MOLECULAR GATE ä TECHNOLOGY
FOR
(SMALLER SCALE) LNG PRETREATMENT

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ABSTRACT

The Molecular Gate adsorption process uses pressure swing adsorption (PSA) to remove nitrogen and carbon dioxide impurities from natural gas while using adsorbents with high selectivity between methane and these impurities. Two systems feeding smaller scale LNG plants are now operating where the methane rich feed is dehydrated and carbon dioxide is removed to 50 ppm or less. The Molecular Gate technology in LNG pretreatment is competitive with TSA based systems for lower carbon dioxide feed levels (such as for pipeline feed based peak shaver plants) and offers cost advantages and simplified operations as compared with amine plus TSA treatment for higher carbon dioxide concentrations. The technology removes water to <1 ppm and carbon dioxide to <50 ppm from any carbon dioxide feed level, with the treatment of carbon dioxide levels of up to 40% having been demonstrated. The Molecular Gate technology is also widely used to remove nitrogen from natural gas and in this application any carbon dioxide in the feed is automatically co-removed to less than 50 ppm. This paper provides an overview of the technology, the basis of the operating plants and outlines the application of the technology to feed streams over a range of carbon dioxide concentrations.

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INTRODUCTION

The Molecular Gate process for removing nitrogen and/or carbon dioxide from contaminated natural gas streams continues to grow in popularity with over thirty systems provided to date. The system operates by adsorbing nitrogen and/or carbon dioxide at 100 - 500 psig (typically 100 psig) while delivering a methane product reduced in these impurities at 10 psi lower than the feed pressure. While most applications deliver pipeline gas, two systems are operating to deliver product gas streams to small liquefiers (10,000 and 13,000 gallons per day).

While large LNG facilities receive the largest share of evaluation and study, small scale LNG facilities are becoming more popular, either for the purpose of distributed LNG or as peak shaver units. Indeed, natural gas storage through peak shavers is well established with well over 100 systems in the United States.

Historical Treatment for Peak Shaver Units Based on Pipeline Gas Feed

Where utilities seek to store natural gas during periods of slack demand for its subsequent use during high demand periods, peak shavers have commonly been used. In these systems, pipeline gas is treated, liquefied and stored by the utility and re-vaporized and injected into the pipeline distribution system as demand dictates. Upgrading pipeline gas as a feed to the liquefier is well established. Since the feed gas is pipeline quality it has already been treated for the removal of the bulk quantity of carbon dioxide, such that the carbon dioxide is two percent or less (more commonly in the one percent range). The pipeline feed gas has also been bulk dehydrated and heavy hydrocarbons have been removed to meet typical pipeline specifications.

Because carbon dioxide freezes in a liquefier at levels above 50 ppm, the pipeline gas fed to a peak shaver unit requires pretreatment for the removal of the residual carbon dioxide in the pipeline gas. Further, the pipeline gas is typically dehydrated to levels of seven pounds per MM SCFD (approximately 150 ppmv) and since water will also freeze in a liquefier, the water level must be reduced to 1 ppm or less. Excess heavy hydrocarbons can form solids in the liquefier and their presence may need to be addressed in the design of the liquefier.

Historically, the treatment for such LNG facilities uses a thermally regenerated molecular sieve adsorption system (TSA) consisting of two or more adsorbent beds. While one bed removes the water and carbon dioxide, a second bed is regenerated by being heated and subsequently cooled before being placed back on the feed step. Because the amount of adsorbent required is large relative to the feed rate, three bed TSA units as shown in Figure 1, are commonly used to allow relatively fast cycle times to minimize the quantity of the regeneration gas and the heating duty.

In the TSA system, the amount of regeneration gas required is a function of the amount of adsorbent required. For this reason, feed streams with high carbon dioxide levels require large adsorbent quantities and high regeneration gas flow rates. Where the carbon dioxide exceeds about two percent, the need to heat and cool the large beds results in using a large portion of the product gas for regeneration, leaving minimal product gas as liquefier feed. For this reason carbon dioxide levels above 2% are not typically treated in TSA systems.

