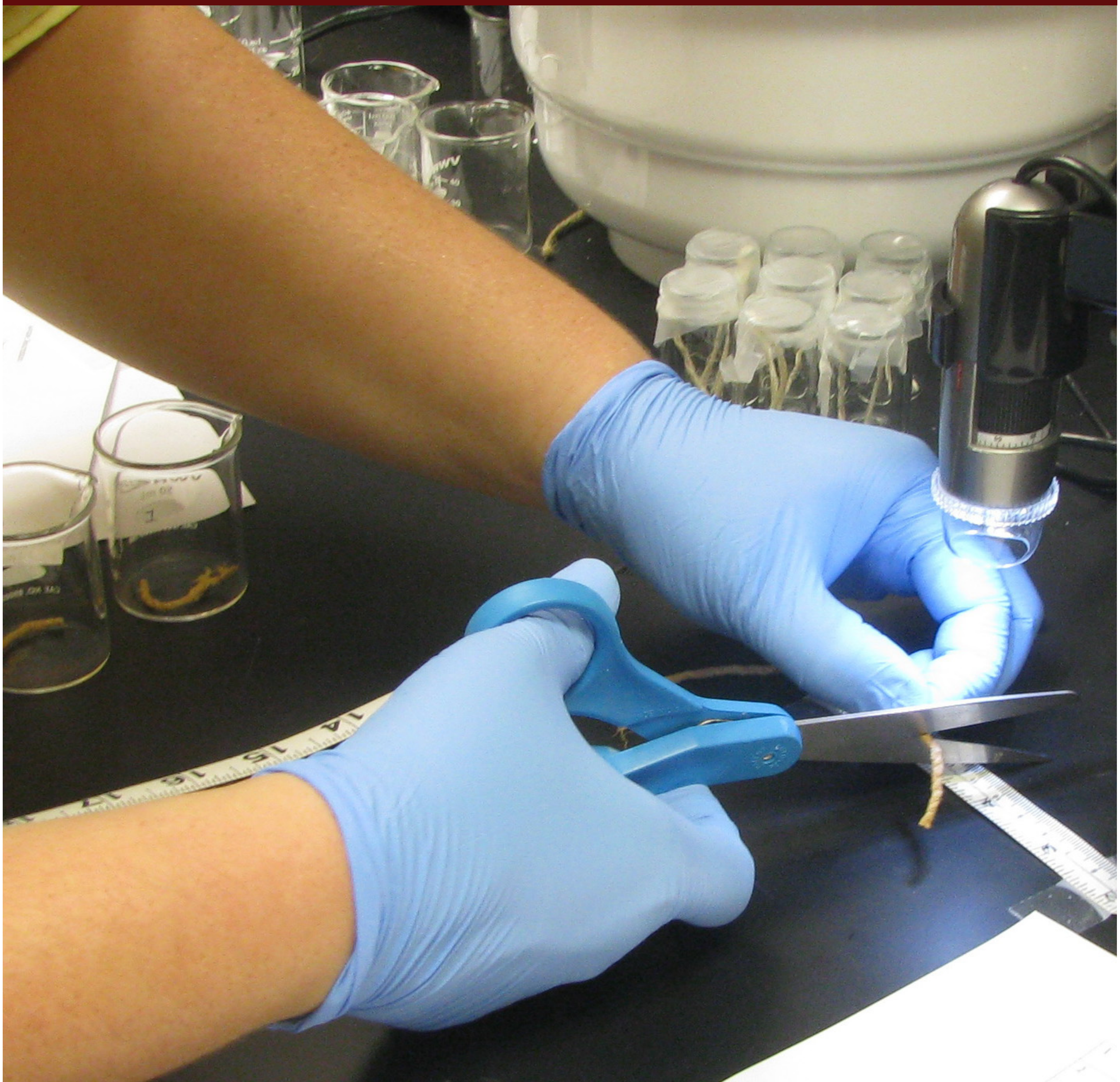
Evaluation of CA(OH)2 Nano-Particle Treatment of Cordage/Basketry | 2011-01

Virginia Department of Historic Resources



National Park Service
U.S. Department of the Interior

National Center for Preservation Technology and Training

Narrative Final Report Format (Attachment C)
NCPTT 2009 Grants
Grant Number: MT-2210-09-NC-06

Project Title: Evaluation of $Ca(OH)_2$ Nano-Particle Treatment of Cordage/Basketry

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Date: December 23, 2010
Revised: January 6, 2010

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Executive Summary

The UA-ASM proposed to evaluate the applicability of nano-sized calcium hydroxides $Ca(OH)_2$ for the treatment of degraded semi-processed cordage objects. This treatment previously found suitability with cellulosic substrates such as paper and wood. During the funded project the following activities were conducted and reported.

