Chapter VI. GAS PURIFICATION

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GAS PURIFICATION

Purification of gas emerging from gasifiers and shift converters is an essential part of the pipeline gas production plant, not only from a pollution point of view, but also toward achieving a high caloric value gas required for pipeline quality.

1. Gas Purification Processes

The processes developed to accomplish gas purification vary from simple, once-through-wash operations to complex multiple-step recycle systems. In many cases, the process complexities arise from the need for recovery of the impurity or reuse of the materials employed to remove it.

The primary operation of the gas purification processes generally falls into one of the following three categories:

(a) Absorption into a liquid.

(b) Chemical conversion to another compound.

(c) Adsorption on solids.

As the background for specific process description, a short discussion of the three unit operations listed above is presented.

1.1 Absorption

Absorption is probably the most commonly used gas purification technique in a great number of processes.

The great majority of absorbers used for this purpose are packed, spray and plate towers. The type of absorbers are interchangeable to a considerable extent with some modification, but certain specific conditions may favor one over another.

The packed tower is considered as more flexible and reliable equipment than others, especially recommended for the following cases; corrosive service, liquid with a tendency to form, high liquid/gas ratio, and low pressure drop desired.

The packing materials commonly used in packed towers are Raschig rings, ceramic saddles and wood grids.

Plate columns are frequently more economical because a higher gas velocity can usually be tolerated and therefore a column of smaller diameter is required. When clean, noncorrosive, nonforming liquid is used under low liquid flow-rate, plate columns are employed.

In order to overcome some of the limiations of simple bubble-cap trays and perforated trays, different types of trays have been developed including Turbogrid, Uniflux, float valve, Flexitray, Kittel plate and shed or shower trays.

Another type of absorber is a spray contactor. This equipment is especially recommended where pressure drop is a major consideration and where solid particles are present in the treated gas.

Since the type of liquid used as the absorbent affects the absorber operation considerably, this must be considered carefully. A number of absorbents are considered in purifying gas from gasification of coal. Natural gas is usually purified by the amine absorber followed by the iron sponge. The hot-potassium carbonate has been recently used commercially for successful absorption.

The iron sponge process which is an absorption process falls into the category (c).

Monoethanol amine solution is preferred over potassium carbonate solution for removal of hydrogen sulfide. However, from the point of heat requirement and flexibility of operation, hot potassium carbonate processes are more economical compared to the amine processes for removal of CO_2.

Combination of various processes with different absorbents will be considered. The object of this phase of study is to determine which of the various schemes proposed is the best for removal of both carbon dioxide and sulfur compounds from the economic point of view.

1.2 Chemical conversion to another compound

Since hydrogen sulfide and other organic sulfur are objectionable not only from legal restriction placed on domestically used gas but also from severe catalyst poisoning of the methanation reaction in the next phase,they must be removed nearly completely.

Dry processes for the removal of hydrogen sulfide and other sulfur compounds such as mercaptans, carbon oxysulfide, carbon disulfide and thiophene from gases by oxidation can be classified into the following two categories:

(a) Oxidation to sulfur

(b) Oxidation to oxides of sulfur

Some of the first type are iron oxide process, activated carbon process and Claus-Chance process. A few examples of the second type are the Katasulf process in which H_2S and a portion of the organic sulfur are oxidized catalytically to SO_2, the North Thames

Gas Board process in which organic sulfur compounds are catalytically converted to SO_2, and the Iron Soda process in which organic sulfur compounds are converted to SO_2 and SO_3.

Iron oxide does not react with organic sulfur compounds such as carbonyl sulfide, carbon disulfide, mercaptans and thiophene at ordinary operation temperatures. Because the concentration of organic sulfur compounds in manufactured gases is always appreciably lower than that of hydrogen sulfide and also because of the less objectionable odor and lower toxicity of these compounds, the removal of organic sulfur is usually of no particular concern.

Practically all legal restrictions for the sulfur content of gas refer to hydrogen sulfide and no limits are usually set for organic-sulfur content.

In spite of the shortcomings of iron oxide, i.e., its ineffectiveness for organic sulfur removal and the poor quality of the sulfur produced, the iron oxide process is widely used because of its capability of satisfying the most stringent H_2S-content requirement of domestically used gas.

This process was installed in Europe around the middle of the nineteenth century. Although it has a long history in practice, there is no theoretical procedure for designing the process.

The activated carbon process, which was developed by I.G. Farbenindustrie during the twenties, takes advantage of the catalytic action of activated carbon in promoting the oxidation of H_2S to elemental sulfur at ordinary temperature.

The rate of reaction of H_2S and oxygen in the presence of activated carbon is known to be much faster than that of the reaction of H_2S and iron oxide.

A higher space velocity for the latter process can be selected than that for the former process. The advantage is that the sulfur produced is of excellent quality, being almost entirely pure under favorable circumstances.

The operation of the demonstration plant by the Bureau of Mines at Louisiana, Mo., where a combination of iron sponge to remove the H_2S and activated carbon to remove the organic sulfur was used, indicates that the iron-sponge method is a feasible way to get the total sulfur content down below the 0.01 grain per hundred cubic feet level [16].

1.3 Adsorption

By adsorption operation, as applied in the gas purification processes, the impurities or organic compounds are removed from the treated gas by concentration on the surface of solid materials. The principles of this operation and the nature of typical adsorbent used are found in a number of standard texts.[1,3,4,57]

Fixed beds are most frequently used for gas purification and dehydration and these are practically designed by rule-of- thumb techniques.

For such installations, the theoretical treatment for gas absorption in a packed tower can be likened to the adsorption operation. But unlike the countercurrent gas absorption process, the unsteady-state condition greatly complicates the mathematical analysis for design of fixed-bed adsorber.

Although many kinds of adsorbents are used in pratical processes, such as gas-purification and dehydration, they are mainly based on some form of silica, alumina, or carbon. One type of silicate adsorbent , the molecular sieves, also to have industrial importance. The silica and alumina-base adsorbents are primarily used for dehydration.

Activated carbon has the specific ability of absorbing organic vapors and is therefore very important for this study. The operation of the removal of organic vapor from air by activated carbon is probably second in importance to dehydration as an industrial application of adsorption

Active carbon has many applications in the adsorption of organic compounds because of its selectivity for them. It is often used in commercial installations to remove benzol and other organic impurities from manufactured and coke-oven gas. It is necessary to remove benzol from the gas not only for its recovery as a valuable by-product but also for improving the gas properties. Benzol has a tendency to burn with a sooty flame.

Whether the process uses the activated carbon or other adsorbent the basic concepts in the design are similar. The gas must be passed through the bed of the adsorbent material at a velocity which will give the required mass transfer but within an allowable pressure drop set by the process requirement. After the bed is fully loaded with the materials removed from the gas, the adsorbent must either be discarded or regenerated.

The detail discussion of this process will be presented in the later section.

1.4 Classification of Absorption Processes

The typical cases presented in this report can be classified into:

(a) Absorption by hot potassium carbonate solution

(b) Absorption by MEA solution

(c) Absorption by the combination of (a) and (b)

In addition, there are other solutions that can be used, such as DEA, H_2O, Caustic solution, Ammoniacal solution, etc.

In each case, these processes are followed by an Activated Carbon Process for removal of organic compounds. If the concentration of H_2S at outlet of an absorber is higher than 0.01 grain/100 SCF it is further purified by an Iron Oxide Process.

The specified compositions of the gas fed to the absorber for the cases considered here are shown in Table VI-1.

Table IV-1 Flow Rate and Composition of Feed Gases

	component	Flow Rate [lb-mole/hr.]	Composition [mole %]
	CO	3180	6.8
Case I	H_2O	1870	4.0
	H_2	11020	23.5
T = 460°F	CO_2	5120	11.0
	CH_4	24670	52.8
	C_6H_6	120	0.3
P = 1050 psi	N_2	720	1.5
	H_2S	50	0.1
	Total	46750	100.0
	CO	6450	7.0
Case II	H_2O	30240	32.7
	H_2	20580	22.3
T = 710°F	CO_2	14330	15.5
	CH_4	19720	21.3
P = 1090 psi	C_6H_6	140	0.3
	N_2	720	0.6
	H_2S	230	0.3
	Total	92410	100.0
	CO	12420	7.5
Case III	H_2O	65450	39.9
	H_2	38650	23.5
	CO_2	31430	19.2
T = 560°F	CH_4	14590	8.9
	C_6H_6	200	0.1
P = 1050 psi	N_2	780	0.5
	H_2S	590	0.4
	Total	164110	100.0

2. Flow System of Hot Potash And Amine Processes for Absorption of CO_2 and H_2S

2.1 Hot Potash Process

A schematic flow diagram of the hot potash process is shown in Figure VI-1. Feed gas is cooled to an optimum temperature before it enters the bottom of the absorber. Steam is passed upward through the absorber, countercurrent to a stream of the hot potash solution.

The absorber is operated at a high pressure while the regenerator is operated at a low pressure. The spent solution from the bottom of the absorber is depressurized in an energy recovery system, which may be a conventional turbine-motor-pump assembly or a flow-work exchanger. The energy recovery system will be discussed later in detail. The work recovered from the spent solution stream is used to make up a great portion of the work required to pressurize the regenerated solution before it enters into the top of the absorber.

The spent solution leaving the energy recovery system is further depressurized in a flash drum. Part of the absorbed CO_2 and H_2S in the liquid are desorbed in the flash drum. Flash drums are advantageous because flash desorption is the most economic method of regeneration.

The remaining CO_2 and H_2S in the partially regenerated solution are then stripped in the regenerator. Open steam is used because it provides higher driving force for the desorption and there is no problem of K_2CO_3 loss through its vapor pressure.

2.2 Amine Process

The amine process employs an amine solution as the solvent for the absorption of CO_2 and H_2S. The flow diagram of this process is shown

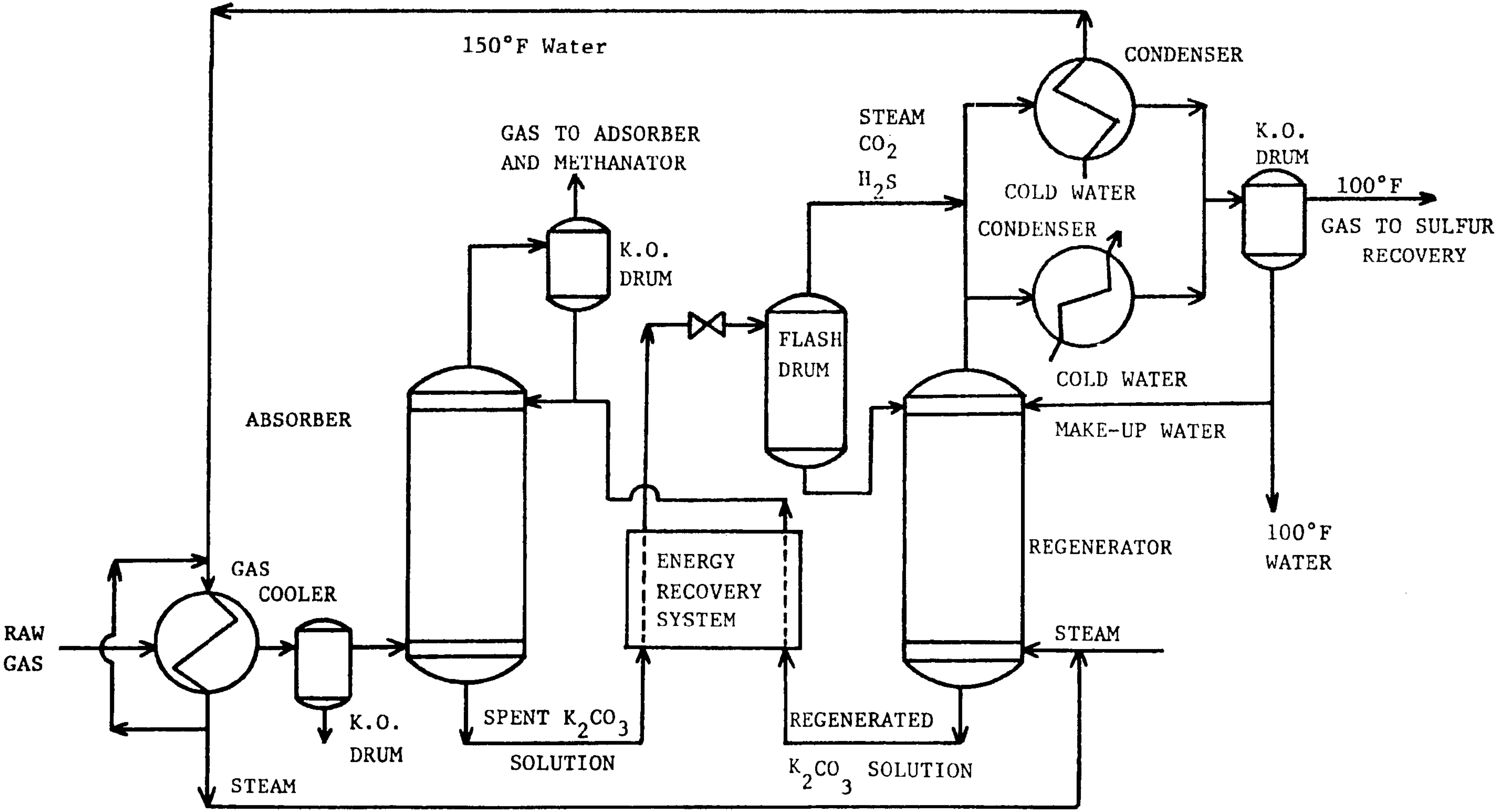


Figure VI-1. Flow Diagram of the Hot Potash Process for Absorption of CO_2 And H_2S

in Figure VI-2. In general, the basic flow diagram of the amine process is similar to that of the hot potash process. Some modifications are included. A water wash is added at the top of the absorber to recover the entrained amine in the purified gas and a draw-off tray is provided to present build-up of water in the system. Because the regenerator is operated at a temperature higher than that of the absorber, heat exchangers are needed for circulating solution streams. The spent solution from the absorber is heated in a solution heat exchanger by the regenerated solution from the reboiler. The regenerated solution is cooled with water in a solution cooler before entering into the top of the abosrber. In order to prevent amine loss in the regenerator and the flash drum, reflux must be returned to the system. Therefore, a reboiler is used. The reboiler is heated by the hot feed gas and the steam supplied for regeneration.

2.3 H_2S and Benzene Removal Processes

A schematic flow diagram is shown in Figure VI-3. If the gas does not meet pipeline gas specifications on H_2S content, the Iron Oxide Process should be used to remove it. The iron oxide granula are discarded and replaced periodically with fresh material when activity is lost. The towers are operated parallel at a temperature below 100°F. To achieve a semi-continuous and smooth operation, standby towers are provided.

The final purification before methanation should be carried out by an Activated Carbon Process because the gas leaving the absorber contains almost the same amount of benzene as that when it enters. The next step, activated carbon adsorption, removes most of the bezene which is recovered as a by-product. Multiple activated carbon towers are used, running in parallel, each operating on a certain hour cycle, a part of the hour for adsorption and the rest for regeneration. The temperature in the towers is at 100°F for adsorption and at 212°F for regeneration. The gas released during depressurization is vented to a surge drum, recompressed, and returned to the main gas stream.

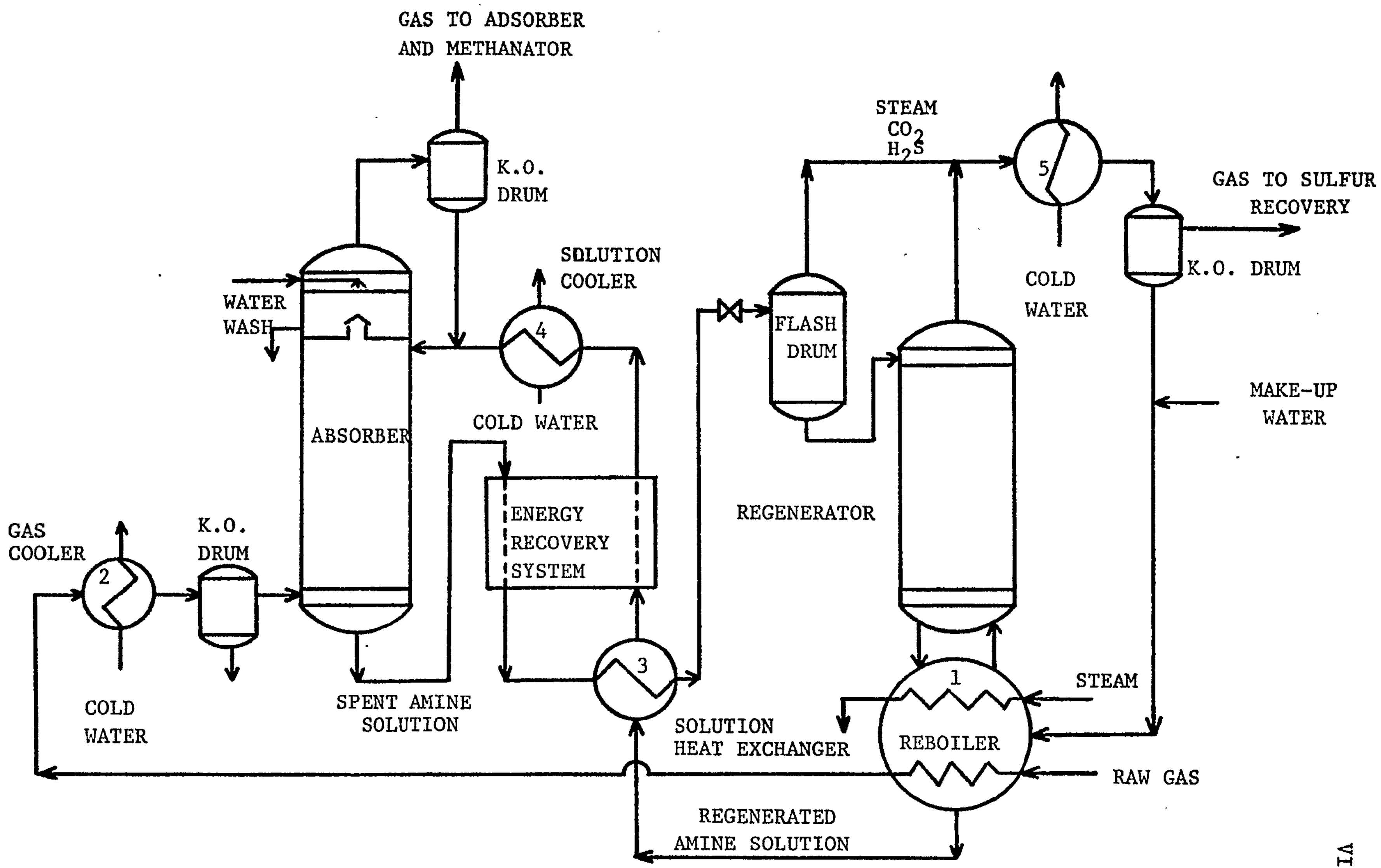


Figure VI-2. Flow Diagram of the Amine Process for Absorption of CO_2 And H_2S

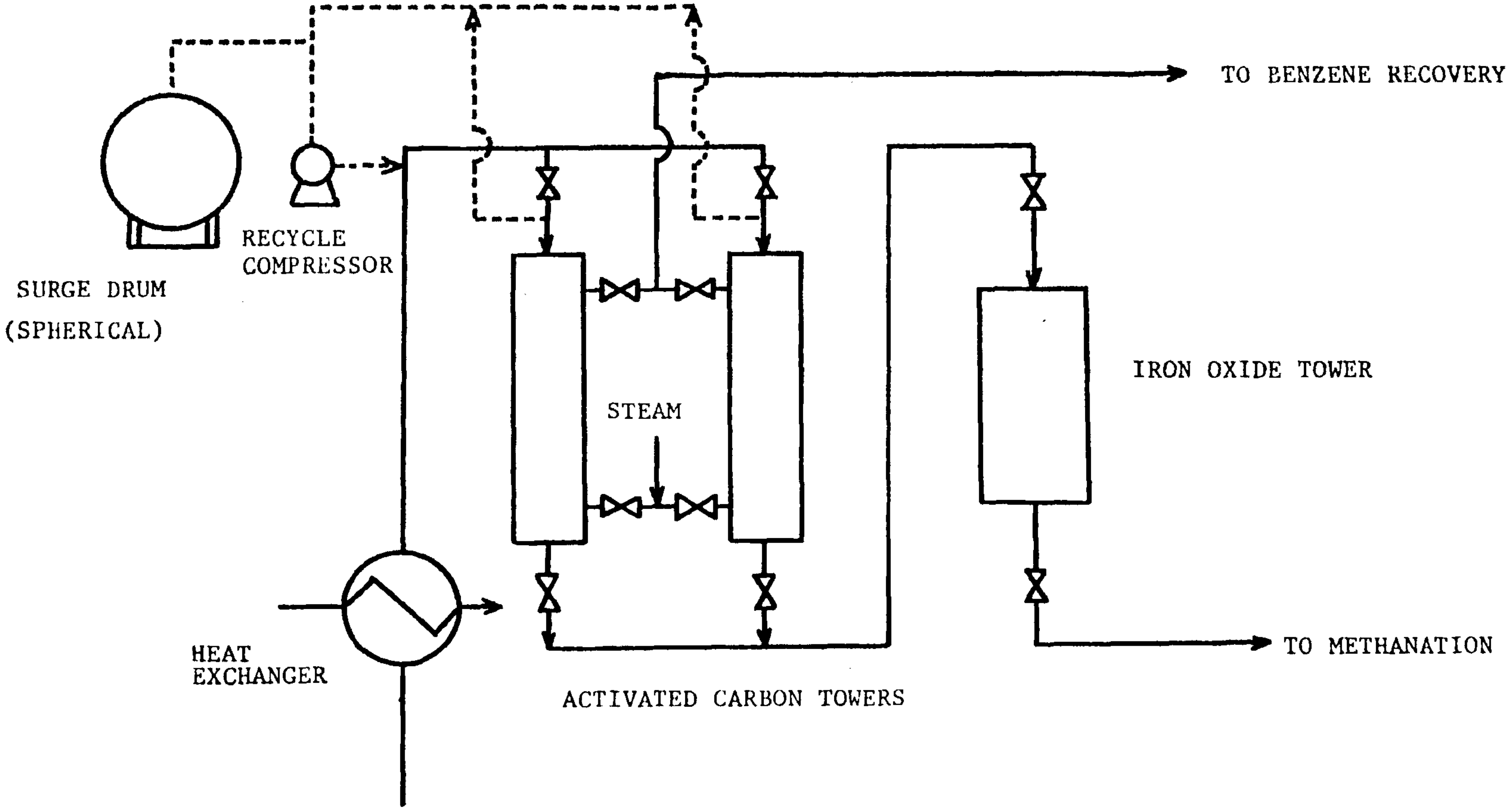


Figure VI-3 Flow Diagram of Adsorption Processes for the Removal of Benzene and Hydrogene Sulfide

3. Basic Thermodynamic Data

3.1 Hot Potash Process

i. Equilibrium and solubility data

(a) Equilibrium relation

Benson, Field, Tosh and Haynes [14] made an equilibrium study of potassium carbonate-potassium bicarbonate-carbon dioxide-water system using solutions of 20, 30, and 40 percent equivalent potassium carbonate concentrations, at temperatures between 158°F and 284°F.

The equilibrium vapor pressure of CO_2 over a solution containing the equivalent of 40 percent potassium carbonate is presented in Fig.VI-4. The abscissa represents the conversion of K_2CO_3 to $KHCO_3$ and covers the range from 10% to 90%. This range is sufficiently wide to cover any actual operating conditions.

The equilibrium partial pressure of CO_2 in various concentrations of K_2CO_3 can be expressed in terms of temperature of the solution, conversion of K_2CO_3 to $KHCO_3$ as,

$$P_{CO_2}^{*} = \frac{X^2}{1 - X} \cdot \frac{1}{S} \cdot \frac{Y_S}{1 - Y_S} \cdot \frac{0.003095}{\exp.\left[6.9\, Y_S - (t_{FL}/150)\right]} \qquad \text{(VI-1)}$$

where

$$S = \frac{1000\,(1 + Y_S)}{\left[18 + (120 + 44X)\, Y_L\right] 2380 \exp\left[(7.1 \times 10^{-3}(t_{FL} - 32) - 1600\right]}$$

$$Y_L = \frac{1}{1 + 7.67\left[(1 - Y_S)/Y_S\right]}$$

Published data for the equilibrium vapor pressure of H_2S over hot potash solution have been very scanty. Buck and Leitch [25] reported

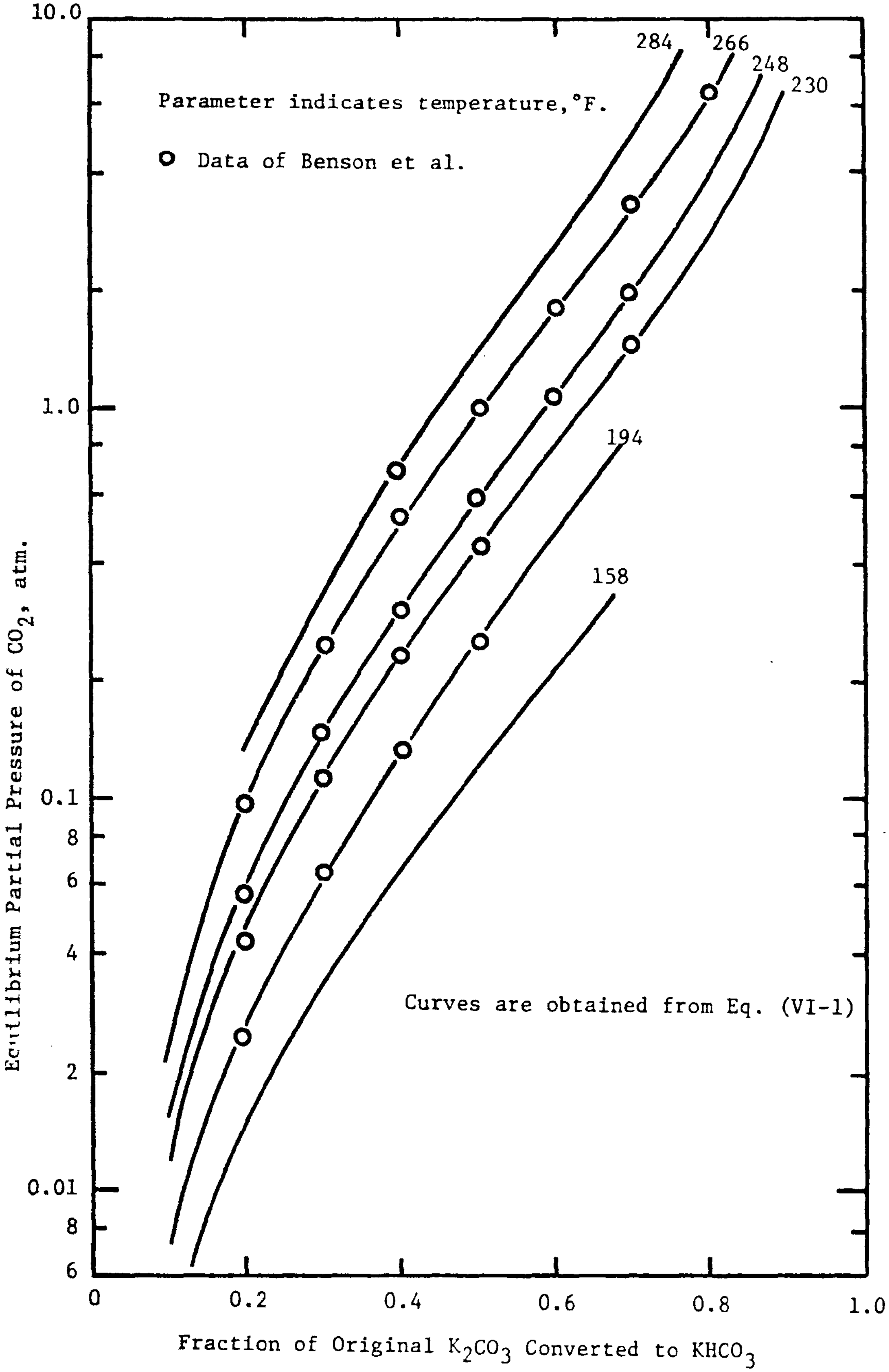


Figure-VI-4 Equilibrium Vapor Pressure of CO_2 Over 40% Equivalent K_2CO_3 Solution [14] equilibrium vapor pressure of H_2S over hot potash solution for a H_2S content of the solution of 1 cubic feet per gallon (SCF/gal). The equilibrium vapor pressure of H_2S over hot potash solution for other H_2S content of the solution is not available. If it is assumed that the equilibrium vapor pressure of H_2S has a linear relation with the H_2S content of the solution, the data of Buck and Leitch can be represented by the equation

$$P^*_{H_2S} = (-0.989 + 9.327 \times 10^{-3}\ T - 1.439 \times 10^{-5} T^2)\ X_{H_2S} \qquad \text{(VI-2)}$$

where $P^*_{H_2S}$ = equilibrium vapor pressure of H_2S ,[atm]

X_{H_2S} = H_2S content of the solution [mole H_2S/mole K_2CO_3 originally presents]

T = temperature,[°F]

(b) Equilibrium Partial Pressure of Water Vapor Over K_2CO_3 Solution

Tosh et al [56] studied the equilibrium partial pressure of water vapor over K_2CO_3 solutions. The equilibrium partial pressure of water vapor over 40% equivalent potassium carbonate solution can be represented by the expression.

$$P^*_{H_2O} = \mathrm{Exp}\left[-\frac{8932.32}{T_R} + 12.9686 + 0.5174\left(X - \frac{1}{3}\right)\right] \qquad \text{(VI-3)}$$

where X = mole CO_2 absorbed/mole K_2CO_3 originally present in the solution

P^*H_2O is in atm.

ii. Solubilities of K_2CO_3 and $KHCO_3$ in Water

The effects of temperature and extent of conversion to bicarbonate on the solubility of the salts in the system have been determined by Benson, Field et. al.[6]. Their data are presented in Fig. VI-5.

