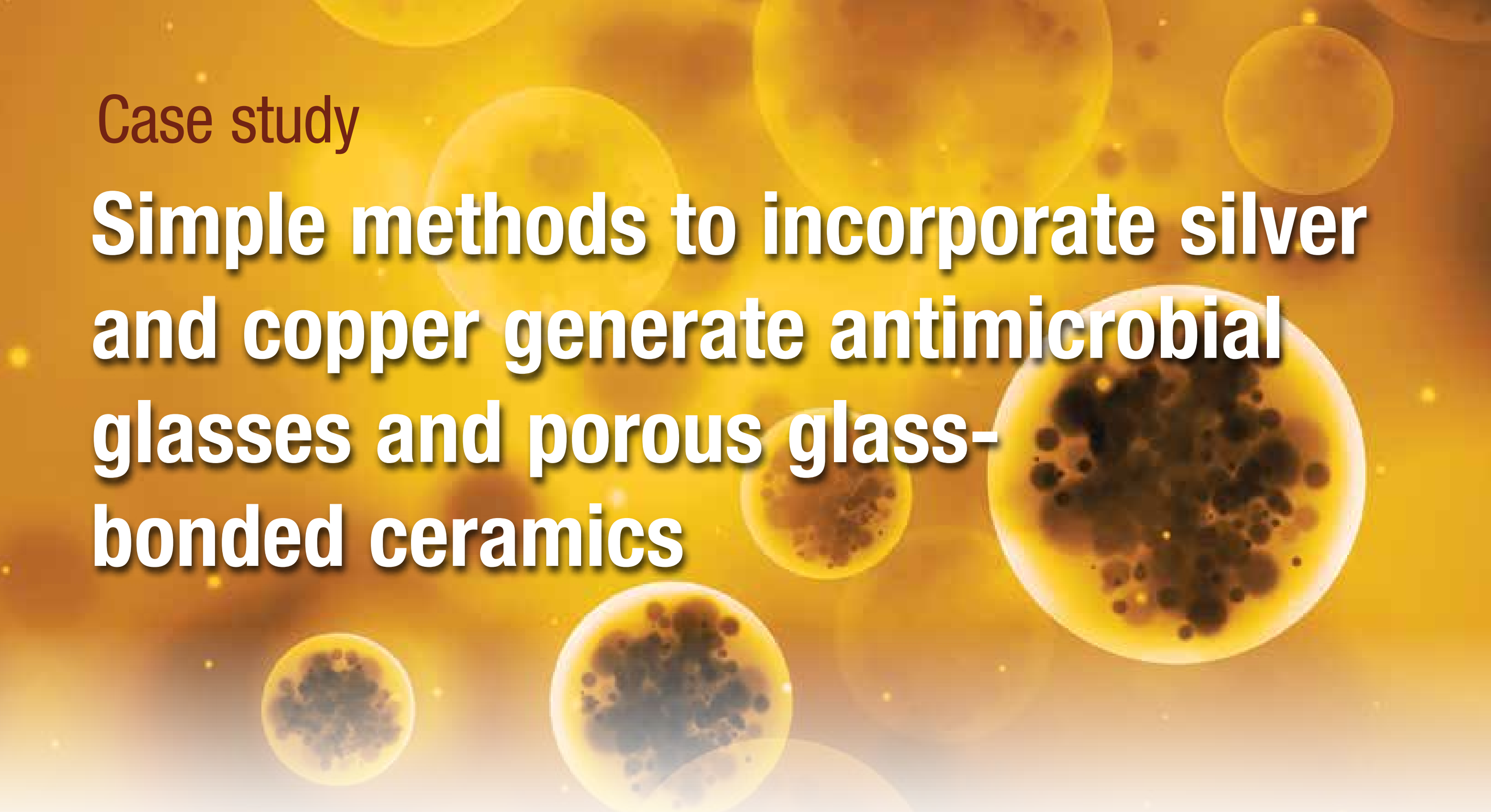


Case study

Simple methods to incorporate silver and copper generate antimicrobial glasses and porous glass-bonded ceramics

By Taki Negas, Dave Hilfiker, and Scott Bartkowski

Simple and flexible techniques show promise for incorporating silver and copper into glass and glass-bonded ceramic materials for novel antimicrobial products.

Credit: Refractron

Figure 1. Typical glass-bonded alumina ceramics produced at Refractron.

