Advancements in Gaskets for HF Acid Alkylation

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Abstract

This paper examines gaskets used in HF Alkylation units in the petroleum refining industry, and demonstrates how the ALKY-ONE® gasket resolves the most difficult issues that have historically plagued these units.

Hazardous Nature of Hydrogen Fluoride

Anhydrous Hydrogen Fluoride (AHF) is used as a chemical catalyst in the reaction that combines C3 and C4 olefins and isobutane to produce alkylates, an important component of gasoline. AHF readily reacts with any available moisture to create the corrosive and toxic Hydrofluoric Acid. So hazardous is this material to humans that OSHA lists the Permissible Exposure Limit (PEL) to 3-ppm averaged over an 8-hour shift[1], while the National Institute for Occupational Safety and Health (NIOSH) lists the IDLH (Immediately Dangerous to Life or Health) concentration at 30-ppm[2]. In and of itself, this hazard level arguably makes HF Acid Alkylation Units the single most dangerous sealing application in modern refining.

In view of this hazard, the first requirement of a gasket for HF Units must be the ability to provide a tight, positive seal to prevent the leakage of HF.

Flange Sealing Problems in Hydrofluoric Acid Units

Anhydrous HF Acid is not corrosive to carbon steel. However as mentioned above, it readily reacts with any available moisture to create Hydrofluoric Acid which is extremely corrosive.

Figure 1. Common flange damage due to HF Acid Erosion.

HF Units periodically must be cleaned, serviced and inspected. At such times water or other aqueous solutions may be used for cleaning up the piping or hydrotesting prior to returning the line to service. Any of this moisture that makes it past the inside of a flange

[1] http://www.osha.gov/dts/hib/hib_data/hib19931119.html
[2] U.S. Department of Health and Human Services, NIOSH Pocket Guide to Chemical Hazards, Publication No. 90-117, Cincinnati, Ohio, June 1990.

gasket – and sits trapped between the flange and the gasket – becomes a potential source of corrosion. When the system is charged with AHF these pockets of moisture can quickly become pockets of aggressive HF Acid, resulting in flange pitting and significant corrosion, especially at the flange ID.

As a result of the prevalence of flange corrosion, flange replacement in HF Acid Alky units is common. One of our clients reported that they replace 1/3rd of all flanges opened in plant turnarounds.

The <u>second requirement</u>, then, of gaskets for HF Units is that they seal against intrusion of liquids between the flange faces. They must have sufficient compression and suppleness to conform to existing imperfections in the flange faces while being able to work in an aggressive chemical environment.

Common HF Acid Gasket Products

One would think that given the dangerous states that can develop due to HF leaks and corrosion that the gasket industry would long ago have responded with a sealing element specifically designed and optimized for HF Acid. However, an examination of the various products offered by major gasket manufacturers showed quite the opposite. In most cases the gaskets marketed for HF Acid services were simple extrapolations of existing gasket designs, with the materials of construction selected to withstand the adverse affects of HF acid. In the few cases where more imaginative modifications were offered, the net effect of the changes were found to be less than positive. These products fall basically into two categories:

1. Spiralwound gaskets with inner rings[3].
2. Spiralwound gasket with inner rings used as secondary sealing elements.

Spiralwound Gaskets with Inner Rings

Spiralwound gaskets with rigid inner rings generally fail to fulfill either of the basic requirements for HF gaskets listed above. Much of the reason for their inadequacy rests upon the fact that this is an antiquated technology (introduced in 1912[4]) that has failed to keep pace with the changing expectation of enhanced sealability.

The requirements for manufacturing spiralwound gaskets for standard flanges are stated in ASME B16.20. While this document gives standard physical dimensions that must be maintained, the only functional requirement is that the gasket compress a certain amount under specified loads. There is no sealability standard. There is no control on the number of metal wraps per inch or the density of the

[3] Spiralwound gaskets without inner rings are not acceptable in critical services because of their susceptibility to inward buckling as demonstrated in the 1996 Exxon study. See Inward Buckling of Flexible Graphite Filled Spiral Wound Gaskets for Piping Flanges, 1996, Rod Mueller, Exxon Research and Engineering. Presented at the 6th Annual Technical Symposium of the Fluid Sealing Association.

[4] http://www.flexitallic.com/company/our-history

final winding. And while the current standard does state that the filler material should not be less wide than the metal winding, there is no reference to the fact that sealability is enhanced when the filler is wider than the metal winding, nor is there a specific standard to accomplish this. A recently released study by Chevron and Teadit[5] has shown that control of these parameters is essential in achieving the kind of "parts-per-million" sealability that is needed in HF Units. When researching and testing spiralwound gaskets produced to the ASME B16.20 standard, the principal researcher in this study, Jose Veiga, determined following facts:

1. These gaskets tend to compress too much, so that the outer edge of the raised flange face rests against the outer centering ring of the spiralwound.
2. Prior to the flanges contacting the outer ring, leakage was measured at or above 65-ppm.
3. The gaskets only seal to "near-zero" leakage levels as the flange faces bite into the outer centering ring. (This metal-to-metal seal is considered inadequate as it is subject to failure due to thermal effects.)

The thought that spiralwound gaskets are actually sealing on the outer guide ring comes as a surprise to many of us in the gasket industry, even though the imprint of the flange is easily seen on a large majority of used spiralwound gaskets. (See Figure 2) To confirm his findings, Mr. Veiga repeated the test with a gasket with a deep radial score, and was unable to achieve a seal.

Figure 2. Flange Imprint on Used Gasket

This joint Chevron/Teadit study demonstrated that by controlling the thickness of the graphite filler material so that it extended a few thousandth of an inch beyond the metal winding, and by winding the sealing element much tighter (so that there are more metal wraps per inch), the sealing response of the gasket could be greatly improved. Such gaskets did not allow the flanges to contact the metal outer ring of the gasket, and were able to achieve "parts-per-million" leakage control on par with the best "cam-profile" designs.

The currently available AMSE B16.20 spiralwound gaskets – tied to the historic manufacturing methods – cannot achieve these results. In fact, gaskets made to Mr. Veiga's recommendations could not receive the ASME B16.20 imprint, as they are not in conformance with the current standard.

