Absorber Design in Sour Natural Gas Treatment Plants: Impact of Process Variables on Operation and Economics

Absorberentwurf für Anlagen zur Behandlung von sauren Erdgasen: Einfluss Prozessparameter auf Betriebsführung und Prozesswirtschaftlichkeit

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Abstract

Two models of absorber have been developed which describe the absorption of H_2S and CO_2 from natural gases by aqueous di-isopropanolamine (DIPA) or methyl-di-ethanolamine (MDEA) solutions. In these models mass transfer, reaction and equilibrium processes as they prevail in conventional tray absorbers and in cascades of trickle bed reactors are incorporated. Owing to the better mass transfer characteristics of the latter type of absorber, i.e. the larger ratio between the gas phase and liquid phase mass transfer coefficients, k_g/k_L , higher selectivities for the absorption of H_2S from sour natural gases are realized.

The influence of variation of a number of operation and design parameters on tray absorber performance, H_2S selectivity and solvent flowrate is demonstrated.

The economics of the above type of absorbers together with a solvent regenerator, sulfur recovery unit and tail-gas unit are explained in detail. From the point of view of the economics trickle bed absorbers are very attractive owing to lower investment costs and higher selectivities, which result in lower operating costs than for tray absorbers under identical conditions.

Kurzfassung

Zwei Absorbermodelle wurden entwickelt zur Beschreibung der Absorption von Schwefelwasserstoff und Kohlendioxid aus Erdgasen mit Hilfe wässriger Di-isopropanolamin (DIPA) oder Methyl-di-äthanolamin (MDEA) Lösungen. In diesen Modellen sind Stoffaustauschvorgänge, Reaktionen und Gleichgewichte verarbeitet wie sie in konventionellen Bodenkolonnen und in Kaskaden von Trickle-bedabsorbern vorliegen. Durch bessere Stoffaustauschcharakteristiken, d.h. einem grösseren Verhältnis zwischen Gasphase- und Flüssigkeitsstoffaustauschkoeffizienten (k_g/k_L), kann im letzteren Absorbertyp eine höhere Selektivität für die Absorption des Schwefelwasserstoffs aus sauren Erdgasen erzielt werden.

Der Einfluss von Variationen mehrerer Betriebs- und Entwurfparameter auf die Bodenkolonnenleistung, H_2S -Selektivität und den Lösungsmitteldurchsatz werden demonstriert.

Die Wirtschaftlichkeit der genannten Absorbertypen in Verbindung mit einem Lösungsmittelregenerator, einer Schwefelrückgewinnungsanlage und einer 'Tail-gas' Anlage werden im Detail erläutert. Aus dem Gesichtspunkt der Wirtschaftlichkeit sind Trickle-bedabsorber sehr attraktiv durch geringere Investitionen und höhere Selektivitäten, die in niedrigeren Betriebskosten resultieren als bei Bodenkolonnen identischer Leistung.

Synopsis

Zur Beschreibung der Hochdruckabsorption (70 bar) von Schwefelwasserstoff und Kohlendioxid aus Erdgasen mit Hilfe wässrigen Di-isopropanolamin (DIPA) und Methyl-di-äthanolamin (MDEA) Lösungen wurden zwei Absorbermodelle entwickelt. Das erste Modell beschreibt relevante physikalische und chemische Prozesse, die in

konventionellen Bodenkolonnen stattfinden (Fig. 2). Das zweite Modell beschreibt diese Prozesse in einer Trickle-bedabsorberkaskade (Fig. 3).

Die Kolonne wird Boden für Boden durchgerechnet. Für jeden ideal vermischt angenommenen Boden werden die physikalischen und chemischen Gleichgewichte, die Reaktions- und Stoffübertragungsgeschwindigkeiten, die Nicht-idealität der Gasphase und die Wärmeeffekte bei den herrschenden Bedingungen berechnet. Die Gleichgewichte werden mit einem relativ einfachen, aber effektiven Modell ermittelt [11]. Die Stoffübertragungs-

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geschwindigkeiten werden sowohl mit einer analytischen Lösung, die Wechselwirkung zwischen und Reversibilität der Flüssigkeitsreaktionen des Schwefelwasserstoffs und Kohlendioxids mit Alkanolamin vernachlässigt, als auch numerisch unter Berücksichtigung dieser Effekte, berechnet [13]. Eine Modifikation der Redlich–Kwong Zustandsgleichung nach Soave beschreibt die Nicht-idealität der Gasphase. Bei der Berechnung der Trickle-bedabsorberkaskade wird jeder Gleichstromabsorber als Reihe ideal vermischter Sektionen angenommen. Jede Sektion wird analog zum Boden berechnet.

Die beiden Methoden zur Beschreibung der Stoffübertragung (analytisch und numerisch) werden an Hand des Modells der Bodenkolonne verglichen. Unter normalen Bedingungen sind die Unterschiede zwischen beiden Modellen vernachlässigbar (Fig. 5–8). Bei extremen Bedingungen ist jedoch das numerische Modell notwendig. Im grössten Teil der Kolonne ist für Schwefelwasserstoff die Stoffübertragungsgeschwindigkeit in der Gasphase limitiert, während für Kohlendioxid die Limitierung in der Flüssigkeit liegt.

Ein Vergleich der Alkanolaminlösungen zeigt, dass das tertiäre Amin, MDEA, nur unwesentlich selektiver ist als das sekundäre DIPA. Für beide Amine liegt die Selektivität, η (definiert durch Gl. (33)), nahe am theoretischen Minimum.

Aus den Berechnungen zeigt sich weiter, dass der Betriebsdruck der Kolonne die Selektivität η und den Lösungsmitteldurchsatz ϕ_Q nicht beeinflusst (Fig. 9). Die anfängliche Beladung des regenerierten Lösungsmittels mit H_2S und CO_2 hat einen ziemlich starken Einfluss auf η und insbesondere auf ϕ_Q (Fig. 10). Die Endbeladung des Lösungsmittels steuert die Selektivität kaum, hat aber einen grossen Einfluss auf den Lösungsmitteldurchsatz (Fig. 11). Bei hohen Aminkonzentrationen und deshalb niedrigen Lösungsmitteldurchsätzen, führt die Wärmeentwicklung zu hohen Temperaturen unten in der Kolonne und kann Kohlendioxid desorbieren (Fig. 13–15).

Nach den Modellberechnungen zeigt die Trickle-bedabsorberkaskade eine deutlich bessere Selektivität und einen günstigeren Lösungsmitteldurchsatz als die Bodenkolonne.

Der Einfluss der Selektivität der Hochdruckabsorber auf die Betriebskosten einer vollständigen Gasbehandlungsanlage, d.h. ein Hochdruckabsorber mit Lösungsmittelregenerator, eine Schwefelrückgewinnungsanlage und eine 'Tail-gas' Anlage (Fig. 1) wird mit Hilfe mathematischer Modelle der Anlagen berechnet. Mit steigender Selektivität der Hochdruckabsorption sinken die Gasbehandlungskosten beträchtlich (Fig. 20). Die Abhängigkeit der Betriebskosten vom Schwefelpreis und von relativen Energiekosten wird aufgezeigt (Fig. 22 und 23).

Trickle-bedabsorberkaskaden sind sehr attraktiv durch niedrigere Investitionen und Betriebskosten als Bodenkolonnen identischer Leistung.

Introduction

Removal of the acid components H_2S and CO_2 from sour natural gases by means of alkanolamine solutions

is studied in this paper. The industrially most important alkanolamines for gas treatment operations are monoethanolamine (MEA), diethanolamine (DEA), diisopropanolamine (DIPA) and methyl-diethanolamine (MDEA) [1, 2]. In general these amines are used in aqueous solutions but for specific applications combined solvents can be more suitable, e.g. water and sulfolane in the Shell 'Sulfinol' process [1, 2].

In view of the high energy consumption in sour natural gas treatment plants, there is considerable incentive for the development of—even slightly—more efficient processes [3, 4]. Large savings in operating and investment costs can be obtained by the selective absorption of H_2S alone from H_2S and CO_2 containing gases. Even in liquid natural gas production, where the CO_2 ultimately also has to be removed in order to avoid plugging of cryogenic equipment, selective absorption of H_2S is economically very attractive using sophisticated treatment schemes as described, for example, by McEwan and Marmin [4].

The selective absorption of H_2S from a sour gas containing CO_2 also offers a number of economical advantages:

- it reduces the solvent circulation rate and, as a consequence, the regeneration costs and investment in equipment are reduced;
- it increases the H_2S/CO_2 ratio in the off-gas to the sulfur recovery unit, which reduces the dimensions of and investment in the sulfur recovery and tail-gas units.

The H_2S selectivity in gas treatment plants using alkanolamine solvents depends largely on three factors:

- the mass transfer properties of the high pressure absorber;
- the (chemical) equilibria in the H_2S – CO_2 –amine system;
- the kinetics of the reactions between H_2S/CO_2 and the amines.

In order to study the effect of these factors on the economics of the treatment operation, we developed a set of mathematical models describing a complete sour natural gas treatment plant. The flow scheme of the plant considered is shown in Fig. 1 and consists of three basic units:

- a high pressure absorber–regenerator unit (ARU);
- a Claus sulfur recovery unit (SRU);
- a Shell Claus off-gas treater (SCOT) tail-gas unit (TGU).

In order to limit the complexity of the calculations and consequently the computer costs involved, we used this relatively simple flowsheet as the basis for this study. We realize, of course, that more sophisticated treatment schemes, involving, for example, cascaded and split-stream solvent flows, are described in the literature and used in commercial operations [1, 4, 5].

As will be shown, the operation of the high pressure absorber is a key parameter in the overall process economics. For this reason the emphasis in this study is put on the relation between the absorber design and the plant performance. Tray column absorbers are used nowadays in large-scale treatment plants. Therefore, the performance of this type of absorber is analysed

Fig. 1. Flow scheme of the treatment plant.

for different operating conditions. Moreover, the properties of a potentially new absorber type for these operations—a cascade of trickle beds—will also be evaluated.

Modifications in process set-ups like those mentioned above can be judged and evaluated only by their impact on the overall process economics. Therefore we incorporated in this study a comparison of the process economics for a number of absorber options. This is carried out on the basis of investment and cost calculations for each of these options, resulting in a cost for the treatment operation per Nm^3 of natural gas.

For a study like this, a vast amount of data is needed. Wherever possible, these data have been extracted from the open literature. Since this study covers a subject of commercial importance, information on the process economics [6, 7], absorber [6, 8] and regenerator design [7] is very scarce. Nevertheless, we are convinced that the results shown in this paper give a good understanding of the impact of absorber design and operation on selectivity and the overall process economics of gas treatment.

For several years now, the fundamentals of (alkanolamine) gas treatment have been one of the subjects of the research programme in our laboratories of Chemical Reaction Engineering at the Twente University of Technology. The emphasis in our research is on improving the selectivity of the absorption of H_2S from H_2S and CO_2 containing gases like natural gas by means of

the mass transfer properties in absorbers. To this end fundamental studies were executed on the following items:

- a general description of the rate of the reaction between CO_2 and aqueous alkanolamines [9, 10];
- the development of a mathematical model for the equilibria in the H_2S — CO_2 —amine—water system [9, 11, 12];
- the mathematical description of the simultaneous mass transfer of H_2S and CO_2 from the gas phase and the complex reversible liquid phase reactions [9, 13].

In the work presented here we apply the knowledge acquired in previous studies [9–13] to the design of a complete treatment plant and also incorporate an evaluation of the economics of the amine treatment process. A summary of the reaction scheme and the pertinent kinetic data is given in Table A.

