

TROUBLESHOOTING AMINE PLANTS USING MASS TRANSFER RATE-BASED SIMULATION TOOLS[§]

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ABSTRACT

Computer simulation models are indispensable tools for designing and troubleshooting amine gas treating plants. These models, especially ones based on *mass transfer* rate calculations, allow users quickly and accurately to design and rate equipment, to identify equipment malfunctions, and to recognize process limitations. Simulation models can also be used to predict areas of performance shortfalls and corrosion concerns, as well as provide considerable physical insight into plant operations and how process parameters interact in sometimes non-obvious ways.

This paper gives some important criteria and strategies for designing and evaluating amine plants. The discussion centers around three commercial case studies using detailed field data from a plant removing CO₂ from synthesis gas, from an off-shore plant processing natural gas, and from a plant removing CO₂ from a high pressure natural gas. Analysis of field data is used to demonstrate effective ways of applying both commercial and proprietary amine simulators to design and operating problems.

Introduction

For most of the time since gases first started to be treated to remove CO₂, H₂S, and other sulfur compounds, treating plants have been built with a 20-tray absorber and 20 tray regenerator, sometimes with two or three water wash trays added to the top of the regenerator. However, the last 20 years or so have seen tremendous improvements to treating technology. These have included (a) the more prevalent use of packing, mostly random but, of late, structured as well and (b) the introduction of a host of new amine chemicals, some highly reactive towards CO₂, and others not reactive at all, yet still quite alkaline. Other solvent advances encompass (c) the use of mixed amines or solvent blends. At present, packing's primary application is tail gas and liquid treating, although there are instances of structured packing being used in fairly high pressure ammonia synthesis gas contactors, as well as low fouling service. In future, the issues of global warming and reduction of greenhouse gases may drive large-scale CO₂ removal from power plant flue gases, and this will require the low pressure drops characteristic of structured packing.

The introduction and acceptance of new amines and solvent blends has been energy driven. For example, the ability to removal selectively H₂S from natural gas allows substantial amounts of CO₂ to remain in the treated gas, thereby reducing the energy required for solvent regeneration (about 80% of

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the cost of operating an amine plant). Another example is the use of MDEA-based solvents promoted by certain amounts of more reactive amines to remove CO₂ from gases while at the same time using much less regeneration energy and lower solvent circulation rates than the older amines. The technology of new amine treating chemicals has even incorporated partial neutralization of the amine with an acid to achieve the counter-intuitive result of much more complete solvent regeneration and higher purity treated gas. These improvements include the use of high efficiency packings (random and structured), use of alternative process configurations, and acceptance of specialty amine solvents that can provide specific treating characteristics. These new approaches to gas treating all depend crucially not just on different rates of reaction, but also on the effect of reaction rates on relative rates of mass transfer. Advanced mass-transfer rate-based simulation models are inherently aligned with, and completely at home in, this world of new gas treating technologies.

Mass-transfer rate-based simulation models use all the basic building blocks of other, more-traditional models, including material balances and phase equilibrium. But what sets them apart is simply that they use the mass transfer rate characteristics of the equipment and its internals to calculate the separation. Mass transfer rate models use the actual number of real trays supplied by the tray vendor, or the actual depth of the particular physical packing fabricated by the packing vendor and installed in the column. One expects a column containing 40 feet of a 1Y-style structured packing to give different mass transfer performance from the same column packed with 40 feet of 4X structured packing or 40 feet of IMTP-25 random packing, or 20 conventional valve trays. And one expects a reliable process simulator to give different answers in each of these circumstances, too. A mass transfer rate-based simulation model marries material balances, phase equilibrium, chemical kinetics, and the mass transfer characteristics of tower internals into a comprehensive, reliable, predictive tool.

The rest of this paper examines three case studies, each of which points out different aspects of gas treating and how mass-transfer rate-based simulation can be used to understand the process, to suggest better ways of operation, and to allow more efficient operation under changing circumstances.

Case Study 1

This study shows how simulation was used in a tricky retrofit situation. A client asked INEOS to assist in an engineering study of an ammonia plant, in which the plant was to be revamped to accommodate an MDEA-based solvent. The processing scheme is unusual in that absorber temperature is not controlled by heat exchangers on streams feeding the absorber, but by directly controlling reboiler energy flow in the regenerator.

Figure 1 shows the process flow diagram of the existing plant. Processing is done in a split flow configuration with a substantial semi-lean stream being drawn from an intermediate point in the regenerator and sent directly to a point near the middle of the absorber, without modulating its temperature. The remaining solvent continues down the regeneration column where it is further stripped to a low acid gas loading. The fully-stripped lean amine is cooled and then sent to the top of the absorber to provide CO₂ polishing. The raw syngas is described in Table 1. The target treated gas is less than 1000 ppmv CO₂.

As is true in all process plants, this unit has equipment limits such as maximum attainable solvent flows, maximum available reboiler energy, and limited cooler capacities. However, the most challenging and interesting aspect of this particular plant is the fact that there is no direct control on the temperature of the semi-lean stream feeding the absorber. The flow of this stream is 2.9–3.3 times greater than the fully-lean stream, so its temperature plays a dominant role in setting the absorber

temperature profile. It determines the performance of the absorber and, indeed, the entire unit. So it *must* be controlled, but how?

