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Author(s): Richard Barden

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Compilers: Julie Lauffenburger and Virginia Greene


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THE ANALYSIS AND RECONSTRUCTION OF ISLAMIC GLASS-FRIT CERAMICS, AND COMPARATIVE METHODS OF DESALINATION

Richard Barden

The Freer Collection

The Freer Gallery of Art has a collection of medieval Islamic glazed glass-frit ceramics, from Raqqa, Syria. Raqqa was a major medieval Islamic ceramics manufacturing city located in the northeast section of Syria. The collection at the Freer Gallery consists mostly of functional wares such as dishes, bottles, and storage containers. There are also a few figurines.

Ceramics with frit as a major component (usually about 20%) of the body are known as glass frit ceramics. Frit is made from a mixture of silica and potash, and/or soda ash, melted together to form a glass, which is ground into a powder.

Numerous pieces in this collection have deteriorating glazes and obvious salt problems. The question of how to treat ceramics with deteriorating glazes and salt problems, can be complicated. The standard, static water bath method of removing salts is effective, but can take several days to several months to be completed. Does this treatment cause a loss of material from a ceramic body or glaze? If there is a loss, is it significant? Is this treatment more detrimental to ceramics with deteriorating glazes?

Regardless of the answers to these questions, the best policy would be to use the least intrusive method with the shortest desalination time. The objective of my research was to reproduce this glass frit ceramic, and compare four methods of desalination. My goal was to determine the most efficient method, including how labor intensive and complicated the methods are.

The tests performed in this research were done with the practicality of treatments in mind. Although the samples were desalinated several times, which would not be true of an actual object, I performed the desalination procedures as I would treat a ceramic object in a museum environment.

Analysis of the Ceramic

Analysis of the Raqqa ceramics was done using ten samples taken from sherds in the Freer's Raqqa study collection, and five samples taken from sherds excavated at Rayy (another major site of medieval Islamic ceramic production) in the collection of the University of Pennsylvania Museum. Analysis was performed using scanning electron microscope and microprobe.

SEM analysis was performed on five of the Freer samples. The elements were identified, and their percentages determined, in the glaze, the inter-particle glass, and the body.
Silica was identified as the largest component in each area of the ceramic, ranging from 71.5 to 77%. The elements that are the modifiers and fluxes make up 21.5% in the glaze, 25% in the inter-particle glass, and 19% in the body.

Using SEM photographs it was possible to see the extent of vitrification, the integration of glaze and body, and the degree to which the components of the body were blended together.

SEM microprobe was used on all fifteen samples to determine which compounds, in what percentage, are present in the ceramic. Ninety-nine percent of the ceramic is made up of the oxides of silica, sodium, calcium and magnesium. The remainder is made up of the oxides of aluminum, iron and potassium.

A small unglazed sample from one of the Raqqa shards was crushed and sieved through various sized mesh screens. Each portion of the sample caught by the individual screens was then weighed. This gave a weight to size ratio. Approximately two thirds of the weight was in particle sizes under 420 microns, one third of the weight had particle sizes greater than 420 microns.

This analysis, in conjunction with the use of historical references and other modern analysis of Islamic ceramics, gave me the data I needed to reproduce this type of glass frit ceramic.

**Reproduction of the Ceramic**

The first step in the reproduction of the ceramic was to create a frit of similar chemical composition as the inter-particle glass. The frit was made from quartz, soda ash, potash, magnesium and calcium carbonates and pyrophyllite clay. These were melted together to form a glass. The molten glass was poured into cold water to shatter it, and then ground into a frit.

After the frit was produced, I mixed the materials for the ceramic body, which is composed of silica, frit, and clay. The silica was of various sizes to match the size to weight ratio of the Raqqa ceramic.

All the constituents for the body were mixed together dry, and water was then added. When the clay body was at an appropriate consistency it was wedged, rolled into 1/4 inch thick sheets and cut into tiles four inches long, and two inches wide.

After the tiles were dry, their tops were dipped into a glaze mix. A blue glaze was made by adding 0.8% copper oxide to the raw materials of the frit.

Historically these ceramics were fired around 1000° C. Various firing times and temperatures were tested using several tiles. After firing, the test tiles were broken open, and a microscopic
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comparison was made between the test tiles and the Raqqa shards. The tile that most resembled the Raqqa ceramic was chosen, and its firing time and temperature used to fire the rest of the tiles. The firing sequence chosen was the following: one hour at 200°C, one hour at 500°C, 20 minutes at 700°C, 20 minutes at 750°C, fifteen minutes at 800°C, and one hour at 1000°C.

In all 34 tiles were successfully fired. Each tile was given a number, 1 through 34, on its bottom. One tile was set aside as a control.

Analysis of the Salts and Choice of Salts for Testing

Salts from the desalination of a Raqqa jug (F 05.243) were reclaimed and analyzed to help select the salts to be used in the desalination tests. The problems of this object were typical of the collection, and I consider these salts representative of salts found in this ceramic collection. A sample of these salts was analyzed by SEM and X-ray diffraction.

The Raqqa jug contained a complex mixture of salts. X-ray diffraction was not able to identify a single, specific mineral to match the salts. However, several minerals came close to matching segments of this analysis, including sodium chloride, potassium sodium chloride, and sodium nitrate sulfate hydrate.

Potassium chloride was chosen as the salt to use in the desalination tests, as potassium and chloride were present in the Raqqa salts, it is commonly found in archaeological ceramics, it is readily soluble in water, and can be easily absorbed into, and removed from, the ceramic tiles.