Design Considerations

General

The flowsheet of the treatment plant studied is shown in Fig. 1. Using aqueous alkanolamine solutions the temperatures in the regenerator are relatively low. Consequently the amine losses due to (high temperature) degradation reactions are low and are assumed to be balanced by the amine make-up for compensation of pump losses and leakages. For this reason an amine

TABLE A. Reaction scheme and data for H₂S + CO₂ absorption in DIPA

1. Equilibrium data:

$$\text{for DIPA: } K = 1.01 \times 10^4 \exp(-3173.9/T)$$

[9]

2. Reaction rate expressions:

$$\text{DIPA: } r = k_{1,1}[\text{CO}_2][\text{DIPA}]$$

[9, 14]

$$\text{where } k_{1,1} = 4.09 \times 10^9 \exp(-4808/T)$$

$$\text{MDEA: } r = k_{1,1}[\text{CO}_2][\text{MDEA}]$$

[9, 10]

$$\text{where } k_{1,1} = 1.02 \times 10^8 \exp(-4808/T)$$

3. Liquid phase viscosities:

$$\mu(\text{DIPA}) = \{1.244 - 5.47 \times 10^{-4}[\text{DIPA}] + 3.668 \times 10^{-7}[\text{DIPA}]^2\} \exp(4549/T - 14.31) \quad \text{cP}$$

[9]

$$\mu(\text{MDEA}) = \{0.7747 - 6.941 \times 10^{-5}[\text{MDEA}] + 1.4934 \times 10^{-7}[\text{MDEA}]^2\} \exp(2977/T - 9.36) \quad \text{cP}$$

[9]

reclaimer is omitted. The capacity of the average gas treatment unit is around 200 000 Nm³ h⁻¹ of natural gas, which we have chosen as the design basis.

TABLE 1. Specification of the feed gases

Capacity: 200 000 Nm³ h⁻¹

Pressure: 70 bar

	H ₂ S (vol.%)	CO ₂ (vol.%)
Gas I	7	7
Gas II	5	10
Specification	4 × 10 ⁻⁴	None

The calculations are carried out for two gas compositions as shown in Table 1, a high H₂S, high CO₂ gas (I) and a low H₂S, high CO₂ gas (II). In the latter case, in particular, selective removal of H₂S is very important.

No other sour gases such as COS or HCN are assumed to be present. In all calculations H₂S is removed to the pipeline specification of 4 ppm vol. [7]. No specification is set for CO₂.

Aqueous solutions of either di-isopropanolamine (DIPA) or methyl-di-ethanolamine (MDEA) are used as solvents.

Absorbers

The absorption process is based on reversible acid–base reactions between H₂S and/or CO₂. These reactions

enhance the rates of mass transfer of the acid components into the liquid phase and also provide absorption capacity.

The reaction between H_2S and the amine involves a proton transfer only and can be regarded as instantaneous and reversible [10, 14]:

Owing to the forward and reverse reactions which are fast compared with the rate of mass transfer, the equilibrium (1) is established everywhere in the liquid.

On the other hand, the reaction between CO_2 and an aqueous amine proceeds at a finite rate. The CO_2 absorption rate is determined by the reaction [9, 10, 14]

for a secondary amine, and [9, 10] by

a base catalysis mechanism for a tertiary amine.

At longer residence times, the carbamate, $R_1R_2NCOO^-$, formed from CO_2 and secondary amines, is hydrolysed [14] and produces bicarbonate and free amine:

The rate of this last reaction, however, is low and therefore it is generally assumed that it does not affect the CO_2 absorption rate significantly.

Two types of high pressure absorbers will be compared: a conventional tray column and a cascade of trickle bed columns. The reason for incorporation of the latter absorber type will be demonstrated later. A tray absorber is used in the TGU calculations.

Tray absorbers

The tray absorbers are calculated by a tray-to-tray procedure. The absorption column is considered as a series of ideally mixed (with respect to both gas and

Fig. 2. Scheme for the tray absorber.

liquid phases) reactors, each corresponding to an *actual* tray (see Fig. 2).

Process conditions and gas and liquid compositions are assumed to be uniform in each reactor. More sophisticated tray models, e.g. with plug flow in the gas phase as proposed, but not used, by Cornelissen [8] are not considered. Gas and liquid phase backmixing between trays as well as pressure drop over the trays are neglected.

The calculation starts with an overall mass balance over the column. For this purpose a CO_2 concentration in the treated gas, $y_{CO_2}^{n+1}$, has to be estimated and then the treated gas flow, ϕ_g^{n+1} , can be calculated by

$$\phi_g^{n+1} = \frac{\phi_g^1(1 - y_{H_2S}^1 - y_{CO_2}^1)}{1 - y_{H_2S}^{n+1} - y_{CO_2}^{n+1}} \quad Nm^3 s^{-1} \quad (5)$$

whereas the H_2S concentration in the treated gas is always taken as 4 ppm vol. The composition and the flow of the treated gas is fixed now. Next, the liquid volumetric flowrate in the column is calculated in such way that the rich solution leaving the column at tray 1 is loaded with acid gases to a preset desired value α_{tot} :

$$\alpha_{tot} = \alpha_{H_2S} + \alpha_{CO_2} = \frac{[H_2S_{tot}]_l^1 + [CO_{2,tot}]_l^1}{[Am_{tot}]} \quad (6)$$

$[H_2S_{tot}]_l^1$, $[CO_{2,tot}]_l^1$ and $[Am_{tot}]$ refer to the *total* concentrations of the respective components in both *reacted* and *unreacted* form.

The liquid flow is obtained from a total acid balance:

$$\begin{aligned} \phi_l = & \{-\phi_g^{n+1}([H_2S]_g^{n+1} + [CO_2]_g^{n+1}) \\ & + \phi_g^1([H_2S]_g^1 + [CO_2]_g^1)\} / \{\alpha_{tot}[Am_{tot}] \\ & - [H_2S]_l^{n+1} - [CO_2]_l^{n+1}\} \quad m^3 s^{-1} \end{aligned} \quad (7)$$

where all gas phase concentrations are expressed in $mol Nm^{-3}$, under standard conditions. We assume ϕ_l to be constant over the column. From the overall mass balances for the individual components the total acid gas concentrations in the rich solution are calculated:

$$\begin{aligned} [H_2S_{tot}]_l^1 = & \frac{\phi_g^1[H_2S]_g^1 - \phi_g^{n+1}[H_2S]_g^{n+1}}{\phi_l} \\ & + [H_2S_{tot}]_l^{n+1} \quad mol m^{-3} \end{aligned} \quad (8)$$

and

$$\begin{aligned} [CO_{2,tot}]_l^1 = & \frac{\phi_g^1[CO_2]_g^1 - \phi_g^{n+1}[H_2S]_g^{n+1}}{\phi_l} \\ & + [CO_{2,tot}]_l^{n+1} \quad mol m^{-3} \end{aligned} \quad (9)$$

The heat capacities of the gas and the liquid are of the same order of magnitude and therefore a heat balance has to be incorporated in the model. The overall heat balance over the absorber is solved assuming that

$$T_g^{n+1} = T_l^{n+1} \quad K \quad (10)$$

which means that the temperature of the top tray is that of the lean amine solution introduced.

This enables us to calculate the temperature of the rich solution, provided that gas and liquid inlet temperatures are specified:

$$T_{\ell}^1 = \frac{(\phi_g^1 T_g^1 - \phi_g^{n+1} T_g^{n+1}) \rho_g C_{pg}}{\phi_{\ell} \rho_{\ell} C_{p\ell}} + \frac{\Delta H_{H_2S} ([H_2S_{tot}]_{\ell}^1 - [H_2S_{tot}]_{\ell}^{n+1})}{\rho_{\ell} C_{p\ell}} + \frac{\Delta H_{CO_2} ([CO_2]_{\ell}^1 - [CO_2]_{\ell}^{n+1})}{\rho_{\ell} C_{p\ell}} + T_g^{n+1} \quad K \quad (11)$$

The ΔH terms represent the sum of the heats of both reaction and adsorption. The gas and liquid compositions and conditions at the absorber bottom are now fixed and provide the starting point for tray-to-tray calculations.

In order to solve the tray heat balance, thermal equilibrium is assumed between the gas and liquid flows leaving the tray:

$$T_g^{i+1} = T_{\ell}^i \quad K \quad (12)$$

At the absorber top, this equation is contradictory to the assumption for the overall heat balance expressed in eqn. (10). This discrepancy is, however, negligible because $T_{\ell}^{n+1} \cong T_{\ell}^n$, as will be demonstrated later.

Now, as the gas temperature on the bottom tray 1 is known from eqn. (12), the liquid phase equilibrium constants, Henry's coefficients, and gas and liquid phase diffusivities are calculated. The liquid phase composition, more specifically the concentrations of unreacted H_2S , CO_2 and amine, is obtained by means of the equilibrium model described by Blauwhoff and van Swaaij [9, 11].

For DIPA, however, the equilibrium of the carbamate hydrolysis reaction (4) will not be (fully) established in the absorber owing to the low rate of this reaction. Therefore, the equilibrium model was modified for DIPA, in order to account for this effect.

Next, H_2S and CO_2 gas phase concentrations at tray 1, i.e. in the gas leaving tray 1, are estimated. Subsequently, gas phase fugacities are calculated by means of the Soave-Redlich-Kwong equation of state [15]. The absorption driving forces are now known. The molar fluxes J_{H_2S} and J_{CO_2} are calculated either using *analytical solutions* of the mass transfer models of Secor and Beutler [16] for H_2S and Hikita and Asai [17] for CO_2 , which do *not* account for *interaction* between the liquid phase reactions, or using the *numerical solution* method for simultaneous mass transfer and *interactive* reversible reactions, developed by Cornelisse *et al.* [13]. It must be noted that the film model solution of Secor and Beutler [16], used for the H_2S absorption rate, was modified to a penetration theory model solution according to the suggestion of Olander [18]. Details are given elsewhere [9].

After the first estimation of the gas phase concentrations and the subsequent molar flux calculations, iteration proceeds using a Newton-Raphson technique, until the following implicit flux balances are satisfied simultaneously:

$$\phi_g^2 [H_2S]_g^2 - \phi_g^1 [H_2S]_g^1 = J_{H_2S} A_{tray} \quad \text{mol s}^{-1} \quad (13)$$

and

$$\phi_g^2 [CO_2]_g^2 - \phi_g^1 [CO_2]_g^1 = J_{CO_2} A_{tray} \quad \text{mol s}^{-1} \quad (14)$$

Using mass and heat balances for tray 1, $[H_2S_{tot}]_{\ell}^2$, $[CO_2]_{\ell}^2$ and T_{ℓ}^2 are then calculated.

The tray-to-tray procedure continues until the H_2S specification is met (4 ppm vol.). If the CO_2 concentration in the treated gas deviates by more than 5% from the initially estimated value, the column calculation is repeated right from the beginning using the calculated CO_2 concentration as a new estimate.

Cascade of trickle bed absorbers

The second absorber type evaluated in this study is a cascade of trickle bed reactors (see Fig. 3). In the reactors, gas and liquid flow cocurrently downward over an inert packing. In this mode of operation flooding does not occur and therefore higher gas throughputs per unit cross-sectional area can be realized than in countercurrent operations.

In cocurrent flow ultimately only one equilibrium stage can be attained in each reactor. This implies that for our very deep H_2S removal several reactor beds are needed which have to be connected to provide overall countercurrent gas and liquid flows, as shown in Fig. 3. This involves the installation of additional pumps.

In the trickle bed calculation procedure each bed is regarded as a series of ideally mixed reactor sections.

Fig. 3. Scheme for the trickle bed cascade reactor.

