

# Chapter 4

# Removal and Use of Ammonia in Gas Purification

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## INTRODUCTION

In previous editions of this book the removal of ammonia from gas streams and the use of ammonia to remove H<sub>2</sub>S and CO<sub>2</sub> were covered in separate chapters. The two subjects have been combined into a single chapter in this edition because (1) the technologies are closely interrelated, (2) the use of aqueous ammonia to absorb H<sub>2</sub>S and CO<sub>2</sub> is declining relative to other, more efficient processes, and (3) the subjects are of most interest with regard to coal gas purification, which is not currently an expanding field.

### Types of Coal Gas

**Table 4-1** lists the principal types of gases produced from coal. Producer gas, water gas, and carburetted water gas represent technology that was widely practiced during the first half of this century to provide fuel gas for residential and industrial use. The availability of abundant supplies of natural gas during the 1950s led to the abandonment of most of these types of coal gasification units in the United States, although their use has continued in other parts of the world. The production of coke-oven gas (COG) continued to grow in the United States during the 1950s and 1960s and is still a major operation worldwide.

The development of processes to produce low- and medium-Btu gas using large pressurized gasifiers received considerable attention during the 1970s and 1980s, but was de-emphasized in the 1990s when oil and natural gas supplies appeared to be ample. Limited development and commercial activities on large, pressurized, oxygen-blown gasifiers are continuing. This type of gasifier is considered to have high potential for future applications to provide fuel for combined cycle power plants and feed gas for the manufacture of ammonia, synthetic natural gas (SNG), and other products.

**Table 4-1**  
**Principal Types of Gas Derived from Coal**

Gas Type	Process Conditions	Approx. HHV (Btu/scf)
Producer Gas	Air blown, moving bed, atmospheric pressure	150
Water Gas	Cyclic process—air to heat, steam to gasify, moving bed, atmospheric pressure	300
Carburetted Water Gas	Similar to water gas with oil added during steam blowing cycle	500
Coke-Oven Gas (COG)	By-product of coal coking process	300
Low-Btu Gas	Air blown; moving, entrained or fluidized bed; usually elevated pressure operation	150
Medium-Btu Gas	Oxygen blown; moving, entrained, or fluidized bed; elevated pressure operation	300

## Sources of Ammonia

During the gasification, carbonization, and thermal treatment of coal, liquid petroleum, shale oil, and tar sands products, a portion of the nitrogenous material contained in the feed is converted to volatile compounds that appear in the gaseous products. The principal nitrogen compounds that have been identified in such gases are ammonia, cyanogen, hydrogen cyanide, pyridine and its homologues, nitric oxide, and free nitrogen. Although the nitrogen present in the fuel is the primary source of these compounds, small amounts of atmospheric nitrogen may also contribute to the presence of nitrogen compounds in the gas stream.

The distribution and concentration of nitrogen compounds in the gaseous products for a given fuel vary over a wide range depending on operating conditions of the gasifier, reactor, or coke oven. The principal operating variables influencing the distribution of nitrogen compounds are temperature, time at temperature, and quantity of steam or oxygen used. For coal carbonization, temperature has the most pronounced effect. For example, the fraction of the nitrogen contained in coal that is converted to ammonia varies from about 2% at a carbonization temperature of 400°C (750°F), which is typical for low-temperature carbonization processes, to 10–15% at 900°C (1,650°F) or higher, the range of typical high temperature carbonization installations.

The approximate distribution of nitrogen in the products under normal, high-temperature coking conditions is shown in **Table 4-2**. Typical concentrations of nitrogen compounds in gases from coal carbonization processes are given in **Table 4-3**. Detailed discussions of the effect of coal carbonization conditions on nitrogen distribution are presented by Kirner (1945) and Hill (1945).

**Table 4-2**  
**Distribution of Nitrogen in Carbonization Products**

Products	Distribution
In the coke	30–50 percent
As ammonia in the gas	10–15 percent
As cyanide compounds in the gas	1–2 percent
In the tar	1–3 percent
As free nitrogen in the gas	Balance

**Table 4-3**  
**Typical Concentrations of Nitrogen Compounds in Coal Gases**

Compound	Volume %
Free nitrogen	0.5–1.5
Ammonia	1.1
Hydrogen cyanide	0.10–0.25
Pyridine bases	0.004
Nitric oxide	0.0001

## Coal Gas Impurities

Ammonia, hydrogen sulfide, and carbon dioxide are major impurities in coke oven gas (COG). In addition to these three components, COG often contains carbon disulfide, carbonyl sulfide, hydrogen cyanide, organic acids, pyridine, phenol, and other impurities, which can cause problems with conventional amine plants. The presence of large quantities of ammonia in these gases naturally led to consideration of its use for removal of H<sub>2</sub>S and CO<sub>2</sub>, and several ammonia-based coke oven gas purification processes have been developed and commercialized.

Processes that use aqueous ammonia to remove H<sub>2</sub>S and CO<sub>2</sub> are still offered for coke-oven gas purification, and many such plants are in operation in the U.S. and Europe; however, it appears that the trend for new operations is toward the use of other absorbents. Other absorption processes that may be applicable for COG purification include the Takahax, Stretford, Vacuum Carbonate, Potassium Carbonate, and Sulfiban (MEA) processes. These processes can be designed to avoid serious adverse effects of trace impurities in the gas, and generally provide somewhat higher H<sub>2</sub>S removal efficiency than ammonia scrubbing. The processes are described in detail in other chapters (see index).

Typical concentrations of major components and impurities in gases derived from coal are given in **Table 4-4**. The principal impurities removed by coal-gas purification processes are hydrogen sulfide and ammonia. These compounds are undesirable because they can cause corrosion, plugging, and ultimately, air pollution. In addition, both H<sub>2</sub>S and NH<sub>3</sub> are relatively valuable chemicals, and their recovery and conversion to useful products, such as elemental sulfur and ammonia, can be of significant economic value. This was particularly true

**Table 4-4**  
**Typical Compositions of Raw Gas Streams from Coal Gasifiers and Coke Ovens**

Component	Oxygen-Blown Gasifiers					COG
	Lurgi	Koppers Topsek	Texaco	BGC/Lurgi	Shell	
C <sub>1</sub> , C <sub>2</sub>	3.6	—	0.3	4.2	—	28.6
H <sub>2</sub>	16.1	18.7	29.8	26.4	30.0	59.0
CO	5.8	43.4	41.0	46.0	60.3	6.0
CO <sub>2</sub>	11.8	6.1	10.2	2.9	1.6	1.3
H <sub>2</sub> S	0.5	0.6	1.0	1.0	1.2	0.4
COS	trace	0.1	0.1	0.1	0.1	—
N <sub>2</sub>	0.1	0.9	0.7	2.8	3.6	1.3
Ar	—	—	0.1	—	1.1	—
H <sub>2</sub> O	61.8	30.2	17.1	16.3	2.0	25.2
NH <sub>3</sub>	0.3	—	0.2	0.3	0.1	0.7
HCN	—	—	—	—	—	0.09

Oxygen-blown gasifier data from Simbeck et al. (1983) based on Illinois #6 coal containing 2.6–3.7% sulfur and 1.1–1.4% nitrogen.

Coke-oven gas (COG) data from Bloem et al. (1990); coal composition not given.

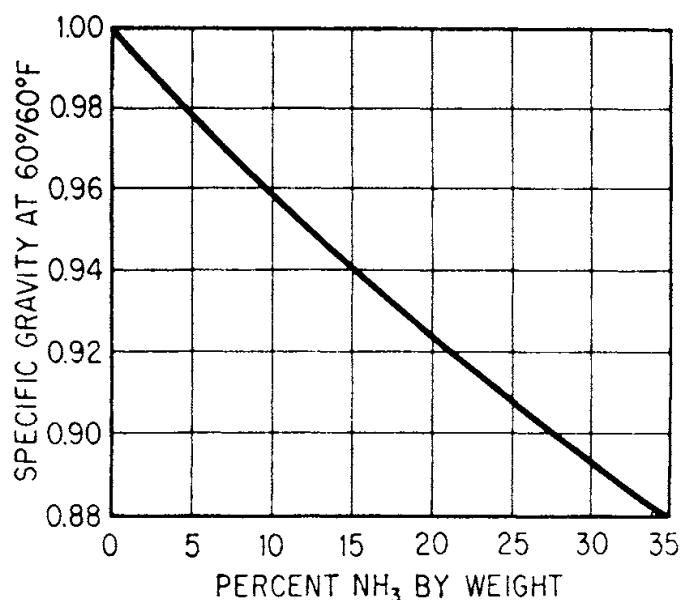
before the advent of synthetic ammonia, when coal gas constituted the largest source of fixed nitrogen.

Carbon dioxide is also a major impurity in coal gas. Although it is not generally necessary to remove CO<sub>2</sub> from gases used as fuels, partial removal is sometimes desirable to improve the heating value. Complete CO<sub>2</sub> elimination is required for gases undergoing processing at very low temperatures, for example, in coke-oven gas purification to provide hydrogen for ammonia synthesis. The removal of other impurities such as HCN, COS, organic acids, and pyridine may also be required when the concentration is high enough to cause pollution or operating problems in downstream systems.

As indicated by the data of **Table 4-4**, gases produced by oxygen-blown gasifiers generally contain appreciably less ammonia than coke oven gas. As a result, the use of aqueous ammonia has not been developed as a gas purification technique for such gases. Gases produced by air-blown gasifiers and by the thermal treatment of petroleum streams (including shale oil and tar sands liquids) are also relatively low in ammonia and are not considered to be appropriate candidates for ammonia-based scrubbing processes.

## Sources of Sour Water

In refinery catalytic cracking operations, oxygen-blown coal gasifiers and similar high temperature processes that produce a gas stream containing both ammonia and hydrogen sulfide, the gas leaving the high temperature step is typically quenched with water or cooled by indirect heat exchange and then scrubbed with water. The resulting "sour water" contains essentially all of the ammonia, but normally contains only a small portion of the H<sub>2</sub>S and CO<sub>2</sub> contained in the gas stream. It also contains water soluble impurities such as organic acids and phenols. Considerable development work has gone into the processing of sour water. Because its processing constitutes an essential step in the overall gas purification scheme, and ammonia is always one component, key processes for sour water treatment are described in the Ammonia Removal section of this chapter.

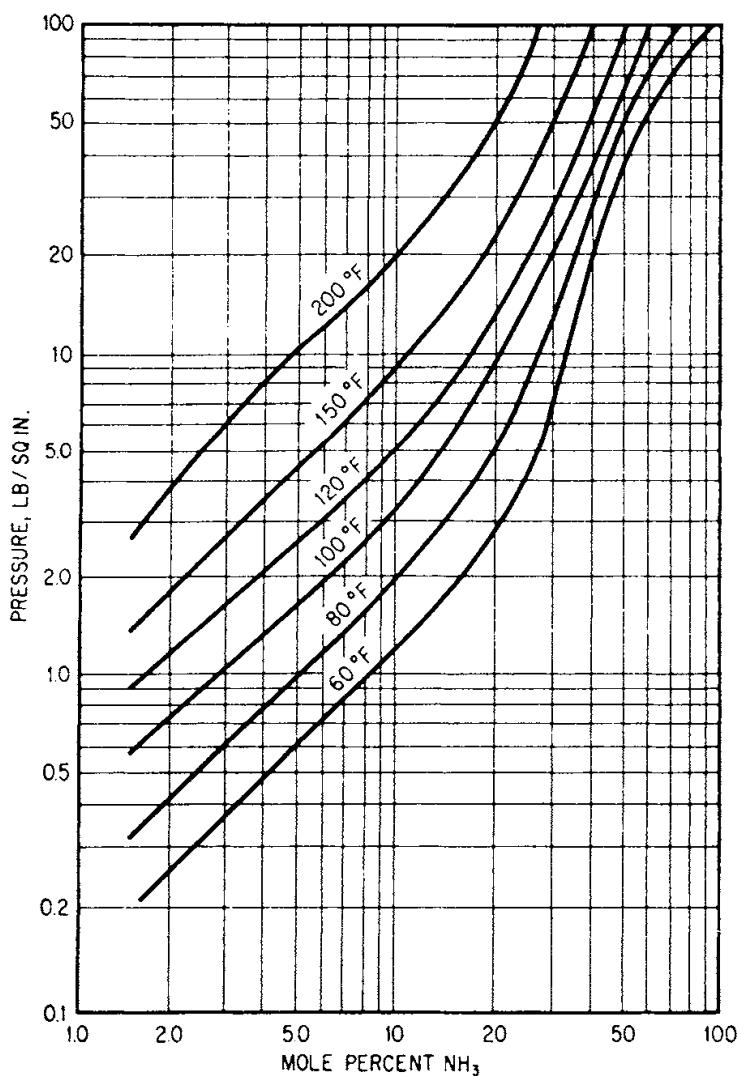


**Figure 4-1.** Specific gravity of aqueous ammonia solutions. *Data of Ferguson (1956)*

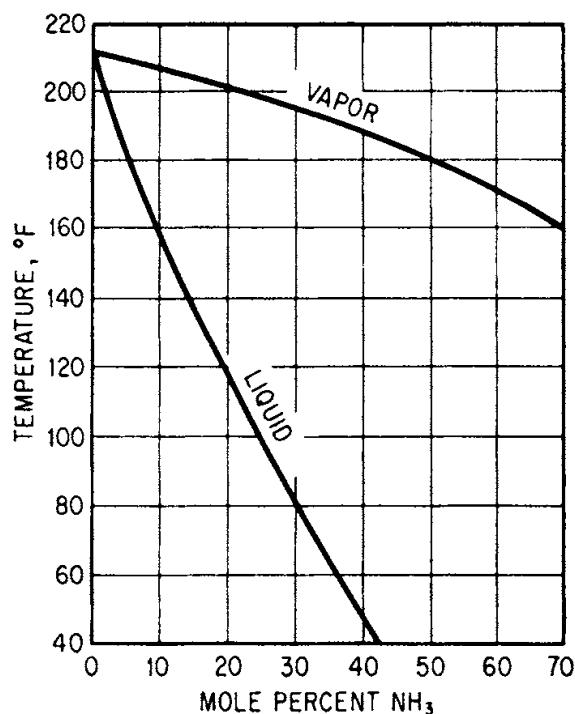
## BASIC DATA

The specific gravity of aqueous ammonia solutions is given in **Figure 4-1**. Vapor pressures of ammonia over aqueous ammonia solutions and vapor-liquid equilibria for such solutions at the atmospheric pressure boiling points are presented in **Figures 4-2** and **4-3**. Vapor-liquid equilibria for the system ammonia-water above about 200°F up to the critical region are given by Sassen et al. (1990). At moderate temperatures, near ambient, dilute solutions of ammonia in water at pH 6 to 10 obey Henry's law, which may be expressed as  $H = 4092/T - 9.70$  (Dasgupta and Dong, 1986). In this equation H is the Henry's law constant ( $M \text{ atm}^{-1}$ ) and T is the absolute temperature (°K).

The vapor pressures of  $\text{H}_2\text{S}$ ,  $\text{CO}_2$ , and  $\text{NH}_3$  over aqueous solutions containing these compounds have been extensively studied. Early investigators included Lohrmann and Stoller (1942), Pexton and Badger (1938), Badger and Silver (1938), Badger (1938), Badger and Wilson (1947), Dryden (1947), and van Krevelen et al. (1949).



**Figure 4-2.** Equilibrium vapor pressure of ammonia over aqueous solutions. *From Perry (1941)*



**Figure 4-3.** Boiling point diagram for aqueous ammonia solutions at 1 atm total pressure. *From Perry (1941)*

The van Krevelen et al. (1949) study is considered to be a pioneering effort in the correlation of vapor-liquid equilibrium data for systems of this type. It has served as the basis for several sour water stripper design procedures, including the widely used approach described by Beychok (1967) and Wild's calculator program for sour water stripper design (1979).

The van Krevelen et al. approach is based on chemical equilibria in the solution with the numerical values for equilibrium coefficients derived from experimental data. For the case of hydrogen sulfide in aqueous ammonia solutions, the correlation is based on the equilibrium relationship between molecular H<sub>2</sub>S and HS<sup>-</sup> ions in an aqueous ammonia solution, which can be defined by the following equation



For a total ammonia content of A moles/liter, a total H<sub>2</sub>S content of S moles/liter, and an equivalent anion concentration of other ammonium salts present of Z equivalents/liter, equations 4-2 and 4-3 can be written in the following forms:

$$(\text{NH}_3) = A - S - Z \quad (4-2)$$

$$(\text{HS}^-) = S \quad (4-3)$$

$$(\text{NH}_4^+) = S + Z \quad (4-4)$$

An equilibrium coefficient K can be expressed as follows:

$$K = \frac{(NH_4^+)(HS^-)}{(NH_3)P_{H_2S}} = \frac{(S + Z)S}{(A - S - Z)P_{H_2S}} \quad (4-5)$$

from which the vapor pressure of H<sub>2</sub>S is

$$P_{H_2S} = \frac{(S + Z)S}{(A - S - Z)K} \text{ mm Hg} \quad (4-6)$$

and from Henry's law,

$$P_{NH_3} = \frac{A - S - Z}{H_{NH_3}} \text{ mm Hg} \quad (4-7)$$

Van Krevelen et al. propose the following equation for estimating Henry coefficients for solutions of the type commonly encountered in H<sub>2</sub>S absorption:

$$-\log \frac{H_{NH_3}}{H_0} = 0.025(NH_3) \quad (4-8)$$

Where: H<sub>0</sub> = Henry coefficient for ammonia in pure water  
(NH<sub>3</sub>) = concentration of free ammonia

The equilibrium coefficient K is not a true constant and varies with the concentration of dissolved salts in the solution. The authors found that this variation can be expressed as a function of the ionic strength (I):

$$I = \frac{1}{2} \sum C_i Z_i \quad (4-9)$$

Where: C<sub>i</sub> = concentration of a given ion  
Z<sub>i</sub> = corresponding valency, by the equation:

$$\log K = a + 0.089I \quad (4-10)$$

Where a has the following values:

t, °C	a
20	-1.10
40	-1.70
60	-2.19

In aqueous solutions containing only ammonia and H<sub>2</sub>S, I equals S, the total H<sub>2</sub>S concentration, and equation 4-10 becomes

$$\log K = a + 0.089S \quad (4-11)$$

Van Krevelen et al. (1949) also proposed correlations to calculate the vapor pressures of components in carbon dioxide-ammonia-water and hydrogen sulfide-carbon dioxide-ammonia-water systems and, in general, results obtained by use of the correlations agree well with experimental data. However, it is important to note that the van Krevelen et al. correlations apply only to ammonia-rich solutions, and are further limited to restricted ranges of acid gas/ammonia ratios and to relatively low temperatures and pressures.

Edwards et al. (1975, 1978A, B) established a molecular-thermodynamic correlation for calculating vapor-liquid equilibria in aqueous solutions containing one or more volatile electrolytes, with special attention to the ternary systems, ammonia-carbon dioxide-water and ammonia-hydrogen sulfide-water. Their 1978 correlation was shown to give results in satisfactory agreement with the limited data then available for temperatures from 0° to 170°C (32° to 338° F) and ionic strengths of about 6 molal (equivalent to total concentrations of the electrolytes between 10 and 20 molal).

