Design & Operation of a Selective Sweetening Plant Using MDEA

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ABSTRACT

Operating data were collected from the Signalta gas sweetening plant. The plant has had an interesting variety of feed gas and operating conditions. The design and operation of the facility for CO₂ slippage are discussed.


INTRODUCTION

The Signalta Resources Forestburg Gas Plant was constructed during the winter of 1983 and placed on stream in April of 1984. A design outlet gas specification of 1/4 grain H₂S /100 scf was requested to ensure meeting the contract commitment of 1 grain/100 scf. The design gas flow rate was 30 MMSCFD containing 0.5% H₂S and 3% CO₂ at 415 psia and 70°F.

The overall plant is configured as shown in Figure 1. Inlet separation facilities are followed by a feed gas heater. The gas stream then flows through a filter separator followed by the amine contactor. Another filter separator is used as a sweet gas scrubber. After sweetening, the gas is routed to a dew point control refrigeration unit. Finally, a single stage of compression is required to boost the gas to 1200 psig maximum pipeline pressure.
The sweetening chemical selected for the Forestburg Plant was methyldiethanolamine (MDEA). This was chosen due to its capability to remove H₂S and leave a portion of the CO₂ in the residue gas. At the time of plant commissioning it was one of the first operating MDEA facilities in Western Canada.

The inlet gas comes from 20 wells and is located in various pipelines up to 6" diameter with a total length of more than 50 miles. Some of the wells produce as much as 2% H₂S and occasionally some oil and asphaltene. The actual feed stream reaching the plant normally contains 0.2 to 0.4% H₂S. Due to demand the flow rate has varied from 6 to 27 MMSCFD.

Several tests of the plant were undertaken to determine the effects of changes in feed point on the contactor. This information can be used to improve the methods and assumptions used in the design of MDEA sweetening systems. Considerable interest is expressed by production companies in the adjustability of CO₂ slippage that can be obtained using MDEA. This opportunity is also used to describe the initial calculation procedures used to develop an MDEA design.

**PROCESS CHEMISTRY**

The methyldiethanolamine (MDEA) process as used for natural gas treating utilizes the selectivity of the chemical for H₂S in preference to CO₂ in a nonequilibrium situation. Several sources of published material are available describing the various reactions that may take place [1-6]. The most significant observation from a plant design perspective is relatively simple. H₂S chemically reacts with MDEA almost instantaneously by proton transfer as is the case with other commonly used amines.

\[ \text{H}_2\text{S} + \text{R}_2\text{NCH}_3 \leftrightarrow \text{R}_2\text{NHCH}_4^+ + \text{HS}^- \]

Since MDEA is a tertiary amine and does not have a hydrogen atom attached to the nitrogen atom, the CO₂ reaction can only occur after the CO₂ has formed bicarbonate with water. It is the formation of the bicarbonate which is generally considered to be the slow reaction which limits the CO₂ reaction to less than equilibrium values at short contact times. The bicarbonate then undertakes an acid-base reaction with the amine to yield an overall CO₂ reaction:

\[ \text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{HCO}_3^- + \text{H}^+ \]

\[ \text{CO}_2 + \text{H}_2\text{O} + \text{R}_2\text{NCH}_3 \leftrightarrow \text{R}_2\text{NHCH}_4^+ + \text{HCO}_3^- \]

Because of the slow intermediate step required for the CO₂ and water it may be assumed that H₂S reaction with MDEA is gas phase limited while the CO₂ reaction is liquid phase limited [2]. It is obvious that to utilize MDEA
effectively in selective situations it is necessary to keep the liquid phase contact time for the reaction to a minimum so that less CO₂ will be absorbed by the amine solution. Several mechanical design considerations must be taken into account in proper absorber vessel design to ensure that this will occur. The mechanical design requirements have an effect on the process operation. Therefore, it is necessary to properly allow reasonable first order estimates of the mechanical influence on the process.

