Evaluation, Selection, and Implementation of CO₂ Removal Technology at a Complex Gas Production Site

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Abstract

This paper discusses the evaluation of technologies to remove CO₂ and the best treatment location for CO₂ removal at a complex gas production site. Types of technologies evaluated in detail include membranes, alkanolamine, and molecular sieve adsorption. Treatment locations considered include treating the raw gas upstream of an NGL plant and high and low pressure locations downstream of the NGL plant to achieve a goal of less than 3% CO₂ in the sales gas stream.

The potential feed stream to the CO₂ removal unit at each of the 3 locations contains similar CO₂ concentrations at different pressures and concentrations of natural gas liquids. The impact of the feed stream quality on pre-treatment and compression requirements is considered. Other key factors considered are ease of operation, capital cost, rejection stream composition and disposal options, and ease of process capacity expansion/turndown.

At the site, a membrane CO₂ removal technology was selected, and the paper discusses the factors leading to the selection. The paper also reviews issues with the CO₂ removal treating unit being integrated into a complex gathering/distribution system while ensuring that treated gas is effectively blended and distributed to all customers.

Background

Carbon dioxide removal from natural gas is a common process in the gas industry and there are many technologies available that remove CO₂ from a gas stream to meet a given pipeline or product specification. Each technology has different benefits and drawbacks. This paper presents an example of the evaluation and selection of CO₂ removal options based on the needs and constraints of a specific gas processing site.

The gas production site in this instance is an older oil and gas field that processes more than 250 MMSCFD of raw natural gas. Figure 1 shows a general block flow diagram of the site. The raw natural gas is processed in three natural gas liquid (NGL) recovery plants where propane, butane, and natural gasoline are extracted from the gas stream and sold as separate products. In addition, two of the three NGL recovery plants dehydrate the natural gas stream at the inlet of the plant and the third dehydrates the residue gas leaving the plant. Residue gas from the three NGL recovery plants is compressed and sold to a number of different customers at various supply pressures.
Figure 1: Simplified Block Flow Diagram of Gas Production Site

Historically, the residue gas from the NGL recovery plants has met the 3 mol% CO₂ sales gas specification required by the operating company’s customers without needing CO₂ removal. As the field has aged, the CO₂ content of the residue gas has risen to concentrations approaching the sales gas specification. Based on reservoir forecasts, the projected CO₂ concentration in the residue gas would be above the sales specification in less than two years. Graphically, this is shown below in Figure 2.
Figure 2: Expected CO₂ Content over Time of Untreated Residue Gas

The existing gas processing units at the site did not provide for CO₂ removal from the gas stream and, if left untreated, the operating company would have to shut-in wells producing high CO₂ gas to prevent customers from shuttering in sales gas pipelines as the CO₂ concentration approached or exceeded 3 mol%. Thus, the operating company had economic justification to install a gas treatment unit designed to ensure the sales gas CO₂ concentration stays below the sales specification in the future.

Technologies Considered

The operating company had several expectations regarding the performance of the proposed gas treatment unit which affected the technology selection process:

- Lifecycle Cost – The chosen technology is to have the lowest forecast lifecycle cost, provided equipment lead time and reliability criteria are satisfied.
- Equipment Lead Time – The chosen technology is to have a short lead time so that the treatment unit can be online before the CO₂ levels rise above 3%. The economic incentives driving the schedule made the lead time of the equipment nearly as important as the overall lifecycle cost.
- Offgas Disposal – Any offgas from the chosen technology cannot be vented or flared, and must either be compressed for reinjection or, if possible, used as a fuel.
- Reliability – The chosen technology needs to be robust and reliable. Since this unit will be the sole process at the site capable of reducing CO₂ levels, the unit needs to be online essentially 100% of the time and there would be no scheduled turnarounds for the unit.
- Scalability – The chosen technology is to be designed such that it can handle or be expanded to handle 150% of forecasted gas flow rate to accommodate the possibility of future off-site gas or additional production wells.

Based on the criteria listed above, a screening study was conducted to compare different CO₂ removal technologies. While there are many processes capable of removing CO₂ from natural gas (e.g. physical solvents, alkaline salts, caustic, batch chemicals, etc.), many of these were excluded early in the screening process for various reasons (unsuitable gas rate, total quantity of CO₂, CO₂ partial pressure, chemical disposal issues, or owner’s preferences). The three processes that passed the initial screening are; amine absorption, molecular sieve adsorption, and membrane treatment. Table 1 shows the expected equipment lead time, lifecycle cost, and major equipment for each option that resulted from the screening study.