Maurer (1980) compared results calculated on the basis of the van Krevelen et al. (1949), Edwards et al. (1978A, B), and Beutier and Renon (1978) correlations with several sets of experimental data. The average deviation of the calculated partial pressures ranged from 10 to 50% depending upon which correlation and which set of experimental data were compared. Kawazuishi and Prausnitz (1987) updated values for some dissociation equilibrium constants and Henry's constants used in the Edwards et al. (1978A, B) correlation with the result that it predicted vapor pressure values in good agreement with the more recent experimental data of Muller (1983).

Because of the importance of sour water processes in the development of substitute natural gas supplies and in refinery operations, the Gas Processors Association (GPA) and American Petroleum Institute (API) supported an extensive program to obtain and correlate design data in this field. In a joint GPA and API-sponsored project, Wilson (1978) developed a program called SWEQ (Sour Water Equilibrium). According to Newman (1991), the SWEQ model is used in several process simulators (e.g. PROCESS, CHEMSHARE, HYSIM, and COADE) and is valid in the temperature range of 70° to 300°F. Newman published a series of charts based on the SWEQ program, which are convenient to use for the preliminary design of sour water systems. Four of his charts representing typical absorption and stripping temperatures are reproduced as **Figures 4-4, 4-5, 4-6 and 4-7**.

After development of the original SWEQ correlation, additional experimental data were obtained by Wilson et al. (1982) and Owens et al. (1983) under GPA sponsorship. The subject is reviewed by Wilson et al. (1985) who present new data on the partial pressure of sour water components at temperatures from 100° to 400°F; and pressures up to 1,000 psia. Sample data are given in **Table 4-5**. Wilson et al. (1985) point out that at temperatures above 300°F, the measured partial pressures of NH<sub>3</sub>, H<sub>2</sub>S, and CO<sub>2</sub> diverge significantly from values predicted by the earlier correlation (Wilson, 1978). They also found the Henry's law coefficients for the inert gases to be the same in sour water as in pure water.

The GPA program culminated with the development of a new model and computer program called GPSWAT (GPA Sour Water Equilibria), which extends the applicability of the precursor SWEQ program from 68°– 284°F to 68°– 600°F and extends the pressure range to 2,000 psia. This program may be purchased from the Gas Processors' Association.

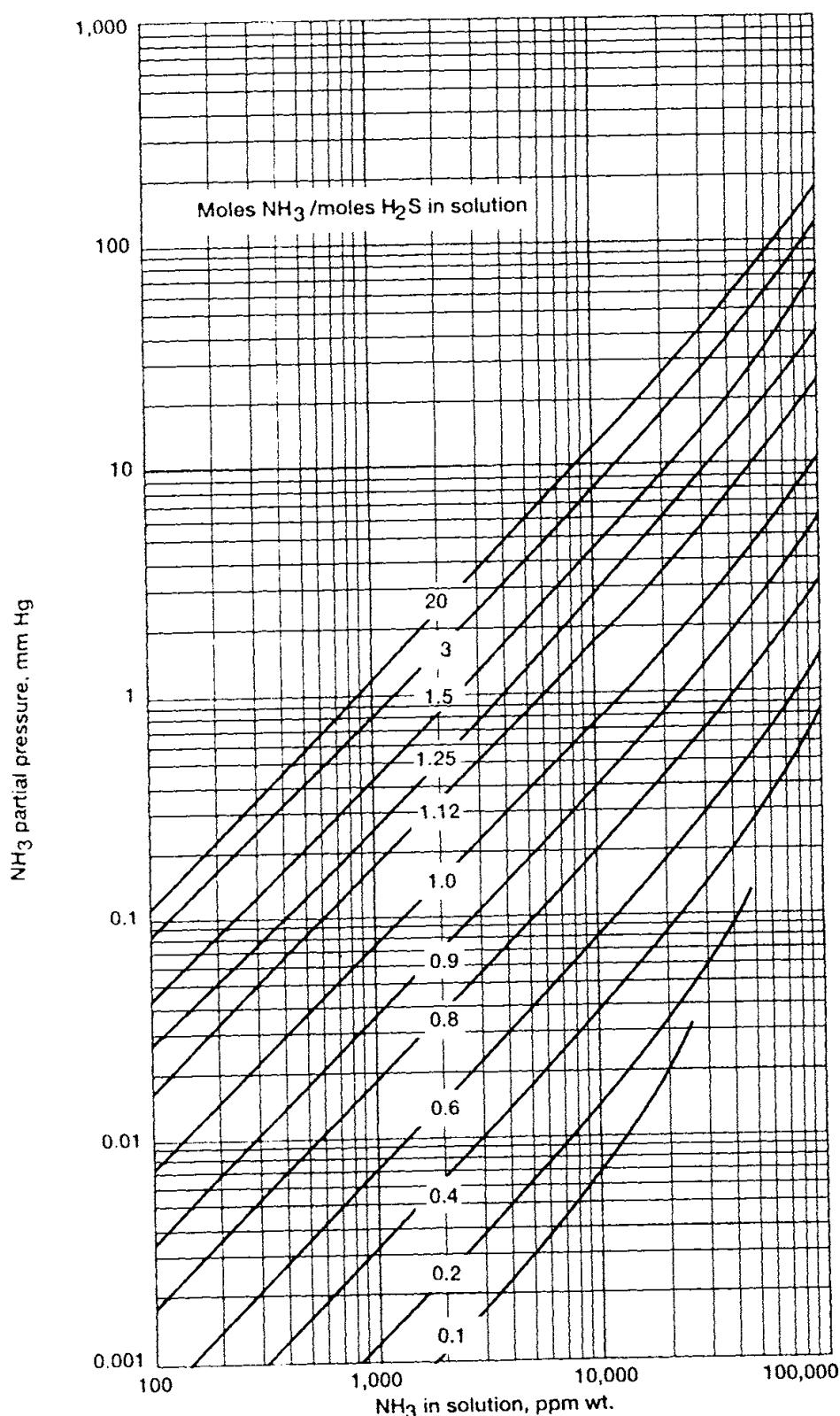
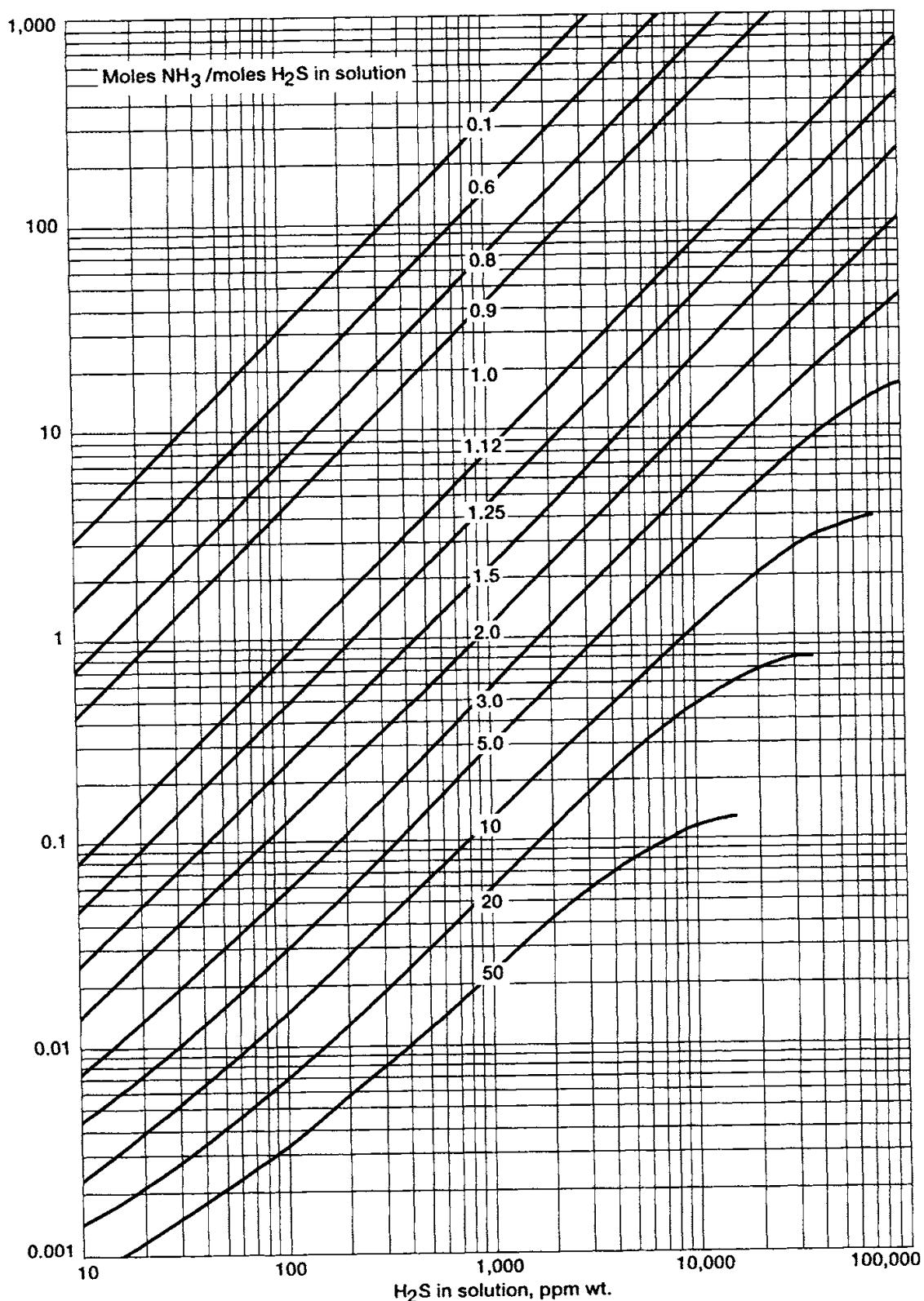


Figure 4-4. Ammonia equilibria at 100°F. Data of Newman (1991). Reproduced with permission from *Hydrocarbon Processing*



**Figure 4-5.** Hydrogen sulfide equilibria at 100°F. *Data of Newman (1991).* Reproduced with permission from *Hydrocarbon Processing*

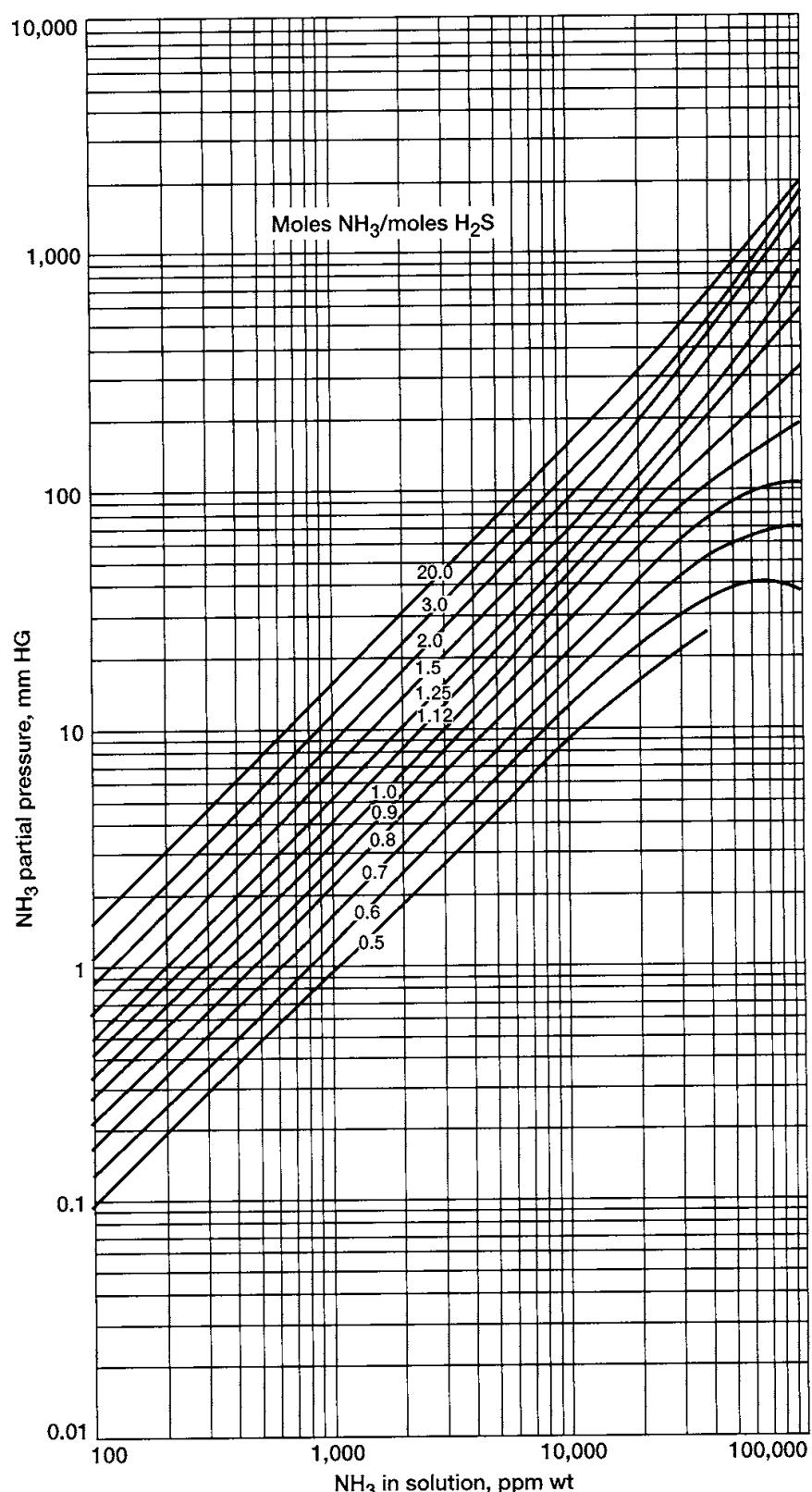
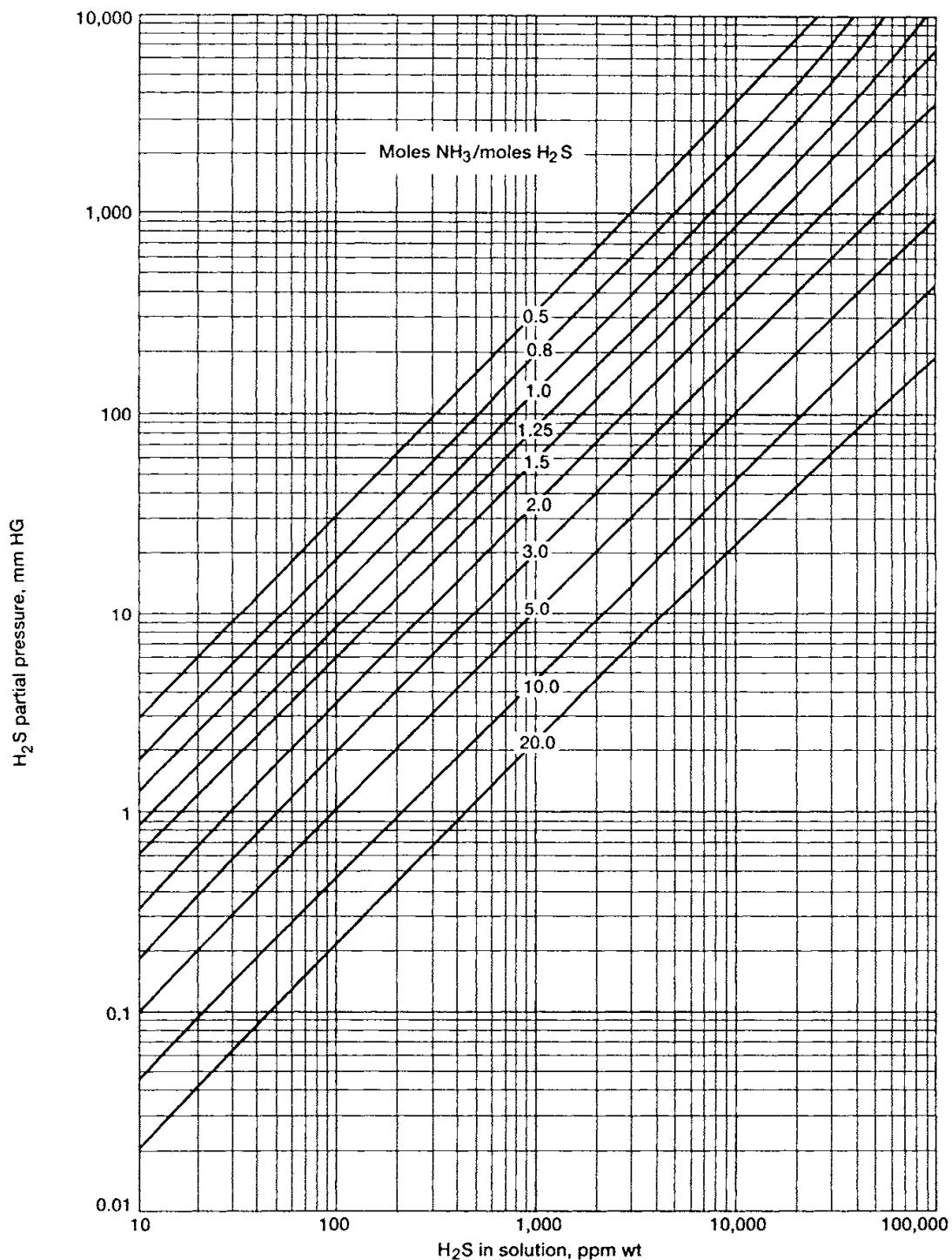


Figure 4-6. Ammonia equilibria at 240°F. Data of Newman (1991). Reproduced with permission from Hydrocarbon Processing



**Figure 4-7.** Hydrogen sulfide equilibria at 240°F. *Data of Newman (1991). Reproduced with permission from Hydrocarbon Processing*

<b>Table 4-5</b> <b>Measured Vapor-Liquid Equilibrium Data for Sour Water with Inerts at Elevated Temperatures and Pressures</b>				
<b>Temperature and Component</b>	<b>Concentration in Liquid, Mole %</b>	<b>Measured Partial Pressure, psia at total pressure of:</b>		
		<b>33.4 psia</b>	<b>500 psia</b>	<b>1,000 psia</b>
<i>100°F</i>				
NH <sub>3</sub>	2.11	0.28	0.34	0.36
CO <sub>2</sub>	0.27	0.022	0.015	0.012
H <sub>2</sub> S	0.53	0.16	0.14	0.15
H <sub>2</sub> O	97.01–97.09	0.78	0.93	0.93
inerts	0–0.08	32.16	498.61	998.6
<i>200°F</i>				
NH <sub>3</sub>	2.05–2.02		2.40	2.75
CO <sub>2</sub>	0.25–0.26		1.61	1.75
H <sub>2</sub> S	0.51–0.52		2.37	2.34
H <sub>2</sub> O	97.15–97.13		11.21	11.20
inerts	0.04–0.07		482.4	981.6
<i>400°F</i>				
NH <sub>3</sub>	2.13			32.7
CO <sub>2</sub>	0.45			222.8
H <sub>2</sub> S	0.84			124.5
H <sub>2</sub> O	96.51			239.8
inerts	0.07			380.2

*Notes: Inerts are CO, N<sub>2</sub>, CH<sub>4</sub>, and H<sub>2</sub> for 100°F and 200°F runs; N<sub>2</sub>, CH<sub>4</sub>, and H<sub>2</sub> for 400°F run.*  
Data from Wilson et al. (1985)

(text continued from page 286)

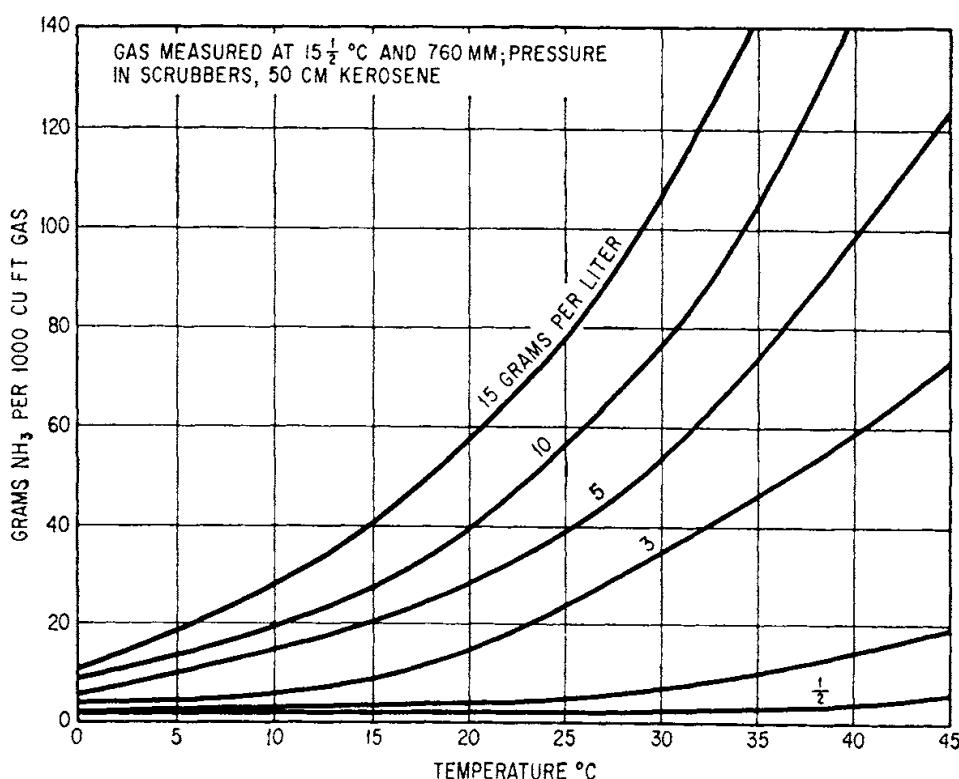
Vapor-liquid equilibria of typical coke-oven gases and liquids obtained in ammonia scrubbers (indirect process) are shown in **Figure 4-8**.

