

The CONTACTOR™

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Approach to Equilibrium: Part 3 — Selective CO₂ Removal

In Parts 1 and 2 of this series we showed how the concept of *Approach to Equilibrium* (A2E) may not always be a good indicator of how much additional useable capacity an absorber has and how resilient it might be to excursions in feed gas quality, and higher acid gas feed rates. These findings were for raw gases containing a single acid component, either CO₂ or H₂S, as well as for ones when the acid gases are present together

In this, the final part in a three-part series of The Contactor™, we first reiterate the definitions of the Approach to Equilibrium, then use a case study to assess the viability of the concept in treating for *selective carbon dioxide removal* using MDEA at relatively high pressure.

Approach to Equilibrium

Briefly, the Approach to Equilibrium is intended to be a measure of the extent to which the solvent leaving an absorber is in equilibrium with the raw gas feed, usually expressed as a percentage. If two gases are present, CO₂ and H₂S, there is a different value of the A2E for each of them. The A2E can be defined in two ways:

Definition 1

Basis is partial pressures of acid gas components:

$$A2E(PP) = \frac{P_{\text{Gas above Rich @ Equilibrium}}}{P_{\text{Gas in Feed}}} \times 100\%$$

Definition 2

Basis is solvent loading:

$$A2E(\text{Loading}) = \frac{\text{Actual Rich Load}}{\text{Equilibrium Rich Load}} \times 100\%$$

When two acid gases are present, the equilibrium rich loading of each gas is calculated at the same time as the other. In other words each acid gas influences the other.

Treating for Selective CO₂ Removal

Because all amines react with H₂S instantaneously but with CO₂ at finite (albeit sometimes

very fast) rate, they are all selective for H₂S over CO₂ to some extent. *N*-methyldiethanolamine (MDEA) is possibly the most selective of the commonly-used, non-proprietary amines.

This ProTreat® simulation study uses 45 wt% MDEA in an absorber with 11.25 ft. of MellapakPlus™ M252.Y structured packing and operating at 890 psig. All basic parameters were kept fixed from case to case. The raw gas H₂S concentration was 0.2 mol% (dry basis), and it was kept constant at this value while the CO₂ concentration was varied between zero and 6.0 mol%.

Figure 1 shows that the CO₂ concentration in the treated gas is *almost* a linear function of the CO₂ content of the raw gas. In other words, a nearly constant percentage of the inlet CO₂ is slipped through the absorber. With H₂S on the other hand, as more CO₂ is absorbed in an absolute sense, more H₂S leaks through the absorber (although the absorber is never in danger of missing a 4 ppmv H₂S treating specification). As CO₂ absorbs, CO₂ loading increases. This removes MDEA and leaves smaller concentrations of amine to absorb H₂S; thus, H₂S leak from the absorber increases.

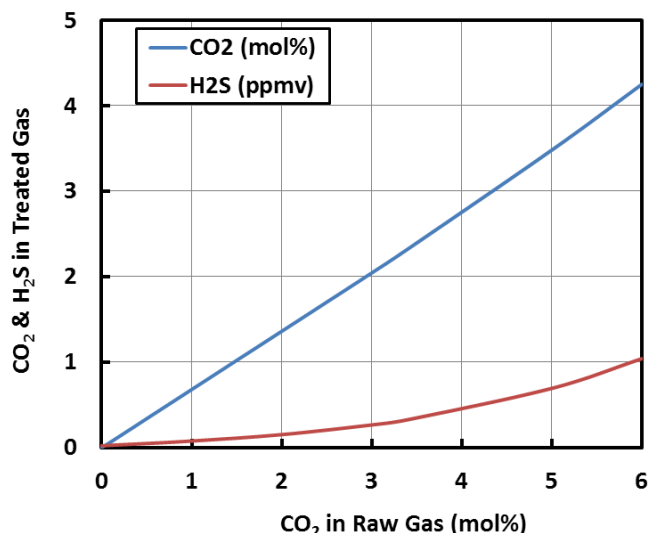


Figure 1 Treating Various CO₂ Levels in Raw Gas

In terms of A2E, Figure 2 shows that for H₂S the A2E reaches 165% of equilibrium with 6% CO₂ in the feed gas, but H₂S is still treated to about 1 ppmv (Figure 1). Does this mean the rich solution is loaded with H₂S to 165% of its equilibrium value? Yes, indeed it does, *but we have to be careful about what equilibrium value is being used as the standard*. In other words, we must be aware of just what is in equilibrium with what.

