



Gas pre-treatment on Molecular Sieves: Floating LNG specificities

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ABSTRACT

Natural gas pre-treatment, prior to liquefaction, typically includes a molecular-sieve-based dehydration unit. Over recent decades, various techniques have led to productivity improvement and unit size optimization (use of split bed, enhancement of product performance, sharper simulation tools, etc.) But the careful study of each design and debottlenecking case show that there are still potential gains to be had in efficiency and size that can extract Opex and Capex savings.

Additionally on Floating LNG units, specific concerns have to be addressed, such as space optimization, enhanced reliability of the process (remote locations), and flexibility of the molecular sieve unit.

This paper describes how to optimize the size and the performance of a molecular sieve unit in this context.

1. Introduction

Floating LNG has become one of the most exciting technical and economic challenge within the natural gas industry.

Since the first studies in the late Seventies^[1], the road to realization has been long, uncertain, and eminently context-dependant. Today the goal is near, and the first Floating LNG projects are under construction, and expected to start production in 2015 or 2016.

Contractors and suppliers are aware of the numerous issues concerning Floating LNG. They can be classified into three main areas:

- Safety,
- Reliability,
- Compactness

And every contractor or supplier has had to confront these constraints, and sometimes reinvent certain aspects of their business to accommodate.

As for any LNG plant, molecular sieves are required to completely dry the gas prior to liquefaction. Even though gas pretreatment has no direct impact on safety (no more than for onshore plants), it may drastically affect the process integrity and the topside footprint.

CECA has been so far involved in 18 Floating LNG projects, and frequently participate in studies, FEEDs and Detailed Engineering on the main ongoing projects. The Petronas FLNG (topside by Technip) will embark CECA molecular sieve in its frontier. The result of this work, based on our experience, and enhanced by our customers questions, led us to an accurate assessment of the design possibilities.

We have been asked:

- How to optimize the adsorption unit size?
- How to extend its lifetime and improve its reliability?
- Is it possible to change out the sieves without stopping the plant?
- What about CO₂ removal in case of low content in the gas, or in case of AGRU upset?

Through a representative case study, this paper's intent is to address these questions.

2. Pretreatment lineup

A typical (not universal) natural gas pre-treatment before liquefaction would include, as a minimum:

- An Acid Gas Removal Unit (AGRU) to remove CO₂ down to the LNG specifications,
- A Dehydration Unit by adsorption on molecular sieve,
- A Mercury Removal Unit (MRU).

Most of the time, CO₂ is removed by an Amine-based absorption process (which is also able to remove H₂S when present). For very high CO₂ contents, permeation systems ("membranes") can also be implemented to first decrease the CO₂ content down to a few percent^[2].

After the Amine unit, the gas is water saturated and needs to be completely dehydrated on molecular sieve (the typical outlet specification ranges from 0.1 to 1 ppmV water).

It has to be noted that CO₂ adsorption on molecular sieve is also a viable method to remove low concentrations.

In addition to the above, some further remarks, specific to a floating structure, can be made:

- Compactness is an important requirement, which calls for the size optimization of all the topside equipment.
- Remoteness brings the necessity for being as self-sufficient as possible, and leads to strong reliability requirements.
- Sea swell-induced motion can have an impact on the Amine unit performance^[3]. Can the downstream molecular sieve unit compensate some limited Amine upset?
- Simplified process is an other important point. Would a single molecular sieve unit (or 2 units in series) be able to de-carbonate and dry, in case of low CO₂ content natural gas fields?

3. Case study

The results of the next chapters are based on the following theoretical case:

- Natural gas, MW = 18.5 kg/kmol
- Flow-rate 21 000 kmol/hr (~ 470 000 Nm³/hr, corresponding to about 2.4 mtpa LNG)
- Operating temperature 25°C / Operating pressure 60 bara.

This can be considered as an average case for a Floating LNG plant. For instance the Petronas FLNG capacity will be 1.2 mtpa^[4] LNG and Shell's Prelude, which is going to be the largest floating structure ever, will be 3.6 mtpa LNG^[5].

The following results and discussions are based on up-to-date state of the art, and on our best calculation tools and simulation models. However, due to the specific operating conditions, gas composition and other constraints of each particular project, they cannot be extrapolated to other cases.

4. Dehydration

In this chapter, it is assumed that an Amine unit first decreases the CO₂ content to less than 50 ppmV. The gas is then chilled to 25°C, and feeds the dehydration at 60 bara. It is water saturated (700 ppmV) and the outlet specification is 0.1 ppmV.

