A Preliminary Investigation into the Effects of Chelators in Accretion Removal from Historic Archaeological Glaze

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Los Angeles 2022

INTRODUCTION

In 2014, a rare *bleu persan* ceramic urn (OBJ-16JA-00008) was excavated by the Colonial Williamsburg Foundation's (CWF) Archaeology Department on the campus of the College of William & Mary in Williamsburg, Virginia. This vessel emerged fragmented and severely delaminated with 2,500+ glaze shards excavated along with almost 60 ceramic sherds.

The urn dates to the late 17th century CE, approximately 1675-1690 CE. It was excavated from various contexts within a sawpit in the South Yard of the Christopher Wren building. The flower urn is a highly delaminated earthenware campana shaped urn with two rope twisted handles that terminate in scrolls, though one handle is dissociated. The urn has a dark cobalt blue lead-tin glaze ground with white floral and scroll decoration in a *chinoiserie* style, known as *bleu persan*. The entire vessel is glazed, though the interior of the body and underside of the foot are plain blue.

After an initial cleaning of the glaze shards, several exhibited thick grey-brown accretions concentrated on the interior surface preventing a flush fit between the glaze and the ceramic body. In this case, the accretion removal was vital for detached glaze fragments to be re-adhered to the ceramic body.

Top: All ceramic sherds and glaze shards before treatment.
Bottom: During treatment of reattaching glaze shards.

GOALS

- To narrow down previous research using chelators on archaeological glass/glaze
- Test chelator efficacy at a neutral pH
- Use a material that is more widely/globally available

Samples tested; Samples A-F with ammonium citrate, Samples G-L with EDTA, and M as control. BT.

MATERIALS & METHODOLOGY

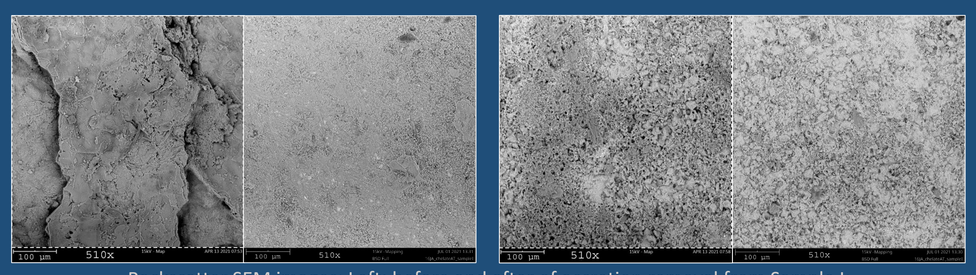
Ammonium Citrate, dibasic $C_6H_{14}N_2O_7$
Disodium EDTA $C_{10}H_{16}N_2Na_2O_8$

Concentrations of 3% and 7% in deionized water, determined by the literature with three different dwell times: 5 minutes, 12.5 minutes, and 20 minutes

The pH of each chelate solution was buffered with sodium hydroxide via titration to neutral to reduce variability. As vitreous objects are subject to various forms of decay in both acidic and alkaline environments, keeping the solution at a neutral pH while determining the best concentration and application time will help inform future treatment decisions. Previous studies on glass tested various pH levels and found that both alkaline and acidic pH affect glass and enhance decay processes.

Chelate solutions were applied via poultice with a Japanese tissue barrier and the solution in cotton wool. Aluminum foil and a crystallizing dish were placed over the sample to decrease the evaporation time. After each application, the surface of the glaze was cleared three times with swabs and deionized water. The pH of the surface was measured before, just following, and after clearance.

The solutions at each concentration and dwell time were tested only once with one sample.



Backscatter SEM images; Left: before and after of accretion removal from Sample I;
Right: Before and after of interior glaze surface of Sample I. The chelators assisted in removal of the accretion with little effect to the glaze.

Left: before and after accretion removal with 7% EDTA for 12.5 minutes in raking light;
Right: Adhering clean shard onto interior of sherd.

RESULTS

While as expected due to pH, the chelator did not fully remove the accretions. The most optimal chelator softened the accretion enough for easy mechanical removal. The chelator solutions that did not pass caused fracturing and difficulty in removal.

After performing twelve tests, results indicate that 7% EDTA for 12.5 minutes worked equally as well as 3% EDTA for 20 minutes. The glaze shards experienced no fracturing and the crusts were easily removed. 7% EDTA for 12.5 minutes was chosen to reduce contact time with the material.

