

EXPECTATIONS FROM SIMULATION

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ABSTRACT

Every EPC firm and most process plant engineering offices have access to at least one, and occasionally several, software packages for simulating a variety of processes and unit operations. This paper addresses two questions:

- Is the simulator you are using matched to your needs and expectations?
- How reliable are the simulation results?

Engineers often use a tool that is either too powerful or expensive for the intended use or, more often, they use one that is woefully inadequate. And they almost invariably struggle with uncertainty about whether their tools are even giving them the right answers. All sorts of methods and approaches, many incorrect, are used to establish and validate the trustworthiness of a given tool.

Simulations are based on models of the physical and chemical processes taking place in equipment. Some types of models are inherently more connected to physical reality than others, a fact that should influence confidence. A familiar parallel is with distributed versus lumped parameter control systems. Nonetheless, models are not reality, a fact that ought to limit one's expectations. How much confidence is really justified?

The key to confidence is validation, and it is critical to understand just what can and cannot be used as a validation standard. We start by discussing just what makes a standard valid or invalid, and why it is necessary that any data themselves first be qualified.

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Introduction

Process calculations and design used to be done with pencil, graph paper, and slide rule but are now done by computer. Coming from a computer perhaps gives the results an undeserved aura of authenticity. If the methodologies remain the same and the calculations have only been relegated to a computer, then the computer merely takes the drudgery out of the work by becoming a substitute for the human calculator. So what should one really expect from a simulator, and what advantages does simulation offer?

Computer simulation offers four principle advantages: (1) greater speed of computation, (2) the ability to look at interactions between process units, (3) the ability to do detailed sensitivity analyses, and (4) implementation of more realistic models enabled by greater computing power. That simulation offers increased speed is unquestioned so unless the calculations are either trivial or superfluous, the first advantage is always realized. Today on a laptop computer, one can run more simulations and can do more computations in an hour than once were possible by slide rule and calculator in 10 years of 24-hour days! But if that's all that simulation provides, it falls well short of its real potential. This presentation examines expectations from simulation from two perspectives:

- Realism of the models used, and
- Reliability of the results.

Both must be considered if a simulator is to deliver what it should.

Realism

A model of any unit operation is just a set of equations that represents one or more principles underlying our understanding of the processes occurring within the unit operation. For example, a centrifugal pump might be thought of as a unit providing an increase in pressure. At the process level, it is not necessary to model the pump using CFD in order to provide the pressure rise and the associated rise in temperature. Thermodynamics will do quite adequately for that. But as a pump designer, one will want a much more realistic model of the pump, maybe even going to the extent of doing a CFD analysis of the flows and potential cavitation within the casing.

Conclusion 1

The necessary level of complexity or realism of the model depends on what one's needs, objectives, and expectations are.

If one is involved in specification and detailed design of heat exchangers, access to advanced software such as HTRI Exchanger Suite® would be of great value. But if it's enough to know that an exchanger in a flowsheet is there only to raise or lower the temperature of a stream, all that needs to be computed is the duty required for a given temperature change (or the temperature change for a given duty), and possibly a specification of the pressure drop. The model can then be extremely simple, involving nothing more than the computation of stream enthalpies. However, if the interest is in exchanger design, then one is in the business of *predicting performance* based on exchanger geometry, fluid properties, and the fundamentals of heat transfer. Heat exchangers have been designed in detail for well over 65 years using a model based on heat transfer rates and additivity of resistances (cf. Kern¹). The model uses individual film coefficients for heat transfer found from generalized charts that are constructed using parameters in the form of dimensionless groups. In today's software those charts are digitized into correlations. Accurate provision is made for two-phase flows, boiling heat transfer, condensation in the presence of inert gases, and a host of other embellishments such as extended heat transfer surfaces, and turbulence promoters. Models based on heat transfer rates use databases of *fundamental* information to allow one actually to *predict* performance with a high degree of reliability. An ideal-stage heat exchanger is an unheard of concept and so is the efficiency of an exchanger modelled this way. Yet in mass transfer separations equipment with its enormously greater cost, ideal stages, stage efficiencies, and height equivalents to a theoretical plate are still considered by many to be state of the art.

There are many simulation applications in which it is perfectly satisfactory to represent a complex column, or a whole set of columns, by a component splitter that allows the feed stream to be divided into any number of outlet streams according to specifications on their compositions, their component flows, or how certain components are to be allocated. But if one is designing a real column to achieve a specific split then one is in the business of *predicting and guaranteeing* how that column will actually perform in the real world of the process plant. To do this, the model of the equipment must consist of a lot more than a fit to data on past performance — it must be truly predictive in no less of a sense than heat exchanger models are predictive. This requires a mass transfer rate basis equivalent to the approach to heat exchanger design routinely used on a daily basis without much thought.

Conclusion 2

If process or revamp guarantees must be made and design fat kept to a minimum, true mass transfer rate based simulation is a must.

To some extent then, perhaps the question “What do you expect from simulation?” should be turned around to read “What do you *want* from simulation?” Matching what you want with what you get requires you to match the simulator to your requirements, i.e., to your expectations. To help answer this question, it may be worth pointing out that there are two types of models: (1) models that perform automated heat and material balances versus (2) models that *predict performance*. In the world of separations — our interest in this presentation — ideal stage based column models must be viewed as usually little more than automated heat and material balancers combined with a (maybe complex) thermodynamic model for the component distribution

between the phases[§]. Truly predictive models must be based on mass and heat transfer *rate* principles, just like their heat exchanger brethren.

