## Separation & Purification Reviews

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597294

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**To cite this Article** Sartori, G. , Ho, W. S. , Savage, D. W. , Chludzinski, G. R. and Wlechert, S.(1987) 'Sterically-Hindered Amines for Acid-Gas Absorption', Separation & Purification Reviews, 16: 2, 171 — 200
**To link to this Article: DOI:** 10.1080/03602548708058543
**URL:** http://dx.doi.org/10.1080/03602548708058543

SEPARATION AND PURIFICATION METHODS, 16(2), 171-200 (1987)

# STERICALLY-HINDERED AMINES FOR ACID-GAS ABSORPTION

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## ABSTRACT

This paper reviews sterically-hindered amines for removal of acid gases such as $CO_2$ and $H_2S$ from gaseous streams. Steric hindrance of amines reduces carbamate stability. Moderately hindered amines are characterized by high rates of $CO_2$ absorption and high capacities for $CO_2$. The moderately hindered amine in use with organic solvent has considerably higher capacity than the conventional amine-solvent system for simultaneous removal of $CO_2$ and $H_2S$ from synthesis gas and natural gas. A severely-hindered-amine absorbent, characterized by a very low rate of $CO_2$ absorption, has much higher capacity and selectivity than the current industry standard, methyldiethanolamine, for selective removal of $H_2S$ from $CO_2$-containing streams. Use of hindered amines represents new advances in gas treating. Hindered amines save energy and capital in gas treating significantly. In addition, hindered amines used commercially have much better stability than

conventional amines. As of today, fourteen commercial plants use hindered amines.

## INTRODUCTION

Acid-gas removal from gaseous streams (gas sweetening) is a very common process and covers broad processing areas in refining, chemical and producing operations(1-5). As illustrated in Figure 1, the fuel gases in a refinery are generally at low pressure with the sum of $CO_2$ and $H_2S$ partial pressures of about 70 kPa or less (70 kPa is about 10 psi). The gases are high in $H_2S$ and low in $CO_2$ and have a $CO_2$ to $H_2S$ mole ratio of about 0.1. These gases are treated to remove $H_2S$ in order to satisfy environmental combustion standards.

The tail gas from a sulfur plant has a $CO_2$ to $H_2S$ ratio of about 10. The tail gas is treated for removing $H_2S$ in order to increase sulfur recovery and to meet environmental regulations. The low-Joule fuel gas produced in Exxon's FLEXICOKING resid conversion process has a similar mole ratio. The gas is desulfurized prior to combustion to reduce sulfur dioxide emission.

In a hydrogen plant, the steam reformer converts methane or other hydrocarbon feed to hydrogen and $CO_2$. $CO_2$ is the only acid gas, and it has a pressure of about 350 kPa. This $CO_2$ is removed to satisfy $H_2$ purity specifications. Similar gas treating requirements are found in ammonia plants and in synthesis gas generators.

Gases associated with producing operations, such as natural gas, and synthetic fuels, such as coal gasification and shale oil, cover broad ranges of both acid gas composition and pressure.

Very often the gas treating agents are amines, such as monoethanolamine (MEA), diethanolamine (DEA), diisopropanolamine (DIPA) and N-methyldiethanolamine (MDEA). They are used in aqueous solution, in aqueous organic medium or in combination with aqueous

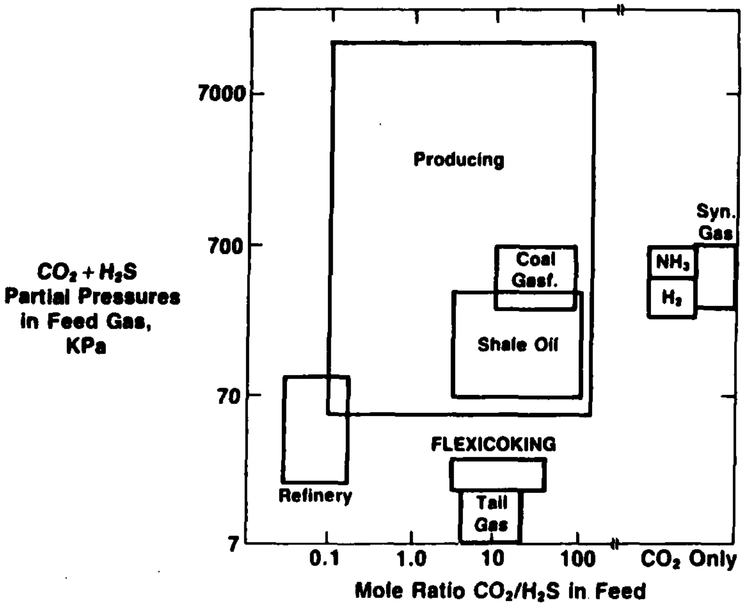


FIGURE 1

Gas treating covers broad processing areas

potassium carbonate. Worldwide, there are hundreds of gas sweetening units.

Most gas treating processes use an integrated absorber-regenerator flowsheet as shown in Figure 2. The impure gas to be treated is contacted countercurrently with the amine solution in a tower, and the treated gas leaves from the top. The rich amine solution is transferred to the desorber (regenerator), where a temperature increase and a pressure decrease cause the acid gases to be desorbed and evolve from the top of the tower. The regenerated amine solution is pumped back to the top of the absorber. Energy is required to pump the solution around and to regenerate it.

Hindered amines show considerable advantages over the conventional alkanolamines listed above. Moderately hindered

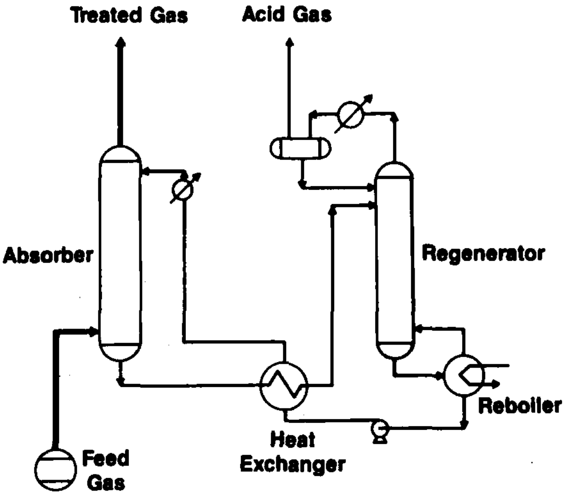


FIGURE 2
Typical acid gas removal process

amines lead to better capacity for $CO_2$ and higher absorption rate. Severely hindered amines have better selectivity for $H_2S$ over $CO_2$ compared to the conventional MDEA.

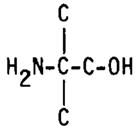
Hindered amines represent the result of cooperative efforts by various Exxon affiliates. The FLEXSORB® SE solvent, based on the use of a severely-hindered amine, won the IR-100 award in 1985 and was one of the five finalists for the 1985 Kirkpatrick award. As of today, fourteen commercial plants use hindered amines.

## 1. Definition and Examples

A hindered amine has a bulky alkyl group attached to the aminogroup. More specifically, we define a hindered amine as belonging to either of these classes:

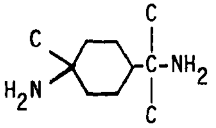
1) a primary amine in which the aminogroup is attached to a tertiary carbon

2) a secondary amine in which the aminogroup is attached to at least one secondary or tertiary carbon.