A computerized approach to the process design calculations is a necessity in order to optimize the design in any reasonable time frame. The program used for the design of the Signalta MDEA process was TSWEET from Bryan Research & Engineering of Bryan, Texas. This program does rigorous tray by tray calculations for the contactor and stripper columns by the Ishii-Otto method and contains a kinetic model to simulate the effects of contact time and the MDEA selectivity. A modified Kent and Eisenberg equilibrium model is used to calculate the vapor pressures of H₂S and CO₂ above the amine solutions. This program also contains the ability to simulate multiple feed points to the absorber, which is one method of control over the selectivity.

PRELIMINARY DESIGN CONSIDERATIONS

Several preliminary considerations should be examined for each sweetening application. These include:

**Circulation Rate**

The ratio of CO₂ to H₂S in the feed gas is of considerable importance in the selection of MDEA as the sweetening agent. The more CO₂ in relation to H₂S, the more attractive economically it will appear to remove only the H₂S. The original CO₂ to H₂S ratio for the Forestburg plant was 6:1 which was the initial indication that MDEA was worth considering. In addition, preliminary simulations indicated that 1/4 grain/100 SCF specification with slightly less than 2% CO₂ in the outlet gas was readily achievable.

When initially designing an MDEA facility, a first estimate of the circulation rate is required. A good approximation is to calculate the amine rate required to remove all the H₂S and half of the CO₂.

\[
GPM = \frac{0.206 \times MM \times (H₂S + CO₂) \times MWT}{ML \times WT}
\]

**MM** = gas flow MMSCFD  
**H₂S** = mol % of H₂S to be removed  
**CO₂** = mol % of CO₂ to be removed  
**MWT** = mole WT of MDEA = 119.9  
**ML** = mol loading, moles acid gas/mole  
**WT** = amine solution weight percent circulated

Using the design feed gas analysis for the Forestburg Plant from Table I as an example case, this is calculated as follows:

\[
GPM = \frac{0.206 \times 0.30 \times (0.5 + 1.5) \times 119.9}{0.3 \times 50}
\]

Thus, a preliminary circulation rate of 100 USGPM is selected. It is worth noting that the 0.3 mol loading was selected due to the relatively low 415 psi operating pressure of the Forestburg contactor. At higher pressures a mole loading of 0.4 to 0.5 would be a more representative initial estimate.

**Tray Residence Time**

The next step is to determine the residence time in the contactor. Because multiple feed points or parallel feeds and drawoffs are often used for selective applications, it is necessary to calculate this value on a stage by stage basis for use in kinetic modeling. The exact tower and tray geometry is not known at the start of the design. The most straightforward procedure is to initially assume two seconds residence time on the trays which receive full amine flow. If multiple feed points are used, the residence time up the column can be calculated by the inverse
ratio of the amine flow rates. Thus, no initial determination of the contactor diameter is required.

Designers who require a closer approximation of the residence time must estimate the contactor diameter by calculating the bubbling area and downcomer area \([7, 8]\) as shown in Figure 2. The required active bubbling area on a tray is primarily dependent on gas flow and secondarily on liquid flow rate. The required bubbling area can be calculated by neglecting the liquid effect and using Souder’s and Brown’s correlation \([7]\):

$$
U_{al} = K \left( \frac{\rho_L - \rho_A}{\rho_A^{0.5}} \right)^{0.5}
$$

Where:
- \(K\) = 0.25 for valve trays, 0.20 for bubble cap trays
- \(U_{al}\) = allowable velocity of gas through bubbling area, ft./sec.
- \(\rho_L\) = density of the amine solution, lb./ft\(^3\)
- \(\rho_A\) = density of the gas at tray conditions, lb./ft\(^3\)

The downcomer area can be calculated from the liquid flow rate assuming a downflow velocity of 0.25 ft./sec. The bubbling area plus two downcomers plus 15% for liquid distribution zone and wastage are used as the total tower cross sectional area. Using the data from Table I:

$$
U_{al} = 0.25 \left( \frac{64.4 - 1.41}{1.41^{0.5}} \right)^{0.5} = 1.87 \text{ ft.} / \text{sec}.
$$