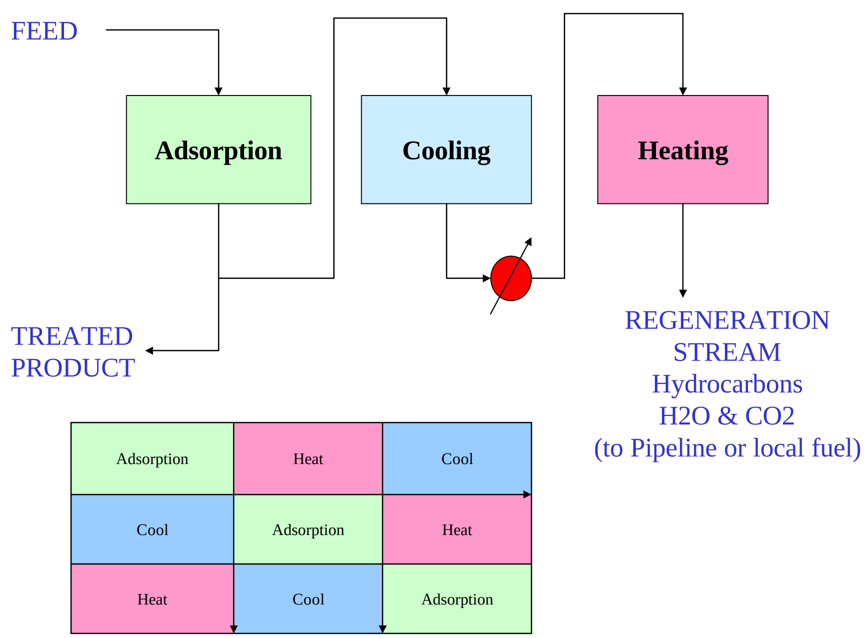

Figure 1 - Three Bed TSA Process

The molecular sieve beds in this process operate at moderate pressure levels as dictated by the design of the liquefier and/or the available pipeline pressure. While the pressure can range widely, 400 psig is a typical operating pressure for historical peak shaver liquefiers, with recent small liquefiers operating at lower pressures. The molecular sieves used in this application are chosen to maximize the capacity for carbon dioxide. Unlike molecular sieves targeted at dehydration alone, a relatively large amount of adsorbent is required to remove the carbon dioxide. This is due to the relatively high carbon dioxide feed concentration and the lower adsorbent capacity for carbon dioxide as compared to the capacity for water vapor. Due to the relatively low capacity of molecular sieves for carbon dioxide in a TSA based system, it is desirable to have the feed gas temperature as low as possible to improve the molecular sieves carbon dioxide capacity. Since pipeline gas is generally at temperatures below summer ambient conditions, there is a temperature advantage in helping to minimize the required adsorbent quantity for pipeline feed streams.

The regeneration of the adsorbent bed takes place at high temperatures, typically in the range of 500 degrees F, and results in a rejected stream containing the previously adsorbed carbon dioxide and water, which is in turn either utilized as local fuel or returned to the pipeline. The treated gas product is commonly used as the regeneration gas, though using the LNG boil-off gas for regeneration is practiced. As with all adsorption systems, finding a home for the regeneration stream is a process optimization and a critical site-specific optimization.

Feed Gases Containing High Carbon Dioxide Levels

Because pipeline gas is already treated for bulk carbon dioxide and water vapor removal the amount of processing to meet the needs for the liquefier is minimal. However, LNG systems are also applied where the feed gas is from wellhead gas. In these applications, the level of carbon dioxide, heavy hydrocarbons and water vapor is higher than that of a pipeline. Pretreatment of such wellhead sites would commonly use amine based systems carbon dioxide removal and since the amine systems are aqueous, the amine system product effluent is saturated in water.

In a wellhead application, the dedicated amine system can be designed to remove the carbon dioxide to levels lower than that required for pipeline specifications. For example, the carbon dioxide can be removed to <50 ppm followed by TSA drying. This low carbon dioxide slip requires a larger amine plant and consideration for specialty amines in the amine plant design should be provided. The carbon dioxide slip into the product can also be balanced against the removal of carbon dioxide in the amine plant versus removal of the carbon dioxide in the TSA dryer. A simplified process flow scheme for an amine/TSA dryer is shown in Figure 2.

Since the product from the amine plant is water saturated, it is possible to install a glycol unit for bulk dehydration prior to the TSA system to limit the size of the molecular sieve TSA system and minimize the quantity of the regeneration stream. In general, membranes in place of the amine system would not be considered since the removal of the carbon dioxide to very low levels is required.

Regardless of the route chosen for carbon dioxide and water removal, the heavy hydrocarbons are not removed and remain with the treated gas. Since heavy hydrocarbons can form solids in the liquefier they require that the liquefier design address the potential impact of heavy hydrocarbons. Since smaller liquefiers do not have the luxury of the economy of scale found with world-scale plants, the additional processing to separately remove heavy hydrocarbons is generally undesirable.

