A Tale of Two Sieves

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Abstract

> *"It was the best of times, it was the worst of times, it was the age of wisdom, it was the age of foolishness…"*
>
> - A Tale of Two Cities - Charles Dickens, Macmillan & Co., LTD, 1922

A reliable molecular sieve system is of paramount importance for any LNG liquefaction facility. While some LNG facilities achieve sieve lives upwards of six years, three years or less is more typical. At the *"the worst of times"*, operation of molecular sieve systems is problematic with drastically reduced sieve life. At *"the best of times",* dehydration systems easily achieve the desired sieve life while operating flawlessly. For example, with the exception of skimming and replacing just the top portion of the beds twice during turnarounds, the Alaska Kenai LNG facility achieved twenty eight consecutive years of relatively trouble free operation on a single sieve charge. How did a 1960's vintage sieve system, designed without modern design tools, ever achieve twenty eight years of sieve life? How did this system operate essentially trouble free for so long without the modern conveniences of a Distributed Control System or automated valve sequencing system?

The answers are not found in fundamental science or sieve integrity. The physical properties of gases and liquids have not changed and the structural integrity of sieves has not diminished. In fact, physical property estimation methods have improved, while newer and more robust sieves have become available. And modern DCS systems offer tremendous advantages over 1960's pneumatic instrumentation systems. Given these advantages, why do modern facilities not achieve similar or better performance? The authors assert that the answers, at least in part, are due to an over-reliance on modern design tools and conveniences, which has led to a general lack of understanding and conservatism. It is evident that some wisdom was lost along with the leap into the information age. In that sense, perhaps we have passed from *"the age of wisdom"* into *"the age of foolishness"*.

This article presents the detailed study results of the Kenai LNG sieve system. Key equipment design and operational criteria applied in the 1960's will be discussed and compared to criteria typically applied to modern systems. This article tells a tale of two sieve systems, past and present, to recapture some of the wisdom lost with the leap into the information age.

Introduction

The Kenai LNG Plant has utilized the Optimized Cascade® process since 1969, achieving exceptional reliability and availability. Key to successful operations is the design of the dehydration system, required to prevent freezing.

With the exception of replacing the top portion of the beds twice during turnarounds, most of the original Kenai molecular sieve lasted 28 years. Similarly, the original sieve at the Sherman Helium Plant in West Texas achieved 15 years life. Since both facilities share the same designers, a cosmic accident is unlikely. The key to reliable sieve performance is design. One cannot ignore the value of operation but successful operation begins in design.

This article compares the key design principles between Kenai and modern dehydration systems. However, it would be unfair to not complete the history. Following an initial 28 year run, sieve life decreased to 3-5 years. While still comparable to modern facilities, the performance decline is dramatic. As discussed later, the reason provides an excellent illustration of a key design principle.

Figure 1: Kenai LNG Facility Dehydrators

Kenai LNG Facility Feed Pretreatment

The Kenai feed is too cold to route directly to the Amine Gas Contactor. An exchanger preheats the contactor feed while chilling the dehydrator inlet gas. The feed is further heated with steam before routing to the Gas Contactor where carbon dioxide is reduced from around 1,000 to 20 ppmv. Treated gas is chilled to ~60°F and routed to the Dehydrator Gas Scrubber to condense and remove as much moisture as possible to reduce adsorption requirements.

The facility utilizes four Molecular Sieve Dehydrators, two in adsorption and two in regeneration. Adsorption and regeneration piping symmetry is maintained. Dry gas is routed through Activated Carbon Filters and Dry Gas Filters for mercury and particulate removal prior to liquefaction.

Regeneration gas taken downstream of the Dry Gas Filters is heated to ~430°F using steam before entering parallel dehydrator beds. Desorbed water is condensed and removed in the Regeneration Gas Cooler and Regeneration Gas Scrubber. The gas is then compressed and recycled upstream of the Gas Contactor. The compressor minimum flow recycle ramps closed over 15 minutes at the beginning of a seven hour heat cycle and open over 15 minutes at the end of a five hour cooling cycle. The heater is bypassed during the cooling cycle. No steam or cooling water leaks impacting the sieve have occurred over the life of the facility.

