Specialized High Performance Butterfly Valve Combats Dendrite Formation in Dry Chlorine Service

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1. ABSTRACT

Dry chlorine gas is found within chlorine production, storage, and transfer facilities, as well as downstream processes such as VCM or phosgene production. Moisture contamination in any of these dry chlorine service areas can result in the formation of small, hard crystals which can be referred to as dendrites. Dendrites can form on critical sliding or sealing surfaces of the most commonly used valve trim materials.

Research shows that dendrite formation on critical sealing surfaces, such as the valves seats and packings combined with extremely harsh operating conditions, leads to a significant increase in potential leak paths due to erosion of seals coming into contact with the dendrites. Dendrites can also form on sliding surfaces causing valves to freeze or to become abrasive to the soft seat which can lead to severe seat damage. In fact, any amount of moisture can lead to dendrite formation and rapid corrosion on moving valve parts.

Recent collaboration between manufacturers of valves and end users has led to deeper understanding of the factors that cause valve failure and factors that can increase service life. To combat moisture contamination and provide enhanced performance in harsh operating conditions, material for each component of the valve was examined for dendrite susceptibility and chosen for optimum reliability. The final design reflects the appropriate combination of super alloys and stainless steel to allow for a cost-effective solution to these issues.

This paper will discuss, in detail, the relationship between dendrite formation and valve life, previous high performance butterfly valve shortcomings, improvements to the design, and best practices for specifying features that will lower total life cycle costs in these critical applications.
2. OVERVIEW

Dry Chlorine can be defined as having less than 150 PPM water containment. Dry chlorine gas is found within chlorine production, storage, and transfer facilities, as well as downstream processes such as VCM or phosgene production. Moisture contamination in any of these dry chlorine service areas can result in the formation of small, hard crystals, or dendrites. With even a small amount of moisture contamination, dendrites can form on critical sliding or sealing surfaces.

This crystal formation (most problematic on critical sealing surfaces, such as the valves seats and packings combined with extremely harsh operating conditions) is likely to lead to a significant increase in potential leak paths. This is due to erosion of seals coming into contact with the dendrites.

Dendrites can also form on sliding surfaces which can cause valves to freeze or to become abrasive to the soft seat which can lead to severe seat damage. Any amount of water, or water vapor, can lead to dendrite formation and rapid corrosion on moving valve parts.

Understanding the factors that cause valve failure and factors that can increase service life led to improved technologies for the standard high performance butterfly valve used in dry chlorine service. To combat moisture contamination and provide enhanced performance in harsh operating conditions, material for each component of the valve was examined for dendrite susceptibility and chosen for optimum reliability. The final design reflects the appropriate combination of super alloys and stainless steel to allow for a cost-effective solution to these issues.
## 2.1. BASICS OF DRY CHLORINE

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorine</td>
<td>Cl₂ (Dichlorine)</td>
</tr>
<tr>
<td>Molecular weight</td>
<td>70.9</td>
</tr>
<tr>
<td>Boiling temperature</td>
<td>-34°C (~-29°F)</td>
</tr>
<tr>
<td>Detectable by smell</td>
<td>3 PPM</td>
</tr>
<tr>
<td>Coughing and vomiting</td>
<td>30 PPM</td>
</tr>
<tr>
<td>Lung damage</td>
<td>60 PPM</td>
</tr>
<tr>
<td>Fatal after a few breaths</td>
<td>1,000 PPM</td>
</tr>
<tr>
<td>Expansion ration</td>
<td>~460 (Liquid to Gas)</td>
</tr>
</tbody>
</table>
3. CUSTOMER REQUIREMENTS FOR A HIGH PERFORMANCE BUTTERFLY VALVE

Moisture contamination of dry chlorine gas in any dry chlorine service area can result in the formation dendrites. As stated previously, dendrites can form on critical sliding or sealing surfaces of the most commonly used valve trim materials.

Research indicates that it is important to understand key valve life issues that end users reportedly experience as associated with dry chlorine service. Understanding the factors that cause valve failure can lead to an increase in service life.

End users identified that real world applications were seldom ideal and that money could potentially be saved by providing a valve that would tolerate less than ideal conditions. A new design would need to address proper materials, cleaning, packaging, external seals that can limit emissions, double packing, and monitoring port.

