

SELECTIVE AMINE TREATING USING TRAYS, STRUCTURED PACKING, AND RANDOM PACKING

Ralph H. Weiland*, **Biliana Oettler****, **Christoph Ender*****, **John C. Dingman******

* Koch-Glitsch, Inc., Dallas, TX, USA

** Koch-Glitsch GmbH., Viernheim, Germany

*** Koch-Glitsch, Inc., Wichita, KS, USA

**** Optimized Gas Treating, Inc., Houston, TX, USA

ABSTRACT

Amine treating-plant selectivity for H₂S removal (and CO₂ rejection) can be greatly influenced by the choice of tower internals, yet this fact seems not to be well-known to most practitioners. A practical example of a case study involving acid gas enrichment to produce a super-rich Claus sulfur-plant feed is presented. The example shows how selectivity can be increased by using packing rather than trays, and the ability of random and structured packings to maximize CO₂ slip is compared and evaluated. The reasons for the superior mass transfer performance of packing in this application are explained in terms of the hydraulics and its effect on the fundamental mass transfer parameters that control the separation process itself.

INTRODUCTION

Total acid gas removal processes are relatively simple to design, build, and operate but their economics are frequently poor. The economics of processes capable of *selective* removal of H₂S and either maximum CO₂ rejection or the production of a treated-gas with a specified CO₂ content (typically 2 to 3%) is usually a major factor in process selection. This is primarily due to the reduction in the amount of CO₂ pickup, resulting in lower solvent circulation rates, better quality sulfur plant feed, and concomitantly lower capital and operating costs.

There are two levels of selectivity: (i) *controlled* selectivity in which the goal is to produce a gas with specified maximum levels of both CO₂ and H₂S, and (ii) *maximum* selectivity where the goal is to maximize the rejection of CO₂ consistent with any maximum H₂S specification on the gas being treated. The majority of natural gas specifications fall into the first category wherein a specified degree of selectivity is required. This can be achieved using mixed (so-called formulated) solvents, many of which are based on mixtures of MDEA with another primary or secondary amine used as an activator (or promoter) to adjust the level of CO₂ absorption. Nevertheless, maximum selectivity is not an uncommon goal.

This paper focuses on maximum rejection of CO₂. One of the most common gas treating applications falling into this category is tail-gas treating. Another somewhat more challenging example is treating natural gas streams with relatively low total acid gas contents and very high CO₂ to H₂S ratios, but where the amount of H₂S necessitates its removal. Single step treatment of high CO₂-to-H₂S-ratio sour gas streams frequently produces an acid gas too low in H₂S content for a satisfactory Claus plant feed. For such applications, it may be desirable to use a selective first-stage H₂S removal process, followed either by a process for bulk CO₂ removal from the remaining high-CO₂ stream, or blending it with other treated gas streams without exceeding the CO₂ specification of the combined streams. An alternative is to upgrade the amine plant regenerator off-gas to produce a super-rich Claus feed or, if the H₂S to CO₂ ratio is extremely low, to concentrate the H₂S into a much smaller volume stream for possible disposal by down-hole reinjection. Off-gas upgrading is an interesting application because the gas being treated is essentially a wet acid gas. The hydrocarbon or inerts content is so low that absorption takes place extremely rapidly, and a very short, well-designed absorber must be used. Whichever approach to high CO₂ rejection is taken, success will be enhanced not only by selecting the right chemical process, but by judicious selection of tower internals, as well. Off-gas upgrading is the example chosen for study in this paper.

In high CO₂-rejection applications, the traditional engineering approach of column over-design is completely unacceptable. First, a column with too many trays or too much packing removes more CO₂ than necessary. Secondly, the additional CO₂ removed by the extra trays can result in abject failure to meet the H₂S specification altogether [4]. There is an optimal number of trays and an optimal depth of packing that maximizes CO₂ rejection while still meeting the H₂S treating goal. In addition, some types and designs of internals are better than others in these applications.

Interstage cooling can also be effective for increasing CO₂ slip because CO₂ absorption continues throughout the height of an absorber used for selective H₂S

removal [2]. Temperature bulges are often large and continue into the upper region of the column where the high temperatures *increase* the CO₂ absorption rate via higher reaction rates with the amine. High temperatures and higher-than-normal solvent CO₂ loadings in the top trays of absorbers frequently require larger solvent circulation rates to reduce the size of the temperature bulge on the top trays.