Conclusion 3

Match the simulator to the use. You don't need a sledgehammer to break a walnut, but you cannot break rocks with a stick either.

If the model is not rate based then it is in some sense fitted because adjustments are required based on either the user's or the simulator developer's experience. Adjustments might take the form of efficiency factors, kinetics factors, heat transfer efficiency, height of a theoretical stage, etc. to force a match between the simulation and known or expected performance. Fitted simulators are best used when tuned to an existing facility where a user wants to explore the potential effects of relatively modest operating changes within a stable operating range. The farther one moves from the set of fitted conditions, however, the less reliable the results become. The benefit of this type of simulator is that a user can apply adjustments that force the simulator to perfectly match his plant data. But in grass roots design they can be completely misleading, or even dangerous if the deviation from fitted conditions falls outside a stable operating range, and they are certainly not predictive.

Predictive simulators are necessarily mass transfer rate based. They calculate results without requiring user-specified adjustments. These simulators are best for designing new facilities, identifying unstable operating conditions, or determining how existing equipment or designs would perform in a new service or under a new set of operating conditions. Examples are revamp projects or for selection of a modular plant for a given service. The advantage of a *real* mass transfer rate-based simulator is that it provides results based on sound engineering principles and thermodynamic properties rather than the user's (or software developer's) experience.

From time to time one hears it said that the mass transfer coefficients used in mass transfer rate models are just alternative fitting parameters to efficiencies and HETPs. Only in the sense that these coefficients have been obtained by fitting them to data, is this true. However, just as with the heat transfer coefficients used in heat exchanger calculations, the correlations are not specific to particular operating conditions and fluid properties. Rather, they are generalized and applicable to a very wide range of conditions. Efficiencies result from an enormously simplified model of what is really a complex process, and they cannot really be correlated in any meaningful way. Mass (and heat) transfer coefficients, on the other hand are connected to mechanistic physical models and lend themselves very well to quite generalized correlation. Philosophically, all models must ultimately rely on the correlation of data, but the reliability and applicability of the model depend on how closely it approximates the mechanistic reality of a situation. In the context of mass transfer separations, the ideal stage is a model of an empty column — a rate-based model uses what is actually in the tower in all its detail. Because rate

[§] There are exceptions, one being distillation involving three phases where the computations to determine even the *existence* of a third phase can be quite complex. Indeed, for many chemical systems, the phase equilibrium models are complex enough that high-quality computer models of the thermodynamics are necessary for accurate results.

models are founded upon physical reality, prediction of physical limitations can naturally be expected.

Conclusion 4

Predictive simulators, whether for heat transfer or mass separations, are necessarily truly transfer *rate based*, not an imitation. If there are stages, efficiencies, or stage calculations, it's a needless oversimplification.

Another way of looking at fitted versus predictive simulators is by analogy with lumped and distributed control systems. An example of a lumped system is a stirred tank reactor with time-varying feed—its behavior can be described as a function of time only because there is no spatial dependence. If the reactor is well mixed the lumped system is an accurate description. An example of a distributed parameter system is a tubular reaction, again with time dependent feed, where conversion depends on both space and time. If the reactor contains catalyst and there is diffusional resistance within the catalyst particles then the details of the catalysis are lumped into simplified kinetics and in that sense the system becomes partially lumped, partially distributed. But what may in fact be essential detail is lost by lumping. If the catalysis is homogeneous and the tubular reactor is modelled as three CSTRs in series the distributed system becomes lumped, and again something is lost in the simplification. The same is true in staged separations. When one replaces four real trays with an ideal stage, much is lost in the translation. Of course, one could always apply an effective efficiency for each component on each ideal stage, but where can one find such data?

Whether it is suitable for a simulator's separations model to be idealized or mechanistic depends on the use to which the simulator is intended. If all that is needed is to fit the model to plant data and then run what-if studies over limited ranges of certain parameters, a fitted model may fulfill the need quite nicely. If one must offer process design guarantees or guarantee the outcome of a revamp, a predictive simulator is an absolute necessity unless there is room to add quite a bit of fat to the design.

Reliability of Simulation Data: What's Data and What's Not

Engineers who use simulation tools are always concerned about whether the results of their simulations are correct or not, or whether they're even reasonably accurate. This kind of concern is only natural and it's certainly justified. After all, you may be called upon to guarantee the design of a 10 million dollar column or a 2,000 million dollar plant, or the performance of certain tower internals, or a solvent formulation. If you're troubleshooting, you certainly don't want to be led up the primrose path to a wrong solution or even to no solution at all because the simulation failed to model real behavior. So what are some of the approaches people have used in trying to establish reliability of a simulator? What are *you* using for benchmarking, and is it valid?

Frequently one hears of comparisons of one simulator with another, or with data from a solvent vendor. Sadly, comparisons between a simulator and real, measured plant performance data are

made much less frequently. Simulators are intended to show what a column or unit *should* be doing if it has been correctly built and it's being operated properly, and that's certainly the case for the ProTreat® simulator.