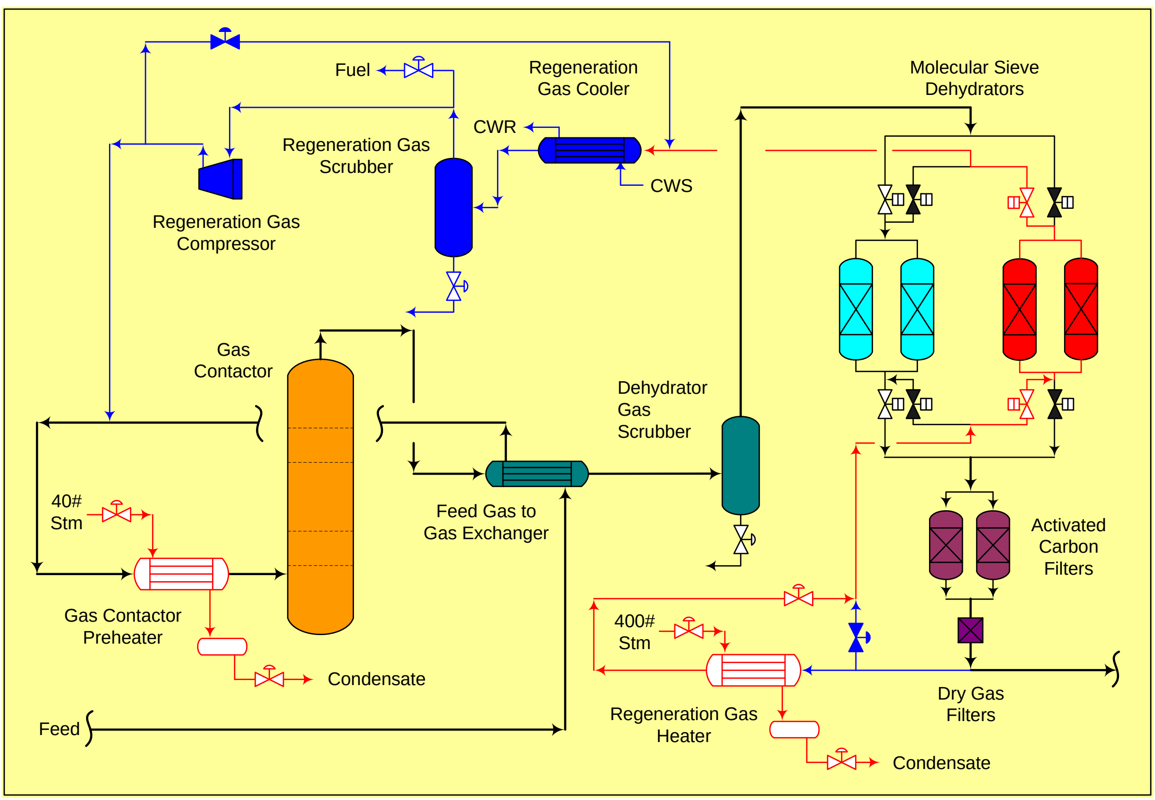

Figure 2: Kenai Acid Gas, Moisture & Mercury Removal System

Modern LNG Facility Feed Pretreatment

Modern facilities employ various pretreatment configurations. A typical arrangement is provided in Figure 3. Comparing Figures 2 and 3 immediately reveals additional equipment. Modern facilities typically include filter/coalescers upstream of both the amine contactor and dehydrators to remove mist, aerosols and particulates to reduce foaming and sieve damage. Free liquids remain the leading cause of sieve damage, leading to increased differential pressure, premature breakthrough and early replacement.