Chevron has long been disenchanted with the performance of spiralwound gaskets manufactured to the ASME B16.20 standard. David Reeves (Chevron's global technology expert on sealing issues) notes that while manufacturers recommend a minimum seating load of 12,500-psi[6], that many of the spiralwound

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[5] The Influence of Winding Density in the Sealing Behavior of Spiral Wound Gaskets, Veiga, Cipolatti, Kavanagh, and Reeves. Presented as PVP2011-57556 at the 2011 Pressure Vessel and Piping Conference.

[6] ASME lists the "Y" value (the Minimum Design Seating Stress) of spiralwound gaskets as 10,000-psi. This is the stress needed to achieve an initial seal against gasses at very low pressure. This value is seen as inadequate for reliable field services.

gaskets in the 150# series cannot be loaded to that level (or just barely exceed that level) due to limitations on the amount of bolt stress available[7]. (See Figure 3.)

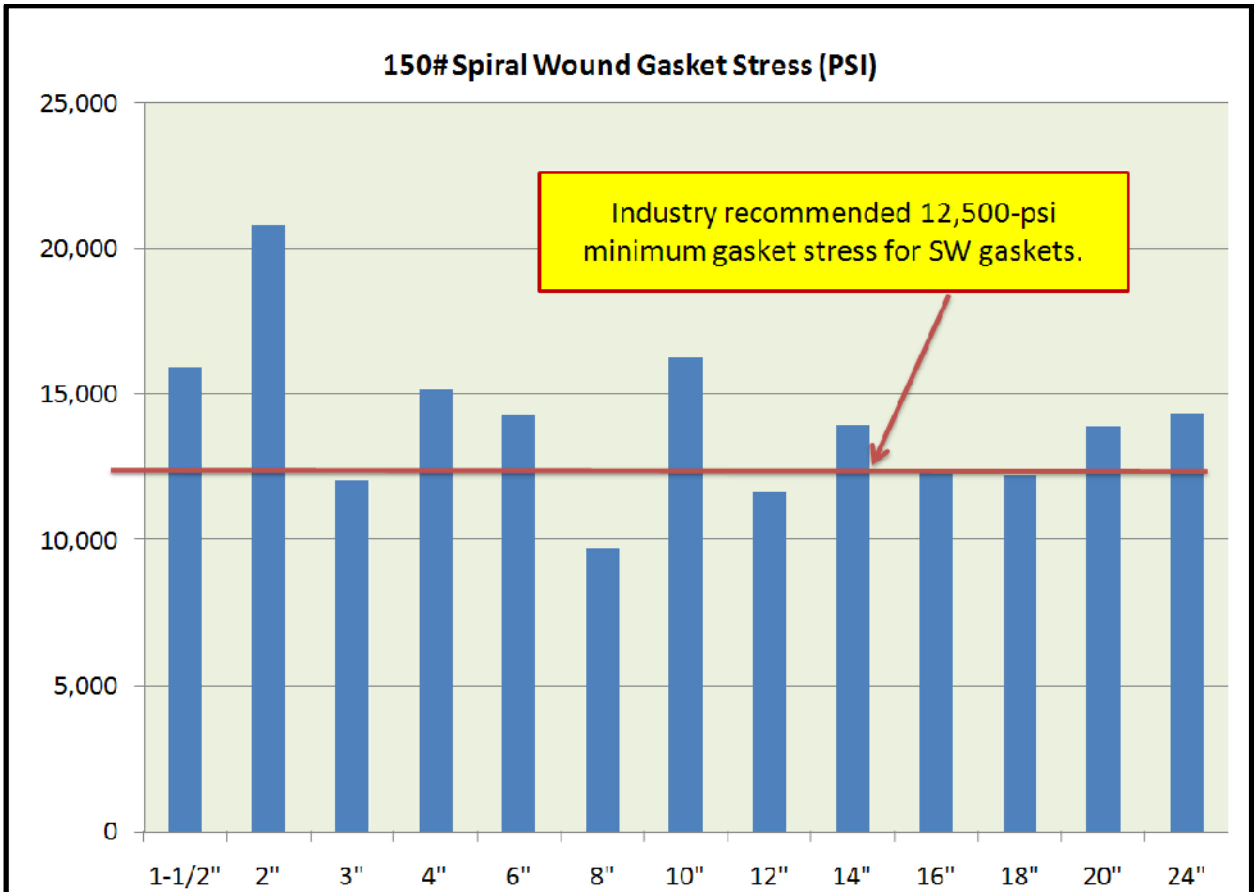

Figure 3. Spiral Wound Gasket Stress at Chevron-Recommended Bolt-up Torques.

This insufficient gasket seating stress is not just troubling because of the difficulties of getting the gasket tight enough to achieve an adequate initial seal, but also because of what it means to the ability of the gasket to remain sealed for the long term. All gasketed joints relax over time. They are also subject to thermal events that create temporary fluctuations (both up and down) in applied stud loads. When any gasket that has been marginally loaded at the onset undergoes extended relaxation – and then experiences thermal fluctuations that result in additional lowering of the available seating stress – that gasket is at risk of leakage. The longer it remains in service, the greater its risk of leakage.

The chart in Figure 3 actually overstates the load on the spiral windings by assuming that all of the bolt load is distributed to the winding. The Teadit/Chevron study cited earlier shows that not to be the case. B16.20 requires the winding to crush down to 0.130" at a stud stress of only 30,000-psi – at which point the flange faces contact the outer compression limiting ring of the gaskets, preventing further loading of the winding. The chart in Figure 4 shows the gasket seating stress at 30,000-psi stud stress for the

[7] Calculated seating stress values are based on full-width averages – and are based on the recommended torque values for Chevron field work at MAWP.

same 150# gaskets shown in Figure 3. The effect of this compression limitation is such that almost all gaskets 4" and larger in the 150#, 300# and 600# classes – made to the B16.20 standard – would fail to meet minimum seating stress requirements at their rated maximum allowable working pressure.