Differential and integral heats of solution of liquid ammonia in water are given in **Tables 4-6 and 4-7**.

The heat of reaction evolved in the saturator during absorption of gaseous ammonia in sulfuric acid, based on heat-of-formation data, is shown in equation 4-12:



In a typical process where ammonia is reacted with sulfuric acid, this heat of reaction is augmented by the heat of dilution of sulfuric acid from 60° Bé (77.6%) to 7% which amounts to 15,000 Btu/lb mole. The total heat effect is, therefore, 101,000 Btu/lb mole of ammonium sulfate.



**Figure 4-8.** Vapor-liquid equilibria of typical coke-oven gases and liquids obtained in ammonia scrubbers (indirect process). *From Pacific Coast Gas Association, Gas Engineers' Handbook (1934)*

In processes where ammonia is reacted with phosphoric acid, the heat evolved in the formation of diammonium phosphate from ammonia and phosphoric acid may be estimated from equation (4-13):



The density, viscosity, and vapor pressure of aqueous ammonium sulfate solutions and the solubility of ammonium sulfate in water can be estimated from the nomogram presented in **Figure 4-9**. To obtain the density, viscosity, and vapor pressure, the temperature on the t scale is selected and aligned with the concentration on the C scale. The intersects of the line of the p, γ, μ, and d scales give the values for vapor pressure, viscosity, and density of the solution. The solubility of ammonium sulfate in water is obtained by aligning the temperature (on the t scale) with the saturation point S and reading the solubility on the C scale. The values obtained by the nomogram agree very closely with published data.

## REMOVAL OF AMMONIA FROM GASES

It is generally necessary to remove ammonia, hydrogen cyanide, and pyridine bases from coal gases prior to industrial or domestic use to meet purity requirements of downstream systems. In addition, ammonia and the pyridine bases are relatively valuable chemicals and their recovery as by-products can be economically attractive when significant quantities are produced. Before the advent of synthetic ammonia processes, by-product ammonia from coal

**Table 4-6**  
**Differential Heats of Solution of Liquid Ammonia**  
**(Btu per pound of ammonia dissolved)**

Concentration, wt %	Heat of solution								
0	347.4	11	302.8	21	253.8	31	197.6	41	135.0
1	343.8	12	298.2	22	248.4	32	191.9	42	127.8
2	340.2	13	293.6	23	243.0	33	186.1	43	120.6
3	336.6	14	289.0	24	237.6	34	180.4	44	113.4
4	333.0	15	284.4	25	232.2	35	174.6	45	106.2
5	329.4	16	279.4	26	226.4	36	168.1	46	99.0
6	325.0	17	274.3	27	220.7	37	161.6	47	91.8
7	320.6	18	269.2	28	214.9	38	155.2	48	84.6
8	316.2	19	264.2	29	209.2	39	148.7	49	77.4
9	311.8	20	259.2	30	203.4	40	142.2	50	70.2
10	307.4								

Source: Perry (1941)

**Table 4-7**  
**Integral Heats of Solution of Liquid Ammonia**

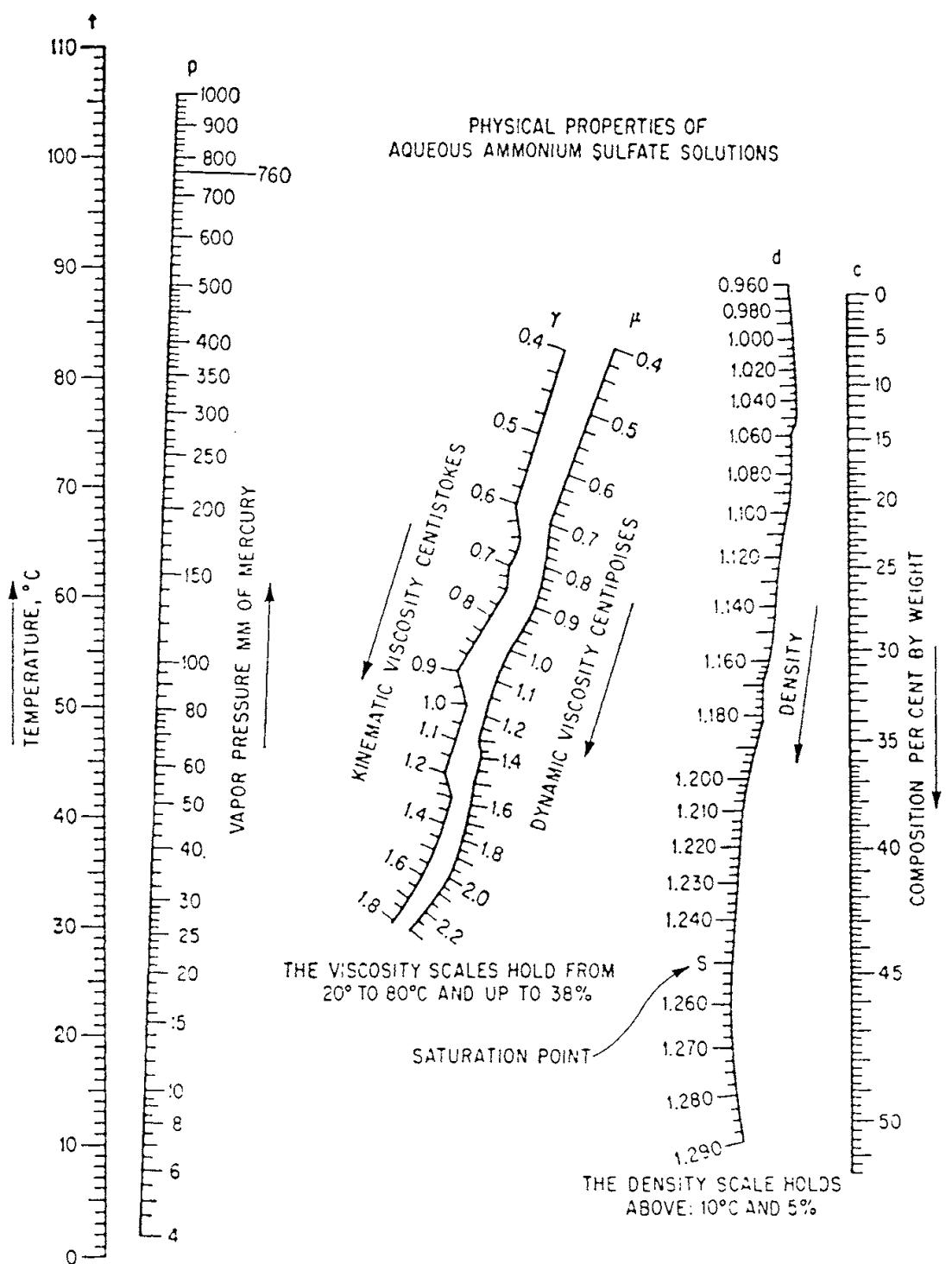
Concentration, wt %	Btu/lb mixture	Btu/lb NH <sub>3</sub>
0	0	358.0
10	34.4	343.8
20	65.7	328.5
30	92.5	308.2
40	108.2	270.0
50	109.4	218.8
60	101.9	169.7
70	84.8	121.1
80	60.7	75.8
90	31.9	35.5
100	0	0

Source: Perry (1941)

carbonization and gasification constituted the most important source of fixed nitrogen. At present, by-product ammonia accounts for only a small percentage of the ammonia produced, and there is a growing trend with small- and medium-sized installations to burn rather than recover ammonia removed from gas streams. Svoboda and Diemer (1990) suggest that ammonium sulfate production is particularly uneconomical in Europe because the acid soils in much of the region preclude the use of sulfate-containing fertilizer.

Since coal gasification has been practiced for many years, it is not surprising that the literature covering the removal of ammonia and other impurities is voluminous and repetitious. No attempt is made in this chapter to discuss all processes that have been developed; instead, detailed descriptions are presented for processes in current use, with emphasis on those that appear to be expanding in application. Comprehensive reviews of earlier technologies applied to coal gas purification in the 1940s and 1950s are given by Hill (1945), Wilson (1945), Wilson and Wells (1948), Bell (1950), and Key (1956). Updates covering coke oven gas and effluent treatment technology as of the mid to late 1970s are provided by Grosick and Kovacic (1981) and Massey and Dunlap (1975).

The proposed construction of very large oxygen- (or air-) blown coal gasifiers to provide feed for combined cycle power plants or for the synthesis of fuels and chemicals is a relatively recent development. Many more such plants have been designed and studied than actually built, and, with the exception of the large Lurgi gasifier installation in South Africa, plants built to date have been aimed primarily at process development and demonstration. The designs typically include a water wash (or quench) step immediately downstream of the gasifier to clean and cool the gas. The resulting sour water contains ammonia, hydrogen sulfide, and other soluble impurities. In most gasification plant designs, the sour water undergoes phenol extraction, steam stripping, and finally biological oxidation before disposal. Vapors from the sour water stripper are generally processed for ammonia recovery. Detailed flow diagrams of typical water processing systems for coal gasification plants are given in the United States DOE *Coal Conversion Systems Technical Data Book* (1982).



**Figure 4-9.** Nomogram for estimating density, viscosity, and vapor pressure of aqueous  $(\text{NH}_4)_2\text{SO}_4$  solutions and the solubility of ammonium sulfate in water. *Data of Tans (1958)*

Petroleum refineries handling heavy crudes, tar sands, or shale oil typically encounter ammonia in the gas streams from catalytic crackers, cokers, and other high temperature operations. It is considered important to remove the ammonia and associated impurities as soon as possible after production to avoid corrosion and plugging of downstream equipment. This

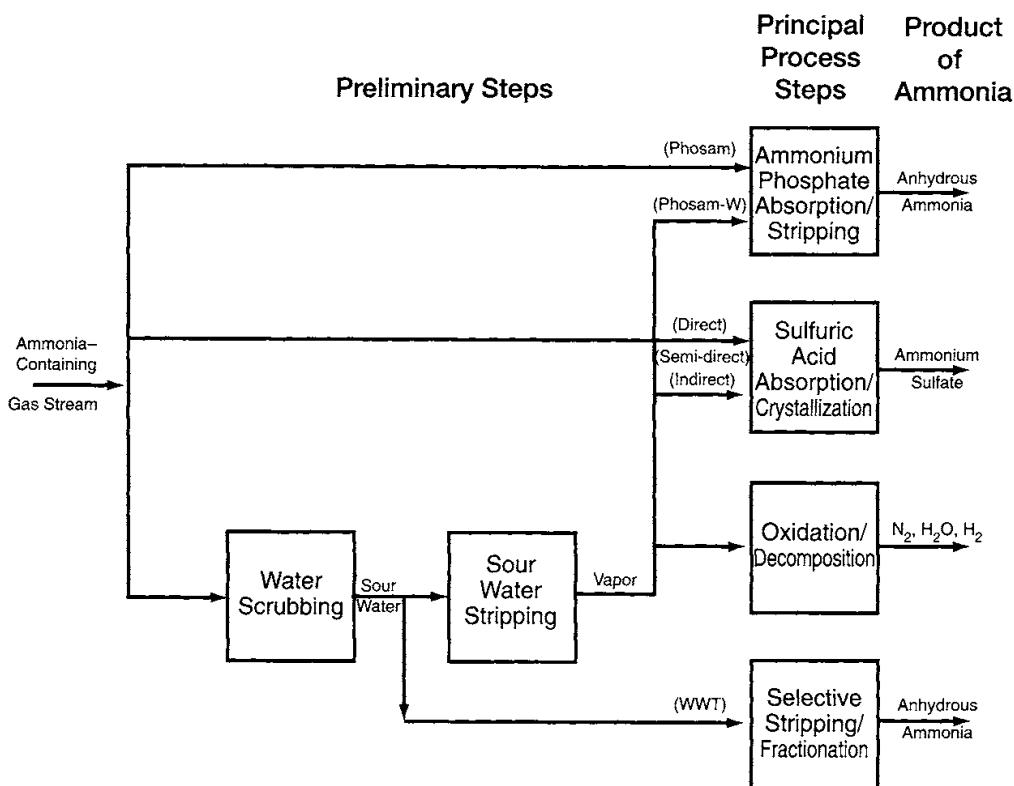
is normally accomplished by water washing. In a fluid catalytic cracker (FCC) system, for example, Strong et al. (1991) suggest injecting water into the main fractionator overhead vapor line and downstream of each stage of gas compression. Sour water containing dissolved ammonia, hydrogen sulfide, chlorides, and cyanides is drawn off at separators located at appropriate points in the circuit and collected for processing in a sour water system.

## Types of Processes

The principal approaches used commercially for ammonia removal from gas streams are shown in **Figure 4-10**. The gas may be contacted with ammonium phosphate solution for the regenerable absorption of ammonia in accordance with the Phosam process, passed through a strong acid solution for the non-regenerable formation of an ammonium salt (direct and semi-direct processes), or scrubbed with water to form a sour water product containing the ammonia along with other impurities.

Although small quantities of sour water may be disposed of by injection into deep wells or by adding to the plant waste water disposal system, these are not viable options for most plants. Normally the sour water is either processed in a sour water stripper (SWS), which produces a vapor phase containing both ammonia and acid gases, or it is selectively stripped in a two-column system such as the Chevron WWT process, which produces separate ammonia and hydrogen sulfide-rich gas streams.

As indicated in **Figure 4-10**, the vapor from a sour water stripper may be processed in a Phosam-W unit, reacted with strong acid (the indirect process) or disposed of by oxidation in



**Figure 4-10. Basic steps in ammonia removal processes.**

an incinerator or sulfur plant or by catalytic decomposition to nitrogen and hydrogen. The ammonia-rich vapor produced in the Chevron WWT process is typically purified to produce anhydrous ammonia as shown in **Figure 4-10**; however, it may also be combusted if ammonia recovery is not economical.

The terms “direct,” “indirect,” and “semi-direct” are used primarily in conjunction with coal-gas purification. In the direct process, the hot gas from the coke ovens is passed directly through concentrated sulfuric acid to produce ammonium sulfate. The process is fraught with operational difficulties and is no longer of commercial interest. In the indirect process, which is the oldest of the three, all of the ammonia is removed from the coke-oven gas by water washing; while in the semi-direct process, the gas is first cooled to condense out tar and a small volume of ammonia-containing water, then reheated and reacted with sulfuric acid as in the direct process. Both the indirect and semi-direct processes are currently used in coking plants. The processes identified in **Figure 4-10** are described in the following sections.

