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Article: Desalination parameters for Harappan ceramics
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Source: *Objects Specialty Group Postprints, Volume Three, 1995*
Pages: 70-76
Compilers: Julie Lauffenburger and Virginia Greene
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# DESALINATION PARAMETERS FOR HARAPPAN CERAMICS

Katherine A. Holbrow, Emily Kaplan and Harriet F. Beaubien

**Abstract**

In a pilot study to determine what soluble salt content would produce minimal damage in porous, low-fired archaeological ceramics, terra cotta bangle bracelet fragments excavated at the Indus Civilization site of Harappa, Pakistan, were desalinated to different controlled salt levels and subjected to various tests. Data from these tests were used to design a long-term study at the site. Preliminary results from the pilot study show that although some soluble salt remains after desalination treatment and in accelerated aging tests, no efflorescence or damage was evident in variously desalinated samples.

## 1. Introduction

Numerous terra cotta artifacts from the Indus Civilization, the earliest fully developed urban society in South Asia, are currently being excavated at the archaeological site of Harappa, Pakistan. The extremely high soluble salt content of the soil, excavated materials, and available water, in combination with severely limited resources, has fostered an ongoing research project intended to determine what soluble salt limits should be considered acceptable in desalination treatments.

The Indus Civilization encompassed a geographic area which included what is now Pakistan, Afghanistan, northwestern India, and parts of Iran and Central Asia. The archaeological site at Harappa includes a walled city which is laid out in a grid and built largely of mud brick and fired brick. Ceramic artifacts commonly found there include not only vessels but small figurines, toys, and ornaments, all displaying extraordinary standardization. Most excavated material from Harappa dates to the civilization's "mature" or flourishing period, roughly 2600-1900 BC.

Conservation at Harappa has been conducted through the Smithsonian Institution's Conservation Analytical Laboratory (CAL) since 1986. Under the auspices of the Archaeological Conservation Internship Program initiated in 1990, interns and fellows have worked at the site under the direction of Harriet F. Beaubien, treating copper alloys, gold, stone, ivory, bone, shell, and faience as well as terra cotta and other types of ceramics.

Research on desalination to date has focussed on evaluating damage to ceramics, identifying salts and their behavior, and designing efficient desalination treatments. Although desalination of ceramics is a conventional conservation treatment, determining a final or "acceptable" level of salt (i.e. salts allowed to remain in the ceramic), has been anecdotal or arbitrary. This is in part because "zero" conductivity, as measured in the final bath, has seemed both the safest option and an attainable goal under most conditions.

Harappa offers a somewhat different perspective on the problems of soluble salts and ceramics, because of a combination of extreme circumstances. Firstly, the salt content of excavated material at the site is extraordinarily high. Conductivity of waste water from the initial baths for ceramics invariably registers over 5000 µmohs/cm. Secondly, available water is very high in soluble salts. Measurements vary, but tap water from wells can have a conductivity of 3000 µmohs/cm, while riverine irrigation canal water can have a conductivity of 300-500 µmohs/cm. To desalinate ceramics below this level, water must be distilled. As at many archaeological sites in remote locations, power to run the stills is limited and expensive, as is access to equipment, parts, and supplies. Finally, the volume of excavated material is enormous: roughly 6000 batches of artifacts were processed through the conservation laboratory in 1994, and over 7000 were processed in 1995 (a batch may contain 30 or more items). Of these objects, about 50% are ceramic, all of which contain substantial amounts of soluble salts. Of these, a very large proportion are low-fired, terra cotta bangle bracelet fragments which are considered study pieces and are not accessioned.

In sum, desalination and processing of such a large quantity of artifacts puts a great strain on all available resources, which in turn can limit treatment of vulnerable accessioned objects. A substantial amount of time, labor, power, and water could be saved if the desalination of study items like bangle fragments were limited without compromising their stability.

## 2. Project Goals

The question which prompted the development of the research project is, therefore, whether some amount of soluble salt could be safely left in a terra cotta object such as a bangle bracelet fragment. This "safe" salt level (as measured by its terminal conductivity level) would not affect the stability of the ceramic under standard storage conditions at the site.

The project was conceived of in two parts: the research design and pilot tests, or "pilot study", and the "long-term study" now taking place at CAL and at Harappa. The pilot study was intended to test procedures; results from these would be used to refine the experimental design for the long-term study. The latter would provide a "real time" basis for evaluating the research question. Other CAL archaeological conservation internship program participants, including Marie Svoboda and Tania Collas, are involved in both the pilot and long-term studies, along with CAL objects conservation staff.