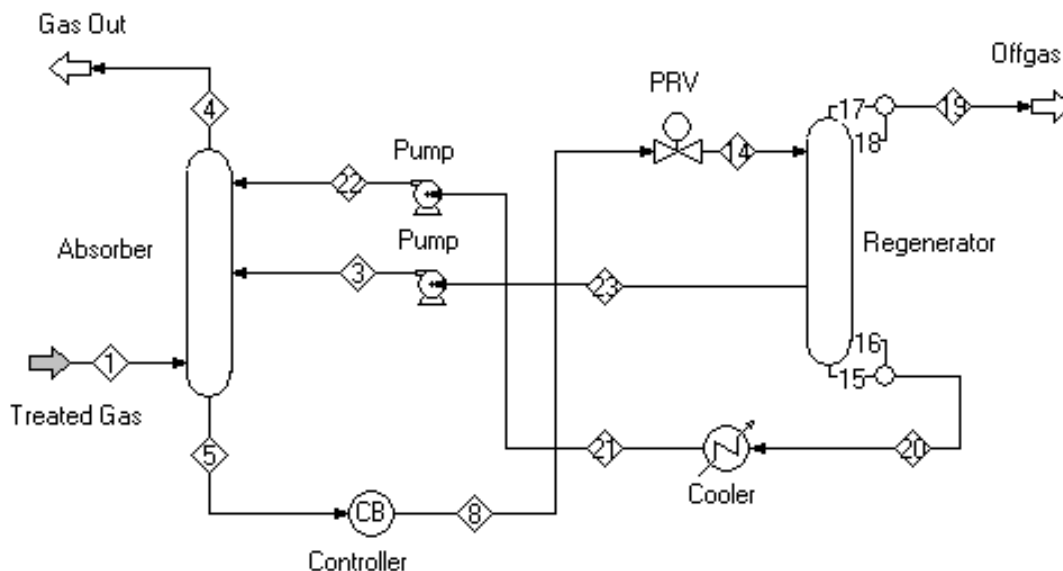


Figure 1 Process Flow Diagram of Ammonia Plant Syngas Treating Unit

It turns out that if this were a conventional regenerator, it would be called severely under boiled at any point within the range of operating conditions of the process. The regenerator is so lightly reboiled relative to the total solvent flow to the column, that the steam flow through the regenerator completely collapses within the first few feet from the bottom. In essence, the rich solvent flashes upon entering the column, and the semi-lean stream has a composition equivalent to the liquid leaving a single-stage nearly-adiabatic flash. However, the reboiler energy flow is certainly adequate to strip sufficiently the 25% of the total solvent represented by the fully-lean amine. As will be shown, the lean solvent is roughly what one would expect from a two-stage flash: the first flash stage is the same flash that produces the semi-lean, while the second stage is essentially a QP flash where Q is the energy flow to the reboiler. Admittedly, there is only a rough equivalence between the regenerator and a two-stage flash, but the comparison is made to guide how we think about the situation.

Table 1 Inlet Gas

Gas Flow	Confidential
Temperature (°F)	158
Pressure (psig)	400
Composition (mol%)	
CO ₂	18.0
H ₂	60.0
N ₂	21.0
CH ₄ , Ar, He, O ₂ , CO	Balance

INEOS GAS/SPEC evaluated the design initially based on MDEA promoted with piperazine, and later with a GAS/SPEC* CS-2000* series solvent. The discussion here is limited to blends with piperazine, specifically to a solvent containing 34 wt% MDEA and 6 wt% piperazine unless noted otherwise. Absorber simulations using the INEOS in-house simulator and using the ProTreat™ simulator, a commercially available package, were found to be quite equivalent. Both packages use a strictly mass and heat transfer rate based approach to tower modeling. Simulation results presented here were obtained using the ProTreat simulator.

The base case simulation pertains to a lean amine temperature of 130°F, a 3:1 split between semi- and fully-lean solvent flow rates, a lean solvent flow rate of X and the reboiler operating with maximum duty. As is common in ammonia plants, both towers were packed but further details cannot be disclosed. Figures 2(a) and (b) show base-case absorber and regenerator temperature profiles. For the purpose of simulation, the packed absorber and regenerator were subdivided into 40 and 24 sections each, and arrows in the figures indicate side-draw and intermediate-feed locations. The treated gas was predicted to contain slightly in excess of 2.7% CO₂ versus the target of < 1000 ppmv, a far from satisfactory result. The temperature in the absorber is obviously much too high and calculations indicate that the rich amine is loaded to within 2.5% of equilibrium with the raw gas. The absorber is severely rich-end pinched as a result of the poor temperature profile. The semi-lean stream is at 88°C (190°F) which is in some part, at least, responsible for the elevated absorber temperatures. There are two obvious ways to reduce the semi-lean temperature: (1) increase the circulation rate and (2) *decrease* reboiler duty. Figure 2(b) indicates that if we increased reboiler duty, the regenerator temperature profile would be pushed further up the column and the semi-lean would become *hotter*, opposite to the desired change. (It would also decrease the lean amine CO₂ loading, but treat is being dictated by the rich-end pinch, not lean quality.) The first approach is the one to try first.

Figure 3 shows a series of absorber temperature profiles corresponding to various increases to the base circulation rate. As flow is increased from 1.113 to 1.117 times base, the temperature profile undergoes a very rapid switch from showing temperature bulges in both the top and bottom sections, to a relatively flat profile over a good part of both sections. (In the transition region, plant operation would be expected to be unstable.) But what is the impact on level of treat? Figure 4 shows treated gas CO₂ content as a function of solvent circulation rate. Small changes from base conditions produce correspondingly small changes in performance. There is a sudden decrease in CO₂ content as circulation rate increases from 1.109X to 1.113X but, referring to Figure 3, this does not require complete removal of the temperature bulge from the top section, but only a much reduced temperature there.

