Dursan's Use in the Food and Beverage Industry: A Walk Through of the Beer Brewing Process

Technical Insight

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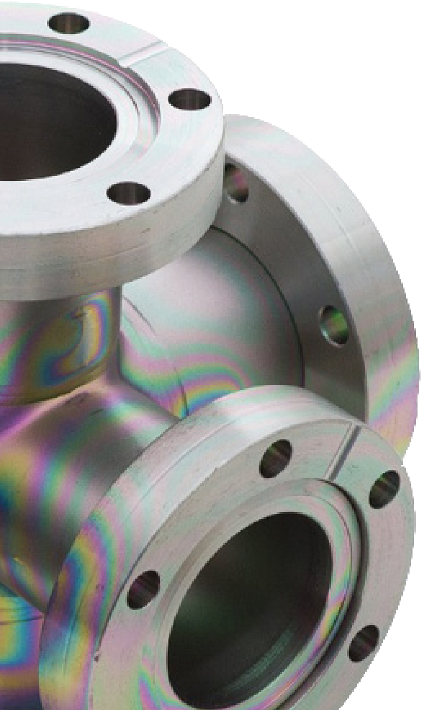
Synopsis

Many of our coatings have shown the ability to block metal ion leaching from a variety of solvents. The ability to block this trace level of metal from entering flow paths has previously shown promise in HPLC applications. In this TI we will focus on what a coating could potentially do in the food and beverage industry if metal ions can be blocked from entering the product. We will specifically look at Dursan as it is SilcoTek's coating that is NSF approved and has passed USP Class VI testing. Additionally, we will focus on beer production as it is an example that SilcoTek can examine in house.

Background

Metals and metal alloys are a fantastic option for equipment in a variety of industrial processes. They are strong, robust, and easily machined, especially when compared to plastics or ceramics. One issue that is seen with most metals are various forms of rust, corrosion, and metal leaching into the product flow path. Figure 1 shows the varying degrees of metals interacting with their chemical environments. Obvious corrosion and rouging are signs of metal ion introduction into the product. Typically, obvious corrosion leads toward structural concerns as well. Both examples are visual; however, alloys can leach trace levels of metal ions into solution. This is often unnoticed and/or overlooked by many users of sophisticated alloys such as stainless steels and specialty alloys. It is certainly of interest to many in the biopharmaceutical industry as the metal ions can cause an increase in impurities and degrade the end product more quickly



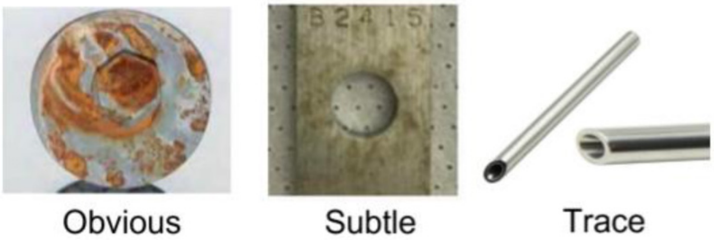


Figure 1: Three examples of metal materials reacting with their environment. Each will have differing levels of concern to different industries, experiments, and individuals.

While this problem is currently not largely considered by those in the food and beverage industry, there are areas where it should be given consideration. It should be highlighted that metals can be split into two categories according to the FDA. There are metals that the human body requires as a part of a recommended daily intake. These include metals found in stainless steel alloys such as iron, chromium, manganese, and molybdenum. The only metal found in stainless steel that the FDA suggest are harmful to health is nickel. This TI will not focus on the health issues associated with metal ions in the food and beverage industry, but rather the impact that metal ions have on the end product and processing of foodstuffs.

Here we will focus on metal ion contamination of beer, and what potential issues this could have in the product, but the issue extends well beyond just beer. Table 1 briefly highlights a few examples where metal ion contamination can cause issues. Most of the examples are due to the oxidative properties of metal ions, and their ability to react with proteins and lipids. This is not an exhaustive list. The book "Oxidation in foods and beverages and antioxidant applications" is recommended reading for more information. The solution for many of these problems involve either the removal of metal ions by means of binding and filtering, or the addition of a variety of preservatives that act as antioxidants in order to limit the damage the metal ions can do to the product. Both of these techniques have shown to have unintended consequences in either sensory differences or regulatory issues as certain metal chelating preservatives can have health impacts.

Table 1: Various issues that metal ion contamination could have on foodstuffs.