Silver and copper ions are well-established antimicrobial agents that combat bacteria, viruses, fungi, and algae. Recently, Corning Incorporated (Corning, N.Y.) researchers discussed the importance of microbial suppression for glass-based touch surfaces on smartphones, ATMs, etc.[1] They demonstrated that silver “bullets” can be ion exchanged into borosilicate glass, resulting in surfaces that effectively control growth of *Escherichia coli* bacteria. To accomplish exchange, Corning immersed glass in a melt of $AgNO_3$–alkali nitrate at 300°C–400°C. Similarly, Borsella et al.[2] used $CuSO_4$–alkali sulfate melts at 518°C–570°C to ion exchange copper into glass slides.

Refractron Technologies Corp. (Newark, N.Y.) manufactures two classes of ceramics: structural zirconias based on dense magnesium-partially-stabilized zirconia (Mg-PSZ) and yttria tetragonal-zirconia polycrystal (YTZP); and alumina (brown- and white-fused grits), silica, and mullite ceramics with precisely controlled porosity (Figure 1). Most of the latter products are bonded with one of several proprietary silicate glasses. These products function as fine bubble diffusers that oxygenate, purify, and filter water in numerous applications. They also transfer gases to liquids under controlled flow for fish farms, aquatic plants, beverages, and

Capsule summary

MOLTEN SALT

Ion exchange of silver or copper ions can generate antimicrobial glasses, but similar processes are not suitable for glass-bonded alumina. Simpler and more flexible manufacturing methods may improve the potential applications of ion-exchanged materials.

NEW MATERIALS

Solution-based ion-exchange and other methods can implant silver and copper ions into the surfaces of a variety of glasses and glass-bonded ceramics.

CAN IT WORK?

Materials tested favorably as antimicrobial agents against *E. coli* and showed potential in antialgal and antifungal tests. These techniques may be able to produce useful antimicrobial products if incorporated into polymers, paints, fertilizers, and more.

aquariums. In addition, saturating the porosity of these materials with ink produces fingerprint touch surfaces.

Refractron porous ceramics typically are bonded with 4–15-wt% silicate glass. Two of the three predominant glasses are borosilicate formulations, and all contain K^+ and Na^+. Thus, they are ideal candidates for potential antimicrobial products if silver and/or copper can be incorporated into glass monoliths, glass frits, or glass-bonded ceramics. However, ion exchange using molten salts is not an option for bonded alumina, because the melts corrode the grits. In addition, parts produced in volume are relatively large, making exchange in and containment of molten salt baths impractical. Simpler and more flexible methods are required.

Credit: Refractron

Figure 2. Examples of non-machined materials used for experiments: (1) porous alumina grit puck bonded with glass (no boron); (2) borosilicate glass produced from frit powder; (3) glass, no boron; (4) borosilicate glass; (5) vesicular borosilicate glass with Cu^{2+}; and (6) borosilicate glass with Cu^+ and roughened surface.

A new experimental approach for silver-ion exchange in glasses

We prepared monolithic buttons (~38-mm diameter × ~8-mm thickness) of three glasses that are used to bond grits—two borosilicate glasses and silicate glass (no boron)—by melting at 800°C–1,300°C. One borosilicate bond formulation was a frit with broad particle-size distribution. Additional experiments used milled and unmilled versions of the frit as well as glass slabs and glass-bonded ceramics (Figure 2).

We used a concentration of 20 g of $AgNO_3$ dissolved in 800 mL of deionized water in all experiments. We broke one button of each formulation into irregular fragments (~7 mm × ~7 mm × ~8 mm), and reserved the balance for additional testing. We placed glass monoliths, broken glass fragments, glass frit, or glass-bonded parts into covered beakers of solution and heated them to 82°C for up to 72 h. We manually stirred frit solutions every 24 h to expose fresh powder surfaces.

Although water evaporation was minimal, we replenished the solution as needed. After each experiment, we rinsed parts repeatedly with deionized water and dried them at 38°C or room temperature. In addition, we tested pucks of 100-grit alumina bonded with boron-free glass using the same procedure. Following the experiment, we ultrasonically rinsed and dried parts (~52-mm diameter × ~28-mm long). We cut one part in half parallel to the length, which allowed us to extract a central slice (~6-mm thick) to analyze silver content in top, middle, and bottom sections.