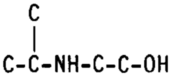


$$\mathrm{H_2N{-}\overset{\displaystyle C}{\underset{\displaystyle C}{C}}{-}C{-}OH}$$

2-amino-2-methyl-1-propanol



1,8-p-menthanediamine



$$\mathrm{C{-}\overset{\displaystyle C}{C}{-}NH{-}C{-}C{-}OH}$$

2-isopropylaminoethanol

In general, only aliphatic and cycloaliphatic amines are suitable for gas treating. Aromatic amines, due to their lower basicity, lead to low absorption capacities and rates. Besides the aminogroup, the amine must contain another functional group to increase solubility and reduce volatility, e.g. a hydroxyl or carboxylic group.

## 2. Amine Carbamate Stability as a Function of Steric Hindrance

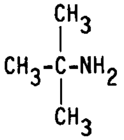
The low tendency of hindered amines to form carbamates owing to the bulkiness of the substituent attached to the aminogroup has been observed by previous investigators. In 1957, Jensen(6) studied the stabilities of the carbamate of butylamines. Addition of barium chloride to an amine solution containing carbon dioxide caused the precipitation of carbonate and bicarbonate, whereas carbamate ions remained in solution. After separation of the precipitate, heating the solution transformed the carbamate ions into carbonate ions, with consequent precipitation. Using that technique, Jensen determined values of the equilibrium constant $K_c$ for carbamate hydrolysis written from right to left; they are given in Table I.

$$\mathrm{RNH_2 + HCO_3^- \rightleftarrows RNHCOO^- + H_2O}$$

$$K_c = \frac{[\mathrm{RNHCOO^-}]}{[\mathrm{RNH_2}][\mathrm{HCO_3^-}]}$$

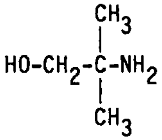
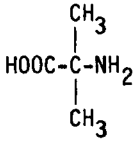
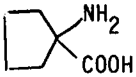
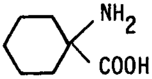
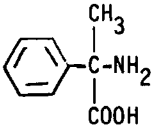
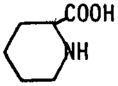
## TABLE I

## Carbamate Stability Equilibrium Constants at 18°C (6)

| Amine | $K_c$ |
|---|---|
| $CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}NH_2$ | 63 |
|  $CH_3\text{-}\overset{CH_3}{\underset{CH_3}{C}}\text{-}NH_2$ | 7 |

## TABLE II

## Hindered Amines Unable to Form Carbamates

| | |
|---|---|
| 2-amino-2-methyl-1-propanol |  $HO\text{-}CH_2\text{-}\overset{CH_3}{\underset{CH_3}{C}}\text{-}NH_2$ |
| 2-amino-2-methylpropionic acid |  $HOOC\text{-}\overset{CH_3}{\underset{CH_3}{C}}\text{-}NH_2$ |
| 1-amino-1-cyclopentanecarboxylic acid |  |
| 1-amino-1-cyclohexanecarboxylic acid |  |
| 2-amino-2-phenylpropionic acid |  |
| pipecolinic acid |  |

## TABLE III

### Carbamate Stability Constants for Hindered and Conventional Amines by Carbon-13 NMR

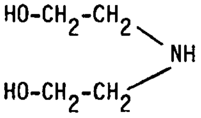
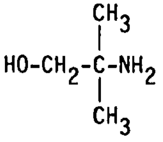
| Amino alcohol | $K_c$ at 40°C |
|---|---|
| $HO\text{-}CH_2\text{-}CH_2\text{-}NH_2$ | 12.5 |
|  | 2.0 |
|  $HO\text{-}CH_2\text{-}\underset{CH_3}{\overset{CH_3}{C}}\text{-}NH_2$ | <0.1 |

Table I shows that the carbamate of the hindered tert. butylamine is much less stable than that of the unhindered n-butylamine.

In 1964 Frahn and Mills(7) showed that certain amines did not form any carbamate under their experimental conditions, see Table II, and attributed that to steric hindrance.

Carbamate stability can be measured by carbon-13 nuclear magnetic resonance (Melchior(8)). Table III shows significant differences in carbamate stability between hindered and conventional amines. The unhindered monoethanolamine and diethanolamine show values of $K_c$ of 12.5 and 2.0, respectively, whereas the hindered 2-amino-2-methyl-1-propanol has a $K_c$ lower than .1.

Space-filling molecular models clearly show the dramatic differences in carbamate stability between hindered and conventional amines.

Figures 3 and 4 show that rotation around the N-COO$^-$ bond is unrestricted in the carbamate of the unhindered n-butylamine,

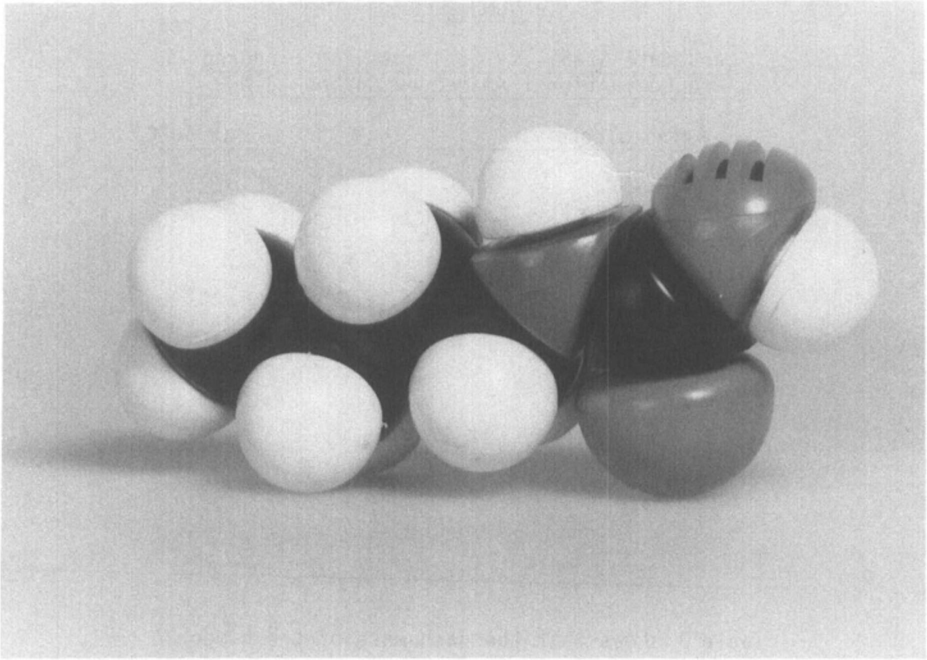


FIGURE 3

Molecular model of carbamate of n-butylamine

whereas rotation around the N-COO$^-$ bond in the carbamate of the hindered tert. butylamine is only possible if the bulky substituent is compressed. Consequently, the carbamate of tert. butylamine is much less stable than that of n-butylamine.