Foodstuff	**Issue that metal ions can cause**
Baby Formula	Formula contains numerous lipids (fats) that are prone to oxidation from iron or copper ions. Lactoferrin (a metal chelating protein) has been used to sequester the iron and limit the lipid oxidation.[1]
Fish OIl	Omega-3 fatty acids are prone to oxidation by excess iron in the oil product. Apotransferrin, phytic acid, and EDTA were shown to inhibit lipid oxidation in a salmon oil-in-water emulsion.[2]
Milk and Mayonnaise	Lipid breakdown was caused by iron metal ions. Lactoferrin, phytic acid, and EDTA were shown to be good preservatives by binding to the iron in solution.[3]
Cooked beef patties	Potato proteins were showed to slow the breakdown of beef proteins and fats when stored in a refrigerated location. The copper and iron were able to selectively bind to the potato protein in the patties and not allow them to attack the fats and beef proteins.[4]
Wine	Transition metal oxidation causes accelerated aging in wines. Often sulfites are added to decrease the rate at which these reactions take place. Many individuals have allergic reactions to these sulfites and thus they are undesirable if unneeded.[5]

The metals present in these foods are likely introduced by some combination of the endogenous metal content of the raw materials to make the product and the processing equipment. The contribution from each source will vary depending on the product and the processing involved. In this TI we investigate the production of beer and where a coated surface could have significant impact on the product. We also identify the chemical differences between a light pilsner brewed in an untreated stainless steel process versus the same beer brewed in a Dursan coated process.

Data and Discussion

Brewing of beer is an age-old art but has become a large industry backed by the science of the brewing process. The brewing process is relatively simple: extract sugars from malted barley, add hops and yeast, and allow the mixture to ferment and age. The impact that metal ions have on beer production have been studied in a variety of ways, but the two areas that have garnered the most interest in literature involve beer flavor stability[6] and the impact that the metal has on the phenolic and polyphenolic composition of the beer.[7-9] Much of the research focuses on the metal content from raw ingredients used in combination with intentional additives of iron, copper, manganese, and other metals. They all make mention that these additive metals are to simulate the introduction of metal ions from the brewing equipment. The degree metal leaching will vary depending on the water, additives, temperature, and quality of the steel. Figure 2 outlines the general steps to get from raw material to finished product. For more detail, here is a great video that outlines the brewing process. The bulk of the metal ion introduction from equipment likely happens in the mash tun, lauter tun, boil kettle, and heat exchanger. In these locations, the liquid is hot or boiling, and the elevated temperatures allow for more metal ions to leach into solution. Most of the materials used in this process is 304 stainless steel. This includes all of the tanks as well as tubing, valves, heat exchangers, blenders, recirculaters, etc.

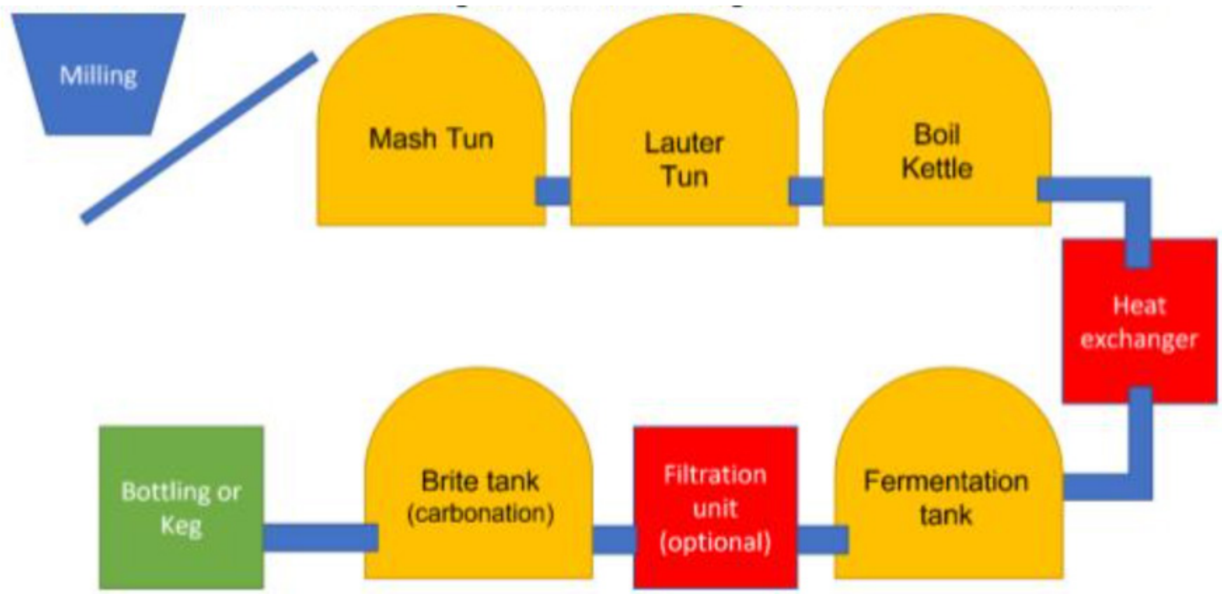


Figure 2: The general process for brewing a beer. The equipment varies in size, shape, and geometry, but this is the general process used at all industrial brewing facilities.