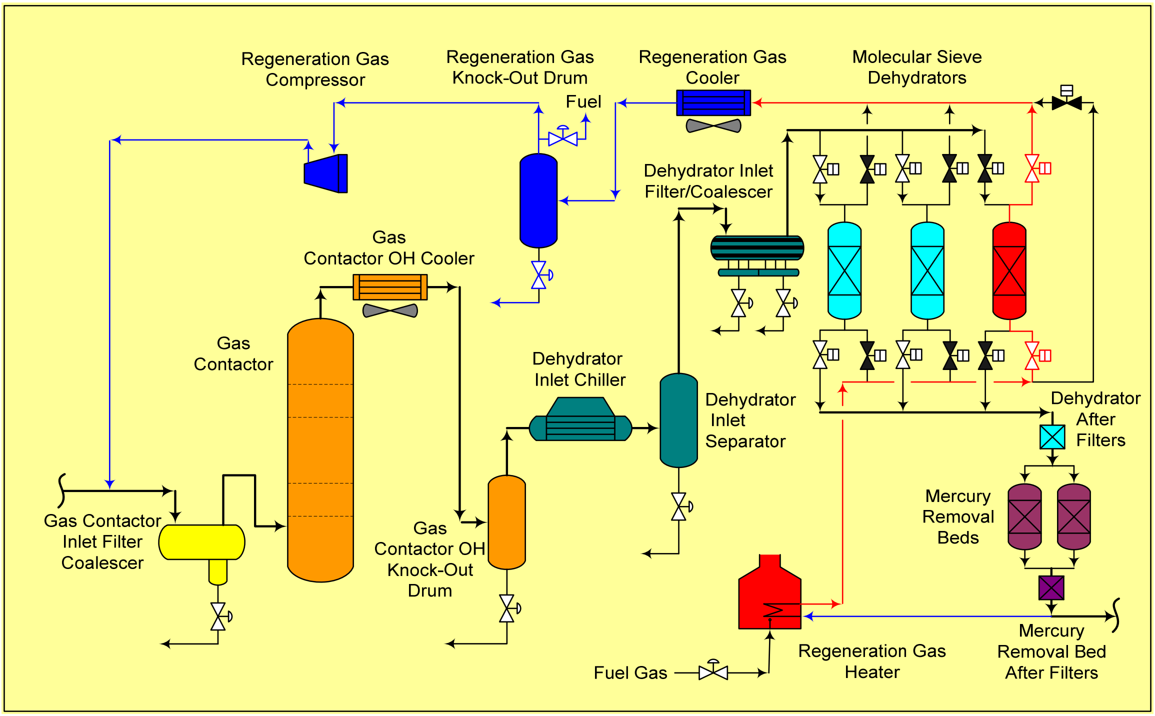

Figure 3: Typical Modern LNG Facility Feed Pretreatment System

Bed arrangement represents another difference. Most facilities employ three or more beds in staggered drying. Care must be taken with the inlet and outlet headers since unlike the Kenai approach, maintaining piping symmetry is impossible.

Given additional equipment, improved controls, enhanced physical property methods, powerful design software, and more robust sieves, performance should improve. Why is this not the case? One tendency is to attribute Kenai's sieve performance to the predominantly methane feed composition. While certainly a factor, this does not entirely explain the performance. The answer is design margin as discussed in the following sections.

Feed Characterization

Many facilities are designed without completing a proper feed characterization, which should be considered of primary importance. A common approach is to select a single C6 component to represent all C6 components, a single C7 component for all C7 components, and so on. A single component is sometimes selected to represent all C6 and heavier components. This approach often results in incorrect physical property predictions, which can result in premature condensation leading to amine foaming, sieve damage and liquefaction freezing. There are excellent references available presenting detailed characterization techniques. (1)(2)(3) While typical for petroleum, feed characterization techniques remain underutilized for gas, despite multiple examples demonstrating the need thereof. (4)(5)(6) Even small temperature deviations near the phase envelope can be detrimental.