Phase 1

- The laboratory at the Arizona State Museum Conservation lab was equipped for the project.
- A synthesis of nano-particles of calcium hydroxide was successful and the process was sustainable.
- All cordage samples used in testing were registered and photographed. These include:
  - -Ethnographic cordage samples purchased from indigenous crafts persons
  - -Archaeological cordage samples from the Arizona State Museum.
  - -Replica cordage samples created using traditional methods and materials.
- A research design and various experimental protocols were developed based on research, trials, and the experience of team members.

Phase 2

- Aged paper samples were treated with nano-particles of calcium hydroxide (aqueous) to replicate the success of the technique as reported.
- Scanning Electron Microscopy was used to study and image the nano-particles in paper. An image processing macro was created to characterize physical properties of the calcium hydroxide nano-particles.
- Cordage samples were treated with nano-particles of calcium hydroxide, both in aqueous and isopropyl dispersions.
- Solvent studies were conducted on Ethnographic cordage samples to evaluate swelling, drying rates.
- Ethnographic cordage samples (treated and untreated) were subjected to Tensile-Strength Tests; to Accelerated Aging using elevated temperature; and to Artificial Aging using a shake table.
- Archaeological cordage samples were subjected to Artificial Aging using a shake table.

- Fourier Transform Infrared Spectroscopy was used to confirm the chemical identity of the calcium hydroxide particles after synthesis.
- Cold extraction pH measurements were conducted on the Archaeological and Ethnographic cordage samples before and after treatment with nano-particles. It was also used before and after Accelerated Aging on the Ethnographic cordage samples.

Phase 3

- Comparative analyses, charts, and graphs for the data and results of this project have been gathered for preparation of presentations and a peer-review publication.
- A presentation was made at the AIC Annual Meeting in Milwaukee 2010.
- An abstract has been submitted for review to the 2011 North American Textile Conservation Society meeting in Oaxaca, Mexico.
- A presentation has been accepted for the College of Engineering spring 2011 seminar series.

Introduction

The Arizona State Museum (ASM) at the University of Arizona in Tucson, Arizona is home to over 22,000 cataloged archaeological basketry, textiles and cordage objects. In previous years, the collection has been organized intellectually into a database and re-housed in acid-free paper trays in museum cabinetry. However, they continue to be threatened by their inherent fragility due to physical, chemical, and biological weakness. The Conservation laboratory sought to investigate a treatment method to further preserve the collection.

Cordage and basketry making in the Southwest is an ongoing tradition that spans over 10,000 years in the archaeological record. Cordage is the term used for any type of rope or string made by twisting fibers together. The fibers are usually referred to as hard or leaf fibers, soft or bast fibers, or seed fibers. Surviving fragments of archaeological cordage in museum collections are typically desiccated, brittle, tangled, shedding, and weak due in part to their low pH.

These conditions are well known in paper-based collections and the use of calcium hydroxide nano-particles, $Ca(OH)_2$, as a basic buffering system has been proven effective as a conservation treatment in paper (Giorgi 2002, Giorgi 2005) and wood (Giorgi 2009). The intent of this project was to evaluate the impact and effectiveness of this method as a treatment on archaeological cordage. However, utilizing calcium hydroxide nano-particles on cordage samples poses unique challenges that are not encountered with paper particularly due to the difference in processing

The major goals of this project involved: laboratory set-up; synthesis of $Ca(OH)_2$ nano-particles; cordage sample acquisition; development of a research design; preliminary testing of solutions and solvents; mechanical and aging studies; analytical characterization; imaging and data collection; and report preparation. The project has demonstrated that aqueous dispersions of calcium hydroxide nano-particles are not an appropriate treatment for archaeological cordage because the cordage swells when treated with water. The study has shown that 2-propanol as a carrier solvent for Calcium hydroxide nano-particles does not swell cordage fibers or inhibit the migration of nano-particles into the matrix, while increasing the pH of the cordage. The results of this funded project suggest that calcium hydroxide nano-particle solutions in isopropyl alcohol is promising as a conservation treatment for archaeological cordage. This study has also confirms that storage that offers the most confinement and immobilization will further reduce damage from handling.