Table 1: Screening Study Results for CO₂ Removal Technologies

<table>
<thead>
<tr>
<th>CO₂ Removal Technology</th>
<th>Lead Time (weeks)</th>
<th>Lifecycle Cost ($MM)</th>
<th>Major Equipment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Membrane Separation</td>
<td>36 - 44</td>
<td>37</td>
<td>Permeate Compression, Inlet Filtration, Membrane Modules, Inlet Cooling</td>
</tr>
<tr>
<td>Amine Solvent</td>
<td>52 - 60</td>
<td>43</td>
<td>Upgraded Metallurgy, Pumps, Fired Heater, Offgas Compression, Residue Gas Dehydration</td>
</tr>
<tr>
<td>Molecular Sieve Adsorption</td>
<td>52+</td>
<td>48</td>
<td>Pressure Vessels, Heaters, Offgas Compression, Valve Skids</td>
</tr>
</tbody>
</table>

Amine absorption presented several problems for the operating company. A previous study found that the incoming gas stream had oxygen present up to 500 ppm and therefore the recommended amine treatment unit would probably need stainless steel vessels and piping in several areas and a permanent reclaimer unit to process degraded amine. The other alternative would be to remove the oxygen from the feed stream to the proposed amine unit catalytically which represented increased lifecycle costs. The amine process, if placed downstream of the NGL recovery plants, would re-saturate the residue gas and require the installation of a residue gas dehydration unit. If placed upstream of the NGL plants, it would be difficult to modify the gas gathering pipeline system to feed a single amine unit. Instead, an amine unit would need to be installed at the inlet to each of the three NGL plants.

The molecular sieve adsorption unit for processing this gas is estimated to be very large which was reflected in the overall lifecycle cost for this option and it had a longer lead time than the
membrane unit option. The operating company also had reservations regarding the reliability of the molecular sieve unit, particularly around the high cycling nature of the valves in this process based on their experience with similar units in the past.

The membrane option was estimated to have the lowest lifecycle cost and shortest lead time of the options considered. The simplicity of a membrane unit gives it an operational advantage over the other options. From an operational standpoint, the membrane unit would be a wide spot in the line that produces a permeate stream which requires recompression. In addition, the requirement for dew point control of the membrane feed stream would be significantly reduced or possibly even eliminated if the unit was installed downstream of the NGL plants.

In addition to the benefits listed above, membrane separation presented the following benefits:

- **Skidded Construction** – The proposed membrane unit would consist of four separate membrane skids. If the operating company deemed it necessary, individual membrane skids could be brought online as they arrived on the site further reducing the lead time for the treatment unit.
- **High Reliability** – Individual membrane “tubes” allow for tube replacement while the overall treatment unit is still online and minimize the downtime required for the CO₂ removal unit.
- **Scalability** – The membrane skids would be designed such that they would meet the 150% flow oversize requirement. This flexibility could be achieved by only increasing membrane tube length and the operating company would only need to purchase additional membrane modules if and when the additional capacity was needed.

Of the three technologies researched, the membrane separation unit provided the lowest lead time to delivery, the lowest lifecycle cost, and the highest reliability. As a result, the operating company moved forward with the detailed design of a single stage membrane separation unit with the option of adding a second membrane stage to minimize hydrocarbon losses.

In the final design, all of the site sales gas would be routed to the membrane unit. A slip stream of gas would be processed through the membranes and the balance of the sales gas would bypass the membrane. The membrane unit would treat 150 MMSCFD of gas at a nominal inlet pressure of 900 psig and reduce the incoming CO₂ content from 3% to 1.5%. The residue gas from the membrane unit would be mixed with the rest of the untreated gas such that the all of the blended sales gas would meet the 3% CO₂ sales gas specification.

The amount of gas that feeds the membrane unit would be controlled by a PLC to ensure CO₂ concentration in the blended sales gas remains below 2.8 mol %. An overall diagram of the single stage membrane unit is shown on the following page in Figure 3.
Feed Streams Evaluation

With the final selection of membrane technology for the CO₂ removal process, the next step was to select which of several possible feed streams to treat. The feed streams were not implicitly considered until after the membrane option was chosen, thus this discussion only considers the feed streams and their impact on membrane technology.