If the cooling of the solution occurs at any point of the system, the precipitation of $KHCO_3$ will prevent the normal operation. Thus the selection of a proper concentration is closely related with the minimum temperature in the system.

iii. Henry's law Constants of CO_2 and H_2S in Pure Water

The Henry's law constant of CO_2 in pure water at total pressure of a few atmospheres or less is given by the expression:

$$H = 0.06243 \exp\left[\frac{32034.5}{T_R} + 12.2\right] \quad [\text{lb-mole/sq.ft atm}] \qquad \text{(VI-4)}$$

The Henry's law constant of H_2S in pure water H' is approximately 3 times that of CO_2. Thus

$$H' = 3H \qquad \text{(VI-5)}$$

iv. Heat of Reaction

Benson et. al.[6] reported the heat of reaction for the absorption of CO_2 into K_2CO_3 solution to be 11,490 BTU/lb-mole of CO_2 absorbed. Ramm[50] reported that the heat of reaction for the absorption of H_2S into K_2CO_3 solution is approximately 5,375 BTU/lb-mole.

v. Other data on properties of the carbonate solution and CO_2

To simulate the performance of CO_2 absorption by carbonate solution, it is necessary to have the reliable data on the thermodynamic properties of solution and CO_2. Such data as heat capacity,viscosity,density of

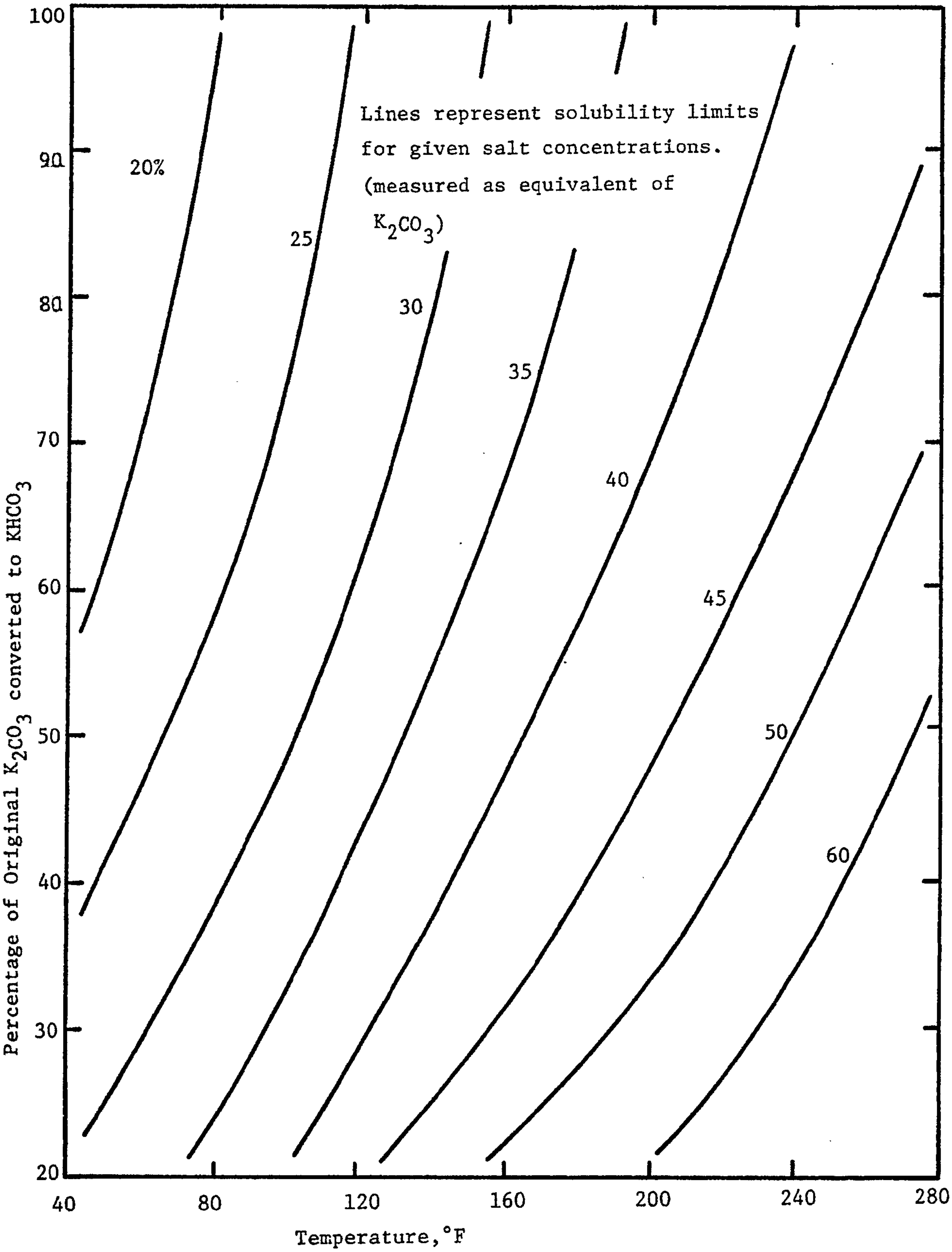


Figure VI- 5 Effect of Temperature and Percentage Conversion of K_2CO_3 to $KHCO_3$ on Solubility of K_2CO_3 plus $KHCO_3$ (obtained from Kohl and Riesenfeld [1]) the solution, and diffusivity and Henry's law constant of CO_2 are essential to the calculation of absorption rates.

Since no data are available at present under the plant operating conditions of 1000 psig and of relatively high temperature, extrapolation of these properties to the desired conditions must be made. Some examples of the extrapolated results are shown in Fig.VI-6 and 7.
These extrapolated values are used in the design of a hot carbonate absorption process.

For convenience of computer calculation, these relations are expressed as follows.

For viscosity of the hot potassium solution,

$$m/\mu = 2.1482\left[\left(\frac{T}{1.8} - 40.435\right) + \sqrt{8078.4 + \frac{T}{1.8} - 40.435^{2}}\right] - 120 \qquad \text{(VI-6)}$$

where m = 2.42 for pure water

m = 9.96 for 40% K_2CO_3 solution

μ = viscosity of K_2CO_3 solution (lb/ft.hr)

T = temperature of K_2CO_3 solution (°R)

For density of the hot potassium solution,

$$\rho_L = -0.01127\,T + 66.5\,Y_o + 66.69 \qquad \text{(VI-7)}$$

where ρ_L = density of the solution (lb/ft.^{3})

Y_o = percentage of K_2CO_3 in the solution (%)

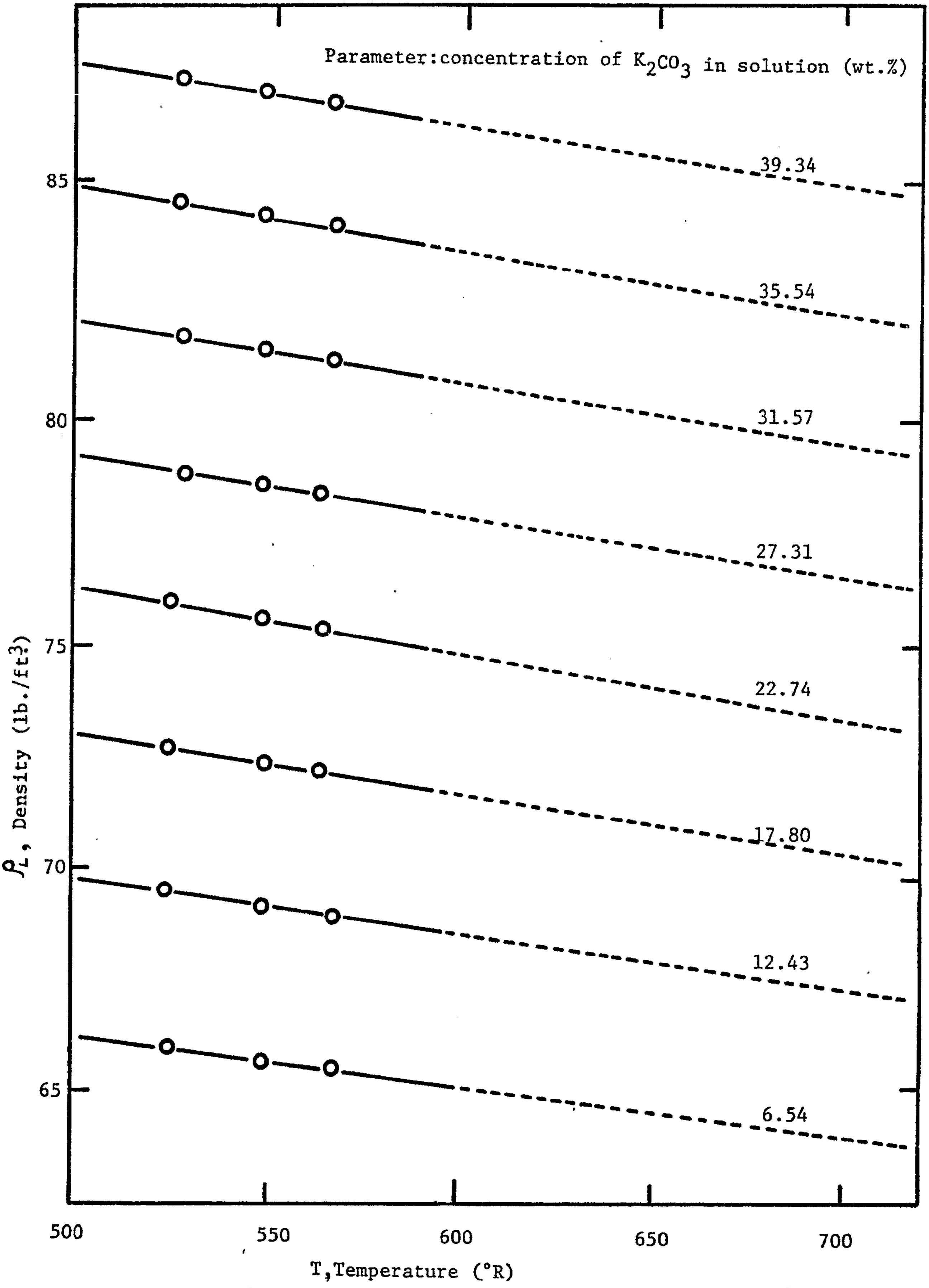


Figure VI- 6. Density of Potassium Carbonate Solution vs. Temperature [28]

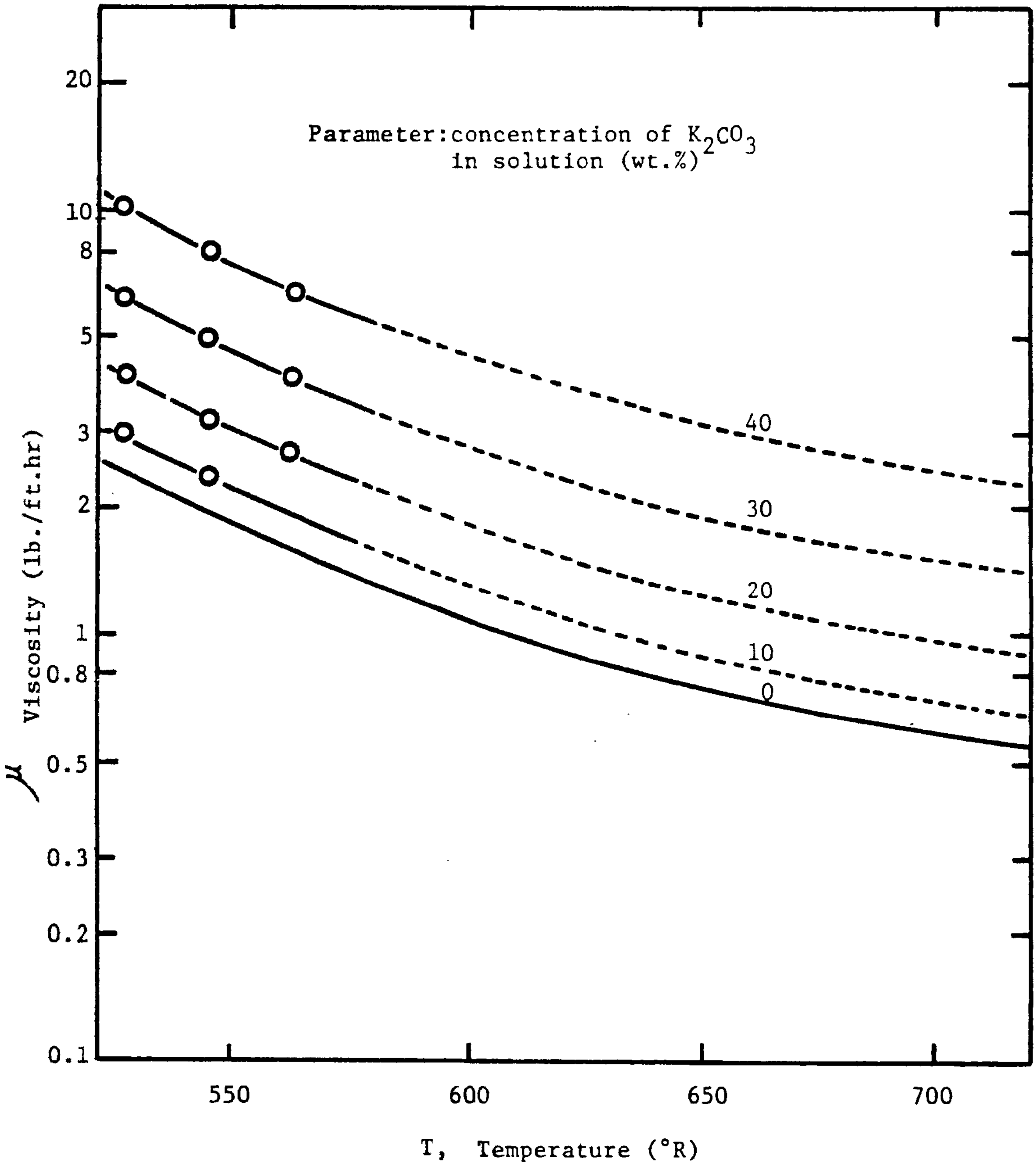


Figure VI-7. Viscosity of Potassium Carbonate Solution vs. Temperature of the Solution

3.2 Amine Process

Monoethanolamine (MEA) and Diethanolamine solutions are frequently used in practice for removing CO_2 and H_2S. In general MEA solutions are the preferred solvents for both CO_2 and H_2S unless special circumstances, which will be discussed later, indicate the desirability of using DEA or other amines. The advantage of MEA lies in its low price, high reactivity, excellent stability, and the ease with which it can be reclaimed from contaminated solutions. Its principal drawback is the fact that it reacts nonregenerably with COS, a common constituent of gas from the cracking operation. Since the gas streams to be treated here are free of COS; MEA solution is a logical choice.

It is noted that increasing the amine concentration will generally reduce the required solution circulation rate and in turn, the plant cost. However, the use of higher amine concentrations results in more corrosion of steel equipment. According to the common practice [44] a maximum of 15 percent of amine should be considered to avoid excessive corrosion. Therefore a 2.5 N mono-ethanolamine solution, which is equivalent to 15.2% MEA concentration, will be used as the solvent for the amine process.

i. Vapor Pressure Data for CO_2 and H_2S over MEA solutions

Published vapor pressure data for CO_2 and H_2S over MEA solution can be found in a book by Kohl and Riesenfeld , Gas Purification [1].

(a) CO_2 Vapor Pressure Over 2.5 N MEA Solution

The operating temperature of the absorber which uses amine solutions as solvents is usually under 140°F. Under this condition, the CO_2 vapor pressure over 2.5N MEA solution is negligibly small compared with the partial pressure of CO_2 in the gas stream. This is particularly true when the gas pressure is high. The regenerator is normally operated at an elevated temperature (about 250°F) such that the CO_2 vapor pressure over MEA solution is relatively high. Accurate vapor pressure data for CO_2 over the MEA solution at about 250°F are needed in the design of a regenerator. Muhlbauer and Monaghan [45] have published vapor pressure data for CO_2 and H_2S over 2.5 MEA solution at 212°F. The presence of H_2S in MEA solution tends to increase CO_2 vapor pressure. However, H_2S concentration is always very low in the present study, the effect of the presence of H_2S on CO_2 vapor pressure is negligibly small and need not be taken into consideration. The CO_2 vapor pressure over 2.5N MEA solution at 212°F in the absence of H_2S can be fitted with the following equation

$$P^*_{CO_2} = \exp(-6.118 + 12.574\,X) \qquad \text{(VI-8)}$$

where $P^*_{CO_2}$ = CO_2 vapor pressure [atm]

X = CO_2 concentration in the solution, [moles CO_2/mole MEA]

This equation is reasonably accurate for concentrations of CO_2, between 0.15 to 0.5.

It is shown in Figure 2-10 of the book, Gas Purification by Kohl and Riesenfeld [1] that the effect of temperature on CO_2 vapor pressure for various CO_2 concentrations in 2N MEA solution can be expressed as

$$\ln P^*_{CO_2} = a + b/T_R;\ (T_R \text{ in } ^\circ F) \qquad \text{(VI-9)}$$

where a and b are constants representing the intercept and the slope in Figure 2-10. The slope b increases almost linearly with decreasing X.

Assuming b to have the same value for 2N and 2.5N MEA solutions at a given X and a linear relation between b and X , the temperature effect can be incorporated into Equation VI-8 as,

$$P^*_{CO_2} = \exp\left\{-6.118 + 12.574X - [18240 - 41500(X - 0.4)](1/T_R - 1/672)\right\} \quad \text{(VI-10)}$$

This equation is used to calculate the vapor pressure of CO_2 between X=0.15 to X=0.5 at regenerator temperatures.

(b) H_2S Vapor Pressure Over 2.5N MEA Solution

In the simultaneous removal of CO and H_2S with an amine solution, the presence of CO_2 in the solution considerably affects the H_2S vapor pressure over the solution.

Published data for H_2S vapor pressure over MEA solutions are available only for relatively high H_2S concentrations in the solution. Since X'is small(X'=mole H_2S/mole amine, less than 0.04) in in the present study, extrapolated data to low H_2S concentrations have to be used. Noting the H_2S vapor pressure, $P^*_{H_2S}$ [atm], at X = 0 to be zero, the H_2S vapor pressure over 2.5N MEA solution at 212°F reported by Muhlbauer and Monaghan [45] can be readily extrapolated to obtain Figure VI- 8 . It is seen from this figure that the curves can be approximated by straight lines for $X' \leq 0.04$. The H_2S vapor pressure over 2.5N MEA at 212°F for $X' \leq 0.04$ can be fitted in the form as

$$P^*_{H_2S} = 310.158X' \cdot X^s \qquad [\text{atm}] \qquad \text{(VI-11)}$$

where $s = [9.4763 + 5.0978 \ln X + 0.9776(\ln X)^2]$

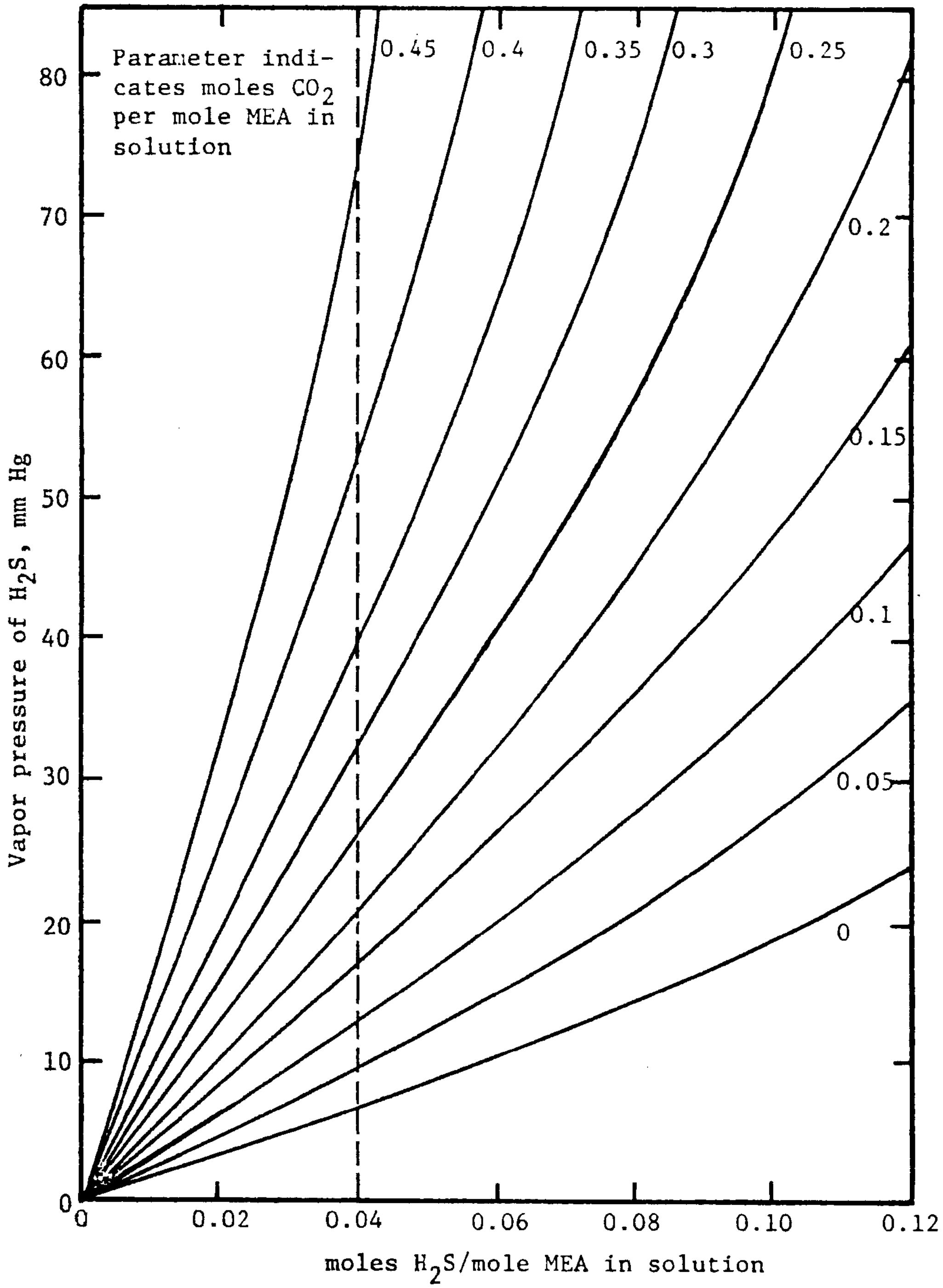


Figure VI-8. Effect of Dissolved Carbon Dioxide on Vapor Pressure of H_2S over 2.5N Monoethanolamine Solution at 202 °F (extrapolated from data of Muhlbauer and Monaghan [45])

This equation is applicable for $X' \leq 0.04$ and $0.05 \leq X \leq 0.5$.

It is noted from Figure 2-19 in Gas Purification by Kohl and Riesenfeld [1], that the effect of temperature on vapor pressure of H_2S over 2N MEA solution can also be expressed in the form:

$$\ln P^*_{H_2S} = a + b/T_R \qquad \text{(VI-12)}$$

where a and b are constants and T_R is temperature in °R. The slope, b, is approximately constant for all CO_2 concentrations in the solution. Assuming the same b for both 2N and 2.5N MEA solutions, the H_2S vapor pressure over 2.5N MEA solution can be expressed as

$$P^*_{H2S} = X' \cdot X^s \cdot \exp \frac{-7079.32}{T_R} + 16.2718 \qquad \text{(VI-13)}$$

Again, this equation is applicable for $X' \leqslant 0.04$ and $0.05 \leq X \leq 0.5$ at regenerator temperatures. s is the same as in Eq. (VI-11).

ii. Heat Capacity, Density, and Viscosity of 2.5N MEA Solution

Heat capacity, density, and viscosity data for MEA solution can also be found in Gas Purification by Kohl and Riesenfeld [1]. The heat capacity of 2.5N MEA solution increases proportionally with increasing temperature. It can be represented by

$$C_{pL} = 0.9028 + 3.875 \times 10^{-4}\ T \qquad \text{(VI-14)}$$

where C_{PL} is in BTU/(lb)(°F) and T, in °F.

The density of 2.5N MEA solution can be fitted with the following equation

$$\rho_L = 63.504 - 1.34 \times 10^{-2}\ T - 5.20 \times 10^{-6}\ T^2 \qquad \text{(VI-15)}$$

where ρ_L is in lb/cu.ft. and T, in °F. The presence of CO_2 and H_2S increases the viscosity of MEA solution. Since no information relating the effect of the presence of CO_2 and H_2S on the viscosity of 2.5N MEA solution is available, and since the concentrations of CO_2 and H_2S in MEA solution change within the absorber and the regenerator, the viscosity data for 20% MEA solution are used for design purpose. The kinematic viscosity for 20% MEA solution are fitted by the following equation

$$\nu_L = \exp\left(10.4838 - 0.1228T + 2.4134 \times 10^{-4}\, T^2\right) \qquad \text{(VI-16)}$$

where ν_L is in ft^2/hr, and T in °F.

iii. <u>Diffusivity of Various Species in Solution</u>

The diffusivity of CO_2 in water at various temperatures have been determined by Thomas and Adams [47]. It can be represented by the equation

$$D = 3.8513 \times 10^{-5} + 7.727 \times 10^{-8} T + 6.8742 \times 10^{-9}\, T^2 \qquad \text{(VI-17)}$$

where D_{CO} is in ft^2/hr, and T is in °F.

The diffusivity of H_2S in water is approximately the same as that of CO_2 at the same temperature.

The diffusivities of MEA(D_o) in water and in 2.5N MEA solution at 77°F are respectively 4.26×10^{-5} ft^2/hr and 2.71×10^{-5} ft^2/hr according to Thomas and Furzer [46].

In the calculation of the rate of CO_2 absorption into MEA solution, D_o and D in the amine solution at various temperatures are needed. Lacking experimental data, Dankwerts [48] suggested that D_o and D in the solution can be estimated as follows. D_o in 2.5N solution at 77°F is 2.71×10^{-5} ft^2/hr . D in water at 77 °F is determined from Equation VI-17 , and is about 7.75×10^{-5} ft^2/hr . D in water at other temperatures can also be determined from

Equation (VI-17). It is assumed that the temperature coefficient of D_o in 2.5N solution is the same as that of D in water. The ratio of the diffusivity of MEA in 2.5N solution to that in pure water at 77°F is 0.64. It is assumed that the ratio of the diffusivity of CO_2 in 2.5N MEA solution to that in pure water is also 0.64 at 77°F, and that it is unchanged at other temperatures. Thus D_o and D in 2.5 MEA solution at various temperatures can be estimated.

Diffusivity data for H_2S in water is not available. Wilke and Chang's correlation [49] can be used to estimate the diffusivity of a solute in solvents when solute concentration is small,accordingly

$$D = 2.16 \times 10^{-7} \frac{\sqrt{\beta M}\ T_R}{\mu\, \bar{V}^{0.6}} \qquad \text{(VI-18)}$$

where D = diffusivity of the solute in the solvent [ft^2/hr]

$\bar{V}$ = the molar volume of the solute as liquid at its normal boiling point, [ft^3/lb-mole]

μ = the viscosity of solution, [lb/ft.hr]

β = an association parameter for solvent, = 2.6 for water

T_R = absolute temperature,[°R]

M = molecular weight of the solvent

iv. Heat of Absorption

Heats of reaction for the absorption of CO_2 and H_2S into MEA solution are respectively 36,300 and 27,800 Btu/lb-mole according to Kohl and Riesenfeld [1].

v. Equilibrium Partial Pressures of MEA Vapor and Water Vapor Over MEA Solution

The equilibrium partial pressure of MEA Vapor over aqueous solution can be found in Figure 3-6 in "Gas Purification," a book by Kohl and Riesenfeld [1]. The equilibrium partial pressure of MEA over 15% aqueous solution of MEA can be represented by the expression

$$P^*_{MEA} = \exp\left(\frac{-15564.5}{T_R} + 17.22\right) \qquad \text{(atm)} \qquad \text{(VI-19)}$$

Data on the equilibrium partial pressure of water vapor over MEA solution $P^*_{H_2O}$ are not available. Therefore, $P^*_{H_2O}$ is calculated by using the Raoult's law.

$$P^*_{H_2O} = P_v X_{H_2O} \qquad \text{(atm)} \qquad \text{(VI-20)}$$

where P_v = vapor pressure of water, (atm)

X_{H_2O} = mole fraction of water in solution

4. Reaction Kinetics and Thermodynamics

4.1 Hot Potash Process

The reaction kinetics of carbon dioxide in aqueous solutions of potassium carbonate is presented in this section.