To evaluate whether the brewing equipment has an impact on the beer quality, we coated two identical all-in-one small-scale fermenters. These can be seen in Figure 3, and encapsulate the mash tun, lauter tun, boil kettle, heat exchanger and fermentation tank steps seen in Figure 2. On the day of brewing, there was no obvious difference between the two when it came to the process. Both beers achieved the same specific gravity (level of sugars extracted from the malt), both appeared to have the same color, and both smelled identical.

Figure 3: Chapman all-in-one brewing systems. On the left is the uncoated example and the right is the Dursan coated system.

Differences between the two beers became aparant when samples were collected for further chemical analysis. Figure 4 shows samples pulled from both beers during the brewing process. These samples were all submitted to Penn State's Laboratory for Isotopes and Metals in the Environment. There, ICP-MS was be performed to determine the total metal ion content of the beer. There was, however, obvious differences in clarity between the beers brewed in the steel container (Sample 1, 3, and 5) versus the beer brewed in the Dursan coated system (Sample 2, 4, and 6). Samples 1 and 2 were pulled after Lauter Tun portion from Figure 2, Samples 3 and 4 were pulled after the boil and cooling, and 5 and 6 were pulled after fermentation had occurred and prior to boiling.

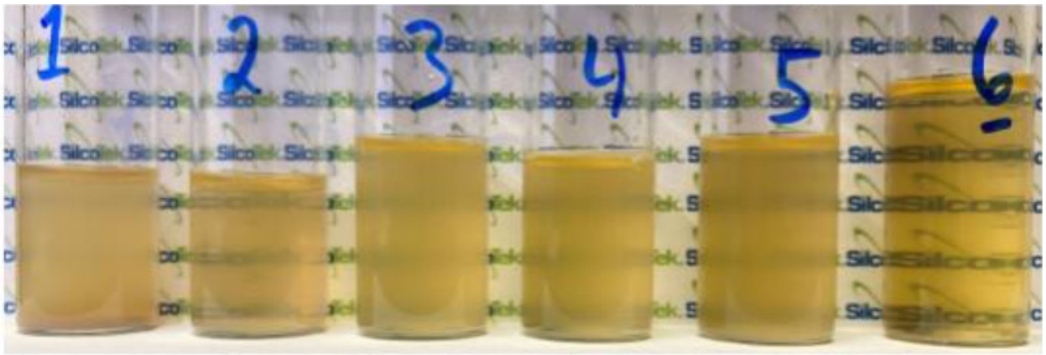


Figure 4: Samples pulled at various stages of the brewing process. The odd numbers are from the steel system and the even numbers are from the Dursan coated system.

This difference in clarity is likely due to a difference in metal concentration in solution. Metals have shown to have a dramatic impact on beer's flavor, appearance, and stability. Frank-Jurgen Methner has extensively studied where the metal ions come from and the impact that they have on beer including: iron and copper accelerating the aging process, iron's ability to impact colloidal stability (haziness), iron's ability to enhance foam stability and its impact in the fermentation process, copper, zinc, nickel, cobalt, manganese, and especially iron in promoting "gushing" reactions.[10]

Metal ion content in the beer

Samples from Figure 4 were analyzed via ICP-MS for metal ion content. The results can be seen in Table 2. The absolute values are not of interest to us as there is substantial literature on the uptake and release of metals throughout the brewing process. What is of interest is the differences between the coated system and the non-coated system.

Table 2: Metal ion content from beer brewed in a stainless steel vessel or a Dursan coated stainless steel vessel.

Sample	Metal content (Fe, Cr, Ni, Mo, Mn) from Steel system	Metal content from Dursan coated system	Apparent metal contribution from the steel
Mash (sugar extraction from the grains)	1207 ppm	815 ppm	33%
After boil (hops added and prior to putting yeast in)	869 ppm	565 ppm	35%
After fermentation	1527 ppm	1144 ppm	25%

UV-Vis Analysis

There are various properties of beer that can be analyzed via a simple UV-Vis instrument. Mettler Toledo has put together a great application brochure on the various experiments that can be done using a UV-Vis. That brochure can be found here. We focused on two measurements that could be impacted by metal ions in solution: total polyphenolic content and antioxidant activity.

