Chemical Injection Technologies
Technical Bulletin

Titanium Fasteners Used in SUPERIOR™ Gas Chlorinators

There has been some debate in recent years regarding the use of Titanium in the manufacture of gas chlorination equipment. Claims run the gamut from the absolutely ridiculous assertions that "dry" chlorine gas will cause Titanium to explode at ambient operating temperatures, to the idea that the Chlorine Institute has disapproved certain brands of products because they use Titanium. Neither of those claims is true.

How Did These *False Claims* Get Started?

While it is always hard to pin down the root cause of any rumor, we have a few good theories about how they began. When Chemical Injection Technologies, Inc. began selling the SUPERIOR™ Gas Chlorinator, and offering a lifetime warranty on the Titanium fasteners, other manufacturers did not think this would be a very important selling feature. They were wrong! After a few years in service, the SUPERIOR™ units proved to be far superior in all-around corrosion resistance to chlorine gas. The Titanium fasteners, in particular, were being demanded by customers because the customers had never before experienced such a total lack of corrosion in this type of equipment. Competitors became alarmed when users told them that they wanted SUPERIOR™ because of their own experience or because they had heard so many good things from other operators.

Faced with a demonstrably improved gas chlorinator, certain competitors have set out on a very negative marketing campaign in which they did not rely on their own product's features and reputation, but rather they tried to create doubt in the minds of potential customers about SUPERIOR™. This has been done by relying on half-truths and even some outright falsehoods. Typical statements included implications that C.I.T. does not carry product liability insurance or that our materials of construction are not "approved" by the Chlorine Institute, among others. These things were easy to prove as lies, and often backfired when the customer learned the truth. Searching for some other negative advertising in which they could point to a fact and then create a complete fiction around it, they chose the Titanium materials in our fasteners. They pointed out that The Chlorine Institute does not recommend the use of Titanium in "Piping Systems For Dry Chlorine", in its Pamphlet 6, Edition 13. This is actually the only truthful statement in the whole debate. However, the truth stops there. It has been amplified to include preposterous statements that dry chlorine gas can cause Titanium bolts in SUPERIOR™ Gas Chlorinators to "explode" or spontaneously ignite, despite the fact that there is no Titanium used in the internal gas stream of the equipment, which is the only place that "dry" chlorine gas can be found. We agree that no Titanium should be used in the interior of a gas chlorinator, or in dry chlorine gas piping. Neither of those uses has anything to do with SUPERIOR's application.

The REAL Story About Titanium and Chlorine Gas

There have been no known, documented instances of Titanium "fires" or "explosions" caused by contact with dry chlorine gas, in any gas chlorination installation. No such instances are known by The International Titanium Association, Hazmat, or the major Titanium producers. Titanium <u>does react</u> with *dry* chlorine gas. For that matter, so does fine silver. Dry chlorine (anhydrous) is defined in the above referenced Chlorine Institute pamphlet 6 and in the Chlorine Institute's Chlorine Manual as "chlorine containing no more than 150 ppm water (by weight)". That is 0.015% water (read fifteen *thousandths* of one percent). That is also a condition not found outside of the "chlorine piping" or the internal gas flow of a chlorinator, and often not even then. Even in a serious leaking situation, the amount of moisture in the air combining immediately with the chlorine is far greater by many orders of magnitude. Titanium is impervious to "wet" chlorine gas. The Titanium industry refers to this as "passivation". It is well documented in papers, research, and publications of the National Association of

Corrosion Engineers, Titanium Corporation of America (TIMET), and the International Nickel Co., among others. Titanium has also been widely used in chlor-alkali cells for decades.

But, let's examine the chemistry and physics taking place here. Titanium will burn in *dry* chlorine at very high temperatures when the surface has been scratched or mechanically damaged. No research has yielded any explosive result. Titanium is reactive in *dry* chlorine gas at lower temperatures when continuously scratched or mechanically damaged. In a series of tests conducted by Titanium Metals Corporation and published by the National Association of Corrosion Engineers continuous scratching of the surface of Titanium test samples in dry chlorine gas produced a brown material over the freshly scratched surface. This material was titanium tetrachloride. With bottled commercially available chlorine gas the reaction was not as pronounced as with dried , crude Hooker cell chlorine.

What are the specific reactions taking place? Titanium itself is actually quite a reactive material. In the presence of any Oxygen or oxidizing acid (HCl or HOCl) a tight oxide layer forms on the Titanium (oxides of Titanium). It is this oxide layer that gives Titanium its corrosion resistance. This is very similar to the corrosion resistance of fine silver which is used in the inlet valves of most gas chlorinators, where the silver forms a tight layer of silver chloride when it comes into contact with chlorine. Silver itself is highly reactive with chlorine, but when the silver chloride layer is formed, it creates a barrier to any further reactivity.

In addition to the TIMET research noted above, a series of extensive experiments were done by Chlorinators, Incorporated, between 1987 and 1990. These experiments were designed to test the resistance of a broad spectrum of materials to all forms of chlorine.

The Test Results

A glass chamber with inlet and outlet valves was constructed to allow observation of test materials. Tests were performed using "dry" chlorine gas as well as chlorine gas with small amounts of water in the bottom of the chamber. It should be noted that no attempt was made in these experiments to create a "dry" chlorine gas condition beyond thorough vacuum evacuation of the test chamber and addition of commercially available bottled chlorine gas. Additional tests were performed on those materials which proved to be non-reactive in either dry or "wet" chlorine gas environments. Those additional tests consisted of exposure to a pressurized, flowing stream of dry chlorine gas as well as exposure to pure liquid chlorine introduced into the vacuum regulator of a gas chlorinator. Titanium showed no noticeable effects from exposure to "wet" chlorine gas for over 1000 hours, from the dry chlorine gas in the chamber for over 48 hours, or to liquid chlorine. Titanium showed noticeable etching and pitting in the exposure to the pressurized flowing stream of dry chlorine gas. As a result of these tests Chlorinators, Incorporated, replaced a stainless steel cap screw in their automatic switchover vacuum regulators with Titanium in 1988 due to the vigorous corrosion of the stainless screws. In the ensuing 5 years there was no instance of chlorine attack on any of these Titanium cap screws.

Tests on Monel in the chamber showed no noticeable effect with dry chlorine gas, but it was very vigorously attacked and pitted when exposed to "wet" chlorine gas for 8 hours. This test bore out observations of chlorine attack on Monel fasteners used in vacuum regulator bodies when low levels of chlorine gas "pocketed" between the body halves. If these small leaks were detected quickly, there was little noticeable attack and most bolts exhibited a dull green film which could be wire brushed to removed the oxidant. However, when the leak persisted undetected for extended periods, the reaction severely damaged the Monel bolts beyond the point where they could be reused.

SUPERIOR™ Offers Lifetime Warranty on Titanium Fasteners

When CIT began the design process that resulted in the SUPERIOR™ Gas Chlorinator, we knew of the shortcomings of Monel and determined that we wanted to use a material we knew would stand up to any conceivable operating environment. Since a pressurized dry chlorine gas stream is virtually impossible in the fastener application, to say nothing of a continuous surface scratching, Titanium was chosen. Our confidence level is so high with this material, that we became the first gas chlorinator manufacturer to extend a lifetime warranty to the Titanium bolts. Even though the cost for these bolts is almost three (3) times that of Monel, we want to provide the user with the best possible material.

