



# The CONTACTOR™

Published Monthly by Optimized Gas Treating, Inc.  
Volume 10, Issue 12, December, 2016

## Approach to Equilibrium: Part 2 — Completely Removing Two Acid Gases

In Part 1 of this series we showed how the concept of *Approach to Equilibrium* (A2E) may not always be a good indicator of how close an absorber is to being rich end pinched. It may not be a reliable measure of how much extra unused capacity the absorber has and how resilient it might be to excursions in feed gas quality, and higher acid gas feed rates. And this was for a raw gas containing a single acid gas, either CO<sub>2</sub> or H<sub>2</sub>S.

As we will see, when a mass transfer rate model is used and there are two acid gases present (usually H<sub>2</sub>S and CO<sub>2</sub>), the A2E concept can range from deceptive to useless as a measure of how close the rich solvent leaving an operating tower is to saturation and how much margin there is to accommodate an increase in acid gas flow. In this issue 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 *total* acid gas removal. In Part 3 we will apply the same kind of analysis to a selective treating case using MDEA.

### Approach to Equilibrium

The Approach to Equilibrium is 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. Commonly there are two gases present, CO<sub>2</sub> and H<sub>2</sub>S, so there is a value of the A2E for each of the two gases. 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 Streams with Two Acid Gases

All amines are selective to an extent that is inversely proportional to the reaction rate between CO<sub>2</sub> and the amine. Thus, even MEA exhibits some degree of selectivity; however, MEA is almost invariably used for total removal of both acid gases. Table 1 shows how the reaction rate constant decreases from MEA (almost negligible selectivity) through to MDEA, the most selective of the commonly-used generic amines.

**Table 1** Rate Constants for Reaction of CO<sub>2</sub> With Gas Treating Amines at 25°C

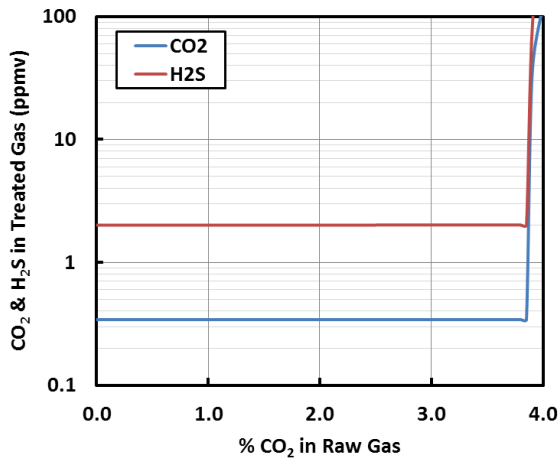
Amine	Rate Constant (L·mol <sup>-1</sup> ·s <sup>-1</sup> )
Piperazine	59,000
MMEA	7,100
MEA	6,000
DGA	4,500
DEA	1,300
DIPA	100
MDEA	4

### Total Acid Gas Removal with MEA

As in Part 1, this ProTreat® simulation study uses 28.8 wt% MEA in an absorber with 44 ft. of a random packing and operating at 533 psig. All basic parameters are kept fixed from case to case. The raw gas H<sub>2</sub>S concentration is held at 2.5 mol% (dry basis), and the feed gas CO<sub>2</sub> content is allowed to vary over the range 0–4 mol%.

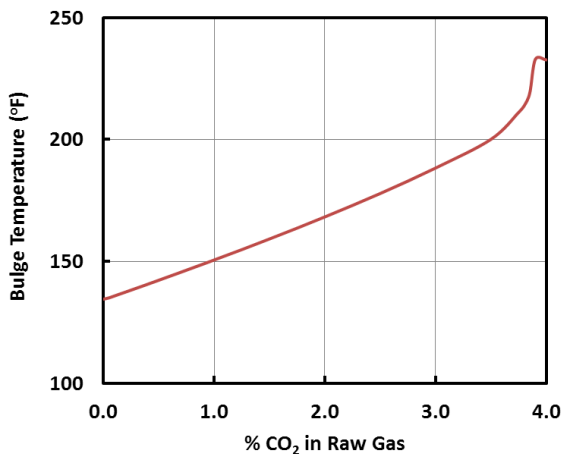
As Figure 1 shows, the CO<sub>2</sub> and H<sub>2</sub>S concentrations in the treated gas both remain constant up to a CO<sub>2</sub> content of 3.8% in the inlet gas—there is virtually complete removal of both components. The treating level is determined by the solvent lean loading. In other words, the absorber under these

conditions is lean end pinched. However, with CO<sub>2</sub> increased beyond about 3.85 mol%, both components escalate to 100s of ppmv in the treated gas.