We used X-ray photoemission (XPS) and wavelength dispersive (WDS) spectroscopies to measure positive results for Ag^+ in two sets of broken glass fragments from exploratory treatments. Semiquantitative WDS analyses revealed a concentration of 3–4-wt% silver depending on the glass composition. For comparison, we treated fragments of one glass with boron and one without using the molten salt method[1] in a dense alumina crucible. The crucible softened near the melt–air interface by corrosion and parted after cooling.

We used WDS to measure 19- and 13-wt% silver for boron and boron-free samples, respectively. However, we found that XPS peak intensities for Ag^+ were similar to those obtained for glasses treated in $AgNO_3$ solution, suggesting similar concentrations.

Nonetheless, we reconciled these discrepancies in the data between XPS and WDS methods. We used XPS almost exclusively to sample surfaces, whereas we used WDS (and energy-dispersive spectroscopy (EDS)) to collect signals


Credit: Refractron

Figure 3. Glass containers with samples suspended in netting after algal test. Central portion of each lid was removed during the test.

from a depth of at least 1 µm. Thus, larger WDS-measured concentrations in the molten salt samples reflect a deeper penetration of ion-exchanged Ag^+, but surface concentrations of all samples do not drastically differ. This distinction is important, because we expect the concentration of Ag^+ at surfaces rather than in the bulk to govern microbial suppression, assuming that it is not rapidly leached in application.

After these encouraging results, we treated another set of glass fragments. We periodically extracted samples from solution and used EDS to analyze silver content.

Although EDS is faster, it is somewhat less accurate. Despite the customary scatter of EDS data, parts saturated at ~4-wt% Ag_2O within ~16 h. A precautionary timeframe of 24 h is reasonable for production.

We also used EDS to confirm the silver content of treated glass buttons, which, along with broken fragments, remained colorless after ion exchange. We then treated glass-bonded, 100-grit porous alumina pucks. EDS spectra from the glass-bond at various locations revealed a uniform distribution of silver.

Finally, we treated unmilled borosilicate glass frit powder, rinsed it thoroughly with deionized water, and dried the product. We repeated this treatment several times to confirm prior results and to accumulate products. We observed during testing that a curious gray material gradually developed on the glass powder surfaces. EDS analysis detected an unusually high concentration of silver (~7-wt% Ag_2O) that cannot be caused entirely by ion exchange enhanced by the larger surface area. Subsequent evidence confirmed this observation.

A new approach for incorporating copper-ions in glasses

We used similar methodologies to attempt ion exchange of copper using 20 g of $Cu(NO_3)_2$ hydrate dissolved in 800 mL of deionized water. Although the attempt failed, interesting reactions occurred during treatment of glass frit powders (more on this later). However, we successfully incorporated copper into glass and glass bonds by formulating an arbitrarily selected amount (2 wt% as CuO) into mixes before processing at elevated temperatures. In addition, we were able to use larger concentrations of copper if necessary.

Glass and glass-bonded silica parts had a blue (Cu^{2+}) hue when processed at <1,000°C, whereas monolithic glass and glass-bonded alumina (brown grit) parts processed at >1,100°C were jet black (Cu^+). We prepared glass slabs of two borosilicates formulated with CuO, one from a <1,000°C melt and one from a >1,100°C melt. The former was blue, suggesting presence of Cu^{2+}, and the latter was jet black, indicating presence of Cu^+ (Figure 2).

We also prepared samples from quartz grit bonded (<1,000°C) with 4-wt% borosilicate plus CuO and from 100-grit alumina bonded (>1,100°C) with 12-wt% boron-free glass plus copper. Although we did not investigate, it is possible that not all CuO dissolved into the glass of the latter, but partitioned to form crystalline phases with the alumina grit or its minor components. Regardless, the modulus of rupture (MOR) did not degrade from a typical value of 30 MPa. In addition, quartz grit did not react with copper oxides to produce crystalline products.

Antimicrobial testing of glass formulations

An independent laboratory measured antimicrobial effectiveness of silver in monolithic glasses, glass-bonded pucks, and glass frit powder using ISO 22196, a standard procedure adapted for ceramic surfaces and powders. The laboratory tested samples in triplicate over 24 h, and it compared the results to identical samples that did not contain silver. The laboratory tested an aqueous culture of *E. coli*, because it bears genetic similarity to numerous bacterial strains. In addition, we challenged copper-containing materials with an antialgal test and a simple but nonstandard antifungal test.

