

Gas Sweetening using DEA

This application brief presents the case of sweetening (purifying) a sour gas from a natural gas well. Several unit operations are employed to simulate a typical gas sweetening process configuration. Once the sour gas components have been removed, the scrubbing liquor is regenerated to remove captured sour components. These components are corrosive and metal selection can be an issue.

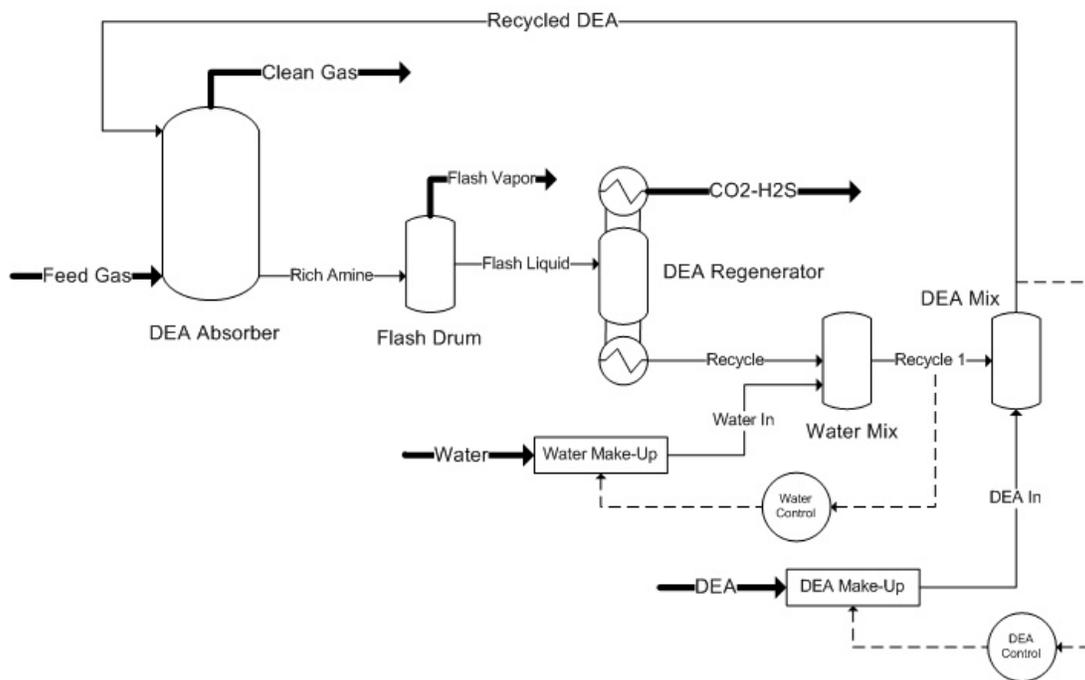


Figure 1 Diethanolamine gas sweetening process flowsheet

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The Application

A natural gas stream is approximately two mole percent (mol%) sour. This means that for every 100 moles of gas there are 2 moles of hydrogen sulfide (H₂S). In addition to H₂S, it is desirable to remove carbon dioxide (CO₂) since this constituent lowers the heating value of the gas and increases the volume of gas that must be transported. Most all alkanolamine plants are designed to maximize the removal of both of these "acid" gases.

In a typical gas cleaning plant, natural gas is fed to an absorber operating at high pressure. The gas is scrubbed using an approximately 58 weight percent (wt%) diethanolamine (DEA) solution. The scrubbed "sweet" gas is sent on for further processing or drying and transport via pipeline.

The rich DEA solution exiting the absorber is sent to a flash drum operating at a much lower pressure. This step removes any light-end hydrocarbons that were captured in the absorber. The light-end gases are sent on for further processing.

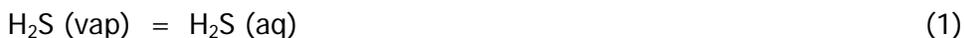
Next, the hydrocarbon-free DEA solution is fed to a regeneration column. Here heat is applied to strip the acid gas components out of the DEA solution. Make-up water and DEA are added to maintain the lean 58 wt% DEA solution. This solution is then recycled to the absorber.

Consider the Chemistry

Why does adding DEA remove H₂S and CO₂?