## 3. $CO_2$-Amine Reaction Stoichiometry, Vapor-Liquid Equilibrium

Carbamate stability has an important effect on the $CO_2$-amine reaction stoichiometry. When $CO_2$ is absorbed in an amine solution, two reactions can occur:

A) $2\text{-}NH_2 + CO_2 \rightarrow R\text{-}NH_3^+ + R\text{-}NH\text{-}COO^-$

B) $R\text{-}NH_2 + CO_2 + H_2O \rightarrow R\text{-}NH_3^+ + HCO_3^-$

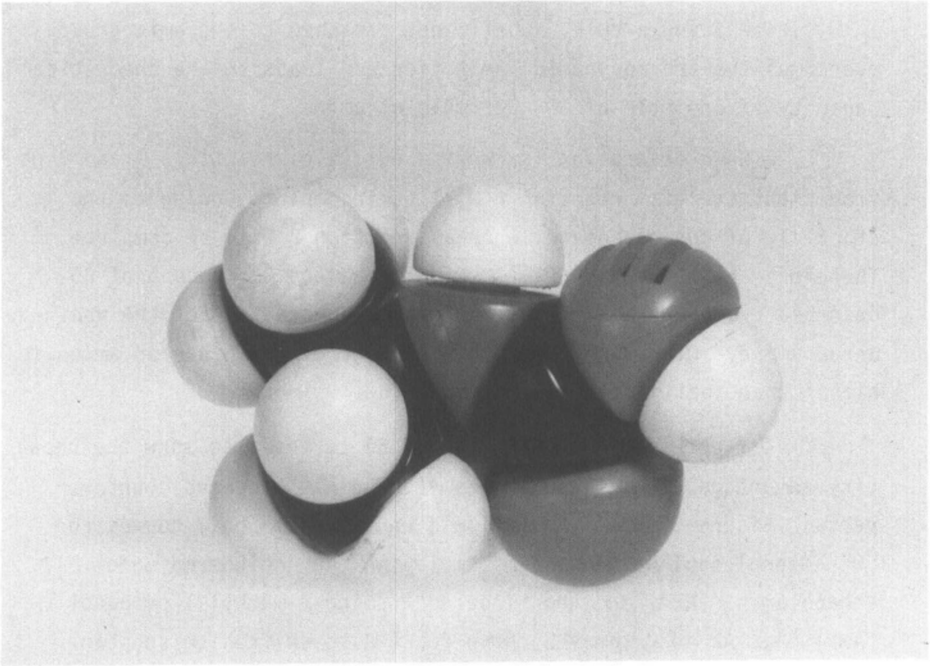


FIGURE 4
Molecular model of carbamate of tert-butylamine

Whether reaction A or B occurs depends on the stability of the carbamate. If the amine is not hindered, i.e. if R is not bulky, the carbamate will be stable and reaction A will occur, which means a half mole of $CO_2$ absorbed per mole of amine. If the amine is hindered, i.e. if R is bulky, the carbamate will be unstable and reaction B will occur, which means one mole of $CO_2$ absorbed per mole of amine. We see how the bulkiness of R has an important effect on the stability of the carbamate and consequently on the stoichiometry of the reaction with $CO_2$. The formation of a stable carbamate is the thermodynamic limitation to the capacity of conventional amines for $CO_2$ removal.

Placing a bulky substituent attached to the aminogroup overcomes the thermodynamic limitation and leads to the theoretical capacity of one mole of $CO_2$ per mole of amine.

When desorption is carried out, i.e. reactions A and B go from right to left, reaction A will be incomplete, owing to the stability of the carbamate, whereas reaction B will be complete. Therefore, both the amount of $CO_2$ absorbed and the amount of $CO_2$ desorbed are higher in the case of the hindered than of the unhindered amine. Otherwise said, the capacity of the hindered amine is higher than that of the unhindered amine.

Vapor-liquid equilibrium (VLE) curves also show the capacity advantage of hindered amines vs. their unhindered counterparts. Figure 5 shows vapor-liquid equilibrium (VLE) curves for $CO_2$-aminoalcohol-water systems employing the unhindered monoethanolamine (MEA) and the hindered 2-amino-2-methyl-1-propanol (AMP)(9). At 40°C the VLE curve for AMP is shifted to substantially higher loadings (the loading is defined as moles of $CO_2$ absorbed per mole of amine) as compared to MEA, especially at high $CO_2$ partial pressures, in agreement with the previous considerations about the reaction stoichiometry. At 120°C, a temperature close to that of regeneration, the VLE curve for AMP is displaced to lower loadings as compared to MEA, also in agreement with the previous considerations about the reaction stoichiometry. Based on carbamate stability, hindered amines can be divided into moderately and severely hindered. Moderately hindered amines form unstable carbamates that are readily hydrolyzed; severely hindered amines do not form any carbamate.

The degree of steric hindrance can be expressed quantitatively by means of Taft's steric hindrance parameter $\sum E_s$(10). Unhindered amines have $\sum E_s < 1.32$. Moderately hindered amines have $\sum E_s$ comprised between 1.32 and 2.0. Severely hindered amines have $\sum E_s > 2.0$.

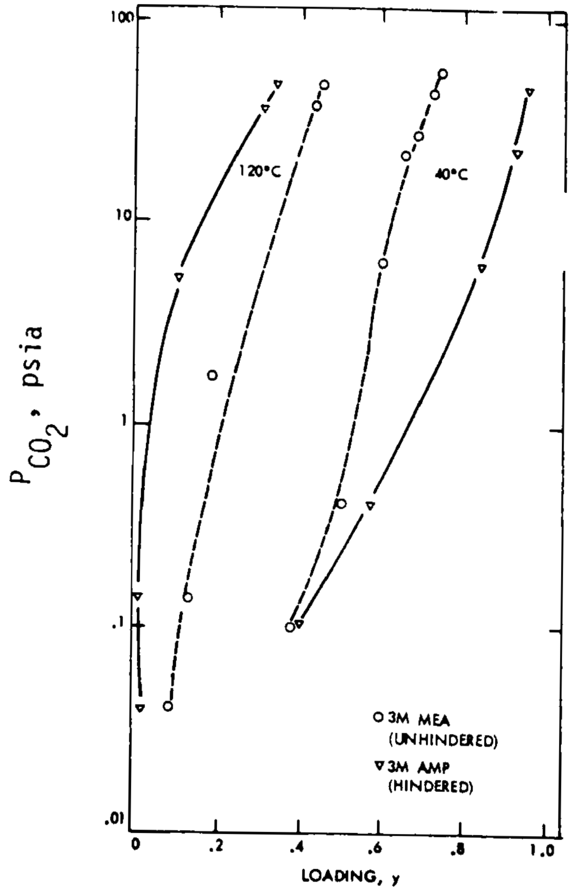


FIGURE 5

Measured $P_{CO_2}$ vs. loading curves for aqueous MEA and AMP

## 4. Effect of Steric Hindrance on $CO_2$-Amine Reaction Rate

In 1965, M. M. Sharma(11) published values of second-order rate constants $k_{AM-CO_2}$ for the reaction of $CO_2$ with a large number of amines. Dividing the amines into classes and plotting $\log_{10}k_{AM-CO_2}$ vs. pKa, some interesting correlations are observed, Figures 6, 7, 8 and 9. In the case of primary amines (Figure 6) at