For microbial testing, we used surface grinding to produce a rough flat patch (24 mm × 24 mm) on the smooth convex exteriors of eight monolithic buttons of each formulation. ISO standard antimicrobial tests revealed that treated glass buttons and glass-bonded 100-grit alumina pucks had 99.98% antimicrobial efficiency, whereas glass frit had 99.97% antimicrobial efficiency. If significant, the reason for this difference remains unclear, because the same glass in a monolithic, low-surface-area configuration had a lower silver content yet a higher efficiency.

We tested samples of borosilicates with CuO only for antialgal growth using a procedure similar to ASTM G29-96 (“Standard practice for algal resistance of plastic films”), but with some differences. We suspended glass slabs containing copper ions (25 mm × 25 mm × 6 mm, see above)—two grits bonded with copper and two without—with polymer netting in 1-L glass jars containing Erie Canal water (Figure 3). The baths contained coarse white alumina grit on the bottom and fish food as a nutrient. A fluorescent light above the baths automatically turned on for 12 h and off for 12 h for 6 weeks. ASTM specifies a 4-week test, which terminates earlier if test samples show evidence of algal growth.

Black and blue glass slabs and black glass-bonded 100-grit alumina parts showed no algal growth (Figure 4). Algae grew on glass-bonded quartz parts with and without copper, loose white alumina grit gravel, and glass-bonded (12 wt%, no copper) 100-grit alumina samples. Thus, antialgal efficiency appears to depend on copper concentration and uniformity in overall distribution, but is independent of copper's valence state. A similar test evaluated samples of a copper compound grown on borosilicate glass frit (see below and Figure 4).

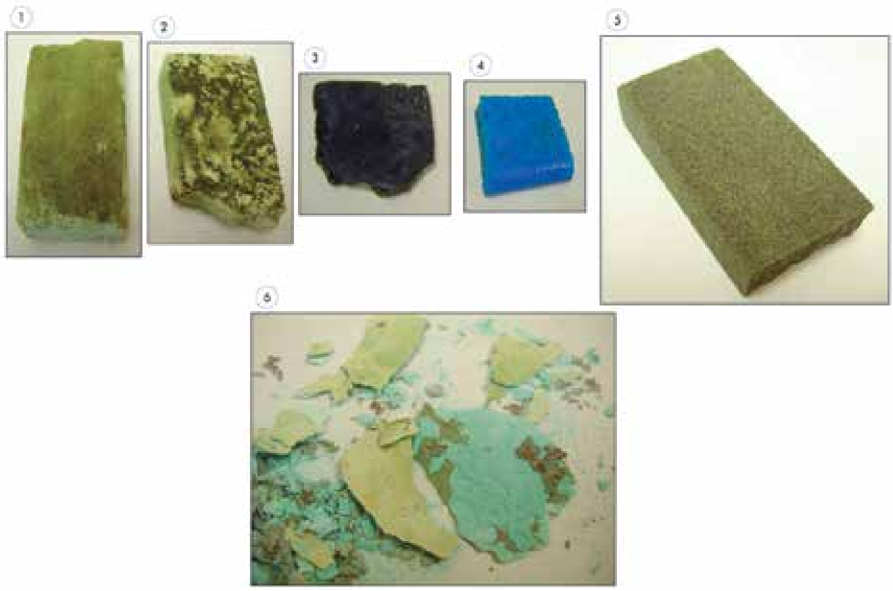


Figure 4. Materials after algal test. Algae grew on SiO_2 (quartz grit) bonded with borosilicate glass with (1) and without (2) Cu^{2+}. Algae did not grow on (3) borosilicate glass with Cu^{+}; (4) vesicular borosilicate glass with Cu^{2+}; and (5) porous brown alumina grit bonded with glass (no boron) containing Cu^{+}. (6) Removed $Cu_2(OH)_3NO_3$ grown on borosilicate glass frit shows light and darker areas of consumed algae.

Credit: Refractron

Silver and copper materials grown on borosilicate glass frit

We used X-ray diffractometry (XRD) to identify the gray material adhered to borosilicate glass frit treated in $AgNO_3$ solution as Ag_2CO_3 plus Ag_2O. We based the identification on two weak broad maxima for the former and two weaker broad lines for the latter, all superimposed on a dominant broad maximum typical of silicate glass.

When we heated it above 200°C, the deposit decomposed to adherent silver metal that imparted a pale-brown hue to the powder. Similarly, an adherent sky-blue deposit developed on the same glass frit when treated with copper nitrate solution. This deposit decomposed to CuO when heated above 200°C.