Materials and Methods

Materials:

Archaeological cordage fragment collection for familiarity study:

In addition to the extensive holdings of cataloged archaeological cordage at the ASM, the museum has a sub-collection of fragmentary pieces that are available for comparative technological studies. These fibers come from six different archaeological areas and range in date from 950 AD-1400AD: Nantack Cave, McEuen Cave, Navajo Mountain, Tsegi Canyon, Chihuahua Cave and Gourd Cave. This collection provides information on the representative types of materials used to make cordage. The large amount of cordage identified as yucca (about 71% of these samples) suggested its importance in traditional cordage manufacture. Use of this reference collection also provided invaluable insight into the locations that archaeological cordage has survived in the southwest and the type of weathering that cordage experienced while exposed to dry elevated temperatures.

Aged Paper Samples used for confirmation tests:

Kraft paper from 1950-1961 was also included in this study as it provided a look at material that relates well to earlier studies, has a high lignin-content paper, and is observably brittle. Kraft paper was tested both with nano-particles made in-house and with micron-sized particles that are commercially available.

The Kraft paper samples were treated with commercially available calcium hydroxide. One piece of paper was not treated, another piece was washed with deionized water, a third was washed with deionized water and then treated with commercially available calcium hydroxide in aqueous dispersion (2g/L). One group of small paper samples was submerged directly into the aqueous nano-particle solution. Another group of small paper samples was submerged directly into a isopropyl alcohol solution of $Ca(OH)_2$ nano-particles. The commercial micron-sized $Ca(OH)_2$ particles in treated Kraft paper were studied and compared with synthesized nano-particles of calcium hydroxide under Scanning Electron Microscopy (SEM). The images indicate that the commercial micron-sized $Ca(OH)_2$ particles do not penetrate past the paper surface.

Replica cordage samples created using traditional methods and materials:

The replication of traditional cordage technology and materials was learned with the guidance of William Randy Haas, Jr., a graduate student in anthropology at the University of Arizona. He completed a master's thesis, *Social Implications of Basketmaker II Cordage Style Distribution*

(2003) and has become quite proficient with cordage technology. Yucca (*yucca elata)* leaves were collected on AZ Highway 77 northwest of Tucson. The yucca leaves were cut, and then placed in water. Over the period of the next month the thick cuticle (outer wax layer) of the leaf was removed by scraping with the back of a butter knife and granite rocks. Then the material was allowed to ret, with water being changed every week. This was placed on a shaded balcony and exposed to all weather in Tucson from February to April. The fibers lost most of their green coloring and soft tissue. The fibers were then "chewed" by mouth in one area for approximately five minutes. This technique is true to tradition and relies on both mechanical action and enzymes to break down any remaining soft tissue of the leaves and gives a cleaner fiber. The fibers were allowed to dry. They were then twisted to form an S-twist by anchoring one end in one hand and rolling the other end against the thigh. There were no additional oils or coatings added to this cordage. These replica cordage samples were useful for testing the preliminary solutions of calcium hydroxide nano-particles and for carrier solvent experiments.

Ethnographic cordage samples purchased from indigenous crafts persons:

An *agave* rope, hand-made in Mexico, was purchased from the *Native Seed Search* store in Tucson in 2010. It is constructed of four sets of double-ply agave cord and has a one plastic core at the center. The four double-plies were separated and used as single cords for many different tests. The fibers were characterized physically, giving an average diameter of 4.23 mm, single ply size of 3.27 mm, and of 2.6 mm ply/cm. Samples of this cordage were treated with calcium hydroxide nano-particle solutions in isopropyl alcohol and tested by artificial aging (shake testing) and by accelerated aging (elevated temperature) before and after the treatment. The cordage samples from this source could be made long enough (80 cm) to conduct Tensile Strength Tests and were of ample quantity to facilitate a broad range of experiments that also included treatment studies, aging studies, analysis with of the Fourier Transform Infrared Spectroscopy (FTIR), and pH testing.

