Why CO_2 Absorbers Go Off Spec[1]

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ABSTRACT

Case studies are used to show why sudden and unexpected failure to remove CO_2 adequately from syngas often results from lean or semi-lean solvents that are allowed to become too hot, perhaps through heat exchanger fouling or ambient air temperatures that are too high to provide adequate solvent cooling. Another cause is trying to squeeze the last economies from a plant by using the absolute minimum solvent flowrate—the unit can run too close to the edge.

Introduction

The majority of CO_2 removal systems in ammonia plants use a piperazine-activated MDEA-based solvent. Frequently the solvent is a proprietary one used in a licensed process—this puts the onus for proper performance on the licensor; nevertheless, it is incumbent on the operator to ensure that process parameters are kept within specified limits, as well as to understand how the process operates and how to troubleshoot it when problems arise. This article explains the 'how' of two of the most common causes for poor CO_2 removal system performance.

It is not uncommon to find that when the lean solvent in a conventional single recycle CO_2 absorption system in an ammonia plant becomes a little too hot, or the solvent flowrate is reduced past a certain point, the treated gas CO_2 level shoots up surprisingly rapidly. The same behavior is sometimes seen when the semi-lean solvent is insufficiently cooled or the solvent rate drops too low in a split flow plant configuration. The reason is connected to the chemical reaction kinetics between carbon dioxide and the reactive components in the solvent.

Piperazine reacts extremely rapidly with CO_2 and is very effective as an absorption promoter even at low concentrations. It allows rapid absorption in a relatively short tower. On the other hand, MDEA reacts with carbon dioxide very slowly, if at all, and it is used at high concentrations (typically 35–50 wt %). It has high capacity for CO_2. It also has relatively low heat of reaction which makes solvent regeneration less energy intensive, one of its main advantages over other amines. Overall, piperazine-promoted MDEA absorbs CO_2 quickly in a short tower and is easy to regenerate. In fact, the absorption rate is so fast that the treated syngas emerges very nearly in equilibrium with the lean solvent entering the tower. Indeed, across the upper reaches of the absorber the gas is at most being polishing to the required CO_2 level if any CO_2 is actually being removed there at all. It is easily shown by simulation that lowering the solvent flow rate reduces the *active* height of the polishing section until the CO_2 breaks through. Beyond that point the carbon dioxide level in the treated gas quickly rises. On the other hand, a solvent that becomes too hot exerts a CO_2 backpressure that prevents the treating specification from being met. Equilibrium CO_2

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backpressure depends exponentially on temperature so the treating response to high temperature can be rapid. Split flow plants are even more sensitive to these effects.

Case Study 1: CO_2 Removal Unit Having a Single Lean Solvent Recycle

Figure 1 shows a simplified flow diagram of this carbon dioxide removal unit which was configured with a single absorber, single regenerator, and single lean amine stream. Over time, the performance of heat exchangers deteriorates. This results in a gradual lessening of heat cross exchange in the exchanger labeled X-Exchanger so as time goes by the lean solvent slowly becomes warmer. The ability of the Cooler to provide additional solvent cooling also becomes increasingly limited. The net result is that the lean amine entering the CO_2 absorber gets hotter with increasing time-on-stream.

An additional problem with the Trim Cooler (Cooler block seen in Figure 1) is that heat exchange is usually against ambient air and regardless of the climate, summer months are the hottest time of the year. Fin-fan coolers have a set area and if cooling is controlled by fan speed, that too has an operating range which limits the maximum amount of cooling possible.