When carbon dioxide is absorbed into a potassium carbonate solution, the following over-all reaction occurs.

$$CO_2 + K_2CO_3 + H_2O \rightleftharpoons 2KHCO_3 \qquad (a)$$

Since the product is a strong electrolyte, the following equation in ionic terms is more convenient in consideration of this system.

$$CO_2 + CO_3^{--} + H_2O \rightleftharpoons 2\ HCO_3^- \qquad (b)$$

This reaction can be considered to occur as the result of the following steps.

$$CO_2 + H_2O \rightleftharpoons HCO_3^- + H^+ \qquad (c)$$

$$CO_2 + OH^- \rightleftharpoons HCO_3^- \qquad (d)$$

$$CO_3^{--} + H^+ \rightleftharpoons HCO_3^- \qquad (e)$$

$$CO_3^{--} + H_2O \rightleftharpoons HCO_3^- + OH^- \qquad (f)$$

All species in reactions (e) and (f) are in ionic forms and thus these reactions may be considered to occur instantaneously. Reaction (c) is rapid dissociation of carbonic acid. Therefore, in this case, reaction (d) is the rate controlling step of the over-all reaction. The rate constants of this reaction were determined by Mills [38] and are presented in Table VI- 2.

Table VI- 2 Rate Constant for the Reaction between CO_2 and OH

Temp. °F	Reaction rate const. k_2, [ft^3/lb-mole hr]
32	5.36×10^7
64.4	2.31×10^8
68	2.88×10^8

At the present time, there seem to be no other data available in the literatures. Therefore these values must be interpolated and extrapolated to estimate the liquid side mass transfer coefficient. Assuming that the temperature effect on k_2 can be represented by

$$k_2 = A_o \exp(-B/RT_R) \tag{VI-21}$$

where A_o and B are constants and T_R is in °R, then the values given in Table VI- 2 can be used to obtain the following relation

$$k_2 = \exp[45.92 - \frac{1.387 \times 10^4}{T_R}] \tag{VI-22}$$

4.2 Amine Process

Excellent discussion of the reaction kinetics of the absorption of CO_2 can be found in the recent publications, such as "The Absorption of Carbon Dioxide into Solution of Alkalis and Amines", by Dankwerts and Sharma [48], "Gas-Liquid Reactions" by Dankwerts, [54] and "Absorption of Gases" by Ramm [50]. Various aspects of the reaction between H_2S and amines were also discussed in these publications.

The product of the reaction between carbon dioxide and primary or secondary amines is the amine salt of the carbamic acid (tertiary amines do not react with carbon dioxide to form carbomates because of the absence of a hydrogen atom attached to nitrogen; they simply act as bases and form bicarbonates).

or $$CO_2 + 2R_2NH \rightleftharpoons R_2NCOO^- + R_2NH_2^+ \qquad (g)$$

The reaction is second order:

Rate of reaction (lb mole/cu.ft. hr) = k_{Am} [Am][CO_2] where k_{Am} is the second-order rate constant for the amine, and [Am] is the concentration of amine [lb mole/cu.ft.]. The contribution of the reactions with water and with hydroxyl ions to the overall rate of reaction are negligible under conditions used in practice for the absorption of carbon dioxide in aqueous MEA or DEA solutions. The rate constant k_{Am} for the reaction between CO_2 and MEA and DEA are given in Table VI-3

Table VI-3 Rate Constant for the Reaction Between CO_2 and Some Amines[48]

	k_{Am}, [cu.ft./lb-mole hr]	
Temperature, °F	MEA	DEA
77	4.38×10^8	8.65×10^7
95	7.50×10^8	1.44×10^8

It can be seen from the table that MEA has higher reactivity than DEA. Assuming that the temperature effect on k_{Am} can be represented by

$$k_{Am} = A_o \exp[B/RT_R] \qquad \text{(VI-23)}$$

then the values given in Table VI- 3 can be used to obtain the following relation for MEA

$$k_{Am} = \exp[36.394 - \frac{8847.59}{T_R}] \qquad \text{(VI-24)}$$

When H_2S reacts with amines, hydrosulfides are formed:

$$H_2S + RNH_2 \rightleftharpoons RH_2NH + HS^- \qquad \text{(h)}$$

It is possible to remove H_2S selectively from gases containing CO_2 by the use of aqueous solutions of tertiary amines, such as triethanolamine, methyl diethanolamine, etc., with which H_2S reacts instantaneously:

$$H_2S + R_3N \rightleftharpoons R_3NH^+ + HS^- \qquad \text{(i)}$$

No information on the rate constants of the reactions between H_2S and amines are available.

Because the processes for the absorption of CO_2 and H_2S involve chemical reactions, it is necessary to know how the rate of mass transfer and reactions influence the overall rate of absorption. Several models have been proposed for the gas-absorption process. Among them the film model has been conveniently used to predict the ratios of the rate of absorption with and that without chemical reactions.

1. Rate of Absorption in the Absorber

The reaction of CO_2 with MEA and DEA is second-order. For industrial gas-absorbers with amine solutions as solvent, the back-pressure of CO_2 in the solution is usually negligibly small. Therefore, the reaction between CO_2 and MEA can be adequately considered as irreversible second-order reaction.

When the concentration of the reactant (MEA) in the neighborhood of the surface is little different from that in the bulk of the liquid, the dissolved gas (CO_2) can be assumed to undergo a pseudo-first order reaction. Using the formula developed by Dankwerts [51], the rate of absorption of the gas per unit interfacial area , R, [lb mole/ft.^{2}hr.] can be approximated by

$$R = C_i \sqrt{k_L^2 + Dk_2 C_o} \qquad \text{(VI-25)}$$

where C_i = concentration of free dissolving gas at interface [lb mole/ft^3]

C_o = concentration of reactant (MEA etc.) [lb mole/ft^3]

D = diffusivity of the dissolving gas in the solution [ft^2/hr]

k_L = liquid-film coefficient in absence of reaction [ft/hr]

k_2 = second-order reaction-rate constant [ft^3/lb mole hr]

The product k_2C_o which can be written as k(hr^{-1}) is the pseudo-first order reaction-rate constant. The condition to be satisfied for a pseudo-first order reaction is

$$\sqrt{Dk_2 C_o} \leq 1/2k_L \left(1 + \frac{C_o}{\alpha C_i}\right) \qquad \text{(VI-26)}$$

where α is number of moles of reactant reacting with each mole of the dissolved gas [e.g. $\alpha = 2$ when CO_2 is absorbed into MEA solution].

The reaction between dissolved gas and reactant can be treated as being instantaneous, if both diffuse to a reaction zone close to the liquid surface where the concentrations approach zero. The absorption rate is then given as

$$R = k_L C_i \left(1 + \frac{D_o}{D} \frac{C_o}{\alpha C_i}\right) \sqrt{\frac{D}{D_o}} \qquad \text{(VI-27)}$$

where D_o is the diffusivity of reactant in liquid [ft^2/hr]. The condition for instantaneous second-order reaction is

$$\sqrt{Dk_2 C_o} \geq 10\, k_2 \left(1 + \frac{C_o}{\alpha C_i}\right) \qquad \text{(VI-28)}$$

For conditions intermediate between those of Equations VI-26 and VI-28 , Van Krevelen and Hoftyzer [52] have shown that R can be calculated from the following equation to within 10%

$$\frac{R}{k_L C_i} = E = \frac{\sqrt{M \dfrac{E_i - E}{E_i - E}}}{\tanh \sqrt{M \dfrac{E_i - E}{E_i - 1}}} \qquad \text{(VI-29)}$$

where $M = \dfrac{Dk_2C_o}{(k_L)^2}$; $E_i = 1 + \dfrac{D_o}{\alpha} \dfrac{C_o}{DC_i}$

When very low gas phase CO_2 concentration at the outlet of the absorber is desired, the back pressure of CO_2 may not be negligible compared to the CO_2 partial pressure. If the condition for pseudo-first order reaction is satisfied the rate of absorption is

$$R = (C_i - C_b) \sqrt{k_L^2 + Dk_2 C_o} \qquad \text{(VI-30)}$$

where C_b = equilibrium concentration of unreacted dissolved CO_2 in the bulk of the liquid.

This equation is the same as that for irreversible first-order reaction given by equation (VI-25), except that the driving force is $(C_i - C_b)$. If the concentration of free CO_2 is much less than that of free MEA, then

$$C_b = \frac{X}{K_c(1 - 2X)^2} \qquad \text{(VI-31)}$$

where K_c is the equilibrium constant of Reaction (g), namely,

$$K_c = \frac{[R_2NCOO^-][R_2NH_2^+]}{[R_2NH]^2 [CO_2]} \qquad \text{(VI-32)}$$

K_c has been given as 1.78×10^6[ft^3/lb-mole] at 68°F by McNeil [53]. For temperature other than 68°F, K_c may be approximated by assuming the same temperature effect on both $P^*_{CO_2}$ and $1/K_c$, namely,

$$1/K_c = \exp\left\{-14.392-[18240-41500(X -0.4)] (1/T_R - 1/528)\right\} \qquad \text{(VI-33)}$$

ii. Rate of Desorption in the Regenerator

Dankwerts [54] in his book "Gas-Liquid Reaction" has discussed the aspect of desorption of gas from liquid with chemical reactions. In the case of desorption with reactions, the dissolved gas is produced instead of being destroyed. The arguments used in absorption can be also used for desorption. If the reaction is of first order, the equation for an irreversible first-order reaction (equation VI-25) can be employed with $(C_i - C_b)$ in place of C_i, where C_i is the concentration of dissolved gas at interface, in equilibrium with gas interface, and C_b is the concentration of the dissolved gas in equilibrium with bulk liquid. Thus the rate of desorption becomes

$$-\bar{R} = (C_b - C_i)\sqrt{k_L^2 + Dk_2 C_o} \qquad \text{(VI-34)}$$

where $(-\bar{R})$ is the rate of desorption.

The condition for this to be applicable is that there is no depletion of reactant at the interface - i.e., C_o is nearly constant. This condition is probably satisfied if the following criterion is met.

$$(C_b - C_i)\sqrt{Dk_2 C_o} \ll k_L C_o / \alpha \tag{VI-35}$$

The arguments used for absorption with an instantaneous reversible reaction can be applied equally well to desorption with the same type of reaction. Provided the diffusivities of all species are equal, the rate of desorption from an agitated liquid is

$$-\bar{R} = k_L (C_t - C_i) \tag{VI-36}$$

where C_t is the total concentration of dissolved gas in reacted and unreacted form in the bulk of liquid.

5. Flooding Velocity, Diameter of Tower and Pressure Drop in Packed Tower

5.1 Flooding velocity and diameter of tower

The flooding velocity in a packed tower must be determined carefully because of its significant effect on the size of the tower. The usual procedure for determining the flooding velocity in a packed tower is to use the graphical correlation of Lobo, Friend, Hashmall and Zenz [30] which is based on earlier work of Sherwood, Shipley, and Holloway [31].

In this correlation a log-log plot of the group $(U_F^2 a \rho_G / g \varepsilon^3 \rho_L) \cdot (\rho_G / \rho_L)^{1/2}$ or $(G_F^2 a / g \varepsilon^3 \rho_L \rho_G)(\mu_L / \mu_W)^{0.2}$ vs. $(L'/G') \cdot (\rho_G / \rho_L)^{1/2}$ is used.

where G_F = flooding mass flow rate, [lb/ft^2.hr]

U_F = flooding velocity of the gas phase based on total tower cross-section. [ft/hr]

a = surface area of packing per unit volume of tower, [ft^{-1}]

g = acceleration due to gravity, [ft^2/hr]

ε = void fraction of the packing

ρ_L = density of the liquid, [lb/ft^3]

ρ_G = density of the gas, [lb/ft^3]

μ_L = viscosity of the liquid, [lb/ft.hr]

μ_W = viscosity of the water at 68°F. [lb/ft.hr]

G' = mass rate of flow of the gas phase, [lb/ft^2.hr]

L' = mass rate of flow of the gas phase, [lb/ft^2.hr]

For computer calculation, however, it is inconvenient to use the graphical method. The following equation proposed by Sawistowski [10] is adopted for calculation of the flooding velocity.

$$\ln \frac{G_F^2 \cdot a}{g \varepsilon^3 \rho_G \rho_L} \left(\frac{\mu_L}{\mu_W} \right)^{0.2} = -4 \left(\frac{L'}{G'} \right)^{1/4} \left(\frac{\rho_G}{\rho_L} \right)^{1/8} \qquad \text{(VI-37)}$$

The diameter of a packed bed is computed on the basis of about 75% of the flooding velocity.

5.2 Pressure drop across packed tower

Although many experimental data for the pressure drop in packed towers has been published, the agreement is often poor.

The pressure drop for gas flowing through dry packings may be represented by an equation of the type

$$\frac{\Delta P}{z} = k v^n \tag{VI-38}$$

where

k = a constant for the packing

n = 2.0 for turbulent flow

$\Delta P/z$ = pressure drop, [lb/ft^2.ft-height]

v = air velocity in empty tower [ft/sec]

For liquid rates up to about 15,000 lb/ft^2.hr this type of equation can represent the experimental data fairly well, but when the liquid rates exceed 15,000 lb/ft^2.hr a simple correlation of this type fails to describe the data. It is found that the exponent n varies with the liquid flow rate.

The extensive data for a variety of packing materials were reproduced by Perry [3]. Leva [32] correlated pressure drop data for ring and saddle packings by the equation

$$\Delta P = \phi \rho_G v^2 \left(10^{\psi L'}\right) \tag{VI-39}$$

where

ϕ, ψ = constants characteristic of the packing

ΔP = pressure drop [in. of water/ft of packing]

v = gas velocity in empty tower [ft/sec]

ρ_G = gas density [lb/ft^3]

The values of the packing constant determined from pressure drop measurements with air and water are given in Table VI-4.

Table VI-4 Packing Constants for Raschig Ring

Size in.	Voidage ft^3/ft^3	Range of Liquid Rate L' lb/ft^2.hr		ϕ	$\psi \times 10^4$	R_g
3/4	.74	1,800	10,800	0.82	0.72	2.7
1	.685	360	27,000	0.80	0.69	2.7
1 1/2	.711	720	18,000	0.30	0.64	2.7
2	.734	720	21.600	0.28	0.47	2.8

Experiments using solutions other than water show that the density and viscosity of the liquid affect the pressure drop. For high density solution, this correlation predicts lower values of the pressure drop than the measured ones.

Lacking other suitable correlations and data, this equation is assumed to be applicable without significant errors.

6. Heat and Mass Transfer Coefficients

6.1 Hot Potash Process

1. Mass transfer coefficient in liquid side

In spite of the industrial importance, the understanding of the kinetics of gas-liquid reaction and design of absorption apparatus from fundamental concepts have not kept the pace with practice. But in the field of physical absorption, relatively reliable theories have been developed. One of the most useful theories is the two-film theory of interphase mass transfer between two fluids.

The general equation for gas absorption is written as

$$N_A = K_G a \Delta P \qquad \text{(VI-40)}$$

where

N_A = rate of absorption of A [lb-moles/ft^2.hr]

K_G = over-all mass transfer coefficient based on gas phase [lb-moles/ft^2.atm.hr]

a = effective surface area [ft^2/ft^3]

ΔP = driving force [atm]

The over-all mass transfer coefficient consists of two individual mass transfer coefficients in the two phases.

$$\frac{1}{K_G} = \frac{1}{k_G} + \frac{1}{Hk_L} \qquad \text{(VI-41)}$$

where H = Henry's law constant [lb-moles/ft^3.atm]

k_L = liquid side mass transfer coefficient [ft/hr]

k_G = gas side mass transfer coefficient [lb-moles/ft^2·atm·hr]

If a physical absorption is mainly gas film controlled, as for example in the absorption of ammonia in water, the addition of a reactant to the liquid would not be expected to influence the over-all coefficient. Changes in the operating condition of gas can affect the rate, however.

The majority of processes involving the absorption of an acid gas by an alkaline liquid are characterized by a fast chemical reaction and for practical purposes the absorption may be regarded as gas film controlled. The mathematical theory was developed by Hatta [36] and was reviewed by Sherwood and Pigford [36].

Carbon dioxide is an exception to this, since its hydrolysis in an aqueous solution is a slow reaction which exerts a controlling influence on the rate of absorption. Thus in the case of the operating condition under normal pressure, Equation (VI-41) becomes

$$K_G a = H k_L a \qquad \text{(VI-42)}$$

This equation is applicable only to the regeneration of spent liquor in the hot potassium process. Since the absorption phase is operated under a high pressure, the gas side resistance becomes significant compared with that in the liquid side.

In this case, the correlation for the gas side mass transfer coefficient proposed by Morris and Jackson[60] is applicable though this equation was obtained for a wetted-wall column.

$$\frac{k_G RT}{v} \cdot \frac{P_{BM}}{P} \cdot \left(\frac{\mu}{\rho \mathcal{D}}\right)^{0.5} = 0.04 \left(\frac{\rho v d}{\mu}\right)^{-0.25} \qquad \text{(VI-43)}$$

where

P_{BM} = logarithmic mean pressure of $(P-P_A)$ and $(P-P_i)$ [atm]

P_i = equilibrium pressure of CO_2 [atm]

P_A = partial pressure of CO_2 in gas stream [atm]

P = total pressure [atm]

d = diameter of the standard column (0.083 ft.)

v = gas velocity relative to the effective surface velocity of the liquid on the wall

In the case of a packed tower, the gas velocity is assumed to be equal to the velocity in the empty tower divided by the fractional voidage of the packing. The coefficient is then multiplied by a packing factor, R_g, given in Table VI-4.

These factors can be used when the liquid flow rate is not less than 0.85 $ft^3/(hr)(ft\ periphery)$ for ring packing up to 3 in. diameter, with the periphery defined as the area of the packing [ft^2] per unit height [ft.].

In equation (42) effective surface area, a, is calculated by the following relationship.

$$\ln \frac{ad - a}{a_d} = -c \frac{L'}{\rho} \qquad \text{(VI-44)}$$

where L'/ρ_L = superficial liquid velocity , [ft/hr]

c = constant with a value of about 6×10^6

a_d = dry surface area

Based on an extensive study of physical absorption, van Krevelen et al. [33] have proposed the following relationship for mass transfer coefficient.

$$\frac{k_L \left(\frac{\mu_L}{g \rho_L^2}\right)^{1/3}}{D} = 0.015 \left(\frac{L'}{a \mu_L}\right)^{2/3} \left(\frac{\mu_L}{\rho_L D}\right) \qquad \text{(VI-45)}$$

where

d = diameter of packing [ft]

g = acceleration due to gravity [ft/hr^2]

ρ_L = density of liquid [lb/ft^3]

ρ_G = density of gas [lb/ft^3]

D = diffusivity of carbon dioxide [ft^2/hr]

L' = mass flow rate of liquid [$lb/ft^2 hr$]

μ_L = viscosity of liquid [lb/ft.hr]
μ_G = viscosity of gas [lb/ft.hr]

Existing data in the literature are correlated satisfactorily by the above equation.

If a slow second order reaction is taking place, the rate of reaction can be considered as $k_2 \cdot C \cdot C_R$, where k_2 is the reaction rate constant, C is the concentration of the solute and C_R is the concentration of the reactant in the solution. If the rate is sufficiently slow compared with the rate of diffusion of the reactant, C_R may be treated as constant.

Van Krevelen and Hofitijzer [12] proposed the following equation on the absorption of CO_2 by carbonate solutions.

$$\frac{k_L\left(\frac{\mu_L^2}{g\rho_L^2}\right)^{1/3}}{D} = 0.0165\left(\frac{L'}{a\mu_L}\right)^{2/3}\left(\frac{\mu_L}{\rho_L D}\right)^{1/3}\frac{\left(\frac{\mu_L}{g\rho_L^2}\right)^{1/3}\left(\frac{k_2 C_R}{D}\right)^{1/2}}{\tanh\left[\left(\frac{\mu_L}{g\rho_L^2}\right)^{1/3}\left(\frac{k_2 C_R}{D}\right)^{1/2}\right]} \quad \text{(VI-46)}$$

This equation was tested based on the data of the absorption of CO_2 in sodium carbonate solution obtained by Payne and Dodge [36], and Furnas and Bellinger and the absorption of CO_2 in potassium carbonate solution by Comstock and Dodge [7].

The comparison between the calculated values and the experimental ones by Comstock and Dodge, and Benson and Field [6] is shown in Fig.VI-9

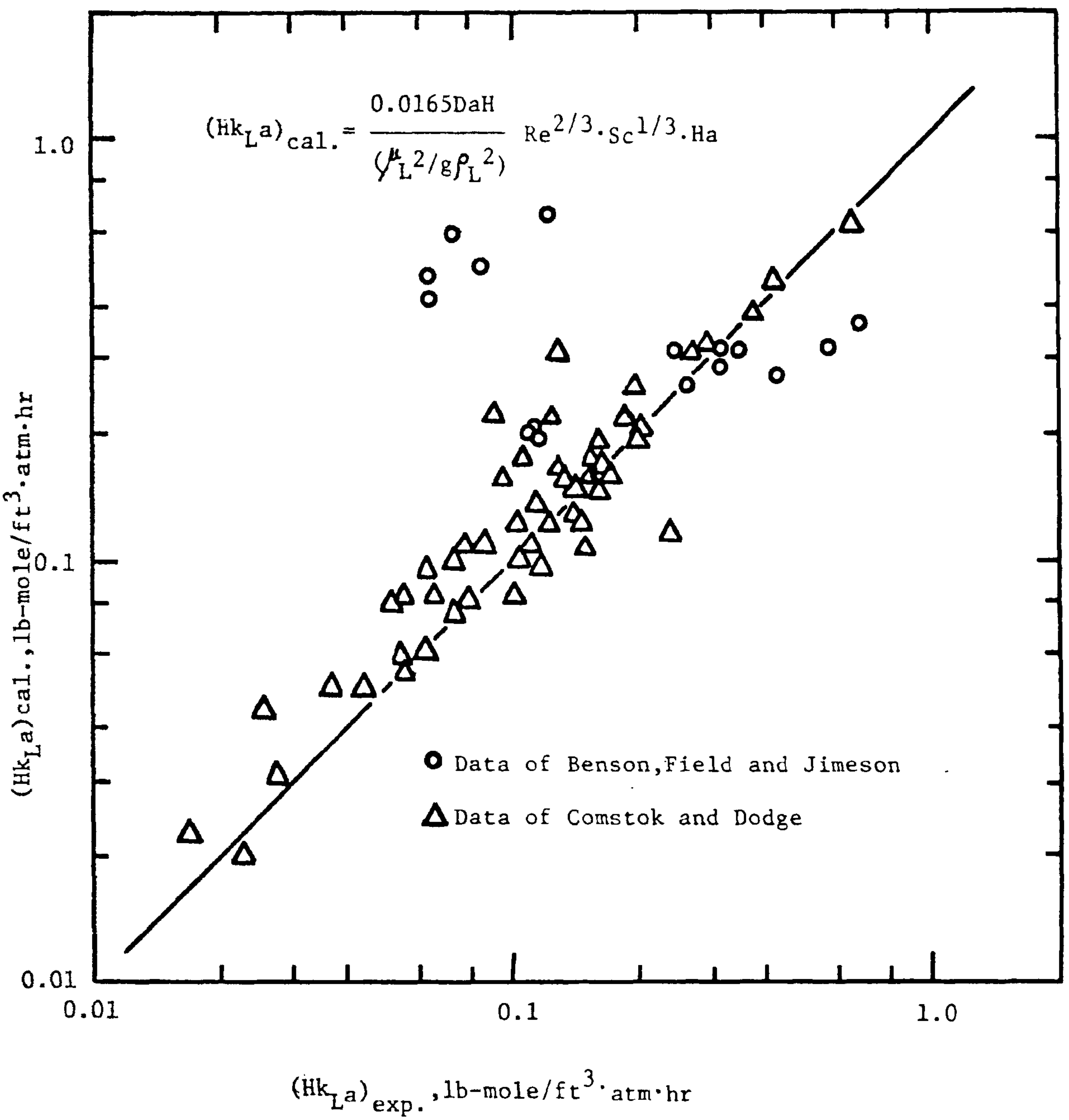


Figure VI-9. Comparison of Calculated and Experimental Values [6,7] of Liquid-side Mass Transfer Coefficient for Absorption of CO_2 by Carbonate Solutions

A limited number of tests were reported by Benson, Field, and Haynes[42] for the adsorption of H_2S by 40% K_2CO_3 solution in a column packed with 1/2" Raschig ring. The average liquid flow rate was 3,350 lb/hr.ft^2. The liquid side mass transfer coefficient of H_2S (Hk_La) calculated from their data has an average value of 0.297 lb-mole/(hr.ft^3. atm). By taking into account the effect of liquid flow rate and packing size, the following relation is obtained for liquid flow rate L' and for 2" Raschig ring

$$Hk_La = 0.297 \left(\frac{L'}{3350} \right)^{0.75} \left(\frac{28}{115} \right) \quad [\text{lb-mole/hr.ft}^3\text{.atm}] \qquad \text{(VI-47)}$$

This equation is used to calculate the overall mass transfer coefficient for the absorption of H_2S by hot potash solution.

ii. Heat transfer coefficient

Due to lack of experimental data on gas-liquid heat transfer coefficient in packed towers, the analogy between heat and mass transfer is used in the calculation.

The analogy between heat and mass transfer, which may be expressed as an equality between the j_H and j_D factors in the following equations, holds within a close approximation for many types of mass transfer apparatus.

For heat transfer,

$$\frac{h}{C_p \rho v} (P_r)^{2/3} = j_H \qquad \text{(VI-48)}$$

where

$P_r = \mu_G C_p/k$, Prandtl number

h = heat transfer coefficient, [Btu/ft^2.hr.°F]

v = average gas velocity, [ft/hr]

C_p = heat capacity of gas, [Btu/lb.°F]

k = heat conductivity of gas, [Btu/ft.hr.°F]

For mass transfer,

$$\frac{k_G}{v}(S_C)^{2/3} = j_D \qquad \text{(VI-49)}$$

where

$S_C = \mu_G/\rho_G D$, Schmidt number

k_G = mass transfer coefficient in gas side, [lb-mole/hr. sq.ft.atm]

Gamson, Thodos, and Hougen (61) studied the evaporation of water into warm air flowing through beds of porous spheres on pellets saturated with water, and found the relation

$$j_H = 1.07\ j_D \approx 1.1\ j_D \qquad \text{(VI-50)}$$

The experiments performed by Heertjes and Ringens [34] and Linch and Wilke [35] also show the following relation

$$j_H = 1.10\ j_D \qquad \text{(VI-51)}$$

6.2 Amine Process

The correlations of heat transfer coefficients, the gas side mass transfer coefficients, and the liquid side mass transfer coefficients without reaction (Eq. VI-45) as discussed in Section 6.1 are also applicable in the amine process.

There is no correlation available for the liquid side mass transfer coefficient for absorption of CO_2 and H_2S into amine solutions in which chemical reactions are involved. Shneerson and Leibush [43] have made a correlation for K_Ga based on the experimental data for the absorption of CO_2 by MEA solutions in a small laboratory column, 1 inch in diameter, packed with 5- to 6-mm glass rings . Kohl and Riesenfeld [1] generalized Shneerson and Leibush's correlation by taking into account the effect of liquid-flow rate and packing size. Unfortunately, these correlations are valid only for CO_2 partial pressure below 0.5 atm, temperatures below 125°F, and mole ratios of CO_2 to amine in the solution below 0.5. In the present study, the CO_2 partial pressure in the absorber can be as high as 20 atm. The K_Ga correlations available for the absorption of CO_2 by MEA solutions under low pressure operation are clearly not applicable for relatively high pressure operation under study. In absence of an adequate K_Ga correlation for the absorption of CO_2 by MEA solutions, the rate of absorption per unit interfacial area, R, based on the method suggested by Dankwerts and Sharma [48], as discussed in section 4.2, will be used to calculate the height of a packed column. For the purpose of checking, the value of K_Ga can be calculated from R by

$$K_Ga=Ra/(PY) \qquad \text{(VI-52)}$$

where Y = mole fraction of CO_2

7. Material and Heat Balances

The material-balance and heat-balance programs are the basic framework on which the design of column height is achieved. In many cases, constant temperature through the whole length of the column is assumed. This greatly simplifies the calculation. However, when the heat of absorption (or heat of reaction) is appreciable as in the cases of CO_2 absorption into K_2CO_3 solutions and amine solutions, the temperature effects can no longer be overlooked. The heat balance therefore incorporated with the material balance in every stage of calculation.