Archaeological cordage samples from the Arizona State Museum:

The Arizona State Museum has un-provenienced and fragmentary bits that are held for experimental and educational purposes. A cluster of six archaeological cordage fragments were requested and approved for this project. They are representative of the materials, technology, and condition of the cataloged specimens in the Arizona State Museum. Samples, 1 inch (2.54cm) length, were treated with calcium hydroxide nano-particle solutions in isopropyl alcohol and tested by artificial aging (shake testing) before and after the treatment.

Methods:

1. Calcium hydroxide synthesis: Choice of Synthetic Method

Two major synthesis methods regarding size and quality of nano-particles are indicated in the conservation literature. (Salvadori 2001) The first method, the use of quick-lime, or heterogeneous synthesis consists of taking calcium oxide and adding stoichiometric quantities of water. There are two options as to where to obtain the calcium oxide, the first is to use commercially available calcium oxide and the second is to reduce calcium carbonate to calcium oxide using high heat. This synthesis route has resulted in large ranges of size in the creation of nano-particles as it is dependent on the size of the initial nano-particles. The second method for creation of nano-particles is the homogeneous synthesis in which dissolved calcium chloride is mixed at moderate temperature with solubilized sodium hydroxide. This is followed by a peptidization step in which the product is sonicated to break up agglomerates. There has been a fair amount of research in this area and it has shown reliably narrow ranges of size of product. This approach to synthesis was what was used in this project to obtain calcium hydroxide nano-particles.

Calcium chloride dihydrate, ACS, 99.0-105.0% (Alfa Aesar) and was used without further purification. Sodium hydroxide, (Fisher Scientific) was used without further purification. Ethylene glycol (Mallinckrodt Chemical Works) was used without further purification. 2-propanol 99+% (Sigma Aldrich) was used without further purification. Silicone oil for baths (Alfa Aesar) and used without further purification. Water was de-ionized with a Culligan unit. A jacketed Buchner filter funnel was created by glass blower Charles Amling from the UA Chemistry and Biochemistry Department. A vacuum pump and oven were purchased from Fisher Scientific.

Synthesis of the Particles and Peptization Procedure:

Reagent $CaCl_2 \cdot 2H_2O$ (2.788 g) was dissolved in 50 mL of ethylene glycol by heating the reactor to 150˚C (~302˚F) in a silicone oil bath. Nitrogen was introduced into the system to exclude carbon dioxide. 17 mL of aqueous NaOH solution (.5682gNaOH/17mL H2O or 0.70 M NaOH) was added drop wise to the Ca^{2+}-containing solution. The reaction went for five minutes under stirring at temperature. (The decisions of molarity, temperature and time come from Salvadori 2001). The calcium hydroxide was filtered using hot filtration (120˚C) in the jacketed Buchner filter funnel under vacuum. The solubility of calcium hydroxide increases with decreasing temperature and thus it is necessary to keep the temperature high. The particles were then peptized by washing with 2-propanol, sonicating for ten minutes and centrifuging for ten minutes. This process was repeated five times to remove ethylene glycol. The particles were then stored in closed containers in isopropyl alcohol. To date the synthesis has been conducted five times in ASM's conservation laboratory.

Physicochemical Characterization:

The identification of calcium hydroxide was conducted using Attenuated Total Reflectance-Fourier Transform Infrared Spectroscopy (ATR-FTIR) on a Nicollet Avatar 360. The physical characterization of the third round of synthesis of calcium nano-particles was done using Scanning Electron Microscopy using a Hitachi 3400N. The particles were coated for two minutes using a platinum coating source. After calcium hydroxide (aqueous) nano-particle synthesis was completed, samples of aged Kraft paper (1950-1961) were obtained at the Arizona State Museum for the purpose of replicating the success of the treatment technique.