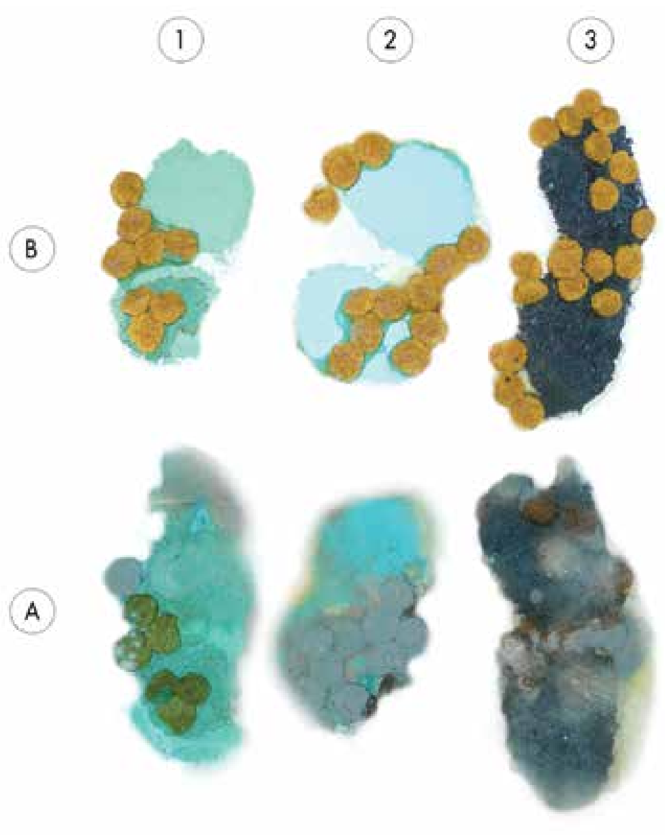
Deposits did not grow in solutions without glass powder or on monolithic glasses or glass-bonded grits. Therefore, higher-surface-area glass appears necessary for their appearance.

Ag_2CO_3 formation requires a supply of $(CO_3)^{2-}$ groups. We can argue that some CO_2 may have dissolved in solution during treatment, despite use of a tight-fitting aluminum foil cover that was infrequently removed. Normally, the color of Ag_2CO_3 is yellowish, and Ag_2O is brown to black. The combination might explain the gray hue, but other phases are not precluded. Amorphous AgOH also is possible, but it cannot be detected by XRD, because its scattering is masked by the broad maximum of glass.

To gain additional insight, we weighed the glass deposit and treated it with 1N HCl. Almost immediately, the gray hue faded to an off-white color and the solution became turbid. There was no obvious effervescence because of CO_2 evolution, which indicated a very low concentration of Ag_2CO_3, if present at all. After rinsing with deionized water and decanting the turbid solution several times, we dried the glass and weighed it. A lower weight revealed that the reaction detached the deposit from glass surfaces. Before each decant, we allowed some of the reaction products in suspension to settle on the glass for XRD analysis.

As we expected, XRD revealed that the only material with the glass was AgCl, which is characterized by intense, sharp maxima. Ag_2CO_3, Ag_2O, and AgOH all produce AgCl upon reaction with HCl. Therefore, the lack of effervescence, high silver concentration on the glass, and large quantity of AgCl generated by HCl indicated to us that Ag_2CO_3 is not a major component of the gray deposit. This also is supported by the absence of a carbon (or nitrogen) signal in EDS spectra. If correctly identified as being present, it is a secondary phase derived from dissolved CO_2 or from reaction of a highly reactive product, such as amorphous AgOH, with air during drying.

After we treated it in copper nitrate solution, we thoroughly washed and dried the glass frit. XRD identified the sky-blue deposit as crystallized $Cu_2(OH)_3NO_3$ from strong lines on a suppressed broad glass maximum. The compound is a well-known mineral with a claylike sheet crystal structure. Normally, it precipitates in solutions containing the pertinent ions. (Stanimirova et al.[3] provide an excellent review and bibliography of the structure, synthesis, and mineralogy of this and



Credit: Refractron

Figure 5. Row B shows samples before fungal tests: (1) $Cu_2(OH)_3Cl$ and (2) $Cu_2(OH)_3NO_3$ grown on borosilicate glass frit; and (3) borosilicate glass grit with black CuO from decomposed $Cu_2(OH)_3NO_3$. Row A shows post-fungal test samples with corresponding frits all moistened periodically under protective plastic. Spherical material is nutrient placed on or adjacent to frits.

related phases.) In this work, Cu^{2+} and $(NO_3)^-$ are the only precursor species. Thus, glass frit surface chemistry had to supply the $(OH)^-$, at least initially. This is not unusual, because the surfaces of silica and silicate glass powders contain complexes of hydroxyl, hydronium, and HOH groups.[4] In turn, this explains why both growths occur only when glass powder is treated in nitrate solutions.