Three difficulties that face the designer are (a) deciding what type of tower internals to use, (b) determining the optimal number of actual trays or depth of packing (of a specific type) and (c) deciding on how to provide enough flexibility to be able to handle the inevitable changes in the volumes and acid gas composition experienced over the life of most plants. For the operator of a high-CO₂-rejection facility, the problems are connected with the counterintuitive nature of some of the strategies used to optimize the operation for a specific case on the one hand, and the flexibility needed to adjust operation for new feed gas conditions and bring an off-specification operation back into conformity, on the other.

Mass transfer rate based simulation provides rigorous, predictive modeling of the process and its columns, and it is an extremely valuable tool for predicting the sensitivity to variations in both design and operating parameters. One of the reasons mass transfer rate based simulation is so valuable is that it makes use of a much more detailed description of the actual mass transfer devices involved. The detailed design and actual number of real trays and packing depth, type, and packing materials replace theoretical idealizations of stages or HETPs [5]. In this paper we use the *ProTreat*[™] gas treating process simulator to uncover ways to maximize CO₂ slip and relate the findings to column internals details and actual column structure. Some changes needed to improve CO₂ slip are counterintuitive.

UNDERSTANDING SELECTIVITY

The key to a basic understanding of selectivity is really quite simple: it is the fact that all alkaline solvents are *thermodynamically* selective towards CO₂ but they are *kinetically* selective towards H₂S. However, if we are to use this understanding to figure out how to increase CO₂ slip (i.e., to improve selectivity) then we must also recognize two other important facts about acid gas-amine systems: (1) CO₂ and H₂S react quite differently in alkaline solution, and (2) their physical absorption rates are controlled by resistances in different phases and depend on the tower internals used.

Reaction Effects

When CO₂ dissolves into the solvent, it binds chemically to the amine at finite rates of reaction, forming reaction products. At low temperatures, these reaction products are stable and require heat and stripping vapor to decompose them and reverse the reactions. On the other hand, when H₂S dissolves into an amine, it converts immediately to sulfide and bisulfide ions via simple instantaneous protonation reactions with hydrogen ions, without directly involving the amine at all. These protonation reactions are immediately reversible and the extent of reversibility depends on solvent alkalinity, not reaction kinetics. While CO₂ reacts relatively slowly and H₂S rapidly, the CO₂ forms stable reaction products, whereas, H₂S forms readily-decomposed products in a reaction that depends only on alkalinity. What do these

[™] *ProTreat* is a trademark of Optimized Gas Treating, Inc.

differences imply for relative absorption rates?

If the gas mixture and the solvent are exposed to each other for only a short time, H₂S absorbs more rapidly than CO₂ because the instantaneous H₂S reaction keeps the H₂S concentration in the unreacted form low in the liquid, and this maintains the driving force high. However, the CO₂ reaction isn't fast enough to prevent its concentration from building up and slowing down its absorption rate. The reaction kinetics have made the process selective towards H₂S. If, on the other hand, we allow the phases to remain in contact for a long time, both gases continue to absorb, but as the CO₂ absorbs it consumes amine and reduces the solvent's alkalinity. At some point as the process continues, this reduced alkalinity becomes too low to keep all the H₂S in a protonated form. Consequently HS⁻ and S⁼ deprotonate and the H₂S starts to desorb. Meanwhile, CO₂, still driven by the (almost) irreversible reaction, continues to absorb and react. Reaction equilibrium favors keeping CO₂ in solution even to the extent of releasing already-absorbed H₂S if necessary. The trick to controlling selectivity is a combination of manipulating the factors affecting the chemistry, because changing the reaction kinetics profoundly affects the CO₂ absorption rate, and partly by controlling contact times. But there is more to the story.

Mass Transfer

Although greatly influenced by CO₂ reaction kinetics, the absorption of both gases is also controlled by diffusion. For CO₂, the diffusional resistance is predominantly in the liquid phase, but for H₂S it is in the gas phase. This means that by cleverly selecting the tower internals to favor mass transfer of an acid gas through one phase over the other, it should be possible to alter the relative absorption rates, hence the selectivity. (There are other reasons for choosing one type of internal over another, such as fouling tendency, pressure drop, and cost; however, the focus here is on their mass transfer characteristics.) Selection of tower internals gives one an additional means to enhance CO₂ slip. This approach has been addressed in a limited way by Darton et al. [1] and Sardar et al. [3]. So, the secret lies in (a) choosing an amine with the right alkalinity and the right reactivity towards CO₂, (b) allowing gas-liquid contact for the right length of time, and (c) using the right kind of equipment with the right internals.