## Water Scrubbing

### Coke-Oven Gas Processing

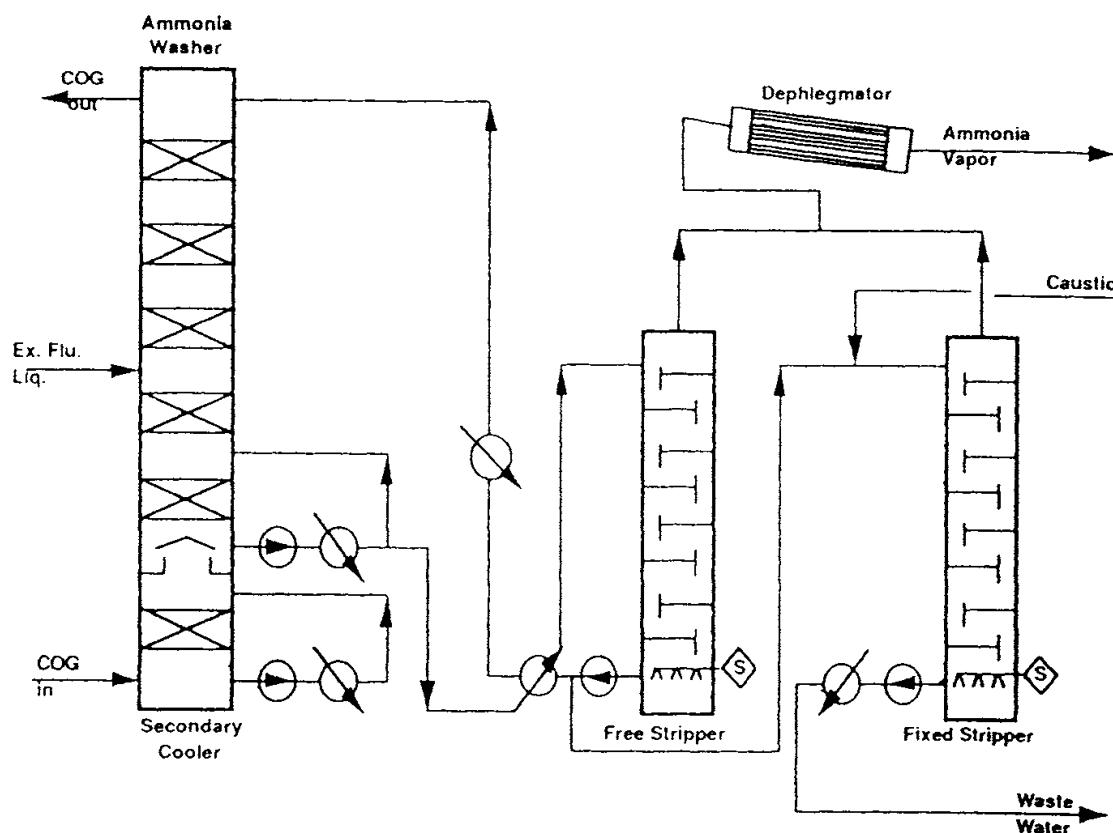
The basic processes used in handling coke-oven gas have not changed greatly in many years. Typically, hot dirty gas from the coke ovens undergoes the following steps prior to ammonia and acid gas removal:

1. The gas is precooled by direct contact with a large volume of a mixture of coal tar and weakly ammoniacal aqueous solution which is sprayed directly into the collection main. During this operation the gases are cooled to about 75° to 100°C (167° to 212°F), and most of the fixed ammonium salts (typically about 30% of the ammonia originally present in the gas) as well as a major quantity of the tar are removed. The liquid, which is known as the “flushing liquor,” is recycled to the collecting main after most of the tar has been decanted. A portion of the flushing liquor is continuously withdrawn from the cycle, combined with other liquid streams containing relatively low concentrations of ammonia (the so-called “weak ammoniacal liquor”) and further processed for recovery of the ammonia. The liquid removed from the cycle is replaced by condensate from subsequent coolers.
2. The gas is further cooled to a temperature of 28°–30°C (82°–86°F) in primary coolers, which may be direct or indirect. Direct coolers are towers in which the gas is cooled by direct contact with a countercurrent stream of weakly ammoniacal solution. Packed towers were formerly used for this service, but naphthalene buildup on the packing caused excessive maintenance, and all recent installations have employed spray towers. The hot solution leaving the bottom of each tower is passed through water-cooled coils and recycled to the top of the tower. A portion of the circulating liquid is continuously withdrawn and added to the flushing liquor. Indirect coolers are shell-and-tube heat exchangers with cooling water flowing through the tubes. Condensate from indirect coolers, which contains some light tar and about 40% of the ammonia originally present in the coal gas, mostly as free ammonia, is collected in a decant tank. The tar is separated and the aqueous phase is added to the circulating flushing liquor.
3. The cooled coke-oven gas is normally passed through an electrostatic precipitator to remove fine droplets of tar, then compressed in an exhauster to a pressure of about 2 psig (Svoboda and Diemer, 1990).

The sequence of these steps may vary depending upon the overall process employed. When the ammonia is to be removed by water scrubbing prior to acid gas removal, the gas must be cooled again to remove the heat of compression. The required secondary cooler is typically installed in the bottom of the ammonia wash tower. A diagram of the water wash ammonia removal process, including the stripping section, is shown in **Figure 4-11**; typical compositions for key flow streams, as reported by Svoboda and Diemer (1990), are given in Table 4-8.

Coke-oven gas from the exhauster, at a temperature of 45°–55°C (113°–131°F), is cooled in the secondary cooler to about 28°C (82°F), then enters the absorption section of the vessel. A portion of the rich solution from the absorber is cooled and recycled over the bottom packed section to remove the heat of reaction and provide a high liquid flow rate in this zone. Cooled excess flushing liquor, which is a dilute solution of ammonia, is fed into the column in the lower third of the vessel. Water from the free ammonia stripper is fed into the top of the absorber. This water still contains fixed ammonia, but since this form of ammonia has a negligible ammonia vapor pressure, it does not significantly affect the gas purity attainable. According to Svoboda and Diemer (1990), this type of washer typically reduces the ammonia content of coke-oven gas from 200–500 g/100 scf to 2–7 g/100 scf.

Rich solution from the bottom of the wash tower is preheated by heat exchange with stripped water then fed to the top of the free ammonia stripper, which operates with direct steam injection at the bottom. Stripped water from this column is cooled and recycled to the top of the wash column. Excess stripped water, which still contains fixed ammonia, is processed in the fixed ammonia stripper before disposal. Caustic soda (or lime) is used to



**Figure 4-11.** Coke-oven gas, water-wash flow diagram. *From Svoboda and Diemer (1990)*

**Table 4-8**  
**Typical Stream Compositions for Water-Wash Process for Ammonia Removal from Coke-Oven Gas**

<b>Component</b>	<b>Process Stream</b>		
	<b>Excess Flushing Liquor g/l</b>	<b>Rich Solution from NH<sub>3</sub> Scrubber g/l</b>	<b>Ammonia Still Vapor vol. %</b>
NH <sub>3</sub> , fixed	2.5–5.0	4.0	—
NH <sub>3</sub> , free	1.0–2.5	0.9	38.7
H <sub>2</sub> S	0.2–0.4	0.6	1.7
HCN	0.1–0.3	0.6	1.4
CO <sub>2</sub>	0.2–0.5	1.6	2.5
H <sub>2</sub> O	balance	balance	55.9

*Data of Svoboda and Diemer (1990)*

react with nonvolatile acids in the liquid feed to the fixed ammonia stripper to release the ammonia and allow it to be steam-stripped from the solution. The design of stripping systems is discussed in a later section entitled "Sour Water Strippers."

Overhead vapors from both the free and fixed ammonia strippers pass through a dephlegmator (partial condenser) and are then available for further processing to recover or dispose of the ammonia and acid gases. Processes for handling the overhead gas product include

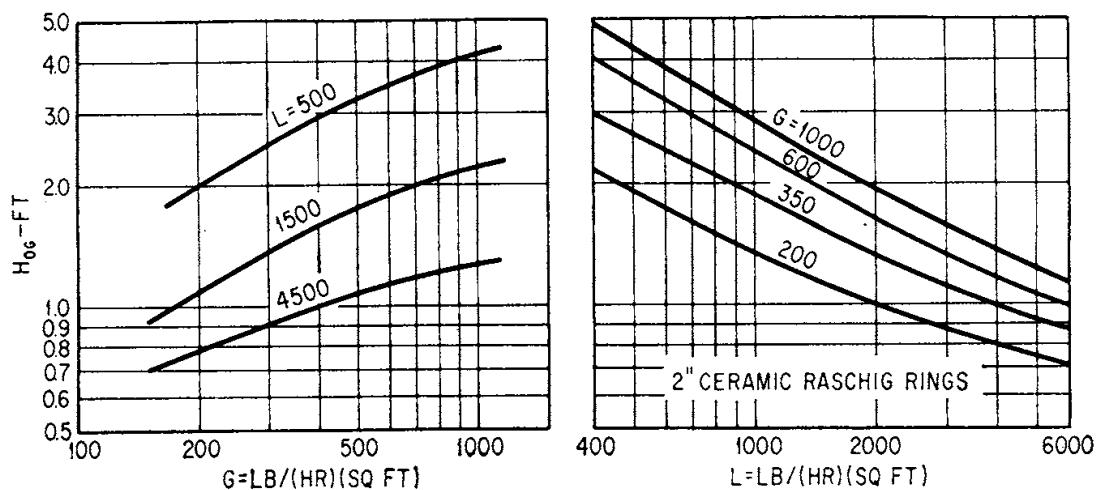
1. Reaction with strong acid to produce ammonium sulfate (or phosphate) salts and a stream of acid gas (the indirect process)
2. Phosam process to produce separate streams of pure ammonia and acid gases
3. Catalytic destruction of ammonia in the presence of H<sub>2</sub>S to produce a single gas stream containing N<sub>2</sub>, H<sub>2</sub>, H<sub>2</sub>S, and other components, which can be recycled to the coke-oven gas stream ahead of the desulfurization unit (Svoboda and Diemer, 1990)
4. Oxidation of both the ammonia and H<sub>2</sub>S in a Claus Plant or incinerator to produce a tail gas containing N<sub>2</sub>, H<sub>2</sub>O, and varying amounts of SO<sub>2</sub>

### **Ammonia Absorption in Water**

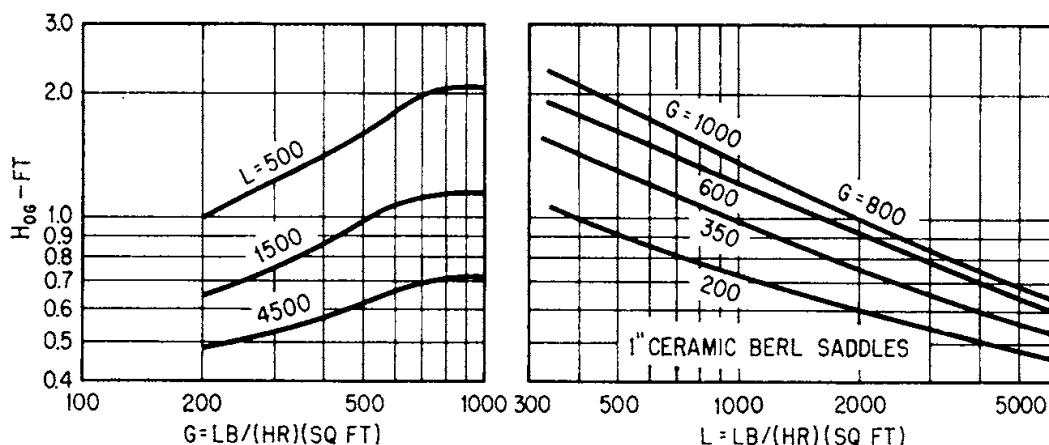
The rate of absorption of ammonia has been studied extensively. A list of key investigations is given in **Table 4-9**. There is general agreement that the operation is gas film-controlled due to the high rate of reaction of dissolved ammonia with water. A wide range of data on the rate of absorption of ammonia in water in packed towers has been presented by Fellinger (1941). Examples of his data, in terms of heights of overall transfer units based on the gas driving force (H<sub>OG</sub>), are given in **Figures 4-12** and **4-13**. Although the charts show that the height of a transfer unit (H<sub>OG</sub>) increases with gas rate (G), indicating poorer performance, the increase in H<sub>OG</sub> is not proportional to the increase in G; therefore, the absorption coefficient also increases. (See Chapter 1 for equations defining H<sub>OG</sub>.)

**Table 4-9**  
**Investigations on the Rate of Absorption of Ammonia in Towers**

Authors	Column diameter in.	Packed height in.	Packing material	Gas	Solvent	Flow rate, lb/(hr) (sq ft)		Temp., °F	Remarks
						Liquid	Gas		
Kowalke, Hougen, and Watson (1925)	16	46	Spray tower Wood grids	Air	Water	30-750	6-150	60	5 "Vermorel" nozzles
	16	41	No. 1 stoneware*	Air	Water	21-670	19-240	68-110	
	16	41	No. 2 stoneware†	Air	Water	30-780	15-240	60-110	
	16	41		Air	Water	30-780	15-240	60-110	
Sherwood and Holloway (1940)	10	19-31	Rings, 1-in.	Air	Water	570-830	55-530	77	Data of Borden and Squires
	{ 10	19-31	Rings, 1-in.	Air	Water	660-710	65-700	54	
		19-31	Rings, 1-in.	Air	0.5-4.5 N H <sub>2</sub> SO <sub>4</sub>	1,520-1,850	210	77	
	10	19-31	Rings and berl saddles, ½-in., 1-in.	Air	3.5-4.5 N H <sub>2</sub> SO <sub>4</sub>	75-480	3,300		
Dwyer and Dodge (1941)	12	48	Rings, ½-in., 1-in., 1½-in.	Air	Water	100-1,000	100-1,000	74-88	
Fellinger (1941)	20	9, 17, 25½, 25½, 23¾	Rings, ¾-in., ½-in., 1-in., 1½-in., 2-in.	Air	Water	500-4,500	200-1,000		
	20	20½, 22, 25	Berl, saddles, ½-in., 1-in., 1½-in.	Air	Water	500-4,500	200-1,000		
	20	26	Triple spiral tile, 3-in.	Air	Water	500-4,500	200-1,000		
			No. 6295 drip-point grid	Air	Water	1,900-15,000	100-1,000		
Pigford and Pyle (1951)	31.5	26, 52	Spray tower	Air	Water	285-900	230-800	6	Sprayco 5-B nozzles



**Figure 4-12.** Values of  $H_{0G}$  for absorption of ammonia in water (packed tower, 2-in. ceramic Raschig rings). *Data of Fellinger (1941)*

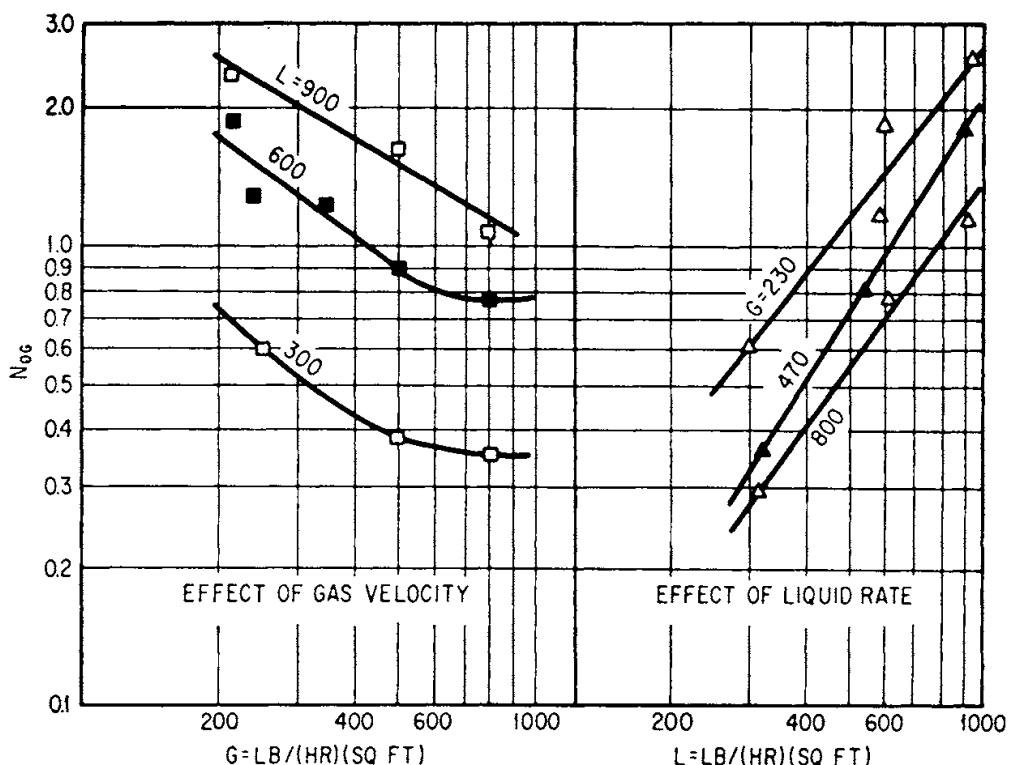


**Figure 4-13.** Values of  $H_{0G}$  for absorption of ammonia in water (packed tower, 1-in. ceramic Berl saddles). *Data of Fellinger (1941)*

Rates of absorption of ammonia in water in countercurrent spray towers have been determined by Kowalke et al. (1925) and Pigford and Pyle (1951). Data obtained by Pigford and Pyle are shown in **Figure 4-14** for a 52-in. high spray tower. In this case the data are given in terms of the number of transfer units because spray column performance is not proportional to height. The indicated number of transfer units for the system is almost directly proportional to the liquid rate because the area for mass transfer increases almost linearly with flow rate in spray units.

Mass transfer data on specific packings and gas/solvent systems of interest can often be obtained from vendors. For example, Jaeger Products, Inc. (1990) gives the following data for the absorption of ammonia by water using Jaeger Tri-Packs, hollow spherical-shaped packings made of injection molded plastic:

G lb/hr ft <sup>2</sup>	L lb/hr ft <sup>2</sup>	Temp. °F	HTU, inches	
			2 & 3½-in.	1-in.
512	1,024	68	8.4	5.6
512	4,096	68	5.4	3.6



**Figure 4-14. Number of transfer units for absorption of ammonia in water in a spray tower, 52-in. high. *Data of Pigford and Pyle (1951)***

The data are for three nominal packing sizes (1-in., 2-in., and 3½-in.) and generally indicate a performance considerably better than comparably sized ring or saddle-type packings. Packing (or tray) performance can also be predicted from correlations based on fundamental data. Available correlations are discussed in Chapter 1.

## Sour Water Stripping Process

Sour water strippers are commonly used in refineries and other operations where a stream of water is produced containing ammonia and hydrogen sulfide. In most cases the sour water also contains carbon dioxide and a number of trace impurities. The principal object of the stripper is to remove the ammonia and hydrogen sulfide, typically to levels below 50 ppmw NH<sub>3</sub> and 10 ppmw H<sub>2</sub>S, so that the water can be reused or disposed of as normal wastewater.

Carbon dioxide is not considered to be a noxious impurity in the water; nevertheless, it is completely removed with the ammonia and hydrogen sulfide during the stripping operation. The presence of phenol in the sour water may require the inclusion of a separate phenol extraction step in the water treatment process, while the presence of strong or nonvolatile acids can usually be handled in the sour water stripping system by the addition of caustic

soda. The caustic soda displaces ammonia by forming stable salts with the acids. As a result the product water contains a small concentration of sodium salts, but no significant quantity of ammonia.

### ***Process Description***

A flow diagram of a typical sour water stripping system is shown in **Figure 4-15**. The sour water feed is passed through a separator where floatable light oil and heavy sludge are removed. It is next collected in a feed storage tank, which serves to smooth out flow rate and composition changes and, after preheating, is fed to the top of the stripping column. Sieve tray columns are probably the most popular, although other types of trays and packed columns are also used successfully. Both the water-cooled overhead condenser/reflux system and the steam-heated reboiler system shown in the flow diagram are optional items. The overhead vapor stream can sometimes be used without condensation as feed to a sulfur plant or incinerator, and stripping vapor can be provided by direct steam (or inert gas) injection; however, economics and practical considerations usually favor the arrangement shown for all but very small installations.

Trends in the design of sour water stripping systems as noted by Won (1982) include

1. Using less steam and more trays to accomplish a given stripping requirement to reduce operating costs
2. Using reboilers instead of direct steam injection to conserve clean condensate and reduce effluent volumes
3. Using an overhead condenser to provide reflux, particularly when the vapor stream is fed to a sulfur plant
4. Using controlled caustic injection to free fixed ammonia

An American Petroleum Institute (API) survey (Gantz, 1975) also noted a trend toward the use of tray columns instead of packed columns. About 75% of the plants surveyed used trays, and all units built after 1970 used trays.

### ***Design Approach***

A detailed procedure for designing sour water strippers is outlined by Beychok (1967). The Beychok approach is a simple tray-by-tray calculation that starts with a preliminary material balance around the tower and assumed values for the number of trays, the column top pressure, the individual tray pressure drop, and the stripping steam flow rate leaving the top tray. The tray-by-tray analysis begins at the top tray with an estimate of the temperature based on the partial pressure of water vapor in the gas phase. An initial value is assumed for the  $\text{NH}_3/\text{H}_2\text{S}$  mole ratio in the liquid on the top tray, then this ratio is adjusted as required until the composition of the gas and liquid phases leaving the tray are in equilibrium. A material balance around the top (first) tray gives the composition of vapor coming from the second tray.

