Selective Absorption Using Amines

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ABSTRACT

The selective removal of H2S from gas streams containing CO2 has become of widespread interest as a means to reduce equipment sizes and operating cost. A selective absorption design capability has been added to the amine sweetening process simulation program, TSWEET. The program results agreed closely with selective absorption data using MEA at contact times of about 0.4 seconds. The program calculations also agreed with a 40% CO2 rejection measured in a DEA absorber operating at 11 psig and 2 seconds residence time per tray. A 6-ft diameter absorber using 15 wt% MDEA was also used for comparison. The calculated H2S in the sweet gas was well within the scatter of the data while the calculated CO2 rejection was about 10% high. The process simulation program accurately represents the selective absorption process including the influence of all process variables.

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INTRODUCTION

Amine sweetening technology has been used on a commercial scale to treat natural gas for over 80 years. Most of the revolutionary innovations available from this process have probably been realized. However, until recently, there has been little impetus to fully explore certain aspects of this technology. Natural gas was cheap enough to allow the operation of amine sweetening units at very poor efficiencies, and environmental considerations did not preclude emission of significant amounts of SO_2 in tailgas streams from a Claus recovery unit.

The traditional method of operating sweetening units has been to remove all the CO_2 along with the H_2S in the sour gas feed. This causes three problems that must now be addressed. First, each lb of CO_2 absorbed by the amine solution requires the expenditure of 200 to 600 Btu’s to remove the CO_2 in the stripper. A larger circulation rate of amine is also required to carry the CO_2 in addition to the H_2S. If the H_2S to CO_2 ratio is 0.1, 90% of the amine circulation is being used to transport CO_2, necessitating oversized pumps, columns, and exchangers.

Second, a high CO_2 concentration will cause problems in the sulfur recovery unit. For example, in Claus units, designs which bypass the burner with part of the acid gas streams must be used for concentrations of less than about 25% because of flame instabilities. Sulfur recovery is much better if the feed stream is close to 50% H_2S. This means that as more CO_2 is rejected, more H_2S can be converted to elemental sulfur in the Claus unit, and therefore, less SO_2 will be vented to the environment (or removed by the tailgas scrubbers).

The third area of concern is in treating the tailgas from a Claus sulfur recovery unit. After passing through a reactor with a reducing atmosphere, the tailgas will primarily consist of CO_2, N_2, H_2S, and water. The CO_2 content is usually on the order of 10%. Since the acid gases from this amine unit are recycled to the front of the Claus unit, minimum CO_2 pickup is absolutely essential for the efficiency of both the Claus and amine units.

These considerations have recently caused an upsurge of interest in selective absorption. Other considerations which have contributed to this interest is the growth of the synthetic fuel industry, which produces sour gases containing significant amounts of CO_2. Several processes, such as Shell's SCOT process and Phillips' HS process, have begun to be used on an increasingly large scale. Both of these processes use modified contactor design and a tertiary amine (MDEA) to selectively remove H_2S from high CO_2, low pressure streams.

The performance data for these units were collected by the companies doing the design work and are held by them as trade secrets. Very little data on the performance of such units are available in the literature. Data have been released showing the rate constants for CO_2 in DEA and MEA for very light loadings and very low wt% amine solutions.

This data is, for the most part, worthless for design purposes, since very extended extrapolations are necessary to reach the operating region for commercial units. The results from the extrapolations show equilibrium residence times on the order of .001 second which is obviously not correct for commercial units.

We have recently added a selectivity capability to our amine sweetening process simulation program, TSWEET. The program will predict the degree of selectivity which can be obtained from MEA, DEA, DGA, or MDEA as a function of solution residence time on a tray. The results from the new capability are being compared to data for as many cases as can be obtained. In this paper, three cases from the literature are used for comparison. Some general trends based on the program are also presented.

