# Thermal Characteristics of $CO_2$ Absorbers[1]

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In a previous article, the use of thermal imaging to determine internal temperatures in $CO_2$ absorbers was discussed, with particular reference to packed columns. Temperatures determined this way are usually within 5°C of simulation. When temperatures are measured using internally-placed thermocouples, the agreement with simulation is significantly closer. The present article continues the discussion by expanding the material to include trayed columns as well as solvents other than piperazine-promoted MDEA. But why do tower internal temperatures matter?

There are at least three situations of importance. Firstly, temperature profiling an absorber can be a superb diagnostic tool to aid in the identification of reasons for poor column performance. In packed towers, solvent and gas maldistribution (and one is always accompanied by the other) is a common cause of performance loss. In trayed towers, the trays can become fouled and downcomers blocked or unsealed, or several trays may be missing altogether; perhaps all the trays have disappeared (only to be partially recovered in filters). With solidly grounded mass transfer rate-based simulation provided by ProTreat®, unexpected deviations between measured temperatures and simulation should be taken as indicative of possible problems with the tower internals.

The second reason absorber (and regenerator) temperature profiles are important is the physical damage to both internals and solvents caused by temperatures that are too hot, especially when acid gas concentrations are high, or $H_2S$ is not present to passivate steel surfaces. The traditional rule-of-thumb is that temperatures should not be allowed to exceed 85°C (185°F) anywhere inside any absorber no matter the solvent and operating conditions. The reasons are twofold: high temperatures mean potential for serious degradation of the solvent with resulting fouling and performance loss, and high temperatures exacerbate corrosion, particularly with mild steel metallurgy. Both solvent degradation and corrosion create avoidable operating costs. Furthermore, undetected corrosion can also represent a safety hazard from suddenly perforated vessel walls or failed piping.

The third reason to be aware of temperature profiles is the clues they provide on how to optimize column operations. For example, if a temperature bulge is towards the bottom of a column and is flat near the top, the tower is probably lean-end pinched so what can be gained by boiling the solvent less vigorously is directly related to lean loading. Changing the gas flow rate will likely have little or no effect on the treated gas composition so it might be quite permissible to increase gas throughput and suffer no penalty.

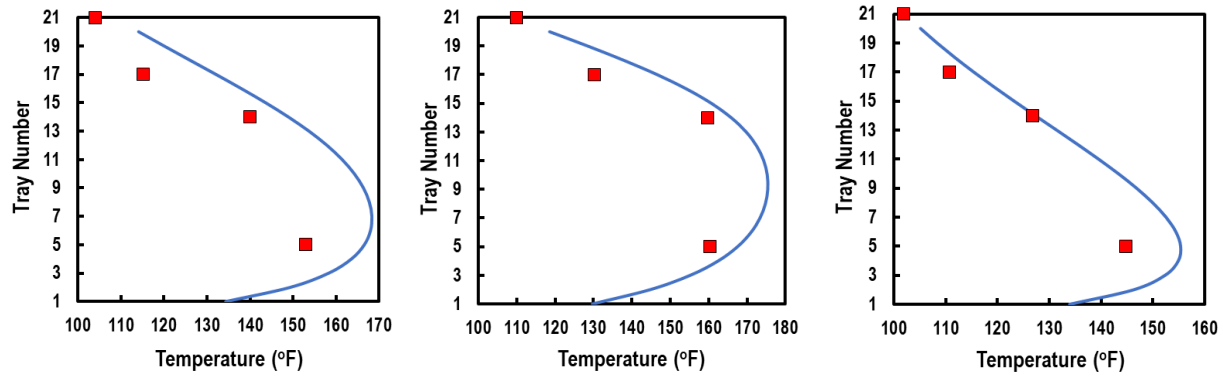
## Trayed Columns

ProTreat has been validated against the temperature profiling of many operating amine absorbers and, with a single exception, found to be in excellent agreement with the measured data. The exception is a $CO_2$ absorber using piperazine–promoted MDEA which, upon subsequently opening the regenerator (which determines lean loading), turned out to have the majority of its trays collapsed into the tower sump. Unfortunately, most of the cases are proprietary to various licensees of the ProTreat simulator and cannot be reported here. However there are a few cases whose data can be revealed but without identifying the plant or its operators.