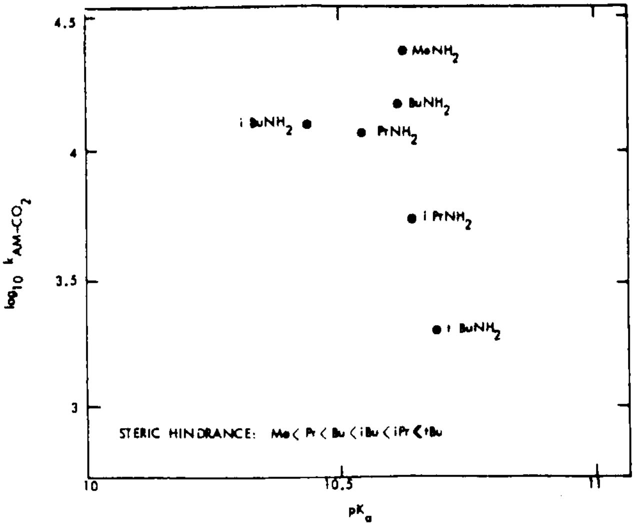


FIGURE 6

Effect of hindrance on $CO_2$ rate constant for primary amines

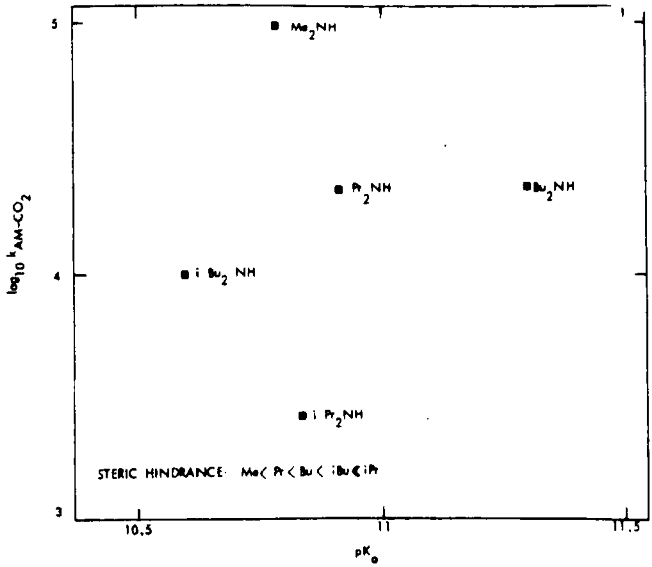


FIGURE 7

Effect of hindrance on $CO_2$ rate constant for secondary amines

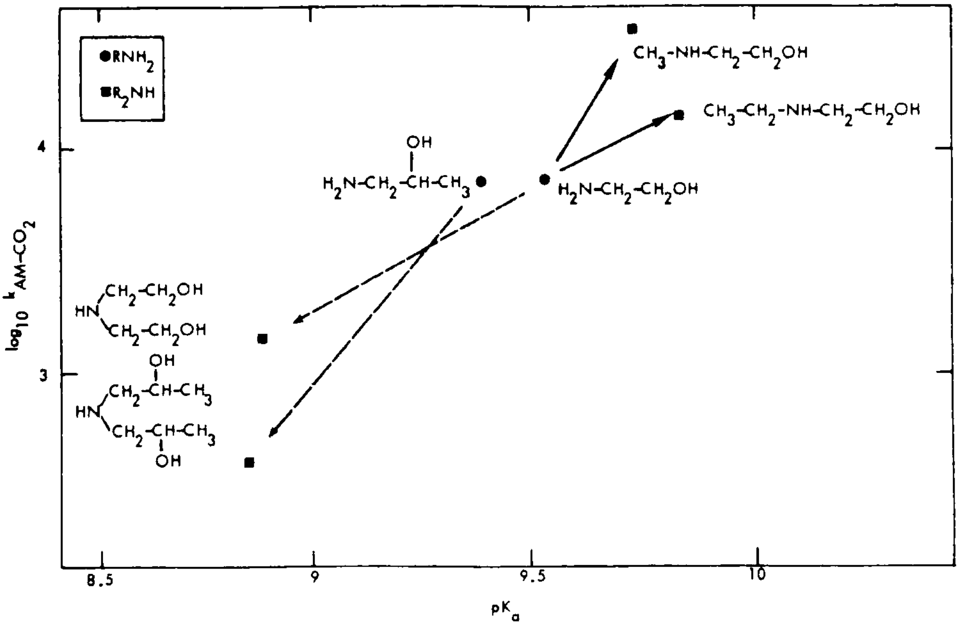


FIGURE 8

Effect of increasing steric hindrance on $CO_2$ rate constant for alkyl amines

constant pKa, the rate constant decreases if steric hindrance increases. The same happens with secondary amines, Figure 7. In going from a primary to the corresponding secondary amine, Figure 8, the rate constant increases only with a non-bulky substituent, e.g. with the methylamines; in the case of bulky substituents, e.g. with the isopropylamines, the rate constant decreases in going from the primary to the secondary amine.

We can observe that diisobutylamine has a lower rate constant than isobutylamine, i.e., going from the primary to the secondary amine implies a considerable steric hindrance increase. This means that branching at the β carbon has little effect on the

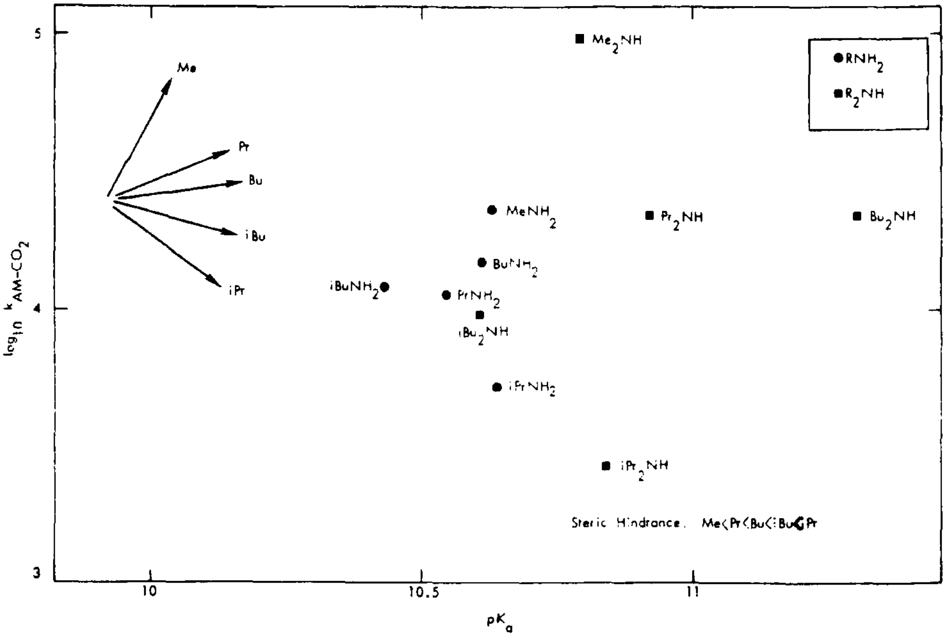


FIGURE 9

$CO_2$ rate constants for aqueous amino alcohol reactions

rate constant in the case of the primary amine, but a significant effect in the case of the secondary amine.