Actual Volumetric Flow of Gas = 11 ft\(^3\)/sec

Bubbling Area = 11/1.67 = 6.6 ft\(^2\)

Area of Downcomer = 100 GPM / 0.25 ft./sec x \((7.48 \text{ gal/ft}^3 \times 60 \text{ sec/min}) = 0.9 \text{ ft}^2\)
Total Required Tower Area = (6.6 + .9 + .9) x 1.15 = 9.66 ft²

This results in a tower I.D. of 42 inches.

The next step in determining the residence time on an actual tray is to calculate the depth of liquid on the tray. The assumption that the weir length is 0.7 times the tower diameter is normally satisfactory for initial calculations. The height of liquid over the weir is calculated using the Francis straight weir relation [7].

\[ h_{ow} = 0.48 \left( \frac{GPM}{L} \right)^{0.67} \quad L = \text{weir length in inches} \]

For the design case:

\[ h_{ow} = 0.48 \left( \frac{100}{(0.7 \times 42)} \right)^{0.67} = 1.1 \text{in.} \]

The standard weir height used by most tray manufacturers is 2.0 inches for a total froth depth of 3.1 inches at the tray outlet. The hydraulic gradient across the tray can also be calculated. However, the error incurred by ignoring it at this point is relatively minor.

The so-called clear liquid residence time can now be calculated.

\[
\text{Clear Liquid Residence Time} = \frac{\text{Bubbling Area} \times \text{Froth Depth}}{\text{Liquid Flow Rate}} \times \text{Froth Gravity}
\]

Design Case:

\[
\text{CLRT} = \frac{6.6 \text{ft}^2 \times (3.1/12) \text{ft} \times 0.3}{100 \text{GPM} \div (7.48 \times 60)} = 2.3 \text{sec}
\]

The product of the froth depth and froth gravity yields the depth of the clear liquid on the tray. These factors must be used since the fluid flowing across the bubbling area is froth of low density due to the contained gas bubbles. The 2.3 second valve is quite close to the 2.0 second residence time recommendation at the beginning of this section. If the designer had used the 2.0 second estimate, the contactor size could be generated by the computer program and the Francis weir equation [7] used to refine the residence time calculations.

**Equilibrium Stages**

The number of actual trays per theoretical stage is always a point of discussion amongst equipment designers. The situation is made more complex when entering the realm of nonequilibrium contact, where one of the components is achieving only a certain percentage of equilibrium. A significant amount of research work has been done and there is more to be done in this area. Rather than belabor the topic with a discussion of point efficiencies, Murphree tray efficiencies and so on, a value of three actual trays per theoretical stage gives realistic comparisons between calculated and actual results. A test of this simplification is the prediction of temperature profiles for absorbers. Prior information published by Daviet, et al. [3] shows reasonable correlation between calculated and actual temperature profiles using the three actual trays per stage approach.

**Contactor Feed Points**

The primary method of adjusting the MDEA system performance with regard to H₂S removal and CO₂ slippage is the location and quantity of amine delivered to different feed points on the contactor. In general, if the amine is
totally supplied to only the bottom few trays, the CO₂ slippage will be quite high, possibly over 80%.

Unfortunately, this may also result in inadequate contact to achieve H₂S specification. The H₂S requirement can be achieved by flowing a lesser amount of amine into a higher feed point in the tower. Some care must be taken with regard to feed temperature and CO₂ absorption heat of reaction. It is possible to create a temperature profile that will not improve the absorption of H₂S due to the elevated temperature and CO₂ content of the amine.

Fortunately, this type of problem becomes apparent when the calculations are rigorously performed by computer. A reasonable level of adjustability is provided by using three feed points. Sour gas entering the Forestburg Plant contacts all the amine on the bottom eight trays followed by a lower amine rate for the next six trays and a final section of six trays at the top of the contactor. Thus the amine feed points are on trays 1, 7 and 13 by process numbering convention. Different feed points could be selected based on the three actual trays per theoretical stage rule and calculations showing a process benefit for the change. Some applications will show that 20 trays are not required, however it is very difficult to convince an experienced amine plant purchaser of this, probably with past bitter experience as justification.