Typical problematic contaminants to identify and quantify are carbon dioxide (CO_2), hydrogen sulfide (H_2S), sulfur dioxide (SO_2), carbonyl sulfide (COS), iron sulfide (FeS & FeS_2 compounds), mercaptans (RSH), tri-methyl arsine $(CH_3)_3As$, mercury compounds, sulfur compounds, methanol (MeOH), and glycols.

The Kenai facility began production in June 1969 as the second base load LNG facility. Triethylene glycol and a tail of heavy components were identified and precautions were included in the initial design. However, since CO_2 was not fully quantified, it was necessary to add an amine system, which came online in September 1970. While the Kenai facility has never missed an LNG shipment, early operations without an amine system proved problematic. (7)

Amine Removal Considerations

Amine contamination of molecular sieves due to foaming and/or entrainment is common. In addition to impingement and sintering/agglomeration, amines create coke during regeneration. The following suggestions are offered to minimize foaming/entrainment.

- Physical properties determined through a thorough feed characterization to prevent internal absorber phase changes.
- Conservative system and flooding factors for the absorber and regenerator
- Upstream water wash for large quantities of glycol, methanol or iron sulfide
- Coalescer/filter removal of 99.99% of particulates larger than 0.3 microns when iron sulfide or aerosols are present
- In addition to normal "lean" solvent filtration, provide 100% "rich" solvent filtration, typically 3-10 microns
- For rich feeds, a minimum of 25 minutes settling time with hydrocarbon skimming capability for the solvent flash and regenerator reflux drums.
- A well designed antifoam injection package
- Dedicated water wash circulation pumps for the amine absorber
- Conservatively sized overhead knock-out drum
- High quality co-knit mesh pads in the amine absorber and overhead knock-out drum
- No condensed hydrocarbons in return streams from downstream equipment

Dehydrator Inlet Gas Chiller

Propane refrigeration or a suitable process stream is often utilized to condense water from the dehydrator feed to reduce adsorption requirements. A control point at least 3-5°F above the hydrocarbon dew point or freeze point, whichever dictates, is recommended. A thorough feed characterization is required to ensure accurate dew point predictions. Tight control is important to avoid hydrocarbon condensation or freezing.

Figure 4: Kenai Gas to Gas Exchanger (Dehydrator Inlet Chiller)

Some practical considerations:

- Elevate the chiller to free drain into the Dehydrator Inlet Separator.
- Avoid high velocities and differential pressures, especially when close to the phase envelope.
- Avoid high inlet and outlet nozzle momentums (ρV^2).
- Utilize RTDs to improve temperature control accuracy.

The Kenai piping and nozzles are conservative. With Kenai's low hydrocarbon dew point, hydrocarbon condensation cannot occur. Tight control is maintained to avoid freezing with sufficient sieve margin to compensate for temperature variations.

Dehydrator Inlet Separator

Successful molecular sieve performance depends upon eliminating liquid contamination. Liquids cause sieve damage through a variety of mechanisms, including impingement, sintering/agglomeration, and coking during regeneration. While gas/liquid separation principles are well understood, sizing in practice is empirical. To reduce cost, age-old experience factors are often abandoned in favor of "proprietary internals". Care is required to adequately size the vessel based on proven long term experience in similar services and conditions, including any internal devices that may be used. A large separator with a co-knit mesh pad is recommended.