Looking at the aminoalcohols, Figure 9, we see that going from a primary amine, in this case monoethanolamine, to its secondary derivatives, in this case 2-methylaminoethanol and 2-ethylaminoethanol, the rate constant increases, especially in the case of the smaller substituent, i.e. the methyl. Although the rate constant for monoisopropanolamine is nearly the same as that for monoethanolamine, the rate constant for diisopropanolamine is definitely lower than that of diethanolamine. The explanation is similar to that proposed for the isobutylamines. The isopropanol group is mildly bulky, therefore it does not decrease the rate

TABLE IV

Amine Steric Hindrance Reduces $CO_2$ Reaction Rate

| Amines | $CO_2$ Reaction Rate Constant at 40°C (Liter/Mole/Sec) |
|---|---|
| ● Unhindered amines | |
| - dimethylamine | $7.9 \times 10^5$ |
| - dipropylamine | $7.1 \times 10^4$ |
| ● Moderately hindered amines | |
| - diisopropylamine | $7.9 \times 10^3$ |
| ● Severely hindered amines | $\sim 1.3 \times 10^2$ |

constant appreciably in the case of the primary amine, but it does decrease it substantially in the case of the secondary amine.

We have determined the rate constants for the reaction of $CO_2$ with some typical secondary amines, Table IV. We see that the increase in steric hindrance accompanying the transition from dimethylamine to dipropylamine is enough to reduce the rate constant by an order of magnitude. The rate constant decreases by nearly another order of magnitude in going from dipropylamine to diisopropylamine. Finally, the rate constant decreases by more than another order of magnitude in going from diisopropylamine to a severely hindered amine.

As mentioned before, an unhindered amine reacts with $CO_2$ according to reaction A:

$$\text{A)}\quad 2\ R\text{-}NH_2 + CO_2 \rightarrow R\text{-}NH_3^+ + R\text{-}NH\text{-}COO^-$$

This means that two moles of amine are tied up for every mole of $CO_2$ absorbed. On the other hand, a hindered amine reacts according to reaction B:

$$\text{B)}\quad R\text{-}NH_2 + CO_2 + H_2O \rightarrow R\text{-}NH_3^+ + HCO_3^-$$

This means one mole of amine tied up per mole of $CO_2$ absorbed. As a consequence, at a certain $CO_2$/amine ratio the fraction of amine tied up will be lower, or in other words, the fraction of free amine will be higher, if the amine is hindered. Therefore, if we look at the expression for the $CO_2$-amine reaction rate:

$$V = k_{AM\text{-}CO_2}\,[\text{Amine}][CO_2]$$

we know that an increase in steric hindrance will cause a decrease in $k_{AM-CO_2}$, but for a moderate degree of hindrance that will be compensated by an increase in free-amine concentration. However, a severely hindered amine has a very low rate constant and consequently a very low $CO_2$ absorption rate.

## 5. Areas of Use of Hindered Amines, Processes

Unlike $CO_2$, $H_2S$ reacts with an amine at a rate unaffected by steric hindrance. The reason is that the reaction is a simple protonation: the rate of addition of a proton to an aminogroup is not affected by the bulkiness of the substituents. As a consequence, moderately hindered amines, characterized with high rates of $CO_2$ absorption and high capacities for $CO_2$, are suitable for the removal of $CO_2$ and the bulk, non-selective removal of $CO_2$ and $H_2S$. Severely hindered amines, characterized with a very low rate of $CO_2$ absorption, are suitable for the kinetically selective removal of $H_2S$ in the presence of $CO_2$ (Figure 10).

Moderately hindered amines can be used in aqueous solution, in aqueous-organic medium and in combination with aqueous potassium carbonate. Severely hindered amines are generally used in aqueous solution, but sometimes they can be used in aqueous-organic medium.

## 6. Hindered-Amine-Based Processes

Two hindered-amine-based gas treating solvents are in commercial use:

FLEXSORB® SE, based on an aqueous severely-hindered amine, selectively removes $H_2S$ in the presence of $CO_2$.

FLEXSORB® PS, based on a moderately-hindered amine in aqueous-organic medium, removes $CO_2$ and $H_2S$ in a non-selective way.

## 7. FLEXSORB® SE

Selective $H_2S$ removal is becoming increasingly important, since there will be more gases with low $H_2S/CO_2$ ratios, such as

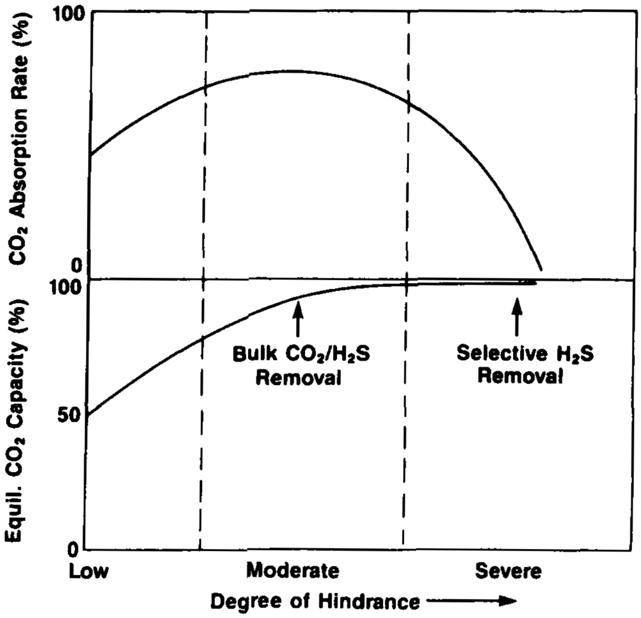


FIGURE 10

Steric hindrance exploitable for both $CO_2$ removal and selective $H_2S$ removal

sulfur plant tail gases, certain natural gases, gases produced in Exxon's FLEXICOKING process and in coal gasification. It is necessary to concentrate $H_2S$ from these streams before feeding to a Claus plant.

Well known processes, Stretford and MDEA, are in commercial use for the selective removal of $H_2S$ in the presence of $CO_2$. The Stretford process is based on the oxidation of $H_2S$ by means of $V^{+5}$ and an anthraquinone derivative, i.e. it is thermodynamically selective. The aqueous methyldiethanolamine (MDEA) process takes advantage of the difference in absorption rates between $H_2S$ and $CO_2$, i.e. it is kinetically selective. Use of a selective amine treating agent, rather than a non-selective agent such as monoethanolamine or diethanolamine, results in lower