2. **Carrier Solvent: Choice of Aqueous and Isopropyl alcohol solutions for treatment**

While $Ca(OH)_2$ nano-particles in aqueous solution have been successful for treatment of paper objects, and Giorgi et al (2005) found isopropyl alcohol to be a suitable non-swelling carrier solvent with nano-particles of calcium hydroxide in the treatment of acidic wood. Cordage is neither paper nor wood so both carrier solvents were tested in this project.

Replica cordage samples (three) made of *yucca elata* were used to observe the effects of aqueous emersion. The samples were cut to a length of 1 inch by about 1/16 inch diameter were submersed in nano-particles. Three samples of the same type and length were submersed in an aqueous dispersion of nano-particles and also in a dispersion in isopropyl alcohol. It was observed that there was an extreme degree of swelling and unwinding of cordage that was exposed to water; the iso-propyl alcohol dispersion caused much less swelling

Ethnographic cordage samples (three) made of *agave* cut to a length of 1 inch by about 1/16 inch diameter were submersed in nano-particles in water. Three samples of the same type and length were submersed in nano-particles in isopropyl alcohol. It was observed that there was an extreme degree of swelling and unwinding of cordage that was exposed to water when compared with that cordage exposed to isopropyl alcohol.

Testing Procedure:

Solvent testing of the cordage samples involved the following protocol. Three samples of modern cordage were cut and their lengths, diameters, ply size and ply/cm measured. The weights were taken of each sample before they were submersed in a beaker with the solvent being tested. They were left in the beaker with the solvent for five minutes then removed from the beaker and left to dry on watch glasses. The samples were weighed every five minutes for 90 minutes and then once more after 120mins. The solvents tested include deionized water and isopropanol as well as ethanol, butanol and acetone for polar solvents, toluene and n-hexane for non-polar solvents. Isopropanol dried readily without significant swelling of the cordage, while water swelled the cordage 2 to 3 times.

Interpretation:

The graphs below show the results of the drying tests for isopropyl alcohol and water in ethnographic cordage samples. The isopropyl alcohol dries quickly, (approaching zero around 35 minutes after removal from the solvent), water has a much longer drying time, and did not finish drying in the two hour window. These studies allow for objective comparison among various solvents. They also provide a better indication of the uptake of solvent by the fiber matrix, in the case of the isopropanol this was 33-40% by weight and in the case of water it was 225-275% uptake. These data made it unnecessary to follow water loss for greater length of time.