We tested the influence of glass surface area using unmilled borosilicate frit ($d50$ = 9 µm; $d90$ = 23 µm) and frit milled in deionized water ($d50$ = 3 µm; $d90$ = 6 µm), both treated with copper nitrate solution. Although we did not measure surface areas, we expect that they were significantly different. We washed frit plus $Cu_2(OH)_3NO_3$ deposits with deionized water and dried them. We then weighed samples, heated them to above 200°C to decompose the compound to CuO, and reweighed samples to calculate concentration of $Cu_2(OH)_3NO_3$ from weight loss. Unmilled frit yielded 0.2 g of compound per gram of glass, whereas milled frit produced 0.7 g of compound per gram of glass.

The larger value signals an overall increase in concentration of available hydroxyls. However, this does not mean that all hydroxyls for both values are provided solely by glass surfaces. For example, 0.7 g requires almost 20% of the weight of glass to be surface $(OH)^-$ and related complexes, whereas 0.2 g indicates only ~5%. Although 5% is possible, 20% is unreasonable. This might indicate that growth of the compound is not limited to frit surfaces—another mechanism may play a role to promote additional growth.

Reactions of Cu^{2+} and $(NO_3)^-$ and of Ag^+ ions with the surface chemistry of glass frit actually are quite complicated. We considered copper, because it offers some insight for the latter. Certainly, at incipient growth of $Cu_2(OH)_3NO_3$, the reaction must proceed according to

$$Cu^{2+}{}_{\text{solution}} + 2(NO_3)^-{}_{\text{solution}} + x(OH)\text{–}_{\text{glass surface}} \rightarrow$$
$$1/3xCu_2(OH)_3NO_3 + 1\text{-}2/3xCu^{2+}{}_{\text{solution}} + 2\text{-}1/3x(NO_3)^-{}_{\text{solution}}$$

We ignored excess H_2O in the above and a subsequent reaction. Although mass balance is maintained (x is unknown), charge neutrality of the solution is not, resulting in a net negative charge. This demands that another reaction or mechanism must cooperate to provide a neutralizing positive charge to the solution. We believe that surface hydrolysis of "Cu-OH-HOH +/- $(NO_3)^-$"-type charged complexes generates H^+ as surfaces evolve.

Surface hydrolysis is well-known in colloid, soil, and clay literature. For example, McBride[5,6] discusses complexes, such as $(CuH_2O)_6{}^{2+}$, $(CuH_2O)_4{}^{2+}$, and $Cu^{2+}\text{–}(H_3O)^+$, that generate H^+ when Cu^{2+} is adsorbed on clays. Liu et al.[7] demonstrate that dendritic Fe_2O_3 grows on the surface of Fe_2O_3 crystals as the complex $2(Fe(CN)_6)^{3-}\text{–}HOH$ releases H^+, which reduces pH from 7.27 to 6.76.

The original surface chemistry of frit changes as growth proceeds. If this model is correct, it follows that growth must continue, likely at an ever decreasing rate, until termination. If $x(OH)^-{}_{\text{glass surface}}$ describes a static concentration of hydroxyls, the reaction must stop when not enough is available to accommodate additional structural Cu^{2+} and $(NO_3)^-$ from solution. On the other hand, surface hydrolysis of copper complexes can produce additional hydroxyls from pre-existing HOH bound to glass and from HOH derived from solution as surfaces of the compound grow. In this case, growth of the compound can continue, but the reaction endpoint remains speculative.