Probably the most common reason people make comparisons between simulators is that they lack reliable data — perhaps they're hoping that two of the simulators will be close to each other, the assumption being that democratically this makes them both right; however, each may be as wrong as the other. From the point of view of an EPC contractor who has been using a specific simulator for years, the reason may be "That's the way we've always done it, it's worked, so why change?" Thinking like this allows plants to continue to be built that are twice the size they need to be, and until such time as the contractor takes a look at some *real plant performance data* (or starts winning fewer bids), that's the way they'll continue to build them.

Two simulators will seldom give the same answers. Simulation software consists principally of models for various unit operations together with methods or procedures for solving the sets of equations that pertain to each such model and the flowsheet as a whole. These equation sets consist of more than just heat and material balances. Even for a simple heat exchanger, physical properties are a necessary part of the model equation set, and the physical properties calculated by the model depend on the database used to fit the properties model in the first place. So already we have two factors that will almost certainly differ between simulators: the properties database (which, incidentally, every user of software should always check against *real data*) and the model (regression) equation used for numerically representing the properties, and that's just for a simple heat exchanger with a single phase!

Two different simulators will calculate unit operations involving vapor-liquid equilibrium (VLE) quite differently just because the phase equilibrium models will differ. Not only will there be differences in the VLE data themselves, but the models can span a huge range of complexity and accuracy, all the way from ideal gas plus ideal liquid solution models to VLE packages that use equations of state and activity coefficient models of various kinds. But, there is yet another, and perhaps more significant difference between models for columns in different simulators.

There are two fundamentally different models for columns: ideal stage and mass transfer rate based, and they will give different answers almost all the time. ProTreat exclusively uses the mass transfer rate-based model. Other commercial simulators use ideal stages, either with user-supplied efficiencies or with other modifications such as ideal stage residence times and thermal efficiencies in an attempt to make a connection between real trays or real packing and ideal stages.

In ProTreat's case, a well-established database of mass transfer performance data for tower internals (trays and packing) is used so there is automatically a direct connection to real trays and packing. With other simulators the user has to supply a best guess for the missing parameters until a match with the intuitively expected performance (or less often with measured field data) is achieved. In any event, all the available commercial simulators will invariably give different answers to the same problem. Making comparisons between simulators, therefore, is an exercise in futility. At the end of the day all one can say with certainty is "They're different". On their own, comparisons between simulators tell you nothing more. So, are simulators data?

Absolutely not! One cannot be used for benchmarking another. They are models, they are most assuredly not data.

Conclusion 5

Simulations are not data, they are models. One cannot be used to benchmark another. By using one simulator to benchmark another, one is making the implicit assumption that the benchmark standard is right. If it is indeed right, why would anyone benchmark anything else against it — after all, one already has the “right” simulator?

Comparisons are often made between a simulator and solvent vendor “data”, but just what is this data? Solvent vendors, too, use simulators to assess the likely performance of their particular solvent in a particular plant configuration. In fact, most of them use a simulator with a mass transfer rate basis. In many cases, solvent vendors have to provide performance guarantees for their solvent. The performance they are guaranteeing is not what their simulator says, but with the results of simulation after a conservative (how far can I stick out my neck) safety factor has been applied. For example, a solvent vendor may project that a solvent CO₂ lean loading of, say, 0.01 moles/mole can be achieved when, in fact, the simulator says 0.003 would be reached. Is the value 0.01 moles/mole data? Indeed, is either value data? Absolutely not! Neither one of them is data. The value 0.01 moles/mole is the guarantee. It’s not data. In fact, it’s a very rare occurrence when a solvent vendor provides a customer with real data at all.

Comparisons between simulators and so-called solvent vendor data are to some extent meaningless as well, although perhaps not quite as meaningless as comparisons between simulators themselves. If your simulation gives better performance than the solvent vendor is guaranteeing, both may be right; but, if simulated performance is considerably poorer than the solvent vendor’s guarantee, something is wrong and further investigation is warranted. The main point though, is that vendor guarantees are most definitely not data. So just what is data?

Conclusion 6

Comparisons against vendor data are almost as meaningless as comparisons against another simulator. Commercially, vendors tend to be conservative. They have to provide guarantees, and they don’t want to have to replace the new solvent with another, so they tend to be conservative. *Vendor reports, however long and official looking, are not data.*

Data are nothing more or less than what is measured in the field from an operating plant. That doesn’t necessarily mean the data are good data, but *by definition they are data*. However, *if it hasn’t been measured in the field (or the laboratory) it cannot be called data!* At a minimum, data to be used for benchmarking a simulator must have been measured using reliable flow, temperature and pressure instrumentation, preferably calibrated (instruments that have been merely zeroed and spanned have *not* been calibrated!). Piping lineups must be correct, on-line analyzers must be calibrated, laboratory procedures validated, trays installed level without too many valves missing, packing properly installed with reliably-uniform liquid distribution. Measured pressure drop values should compare favorably with internals vendor calculations so

as to minimize (but not eliminate) the possibility of foaming and fouling. Reasonable material and energy balance closure is a requirement. These are some of the things that characterize good data.

Conclusion 7

Data is what is measured in the field from an operating plant. Heat and material balances must close to within reasonable tolerances for data to be valid as a benchmark. As users of simulation tools, we all want to be convinced that the tool we're using is reliable and accurate. The only truly valid benchmark for a simulator is real data measured in the field.

Conclusion 8

The simulator should compare reasonably closely with the measured performance data without adjusting or providing any factors to force agreement (in other words, the simulator must be truly predictive).