**Stripping Rates**

Amine plants have been designed for many years using a rule of thumb of one lb. of steam per gallon of amine circulated. The final requirements for stripping steam rate must be determined from the rigorous computer calculations. The stripping rate required is highly variable depending on CO₂/H₂S ratio and may be as low as 0.8 to meet a 1 grain/100 SCF H₂S specification and as high as 1.5 to meet 1/4 grain/100 SCF H₂S specification. In general, MDEA is easier to strip than other amines and an operating rate of less than one lb. steam/gallon will meet 1/4 grain requirements. The design of the stripper and reboiler is conventional with respect to other amine system designs. In the stripper, the trays have been found to be more efficient and two actual trays per theoretical stage should be used. Packed towers are often used in stripping applications and an HETP of three feet is a conservative value.

**Design Optimization**

The previous sections have outlined some basic assumptions and methods of calculating first trials for the various design parameters. The design is then finalized by providing the data to the computer program for rigorous calculation. When the initial simulation results are obtained they can be inspected and some of the parameters modified accordingly. For example, the stripping rate can be reduced if H₂S content of the outlet gas is significantly below 1/4 grain per 100 SCF. The circulation rate can be reduced to improve the CO₂ slippage. Residence times on the trays can be changed within the limits of contactor diameter by a factor of about −50 to +100 percent by selecting alternate weir heights. Changing the quantity of amine supplied to different feed points will show changes in CO₂ slippage and H₂S sweetness. More H₂S and CO₂ are removed from the gas stream by increasing amine flow rates to more contact stages. It should be noticed that it is necessary to revise the contact times for each new amine flow rate tested. This process of making slight alterations to the calculations is a valuable exercise for the designer to perform so that critical limitations in the final design can be avoided. Selection of a process design which has some flexibility will simplify the selection of the mechanical equipment.

**MECHANICAL EQUIPMENT**

The selection of heat exchange and mechanical equipment is often specific to a given plant process design however some discussion of the equipment used at the Forestburg Plant is of some interest.

**Lean Rich Exchanger**

A plate/plate exchanger was used as the lean/rich amine exchanger. This type of exchanger offers large surface areas and high transfer rates in a small volume. The designer should be careful to allow for acid gas breakout on the rich amine side of the exchanger. This factor is important for both pressure drop and heat exchange considerations. The pressure drop through the lean side should be kept below two psi to prevent pumping problems associated with reducing the lean amine below its vapor pressure at the exchanger inlet nozzle. On the other hand it is advisable to keep velocities high enough that the exchanger does not collect dirt. A single pass
configuration on both sides of this exchanger is advisable. The plates should be 316 SS, EPDM gaskets are recommended. A few years ago, gasket leaks were the plague of plate/plate exchangers. In general, this situation has been corrected. It is still necessary to have a spare set of gaskets readily available.

**Booster Pumps**

The common practice of placing the booster pumps downstream of the lean/rich exchanger was not followed in the Forestburg design. Sufficient NPSH was available to allow these pumps to operate properly with the hot lean amine directly from the reboiler. This was done in an attempt to overcome the problem mentioned in the previous paragraph. It also allowed the use of higher pressure drop in the plate exchanger and subsequent reduction in size of that unit. The use of high temperature seals and seal cooling was required, however. Although there have been no problems with the selected arrangement, the more common practice is probably less expensive and less prone to design oversights which might cause pump cavitation. It is interesting to note that some amine plants have no booster pumps on the basis that sufficient NPSH is available for the charge pumps without using a booster. Very often these designs ultimately have cavitation problems. The reason for this is the presence of hydrocarbons in the amine which can reduce the NPSH available to half of what would be expected from the amine solution vapor pressure calculations.

