Which Regime Is Right?[1]

Clay Jones & Matt Bailey
Optimized Gas Treating, Inc.
212 Cimarron Park Loop, Buda, TX 78610

The CO_2 absorber in an LNG plant is a critical piece of equipment where the product CO_2 spec is met – or not – affecting downstream production and revenue. Inside this vessel, a highly non-ideal and non-linear mass transfer process takes place: the acid gas CO_2 is physically and chemically absorbed into an alkaline aqueous solvent. Depending on the operating regime of an absorber, its overall performance is determined by its particular conditions. This article provides a practical review of

- Operating regimes (mass transfer limited, lean-end pinch, bulge pinch, rich-end pinch)
- How to identify the absorber's operating regime
- Implications for operating the absorber

None of these regimes is necessarily good or bad. Any absorber that meets its operating targets could be considered acceptable, regardless of its operating regime. However, the regime that it is in determines the likely effect of changes to operating variables.

There are other considerations of operating regime which have important implications for long-term reliability of the plant (for example the relationship of temperature and loading with corrosion rate) that are outside the scope of this article.

Operating regimes

To some extent, the performance of the absorber in a CO_2 removal system depends on all the operating variables in the plant including lean loading, lean solvent temperature, lean amine circulation rate, total amine concentration, promotor (e.g., piperazine) strength in a promoted MDEA solvent, feed gas temperature, inlet CO_2 concentration, operating pressure, and internal hardware. However, in a practical sense, in each particular absorber not all variables will exert a significant influence. Recognizing the operating regime of an absorber unlocks the knowledge of which parameters are the most important and which ones have less influence on absorber performance. With this information, engineers can make decisions in the field to improve treatment and judge the impact of potential changes to hardware and operating conditions.

As the operating conditions of a tower change, one operating regime can morph into another, not always smoothly but sometimes rather abruptly. Figure 1 shows that the operating regimes are interrelated through process variables. Each regime is discussed individually later, but here we consider how they are related to each other from a high-level perspective.

The first major division between operating regimes is whether performance is determined by mass transfer rate or a vapor-liquid equilibrium pinch. If the rate of absorption is slow enough and the amount of vapor liquid contact is small enough, any absorber can find itself in the mass transfer rate-limited regime, meaning that more absorption could occur in the tower if only there was more contact between the phases or the absorption rate could be increased. Conversely, if enough mass transfer area is provided then any absorber will eventually become pinched. A pinch occurs when the solvent and gas are in equilibrium somewhere in the absorber. Once equilibrium exists, there is no further absorption. Therefore, the absorber's performance can be manipulated only by influencing the equilibrium conditions

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at the pinch point. If a pinch point exists, it might occur at the lean end (top), the temperature bulge (middle) or rich end (bottom) of the absorber.