THE SIMULATION PROGRAM

TSWEET is an advanced process simulation program using the flexible flowsheet concept. Beginning with the process flowsheet and operating parameters, complete material and energy balances for the steady state operating conditions can be performed. Rigorous tray by tray calculations using the Ishii-Otto method are used to predict the design of the stripper and absorber columns. Some 21 chemical species are allowed, including the four amines mentioned above, water, H_2S, CO_2, and an assortment of gases commonly present in natural and synthetic gases.

Vapor pressures of H_2S and CO_2 over the amine solutions are calculated by a modified Kent and Eisenburg equilibrium model. A kinetic model was developed to predict the effect of residence time, temperature, solution concentration, pressure and type of amine on the rate of CO_2 absorption. Henry's law constants are used to determine the solubility of the other vapor species in the liquid phase. We are presently working on extending this model to liquid sweetening systems.

The program has been demonstrated to be very reliable in calculating the performance of amine sweetening plants where essentially all of the acid gases are removed. In these plants, residence times are long and usually have little effect on the performance of the plant. For selective absorption units, performance data are limited.

DISCUSSION OF RESULTS

The results from the new selective absorption capability are compared to the data for three cases reported in the literature. In addition, some general selective absorption trends based on the program are presented.

Selective absorption with MEA

Gregory and Wichert[1] demonstrated a method to achieve selective absorption with MEA, the most common amine which has shown little tendency for selectivity in 80 years of use. The method involved injecting MEA solution into a "precontactor" at the bottom of a conventional absorber. The precontactor consisted of a static mixer as shown in Fig. 1. This mixer allowed about a 0.4 second contact time between the amine and the sour feed gas. The precontactor removed a sizeable fraction of the acid gases and thereby significantly reduced the load on the absorber.

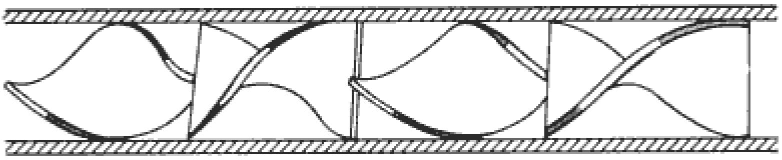

Figure 1. Typical static mixer section used by Gregory and Wichert.[1]

The precontactor was simulated as one ideal stage with a residence time of 0.4 second. The program results are compared to the data in Fig. 2. The H_2S curve produced from the program exhibits the same trend as the data and is within the scatter of the data. The CO_2 curve is also within the scatter of the data and has essentially the same trend. Due to the larger scatter, the trend of the CO_2 data is not as well defined as for the H_2S.

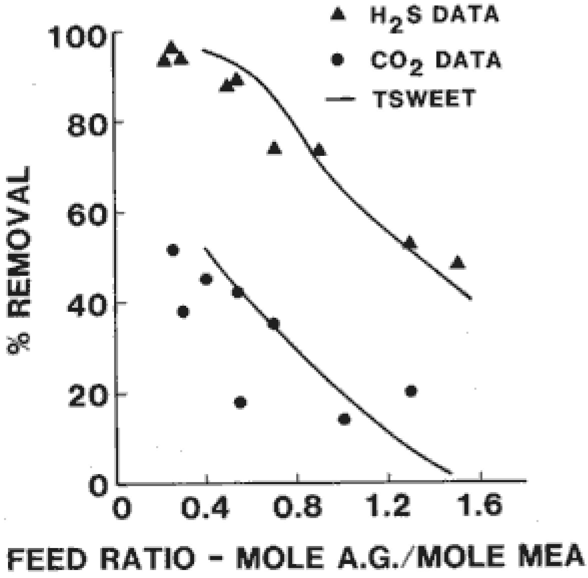

Figure 2. Comparison of TSWEET to static mixer absorption data of Gregory and Wichert.[1]

Thus, selective absorption can be obtained for MEA under the proper conditions of very short contact times. Furthermore, the simulation program is able to accurately represent the selective absorption process with MEA.

