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Hard water vs hard liquor

Brandon Aldinger shares results from American Glass Research's study exploring the cause of white deposits that can adhere to the inside surfaces of filled vodka and gin bottles, giving the glass a hazy appearance.

In the past ten years, American Glass Research has received multiple requests to analyse filled vodka and gin bottles that exhibited white deposits adhered to the inside surface, creating a visually hazy appearance. The deposits are reported to appear within 24 hours after filling, but were not previously visible in the empty bottle prior to filling. Moreover, not all of the bottles in the same lot were affected.

In most cases, the white deposits occur on the interior upper sidewall of the container and not the bottom or heel areas. The deposits are patchy and do not cover the entire inner surface. As shown in Figure 1, boundaries between the deposits and clear, unaffected areas are usually sharp. Within the deposits, irregular elliptical or circular features are present, with the outlines of the features consisting of clear areas.

When analysed via SEM-EDX [Scanning Electron Microscopy (SEM) with Energy Dispersive X-Ray Analysis (EDX)], as shown in Figure 2, the deposits are found to consist of pointed crystals with concave, triangular faces that resemble tetrahedrons. The crystals are approximately 2–4µm in size, and are remarkably consistent in their morphology even for samples produced by different manufacturers and filled by different beverage companies. Spectral analysis of the crystals has shown that they are composed primarily of calcium carbonate ($CaCO_3$), with minor and variable amounts of magnesium, phosphorous and sulphur.

A published source relevant to this phenomenon was found in a home distiller's guide (*Making Gin and Vodka*, John Stone; Brewhaus; Calgary, AB 2004). Similar deposits were claimed to be caused by precipitation of solutes out of hard water used to dilute the alcohol to the desired concentration; however, no mention of deposits adhering to the sides of the container was made. Calcium carbonate – the primary solute in hard water – has a solubility of only 0.0014g/100ml in cold water, and is even less soluble in alcohol. Thus, precipitation of $CaCO_3$ upon addition of hard water to alcohol was a plausible mechanism for the issue observed by commercial fillers. Yet the hard water theory still left some observations unexplained. For instance, why did the deposits occur only in some bottles within a lot, and not in all?

A study was therefore designed to explore the mechanism for creation of the white deposits. Water hardness was the primary variable under consideration, while secondary variables of internal treatment (IT) and inside surface roughness were also tested.

Experimental procedures

For the experiment, 1l round stock liquor bottles that had been collected directly off the lehr were used. Some of the stock bottles had been internally treated with difluoroethane as per the glass manufacturer's standard process, and some were untreated. To test the effect of inside surface roughness, bottles in each trial were abraded on the inside surface by wrapping a ball-tipped probe with 150- and/or 600-grit sandpaper and sliding it against the interior sidewall.

A common recipe for simulating hard water was found on a brewing reference site: Epsom salt (magnesium sulphate, Mg_2SO_4) was first added to reverse osmosis (RO) water while stirring. After that component had dissolved, baking soda (sodium bicarbonate, $NaHCO_3$) was added, followed by calcium chloride ($CaCl_2$).

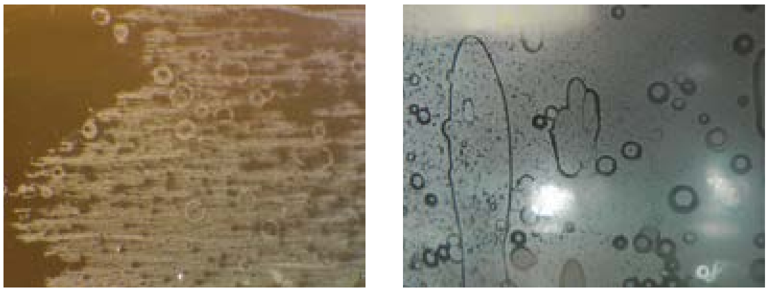

Figure 1: Photomicrographs of white deposits from trade samples (10X magnification).

The bottles for each trial were first filled halfway with 500ml of 95% denatured ethanol. Then, hard water solutions were poured into the bottles up to the approximate fill-point, for a final alcohol concentration of 47.5%. Adding the water to the alcohol was intentional to mirror the commercial dilution process. The filled bottles were then allowed to sit undisturbed while being monitored over the next 72 hours.

The most applicable results were obtained with a hard water solution of 0.025g/l Mg_2SO_4, 0.250g/l $NaHCO_3$, and 0.100g/l $CaCl_2$. Higher concentrations of solutes caused cloudiness or precipitation to appear upon addition to the alcohol, which was not reported to occur in the trade.