The total pressure at the second tray is estimated by assuming a pressure drop of about 0.50 psi per theoretical tray (based on 0.25 psi per actual tray and 50% tray efficiency) and the above procedure repeated. The tray-by-tray analysis is continued down the column until the liquid leaving a tray meets the product water specification with regard to ammonia and hydrogen sulfide content. If necessary, the entire process is repeated with different initial

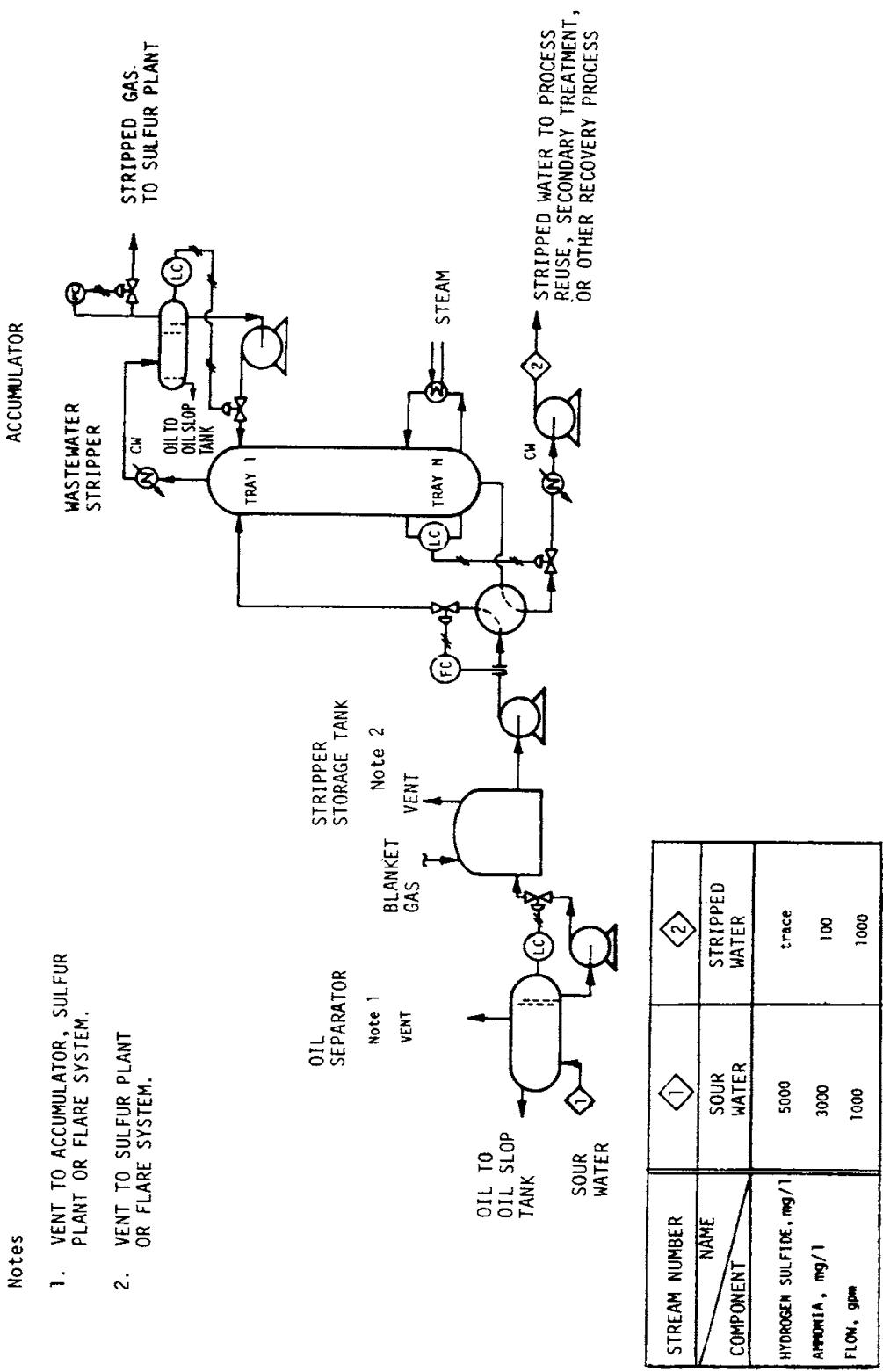


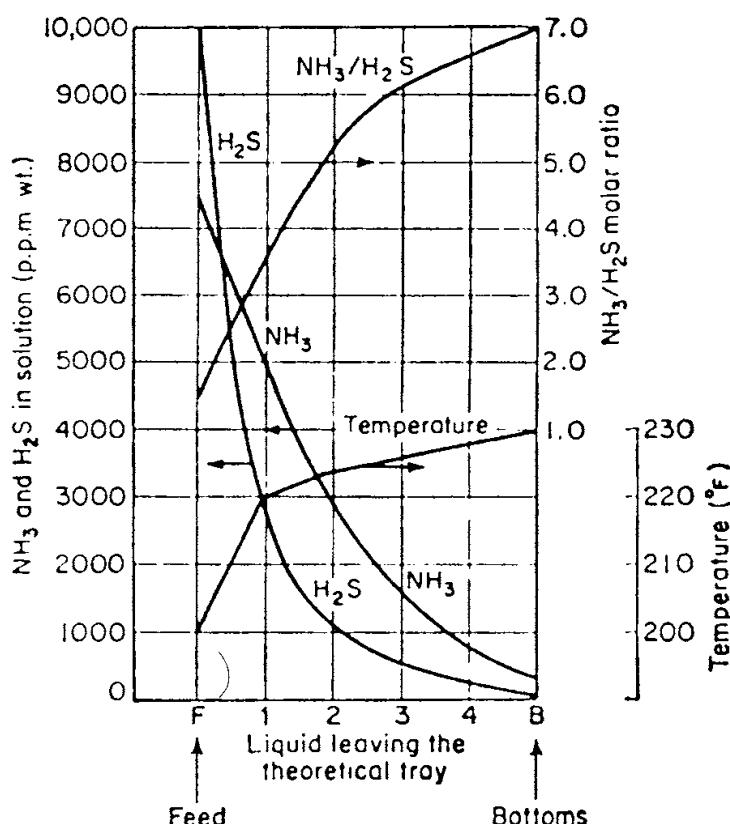
Figure 4-15. Flow diagram of sour water stripper system. From U.S. DOE, Coal Conversion Systems Data Book (1982)

assumptions until good agreement is obtained and optimum design conditions are established. Composition and temperature profiles calculated by Beychok for a sour water stripper operating with feed to the top tray and no reflux are shown in **Figure 4-16**.

Wild (1979) adapted the Beychok design procedure to a hand calculator. His sample calculation is of interest in defining typical design and performance parameters for a commercial sour water stripper. The design is for a stripper to process 100,000 lb/hr of sour water containing 0.73 wt% H<sub>2</sub>S and 0.556 wt% NH<sub>3</sub> and produce water containing 5 ppm and 20 ppm of H<sub>2</sub>S and NH<sub>3</sub>, respectively. The initial design assumptions are a stripping steam rate at the top of the column of 10.2% of the feed (10,200 lb/hr), a column top pressure of 30 psia, and a pressure drop per theoretical tray of 0.45 psia. Results of the calculation, which are reported to compare favorably with the results from a commercial computer program, are summarized in **Table 4-10**.

The effect of the quantity of stripping steam and the number of theoretical trays on the amount of ammonia remaining in the bottoms liquid of a typical stripper is shown in **Figure 4-17** (Gantz, 1975). For comparison, actual data from a refinery installation (questionnaire No. 34 of the API survey) are included on the chart. The actual column, which contains 15 ft. of 3-in. raschig rings, appears to behave as predicted for a 4.7 theoretical tray column, indicating a height equivalent to a theoretical tray (HETP) of 3.2 ft. In most cases studied, HETPs for 3-in. raschig rings averaged 2.5 to 3.5 ft and overall tray efficiencies ranged between 30 and 50% (Gantz, 1975).

The API-sponsored survey of more than 80 sour water stripping operations found that the Beychok calculation model correlates satisfactorily with observed results down to an ammo-



**Figure 4-16.** Calculated composition and temperature profile in sour water stripper. From Beychok (1967). Used with permission from John Wiley & Sons, New York

**Table 4-10**  
**Sour Water Stripper Design Calculations; Input Data and Results**

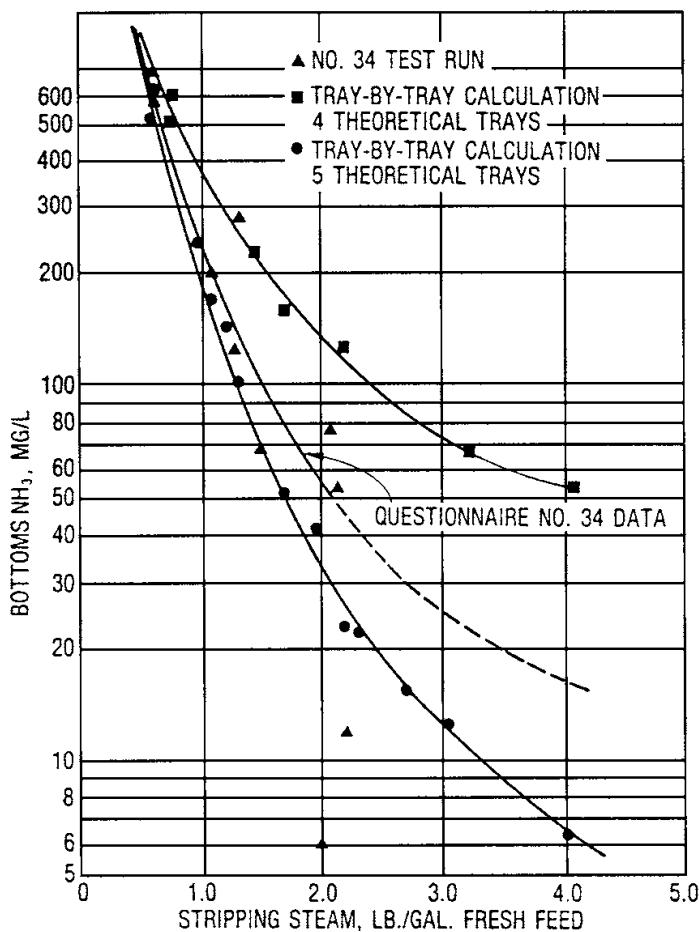
<b>Material Balance Stream</b>	<b>Pounds per hour</b>		
	<b>H<sub>2</sub>O</b>	<b>NH<sub>3</sub></b>	<b>H<sub>2</sub>S</b>
Sour water feed	98,714.00	556.00	730.00
Tower bottoms	98,292.43	1.97	0.49
Overhead vapors	10,200.00	1,740.82	1,451.06
Reflux	9,778.43	1,186.79	721.55
Tail gas	421.57	554.03	729.51
<b>Temperatures, °F</b>			
Feed		199	
Reflux drum		184	
Bottoms		259	
<b>Pressures, psia</b>			
Tower top		30	
Reflux drum		27.2	
Pressure drop per theoretical tray		0.45	
Reboiler		35.00	
Steam rate from reboiler, lb/hr		18,158	
Number of theoretical trays needed		11	
<i>Data of Wild (1979)</i>			

nia concentration in the liquid phase approaching that of the fixed ammonia (Gantz, 1975). Measured H<sub>2</sub>S and NH<sub>3</sub> concentrations in the reflux drum were found to be considerably less than predicted by extrapolation of the van Krevelen et al. (1949) data. Obviously, the accuracy of the design predictions is influenced by the quality of the equilibrium data used.

Both the Beychok (1967) and Wild (1979) design procedures make use of the van Krevelen et al. (1949) vapor-liquid equilibrium correlation; however, the same basic tray-by-tray approach can be used with any consistent set of equilibrium data. The SWEQ correlation (see Figures 4-4, 4-5, 4-6, and 4-7) is believed to be adequate for most preliminary designs; however, the GPSWAT program described by Gerdes et al. (1989) probably represents the most comprehensive and accurate data currently available.

The GPSWAT program is written in standard Fortran 77 and consists of a major program and 17 subroutines. It is set up for five calculation options:

1. Equilibrium flash, with the stream composition, temperature, and pressure specified
2. Bubble point, with the liquid composition and temperature specified
3. Bubble point, with the liquid composition and pressure specified
4. Dew point, with the gas composition and temperature specified
5. Dew point, with the gas composition and temperature specified



**Figure 4-17.** Effect of stripping steam and number of trays on sour water stripper performance. *From Gantz (1975). Reproduced with permission from Hydrocarbon Processing*

In each case, the unspecified temperature, pressure, and composition will be calculated. The pH can also be calculated, or a specified pH can be imposed on the calculation in which case the required amount of caustic will be calculated. The GPSWAT model is useful in predicting the composition of sour water that will result from a high pressure gas/water contact or in designing a sour water stripping system using either manual or computerized column design techniques.

### Plant Operations

The sour water stripper system represents a very simple separation process, which generally operates in a predictable and straightforward manner. The three main problems encountered in many installations are: (1) the presence of fixed ammonia, (2) the presence of phenols, and (3) corrosion.

Ammonia is fixed, so it is not readily vaporized in the stripper, by the presence of non-volatile or strong acids in the feed stream. The acids may be weak (e.g., benzoic acid) or strong (e.g., hydrochloric acid). One source of acid is the oxidation of sulfur compounds in the sour water to form, for example, thiosulfuric acid. This source can be minimized by preventing contact of the sour water with air at any point in its gathering and processing.

Fixed ammonia can be released during stripping by the addition of caustic soda. A study of caustic addition by Bomberger and Smith (1977) indicates that the addition of caustic does not interfere with hydrogen sulfide removal provided the caustic is added in an amount equivalent (on a molar basis) to the fixed ammonia in solution. They conclude that it is more efficient to add the caustic at the top of the column with the feed stream than to add it lower in the column in practice, an excess of caustic is added near the bottom to avoid interference with hydrogen sulfide stripping.

One problem with phenol in the sour water is that a column designed specifically to remove a high percentage of the ammonia and hydrogen sulfide is capable of removing only a relatively small fraction of the phenol. This is due to the low volatility of phenol, not to a low tray efficiency for phenol removal. Won (1982) studied the individual tray efficiencies for ammonia, hydrogen sulfide, hydrogen cyanide, and phenol in sour water strippers and found that ammonia and phenol have relatively high tray efficiencies (about 70%) while hydrogen sulfide, hydrogen cyanide, and a phenolic mixture have low efficiencies (about 20 to 40%). He used commercial column performance data published by the API which generally showed that 8- to 10-tray (actual) columns removed only about one-half the phenol when operated at steam rates of 1.0 to 2.7 lb/gal. If this level of phenol removal is not adequate, the column can be designed specifically for phenol removal, or a phenol extraction system can be installed to treat the sour water feed before it enters the stripper. The latter approach is generally preferred if significant amounts of phenol are present.

Sour water strippers are generally constructed of carbon steel and only minor corrosion is reported in the tower, trays, and feed-to-bottoms heat exchangers (Gantz, 1975). Materials experience and corrosion problems in sour water strippers are discussed in two API reports (1974, 1976). Significant corrosion has been encountered in the overhead systems of refluxed towers when the overhead systems were constructed of carbon steel. The API reports indicate that titanium is very resistant to corrosion in such situations.

## Ammonium Salt Production

### *The Direct Process*

This process, which was proposed by Brunck (1903), is designed to eliminate the necessity of recovering ammonia from aqueous solutions before its conversion to ammonium sulfate. The hot gas leaving the retorts or coke-ovens is kept at a temperature above its water dew point and passed directly through concentrated sulfuric acid. During absorption of the ammonia, an appreciable portion of the tar is also removed from the gas; this results not only in serious contamination of the ammonium sulfate, but also in acid degradation and contamination of tar. In addition, ammonium chloride contained in the gas is decomposed by the concentrated sulfuric acid, and the hydrogen chloride evolved causes extremely severe corrosion of the equipment. Some of the difficulties of the process can be alleviated by installation of very elaborate tar-separation systems; others, however, have proved to be almost insurmountable, and, as a result, the process has only been used in a few installations. The relative merits of the process as compared with the indirect and semi-direct methods are discussed in some detail by Ohnesorge (1910, 1923).

### *The Indirect and Semi-direct Processes*

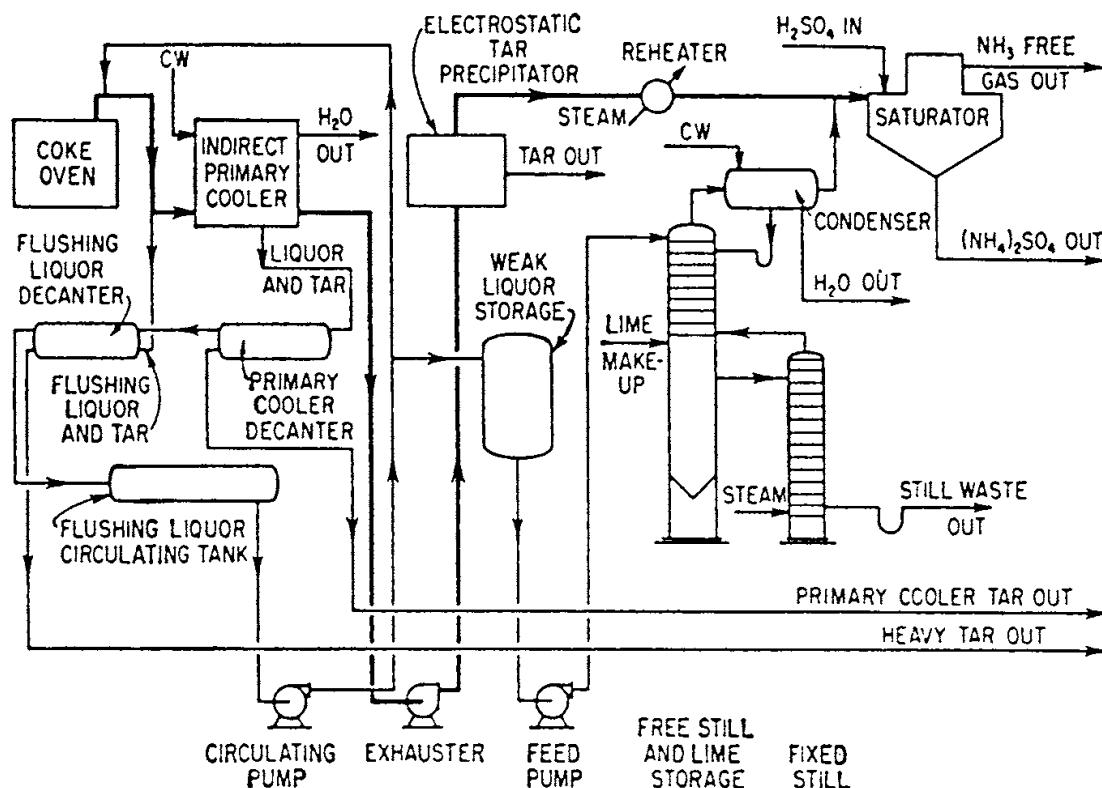
The indirect process requires that the ammonia in the gas first be removed by a water wash operation as described in the previous section entitled "Coke-Oven Gas Processing."