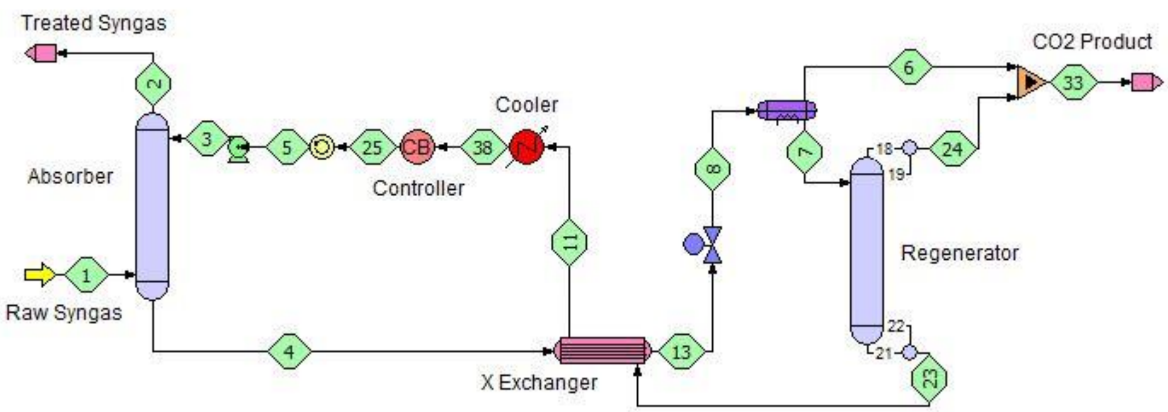


Figure 1 Simplified Process Flow Diagram for Single Recycle Case

Single recycle CO_2 removal systems like the one shown here are generally simple to operate and are usually immune from rapid responses to seemingly small variations in flows and temperatures over a fairly wide operating range. In the case study considered here, the CO_2 removal unit operates in a plant producing about 1,350 tonne/d ammonia from 208,000 Nm^3/h of raw syngas with 17.86% CO_2. The solvent is 42 wt% MDEA promoted with 3 wt% piperazine flowing at 375 L/s measured at the lean solvent inlet stream temperature. The reboiler in the trayed regenerator consumes 215 GJ/h provided by steam. The 12-ft (3.66-m) absorber holds a 40-ft (12.2-m) deep bed of IMTP®-50 random packing.

Performance as a function of lean amine temperature was assessed using the ProTreat® simulator which is completely mass and heat transfer rate based and depends on absolutely no adjustable of parameters to achieve any kind of fit or agreement with measured data. Agreement with data is simply a natural consequence of the predictability of the models. Figure 2 shows the simulated response of the treated gas CO_2 level to variation in the lean amine temperature.

There is an optimal lean temperature at about 45°C. As temperature is lowered from this value treating gets worse, slowly at first, but more and more rapidly as temperature continues to fall. The cause is two-fold: the kinetics of the reaction between carbon dioxide and piperazine slows, and the solvent becomes more viscous which inhibits the absorption *rate* of CO_2 into the solvent. As lean solvent temperature is raised above 45°C treating again worsens.

This time it's because the equilibrium solubility of CO_2 rises with temperature. But above 73–74°C, treating starts to go badly wrong. The reason is simply because the solvent is now holding as much CO_2 as it possible can at absorber conditions. Its capacity is even lower at higher temperatures and what cannot be absorbed has to leave with the treated gas. The solvent temperature at which this happens is the breakthrough temperature and beyond it further CO_2 removal fails miserably and the treated gas goes wildly off specification. Note also that controlling to a set point temperature of 73–74°C will be quite impossible.

Too cold, and especially too hot have dire consequences; however, solvent temperature has a wide operating range, at least in this removal plant. Nevertheless, it is critical to keep the lean amine temperature below 73–74°C, something that may prove hard to do in very hot environments, especially if the exchanger has been undersized, or it has become fouled. These problems are exacerbated if plant throughput is pushed beyond reasonable levels. Sensitivity analysis by rate-based simulation is the most assured way to analyse operations and set limits before changes are implemented and promises of higher production rates are made.