7.1 Hot Potash Process

i. Material and Heat Balances for the Absorber

Figure VI-10 shows the diagrammatric representation of material balance for the absorber of the hot potash process. It is assumed that H_2 , CH_4, CO, and N_2 are not absorbed into the liquid stream. Since the absorber is operated at high pressure, it can also be assumed that the amount of water vaporized from the liquid stream and the amount of water condensed from the gas stream are negligibly small. Therefore CH_4, CO, N_2, H_2 , and water vapor can be considered as inert gases in the absorber. The material balance for CO_2 around the absorber gives

$$F \cdot X_{ab} + G_{at}\, y_{at} = F \cdot X_{at} + G_{ab}\, y_{ab} \qquad \text{(VI-58)}$$

where

F = molar flow-rate of the reactant (K_2CO_3 in this case) in the original solution, [lb-mole/hr]

= L · Z

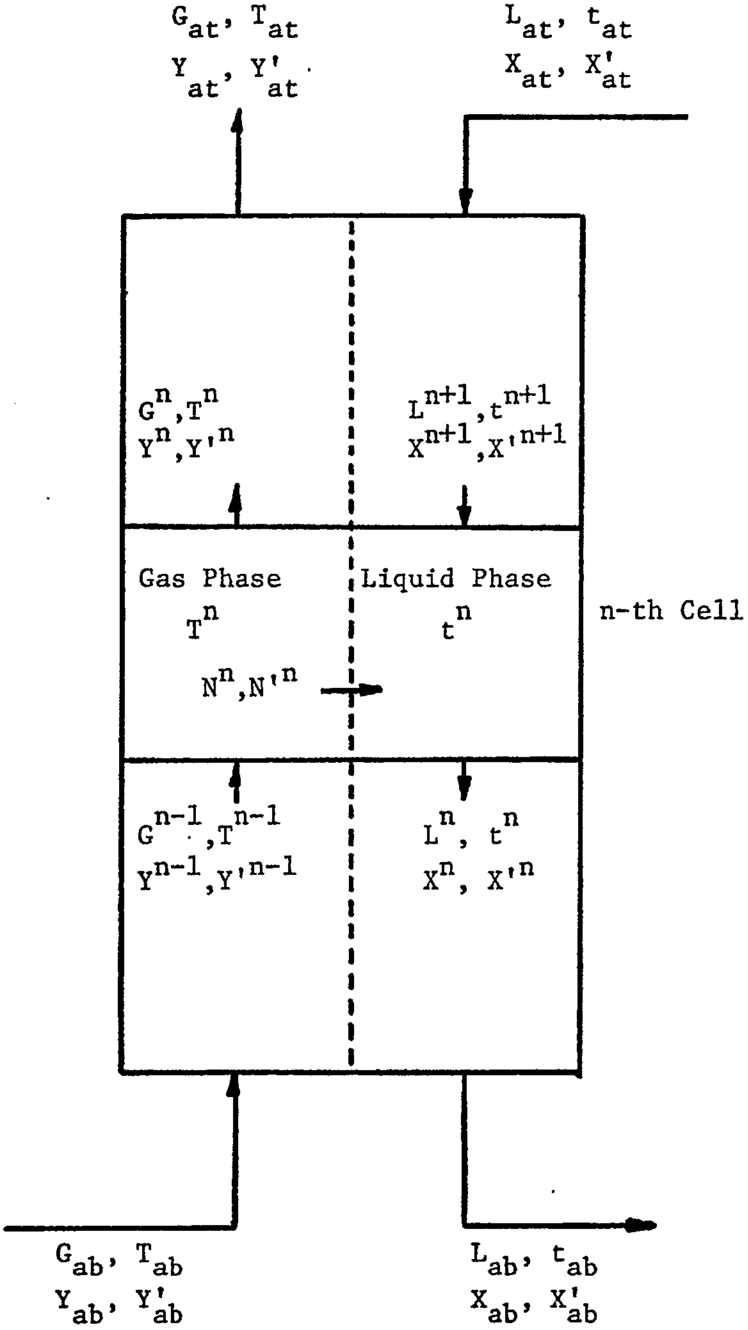


Figure VI-10 Diagrammatic Representation of Material Balance for The Absorber of The Hot Potash Process

L = molar liquid flow-rate including water and reactant (in both reacted and unreacted forms), [lb-mole/hr]

Z = mole fraction of reactant (in both reacted and unreacted forms) in the solution

X = carbonation ratio - i.e., moles CO_2 absorbed per mole reactant originally present in solution

y = mole fraction of CO_2 in gas

G = molar gas flow rate [lb-mole/hr]

Subscripts ab and at denote quantities at the bottom of the absorber and quantities at the top of the absorber, respectively.

According to the assumption, L and Z are constant in the absorber and

$$F = L_{ab} \cdot Z_{ab} = L_{at} \cdot Z_{at} = L \cdot Z \qquad \text{(VI-54)}$$

By introducing a constant gas flow-rate basis, G_i, Equation (VI-53) can be rewritten as

$$\frac{Y_{ab} - Y_{at}}{X_{ab} - X_{at}} = \frac{L \cdot Z}{G_i} \qquad \text{(VI-55)}$$

where G_i = molar flow rate of inert gas in the absorber, [lb-mole/hr]

Y = mole CO_2 per mole inert gas

$= \dfrac{y}{1 - y - y'}$

y' = mole fraction of H_2S in gas stream

Likewise, the material balance for H_2S around the absorber gives

$$\frac{Y'_{ab} - Y'_{at}}{X'_{ab} - X'_{at}} = \frac{L \cdot Z}{G_i} \qquad \text{(VI-56)}$$

where $Y' =$ mole H_2S per mole inert gas $= \dfrac{y'}{1 - y - y'}$

X' = mole H_2S absorbed per mole reactant original present in solution

As will be seen later, after sufficient contact between gas and liquid, the gas temperature (T) and liquid temperature (t) at the top of the absorber are approximately equal, thus, $T_{at} = t_{at}$. The heat balance around the absorber can be written as

$$G_{ab} \cdot \overline{Cp} \; T_{ab} + L_{at}\overline{CpL} \; t_{at} + F \cdot (X_{ab} - X_{at})\Delta H + F \cdot (X'_{ab} - X'_{at})\Delta H'$$
$$= L_{ab} \overline{CpL} \cdot t_{ab} + G_{at} \cdot \overline{Cp} \cdot T_{at} \qquad \text{(VI-57)}$$

where $\overline{Cp}$ and $\overline{CpL}$ are mean heat capacities in BTU/lb-mole °F of gas stream and liquid stream, respectively, for the temperature range from 0°F to the corresponding temperature.

A considerable amount of data on absorption-column performance is presented in term of the "height of transfer unit" (HTU) and the design procedures based on their simplicity and similarity to plate-column calculation methods. The basic concept is that the calculation of column height invariably requires the integration of some gas phase composition relationship. In the design of a gas purifier using K_2CO_3 solution as solvent, the "compartment-in-series" model is more convenient for simultaneous calculations of material and heat balances along the length of the absorber and the regenerator. This is particularly true when the mass transfer coefficient can be readily obtained from some correlation as in the case of CO_2 absorption into hot potash solution. To make use of this model, the absorber and the regenerator are divided into small compartments (or cells) of equal volume in each of which the fluid is completely mixed. The composition and temperature of each fluid are assumed to remain constant within each compartment. A cell-to-cell calculation of material and heat balances can be carried out from bottom up to top of the absorber and the regenerator. If the height of each cell is small enough, it can be shown that both "HTU" and "compartment-in-series" methods give approximately the same result. Since mass and heat transfer interact with each other, material and heat balances cannot be fully separated and it is necessary to iterate in the temperature and the gas phase composition in each cell to obtain consistent material and heat balances.

The rates of CO_2 and H_2S transfer from the body of the gas to the body of the liquid in the n-th cell can be expressed as

$$N^n = (K_G a)^n \cdot \Delta h \cdot (P^n_{CO_2} - P^{*n}_{CO_2}) \qquad \text{(VI-58)}$$

$$N'^n = (K_G a)'^n \cdot \Delta h \cdot (P^n_{H_2S} - P^*_{H_2S}) \qquad \text{(VI-59)}$$

where N = rate of CO_2 mass flux from bulk of gas to bulk of liquid [lb mole/hr ft^2]

$K_G a$ = gas side over-all mass transfer coefficient [lb mole/ft^3 hr atm]

Δh = height of each cell, [ft]

P_{CO_2}, P_{H_2S} = partial pressures of CO_2 and H_2S, respectively, in gas phase, [atm]

$P^*_{CO_2}, P^*_{H_2S}$ = equilibrium partial pressures of CO_2 and H_2S respectively, [atm].

Prime denotes quantity of H_2S and superscript n denotes the cell number.

Defining L_o as the superficial molar liquid flow rate (lb mole of reactant and water originally present/ft^2 hr), and G_o the superficial molar flow rate of the inert gases (lb mole/hr ft^2) material balances can be written for liquid side and gas side as

$$N^n = L_o \cdot Z\ (X^n - X^{n+1}) = G_o\ (Y^{n-1} - Y^n) \qquad \text{(VI-60)}$$

$$N'^n = L_o \cdot Z\ (X'^n - X'^{n+1}) = G_o\ (y'^{n-1} - Y'^n) \qquad \text{(VI-61)}$$

The heat balance around the n-cell is given as (VI-62)

$$G^n\ \overline{Cp}^n\ T^n + q_g^n + q_t^n = G^{n-1}\ \overline{Cp}^{n-1}\ T^{n-1}$$

for the gas side and

$$L^n\ \overline{Cp_L}^n\ t^n = q_r^n + q_g^n + q_t^n + L^{n+1}\ \overline{Cp_L}^{n+1}\ t^{n+1} \quad \text{for the liquid side} \qquad \text{(VI-63)}$$

where q_g^n = rate of heat carried by CO_2 and H_2S from gas phase to liquid phase in n-th cell due to absorption of CO_2 and H_2S

= $(N^n\ \overline{Cp_c}^n + N'^n \cdot \overline{Cp_h}^n)\ T^n$, [BTU/hr]

q_t^n = rate of heat transferred from gas phase to liquid phase in n-th cell

= $h \cdot a \cdot \Delta h \cdot S_a \cdot (T^n - t^n)$, [BTU/hr]

h = heat transfer coefficient, [BTU/ft^2-hr-°F]

a = effective interfacial area per unit volume of packing, [ft^2/ft^3]

S_a = total cross-sectional area of the absorber, [ft^2]

q_r^n = rate of heat generated due to absorption in n-th cell,

= $(N^n\ \Delta H + N'^n\ \Delta H')\ S_a$ [BTU/hr]

T^n, t^n = gas temperature and liquid temperature, respectively, in n-th cell

$\overline{Cp}^n$, $\overline{Cp}_c^n$, $\overline{Cp}_h^n$, $\overline{Cp}_L^n$ = mean heat capacities of gas mixture, CO_2, H_2S, and liquid stream, respectively in the temperature range 0 to T^n or t^n, whichever applies [BTU/lb mole°F]

For each cell, the material and heat balances must be calculated simultaneously to obtain X, X', Y, Y', T, and t. The calculation can be started from the first cell (bottom cell) with n = 1

$X^1 = X_{ab}$, $X'^1 = X'_{ab}$; $Y^\circ = Y_{ab}$, $Y'^\circ = Y'_{ab}$

$T^\circ = T_{ab}$, $t^1 = t_{ab}$

An iteration procedure is required for each cell.

ii. Material and Heat Balances for the Regenerating System

Figure VI-11 shows the diagrammatic representation of material balance for the regenerating system of the hot potash process. Flash regeneration is the most economical regeneration method because it does not require gas stripping. Therefore, it is desirable to incorporate a flash drum (or chamber) into the regenerating system. The flash drum may be either a separate unit or an integral part of the regenerator. The spent solution is first flashed nearly to the operating pressure of the regenerator and subsequently the regeneration is carried out by stripping with steam in the regenerator. Theoretically, equilibrium can be achieved in the flash drum although practical desorption in the flash drum is seldom carried out to equilibrium. There is practically no information in the literature regarding the design of a flash drum. For material balance purpose, it may be assumed that equilibrium exists between gas phase and liquid phase in the flash drum.

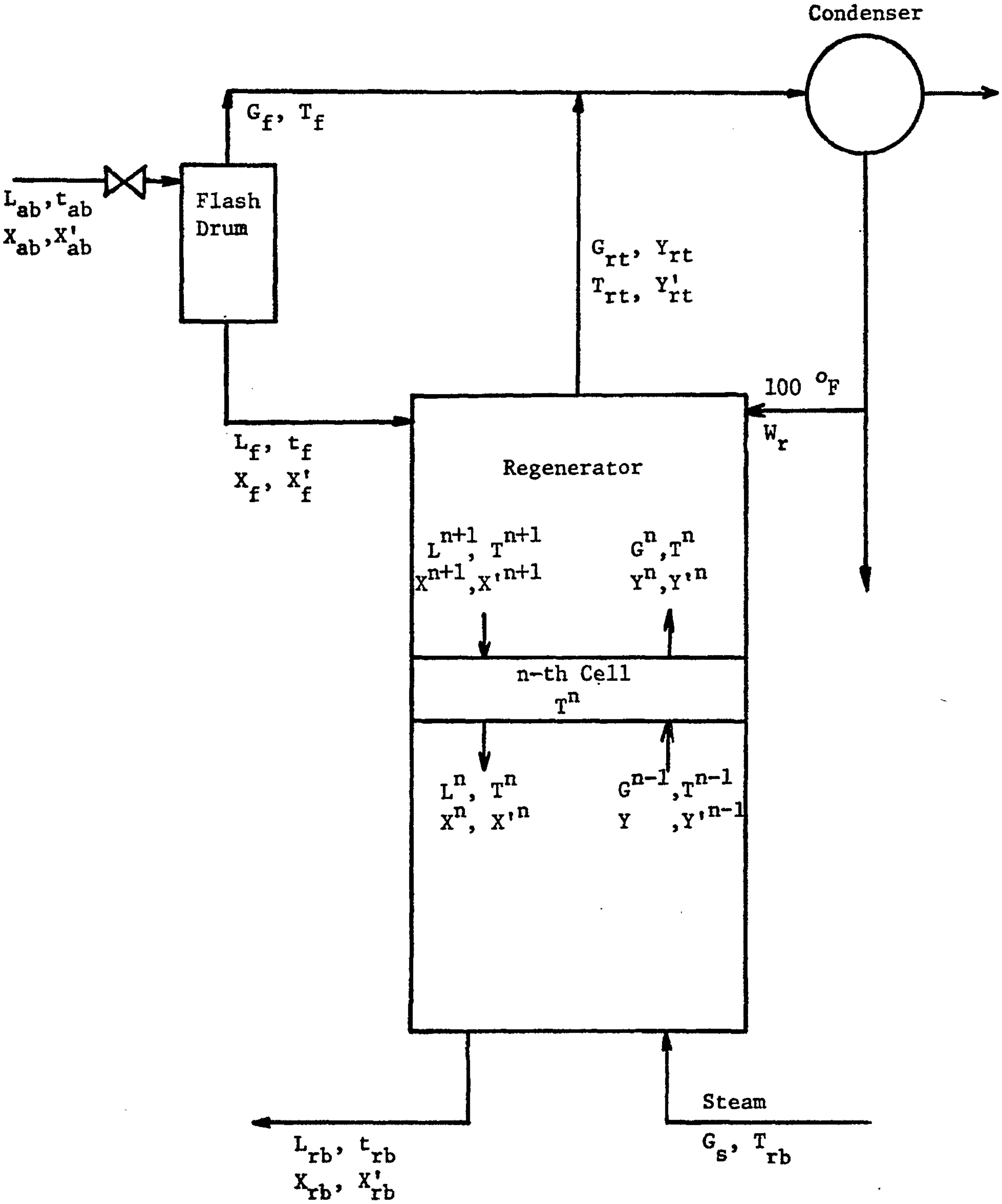


Figure VI-11 Diagrammatic Representation of Material Balance for the Regenerating System of The Hot Potash Process

Thus, material balance and heat balance around the flash drum can be given as follows:

Material balance for CO_2:

$$F X_{ab} = FX_f + Gc_f \qquad \text{(VI-64)}$$

Material balance for H_2S:

$$F X'_{ab} = FX'_f + G_{h_f} \qquad \text{(VI-65)}$$

Material balance for water:

$$L_{ab} = L_f + Gw_f \qquad \text{(VI-66)}$$

Heat balance:

$$L_{ab}\,\overline{C}_{pL}\,t_{ab} = L_f\,\overline{C}_{pL}\,t_f + G_f\,\overline{C_p}\,T_f + G_{cf}\,\Delta H + G_{hf}\,\Delta H' + G_{wf}\,\Delta H_v \qquad \text{(VI-67)}$$

G_f = molar flow rate of gas leaving the flash drum

$= G_{cf} + G_{hf} + G_{wf}$ [lb-mole/hr]

where G_{cf}, G_{hf}, G_{wf} = molar flow rates of CO_2, H_2S, and water vapor. respectively leaving the top of the flash drum [lb-mole/hr]

X_f, X'_f = mole CO_2/mole reactant and mole H_2S/ mole reactant, respectively, in liquid stream leaving the flash drum

L_f = molar flow rate of liquid stream leaving the flash drum, [lb-mole/hr]

$T_f = t_f$ = flash drum temperature

ΔH_v = heat of vaporization of water, [BTU/lb-mole]

Gc_f, Gc_h, and Gw_f are related by

$$G_{hf} = \frac{P^*_{H_2S}}{P^*_{CO_2}}\,G_{c_f} \qquad \text{(VI-68)}$$

$$G_{wf} = \frac{P^*_{H_2O}}{P^*}\,G_{c_f} \text{ and} \qquad \text{(VI-69)}$$

$$P^*_{H_2S} + P^*_{CO_2} + P^*_{H_2O} = P_r \qquad \text{(VI-70)}$$

where $P^*_{CO_2}$, $P^*_{H_2S}$ and $P^*_{H_2O}$ are the equilibrium partial pressures of CO_2, H_2S, and water, respectively, in the flash drum. Pr is the operating pressure of the regenerator. t_f, Gc_f, G_{h_f}, G_{w_f}, X_f, X_f' and L_f can be calculated from Eqs. (VI-64) to (VI-70) by iteration.

The heat transfer coefficient h for the regenerator is in the order of 500 BTU/ft^2-hr-°F. With this high heat transfer coefficient, gas temperature and liquid temperature in the regenerator are essentially equal, except near the bottom of the regenerator when superheated steam is used. Saturated steam will be used directly to strip the spent solution in the regenerator. Therefore, it can be assumed that gas temperature and liquid temperature are equal throughout the regenerator.

The temperature in the regenerator should be maintained as high as possible to achieve the most effective desorption. But the temperature can not exceed the boiling point of the liquid. Therefore, the temperature at the bottom of the regenerator T_{rt} is equal to the boiling temperature of the liquid at the bottom of the regenerator. T_{rt} can be chosen such that the following relation is satisfied:

$$(P^*_{CO_2} + P^*_{H_2S} + P^*_{H_2O}) \Big|_{T=T_{rt}} = Pr \qquad \text{(VI-71)}$$

In the stripping process, some amount of steam must be condensed to supply the heat to raise the liquid temperature and to dissociate CO_2 and H_2S from the solution. The rate of condensation of steam is denoted by W_c, (lb-mole/hr). In the hot potash process considered here, G_{wf} is greater than W_c. Therefore some reflux must be returned to make up the water balance. If W_r is the flow rate of water returned to the top of the regenerator, then

$$W_r = G_{wf} - W_c \qquad \text{(VI-72)}$$

The water returned at 100°F will be mixed with the solution coming from the flash drum at t_f. The resulting liquid temperature at the top of the regenerator is T_{rt}. Thus

$$L_f \; \overline{C_{pL}} \; (t_f - T_{rt}) = W_r \; \overline{C_{pw}} \; (100 - T_{rt}) \qquad \text{(VI-73)}$$

where T_{rt} = temperature at top of the regenerator,[°F]

$\overline{C_{pw}}$ = average heat capacity of water, (BTU/lb mole °F)

Heat balance around the regenerator gives

$$L_f \cdot \overline{C_{pL}} \cdot t_f + W_r \overline{C_{pW}}(100) + G_s \cdot \overline{C_{ps}} \; Trb + W_r \Delta H_v = L_{rb} \; \overline{C_{pL}} \; T_{rb} \; +$$
$$(G_s - W_r)\overline{C_{ps}} \; T_{rt} + F(X_f - X_{rb})(\Delta H + \overline{C_{pc}} \; T_{rt}) + F(X'_f - X'_{rb})(\Delta H' + \overline{C_{ph}} \; T_{rt})$$

where G_s = molar flow rate of steam at bottom of the regenerator [lb-mole/hr]

$\overline{C_{ps}}$ = mean heat capacity of steam, [BTU/lb-mole-°F]

L_{rb} = molar flow rate of liquid at bottom of regenerator

= L_{at}, [lb mole/hr]

X_{rb} = mole CO_2/mole reactant in liquid at bottom of the regenerator

= X_{at}

X'_{rb} = mole H_2S/mole reactant in liquid at bottom of the regenerator

= X'_{at}

Eqs. (VI-72) to (VI-74) can be used to solve for T_{rt}, Wc, and Wr.

The molar flow rate of the off gas from the regenerator, G_{rt} is obtained by the equation

$$G_{rt} = (G_s - W_c) + F(X_f - X_{rb}) + F(X'_f - X_{rb}) \qquad \text{(VI-75)}$$

The mole fractions of CO_2 and H_2S in the off gas of the regenerator are, respectively,

$$y_{rt} = \frac{F(X_f - X_{rb})}{G_{rt}} \quad \text{and} \qquad \text{(VI-76)}$$

$$y'_{rt} = \frac{F(X'_f - X'_{rb})}{G_{rt}} \qquad \text{(VI-77)}$$

The material balances for the nth cell of the regenerator are given as:

$$-N^n = (K_Ga)^n \cdot \Delta h \cdot (P^*_{CO_2} - P^n_{CO_2}) = \frac{F(X^{n+1} - X^n)}{S_r}$$

$$= \frac{G^n y^n - G^{n-1} y^{n-1}}{S_r} \qquad \text{(VI-78)}$$

$$-N'^n = (K_Ga)'^n \cdot h \cdot (P^*_{H_2S} - P^n_{H_2S}) = \frac{F(X'^{n+1} - X')}{S_r}$$

$$= \frac{G^n y'^n - G'^{n-1} y'^{n-1}}{S_r} \qquad \text{(VI-79)}$$

where G^n = molar gas flow rate in the n-th cell

$= G^n_c + G^n_h + G^n_w$, [lb mole/hr]

G^n_c = molar flow rate of CO_2 in gas stream in the n-th cell

$= F(X^n - X_{rb})$, [lb mole/hr]

G^n_h = molar flow rate of H_2S in gas stream in the n-th cell

$= F(X'^n - X_{rb})$, [lb mole/hr]

G^n_w = molar flow rate of steam in the n-th cell

$= G_s - W^n_c$

W_c^n = total condensation rate of steam in cells 1 to n, [lb mole/hr]

$y^n = G_c^n / G^n$

$y'^n = G_h'^n / G^n$

S_r = total cross-sectional area of the regenerator, [ft^2]

The temperature of the nth cell T^n can be assumed to be at the boiling point of the solution in the nth cell. W_c^n can then be calculated from heat balance equation

$$L_{rb} \cdot \overline{Cp}_L \cdot T_{rb} + G^n \overline{Cp} \cdot T^n + F(X^{n+1} - X_{rb}) \cdot \Delta H + F(X'^{n+1} - X'_{rb}) \cdot \Delta H'$$

$$= L^{n+1} \overline{Cp}_L \cdot T^{n+1} + G_s \cdot \overline{Cp}_s \cdot T_{rb} + W_c^n \Delta H_v \qquad \text{(VI-80)}$$

where L^{n+1} = molar liquid flow rate in the (n+1)-th cell

$= L_{rb} - W_c^n$

Calculation of X, X', y, y', and T distribution in the regenerator can be started from the first cell with

$n = 1$

$W_c^{n-1} = G_c^{n-1} = G_h^{n-1} = Y^{n-1} = Y'^{n-1} = 0$

$L^1 = L_{rb} = L_{at} = L$

$X^1 = X_{rb}$

$X'^1 = X'_{rb}$

$G^1 = G_s$

Again, an iteration procedure is required for each cell.

7.2 Amine Process

i. Material and Heat Balances for the Absorber

Figure VI-12 shows the diagrammatic representation of material balance for the absorber of the amine process. The equations for the material and heat balances around the absorber of the hot potash process [Eqs. (VI-53) to (VI-57)] are applicable to the amine process. Since adequate K_Ga correlations for the absorption of CO_2 and H_2S by MEA solutions are not available as indicated in Section 6.2, the method of the rate of absorption per unit interfacial area, R, proposed by Dankwerts and Sherman [48] is used to calculate the height of the column. The following simple procedure can be used to calculate the height of the packed column for CO_2 absorption under isothermal condition:

(a) Calculate the composition of liquid and gas through the column by material balance.

(b) Estimate the rate of absorption per unit interfacial area, R

(c) Determine the height of the column by

$$h_c = \frac{L_o}{\alpha a \rho_m} \int_{C_2}^{C_1} \frac{d\, C_o}{R} \qquad \text{(VI-81)}$$

where h_c = height of column, [ft]

L_o = superficial molar flow rate of liquid, [lb mole/hr ft^2]

ρ_m = molar density of liquid, [lb mole/ft^3]

C_o = concentration of free MEA in the solution, [lb mole/ft^3]

C_1, C_2 = values of C_o at the top and bottom, respectively of the column, [lb mole/ft^3]

α = number of moles of reactant reacting with each mole of dissolved gas

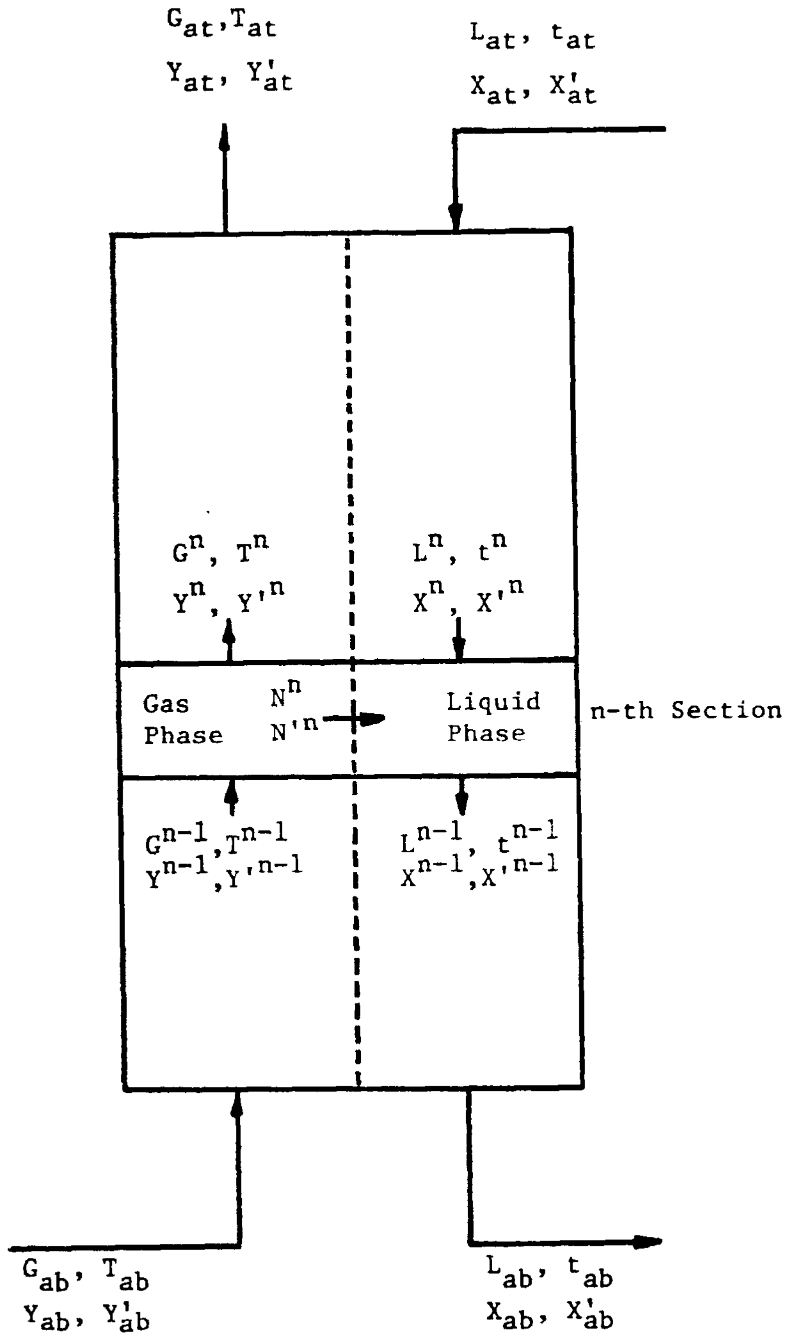


Figure VI-12 Diagrammatic Representation of Material Balance for The Absorber of The Amine Process

For simultaneous absorption of CO_2 and H_2S by a MEA solution under the adiabatic condition, the material and heat balance must be calculated over the entire length of the column. It is convenient to divide the column into a number of sections. The height of each section is usually not equal. A procedure is presented for the computation of absorption of CO_2 and H_2S under adiabatic condition, as follows:

(a) Divide $(y_{ab} - y_{at})$ into N portions so that $(y^{n-1} - y^n)$ is small enough, where y is the mole fraction of CO_2, superscripts n-1 and n denote quantities at the top of the (n-1)-th section and the n-th section, respectively, of the column, and subscripts ab and at denote quantities at the bottom and the top, respectively, of the column.

(b) Calculate the compositions of liquid and gas at the top of the n-th section by the following material balance equations:

$$N^n = (Y^{n-1} - Y^n)\, G_o = (X^{n-1} - X^n)\, F \tag{VI-82}$$

$$N'^n = (Y'^{n-1} - Y'^n)\, G_o = (X'^{n-1} - X'^n) \tag{VI-83}$$

$$C_o^n = (1 - 2\, X^n - X'^n) Z\, \rho_m \tag{VI-84}$$

where $Y = y/(1 - y - y')$; $Y' = y'/(1 - y - y')$ (VI-85)

Since y'^n, the mole fraction of H_2S at the top of the n-th section, is not known initially, y'^r is used as the first approximation for y'^n. The approximate value of C_o^n can then be calculated.