The gas streams available for consideration as a feed stream to the membrane unit are:

1. Field gas – 3% to 4% CO₂, unprocessed ~ 1400 btu/scf gas at 350 psig
2. Residue gas – 3% to 4% CO₂, processed ~ 1080 btu/scf gas at 300 psig
3. Sales gas – 3% to 4% CO₂, processed ~ 1080 btu/scf gas at 900 psig

Due to the complex nature of the gas gathering and sales gas systems the operating company considered treating either the gas entering the NGL plants (field gas) or the gas leaving the NGL plants (residue or sales gas). Both options require consideration be given to feed gas gathering and low CO₂ gas distribution to ensure all of the sales gas customers received gas meeting the CO₂ specification. Dew point control pretreatment requirements for the hydrocarbon rich field gas would be similar in function to the NGL plants that produce the residue and sales gas streams. For the residue and sales gas streams, the NGL plants would provide the bulk of the membrane pretreatment. As a result, processing the field gas in the membrane unit would be the highest cost option of the three due to higher pretreatment costs, thus it was eliminated from consideration.
The remaining two feed options, residue gas and sales gas, are similar in composition and CO₂ concentration (with the possible exception of entrained compressor lube oil), but are available at different pressures. Ultimately the operating company chose to treat the sales gas because the higher pressure sales gas produces a smaller permeate stream and it is easier to manifold all of the sales gas to a single location for treatment. Figure 4 shows the location proposed for the membrane treatment unit in the site’s overall gas process.

![Figure 4: Proposed Location for Membrane Separation Unit]

By locating the membrane unit downstream of the NGL recovery plants and residue gas compressors, the project realized the following benefits:

- Elimination of potential feed compression requirements, a typical cost associated with membrane units.
- Minimizing the possibility of damaging the membrane tubes with liquids or particles as the low dewpoint liquids had already been removed in the NGL recovery plants.
- Reduced low CO₂ distribution issues by sending all of the sales gas through a single treatment unit. Note: A portion of the sales gas is bypassed around the membranes inside the membrane unit as shown in Figure 3

**Process Engineering Challenges during Detailed Design**

Early in the detailed design phase, the project team estimated that a single stage membrane unit would produce a permeate gas suitable for use as a fuel to the on-site cogeneration unit and a nearby power plant customer. The power plant has a very tight specification related to the fuel’s Modified Wobbe Index (MWI of fuel gas is equal to the lower heating value divided by the square root of the specific gravity of the gas times the absolute temperature of the gas). Therefore the operating company has to carefully blend the permeate gas with sales gas to be sure that the gas delivered to the power plant meets the MWI specification. The power plant also frequently reduces fuel demands to meet their power forecasts and therefore the amount of permeate gas that could be blended into the power plant fuel is variable and cannot be relied on as the only outlet for the permeate stream.
An evaluation of the cogeneration unit estimated that the unit could potentially consume close to 100% of the permeate stream that the membrane unit produced if the cogeneration unit operated at maximum capacity. In this case, the permeate stream would be close to 100% of the cogeneration unit’s feed stream. Since the stream would not be available until after the membrane process was started up and there were no process streams available at the site to simulate the permeate stream, the operation of the cogeneration unit on permeate gas could not be tested until after the start-up of the membrane unit. Therefore the project team decided to move forward with the option to send permeate gas to the cogeneration unit but it would not be confirmed until after a future test run.

Since the power plant and the cogeneration units could not be guaranteed to accommodate all of the permeate gas stream at all times, the low pressure injection option (see Figure 5) remained in the project scope as the back-up option for permeate handling. Since there are three possible outlets for the permeate stream, careful consideration has to be given to the permeate control scheme to protect the power plant and cogeneration plants from upsets due to changes in permeate stream demand while minimizing the amount of permeate sent to low pressure injection.

The project team proposed to control the permeate gas flow going to the power plant customer using a ratio control which modulated the permeate gas flow as the total fuel to the power plant varied. The remainder of the permeate gas would be sent to the cogeneration unit for consumption or if neither plant could consume the gas, it would flow to low pressure injection. During normal operation, the cogeneration unit and the power plant are expected to consume the entire permeate gas flow from the membrane separation unit. By disposing of the permeate gas in this manner, the project maximized the economics of the membrane unit by normally selling or consuming all or most of the gas produced out of the membrane separation unit. Figure 5 shows the final configuration of the production site.