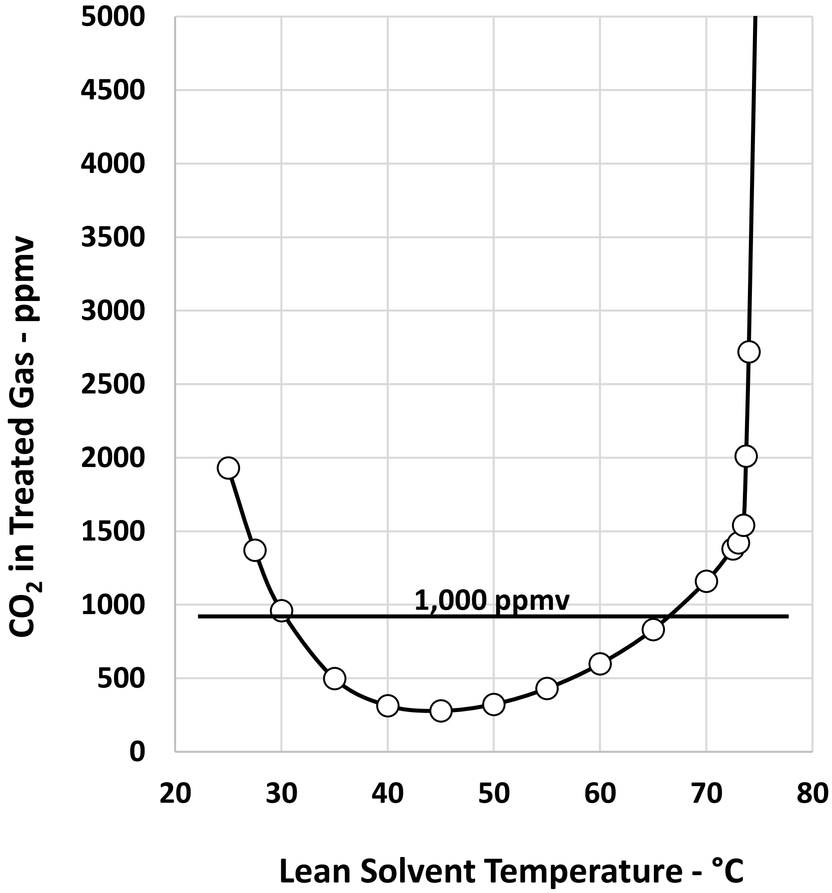


Figure 2 Treating Response to Lean Solvent Temperature

Case Study 2: CO_2 Removal Unit in a Split-Flow Configured Unit

This case study is of a much larger plant in the Middle East, one with a nominal 3,500 tonne/d capacity. The process is in a split-flow configuration. In a conventional split-flow plant (Figure 3), a semi-lean amine stream is drawn from part way down the regenerator, cross exchanged with part of the rich feed to the regenerator, and enters the absorber mid tower. The remaining solvent continues down the regenerator and leaves the reboiler in a fully-stripped state. It returns to the absorber top where is removes the residual CO_2 not yet captured by the semi-lean solvent.