If all you're doing is comparing with another simulator, or comparing with so-called solvent vendor data, you do not have a valid benchmark. This makes the comparison worthless for the validation purpose intended. Results from simulations and solvent vendor guarantees are not data. Only measured data are data! The four case studies now to be presented all involve real process and performance data as measured in operating plants and compared with simulations that have not been fitted in any way.

Case Studies

The case studies have been selected to feature a range of treating applications, namely, (1) treating gas typical of a refinery, (2) the effect of heat stable salts and tower internals on hydrogen sulfide removal from fuel gas using MDEA, (3) carbon dioxide removal in a Middle Eastern LNG unit using piperazine-promoted MDEA, and (4) selective hydrogen sulfide removal using structured packing in a TGTU.

Hellenic Petroleum Refinery Revamp

The refinery is located in Thessaloniki on the Aegean Sea in far northern Greece. This refinery was the subject of a large-scale revamp. Siirtec Nigi was engaged to investigate the impact of the revamping project on the amine system and the downstream Sulphur Recovery Unit (SRU). The results of the study were reported at the Vienna 2014 Brimstone Sulfur Symposium, and the information given here is taken from the conference proceedings².

As a consequence of the Upgrading Project, the feedstock to the amine absorbers towers changed: the total amount of hydrogen sulfide coming from the crude oil increased as well as many sour gas streams flow rates. Siirtec Nigi proposed the replacement of the old monoethanolamine (MEA) with methyldiethanolamine (MDEA) in the refinery amine system and the implementation of an oxygen enriched Claus process for the SRU. In 2012 the Refinery completed the first part of the amine system revamping. Of interest to us here is the overall comparison between the actual plant performance and the expected plant behaviour based on the process simulation results presented in the Brimstone paper.

As background, the revamp project consisted of increasing the refinery crude processing capacity from 70 KBPSD to 100 KBPSD. Consequently, the amine treating system and the downstream SRU capacities had to be increased accordingly. In addition, as part of the revamping project, the crude types and blends were changed and the refining operations modified. As a result, the gas and liquid streams to be treated in the amine absorbers changed in composition (mainly the H₂S concentration). This led to significant modification of the amine system configuration.

The feeds to the amine scrubbers after revamping are shown in Table 1 together with the solvent flows and the types of tower internals. Towers T-170 and T-1902 are both high pressure columns, the others are low pressure. There is also a mix of trayed and packed absorbers, with T-407 having been repacked with Pall Rings as part of the revamp. In the context of this paper, having shown some of the operating details for the columns, what is important is the fact that we have field data available with which to benchmark the simulator.

With the exception of T-170 for which no performance data are available, the simulator matches the field data quite well. It deserves to be pointed out that the simulations were not adjusted to match the data — *the simulations are pure out-of-the-box predictions*.

Table 1 Amine Treater Performance Data

Scrubber	T-407	T-170	T-410	T-1902
Internals	Pall Rings	Trays	Packing	Trays
Gas Conditions				
Temperature, °C	46	43	43	49
Pressure, kg/cm²g	18.6	42	4.1	53
Mass Flow, kg/h	1,036	6,700	3,119	8,458
Composition, mol%				
Hydrogen	71.8	68.7	51.2	88.2
Methane	14.4	22.5	16.5	6.3
Ethane	7.6	4.8	8.3	1.4
Propane	2.5	1.7	5.8	0.6
n-butane	0.4	0	3.5	0.3
i-butane	0.1	0.5	1.0	0
n-pentane	0.2	0	2.1	0
i-pentane	0.1	0.2	1.2	0
C₆+	0.6	0.2	2.5	0.3
H₂S	1.9	1.2	6.1	2.6
Water	0.5	0.2	1.8	0.3
Solvent				
Flow Rate, m³/h	6	8	8	10
Treated Gas				
Measured H₂S, ppmv	25	N/A	70	10
ProTreat® H₂S, ppmv	26	8	60	8

Conclusion 9

The mass transfer rate-based simulations predict the *performance data* quite well. Because these are actual measured data one can have considerable confidence in the validation.

Treating a Refinery Fuel Gas

This case involves hydrogen sulfide removal in one of two fuel gas treaters in a West Coast USA refinery. To take advantage of the lower regeneration energy required by MDEA, the refinery had switched out the DEA solvent to 38 wt% generic MDEA. At the same time, trays were replaced with #2.5 CASCADE MINI-RING™ (CMR™) packing in both treaters. The treater of interest here was 2.5 ft diameter, and its original 17 valve trays were replaced with 25 ft of CMRs. The gas to the treater was 0.2 mol% CO₂ and 0.5 mol% H₂S at 200 psig with the balance two-thirds hydrogen with 17% methane and minor amounts of C₁ – C₅ hydrocarbons.

Performance after the revamp was disappointing — despite the low, acid-gas, lean loadings (0.0009 for H₂S and 0.008 for CO₂) the H₂S leak from the absorber was measured at 26 ppmv; whereas, a value closer to three or four parts per million was expected. Simulation indicated the hydrogen sulfide in the treated gas should have been less than 1 ppmv, in disagreement with actual measured data. A consultant tasked by the refiner to determine the cause for the larger than expected H₂S leak suggested that the residence time on the packing was too short to achieve good treating and he recommended the refinery return to using trays. However, after reinstalling the 17 trays, the H₂S leak remained stubbornly at 25–26 ppmv. The costly shutdown and revamp back to trays produced no beneficial result.