CASE STUDY: REGENERATOR OFF-GAS CONCENTRATION

The study is concerned with enriching a dilute regenerator off-gas to turn it into a suitable sulfur-plant feed. This is a very difficult situation to simulate, not only because the component separation is completely dependent on relative *rates* of mass transfer, but because the entire gas phase is capable of being absorbed if too much solvent is used. The gas being enriched is essentially a wet H₂S-CO₂ stream at 43C and 170 kPa, flowing at 300,000 Nm³/day. The solvent is 40 wt% MDEA at 50C. A conventional absorber-regenerator flowsheet is used with a 1.5-m diameter regenerator with up to 20 two-pass Koch FLEXITRAYS. Reboiler duty is 7.3 MW.

Three feed gas dry-basis analyses are considered: 1, 2, and 5 vol% H₂S with the balance CO₂ and, for the case of 1 vol% H₂S in the feed gas, three solvent rates are examined: 70, 80, and 90 m³/hr. Both the trayed and packed contactors were sized for 80% flood.

Performance of Trays

Figure 1 shows the effect of tray count (FLEXITRAYS) and solvent flow on the residual H₂S in the treated gas. The absorber here contained two-pass Koch FLEXITRAYS trays in a 1.67-m diameter shell. Higher solvent rates give lower residual H₂S levels, as expected. However, in each case there is an optimal number of trays for which the H₂S content is minimum. For very small tray counts there is insufficient contact to get to very low H₂S levels and, as the number of trays is increased, H₂S pickup improves; however, as the number of trays continues to increase, performance starts to deteriorate. This is because the increased contact results in increased CO₂ pickup which is detrimental to H₂S removal.

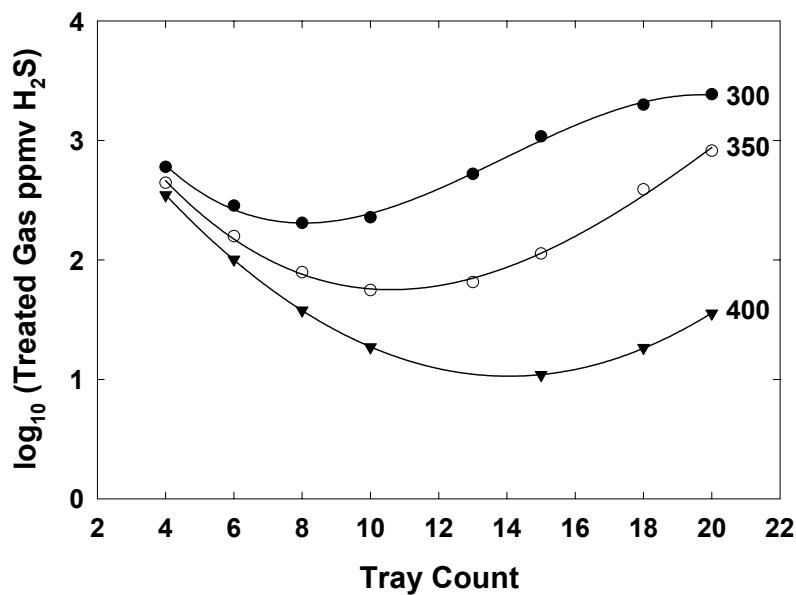


Figure 1 Residual H₂S in Treated Gas at Three Circulation Rates (m³/hr); Feed Gas Is Being Enriched From 1% H₂S. Note Logarithmic Y-Axis.

This can be seen in Figure 2 which shows deteriorating sulfur-plant feed quality as the tray count is increased. Because higher solvent flows can pick up more acid gas, the optimum tray count for best H₂S removal is an increasing function of solvent flow. Of course, the limit is zero enrichment which occurs when the tray count and solvent rate becomes high enough for total acid gas pickup.