Like in the tray-to-tray calculations, backmixing in the gas and liquid phases as well as pressure drop over the sections are neglected.

By means of mass and heat balances over the cascade of reactors, which are essentially identical with those for the tray absorber, the temperature of the rich solution leaving the reactor 1 and the total H_2S and CO_2 concentrations in it are derived.

As far as the reactor balances for H_2S and CO_2 are concerned, the procedure now proceeds slightly differently.

Flowing cocurrently in a reactor, the H_2S gas concentration will decrease and the (unreacted) H_2S liquid concentration will increase owing to the mass transfer. Ultimately, the mass transfer driving force of H_2S will be zero and only CO_2 will still be absorbed at a relatively high rate. In order to avoid this (for selectivity) extremely unfavourable situation, the calculations are stopped at a preset positive absorption driving force for H_2S . This is realized, for example, for reactor i , by calculating the unreacted H_2S concentration $[H_2S]_g^{i,n+1}$, in the liquid from temperature, total H_2S and CO_2 concentrations using the equilibrium model mentioned earlier [9, 11]. The H_2S gas phase concentration, $[H_2S]_g^{i,n+1}$, at which the reactor calculations are stopped, has been using an arbitrary but effective algorithm:

$$[H_2S]_g^{i,n+1} = f^i \frac{[H_2S]_l^{i,n+1}}{m_{H_2S}} \quad \text{mol Nm}^{-3} \quad (15)$$

where

$$m_{H_2S} = \frac{[H_2S]_l}{[H_2S]_g} \quad \text{at the interface} \quad (16)$$

and where f^i is a constant >1 which may have different values for each reactor. Condition (15) ensures a positive driving force for the H_2S absorption in each reactor section and terminates the reactor calculations when the H_2S equilibrium is approached too closely.

An initial estimation of the CO_2 gas phase concentration leaving reactor i , $[CO_2]_g^{i,n+1}$, now provides sufficient data to complete the reactor mass and heat balances and the inlet data can be obtained. Next, a section-to-section calculation proceeds until the H_2S gas phase concentration falls below the value calculated by eqn. (15). If the calculated CO_2 gas concentration deviates by more than 3% from the initial estimate the procedure is repeated using the calculated value as a new estimation. New reactors are added until the H_2S specification is met (Table 1). If the CO_2 concentration in the treated gas deviates by more than 5% from the initial estimation, the overall calculations are repeated. It will be understood that the choice of the factor f^i and the number of beds and their lengths in this cascaded reactor are interrelated. This requires a sub-optimization of the economics of this reactor type not presented here.

Regenerator

In the regenerator the H_2S and CO_2 components are stripped out of the solution at low pressure and high

temperature. Under the prevailing conditions, the absorption reactions (1) and (2) are reversed, the acid gases are entrained with the water vapour and pass overhead where the water vapour is condensed and returned to the regenerator.

The basis of the regenerator design used in this study is the method introduced by Ouwkerk [7]. Two operating regimes for the regenerator are distinguished: heat limited and stripping limited operation.

In the *heat limited regime*, the steam flowrate for the regeneration of the rich solution is entirely determined by the amount of heat required to provide the latent heat for the desorption reactions, the sensible heat difference between entering and leaving liquid flows and the reflux flow. The steam rate is described by [7]

$$\begin{aligned} \phi_{st}^{HL} = & \phi_L M_{st} \{ \alpha_{H_2S} [Am_{tot}] \Delta H_{H_2S} \\ & + \alpha_{CO_2} [Am_{tot}] \Delta H_{CO_2} + \\ & + \rho_L C_{pL} (T_L^{out} - T_L^{in}) \} / \Delta H_{st} \\ & + \phi_{reflux} \quad \text{kg s}^{-1} \end{aligned} \quad (17)$$

where

$$\phi_{reflux} = R \alpha_{tot} [Am_{tot}] \phi_L M_{st} \quad \text{kg s}^{-1} \quad (18)$$

R represents a reflux factor defined by

$$R = \frac{\text{moles of steam in regenerator off-gas}}{\text{moles of acid gas in regenerator off-gas}} \quad (19)$$

A value of $R = 1.2$ is used throughout this study [1]. Since the heats of reaction ΔH_{H_2S} and ΔH_{CO_2} are almost equal [1], eqns. (17) and (18) may be combined to give

$$\begin{aligned} \phi_{st}^{HL} = & \phi_L M_{st} \left\{ \alpha_{tot} [Am_{tot}] \left(\frac{\Delta H_r}{\Delta H_{st}} + R \right) \right. \\ & \left. + \frac{\rho_L C_{pL}}{\Delta H_{st}} (T_L^{out} - T_L^{in}) \right\} \quad \text{kg s}^{-1} \end{aligned} \quad (20)$$

In the *stripping limited regime*, regenerator operation is controlled by the minimum gas (steam) flow required to dilute the gas components at the regenerator bottom sufficiently to provide a driving force for the desorption. This minimum gas flow can be obtained from the operating line tangent to the equilibrium curve at the desired residual acid gas load α_0 (see Fig. 4) [7]:

$$\phi_{st}^{SL} = \phi_L \rho_{st} [Am_{tot}] \left. \frac{d\alpha_{H_2S}}{d[H_2S]_g} \right|_{\alpha_0} \quad \text{kg s}^{-1} \quad (21)$$

The operating line can be considered as a straight line near the regenerator bottom only where the heat needed for the desorption reactions, and hence the condensation of steam, is still negligible. At higher trays large amounts of heat are transferred to the solvent by condensation of the steam and consequently the operating line will curve upward. The solvent temperature at the regenerator bottom is assumed to be the boiling temperature of water at the prevailing pressure. Equilibrium curves are generated by the equilibrium model [9, 11] at this temperature, assuming equal amounts of H_2S and CO_2 in the lean solution. The higher value of either the heat limited or the stripping limited steam rate has to be applied.

Fig. 4. Determination of minimum steam rate in the stripping limited regime.

Sulfur recovery unit

The hydrogen sulfide in the regenerator off-gas is converted to elemental sulfur in a split-stream three-stage Claus unit (see Fig. 1). In this configuration one-third of the Claus feed gas is fed to a burner and converted with oxygen from air into SO_2 according to the exothermic reaction [19]

The larger part of this hot gas stream is cooled in a waste heat boiler to such an extent that after mixing with the unconverted main gas stream the temperature of the gas to the first catalytic converter is 230°C , the optimum inlet temperature for the first converter [2]. A small part of the hot gas stream is bypassed to reheat the feed to the second and third converters (see Fig. 1).

In the catalytic converters elemental sulfur is produced by the equilibrium reaction [19]

For reasons of simplicity, we assumed $\text{S}_x = \text{S}_8$, which is a good approximation at $T < 330^\circ\text{C}$ [19]. The conversion of H_2S in each catalytic converter is assumed to be 95% of the thermodynamic equilibrium conversion.

After each converter the gas is cooled to 155°C to condense the sulfur vapour. The removal of sulfur from the gas stream favours conversion of H_2S by the equilibrium reaction (23) in the next converter, which is entered after reheating the gas to 230°C by the bypassed hot gas.

The dimensions of the converters are derived by the relation for the required amount of catalyst either by Kohl and Riesenfeld [1] or by Fisher [20]. The most conservative of the two results is used in our calculations.

Tail-gas unit

In the tail-gas unit, based on the Shell Claus off-gas treatment (SCOT) process, SO_2 in the gas leaving the SRU is first catalytically reduced to H_2S [1]. This reaction occurs at $\sim 285^\circ\text{C}$ by means of a CO/H_2 gas

mixture obtained, for example, by partial combustion of natural gas [1, 2]:

The volume of the catalyst in the reduction reactor is estimated by the same procedure as used for the Claus converters. The gas leaving the reactor is then cooled to 155°C in a waste heat boiler in which steam is generated. After further cooling in a feed water preheater the excess water vapour in the gas is condensed in a packed cooling tower by means of circulating water. The dimensions of the tower are determined by the procedure described by Treybal [21]. The cooled gas now enters the SCOT absorber, specifications of which are calculated by means of the procedure described earlier. The H_2S specification for the absorber off-gas is set at 160 ppm vol. [22].

Heat exchange equipment

Parameters of the heat exchange equipment are not calculated in detail. Overall exchange areas are obtained by the 'e-NTU' method described by Kays and London [23] for countercurrent operations. Heat transfer coefficients of $600 \text{ W m}^{-2} ^\circ\text{C}^{-1}$ are used for liquid-liquid heat exchange, of $1500 \text{ W m}^{-2} ^\circ\text{C}^{-1}$ for exchangers involving condensing or evaporating media and of $300 \text{ W m}^{-2} ^\circ\text{C}^{-1}$ for condensing vapours containing non-condensable gases.

Physico-chemical data

A large amount of physico-chemical data is used in the absorber calculation procedures. In this section sources of data and pressure/temperature dependences will be summarized briefly.

The liquid phase

The composition of the liquid phase at each tray or section is calculated by the equilibrium model of Blauwhoff and van Swaaij [11]. Equilibrium constants and Henry's coefficients for this model as a function of temperature are obtained from Edwards *et al.* [24], Blauwhoff and Bos [12], Schwabe *et al.* [25] and Blauwhoff [9]. Pressure corrections for Henry's coefficients are taken from Edwards *et al.* [24].

Rate constants for the CO_2 -amine reactions are obtained from Danckwerts and Sharma [14], Blauwhoff *et al.* [10] and Blauwhoff [9]. Heats of reaction are summarized by Kohl and Riesenfeld [1].

The liquid phase viscosities for aqueous DIPA and MDEA solutions were measured by Blauwhoff [9]. The simple Andrade correlation is used for extrapolation to higher temperatures [26]. Pressure dependence of the viscosity is considered to be negligible in the relevant pressure range [26].

The diffusivities of H_2S , CO_2 and DIPA in aqueous solutions are correlated with the liquid viscosities and temperatures by a modified Stokes-Einstein relation [26]:

$$\frac{D\eta^{2/3}}{T} = \text{constant} \quad (25)$$

The diffusivities in pure water serve as a basis for this correlation [14, 27]. The diffusivities of the ionic species in the solution and of MDEA are assumed to be equal to the diffusivity of DIPA [14]. Properties not mentioned explicitly are taken to be the same as for water under the prevailing conditions.

The gas phase

The gas phase is described by the Soave modification of the Redlich–Kwong equation of state [15]. Constants and critical properties for this equation can be found in Reid *et al.* [26]. Gas phase diffusivities are calculated by the Chapman–Enskog relation [26] and are assumed to be inversely proportional to the operating pressure.

The mass transfer parameters

High pressure mass transfer coefficient and interfacial area correlations for tray and trickle bed absorbers are not available in the open literature. Therefore we used correlations on the dependence of the mass transfer coefficients on the hydrodynamic conditions, derived at atmospheric pressures, and extrapolated to higher pressures. For the tray absorber calculations we employed the sieve tray correlations of Sharma and Gupta [28] as a basis for the influence of v_L , v_g , ρ_L , ρ_g and HeCO_2 on $k_L a$ and $k_g a$:

$$k_L a = c_1 (v_L \rho_L)^{0.6} v_g^{1.2} \quad \text{s}^{-1} \quad (26)$$

and

$$k_g a = c_2 (v_L \rho_L)^{0.6} v_g^{1.2} \text{HeCO}_2 \quad \text{s}^{-1} \quad (27)$$

where $c_1 = 4.9 \times 10^{-7} \text{ s}^{0.8} \text{ kg}^{-0.6}$ and $c_2 = 1.0 \times 10^{-6} \text{ m}^3 \text{ bar s}^{0.8} \text{ kg}^{-0.6} \text{ mol}^{-1}$ at 70 bar and $c_1 = 5.5 \times 10^{-8} \text{ s}^{0.8} \text{ kg}^{-0.6}$ and $c_2 = 1.1 \times 10^{-7} \text{ m}^3 \text{ bar s}^{0.8} \text{ kg}^{-0.6} \text{ mol}^{-1}$ at low pressures respectively.