4.1. Size optimization

Several criteria help to define the best unit arrangement and the vessel size. The flow-rate and the water inlet content are of course the most obvious, but a few others also impact the design:

- Vessel size limitations (construction cost, transportation, available deck space, weight limits, etc.),
- Allowable pressure drop (depends on the flow-rate, gas characteristics and vessel dimensions),
- Requested lifetime (adsorbents ageing effects increase with the number of regenerations),
- Adsorbents shape, size and density.

The following will mainly focus on the latter two: we will see how to optimize the size of the bed to get the most compact unit, and we will see the impact of doubling the requested lifetime of the products.

In this example the best fitted layout is a "2+1 system" arrangement: 2 beds are in adsorption mode and 1 bed is in regeneration. The adsorption time is assumed to be 20 hours down-flow (therefore the time lag between the beds, which corresponds to the time allocated to up-flow regeneration, is 10 hrs).

The maximum allowable pressure drop is 0.25 bar at the beginning of the lifetime. Regeneration is performed by heating a slip stream of the product gas which is then cooled down and recycled to the dehydration unit inlet.

4.1.1. Product size and density

Products size and split:

In order to optimize the height of the Mass Transfer Zone (MTZ), it is now common (if not standard), to implement “split beds”. Split beds are made of large particles (typically 1/8” beads or pellets) in the Equilibrium Zone (EZ), followed by small ones (typically 1/16” beads or pellets) in the MTZ. Since the small particles show a much larger overall surface, the MTZ is shorter compared to large beads or pellets. From a pressure drop point of view, even though the small particles create more resistance, it is completely offset by the overall height reduction of the bed.

The below chart (Chart 1) shows, for the given case study, the vessel size comparison between a full 1/8” pellets bed and a split bed, both with typical pellets. The difference is very significant with a gain of about 20%.

Chart 1	1/8 “ pellets only	Split bed	Ratio (%)
Molecular Sieve quantity / vessel (kg)	27 000	21 250	- 21.3
Vessel internal diameter (mm)	3 300	3 300	0.0
Molecular Sieve bed height (mm)	4 470	3 650	- 18.3
Molecular Sieve volume (m³)	38.2	31.2	- 18.3

Density:

It is possible to further reduce the vessel size by using dense adsorbents. As a matter of fact, the adsorption capacity is expressed as a mass percentage (for example mass of water adsorbed by 100 kg of adsorbent). The calculated required mass then has to be loaded in a given volume (for existing units), or in a calculated volume based on products’ density (for new units).

Chart 2 gives, for our studied case, the vessel size comparison between the previous split bed (with typical pellets available on the market) and an optimized split bed using dense particles.

Chart 2	Split bed	Optimized bed	Ratio (%)
Molecular Sieve quantity / vessel (kg)	21 250	21 200	-1.5
Vessel internal diameter (mm)	3 300	3 150	- 4.5
Molecular Sieve bed height (mm)	3 650	3 400	- 6.9
Molecular Sieve volume (m³)	31.2	26.5	- 15.1

Conclusion:

The potential overall reduction on the adsorbent bed volume, from a conservative design to an optimized split bed with dense particles is here of 31%. Depending on the specific cases, it has been found to be ranging from about 25 to 35%.

Even from a split bed to another split bed, and depending on the type and density of product, the reduction of the needed volume can be as high as 15%.

4.1.2. Requested lifetime

Ageing and slow damaging of a molecular sieve bed is linked essentially to the high temperature regeneration and its associated effects. The longer the lifetime, the more regeneration steps, and

therefore the necessity to compensate these ageing phenomena by some margin on the products quantity installed.

Chart 3 is a comparison between 2 optimized designs, the first one with a 4 to 5 years lifetime expectation, the second one with a more than 7 year lifetime expectation.

Chart 3	> 4 yrs lifetime	> 7 yrs lifetime	Ratio (%)
Molecular Sieve quantity / vessel (kg)	21 200	23 000	+8.5
Vessel internal diameter (mm)	3 150	3 200	+ 1.6
Molecular Sieve bed height (mm)	3 400	3 580	+ 5.3
Molecular Sieve volume (m³)	26.5	28.8	+ 8.7

In this example, should the project request a long lifetime design, this would involve between 8.5 and 9% more volume of product.

4.2. Reliability

Due to the remoteness of the facilities, Floating LNG plants require a high degree of reliability. From the molecular sieves point of view, and specifically considering the case study unit, a few parameters have to be taken into account:

- Molecular sieve quantity margin. This is of course the most obvious: have larger beds with greater than necessary quantity of molecular sieve. This solution is efficient and reliable to certain extent, for example to withstand a slightly faster than normal ageing rate, or to face occasional upset conditions (see § 5.2 below). However, it cannot be seen as an absolute panacea, for example in case of massive hydrothermal damaging or acid attack destroying the sieves and turning them to powder.