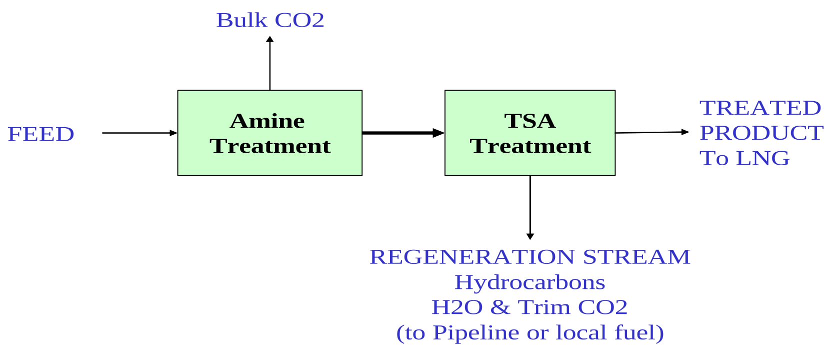

Figure 2 -Amine plus TSA Treatment

Molecular Gate Technology for Carbon Dioxide Removal

The Molecular Gate Technology for carbon dioxide removal uses a highly selective adsorbent with a high affinity for carbon dioxide over that of methane which is applied in a pressure swing adsorption system. Feed gas is introduced into the Molecular Gate Unit at feed pressure, which is typically 100 psig but can range as high as 500 psig or more, and the product methane stream is delivered at near feed pressure. In the Molecular Gate System, water vapor and carbon dioxide is adsorbed in much the same way as in a TSA dryer and a product of less than one ppm water vapor and less than 50 ppm carbon dioxide is produced. The Molecular Gate System regenerates using pressure reduction rather than thermal regeneration and the feed stream is split into a product stream at near feed pressure and a reject regeneration stream that is delivered after a vacuum pump at a few psi above atmospheric pressure. A photo of a typical Molecular Gate system is shown in Figure 3.

Figure 3: Typical installation for a 2 - 5 MM SCFD Molecular Gate Unit

Because the Molecular Gate system operates with rapid cycles, on the order of a few minutes, and the feed/regeneration pressures can be changed rapidly, the technology allows both bulk and trace removal of impurities. The attributes of the pressure swing adsorption technology allows the amount of carbon dioxide that can be removed in a single step to be much higher than that achieved by the TSA system. This is compared to the hours-long cycle times of thermally regenerated systems which are more appropriate for the removal of low quantities of impurities.

Historically, conventional adsorbents in PSA service have high methane adsorption capacities which upon regeneration result in high methane losses. However, the very high selectivity between methane and carbon dioxide of the Molecular Gate adsorbent allows the delivery of a product that contains ppm levels of carbon dioxide while also achieving high methane recovery rates. The inherent higher adsorption for carbon dioxide over methane of all adsorbents is enhanced in the Molecular Gate system due to the pore size control which limits adsorption of methane. This size selective effect is shown in Figure 4.

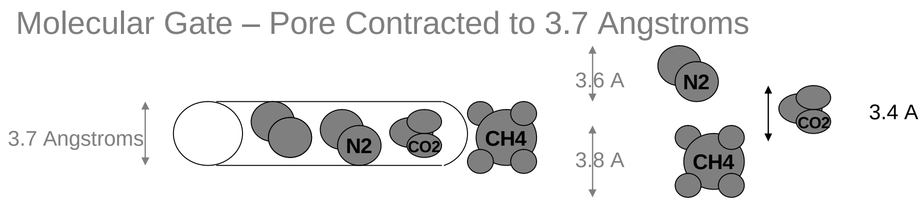

Figure 4 - Schematic of the Molecular Gate Adsorbent Separation

In the Molecular Gate process, nearly any level of carbon dioxide can be removed to 50 ppm or less in a single step. As a high carbon dioxide feed example the removal of 40% carbon dioxide, such as from a digester gas, to less than 50 ppm of carbon dioxide has been demonstrated.

In a single step Molecular Gate Unit, the methane recovery to the LNG facility is, in part, a function of the amount of carbon dioxide in the feed stream. For example, feed stocks containing one to two percent carbon dioxide such as pipeline gas can achieve methane recovery rates of 95%, while higher levels of carbon dioxide such as five to ten percent would have recovery rates in the 90% range. In some cases where the tail gas is to be returned to the pipeline, high recovery is not desired since the returned tail gas must be diluted to meet the pipeline carbon dioxide limits. Thus, the Molecular Gate design and hydrocarbon recovery is a site-specific optimization depending largely upon the uses of the regeneration stream. A single stage flow sheet is shown in Figure 5.