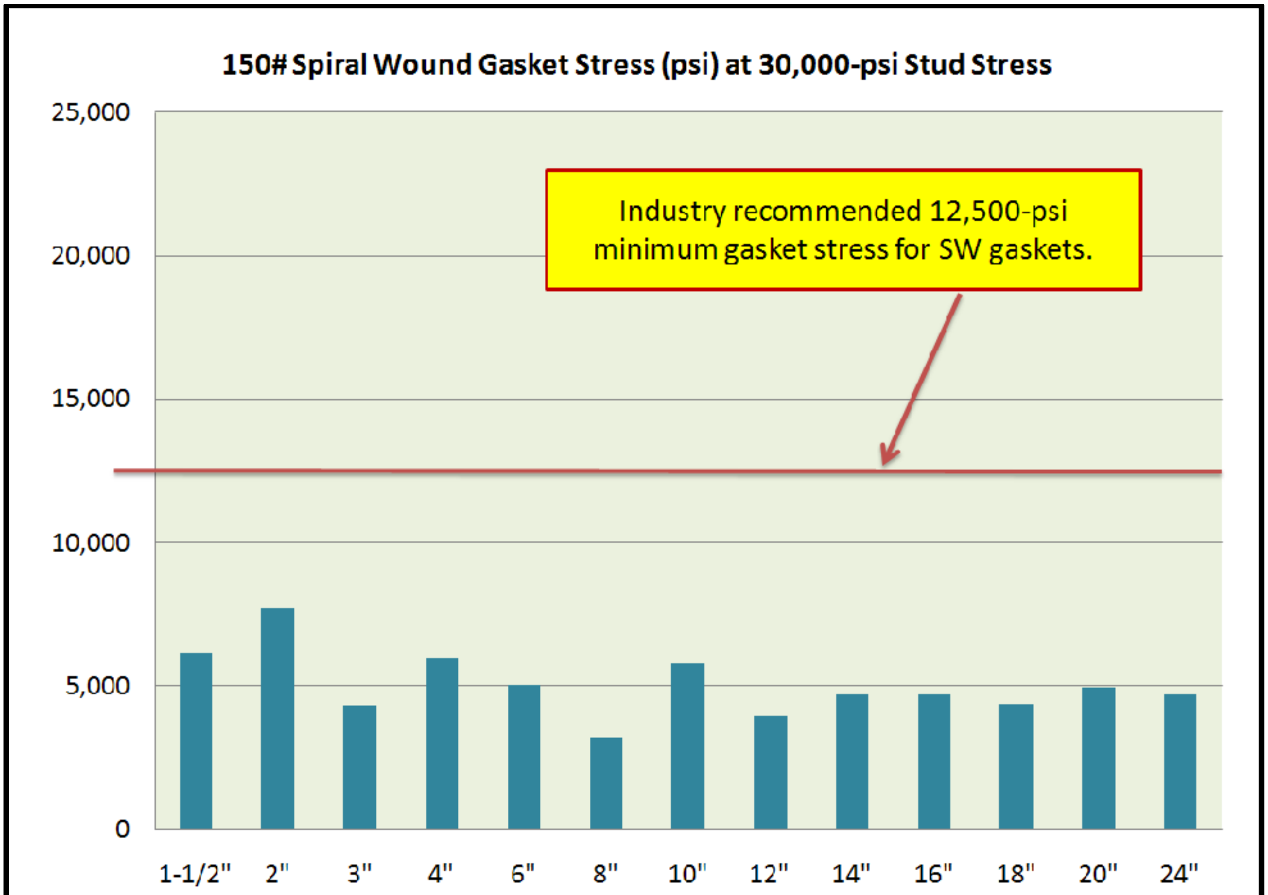

Figure 4. Spiral Wound Gasket Stress at 30,000-psi stud stress.

As stated earlier, the first essential characteristic of gaskets for HF acid is the ability to provide a positive, permanent, leak-free seal to prevent the release of HF acid to the atmosphere. However, as shown above, spiralwound gaskets are manufactured under a standard that actually prevents the winding from developing the high levels of seating stress needed to ensure leak-free performance. This lack of gasket seating stress not only impacts the ability of spiralwound gaskets to seal upon initial installation and start up, but makes it unlikely that the gasket will remain leak-free in the face of relaxation and other thermal effects. As a result, they leak.

As to the second essential characteristic – protecting the flange against acid intrusion – spiralwound gaskets that utilize rigid 1/8" thick inner rings have an inherent weakness. Figure 5 shows the way a spiralwound gasket registers on a standard raised-face flange.

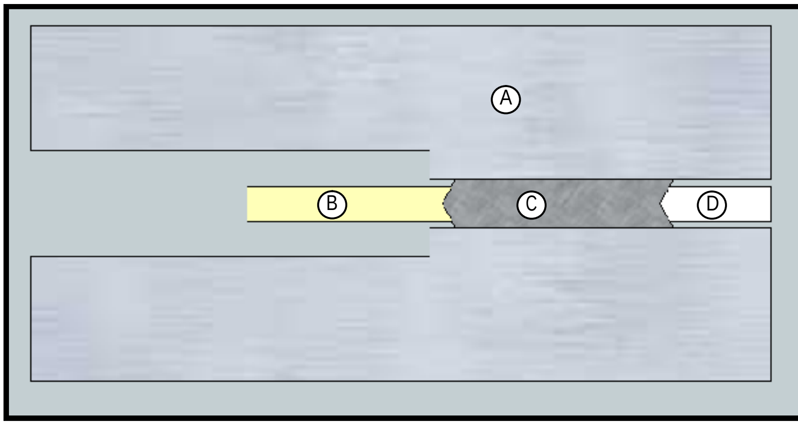

Figure 5.

A – Raised Face Flanges

B – Outer Ring

C – Spiral Wound Sealing Element

D – Inner Ring

The inner ring of a standard spiralwound gasket is the same thickness (1/8") as the outer ring. The outer ring is intended both to center the gaskets in the bolt circle and to provide a compression limiting stop to the flanges, while the inner ring protects against inward buckling of the winding and serves as a gap-filler on the ID of the flanges.

As the winding is compressed under stud load, the space between the flanges and the inner ring narrows until the winding is pressed down to the same thickness as the inner and outer rings. But since it requires a significant percentage of the stud load just to compress the winding to this point, it is clear that only a small percentage of the stud load is available to compress the inner ring – and without significant loading it is impossible to deform the inner ring to the degree needed to provide positive sealing on the inner ring. Furthermore – as the Chevron/Teadit study shows – as additional bolt load continues to be applied the flanges tend to rotate, pressing the outer edge of the raised faces into the outer ring, which actually unloads the compressive forces on the inner ring.