Results

For the hard water concentration noted above, the water/alcohol solution remained clear upon filling, and no deposits were present within several hours. White deposits were then observed on the sidewalls of the containers the next day after filling, as shown in Figure 3.

For the internally treated bottles, the white deposits preferentially occurred within abrasions. The non- ▸

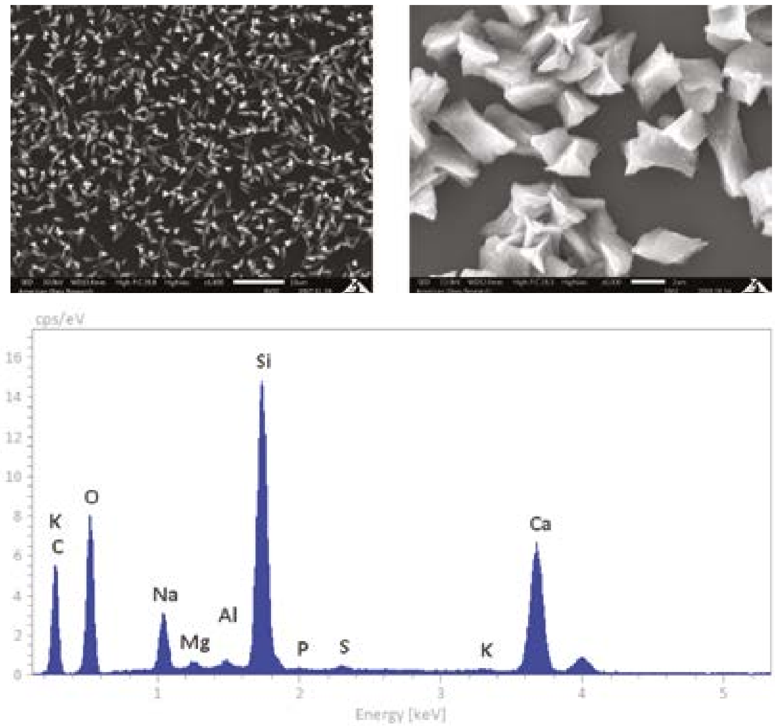

Figure 2: SEM-EDX micrographs of white deposits from trade samples. The EDX spectrum of a typical crystal is also shown; the silicon, sodium, and aluminium peaks are due to the underlying glass and not the crystals.

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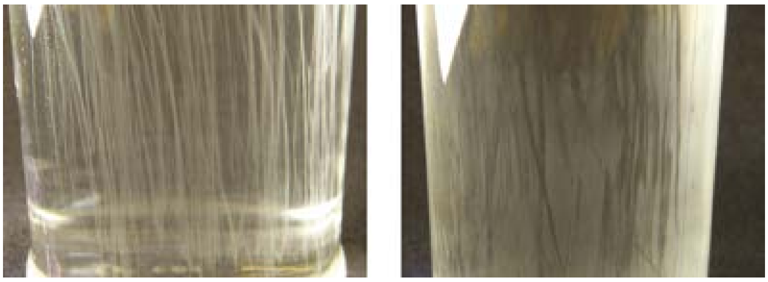
Figure 3: Photographs of representative bottles showing IT-abraded (left) and non-abraded (right).

abraded samples generally contained uniform patches of deposits with well-defined boundaries, generally similar to commercial samples but lacking the complex 'droplet' shapes seen on containers from the trade. For the untreated bottles, the deposits preferentially occurred on smooth areas without abrasions.

After draining the liquid, portions of the white deposits were examined with a scanning electron microscope with X-ray capabilities (SEM-EDX).

As shown in Figure 4, the deposits consisted of crystals that were either small and rounded (No-IT) or hexagonal and crystalline (IT). Despite their differing morphologies, the crystals on both types of bottles had the same composition: $CaCO_3$ with a minor amount of sulphur.

Discussion

Several aspects of the white deposits reported from the trade were successfully reproduced through dilution of alcohol with a hard water simulant:

1. The lab-created white deposits were composed primarily of $CaCO_3$ crystals, which is the same composition for the deposits found in trade samples.
2. It was possible to cause delayed deposition of crystals on the interior sidewall of containers, even when the liquid initially appeared clear. The delay time between filling and the appearance of the deposits was similar to the fillers' reports.
3. Crystals of $CaCO_3$ were created on both IT-treated and untreated bottles, which mirrors samples obtained from the trade.
4. For some bottles, surface roughness in the form of abrasions provided nucleation sites for the crystals. Although as-produced inside surfaces would not have roughness as severe as an abrasion, varying amounts of roughness may explain why some bottles in the trade develop deposits and others do not.