The first case[2], originally reported in 2007, involves using 48 mass% generic MDEA to remove $CO_2$ from a gas containing nominally 4.3% $CO_2$ (no $H_2S$) at 69 barg (998 psig) at the gas and solvent flow rates shown in

[1] Published in LNG Industry, June, 2019
[2] Jenny Seagraves and Ralph Weiland, *Troubleshooting Amine Plants Using Mass Transfer Rate-Based Simulation Tools*, Laurence Reid Gas Conditioning Conference, Norman, OK, 2007.

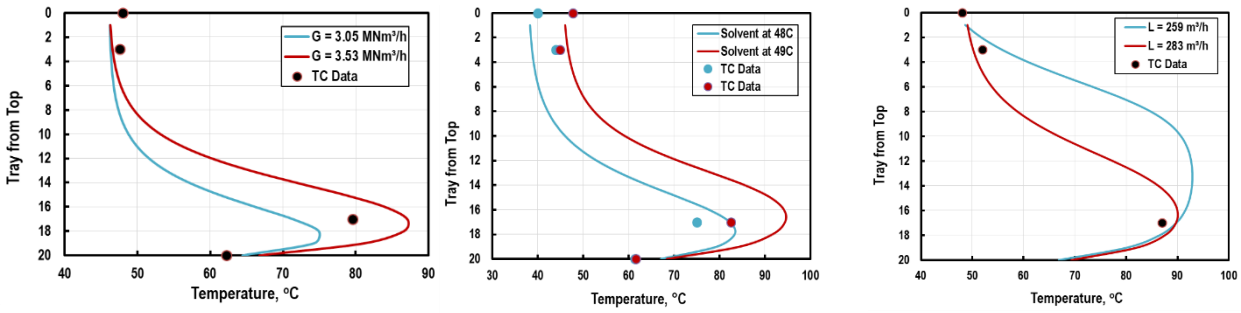
Figure 1. MDEA alone was used as the solvent because the objective was to remove $CO_2$ to below 2 mole%, the pipeline specification. Tray 21 corresponds to the inlet solvent. Simulation trends slightly above the data, although the measured temperature on Tray 14 is always closest to the simulated profile while Trays 5 and 17 are farthest away. These were not calibrated thermocouples and discrepancies may reflect thermocouple error; however, discrepancies may be genuine departures of the simulation from reality.




*L = 227 m³/h; G = 5.65 x 10⁶ sm³/d* *L = 186 m³/h; G = 5.57 x 10⁶ sm³/d* *L = 226 m³/h; G = 4.82 x 10⁶ sm³/d*

***Figure 1*** ***Measured vs. Simulated Temperature Profiles in a High Pressure $CO_2$ Absorber using MDEA. Trays Numbered Bottom Up.***