The gas–liquid interfacial area per m^2 tray is calculated with the correlation of Nonhebel [29] for sieve trays:

$$a'' = 30 (\rho_g v_g)^{0.5} \rho_g^{0.25} \quad \text{m}^2 (\text{m}^2 \text{ tray})^{-1} \quad (28)$$

By combination of eqns. (26), (27) and (28) and assuming an average froth height of 0.3 m, values of the mass transfer coefficients k_L and k_g are obtained. We are aware that using different sources for the derivation of k_L and k_g may lead to erroneous values for these parameters. In fact, we adjusted the values of c_1 and c_2 in eqns. (26) and (27), as compared with the original values [28], in order to obtain realistic values for k_g and k_L in the relevant pressure ranges while maintaining their dependence on the hydrodynamic conditions.

In the calculation procedure for the cascade of trickle bed reactors the correlations of Fukushima and Kusaka [30–32] for k_L and k_g in the pulsing flow regime are incorporated:

$$k_L = 5 \times 10^2 \phi^{0.33} \text{Re}_L^{0.33} \text{Re}_g^{0.20} \text{Sc}_g^{0.5} \times \left(\frac{d_p}{d_c} \right)^{2.2} \frac{D_{\text{CO}_2}^g}{d_p} \quad \text{m s}^{-1} \quad (29)$$

and

$$k_g = 8.0 \times 10^2 \phi^{-0.4} \text{Re}_g^{0.4} \text{Sc}_g^{0.5} \times \left(\frac{d_p}{d_c} \right)^{2.3} \frac{D_{\text{CO}_2}^g}{d_p} \quad \text{m s}^{-1} \quad (30)$$

Since we considered the influence of the ratio d_p/d_c on k_L and k_g to be unrealistically high, we replaced this ratio by a fixed value of 0.075 in our calculations. This is a typical value for the geometries used by Fukushima and Kusaka [30–32].

For the interfacial area we have chosen a conservative value of 200 m^2 per m^3 of reactor for all trickle bed calculations. This value corresponds to the geometric packing area of 1 inch Raschig rings.

The mass transfer coefficients are converted to the operating pressures and temperatures by assuming a penetration theory dependence of k_L and k_g on the diffusivity:

$$k_{L/g}^P T = k_{L/g}^* \sqrt{D^P T / D^*} \quad \text{m s}^{-1} \quad (31)$$

where D^* refers to the diffusion coefficient under the conditions at which the mass transfer coefficient relations (26)–(30) were obtained. The interfacial areas were assumed to be independent of pressure [33] and temperature.

Results of the High Pressure Tray Absorber Calculations

Comparison of the non-interactive and interactive mass transfer models

A set of calculations for the high pressure tray absorber model was carried out in order to compare the results for the analytical non-interactive and numerical interactive solutions of the mass transfer model. In the analytical solution the H_2S and CO_2 liquid phase reactions are regarded as non-interacting and hence the mass transfer rates of H_2S and CO_2 are independent of each other. The numerical solution method, however, does account for interacting reactions. Calculations were carried out using feed gas composition I (see Table 1) and two amine solutions of 2.0 M DIPA and 2.0 M MDEA at absorber conditions as specified in Table 2, in order to compare both methods. The tray-to-tray gas phase compositions calculated by both methods are shown in Figs. 5 and 6 for DIPA and MDEA respectively. The difference between the results obtained by the two methods is only marginal. The maximum deviation of 13% in the CO_2 concentration in the treated gas is found when using DIPA.

A comparison of the two methods of calculation can be illustrated more clearly on the basis of the overall mass transfer resistances for H_2S and CO_2 , as defined by

$$R_i^{\text{ov}} = R_i^g + R_i^L = \frac{[C]_g - [C]_L / m_i}{J_i} = \frac{1}{k_{\text{ov}}} = \frac{1}{k_{g,i}} + \frac{1}{m_i k_{L,i} E_i} \quad \text{s m}^{-1} \quad (32)$$

TABLE 2. Standard design parameters and operating conditions for the high pressure tray absorber

General	P	70 bar
	$[Am_{tot}]$	2 kmol m^{-3}
Gas in:	ϕ_g^1	$55.56 \text{ Nm}^3 \text{ s}^{-1}$ ($= 200\,000 \text{ Nm}^3 \text{ h}^{-1}$)
	T_g^1	293 K
Gas out:	$y_{H_2S}^{n+1}$	4 ppm vol.
Liquid in:	T_L^{n+1}	313 K
DIPA:	$[H_2S_{tot}]_L^{n+1}$	20 mol m^{-3}
	$[CO_{2,tot}]_L^{n+1}$	20 mol m^{-3}
MDEA:	$[H_2S_{tot}]_L^{n+1}$	10 mol m^{-3}
	$[CO_{2,tot}]_L^{n+1}$	10 mol m^{-3}
Liquid out:	α_{tot}^1	0.7

in which

$$m_i = \frac{[C_i]_l}{[C_i]_g} \bigg|_{\text{at interface}} \quad (16)$$

E_i is the enhancement factor obtained from the analytical and numerical mass transfer model respectively. The calculated overall resistances are shown in Figs. 7 for DIPA and 8 for MDEA, together with the temperature profile. On the first few trays in the bottom section, both the H_2S and CO_2 driving forces for the absorption are high. On the other hand the solution is loaded with acid gases, so that the concentration of unreacted amine, the alkaline liquid phase reactant, is low. These two factors cause the amine transport from the liquid bulk into the reaction zone near the gas-liquid interface to be controlled by diffusion, so that the amine is depleted in the reaction zone. Owing to this depletion H_2S has to diffuse into the liquid phase before it can react with amine. Consequently, the H_2S transport

Fig. 5. Comparison of tray-to-tray gas phase compositions for the interactive and non-interactive mass transfer models (DIPA, feed gas I).

Fig. 6. Comparison of tray-to-tray gas phase compositions for the interactive and non-interactive mass transfer models (MDEA, feed gas I).

Fig. 7. Comparison of overall mass transfer resistances for the interactive and non-interactive mass transfer models (DIPA, feed gas I).

is partially liquid phase limited at the bottom trays both for DIPA and MDEA.

Higher up in the column, the H_2S gas phase concentration along with its driving force falls rapidly (see Figs. 5 and 6). The unreacted amine concentration increases upwards to the absorber top. This results in an increasing H_2S enhancement factor E_{H_2S} , so that the overall mass transfer resistance $R_{H_2S}^{ov}$ drops according to eqn. (32). Finally, at very large values of E_{H_2S} , the overall mass transfer resistance approaches the limit of

Fig. 8. Comparison of overall mass transfer resistances for the interactive and non-interactive mass transfer models (MDEA, feed gas I).

complete gas phase resistance indicated by the lines drawn in Figs. 7 and 8. Generally speaking, the H_2S mass transfer in the high pressure absorber can be considered to be gas phase controlled on a column scale.

Both model calculations agree well for H_2S in the regime where distinctions—if present—would have been expected, i.e. in the partially liquid phase limited mass transfer regime at the absorber bottom. The H_2S mass transfer is obviously entirely determined by the diffusion rate of amine and therefore independent of the model used. In the gas phase limited regime (tray > 8), of course, no distinction between the models is observed. Only at the top of the column the H_2S overall mass transfer resistance calculated by the numerical method slightly increases. This effect is due to a decrease of the H_2S enhancement factor, caused by the relatively high CO_2 molar flux.

For the CO_2 mass transfer resistance profiles the situation is different. In general the CO_2 absorption rate is almost exclusively liquid phase limited ($R_{CO_2}^{ov} > 0.8R_{CO_2}^{ov}$ for DIPA and $R_{CO_2}^{ov} > 0.9R_{CO_2}^{ov}$ for MDEA). As for H_2S , the two methods of solution agree well and only minor distinctions can be observed.

At the bottom tray the amine depletion is extreme and therefore the CO_2 overall mass transfer resistances are highest here. At higher trays the depletion decreases and the resistances fall steadily. With the analytical method a local minimum value of $R_{CO_2}^{ov}$ is observed at tray 2. This is caused by the high liquid phase temperatures (see Figs. 7 and 8) and the correspondingly high

CO_2 -amine rate of reaction. Obviously this is levelled out in the results obtained by the numerical method as caused by the H_2S co-absorption.

At first sight, it is surprising that the analytical mass transfer methods of calculation, which do not account for the interaction of the liquid phase reactions, agree so well with the more sophisticated numerical method. This can be understood, however, by realizing that at the column bottom the molar fluxes of H_2S and CO_2 are high, so that the mass transfer rates are determined only by the diffusion limitation of the amine and therefore are independent of the rates of the interacting reactions. In the upper part of the column the H_2S mass transfer rate is exclusively gas phase limited and, therefore, independent of the model chosen for the liquid phase, whereas the CO_2 absorption rate is not influenced at all by the simultaneous H_2S absorption due to the low H_2S molar fluxes. Because of the good agreement between the two methods, wherever possible, we thenceforward used the analytical method which consumed the least computer time.

Influence of design and operating variables on the absorber performance

Extensive calculations on the high pressure tray absorber were carried out in order to determine the influence of a number of design and operating parameters on the overall absorber performance. Two parameters are used to characterize this performance: firstly, the overall absorber selectivity defined by

$$\begin{aligned} \eta &= \frac{\text{moles } H_2S \text{ absorbed}}{\text{moles } H_2S + CO_2 \text{ absorbed}} \\ &= \frac{\alpha_{H_2S}^{out} - \alpha_{H_2S}^{in}}{\alpha_{H_2S}^{out} - \alpha_{H_2S}^{in} + \alpha_{CO_2}^{out} - \alpha_{CO_2}^{in}} \left(\approx \frac{\alpha_{H_2S}^{out}}{\alpha_{H_2S}^{out} + \alpha_{CO_2}^{out}} \right) \\ &= \frac{\phi_g^{in} y_{H_2S}^{in} - \phi_g^{out} y_{H_2S}^{out}}{\phi_g^{in} (y_{H_2S}^{in} + y_{CO_2}^{in}) - \phi_g^{out} (y_{H_2S}^{out} + y_{CO_2}^{out})} \end{aligned} \quad (33)$$

and, secondly, the solvent flowrate ϕ_0 .

The first parameter η equals in fact the fraction H_2S in the regenerator off-gases and therefore virtually controls the dimensions of the process equipment linked to the regenerator in the SRU and the TGU. Low values of η result in low H_2S and high inert CO_2 concentrations in the SRU feed gas and have a detrimental effect on the dimensions of SRU and TGU. The minimum value of η is obtained when all acid gases are totally absorbed and is solely determined by the ARU feed gas composition:

$$\eta_{min} = \frac{y_{H_2S}^{in}}{y_{H_2S}^{in} + y_{CO_2}^{in}} \quad (34)$$

The values for η_{min} are 0.50 and 0.333 for gas compositions I and II respectively (see Table 1). The maximum value of the selectivity on the other hand is unity, if no CO_2 is absorbed at all.

The lower the selectivity the more CO_2 is co-absorbed and the more steam is wasted for the CO_2 desorption in the regenerator. Thus the incentive for improving the absorption process increases rapidly with decreasing η .

