



The CONTACTOR™

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Conflicted Meanings of “Rate Based”

The term “Rate Based” has different meanings to different people and can be used inappropriately to give the rate-based qualification to a simulation model when, in fact, the model is not rate based at all. This applies in particular to models for columns. A model deserves the name rate-based only if it is firmly grounded in **mass transfer rate** calculations. In other words, *it must be a mass and heat transfer rate model*. It's not good enough that it might use chemical reaction kinetics as an element in the overall model—it must directly use mass transfer rates as well. Simulation software that relies on liquid residence time for its calculations on trays or packing is a case in point.

One approach to treating the absorption of slowly reacting species such as CO₂ take-up by MDEA is to treat the liquid on a tray, for example, as the equivalent of a continuous stirred tank reactor (CSTR). The dissolved molecular CO₂ with concentration C_{CO_2} reacts with MDEA (concentration = C_{MDEA}) at the rate (mol/m³·s)

$$\text{Reaction Rate} = k_2 \times C_{CO_2} \times C_{MDEA}$$

If the holdup volume of liquid on the tray is V , (equal to volumetric liquid flow rate multiplied by the residence time) then the rate at which CO₂ disappears by reaction on the tray is (mol/s)

$$\text{Removal Rate} = k_2 \times C_{CO_2} \times C_{MDEA} \times V$$

In principle at least, this calculated removal rate now can be used in a simple CO₂ balance around the tray. From it, one can calculate the change in total CO₂ concentration in the liquid (and the gas) between inlet and outlet, i.e., the separation. So is the problem solved? Not quite! There are two issues with the whole approach.

First, simulators that use this approach also use theoretical (ideal) stages. Indeed, if they were truly mass transfer rate models they wouldn't have to resort to a CSTR analysis in the first place. There is

a fundamental disconnect between theoretical stages and real trays in a CSTR model. Does the residence time refer to the real tray or to enough real trays to add up to one ideal stage? But the second issue is far more telling.

The concentration of physically dissolved (but unreacted) CO₂ in the solvent is completely unknown! As the CO₂ reacts with MDEA, it is replenished by more CO₂ dissolving into the liquid. But what is its concentration in the bulk well-mixed liquid? If the reaction is fast enough, it could be nearly zero. If there is no reaction at all and the residence time is long, it could be the value in physical equilibrium with the CO₂ in the gas ($C_{CO_2}^*$). *The model can be used only if C_{CO_2} is known* and the simplest assumption is that it has the phase equilibrium value, $C_{CO_2}^*$. Implicit in this model is that (1) the mass transfer resistance is too small for mass transfer to be the limiting step, and (2) the limiting step is the reaction of CO₂ with MDEA. In other words, CO₂ removal is a two-step process of dissolving into the liquid followed by reaction, and incorrectly, that the reaction rate is the limiting step. This is the only assumption available to an ideal stage model because ideal stage models neither calculate nor use mass transfer rates, so applying them here is out of the question. Despite attempting to use kinetics, **models that use ideal stages are simply not rate based** in any sense of the term.

Trying to account for reaction kinetics via a CSTR type of model focuses on the wrong process as the controlling or limiting step. In fact, CO₂ slip from MDEA contactors is **not controlled** by reaction kinetics at all—it's controlled by mass transfer resistance to CO₂ absorption. The resistance is on the liquid side of the interface, it is diffusional, and it sets the absorption rate. By ignoring the mass transfer resistance, absorption calculated on the basis of just reaction kinetics and residence time gives the highest possible rate—any mass transfer

resistance will lower absorption. This is the reason these so-called rate-based models often can match performance data only by using physically impossible tray residence times (small fractions of a second for example, when the real residence time is known to be several seconds). For absorption of CO₂ by MDEA under the most common operating conditions, the value of residence time that generates a reasonable model fit to data is well established. But as plant parameters move away from the common operating range, such models become less and less reliable and for the most part tend to produce increasingly optimistic amounts of CO₂ removal simply because they completely ignore the crucial and determining role played by resistance to mass transfer in the liquid phase.

Case Study

This plant was designed using an ideal stage column model incorporating tray residence time with CO₂-MDEA reaction kinetics. The plant was intended to take gas containing 9.5% CO₂ at 765 psig down to 0.5% CO₂ for subsequent blending with another gas to produce a 2% CO₂ product. The contactor was sized with 22 trays having 2-in weirs. Prior to startup, the engineering contractor asked a solvent vendor to verify that the 22 tray column would meet treat. The solvent vendor used the ProTreat simulation package for this work. Simulations indicated **it would take 50 trays to reach the 0.5% CO₂ target**. At design rates with only 22 trays, the plant would be struggling to achieve even 2% CO₂, let alone the 0.5% target. Since construction was nearing completion, the solvent vendor recommended 5-in weirs to provide at least some relief. However, the original simulations on which the design was based appeared to be optimistic, at least relative to ProTreat. However, simulations are NOT data and the validity of these two very different models can really be determined only by comparison with actual, carefully-taken, performance data. Unfortunately, there are no comparisons of ideal-stage calculations with actual performance data; however, the ideal stage *design* results for 2- and 5-in weirs were 0.68 and 0.20% CO₂, respectively, vs. 2.08 and 1.72% CO₂ via ProTreat simulation. There is roughly a factor of 10 spread between the two models with 5-in weirs.

The results of a performance test at 9 MMscfd flow (close to the design gas rate of 10 MMscfd) but with

a reduced raw gas CO₂ content, are shown in Table 1. Although not a perfect match, ProTreat nonetheless comes quite close to reproducing the measured CO₂ level in the treated gas.

Table 1 Performance at Near Maximum Rates

	Maximum Rate (Aug 2008)	ProTreat Simulation
Gas Flow, MMscfd (Nm ³ /s)	9 (2.95)	9 (2.95)
Pressure, psig (barg)	830 (57.2)	830 (57.2)
Inlet Gas, °F (°C)	66 (18.9)	66 (18.9)
In CO ₂ , mol%	8	8
Outlet Gas, °F (°C)	114 (45.6)	115 (46.1)
Outlet CO ₂ , mol%	1.72	1.34
MDEA Strength, wt%	52	52
Amine, USgpm (m ³ /h)	100 (22.7)	100 (22.7)
Lean Temp, °F (°C)	114 (45.6)	114 (45.6)
Lean Load, mol/mol	NA	0.0044
Rich Load, mol/mol	NA	0.287

The consequences of the incorrect original design were mitigated in part by a last-minute tray modification, and by the fact that the actual gas flow and composition when taken together were over 30% lower than the design was supposed to accommodate. Only after two years of operation, when original design conditions *had* to be met, did the real consequence of using a modified-equilibrium-stage-based model for this type of application come to a head. The only sensible solution was a solvent change-out to a specialty amine. Fortunately, ProTreat's mass transfer rate based simulations allowed the operators of this facility to anticipate what was coming and to plan for the right corrective action well in advance.

ProTreat actually calculates and uses the mass transfer rate of CO₂ into the solvent, and it uses the chemical reaction kinetics as well. No assumptions are made about the dominant resistance or limiting step in the process, so there is no inherent or insidious optimism built into the calculations. Full account is taken of the mass transfer characteristics of the trays or packing that are actually in the column. **ProTreat calculations are completely predictive**—there are *no* adjustable parameters.

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