**Filtration**

A full flow amine filter was incorporated into the Forestburg Amine Plant. A 5% flow charcoal filter was also installed in the amine stream. Directly ahead of the amine contactor in the gas stream a large filter separator removes any particulate or liquid mists that might be present after inlet separation. Even with all of the above filters and a double system wash before start-up, the Forestburg Plant encountered foaming problems for the first several weeks after start-up. As this problem has almost entirely disappeared without any mechanical modification, it is presumed that well completion fluids or oil entrainment were the culprits. An asphaltene dispersant of unknown chemical composition injected at some of the wellheads seems to have helped eliminate this problem as well. The use of antifoam agents in the plant has been reduced to nil.

**Air Coolers**

The overhead condenser and the lean amine cooler were mounted in a common unit. Air recirculation and two-speed fan motors were also used to prevent freezing problems at low ambient conditions. This is also the reason that a 50% MDEA solution was used in the original design.

**Charge Pumps**

The highest maintenance items on the amine plant are generally the charge pumps. The Forestburg Plant operating pressure was sufficiently low that high-speed centrifugal pumps could be economically used to pump the amine solution up to contactor pressure. This type of pump is highly recommended from a maintenance viewpoint. Most of the inherent problems with the more commonly used plunger pumps in amine service are a result of the packing glands filtering iron sulfides out of the amine solution. Build-up of these particles results in abrasion of the plungers and frequent replacement. The drawback of the centrifugal pump is its relatively low pumping efficiency which increases the horsepower consumption by a factor of approximately two. At high operating pressures the plunger pumps are still the best choice due to the high comparative cost of multistage centrifugal pumps. The acceleration head requirements and possible use of pulsation dampening should not be overlooked when using plunger pumps.

![Table I. Design & Test Data for Signalta Plant](image-url)
DISCUSSION OF PLANT TEST

The design considerations and methods previously discussed were used to design an MDEA facility for the Signalta Forestburg Plant. The design information as determined by final computer simulation is shown in the first column of Table I. The process flow diagram for the amine process is shown in Figure 3.

<table>
<thead>
<tr>
<th>Contactor:</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas In Temp, °F</td>
<td>70</td>
<td>59</td>
<td>60</td>
</tr>
<tr>
<td>Gas Out Temp, °F</td>
<td>125</td>
<td>85</td>
<td>86</td>
</tr>
<tr>
<td>L. Amine In Temp, °F</td>
<td>110</td>
<td>74</td>
<td>79</td>
</tr>
<tr>
<td>R. Amine Out Temp, °F</td>
<td>106</td>
<td>80</td>
<td>77</td>
</tr>
<tr>
<td>Gas In Press, PSIA</td>
<td>428</td>
<td>432</td>
<td>393</td>
</tr>
<tr>
<td>Avg. Gas #/ft³</td>
<td>1.41</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Amine Rate, GPM</td>
<td>100</td>
<td>72</td>
<td>70</td>
</tr>
<tr>
<td>% to Tray 1</td>
<td>100</td>
<td>36</td>
<td>39</td>
</tr>
<tr>
<td>% to Tray 7</td>
<td>-</td>
<td>64</td>
<td>61</td>
</tr>
<tr>
<td>% to Tray 13</td>
<td>-</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Reboiler:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Steam, lb/gal</td>
<td>1.2</td>
<td>1.5</td>
<td>1.55</td>
</tr>
<tr>
<td>Press, PSIA</td>
<td>27.7</td>
<td>22</td>
<td>23</td>
</tr>
<tr>
<td>Amine Wt %</td>
<td>50</td>
<td>36.2</td>
<td>32.4</td>
</tr>
</tbody>
</table>

Stripper:

| Feed Temp, °F                    | 220| 204| 205|
| O/H Cond. Temp.                  | 120| 88| 87|
| Residence Time (secs.):          |  |  |  |
| Tray 1-6                         | 2.3| 6.7| 6.5|
| Tray 7-12                        | 2.3| 2.9| 2.9|
| Tray 13-20                       | 2.3| 2.9| 2.9|