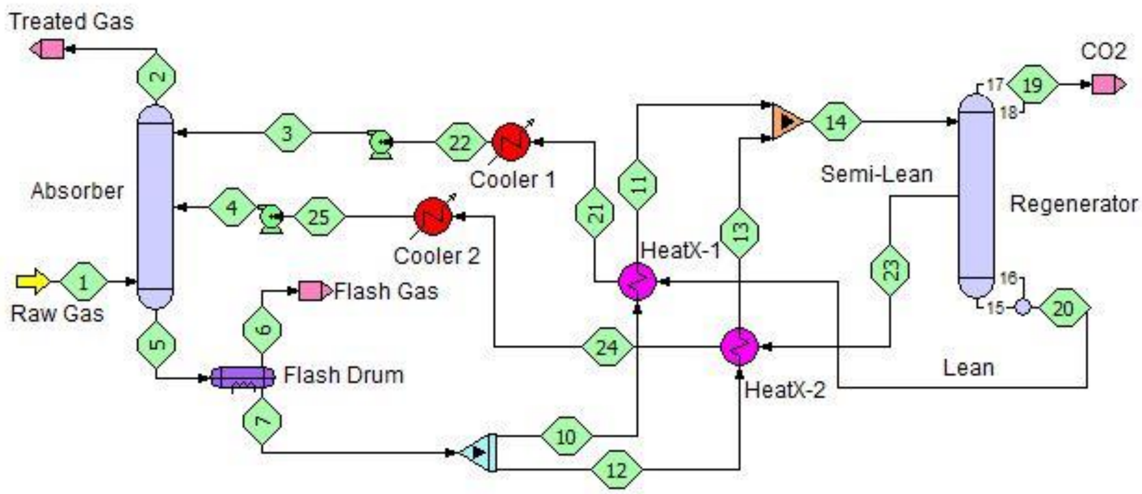


Figure 3 Split Flow CO_2 Removal Unit

In this particular plant, the single absorber is actually build as two side-by-side columns of 4-m (Polishing) and 6-m (Bulk Removal) diameter, containing different packings but each with the same 11-m total bed depth (Figure 4). The absorber was also simulated this way although ProTreat is perfectly capable of modeling this setup as a single tower, swaged at the semi-lean feed point and containing different packings. The simulation of the Polishing column included two bubble cap trays at the top which serve to capture potential solvent that would otherwise be carried over with the treated gas. Lean and semi-lean solvent flows are 770 and 4480 tonne/h, respectively. The solvent is nominally 37 wt% MDEA with 3 wt% piperazine as promoter.

The parameter of greatest interest is the temperature of the semi-lean solvent stream because it was the one variable the plant was having the greatest difficulty getting down to a satisfactory level. Figure 5 shows how treating is simulated to respond to semi-lean amine temperature, and the simulation predicts that the absorber system operates quite satisfactorily as long as this temperature is kept below about 77°C. Unfortunately, the trim cooler (Cooler 2 in Figure 3) was undersized for the throughput desired and in the summer months with very hot ambient air temperatures, the temperature could not be brought to below the process licensor's recommended maximum of 74°C. A higher solvent rate would have fixed this problem but the solvent pumps were already operating at capacity.

One of the interesting aspects of Figure 5 is that a unit operating below 77°C would give *absolutely no indication* of the existence of the critical temperature of 77°C, and that if it were exceeded, treating would rapidly go off specification without warning of any kind. There is a critical temperature, *not a temperature range*, and given the inherent margin in any control system, one might find sudden unexpected and inexplicable excursions in treating with a temperature change of less than 1°C.

Like any commodity, the price of tonnage ammonia can fluctuation markedly, but at a nominal value of USD 600 per metric tonne, the value of lost production from this plant is not less than USD 2,000,000 per day. There is high incentive to understand any problem plaguing a unit and to permit recommendations to be made with some certainty of their success. Most will agree that simulation offers the best chance for identifying and understanding the cause of poor treating well enough for remedial action to be taken to keep the unit producing until bottlenecked or compromised equipment can be upgraded or replaced during a scheduled shutdown. The authors contend that a real mass transfer rate-based simulator is the *best and only* choice. So what is the cause of the failure in this case, and given the inherent constraints within the unit, what are the possibilities for avoiding or at least minimizing lost production?