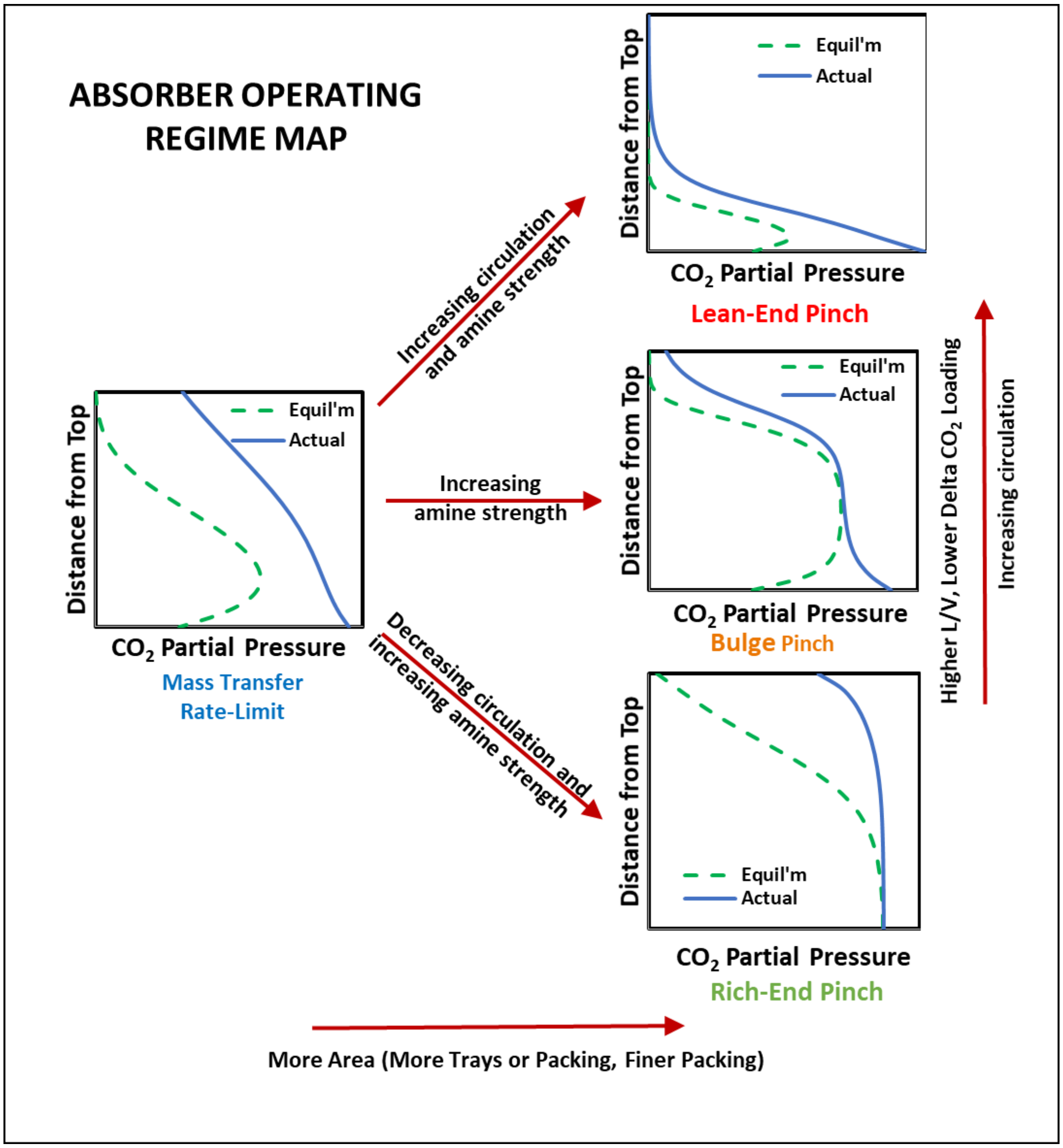

Figure 1 - Typical relationship between absorber operating regimes

The map in Figure 1 shows a general relationship between operating regimes that are quantitatively different for each absorber. Note that the bulge pinch regime is not possible for all absorbers. Generally, to become bulge pinched, a sufficiently reactive solvent must be used, i.e., in the context of LNG production, the piperazine content of a promoted MDEA-based solvent must be high enough.

It isn't always easy to know the operating regime, and an absorber can operate on the border between regimes where its behavior may be a combination of the two. For a new design or revamp project, the only way to know the operating regime with certainty is to use a mass transfer rate-based simulation tool such as the ProTreat® simulator—ProTreat was used to determine the profiles shown throughout this article. For an operating unit, the regime can also be determined by doing step-tests to find out which process variables are the most effective at controlling CO_2 absorber performance.