*Calculated by CO2 balance
**Calculated from acid gas composition

Figure 3. Process flow diagram for Forestburg sweetening plant.
Inlet, residue and acid gas samples were analyzed by gas chromatograph. During test A, discrepancies were found between the inlet H2S measurements and the acid gas flow rates. Investigation into this problem uncovered acid gas metering errors and variance between chromatograph and Tutweiler H2S measurements. Therefore, it was necessary to calculate the acid gas rate based on the CO2 concentration (a relatively large number) and then back calculate the inlet H2S from the acid gas flow rate. This corresponded with Gastec sample tube readings taken during the test. For the subsequent B and C tests, H2S readings were taken by gas chromatograph, Tutweiler apparatus and Gastec indicator tubes. Due to variations in the different methods, the low and high readings were discarded and the remaining readings were averaged to show the results in Table I.

As with most operating facilities of this type, the final operating conditions are never quite the same as were estimated in the original design. As can be seen from the Test Data columns of Table I, the plant operating pressures, temperatures and flow rates were quite different from the original design.

This type of disparity in the design and test conditions is probably the best test of the simulation program used to design the plant. Table II shows that the TSWEET program results conformed very closely to the test data when actual operating conditions are simulated. The primary effect for investigation was the influence of feed point and contact time on the CO2 slippage and H2S sweetness. Thus the tests were conducted using a high stripping rate to minimize the effects of changes in lean amine loadings. It is important to vary as few parameters as possible to obtain meaningful data. The simulation results proved to be very accurate within 5% for the CO2 slippage and were conservative for the H2S calculations. It is difficult to quantify the results concerning the H2S content in the outlet gas as the H2S monitor at the site sampled the residue gas every few seconds and variations of 1 ppm were not unusual between consecutive readings. We were pleased that the prediction was slightly conservative.

### Table II. Comparison of test data & simulation results

<table>
<thead>
<tr>
<th>Test</th>
<th>Plant Test</th>
<th>Predicted by TSWEET</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO2 out</td>
<td>2.05%</td>
<td>2.14%</td>
</tr>
<tr>
<td>H2S out</td>
<td>2.8ppm</td>
<td>3.2ppm</td>
</tr>
<tr>
<td>CO2 mass balance</td>
<td>*</td>
<td>-</td>
</tr>
<tr>
<td>H2S mass balance</td>
<td>*</td>
<td>-</td>
</tr>
<tr>
<td>CO2 out</td>
<td>1.95%</td>
<td>1.92%</td>
</tr>
<tr>
<td>H2S out</td>
<td>0.6-1.5ppm</td>
<td>1.94ppm</td>
</tr>
<tr>
<td>CO2 mass balance</td>
<td>-1.5%</td>
<td>-</td>
</tr>
<tr>
<td>H2S mass balance</td>
<td>-2.5%</td>
<td>-</td>
</tr>
<tr>
<td>CO2 out</td>
<td>2.13%</td>
<td>2.01%</td>
</tr>
<tr>
<td>H2S out</td>
<td>3.2-3.7ppm</td>
<td>4.5ppm</td>
</tr>
<tr>
<td>CO2 mass balance</td>
<td>+1.0%</td>
<td>-</td>
</tr>
<tr>
<td>H2S mass balance</td>
<td>+1.5%</td>
<td>-</td>
</tr>
</tbody>
</table>

*Test A meter errors required CO2 and H2S be used to calculate acid gas flow rate.

### CONCLUSION

The use of basic design parameters outlined earlier in this paper allows the designer of an MDEA plant to approximate the required circulation rates and heat loads. Subsequent use of a computerized simulation model, which accounts for kinetic effects and performs rigorous equilibrium calculations enables a large degree of refinement in the final design. The capability of modifying several parameters allows the designer to identify
potential limitations in the overall scheme and avoid deficiencies in the final plant equipment selection.

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LITERATURE CITED


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