Interestingly, semi-lean temperature went from 84°C to 76 °C in going from 1.092X to 1.109X (and treat improved from 1.28% to 1130 ppmv) but the temperature dropped only one degree further between 1.109X and 1.113X. Yet treat improved from 1130 ppmv to 40 ppmv. In going from 1.113X to 1.117X, neither treat nor semi-lean temperature changed significantly, yet the temperature profile showed quite a dramatic switch, showing no temperature bulges anywhere save at the very bottom of the absorber. And in every case, the rich-end approach to equilibrium was always above 97%.

There appear to be two major factors at play: (1) lower semi-lean temperatures reduce the temperature bulges, and (2) increased solvent flow drags heat of reaction down the column instead of allowing it to exit with the gas. Both are important effects and manifest in different ways. This conjecture prompted the second part of the study.

The point in the regenerator at which the steam flow collapses can be pushed further down the tower simply by reducing the reboiler duty and leaving the circulation rate unchanged. Five simulations were run at the base-case circulation rate, but at reduced reboiler duties of 82.5%, 87.6%, 92.8% and

* GAS/SPEC and CS-2000 are trademarks of INEOS Oxide LLC. ProTreat is a trademark of Optimized Gas Treating, Inc.

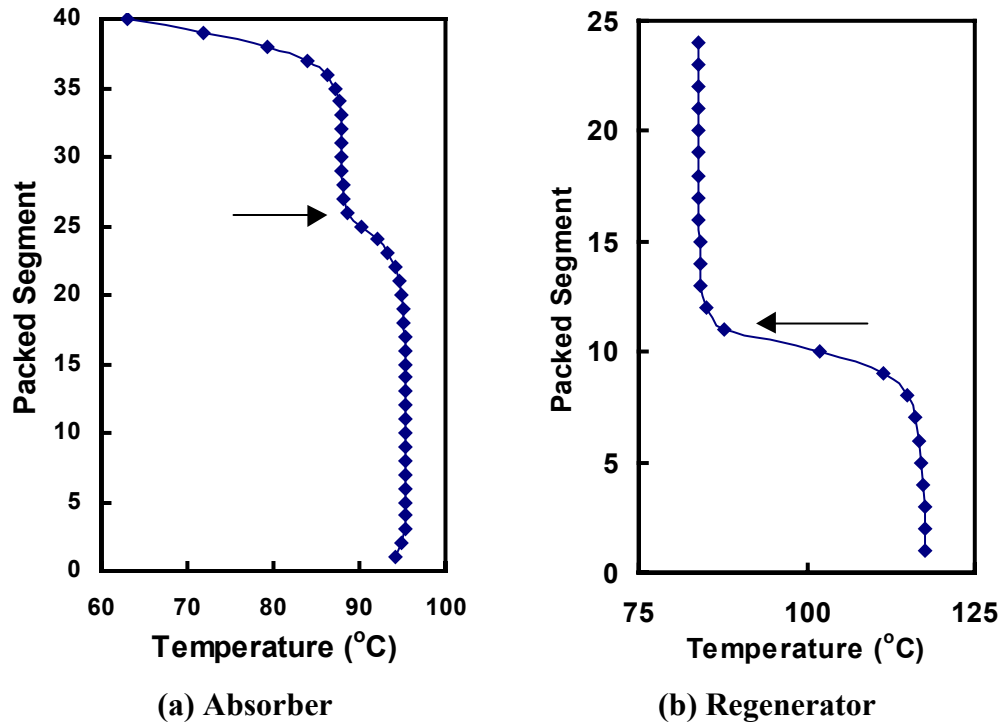


Figure 2 Base-Case Temperature Profiles. Arrows Mark Absorber Feed and Stripper Draw Positions

