12th International Congress on the Deterioration and Conservation of Stone
Columbia University, New York, 2012

THE PRESERVATION OF SANDSTONE RELIEFS AT THE ARCHAEOLOGICAL SITE OF TAJÍN, MEXICO, USING COLLOIDAL SILICA

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Abstract

The Archaeological Site of Tajín was the biggest and most important prehispanic city of the north coast of the Mexican Gulf; it reached its peak from the early ninth to the early thirteenth century C.E. Currently, it is surrounded by jungle and stands in the vicinity of areas of petroleum extraction. At this World Heritage Site several constructions have detailed religious and symbolic scenes carved on carbonate-cemented sandstone, which suffers from diverse deterioration, mainly weathering, flaking, and often extensive loss.

The first plasters applied in the conservation of these reliefs were made of synthetic polymers or lime without good results. These materials differed in color, texture and porosity from the original material; they were difficult to apply and often stained the stone during application and after weathering. After time, they also suffered from cracking and detachment.

Fills prepared with colloidal silica showed good initial results for the treatment of the sandstone reliefs subject to tropical environmental conditions and air pollution. Colloidal silica-based plasters have been tested for one year on site and have shown better endurance, stability, and appearance than the previously applied plasters. The plasters were also tested as protective surface coatings for the sandstone against environmental deterioration and acidic pollution at the site.

Petrographic studies and nitrogen adsorption-desorption techniques were used to characterize the plasters in order to evaluate their long term durability and compatibility with the original sandstone, as well as future alteration.

Keywords: colloidal silica, sandstone, Tajín reliefs

1. Introduction

Sandstone was extensively used at the archaeological site of Tajín, the biggest and most important prehispanic city of the north coast of the Gulf of Mexico. Here, most of the buildings have a core constructed of stone and earth rubble covered with close-fitting sandstone flagstones assembled with minimal use of mortar. At this World Heritage Site, detailed bas-reliefs on tablets, columns, friezes, panels and altars depict religious and mythological scenes that illustrate the beliefs of its inhabitants.

Tajín reached its peak between the early ninth and early thirteenth centuries C.E. While originally related to the important site of Teotihuacan, Tajín was able to survive the fall of its powerful neighbor, probably due to its own strategic location along the trade routes of Mesoamerica. Although the collapse of Tajín started around the eleventh century (Soto 2009), it was not completely abandoned; even today small communities have survived around the site, and it is still part of the inhabitants' daily walk to school and work.

Tajín is undergoing formal preservation of its wall painting and stone elements through a project carried out by Mexico's Instituto Nacional de Antropología e Historia (INAH) Department of Conservation (CNCPC). This project, which started in 2008 and is slated to last until 2020, includes not only preservation and restoration procedures but also documentation, maintenance, dissemination, training of local employees and applied research for conservation issues. This paper describes the preliminary results of ongoing research for the use of colloidal silica for the conservation of the sandstone reliefs at Tajín.

2. The sandstone problem at Tajín

The sandstone at Tajín is affected by various types of deterioration, presumably caused mainly by environmental conditions and intensive weathering. Deterioration is manifested mainly by exfoliation, detachment and erosion, which have resulted in the extensive loss of material from both flagstones and relief. The decay also includes cracking, deformation, efflorescence, discoloration and diverse biological colonization (Figure 1).

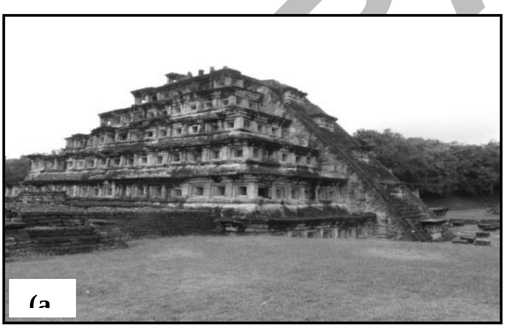

Figure 1. (a) Pyramid of the Niches, best known building at Tajín **(b)** Exfoliation, flaking, and weathering at one niche. *Courtesy of INAH.*