(c) Estimate R^n and R'^n, the rates of absorption of CO_2 and H_2S, respectively, per unit interfacial area, by the method given in Section 4.2. Because the initial values of t^n and T^n are not known,

t^{n-1} and T^{n-1} are used as the first approximated values to evaluate R^n and R'^n. If

Eq. (VI-26) is satisfied, the reaction is a pseudo-first order reaction and the absorption rate of CO_2 can be expressed as

$$\begin{aligned} R^n a &= a\ C_i^n \sqrt{k_L{}^2 + D\ k_2\ C_o^n} \\ &= k_G a\ P\ (y^n - y_i^n) \end{aligned} \qquad \text{(VI-86)}$$

where C_i = concentration of CO_2 in liquid at interface

= $H \cdot P \cdot y_i$, [lb mole/ft^3]

y_i = mole-fraction of CO_2 in gas at interface

k_2 = k_{Am} = 2nd-order reaction ration rate constant for the reaction between CO_2 and amine, [ft^3/lb mole hr]

D = diffusivity of the disolving CO_2 in the solution, [ft^2/hr]

Eq. (VI-86) can be rewritten as

$$R^n = \frac{k_G a\ H\ P\ y^n \sqrt{k_L{}^2 + D\ k_2\ C_o^n}}{k_G a + a\ H\ \overline{k_L^2 + D\ k_2\ C_0^n}} \qquad \text{(VI-87)}$$

If Eq. (VI-28) is satisfied, the reaction is an instantaneous second-order reaction and the absorption rate of CO_2 can be expressed as

$$\begin{aligned} R^n a &= a\ k_L C_i^n\ [\sqrt{D/D_o} + \sqrt{D_o/D}\ C_o^n/(2\ C_i^n)] \\ &= k_G a\ P\ (y^n - y_i^n) \end{aligned} \qquad \text{(VI-88)}$$

where D_o is the diffusivity of amine in the solution, (ft^2/hr)

hence

$$R^n = \frac{H\ P\ y^n - C_o^n/(2\ k_L)\ \ D_o/D}{1/k_L \sqrt{D_o/D} + a\ H/k_G a} \qquad \text{(VI-89)}$$

If neither of Eqs. (VI-26) and (VI-28) is satisfied, Equation (VI-29) should be used to calculate R^n. From Equation (VI-29)

$$R^n a = k_G a P (y^n - y_i^n) = a E k_L H P y_i^n \tag{VI-90}$$

Thus

$$R^n = \frac{E k_L H P y^n}{1 + \frac{E k_L a H}{k_G a}} \tag{VI-91}$$

$$y_i^n = y^n - \frac{R^n}{k_G a P} \tag{VI-92}$$

To calculate R^n, let $y_i^n = y^n$ as a first approximation. Then R^n is evaluated from Eq. (VI-90). Calculate the second approximation for y_i^n by Equation (VI-91) and repeat the procedure until the successive values of R^n are nearly equal within a given tolerance.

Similar methods can be used to calculate R'^n. The only difficulty is that the data on the second-order reaction rate constant for the reaction between H_2S and MEA are not available. Leibush and Shneerson [55] conducted a study of simultaneous absorption of CO_2 and H_2S in MEA solutions. With a mixed gas containing 2.5 to 20 times as much CO_2 as H_2S, they found that H_2S has an absorption coefficient 6 to 10 times greater than that of CO_2. If k_{Am} is used to calculate R' and thus $K_G a$ for H_2S absorption using their experimental conditions, conservative $K_G a$ values are obtained compared to their $K_G a$ data for H_2S absorption. This indicates that the second-order reaction rate constant for the reaction between H_2S and MEA should be somewhat greater than k_{Am}. For a conservative design, k_{Am} is used in the calculation of R'. Since Y' is always very small in the present study, Equation (VI-26) is always satisfied. Therefore, pseudo-first order reaction assumption is valid.

Equations (VI-87), (VI-89), and (VI-91) are obtained based on the assumption that back pressure of the dissolved gas is negligible compared to its partial pressure in the gas phase. When very high purity of the treated gas is required, back pressure of the gas must be considered in calculating R near the top of the absorber The reaction near the top of the absorber is usually pseudo-first order reaction and Equation VI-30 is applicable.

(d) Calculate the height of the n-th section Δh^n by the equation

$$\Delta h^n = \frac{L_o}{2 a \rho_m} \int_{C_o^{n-1}}^{C_o^n} \frac{d C_o}{R} \tag{VI-93}$$

Trapezoidal rule can be used for the numerical integration. Thus

$$\Delta h^n = \frac{L_o}{4 a \rho_m} (C_o^n - C_o^{n-1}) \left(\frac{1}{R^n} + \frac{1}{R^{n-1}} \right) \tag{VI-94}$$

(e) Calculate y'^n and X'^n by the material balance equations for H_2S

$$N'^n = 0.5 \, a \, \Delta h^n (R'^{n-1} + R'^n) \tag{VI-95}$$

$$Y'^n = Y'^{n-1} - \frac{N'^n}{G_o} \tag{VI-96}$$

$$y'^n = \frac{Y'^n}{1 - Y^n - Y'^n} \tag{VI-97}$$

$$X'^n = X'^{n-1} - \frac{N'^n}{L_o Z} \tag{VI-98}$$

(f) Calculate gas temperature and liquid temperature at the top of the n-th section, T^n and t^n, respectively, by the following heat balance equations,

$$G^n \overline{C_p}^n T^n + (N^n \overline{C_{pc}}^n + N'^n \overline{C_{ph}}^n)(T^n + T^{n-1})\, S_a/2$$

$$+ \; h\, a\, \Delta h^n S_a (T^n - t^n + T^{n-1} - t^{n-1})/2 = G^{n-1} \overline{C_p}^{n-1} T^{n-1} \qquad \text{(VI-99)}$$

$$L^n \overline{C_{pL}}^n t^n + [(N^n \overline{C_{pc}}^n + N'^n \overline{C_{ph}}^n)(T^n + T^{n-1})/2 + (N^n \Delta H + N'^n \Delta H')$$

$$+ \; h\, a\, \Delta h^n (T^n - t^n + T^{n-1} - t^{n-1})/2]\, S_a = L^{n-1} \overline{C_{pL}}^{n-1} t^{n-1} \qquad \text{(VI-100)}$$

Steps (b) through (f) must be iterated for each section to obtain consistent material and heat balances. After the height of every section is calculated, the packed height of the column can be calculated by

$$h_t = \sum_{n=1}^{N} \Delta h^n \qquad \text{(VI-101)}$$

ii. Material and Heat Balance for the Regenerating System

Figure VI-13 shows the diagrammatic representation of material balance for the regenerating system of the amine process. Again, it is assumed that gas temperature and liquid temperature are equal and are at the local boiling point of the liquid throughout the regenerator. Since the partial pressure of MEA over aqueous solution is very low (Eq VI-19) it can be assumed that MEA does not vaporize in the regenerator. Material balance and heat balance equations around the flash drum of the amine process are similar to those of the hot potash process. The temperature of the reboiler T_b is the boiling point of

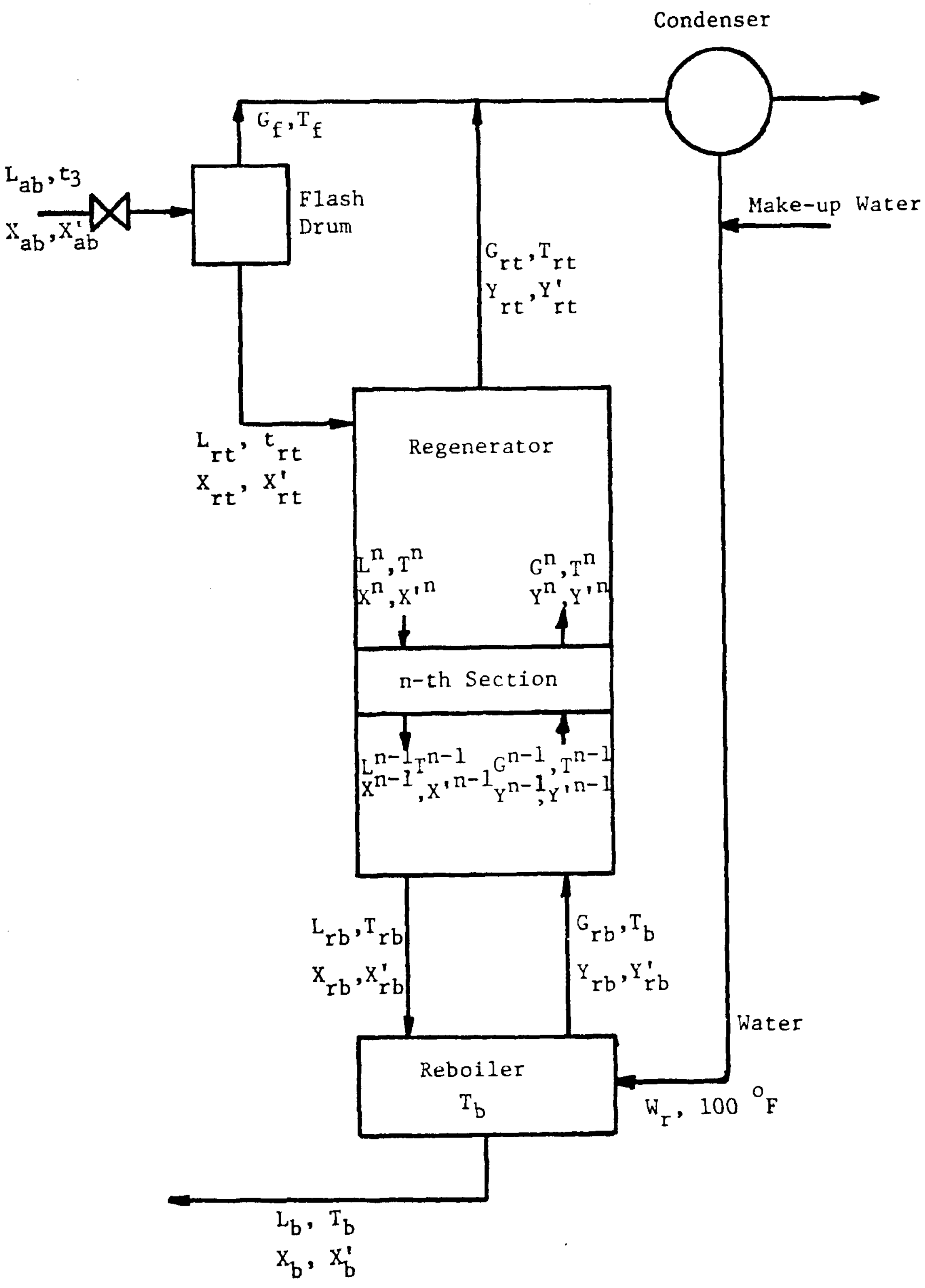


Figure VI-13 Diagrammatic Representation of Material Balance for The Regenerating System of The Amine Process the liquid leaving the reboiler. It is also assumed that equilibrium exists between the gas phase and liquid phase in the reboiler. The reflux is returned to the reboiler saturated with CO_2 and H_2S. But their quantities are small and can be neglected for the purpose of material balance calculation. The material balance and heat balance around the reboiler can be given as follows:

Material balance for CO_2:

$$F X_{rb} = F X_b + G_{cb} \tag{VI-102}$$

Material balance for H_2S:

$$F X'_{rb} = F X'_b + G_{hb} \tag{VI-103}$$

Material balance for water:

$$L_b = L_{rb} + W_r - G_s \tag{VI-104}$$

Heat balance:

$$\begin{aligned} L_b \overline{C_{pL}} T_b + G_{rb} \overline{C_p} T_b + G_{cb} \Delta H + G_s \quad H + G_{hb} \Delta H' \\ = Q_b + W_r \overline{C_{pw}} (100) + L_{rb} \overline{C_{pL}} T_{rb} \end{aligned} \tag{VI-105}$$

where G_{cb}, G_{hb}, G_s = molar flow rates of CO_2, H_2S and steam, respectively, [lb mole/hr]

X_b = mole CO_2/mole reaction in liquid leaving the reboiler

= X_{at}

X'_b = mole H_2S/mole reactant in liquid leaving the reboiler

= X'_{at}

L_b = molar flow rate of liquid leaving the reboiler, [lb mole/hr]

L_{rb} = molar flow rate of liquid leaving the bottom of the regenerator, [lb mole/hr]

W_r = molar flow rate of the reflux, [lb mole/hr]

G_{rb} = molar flow rate of gas entering the bottom of the regenerator, [lb mole/hr]

$= G_s + G_{cb} + G_{hb}$

T_b = temperature of the reboiler, [°F]

T_{rb} = temperature at the bottom of the regenerator, [°F]

Q_b = heat duty of the reboiler, [BTU/hr]

The value, 100, is the temperature of reflux, [^oF]

G_{cb}, G_{hb}, and G_s are related by

$$G_{cb} = G_s \, (P^*_{CO_2}/P^*_{H_2O}) \quad \text{(VI-106)}$$

$$G_{hb} = G_s \, (P^*_{CO_2}/P^*_{H_2O}) \quad \text{(VI-107)}$$

$$P^*_{H_2O} + P^*_{CO_2} + P^*_{H_2S} = P_r \quad \text{(VI-108)}$$

where $P^*_{H_2O}$, $P^*_{CO_2}$, and $P^*_{H_2S}$ are the equilibrium partial pressures of H_2O, CO_2 and H_2S, respectively, in the reboiler and P_r, the operating pressure of the regenerator.

The material balance around the regenerator and the reboiler gives

$$F\,(X_{rt} - X_b) = G_{rt}\, y_{rt} \quad \text{(VI-109)}$$

$$F\,(X'_{rt} - X'_b) = G_{rt}\, y'_{rt} \quad \text{(VI-110)}$$

$$G_{rt} = F(X_{rt} - X_b) + F\,(X'_{rt} - X'_b) + (G_s - W_c) \quad \text{(VI-111)}$$

where G_{rt} = molar gas flow rate leaving the top of the regenerator, [lb mole/hr]

W_c = rate of condensation of steam in the regenerator, [lb mole/hr]

The subscript rt denotes quantities at the top of regenerator

The flow rate of the reflux can be determined by the equation

$$W_r = G_s - W_c + G_{wf} \quad \text{(VI-112)}$$

The heat balance around the regenerator and the reboiler can be written as

$$L_b\overline{C_{pL}}T_b + F\,(X_{rt} - X_b)\Delta H + F(X'_{rt} - X'_b)\Delta H' + (G_s - W_c)\Delta H_v + G_{rt}\overline{C_p}\,T_{rt} = L_{rt}\,\overline{C_{pL}}T_{rt} + W_r\,\overline{C_{pw}}(100) + Q_b \qquad \text{(VI-113)}$$

and heat balance around the regenerator,

$$L_{rb}\overline{C_{pL}}T_{rb} + F(X_{rt} - X_{rb})\Delta H + F(X'_{rt} - X'_{rb})\Delta H' + G_{rt}\overline{C_p}T_{rt} = L_{rt}\overline{C_{pL}}T_{rt} + G_{rb}\overline{C_p}\,T_b + W_c\,\Delta H_v \qquad \text{(VI-114)}$$

The three heat balance equations, Eqs. (VI-105), (VI-113), and (VI-114), be rewritten to obtain three simultaneous equations with three unknowns Q_b W_c, and T_{rb}, which are easily solved.

The height of the regenerator can also be calculated by the method of the rate of absorption per unit interfacial area, R. The local temperature in the regenerator is assumed to equal the local liquid boiling point. The material balance equations for each section of the regenerator of the amine process are similar to those for each cell of the regenerator of the hot potash process Thus

$$-N^n = F\,(X^n - X^{n-1})/S_r = (G^n\,y^n - G^{n-1}y^{n-1})/S_r \qquad \text{(VI-115)}$$

$$-N'^n = F\,(X'^n - X'^{n-1})/S_r = (G^n\,y'^n - G^{n-1}y'^{n-1})/S_r \qquad \text{(VI-116)}$$

$$G^n = G^n_c + G^n_h + (G_s - W^n_c) \qquad \text{(VI-117)}$$

$$W^n_c\Delta H_v + G_{rb}\,\overline{C_p}\,T_{rb} + L^n\,\overline{C^n_{pL}}T^n = L_{rb}\overline{C_{pL}}T_{rb} + G^n\overline{C^n_p}T^n + F(X^n - X_{rb})\Delta H + F(X'^n - X'_{rb})\,\Delta H' \qquad \text{(VI-118)}$$

Note that the superscript n indicates the quantities at the top of the n-th section instead of in the n-th section.

8. Heat Exchanger Design

8.1 Hot Potash Process

i. Feed Gas Cooler

The temperature of the feed gas from the water gas shift converter is too high for proper gas purification operation in absorbers. Therefore, a heat exchanger is required to reduce the feed gas temperature before it enters the bottom of the absorber. The arrangement of the feed gas cooler is shown in Figure VI-1. Treated water from the exit of a condenser at 150°F is used as cooling water. Steam at T_{rb} is recovered from the heat excahnger. This steam is to be used to regenerate the spent potash solution. The amount of water condensed from the gas stream is

$$D_W = \frac{G_1(y_W - P_v/P)}{1 - P_v/P} \quad [\text{lb-mole/hr}] \qquad \text{(VI-119)}$$

where G_1, P, y_W, and P_v are molar flow rate of the feed gas [lb.mole/hr], feed gas pressure [atm], mole fraction of H_2O in feed gas, and vapor pressure of water at $(T_g)_{ab}$ [atm], respectively. The heat duty of the feed gas cooler is given by

$$Q_1 = G_1\overline{C}_p\,[T_1 - T_{ab}] + D_w \Delta H_v \quad [\text{BTU/hr}] \qquad \text{(VI-120)}$$

where

$\overline{C}_p$ = mean molar heat capacity of the gas stream [BTU/lb.mole°F]

T_1 = feed gas temperature [°F]

ΔH_v = heat of vaporization of water [BTU/lb-mole]

The water flow rate through the feed gas cooler can be calculated from Q_1 as

$$W_1 = \frac{Q_1}{T_{rb} - T_c + \frac{0.5\Delta H_v}{18}} \quad [\text{lb/hr}] \qquad \text{(VI-121)}$$

where T_c = temperature of entering water [°F]

Note that in developing this equation, one half of the water passed is considered to be vaporized while the other half is recycled (see Figure VI-1). Therefore the amount of steam produced in the feed gas cooler is 0.5 W_1 [lb/hr] and

$$T_c = 0.5\,[150 + T_{rb}] \quad [°\text{F}] \qquad \text{(VI-122)}$$

The gas temperature in the cooler at the point where water starts to vaporize (T_m) can be calculated from

$$T_m = T_1 - \frac{\frac{0.5W_1\Delta H_v}{18} - G_1\Delta H_v \frac{y_W - \frac{P_{vm}}{P}}{1 - \frac{P_{vm}}{P}}}{G_1 \cdot \bar{C}_p} \qquad \text{(VI-123)}$$

where

P_{vm} and ΔH_v are, respectively, the vapor pressure and the heat of vaporization of water at T_m.

The heat transfer area of the feed gas cooler is

$$A_1 = \frac{W_1}{U_1}\left[\frac{T_{ab} - T_c}{\Delta t_1} + \frac{\frac{0.5\Delta H_v}{18}}{\Delta t_2}\right] \qquad \text{(VI-124)}$$

where

$$\Delta t_1 = \frac{(T_m - T_{rb}) - (T_{ab} - T_c)}{\ln \frac{T_m - T_{rb}}{T_{ab} - T_c}} \quad ; \Delta t_2 = \frac{(T_1 - T_{rb}) - (T_m - T_{rb})}{\ln \frac{T_1 - T_{rb}}{T_m - T_{rb}}}$$

U_1 = over-all heat transfer coefficient [Btu/sq. ft-hr-^oF]

(An estimated value of 85 is used)

ii. Overhead Condensers

Two overhead condensers in parallel are used in the regenerating system to cool the off gases of the flash drum and the regenerator. Cooling water enters the condensers at 85 ^oF and leaves at 150 ^oF. The treated water from the exit of the first condenser is to be used as the cooling water for the feed gas cooler. Therefore the heat duty of the first condenser is

$$Q_{c1} = W_1 (150 - 85) \qquad \text{[Btu/hr]} \qquad \text{(VI-125)}$$

where W_1 is the treated cooling water flow rate required for the feed gas cooler.

The total molar flow rate of the gas entering the condensers is

$$G_{con} = G_{rt} + G_f \qquad \text{[lb-mole/hr]} \qquad \text{(VI-126)}$$

and the total molar flow rate of water vapor in the gas entering the condensers is

$$G_{wc} = G_s - W_c + G_{wf} \qquad \text{[lb-mole/hr]} \qquad \text{(VI-127)}$$

The off gases of the flash drum and the regenerator are to be cooled to 100 ^oF. The rate of water condensation from the gas stream is

$$D_{wc} = \frac{G_{wc}/G_{con} - P_{vc}/P_c}{1 - P_{vc}/P_c} G_{con} \qquad [\text{lb-mole/hr}] \qquad (\text{VI-128})$$

where P_c is the gas pressure in the condensers and P_{vc} is the vapor pressure of water at 100 ^oF.

The total heat duty of the two condensers is given by

$$Q_c = G_f \overline{C}_p (T_f - 100) + G_{rt} \overline{C} (T_{rt} - 100) + D_{wc} H_v \; [\text{Btu/hr}] \qquad (\text{VI-129})$$

The heat duty of the second condenser is

$$Q_{c2} = Q_c - Q_{c1} \qquad [\text{Btu/hr}] \qquad (\text{VI-130})$$

The flow rate of the untreated water required for the second condenser is

$$W_{c2} = Q_{c2}/(150 - 85) \qquad [\text{lb/hr}] \qquad (\text{VI-131})$$

The heat transfer areas of the first and second condensers are respectively

$$A_{c1} = \frac{Q_{c1}}{U_c \Delta t_c} \quad \text{and} \quad A_{c2} = \frac{Q_{c2}}{U_c \Delta t_c} \qquad [\text{sq.ft.}] \qquad (\text{VI-132,133})$$

where

$$t_c = \frac{(T_{ci} - 150) - (100 - 85)}{\ln \dfrac{T_{ci} - 150}{100 - 85}} \qquad [^oF]$$

$$T_{ci} = (G_f \overline{C}_p T_f + G_{rt} \overline{C}_p T_{rt}) / (G_f + G_{rt})$$

U_c = overall heat transfer coefficient of the condensers [Btu/sq ft-hr-^oF] (An estimated value of 200 is used)

8.2 Amine Process

The amine process usually requires a feed gas cooler, a solution heat exchanger, a solution cooler, a reboiler, and a condenser. In some cases, one or all of the feed gas cooler, the solution heat exchanger and the solution cooler are not needed.

i. Reboiler

The raw gas is first introduced into the reboiler to supply part of the heat required for the reboiler. The rate of heat recovered from the raw gas is

$$Q_{bg} = G_1 \bar{C}_p (T_1 - T_2) + D_{wg} H_v \qquad \text{(VI-134)}$$

where T_2 = temperature of gas leaving the reboiler, [°F]

D_{wb} = rate of condensation of water vapor from the raw gas in the reboiler, [lb mole/hr]

$$= \frac{G_1(Y_w - P_v/P)}{1 - P_v/P}$$

Low pressure steam at 265° from the methanator is used to supply the rest of heat required for the reboiler. If Q_b and Q_{bs} are respectively the heat duty of the reboiler and the rate of heat supplied by the steam, then

$$Q_{bg} = Q_b - Q_{b_s} \qquad \text{[BTU/hr]} \qquad \text{(VI-135)}$$

The rate of steam required can be calculated by

$$G_{bs} = \frac{18\, Q_{bs}}{H_v} \qquad \text{[lb/hr]} \qquad \text{(VI-136)}$$

The heating area of the reboiler is given by

$$A_b = \frac{Q_{bg}}{U_g t_g} + \frac{Q_{bs}}{U_s t_s} \qquad \text{[sq.ft]} \qquad \text{(VI-137)}$$

where U and t are respectively the over-all heat transfer coefficient and logarithmic mean temperature difference, and the subscripts g and s denote heating mediums raw gas and steam respectively. Estimated values of 75 and 200 (BTU/ft^2 hr °F) are used for U_g and U_s respectively. t_g and t_s are calculated from the following equations:

$$t_g = \frac{(T_1-T_b) - (T_2-T_b)}{\ln((T_1-T_b)/(T_2-T_b))} \; ; \qquad t_s = 265 - T_b \qquad \text{(VI-138)}$$

If the gas to be treated by the amine process is an effluent from the hot potash process, then the reboiler is not needed. Thus $Q_g = 0$ and $Q_r = Q_s$.

ii. Feed Gas Cooler

The feed gas cooler is used to cool the feed gas from T_2 to T_{ab}. The design of this feed gas cooler is similar to that of the feed gas cooler used in the hot potash process

iii. Solution Heat Exchanger

The solution heat exchanger is used to exchange heat between the spent solution stream from the bottom of the absorber and the regenerated solution stream from the reboiler. A minimum temperature difference of 15°F is allowed between the solution streams. If the spent solution is heated from t_{ab} to t_3 and the regenerated solution is cooled from t_b to t_4 then

$$t_3 = T_b - 15 \qquad [°F] \qquad \text{(VI-139)}$$

$$t_4 = t_{ab} + 15 \qquad [°F] \qquad \text{(VI-140)}$$

$$Q_{se} = L_{ab}\,\overline{C}_{PL}(t_3 - t_{ab}) \qquad [\text{BTU/hr}] \qquad \text{(VI-141)}$$

where Q_{se} = heat duty of the solution heat exchanger, [BTU/hr]

The heat transfer area of the solution heat exchanger is

$$A_{se} = \frac{Q_{se}}{15\,U_{se}} \qquad \text{(VI-142)}$$

An estimated value of 200 BTU/ft^2 hr °F is used for U_{se}, the over-all heat transfer coefficient of the solution heat exchanger.

iv. Solution Cooler

The solution cooler is used to cool the regenerated solution from t_4 to t_{at} with untreated water entering at 85°F and leaving at 120°F. Its heat duty, Q_x, and heat transfer area A_{sc} are given as

$$Q_{sc} = L_{at}\overline{C}_{pL}(t_4 - T_{at}) \tag{VI-143}$$

$$A_{sc} = \frac{Q_{sc}}{t_{sc}U_{sc}} \tag{VI-144}$$

where

$$t_{sc} = \frac{(T_4 - 120) - (T_{at} - 85)}{\ln \dfrac{t_4 - 120}{T_{at} - 85}}$$

U_{sc} = over-all heat transfer coefficient of the solution cooler (an estimated value of 200 is used), [BTU/ft^2 hr °F]

v. Condenser

The gaseous effluents from the regenerator and the flash drum are cooled to 100°F in the condenser with untreated cooling water entering at 85°F and leaving at 150°F. The design of a condenser in the amine process is similar to the design of the condensers in the hot potash process, except that only one condenser is used in the amine process.

9. Energy-Recovery System

The wet gas purification process studied in this chapter involves two pressure level operations: (1) liquid is pumped to a high pressure, for treatment at that high pressure, and then (2) the treated liquid is depressurized for further processing. This pressure-reduction step is a source of energy that can not be overlooked in large modern plants. The lean solution (K_2CO_3 or MEA solution) from the bottom of the regenerator must be pressurized to the operating pressure of the absorber (about 1050 psia) to scrub CO_2 and H_2S from the gas stream in the absorber, and the spent solution discharged from the bottom of the absorber has to be depressurized before being regenerated in the regenerator. Therefore, the problem of simultaneously pressurizing a liquid stream and depressurizing another liquid stream must be considered. Power recovered from the spent solution stream can be used to reduce the overall energy requirement of the process.

The conventional machines used for recovering this energy have been reverse-running pumps and hydraulic turbines. Franzke [40] reported that hydraulic turbines, which use reverse impellers to recover power from pressure-based potential energy, have a definite advantage over reverse-running pumps-they can operate over a wide range of processing conditions. Figure VI-14 shows an energy recovery system that uses a hydraulic turbine.

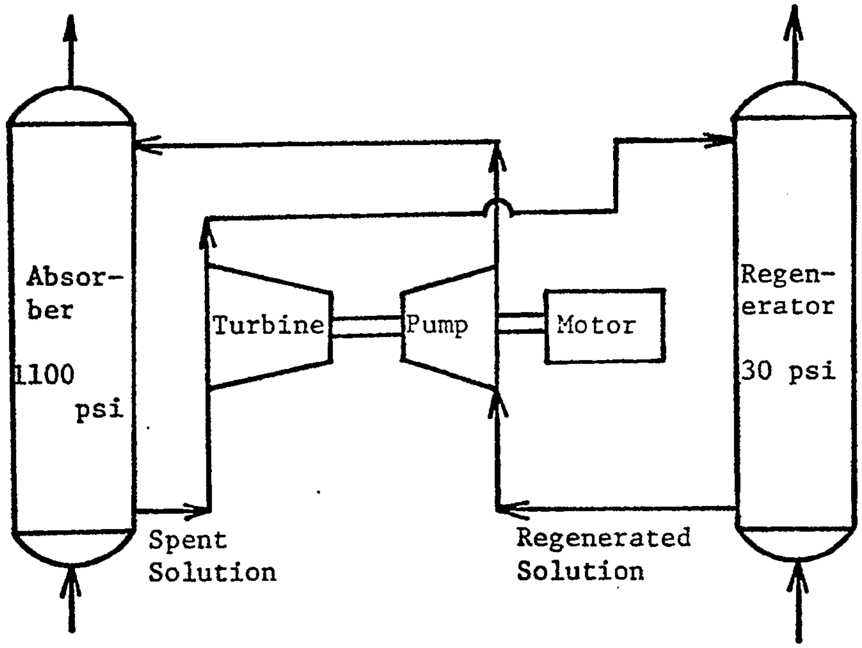


Figure VI-14 Hydraulic Power recovery With a Turbine

The turbine is directly coupled to the pumping unit being used to pressurize the lean solution. Since the pump requires more power than that produced by the turbine, a motor is required to supply the balance. The overall efficiency is estimated to be less than 70%

Recently, a high efficiency energy recovering system called a "flow-work exchanger" was developed by Cheng, Fan, and Hunter [41]. Unlike the conventional energy recovery system, a flow-work exchanger is a unified piece of equipment which simultaneously pressurizes a liquid stream and depressurizes a substantially equivalent volume of another liquid stream. A flow-work exchanger uses one or more displacement vessels to form closed loops with the absorber and the regenerator as shown in Figure VI-15. Figure VI-16 shows two types of displacement vessels. As shown in Figure VI-17 each of the displacement vessels is alternately filled by a low-pressure lean solution and a high-pressure spent solution, both pressurized and depressured, respectively, by substantially non-flow processes. The pressurized lean solution is pushed into the absorber by the high-pressure spent solution stream and the depressurized spent solution stream is pushed out of the displacement vessel by the low-pressure lean solution stream. Since the flow-work exchanger pressurizes and depressurizes liquid streams by substantially non-flow processes, the efficiency of the flow-work exchanger is exceptionally high. The prototype units built by Cheng, Fan, and Hunter [41] required a make-up energy of less than 6% of the energy exchanged.