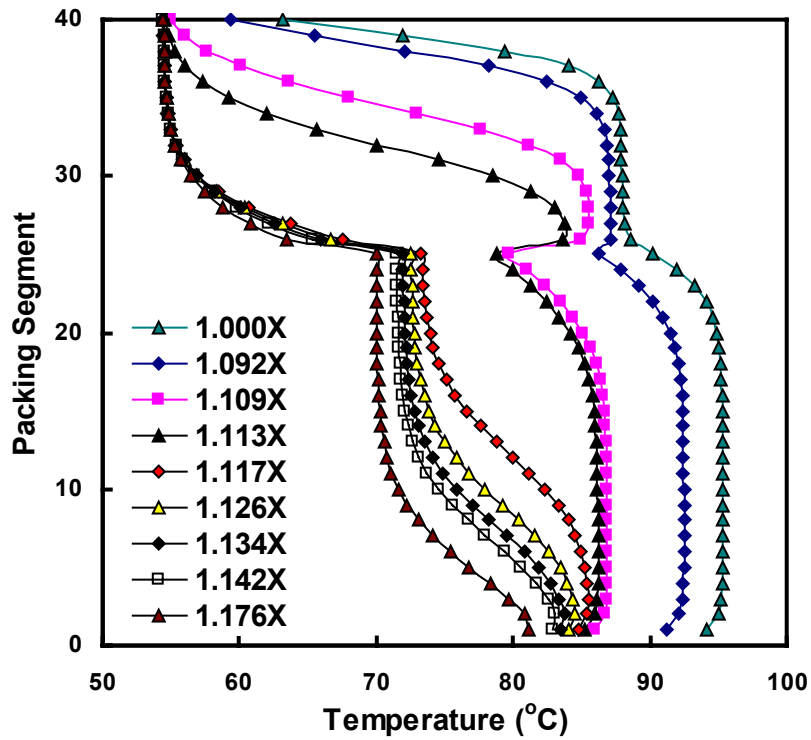


Figure 3 Effect Of Increasing Circulation On Absorber Temperatures

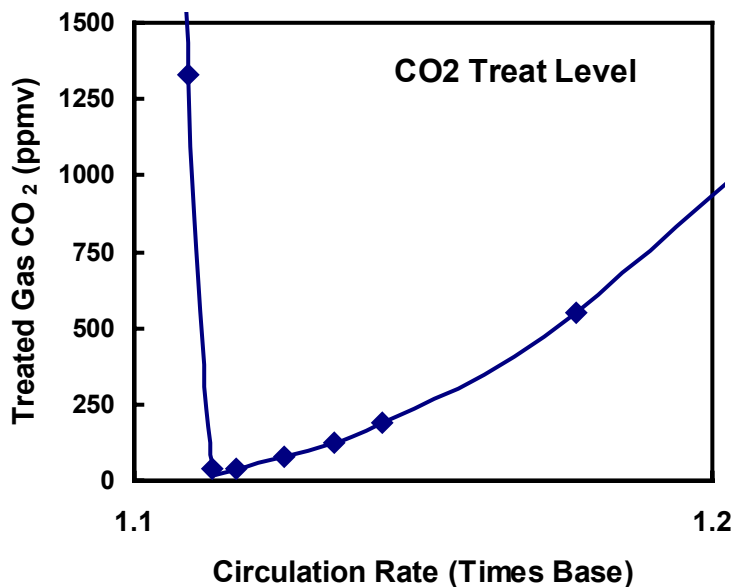
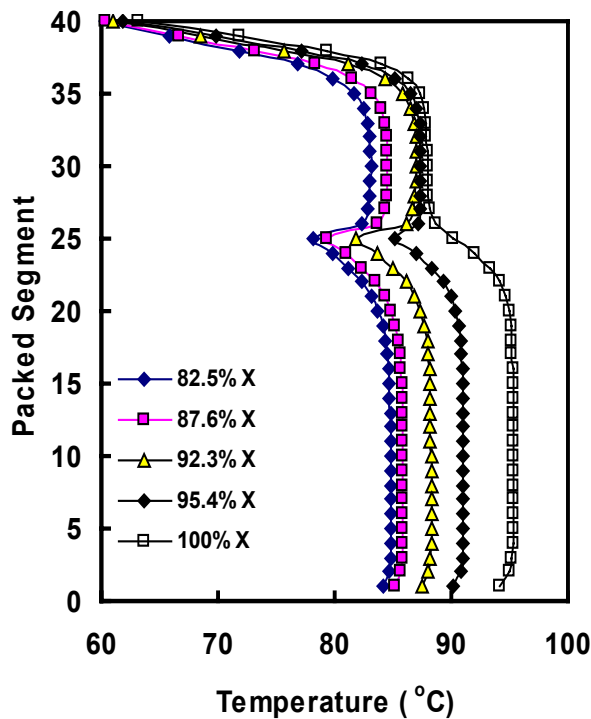


Figure 4 Effect Of Circulation Rate on Treat

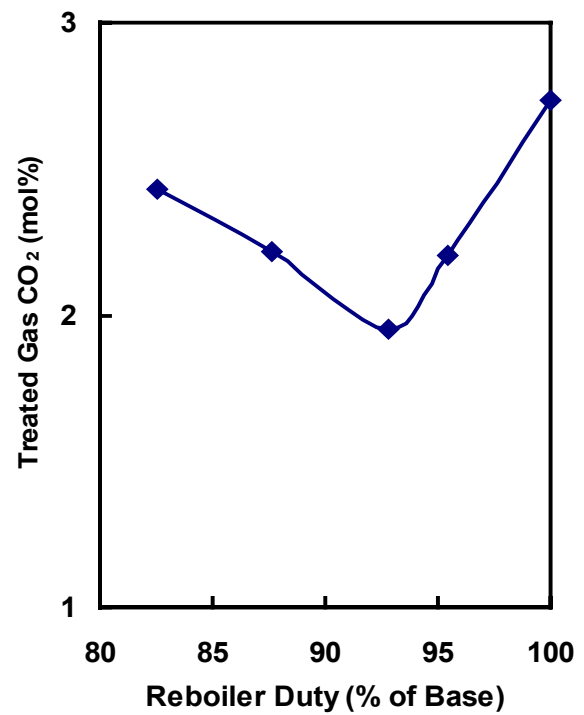
95.4% of base. Simulated semi-lean temperatures were 74.5 °C, 75 °C, 78 °C, and 82 °C, respectively, which are quite comparable to those in the circulation rate study. But the effect on absorber temperature profiles (Figure 5) and level of treat (Figure 6) are nothing like the effect of semi-lean temperature obtained by varying solvent rate. Dropping reboiler duty produced a colder semi-lean which generated a cooler region in the absorber near its point of introduction. However, even though the approach to equilibrium was always in the high 90s, it would appear that poor treating was really caused by too low a solvent circulation rate to drive the heat of reaction out the bottom of the column and develop a favorable temperature profile. The effect on treat of lowering the reboiler duty was negligible in the absence of sufficient circulation.

Several further studies could be done to find the optimal conditions for a piperazine-promoted MDEA solvent. For example, increasing the piperazine content from 6% to 8% results in a great improvement to simulated treat. However, higher piperazine level would increase the likelihood of higher losses due to vaporization and precipitation of the piperazine carbamate salt. On the other hand, increasing both piperazine and MDEA concentrations to a total of 53 wt% while maintaining the MDEA to piperazine ratio constant leads to much worse treat, because of much higher solvent viscosity, hence increased resistance to mass transfer. One of the conclusions is that the solvent being used for the simulations (34 wt% MDEA with 6 wt% piperazine) just doesn't have enough capacity at the plant's battery limit conditions to treat the gas successfully. What is more, neither increasing the solvent strength nor increasing the promoter content leads to success.