Mass transfer rate limited

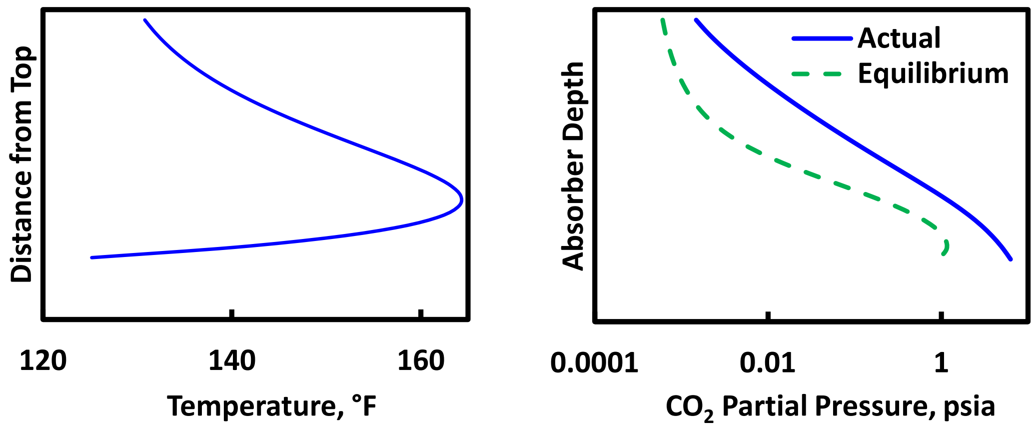

Figure 2 - Profiles for mass transfer rate limit for bulk removal

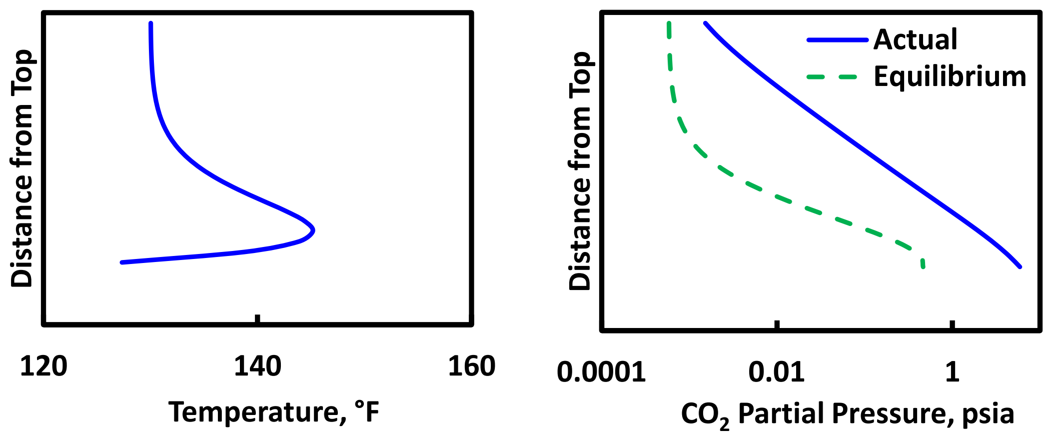

Figure 3 - Profiles for mass transfer rate limit for deep CO_2 removal. Note the flat temperature profile near the top.

<u>How to identify</u>

Absorbers that are mass-transfer rate limited have a significant driving force for CO_2 absorption along the entire height of the absorber. In these towers, the actual CO_2 partial pressure is significantly higher than the equilibrium value at every level in the tower.

For bulk absorption applications, there will be a substantial absorption rate of CO_2 even in the top of the tower resulting in a rising temperature as the solvent flows through the column as shown in Figure 2. However, the temperature profile alone isn't always enough information for applications where CO_2 is being removed to a very small concentration. Figure 3 shows a situation where the absorption rate of CO_2 at the top of the tower is so small that it doesn't cause much temperature rise, even though the tower is in the mass transfer rate limited regime throughout its entirety.

<u>Operating Implications</u>

For a tower that is mass transfer rate limited, changes to different operating parameters will have effects of different magnitude depending on the particulars of the absorber. In general, any strategies expected to improve treating will succeed to some extent, but operating experience or predictive simulation will be needed to know quantitatively which strategies will give the greatest result.

One important feature of towers operating in the mass transfer rate-limited regime is that additional absorption will take place if improved contacting hardware is installed in the absorber. These towers are candidates to be improved with capital projects to add trays, switch from trays to packing, or otherwise upgrade the packing to a variety with better mass transfer characteristics.