Selective absorption with DEA

Donnelly and Henderson[2] report on a DEA contactor system where selective absorption was obtained unexpectedly. The system consisted of two contactors operating in series with a compressor between them. The first contactor was operated at low pressure (LP) and was used to reduce the acid gases sufficiently to eliminate the exotic materials requirement in the compressor. The second contactor was operated at a higher pressure

(HP) and was used to produce pipeline specification gas. The feed gas for this plant contained 7% H_2S and 2% CO_2.

The gas was fed to the LP contactor at 11 psig and boosted to 515 psig for the HP contactor. Equilibrium calculations based on conditions at the bottom of the LP contactor showed that 95% of the CO_2 should have been picked up. Instead, only 60% was picked up and 40% was rejected overhead from this unit. Table 1 shows the results from the actual operating data and the program calculations based on a residence time of 2 seconds per tray in the LP absorber.

Table 1. Comparison of Donnelly data to TSWEET results.

	Plant data	**TSWEET results**
Low pressure gas		
H2S, gr/100scf	2.1	17
CO2, %	0.72	0.78
Circulation Rate	112.5	112.5
High pressure gas		
H2S, gr/100scf	0.5*	0.3
CO2, %	Trace	2.0
Circulation Rate	~30	28
Lean amine		
H2S, gr/gal	50	50
CO2, mol/mol	0.005	0.005

*Specification was 1.0 gr/100 scf

As can be seen, the CO_2 rejection calculated by the program agrees very closely with the data. The H_2S concentration calculated by the program for the LP contactor does not agree with the data. According to our vapor-liquid equilibrium model which was verified with the Lee, Otto and Mather[3] data, the 2.1 gr H_2S/100 scf from the LP absorber would be in equilibrium with the lean amine from the stripper.

This would require that no CO_2 could be picked up on the top tray of the LP contactor, since any increase in the CO_2 loading of the amine would further increase the equilibrium partial pressure of H_2S over the stage. But this stage is where the maximum CO_2 pickup can be expected, since the CO_2 loading of the amine is at its lowest and the CO_2 partial pressure over the solution is at 40% of its feed value. Thus, the 2.1 gr/100 scf is believed to be an error in the data.

The behavior of the HP absorber is also very interesting even though no selectivity is exhibited. A solution flow rate of about 30 gpm resulted in a residence time of 2 seconds. The calculated H_2S concentration in the sweet gas is slightly lower than the value reported in the data. The H_2S was found to depend very strongly on solution flow rate. Figure 3 shows the results of several runs with different flow rates. At flow rates less than 23 gpm, the column suddenly fails to produce specification gas, since the H_2S concentration has increased by nearly an order of magnitude.

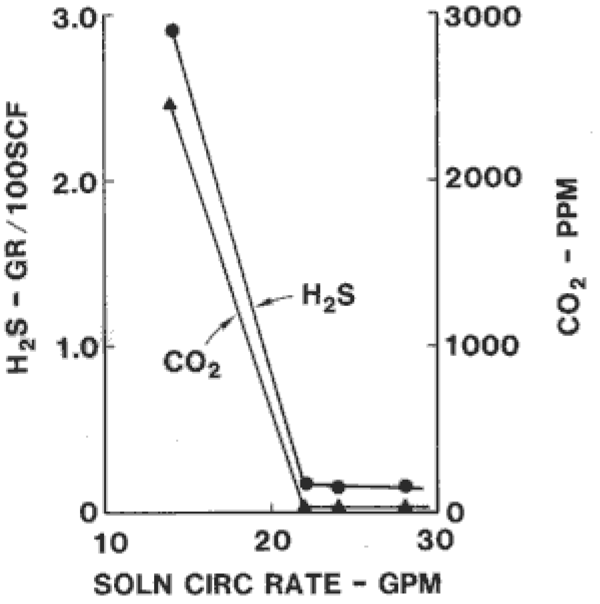

Figure 3. Calculated high pressure absorber performance at various solution circulation rates.

The printout for the column internal conditions for the HP absorber showed that the H_2S concentration in the gas does not begin to significantly decrease until the CO_2 has been reduced to less than about .001%. At flow rates of less than 23 gpm, there is not sufficient amine to collect all the CO_2. Thus, the column cannot pick up any significant amount of H_2S at the lower flow rates.