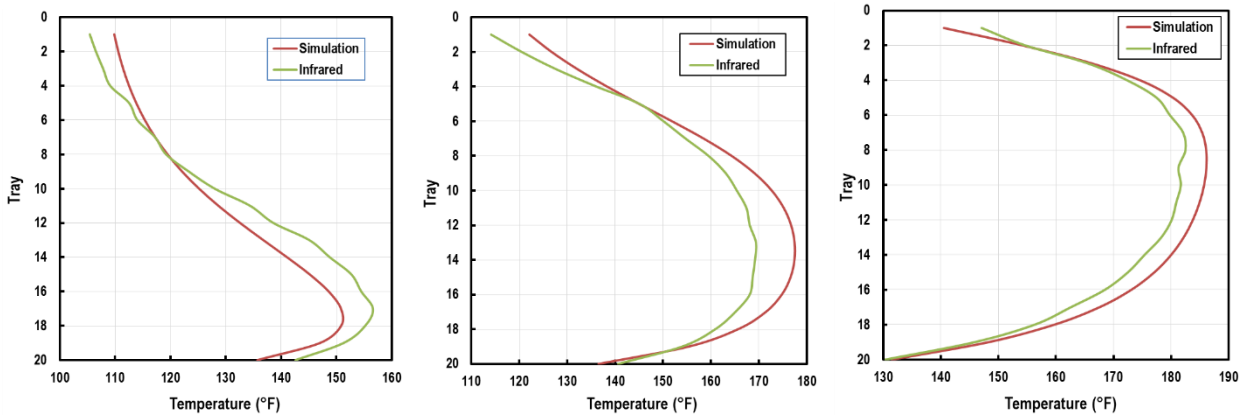
The second case uses a roughly 30 mass % MDEA plus 20 mass % DEA mixed solvent to remove $CO_2$ from a 70 bara (1,015 psia) gas using a 20-tray column. The plant had several parallel identical trains. Figure 2 shows simulated temperature profiles with thermocouple measurements indicated by the data points. In Cases (a) and (c) the thermocouples read almost identical temperatures regardless of gas and solvent flows, and the temperature profiles indicate this would be expected except for the bulge temperature in Case (a) where about a 10°C difference should be expected. Note too that there is significant thermocouple error around the top of the absorbers in Cases (a) and (b) — measured temperatures are shown decreasing with distance away from the top of the column, a physical impossibility. There would appear to be sizeable errors associated with many of the thermocouple measurements




*(a) L = 173 m³/h* *(b) L = 193 m³/h; G = 4.4 x 10⁶ sm³/d* *(c) G = 5.6 x 10⁶ sm³/d*

***Figure 2*** ***Measured vs. Simulated Temperature Profiles in a High Pressure $CO_2$ Absorber using MDEA/DEA Blended Solvent. Trays Numbered Top Down.***

The third case compares measured and simulated absorber temperature profiles in a 1.8-m diameter absorber treating gas from about 4% $CO_2$ to LNG quality at moderate pressure. The solvent is piperazine-promoted MDEA. Absorber temperature profiles were translated from thermal scans of the absorber and Figure 3 compares absorber temperature profiles taken from a thermal image of the absorber (—) with mass transfer rate-based simulation (—) at three different gas treating rates, all at the same solvent flow rate.




*(a) G = 1.6 x $10^6$ $sm^3/d$* *(b) G = 2.0 x $10^6$ $sm^3/d$* *(c) G = 2.7 x $10^6$ $sm^3/d$*

***Figure 3 Measured vs. Simulated Temperature Profiles in a Moderate Pressure $CO_2$ Absorber Using Piperazine-promoted MDEA Solvent in LNG Production. Trays Numbered Top Down.***

Not only do the simulations track the shape of the measured temperature profiles, but they are generally within better than five to seven degrees of measured. As discussed in a previous article[3], infrared measurements (which correspond to temperatures on the exterior of the tower shell) generally need to be corrected upwards by several degrees to account for the effect of temperature gradients through thick steel shells and to adjust for cooling by the wind. In Figure 3, the lowest gas rate shows a temperature bulge on the bottom trays, the highest gas rate towards the upper trays, and the intermediate gas rate more centred in the tower. This is expected because temperature bulges locate themselves according to how much heat is conveyed upwards by the gas flow versus how much is convey downwards by the liquid. This has been examined in detail elsewhere[4] where a quantitative criterion was presented that can be used to predict at which end of a column a temperature bulge is likely to occur. This kind of information can be valuable for determining exactly where a thermowell should best be placed to use temperature as a corrosion indicator, or for control purposes, for example.