By working through the critical pain points, it was learned that the dendrites were forming on the surface of Monel® discs, causing damage to the soft seats. When these crystals form on frictional surfaces, they cause binding and seizing of mating parts. An example is a simple component like the disc spacers that keep the disc centered. The shaft is turning inside the bearings and packing. Any crystal formation will quickly deteriorate these critical components. When these crystals form on hard surfaces that mate with soft seals, they erode the seals (similar to sandpaper). This is what occurs when crystals form on the disc sealing surface.

Additionally, while Monel® performs well in dry chlorine service, any amount of moisture can lead to rapid corrosion on the moving parts. For these two reasons, engineers determined that Hastelloy®C is the preferred disc and stem material (see Valve Materials Selection Guide on the following page).

For the valve body, CF8M stainless steel was selected as the new standard. All other valve components (pin, gland, bolts, etc.) were reviewed individually to determine the exact material requirements.

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Using Hastelloy® for key parts means the valve will tolerate moisture infiltration. Using stainless for the body meant that the exterior system would stay cleaner and it would provide visual confidence that the system is intact.

### Table 4-8. Valve Material Selection Guide

<table>
<thead>
<tr>
<th>Product Forms</th>
<th>Parts</th>
<th>Classes I &amp; IV</th>
<th>Classes II &amp; V</th>
<th>Classes III &amp; VI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Body, Bonnet &amp; Cover Bolting</td>
<td>Bolts &amp; Stud Bolts</td>
<td>ASTM A193 Grade B7</td>
<td>ASTM A320 Grade L7 (Charpy test at -150°F/-101°C) [See Notes 13 and 14]</td>
<td>ASTM A320 Grade L7 (Charpy test at -150°F/-101°C)</td>
</tr>
<tr>
<td></td>
<td>Nuts</td>
<td>ASTM A194 Grade 2H heavy hex nuts</td>
<td>ASTM A194 Grade 4 heavy hex nuts (Charpy test at -150°F/-101°C) [See Note 13]</td>
<td>ASTM A194 Grade 4 heavy hex nuts (Charpy test at -150°F/-101°C) [See Note 13]</td>
</tr>
<tr>
<td>Other Metal Parts</td>
<td>Stems (Shafts)</td>
<td>Hastelloy C22 (UNS N06022), C-276 (UNS N10276) Monel 500 (UNS N05500) Monel 400, R405 (UNS N04400 &amp; N04405) [See Note 6]</td>
<td>Hastelloy C22 (UNS N06022), C-276 (UNS N10276) Monel 500 (UNS N05500) Monel 400, R405 (UNS N04400 &amp; N04405) [See Note 6]</td>
<td>Hastelloy C22 (UNS N06022), C-276 (UNS N10276) Monel 500 (UNS N05500) Monel 400, R405 (UNS N04400 &amp; N04405) [See Note 6]</td>
</tr>
<tr>
<td>[See Note 3]</td>
<td>Balls, Tapered Plugs, &amp; Discs</td>
<td>Monel 400 (UNS N04400) [See Note 2]</td>
<td>Monel 400 (UNS N04400) [See Note 2]</td>
<td>Monel 400 (UNS N04400) [See Note 2]</td>
</tr>
<tr>
<td>[See Note 3]</td>
<td>Seats &amp; Discs, Wedge Facings</td>
<td>[See Notes 4 &amp; 5]</td>
<td>[See Notes 4 &amp; 5]</td>
<td>[See Notes 4 &amp; 5]</td>
</tr>
<tr>
<td>Non-Metallic Parts</td>
<td>Other Parts</td>
<td>[See Note 5]</td>
<td>[See Note 5]</td>
<td>[See Note 5]</td>
</tr>
<tr>
<td></td>
<td>Seats, Sleeves &amp; Seals</td>
<td>Fluoropolymer Resin</td>
<td>Fluoropolymer Resin</td>
<td>Fluoropolymer Resin</td>
</tr>
<tr>
<td></td>
<td>Packing</td>
<td>Flexible graphite Fluoropolymer resin or asbestos [See Note 10]</td>
<td>Flexible graphite Fluoropolymer resin or asbestos [See Note 10]</td>
<td>Flexible graphite Fluoropolymer resin or asbestos [See Note 10]</td>
</tr>
<tr>
<td></td>
<td>Bonnet/Bonnet Gasket</td>
<td>Flexible graphite Fluoropolymer resin or asbestos [See Notes 7, 9, 10]</td>
<td>Flexible graphite Fluoropolymer resin or asbestos [See Notes 7, 9, 10]</td>
<td>Flexible graphite Fluoropolymer resin or asbestos [See Notes 7, 9, 10]</td>
</tr>
</tbody>
</table>