Lean-end pinch

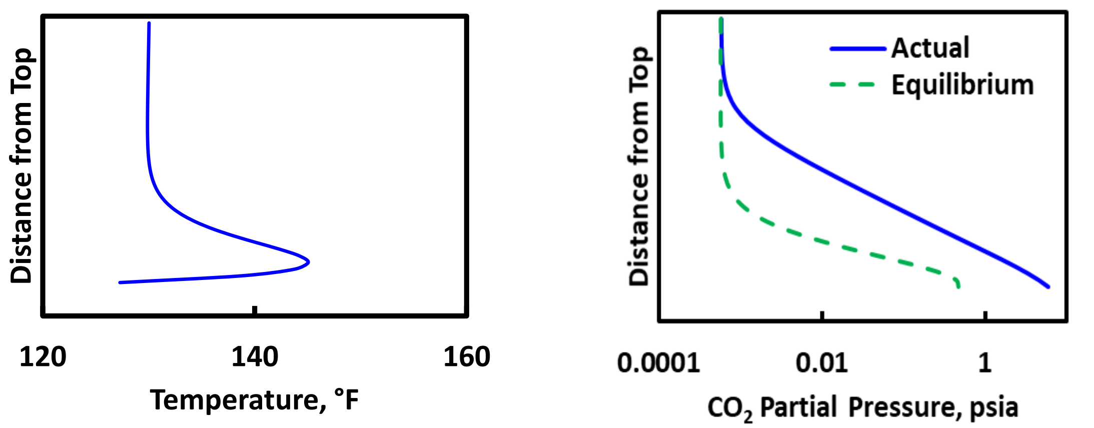

Figure 4 - Profiles for lean-end pinch

How to identify

Since LNG CO_2 treating targets correspond to deep removal, it is common for the absorber to fall into this regime. The defining characteristic of a lean-end pinch is that at the lean end of the tower the treated gas is in equilibrium with the lean amine. In other words, actual and equilibrium CO_2 partial pressures are the same close to the top of the tower as shown in Figure 4. This tends to happen when there's a higher L/V ratio to push the temperature bulge lower into the tower and when the overall change in loading is somewhat smaller, leading to lower heat of absorption.

Lean-end pinches usually exhibit a vertical temperature profile in the region near the top of the tower as shown in Figure 4; however, temperature profiles alone can be deceiving as exemplified by Figure 3.

Operating Implications

Operating parameters that affect the performance of a lean-end pinched tower are the same ones that affect equilibrium at the top of the tower. Better treating can be had with lower lean loading (increased reboiler steam) and cooler lean amine temperature. Other changes such as increasing the solvent circulation rate or adding more contact area by upgrading trays/packing will be ineffective.

Bulge pinch

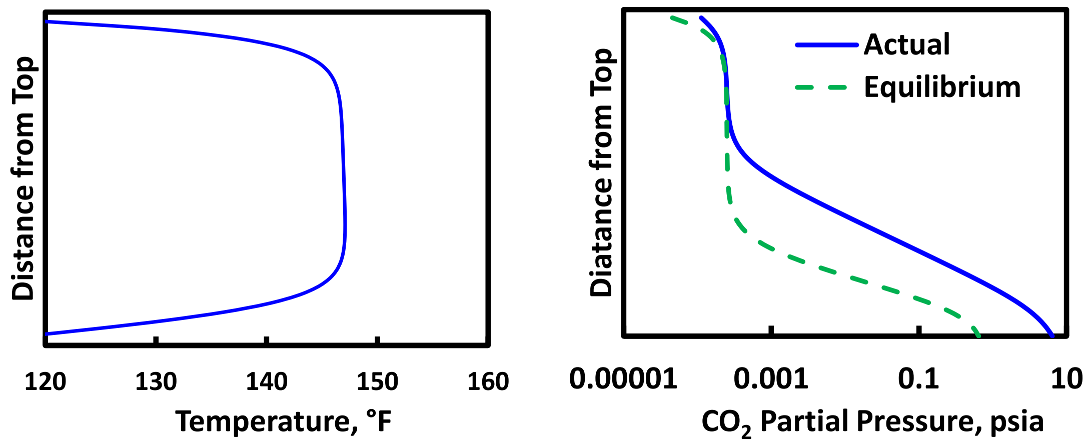

Figure 5 - Profiles for bulge pinch

How to identify

The bulge pinch condition is characteristic of optimized units where highly reactive solvents are used at minimal circulation rates. This combination of conditions results in a "heat bubble" where rapidly released heat of absorption at the bottom of the tower rises in the vapor only to be reabsorbed and pushed back down by cool lean solvent entering at the top. While almost all absorbers will exhibit some degree of temperature bulging, a bulge-pinched condition is characterized by a broad, relatively flat temperature bulge, often approaching regenerator temperatures. Across the whole temperature bulge, the actual and equilibrium partial pressure of CO_2 are essentially the same.