The feed pressure used is commonly 100 psig, though higher pressure can also be accommodated. In general, higher pressure operations would include a recycle compressor to allow high methane recovery and minimize hydrocarbon losses.

An example of performance when treating pipeline gas is in Table 1.

	Pipeline Feed	Product to Liquefier	Tail Gas
Flow	100	91	9
Pressure, psig	100 - 500	90 - 490	3
Temperature, F	As available	80 - 120	150
Composition, Mole %			
C1	94.0	97.3	61.6
CO2	2.0	<50 ppm	21.8
C2	3.0	2.5	8.2
C3	0.7	0.2	5.4
C4+	0.3	< 0.1	3.0
H2O	7 lb/ MM SCFD	<1 ppm	By Difference
HHV, BTU/FT3	1030	1033	1000

Table 1 - Typical Pipeline Feed Stream Treatment

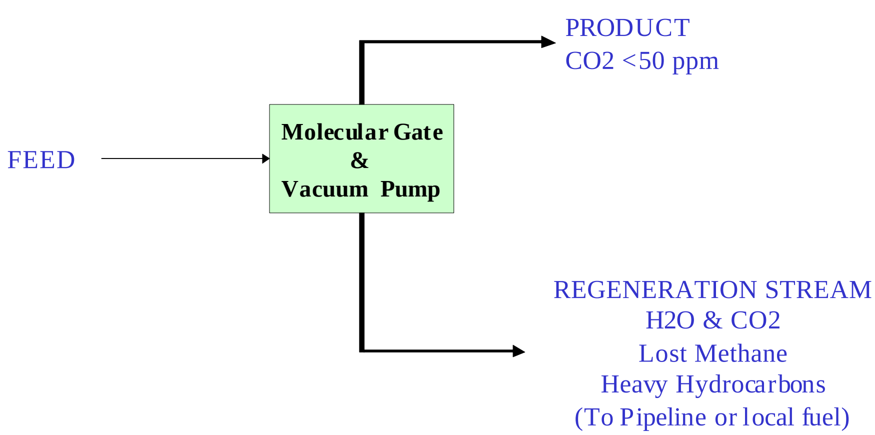

Figure 5 - Typical Single Stage Molecular Gate Processing

As with most separation processes, there are considerable flexibilities in the design performance and the use of a recycle stream or two-stage processing allows the adjustment of the hydrocarbon recovery rates to be higher or lower as needed to optimize the process for a particular site.

In treating streams with high carbon dioxide or where the highest methane recovery is desired, two stage processing can be considered. Such a process is shown in Figure 6 where a first stage unit removes the bulk of the carbon dioxide while the second stage polishes the carbon dioxide to ppm levels. The opportunity to recycle the tail gas from the second stage allows for minimizing the hydrocarbon losses.