Figure 3 shows the effect of feed-gas H₂S content on the degree of enrichment as a function of tray count and Figure 4 shows the corresponding treated gas residual H₂S concentration. Again, there is an optimal number of trays for maximum H₂S recovery. However, as expected from the kinetic preference for H₂S versus the thermodynamic selectivity for CO₂, the highest degree of enrichment corresponds to the fewest number of trays, but then the H₂S recovery is poor. Thus, when it comes to tray count, there is always a tradeoff between fractional recovery and enrichment.

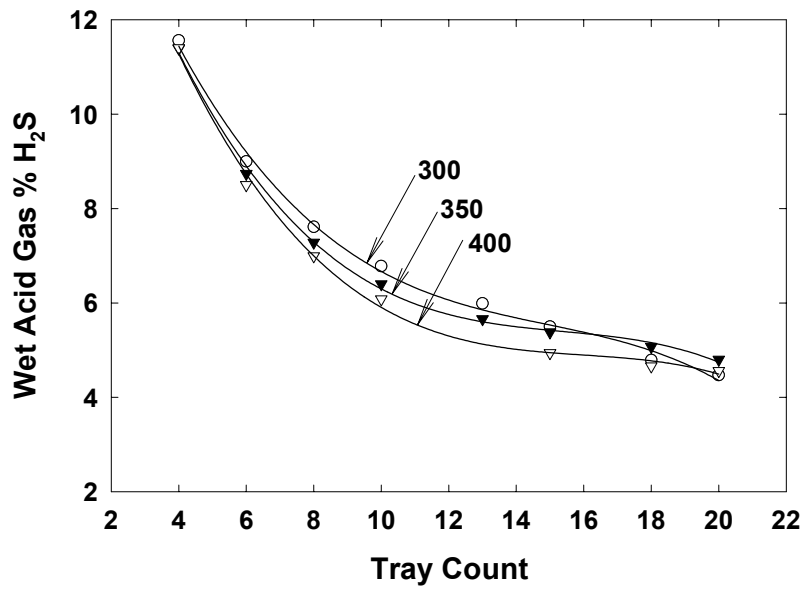


Figure 2 Effect of Tray Count on Enrichment of a 1% H₂S Feed Gas at Three Circulation Rates

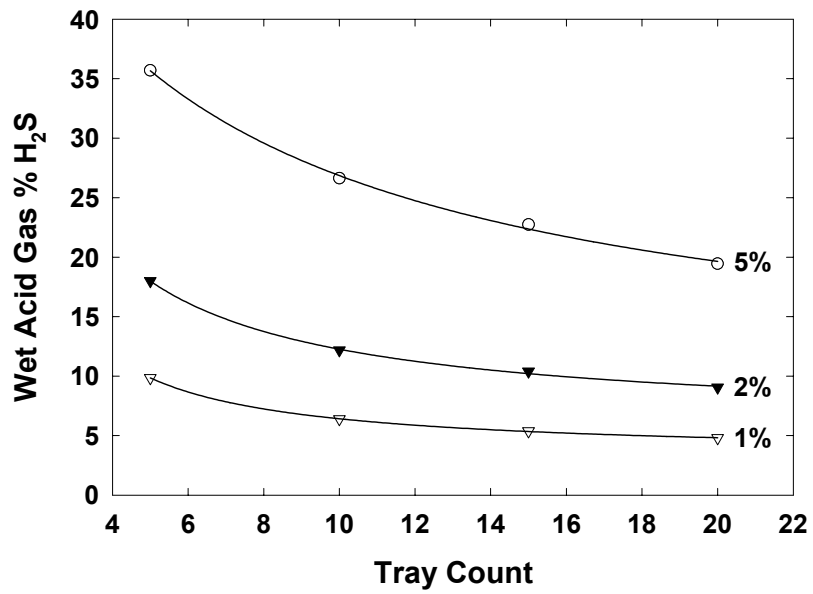


Figure 3 Effect of Tray Count on Enrichment of 1%, 2%, and 5% H₂S Feed Gas at 80 m³/hr