Ammonium citrate samples experienced fracturing during mechanical removal and no particular test increased the ease of crust removal. The fracturing is most likely due to the creation of a lower pH atmosphere around the area of the glaze as it dissolves.

SEM-EDS results indicate the accretion itself is calcium carbonate based with trace amounts of silica, aluminum, iron, lead, manganese, potassium, sulfur, and yttrium.

SEM-EDS analysis of the soil indicates considerable amounts of calcium and elevated levels of magnesium due to burned material and a large cache of oyster shells, possibly contributing to the development of the accretion.

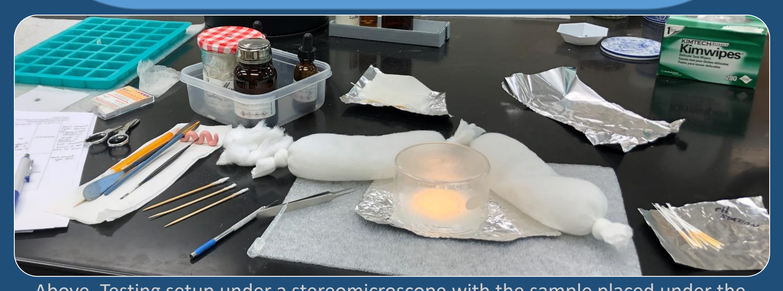
Completed treatment, Photos by Jason Copes. Copyright Colonial Williamsburg Foundation.

CHARACTERIZATION

Experimental samples were characterized and evaluated for optical and chemical changes with optical microscopy (OM) and scanning electron microscopy coupled with energy dispersive spectroscopy (SEM-EDS) before and after treatment.

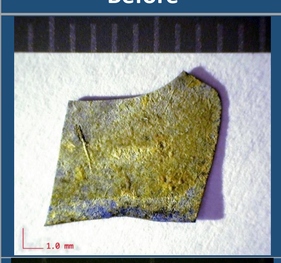
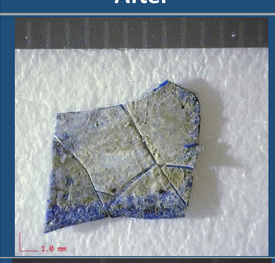
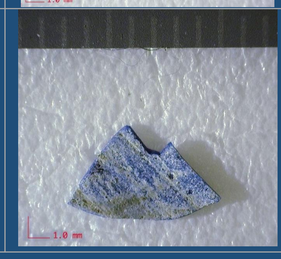
The glaze, accretion, and ceramic body were characterized with these methods. Each one was characterized in three locations within each sample. Focus was given to the effects on the glaze as well as the ease of accretion removal.

Identification of the crusts present on all glass samples was necessary to determine the effectiveness of the various concentrations applied. The ceramic body was characterized with SEM-EDS to ensure that crusts are not part of the ceramic itself.



Above, Testing setup under a stereomicroscope with the sample placed under the aluminum foil and a crystallizing dish with clean cotton swabs and pH strips prepared.

Below, table demonstrating the average effects of each chelate solution

Sample	Before	After
C Ammonium Citrate 3% 20 minutes		
I EDTA 3% 20 minutes		

Various glaze sherds exhibiting the accretion on the interior, prior to cleaning

CONCLUSIONS

While chelators remove different metallic salts more effectively at specific pHs, the outcomes from treatment at neutral pH demonstrates that chelation is still successful enough for treatment to be carried out on calcium-based accretions.

These glaze shards exhibited few condition issues, the methodology may need to change and adapt to treat more deteriorated glaze/glass.

Further tests with each chelator solution can be tested with more samples with varying condition issues to narrow down efficacy and a more optimal pH, as well as more diverse accretion compositions and burial environments.

Future research includes performing a field test under non-laboratory environmental conditions. Field testing is beneficial and necessary to determine efficacy and ease of use in non-ideal conditions.

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This research was conducted during a Kress Fellowship undertaken in Archaeological Conservation 2020-21 at Colonial Williamsburg under the supervision of Kate McEnroe.

ACKNOWLEDGMENTS

Samuel H. Kress Foundation, Colonial Williamsburg Foundation, College of William & Mary, Kate McEnroe, Jack Gary, Sean Devlin, Patricia Silence, Kirsten Moffitt, Kelly Ladd-Costro, Susan Kern, Jason Kirk, Jay Stephens, Angelika Kuettner, Emily Zimmerman, and Melanie Pereira