Operating Implications

To improve the performance of a bulge-pinched absorber, the internal heat balance must be reconfigured to reduce the magnitude of the temperature bulge. The most effective way to do this is by increasing amine circulation rate. This step extends the reach of the lean amine's cooling effects. By pushing the heat balance towards a cooler profile, the temperature bulge is reduced and the improved equilibrium allows more CO_2 to be absorbed. Some optimized designs make use of external cooling through a pump-around circuit to alleviate a bulge pinch.

Similar to other pinched absorbers, the addition of trays or packing improvements will not improve the performance of bulge-pinched absorbers; instead, it will just stretch the bulge across more of the column.

Rich-end pinch

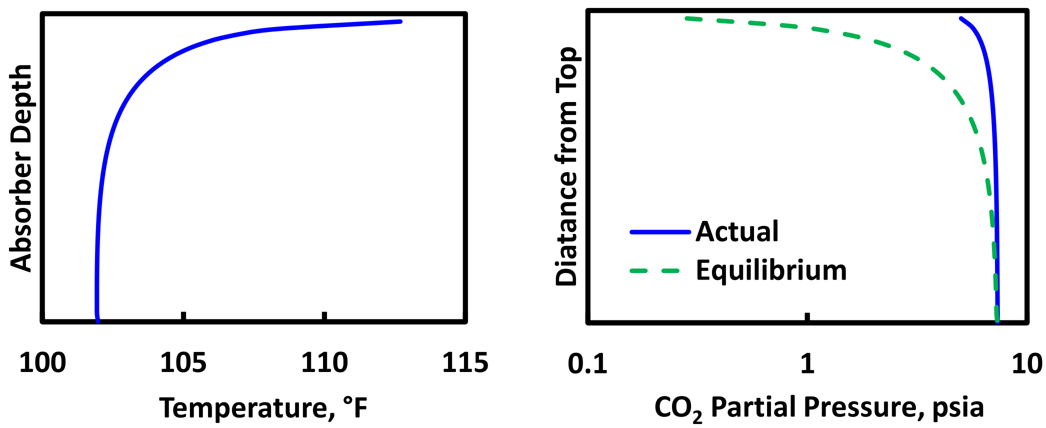

Figure 6 - Profiles for rich-end pinch

<u>How to identify</u>

Rich-end pinches occur when the actual and equilibrium partial pressure are the same at the bottom of the absorber. Completely opposite to a lean-end pinch, the maximum temperature now is located at the top of the column. The combination of large residual amounts of acid gas remaining in the treated gas, high rich-amine loading, and under-circulated amine are the hallmarks of a rich-end pinch.

<u>Operating Implications</u>

Increasing amine circulation to push the temperature bulge downwards to lower in the column will improve treatment. Since the treated gas is far from equilibrium, lower lean loading (additional steam to the regenerator) will not have much effect.

Conclusion

The four operating regimes and their characteristic features together with the most important operating variables have been described for each regime. Table 1 summarises all this information by showing which variables are typically the most effective at influencing the performance for operation within each regime.

	Lean Loading	Lean Temperature	Amine Circulation Rate	Total Amine Strength	Promotor Concentration	Number of trays, depth/size of packing
Mass transfer rate limited	✓	✓	✓	✓*	✓	✓
Lean end pinch	✓	✓	✗	✓	✓	✗
Bulge pinch	✓	✓	✓	✓	✓	✗
Rich end pinch	✗	✗	✓	✓	✓	✗

** In a mass transfer rate-limited tower, higher total amine strength might help by providing higher capacity but it might also hurt by causing higher viscosity, hence greater resistance to mass transfer*

Table 1 - Most effective influences for each operating regime

Knowing an absorber's operating regime provides valuable information about how the absorption process is taking place, and how one can influence the process by using effective controls in the unit. For any operating plant, the operating regime can be ascertained either through expensive plant-scale step testing of the various control variables, or alternatively via the much less costly and less disruptive approach of using a predictive mass transfer rate-based simulator. The latter tactic provides tremendous additional insights such as just how sensitive and responsive to various strategies the plant actually is. As a result, focus can be directed to the most important parameters. For plants still in the design phase, predictive modelling is the only way to know the expected regime for the anticipated operating conditions and, therefore, what parameters require the closest attention, not only to provide an optimal design, but one that has been constructed to be the most resilient to changes outside original battery limits.