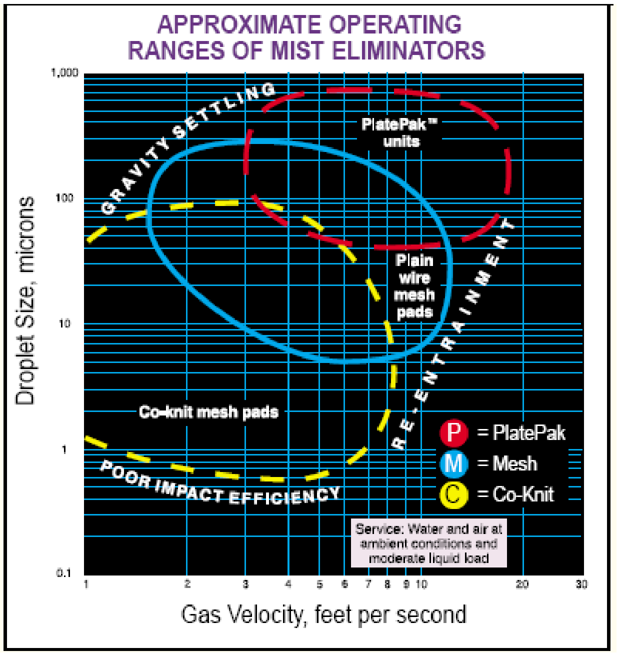

Figure 5: Approximate Operating Ranges of Mist Eliminators (8) – Reprinted With Permission from ACS Industries, LP

Figure 5 reveals a relatively large operational range for co-knit mesh pads. The authors of the cited publication correctly state that designers typically assume droplet distribution based on empirical data, experience, and/or application. Also noted is the data was compiled for air and water at ambient conditions. (8) Gas/liquid separation is not an exact science and relies on experience.

Bulk liquids and droplets ranging anywhere from submicron to 500+ microns form in the upstream chiller. It is therefore recommended to lower the velocity and utilize gravity for bulk liquid and large droplet separation before reliance on mist elimination devices. A high quality co-knit mesh pad is recommended for small droplets and mist.

Even though Kenai utilizes a large Dehydrator Inlet Separator with a vane pack, entrainment remains the leading cause of damage. However, other than replacing the top portion after seven years and again after 27 years, most of the initial sieve lasted 28 years before full replacement in 1997. A particularly noteworthy foaming event in 1992 resulted in high differential pressures on one pair of beds. Additional surge volume may have prevented sieve damage, but the separator protects the sieve rather well, especially since there is no downstream coalescer.

Following a 1993 capacity increase, sieve life declined to 3-5 years. Visible sintering at the top of the beds reveals accelerated liquid contamination. The differences presented below appear mild but are sufficient for increased entrainment.

Dehydrator Gas Scrubber Sizing Criteria	Before 1993 Capacity Increase	After 1993 Capacity Increase
Vessel K Factor (ft/sec)	0.168	0.203
Vessel Internal Velocity (ft/sec)	0.89	1.07
Vane Pack K Factor (ft/sec)	0.46	0.56
Vane Pack Velocity (ft/sec)	2.4	3.0
Nozzle Momentum, ρV^2 [$lb_m/(ft \bullet sec^2)$]	1,167	1,697
Nozzle Velocity (ft/sec)	23.1	27.9

Table 1: Kenai Dehydrator Gas Scrubber Criteria Before & After 1993 Capacity Increase

Dehydrator Coalescer/Filter

Most coalescer/filters are designed to remove mist and aerosols. Coalescing is impeded when the elements become saturated. It is instructive to envision droplets beading on the windshield of a slow moving automobile. As smaller droplets coalesce into larger droplets, gravity pulls them downward. At higher velocities, the wind pushes droplets upwards, overcoming gravity. In a downpour the windshield becomes sheeted which impedes coalescing. These principles apply within coalescer/filters. It is important to:

- Remove bulk liquids and large droplets upstream
- Avoid exceeding internal velocity constraints

Reducing equipment size to reduce cost is ill-advised. Since coalescer/filters provide the last line of defense, conservatism is warranted. Recommended specifications are:

- Remove 99.99% of droplets $\geq$0.3 microns
- Inlet and outlet nozzle momentums: $\rho V^2 \leq 1{,}500\ lb_m/(ft \bullet sec^2)$

The inlet piping should be free draining without excessive pressure loss, especially if operating near the phase envelope. If multiple coalescer/filters are required, the inlet and outlet piping should be symmetric without liquid collection points.