The Chlorine Institute, Pamphlet 6, Piping Systems for Dry Chlorine
4. TECHNICAL DESIGN REALIZATION AND IMPLEMENTATION

The Chlorine Institute recommends the use of WCB bodies and Monel® internals for dry chlorine service. For wet chlorine, Hastelloy®C internals must be used. This is per The Chlorine Institute, Inc. Pamphlet 6 on Piping Systems for Dry Chlorine.

Research indicates that even in dry chlorine service, systems are prone to moisture contamination during installation or whenever connections are made. This contamination reacts with the chlorine and forms hard, microscopic metallic chloride crystals on metal surfaces. This even occurs on Monel® surfaces which are considered acceptable with perfectly dry chlorine.

To combat the corrosion, the use of Hastelloy®C is the better option for dynamic surfaces between metal and soft parts. It is a more costly, very hard material that also increases machining costs, but it is critical to long life and total life-cycle costs.

WCB valve bodies are typically recommended for use with dry chlorine since stainless steel is subject to chloride stress cracking. Pamphlet 6 (section 2.3) recognizes the usefulness of 300 Series stainless steel for its low temperature suitability, but also cautions about the potential for failure due to chloride-stress corrosion-cracking in the presence of moisture, particularly at ambient or elevated temperatures. CF8M bodies, on high performance butterfly valves, have proven to offer great tolerance of corrosive environments while being robust enough to resist the failures associated with stress-cracking.

Live-loaded, double-packing with monitoring ports include Inconel® spring (Belleville) washers. The packing gland is made from Hastelloy®C to prevent the possibility of it freezing in the packing bore which would nullify the live loading. The packing gland is a simple part on the outside of a valve that would seem isolated from possible contamination. Experience indicates, however, that it is exposed to high moisture and even minute traces of chlorine vapor permeating from the system, can cause it to seize. Once this happens, it no longer serves its function of pressurizing the packing, and potential leakage is the result. As such, Alloy 20 bolting should be used for packing gland studs and nuts to minimize corrosion on these stressed parts while avoiding the stress cracking concern if stainless steel was used.

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A lantern ring between the sets of packing allows any leakage from the flow path to accumulate in an area before the second packing set. A small sampling valve can be threaded to a monitoring port channeled to this area so that it can be periodically checked for early signs of weakening. The lantern ring should be made from Hastelloy®C to ensure long term operation.

For seating, the use of Teflon® provides a compliant, inert seal that provides bubble tight shutoff. Use of an axially pliant seat allows the use of reinforced PTFE seats to maximize resistance to abrasion while maintaining the chemical compatibility of Teflon®. An axially pliant seat flexes but is not subject to hoop stretch. Since Teflon® does not have memory, it is important to avoid stretching the material. Chlorine systems often have rust or scale in the system and valve seats must be tolerant. Moleculely enhanced PTFE (TFM) has the disadvantage of performing poorly at low temperatures whereas the R-PTFE ensures the valves perform well during temperature cycling and in cold environments.

Systems often require bidirectional sealing as well as the ability to be used in end-of-line service with pressure contained behind a closed valve regardless of which side piping is removed.

Eliminating all potential leak paths is important to control fugitive emissions. The use of a closed bottom design is a good way to remove any leakage that might occur if the shaft bore protrudes through the bottom of the valve. This is the best design for valves 12” and under. For larger valves, where it is not practical to bore the bottom shaft hole from the top of the valve, a bolted plate with a static PTFE seal is preferred over a threaded plug. A threaded plug has the undesirable tendency to grab a seal and twist it during assembly.
4.1. Cleaning and Packaging

It is also important that the valves meet industry standards for cleaning and packaging. Chlorine can react with oils, grease, paint, rust and moisture to cause fire, corrosion, pressure increase or harmful deposits. Special cleaning and inspection is essential to preparation of a valve that will be used in chlorine service. This involves cleaning all parts before assembly, and again after the valve is assembled and tested. A high standard of cleanliness must be observed by all personnel handling the valves and components.