The upshot of this dynamic is that while a solid inner ring in a spiralwound gasket may in fact be able to significantly fill the gap on the inside of the flange so as to reduce turbulence at that point, it cannot be relied upon as a primary seal to prevent intrusion of fluid onto the flange faces. Spiralwound gaskets with solid inner rings will not be able to fulfill the second primary objective for HF gaskets.

<u>Spiralwound Gaskets with Inner Rings Used as Secondary Sealing Elements</u>

To address these concerns, some manufacturers have introduced spiralwound gaskets with soft facing materials on the inner rings. This move essentially turns the inner ring into a secondary sealing element, so that one gasket (the faced inner ring) sits inside another (the spiral winding). The benefits they hope to achieve are:

1. By adding soft graphite or PTFE facings to the inner ring they increase the amount of deformation possible at the inside of the flange, creating a better – more positive – seal to prevent acid intrusion between the flange faces.

2. The added thickness of material means that the flanges will contact these soft surfaces at an earlier point in the compression of the spiral winding, meaning that additional bolt load will be available to deform and compress these soft surfaces.

One manufacturer simply adds soft faces to the standard 1/8" inner ring, while another (as shown in Figure 6) takes the additional step of machining serrations on the inner ring prior to adding the facing material. Either way, the purpose is to turn the inner ring into an effective gasket.

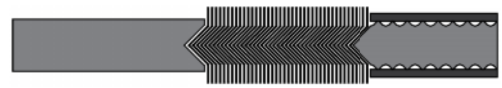

Figure 6.
Inner ring serrated and faced w/PTFE

It is possible that this design innovation improves the gasket performance in terms of limiting acid intrusion between the flange faces, and may therefore help reduce the incidence of flange corrosion and subsequent flange replacement. However there is an inherent trade-off in this design that negatively impacts the overall sealability of the gasket. The unintended side effects of this modification are:

1. As the added facing materials are compressed they become more and more dense, requiring increasing amounts of stud load to further compress. The load required to compress the inner ring is redirected from the task of compressing the spiral winding.
2. The added thickness of the facing materials limits the amount of compression that the spiral winding can undergo. It compresses less because the flange is essentially held open by the added material.
3. The overall gasket seating stress is diluted by requiring the studs to compress a greater area of gasket material. The net result is to reduce the average full-width gasket stress.

High gasket seating stresses are essential for long term sealability because they compensate for losses due to stud and gasket relaxation. But this design increases the area of gasket material that has to be compressed, thus lowering the average gasket seating stress. Given the fact that many sizes of spiral wound flange gaskets are only marginally loaded under the best of circumstances, this broadening of the seating area with its resulting drop of gasket stress is definitely a move in the wrong direction.

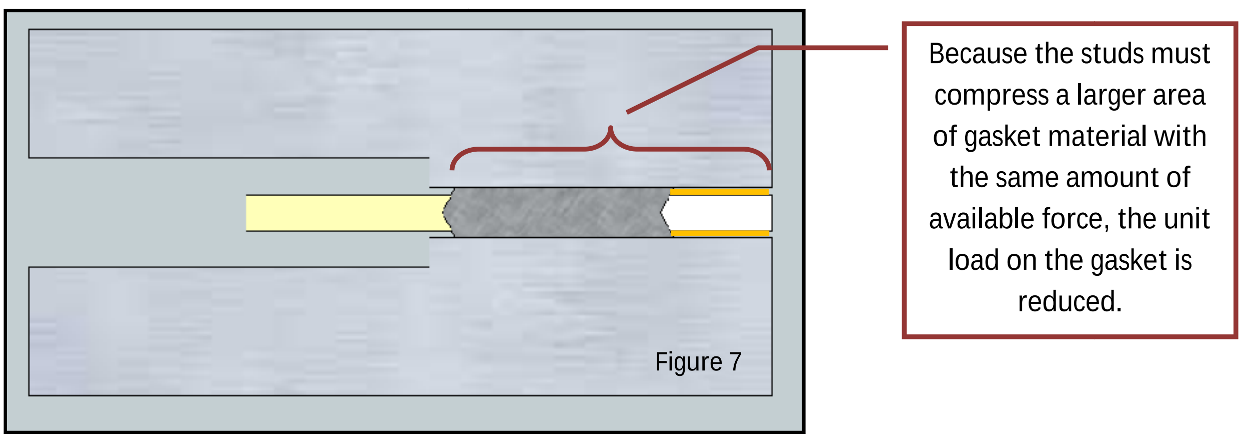

Figure 7

Figure 8 shows the impact this design change makes on the full-width gasket seating stress for the 150# series. The blue series is the same data as shown in Figure 4. The maroon series is the average full-width gasket seating stress that results when the stud load is asked to squeeze both the winding and the inner ring.

It's bad enough that on average the seating stress drops over 37% (from 14,050-psi to 8,825-psi). It's even more alarming that in every case the resulting gasket load is lower than the industry recommended minimum value for spiralwound gaskets!