## 3. Pilot Study

In the pilot study, procedures in four areas of experimental design were considered and selected for the preparation of samples at Harappa, and for preliminary analysis at Harappa and CAL. These areas were sample selection and treatment, characterization of the samples, evaluation of

change, and aging methods.

**Sample selection and treatment**

Two commonly found bangle types were used as samples: one small (approximately 1 cm) in diameter, and the other larger (1.5 to 2 cm in diameter). Five of each type of bangle were cut into six pieces, then pieces from each bangle were desalinated in groups to levels of 400, 300, 200, 100, and zero μmohs/cm. Remaining samples (one from each bangle) were left untreated, as controls. Two additional examples of the large type were also processed for destructive analysis. During desalination, the water-to-ceramic ratio used was 2:1 by weight, and salt levels were measured with a LaMotte conductivity meter. Conductivity levels of the final baths were maintained for 24 hours.

This range of salt levels was selected because of the significant implications for water usage. The higher end -- 400 μmohs/cm -- could be achieved at Harappa using a substantial amount of irrigation canal water and a minimal amount of distilled water or, conceivably, no distilled water at all. If desalination of bangle fragments could be terminated at this level, it was estimated that current distilled water use could be cut by approximately 90%, saving considerable time and energy. Even desalinating bangle fragments to 100 μmohs/cm rather than zero would result in substantial savings. In addition, each drop of water with a conductivity between 100 and 400 μmohs/cm could be re-used in the desalination process. The 100 μmohs/cm increments were chosen because they made the tests easier to execute and interpret.

**Characterization of the samples**

Because paste composition, porosity, and firing temperature can all affect the response of a ceramic to soluble salts, visual examination and several instrumental techniques were used to characterize the paste of the bangles. Variations in firing conditions were apparent from the presence of black cores in samples from one small and two large bangles.

Scanning electron microscopy (SEM), performed on the control and the "zero" samples from the two extra bangles, was used to assess porosity and variations in firing; the black-cored bangle appeared noticeably more vitreous. Energy dispersive x-ray spectrometry (EDS) showed elements typical of a ceramic including silicon, aluminum, oxygen, iron, and magnesium. CAL research chemist M. James Blackman, who has performed earlier analyses of Harappan ceramics (Blackman and Vidale, 1989), assisted in examining petrographic thin sections to better understand porosity, temper, and other inclusions. Thin sections were prepared from the "zero" samples of three small and three large bangle fragments. Examined under crossed polars, these showed a highly porous ceramic, with numerous calcitic inclusions and fold lines indicating manufacture by rolling.

Characterization of the salts found in Harappan ceramics has been carried out at CAL in previous years using efflorescent salt samples, examined with x-ray diffraction (XRD) by Harriet F. Beaubien (Beaubien, 1989-1993, unpublished). High proportions of sodium chloride and potassium chloride were found, as well as sodium sulfate and calcium sulfate. During the SEM/EDS examination of the bangle samples, sodium chloride was clearly identified. In a related research project using an unprocessed bangle and a sherd, salts were collected at CAL from sequential desalination baths. These are being analyzed to investigate the dissolution and diffusion trends of the constituent salt species; sodium and potassium chlorides and calcium sulfate were identified using XRD with EDS.

SEM/EDS provided important information and will continue to be used. During SEM examination of the ceramic structure of the bangle fragments, salt crystals in the matrix were observed before and after desalination and aging. A significant result of this examination was the recognition that salts were present in all samples examined, even those desalinated to a conductivity of "zero" μmohs/cm. Pockets of salt crystals, identified as sodium chloride using EDS, were visible throughout the "zero" sample.

## Evaluating change

Weight measurements were selected as a method to measure loss of ceramic material through the action of salts, but it is not yet clear that changes will be detectable on the equipment available at the site. Scratch tests, stress tests, and indentation or puncture tests were considered as means to evaluate mechanical change. While scratch tests carried out on the "zero" samples generally distinguished the harder black-cored samples from the others, no consensus could be reached on the validity of scratch or indentation tests for damage evaluation purposes. Given the small size and irregular shape of the samples, meaningful results would be difficult to obtain with standard mechanical testing equipment and these tests were discarded.

Visual examination was selected as the primary method for evaluating the samples. At the site, a simple comparison of treated and control samples with the naked eye was performed by excavation participants. However, differences between samples desalinated to different salt levels were not apparent before aging. Examination with a binocular microscope at the site proved useful for fine distinctions between samples, and samples brought back to CAL will be further examined in this way. To assist in the evaluation of change over time, a system of degradation with the use of photographic standards is being developed.