Molecular Sieve Selection

Adsorbents are available to address a variety of requirements such as mercaptan removal, simultaneous removal of mercury and water, minimizing carbonyl sulfide formation, and resisting acidic attack. Since some contaminants may be removed by acid gas solvents and adsorbents, the selection of both should be completed simultaneously.

Pellets and beads are the most commonly selected shapes. Pellets are extruded to a specific diameter while beads are manufactured within a range of particle sizes. Beads expand during manufacturing and are screened into 8x12 mesh (nominal 1/16") and 4x8 mesh (nominal 1/8") sizes. An 8x12 designation describes particles that pass through 8 mesh screen and retain on 12 mesh screen. UOP, who offers pellets and beads, compared their relative performance and determined that beads require a larger mass transfer zone and offer no differential pressure advantage. The volumetric capacity is approximately the same for both, but beads have higher density and therefore remove less water per pound. (9)

The most common adsorbents for LNG facilities are 4A sieves, due to high moisture capacity and robust performance. 3A sieves are often rejected for saturated water conditions due to lower moisture capacity and lower regeneration temperatures than 4A. As such, 3A sieves require higher regeneration rates for the same regeneration temperature and heating time.

Amount of Molecular Sieve Required

The highest moisture case, not the highest flow, determines sieve requirements. For many facilities the highest moisture case is the highest temperature case. Even small temperature differences dramatically impact moisture content. A common mistake is to base gas moisture content on equilibrium calculations. Dehydrator feed gas frequently contains more moisture than equilibrium calculations indicate. UOP has developed a proprietary method to predict moisture based on composition and operating conditions.

To prevent premature breakthrough, the design must consider end of life sieve capacity. Because sieve capacity deteriorates over time as a function of the number of regenerations, it is recommended to establish a realistic end of life capacity working with the sieve supplier. For typical LNG designs using 4A sieves, ConocoPhillips LNG Licensing recommends establishing a ceiling no higher than 9.8-10 lbs of water per 100 lbs of sieve.

The Kenai dehydrators contain almost twice the sieve required. While some of the top sieve was replaced twice during the first 28 years, this included most of the active sieve. The longest "active" sieve life of 20 years was still exceptional. While doubling the sieve seems excessive, no moisture breakthroughs occurred in over 41 years. Considering all associated defrost downtime was avoided over the life of the facility, the additional sieve was justified, especially since it was rarely replaced.

Additional sieve is not necessary if proper precautions are followed. However, additional sieve provides insurance against unforeseen conditions, but must be included in the initial design to allow accurate equipment sizing.

Number & Size of Dehydrators

Many assume that two or three beds are more economical than four or more. The Kenai designers selected four based on cost and other considerations. In some cases, additional dehydrators reduce both capital and operational expenditures. Wall thickness requirements increase with diameter such that three larger vessels may require more steel than four smaller vessels. While additional valves are required, the sizes decrease. Smaller beds also require less regeneration gas, which requires smaller regeneration equipment and improves process efficiency.

Additional beds also improve life-cycle availability. It is rare when adding equipment improves both capital and/or operating expenditures, but it does sometimes happen. As such, a life-cycle Net Present Value approach is recommended to select the best option. The following criteria are advised.

- Determine sieve requirements using the highest moisture case.
- Establish a maximum differential pressure of 5 psi using the highest velocity case, including regeneration gas.
- Establish a maximum end of life differential pressure of 10 psi. An increase of ~60% over a new bed is reasonable.
- Maintain sieve bed L/D>1.0.

Compound Beds

Many facilities employ a silica gel layer as protection against contaminants. This tactic has proven largely ineffective. (9) While initially effective, silica gel often breaks down and increases differential pressure. Silica gels also lose effectiveness faster than molecular sieves such that liquid contaminants pass through and damage the underlying sieve.