- Suitable regeneration procedure. Your molecular sieve manufacturer is able to recommend the most suitable regeneration protocol specific to your case. This could involve temperature ramping, preliminary heating steps, criteria to make sure the regeneration is complete, etc.

- Upstream filtration equipment is paramount to avoid water, liquid hydrocarbon or amine foams carry-over. CECA strongly recommends the implementation of a coalescer with a liquid droplets specification of less than 0.1 ppmWT.

- On top of the molecular sieve bed, we also recommend to load a protective layer of alumina or silica gel. This layer will prevent the sieve from being directly accessible to liquids, and can be an efficient shield in case of occasional carry over.

All the above solutions are partial; and enhanced plant reliability is the result of gathering them all.

Last but not least, a periodic follow-up of the unit performance by your molecular sieve supplier (including regeneration curves review and breakthrough testing) usually keeps the serious troubles away, and is often the best source of optimization and improvement.

4.3. Vessel change out during operation

It is often asked if changing molecular sieve is possible without stopping the plant completely. Doing so requires a system having more than one vessel in adsorption. In our case study, what are the operating conditions that would allow only one vessel in adsorption, while the second one is in regeneration and the third in maintenance?

Processing the whole flow-rate through only one bed would multiply the pressure drop by 4, bringing it to more than 1 bar at the beginning of the lifetime (and potentially up to 2 bars near the end of the lifetime). Additionally, the adsorption time would be divided by more than 2 (taking into account the dramatic increase of the MTZ).

Therefore there is scope to assess the best compromise in terms of flow-rate and adsorption time, that would stay within an acceptable pressure drop range, whilst minimizing the impact of MTZ elongation.

Chart 4 gives, in our case study, what could be still acceptable. However, one should keep in mind that the indicated pressure drop is at the beginning of the lifetime, while such a change out is usually performed at the end of the lifetime. Therefore if the vessel that is in adsorption mode is aged the same as the one being changed out, some margin has to be considered (with the real pressure drop being potentially double)

Chart 4	Normal operation (2+1 system)	“On the fly” change out (1+1 system)	Ratio (%)
Flow-rate (Kmol/hr)	21 000	12 300	- 41.4
Pressure drop (bar, new product)	0.25	0.35	+ 40.0
Adsorption time (hr)	20	16	+ 5.3

Even if the plant is not stopped, the feed flow-rate has to be reduced by about 40%, and the pressure drop is also 40% higher. Last but not least, the time requested for the change out (typically a few days), and the logistics/safety issues involved have to be considered.

5. Carbon dioxide removal

In this section we will study how the molecular sieve unit, which is required anyway for dehydration, can be used to totally or partially remove CO₂ from the inlet gas. Some previous preparative work on the subject has already been presented by CECA earlier^[6]. It is assumed that the gas contains no H₂S. Two scenarios can be envisioned:

- Low CO₂ content gas fields (0.1 to 0.2 vol%), where no Amine unit is implemented. All the de-carbonation and water removal are performed by molecular sieve. We will call this case the “by design” case.
- Standard unit, with an Amine unit bringing the CO₂ down to the LNG specification level of less than 50 ppmV. The question will be: can the molecular sieve unit compensate an upset in the Amine unit performance? If yes, to which extent, and does it have to be anticipated in advance at design stage? This case is called the “Amine upset case”.

5.1. By design case

As already stated, the adsorption capacity of molecular sieve for CO₂ is limited, and it is not possible to treat high CO₂ contents.

However, in the case of low CO₂ content gas fields, it is a viable solution, for several reasons - global plant layout simplification, less emissions, global footprint, avoid Amine-based solution sensitivity to sea swell-induced motion, etc.

One of the main issue is that the regeneration gas (containing all the CO₂ desorbed) cannot be recycled as it is for dehydration only. It has to be flared, or used as a fuel gas when the CO₂ content allows it. This amount of regeneration gas depends on the regeneration duty and, therefore, mainly on the vessel size, pressure, and allowable regeneration time. It is possible, to minimize it, by to internally insulating the vessels and thus reduce the steel heating duty. It is also common to add a vessel and to

regenerate 2 vessels at the same time (one in cooling in series with a second one in heating mode). Doing so, the regeneration time allocated to heating is extended and the regeneration flow-rate can be minimized.

The following chart (Chart 5) compares 3 different designs:

- Design 1: - 0.1 vol% CO₂ + 700 ppmV water in the feed,
 - 2 vessels in adsorption, 1 in regeneration,
 - external insulation.
- Design 2: - 0.1 vol% CO₂ + 700 ppmV water in the feed,
 - 2 vessels in adsorption, 2 in regeneration in series,
 - **internal** insulation.
- Design 3: - **0.2 vol%** CO₂ + 700 ppmV water in the feed,
 - 2 vessels in adsorption, 2 in regeneration in series,
 - internal insulation.