## Aging methods

Short term accelerated aging in a commercial cycling humidity and temperature chamber at CAL was attempted, but the chamber proved difficult to control, and no changes were noted in the

control and "zero" samples from the two extra bangles. More successful was cycling in chambers regulated by desiccated silica gel and containers of water. In an ongoing experiment at CAL, the small bangle samples were cycled between 10% and 90% RH at one week intervals, for six months, at ambient temperature. Preliminary results show that only the control samples (i.e., those not desalinated) exhibit any visible efflorescence or damage. All samples desalinated to 400 μmhos/cm or lower appeared unchanged.

## 4. Long-term Study

The long-term study began in the spring of 1995 and is now underway at Harappa and at CAL. The results of the pilot study were used to support this longer study and suggested modifications in the experimental design.

### Sample selection

To reduce variables introduced by differences in bangle types and firing history, the sample pool for the long-term study was narrowed to the small bangle type only. The number of samples was increased to 60 bangles of a uniform appearance and size, cut into 378 samples, to allow for periodic destructive analysis. Groups of samples were treated by desalination to different controlled conductivity levels, again requiring maintenance at the final level for 24 hours. Conductivity of the different groups measured zero, 100, 200, 300, and 400 μmhos/cm; undesalinated controls are estimated to have a conductivity of greater than 5000 μmhos/cm.

### Characterization of the samples

Characterization of both the ceramic and the salts will continue at CAL. Eighteen sample pieces will be sent to Blackman for neutron activation analysis of the paste and for thin section petrography. Continuation of systematic analysis of soluble salts and their diffusion rates is planned at CAL, using evaporates from sequential desalination baths of the bangle samples processed for the long-term study.

### Evaluation of change

The samples will be examined periodically for changes in visible salt efflorescence, surface and structural change, and changes in weight. Visual changes will be quantified by comparing samples to photographs of a series in increasingly degraded condition. Analysis using SEM will continue on selected samples as they age, both for characterization and for indications of microstructural damage.

**Aging methods**

For the long-term study, real-time aging of the treated samples is taking place under real storage conditions at Harappa. Like most buildings at the site, the ceramics storeroom at Harappa is brick, which serves to insulate it somewhat. However, Pakistan's temperature and relative humidity fluctuations are extreme, and salts are likely to deliquesce many times during a year. The samples will be examined annually at Harappa, over five to ten years, with selected samples periodically brought back to CAL for analysis. Accelerated aging tests are planned at CAL to support possible expansion of the study's selected desalination levels.

## 5. Conclusions

While the long-term project is in its earliest stages, the pilot study provided many useful indicators for experimental design as well as some interesting conclusions. The presence of salt crystals in all samples, including the one desalinated to the lowest detectable conductivity limits, suggests that desalination treatments are not as effective as may have been thought. The fact that preliminary aging tests produced damage over time only in the "control" (i.e. undesalinated) samples, while all others remained in stable condition, suggests that leaving some salt in these ceramics may well be a safe conservation option. Determining how much salt can safely remain, and under what environmental conditions, will require further research.

The absence of damage and efflorescent crystal growth in the aged, partly-desalinated samples needs to be considered in another light as well. Situations arising in the field can be difficult or impossible to replicate in the laboratory; the conditions, durations, and results of accelerated aging cannot be correlated specifically with real conditions. Although damage was evident in the laboratory-aged undesalinated samples, they did not show salt growth comparable to that seen at Harappa despite their high salt content. The largest salt crystals obtained in the laboratory were minuscule in volume compared to salts found at the site. Similar failures have been reported anecdotally by other conservators. The pilot study prompted a prioritization of goals, and it was resolved that the central focus of the project was *not* to mimic soluble salt growth in the laboratory, but to determine practical desalination limits in a specific situation. This resolution underlies the decision to use real-time aging on the samples in storage at Harappa.

A real-time aging study is rewarding and possible in this case, where the value of obtaining useful results outweighs the disadvantage of the time needed to get these results. The Harappa excavation offers a unique research opportunity including the extreme nature of the salt problems, and the availability of sample material for use in tests. More importantly, Harappa is an established, ongoing excavation and closely affiliated to the conservation research community at CAL. Such fortunate circumstances make a five- to ten-year study possible.

**Acknowledgements**

We offer sincere thanks to everyone who participated in this project, especially to Carol Grissom, head of objects conservation at the Smithsonian Institution's Conservation Analytical Laboratory; to Drs. Richard Meadow, J. Mark Kenoyer, and Rita Wright, directors of the Harappa Archaeological Research Project; and to the Samuel H. Kress Foundation. The generous support and encouragement of all made this project possible.

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