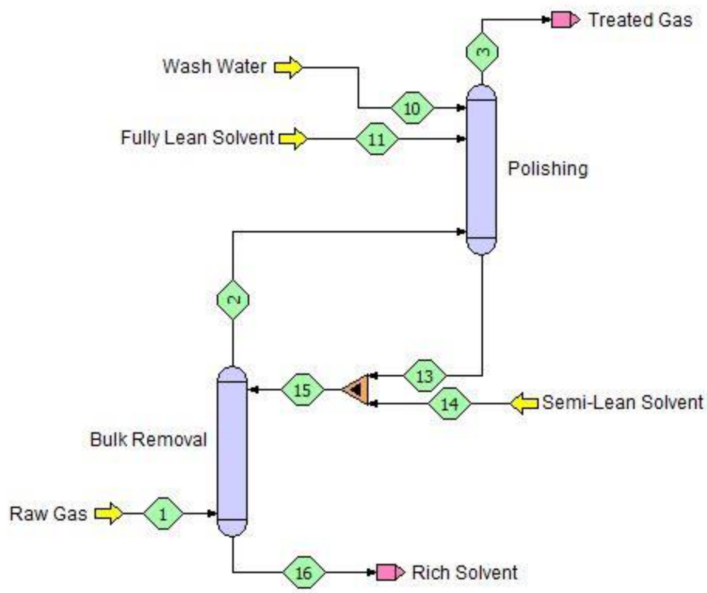


Figure 4 Absorber As-Built

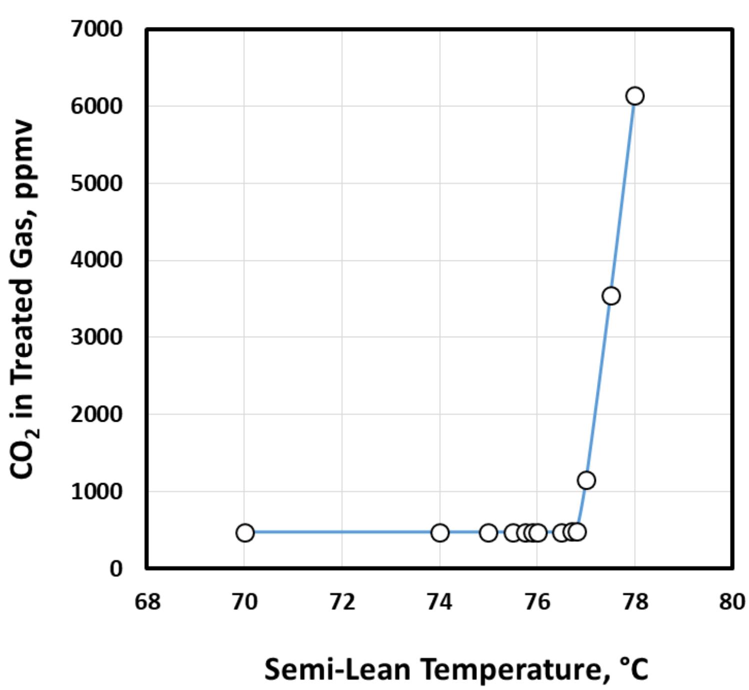


Figure 5 Response of Treating to Semi-Lean Temperature

Figure 5 shows CO_2 breakthrough from the polishing column, apparently caused by excessively high semi-lean solvent temperature. Breakthroughs of this type almost invariably correspond to a solvent capacity limit being exceeded. In the present case, as the semi-lean temperature increases the Bulk column is able to remove less and less CO_2 and what cannot be removed spills over into the Polishing Column. At conditions corresponding to 76.8°C the Polishing Column's absorption capacity has been reached and breakthrough occurs. Figure 6 shows the CO_2 content of the gas leaving the Bulk Removal column as a function of semi-lean temperature. The slow increase that can be seen below the break (~ 76.5°C) results simply from elevated equilibrium pressure caused by higher temperature. The rapid rise to the right of that temperature is the result of CO_2 breakthrough, i.e., the solvent capacity in the Bulk Removal column has been reached and then exceeded.