Consider the vapor-liquid equilibrium and acid/base chemistry for hydrogen sulfide and carbon dioxide.

The absorption of hydrogen sulfide gas follows these equilibria:



Adding a basic reagent such as DEA increases the pH of the solution. pH is defined as:

$$\text{pH} = -\log a_{\text{H}^+} \quad (4)$$

where a_{H^+} is the activity of the hydrogen ion. The activity of the hydrogen ion is defined as:

$$a_{\text{H}^+} = \gamma_{\text{H}^+} [\text{H}^+] \quad (5)$$

where γ_{H^+} is the activity coefficient for hydrogen ion and $[H^+]$ is the concentration of hydrogen ion.

As pH increases, the concentration of hydrogen ion decreases. As hydrogen ion decreases, the equilibria above shift to restore the equilibrium. Let's look at each reaction individually:



As hydrogen ion concentration decreases, this equilibrium will dissociate more bisulfide ion (HS^-) to replace the hydrogen ion. We see that the bisulfide ion concentration will also decrease as the hydrogen ion decreases.



This equilibrium will also shift to the right (decreasing the hydrogen sulfide concentration) as the hydrogen ion concentration decreases. A double effect occurs since the bisulfide ion is also decreasing.



As the aqueous hydrogen sulfide concentration decreases, the amount of hydrogen sulfide remaining in the vapor phase will also decrease. This is why scrubbing of an acid gas using a basic solution works.

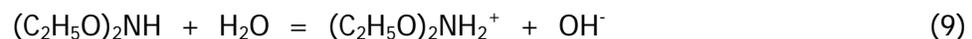
Carbon dioxide follows a similar equation path:



For similar reasons as with hydrogen sulfide, increasing the solution pH will cause more carbon dioxide to be absorbed.

Where does the basic reagent come from?

Adding DEA ($(C_2H_5O)_2NH$) to a solution will make it more basic:



Adding DEA to the solution forces water to dissociate (Eq. 10). The hydrogen ion is complexed with the DEA molecule to create a protonated species and leaving free

hydroxide ions. This increases the pH and all of the vapor-liquid equilibria described above (by Equations 1, 2, 3, 5, 6 and 7) will shift to the right.

There is a secondary equilibrium involving DEA carbamate ((C₂H₅O)₂NCO₂⁻):



This species is stable at low temperatures and helps to remove carbon dioxide from the natural gas.

How can DEA solution be regenerated?

One interesting feature of alkanolamine solutions in general is that the stability of the complexes are temperature dependent. The complexes tend to be less stable as the temperature increases.

We have taken a stream from the above process (**Rich Amine**) to illustrate solution temperature stability.

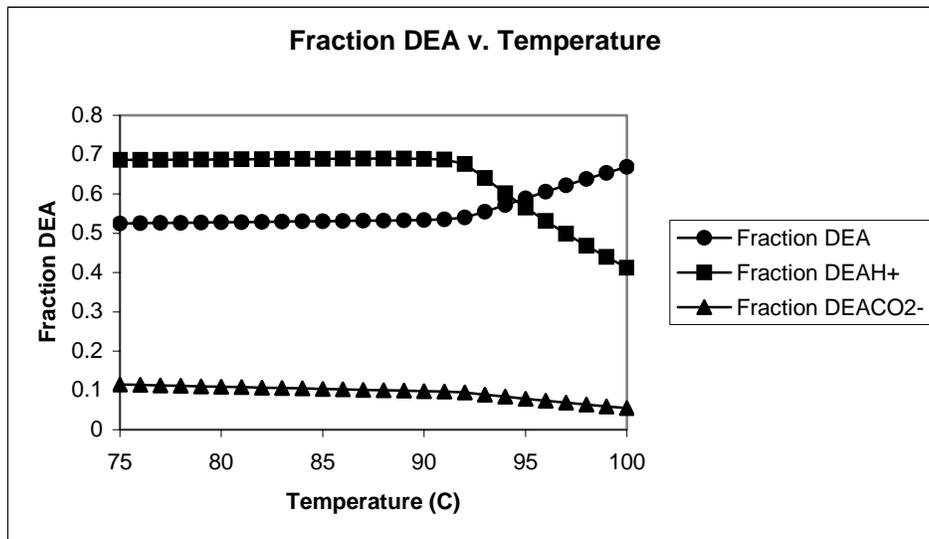


Figure 2 Temperature dependence of DEA complexes

Figure 2 illustrates the advantages of using heat to regenerate the DEA. As the temperature increases above 95 °C, the protonated form of DEA (DEAH+) rapidly decreases (the squares in Figure 2) while the neutral DEA rapidly increases (the circles in the Figure 2). The DEA carbamate species (see Eq. 11) also decreases but is a much weaker function of temperature. So, we see that applying heat facilitates recovery of the amine.