While further research is required to fully understand the causes of deterioration at Tajín, a number of factors undoubtedly play a role. Variations in the composition of construction materials may account for some of the observed diversity in deterioration. Tajín is surrounded by rainforest, with a Senegal-type climate characterized by high heat and humidity throughout most of the year. Hurricane season runs from June to October, while the "nortes", cold fronts with winds and sometimes rain that come from the north, can occur during the rest of the year. The geologic stratigraphy comprises three levels: the middle layer is semi-permeable, while the third is impermeable due to the presence of clay, which means that the large quantities of water which fall during the rainy season are trapped in the uppermost level. During the 1981-1983 season, a drainage system was installed to reduce the problem (Bruggermann 1992), but lack of maintenance of the system has caused water levels to rise again, favoring mobilization and efflorescence of salts from sources such as cement from previous interventions, while flagstones suffer stress from the contraction-expansion of their autochthonous clays during wetting and drying cycles (Bruggermann 1992).

Concern towards air pollution and acid rain at this area has favored a daily monitoring. Large-scale and local meteorological conditions in the region of Tajín favor transport from the east and north and are a source of potential acid precursor emissions. However, the relationship between transport pathway and precipitation acidity is still not clear and ongoing research is done (Kahl et al. 2007).

3. Selection of conservation materials

Around the 1970´s several panels decorated with reliefs were first treated (Bruggermann 1992). At that time, cement plasters were used for structural consolidation, while plasters for fills and edging were made with lime combined with synthetic polymers. These materials differed in color, texture and porosity from the original material; they have often stained the stone during application. After time, they also suffered from weathering, cracking and detachment.

During 2008, some of the most decayed reliefs were again treated to prevent further deterioration. The treatment included the edging of flakes to prevent detachment, the filling of areas of loss and the application of a protective surface coating in extensively weathered areas. Lime, crushed sandstone, earth and sand were employed as the conservation material for treatment in 2008-2010. The plasters were evaluated immediately after application as well as every three months, and showed unsatisfactory results for the treatment: edging and fill plasters suffered weathering, cracking and detachment, while the protective surface coating was aesthetically incompatible with sandstone, even although pigments and sand were used to match colors and texture as much as possible.

In 2011, an effort was made to find an alternative to the unsatisfactory materials used in previous treatments. Colloidal silica was selected as a test binder for plasters, due to its chemical and aesthetic compatibility with the silica stone system, its low toxicity and ease of use. It was selected over ethyl silicate-type binders because it does not react chemically with the stone substrate, resulting in a softer and more reversible plaster material.

4. Colloidal silica in conservation

Colloidal silica is a suspension with a determined volume fraction of SiO_2 spheres in various solvents. The particle size of the silica colloids ranges from 30 to 100 nm. Depending on the solvent, temperature and humidity, the drying and sedimentation of the SiO_2 particles differs (Okubo et al. 2008; Okubo et al. 2006). Colloidal silica is used in many industrial applications such as polishing slurries, catalysts, composite coatings and adsorbents (Kobayashi et al. 2005).

Colloidal silica has most often been applied in conservation as consolidant for stone, plasters and paint layers (Biscontin 2002; Chandra and Liping 1999; Malaga et al. 2000, Mangio and Lind 1997; Moropoulou et al. 2000; Mosquera et al. 2005; Schindler 2005; Zendri et al. 2006; Lithgow and Stewart 2001), although it also has been used as a component in grouts (Christaras et al. 2002). Colloidal silica has also been applied to limestones and lime plasters, sandstone and volcanic tuffs (Elías 2007).