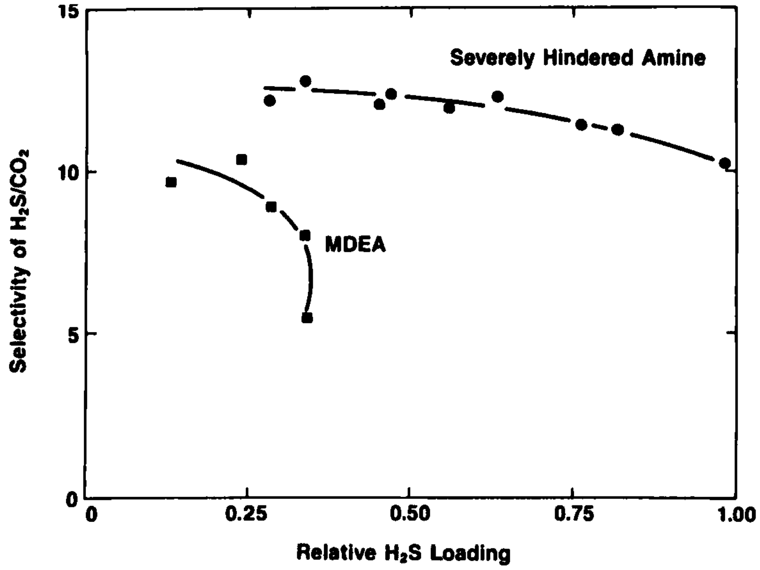


FIGURE 11

Severely hindered amine outperforms MDEA for selective $H_2S$ removal

amine circulation rate, smaller equipment and lower operating costs. This occurs because the amine preferentially absorbs $H_2S$, therefore is not tied up in unnecessary $CO_2$ removal.

Both the Stretford and MDEA processes have some limitations. The Stretford process produces low-quality sulfur, and side reactions lead to formation of thiocyanides and thiosulfates which are difficult to dispose of. A drawback of the aqueous methyldiethanolamine process is that it has a good selectivity only at low loadings, i.e. selectivity decreases rapidly as $H_2S$ and $CO_2$ are absorbed. We have shown before that severely-hindered amines are characterized by a very low rate of reaction with $CO_2$ and a very high rate of reaction with $H_2S$, therefore they are suitable for the kinetically selective removal of $H_2S$ in the presence of $CO_2$. Exxon's FLEXSORB® SE amine, besides showing good $H_2S$ selec-

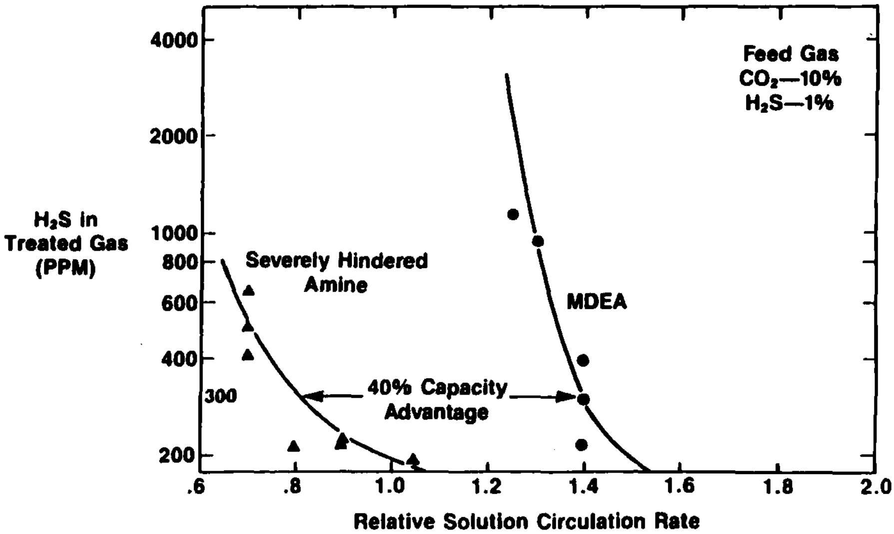


FIGURE 12
Severely hindered amine commercial data show significant capacity advantage

tivity and high capacity, has high solubility, low volatility, excellent chemical stability, no corrosivity and low foaminess. Figure 11 shows that the severely-hindered FLEXSORB® SE outperforms MDEA as regards selectivity at high loading. Selectivity is defined as:

$$\text{selectivity} = \frac{H_2S/CO_2 \text{ ratio in solution}}{H_2S/CO_2 \text{ ratio in gas phase}}$$

The advantage of FLEXSORB® SE over MDEA has been confirmed in commercial tests(12,13). Figure 12 shows the results. All data are at constant ratio of regeneration steam rate to amine solution circulation rate (Kg steam/$m^3$ of amine solution). FLEXSORB® SE shows a 40% capacity advantage over MDEA at the design point of 300 ppm of $H_2S$ in the treated gas. Since

## TABLE V

## FLEXSORB® SE is Economically Attractive

Basis

- Desulfurization of 7.9M m$^3$/d (280 MSCF/D) low joule gas
- Desulfurization of 1.0M m$^3$/d(35 MSCF/D) Claus tail gas
- Total sulfur removed, 0.125 Gg/d(123 T/D)

| | FLEXSORB® SE, % of MDEA |
|---|---|
| • Amine circ. rate | 41% |
| • Steam rate | 51% |
| • Regenerator | |
| - Diameter | 69% |
| - Height | 87% |
| • Investment | 74% |
| • Operating Cost | 57% |

all data are at a constant ratio of regeneration steam to amine solution volume, this 40% capacity advantage translates into a 40% energy saving. In a grass-roots design this 40% capacity advantage results in significantly smaller equipment and lower investment. An example is given in Table V.

Some plants use diisopropanolamine (DIPA) rather than MDEA for the selective removal of $H_2S$. Table VI shows a retrofit application in which FLEXSORB® SE is used to replace DIPA in a small tail gas cleanup unit. The objective is to achieve energy savings. FLEXSORB® SE requires only 32% of the DIPA circulation rate and only 25% of the DIPA reboiler duty.

## 8. FLEXSORB® PS

FLEXSORB® PS consists of a moderately hindered amine in an organic solvent plus water. The proportions of the three ingredients depend on the acid gases to be removed and the degree of purification desired. Compared to the conventional non-hindered amines with which it competes, FLEXSORB® PS is considerably more stable under the operating conditions. In order to confirm the

TABLE VI

FLEXSORB® SE Incentives Versus DIPA Are Very Large

Basis:

- Desulfurization of 3.2 MSCF/D Claus Tail Gas to 500 vppm $H_2S$
- Feed Conditions: 16.2 psia, 120°F

| Component | Mole % |
|---|---|
| $N_2$ | 76.9 |
| $H_2O$ | 10.2 |
| $CO_2$ | 9.8 |
| $H_2S$ | 1.6 |
| $H_2$ | 1.5 |
| | 100.0 |

| | FLEXSORB® SE, % of DIPA |
|---|---|
| Solution Circulation Rate | 32% |
| Regenerator Reboiler Duty | 25% |

laboratory results, a severe degradation test was carried out in parallel with a conventional amine-solvent system(13,14,15). In the test, each solution was allowed to equilibrate at 255°F with a natural gas slipstream containing 82 psia of $H_2S$ and 37.4 psia of $CO_2$. After only 15 days of exposure, Figure 13, about 90% of the initial amine contained in the conventional amine-solvent system had undergone degradation. During that same period of time the FLEXSORB® PS amine showed only slight degradation.

Development of FLEXSORB® PS absorbent involved extensive pilot unit testing. Test work was carried out to verify and quantify the capacity and mass transfer advantages observed in the laboratory for hindered amines and to confirm operability regarding foaming, corrosion, and amine degradation. Comparative tests at similar conditions were carried out between FLEXSORB® PS and a conventional amine-solvent system.