As part of a new, independent investigation, we ran ProTreat against the data but it too predicted better than 1 ppmv H₂S in the treated fuel gas. Then we asked for a solvent analysis (shown in Table 2). When the real solvent composition was used in the simulation, the predicted H₂S leak rose to 22 ppmv when the absorber was packed and 26 ppmv when it was trayed. It is worth noting that the predicted H₂S leak and the measured value from the trayed absorber are virtually identical! (Incidentally, the presence of heat stable salts — HSSs — led to several percent *more* CO₂ slip for both trays and packing.)

Table 2 Fuel Gas Treater: Solvent Analysis

MDEA (wt%)	38
Carbon Dioxide (Loading)	0.00014
Hydrogen Sulfide (Loading)	0.0009
Acetate (ppmw)	2,580
Formate (ppmw)	14,305
Sulfate (ppmw)	230
Thiocyanate (ppmw)	3,225
Chloride (ppmw)	1,675

Without a proper solvent analysis of course, one generates the wrong results. Treating is very optimistic because HSSs effectively create higher acid gas vapor pressures in the absorber than a

HSS-free solvent would. Naturally, they also create higher backpressures in the regenerator and this assists solvent regeneration, hence the relatively low lean loadings, even for MDEA. It is also revealing to compare the hydrogen sulfide partial pressure profiles with and without HSSs. A comparison for packing is sufficient as the effects are qualitatively the same for trays. Figures 1a and 1b show the actual H_2S partial pressures and the equilibrium partial pressures with and without HSSs, respectively. Figure 1a shows that with HSSs the equilibrium backpressure of hydrogen sulfide is very much higher throughout the absorber. This causes higher H_2S leak from the absorber and a reduced concentration difference driving force for absorption everywhere. With no HSSs, the driving force is so much higher that absorption is essentially complete by the time the gas reaches just half way up the column — the absorber is severely lean end pinched because the actual hydrogen sulfide concentration is very nearly equal to its equilibrium value in the upper half the bed (and near the very top of the bed in Figure 1a). The non-verticality of the profile in the upper half of the bed shown in Figure 1b is caused by continued absorption of carbon dioxide which affects the equilibrium of hydrogen sulfide. In both cases then, treating is dictated almost entirely by lean loading, i.e., vapor-liquid equilibrium, although the way the profiles develop (and the shape of the temperature bulge) are determined by mass transfer rates.

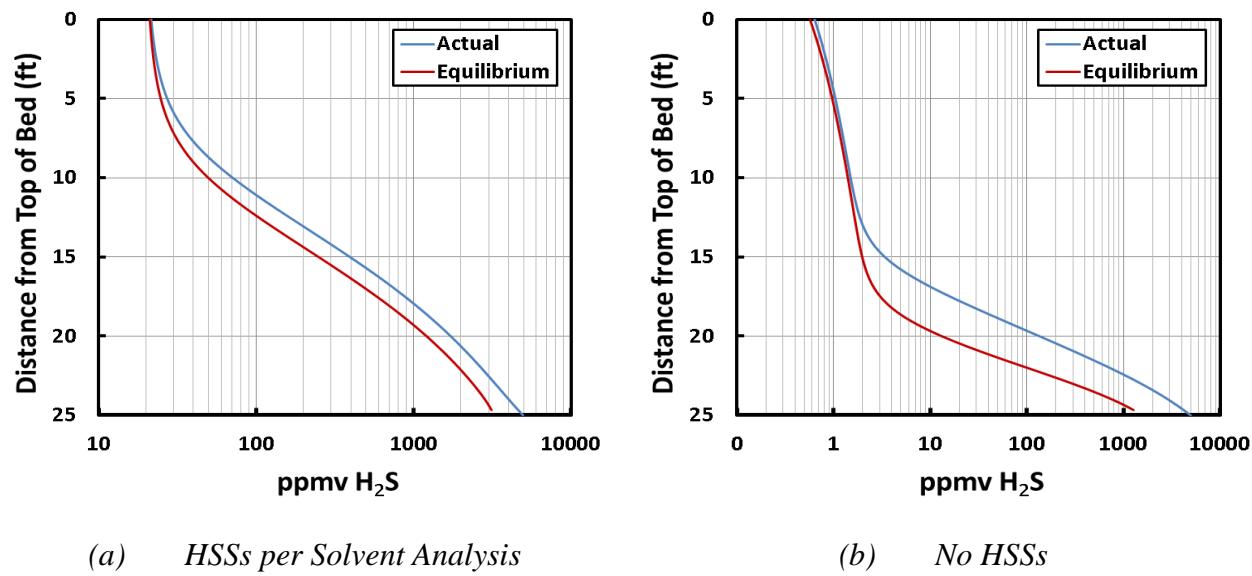


Figure 1 **Simulated Actual and Equilibrium H_2S Profiles with and without HSSs**

Any simulation based on ideal stages fails to reveal the existence of pinches because it treats the column as a black box, an empty shell. What is inside the tower makes a huge difference to treating performance. Four-inch Raschig rings perform completely differently from a small or medium crimp structured packing, both perform differently from trays, and what type of tray and its physical features affect performance, too. It is unrealistic to expect to be able to diagnose internals problems using ideal stage simulation (with or without efficiencies) because such simulations are blind to what is actually in the tower.