Therefore, a flow-work exchanger will be used to circulate solutions between the absorber and the regenerator. For design purpose, a make-up energy of 10% of the energy exchanged will be assumed. If q is the liquid flow rate in gpm (both liquid streams are essentially the same in this application), and P_a and P_o are the inlet pressure and outlet pressure, respectively, in psi, then the work exchanged will be

$$We = \frac{144 \cdot q \, (P_a - P_o)}{246800} \qquad [hp] \qquad (VI-145)$$

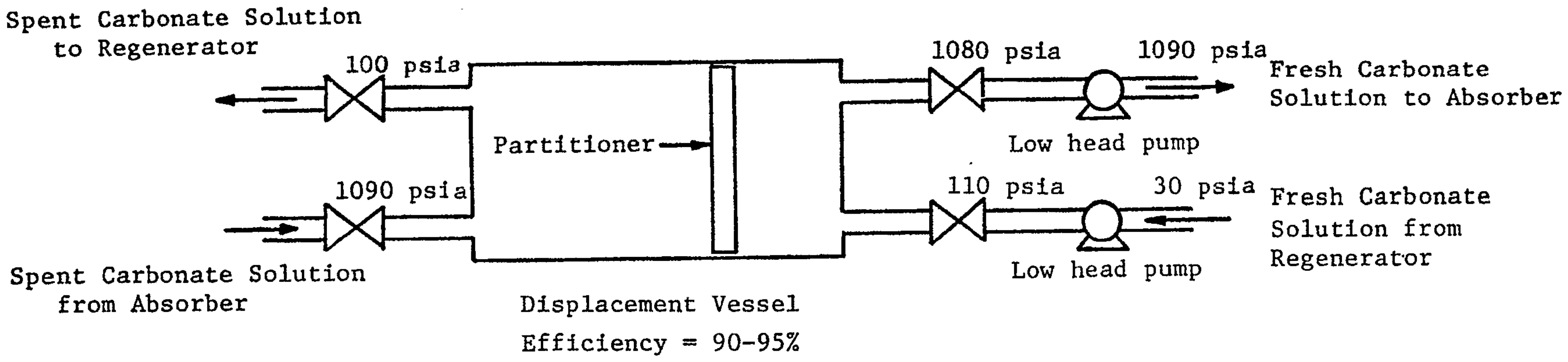
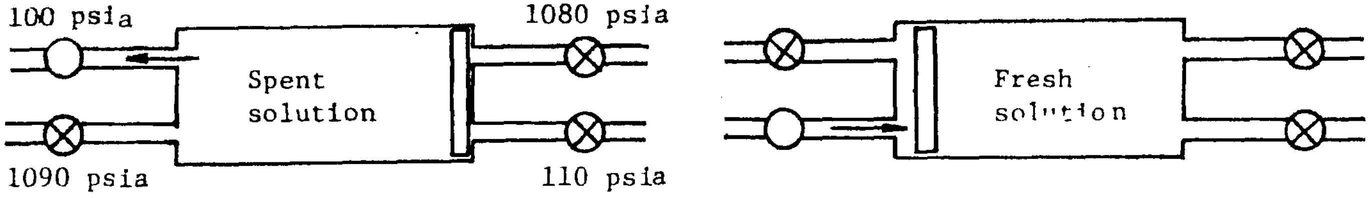


Figure VI-15 Flow Work Exchanger

Floating Piston Type

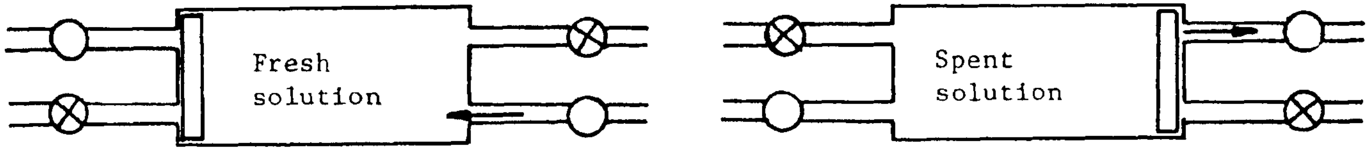
Diaphragm Type

Figure VI-16 CONSTRUCTION OF A DISPLACEMENT VESSEL



Step 1: Depressurization

Step 3: Pressurization



Step 2: Low-Pressure Displacement

Step 4: High-Pressure Displacement

Figure VI- 17. OPERATION OF THE DISPLACEMENT VESSEL

(4 in parallel)

The brake horse power required for the pump to pressurize the lean solution from the regenerator pressure P_r [psi] to P_o and to lift the lean solution to the top of the absorber is

$$B'_p = \frac{q \quad 144(P_o - P_r) + \rho h_c}{246800 \ E_p} \qquad [\text{hp}] \qquad (\text{VI-146})$$

in which h_c is height of the absorber [ft] and E_p the efficiency of the pump (assumed to equal to 0.8). B'_p and 10% of W_e will be supplied by electric motors. Therefore the rating horse power of the motors is

$$B_m = \frac{W_e + B'_p}{E_m} \qquad (\text{VI-147})$$

where E_m , the motor efficiency is assumed to be 0.9. This is also the make-up energy for the flow-work enchanger.

Since there is no commercial flow-work exchanger available, the cost of the flow-work exchanger is also not available. However, it is certain that the cost of the flow-work exchanger will be less than the total cost of turbine, pump, and motor assembly. Therefore the cost of the flow-work exchanger will be assumed to be equal to the total cost of the equivalent turbine, pump and motor assembly. The total brake horse power of the pump in the assembly would be

$$B_p = \frac{q \quad 144\ (P_a - P_o) + \rho_L h_c}{246800 \cdot E_p} \qquad (\text{VI-148})$$

where ρ_L is the density of the liquid [lb/ft^3]

The capacity of a pump is assumed to be 2,000 gpm . The number of the pump can then be determined. The numbers of turbines and motors are assumed to be equal to that of pumps. The cost of pumps E_p, and the cost of motors, E_m, are calculated from B_p and B_m by Eqs.(II-8,9),respectively. A hydraulic turbine is slightly more expensive than a reverse-running pump. However, the total horse power of the turbines is less than that of the pumps. It is reasonable to assume that the cost of turbines, E_t is equal to the cost of pumps, E_p. Therefore the cost of the flow-work exchanger is

$$E_w = E_p + E_m + E_t \tag{VI-149}$$

The make-up energy can be calculated from B_m.

10. Removal of Sulfur Compounds by Iron Oxide Process

The removal of sulfur compounds in the gas is an important and difficult part of the gas purification, especially because it will affect the catalyst activity in the successive methanation process.

The processes for hydrogen sulfide removal can be broadly classified into two methods, solid adsorbent process and liquid process.

Some of the examples of the solid adsorbent processes are Iron Oxide Process, Claus-Chance Process, Katasulf Process, North-Thames Gas Boad Process etc. The examples of liquid processes include the Ferrox Process, the Giammanro Veterocoke Process, Monoethanol Amine Process etc.[1]

As mentioned earlier, Iron Oxide Process has the capability of satisfying the most stringent requirement of maximum concentration of hydrogen sulfide in the domestically used gas.

10.1 Reaction Kinetics and Analysis of Iron Oxide Process

The basic chemistry of this process can be represented by the following equations.

$$2Fe_2O_3 + 6H_2S = 2Fe_2S_3 + 6H_2O \qquad (j)$$

$$2Fe_2S_3 + 3O_2 = 2Fe_2O_3 + 6S \qquad (k)$$

Combination of both equations gives

$$6H_2S + 3O_2 \longrightarrow 6H_2O + 6S \qquad (1)$$

According to equation (j), H_2S can be removed almost completely while equation(k) describes the regeneration step.

There are several forms of ferric oxide but only two, $\alpha\ Fe_2O_3 \cdot H_2O$ and $\gamma\ Fe_2O_3 \cdot H_2O$, are useful for the purpose of gas purification. These two forms react readily with hydrogen sulfide to form ferric sulfide, Fe_2S_3. Ferric sulfide can be easily regenerated to recover its activity for adsorption. At temperatures above 120°F and in neutral or acid environment, ferric sulfide loses its water of crystallization and is converted to FeS_2 and Fe_8S_9, neither of which can be readily reconverted to hydrated ferric oxide. Also α-, and γ-ferric oxides at high temperatures above 105°F decompose to lose the water of crystallization. From these facts, the process should be operated under a certain temperature, approximately 105°F, and in an alkaline environment.

The iron oxides used for gas purification can be classified as unmixed and mixed oxides. Unmixed oxides contain essentially pure hydrated ferric oxides with water. Mixed oxides, on the other hand, are artificially made by supporting finely floured iron oxides on media such as wood shavings and granulated or crushed slugs. The advantage of iron oxides or iron-sponges is that the density, moisture content, pH of the materials can be more easily controlled than in the unmixed oxides. Moreover, less pressure drop in the bed and high final sulfur loading can be expected.

The recovery of sulfur from the adsorber is common practice in European installations, but in the United States, it is usually considered uneconomical to recover sulfur from spent oxides, especially if the materials are used for purifying gases of low sulfur content.

10.2 Pressure Drop in Bed

A major factor in the design of iron oxide beds is the selection of the proper particle size of iron oxide. Iron oxide pellet size is also related to the pressure drop through the beds. The pressure drop through porous masses is usually related to the Reynolds number by means of a friction factor. Though there are several correlations for pressure drop, Ergun's equation

$$\frac{\Delta P g_c}{z} = 150\left(\frac{(1-\varepsilon)^2}{3}\right)\left(\frac{\mu u}{D_p^2}\right) + 1.75\left(1-\frac{\varepsilon}{\varepsilon^3}\right)\left(\frac{Gu}{D_p}\right) \qquad \text{(VI-150)}$$

is used in this study.

Equation (VI-150) is also written by using the correlated friction factor f_k and Reynolds number as

$$f_k = 150\,\frac{(1-\varepsilon)}{R_e} + 1.75 \qquad \text{(VI-151)}$$

where D_p = diameter of the particle,(ft.)

z = height of bed,(ft.)

P = pressure drop,(lb_f/sq.in.)

g_c = gravitational conversion factor,(lb_m.ft./lb_f.hr.)

ε = fractional void space,(-)

μ = viscosity of gas,(lb./ft.hr.)

G = superficial mass velocity of gas,(lb./ft.sq.ft.)

u = superficial gas velocity,(ft./hr.)

$Re = D_pG/\mu$, Reynolds number,(-)

11. Optimization of CO_2 and H_2S Removal Processes

The purpose of gas purification is to remove vapor phase impurities, mainly CO_2 and H_2S from the gas stream in order to meet the purity requirements for pipe-line gas. CO_2 is a diluent which lowers the heating value of pipe-line gas. The CO_2 content of the purified gas should not be greater than 1 per cent. Sulfur compounds not only are toxic but also can poison nickel catalyst used in the methanator. A maximum H_2S content of 0.25 grain/100 SCF (standard cubic feet) is frequently specified for pipe-line gas. To make coal gas suitable for catalytic methanation reaction a maximum H_2S content of 0.01 grain/100 SCF is required [16].

Benzene is a valuable by product of coal gasification. Removing benzene from the gas stream can also improve gas quality. Since the benzene removing process does not affect the optimization of CO_2 and H_2S removing processes, the benzene removal can be studied independently.

11.1 Selection of Processes

Optimization of gas purification processes begins with the preliminary selection of a process or a combination of several processes from a number of alternatives. In this respect, books that deal with gas purification such as "Gas Purification" by Kohl and Riesenfeld [1], "Gas-Liquid Reaction" by Danckwerts [54], and "Absorption of Gases" by Ramm [50], etc. are helpful.

The hot potash process seems the most economical for removal of CO_2 to 1 per cent but is not selective for H_2S absorption. The amine process has been widely used to remove CO_2

and H_2S from natural gas. It has high selectivity for the absorption of H_2S. The iron oxide process is a relatively expensive process for the removal of H_2S from gas streams. But it can remove H_2S almost completely. These three processes are investigated in this section for the optimum process design.

To achieve the required gas purity, one single process or a combination of two or three processes may be needed. Since iron oxide process does not remove CO_2, it cannot be used alone. The following six process schemes are possible:

Scheme 1: hot potash process

Scheme 2: hot potash process + iron oxide process

Scheme 3: amine process

Scheme 4: amine process + iron oxide process

Scheme 5: hot potash process + amine process + iron oxide process

Scheme 6: hot potash process followed by amine process

The best process scheme is the one that can achieve the gas purity required at the lowest cost when being operated under optimum condition. Therefore, in order to choose the best process scheme every possible scheme has to be optimized and compared with other process schemes.

11.2 Optimization Technique and Calculation Procedure

The objective of process optimization is to choose process variables subject to some constraints so that the revenue requirement is minimized. The cost information and method of calculating revenue requirement are presented in Chapter II. Many search methods have been successfully used to solve constrained minimization problems. These include the univariate search method, sequential simplex method, complex method, etc. Among these methods, the univariate search method is the easiest to use. It utilizes succession of one dimensional searches for minima along sequence of directions. The simplest way is probably to search in turn along separate independent variables cyclically, keeping (n-1) variables constant at each stage. The advantage of this type of univariate search method is that during the calculation the effect of each variable on the objective function can be observed and error can be easily located. The disadvantage of this method is that it progresses slowly near valleys and can stall at the bottom of the valley. This method is used in the search of the optimum designs of the purification processes.

With the insight on choice of initial values of variables, two or three cycles of search will lead to the optimum. Different starting points are tried to see if an optimum is a true one.

When two or more processes are used as in the process schemes, 3 to 5, each process can be considered as a subsystem. Since there is recycle between subsystems, each subsystem must be optimized in order to obtain the optimum of the whole process scheme and the concept of dynamic programming can be applied.

11.3 Process Variables

Before calculation, some process variables can be fixed by imposed restraints and by preliminary survey. Columns packed with Raschig ring are used in the design of absorption process. Although small packing size offers large interfacial contact area, the column is easily flooded. Therefore, large total cross-section of columns is needed if small packing size is to be used. According to the preliminary comparison, 2-inch packing size is best suited to the design of the absorber and the regenerator. Total cross-sectional area can be determined by 75 per cent of the flooding velocity (Eq. VI-37).

i. Hot Potash Process

The concentration of K_2CO_3 in the original solution is one of the design variables. In general, increasing the K_2CO_3 concentration will reduce the required circulation rate of the solution and in turn the plant cost. However, the use of higher K_2CO_3 concentration may result in precipitation of $KHCO_3$. On the basis of the solubility data of K_2CO_3 and $KHCO_3$ (Fig. VI-5), it is concluded that a 40 per cent K_2CO_3 concentration in the original solution is about the maximum that can be used for operation without precipitation. Therefore, 40% K_2CO_3 solution is used in the design of the hot potash process.

The flow diagram of the hot potash process is shown in Figure VI-1. Y_{at} or Y'_{at} is chosen as a parameter. The independent variables are:

X_{ab}, X_{at}, X'_{ab}, X'_{at}, T_{ab}, T_{at}, G_s, Pr, T_2, T_3, da (inside diameter of absorber) and dr (diameter of regenerator).

Among the independent variables, da and dr can be treated separately as they do not affect other independent variables.

The constraints are:

(a) Pr $\geqslant$ 10 psig to allow for pressure drop

(b) $T_{ab} - T_{rb} \geqslant$ 15°F to maintain a minimum temperature driving force for the feed gas cooler

(c) $0 < X < 1.0$; $0 < X' < 1.0$

(d) $P_{CO_2} > P^*_{CO_2}$; $P_{H_2S} > P^*_{H_2S}$ in the absorber

(e) $P_{CO_2} < P^*_{CO_2}$; $P_{H_2S} < P^*_{H_2S}$ in the regenerator

(f) $n_a \pi (\frac{da}{2})^2 = S_a \quad n_r \pi (\frac{dr}{2})^2 = S_r$

where n_a and n_r are numbers of the absorbers and regenerators, respectively.

(g) X should be low enough and t high enough so that no precipitation of $KHCO_3$ will occur.

ii. Amine Process

As discussed in Section 3.2, 2.5N-MEA solution is chosen as the solvent for the amine process. The flow diagram of the amine process is presented in Section VI-2. Again, Y_{at} or Y'_{at} is chosen as the system parameter.

The independent variables are:

X_{ab}, X_{at}, X'_{ab}, X'_{at}, T_2, T_{ab}. T_{at}, T_3, P_r, G_s, d_a and d_r.

As in the hot potash process, da and dr can be treated separately. T_2, T_3 and P_r can be fixed at their minimum or maximum allowable values because they happen to be the optimum ones. Therefore

$T_2 = T_b + 15$: to allow for the minimum temperature driving force of 15°F for the reboiler and to recover the maximum amount of heat from the feed gas

$T_3 = T_b - 15$: to allow for the minimum temperature driving force of 15°F for the solution heat exchanger and to obtain maximum T_3

$P_r = 10$ psig: to obtain maximum pressure driving force for desorption in the regenerator.

Thus, T_2, T_3 and P_r are eliminated from the independent variables. The constraints are:

(a) $0 < X < 0.5$; $0 < X' < 1.0$

(b) $P_{CO_2} > P^*_{CO_2}$; $P_{H_2S} > P^*_{H_2S}$ in the absorber

(c) $P_{CO_2} < P^*_{CO_2}$; $P_{H_2S} < P^*_{H_2S}$ in the regenerator

(d) $n_a \pi (\frac{da}{2})^2 = Sa$; $n_r \pi (\frac{dr}{2})^2 = S_r$

iii Iron Oxide Process

Although many Iron Oxide Processes have been installed and used, there is no theoretical base for the design procedure. But from the experience of using this process in the industries, several empirical rules can be provided as follows. [1, 16, 17]

The tower should be of such diameter as to limit sulfur deposition to a maximum of 15 grains per square foot cross-sectional area of the bed per minute. This is necessary because the reaction of H_2S with Fe_2O_3 to form Fe_2S_3 and water is an exothermic one; and if too much heat is evolved, the water of crystallization in the Fe_2O_3 molecule will be driven off and the activity of the material is destroyed.

For this reason, the operating temperature of the bed should be always below 105°F. However, if the temperature should exceed 120°F, a water spray must be used in the top section of the tower to keep the material wet in order to prevent dehydration. A water spray is usually not necessary if temperature is below 105°F.

The height of the tower is recommended to be at least 10 feet to produce pressure drop sufficient for proper gas distribution over the entire cross-section area of the tower.

Flow diagram of the Iron Oxide Process is shown in Fig. VI-3.

The decision variables for optimazation of this process are; C_{Ag} (inlet concentration of hydrogen sulfide), D_B (diameter of the tower), H_B (height of the bed), D_p (particle diameter of iron oxide), and t_B (life time of iron oxide-changeout time).

The constraints are:

(a) $T_B < 105°F$ in the iron oxide tower

(b) $H_B > 10$ ft. for height of iron oxide bed

(c) C_{H_2S} [grains]/ $\frac{\pi}{4} D_B^2 < 15$ [grains/ft.]

11.4 Results and Discussion

i. Iron Oxide Process

Although the iron oxide process is employed in connection with the hot potash process and the amine process for removal of hydrogen sulfide, it can be treated independently since the temperature and pressure in the iron oxide process are nearly constant. A predominant factor which affects the cost of this process is the inlet concentration of hydrogen sulfide. Lowering the inlet concentration lowers the total cost if all of the other conditions are the same.

This process is, therefore, optimized first under the various hydrogen sulfide concentration of inlet gas.

The results of several cases obtained from the computer study indicating the relation between the inlet concentration of H_2S versus the revenue requirement for Iron Oxide Process are shown in Figs. VI-18 and VI-19.

These results are used to calculate the revenue requirement of Scheme-2, 4 and 5.

ii. Hot Potash Process and Amine Process

To compare the performances of the hot potash process and the amine process, the two processes were first optimized with parameter Y_{at}=0.0101 or Y = 0.01. One of the results of CO_2 concentration and temperature profiles along the absorber is shown in Figure VI-23 for the hot potash process and in Figure VI-24 for the amine process. The minimum revenue requirements for both processes are listed in Table VI-5.

It is found that the minimum revenue requirement for the amine process is more than twice that for the hot potash process for every case of feed gas. This is due to the fact that the amine process requires a larger circulation rate of the solution and a larger steam cost. It is also found that the H_2S contents of the exist gas from the amine process is much less than that of the corresponding exit gas from the hot potash process. This comes from the fact that the amine process has much higher selectivity for the absorption of H_2S than the hot potash process. Therefore, in process schemes 3 and 5, the hot potash process must precede the amine process so that most of the CO_2 in the gas can be first removed by the hot potash which can be operated at a lower cost. The following amine process will effectively reduce the H_2S content without the need of large circulation rate of the solution.

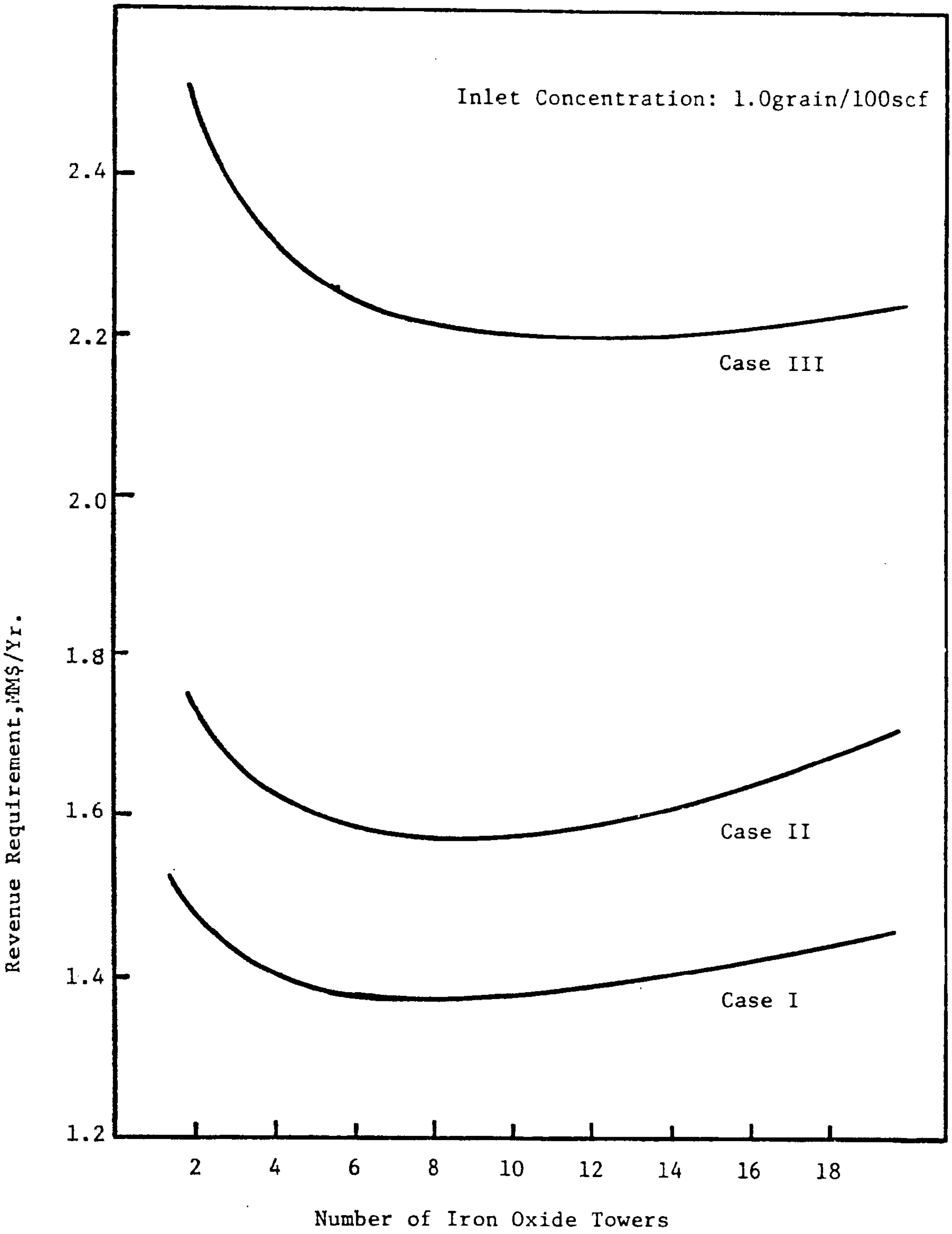


Figure VI-18. Effect of Number of Towers on Revenue Requirement in Iron Oxide Process

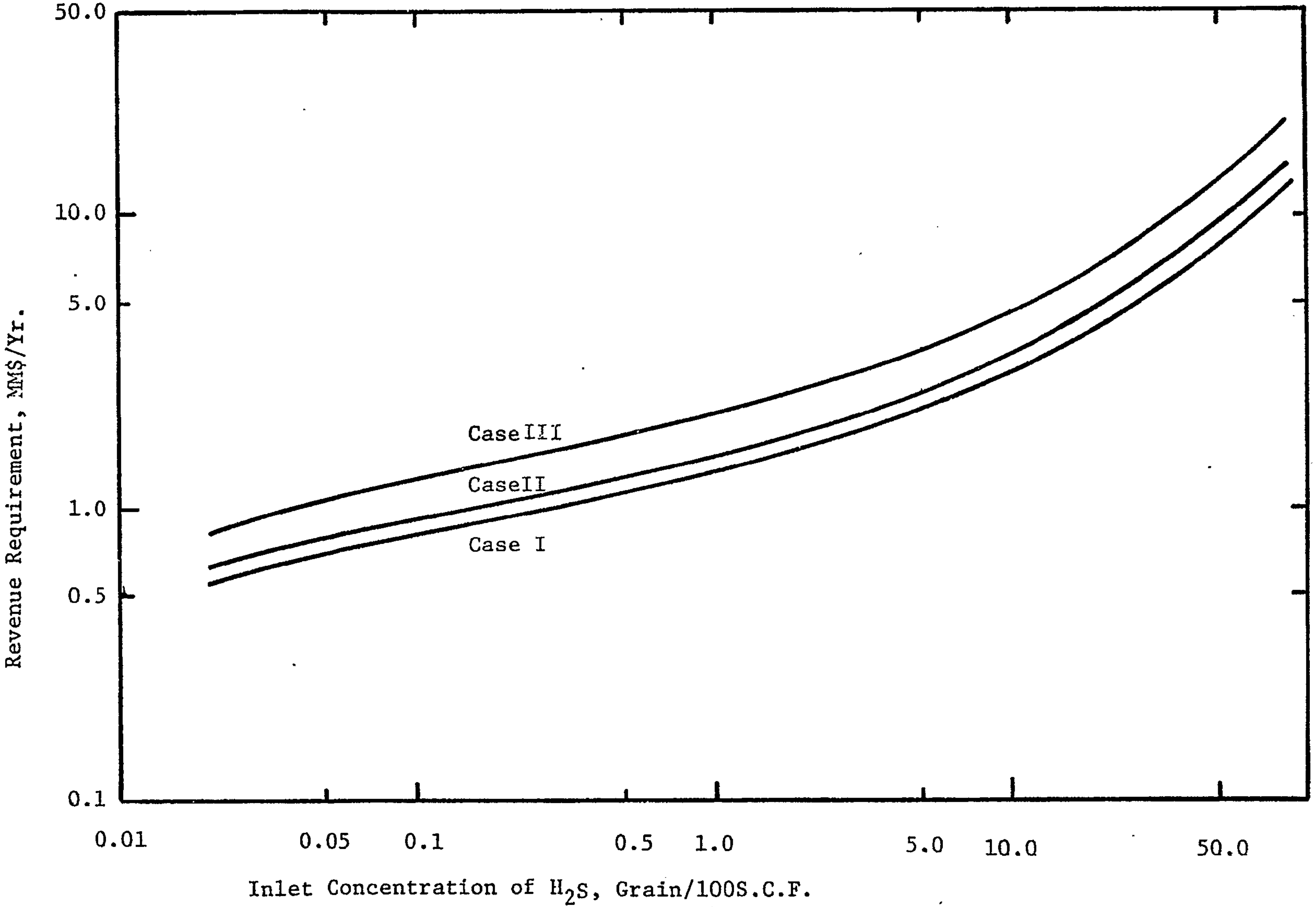


Figure VI-19. EFFECT OF INLET CONCENTRATION OF H_2S ON REVENUE REQUIREMENT OF IRON OXIDE PROCESS

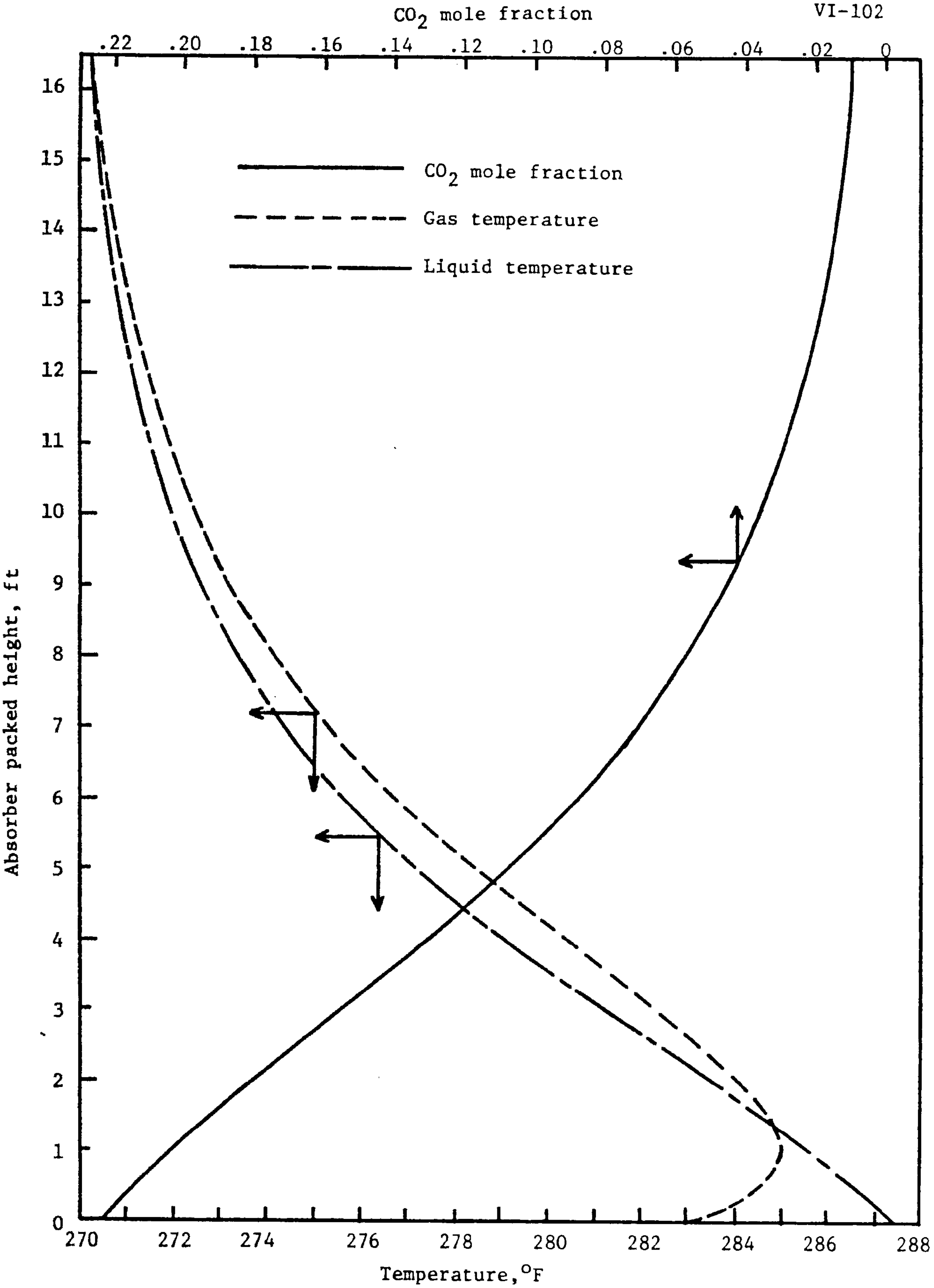


Figure VI-20. Carbon Dioxide Concentration And Temperatures Profiles along the Absorber of Hot Potash Process which Reduces Carbon Dioxide to 1 % (Case II)