The second parameter ϕ_L at a constant acid gas loading α_{tot} controls directly the amount of steam required for the regeneration of the rich solution, as can be seen from the eqns. (20) and (21). As steam costs are the major item in the operating costs for gas treatment, we must reduce the solvent rate as far as possible.

In the Figures to this section these two parameters η and ϕ_L together with CO_2 concentration in the treated gas and the number of trays required for the H_2S specification, are plotted as a function of the most important design and operating parameters. The design conditions are summarized in Table 2.

Operating pressure of the tray absorber

The operating pressure of the tray absorber affects a number of parameters. By increasing the pressure the driving forces for the H_2S and CO_2 absorption become approximately proportionally larger, whereas the mass transfer coefficients and interfacial areas decrease owing to the lower volumetric gas throughput (see eqns. (26)–(28)). Moreover, the gas phase diffusivities decrease and hence the gas phase mass transfer coefficients will also decrease (see eqn. (31)). The overall influence of the operating pressure on the absorber performance is shown in Fig. 9 for the feed gas compositions I and II and for DIPA and MDEA solutions. In general it may be concluded that the pressure does not affect the absorber performance. For the DIPA solutions the selectivities for the gas compositions I and II are close to the corresponding minimum values 0.50 for gas I and 0.33 for gas II, as is also indicated by the low CO_2 concentration in the treated gas. By using MDEA solutions the absorber operation is only marginally more selective (11%–14%)

Fig. 9. The influence of the operating pressure on the tray absorber performance.

and the solvent flowrate at constant α_{tot} can correspondingly be reduced.

The regenerator effectiveness—the acid gas loading of the lean solvent, α_{tot}^{in}

For reasons of simplicity, we assumed the lean solvent in the regenerator bottom to contain equal quantities of H_2S and CO_2 :

$$\alpha_{tot} = \alpha_{H_2S} + \alpha_{CO_2} \quad (35)$$

where

$$\alpha_{H_2S} = \alpha_{CO_2} \quad \text{or} \quad [H_2S_{tot}]_L = [CO_2_{tot}]_L \quad (36)$$

The results of the calculations at varying acid gas loadings of the lean solvent are summarized in Fig. 10.

Fig. 10. The influence of the acid gas loading of lean solvent on tray absorber performance.

An increase of the acid gas loading is detrimental to the driving force for H_2S absorption at the top of the column, whereas the CO_2 driving force is hardly affected. To meet the H_2S specification more trays are needed and therefore the CO_2 co-absorption also increases. As a result the selectivity decreases and the solvent flow increases. For DIPA solutions these effects are less marked since the absorbers already operate close to minimum selectivity and maximum solvent flow. For MDEA, however, the effects are quite pronounced and these solutions, therefore, should generally be regenerated to lower acid gas loadings. The optimum α_{tot} follows from an optimization of the steam consumption in the regenerator. This latter subject will be discussed later.

Acid gas loading of the rich solution, α_{tot}^1

The acid gas loading of the rich solution is a very important parameter in the absorber operation. Results are shown in Fig. 11. An increase of the α_{tot}^1 results in a reduction of solvent rate ϕ_g without affecting the process selectivity. The approximately constant CO_2 concentration in the treated gas, $y_{CO_2}^{n+1}$, implies that the total acid gas pick-up by the solvents is constant at varying α_{tot}^1 . If the acid balance over the absorber (7) is rewritten in the form

$$\begin{aligned} \phi_g [Am_{tot}] (\alpha_{tot}^1 - \alpha_{tot}^{n+1}) \\ = \phi_g^1 \{ [H_2S]_g^1 + [CO_2]_g^1 \} \\ - \phi_g^{n+1} \{ [H_2S]_g^{n+1} + [CO_2]_g^{n+1} \} \quad \text{mol s}^{-1} \quad (37) \end{aligned}$$

and as the right-hand side of this equation appears to be constant, relation (37) can be simplified to

$$\begin{aligned} \phi_g [Am_{tot}] (\alpha_{tot}^1 - \alpha_{tot}^{n+1}) &\cong \phi_g [Am_{tot}] \alpha_{tot}^1 \\ &= \text{constant} \quad (38) \end{aligned}$$

This equation relates α_{tot}^1 directly to the solvent rate. The constant in eqn. (38) is obtained from the results of the absorber calculations and is summarized in Table 3 for all four gas-solvent combinations.

In heat limited regenerator operation, the reduction of steam consumption by increasing α_{tot}^1 will generally be rather low. This is caused by the fact that, although the solvent flow is reduced, the product $\phi_g \alpha_{tot}^1$ is fixed (see eqn. (38)) and hence the amount of steam required to provide for the heats of reaction and the reflux is

Fig. 11. The influence of the acid gas loading of rich solvent on tray absorber performance.

TABLE 3. Values of the constants in kmol s^{-1} in eqn. (38)

	Solvent	
	DIPA	MDEA
Gas I	0.352	0.315
Gas II	0.374	0.326

also almost fixed (see eqn. (20)). In this heat limited regime of the regenerator operation, the reduction of steam consumption will therefore only originate from the smaller amount of sensible heat to be supplied to the solvent.

In the stripping limited regime the steam consumption is proportional to the solvent flowrate only (see eqn. (21)) and hence inversely proportional to α_{tot}^1 at constant $[Am_{tot}]$. An increase of α_{tot}^1 in this regime is far more effective in reducing the steam consumption than it is in the heat limited regime.

Though not shown explicitly in Fig. 11, there exists a maximum limit of the acid gas loading for given operating conditions. This maximum is determined by operation of the bottom trays of the absorber. With increasing gas loading α_{tot}^1 , the liquid phase temperature at the bottom trays rapidly rises. The combined result of increased loading and rising temperatures causes the unreacted H_2S concentration to be higher and reduces the H_2S absorption driving force. The maximum acid gas loading is obtained if the driving force at one of the bottom trays becomes zero and a pinch between equilibrium and operating lines of the absorber results. This phenomenon is not bound to occur at the first tray, because its temperature is usually appreciably lower, owing to the introduction of the cold feed gas, than the temperatures of 2nd and 3rd trays (see Figs. 7 and 8). For our specific calculations the maximum acid gas loading will be around $\alpha_{tot}^1 \cong 0.85$.

Total amine concentration $[Am_{tot}]$

The total amine concentration is a parameter with a most complicated influence on the absorber operation. In Fig. 12 results are shown for varying amine concentrations. The influence of the amine concentration is roughly twofold. Firstly, increasing $[Am_{tot}]$ proportionally decreases the solvent flow, identically to the effect of the acid gas loading of the rich solution. Since the CO_2 concentration in the treated gas is almost constant, eqn. (38) and the constants summarized in Table 3 can be used for correlating the solvent flow and the amine concentration. With respect to the reduction of the steam rate in the regenerator as affected by lower solvent rates the same remarks as were made for the influence of α_{tot}^1 are valid. Secondly, with increasing amine concentration the solvent flow and therewith its capacity for heat absorption are reduced; consequently, the temperature profiles over the column become more pronounced. This is clearly demonstrated in Fig. 13 for three MDEA solutions and for gas I. With increasing MDEA concentration the absorber temperature level

Fig. 12. The influence of the amine concentration on tray absorber performance.

Fig. 13. The influence of MDEA concentration on temperature profiles in the tray absorber.

risers and the maximum shifts to higher trays. This change of temperature profiles affects the liquid phase equilibria and thus the absorption driving forces. In Fig. 14, gas phase and unreacted liquid phase concentration $[H_2S]_g$ and $[H_2S]_l/m_{H_2S}$, respectively, are plotted as a function of the tray number for the MDEA concentrations. The difference between the gas and liquid phase profiles represents the H_2S absorption driving force. Be aware of the logarithmic scale for the concentration. With increasing MDEA concentration $[H_2S]_l/m_{H_2S}$ increases and the absorption driving forces,

Fig. 14. H_2S concentrations in the gas phase and unreacted in the liquid phase as a function of the tray number and the MDEA concentration ($\alpha_{tot}^{out} = 0.7$).

particularly in the absorber bottom, are reduced. Consequently, the H_2S molar fluxes are reduced and additional trays are required to meet the H_2S specification.

The CO_2 concentration profiles show a more significant sensitivity towards the temperature or MDEA concentration (see Fig. 15). As a result the CO_2 liquid concentration, $[CO_2]_l/m_{CO_2}$, rapidly increases with the MDEA molarity in the lower part of the absorber. For the 3.2 M MDEA solution this concentration even exceeds the gas phase concentration at trays 2, 3 and 4, resulting in a desorption of CO_2 and increasing CO_2 gas concentrations. Unfortunately, this selectivity favouring effect is almost completely nullified by the larger CO_2 driving forces at higher trays and the extra trays required for the H_2S specification. Similar results are obtained for DIPA solutions.

Fig. 15. CO_2 concentrations in the gas phase and unreacted in the liquid phase as a function of the tray number and the MDEA concentration ($\alpha_{tot}^{out} = 0.7$).

With an increase of the amine concentration at a fixed acid gas loading α_{tot}^1 , unreacted H_2S and CO_2 liquid phase concentrations rise rapidly and reduce, in particular, the absorption driving forces at the absorber bottom, as has been shown already for MDEA (see Figs. 14 and 15). The increase of amine concentrations is limited to the point where the absorption driving force for H_2S at the absorber bottom is reduced to zero and where a pinch between equilibrium and operating lines is developed. This limit is attained for $\alpha_{\text{tot}}^1 = 0.7$ at ~ 3 M DIPA and ~ 3.5 M MDEA molarities both for gas I and II.

General Remarks

From the results discussed it is evident that the three parameters $\alpha_{\text{tot}}^{n+1}$, α_{tot}^1 and $[\text{Am}_{\text{tot}}]$ affect the solvent flowrate and only $\alpha_{\text{tot}}^{n+1}$ influences the selectivity. Although not every reduction of the solvent rate results in a proportional decrease of the steam rate, it is in general favourable to reduce the solvent rate as far as possible. This is realized by operating at the highest possible acid loadings in the rich solution and amine concentrations and at the lowest possible gas loadings in the lean solution. Whether the latter is feasible can be judged only on the basis of an overall evaluation of the economics.

The, commonly referred to as selective, tertiary amine MDEA in general is some 10%–15% more selective and requires corresponding lower solvent rates than DIPA under our process conditions. High pressure tray absorbers using MDEA solutions still operate fairly close to the minimum theoretical selectivity. A closer look at our results shows that the enhancement factor for the CO_2 -aqueous MDEA absorption is rather close to unity—typically $1.1 < E_{\text{CO}_2} < 1.3$. This implies that the CO_2 mass transfer rate is controlled by the liquid phase mass transfer coefficient and the absorption driving force only and can be expressed by

$$J_{\text{CO}_2} \cong k_{\text{L}} \left([\text{CO}_2]_{\text{g}} - \frac{[\text{CO}_2]_{\text{L}}}{m_{\text{CO}_2}} \right) \quad \text{mol m}^{-2} \text{ s}^{-1} \quad (39)$$

On the other hand, the H_2S mass transfer rate is gas phase limited in the larger part of the absorber and is thus described by

$$J_{\text{H}_2\text{S}} = k_{\text{g}} \left([\text{H}_2\text{S}]_{\text{g}} - \frac{[\text{H}_2\text{S}]_{\text{L}}}{m_{\text{H}_2\text{S}}} \right) \quad \text{mol m}^{-2} \text{ s}^{-1} \quad (40)$$

Since the absorber selectivity is directly related to the ratio of $J_{\text{H}_2\text{S}}$ to J_{CO_2} , the selectivity for MDEA can obviously be improved by increasing the ratio of the H_2S and CO_2 driving forces and the ratio $k_{\text{g}}/k_{\text{L}}$. The first ratio may be improved by the application of different amines which almost do not react with CO_2 , resulting in high $[\text{CO}_2]_{\text{L}}$ values. Further improvement in this respect may be obtained by the use of solvents which affect the solubilities $m_{\text{H}_2\text{S}}$ and m_{CO_2} .