Conclusion 10

Failure to account for heat stable salt contamination of the solvent can lead to completely erroneous simulation results and to expensive but unsuccessful revamps to cure a problem whose cause lies in the solvent, not the tower internals.

Conclusion 11

A column that is lean-end pinched cannot have its performance altered by changing or modifying the internals. Pinch conditions are revealed only by mass transfer rate-based simulation which, in the present case, points unmistakably to the correct solution to poor performance — a cleaner solvent.

Carbon Dioxide Removal in an LNG Unit

Careful examination of the behavior of a carbon dioxide absorber in an LNG facility that uses piperazine-promoted MDEA reveals the existence of a bulge pinch and a surprising operational instability, and the real cause for an observed failure to meet the treating objective. LNG production is a typical deep CO₂ removal application. Others include ammonia and methanol production, and the purification of various other synthesis gases. In LNG the goal is usually a treated gas containing less than 50 ppmv of carbon dioxide. Most solvents are based on *N*-methyldiethanolamine (MDEA) promoted with lesser amounts of piperazine, although 2-(2-aminoethoxy)ethanol, known commercially as Huntsman's DIGLYCOLAMINE® agent (DGA®) and BASF's ADEG, have found use in this application.

Split flow processing schemes such as the one in Figure 2 are one approach to minimizing regenerator energy consumption, especially when the inlet gas is high in carbon dioxide. There is no need to use a highly stripped solvent to remove the bulk of the CO₂ — a high flow rate of only partially regenerated solvent will do as well. This can be obtained by drawing off the bulk of the solvent from part way down the regenerator (or from a pre-regenerator heated flash stage) and sending it to a point part way down the absorber. The remainder of the solvent is thoroughly stripped and is used in the top section of the absorber to “polish” the gas from which the bulk of the carbon dioxide has already been removed in the lower section. Further benefit can be had from the low liquid load in the polishing section by reducing the column diameter there, thus saving on the cost of the shell and, if the column is trayed then smaller trays, or if it is packed, less packing volume.

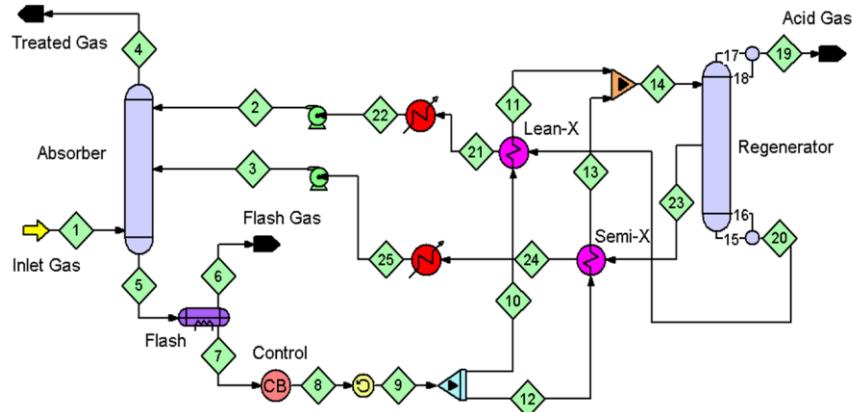


Figure 2 Split Flow CO₂ Removal Flowsheet

One has the option of swaging the absorber diameter at the semi-lean feed position (the point of entry of Stream 3 in the drawing) or of having a completely separate polishing column in series with the Bulk Removal column, as was done in the present plant. Figure 3 shows the flowsheet for the absorption side of the removal unit as it was actually built. The semi-lean amine comes from a semi-lean cooler and joins the solvent flow coming from the bottom of the Polishing column before entering the top of the Bulk Removal column.

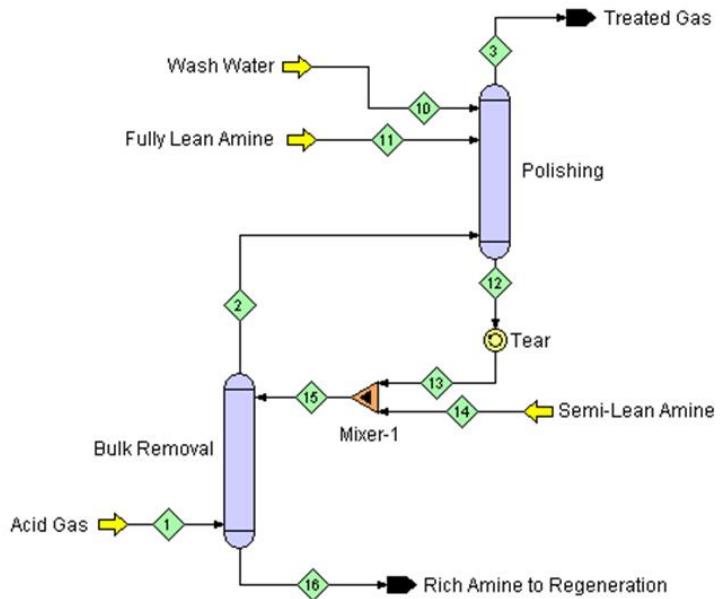


Figure 3 Two CO₂ Absorbers Connected in a Split-Flow Configuration

The 4-m diameter Polishing column contained two 5.5-m deep beds of 25-5 Rauschert HIFLOW® rings as well as two bubble-cap trays at the top of the column. The top tray was fed with makeup water and the trays were intended to remove vaporized and entrained solvent. The

packed section received solvent at 769,000 kg/h. Figure 4 is a photograph of several sizes of HIFLOW rings.