To provide the client with a workable option, INEOS will be proposing a GAS/SPEC solvent for this application because of its much higher capacity and fast mass transfer. Additional in-house and ProTreat simulations will be performed to evaluate a variety of modifications to enhance this plant's treating capacity and reliability.



(a) Absorber temperature profiles



(b) Treating levels

Figure 5 Effect of Reboiler Duty on Treating Unit Performance, Constant Circulation

Case Study 2

The ability to predict future performance and identify process limitations can be extremely useful in natural gas applications where flows and compositions are likely to change drastically as new wells are being brought into production or as treating requirements change. The following case study of an offshore application demonstrates how simulations were used to design an amine plant to accommodate expected (and somewhat unexpected) changes in process conditions. Table 2 shows the original design treating conditions. A process flow diagram is shown in Figure 6.

Table 2 Original Design Treating Conditions

Inlet Gas Flow (MMscfd)	450
Inlet Gas Pressure (psia)	1076
Inlet Gas Temp (°F)	120
Gas Composition:	
CO ₂ (mol%)	3.25
H ₂ S (mol%)	1.35
Treated Gas Specification:	< 1.0
CO ₂ (mol%)	< 1
H ₂ S (ppmv)	< 4

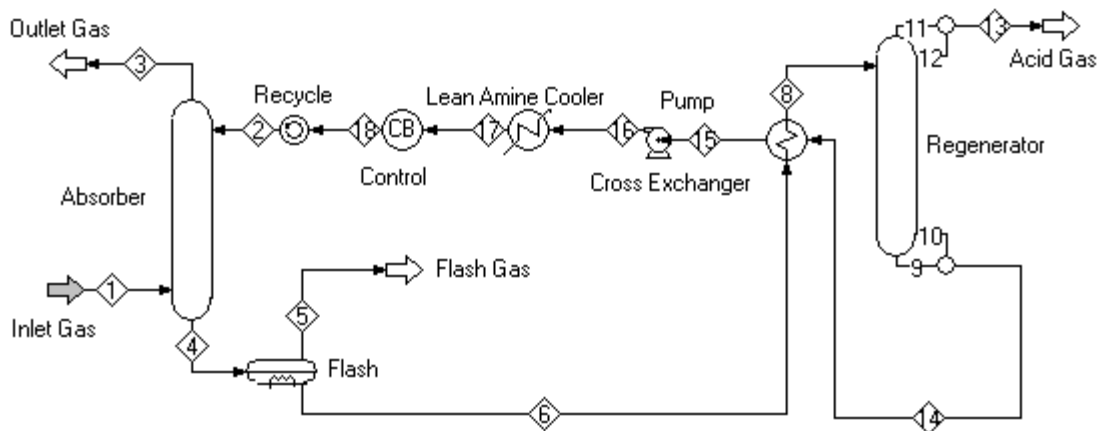


Figure 6 PFD of Natural Gas Plant

Prior to INEOS' involvement with the project, the customer, together with the engineering company, had made some key design decisions, including specifying the maximum circulation rate, the maximum reboiler duty, and the use of a 30-tray absorber. The plant was designed to use generic MDEA, and simulations confirmed that the treating requirements could be adequately met with MDEA. This forms the design-case basis.

With maximum rates established, INEOS was tasked with considering the plant's performance under a range of other operating conditions. One of the main considerations was the possibility that the heat supply to the reboiler could become limited to about 57% of design at certain times. Under this, and other circumstances, the plant was to operate at the reduced rate of 250 MMscfd. At this stage, the engineers recognized the advantages of implementing additional feed points to the absorber to control CO₂ slip. Table 3 shows the effect of varying the feed point on treat at both design and reduced flow rates. Feed nozzles were subsequently added to trays 24 and 19 of the absorber.

Table 3 Performance at Design and Reduced Rates from ProTreat Simulation

	Design Rate	Simulation Scenario 1	Simulation Scenario 2
Gas Flow (MMscfd)	450	250	250
Feed Tray from Top	30	30	19
MDEA Conc. (wt%)	50%	50%	50%
Circulation Rate (gpm)	2400	1500	1500
Treated Gas			
CO ₂ (mol%)	0.92	0.59	0.99
H ₂ S (ppmv)	< 1 ppm	<1 ppm	< 1 ppm
Lean Loadings			
H ₂ S (mol/mol)	0.0002	0.0002	0.0002
CO ₂ (mol/mol)	0.005	0.005	0.005
Rich Loadings			
H ₂ S (mol/mol)	0.13	0.11	0.11
CO ₂ (mol/mol)	0.23	0.23	0.22
Reboiler Duty	X	0.57 X	0.57 X

Just before the plant started up, the customer found that a much lower CO₂ level was needed in order to minimize corrosion in the downstream pipeline. Therefore, instead of 1% CO₂, the plant would now have to meet a 1000 ppmv CO₂ specification. Clearly, the plant would not be able to meet this more stringent specification with generic MDEA. Since engineering and construction were already completed, the customer decided to proceed with MDEA to test the capabilities of the plant, and then eventually to upgrade to a specialty solvent to meet the 1000 ppmv CO₂ specification.