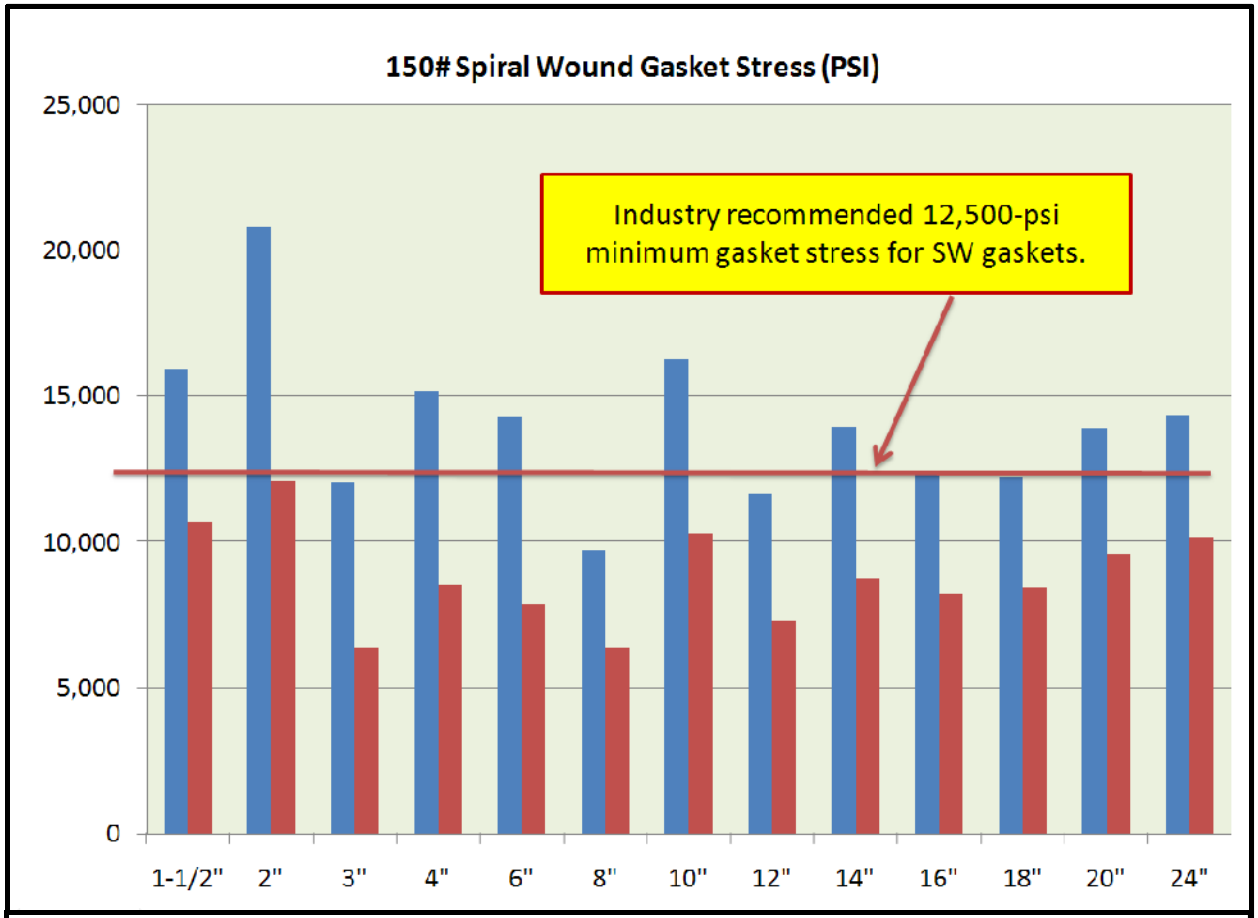

Figure 8. Spiral Wound Gasket Stress at Chevron-Recommended Bolt-up Torques.

Idealized Criteria

In our work with Chevron to conceptualize an "ideal" HF acid gasket, we developed the following list of desirable design criteria.

1. Achieve a high seating load on the primary seal to prevent leakage – both short term and long term. (Based on the first imperative.)
2. Eliminate chemical intrusion between the flanges, thus reducing flange corrosion and replacement. (Based on the second imperative.)

3. Utilize the gasket style known to have the lowest fugitive emission leakage.
4. Incorporate the highest grade materials.
5. Seal against the best part of the flange face.
6. Utilize acid-revealing paint to ensure worker safety.
7. Create a fire-safe seal.

Since successful sealing of HF Acid requires both external sealing (point #1 above) and internal sealing (point #2 above) are required, it was clear to us from the outset that the gasket would need two seals. The primary seal would need to be designed in a manner that satisfied the primary function of HF gaskets – that of providing uncompromising sealing for the long haul – and the secondary seal would need to perform the secondary function – that of preventing flange damage due to acid intrusion. To correct the design weaknesses of existing products, the secondary seal must satisfy its function without negatively impacting the function of the primary seal.

The ALKY-ONE® Gasket

The ALKY-ONE® gasket by Advanced Sealing was specifically designed to meet the demands of HF Acid units in petroleum refining. It is the only gasket of its kind, custom-designed to provide the safest, most reliable seal for HF Acid.

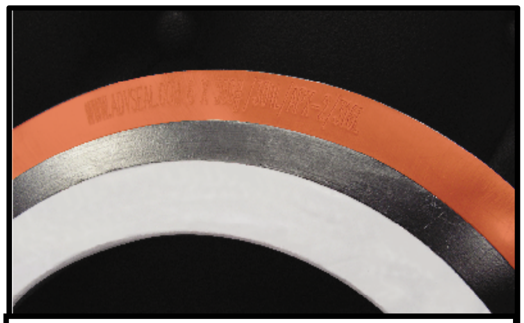

Figure 9. ALKY-ONE® Photograph

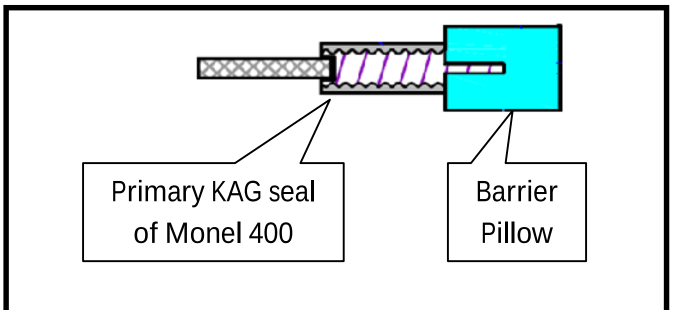

Figure 10. ALKY-ONE® Cross-Section

ALKY-ONE® Design

Primary Seal – KAG The decision to use a "cam-profile" style of gasket for the primary seal was driven by a number of factors.

First, Chevron has had a great deal of positive experience with this style of gasket. One of the material designations on Chevron's gasket specification is "KAG" – a cam-profile gasket made to very exacting specifications. The KAG gasket has a 1/8" thick metal core that is serrated with 0.012" to 0.016" deep grooves on a 0.040" pitch. It is overlaid with 0.020" thick facings of APX2 flexible graphite. KAG gaskets are used in heat exchangers worldwide, and a KAG sealing element is used to eliminate the spiral winding in Chevron's "CPFG" style of flange gasket. When properly installed and loaded, the KAG style of gasket provides a positive seal that is able to withstand years of thermal effects without degradation.

Second, the KAG style gasket had already been submitted to Yarmouth Research Laboratory for emission testing, where it had generated the lowest emission results in the lab's history – an average of 1-ppm over five thermal cycles.