A number of studies describe the use of colloidal silica as a binder for fills and sacrificial layers, and provided useful information for the tests described here. In examples, which included colloidal silica in sacrificial layers, it was found that the penetration of the silica and therefore adhesion of the protective layer can be controlled through silica dilution, and by exploiting differences between the silica solution and substrate pHs (Kozlowski et al. 1992; Stepien et al. 1993). There is also an interesting example of colloidal silica used as a binder for sandstone repair mortars and sacrificial layers, in which the compositions of the mortar and sacrificial layer were based on the tested properties of the sandstone to be repaired. The sacrificial layer was composed of ground sandstone and silica. This study noted that treatment with high pH silica solutions may cause severe color changes in stones containing iron compounds sensitive to changes in pH (Kuhlenthal et al. 2000; Simon et al. 2006; Snethlage 2000).

Although many are case studies, most published applications of colloidal silica include laboratory testing of proposed treatment systems, including studies of properties such as penetration, water vapor permeability, salt resistance and optical effects, in relation to the properties of the materials they have been used to conserve. Generally results suggest that colloidal silica has a minimal impact on water vapor permeability, is stable over time, and improves the weathering resistance of stone. No particular negative impacts have been stated, although this may be due to lack of reported observations over time in the field. A few studies offer an evaluation of behavior over time, up to two years after the application of colloidal silica-based tests or treatments *in situ*. These authors generally found the tests to be stable and relatively unaffected by deterioration (Kuhlenthal et al. 2000; Stepien 1993).

5. Materials preparation and testing methodology

Ludox HS40®, a suspension of 30% wt. colloidal silica in water, was selected as a binder for test plasters in this research, since it has already been applied in conservation It has a density of 1.2 g/cm^3 and pH 9.

Several Ludox-based plasters were made using varying proportions of sand, crushed sandstone and sometimes a local earth. The results for plasters made with a binder: aggregate ratio of 2:3 and 1:3 by volume are presented here. The proportions of the aggregates were changed according to the color and texture of the sandstone substrate to which they were applied. Test plasters were first applied to sandstone fragments collected around the archaeological site and characterized in the laboratory during and after application. Plaster mixes with desirable characteristics were then applied *in situ* to sandstone blocks for exposure to natural weathering and evaluation over time.

A year after application of the test plasters in the laboratory and in situ, petrographic analysis was performed in order to observe and compare the crystallization of the plaster with the original sandstone. Optical microscopy was used to observe the texture and cohesion degree of the plasters. To ensure that the plaster does not affect the physisorption properties of the stone, the nitrogen adsorption-desorption technique was used.

A desired property in conservation materials is reversibility, and therefore removal tests of the plasters were made in laboratory samples and on site using wooden sticks, after previous moistening of the plaster. The cleaned surface was observed in the optic microscope to determine changes in the surface's texture. The colloidal silica plasters were compared with the former lime based plasters.

6. Results

Based on petrographic analysis the Tajín's sandstone can be classified as a calcareous litarenite with fragments of sedimentary rocks, quartz and feldspars on a clay matrix, and partially cemented by calcite. The proportion of quartz and calcite varies according to the selected stone. Therefore, the inclusion of colloidal silica in the plaster´s composition is important to assess chemical compatibility with the original.

In the petrographic analysis we could observe that the plasters have good integration with the stone substrate. Colloidal silica plaster can be applied to form thin layers like a lime plaster would do, or thick layers, as can be seen in Figure 2. The petrographic description of the first plaster shows the presence of quartz, feldspar and glass that are the components of the aggregates, and these materials are in a matrix formed from quartz microcrystals, which is a 39% of the plaster's composition. The second plaster has also lithic fragments and pyroxenes that come from the mixed earth, the matrix is formed from the quartz microcrystals of the colloidal silica, but they are a 15% of the plaster, accordingly to the plaster's preparation.