This comparison has two important features. First, it shows that in the HP absorber, no significant selectivity could be obtained. This is consistent with statements in the literature that selectivity is best accomplished at low pressures and low amine loadings. Second, it shows that under the proper conditions, DEA can function in a selective role. The LP absorber, operating at 11 psig, was able to remove virtually all of the 7% H_2S in the inlet stream, while leaving 0.5% CO_2 in the outlet gas stream. Under most conditions this degree of selectivity could be used to significantly reduce the amine circulation rate and heat load on a sweetening plant. However, it is probably not sufficient for tailgas treating.

Selective absorption with MDEA

Vidaurri and Kahre[4] report on a number of tests related to selective absorption. The authors conducted three series of experiments. The first series consisted of batch absorptions using four different amines. This data showed that all amines could be used selectively if conditions could be arranged properly. The next phase consisted of operating a small scale pilot plant with various amines under a wide variety of conditions.

This phase showed that MDEA could give the best selectivity under typical operating conditions encountered in the industry. The last phase consisted of the conversion of an industrial sweetening unit from DEA to MDEA. The data showed that significant selectivity was obtained from the updated unit. The data from this unit are used for comparison in the present work.

The inlet gas was at 78 psig and contained 8% H_2S and 1.5% CO_2. The absorber was 6 ft in diameter with 20 trays and a pressure drop of 3.5 in. of water per tray. The scrubbing solution was 15 wt% MDEA. Average operating conditions and a residence time of 2.5 seconds per tray were used for the simulation.

The data for the H_2S in the sweet gas are shown in Fig. 4 along with the program results. The values calculated by the program are well within the scatter of the data. The scatter is about +/-6 ppm about the data curve. The total solution loading where H_2S breakthrough occurs can also be compared in Fig. 4. The breakthrough value of 0.76 mole a.g./mole MDEA calculated by the program is about 6% lower than the value of about 0.81 mole a.g./mole MDEA from the data.

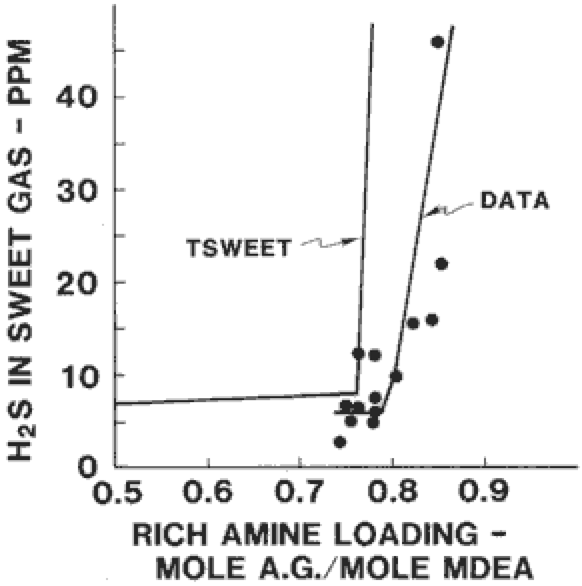

Figure 4. Comparison of TSWEET to data of Vidaurri and Kahre.[4]

CO_2 rejections of about 70% were reported for the absorber. The values calculated by the program were near 80% and were thus about 10% high. As can be seen from Fig. 2, all of the loadings reported for the data were near the maximum loading of about 0.8 moles acid gas/mole of amine. These loadings are much higher than for most industrial applications. Under conditions of very high and near equilibrium loadings, small changes in operating parameters tend to cause a much larger change in the column performance. This is probably the reason for most of the scatter in the data. Thus, one can conclude that the CO_2 rejection calculated by the program matches the data to within about 10%, which is essentially within the scatter of the data.

GENERAL TRENDS FOR SELECTIVE ABSORPTION WITH MDEA

Selective absorption is dependent on several process variables, some of which cannot be specified or controlled by the design engineer. The variables include absorber pressure, amine temperature, concentration of acid gases, residuals in lean amine, residence time and wt% of amine. Furthermore, each of these variables interacts to give a very complex system.