Third, the KAG gasket does not fall under ASME B16.20 standards, so its dimensions can be modified and adapted to meet the specific requirements of an application. This allowed the sealing element to be designed to generate seating loads far higher than what are generated in most spiralwounds. This freedom of design also permitted the outer diameter of the KAG sealing element to be sized to take advantage of the best part of the raised faces – the area that typically lies just beyond the outside of the windings in a spiralwound gasket.

Fourth, the Minimum Design Seating Stress (or "Y" Value) of the KAG gasket is half that of spiralwounds. So not only will it achieve an initial seal with less stud load, but the margin of safety between the initial seating stress and the final generated seating stress is more than 2-1/2 times higher than seen in a spiralwound. (See Figure 11.) It is this "extra" stress in the gasket above the amount needed to achieve a minimum seal that is available to keep the gasket tight against pressure fluctuations and relaxation.

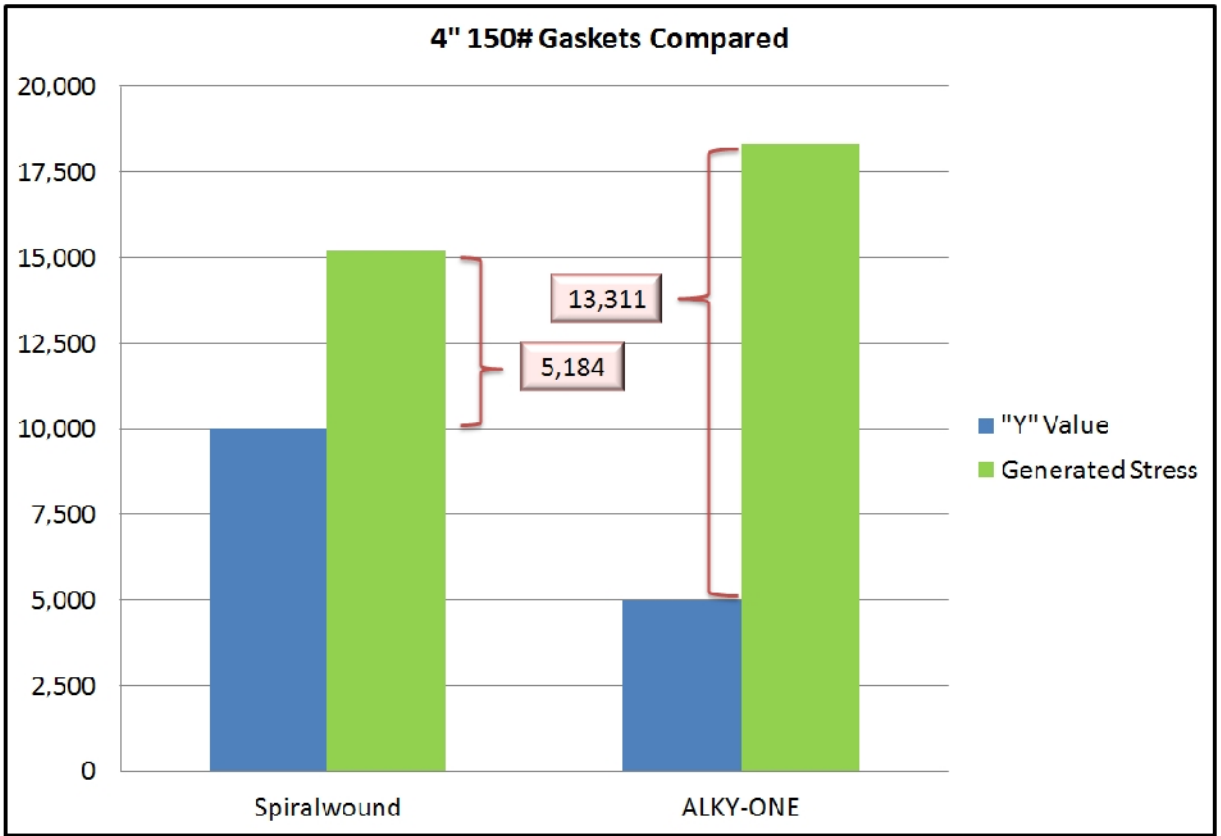

Figure 11. Generated Seating Stress Compared to "Y" Value

Secondary Seal – E-PTFE (Barrier Pillow) The natural choice for the secondary seal – used to prevent acids from reaching the flange faces – is expanded polytetrafluoroethylene (or E-PTFE). Best known by its DuPont trade name Teflon®, this material is virtually inert to a wide range of chemicals. The expanded form of this material is soft and supple, and easily conforms to metal flange faces. From the point of first flange contact until the ALKY-ONE® gasket is fully compressed, the ¼" thick barrier pillow undergoes 0.110" compression – much more than is seen on other styles of alkylation gaskets. This high amount of deformation – combined with the suppleness of the material – allows excellent conformation to the flange faces.

This barrier pillow is joined to the primary seal by use of an attachment ring that is machined onto the KAG element. The overlapping fit provides a secure, permanent joining without the use of adhesives.

The soft, compressible nature of E-PTFE also enhances the performance of the primary KAG seal. Since the force to compress the barrier pillow comes from the same studs that compress the KAG seal, any load required by the pillow takes away from the amount of stud stress available to compress the primary seal. Stress/Compression tests performed on the Flange Assembly Demonstration Unit (discussed below) show that the barrier pillow takes only a small fraction of the bolt load, ensuring that the KAG seal develops the stress needed to do its job.

Fire Safety Testing

Yarmouth Research Laboratory was commissioned to determine if the ALKY-ONE® is a fire-safe gasket. The test was performed on a 6" 300# gasket using the API 6FB test protocol. In this test a flange pressurized to 550-psi is held at 1200°F for 15 minutes. The flange is then cooled, depressurized and repressurized. To be considered fire safe, the leakage at the flange after repressurization can be no more than 25.6 ml/min. The ALKY-ONE® gasket passed the test with a leak rate of 0 ml/min. (Results available on request.)

The ease with which the ALKY-ONE® passed this fiery ordeal was not unanticipated, as both the Monel 400 base metal and the APX2 flexible graphite are fire-safe materials. Furthermore, the design of the KAG seal element produces a much higher clamping load than normal gaskets – providing reserve stress to help it resist any thermally induced relaxation at the joint.