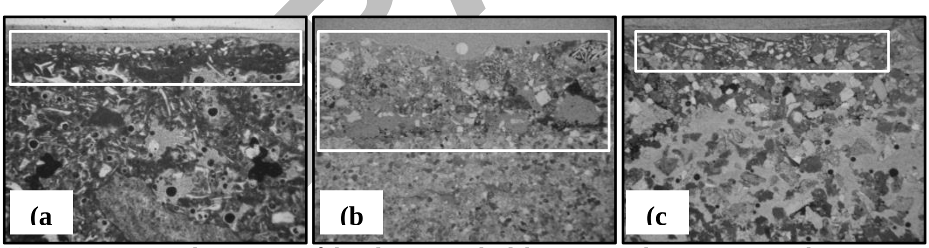

Figure 2. Petrographic images of the plasters on the laboratory probes. 2.5X, 10X objective. The plasters are marked with a rectangle.
(a) Colloidal silica plaster with proportion 2:3, **(b)** Colloidal silica plaster with proportion 1:3, **(c)** Lime plaster with proportion 1:2. *Courtesy of INAH.*

In the optical microscope, the difference between the colloidal silica and lime plasters was evident (Table 1). The silica-based plasters had a texture similar to the original stone, mostly due to the particle size of the aggregates. The cohesion of the plaster was also determined by the size and form of the aggregate particles, since all the water in the colloidal silica evaporates and only the SiO_2 crystals remain, causing cohesion properties to be determined largely by the arrangement between aggregate particles.

Table 1. Properties of the plasters observed in the optical microscope. Cohesion, particle size and distribution are before removal tests.

Composition	Cohesion	SiO_2 Particle size	SiO_2 Particle distribution	Cleaned surface appearance
2 colloidal silica: 3 aggregates	good	homogeneous and medium	homogeneous	original surface texture
1 colloidal silica: 3 aggregates	regular	homogeneous and small	homogeneous	original surface texture
1 lime: 2 aggregates	very good			abrasion on surface and surface holes filled with lime

The texture of the lime plasters varied significantly from that of the sandstone, but these plasters showed very good cohesion, since the lime acts directly as a binder between the particles.

The nitrogen adsorption-desorption isotherms for the colloidal silica and lime plaster showed that the materials are mesoporous, the desorption rate was lower for the lime plaster than for the colloidal silica plaster. The stone presented a type II isotherm with a type H3 hysteresis loop (Rouquérol 1999), which is also for mesoporous materials. These results indicates that the physisorption dynamic is similar for the three materials, but since the desorption rate in the lime plaster is the lowest, it could be expected a change in the material while it is wet.

Table 2. Comparison of lime plasters in respect to colloidal silica plasters.

Characteristic	Lime plasters	Colloidal silica plasters
Color and texture	Always whitish compared to sandstone. Pigments were used to match color, something that can cause undesirable long term changes	Easy to match when mixed with sand, crushed sandstone and local earth.
Reversibility	Not so easy to remove by mechanical means. Leaves white color residues difficult to remove as lime penetrates in the sandstone pores.	Easy to remove by mechanical means after application of water on it. Leaves no color residues. The only change in color of the original surface is due to the removal of surface patina.
Ease for application	Easy to manipulate and store.	Requires familiarity with the material as small amount of plaster can be prepared at a time. Dries fast.
Endurance	It cannot endure the constant movement of sandstone at the tropical environment so it finally detaches.	Good endurance. It can fail if too much sand is added or if large aggregate is used.
Cracking after	Requires setting under controlled	Good. High earth content causes

application	conditions as can easily crack under tropical environment.	cracking.

The reversibility of the treatment was determined by the cohesion of the plaster and its adhesion with the stone, since the interaction of the plaster and the stone is mechanical. The lime effectively bound not only the aggregates, but also the plaster to the stone making it difficult to remove and leaving remains of lime in the smaller pores, changing the appearance of the stone. This was not a problem for stones with a higher proportion of calcite, but for the ones with a higher content of feldspars and quartz, the color changed dramatically.

The colloidal silica plasters were well attached to the stone, but it was very easy to remove them, since the interaction was only mechanical and was directly related to the surface texture and the arrangement of the particles.

If the aggregate particles were not sieved, the plaster was easier to remove since the arrangement was less strong than with a finer particle size. These plasters did not leave remains on the stone, at least visible at a microscopic level, and after the removal the texture was the same as the untreated stone. The difference in the particle size also had an effect in the plasticity of the material, and therefore, in the handling of the plaster in the application on the reliefs. The comparison of the evaluated properties of the plasters is presented in Table 2.