Formulating the Process

DEA Absorber

This process can be simulated entirely using ESP. Figure 1 shows the process flowsheet model in detail. The natural gas stream **Feed Gas** has the following composition:

Table 1 Feed Gas composition

Temperature	30 °C
Pressure	20 atm
CH4	925 mole/hr
C2H6	20 mole/hr
C3H8	10 mole/hr
C4H10	5 mole/hr
CO2	20 mole/hr
H2S	20 mole/hr

This gas is fed to the bottom of the **DEA Absorber**. The absorber is modeled as a column with 10 theoretical stages. **Clean Gas** leaves the top of this absorber. The composition of the **Clean Gas** is:

Table 2 Clean Gas composition

Temperature	42 °C
Pressure	20 atm
CH4	925 mole/hr
C2H6	20 mole/hr
C3H8	10 mole/hr
C4H10	5 mole/hr
CO2	7×10^{-6} mole/hr
H2S	2×10^{-4} mole/hr
H2O	2.9 mole/hr
DEA	5×10^{-4} mole/hr

Note that some DEA is carried up the column and lost in the overhead.

Flash Drum / DEA Regenerator

The **Rich Amine** solution flows to the **Flash Drum** where the pressure is reduced from 20 atm to 1.5 atm. Any remaining light-end hydrocarbons are removed at this point. The **Flash Liquid** is sent to the **DEA Regenerator** where 4.6 MMcal/hr of heat is applied to the reboiler to strip hydrogen sulfide and carbon dioxide out of the rich amine solution.

The overhead of the **DEA Regenerator (CO₂-H₂S)** contains the acid gas components. The composition of this stream is:

Table 3 CO₂-H₂S composition

Temperature	86 °C
Pressure	1.2 atm
CH ₄	0.01 mole/hr
C ₂ H ₆	2 x 10 ⁻⁴ mole/hr
C ₃ H ₈	5 x 10 ⁻⁴ mole/hr
C ₄ H ₁₀	1 x 10 ⁻⁴ mole/hr
CO ₂	20 mole/hr
H ₂ S	20 mole/hr
H ₂ O	40 mole/hr
DEA	3 x 10 ⁻⁹ mole/hr

As you can see, very little DEA is lost in the overhead product of this column. Most of the DEA is recycled back to the **DEA Absorber**. The hydrogen sulfide and carbon dioxide can now be treated separately from the hydrocarbon gas.

Make-up and Recycle

The **Recycle** stream leaving the bottom of the **DEA Regenerator** loses some water and amine. Both need to be replenished. Two feedback control loops are used to adjust water and DEA make-up. An additional 43 moles of water and only 5.4 x 10⁻⁴ moles of DEA are needed to maintain the **Recycled DEA** stream at a concentration of approximately 58 wt% DEA.

The **Recycled DEA** stream has the following composition (true basis) and properties:

Table 4 Recycled DEA stream

Temperature, °C	30.0
Pressure, atm	20.0
pH	11.675
Total Flow, mole/hr	620.2164
Flow Units	mole/hr
H ₂ O	500.159
C ₃ H ₈	5.77E-11
C ₄ H ₁₀	5.77E-11
CH ₄	5.79E-08
CO ₂	4.54E-09
DEA	119.206
H ₂ S	8.05E-07
OH ⁻	0.055032
(C ₂ H ₅ O) ₂ NCO ₂ ⁻	0.14022

$(C_2H_5O)_2NH_2^+$	0.453815
HCO_3^-	9.29E-04
H^+	2.36E-11
HS^-	0.145074
CO_3^{-2}	0.0458573
S^{-2}	0.0104223
C_2H_6	0.0
Total g/hr	21621.4
Volume, m3/hr	0.0111339
Enthalpy, cal/hr	-4.63E+07
Density, g/m3	1.94E+06
Osmotic Pres, atm	489.581
Ionic Strength	0.0566113

Corrosion Considerations

The acid gas components have been removed from the natural gas stream and stripped from the DEA solution. These gases may be treated then vented. One major concern is that piping for this overhead gas (**CO2-H2S**) may be subject to corrosion.