The pilot plant used contained the basic parts of a conventional gas treating plant: absorber, regenerator, reboiler and lean solution pump. A feed gas saturator and overhead condensers/ knockouts were used to maintain solution water balance. A gas

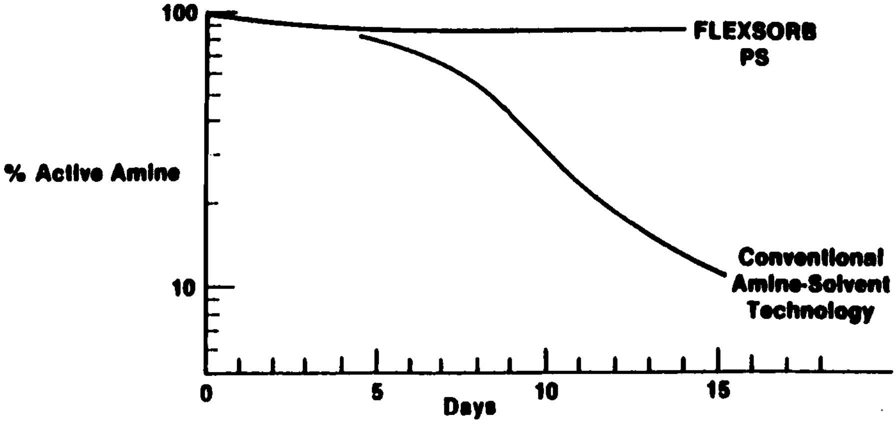


FIGURE 13

Stability demonstrated under severe field conditions

manifold allowed mixing $H_2S$, $CO_2$ and $N_2$ over a wide range of concentrations. $N_2$ was used to simulate the "non-acid gas" components. Both the absorber and regenerator were packed columns equipped with intermediate liquid inlets which allowed varying the packing height. On-line gas analyses by gas chromatography and data logging provided data for material balance and performance calculations.

The capacity advantages discussed earlier were demonstrated in the pilot unit by operating at the rich end pinch. The minimum solution rate can be determined by holding the feed gas rate constant and decreasing the solution rate until the acid gas concentration in the absorber treated gas rises dramatically. At this pinched condition, the solution has the maximum acid gas loading and the mass transfer driving force at the absorber bottom approaches zero. Regeneration steam during these tests would be at a level to provide adequate regeneration. Rich end capacity tests were completed for FLEXSORB® PS and a conventional amine-solvent system. Solution compositions were chosen to give equivalent amine

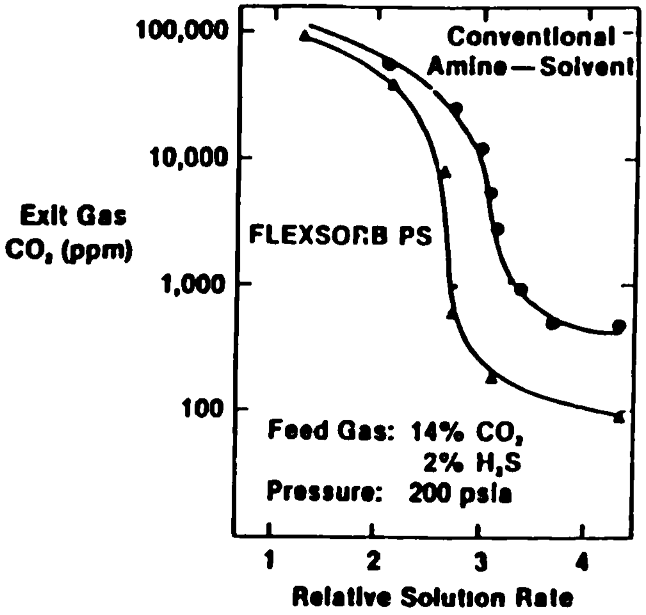


FIGURE 14

Capacity advantage for FLEXSORB® PS absorbent

normalities and physical solvent concentrations. In both cases feed gas compositions and process conditions were similar. As shown in Figure 14 at a $CO_2$ leak of 100 vppm, the FLEXSORB® PS solvent operated at the same steam rate in terms of lbs of steam per gallon of solution circulation; the lower circulation rate translates into a direct steam savings.

Mass transfer data were obtained by operating with a short absorber thereby avoiding equilibrium pinches at either end of the absorber. As a result large driving forces exist across the absorber so that accurate mass transfer coefficients can be determined. Overall mass transfer coefficients were determined based on log mean driving forces and gas phase partial pressures. Figure 15 compares mass transfer coefficients for $CO_2$ absorption for the

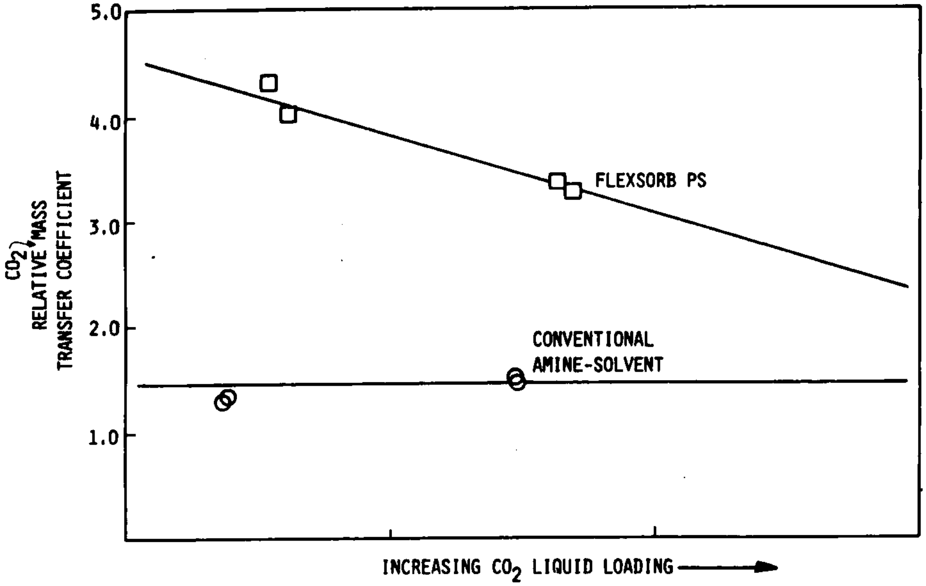


FIGURE 15

Increased $CO_2$ mass transfer rate of FLEXSORB® PS absorbent vs. conventional amine-solvent system

FLEXSORB® PS absorbent and a conventional amine-solvent system. The mass transfer coefficient for FLEXSORB® PS exhibited a strong dependence on average loading indicating the effect of the free amine concentration on mass transfer. In general, the observed $CO_2$ mass transfer rate for FLEXSORB® PS was a factor of 2 to 3 higher than that observed for a conventional amine-solvent system.