In turn, the solution must become more acidic with increasing contribution of H^+. Although we conducted reactions only for 72 h, the unusually large concentration of $Cu_2(OH)_3NO_3$ discussed above supports continued growth. In addition, pH of the solution becomes somewhat more acidic (Table 1). In addition, pH of glass frit in deionized water becomes less basic

Table 1. pH of deionized water solutions containing borosilicate glass frit, $Cu_2(OH)_3NO_3$, and dissolved copper nitrate

Material	Conditions	pH
a. 30-g borosilicate glass frit, not milled	Soaked 24 h in 200-mL deionized water	10.4
b. 20-g $Cu(NO_3)_2$ hydrate	Dissolved in 600-mL deionized water	3.65
c. Combined a and b	In 800-mL total deionized water	4.64
d. Combination c	3 days at 82°C; growth of $Cu_2(OH)_3NO_3$ on frit	4.43
e. $Cu_2(OH)_3NO_3$ + glass from d	Washed repeatedly with deionized water and soaked 24 h in 200-mL deionized water	7.15
f. Deionized water		6.9

when $Cu_2(OH)_3NO_3$ is present, showing that the original surface chemistry is altered.

In antialgal tests of $Cu_2(OH)_3NO_3$ bonded to glass powder, the water remained clear for 6 weeks, but then a yellow-white material developed and covered the compound spread on the bottom of the glass container. At the container–compound interface, the material was discontinuous and gray-brown. Both yellow-white and gray-brown materials indicate annihilated or consumed algae.

We also grew the isostructural compound $Cu_2(OH)_3Cl$ on the same glass frit heated in a solution of dissolved $CuCl_2$. The reaction is subject to the same phenomena discussed for the nitrate analogue. This chloride is an alternative fungicide for crops,[8] but it is not phytotoxic, because it is relatively insoluble, in contrast to banned chemicals containing soluble phases, such as $CuSO_4$, that disperse through the environment (e.g., Bordeaux mix in vineyards). Antifungal testing confirmed that both compounds prevented growth of white and black fungi during a 1-month trial. In contrast, the CuO-glass product resulting from decomposition of both compounds above 200°C was less effective (Figure 5).

After an early stage of simultaneous ion exchange and reaction of silver with glass surface chemistry, we expected the latter process to hinder, if not eventually block, the former. Despite the minor issue involving Ag_2CO_3, we propose that the reaction proceeds similar to that of copper and, in simplest form, involves $(OH)^-$ according to

$$\mathrm{Ag}^+_{\text{solution}} + (\mathrm{NO}_3)^-_{\text{solution}} + x(\mathrm{OH})^-_{\text{glass surface}} \rightarrow x\mathrm{AgOH} + (1 - x)\mathrm{Ag}^+_{\text{solution}} + (\mathrm{NO}_3)^-_{\text{solution}}$$

We believe AgOH to be amorphous, but it is likely to have a more complicated chemistry associated with additional $(OH)^-$ or HOH. Amorphous phases are not unusual in colloid and clay chemistry. For example, Arias et al.[9] report “amorphous iron-precipitates,” also described as iron hydroxide, on the surfaces of kaolin treated in iron nitrate solution. To maintain charge neutrality in the above reaction, H^+ is provided by surface hydrolysis of charged surface complexes assumed to be similar to “Ag-OH-HOH” or “Ag-O-OH-HOH.” The latter could yield the observed Ag_2O as an intermediate product. If this model is correct, the same phenomena (e.g., continued reaction/deposition, evolving surface chemistry, and decreased pH) discussed for copper follow.

Summary

We implanted Ag^+ into the surfaces of a variety of glasses and glass-bonded ceramics by ion exchange, simply using an aqueous solution of $AgNO_3$ heated to 82°C. Ion-exchange kinetics can be altered by varying temperature and concentration of $AgNO_3$. These materials tested favorably as antimicrobial agents against *E. coli*.

We could not exchange copper ions using this method, but they were incorporated into bulk materials by addition to mixes before final processing at high temperature and by reactions of glass frit surfaces with nitrate solution. Some of the copper materials resisted growth of algae and fungus. Although not discussed, it should be appreciated that Ag^+ and Cu ions can be incorporated into glasses and glass bonds, the latter via addition to formulations before final processing followed later by ion exchange with the former.

Based on these observations, Refractron is developing another simple method to implant silver and copper on the surface of glass that bonds fingerprint pads (Figure 1, rectangular part at lower left).

Ag^+ and Cu^{2+}-$(NO_3)^-$ in solutions react with surface chemistry of glass frit to produce potentially useful adherent products if incorporated, for example, into polymers, paints, or fertilizers. Proposed reactions require surface hydrolysis of charged surface complexes that donate H^+ to maintain charge neutrality of solutions. The results warrant further study by interested researchers using more sophisticated methods.

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