The influence of residence time and acid gas loading were chosen for presentation in the current work. The effect of residence time on each tray for a typical example is shown in Fig. 5. Obviously, the amine loading also varies as the CO_2 pickup increases. The H_2S concentration is nearly constant over the 1 to 5-second range for this case.

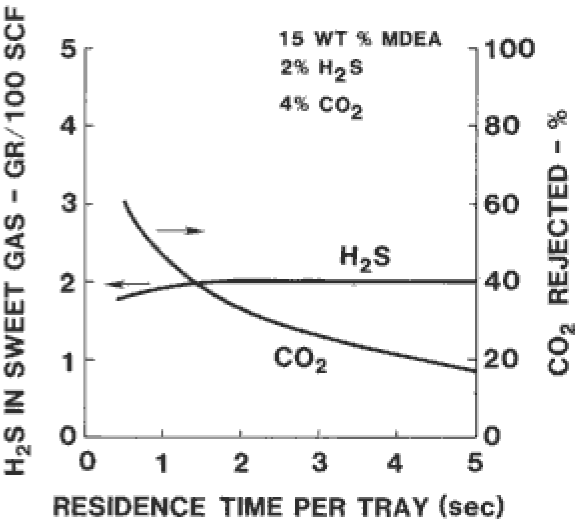

Figure 5. Effect of residence time on CO2 rejection.

The effect of amine loading is shown in Fig. 6. The CO_2 rejection increases sharply with loading. The H_2S in the sweet gas also increases with loading over this range.

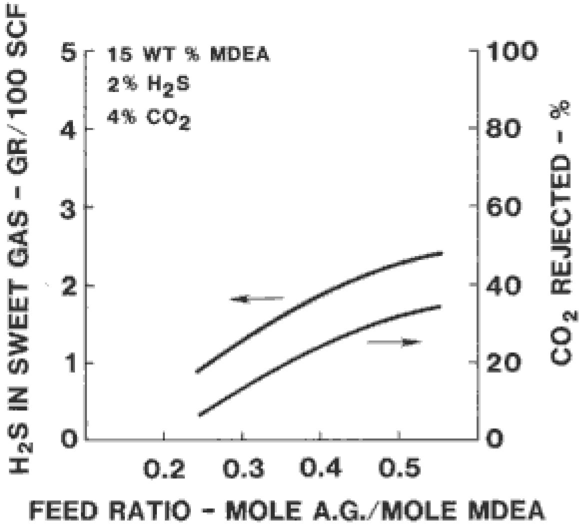

Figure 6. Effect of amine loading on CO2 rejection.

SUMMARY AND CONCLUSIONS

Selective absorption of H_2S from streams containing CO_2 has become of paramount interest. Although all amines have been known to be selective, their selective capability has not been commonly demonstrated on an industrial scale. A selective absorption capability has been added to the amine sweetening process simulation program, TSWEET. The program results agreed very closely with data for selective absorption of H_2S using MEA in a precontactor (static mixer) on an industrial absorber. The contact time was 0.4 second.

Good agreement was also found when the program was compared to an absorber using DEA and operating at 11 psig. The residence time was 2 seconds per tray. The CO_2 rejection in the absorber was about 40%. The overhead concentration was 0.72% CO_2 from the data compared to 0.78% calculated by the program.

A comparison was also made for a 6-ft diameter absorber using 15 wt% MDEA. The H_2S concentration calculated by the program for the sweet gas was well within the scatter of the experimental data. The H_2S breakthrough value of 0.76 mole a.g./mole MDEA was 6% below the data. The calculated CO_2 rejection from the absorber was about 10% above the data.

The process simulation program, TSWEET, has been demonstrated to accurately represent the selective absorption process. The model accommodates the influence of all process variables on the selective absorption process including pressure, temperature, amine type, acid gas concentration, amine concentration and residence times.

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