Several characteristics of the deposits analysed in trade samples could not be fully reproduced in the laboratory experiments, including the crystal morphologies and circular deposition features. Because the exact filling conditions used by distillers were not known, it is possible that these differences are due to peculiarities of the filling process.

No noticeable difference in the creation or amount of $CaCO_3$ deposits was found between IT-treated and untreated bottles. Internal treatment is performed to reduce the amount of surface available alkali in the glass; thus, its lack of effect on deposit formation provides strong evidence that the primary source of calcium is from the water used for dilution. This result is of use to distillers who use water high in dissolved minerals for dilution, thereby risking $CaCO_3$ deposit formation regardless of the presence of treatment in their glass containers.

Conclusion

In conclusion, the white deposits observed in filled vodka and gin glass bottles are composed mainly of $CaCO_3$ crystals. The primary cause of these crystals is the addition of hard water to the distilled alcohol during filling. Several characteristics of the deposits found in trade samples could be reproduced in the laboratory via dilution of alcohol with a hard water simulant. Properties of the crystals that could not be fully reproduced, such as crystal structure and deposition pattern, may be due to differences in the filling environment versus the experimental conditions. Finally, the presence of weathering products in the bottles, microscopic surface roughness, and the extent of internal treatment were not fully explored, and may play a secondary role in occurrence of the deposits within a particular bottle or lot of bottles. Despite these remaining questions, it can be concluded that hard water – and not the bottle – is the main driver for creation of the $CaCO_3$ deposits. ●

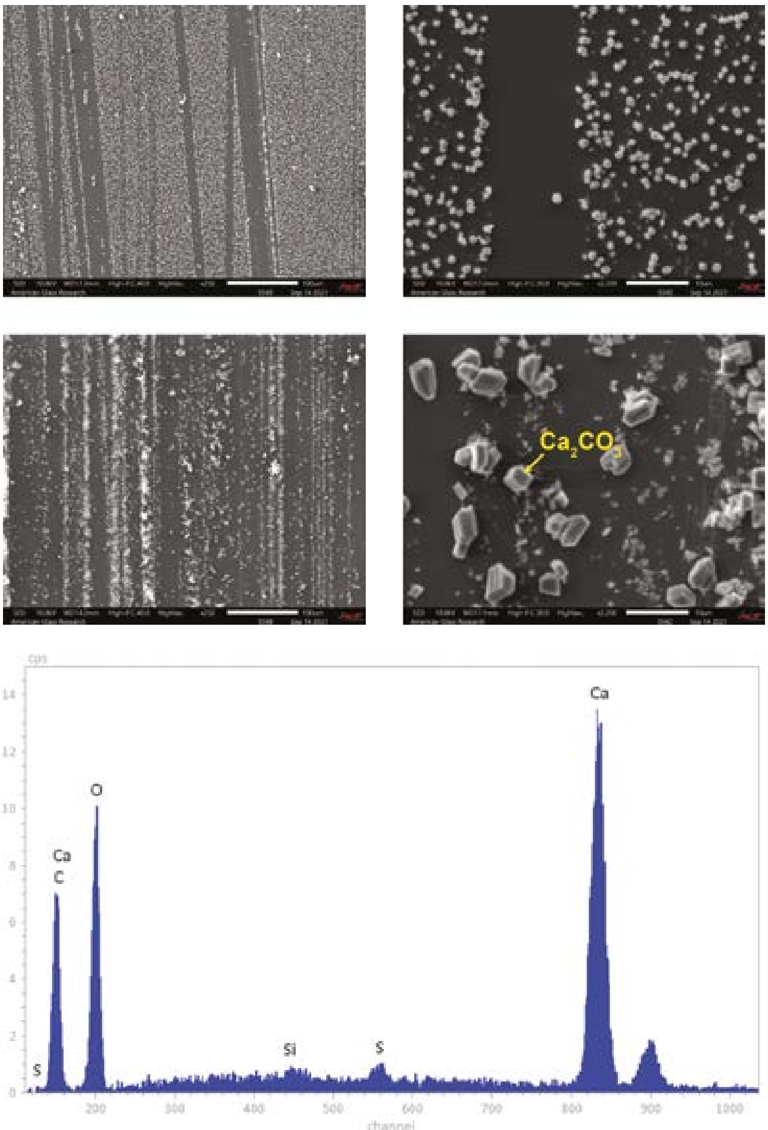

Figure 4: Representative SEM micrographs: no-IT (top) and IT-abraded, along with the EDX spectrum of a crystal.

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