Pretreatment System Modifications for Improving CO₂ Removal in the Feedgas for 3 Gas Utility Peak-Shaving Plants

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Abstract

Natural gas transmission systems are being extended to new sources of natural gas to satisfy the additional needs of more gas-fueled power generation systems throughout the US. However, some of these new gas sources have gas compositions which stretch the pipeline tariff limits. Three major Utility-owned LNG Liquefaction/Peak shaving plants in Omaha, Nebraska and Minneapolis, Minnesota were notified of increased CO₂ levels in the feedgas to these plants, which would exceed the design capabilities of these plants. Designed in the early 1970's for typical feedgas conditions, which included a CO₂ content of less than 1%, and these facilities operated over 30 years without issues. Once notified that new gas supply CO₂ concentrations would reach up to 3% in Omaha and up to 2% in Minneapolis, each utility decided to replace their original Molecular Sieve with a Sieve material capable of CO₂ removal at these high concentrations. This presentation briefly outlines the situations and the efforts of these 3 LNG facilities to quickly modify their Pretreatment systems in order to continue to operate their existing Liquefaction plants without complete replacement of their Pretreatment system.

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Natural gas transmission systems are being extended to new sources of natural gas to satisfy the additional needs of more natural gas-fueled power generation systems throughout the US. However, some of these new gas supplies are stretching the CO₂ allowable limits of the natural gas pipelines delivering gas to major cities in the Upper Midwest region of the United States. These areas are served by 3 major gas utilities, each operating their own LNG Liquefaction/gas peak shaving plant.

This presentation outlines how the higher CO₂ levels in the feedgas affect the operability of these LNG Liquefaction facilities, and what considerations were needed in order to continue operating these plants. A brief review of the results and a few pictures of the process are also included.
All of these LNG facilities were designed and built in the mid 1970’s to liquefy pipeline quality natural gas, with a CO₂ content of less than 1%. The Liquefied Natural Gas, LNG is then stored for use during the heating season when natural gas supplies are not in balance with the Gas Utility system’s demand.

During the Liquefaction process the temperature of the feedgas is reduced to approximately -260 degrees Fahrenheit, therefore the H₂O and CO₂ in the feedgas must be removed prior to liquefaction as their freezing will create blockages in the process piping at these cryogenic temperatures.

The 2 primary methods for the removal of CO₂ and water from natural gas for liquefaction are:

- Amine gas treating systems
- Zeolite molecular sieve systems.

Amine systems utilize liquid removal of high concentrations of H₂S and CO₂ from the Sour Gas that typically may be found in raw gases at the well head. This illustration shows the process flow of the amine solution and “sour” gas being treated, as well as the waste stream of Sulfur and CO₂.
These Amine systems require the use of hazardous chemicals in the stripping process, which must be periodically refreshed. These systems must also have a means for disposing of the byproducts (sulfur and CO₂) that has been stripped from the gas. This coupled with the high initial investment, and close management of the chemicals used for the system’s operation make these systems impractical for the gas utility-owned LNG facilities.

Temperature Swing Adsorber systems utilizing zeolite molecular sieve material are also used in large scale applications, however they are also well suited for the seasonal operations of the gas utility-operated LNG plants.
Zeolite molecular sieves have the ability to adsorb water and CO₂ when cool, and then release these elements once heated. This feature enables the gas processing system to remain idle for extended periods of time without any detrimental effects on the zeolite. This picture shows what some of the different types of molecular sieve materials look like.

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The common decision of these three gas utilities was to modify the adsorber pretreatment system by changing their operating procedures, and replacing their current molecular sieve with a newly developed zeolite sieve material capable of CO2 removal at 30% higher concentrations than before.

**Adsorber principles of operation**

Each adsorber system consists of:

- Several vertical, and internally insulated pressure vessels containing the zeolite molecular sieve
- Associated flow control valves and gas piping to and from the vessels
- A gas heater for heating the regeneration “purge” gas that passes through the bed to heat the zeolite during regeneration
- A gas cooler to remove the heat from the hot regeneration gas after it passes through the adsorber beds, and before sending the gas back out as “tailgas” into the gas distribution pipeline system.

This chart above shows that the zeolite has a higher affinity for water than other elements. Therefore the water will be adsorbed first from the feed, and will displace the other elements which had already been...
adsorbed in the molecular sieve material as it passes through the zeolite material. These other elements will then be adsorbed at another area of the adsorber bed.

This creates a virtual “wave front” that will move through the adsorber bed during the adsorption process. The illustration shows how this moves down through the Adsorber vessel as the molecular sieve is “loaded” by the water and CO₂.

These adsorber systems require a substantial amount of purge gas, and heat for regenerating the molecular sieve material for continued use. While the design flow rate, and temperature of the “regeneration” gas used for purging the beds varies greatly, the result remains the same in removing the H₂O and CO₂ from the feedgas.

There are several designs for the Adsorber systems, but in these facilities there are just the “Two Bed” and “Three Bed” Temperature Swing Adsorber systems.