**Packed Columns**

Our reference list of temperature profiles measured in packed columns pertinent to LNG production is a little less extensive than it is for trays; however, as indicated elsewhere[2], simulation has proven to be just as accurate for packed tower operations. But packed towers present a different challenge—axial dispersion or back-mixing *within* packed beds must be accounted for because it has a profound effect on treating and on the ability of a mass transfer rate-based simulator to reproduce observed temperature profiles and overall performance metrics. To those more conversant with tray efficiencies and HETP concepts for packing, the accuracy of tray efficiency predictions is highly dependent on understanding liquid mixing on the trays. Completely back-mixed and plug-flow liquid models give quite different answers. To that extent, efficiencies depend on tray construction details such as efforts made to

[3] Steven Fulk, Clayton Jones & Ralph Weiland, *Beyond What the Eye Can See*, LNG Industry, p. 19, June, 2019.

[4] Ralph Weiland & Nathan Hatcher, *Understanding Temperature Profiles*, Hydrocarbon Engineering, February, 2017.

prevent back mixing (e.g., using push valves), although not to any great extent on tray type. Similarly, packed beds can have back-mixed or plug-flow gas and liquid flows with these extremes leading to significantly different effects on the HETP. However, packed bed performance depends profoundly on the packing type (random vs. structured, brand, surface treatment, perforations) and size. The basic hydraulic models used in the ProTreat simulator are pretty much the same between trays and packing. The liquid on any tray is taken to be completely mixed while vapour is assumed to be in plug flow. In a packed segment liquid is back-mixed and vapour is taken to be in plug flow. So a real tray and a packed segment make similar assumptions about how the phases flow and what averaging needs to be done to allow calculations on a whole tray or a whole packed segment. All this is without reference to subtleties of axial dispersion on trays and within packing segments. However, mass transfer is still treated as a rate process driven by concentration differences and responding to mass transfer coefficients and interfacial areas, but the *mass transfer characteristics* of trays and packing are radically different.

Packed beds are simulated by discretizing the total bed depth into a number of segments. A single segment would correspond to completely back-mixed flow of liquid. At the other extreme, an infinite number of segments in a tower would correspond to perfect plug flow of both phases. The truth is somewhere between these limits. ProTreat® segments packed towers according to general rules of thumb and internally chosen generalised heuristics to achieve best agreement with performance data. There is a rough equivalence between a packed segment and a real tray but they have very different mass transfer characteristics so they perform quite differently.

Both demonstration cases are LNG plants operating in Australia. The first case uses the thermal image of the bare-shell absorber containing Mellapak M250.X structured packing in a 4-m diameter shell. The solvent is a piperazine-promoted MDEA mixture removing 2.8 mole% $CO_2$. Figure 4 shows the data (●) garnered from four repeat images of the tower, after correction for the temperature gradient through the tower shell and for the effect of a 20 km/h wind on the skin temperature. Repeat measurements span a range of at least 8°C, giving some indication of repeatability. Lines on the figure are simulations from which it can be seen that the simulated temperature is quite sensitive to small metering errors in solvent flow. Lowering the solvent flow for the simulation by only 2% (well within the measuring error of most industrial flow meters) puts the simulation into close agreement with the data.