The stripper overhead vapor from this process is then passed through a "saturator" containing sulfuric acid to produce ammonium sulfate crystals.

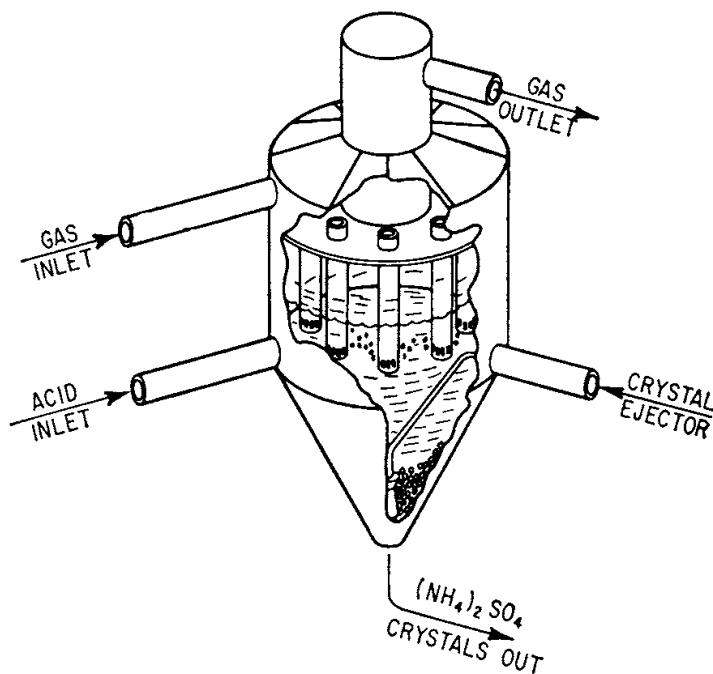
The semi-direct process, which was developed by the Koppers Company, Inc. (1907) and is now licensed by ICF Kaiser Engineers, is a combination of the direct and indirect processes. A schematic flow diagram is shown in **Figure 4-18**. Gas evolved in the coke ovens is first treated in a manner similar to that described in the "Coke-Oven Gas Processing" section, steps 1 through 3.

After flowing through the electrostatic tar precipitator and exhauster, the gas flows through a reheater where its temperature is raised above its dew point, usually to about 60°C (180°F). The reheated gas (which may also contain the overhead vapor from an ammonia still) flows to the saturator where the ammonia is removed by reaction with a strong acid, in most cases sulfuric acid. The ammonia-free gas, which still contains most of the originally present weakly acidic gases, passes to the light-oil recovery and desulfurization operations.

Absorption of ammonia in acid (typically sulfuric acid) is carried out in a vessel called the "saturator." A diagrammatic view of a typical unit is shown in **Figure 4-19**. A discussion of different saturator designs is presented by Otto (1949). Saturators are usually lead- or stainless steel-lined, although other materials such as Monel or acid-resistant refractories may also be used. A concentration of approximately 5 to 7% free acid is maintained in the saturator liquid by continuous addition of 60° Bé (77.6%) sulfuric acid. Periodically, usually every 24 hr, the liquid level in the saturator is raised and the free-acid content is increased to 10 to 12%. This is done to dissolve crystals of ammonium sulfate which have accumulated on the vessel walls



**Figure 4-18.** Diagrammatic flow sheet of semi-direct ammonia-removal process.



**Figure 4-19.** Saturator for production of ammonium sulfate.

and in the distributor pipes. The salt crystals formed are continuously removed from the bottom of the saturator by means of a compressed-air ejector. Liquid adhering to the crystals is first removed in a settling tank, then in a centrifuge, and is recycled to the saturator.

In the semidirect process the gas enters the saturator at a temperature of 50° to 60°C (122° to 140°F) which, together with the heat liberated by the reaction, is sufficient to maintain the saturator-bath temperature at approximately 60°C (140°F). Since the gas entering the saturator is unsaturated with water vapor, a considerable amount of water is evaporated from the aqueous acid solution, and the saturator functions in effect as an evaporator. Much higher temperatures—about 100°C (212°F)—are required in saturators operating in conjunction with installations using the indirect process, in which the effluent gases from the ammonia still are saturated with water at 75° to 80°C (167° to 176°F). Thermal equilibria in saturators operating in indirect, direct, and semidirect processes are discussed in detail by Terres and Patscheke (1931). A comprehensive review of ammonium sulfate production from by-product ammonia is given by Hill (1945).

Diammonium phosphate may be obtained by using furnace phosphoric acid in conventional saturators. However, temperature control is somewhat more critical, and Monel is not suitable as a construction material. Production of many other ammonium salts, such as nitrate, bicarbonate, monophosphate, and others, has been proposed, but none of these are being manufactured on a large commercial scale.

The main advantage of the semi-direct process over the indirect process is the fact that less than half the volume of aqueous ammonia solution is produced, and, therefore, the steam requirements for the ammonia distillation and operating costs are appreciably lower. In addition, the process has some flexibility because part of the ammonia can be converted to products other than the ammonium salts of strong acids. Furthermore, first cost and ground-space requirements are less than for installations using the indirect process, and, finally, smaller ammonia losses are incurred.

## Phosam and Phosam-W Processes

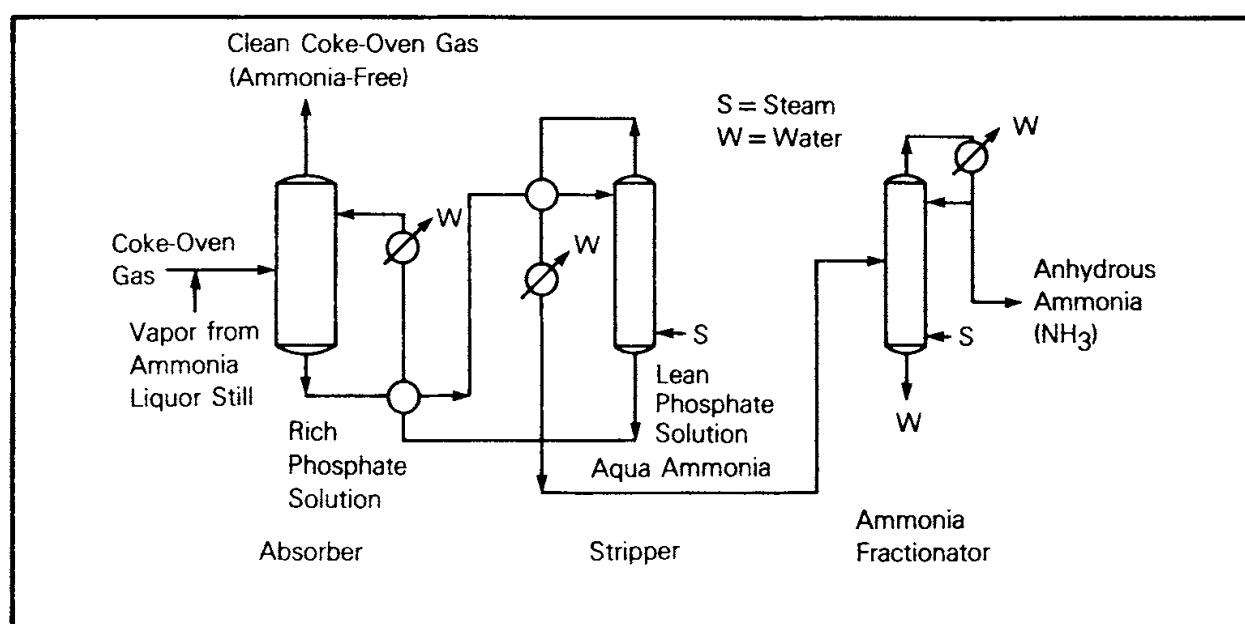
The Phosam technology was initially developed by USX Corporation to remove ammonia from coke-oven gas and recover it as pure anhydrous ammonia. It is called the Phosam process when applied to coke plants (i.e., removal of ammonia from coke-oven gas, removal of ammonia from the overhead vapor stream of an ammonia liquor distillation column, or removal of ammonia from the overhead stream of a deacidifier column ahead of a Claus plant). It is designated as the Phosam-W process when used for any other application (i.e., chemical plants, coal gasification systems, shale oil processing plants, and petroleum refineries). The W in Phosam-W is related to its use for the treatment of sour water (Busa, 1992).

The technology is covered by U.S. Patents 3,024,090, 3,186,795, and 3,985,863 as well as patents in Canada, Germany and, Great Britain. Aristech Chemical Corporation is the proprietor of the Phosam and Phosam-W processes, and USX Engineers and Consultants, Inc. (UEC) has exclusive licensing rights worldwide. Detailed descriptions are given in UEC sales literature and in papers by Rice and Busa (1984, 1985) and Busa and Cole (1986).

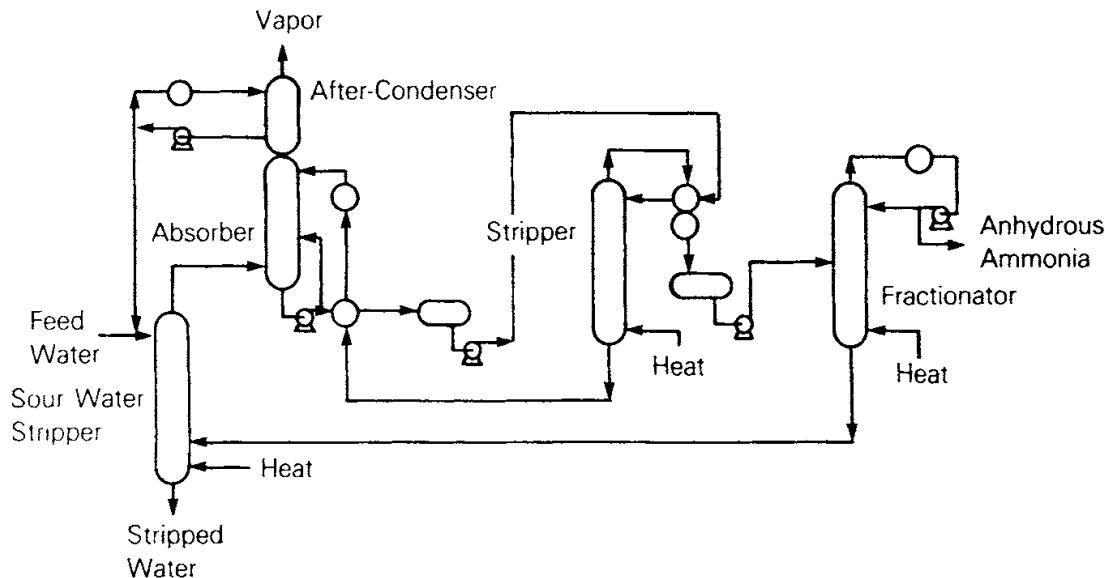
Work on the Phosam Process began in the late 1950s and the first full-scale commercial plant was started up at USS Clairton Works in 1968. By 1994, twenty-four different companies worldwide had installed or licensed the Phosam process, while ten companies had installed or licensed the Phosam-W version.

### Process Description

Typical flow diagrams for the Phosam and Phosam-W processes are given in Figures 4-20 and 4-21. It should be noted that the processes are identified by application, not flow arrangement, and the illustrated diagrams are not the only possible systems for either version. For example, when ammonia is removed from coke-oven gas by water washing and stripping,



**Figure 4-20.** Flow diagram of typical Phosam process in a coke plant. *From USX Engineers and Consultants, Inc. (1991)*



**Figure 4-21.** Flow diagram of Phosam-W process. *From USX Engineers and Consultants, Inc. (1991)*

the Phosam absorber would be installed to scrub ammonia from the stripper overhead vapor as illustrated for the Phosam-W case.

Referring to **Figure 4-20**, which represents a typical Phosam plant, the coke-oven gas (after cooling and cleaning to remove entrained solids, water, and tar) enters the bottom of the absorber where it is contacted countercurrently with an aqueous solution of ammonium phosphate. About 99% of the ammonia is removed from the gas stream in the absorber. The ammonia-free product gas is suitable as feed for a variety of processes to remove hydrogen sulfide and other impurities. The ammonia-rich solution is drawn off the bottom of the absorber for regeneration.

The Phosam absorber generally operates at the pressure and temperature of the coke-oven gas at that point in its circuit. A temperature of about 50°C (122°F) is typical, although effective absorption can be attained at temperatures as high as 100°C (212°F).

Ammonia-rich solution from the bottom of the absorber is pumped through heat exchangers where its temperature is increased by the absorption of heat from stripper off-gas and lean solution streams. It then enters the stripper, which operates at an elevated temperature of about 170° to 200°C (338° to 392°F) and a high pressure—typically 1,300 kPa (190 psig)—to assure separation of the ammonia from the aqueous solution of ammonium phosphates (Rice and Busa, 1984). Heat and stripping vapor may be provided by a reboiler, the direct injection of steam, or a combination of both.

Overhead vapor from the stripper, containing typically about 20% ammonia, 80% water vapor, and a small amount of impurities is condensed in two stages to produce impure aqua ammonia. When anhydrous ammonia is the desired end product, the aqua ammonia is pumped to a fractionator which separates ammonia and water. The fractionator is typically operated at a high enough pressure to permit the ammonia overhead vapor to be condensed

at the temperature of the available cooling water. Part of the liquid ammonia is used as reflux and the balance is taken off as a salable product.

The Phosam-W process shown in **Figure 4-21** differs from the system of **Figure 4-20** primarily in the front-end configuration. Sour water from the refinery or other non-coke-oven operation is processed in a conventional sour water stripper. The stripped water can be reused in the plant or further processed for disposal. The vapor phase, containing, for example, 10% NH<sub>3</sub>, 10% H<sub>2</sub>S and CO<sub>2</sub>, and the balance steam with traces of HCN and volatile organics, is fed into the Phosam absorber. Absorber conditions for this case are approximately 90°–100°C (194°–212°F) and 35–70 kPa (5–10 psig). About 95–99% of the ammonia is removed from the vapor phase passing through the absorber.

Vapor leaving the top of the absorber is next passed through an after-condenser where a small portion of the water vapor is condensed. The resulting small stream of sour water is recycled to the sour water stripper. Rich solution from the absorber is recycled around the bottom of the absorber to maximize its loading with ammonia. The net rich solution product is fed to the regeneration stage which is similar to that of the Phosam process.

### **Process Chemistry**

The process uses a conventional absorption-regeneration cycle in which a thermally unstable compound is formed during absorption and decomposed by an increase in temperature and the presence of stripping vapor during regeneration. The chemistry is simple and can be represented approximately by the conversion of monoammonium phosphate to diammonium phosphate as follows:



In practice, the reactions are not carried to completion in either direction. The mole ratio NH<sub>3</sub>/HPO<sub>4</sub> shifts from the range of 1.2–1.4 in the lean solution to 1.7–2.0 in the rich solution (Rice and Busa, 1984). In effect the dissolved salt has the formula, (NH<sub>4</sub>)<sub>n</sub>H<sub>3-n</sub>PO<sub>4</sub>, where n varies from less than 1.4 in the lean solution to over 1.7 in the rich solution. The concentration of salt in the circulating solution is maintained well below the limit of solubility of the existing salt form at all points in the circuit to avoid the formation of solid salt crystals.

Since phosphoric acid is essentially nonvolatile, thermal decomposition of diammonium phosphate in solution yields only ammonia gas in the vapor phase. The phosphate ion is extremely stable and is not altered in the process; therefore, no blowdown is required and only a small makeup of phosphoric acid is needed to compensate for unavoidable mechanical losses. The small amount of acid gases, acidic organics, and neutral compounds that are co-absorbed with the ammonia are either recycled to the absorber or reacted with caustic soda to prevent corrosion and ammonia product contamination in the fractionator.

### **Performance**

Ammonia produced by the process will readily meet commercial or fertilizer grade specifications (99.5% minimum ammonia content, 0.2–0.5% wt. water, 5 ppm max. oil) for which there is a ready market. The fractionation system has the capability of producing an even purer ammonia when a market exists for such a product.

In plants where the hydrogen sulfide is ultimately converted to elemental sulfur, removal of ammonia from the acid gas stream greatly improves the operation and economics of the sulfur

plant. This is because ammonia tends to form compounds that plug the catalyst beds and extra air is required to completely oxidize any ammonia in the feed gas. The presence of ammonia in the feed to a sulfur plant also requires the use of high efficiency burners to assure the complete destruction of ammonia before all oxygen is consumed by hydrogen sulfide.

### **Capital and Operating Costs**

According to USX Engineers and Consultants, Inc. (1991), a Phosam Process plant is competitive with other available processes for removing ammonia from coke-oven gas, including ammonium sulfate production and ammonia destruction by incineration, and is a more compact system than either of these alternatives. They have provided the data given in **Table 4-11** as an aid to estimating projected operating costs. Data are not provided for Phosam-W installations because they are normally very site specific.

### **Chevron WWT Process**

A process for treating ammonia-containing sour water generated during petroleum refining operations has been developed by the Chevron Research and Technology Company. It is anticipated that the process will also be applicable to the high-ammonia sour water produced in shale oil and tar sands processing plants. In this concept, which is called the Chevron WWT (waste water treatment) process, relatively pure streams of ammonia, acid gas, and stripped water are produced. According to the developer, approximately one new WWT plant per year is licensed; as of mid-1992 approximately 20 plants were operating worldwide. Descriptions of the process are given by Annessen and Gould (1971), Leonard et al. (1984, 1985), Busa and Cole (1986), and, more recently, by Bea and Wardell (1989).

Conventional sour water stripping systems use a single column and produce a vapor stream containing both ammonia and hydrogen sulfide. This mixed vapor stream may be fed to a Phosam unit, passed through a strong acid ammonia absorber, fed to a sulfur recovery unit, or incinerated. The WWT process also accomplishes sour water stripping, but uses a two-column stripping system that separates the ammonia and acid gases.