### Typical Range of Design and Operating Conditions

#### Adsorption (Feed) Conditions
- Source: pipeline quality natural gas
- Flow Rate: ~ 5 to 30 MMSCFD
- Pressure: ~ 300 to 800 psig
- Temperature: 60 to 100 °F
- CO₂ Content: 0.5 to 1.5 (mole)%

#### Regeneration (Purge) Conditions
- Source: adsorption product or plant flash gas
- Flow Rate: ~ 20% to 50% of feed rate
- Pressure: feed or lower
- Temperature: ~ 300 to 600 °F
Two bed adsorber system

- Minneapolis, Minnesota - Centerpoint Energy LNG plant’s details
- Built by CB&I and operational in 1976.
- 1 BCF LNG storage tank
- Liquefaction design - 5 MMCF per day
- 2 bed adsorption system for feedgas pretreatment for liquefaction with a regeneration gas flow of 8.4 MMCFD.
- The typical feedgas processed by this plant had a CO2 content of 0.5 to 0.6%.

Two Bed Cycle, Open Loop Regeneration

Wet Feed

<table>
<thead>
<tr>
<th>Adsorption</th>
<th>Regeneration</th>
</tr>
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<tbody>
<tr>
<td>(H₂O &amp; CO₂ Removal)</td>
<td>(H₂O &amp; CO₂ Removal)</td>
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Heater

Product (to LNG)

To Fuel/Pipeline

The 2 bed Adsorber system illustration shows the process flow through the 4 components of the system. This system is designed so that the adsorption time required in the first Adsorber bed is the same as the heating and cooling times in the other Adsorber bed.
While the frequency of the changing feedgas content is now unpredictable, the results thus far have been satisfactory for the Centerpoint Energy facility.

- They have been able to operate the Liquefaction facility with CO₂ levels up to 1.55% without any issues to their process.
- They have made some process changes, such as timing of the Adsorber bed switching.
- They are considering the conversion to a Three Bed system if the CO₂ content should increase further.

**Results of Molecular Sieve changeout**

- Results;
- The CO₂ capacity of the adsorber system was improved by 30%.
- The maximum CO₂ content successfully processed had a CO₂ content of 1.55% without breakthrough.
- Future considerations include;
  - lengthening bed switching times
  - adding a third bed if higher CO₂ levels develop

**Three bed adsorber system**

- **St. Paul, MN- Xcel Energy LNG plant’s details**
  - The Xcel Energy plant was built by CB&I and operational in 1974.
  - The plant includes;
  - 2 BCF LNG storage tank
  - Liquefaction design- 10 MMCF per day
  - 3 bed adsorption system to pretreat the feedgas for liquefaction with a regeneration gas flow of 23 MMCFD.
  - The typical feedgas processed by this plant had a CO₂ content of 0.5 to 0.6%.
The 3 bed Adsorber system illustration shows the process flow through the 4 components of the system. This system is designed so that the adsorption time required in the first Adsorber is the same as the Heating and cooling times in the other 2 adsorber beds.

### Results of Molecular Sieve changeout

- **Results:**
- The CO2 capacity of the adsorber system was improved, but testing has not been completed.
- The maximum CO2 content while on line was at 1.2% without an issue.
- Experience operating the system with lengthening bed switching times has been successful with CO2 levels below 1%.

While the frequency of the changing feedgas content is now unpredictable, the results thus far have been satisfactory for the Xcel Energy facility.

- They have been able to operate the Liquefaction facility with CO2 levels up to 1.2% without any issues to their process.
- They have made some process changes, and have extended their Adsorber bed switching time from 60 minutes to 120 minutes when operating at CO2 content levels below 1%.
- They have reconfigured the gas analyzing system for faster response to possible CO2 breakthroughs.

Prolonged usable life of the zeolite is anticipated by extending the Adsorber bed switching time and reducing the thermal cycles.
Again, the 3 bed Adsorber system illustration (page 9) shows the process flow through the 4 components of the system. This system is designed so that the adsorption time required in the first Adsorber is the same as the Heating and cooling times in the other 2 adsorber beds.

While the frequency of the changing feedgas content is now unpredictable, the results thus far have been satisfactory for the Metropolitan Utilities District facility.

- Testing has shown that CO₂ breakthrough has improved from 90 minutes at 0.58% CO₂ to 150 minutes at 1.1% CO₂.
- They are able to maintain normal Liquefaction plant operations up to 1.6% CO₂ content.
- They are reviewing other options to be able to operate at 2% CO₂ content level.

**SUMMARY**

None of the Liquefaction plants have experienced feedgas containing the maximum CO₂ content levels during liquefaction, and they will be required to occasionally stop their processes if these maximum levels develop.
However, all plants have been able to modify their systems which will greatly extend the number of days available for plant operations, and each have found this solution successful at this point. Only a few options exist for processing natural gas at such high CO\textsubscript{2} content, and they will require major investment into the existing systems.

[Graphics and Zeolite Molecular Sieve specifications provided by UOP.]

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These pictures illustrate the change out process. The stainless steel liquid nitrogen tanks with the nitrogen used for purging the adsorber vessels, and a vacuum truck used to remove the molecular sieve from the Adsorber vessels are seen in the upper left picture. Loading the removed sieve material into containers for disposal is shown in the lower right picture.

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Entry into the Adsorber for internal inspection is shown in the upper left picture. Loading the new molecular sieve from the transport sacks is shown in the lower left picture.