Another approach utilizes 1/8" sieve for the saturation zone and 1/16" sieve for the mass transfer zone, which shortens the mass transfer zone and reduces bed height requirements. This approach should be avoided for new designs to maintain future flexibility but remains valid for retrofits.

Silica gel was originally utilized at Kenai but ultimately discontinued due to fracturing and increased differential pressures. The facility recently installed UOP MOLSIV™ UI-94 Adsorbent, a 4A product developed by UOP to resist breakup and coking from liquid contamination, with good results thus far.

Regeneration Cycles

For water saturated conditions, ConocoPhillips LNG Licensing recommends a design maximum of 1,000 regenerations per bed. While possible to exceed 1,000 regenerations, it should not be assumed during design.

Considering only heating and cooling time with no allowance for sequencing, pressurization/depressurization, ramping, hold(s) or standby is common. This does not allow operational flexibility and should be avoided. The following are recommended.

- Sequencing: 0.25-0.5 hours
- Pressurization/depressurization: Downward direction only - not to exceed 0.833 psi/sec
- Ramping: 0.25 hours at beginning of heat cycle
- Standby: 1-2 hours
- Holds: 2-3 hours below decomposition temperature of "known" contaminate.

The Kenai regeneration cycle is seven hours heating and five hours cooling. The valves are manually sequenced to pressurize and depressurize in the downward direction. Regeneration gas ramps up over 15 minutes at beginning of heating cycle and down at completion of cooling cycle. The regeneration sequence and flow have remained unchanged over the life of the facility.

Regeneration Equipment

Adsorbents must be heated to desorb water and cooled prior to another adsorption cycle. Unfortunately, water desorption is not the only heat requirement. The vessel, internals and piping must be heated and cooled during each cycle. It is necessary to accurately determine the mass of the vessel, piping, support balls, sieve and system heat losses. In some designs, the duty for large high pressure vessels may exceed that required to desorb water. Therefore, sufficient detail must be provided to accurately determine vessel mass. In addition to providing the required heat/cooling duty, the regeneration gas must provide at least 0.01 psi/ft of sieve for adequate distribution. Regeneration flow requirements are a function of temperature and time, with lower temperatures or flow requiring longer heating times.

The Regeneration Cooler must cool the regeneration gas and condense desorbed water. Since the majority of water desorbs within 30 minutes to an hour, peak load must be considered. However, it is not possible to remove more heat than supplied. In practice, the Regeneration Cooler duty is slightly less than or equal to the Regeneration Heater duty.

If regeneration gas originates downstream of the adsorption bed(s), physical properties at the Regeneration Gas Knock-Out Drum will be similar to those at the Dehydrator Inlet Separator. It is therefore logical to utilize the same sizing criteria. The Regeneration Gas Scrubber is slightly more conservative than the Inlet Gas Scrubber.

Regeneration Gas Scrubber Sizing Criteria	Value
Vessel K Factor (ft/sec)	0.136
Vessel Internal Velocity (ft/sec)	0.66
Vane Pack K Factor (ft/sec)	0.35
Vane Pack Velocity (ft/sec)	1.7
Nozzle Momentum, ρV^2 [$lb_m/(ft \cdot sec^2)$]	816
Nozzle Velocity (ft/sec)	18

Table 2: Kenai Regeneration Gas Scrubber Criteria

Conclusions

LNG plant availability depends on reliable sieve performance, which is achievable if key separation and adsorption principles are properly understood and followed. The Kenai designers understood the value of reliable performance and were wise enough to include sufficient design margin, which ultimately ensured over 41 years without a single moisture breakthrough or missed LNG shipment. The Kenai design regeneration rate, cycles and heater/cooler duties remain unchanged. In today's environment, there is increased pressure to reduce cost by reducing design margin. And advances in computational methods allow engineers to "optimize" to a degree unavailable in previous eras, which can provide the designer with a false sense of comfort. Today's project teams must recapture the wisdom of including sufficient margin to ensure certainty of outcome, not only for cost but also long term performance.

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