Deburring is a critical first step to remove edges that might break off and to blend areas that might be difficult or impossible to clean. Isopropyl alcohol works well but clean water can also be effective, especially in an intense spray. Hydrostatic testing can be performed using clean water, but it must be disassembled and cleaned afterward. On valves up to pressure class 150, Nitrogen should be used for testing. A plastic bristle brush is helpful for any necessary scrubbing. Blotting is the preferred method of drying as heated evaporation can leave any dissolved materials behind. Using low pressure nitrogen is also acceptable. This is especially helpful for any holes or crevices.

The cleaning and assembly should be done in a clean room environment. New polyethylene sheeting is a good choice to line work surfaces. All tools need to be cleaned before use and new lint-free gloves need to be worn. Inspection in a dark room under a black light is required to confirm that all contamination has been removed. It is best to avoid the use of any lubricants in the assembly of the valves. It helps to have an air conditioned space to perform the work because even perspiration from assemblers could negate all the work done to clean the valves.

Material handling aids, such as a crane, also need special consideration. Touching a contaminated chain, or crane control, and then touching the valve will necessitate that the entire cleaning procedure be redone. Brass is the preferred material for tagging.

Special packaging is essential to protect the valves and maintain their cleanliness. Valve openings should be closed and ends protected. Any covers should be designed to prevent the possibility of installation without first removing them. Smaller valves can be placed in thick polyethylene bags while larger valves are more appropriately wrapped in shrink wrap. Desiccant packets should be placed around the valve and protected against rupture during shipping. Of course the wrapped, or bagged, valves also need to be boxed with care to
ensure arrival at their destination without damage to the wrapping and the resulting contamination.
5. PRACTICAL RESULTS

Based on this research, a new high performance butterfly valve has been created. This new HPBV for use in dry chlorine service is a break-through product designed to prevent valve damage due to moisture contamination. The reaction of moisture with the chlorine gas can cause the formation of dendrites on the critical sealing surfaces of most commonly used disc and stem materials; this causes the valve to freeze, or to become abrasive to the soft seat which can lead to severe seat damage.

To combat moisture contamination and provide enhanced protection against harsh operating conditions, each component of the valve was examined to determine which were directly affected by dendrites. The disc and shaft materials were upgraded to Hastelloy® to maintain the integrity of the sealing surfaces because Hastelloy® is not susceptible to the formation of dendrites. All other valve components, including the pin, gland, and bolts, were reviewed individually to determine the exact material requirements.

To minimize the potential of fugitive emissions, a double packing is employed and live-loaded to ensure proper compression over time. Finally, a monitoring port is incorporated to detect early signs of failure before any leakage can occur.

5.1. New HPBV for Dry Chlorine Service Component Overview

- Hastelloy® Gland to prevent dendrite formation
- Hastelloy® Lantern Ring to prevent corrosion due to chlorine gas migration
- Hastelloy® Disc and Shaft to prevent dendrite formation on sealing surface (most important location for dendrite formation)
- Alloy 20 Nuts and Bolts to resist external corrosion; Inconel spring washers
- Stainless Steel Bearings with Teflon® liner is a non-moving part and is not at risk for dendrite formation; Teflon® liner rides on Hastelloy® shaft
The distinctive design of this High Performance Butterfly Valve offers the following benefits:

1. Hastelloy® disc and stem provide extended integrity of sealing surfaces
2. Live-loaded, double packing with optional monitoring port to minimize emissions
3. Closed bottom design (up to 12”) decreases potential leak paths for ultimate reliability
4. Each valve component was carefully examined to ensure optimum material selection to make this the top valve option for dry chlorine service.

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6. CONCLUSIONS

High performance butterfly valves perform well in dry chlorine service provided careful consideration is given to materials of construction, features, and valve design. All systems are prone to moisture contamination and the use of Hastelloy®C on critical sealing and sliding surfaces will contribute significantly to lowering overall life cycle system costs. Selection of an emissions limiting packing is important as is the choice of a valve design with a proven long life seat.
REFERENCES

The Chlorine Institute, Inc. Pamphlet 6 – Piping Systems for Dry Chlorine (Edition 15)

Xomox Manufacturing Control Manual – Level III Cleanliness Requirements Chlorine, Food, Std. Oxygen, and Vacuum Service Valves