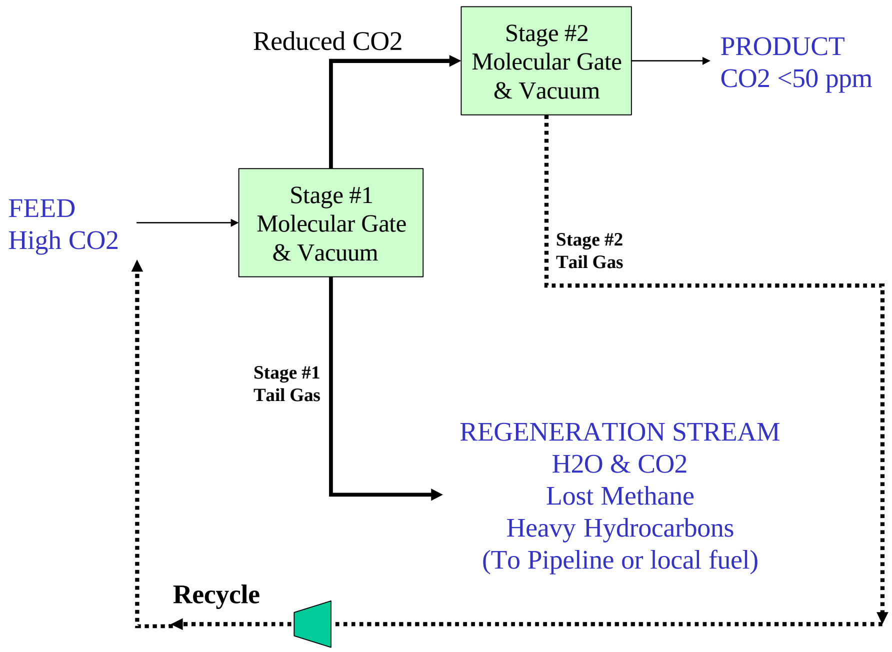

Figure 6 - Two Stage Processing Schematic #1

Figure 7 shows an alternate two stage approach targeted at moderate feed levels of carbon dioxide but where high recovery rates are desired. In such a design, recovery rates of 98% or more can be achieved. In this configuration, the first stage unit produces the treated product while the second stage treats the compressed tail gas from the first stage for bulk carbon dioxide removal with hydrocarbon recycle to the first stage to allow additional methane recovery.

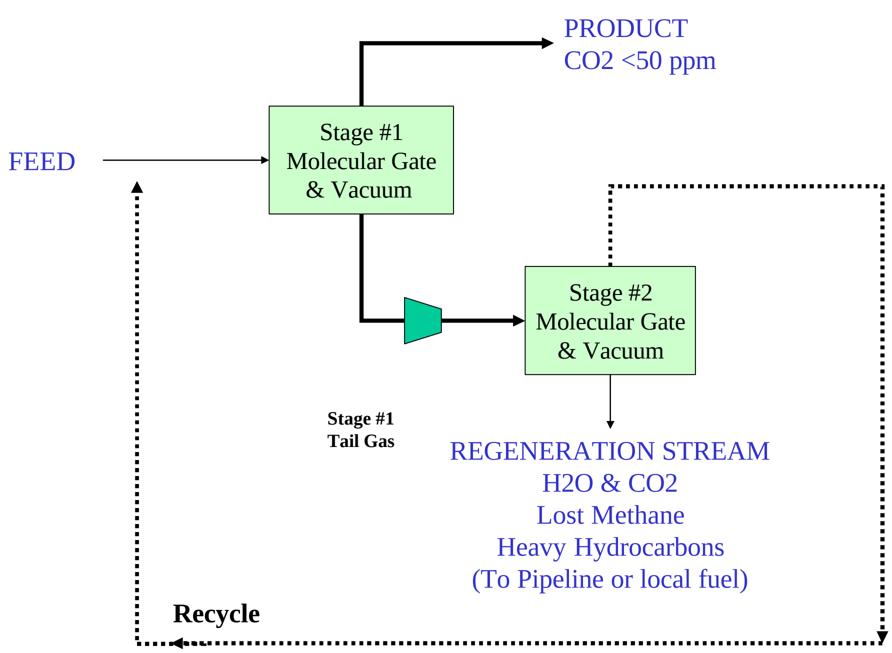

Figure 7 - Two Stage Processing Schematic #2

In the examples above, a two stage Molecular Gate process is considered, however, one of the stages can be amine, membrane or TSA based. The use of two-stage processing adds cost and the overall cost must be balanced against the value of the recovered hydrocarbons as LNG and the site-specific use of the regeneration stream.

Heavy Hydrocarbon Removal

An advantage that the Molecular Gate Technology brings to LNG facilities is the ability to remove heavy hydrocarbons along with the carbon dioxide and water vapor. Though heavy hydrocarbons do not fit with the pore they adsorb on the surface of the Molecular Gate adsorbent. The Molecular Gate technology can target the relative removal quantity of these heavy hydrocarbons which can be adjusted to that desired for the liquefier. In our experience, we have seen requests for C6+ removal to levels as low as 10 ppm.

In removing heavy hydrocarbons, the system is flexible and can be designed to target the removal of the C5 and C6+ fractions while leaving behind the bulk of the ethane, propane and a portion of the butane in the product to the liquefier. Since heavy hydrocarbons can form solids in the LNG plant and since controlling the heating value of the LNG product can be desirable, this flexibility can be an attractive benefit.

The Molecular Gate system can also be designed to remove mid-range hydrocarbons to match the desired product LNG heating value. Systems have been provided to treat feeds with high levels of ethane and propane to remove a portion of these components (along with essentially all the C6+) to meet CARB standards for CNG product quality.

An example of treatment for a rich, 5% carbon dioxide feed stream is shown in Table 2.