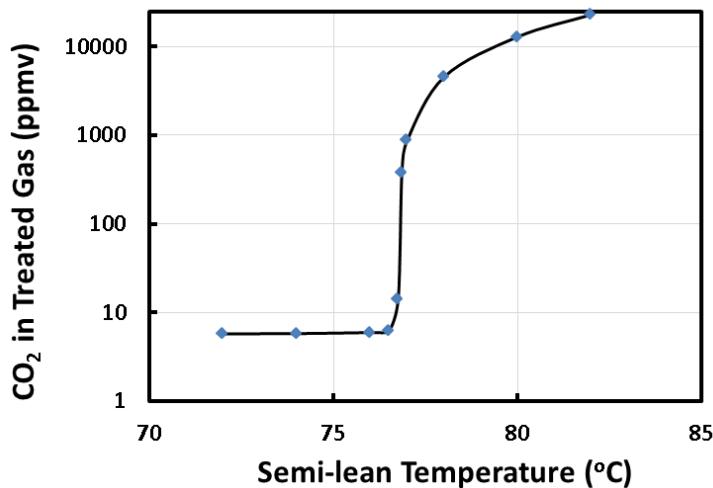


Figure 4 Metal HIFLOW® Rings

The Bulk Removal absorber was 6-m diameter and it contained two beds of 50-5 HIFLOW rings, each of 5.5-m depth handling solvent at 4,480,000 kg/h, some 5.8 times the fully-lean amine flow rate. Both absorbers operated at roughly the same pressure (45 barg). The solvent was a 37 wt% MDEA + 3 wt% piperazine blend and the fully-lean and semi-lean loadings were 0.021 and 0.388 moles CO₂ per mole of total amine, respectively. The rich solvent was loaded to 0.54 moles per mole which required stainless metallurgy in certain parts of the unit. Both the Bulk Removal and Polishing columns were comfortably oversized at 64% and 52% of flood, respectively.

The plant was designed to treat 330,000 kg/h of raw gas containing 17.5% CO₂ with the balance methane and smaller amounts of C₂ to C₆ hydrocarbons. However, at nameplate rates the unit fell far short of meeting the < 50 ppmv specification. The best it could achieve was several *thousands* of parts per million. Needless to say, the owners were up in arms and the usual round of finger pointing ensued. As is typical, the internals supplier was the first party stood against the wall but the verdict was ‘not guilty’. It took mass transfer rate-based simulation to diagnose the cause.

The process licensor’s original recommendation was that the semi-lean amine temperature be cooled to at least 70°C; however, the semi-lean cooler was undersized and the lowest achievable temperature was 80°C. This was a Middle Eastern plant faced with the usual challenges of heat exchange against very hot air. A simulation study of this plant was carried out using the ProTreat® mass transfer rate-based simulator. As the chart of Figure 5 shows, there is a critical temperature of about 76.8°C above which treating is predicted to fail precipitously. The licensor’s recommendation was well founded.



**Figure 5 Effect of Semi-lean Temperature on Treating
in a Split-flow CO₂ Absorber System**

What is disconcerting about the situation is that failure seems to occur almost without any warning. Below a temperature of 76.5°C treating is nothing short of excellent; in fact it is much better than required, but with the temperature only $\frac{1}{2}$ a degree hotter the treated gas contains 1,000s of ppm carbon dioxide. The extreme sensitivity to semi-lean temperature was certainly unexpected and at first a little hard to believe, but the explanation is fairly simple.

Somewhere several degrees below 76.5°C the Bulk Removal column has absorbed all the CO₂ it is capable of doing. When the temperature goes up just a little the solvent capacity experiences a corresponding drop. Of necessity, the CO₂ that now cannot be absorbed by the Bulk column passes through to the Polishing column. However, the Polishing column is running with a low solvent flow rate, and so it has very limited absorption capacity for carbon dioxide. It too finally reaches its limit and CO₂ breaks through. Figure 6 explains why the breakthrough is so precipitous. The reaction of carbon dioxide with a piperazine-containing amine is very fast and this confines the absorption zone to a fairly narrow part of the packed bed. Thus, the CO₂ profiles in the column show rapid change across a relatively short section of the bed. Although the absorption zone is being forced up the Polishing column with increasing semi-lean temperature, only parts per million of CO₂ remain unabsorbed until the breakthrough temperature is reached. At that point the carbon dioxide content of the treated gas suffers a large excursion. The column goes from lean-end pinched at low temperatures to *bulge pinched* when the solvent becomes hot enough. At temperatures much above 76.5°C the Polishing absorber becomes bulge pinched. This interesting and dangerous phenomenon is revealed only by real mass transfer rate-based simulation.

