

Removing Beerstone: A look at alternative cleaning methods

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A big problem encountered by breweries is removing the scale that forms in aging tanks, serving tanks and kegs. This particular type of scale is known in the industry as beerstone. Beerstone can be incredibly difficult to remove, especially after the buildup becomes visible to the naked eye. Why is beerstone different than other types of inorganic scale? Why is beerstone so difficult to remove? This article will detail the chemical composition of beerstone and give some alternative cleaning methods to remove this tenacious scale. Once free of beerstone, metal surfaces then typically require less aggressive chemicals to keep the problem from reoccurring.

Beerstone is a type of scale known as calcium oxalate (C_2CaO_4) in the brewing industry, calcium oxalate is a precipitate. This precipitate is largely due to a reaction between alkaline cleaners (caustic), hard water minerals (calcium and magnesium) and protein (amino acids). (1,2) To be sure, there are other factors involved as well, but for the purpose of this article, I will focus on traditional cleaning methods which assist in creating a beerstone problem. If left unchecked, beerstone can have disastrous consequences for the beer.

If not completely removed in the cleaning process, beerstone leaves an unsanitary surface that can harbor microorganisms. (2) An unsanitary surface in the aging, serving tank or keg will infect the beer. Minimally, beerstone can cause "off flavors" or shorten the shelf life of beer. In the worst case scenario, undesirable organisms can ruin an entire batch of beer, costing time and money to replace. This situation is best to be avoided, so let's take a look at so-called "normal" cleaning methods used in the brewery that may assist in creating a beerstone buildup.

TRADITIONAL CLEANING METHODS

Caustic based products have traditionally been the standard in most breweries to remove soil. Generally speaking, in CIP (clean in place) applications, the caustic based product is used at a concentration of 2-4% with hot water. The solution is then rinsed and followed with a phosphoric based acid to neutralize the caustic to remove any beerstone or hard water scale left behind by the caustic. In cleaning primary fermentors and uni tanks this approach usually works just fine.

The caustic is subsequently rinsed out and followed with a phosphoric acid rinse. Some brewers also consider the phosphoric acid step as the sanitizing step, as most

organisms cannot withstand the extreme temperature and pH swings involved in the cleaning process. Most brewers, however, use a sanitizing compound (such as iodophor) to ensure that any surviving bacteria, yeast or mold do not create a problem later. Even if a sanitizer is used, however, the surface will still harbor organisms if a beerstone problem exists. (The organisms simply "hide" in the cracks and crevices of the beerstone. When conditions later improve, the organisms then proliferate).

THE PROBLEM WITH BEERSTONE

Beerstone is not a straight inorganic scale like a hard water scale (which tends to be calcium and or magnesium based). Beerstone also contains carbon in the form of protein. Protein acts as the "binder", making the scale tenacious. To remove protein soil, sodium hydroxide (caustic) is typically the chemical of choice. (2) Using a form of hydrolysis known as saponification, the protein soil is hydrolyzed by the caustic to form soap. Once this reaction has taken place, the soil can then be termed, "saponified". In hard water, the calcium and magnesium can attach to these soaps. If the resulting molecule becomes too large to stay in solution, it will deposit on the surface.

Beerstone contains calcium. Calcium, in general, has an extremely limited solubility in hot water. (An example of this phenomenon is hot water pipes that become clogged with precipitated hard water deposits). While calcium is at least slightly soluble in cold water, the hydrated form of calcium oxalate is completely insoluble in both hot and cold water. (3)

Herein lies the problem with removing beerstone. How do we clean the equipment and remove beerstone without setting either the calcium, protein or both? We know that caustic does a good job of removing protein soil. However, at the same time, we also know that inadequately formulated caustic solutions tend to increase the alkaline formation of beerstone by precipitating calcium and magnesium. In cleaning a vessel such as a serving or aging tank, for example, where the problem is primarily scale, using caustic may not be the best choice. (4)

Caustic cleaners without help from water softening/conditioning ingredients such as chelators and sequestrants can actually precipitate calcium, thereby adding to the beerstone problem. If extremely hot water (>180° F). is used in the cleaning cycle, this will also promote the precipitation of calcium. (2)

A NEW APPROACH

We have discovered a new way to keep beerstone from becoming a problem in aging, serving tanks and kegs using the following procedure:

- Rinse out beer and yeast with ambient temperature water.
- Use a 1-2 ounce per gallon phosphoric/nitric acid mixture (140° F maximum temperature) for 15-30 minutes.
- No rinse.
- Use a noncaustic alkaline cleaner at 1-2 ounces per gallon of warm (120-140° F) to start. CIP for 15-30 minutes depending on conditions.
- Rinse with ambient temperature water until the pH of the rinse water is neutral (same pH as the tap water coming in).

If a straight phosphoric acid (without nitric) is used the above procedure may not work. The reason phosphoric by itself is not as effective on beerstone is that it is not an oxidizing acid. Phosphoric acid is a mineral acid and, consequently, offers only hydrolysis, not oxidation. Oxidation is required to assist in breaking apart the amino acid groups making up the protein. Since nitric acid oxidizes as well as hydrolyzes, it is much more effective in loosening protein deposits. For this reason, many beerstone and milkstone removing acid cleaners incorporate nitric acid. An added benefit of using an acid with nitric acid is that nitric acid has a passivating effect on stainless steel.