During startup, the plant experienced operational problems associated with foaming—higher than expected amounts of high-molecular-weight hydrocarbon in the feed resulted in severe foaming throughout the plant. Even with inlet gas separators and carbon filtration, the plant could not process more than 180 MMscfd and still remain below the 1% CO₂ product specification. Plant personnel observed that the hydrocarbon level increased with increasing number of trays in the absorber, indicating that longer residence time in the absorber increased the condensation of heavy hydrocarbons¹. To maintain stable operation, plant operators fed the amine to tray 19, while minimizing the amount of circulating solution. Foaming also hindered the ability to strip the MDEA solvent adequately. Table 4 shows ProTreat simulations of two plant data sets. Unfortunately, the actual reboiler duties were not known, so in the simulation the reboiler duty was adjusted to give lean H₂S loadings in agreement with plant measurements.

Despite the occurrence of foaming, the ProTreat simulator predicts the measured treated gas compositions with high accuracy. It should be noted that in both plant trials, the measured H₂S loading exceeded 0.002 mol/mol and the H₂S exceeded 4 ppmv in the treated gas. In order to meet specifications, the solvent would have to be stripped to a lower H₂S level than 0.002 mol/mol loading.

Table 4 Plant Trial Data Compared with ProTreat Simulations

	April	June
Inlet Gas (MMscfd)	180	170
Inlet Temp (°F)	118	95
Inlet Gas Composition		
H ₂ S (mol%)	2.0	2.0
CO ₂ (mol%)	2.2	3.25
Solvent		
Feed Tray (from Bottom)	19	19
MDEA (wt%)	56	48
Circulation Rate (gpm)	1040	1039
Treated Gas		
H ₂ S Measured (ppm)	10	5
H ₂ S ProTreat Simulation (ppmv)	6	7
CO ₂ Measured [§] (mol%)	1.0 - 1.2	1.0 - 1.2
CO ₂ ProTreat Simulation (mol%)	0.9	1.2
Lean Solvent Loadings		
H ₂ S Measured (mol/mol)	0.0023	0.0026
H ₂ S ProTreat Simulation (mol/mol)	0.0023	0.0027

[§] Plant does not have continuous outlet CO₂ measurement—Periodic basis only.

¹ The ProTreat simulator accurately accounts for the effect of solvent type and strength, and acid gas loadings on hydrocarbon and BTEX solubility in amine treating solutions, but does not deal with a second, liquid-hydrocarbon phase.

After 5 months of operation with MDEA and little or no improvement in either the foaming tendency or the CO₂ treat, it was time to look at alternatives. The customer decided to undertake a running conversion to GAS/SPEC CS-2000 solvent. Because this solvent is much more reactive toward CO₂ than MDEA, the plant was able to meet the 1000 ppmv CO₂ specification with only 19 trays and at reduced circulation rate. An added benefit was that the higher rich loading reduced the solubility of the hydrocarbon in the amine and decreased the foaming.

Two years after the conversion, the plant regenerator runs quite stably and continues to meet specifications. It is now able to treat up to 450 MMscfd of gas within the design circulation rate and equipment parameters.

Case Study 3

Simulation of the current plant condition is an important step in determining whether the plant is performing to expectations. Comparisons of actual process data with a process model would often reveal areas of performance shortfalls or identify opportunities for optimization. Taken one step further, simulations can also be used to make decisions on the economics of a project or how best to utilize existing assets.

The plant in this study uses a conventional processing scheme to remove CO₂ from high-pressure coal bed methane gas. The facility was originally designed to process 250 MMscfd of gas containing 5 mol% CO₂. The plant meets pipeline specifications by drawing a portion of the 250 MMscfd of raw gas supply and processing it to a low CO₂ content. The treated gas is then blended with the remaining untreated gas to produce a 3 mol% CO₂ product gas. The amine plant was originally sized to use either DEA or a specialty solvent. However, prior to startup, the client decided to use MDEA instead due to the low CO₂ content of the feed gas. After a year of operation, the client became concerned with the consequences of future increases in the CO₂ and, of course, wanted to maximize throughput. The inlet CO₂ content has now risen to close to the original design of 5 mol% CO₂.

To test the processing capabilities of the plant, INEOS and an engineering contractor assisted the customer in running a set of plant trials. As part of the exercise, the ProTreat gas treating simulator was used to benchmark the performance data collected. A simplified PFD is shown in Figure 7 together with a few of the more important equipment parameters.

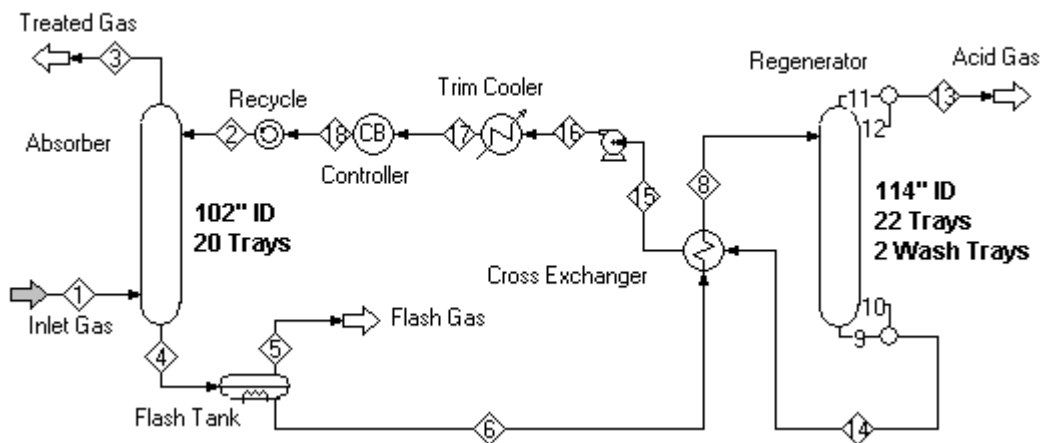


Figure 7 PFD of High Pressure CO₂ Removal Unit

Conditions for the three tests are shown in Table 5. Test 3 was run at maximum design rates for the amine plant; Tests 1 and 2 were run at higher gas rates and in the case of test 2, at a much reduced solvent rate. Thermocouples located on trays 3, 6 and 15 from the top of the column enabled the efficacy of the ProTreat simulations to be checked not only against the overall treating performance, but also against measured tower internal temperature profiles.