The wet gas leaving the **DEA Regenerator** is at 86.24 °C. What is the dew point of this gas? We used ESP's companion product **Corrosion Analyzer™** to find out...

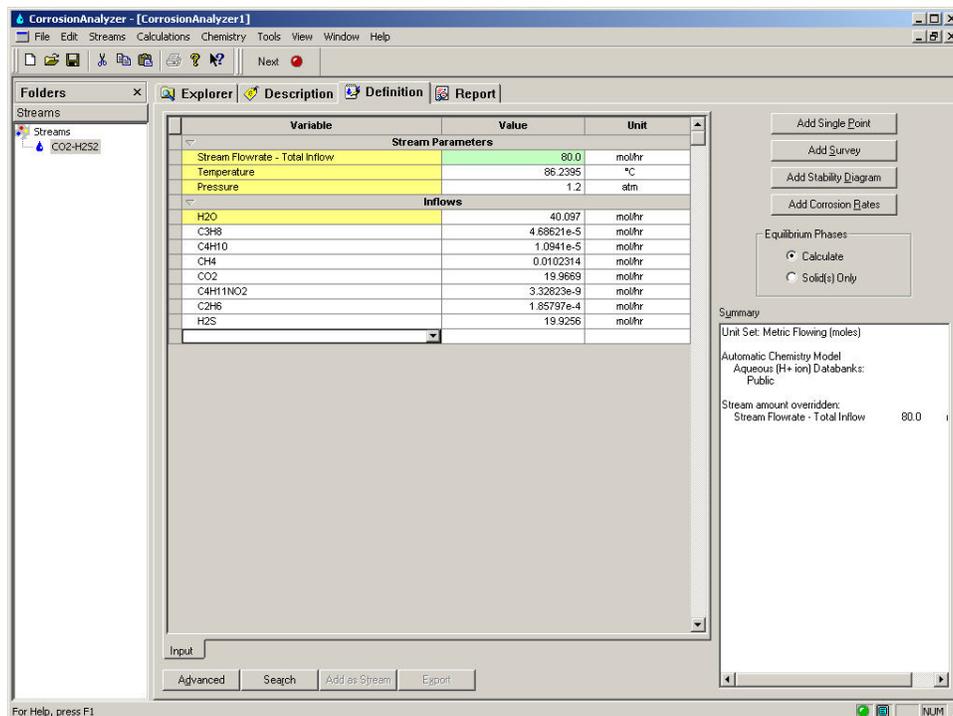


Figure 3 CO2-H2S stream imported into **Corrosion Analyzer™**

Aqueous Dew Point

The stream **CO2-H2S** was imported into *Corrosion Analyzer™* and a single-point calculation was performed to determine the dew point temperature for this gas at 1.2 atm.

The calculated dew point temperature was 86.24 °C which means the regenerator overhead gas is fully saturated with respect to water. This means that there may be corrosion problems if the temperature of the inner surface of the pipe falls below this temperature.

Corrosion Rates

Next, we used *Corrosion Analyzer™* to estimate the general corrosion rate for carbon steel and two steel alloys:

Table 5 General corrosion rate for the CO2-H2S dew-point composition

Material	Corrosion, mil/yr
Carbon steel	18.9
13% chrome steel	1.0
304 stainless steel	0.3

From these results, the largest beneficial reduction in general corrosion rate seems to be to switch from carbon steel to 13% chrome steel.

Conclusions

Using ESP with companion program *Corrosion Analyzer™*, you can simulate typical gas sweetening plants and investigate the potential for corrosion problems and investigate corrosion mitigation strategies.

Trends in the gas processing industry are tending towards using different amines to achieve different absorption profiles and for using mixtures of amines to achieve more selective absorption. ESP can readily be applied to simulate these situations as well.