In this study we focused our attention on the second ratio, $k_{\text{g}}/k_{\text{L}}$. Using tray columns this ratio is typically around 50 at atmospheric pressure and around 6 at 70

bar. From the aspect of this $k_{\text{g}}/k_{\text{L}}$ ratio, tray absorbers perform worse than almost any other type of gas–liquid reactor. Therefore we compared the tray absorber with a cascade of trickle bed reactors. The $k_{\text{g}}/k_{\text{L}}$ ratio for this type of absorber is typically around 80 at atmospheric pressure and around 10 at 70 bar and leaves room for further optimization owing to the absence of flooding phenomena. This improvement in the $k_{\text{g}}/k_{\text{L}}$ ratio, however, may be partially offset by the fact that in each reactor H_2S equilibrium is approached, which is undesirable from the point of view of selectivity.

Comparison between the Tray Absorber and a Cascade of Cocurrent Trickle Bed Reactors

The performances of the tray absorber and cocurrent trickle bed cascades are compared under the standard conditions given in Tables 2 and 4, respectively. The results of the calculations are summarized in Table 5 for two gas compositions and for both DIPA and MDEA solutions.

In all situations the trickle bed cascades perform better—in terms of selectivity and solvent rates—than their tray absorber counterparts. The solvent rates can be reduced by around 6%–8.5% for DIPA and around 9%–18% for MDEA solutions owing to the improved H_2S selectivities. Moreover, the absorber diameters required are much smaller, which is an advantage in the plant economics.

TABLE 4. Standard design parameters and operating conditions for the trickle bed cascade reactor

General:	P [Am _{tot}]	70 bar 2 kmol m ⁻³
Gas in:	ϕ_{g}^1 T_{g}^1	55.56 Nm ⁻³ s ⁻¹ (= 200 000 Nm ³ h ⁻¹) 293 K
Gas out:	$y_{\text{H}_2\text{S}}^{n+1}$	4 ppm vol.
Liquid in:	T_{L}^{n+1}	313 K
DIPA:	$[\text{H}_2\text{S}_{\text{tot}}]_{\text{L}}^{n+1}$ $[\text{CO}_2]_{\text{tot}}]_{\text{L}}^{n+1}$	20 mol m ⁻³ 20 mol m ⁻³
MDEA:	$[\text{H}_2\text{S}_{\text{tot}}]_{\text{L}}^{n+1}$ $[\text{CO}_2]_{\text{tot}}]_{\text{L}}^{n+1}$	10 mol m ⁻³ 10 mol m ⁻³
	ν_{L}	0.1 m s ⁻¹
Liquid out:	α_{tot}^1	0.7

The difference in the absorption characteristics between the tray and cocurrent trickle bed absorbers is illustrated on the basis of gas concentration and mass transfer resistance profiles which are plotted as a function of the cumulative interfacial area in Figs. 16, 17(a) and 17(b) respectively. Owing to higher mass transfer coefficients and hence lower mass transfer resistances the gas–liquid interfacial areas required to bring the gas on H_2S specification in the trickle bed reactors are reduced to less than half of the area needed in the tray absorber (see Fig. 16). The higher $k_{\text{g}}/k_{\text{L}}$ ratios

TABLE 5. Comparison of dimensions and performance of tray absorbers

Gas composition	I				II			
Amine	DIPA		MDEA		DIPA		MDEA	
Reactor type	Tray	Trickle	Tray	Trickle	Tray	Trickle	Tray	Trickle
Absorber diameter (m)	3.45	1.75	3.34	1.62	3.55	1.75	3.40	1.56
Number of trays, sections	22	5	22	5	22	6	23	6
Absorber length (m)	19	17	19	17.5	19	19	19.5	21
Total interfacial area (m ²)	6400	3050	6120	2890	6600	3100	6550	4000
Selectivity η	0.511	0.547	0.568	0.637	0.346	0.383	0.393	0.486
Solvent flow ϕ_Q (m ³ s ⁻¹)	0.250	0.236	0.225	0.205	0.265	0.243	0.234	0.192
$y_{CO_2}^{out}$ (%)	0.30	1.21	1.68	3.01	0.53	1.96	2.29	4.71
$\phi_Q, trickle/\phi_Q, tray$	0.944		0.911		0.917		0.821	
$\eta_{trickle}/\eta_{tray}$	1.070		1.121		1.107		1.237

Fig. 16. Gas concentration profiles as a function of the cumulative interfacial area in tray and trickle bed absorbers (DIPA and MDEA, gas I).

realized in the trickle beds result in an improvement of the ratio of mass transfer resistances $R_{CO_2}^{ov}/R_{H_2S}^{ov}$, which forms virtually the basis of the higher selectivity obtained in the cascade of trickle bed reactors (see Figs. 17(a) and (b)).

The influence of the design and operating parameters P , α_{tot}^{in} , α_{tot}^{out} , and $[Am_{tot}]$ on the trickle bed absorber performance is roughly identical to that for the tray absorber set-up. However, in the design of cascades of trickle bed absorbers additional degrees of freedom are available, i.e. the superficial gas and liquid velocities, the packing size and the equilibrium approach factor f^i used in eqn. (15). The first three degrees of freedom can be used to optimize the k_g/k_Q ratio even more. This ratio can be derived from eqns. (29) and (30) and predicts the following proportionality after elimination of d_c :

$$k_g/k_Q \cong v_Q^{-0.33} v_g^{0.15} d_p^{-0.03} \quad (41)$$

Since in our set-up the total amounts of liquid and gas pass through all reactors, v_Q and v_g are directly proportional to each other by the overall mass balance eqn. (7), so that virtually only one really effective parameter remains:

$$k_g/k_Q \cong v_Q^{-0.18} \quad \text{or} \quad \cong v_g^{-0.18} \quad (42)$$

According to eqn. (42), a superficial velocity which is as low as possible is required in order to obtain a high k_g/k_Q ratio and hence a high selectivity. This inevitably leads to larger trickle bed diameters and hence to larger investments. An economic optimization is needed to determine the optimum design and operating conditions as far as the k_g/k_Q ratio is concerned.

In fact, v_Q and v_g are only directly coupled in the first reactor where the feed gas enters and the rich solution leaves the cascade at a preset acid gas loading α_{tot}^{out} (see Fig. 3). This implies that the effective superficial liquid velocities in the following reactors (2 to n) may be

Fig. 17(a). Overall mass transfer resistance profiles as a function of the cumulative interfacial area in tray and trickle bed absorbers (DIPA and MDEA, gas I).

Fig. 17(b). Ratios of overall mass transfer resistances $R_{CO_2}^{OV}/R_{H_2S}^{OV}$ as a function of the cumulative interfacial areas in tray and trickle bed absorbers (DIPA and MDEA, gas I).

reduced. This will result in an increased k_g/k_L ratio for these reactors and in a reduced CO_2 removal per reactor as well. Again an evaluation of the economics will yield the optimum superficial liquid velocities for each reactor.

The last degree of freedom mentioned above, the equilibrium approach factor f^i , hardly affects the selectivity of the operation, but largely controls the layout of the cascade. The optimum values of f^i for each reactor bed can be determined by an evaluation of the economics and will probably result in a set of beds of equal lengths.

Results and Discussion of Regenerator Calculations

The regenerator operation is illustrated for the regeneration of the rich DIPA solution after absorption, as summarized in Table 5, column 1. Some results are shown in Fig. 18. In this Figure, two sets of lines can be distinguished: the set of horizontal lines (HL) describes the heat limited operation of the regenerator according to eqn. (17). It can be seen that the heat transfer in the lean/rich exchanger or the temperature difference between the leaving and entering liquid flows (temperature approach) has a substantial effect on the amount of heat limited steam required. The lower this temperature difference the lower the amount of steam required, but at the same time the investment in the lean/rich exchanger increases.

The second set of lines (SL) represents the amount of stripping limited steam required as calculated from eqn. (21). As mentioned before, the amount of steam required for the regeneration of the rich solution is the higher of either the stripping or the heat limited steam rate. For example, at a regenerator pressure of 1.5 bar and with a temperature approach of 8 °C, the regenerator operates in the heat limited regime, if we want to achieve residual acid gas loadings of around 22 mol m^{-3} and higher. However, if a steeper reduction of this residual acid gas

Fig. 18. Steam consumption curves for the regeneration of a rich 2.0 M DIPA solution ($\alpha_{tot}^{out} = 0.7$, $\phi_Q = 0.25 m^3 s^{-1}$).

loading is desired, the steam rate is determined by the stripping limited curve at 1.5 bar.

If, for example, a residual loading of around 15 mol m^{-3} is required, under the above conditions (1.5 bar and $\Delta T = 8$ °C) around 105 kg of steam per m^3 of solvent is required. However, by increasing the pressure in the regenerator to around 2.5 bar, the operation obviously becomes heat limited again and only around 74 kg of steam per m^3 of solvent is needed!

Since the regenerator operates at the boiling temperature of water at the prevailing pressure, the higher temperature at 2.5 bar (401 K) as compared with that at 1.5 bar (385 K) provides a substantially increased shift in the equilibria of the desorption reactions (1) and (2). This shift produces more free, now unreacted H_2S and CO_2 in the solution and increases the desorption driving forces, even though the operating pressure is higher, *i.e.* the temperature effect on the equilibria overrides the pressure effect on the gas phase concentrations. In all our following calculations we used this effect and increased the regenerator pressures in order to reduce the steam rate to the heat limited minimum.

Economical Consequences for Sour Natural Gas Treatment

Introduction

In this section, the eight absorber–solvent–gas combinations, which have been compared with respect to their technical performance in Table 5, are evaluated with respect to the economics.

This necessitates an analysis of the economics, not for the absorbers alone, but for the entire gas treatment plant including the absorber–regenerator unit (ARU), the sulfur recovery unit (SRU) and the tail-gas unit (TGU).

The evaluation of the economics requires an estimate of the investments in process equipment and working

capital and the manufacturing costs per unit product treated. The above will be dealt with for a treatment plant to be situated in The Netherlands with an operating time efficiency (OTE) of 90%.

Estimate of investments in process equipment

To estimate the investments in chemical process equipment and plants several methods are available in the literature. The degree of accuracy of these methods depends by and large on the amount and reliability of the information on plant design. Three categories of methods of estimation may be distinguished:

- order-of-magnitude estimates (typical accuracy around 40% of investment) applied when only limited information on the process is available;
- study-type estimates, based on process flowsheets and global design data of the main process equipment (typical accuracy around 25%); and
- detailed estimates, based on detailed engineering (typical accuracy around 5%–10%).

In this study we are clearly confined to study-type methods of estimation. All methods in this category are based on the approach described by Lang [34]: the investment in a chemical plant is assumed to be the product of the equipment cost and a so-called Lang factor, which adds costs of installation, piping, instrumentation, plant construction, *etc.*:

$$\text{Investment} = \text{Lang factor} \times \text{equipment costs} \quad (43)$$

An estimate of total investment is thus divided into the derivation of a Lang factor and an estimate of the equipment costs.

The Lang factor

Several authors derive Lang factors from cost analyses of existing chemical plants. These analyses vary between a global cost breakdown of a limited number of items [34] and more sophisticated detailed cost engineering [35].