Chart 5	Design 1	Design 2	Design 3
CO₂ content (ppmV)	1000	1000	2000
Vessels in adsorption / regeneration	2 / 1	2 / 2	2 / 2
Adsorption time (hr)	8	8	6
Molecular sieve volume per vessel (m³)	122.6	122.1	150.3
Regeneration flow-rate (% of feed)	36	15	24

Considering the scale, internal diameters range from 4600 to 4800 mm, and the product height from 7300 to 8300 mm. These are very large vessels, quite rare (even onshore), but existing and realistic. Of course, the lower the flow-rate the smaller the vessels. It is also possible to envision 2 different molecular sieve trains, each treating half of the flow.

In conclusion, removing water and CO₂ in a single plant seems feasible for medium to low CO₂ contents, but the main issue is to be able to minimize, as much as possible, the regeneration flow-rate. In some cases, it has been possible to accommodate less than 10% regeneration flow-rate.

Notes:

1- To simplify our assumptions, and to better compare section 4 and 5, we considered the gas saturated with water. However since it doesn't come from an aqueous process, it is not necessarily the case.

2- An alternative solution, which is not detailed here, would be to implement 2 distinct molecular sieve units: 1 for water (for example on 3A type product), and 1 downstream for CO₂. In spite of having 2 units, a first advantage could be to decrease the CO₂-rich regeneration flow-rate, and a second one could be to benefit a longer adsorption time on the water unit (and therefore a longer lifetime). It is even possible to imagine more complex arrangements where the CO₂ unit regeneration gas is also used to regenerate the dehydration unit. Such a solution can provide significant savings in terms of investment and energy, but is not easy to implement as the 2 units have to be perfectly synchronized.

5.2. Amine upset case

In this scenario, it is assumed that in a normal situation, an Amine absorption system and a chiller bring the gas to less than 50 ppmV CO₂ and 25°C / 60 bara (700 ppmV water).

What would happen in the case of upset (for instance due to sea motion), if the Amine unit was not able to deliver the CO₂ specification during a given duration? Would the molecular sieve unit be able

to cope with both water and the additional CO₂? If yes for how long? If not, would that have to be considered at design stage?

5.2.1. Amine upset and regular dehydration unit

A dehydration unit is designed to ensure a given water specification for a given lifetime. At the beginning of the lifetime, the bed's capacity is maximized because the product is not significantly aged. Therefore at the end of an adsorption cycle, there is still some fresh sieve that can cope with additional CO₂.

Let's consider the example of an Amine unit upset event that would deliver 200 ppmV CO₂ during 30 min. What would happen in the case of the "optimized bed" discussed in section 4.1.1 (Chart 2), at the beginning of its lifetime ?

- The 50 ppmV CO₂ specification could only be met provided the upset would happen quite early in the cycle (here, after a maximum of about 75% of the adsorption time). Besides, the problem would have to be identified immediately, and the cycle would have to be stopped just after the upset.

- If the upset happens close to the end of the adsorption time, the CO₂ breakthrough would reach 70 ppmV at the beginning of the upset, and 80 ppmV after 30 min.

It is of course not acceptable to let "good luck" be such a key factor. Besides, the above described ability for the bed to retain some of the additional CO₂ is decreasing as the sieves become aged.

5.2.2. Amine upset and enlarged dehydration unit

Considering the same dehydration duty as per the above cases, the present chapter looks at how much larger the molecular sieve unit must be to treat, any time, an upset of 500 ppmV CO₂ during 60 min. Chart 6 below compares the optimum design for dehydration only ("optimized bed" of chart 2), with the unit that would be required to treat such an upset and still meet the < 50 ppmV specification.

Chart 6	Optimized bed	Enlarged bed
Inlet CO₂ content (ppmV)	50 always	500 for 60 min
Molecular Sieve quantity / vessel (kg)	21 200	37 000
Vessel internal diameter (mm)	3 150	3 600
Molecular Sieve bed height (mm)	3 400	4 550
Molecular Sieve volume per vessel (m³)	26.5	46.2

The enlarged beds are 75% greater in volume than the regular ones. Even in the case of normal CO₂ content (no upset), the regeneration duty will therefore be much higher compared to the regular unit (+35%)

6. Conclusion

Even though the liquefaction of natural gas is a very well known process, marinization brings new constraints, including the gas pre-treatment chain. Whether to optimize the footprint, the global weight, to simplify the process and make it more reliable, or to build in contingencies for upstream processes, solutions exist and molecular sieve can be part of it. Dense adsorbents can significantly reduce the size of the dehydration unit. Molecular sieve can also be used to remove low CO₂ contents, or to cope with limited Amine unit upsets. In any case the most important aspect is to clearly define the requested service at design stage.

References

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