	Pipeline Feed	Product to Liquefier	Tail Gas
Flow	100	83	17
Pressure, psig	100 - 500	90 - 490	3
Temperature, F	As available	80 - 120	150
Composition, Mole %			
C1	83.5	92.6	39.1
CO2	5.0	<50 ppm	29.3
C2	6.0	6.0	6.0
C3	3.0	1.1	11.9
C4	1.6	0.2	8.6
C5	0.6	<0.1	3.3
C6+	0.3	Trace	1.8
H2O	Saturated	<1 ppm	By Difference
HHV, BTU/FT3	1115	1078	1298

Table 2 - Typical Higher Carbon Dioxide / Rich Gas Treatment

The adsorbent also has a high affinity for hydrogen sulfide and when carbon dioxide is removed below 50 ppm, any hydrogen sulfide in the feed is removed from the methane product. To date, feed streams with up to 6000 ppmv of hydrogen sulfide have been treated.

Mercaptan and Mercury Removal

Where the feed contains mercaptans they are adsorbed and removed from the product to the liquefier. At the current time, data on mercury remo6val is lacking, however, where mercury is present in the feed stream it is expected to be removed (at least in part).

Nitrogen plus Carbon Dioxide Rejection

Of the thirty Molecular Gate Systems in operation, more than half have been designed for the removal of nitrogen (1) to typical pipeline standards of three to four percent. For all the nitrogen rejection units, the feed stream contains a level of carbon dioxide ranging from a few thousand ppm to several percent. Because carbon dioxide adsorbs more strongly than nitrogen in the Molecular Gate process, inherently a feed stock containing mixed nitrogen plus carbon dioxide will contain a product with less than 50 ppm carbon dioxide when the nitrogen is removed to typical pipeline specifications. Thus, the Molecular Gate Unit removes both carbon dioxide and nitrogen in a single step.

Nitrogen in the feed stream to a liquefier is undesirable because nitrogen is soluble in the LNG and thus increases the refrigeration duty or lowers the heating value of the LNG product. While nitrogen removal by flash from the LNG is possible (and studies using the Molecular Gate process to purify the flash gas or boil-off gas have been conducted) the Molecular Gate process allows removal of nitrogen before it reaches the liquefier which can be attractive in the liquefier design.

In our experience, small scale LNG plants target nitrogen levels in the three to four percent range and, thus, the typical product nitrogen levels from Molecular Gate units match that required by LNG facilities. To date, there are two operating Molecular Gate units that feed small scale liquefiers with both of these in landfill gas service.

In upgrading the landfill gas to feed the liquefiers, the gas is available near atmospheric pressure and contains about 50% methane along with water vapor, a wide variety of VOC's, hydrogen sulfide, ~40% carbon dioxide, ~1% oxygen and nitrogen in the 6% to 15% range. The typical process steps are (1) compression (2) pre-treatment to remove the VOC's and hydrogen sulfide (3) treatment to remove the bulk of the carbon dioxide (using either membranes or a first stage Molecular Gate system) and (4) nitrogen rejection. In the feed to the Molecular Gate unit removing the nitrogen and carbon dioxide the resultant gas after steps 1 to 3 contains a few percent of carbon dioxide and 10 to 25 percent nitrogen (dependent on the raw feed nitrogen concentration). In the two existing Molecular Gate Units, the nitrogen is removed to three to four percent and the carbon dioxide is essentially completely removed. In both applications, the Molecular Gate Unit is the final treatment system before feeding the liquefier. In this demonstrated service, the first unit treating a contaminated feed of approximately 1.2 MM SCFD has been in operation in the UK for over two years while a second unit treating a contaminated feed of 1.8 MM SCFD has been operating in California since last year.

Conclusions

Peak shavers and small scale LNG units have been a common and growing process for the natural gas industry. The Molecular Gate technology offers a new route for feed gas pre-treating. The technology brings the advantage of removing water vapor and any level of carbon dioxide while offering a flexible design that can be targeted to remove a desired amount of heavy hydrocarbons while also removing other impurities. Where the feed gas contains nitrogen, Molecular Gate Systems can remove nitrogen and deliver methane product to the LNG facility at a typical three to four percent nitrogen concentration, while inherently removing carbon dioxide in the feed to the ppm levels required for the liquefier.

References

1. Mitariten, M.J., "Nitrogen Removal from Natural Gas with the Molecular Gate Adsorption Process", 88th GPA Proceedings, San Antonio, TX, 2009.