The acid first step does not remove the beerstone. Rather, beerstone is merely loosened for the next step. If the acid is drained and followed with a rinse, a pH of about 4.5 makes protein insoluble. (1) For this reason, it is best to skip the rinse and proceed immediately to the alkaline step.

NONCAUSTIC STEP

After the acid step, the scale is ready for the noncaustic step. Since noncaustic cleaners do not contain sodium hydroxide, violent reactions will not occur even if there is a little acid left in the system.

For best results, the noncaustic cleaner is used at around 1-2 ounces per gallon of warm water for low to moderate deposits. For worst case scenarios, (beerstone buildups that have accumulated for a long period of time) up to 4 ounces of cleaner can be used. At the end of the alkaline cleaning step, the noncaustic cleaner is discarded and can be mixed with the spent acid solution for pH neutralization. Any remaining soil adhered to the metal will generally be very soft and can be removed with a high-pressure hot water rinse or simply wiped off. Rinsing with acid after the noncaustic step is unnecessary. Most noncaustic cleaners currently on the market leave a pH neutral surface with a normal tap water rinse. Following the noncaustic cleaner with an acid may strip the silicate coating, leaving the surface more prone to scale (beerstone) adhesion.

Depending on the amount of scale to remove, cleaning times will vary. Light buildups typically only take 15-30 minutes per step to remove. Heavier buildups will require at least 30-45 minutes (or longer) to remove and may not be totally removed on the first pass. If the scale is extremely heavy, hand scrubbing or soaking with acid may be required.

ADVANTAGES

One of the biggest advantages of this method is that it can reduce the amount of time, chemical and water required in the equipment cleaning process. It works well to keep from setting the scale. Since no caustic is involved in the procedure, it is a little safer, too.

The approach is very effective to keep beerstone from building up on new equipment surfaces. Since sodium hydroxide is not used in the procedure, it is less corrosive and typically safer as well. Plus, properly formulated noncaustic cleaners will not promote the formation of beerstone. The spent cleaning solutions can be combined to neutralize one another prior to being disposed. A pH neutral effluent is important regardless of whether the brewery is checked for it or not.

TENACIOUS BEERSTONE BUILDUPS

If the beerstone buildup has accumulated over a long period of time, it will be extremely difficult to remove. Aging and serving tanks and kegs can have beerstone buildups that are tough to remove. There are many reasons for this. Since the beer can spend a long period of time in a refrigerated environment, there is a lot of time for the scale to combine with beerstone already deposited on the surface. The cold temperatures encountered in the cellar make it difficult to maintain a warm cleaning solution. Consequently, if the beerstone is not removed in the cleaning process, the scale will continue to build up on the surface much like layers of paint, stacked one on top of the other.

The resulting whitish layer has a texture that resembles sandpaper. If the beerstone situation degrades to this point, drastic measures are called for to remove the scale.

Using strong acid solutions are the quickest and most effective way to remove beerstone from stainless steel surfaces. Care has to be taken, however, when using strong acids because of their corrosiveness. Hydrochloric acid, for example, is an excellent acid for removing calcium-based scale. The chloride ion, however, is extremely corrosive to stainless steel and can cause pitting. Routine cleaning of stainless steel with hydrochloric acid is not recommended. Other inorganic acids such as nitric, gluconic and sulfamic can be effective on beerstone and are less harmful to stainless steel, especially when corrosion inhibitors are incorporated into the formula. For hand scrubbing, a 10% nitric acid and koalin can be applied as a paste. (2) Check with your chemical supplier for specific recommendations.

SUMMARY

Brewing has become more science than art these days. It is important, however, to not discount sensory evaluations. Does the equipment look clean? (Heat exchangers can be difficult to evaluate unless they are dismantled.) Are you detecting beerstone building up in your aging, serving tank or keg? Does the metal feel smooth to the touch? If the surface is rough, the cleaning has not been adequate to remove the scale buildup, and this condition will only continue to deteriorate.

The old saying, "An ounce of prevention is worth a pound of cure" is as true today as it ever was. A little extra chemical cost now may save an entire batch of beer (and your reputation) later. The flavor and shelf-life of the beer will be much better if the equipment is kept clean and sanitized. The best news is that once beerstone is completely removed, it is much easier to keep it from coming back in the future with a proper cleaning regimen.

References:

1. Fred Holzhauer, Dana Johnson, "Noncaustic Cleaning in the Brewery", *The New Brewer*, March/April, 1996, page 77.
2. Norman G. Marriott, *Principles of Food Sanitation*, Second Edition, 1989, Van Nostrand Reinhold, New York, pages 82-83, 285, 290.
3. Robert C. Weast, Ph. D., Melvin J. Astle, Ph. D., *Handbook of Chemistry and Physics* (63rd Edition) 1982-1983. CRC Press, Inc. Boca Raton, FL, page B-88.
4. Greg Foss, "The Dirt on Brewery Cleaning-A Review of Procedures and Chemicals", *Brewing Techniques*, March/April, 1997, page 68.