Desalination Methods and Procedures

Salts were absorbed into the tiles through capillary action using a two molar potassium chloride solution. The tiles were placed on their short side in the salt solution. The solution covered approximately one inch of the tile, leaving most of the tile open to the atmosphere. To keep the salts evenly distributed in the solution, and to aid in their absorption, the bath was kept under constant mild agitation using magnetic stir-bars. The tiles were in each salt absorption bath for five days.

The tiles were infused with salts and desalinated three times. The average amount of salts impregnated into the tiles varied with each infusion. The average weight gain was 2.4 grams, about 3% of the average tile weight.

Each desalination bath contained 1.5 liters of distilled water. Conductivity was used to determine the end point of the desalination. Because of the relatively quick desalination times the end point chosen was a conductivity measurement below 50 micromohs after 24 hours of soaking.
After each absorption or desalination bath, the tiles were air dried for two days, oven dried at 100° C for one day, and left for three days to return to ambient temperature and relative humidity.

As a measure of the amount of salts absorbed into and removed from the tiles, the tiles were weighed before any tests were performed, after each salt infusion, and after each desalination test. The tiles were weighed dry, and to a 10,000th of a gram.

Four desalination methods were compared: (1) the standard method, (2) the bath changes method, (3) a circulating bath with bath changes, and (4) electrophoresis with bath changes.

The standard method consists of placing the tile on risers, and then immersing it in a distilled water bath. After 24 hours, the conductivity of the solution is measured, and the bath water changed. This continues until the treatment is complete.

The second method of desalination, "bath changes", uses the standard method, with the bath water changed between one and five times in the first eight hours. The baths were then changed every 24 hours until the treatment was completed.

The third method of desalination combined circulating water with bath changes. Using a peristaltic pump and plastic hose the water was circulated through the container six times per hour. The water entered at the top of the bath on one side, and was withdrawn from the bottom on the opposite side of the container. The bath water was changed after the first half hour, and then after every 24 hours.

The final method of desalination was electrophoresis with bath changes. Electrophoresis is the use of electronic fields to attract ions. This method speeds up the dissolution of the salts and increases their migration away from the ceramic. As the salts dissolve the ions are attracted to electronic fields of opposite charge, and repulsed by the fields with the same charge. The bath water was changed after the first half hour, and then after every 24 hours. Carbon electrodes were used, and a current of one tenth of an amp with enough voltage to complete the circuit. The electrophoresis ran for the entire time the tiles were immersed.

Results of desalination

Before any tests were performed, the first step was to immerse the recently fired tiles in static distilled water baths to insure that all soluble material was removed. This created a more uniform standard, and an equalized, beginning, conductivity level. The tiles were immersed for a total of thirteen days, until conductivity was below 100 micromohs for three consecutive days. Ending conductivity was 33 micromohs for the thirty-three tiles.
A total of 84 desalination tests were performed.

Of the tiles that were desalinated using the standard method, only seven percent were desalinated in 48 hours, seventy-three percent in 72 hours, and the remaining twenty percent took 96 hours. No other method took 96 hours to desalinate a tile.

For the bath changes method, sixty-four percent of the tiles were desalinated in 48 hours, the remaining thirty-six percent in 72 hours.

To break down the results of this method further, of the tiles with two baths in the first eight hours, sixty-four percent were desalinated in 48 hours, and thirty-six percent in 72 hours. After 5 bath changes, the desalination rate increases to seventy-three percent desalinated in 48 hours, and twenty-seven percent in 72 hours.

The circulating bath tests desalinated eighty-six percent of the tiles in 48 hours; the remaining fourteen percent took 72 hours.

The combination of electrophoresis and bath changes resulted in ninety-three percent of the tiles desalinated in 48 hours.

**Conclusions**

Compared to the standard method, all the other desalination methods were more efficient. The bath changes method is fifty-seven percent more efficient than the standard method. Even one bath change within the first eight hours greatly decreased the desalination time.

However, increasing the bath changes to five times in the first eight hours decreased the desalination time by only nine percent. This decrease is not significant enough to justify the added labor or the possible harmful consequences to the ceramic due to the added handling.

The circulating bath method was twenty-two percent more efficient than bath changes, and electrophoresis twenty-nine percent more efficient. However, both methods are more work-intensive, requiring more equipment, monitoring, and electricity.

The tubes for the circulating bath cracked several times from the action of the peristaltic pump. The water was then completely pumped out of the container and the tile dried. The possible damage to an object if the ceramic dries out before the salts are removed needs to be considered. The pump should be operated only during working hours, and the hoses examined periodically and replaced at the first sign of wear.

During electrophoresis, excessively high current caused the cathode to deteriorate, and particles
from the electrode transferred to the tiles. Therefore the current must be set at proper levels and monitored.

Another question concerns the loss of ceramic material due to desalination, and its significance. In my tests the tiles weighed less after the desalination, but the average weight loss was 9/100 of a gram, approximately one tenth of one percent of the average tile weight. This loss occurred after repeated baths and oven drying which is not normally done.

Other questions have not yet been answered: Would the circulating bath remove more ceramic material than a static bath? When using electrophoresis, do the electric fields pull out soluble ions from the ceramic that would be unaffected by a static bath? I hope that further research will be performed to find the answers.

I would not hesitate to use the bath changes method. Changing the bath one time within the first eight hours will greatly decrease the desalination time, and this method will not harm the ceramic any more than the standard method. I would also use a circulating bath once the problem of the hoses had been solved.

Electrophoresis appears to be the most efficient method, though I have reservations regarding its use. I would like to find better electrodes, and feel more research should be performed before this method is widely used.

Author's Address