Of course fire-safety isn't just about bragging rights. In an HF Alkylation Unit a fire would be a huge threat to human safety – especially if the gaskets failed in a manner that released HF Acid to the atmosphere. Fire fighting is hazardous enough under the best of conditions, but the addition of HF Acid could create a nightmare scenario.

Since the E-PTFE barrier pillow of the ALKY-ONE® gasket will not stand up to the heat of a fire – a problem common to all PTFE-based gaskets – the gaskets would need to be replaced as a part of a planned maintenance turnaround to restore the unit's integrity following a fire. However because the gasket is fire-safe – because the primary seal does not leak – gasket replacement can be done under controlled conditions after process lines have been cleaned up and depressurized. Cleaning up process lines is a lot harder if all the gaskets are leaking!

Comparative Test Result to Brand X

Since the spiralwound gasket with the serrated and faced inner ring (shown in Figure 6) is aggressively marketed to the Alkylation industry, Chevron conducted a head-to-head comparison of that gasket with the ALKY-ONE® gasket. This was done through the use of a FADU (Flange Assembly Demonstration Unit[8]) test fixture. This equipment measures gasket compression as a function of stud stress in real-time.

The stress/compression data from both gaskets is shown below in Figure 12.

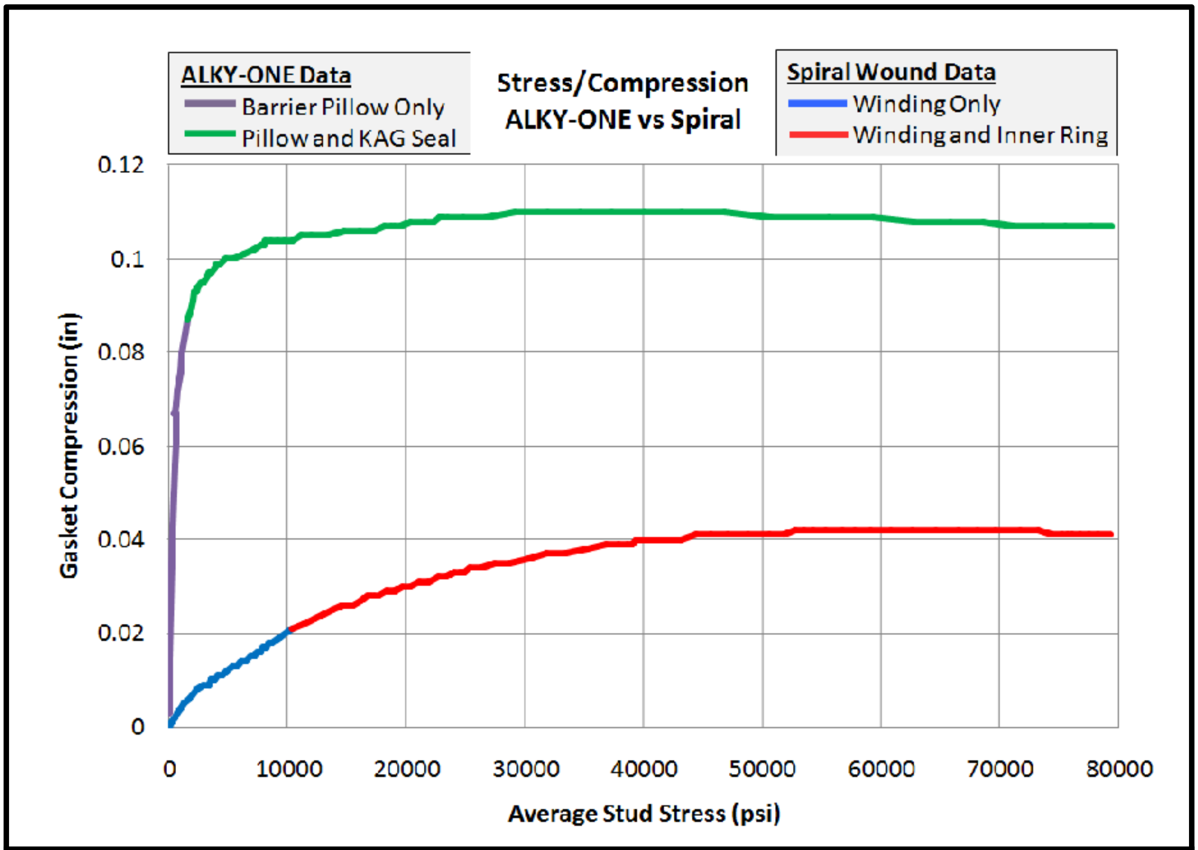

Figure 12. FADU Test Results

This side-by-side display allows an easy comparison of key attributes of these gaskets. In particular note:

[8] Designed and manufactured by John Jenco. See http://www.jjenco.com/fadu.html

1. The total amount of compression that the gaskets undergo is dramatically different. The spiralwound sees a total of 0.042" compression, while the ALKY-ONE® gasket sees about 0.110" – over 2-1/2 times as much!
2. The amount of compression on the inner seal – the component that prevents HF acid from reaching the sealing surfaces – is even more dramatic. The inner portion of the spiralwound only compresses in the upper part of the curve – the portion in red. That compression is about 0.022". On the ALKY-ONE® gasket the inner pillow is being compressed throughout the entire tightening operation, or about 0.110" – 5 times as much! It is this degree of compression that allows the barrier pillow to conform to irregularities in the flange faces, providing a positive inner seal.
3. The amount of force required to compress the inner seal is also dramatically different. The barrier pillow on the ALKY-ONE® gasket compresses quickly with very little stud force, as shown by the quickly ascending purple portion of the curve. This demonstrates that once the flanges contact the KAG seal very little of the stud load is diverted into further compression of the barrier pillow. On the spiralwound the exact force required by the inner seal is hard to separate, because it is only compressed in the top portion of the curve (in red) when both the spiralwound and inner ring are being compressed at the same time. However as the faces of the inner ring are more densely compressed they require an increasing amount of stud load. Since the inner ring becomes the "high point" in the joint preventing the spiral winding from further compression, it is assumed that a large portion of the bolt load is transferred to the inner ring instead of the outer spiralwound winding.
4. The point at which the gaskets reach maximum compression is telling. The ALKY-ONE® gasket reaches this point with only 29,000-psi stud stress. The spiralwound gasket requires almost 53,000-psi stud stress – almost twice as much. The reason for this is simply that the spiralwound gasket with the inner cam-profile seal is spreading the stud load over a much larger gasket area, so it is less efficient in compressing the gasket. With the ALKY-ONE® gasket the reverse is true. Since the area of compression is smaller than even a standard spiralwound gasket, it more efficiently compresses the primary seal. This enables it to quickly consolidate the flexible graphite faces and come to tightness.