**Table 4-11**  
**Operating Requirements for Phosam Process Plants**

<b>Chemicals and Utilities</b>	<b>Per kg NH<sub>3</sub></b>
H <sub>3</sub> PO <sub>4</sub> Makeup (as 100%)	0.0075 kg
NaOH (as 100%)	0.01 kg
Steam (250 psig)	10–11 kg
Electricity	0.22 kW
Cooling Water (per °C temp rise)	3.5–5.0 m <sup>3</sup>
<b>Labor for Operation and Analytical Control</b>	
Men per shift	less than 2

*Data provided by USX Engineers and Consultants, Inc. (1991)*

The production of separate ammonia-rich and acid gas-rich streams offers the following advantages:

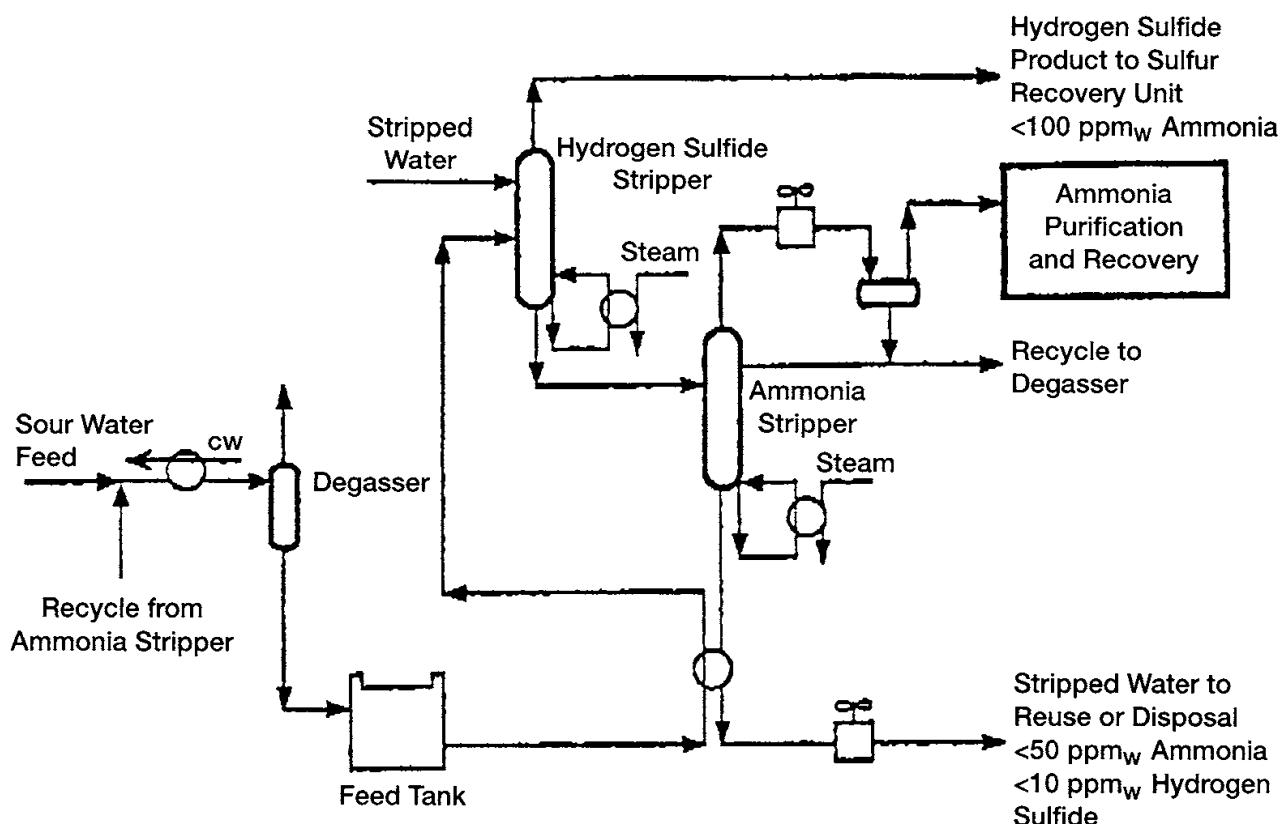
1. Removal of ammonia from feed to a conventional sulfur recovery plant reduces sulfur plant operating problems and improves economics.
2. Ammonia-free hydrogen sulfide can be used as feed to a sulfuric acid plant.
3. The ammonia stream can be converted to a salable byproduct or burned without producing  $\text{SO}_2$ .

### ***Process Description***

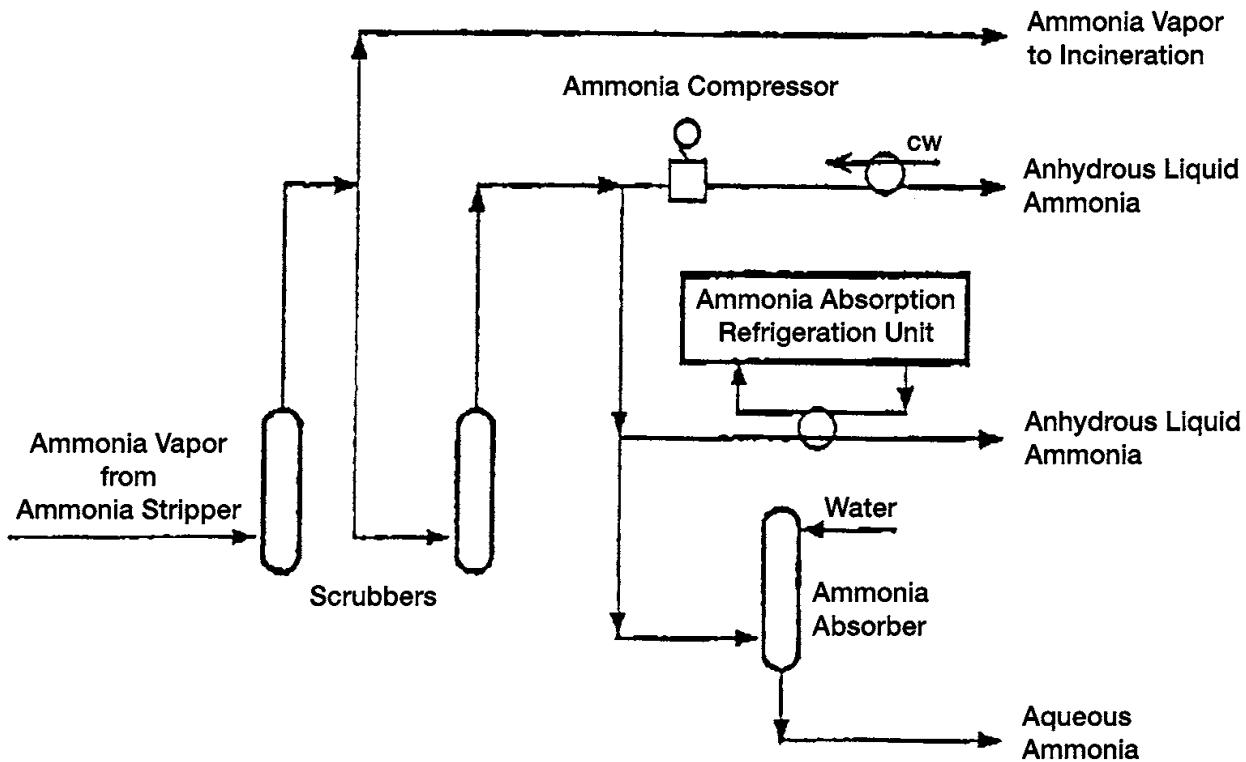
As shown in **Figures 4-22 and 4-23**, the Chevron WWT process incorporates the following steps:

1. Degassing and feed storage
2. Acid gas stripping
3. Ammonia stripping
4. Ammonia purification and recovery

Plants have been designed to handle sour water feeds containing 0.3 to 6.0 wt%  $\text{NH}_3$  and 0.3 to 10 wt%  $\text{H}_2\text{S}$  and can be designed to handle even higher concentrations of these two ingredients as well as high levels of  $\text{CO}_2$  (Bea et al., 1989). When large volumes of dilute sour water are to be processed, it is often economical to use a preconcentrator ahead of the



**Figure 4-22.** Flow diagram of Chevron WWT process. *From Bea et al. (1989)*



**Figure 4-23.** Chevron WWT process; ammonia recovery options. *From Bea et al. (1989)*

system illustrated in **Figure 4-22**. The preconcentrator consists of a distillation column, which produces a bottom product of stripped water of equal quality to that produced in the WWT plant, and an overhead product, which contains essentially all the ammonia and hydrogen sulfide contained in the original feed, but in a more concentrated form. This concentrated sour water then serves as feed to the WWT plant.

In a typical WWT plant, as illustrated in **Figure 4-22**, the sour water feed is diluted with a recycle stream of condensate from the ammonia stripper; cooled and fed to a degassing unit, which removes dissolved inert gases; and then directed to a feed storage tank. The recycle condensate contains a significant concentration of ammonia and this helps hold acid gases in solution in the degassing unit and feed storage system. The feed storage tank smooths out fluctuations in sour water feed rate and composition and, in addition, provides time for liquid hydrocarbons and solid particles to separate from the aqueous phase.

Sour water from the feed storage tank is pumped at a constant rate through a heat exchanger, which raises its temperature while cooling water from the ammonia stripper, and then fed into the H<sub>2</sub>S stripper. The H<sub>2</sub>S stripper is a distillation column, operating at a pressure of about 100 psig, with a steam-heated reboiler at the bottom and a flow of stripped water at the top to provide reflux. Overhead vapor from the H<sub>2</sub>S stripper is primarily H<sub>2</sub>S, containing less than 100 ppm NH<sub>3</sub> and saturated with water vapor at the operating temperature of about 100°F. It also contains any CO<sub>2</sub> that is present in the sour water feed.

The liquid aqueous stream from the bottom of the H<sub>2</sub>S stripper, containing essentially all of the NH<sub>3</sub> and some of the H<sub>2</sub>S, flows to the NH<sub>3</sub> stripper, which operates at a lower pressure (typically 50 psig). This stripper is also a reboiled distillation column. Reflux is provided by recycling water condensed from the overhead vapor stream. Part of this condensate is

recycled to the sour water feed to the plant. The vapor stream, which is primarily ammonia saturated with water vapor at the condenser temperature, is sent to the ammonia disposal or recovery system.

The liquid product from the bottom of the ammonia stripper is clean water containing less than 50 ppm NH<sub>3</sub> and less than 10 ppm H<sub>2</sub>S. After passing through a heat exchanger, where it is cooled while heating the sour water feed stream, and after further cooling, if necessary, the water is suitable for reuse in refinery processes or for disposal with other waste waters.

The vapor product from the ammonia stripper can be processed by one of the options shown in **Figure 4-23** for recovery or disposal of ammonia. When the quantity of ammonia produced or the local ammonia market make the production of salable ammonia uneconomical, the ammonia-rich vapor can be incinerated by using it as fuel in a process furnace or boiler. To prevent air pollution it may be necessary to scrub the ammonia-rich stream with water before burning it. This generates a small amount of sour water, which can be recycled to the plant feed stream.

The production of anhydrous or aqueous ammonia requires that the ammonia stripper overhead stream be further purified to remove H<sub>2</sub>S. Two steps of water scrubbing are required for the production of anhydrous ammonia, while the production of aqueous ammonia may be accomplished with either one or two scrubbing steps depending on the desired product purity. Typical product specifications for the Chevron WWT process are given in **Table 4-12**.

### **Process Economics**

Plant investment and utility requirements for a typical 200 gpm sour water WWT plant are given in **Table 4-13**. In many cases the higher investment cost and utility requirements of the ammonia recovery option are more than offset by the byproduct value of the ammonia product. The disposition of the ammonia product from 15 WWT plants was reported by Bea et al. (1989) to be as follows: seven utilized ammonia incineration; four produced ammonia for industry, and agriculture; and four used the ammonia to produce nitric acid.

**Table 4-12**  
**Typical Product Specifications: Chevron WWT Process**

	Hydrogen Sulfide	Stripped Water	Anhydrous** Ammonia	Anhydrous Ammonia	Aqueous Ammonia
Form	Gas	Liquid	Gas	Liquid	Liquid
Ammonia, ppm	<100	<50	—	—	—
Hydrogen Sulfide, ppm	—	<10	<1500	<5	<2
Water, Wt %	0.1	—	1.5	0.4	75*
Temperature, °F	100	100–200*	100	100	100
Pressure, psig	25–100*	—	40	200	35

\*As required

\*\*For incineration

From Bea et al. (1989)

**Table 4-13**  
**Chevron WWT Process Economics; Ammonia Incineration vs. Ammonia Recovery**

	<b>NH<sub>3</sub> Incineration</b>	<b>NH<sub>3</sub> Recovery</b>
Investment, \$	5,100,000	7,100,000
Utilities		
150 psig Steam, lb/hr	45,700	46,100
Cooling Water, gpm	4,600	5,100
Electric Power, kW	74	278
Deraerated Condensate, gpm	20	20
<b>Design Basis</b>		
Sour Water, Rate, gpm	200	
Ammonia		
Wt %	2.5	
Tons/day	30	
Hydrogen Sulfide		
Wt %	5.0	
Tons/day	60	
<i>From Bea et al. (1989)</i>		

Leonard et al. (1984) present a comparison of the economics of using the WWT process to produce ammonia versus the use of a sour water stripper with the product gas going to a sulfur recovery plant. The study is based on plants processing 285 gpm of sour water containing 3.1 wt% ammonia (47 tons/day) and 6.2 wt% H<sub>2</sub>S (94 tons/day). They conclude that the investment cost for a sour water stripper system would be about \$1 million (12%) more than for a WWT system when the extra costs to enable the sulfur and tail gas plants to handle the ammonia are added to the base cost of the SWS system. Operating costs are about \$120,000 per year higher for the WWT system assuming credits of \$2.6 million per year for ammonia sold (at \$165/ton), and \$1.4 million per year for ammonia burned to produce steam in the sulfur plant. Clearly, generalizations cannot be made with regard to the most economical approach; each case requires a site-specific evaluation.

The recent development of Claus plant sulfur furnace burners that can handle acid gas streams containing significant percentages of ammonia can improve the economics of simple sour water stripper-sulfur recovery unit systems. Such burners are available from LD Duiker, B. V. of Holland (1990) and Lurgi Corporation (Fischer and Kriebel, 1988). See Chapter 8 for additional information on sulfur plant burners.

## **USE OF AMMONIA TO REMOVE ACID GASES**

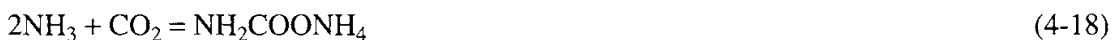
The use of ammonia to remove hydrogen sulfide and carbon dioxide from gas streams has declined in recent years; however, the process is still used to desulfurize coke-oven gas in a number of installations. Ammonia-based hydrogen sulfide removal processes are offered by

the Krupp Wilputte Corporation (1988), Davy-Still Otto (1992), and Mitsubishi Kakoki Kaisha, Ltd. (Fumio, 1986).

Processes have also been developed which use aqueous ammonia solutions to remove carbon dioxide from synthesis gas. The use and relative economics of ammonia-based carbon dioxide processes as of the late 1950s have been described by Mullowney (1957). Ammonia has the advantage for such applications of being essentially unaffected by the presence of carbonyl sulfide, carbon disulfide, hydrogen cyanide, and hydrogen sulfide. However, the process is more complex than those based on nonvolatile alkaline absorbents and is not capable of providing very low levels of carbon dioxide in the product gas. As a result, the process is seldom considered for new commercial applications. A detailed discussion of the history of ammonia use for acid gas removal and descriptions of many processes that are no longer of industrial significance are given in previous editions of this book and in the *Chemistry of Coal Utilization* (Lowry, 1945), including the first and second supplements (Lowry, 1963; Elliott, 1981).

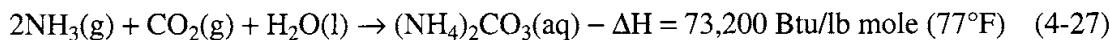
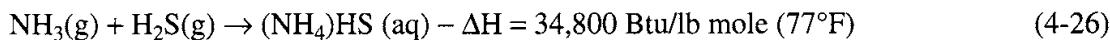
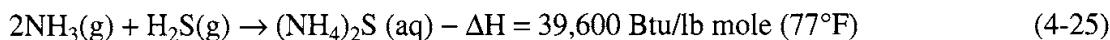
## Basic Chemistry

The reactions occurring in the system comprised of ammonia, hydrogen sulfide, carbon dioxide, and water can be represented by the following equations:



Van Krevelen et al. (1949) have shown that under equilibrium conditions the ionic species  $\text{NH}_4^+$ ,  $\text{HCO}_3^-$ ,  $\text{NH}_2\text{COO}^-$ , and  $\text{CO}_3^{=}$ , as well as undissociated  $\text{NH}_3$ , are present in aqueous solution in measurable quantities. The same authors state that under most conditions  $\text{H}_2\text{S}$  is present in the form of  $\text{HS}^-$  ions. When the pH of the solution is below 12 the sulfide ion concentration is negligible, and even at pH 12 this ionic species amounts to only 0.1% of the fixed hydrogen sulfide.

The following equations present heats of reaction (based on published heats of formation) for the four reactions most predominant in processes using ammonia for the removal of hydrogen sulfide and carbon dioxide from gases:



The absorption of ammonia into water is quite rapid and governed almost entirely by the gas-film resistance; in fact, this is the classical system for chemical engineering studies of gas-film resistance. The rate of absorption of hydrogen sulfide into aqueous ammonia solutions is also rapid although it is dependent upon the ammonia concentration. In the presence of an adequate concentration of ammonia at the interface, it is probable that the rate of this absorption is also governed by the gas-film resistance. On the other hand, absorption of carbon dioxide into water or weak alkaline solutions is considered typical of liquid-film controlled systems, not because its gas-film resistance is any lower than that of  $\text{H}_2\text{S}$  and ammonia, but because its liquid-film resistance is very much greater. The net result is that when gases containing  $\text{H}_2\text{S}$ , ammonia, and  $\text{CO}_2$  are contacted with water, the ammonia and  $\text{H}_2\text{S}$  are absorbed much more rapidly than the  $\text{CO}_2$  and this difference can be accentuated by operating under conditions which reduce the gas-film resistance or increase the liquid-film resistance.

The absorption of  $\text{CO}_2$  into water and dilute alkaline solutions is hindered by a slow chemical reaction which is required to convert the dissolved carbon dioxide molecules into the more reactive ionic species. In effect, the  $\text{CO}_2$  molecules are absorbed until some molecules are removed by the hydration reaction. The efficiency of  $\text{CO}_2$  absorption can, therefore, be improved by turbulence in the liquid film (this aids diffusion of unreacted molecules into the body of the liquid) and by an extended hold-time of liquid in the absorption zone (this provides for the continuous reaction of  $\text{CO}_2$  molecules that do enter the liquid phase). These conditions can be met, for example, by a tall, packed column operating at a relatively high liquid-flow rate or by a liquid-filled column through which bubbles of gas are made to pass.

The hydrogen sulfide and ammonia-absorption rates can be increased by inducing turbulence in the gas phase at the interface, a condition that requires a high relative velocity between gas and liquid. This can be achieved by the use of high-pressure spray nozzles, which produce a much higher relative velocity than can be realized with gravity flow devices. If maximum selectivity for  $\text{H}_2\text{S}$  and ammonia is desired, the use of spray column in combination with relatively short contact-time is indicated.