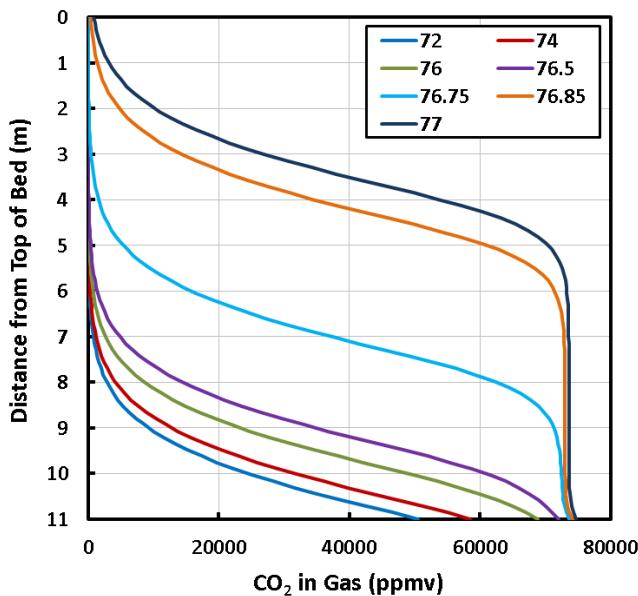


Figure 4 Profiles of CO₂ Concentration in the Polishing Column as a Function of Semi-Lean Amine Temperature

Lean and semi-lean amine temperatures were already as low as achievable in the plant, and solvent circulation pumps were already operating at capacity so, short of a larger semi-lean exchanger, treating could be brought back on specification only by reducing the gas flow (production). This case demonstrates the power of mass transfer rate-based simulation in diagnosing plant operating problems. What was initially attributed to malfunctioning tower internals turned out to be caused by inherent process sensitivity to an (unachievable) operating temperature. A simulation based on mass transfer rates can predict unanticipated phenomena such as this, but a simulation based on efficiency or HETP could not reveal this critical aspect of the process. To create confident and successful designs and to troubleshoot existing processes efficiently, it is necessary to know which parameters control performance in different parts of the process.

Conclusion 12

Bulge pinches may be associated with an unstable operating region. The Cure: recognise and stay away from instabilities.

Conclusion 13

If a small change in a variable causes a huge change in a simulated performance parameter, your simulator may not have gone crazy — it may be telling you something important. Only mass transfer rate-based simulation is capable of revealing bulge pinches. Such cases deserve close scrutiny.

Tail Gas Treating

The final case is a Texas Gulf coast refinery 6-ft diameter TGTU packed with 20 ft of FLEXIPAC® 2Y structured packing and treating 3 MMscfd of 1 psig gas containing 3.4 mol% carbon dioxide and 1.7 mol% hydrogen sulfide. The refinery claims the gas to the thermal oxidizer was only 3 ppmv H₂S until they cleaned the solvent. Treating is now horrible and the refinery's sulfur emissions are up against the permitted limit.

The original solvent was 34 wt% MDEA with the solvent analysis shown in Table 2. There were over 8,000 ppmw HSSs in the solvent. After cleaning there were virtually none.

Table 3 Solvent Analysis: Heat Stable Salts

MDEA, wt%	33.374
DEA, wt%	0.338
Thiosulfate, ppmw	5,930
Oxalate, ppmw	220
Acetate, ppmw	1,150
Formate, ppmw	815

ProTreat simulation using the as-reported solvent analysis predicted the treated gas should contain 3.8 ppmv H₂S, very close to the refinery's claim of 3 ppmv. (The H₂S lean loading was predicted at 0.00008.) Again, this is an out-of-the-box prediction — absolutely no adjustments or fitting of any kind. This is plant performance data and is therefore a valid point of reference against which to benchmark a simulator.

Beyond stating that after solvent cleaning the treating was horrible, the refinery did not provide actual data on H₂S leakage from the TGTU. However, simulation with the HSSs removed from the solvent but with all other conditions the same, predicted there should be 80 ppmv H₂S in the treated gas. (The predicted H₂S lean loading was 0.009.) Treating is certainly "horrible" compared with the HSS contaminated solvent and provides at least anecdotal evidence of the effect of heat stable salts. The HSSs greatly reduce lean loading which is responsible for better treating in this application. Depending upon the specific system and operating conditions, this may not always be the case.

Conclusion 14

The performance of structured packing was very successfully simulated in a TGTU application and the observed H₂S leak was predicted to within better than 1 ppmv.

Conclusion 15

Modest concentrations of heat stable salts in an MDEA treating solvent appear to have quite a beneficial effect on tail gas treating unit performance.

Concluding Remarks

Relevant conclusions have been scattered throughout the paper and will not be repeated here. Suffice it to underscore the facts that

- Simulators cannot be validated by comparison with other simulators. Doing so assumes one of them is correct when, in fact, both may be wrong. Comparing three simulators and assuming the two closest to each other are the best ones is tantamount to taking the foolish position that correctness can be established by democratic vote. We are engineers, not politicians.
- Simulators cannot be validated against “vendor data”. Vendors provide process and solvent performance guarantees. These are not data — they represent the extent to which the vendor is willing to stick out his neck.
- Simulators can be validated only against real plant performance data measured in the field. One is not permitted to adjust or fit the simulation to the measured data and then claim an accurate prediction. Using adjustments, the best one could say is that one has achieved an accurate fit but to call it a prediction is disingenuous.
- An achievable expectation from simulation is that one should be able to predict the performance of existing plants as measured in the field, without simulator adjustments. Experience and rules-of-thumb are valuable adjuncts to simulation but they are not reliably predictive, especially in new circumstances. If they are necessary in order to provide input information to the simulator then the simulation is not nearly as reliable as imagined.

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