What is important to note is that radical differences in the shape of the charted data for these two products is a reflection of the very real physical differences in the products. The quick ascension of the ALKY-ONE® graph line shows the soft, supple barrier pillow. But when the graphite faces of the KAG seal are contacted, the line immediately begins a rapid curve as the faces are quickly consolidated and the gasket begins to build seating stress. The gasket comes to tightness quickly because the size of the KAG seal has been purposely designed to produce this result.

The opposite is true for the spiralwound gasket with the inner seal. The very flat curve shows that it takes a lot of bolt force to compress. The fact that the red portion of the curve takes so long to flatten just shows that the bolt load is gradually being spread out over a larger area.

All of this is readily seen on this FADU comparison.

The FADU test, however, does not show the gasket seating stress that is developed at full torque. Figure 13 compares the generated gasket seating stress for the ALKY-ONE® gasket to the spiralwound gasket with a cam-profile inner rings. The values displayed were calculated at Chevron's recommended bolt torque for the given flange size.

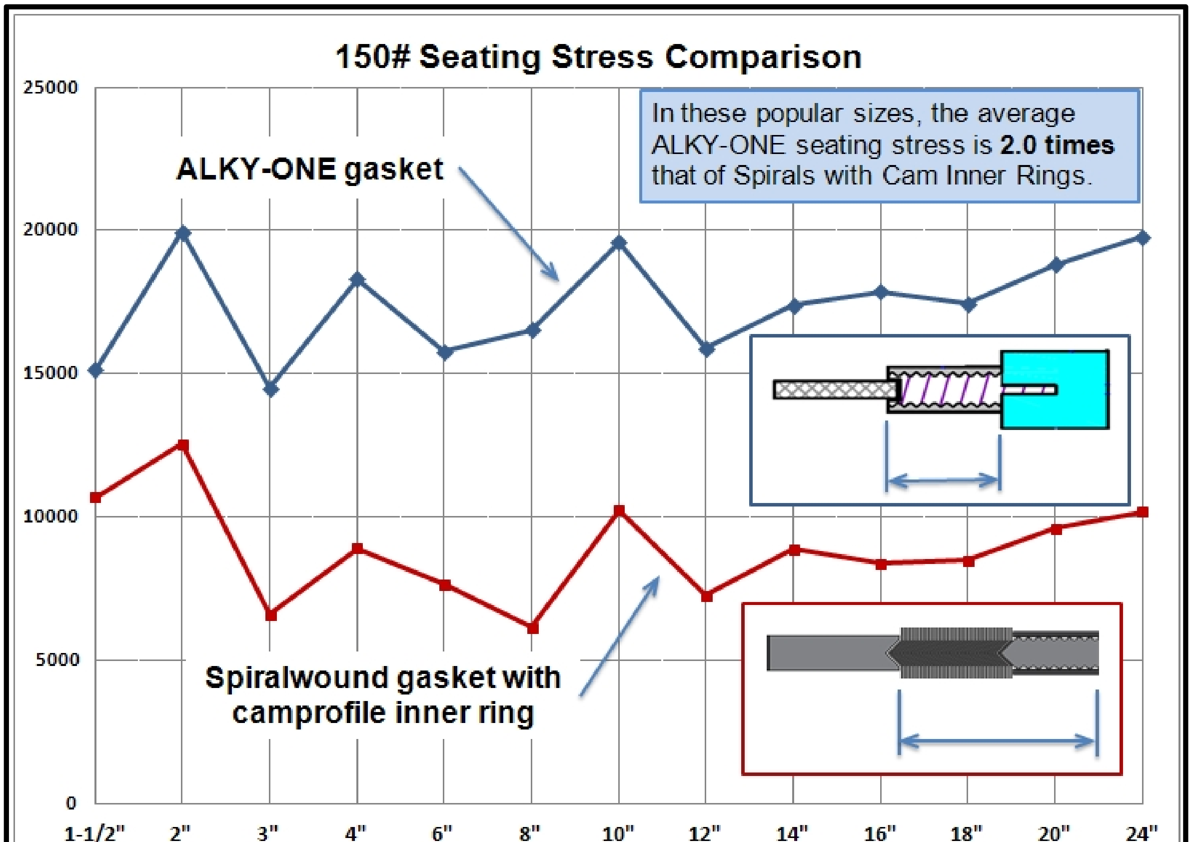

Figure 13. Seating Stresses at Full Torque Compared

Chevron recommends torquing the 5/8" studs on a 4" 150# gasket (the size tested in the FADU test) to 120 ft-lbs. At that level of tightness the primary seal on the ALKY-ONE® gasket experiences about 18,300-psi of seating stress – a level high enough to ensure long-term sealing in spite of relaxation and other thermal effects. By comparison, the spiralwound that has been "enhanced" by the inclusion of an inner cam-profile gasket is attempting to seal a much wider area. As a result, the average full-width gasket seating stress is reduced to only 8,900-psi – which is much less than the recommended minimum load on a spiral sealing element. Furthermore, the gasket lacks reserve stress to keep it tight when it undergoes relaxation.

While gasket stresses will vary significantly for 300# and higher class spiralwound gaskets across the different pipe sizes, the ALKY-ONE® gasket has been engineered to obtain a consistently high gasket stress at the maximum pressure the flanges is rated for when recommended stud stresses are applied.

These stud stresses have been engineered to work effectively with both B7 and B7M studs (which have an 80,000 psi minimum yield strength) in weld neck flanges.

Conclusion

The ALKY-ONE® gasket, designed specifically for HF Alkylation services, addresses and resolves the major sources of sealing difficulty that have plagued that industry. It develops a more-positive seal to prevent leakage of HF Acid, while also providing a more supple, adaptive seal to prevent acid intrusion into the flange interface. Its construction from only premium grade materials ensures resistance to environmental degradation, while its inherent fire-safety provides an extra level of protection against unforeseen incidents.