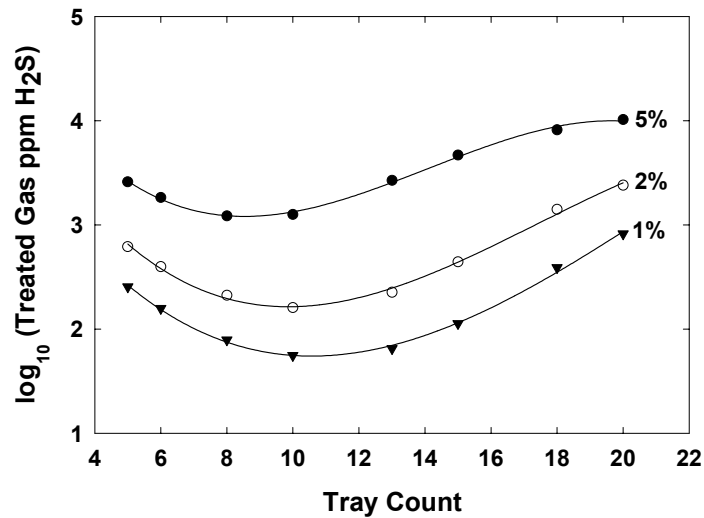


Figure 4 Treated Gas H₂S Content After Enrichment of 1%, 2% and 5% Feed Streams with Solvent at 80 m³/hr. Note Logarithmic Y-Axis.

Performance of FLEXIRING Random Packing

This section discusses the use of 50-mm steel FLEXIRINGS in the same acid gas enrichment operation with 40 wt% MDEA. In this case, the tower diameter required for 80% flood at the highest flows was only 1.37 m. Figure 5 shows that the residual H₂S in the treated gas decreases exponentially with increasing depth of packed bed (note that the y-axis is logarithmic). Solvent circulation rate appears to have very little effect on treated gas quality.

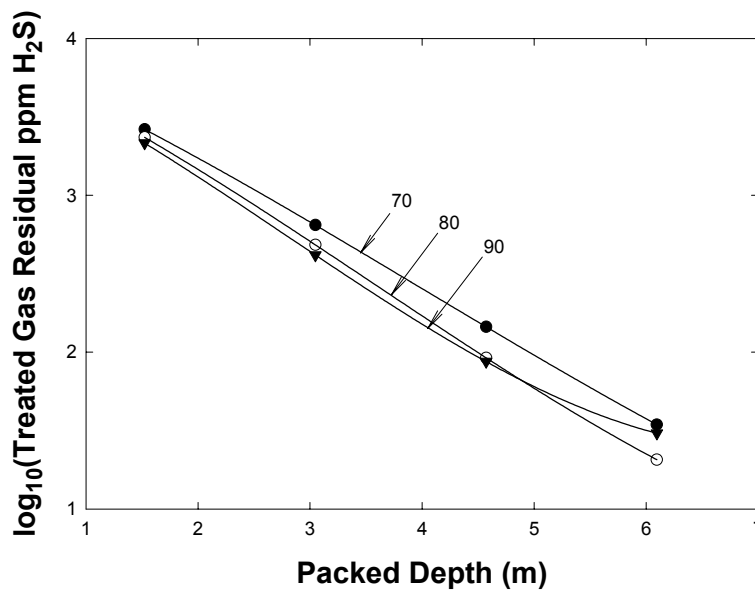


Figure 5 Effect of Bed Depth on Treated Gas Quality After Enrichment at Three Solvent Rates (m³/hr). Note Logarithmic Y-Axis.

The quality of the enriched gas stream is shown in Figure 6. The improvement that random packing affords over trays is truly remarkable. Referring to Figure 2, the best that could be achieved under these same circumstances using trays was about a tenfold enrichment. FLEXIRINGS produce a thirty-fold enrichment, taking a stream of 1% H₂S in 99% CO₂ and enriching it to about 30 mol% H₂S. Depending on the solvent rate, trays may or may not achieve a cleaner treated gas; however, the cost is always a tremendously reduced quality of Claus sulfur plant feed.