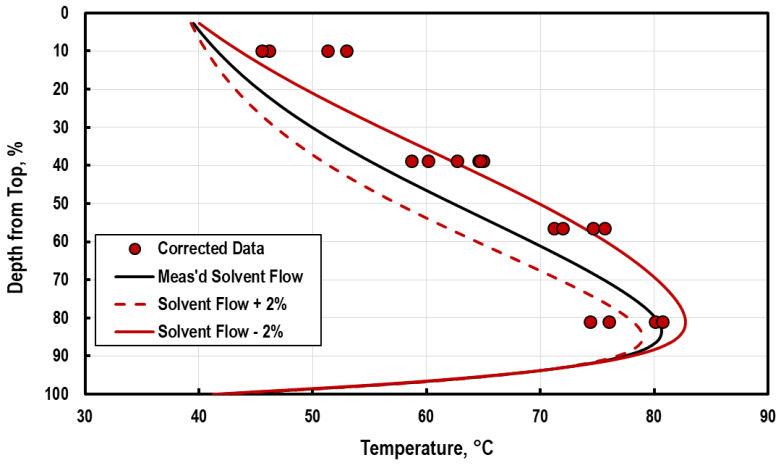



**Figure 4 Simulation Compared with Temperatures Measured from Thermal Images. Structured Packing**

The second example is a 4.5-m diameter absorber containing two beds of Raschig Super-Rings No. 1.5, a modern random packing. Piperazine-promoted MDEA solvent is used to remove 6.3 mole% $CO_2$. Measured and simulated bed temperatures are in excellent agreement. Because directly measured temperatures using thermocouples require no corrections for thermal gradients through tower shells or corrections for cooling by radiation

and by natural and forced convection (forced by a varying wind velocity and direction), direct measurement is certainly to be preferred over indirect methods. Furthermore, unlike thermal imaging, measurement by internally placed thermocouples is independent of the presence of column insulation and appendant items such as pipe fittings, platforms, hangers, and flanges.

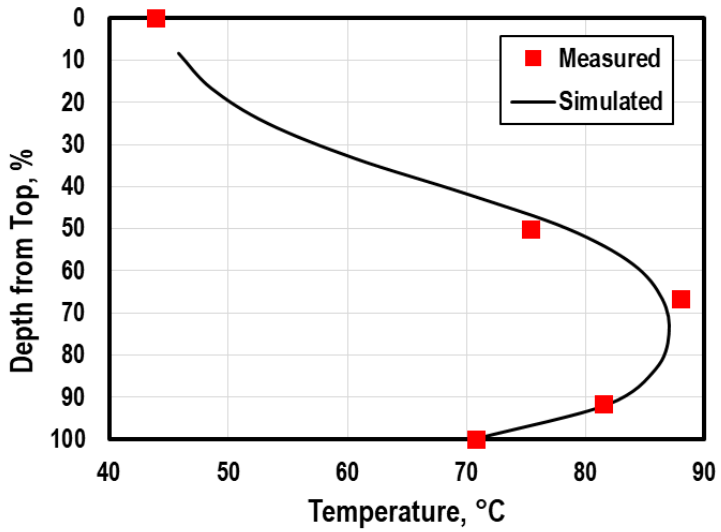



**Figure 5 Simulation Compared with TC-measured Temperatures. Raschig Super-Rings No. 1.5**

## Summary

Typical carbon dioxide absorbers in amine service are characterised by a large temperature bulge somewhere in the tower. The bulge will be positioned in the tower at a location dictated by the relative convection of the heat released by absorption via the gas and liquid flows. Temperatures are at their highest when the gas and liquid convey heat at about equal rates[3]. This is because each phase carries heat to one end of the column or the other but as it arrives towards its outlet end, the opposite phase (being relatively cold) picks up the heat and carries it right back into the interior of the column. Both phases perform this dance in tandem. Peak temperature, however, is also determined by the heat of absorption so it will depend on the solvent composition and the ***rate*** of absorption, which determines the location of most of the heat release. Absorption rate depends on the specifics of the packing—for example, small packings have higher surface areas so they absorb faster and result in higher temperatures. Absorption rate also depends on tray geometry at least insofar as it affects interfacial area between gas and solvent. Regardless, temperatures can become hot enough seriously to exacerbate corrosion of equipment and cause rapid thermal degradation of solvent components. It would be prudent to monitor absorber temperatures via thermal imaging and perform mass transfer rate-based ProTreat® simulation of the whole amine plant before any significant change is made to new operating conditions of flow rates and temperatures. Incidentally, it is important to include the regenerator in amine plant simulations because solvent lean loading greatly affects absorber behaviour.