The first commercial use of FLEXSORB® PS absorbent was at Exxon Chemical Americas' plant in Baton Rouge, Louisiana. FLEXSORB® PS absorbent replaced a conventional amine solvent system in order to achieve energy savings, increase capacity and avoid solution reclaiming. The plant removes $H_2S$ and $CO_2$ from a partial oxidation synthesis gas. Conversion to FLEXSORB® PS absorbent included draining the original solution, followed by water wash and

## TABLE VII

## FLEXSORB® PS Absorbent Demonstrates Capacity and Energy Credits in Commercial Syngas Plant

| | Conventional Amine-Solvent | FLEXSORB® PS Absorbent |
|---|---|---|
| Feed Rate | Base | 120% Base |
| Product | | |
| $CO_2$, vppm (feed = 6.5 mol%) | ---------- 10 ---------- | |
| $H_2S$, vppm (feed = 400 vppm) | ---------- 2.0 ---------- | |
| $CO_2$ removal | Base | 125% Base |
| Solution circulation rate | Base | 50% Base |
| Steam Rate | Base | 50% Base |

charging the FLEXSORB® PS solution. No mechanical modifications were required. Table VII compares the process performance of the FLEXSORB® PS absorbent and the conventional system it replaced. Despite removing 25% more $CO_2$, the required solvent circulation rate for the FLEXSORB® PS absorbent was 50% of that required with the existing conventional amine-solvent system. Since the tests were conducted at a constant steam ratio, i.e. lbs of steam per gallon of solution circulation, a 50% energy savings was realized with the FLEXSORB® PS absorbent. At the time of testing, the conventional solvent system had undergone considerable degradation which required higher circulation rates and steam rates relative to fresh solution. Had the conventional solvent been fresh solution, a 30% energy savings would have been expected.

The FLEXSORB® PS solvent has completed over four years of commercial operation in this unit. Overall operability of the solvent has been excellent. Amine degradation, which previously had been a serious problem, quickly reached equilibrium at a low level. Amine losses attributed to volatility or solution losses have been about 5% of the initial amine inventory per year.

FLEXSORB® PS absorbent has also been applied for treating natural gas at Esso Resources Canada Limited's Quirk Creek gas plant. This plant was designed to process 90M SCF/D of gas containing 8.9 vol% $H_2S$ using a commercially proven amine-solvent system. However, operation at the plant had been restricted to approximately 75% of design due to limitations in lean solution cooling capacity. Because of declining production at the fields, the loss in capacity was not a bottleneck. However, the Quirk Creek plant received approval to process additional gas from a nearby field. Processing the additional gas would require the full design capacity.

Mechanical modifications to increase the lean solution cooling capacity by 68% were initially considered to debottleneck the plant. However, subsequent engineering studies indicated that changeout to the FLEXSORB® PS solvent could achieve the necessary plant debottleneck with no mechanical modifications.

During March of 1985 the Quirk Creek plant was converted to FLEXSORB® PS absorbent. Although the complete allocation of production gas was not available at the time of startup, sufficient reductions in both solution circulation rate and reboiler duty were demonstrated in order to ensure satisfactory operation at design capacity. Table VIII compares performance of the FLEXSORB® PS solvent with the conventional system. Because of declining gas supply, the gas rate for the conventional solvent test carried out in 1980 was 30% higher than for the FLEXSORB® PS absorbent test period. As a result, circulation rate and reboiler duties for FLEXSORB® PS absorbent were normalized upward so that comparisons could be made on a constant feed basis. FLEXSORB® PS solvent achieved the desired cleanup to 1/4 grain $H_2S$ and 3 ppm mercaptan at 61% of the circulation rate required for the conventional solvent. Reboiler duty was reduced by 20%. In addition, plant experience with the conventional solvent indicated that rich solution acid gas loading and temperature had to be limited in order to alleviate equipment fouling caused by amine degradation.

TABLE VIII

FLEXSORB® PS Absorbent Application at Quirk Creek Natural Gas Plant

| | Conventional Amine-Solvent | FLEXSORB® PS Absorbent |
|---|---|---|
| Inlet Gas Rate, MSCF/SD | 70 | 52 |
| Inlet gas composition, mol pct | | |
| $H_2S$ | 9-10 | 9-10 |
| $CO_2$ | 4.1 | 4.1 |
| Sales Gas Quality | | |
| $H_2S$, vppm | 1 | 1 |
| RSH/ vppm | 3 | 3 |
| Process Parameters | | |
| Solvent Circulation Rate | Base | 61% Base* |
| Reboiler Duty | Base | 80% Base* |
| Projected Maximum Inlet Gas Rate, MSCF/SD | 70 | 90.0 |

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*Normalized to constant feed rate

No such fouling or sludge formation was experienced with FLEXSORB® PS solution even though rich acid gas loadings and temperatures were substantially higher. Latest operations with the complete allocation of gas indicate that the FLEXSORB® PS solvent has achieved the desired debottleneck (see Table VIII).

While the FLEXSORB® PS solvent has found the initial use in retrofit applications, the benefits of the high capacity solvent can be sometimes best realized in grassroots applications where significant reductions in capital equipment are possible. Table IX compares the use of FLEXSORB® PS absorbent to conventional technology for acid gas cleanup in a large liquefied natural gas plant. FLEXSORB® PS solvent circulation rate was 24% lower than the conventional amine-solvent system. In a grassroot design, this

TABLE IX

FLEXSORB® PS Absorbent Has Significant Credits in Grassroots Applications

Basis: 60 MSCF/SD. 850 psig natural gas

| | Feed Mole % | Treated Gas VPPM |
|---|---|---|
| $CO_2$ | 18.5 | 50 |
| $H_2S$ | 0.1 | 4 |

| | Conventional Amine Solvent | FLEXSORB® PS Absorbent |
|---|---|---|
| Process | | |
| ● Solution GPM | 124% Base | Base |
| ● Steam | 104% Base | Base |
| ● Power | 120% Base | Base |
| Economics | | |
| ● Investment, M$ | +12 | Base |
| ● Operating Costs, M$/Yr | +2.2 | Base |

lower circulation rate would result in significantly smaller equipment designs. Estimated equipment savings of 12 million dollars were calculated. Energy use including regeneration steam and power for solution circulation were lower, resulting in estimated annual energy savings of 2.2 million dollars.

## CONCLUSIONS

Exxon researchers were the first to recognize the dimensions and practical importance of the new area represented by hindered amines. Before we began our research on gas treating, some investigators(6,7) had observed that hindered amines give unstable carbamates. Other investigators(16) had pointed out the importance of a low carbamate stability (low $K_c$) in order to obtain high capacity.

The discovery of hindered amines represents an example of how application of first principles and experimental observations led to new industrial gas treating absorbents. As of today, fourteen commercial units are using hindered-amine-based absorbents. Additional commercializations are in preparation.

At the very beginning of our investigations, we decided to look for a drop-in application, i.e. an application that could be used in existing plants. In addition to lowering energy consumption, hindered amines increase the output of existing plants, i.e. they can debottleneck the plant. In the case of new plants, the higher solution capacity leads to lower solution circulation and lower energy consumption which is reflected in smaller equipment and capital savings.

Use of hindered amines represents new advances in gas treating. Steric hindrance of amines improves acid gas removal by lowering carbamate stability. In addition to saving energy and capital in gas treating significantly, the hindered amines used in practice have much better stability than conventional amines. Hindered amines have low or no amine degradation.

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