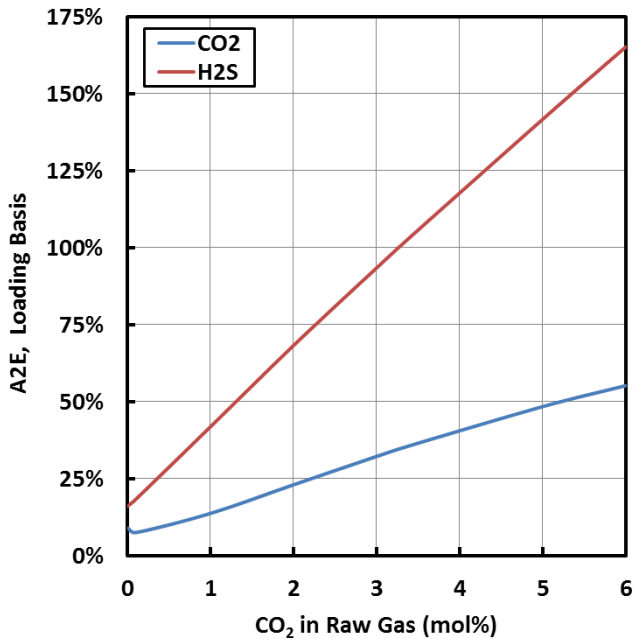


Figure 2 Loading-based Approach to Equilibrium

The definitions used in calculating A2E are the acid gas loadings that *would* be in equilibrium with the raw gas feed *if the two were allowed to equilibrate*. If the liquid were actually allowed to equilibrate with the gas, the CO₂ loading would be considerably higher than the loading of the liquid really leaving the absorber. Consequently, the equilibrium H₂S loading would be a lot smaller than the loading of the real rich solvent.

Carbon dioxide absorbs so slowly it cannot possibly equilibrate with the raw gas, i.e., the solvent cannot become saturated with CO₂. Hydrogen sulfide takes advantage of this by using all the residual loading still available as a result of CO₂'s slowness to absorb. So, one ought to expect the loading-based A2E for H₂S will sometimes greatly exceed 100%. Unfortunately, this leaves the numerical values of A2E with little practical utility.

The fact that CO₂ is nowhere near at equilibrium with the inlet raw gas is substantiated by values of its A2E much below 100%. At an inlet CO₂ concentration of 6 mole%, CO₂ in the solvent

phase is at only 50% or so of its equilibrium value. If it had the wherewithal to equilibrate, already absorbed and dissolved H₂S would eventually be pushed from the solvent back into the gas.

Figure 3 shows the A2E for this case based on acid gas partial pressures. On a loading basis, A2E refers to actual ÷ equilibrium values; whereas, on a partial pressure basis the definition is the inverted—it is equilibrium ÷ actual. Thus, a partial-pressure based A2E for H₂S of 20% means the equilibrium partial pressure exerted by the H₂S in the *actual* solvent is only 20% of the partial pressure in the raw gas. There is still, plenty of capacity for further absorption. The rich solvent also has even more capacity for CO₂; however, CO₂ absorbs so slowly, the solvent's equilibrium capacity for that gas will never be realized under even the most optimistic circumstances.

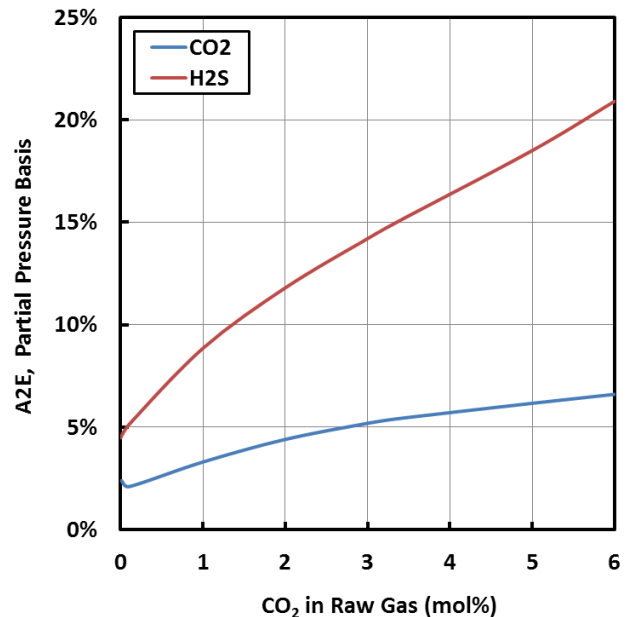


Figure 3 A2E Based on Partial Pressure

In selective treating, the *Approach to Equilibrium* is even less meaningful than in systems for complete acid gas removal. Nevertheless, it is still a commonly used metric, even by those well versed in gas treating. One has to wonder why.

To learn more about this and other aspects of gas treating, plan to attend one of our training seminars. Visit www.protreat.com/seminars for details.

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