In Table 6 we compare four sources of Lang factor (inside battery limits) for our treatment plant, consisting of some 40% pressure vessels and columns, some 40% heat exchange equipment and around 20% for pumps. The Lang factors coincide surprisingly well despite variations in basic assumptions. In this study the original Lang factor will be used adding 10% for the offsites,

as proposed by Lang. The Lang factor obtained in this way overestimates the investment in special, non-conventionally costed equipment such as the high pressure absorbers in our study.

For this type of equipment a modified approach is used.

(a) Columns and (reactor) vessels

In cost estimates of absorber/regenerator columns and (reactor) vessels the equipment is divided into the (pressure) vessel and the internals. The cost of the (pressure) vessel is generally correlated either with the vessel weight [37–39] or the vessel dimensions [35, 40]. We used a weight based correlation, given by Peters and Timmerhaus [37]. The effective cross-sectional areas of the tray absorbers and regenerators in the flow scheme are obtained from gas and liquid loads using the flooding correlation given by Treybal [21] for a 0.75 m tray spacing. These effective areas are then multiplied by a factor of 1.25 for downcomers, *etc.*, to obtain the actual areas. The column height follows from the number of trays, the 0.75 m tray spacing and a 3 m length added for gas and liquid inlets and outlets at the top and bottom of the column. The number of trays for the regenerator is set at 20 [1]. The length of the cascade of trickle bed absorbers is decided from the number of beds required to reach the H₂S specifications and the height of each bed, adding a length of 2 m per bed for inlets and outlets.

The dimensions of the flash vessel follow from the residence time of the liquid, which is set at 3 minutes in this study. For the reactor vessels the dimensions are obtained from the respective catalyst inventories. The weight of the pressure vessels is determined using the ASME standard for the calculation of the wall thickness. The weight thus obtained is multiplied by a factor of 1.2 for manholes, flanges, *etc.* The installed costs for internals are added to the vessel costs. The expenditure on sieve trays as used in the absorbers and regenerators is averaged at US \$ 1600 per unit at 3 m diameter. Correction for different diameters is taken to be proportional to the column cross-sectional area. For the trickle bed absorbers packing costs are taken at US \$ 900 per m³. An example calculation for the absorbers is given in Table 7.

(b) Other items of equipment

Heat exchange equipment costs are related to the exchange areas [35]. Correction factors are incorporated

TABLE 6. Comparison of Lang factors

	Guthrie [35]	Hirsh and Glazier [36]	Lang [34]	Peters and Timmerhaus [37]
Equipment cost	1.0	1.0	1.0	1.0
– direct plant costs excluding piping material	2.75	2.39	2.52	2.51
– piping material	0.48	0.56	0.60	0.66
– overheads	1.12	1.18	1.19	0.86
Total Lang factor (ISBL)*	4.35	4.13	4.31	4.03

*ISBL = inside battery limits.

TABLE 7. Example of investment in tray and trickle bed absorbers

Basis: tray absorber (3.45 m × 18.5 m, 22 trays) and trickle bed absorber (1.75 m × 17 m, five sections with a total packed height of 7.05 m).

	Investments in US k\$			
	Tray		Trickle bed	
1. Pressure vessel				
(a) Vessel costs [37]		463		176
2. Internals and extra pumps				
(a) Tray/packing support material	45		4	
(b) Tray/packing support labour	+ 11		+ 1	
(c) Tray/packing support costs	56	56	5	5
(d) Packing material including installation				54
(e) Extra pumps including installation				26
3. Installation				
3.1. Materials				
(a) Installation materials column 10 bar [37, 40]	125		51	
(b) Tray/packing support installation materials	+ 56		+ 5	
(c) Installation materials costs at 10 bar	181		56	
Installation materials costs at 70 bar: $2.68 \times$ item 3.1(c)		485		150
3.2. Labour				
(a) Labour in Europe (= $1.3 \times$ US at 20 \$/man-hour [40])	510		156	
(b) Overheads (80% of item 3.2(a))	+ 408		+ 125	
(c) Total labour	918	+ 918	281	+ 281
Sub-total		1922		692
4. Contingency and fees (45% of sub-total)		+ 865		+ 311
5. Total installed column costs		2787		1003

for exchanger type, the construction materials and the operating pressures [35]. The maximum exchange area is limited to 1000 m² per unit.

The capacity factor, being the product of flowrate (m³ s⁻¹) and head (bar), is representative of the costs of standard rotating equipment [37]. The high flowrate (0.25 m³ s⁻¹), high head (70 bar) booster pumps between the regenerator and the high pressure absorber do not fit in the standard manufacturing programs and have to be manufactured on request. The estimated cost, including drive and appendages, is US \$ 130 000 per set.

The working capital is calculated by:

Working capital = chemicals hold-up

$$+ 0.5 \times \text{monthly salaries} + 0.025 \times \text{investment} \quad (44)$$

Costing of the treatment operation

The cost elements in gas treatment are: raw materials, energy, labour, maintenance, miscellaneous, depreciation and capital charges.

1. *Raw materials* comprise amine costs owing to pump losses, natural gas consumption in the TGU and catalyst replacement. The amine solvent hold-ups in the ARU and the TGU are estimated at 150 m³ each (absorber 35 m³, regenerator 40 m³, flash vessel 45 m³, piping, etc., 30 m³). Monthly pump losses are taken at 10% of total inventory. Annually, around 80×10^3 kg of amine is consumed in the two units at a cost of US \$ 0.90 kg⁻¹ [1]. The natural gas consumption for the production of reducing gas is rated at US \$ 0.13 Nm⁻³. Catalyst life-

time in the SRU is reported to be 5 years [20]. For the reduction catalyst in the TGU the same lifetime is assumed. Thus an annual 20% of the catalyst inventory has to be replaced at US \$ 2200/m³ for both the Claus and the TGU catalysts. The sulfur proceeds are credited at US \$ 90/10³ kg.

2. The *energy costs* involve electricity, steam, process and cooling water expenses. The electricity costs are rated at US \$ 0.071/kW h. The treating process both consumes and produces steam in the regenerators and sulfur condensers respectively. The steam costs and proceeds are estimated at US \$ 15/10³ kg. The amount of process water used for steam make-up in the sulfur condensers is assumed to be 10% of steam consumed at a cost of US \$ 2.00/m³. The cooling water costs are US \$ 0.013/m³.

3. A total *staff* of 27 persons is assumed to involve an average salary cost of US \$ 34 000/man-year [41]. 5.5% is added for personnel charges and another 7% for tools, etc.

4. The cost of *plant maintenance* is set at 4% of the investments [37, 42, 43].

5. *Other costs* include insurances, local taxes and disposal. Insurances plus local taxes are 2% of the investments [37, 43] and waste disposal is estimated at 2% of the investments plus 2% of the costs of amine and catalyst consumed.

The plant depreciates linearly over 10 years and capital charges are taken at 15% of investment plus working capital.

Results and Discussion of Calculations

Several operating parameters in the flow schema of Fig. 1 (e.g. temperature and acid loading of the lean amine to the absorber, condensation temperature of the sulfur in the SRU) may be chosen at will within certain limits. By an overall optimization of the economics of the entire gas treatment plant, values for these operating parameters are assessed; an extensive optimization establishing all degrees of freedom is not envisaged. As an example, however, the influence of a partial economical optimization of the temperature approach of the lean, hot and rich, cold amine solutions at the regenerator outlets and inlets, respectively, is elaborated.

Optimization of the exchanger temperature approach

The parameter to be chosen freely is the temperature approach of the amine flows at the regenerator inlet and outlet. The smaller this temperature approach, the larger the amount of heat to be transferred and the smaller the average heat transfer driving force. Hence, the exchanger area becomes larger, as do the investments in the lean/rich exchanger. On the other hand, less steam is needed in the regenerator to balance the sensible heat difference between the entering and leaving streams (see eqn. (17)), so that smaller sized reboilers and regenerator columns can be installed. Obviously, an optimization of investments (exchange equipment plus regeneration) versus variable costs (steam) is at hand.

For gas I and DIPA as the solvent at absorber conditions as in Table 2 a breakdown of the costs is given in Table 8 and shown graphically in Fig. 19.

With increasing temperature approach the investment in the lean/rich exchanger decreases, as do the capital charges. On the other hand, steam consumption rises rapidly with an increasing temperature approach. The flat optimum of the total costs is found at a temperature approach of 8 °C. It must be emphasized that, in

Fig. 19. Economical optimization of the temperature of the lean/rich heat exchanger.

principle, for each absorber–solvent–gas combination in Table 5 a different optimum temperature approach can be found. Considering the relative flatness of the optimum, however, we used the value of 8 °C for all further evaluations.

Comparison of the different combinations

Eight absorber–solvent–gas combinations have been evaluated and compared with respect to the operating economics. The technical details are summarized in Table 5 and the costs breakdown is shown in Tables 9 + 10 and 11 + 12 for gas I and II respectively.

Comparison of the investments in equipment for gas I and gas II (Tables 9 and 11 respectively) leads to the conclusion that the investments in plants with trickle bed absorbers are considerably lower than in the corresponding plants with tray absorbers. These investment

TABLE 8. Breakdown of costs vs. temperature approach (DIPA, gas I)

	Temperature approach (°C)					
	4	6	8	10	12	14
1. Investments (M\$)						
(a) Lean/rich heat exchanger	8.33	5.42	3.96	3.02	2.39	1.99
(b) Regenerator	1.87	1.92	1.98	2.03	2.09	2.14
(c) Reboiler	0.41	0.42	0.43	0.45	0.46	0.48
(d) Amine cooler	0.95	0.98	1.01	1.03	1.21	1.24
(e) Absorber flash vessel, pumps compressor, condenser, reflux drum	5.4 +	5.4 +	5.4 +	5.4 +	5.4 +	5.4 +
	17.0	14.1	12.8	11.9	11.6	11.2
2. Energy requirements						
(a) Steam (kg s^{-1})	16.66	17.54	18.44	19.44	20.40	21.35
(b) Electricity (kW h s^{-1})	0.70	0.70	0.70	0.70	0.70	0.70
(c) Cooling water ($\text{m}^3 \text{s}^{-1}$)	0.52	0.55	0.54	0.62	0.65	0.68
Annual energy costs (M\$/year)	8.77	9.16	9.54	10.00	10.43	10.85
Annual fixed costs (33% of investment) (M\$/year)	5.61	4.65	4.22	3.93	3.83	3.70
Total annual costs (M\$/year)	14.38	13.80	13.76	13.93	14.26	14.55

TABLE 9. Investment costs for a gas I treatment plant (7% H₂S and 10% CO₂)

Amine	DIPA		MDEA	
	Tray	Trickle	Tray	Trickle
Absorber type				
(a) Relative selectivity η_{rel} ($\eta/\eta_{tray, DIPA}$, see Table 5)	1.00	1.07	1.11	1.25
(b) Relative solvent circulation ($\phi_{\ell}/\phi_{\ell, tray, DIPA}$, see Table 5)	1.00	0.94	0.90	0.82
Investments (M\$)				
(1) Absorber-regenerator unit	12.8	10.2	16.2	11.8
(2) Sulfur recovery unit (Claus plant)	5.8	5.8	5.4	5.0
(3) Tail-gas unit (SCOT)	8.0	7.5	5.4	4.2
(4) Working capital	2.3	2.2	2.3	2.1
	+ ———	+ ———	+ ———	+ ———
Total investment costs	28.9	25.7	29.3	23.1