**Figure 1 Treating Various CO<sub>2</sub> Levels in Raw Gas**

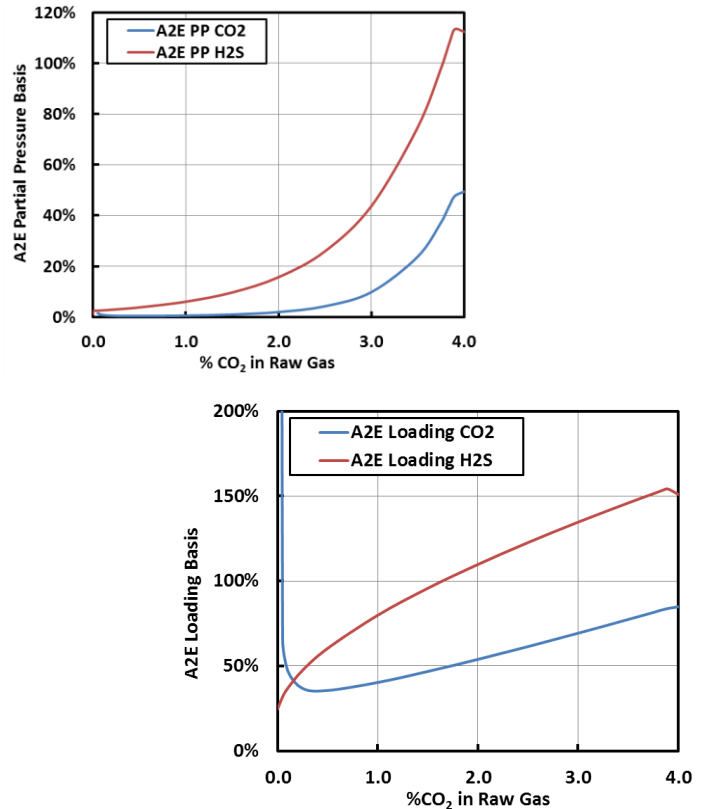
Absorber temperature profiles provide ready explanation for the sudden deterioration in treating—at and below 3.85 mol% CO<sub>2</sub>, there is a sharp temperature bulge near the base of the packed bed and its magnitude increases with amount absorbed (Figure 2). The profile slowly broadens with amount of CO<sub>2</sub> absorbed, but at 3.85 mol% CO<sub>2</sub> the sharp profile changes to a broad one that occupies 80–90% of the bed.



**Figure 2 Bulge Temperature at Various CO<sub>2</sub> Levels**

What does the A2E metric say about this sudden loss of treating? The plots in Figure 3 show no corresponding change in the A2E by either measure. Although the A2E for H<sub>2</sub>S based on partial pressure shows a value close to 100%, for CO<sub>2</sub> it is a long way below 100%. On a loading basis, the A2E is a long way above and below 100% for CO<sub>2</sub> and H<sub>2</sub>S, respectively. The Approach to Equilibrium really has nothing to say at all about this

absorber's ability to handle upsets and higher acid gas flow rates.



**Figure 3 Partial Pressure and Loading-based A2E for CO<sub>2</sub> and H<sub>2</sub>S Absorption**

In the case of two acid gases being competitively absorbed, an A2E value above 100% does not mean the column is operating at more than 100% capacity—that would be absurd. Because CO<sub>2</sub> is a stronger acid than H<sub>2</sub>S, and it forms a carbamate, the *equilibrium* solvent will contain more CO<sub>2</sub> and less H<sub>2</sub>S than the real physical column. Since the real column is usually far from equilibrium, especially at the rich end, *the real H<sub>2</sub>S loading of the solvent can be a lot higher than the equilibrium value*. Therefore, the A2E for H<sub>2</sub>S on a loading basis can considerably exceed 100% *just because of the definition of A2E*. Indeed, it can be considerably greater than 100% long before the condition of rich solvent saturation occurs. This makes the A2E concept unfit for its intended purpose in two-gas applications. And this is with MEA, usually considered to be nonselective.

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

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