7. Discussion

Aggregate particle size significantly affected the adequate composition and good handling characteristics of the plasters, as well as their behavior once dried. The interface between the stone and plasters made with fine aggregates was difficult to distinguish, even at the microscopic level. Fine grained plasters were easy to apply, even as thin layers that conformed well to the details of the relief. They also formed stable plasters, since they had good cohesion, which was noticeably influenced the durability of the material: after one year of weathering in the extreme conditions of Tajín, finer plasters remained unchanged.

Another important factor was the proportion of different aggregates. Plasters made with higher proportions of sand lost cohesion and showed diminished durability. Higher proportions of earth caused cracking during the setting of the plaster. Finally, crushed sandstone provided both plasticity and good color and texture matching.

It was easy to match the color and texture of the silica-based plasters with the sandstone. In Figure 3(b) several colors were achieved by varying the proportion of aggregates, in order to obtain the plaster with best aesthetic results. The restoration of the relief at Figure 3(a) included filling the lost areas and providing preventive care for the rest of the damaged edges. Other areas of this relief were successfully treated with the same plaster as a protective surface coating. The colloidal silica plaster proved to be a compatible material Figure 3(c) that helps to recover and preserve the relief´s value.

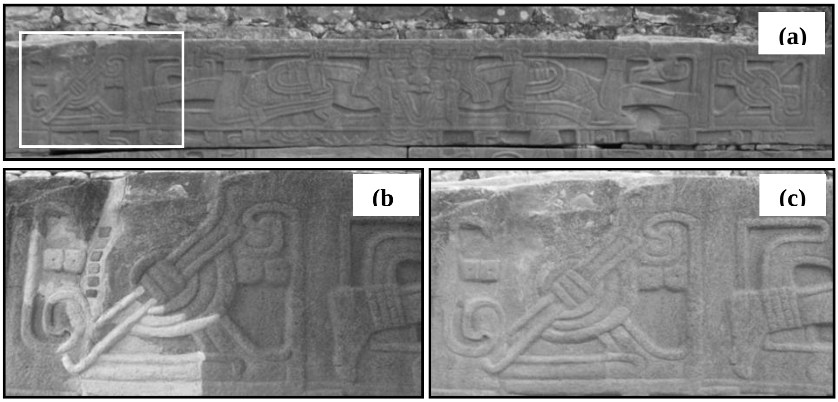

Figure 3. On site application of colloidal silica at the central south panel from the South Ballgame. **(a)** Upper frame with the depiction of a dual body related to Quetzalcoatl. On the left edge the treated area. **(b)** Color and texture testing for filler material with colloidal silica. **(c)** Same area after treatment. *Courtesy of INAH.*

Colloidal silica provided a good microcrystalline matrix for aggregate cohesion and therefore it resembles the original sandstone composition, as it can be seen in petrographic analyses. Reversibility is one of the main desired characteristics that were achieved using this plaster.

8. Conclusions

Colloidal silica-based plasters and protective surface coatings were evaluated after one year of exposure to tropical conditions and air pollution in Tajín. The plasters proved to have good endurance, stability, and appearance characteristics, and laboratory testing suggests that they are more compatible with the sandstone substrate than lime-based materials. They are therefore considered much more successful than the previously applied lime plasters, and are now considered acceptable for use in future conservation treatments at Tajín.

The tests conducted in this study and future treatments will continue to be monitored and evaluated over the remainder of the conservation project at the site, which will end in 2020. It is hoped that the continued study of these treatments will provide a more thorough evaluation of the long-term success and viability of colloidal silica-based plasters in conservation.

Acknowledgements

Thanks to the authorities of INAH (CNCPC, Tajín Archaeological Site, and Centro INAH Veracruz) who encouraged this research on behalf of Tajín´s cultural patrimony.

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