![Figure 5: Block Flow Diagram of Final Membrane Separation Unit](image-url)
During the technology selection process, the operating company decided to use a pair of mothballed reciprocating compressors to compress permeate gas from the membrane unit up to the fuel header pressure. While this saved a significant capital expense, the compressors were not originally designed for this service and would have affected the expected performance of the membrane unit in several ways. Most significantly, the compressors are required to operate at an elevated suction pressure, nearly 50 psig, which is well above the initial design case of 15 psig for the compressors. Figure 6 shows the expected capacity of the permeate compressors as a function of suction pressure.

![Figure 6: Permeate Compressor Capacity as a Function of Suction Pressure at Constant Temperature, Composition, and Discharge Pressure](image)

The project team created a dynamic mass balance around the membrane separation unit using the predicted feed gas flow rate and composition from the site, the expected separation performance of the membrane unit from the membrane vendor, and the capacity of the permeate compressors as a function of suction pressure. For a given permeate pressure, the mass balance calculated the expected permeate gas flow from the membrane unit. This calculated flow was then compared to the capacity of the permeate compressors at the permeate pressure less the line pressure loss between the membrane unit and the compressors. If the compressor capacity at the given pressure was less than the permeate gas flow rate, the mass balance increased the permeate pressure and the calculation repeated itself until the compressor capacity met or exceeded the permeate flow rate. The final membrane unit performance is shown in Table 2.
Table 2: Expected Membrane Performance at 900 psig Feed Pressure with 2.8% CO₂ Content in Blended Gas (Based on the Expected CO₂ Content Shown in Figure 2)

<table>
<thead>
<tr>
<th>Year</th>
<th>Total Membrane Unit Feed (MMSCFD)</th>
<th>Feed to Membrane Elements (MMSCFD)</th>
<th>Membrane Element Bypass (MMSCFD)</th>
<th>Permeate Pressure (psig)</th>
<th>Permeate Flow Rate (MMSCFD)</th>
<th>Membrane Element Residue Gas (MMSCFD)</th>
<th>Total Membrane Unit Blended Gas (MMSCFD)</th>
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Start Up and Operation to Date of Membrane Separation Unit

Commissioning and start up of the membrane unit took place during the spring of 2009. The first week of operation was spent proving out the membrane units. Overall the unit started up without any major problems. Some of the minor problems encountered included typical issues with instrumentation such as bad I/O and the bypass control valve not fully closing. A few minor issues were also encountered with the permeate compressors, however these did not delay start-up of the unit.

By the end of the first week of start-up, the membrane unit was online and the site was producing sales gas at the target CO₂ concentration of 2.8 mole % in the blended sales gas.

During the first week of operation, the permeate gas was sent to low pressure injection until testing of each membrane skid had been completed and the membrane unit was proven to produce a permeate stream suitable for power plant fuel. By the end of the first week the membrane unit was fully operational and the permeate stream was going to power plant sales without any issues. The Modified Wobbe Index of the power plant feed was stable and within the required specifications.

During the second week of operation, a performance test was conducted to test the cogeneration unit’s capacity to operate on permeate gas from the membrane unit. Until this test was conducted, the amount of permeate gas the cogeneration unit could feed while staying within the operating specifications and environmental requirements of the cogeneration unit was purely speculative. Test runs in the cogeneration unit confirmed that the unit can take the full permeate stream without any operational issues or environmental excursions. After the cogeneration unit performance test was complete, the operating company decided to send half of the permeate stream to power plant sales and the other half to the cogeneration unit during normal operations. This mode of operation provides additional tolerance for upsets at either location since the upsets would typically only impact up to half of the permeate stream.
Operation of the membrane unit to date has been without issue and very reliable. Since start-up, the membrane unit has been online without any major maintenance issues or operational upsets. During normal operations the unit is unattended, however operators from one of the NGL plants are responsible for operations at the membrane unit and they perform rounds through the unit multiple times per day. In addition, the unit is monitored remotely by the operating company at all times. The operating company has been very pleased with the performance and reliability of the CO$_2$ removal process.