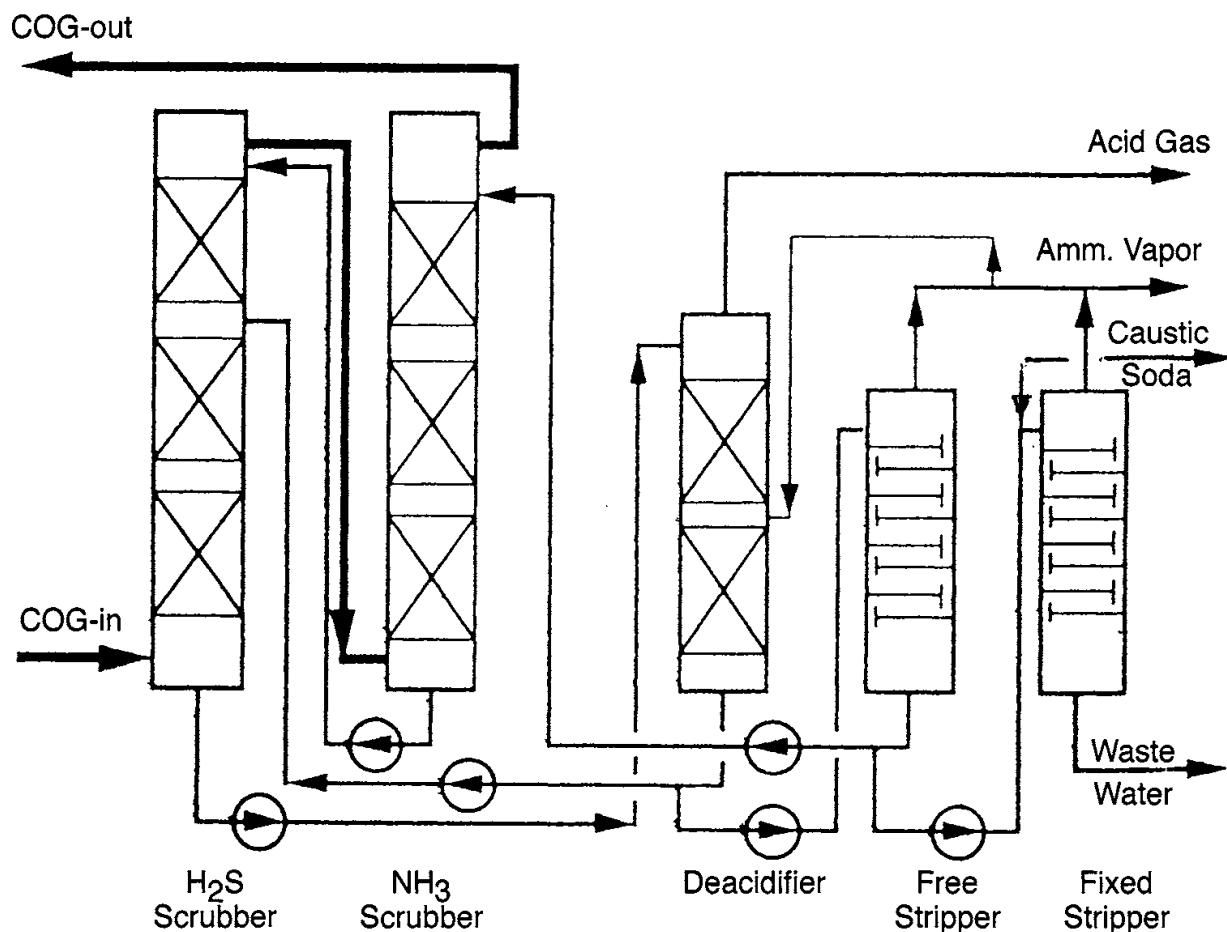
An additional factor that bears on the selectivity of the process is the fact that, once in solution,  $\text{CO}_2$  is an appreciably stronger acid than  $\text{H}_2\text{S}$  and, under equilibrium conditions, the process would actually be expected to be selective for  $\text{CO}_2$ . If the ammonia is added with the wash water, this is indeed possible providing that a sufficiently tall column is used. When the ammonia enters with the feed gas, however, it is absorbed near the bottom of the column and, because very little absorption of  $\text{CO}_2$  can occur in pure water, additional column height will have little effect on the selectivity or on the total amount of acid gases absorbed.

With proper design and operation, most of the H<sub>2</sub>S can be eliminated from the gas in a selective absorber. Removal of H<sub>2</sub>S, CO<sub>2</sub>, and HCN from the ammonia solution in a stripping column located ahead of the ammonia-distillation column permits completely separate processing of the ammonia and the acid gases. This serves to prevent some difficulties in the operation of the saturator or, if strong ammoniacal liquor is produced, results in much higher purity of the crude liquor. Finally, selective absorption of H<sub>2</sub>S yields an acid-gas stream of high H<sub>2</sub>S concentration, which is desirable in the further processing to sulfur or sulfuric acid.

Selective H<sub>2</sub>S-removal processes do not result in complete elimination of H<sub>2</sub>S and, if the treated gas is intended for use as a domestic fuel or in synthesis processes, a final purification step is required. The degree of H<sub>2</sub>S removal depends on several operating variables, but it appears that elimination of about 90% of the H<sub>2</sub>S is the maximum that can be attained economically. Substantial amounts of hydrogen cyanide are also removed in the selective absorber.

## Process Descriptions

A basic flow diagram of the process for removing H<sub>2</sub>S from coke-oven gas using aqueous ammonia solution is shown in **Figure 4-24**. In the process the gas passes through a hydrogen sulfide scrubber and an ammonia scrubber in series. Stripped water is fed to the top of the



**Figure 4-24.** Basic flow diagram for coke-oven gas desulfurization with aqueous ammonia.

ammonia scrubber where it absorbs ammonia from the gas. The resulting ammonia solution is then used as the alkaline absorbent for H<sub>2</sub>S in the hydrogen sulfide absorber. The rich solution from this unit, containing ammonium sulfide in solution, is fed to a deacidifier which decomposes the ammonium sulfide to produce a hydrogen sulfide-rich vapor and an ammonia-rich liquor. Part of the ammonia-rich liquor is fed to an intermediate point in the hydrogen sulfide absorber and the surplus is fed to an ammonia stripper where ammonia vapors are steam stripped from the solution. Caustic soda is normally added to the ammonia stripper or to a separate fixed-ammonia stripper to release ammonia that is present as the salt of a nonvolatile acid. The various processes differ in the details of heat exchange, recycle streams, wash steps, hardware designs, and process conditions; however, the basic operations and chemical reactions are essentially the same.

### ***Still Otto Process***

A more detailed diagram of the hydrogen sulfide and ammonia scrubber systems of the Still Otto process is shown in **Figure 4-25** (Davy/Still Otto, 1992). In this arrangement the ammonia-rich deacidified water is fed to the hydrogen sulfide scrubber near the bottom to minimize absorption of carbon dioxide; while the wash water product from the ammonia scrubber, which contains much less ammonia, is fed to the top of the scrubber to maximize the total amount of H<sub>2</sub>S removed. The liquid flowing down through the H<sub>2</sub>S scrubber is removed, cooled, and returned to the column in at least two separate places to remove the heat of reaction of H<sub>2</sub>S with ammonia and maintain a suitably low temperature for absorption.

After leaving the hydrogen sulfide scrubber, the gas enters the bottom of the ammonia scrubber, which is actually three separate absorption zones in a single vessel. In the first (bottom) zone, the bulk of the ammonia is removed from the gas by countercurrent contact with water from the ammonia stripper and from the third (top) zone. Both of these water sources contain low concentrations of ammonia. Other low-ammonia-concentration waste water streams may be fed into the ammonia absorption zone if available. In the second (middle) zone the gas is contacted with a solution of caustic soda for the purpose of further reducing its hydrogen sulfide content before discharge. The spent caustic soda removed from this zone can still be used to release ammonia from fixed salts in the fixed ammonia stripper by reactions such as



In the third (top) absorption zone the gas is washed with ammonia-free water to remove as much residual ammonia as possible before final release as purified coke-oven gas.

A commercial application of the Carl Still process (predecessor to the Still Otto process) is described by Snook (1977). The plant, which is located at the ARMCO Steel Corporation in Middletown, Ohio, uses a circulating solution containing 2 wt% ammonia, and reduces the hydrogen sulfide content of the coke-oven gas from 350 to 50 grains per 100 scf. At the ARMCO plant the ammonia is removed from the acid gas with the Phosam process, and the remaining acid gases are fed to a sulfuric acid plant.

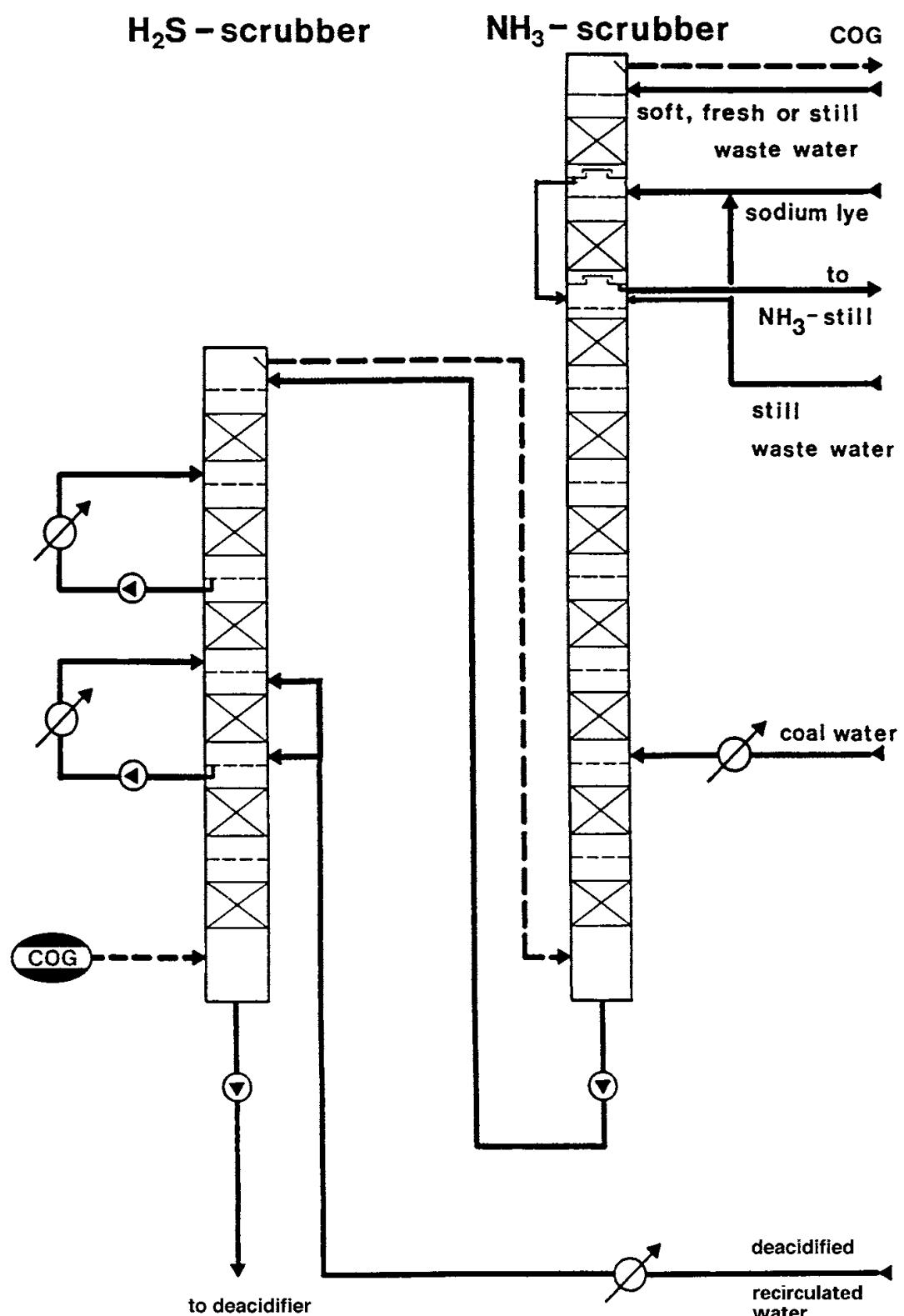


Figure 4-25. Diagram of Still Otto process hydrogen sulfide and ammonia scrubber system. Davy/Still Otto (1992)

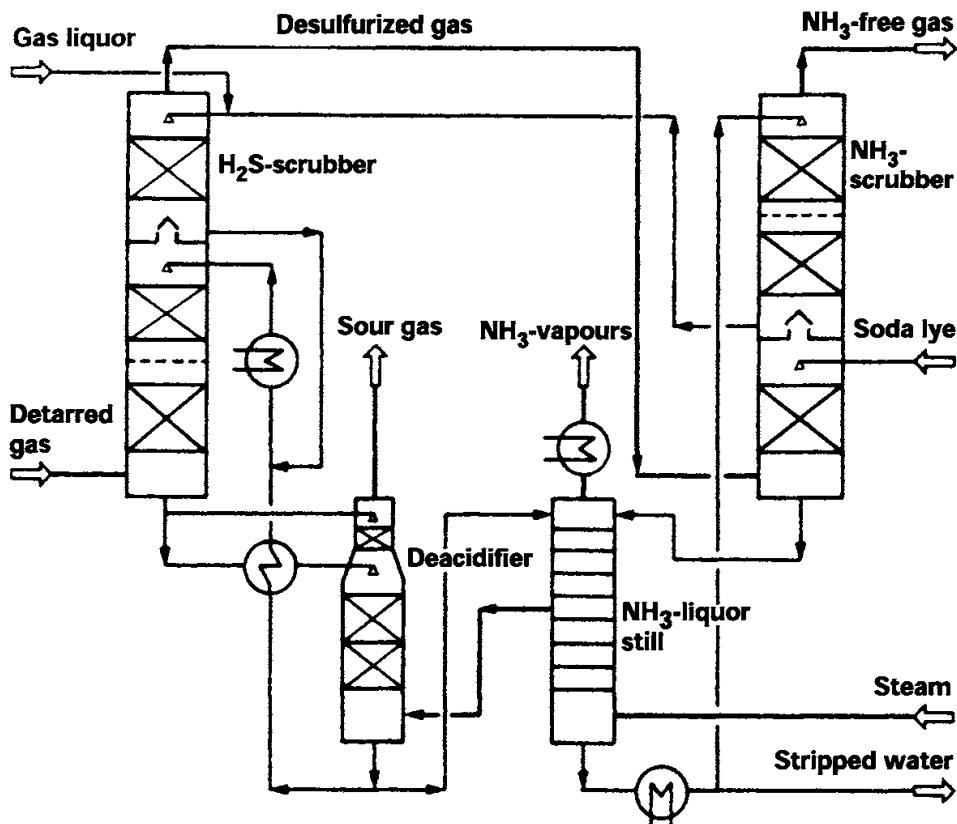
### Krupp Wilputte Process

A flow diagram of the Krupp Wilputte H<sub>2</sub>S/NH<sub>3</sub> circulation scrubbing process is shown in **Figure 4-26** (Krupp Wilputte, 1988). The basic process is similar to those described above; however, there are some differences in the flow arrangement. For example, the caustic soda scrubbing zone is at the bottom of the ammonia scrubber rather than between two water wash zones, and the free-and fixed-ammonia strippers are combined into a single vessel. Another detail shown on the Krupp Wilputte flow diagram is a small contact zone at the top of the deacidifier where the sour gas product is washed with a stream of unheated rich solution from the H<sub>2</sub>S scrubber. This serves to reduce ammonia loss and condense some water from the deacidifier off-gas stream.

### DIAMOX Process

The DIAMOX process, which was developed jointly by Mitsubishi Chemical Industries (MCI) and Mitsubishi Kakoki Kaisha (MKK) in Japan, is described by Hiraoka et al. (1977) and Fumio (1986). The flow arrangement is similar to the basic scheme shown in **Figure 4-24**. It is claimed that the process will remove over 98% of the hydrogen sulfide from coke-oven gas and produce a purified gas stream containing less than 8 grains of hydrogen sulfide per 100 scf.

**Tables 4-14** and **4-15** summarize operating and utility consumption data for a DIAMOX plant. Although there is about seven times as much carbon dioxide as hydrogen sulfide in the



**Figure 4-26.** Krupp Wilputte H<sub>2</sub>S/NH<sub>3</sub>-circulation scrubbing process for desulfurization and ammonia removal. *Krupp Wilputte Corp. (1988)*

COG treated by this plant, the data show that the DIAMOX process selectively removes the hydrogen sulfide. Operating data from the MCI Kurosaki plant in **Table 4-14** show the amount of ammonia, hydrogen sulfide, and carbon dioxide present in the rich and lean liquors as a function of absorption liquor temperature and percent hydrogen sulfide removed from the COG. The data indicate that the lower the operating temperature, the greater the percent of desulfurization. Equal concentrations of hydrogen sulfide and carbon dioxide exist in the rich and lean solutions indicating that hydrogen sulfide is selectively removed over carbon dioxide. Only about 30% of the hydrogen cyanide present in the COG is absorbed during desulfurization and hydrolyzed into ammonia and other by-products.

The acid gas produced contains more than 45 vol% hydrogen sulfide with the balance being carbon dioxide and a small amount of other impurities such as 0.1 vol% hydrogen cyanide, .01 vol% ammonia, and 1.1 vol% aromatics. Consequently, the acid gas is a suitable feed for a typical Claus unit. Operating problems such as plugging and corrosion associated with larger concentrations of these impurities are avoided. As an alternative, the acid gas is a suitable feed for a sulfuric acid plant.

**Table 4-15** shows the utility requirements for the DIAMOX process for two levels of COG desulfurization. The DIAMOX process does not require any chemicals since the absorption liquor is generated from the ammonia present in the COG.

Absorption Liquor Temp., °F	% Removal H <sub>2</sub> S	Solution Analysis, Grains/U.S. Gal.					
		NH <sub>3</sub>		H <sub>2</sub> S		CO <sub>2</sub>	
		Rich	Lean	Rich	Lean	Rich	Lean
90	96.2	473	473	118	12.3	117	2.3
98	91.1	436	417	108	14.6	123	2.3
104	86.0	418	386	102	16.4	106	5.2

*Data from Hiraoka (1977)*

<b>Table 4-15</b> Utilities for DIAMOX Process for Two COG Desulfurization Levels (Basis: 500 grains H <sub>2</sub> S/100 SCF at inlet, 90 MMSCFD capacity)			
Utility	H <sub>2</sub> S at Absorber Outlet	8 Grains/100 SCF	30 Grains/100 SCF
L.P. Steam, Lb/Hr		34,180	20,950
Cooling Water, GPM		2,910	1,590
Boiler Water, GPM		7	33
Electric Power, kW		1,000	570

*Data from Hiraoka (1977)*

## Design and Operation

A simulation model for an ammonia-based coke-oven gas desulfurization plant is described by Bloem et al. (1990). The model was developed within the capabilities of Aspen-Plus, a widely used software package for chemical process flowsheet simulation. The two scrubbers were simulated on the basis of six theoretical stages for the hydrogen sulfide absorber and five stages for each of the two ammonia scrubbers. All important chemical reactions were included and equilibrium assumed. The difference in the absorption rates of carbon dioxide and hydrogen sulfide was corrected by adjusting the vaporization efficiency of carbon dioxide. The model was verified and adjusted on the basis of experimental data. It has been used to optimize the performance of a large coke-oven gas desulfurization plant and reduce sulfur emissions.

Corrosion problems in ammonia-based desulfurization plants are confined primarily to the elevated temperature zones, and are aggravated by the presence of HCN in solution and by the use of more concentrated ammonia (and acid gas) solutions. According to Massey and Dunlap (1975), the absorber and most heat exchangers are constructed of aluminum-killed carbon steel. Commercially pure aluminum is used for the deactivator vessel with the internals fabricated out of Haveg reinforced phenolic resin. Hastelloy is used for steam spargers, hot-solution circulation pumps, and high-temperature heat exchangers. Ammonia stripping columns are typically fabricated out of cast iron. Ceramics can be used for accessories with solutions containing high concentrations of ammonia and HCN.

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