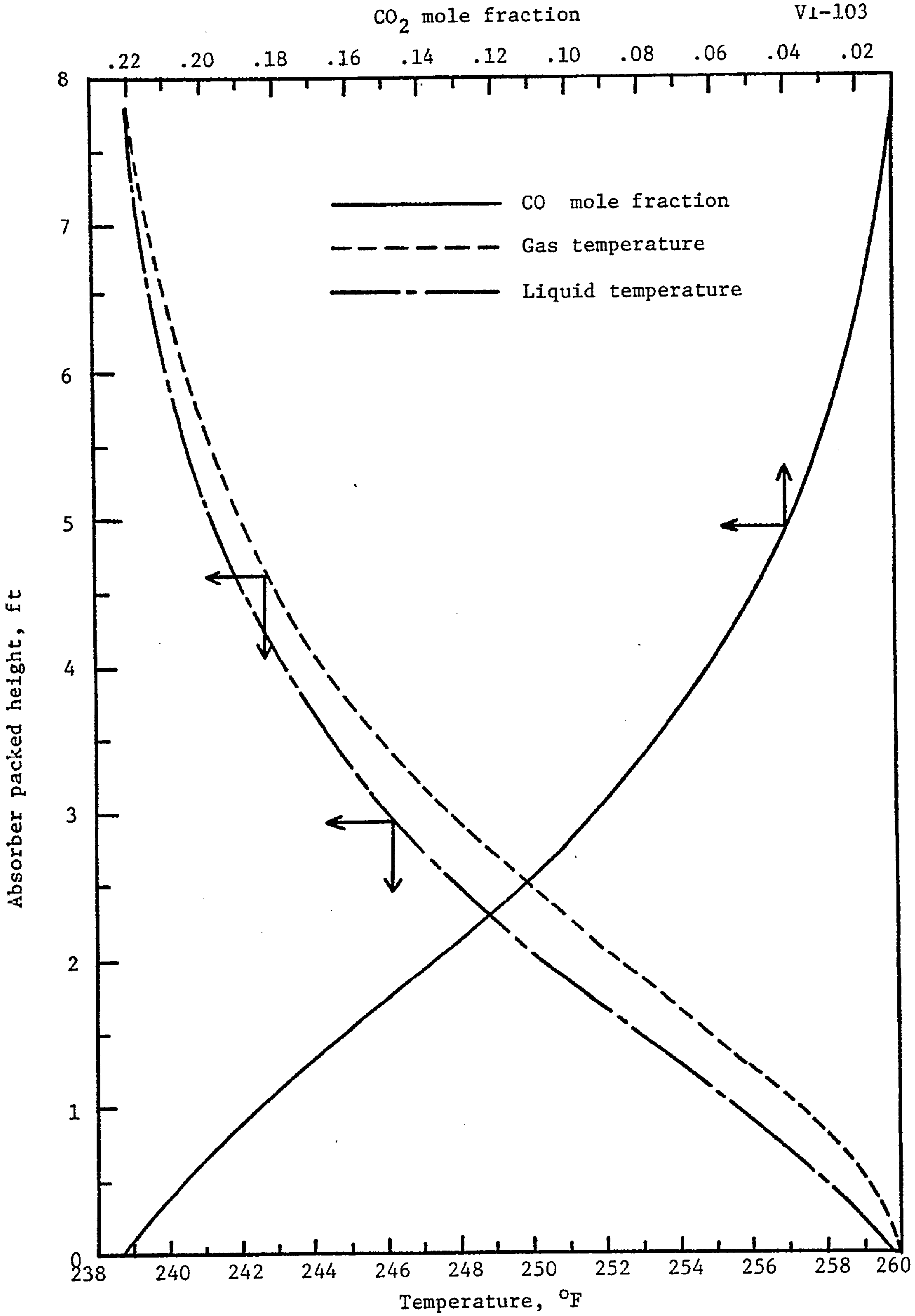


Figure VI-21. Carbon Dioxide Concentration And Temperature Profiles along the Absorber of Amine Process Which Reduces Carbon Dioxide to One Percent (Case II)

Table VI-5 Minimum Revenue Requirement for the Hot Potash Process and that for the Amine Process. CO_2 content of outlet gases is 1.0%.

Process	Case	Minimum Revenue Requirements, M$/Yr.	H_2S Content of Exit Gas, Grain/100 SCF
hot potash process	I	720	17.0
	II	1,470	28.4
	III	2,940	28.6
amine process	I	1,640	2.2
	II	3,320	7.7
	III	7,650	11.9

Scheme 1 is then optimized with H_2S content of the exit gas as the parameter and with $Y_{at} < 0.01$. The minimum revenue requirement for this scheme for various H_2S content of the exit gas is shown in Figure VI-22. It is seen from this figure that if the H_2S content of the exit gas is lower than 1 grain/100 SCF this process becomes very expensive. Therefore, the hot potash process alone does not seem to be able to achieve the required gas purity economically.

The iron oxide process is also extremely expensive if the inlet H_2S concentration of the gas is relatively high (Figure VI-19). Therefore, when Scheme 2 is used, the H_2S content of the gas must be reduced with the hot potash process to a reasonably low value. The minimum revenue requirements of Scheme 2 is listed in Table VI-6. Here the H_2S content of the outlet gas of the hot potash process is selected as parameter.

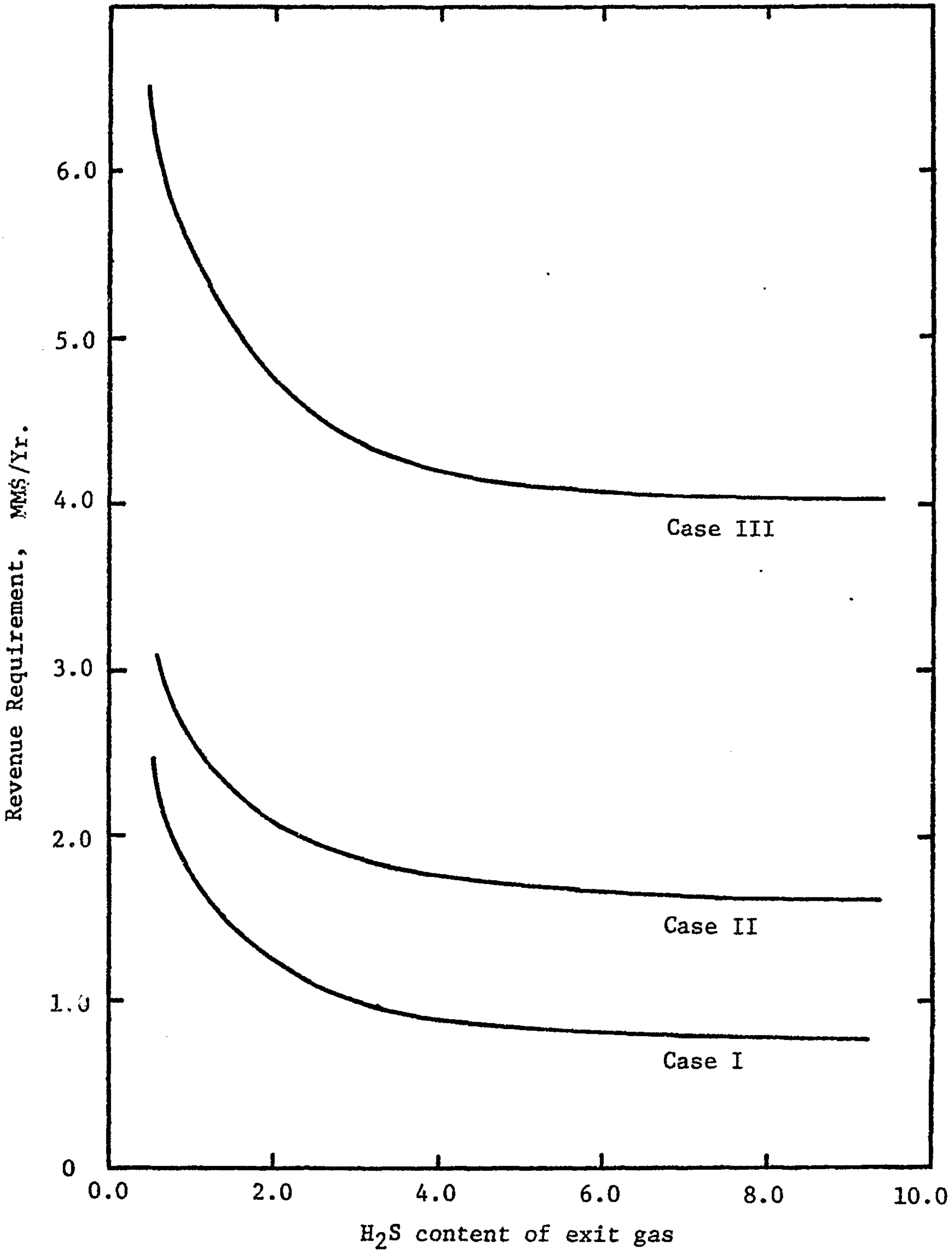
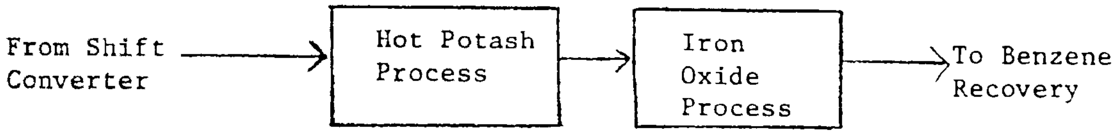


Figure VI-22. Revenue Requirement of Hot Potash Process vs. H_2S content of exit gas (Scheme-1)

Table VI-6. Revenue Requirement for Scheme-2.

Case	H_2S Content of outlet gas of Hot Potash Process grain/100 SCF	Revenue requirement for Hot Potash Process M$/Yr.	Revenue requirement for Iron Oxide Process M$/Yr.	Minimum total revenue requirement for Scheme-2 M$/Yr.
I	2.0	1,230	1,630	2,860
II	1.0	2,560	1,520	4,080
III	5.0	3,800	3,500	7,300



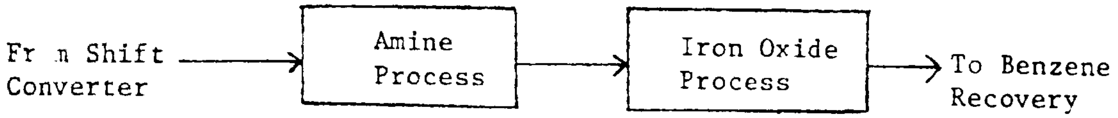
Scheme-2

Scheme 3 (amine process alone) can achieve the required gas purity with the resulting minimum revenue requirements of $2,900 M, $8,520 M, and $18,730 M for case I, II, and III, respectively.

The minimum revenue requirements for Scheme 4 (amine process followed by iron oxide process) with $Y \ll 0.01$ and with the H_2S content of the outlet gas of the amine process is listed in Table VI-7.

Table VI-7. Revenue Requirements for Scheme-4.

Case	Revenue requirement for Amine process, M$/Yr.	Revenue requirement for Iron Oxide Process M$/Yr.	Total revenue requirement for Scheme-4 M$/Yr.
I	2,900	420	3,320
II	8,340	540	8,880
III	18,340	700	19,040



Scheme-4

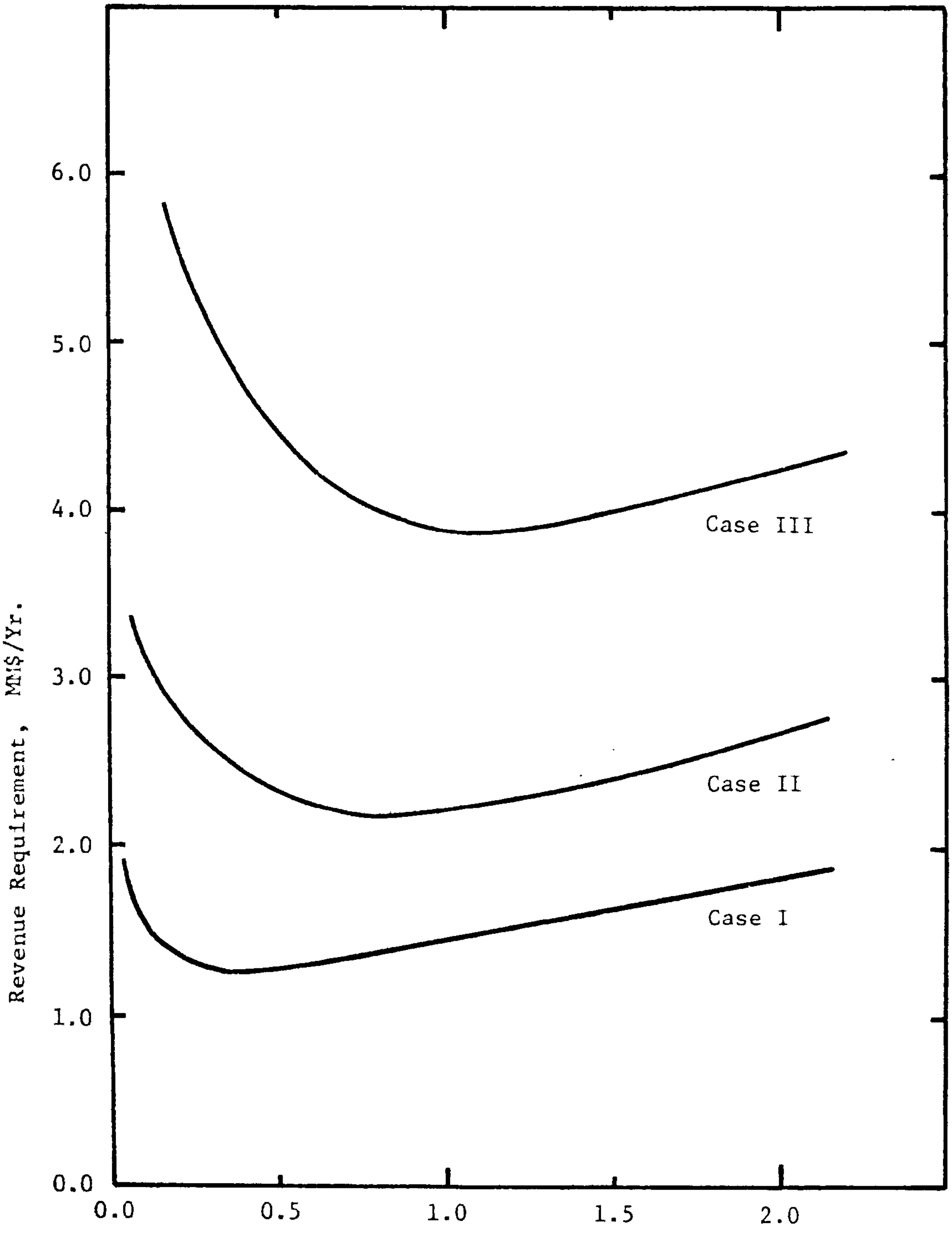
It can be seen that the amine process alone can achieve the required gas purity at costs lower than that of the combination of the amine process and the iron oxide process.

Next, Scheme-5 is considered. Table VI-8 lists the minimum revenue requirements for Scheme-5 with various values of CO_2 content of outlet gas from the hot potash process and H_2S content of outlet gas from the amine process. Again, for every case, the lowest revenue requirement is obtained with the H_2S content of outlet gas from the amine process equal to 0.01 grain/100 SCF.

Scheme-5 without the iron oxide process reduces to Scheme-6 namely the hot potash process followed by the amine process. The CO_2 in raw gas is first reduced by the hot potash process to a certain conentration. Then the partially purified gas is further treated with the amine process to achieve the gas purity required. The revenue requirements for Scheme-6 with CO_2 concentration in the outlet gas from the hot potash process are listed in Table VI-9. The same results are also represented in Figure VI-23.

The best process scheme is found to be the hot potash process, (which reduces the CO_2 content of the gas to 0.36%, 0.8% and 1.1% for cases I, II, and III, respectively), followed by the amine process, which further purifies the gas to the required purity.

The minimum revenue requirements for removing CO_2 and H_2S in the gases in case I, II, and III are respectively \$1,280M, \$2,180M, and \$3,870M.

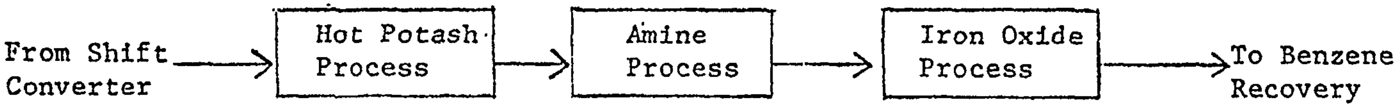


CO_2 concentration of outlet gas from hot potash process, Grain/100SCF

Figure VI-23. Relationship between Revenue Requirement and CO_2 concentration of outlet gas of absorber of hot potash-process

Table VI-8 Revenue Requirements for Scheme-5.

Case	CO_2 content of outlet gas of Hot Potash Process, %	H_2S content of outlet gas of Amine Process, Grain/100SCF	Revenue requirement for Hot Potash Process, M$/Yr.	Revenue requirement for Amine Process, M$/Yr.	Revenue requirement for Iron Oxide Process M$/Yr.	Total Revenue requirement for Scheme-5, M$/Yr.
I	0.4	0.01	860	460	420	1,740
II	1.0	0.01	1,470	730	470	2,670
III	1.0	0.01	2,940	890	630	4,460



Scheme-5

Table VI-9. Revenue Requirements for Scheme-6 varying CO_2 Concentration of Outlet Gas from Hot Potash Process.

Case	CO_2 content of outlet gas from hot potash process, %	Revenue requirement for hot potash process, M$/Yr	Revenue requirement for amine process, M$/Yr.	Total revenue requirement for Scheme-6, M$/Yr.
I	3.0	620	1,250	1,870
	2.0	680	990	1,670
	1.0	720	630	1,350
	0.5	810	510	1,320
	0.36	840	440	1,280
	0.2	940	400	1,340
	0.1	1,160	370	1,530
II	3.0	1,350	1,460	2,810
	2.0	1,460	1,100	2,560
	1.0	1,470	730	2,200
	0.8	1,550	630	2,180
	0.5	1,740	600	2,340
	0.2	1,930	450	2,380
	0.1	2,710	440	3,150
III	3.0	2,740	1,960	4,700
	2.0	2,930	1,560	3,490
	1.1	2,940	930	3,870
	1.0	3,020	890	3,910
	0.5	4,050	760	4,810
	0.2	4,860	580	5,440
	0.1	6,570	560	7,130

12. Removal of Benzene by Activated Carbon Process

As mentioned previously, Activated Carbon Process has been used for the recovery of organic compounds in many commercial installations since the 1920's.

The adsorption bed may be designed based on the similar concept developed for gas absorption in a packed tower using a mass transfer coefficient and a mass transfer unit. However, the reliable information on the mass transfer coefficient in the adsorption bed using activated carbon is not available.

Since the activated carbon process is employed frequently in the industries, basic physical data such as equilibrium relations and properties are available.

12.1 Properties of Activated Carbon

The quantity of benzene adsorbed per unit weight of carbon is dependent on the carbon-benzene equilibrium relationship and the operating conditions. The equilibrium data for benzene on activated coconut-shell charcoal are presented in Figure VI-24. This figure illustrates the effect of the partial pressure of benzene and temperature on the quantity adsorbed [58].

The other properties of commercial activated carbons such as density, diameter of the particles, hardness, porosity, etc. are available in references [1, 3, 4]

12.2 Theoretical Treatment [3, 4]

(i) Height of bed and breakthrough time

Basic equation for material balance in the fixed bed is given as

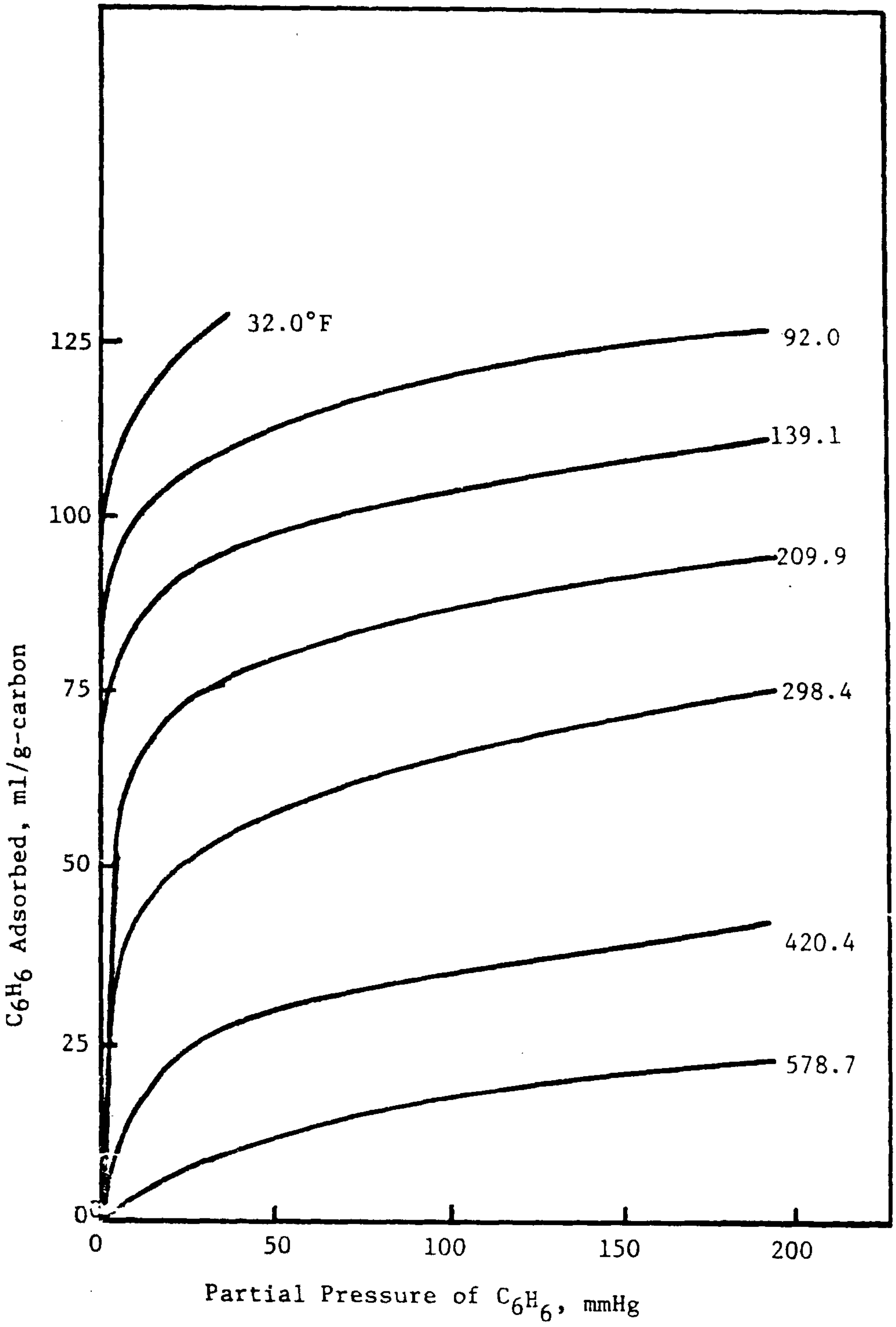


Figure VI-24. ADSORPTION EQUILIBRIA ON AN ACTIVATED CARBON

$$\gamma \frac{\partial x}{\partial t} + \varepsilon \frac{\partial c}{\partial t} + U \frac{\partial c}{\partial z} = \varepsilon D \frac{\partial^2 c}{\partial z^2} \qquad \text{(VI-152)}$$

where γ = packing density, [lb/cu.ft]

x = amount of benzene adsorbed per unit mass of carbon [lb / lb]

t = time, [hr]

ε = void fraction in bed, [-]

c = concentration of benzene adsorbed per unit volume of gas, [lb/cu.ft]

U = superficial velocity, [ft/hr]

Z = height of bed, [ft]

D = diffusivity of benzene in gas, [sq. ft/hr]

The term on the right-hand side, which represents the longitudinal dispersion of gas in a packed bed, is small and can be neglected when the bed height is large compared to the bed diameter.

Thus,

$$\gamma \frac{\partial x}{\partial t} + \varepsilon \frac{\partial c}{\partial t} + U \frac{\partial c}{\partial z} = 0 \qquad \text{(VI-153)}$$

The rate of adsorption is given by

$$\begin{aligned} \gamma \frac{\partial x}{\partial t} &= K_F A_v (C-C^*) \\ &= k_F A_v (C-C_i) \qquad \text{(VI-154)} \\ &= k_s A_v (X_i-X) \end{aligned}$$

where K_F = over-all mass transfer coefficient based on the concentration difference in gas, [lb/sq.ft hr ΔC]

A_v = interfacial area per unit volume of bed, [sq.ft/cu. ft]

k_F = mass transfer coefficient in gas side, [lb/sq. ft hr ΔC]

k_s = mass transfer coefficient in particle, [lb/sq. ft/hr ΔC]

ΔC = concentration difference or driving force [lb/cu. ft]

C^* = concentration of benzene in equilibrium with x, [lb/cu. ft]

C_i = interfacial concentration of benzene adsorbed, [lb/cu. ft]

X_i = amount of benzene adsorbed per unit mass of adsorbent at interface, [lb/lb]

If the shape of adsorption isotherm is favorable equilibrium, the height where mass transfer occurs can be given by the following equation.

$$Za = \frac{U}{K_F a_v} \int_{C_b}^{C_o - C_b} \frac{dc}{C - C^*} = \frac{UNm}{K_F A_v} \qquad \text{(VI-155)}$$

where Za = height of bed where mass transfer occurs, [ft]

C_b = outlet concentration of benzene at breakthrough time, [lb/cu.ft]

C_o = inlet concentration of benzene, [lb/cu.ft]

$Nm = \int_{C_b}^{C_o - C_b} \frac{dc}{C - C^*}$, number of transfer unit

The breakthrough time is given as

$$t_b = \frac{XoZ}{UCo}\left(1 - \frac{Za}{2Z}\right) \qquad \text{(VI-156)}$$

where t_b = breakthrough time, [hr]

X_o = amount of benzene in solid which is in equilibrium with Co, [lb/lb-C]

Therefore, the height of the bed can be calculated by

$$Z = \frac{UCo}{Xo} \cdot t_b + \frac{Za}{2} \qquad \text{(VI-157)}$$

(ii) Over-all mass transfer coefficient [59]

The over-all mass transfer coefficient for adsorption of benzene in the activated carbon bed is given by the following correlation [59]

$$\frac{K_F a_v d_p^2}{D} = 3.110 \, Re^{0.477} , \quad 15 < Re < 150 \qquad \text{(VI-158)}$$

where d_p = diameter of particle, [ft]

Re = $d_p U \rho / \mu$, Reynolds number, [-]

(ρ = density of gas, [lb/cu.ft]; μ = viscosity of gas, [lb/ft.hr])

(iii) Pressure drop

The pressure drop in the bed can be calculated by eq. (150) in Section 10.2.