The phenolic composition of a beer plays crucial roles in flavor and stability of a beer over time. While individual phenolic compounds will be analyzed in the future via HPLC, the measurement of the total number of polyphenols can be measured via UV-Vis. Previous studies have shown that high polyphenol concentrations can lead to better quality, more stable sensory properties, and longer shelf life than beers that contain lower polyphenol content.7 Measurements were performed utilizing a European Brewery Convention method to measure total polyphenol content. Briefly, 10 mL of beer is combined with 8 mL of carboxymethyl cellulose sodium salt and EDTA solution in a flask and thoroughly mixed. Then 0.5 mL of an ammonium iron citrate solution was added and again mixed. Finally, 0.5 mL of ammonia is added followed by distilled water to dilute to 50 mL total volume. The mixture was allowed to stand at room temperature for 10 minutes and the absorbance was measured at 600 nm. The absorbance value is then multiplied by 820 to determine the total polyphenolic content in mg/L. The results of the two beers were:

Total polyphenols
Dursan coated system: 140 mg/L
Steel system: 120 mg/L

For two beers that were brewed in identical manners, a difference of 20 mg/L is quite significant. Polyphenol concentrations can range from just over 400 mg/L for dark beers down to under 100 mg/L for near beer (beer that has less than 0.5% ABV).[11] Typically, the differences in polyphenol content is due to differences in raw ingredients, brewing processes, and yeast types. Here these were all identical, so the difference can be attributed to the metal interactions with the brewing process.

Antioxidant activity is of interest for shelf-life concerns. Typically, the more antioxidants a beer has, the longer it can stay on shelves before aging to the point of being dramatically different in its sensory profile. Here, a slightly modified version of Zhao's method9 was used to measure the antioxidant activity in the beer. DPPH (2,2-diphenyl1-picrylhydrazyl) is a stable radical that is commonly used as an oxidizing agent. The deep purple color DPPH turns yellow when exposed to antioxidants (or reducing agents). This color change can be measured at 517 nm on a UV-Vis and is plotted on a calibration curve of Trolox equivalency (TE). Trolox is an antioxidant compound, similar to Vitamin E, that is the industry standard for the measurement of antioxidant activity. The results of the two beers were:

Antioxidant activity
Dursan coated system: 0.89 mmol/L TE
Steel system: 0.55 mmol/L TE

When compared to commercially available Czech lagers, the beer brewed in the Dursan coated system had a value closer to larger breweries in the Czech Republic, where the beer coated in the steel system was more in line with wheat beers rather than Czech lagers.[12]

It should be noted that both of these measurements were taken 1 week into the aging and carbonation process. Both total polyphenol content and antioxidant activity diminish over time. Bottles of both beers are currently aging at room temperature and awaiting a measurement at the 8-week point to see how the beer changes in that natural aging process.

Sensory analysis

The beers were allowed to age for 8 weeks in a refrigeration unit that was set to 40° F. SilcoTek employees were asked to volunteer to sample the beers, and 31 participants agreed to taste the beers. Participants were given 3 samples in opaque cups (the opaque cups were used to eliminate any visual differences between the beers). Two of the beers were the same and one beer was different. The participants were asked to identify the beer that was different from the other two. This method is known as a triangle test and a video here further describes how this testing is used.

Triangle test theory tells us that if someone is given 2 samples, the taste tester knows that one is different from the other. Consequently, the tester may start making up differences based on the knowledge that the two are different. With three samples (2 of one sample and 1 of the other sample), the taste tester won't know which one is different unless they can actually taste a difference. Participants were instructed to judge the 3 beers regardless of whether they could taste a difference or couldn't taste a difference but guessed. Participants were asked to identify the odd one out of the three samples. Participants were also asked to describe why they chose that sample or just guessed.

In sensory analysis and a triangle test like this, the cutoff to determine whether the results are statistically relevant is a p-value of less than 0.05. With 31 participants, 16 participants would have had to correctly identify the odd beer out to meet this criterion. The results showed 17 employees correctly identified the odd beer out, showing that there is a difference in the taste and smell of the two beers. Of the participants that correctly identified the beer that was different 5 reported that the two beers smelled different from one another.

In fact, one participant did not taste any of the three beers, she only utilized smell to differentiate them. The odor was reported to be cleaner for the Dursan beer, and a little more sour on the nose for the steel beer. 10 participants reported that the taste was different. They largely identified the Dursan beer by having upfront taste with a clean, quick finish where the steel beer did not have much taste upfront, but a longer lingering aftertaste. Two participants admitted that they simply guessed and could not identify a difference.

Conclusion:

The beer brewed in the Dursan coated system and the bare steel system showed a variety of differences, despite being the same recipe and brewed at the exact same time. Future measurements will include total polyphenol content and antioxidant activity of aged beer as well as HPLC analysis of the flavor compounds from both beers. As with any scientific experiment, it needs to be replicated to ensure that the results are repeatable. We plan to brew a hop forward beer, such as an IPA, to see if there is an impact on the hop flavor compounds as the beer ages. We also plan to look at a beverage that has higher amounts of antioxidants and polyphenols such as a dark beer, like a stout, and/or explore other beverages such as hard cider or wine which have orders of magnitude higher antioxidant activity.

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