Simulated overall performance of both the absorber and regenerator is compared with measured test data in Table 6. Figure 8 shows temperature profiles calculated by the ProTreat simulator. The points on these plots correspond to field temperature measurements. It can be seen that the level of CO₂ treat is quite accurately reproduced by the models, and even the calculated lean loads are remarkably close to laboratory measured values. In terms of temperature profiles, agreement is not perfect, but the absorber simulations fall pretty well through the middle of the data.

Once we had established that the model accurately simulated this system, the next step was to simulate future conditions. As indicated earlier, the CO₂ content of the gas is slowly rising. In order to understand the effect of this on treating performance, a number of simulations were performed to determine the maximum volume of gas the plant could treat at increasing increments of CO₂ concentration. For this sensitivity study, the target CO₂ level for the treated gas from the absorber was set at 2 mol% and the blended gas at 3 mol%. Figure 9 shows the effect of the inlet CO₂ content on plant capacity.

Table 5 Operating Conditions for Plant Trials

	Test 1	Test 2	Test 3
<i>Raw Gas</i>			
Flow (MMscfd)	211	208	180
Temperature (°F)	104	104	104
Pressure (psia)	998	998	997
CO₂ (mol%)	4.29	4.29	4.21
Lean Solvent			
Flow (gpm)	1000	819	998
Temperature (°F)	104	110	101.8
Wt% MDEA	48	48	48
Acetate (ppmw)	975	975	975
Formate (ppmw)	225	225	225
Chloride (ppmw)	45	45	45

Table 6 Overall Performance Compared With ProTreat Simulation

	Test 1	Test 2	Test 3
Solvent Rate (gpm)	1000	819	998
Gas Rate (MMscfd)	211	208	180
Treated Gas			
Measured CO₂ (mol%)	1.54	1.98	1.20
ProTreat CO₂ (mol%)	1.57	1.95	1.20
Lean Amine			
Measured CO₂ Loading (mol/mol)	0.008	0.008	0.007
ProTreat CO₂ Loading (mol/mol)	0.0075	0.0059	0.0046
Rich Amine			
ProTreat CO₂ Loading (mol/mol)	0.310	0.403	0.294

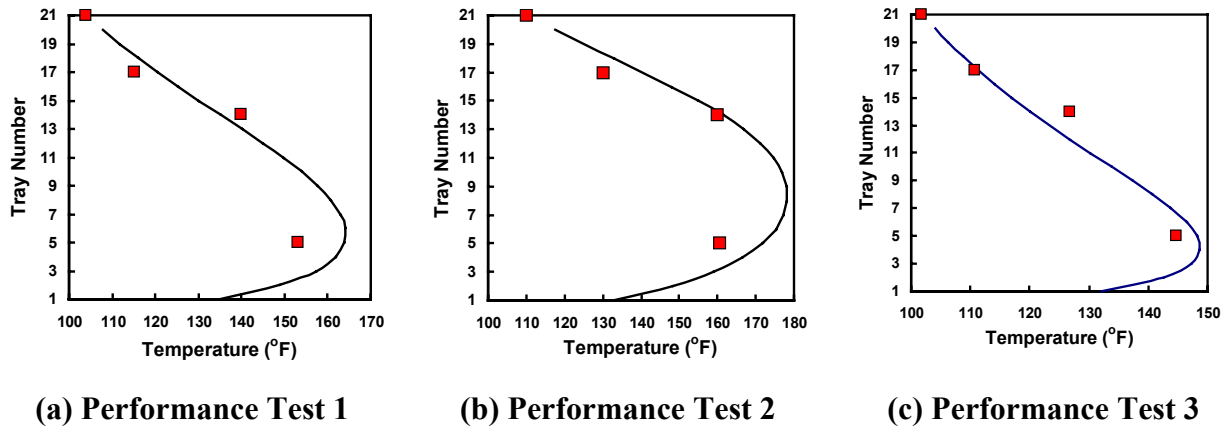


Figure 8 Simulated Temperature Profiles Compared With Measured Data

Figure 9 shows why MDEA makes economic sense when the CO₂ level is low. At CO₂ concentrations below 4.1 mol%, the plant can easily fill the trunk line system with its design capacity of 450 MMscfd. However, increasing CO₂ level can significantly reduce the capacity of the facility. At 5.5% CO₂, for example, the combined gas volume to the trunk line is cut in half.

To maximize gas production, the customer is now considering a proposal to convert from MDEA to a specialty solvent. The scenario shown in Figure 10 assumes that, a specialty solvent will reduce the CO₂ level to 1000 ppmv instead of 2 mol%. The change in solvent will require less gas flow through the amine plant, and will enable the facility to meet the 3 mol% CO₂ specification by using a higher by-passed gas flow. Projections of the expected treating capacity are shown in Figure 10.