TABLE 10. Treatment costs of gas I in M\$/year

Amine	DIPA		MDEA	
	Tray	Trickle	Tray	Trickle
Absorber type				
(a) Relative selectivity η_{rel} ($\eta/\eta_{tray, DIPA}$)	1.00	1.07	1.11	1.25
(b) Relative solvent circulation	1.00	0.94	0.90	0.82
1. Raw materials				
1.1. Absorber-regenerator unit				
(a) Replacement amine	0.04	0.04	0.04	0.04
1.2. Sulfur recovery unit				
(a) Catalyst replacement	0.41	0.41	0.34	0.33
(b) Sulfur produced	-13.50	-13.50	-13.50	-13.50
1.3. Tail-gas unit				
(a) Replacement reducing catalyst	0.04	0.04	0.03	0.03
(b) Reducing agent	0.60	0.59	0.54	0.49
(c) Replacement amine	0.04	0.04	0.04	0.04
2. Energy				
2.1. Absorber-regenerator unit				
(a) Steam reboiler	7.95	7.48	7.12	5.75
(b) Electricity	1.41	1.33	1.26	1.03
(c) Cooling water	0.22	0.21	0.20	0.16
2.2. Sulfur recovery unit				
(a) Steam produced	-6.38	-6.34	-6.35	-6.19
(b) Electricity	0.73	0.73	1.06	1.06
(c) Process water	0.07	0.07	0.07	0.07
2.3. Tail-gas unit				
(a) Steam reboiler	1.64	1.62	0.88	0.58
(b) Electricity	0.07	0.06	0.04	0.01
(c) Cooling water	0.11	0.10	0.08	0.06
3. Labour	1.05	1.05	1.05	1.05
4. Maintenance	1.16	1.03	1.17	0.92
5. Other				
(a) Insurance, rents, local taxes	0.58	0.51	0.59	0.46
(b) Waste removal/destruction	0.59	0.52	0.60	0.47
6. Depreciation	2.66	2.35	2.70	2.10
7. Capital charges	+ 4.34	+ 3.86	+ 4.40	+ 3.47
Annual operating costs (M\$/year)	3.83	2.20	2.36	-1.57
Cost of treating 1 Nm ³ gas (¢/Nm ³)	0.24	0.14	0.15	-0.10

reductions are caused by lower absorber costs in the ARU, and smaller SRUs and TGUs owing to the increased selectivities. The investments for MDEA ARUs are higher than for their DIPA counterparts because of the higher

temperatures required for the MDEA regeneration and the consequently considerably larger lean/rich exchangers.

The treatment costs are summarized for eight combinations in Tables 10 and 12 for gas I and II respectively.

TABLE 11. Investment costs for a gas II treatment plant (5% H₂S and 10% CO₂)

Amine	DIPA		MDEA	
	Tray	Trickle	Tray	Trickle
Absorber type				
(a) Relative selectivity η_{rel}	1.00	1.11	1.14	1.40
(b) Relative solvent circulation	1.00	0.92	0.88	0.72
Investments (M\$)				
(1) Absorber–regenerator unit	13.3	10.5	16.8	11.4
(2) Sulfur recovery unit (Claus plant)	4.8	4.7	4.3	3.9
(3) Tail-gas unit (SCOT)	10.8	9.5	7.0	4.4
(4) Working capital	+ 2.3	+ 2.2	+ 2.3	+ 2.1
Total investment costs	31.2	26.9	30.4	21.8

TABLE 12. Annual treatment costs for gas II in M\$/year

Amine	DIPA		MDEA	
	Tray	Trickle	Tray	Trickle
Absorber type				
(a) Relative selectivity η_{rel}	1.00	1.11	1.14	1.40
(b) Relative solvent circulation	1.00	0.92	0.88	0.72
1. Raw materials				
1.1. Absorber–regenerator unit				
(a) Replacement amine	0.04	0.04	0.04	0.04
1.2. Sulfur recovery unit				
(a) Catalyst replacement	0.35	0.33	0.27	0.25
(b) Sulfur produced	−9.72	−9.72	−9.72	−9.72
1.3. Tail-gas unit				
(a) Reducing agent	0.52	0.49	0.45	0.37
(b) Others	0.06	0.06	0.06	0.06
2. Energy				
2.1. Absorber–regenerator unit				
(a) Steam reboiler	8.50	7.77	7.48	5.46
(b) Others	1.73	1.58	1.52	1.13
2.2. Sulfur recovery unit				
(a) Steam produced	−4.49	−4.41	−4.43	−4.25
(b) Others	0.57	0.57	0.81	0.81
2.3. Tail-gas unit				
(a) Steam reboiler	2.67	2.50	1.56	0.71
(b) Others	0.24	0.21	0.16	0.09
3. Labour	1.05	1.05	1.05	1.05
4. Maintenance	1.25	1.08	1.22	0.87
5. Other	1.25	1.09	1.23	0.89
6. Depreciation	2.89	2.47	2.81	1.97
7. Capital charge	+ 4.68	+ 4.04	+ 4.56	+ 3.27
Annual operating costs (M\$/year)	11.59	9.15	9.07	3.00
Cost of treating 1 Nm ³ gas (¢/Nm ³)	0.74	0.58	0.58	0.19

In fact three costs items are overruling in each case: energy (in particular steam) costs, sulfur proceeds and depreciation + capital charges. The treatment costs per Nm³ of natural gas are shown as a function of the relative selectivity η_{rel} ($=\eta/\eta_{tray, DIPA}$) in Fig. 20. Two very important conclusions can be drawn from this Figure. Firstly, the treatment costs at a fixed feed gas composition decrease considerably with increasing selectivity in the high pressure absorber. These costs can even be converted into a net income at higher relative

selectivities: $\eta_{rel} > 1.2$ for gas I and $\eta_{rel} > 1.55$ for gas II. Secondly, the more H₂S in the feed gas (H₂S, gas I > H₂S, gas II), the lower the treatment costs. This effect is mainly due to higher sulfur proceeds and lower overall energy costs in treating the H₂S rich gas. The latter is illustrated in Fig. 21, where the energy costs for the ARU, SRU, and TGU are plotted as a function of the relative selectivity. The ARU energy costs for gas II are 5%–10% higher than for gas I at equal η_{rel} because in treating gas II roughly 5%–10% more acid gases are

Fig. 20. Treatment costs per Nm^3 of natural gas as a function of the relative selectivities.

Fig. 21. Energy costs for treating gas I and gas II.

absorbed since gas II contains 15% and gas I only 14% of H_2S plus CO_2 (see Table 5). In the SRU, more steam is produced in processing gas I because of the higher amounts of H_2S converted. Hence the SRU steam generation is larger for gas I. After the reduction of unconverted SO_2 to H_2S , the H_2S concentration to the TGU absorber is higher for gas I than for gas II and higher selectivities are thus obtained. This effect results in lower TGU solvent flowrates and therefore reduced steam requirements for gas I in the TGU regenerator. The overall energy picture for ARU + SRU + TGU results in energy costs which are ~ 3 M\$/year, or 0.2 US $\text{\$/Nm}^3$ of treated gas, lower for gas I. Combination of these costs with the difference in sulfur proceeds, i.e. 3.78 M\$/year or 0.24 $\text{\$/Nm}^3$ of treated gas, brings the total difference between the treatment costs of gas I and II to 6.8 M\$/year, which is equivalent to 0.44 $\text{\$/Nm}^3$ of treated gas.

Sulfur proceeds have a considerable impact on the treatment economics (see Tables 10 and 12). Since the

sulfur price is established by a market mechanism, the proceeds will fluctuate and will have a varying beneficial contribution to the treatment costs. The influence of the sulfur price on the treatment costs is shown in Fig. 22. At increasingly higher sulfur prices the treatment processes will eventually become profitable, the H_2S rich gas I being more dependent on the sulfur price.

In Fig. 23 the treatment costs are shown as a function of the relative energy costs, defined as energy costs/energy costs used in this study. These relative energy costs evidently exercise a large influence on the energy intensive, low selectivity process operations, e.g. treating gas II in the tray absorber using DIPA as the solvent (see also Fig. 21). In the high selectivity operations using trickle bed absorbers and MDEA as the solvent, the energy consumption and thus the impact of energy costs on the treatment economics is relatively low. This is an extra incentive for using more selective high pressure absorption equipment, such as the cascade of trickle bed absorbers.

Fig. 22. Influence of sulfur price on treatment costs.

Fig. 23. Treatment costs as a function of the relative energy costs.

Conclusions

Two models have been developed which describe the combined mass transfer, reaction and equilibrium processes in the absorption of H_2S and CO_2 by aqueous amine solutions in tray and cocurrent trickle bed absorbers respectively. The analytical and numerical solutions of the two mass transfer models used in these absorber calculations give almost equal results despite their essentially different principal assumptions and complexity.

The impact of variations in design and operating parameters on the tray absorber performance has been established. The operating pressure of the absorber exercises a negligible influence on the absorber selectivity and the solvent rate. The acid gas loadings of lean and rich amine solvents and the total amine concentration have a significant effect on selectivities and solvent flowrates.

A cascade of trickle bed reactors produces higher H_2S absorption selectivities than tray absorbers at identical operating and design conditions. This effect is mainly due to the increased k_g/k_L ratio realized in trickle bed reactors.

In the evaluation of the economics of the use of eight absorber-solvent-gas combinations it is shown that the investments for the trickle bed absorbers are considerably lower than for their tray absorber counterparts. Moreover, as a result of the increased selectivity and lower investment in the trickle bed absorbers, the annual operating costs for the treatment plant are considerably lower with this absorber type. The use of MDEA solutions is economically more attractive than of DIPA solutions.

Nomenclature

A_{tray}	gas-liquid interfacial area on tray, m^2
a	specific gas-liquid interfacial area, m^2/m^3
a''	gas-liquid interfacial area, m^2/m^2 tray
C_1	constant in eqn. (26)
C_2	constant in eqn. (27)
C_p	specific heat, $kJ\ kg^{-1}\ ^\circ C^{-1}$
D	diffusion coefficient, $m^2\ s^{-1}$
d_p	particle diameter, m
d_c	column diameter, m
d_s	equivalent spherical packing diameter [32], m
E	enhancement factor
f^i	equilibrium approach factor, defined by eqn. (15)
ΔH	heat of reaction + absorption, $kJ\ mol^{-1}$
ΔH_{st}	latent heat of steam, $kJ\ mol^{-1}$
He	Henry's coefficient, $mol\ m^{-3}\ bar^{-1}$
J	molar flux, $mol\ m^{-2}\ s^{-1}$
k	mass transfer coefficient, $m\ s^{-1}$
M	molar mass, $kg\ mol^{-1}$
m	dimensionless solubility, defined by eqn. (16)
n	total number of trays
P	pressure, bar
R	ratio, defined by eqn. (19)

R^{ov}, R^L	overall, liquid and gas phase mass transfer resistances, defined by eqn. (32), $s\ m^{-1}$
Re	$= d_g v \rho / \mu$, Reynolds number
Sc	$= \mu / D \rho$, Schmidt number
T	temperature, K
v	superficial velocity, $m\ s^{-1}$
x	liquid phase molar fraction
y	gas phase volume fraction
$[]$	concentration, $mol\ m^{-3}$
α	acid gas loading, defined by eqn. (6)
η	selectivity defined by eqn. (33)
μ	viscosity, $kg\ m^{-1}\ s^{-1}$
ρ	density, $kg\ m^{-3}$
ϕ	packing constant in eqns. (28) and (29)
ϕ_g^i	gas flowrate to tray i , $Nm^3\ s^{-1}$
ϕ_L	solvent flowrate, $m^3\ s^{-1}$
ϕ_{st}	steam flowrate, $kg\ s^{-1}$
ϕ_{st}^L	steam flowrate, $kg\ (m^3\ solvent)^{-1}$

Indices

g	gas phase
HL	heat limited
L	liquid phase
ov	overall
SL	stripping limited
st	steam
tot	total (in reacted and unreacted form)

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