(iv) Surge drum [62]

The gas released during depressurization should be vented to surge drums. The diameter of a surge drum is given by the following equation.

$$D_s = 2 \left[\frac{3V_A}{4\pi} \left(\frac{P_B}{P_d} - 1 \right) \right]^{1/3} \qquad \text{(VI-159)}$$

where D_s = diameter of surge drum, [ft]

V_A = volume of activated carbon tower, [cu.ft]

P_B = operating pressure in bed, [psi]

P_d = pressure in surge drum, [psi]

The thickness of the drum can be calculated by

$$T_s = \frac{1}{12} \left[\frac{P_d D_s}{2(2SE - 0.2P_d)} + 0.25 \right] \qquad \text{(VI-160)}$$

where T_s = thickness or surge drum, [ft]

S = maximum allowable stress value, [psi]

E = efficiency of joint, [-]

(SE = 15105 is used)

(v) Regeneration of Activated Carbon Bed by Steam

Regeneration is accomplished by passing low-pressure steam upward through the bed. The steam raises the temperature of the bed thereby reducing its equilibrium capacity for benzene. It also provides the latent heat of vaporization for benzene. The steam consumption for the regeneration is estimated by the following relation and Fig. VI-24.

$$\frac{Ws}{M} = \frac{Mw}{Mv} (P_T - P_V) \cdot \frac{dX^*}{dPv} \qquad \text{(VI-161)}$$

where W_S = amount of steam, [lb]

M = total amount of activated carbon in bed, [lb]

M_w = molecular weight of water, (=18)

M_v = molecular weight of benzene, (=78)

P_T = total pressure, [psi]

P_V = partial pressure of benzene, [psi]

X^* = amount of benzene in equilibrium with vapor having vapor pressure, P_v, [lb/lb-C]

12.3 Optimization of Activated Carbon Process

(i) Optimization technique and calculation procedure

The policy for optimization of this process is the same as that for Hot Potash Process, Amine Process and Iron Oxide Process. The cost information and calculation procedure of the revenue requirement presented in Chapter II can be used for this process.

The optimization technique applicable to this process is limited to univariable search method due to many process variables discusses in the next section.

(ii) Process variables

The flow diagram for Activated Carbon Process is shown in Fig. VI-3. The independent variables are :

Z, D_T, Number of tower, t_b, d_p, P_s (steam pressure)

T_G (temperature of gas), D_s, P_d

Among these variables, Z, D_T, t_b and D_s are related to each other by Eqs. (VI-156) and (VI-159). Thus, t_b and D_s are eliminated from the independent variables.

(iii) Results

The results of optimum design of Activated Carbon Process for various benzene content of inlet gas are shown in Figs. VI-25 and VI-26. For the feed gas containing 0.3% of benzene, the optimum operating conditions, the equipment cost and the revenue requirement for this process are listed in Table VI-10 and VI-11. The optimum operating cycle of the process is 2 hours with 1 hour for adsorption and 1 hour for regeneration.

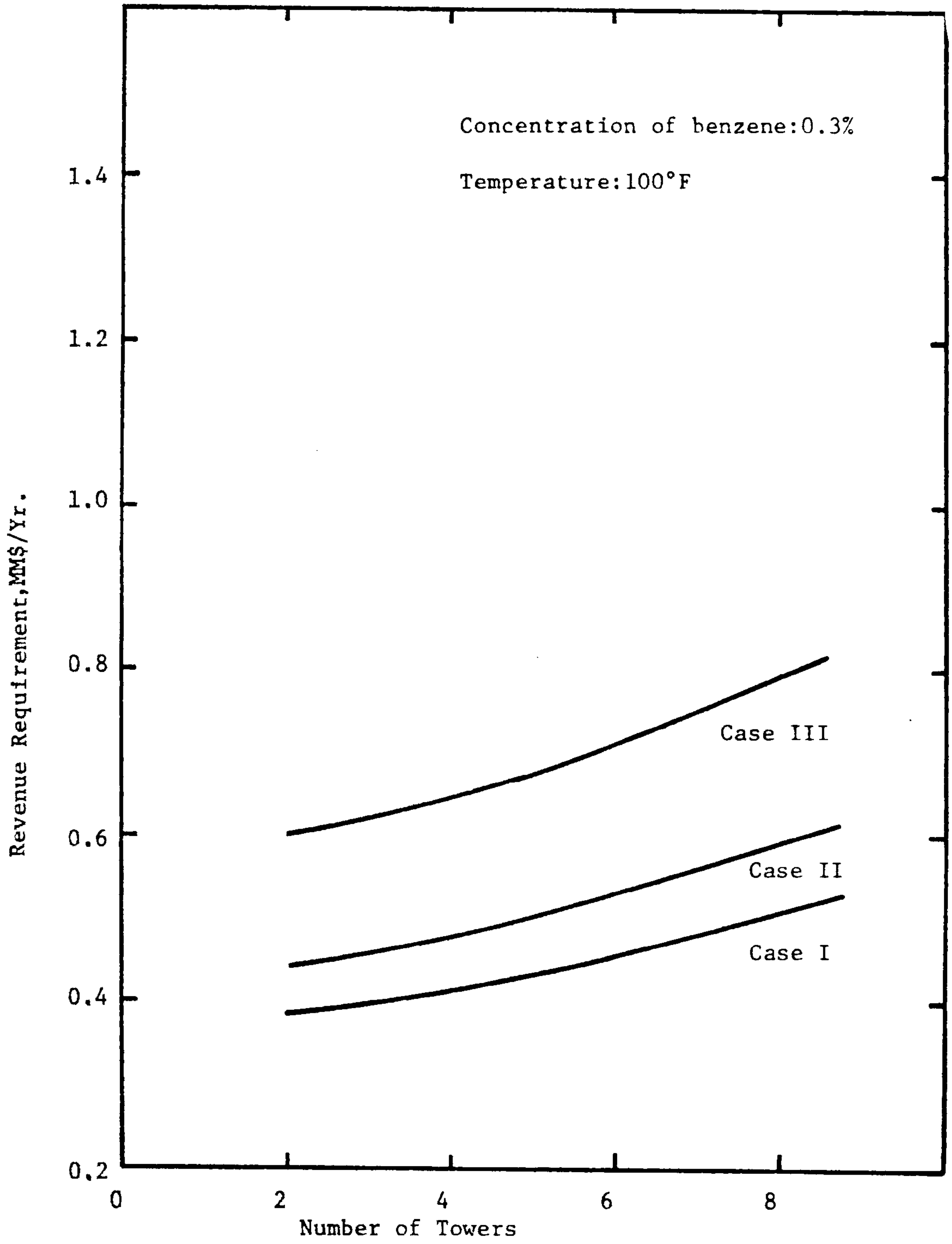


Figure VI-25. Effect of Number of Towers on Revenue Requirement in Activated Carbon Process

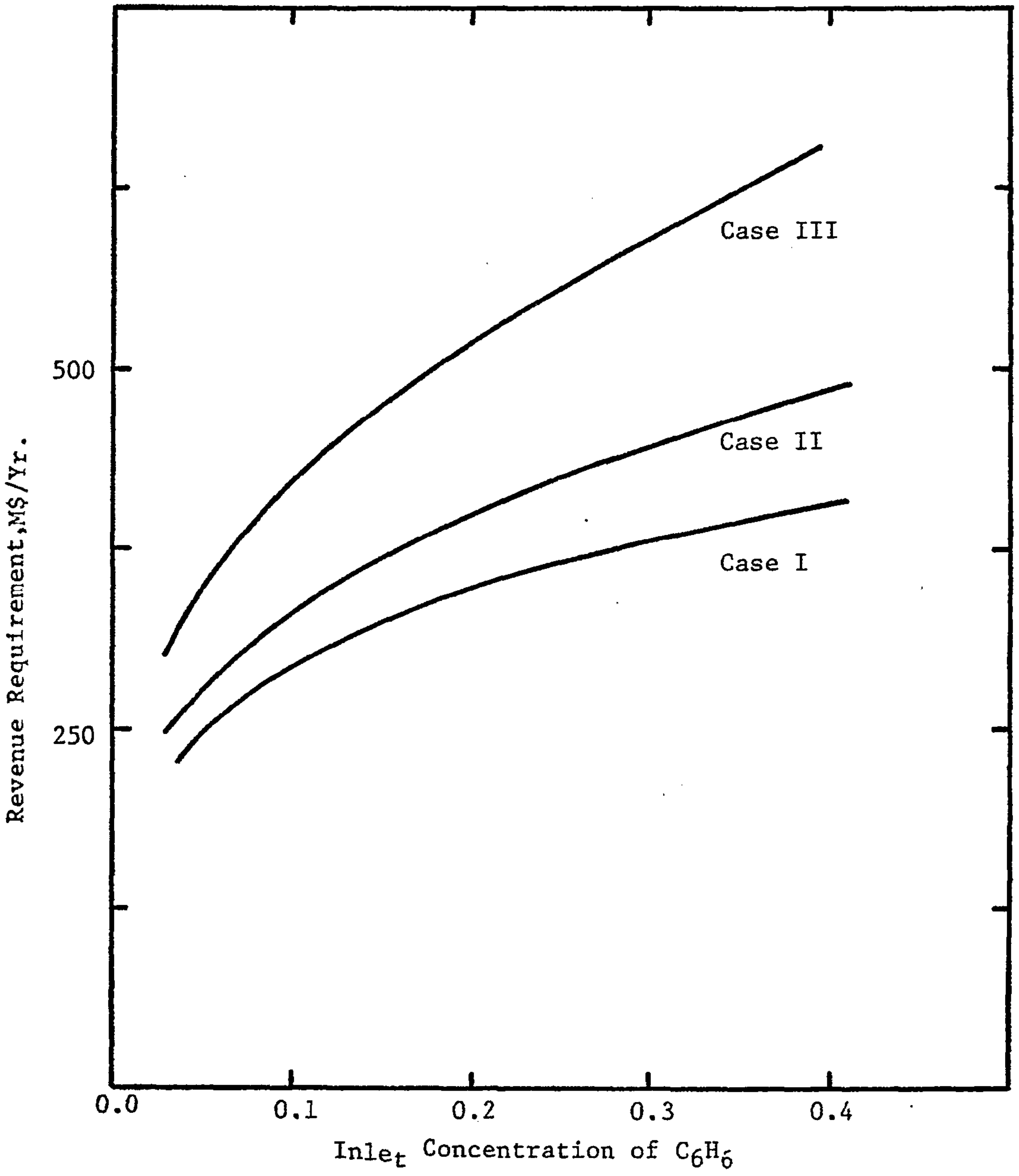


Figure VI-26. Effect of Inlet Concentration of Benzene on Revenue Requirement of Activated Carbon Process.

13. Conclusion and Recommendation for Further Investigation

Process optimization of gas purification has been carried out. The most economical process scheme for the purification of the coal gas in the present study was found to be hot potash process followed by monoethanolamine process. The activated carbon process for removal of benzene has been studied independently.

The optimum operating conditions and equipment costs are listed in Table VI-10 with over-all revenue requirements including that for activated carbon process. The flow rate and composition of the purified gas are also listed in Table VI-11. The use of hot potash process to first remove CO_2 to a low concentration takes the maximum advantage of the inlet synthesis-gas conditions, i.e., high CO_2 partial pressure and high temperature. The scheme of the amine process after substantial removal of CO_2 by the hot potash process takes the advantage of the high selectivity of amine process for the absorption of H_2S and avoids the disadvantage of the high solution circulation rate required by amine process to remove CO_2. However, it is not intended herin, that the process scheme and the operating conditions presented are the absolute ultimate optima due to the following facts:

(a) The computer optimization was performed based on available, as well as extrapolated data and some assumptions. When experimental data are not available, more or less conservative assumptions have to be made. This undoubtedly leads to an over design.

(b) Some new processes, which utilize the catalytic properties of organic or inorganic additives in the conventional gas purifying solutions, are claimed to have high rates of CO_2 and H_2S absorption and desorption and consequently require smaller absorbers and regenerators than their conventional counterparts. However, the kinetics of these new processes are not clear at this stage. Therefore, they are not suitable for, and are not included in the computer optimization.

Further investigation should include the following aspects:

(a) Equilibrium properties and kinetics of H_2S over K_2CO_3 and amine solutions and rates of H_2S absorption into these solutions are very scanty. To remove H_2S from the gas to an extremely low concentration, accurate data for the equilibrium vapor pressure of H_2S over amine solutions at low temperature are important. Tertiary amines do not react with CO_2 and can be used to remove H_2S selectively. Therefore, special attention should be given to tertiary amines. Solid adsorbents such as activated carbon and iron oxide can essentially remove H_2S completely. The adsorption isotherms and the rate of H_2S adsorption on some good adsorbents should also be investigated.

(b) Regeneration of spent solutions

No data are available on the regeneration of the spent solution.

The information pertaining to mass transfer in desorption of CO_2 from amine solution should be especially developed for a reliable regenerator design.

(c) Corrosion of equipment

Accurate corrosion data for absorbers, regenerators, and heat exchangers are needed to provide reliable design from materials point of view.

(d) New and improved processes

Data for simultaneous removal of CO_2 and H_2S by new and improved processes should be established.

It is hoped that more reliable data will become available in the near future, particularly for the newly developed gas purification processes, so that a more economical scheme and better process design for gas purification will be possible.

Table VI-10. Optimum Operating Conditions and Equipment Costs for <u>Hot Potash Process</u>.

Equipment	Case I	Case II	Case III
Absorber			
Number	3	5	10
Height, [ft]	26.5	17.0	18.5
Diameter, [ft]	8.7	9.5	9.6
Inlet Gas Temperature, [°F]	289.8	295.8	279.0
Outlet Gas Temperature, [°F]	274.9	280.9	267.2
Inlet Liquid Temperature, [°F]	294.2	299.0	285.2
Outlet Liquid Temperature, [°F]	274.8	280.9	267.2
Total Cost, [M$]	802.0	1,240.0	2,608.0
Regenerator			
Number	2	4	7
Height, [ft]	68.0	39.0	50.5
Diameter, [ft]	13.1	14.1	14.1
Inlet Liquid Temperature, [°F]	267.2	280.8	267.2
Outlet Liquid Temperature, [°F]	246.8	259.3	246.9
Total Cost, [M$]	284.0	484.0	850.0
Turbine-Motor-Pump System			
Number of Pumps	3	8	17
HP of Pump	1300	1500	1500
Total Cost, [M$]	238.0	682.0	1,404.0
Condenser 1 & 2			
Heat Duty, [MM BTU/hr]	254.4	56 .5	1,077.0
Cost, [M$]	129.1	196.1	291.8
Feed Gas Cooler			
Heat Duty, [MM BTU/hr]	375.8	791.4	1,246.0
Cost, [M$]	142.8	161.5	241.8

Table VI-10.(Continued) Optimum Operating Conditions and Equipment Costs for Amine Process.

Equipment	Case I	Case II	Case III
Absorber			
number	1	2	2
Height,[ft]	69.4	71.5	68.7
Diameter,[ft]	8.5	7.1	8.5
Inlet Gas Temperature	146.0	143.0	146.0
Outlet Gas Temperature,[°F]			
Inlet Liquid Temperature,[°F]	141.3	170.2	160.7
Outlet Liquid Temperature,[°F]	107.5	107.5	102.5
Total Cost,[m$]	528.7	765.2	1,036.5
Regenerator			
Number	1	1	1
Height,[ft]	35.5	38.0	27.8
Diameter,[ft]	5.4	8.6	12.0
Inlet Liquid Temperature,[°F]	237.1	236.8	236.2
Outlet Liquid Temperature,[°F]	219.2	216.7	216.7
Total Cost,[M$]	15.2	29.9	41.1
Turbine-Motor-Pump System			
Number of Pumps	1	1	1
HP of Pump,[HP]	300	500	1200
Total Cost,[M$]	36	59	78
Condenser			
Heat Duty,[MM BTU/hr]	23.6	57.2	107.2
Cost,[M$]	32.4	54.0	76.8
Feed Gas Cooler			
Heat Duty,[MM BTU/hr]	88.4	94.9	113.2
Cost,[M$]	82.1	68.5	76.8
Heat Exchanger(No.3)			
Heat Duty,[MM BTU/hr]	14.2	23.4	44.5
Cost,[M$]	39.4	52.3	75.0
Heat Exchanger(No.4)			
Heat Duty,[MM BTU/hr]	7.7	30.6	54.2
Cost,[M$]	19.4	35.0	54.0

Table VI-10.(Continued) Optimum Operating Conditions and Costs of Miscellaneous Equipments.

Equipment	Case I	Case II	Case III
Activated Carbon Tower			
Number	2	2	2
Packing Height,[ft]	5.4	5.6	5.9
Diameter,[ft]	15.6	16.8	19.6
Total Cost,[M$]	992.0	1,211.9	1,823.3
Surge Drum			
Number	1	1	1
Diameter,[ft]	38.2	40.8	45.7
Total Cost,[M$]	93.0	108.1	142.1
Compressor			
Number	1	1	1
Cost,[M$]	23.9	27.9	37.2
Hot Potash Process:			
Revenue Requirement,[M$/yr]	837.8	1,550.2	2,944.6
Equipment Cost,[M$]	1,931.6	3,264.1	6,445.9
Utility Cost,[M$/yr]	291.0	712.0	1,404.0
Amine Process:			
Revenue Requirement,[M$/yr]	436.8	634.8	893.0
Equipment Cost,[M$]	853.0	1,220.8	1,638.9
Utility Cost,[M$/yr]	151.0	271.2	440.7
Activated Carbon Process:			
Revenue Requirement,[M$/yr]	382.3	439.8	594.9
Equipment Cost,[M$]	1,126.3	1,365.1	2,020.7
Utility Cost,	44.7	53.6	75.2

Table VI-11. Flow Rate and Composition of Purified Gases

	component	Flow Rate [lb-moles/hr.]	Composition [mole %]
Case I	CO	3,180	8.0
	H_2O	40	0.1
T = 105°F	H_2	11,020	27.5
	CO_2	400	1.0
P = 1047 psi	CH_4	24,670	61.6
	C_6H_6	-	-
	N_2	720	1.8
	H_2S	-	-
	Total	40,030	100.0
Case II	CO	6,450	13.4
T = 106°F	H_2O	50	0.1
P = 1087 psi	H_2	20,580	42.9
	CO_2	480	1.8
	CH_4	19,720	41.1
	C_6H_6	-	-
	N_2	720	1.5
	H_2S	-	-
	Total	48,000	100.0
Case III	CO	12,420	18.5
	H_2O	70	0.1
T = 100°F	H_2	38,650	57.5
	CO_2	670	1.0
P = 1047 psi	CH_4	14,590	21.7
	C_6H_6	-	-
	N_2	780	1.2
	H_2S	-	-
	Total	67,180	100.0

NOTATION

a	effective surface area of packing per unit volume of tower,(sq.ft./cu.ft.)
$[A_m]$	concentration of amine,(lb-mole/cu.ft.)
A_j	heat transfer area of j-th heat exchanger,(sq.ft.)
a_v	interfacial area per unit volume of bed,(sq.ft./cu.ft.)
c	concentration of disolved CO_2 in solution,(lb-mole/cu.ft.)
c	concentration of disolving H_2S in solution,(lb-mole/cu.ft.)
c	concentration of benzene adsorbed per unit volume of gas,(lb./cu.ft.)
c^*	concentration of benzene in equilibrium with X,(lb./cu.ft.)
c	concentration difference of benzene or driving force,(lb./cu.ft.)
c_b	equilibrium concentration of unreacted dissolving CO_2 in bulk of liquid,(lb-mole/cu.ft.), or outlet concentration of benzene at breakthrough time,(lb./cu.ft.)
c_i	concentration of dissolving H_2S at interface,(lb-mole/cu.ft.)
c_i	concentration of dissolving CO_2 at interface,(lb-mole/cu.ft.) or interfacial concentration of benzene adsorbed,(lb./cu.ft.)
c_o	concentration of amine in solution,(lb-mole/cu.ft.) or inlet concentration of benzene,(lb./cu.ft.)
C_p	mean molar heat capacity of gas stream,(BTU/lb-mole °F)
C_{pL}	mean molar heat capacity of amine solution,(BTU/lb-mole°F)
C_{pL}	heat capacity of liquid,(BTU/lb.°F)
c_R	concentration of reactant in solution,(lb-mole/cu.ft.)
c_{H_2S}	H_2S concentration of inlet gas to iron oxide bed,(grain)
c_1,c_2	value of C_o at top and bottom, respectively, of column,(lb-mole/cu.ft.)
d	diameter of packing,(ft.)
D	diffusivity of solute or CO_2 in solvent,(sq.ft./hr.) or diffusivity of benzene,(sq.ft./hr.)
D'	diffusivity of H_2S in solvent,(sq.ft./hr.)

D_B	diameter of iron oxide bed,(ft.)
D_o	diffusivity of amine in solvent,(sq.ft./hr.)
d_p	diameter of particle,(ft.) in Eq. (VI-158)
D_p	diameter of particle,(ft.)
D_s	diameter of surge drum,(ft.)
D_{wj}	amount of water condenced from gas stream in j-th heat exchanger,(lb)
E	efficiency of joint of sphere,(-)
g	acceleration due to gravity,(ft./sq.ft.)
G	molar gas flow rate,(lb-mole/hr.), or superficial mass velocity of gas,(lb./sq.ft.hr.)
g_c	gravitational conversion factor,(lb_m.ft./lb_f.hr.)
G_F	flooding gas velocity,(lb./sq.ft.hr.)
G_i	molar flow rate of inert gas in absorber,(lb-mole/hr.)
G_j	molar flow rate of gas entering j-th heat exchanger,(lb-mole/hr.)
G_o	superficial molar flow rate of inert gas ,(lb-mole/sq.ft.hr.)
G_s	molar steam flow rate,(lb-mole/hr.)
G_1	molar flow rate of feed gas,(lb-mole/hr.)
h	heat transfer coefficient,(BTU/sq.ft.hr.°F)
H	Henry's law constant,(lb-mole/cu.ft.atm.)
H_B	height of iron oxide bed,(ft.)
h_c	height of column,(ft.)
h^n	height of n-th section,(ft.)
H_{va}	heat of vaporization of water at $(T_g)_{ab}$,(BTU/lb.)
H_{vj}	heat of vaporization of water at T_j,(BTU/lb.)
H_{vm}	heat of vaporization of water at T_m,(BTU/lb.)
H_{vr}	heat of vaporization of water at $(T_g)_{rb}$,(BTU/lb.)

j_D	j-factor for mass transfer
j_H	j-factor for heat transfer
K_c	equilibrium constant of reaction $2R_2NH + CO_2 \rightleftharpoons R_2NCOO + R_2NH_2$, (cu.ft./lb-mole)
k_c	mass transfer coefficient in particle,(lb./sq.ft.hr. C)
k_F	mass transfer coefficient in gas side,(lb./sq.ft.hr. C)
K_F	over-all mass transfer coefficient based on the concentration difference in gas,(lb./sq.ft.hr. C)
K_Ga	over-all mass transfer coefficient in gas side,(lb-mole/cu.ft.hr.atm)
k_L	liquid side mass transfer coefficient,(ft./hr.)
L	molar liquid rate,(lb-mole/hr.)
L_o	superficial molar liquid flow rate,(lb-mole/sq.ft.hr.)
m	total amount of activated carbon in bed,(lb.)
M	molecular weight of solvent,(lb./lb-mole)
M_v	molecular weight of benzene,(=78)
M_w	molecular weight of water,(=18)
N	mass flux,(lb-mole/sq.ft.hr.)
N_A	mass flux of component A,(lb-mole/sq.ft.hr.)
N_m	number of transfer unit,(lb-mole/cu.ft.)
p	pressure drop,(atm. or psi)
P	total pressure,(atm. or psi)
p_B	operating pressure in activated carbon bed,(psi)
p_{CO_2}	partial pressure of CO_2,(atm or psi)
p_{CO_2}	equilibrium pressure of CO_2,(atm or psi)
p_d	pressure in surge drum,(psi)
p_{H2S}	partial pressure of H_2S,(atm or psi)
p_{MEA}	partial pressure of monoethanolamine,(atm or psi)

P_r	pressure in regenerator or Prandle number,(atm or psi,or –)
P_T	total pressure,(psi)
P_v	vapor pressure of water or partial pressure of benzene,(atm or psi)
P_{vm}	vapor pressure of water at T_m,(atm or psi)
P_{vj}	vapor pressure of water at T_j,(atm or psi)
P_c	vapor pressure of water in condenser,(atm or psi)
q_r	heat generated due to absorption,(BTU/sq.ft.)
q_t	heat transfered from gas phase to liquid phase,(BTU/sq.ft.)
q_g	heat carried by CO_2 and H_2S from gas phase to liquid phase due to absorption,(BTU/sq.ft.)
Q_a	heat generated in absorber due to CO_2 and H_2S absorption into solution,(BTU)
Q_r	heat disappeared in regenerator due to CO_2 and H_2S desorption from solution,(BTU)
Q_v	heat disappeared in flash drum due to vaporization of CO_2,$Q_a - Q_r$,(BTU)
Q_j	heat duty of j-th exchanger,(BTU/hr.)
R	rate of absorption,(lb-mole/sq.ft.hr.)
S	maximum allowable stress value,(psi)
t	time,(hr.)
t_b	breakthrough time,(hr.)
T_B	temperature of iron oxide bed,(°F)
t_j	logarithmic-mean temperature difference,(°F)
T_j	gas temperature at inlet of j-th heat exchanger,(°F)
T_1	feed gas temperature,(°F)
T_c	temperature of entering water,(°F)
T_R	absolute temperature,(°F)
t_{FL}	temperature of liquid,(°F)

T_s	thickness of surge drum,(ft.)
u	superficial velocity,(ft./hr.)
U_F	flooding velocity of gas phase based on total tower cross-sectional area,(lb./sq.ft.hr.)
U_1	over-all heat transfer coefficient,(BTU/sq.ft.hr.°F)
U_2	over-all heat transfer coefficient of condensers,(BTU/sq.ft.hr.°F)
U_j	over-all heat transfer coefficient of j-th heat exchanger,(BTU/sq.ft.hr.°F)
v	gas velocity in empty tower,(ft./sec.)
V	mole volume of solute as liquid at its normal boiling point,(cu.ft./lb-mole)
V_A	volume of activated carbon tower,(cu.ft.)
W_1	water flow rate,(lb./hr.)
W_j	coolant water flow rate through heat exchanger,(lb./hr.)
W_s	amount of steam,(lb.)
X	amount of benzene adsorbed per unit mass of activated carbon,(lb./lb.-C) or mole ratio of CO_2 to MEA in liquid,(-)
X_{ab}	mole ratio of CO_2 to MEA in liquid at bottom of absorber,(moles-CO_2/mole-MEA)
X_{at}	mole ratio of CO_2 to MEA at top of absorber,(moles-CO_2/mole-MEA)
X^*	amount of benzene in equilibrium with vapor having vapor pressure p_v,(lb./lb.-C)
X_i	amount of benzene adsorbed per unit mass of adsorbent,activated carbon, at interface,(lb./lb.-C)
X_o	amount of benzene in equilibrium with C_o,(lb./lb.-C)
X'	mole ratio of H_2S to MEA in liquid,(-)
Y_s	mole fraction of K_2CO_3 in original solution
Y_o	concentration of K_2CO_3 in solution,(%)
y'^n	mole fraction of H_2S at top of n-th section

Y_{ab}	moles-CO_2 per mole inert gas at bottom of absorber,(-)
Y_{at}	moles-CO_2 per mole inert gas at top of absorber,(-)
Y_{rt}	moles-CO_2 per mole steam in gas at top of regenerator,(-)
Y_{rb}	moles-CO_2 per mole steam in gas at bottom of regenerator,(-)
Y_{wj}	mole fraction of water vapor in gas stream entering j-th heat exchanger,(-)
y_w	mole fraction of H_2S in feed gas,(-)
Z	height of activated carbon bed,(ft.) or height of iron oxide bed,(ft.)
z	mole fraction of amine in original solution,(-)
Z_a	height of bed where mass transfer occurs,(ft.)

Greek Letters:

α	number of moles of reactant reacting with each mole of dissolved gas
β	association parameter for solvent
γ	packing density,(lb./cu.ft.)
ε	void fraction of bed or packing,(-)
μ_g	viscosity of gas,(lb./ft.hr.)
μ_w	viscosity of water,(lb./ft.hr.)
ρ_L	density of liquid,(lb./cu.ft.)
ρ_G	density of gas,(lb./cu.ft.)
ρ_M	molar density of liquid,(lb.-moles/cu.ft.)
ϕ,ψ	characteristic constants for packing

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