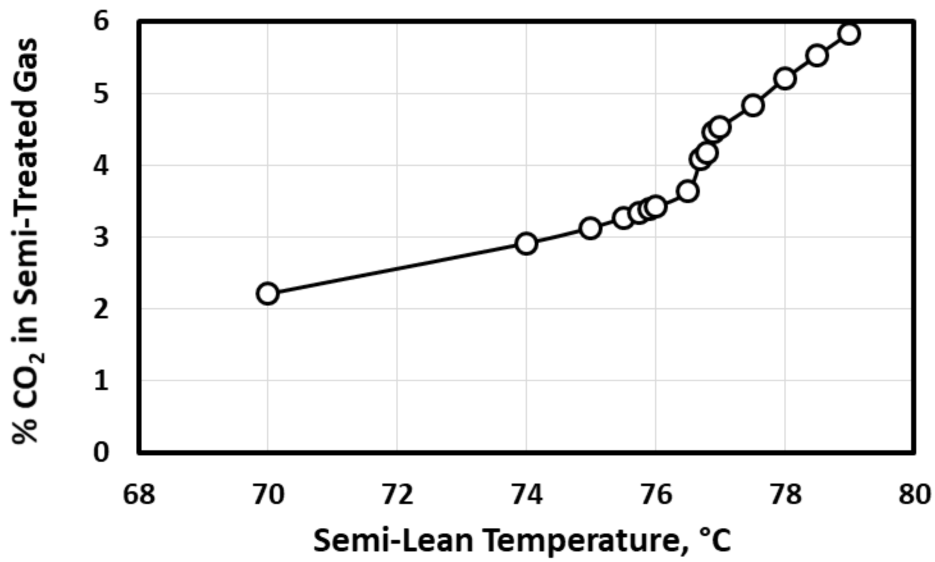
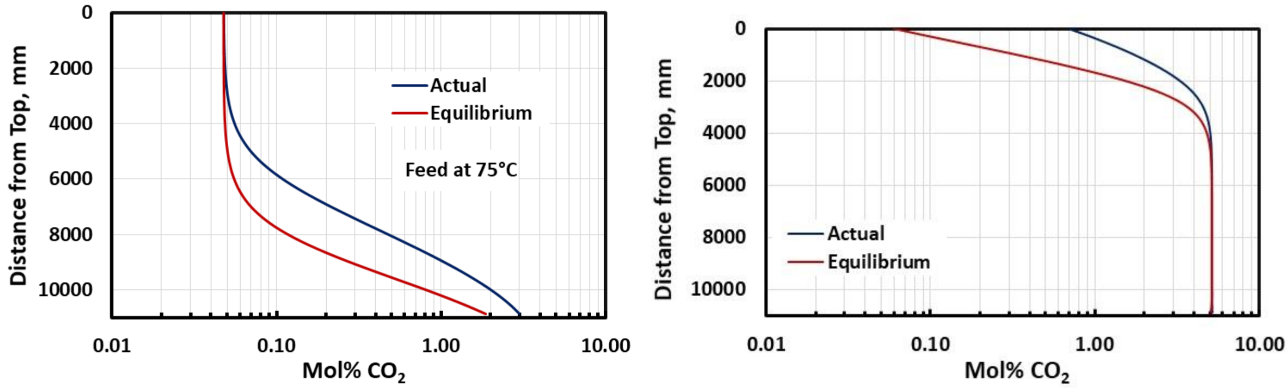


Figure 6 CO_2 from Bulk Removal Column vs. Semi-Lean Temperature

In the vicinity of 77°C, both columns go from having their performance pinched at the top, to pinched at the bottom. Figure 7 shows CO_2 profiles interior to the Polishing column before and after the switch from being lean-end to rich-end pinched. Pinching is a condition that occurs when the actual concentration of CO_2 in the gas and its equilibrium concentration coincide. When that happens, there is no driving force (no concentration difference) to force or drive absorption through mass transfer. Consequently, absorption stops and that region of the column is said to be pinched. The kind of profiles and the type of pinching shown in Figure 7 for the Polishing column occur simultaneously in the Bulk Removal column, too.



(a) Lean Pinched — Cold Semi-lean **(b) Rich Pinched — Hot Semi-lean**

Figure 7 CO_2 from Bulk Removal Column vs. Semi-Lean Temperature

Summary

When a CO_2 absorber stops treating properly, one of the first things to do is run a simulation of the system using predictive simulation software such as ProTreat® with its real mass and heat transfer rate based tower model. ProTreat simulation will tell you how the column *should* be performing, and interpretation of its predictions will help a great deal to reveal the root cause of the poor performance. High lean solvent temperature from fouled heat transfer equipment is a common cause of failure that's hard to diagnose any other way. So are reduced solvent flows, degraded solvent, corroded tower internals, and inadequate reboiler steam flow. This highly reliable, predictive tool is certainly worth its miniscule cost when compared to USD 500 to USD 1,500 *per minute* in lost production.