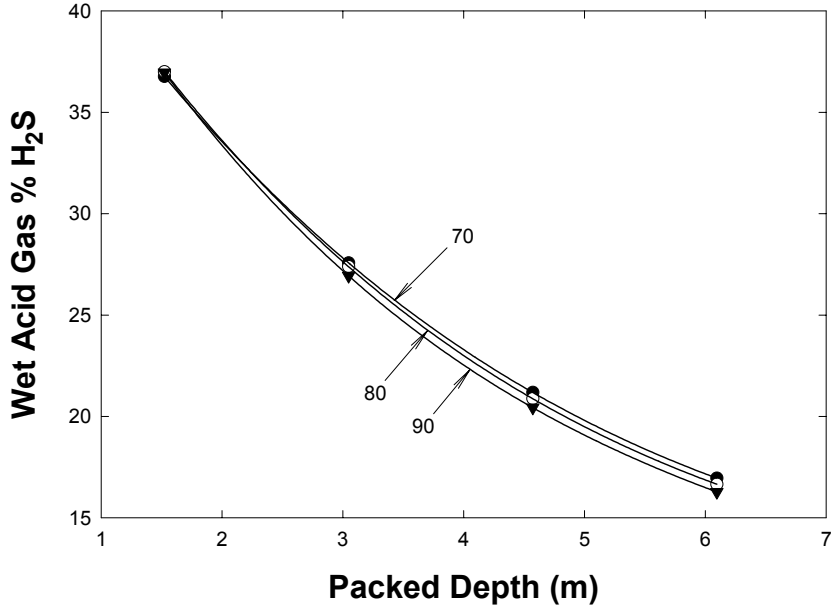


Figure 6 Enriched Wet Acid Gas Stream Obtained at Various Bed Depths of FLEXIRINGS and Solvent Rates (m³/hr) with 1% H₂S in Feed Gas

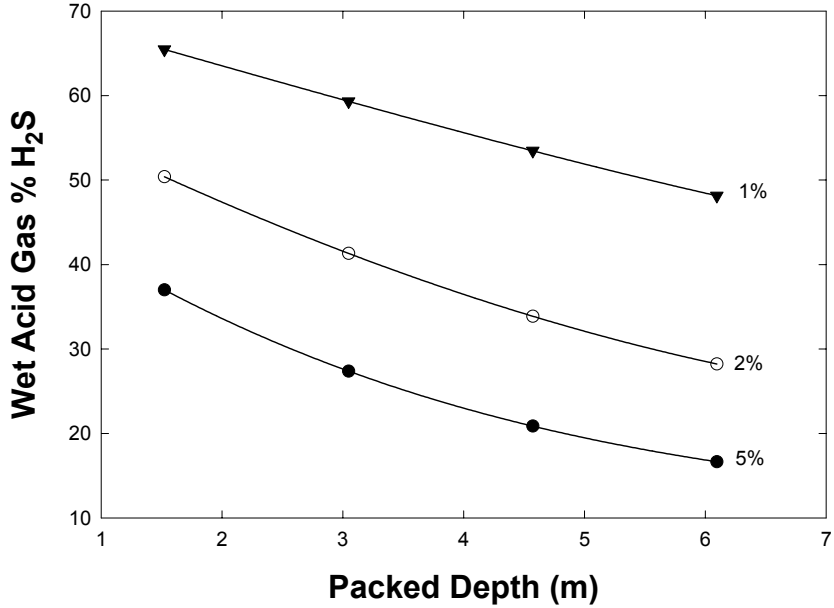


Figure 7 Effect of FLEXIRING Bed Depth on Enrichment Achievable From Feed Streams Containing 1%, 2%, and 5% H₂S in CO₂

Figures 7 and 8 show the enrichment possible from acid gas streams containing 1%, 2% and 5% H₂S in CO₂, and concomitant level of treating, respectively. Figure 7 shows that the production of sulfur plant feed of outstanding quality from problem off-gas streams is quite achievable. As shown in Figure 8, residual levels of H₂S in the treated gas comparable to those produced with trays can also be reached.