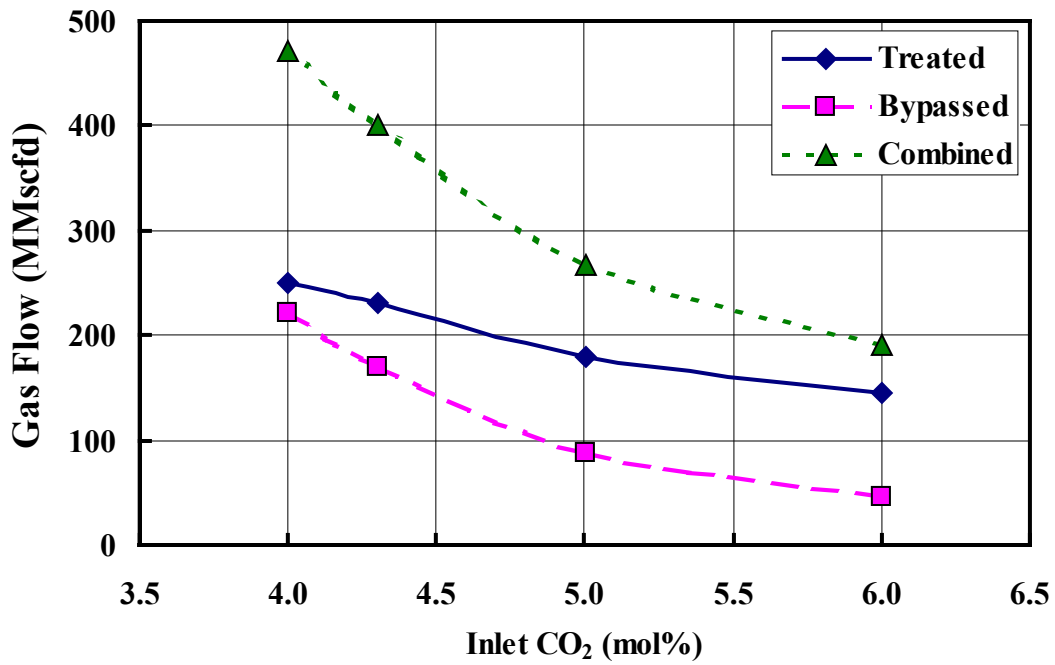


Figure 9 Treating Capacity Using 50 Wt% MDEA

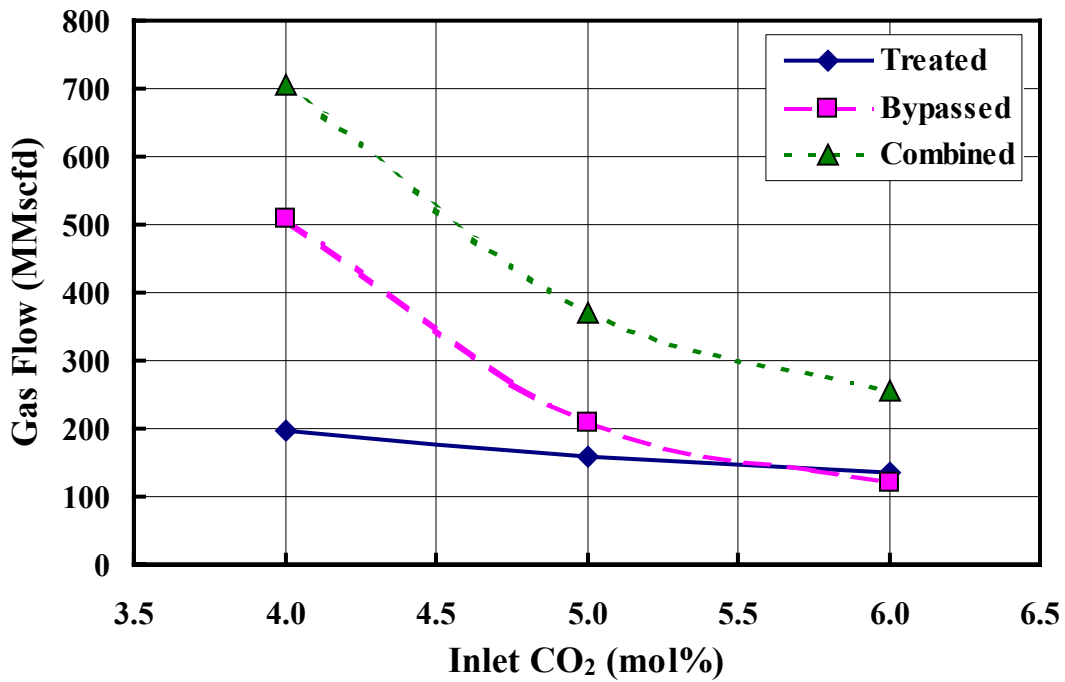


Figure 10 Treating Capacity Using 50 Wt% GAS/SPEC CS-2010

Summary

A mass transfer rate based simulator can be a very powerful tool in retrofitting existing facilities to new process conditions using either the existing treating solution or new specialty solvents. Mass transfer rate based amine simulation capabilities are also invaluable in troubleshooting a problem operation. It allows the engineer to carry out a wide ranging what-if study to find better, more energy conserving operating conditions or to determine the cause of malfunction or poor performance.

As shown by the examples, an existing plant using one solvent can be revamped with a new solvent and have its performance improved in several ways. Errors made in design, or decisions taken too early that prove limiting can be overcome by accurate and appropriate simulation. New gas streams and changed treating goals can be accommodated sometime by relatively simple changes, suggested by applying a reliable, gas treating process simulation tool.

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