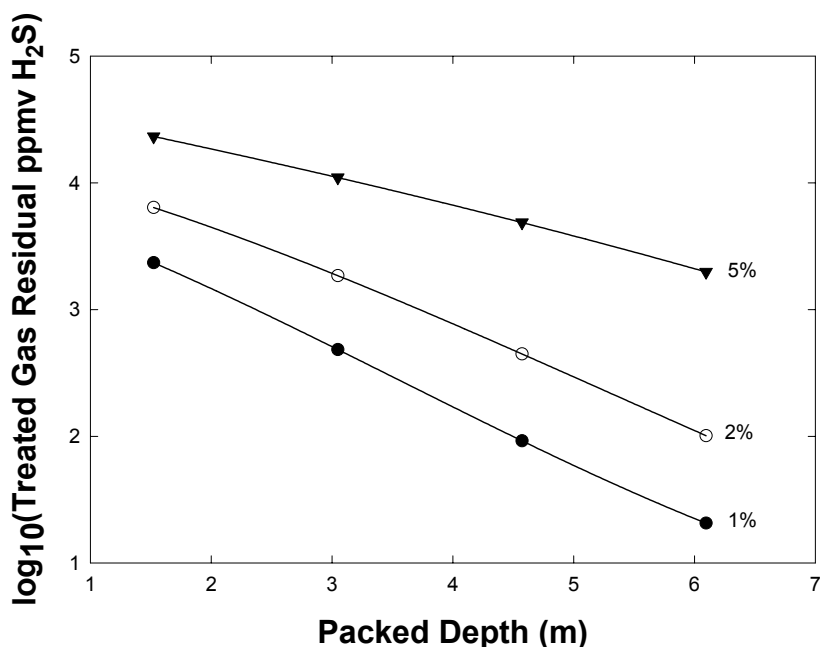


Figure 8 Residual H₂S in Treated Gas for Various Feed Gas H₂S Concentrations.
Note Logarithmic Y-Axis

What has been done here is to take a problem off-gas stream containing levels of H₂S that are hopelessly low for use in a sulfur plant (and probably too high to make a sulfur scavenger economic) and produce a very high quality sulfur plant feed. The residue is a very dilute stream of H₂S in CO₂ which must be disposed of, but at these small concentrations of H₂S, both flaring and scavengers become more attractive.

Structured Packing

FLEXIPAC[®] 3Y is a structured packing with a specific surface area similar to 50-mm FLEXIRINGS. Both its gas- and liquid-side mass transfer coefficients are a little higher than 50-mm FLEXIRINGS, and its wetted surface area is also greater. This means that a shorter bed of FLEXIPAC will provide about the same selectivity as FLEXIRINGS. However, the pressure drop per unit of packed depth for FLEXIPAC is lower for the same gas and liquid traffic and, because a shorter bed can be used, the overall pressure drop will be reduced even more. This is an important factor in very low pressure applications such as tail gas treating and CO₂ recovery from power plant exhaust gases; it is unimportant in most other applications. However, the shortness of the packed bed can represent significant cost savings in tower shell.

Summary

Process selectivity for H₂S and the ability to reject CO₂ are well known to be dependent on the amine's reactivity towards CO₂. A fact generally ignored (and apparently little-known) by practitioners in the field, however, is that choosing the right tower internals also has a profound effect on selectivity. Because of inherently

better mass transfer characteristics (high vapor- and low liquid-film coefficients) packed columns are much more selective towards H₂S than trays. Improved selectivity is achieved by high CO₂ rejection and this results in lower solvent circulation requirements and, therefore, smaller columns.

The ability to predict quantitatively the kinds of effects described here depends on the use of mass transfer rate based modeling. This is a very powerful simulation tool that accounts not only for process conditions, but also for the type of tower internals and the physical details of construction. A mass transfer rate based absorber model is essential to the success of simulation of acid gas enrichment simply because competitive mass transfer rates, not phase equilibrium, determines the actual separation and the degree of enrichment achieved. This is especially true when packing is used because current equilibrium stage simulation tools are completely unable to recommend the depth of packing needed to achieve a given treating goal. A true mass transfer rate model such as *ProTreat* is required.

REFERENCES

1. Darton, R.G.; Hoek, P.J.; Spaniuk, J.A.M.; Suenson, M.M.; Wijn, E.F.; *The Effect of Equipment on Selectivity in Amine Treating*, I. Chem. E. Symp. Ser. No. 104, pp A323-A345, (1987)
2. Katti, Sanjeev S.; Langfitt, Bruce D.; *Effect of Design and Operating Variables on the Performance of Commercial Absorbers Used for Selective Chemical Absorption*, Paper Presented at AIChE Spring National Meeting, New Orleans, LA, March 6-10 (1986).
3. Sardar, H.; Sivasubramanian, M. S.; Weiland, R. H.; *Simulation of Commercial Amine Treating Units*, 35th Annual Laurance Reid Gas Conditioning Conference, Norman, Oklahoma, March 4-6, 1985.
4. Weiland, R. H.; Dingman, J. C.; *Column Design Using Mass Transfer Rate Simulation*, Pet. Technol. Quarterly, 139-143 (2002).
5. Weiland, R.; Hardy, R.; *Use Packing to Improve Selectivity in Amine Treating*, paper presented at Annual AIChE Meeting, Reno, NV, Nov. 2001.