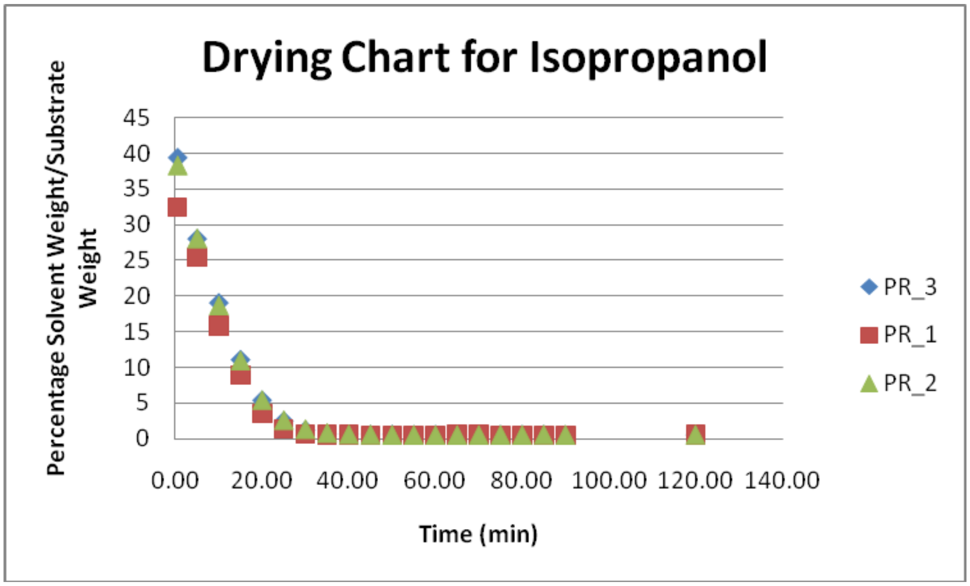

Figure 1. Isopropyl alcohol drying chart

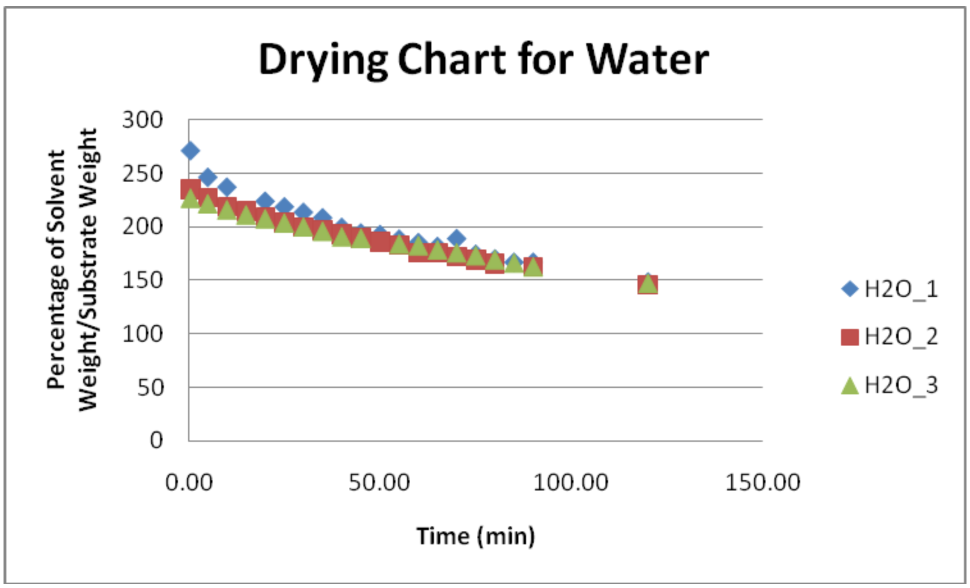

Figure 2. Water drying chart

3. **Attenuated Total Reflectance-Fourier Transform Infrared Spectroscopy (ATR-FTIR)**

Sample testing using attenuated total reflectance-Fourier transform infrared spectroscopy or ATR-FTIR was conducted in the Arizona State Museum Conservation Laboratory using a Nicollet Avatar 360 instrument.

FTIR was useful in confirming the composition of calcium hydroxide. The $Ca(OH)_2$ nano-particle solution in isopropyl alcohol sample from the fourth round of synthesis was prepared by sonicating for ten minutes, then centrifuging for ten minutes, decanting the isopropyl alcohol and then process was repeated five times. The sample was stored in isopropyl alcohol. This sample was removed from isopropyl alcohol allowed to dry for a few minutes and then put on to the instrument with ATR attachment. The background was taken prior to the sample and then the sample was scanned for 64 scans. (3642.16 O-H of solid $Ca(OH)_2$, 2359.91 CO_2, 1489.91 $CaCO_3$, 1086.78 $CaCO_3$, 872.14 $CaCO_3$)

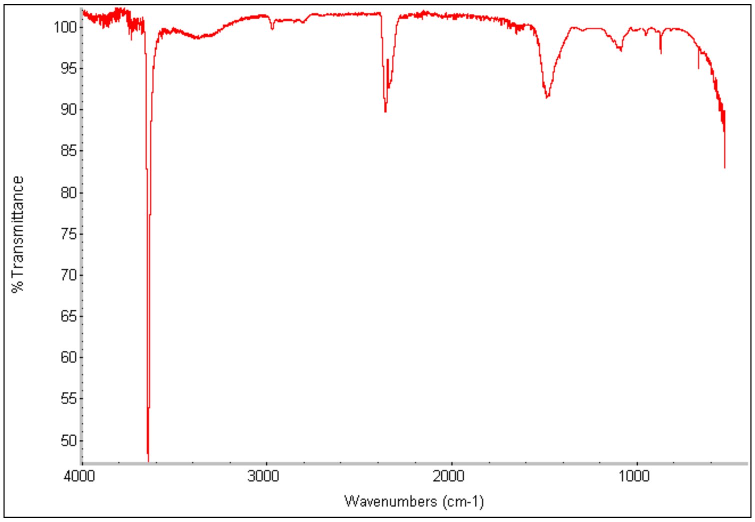

Figure 3. FTIR of calcium hydroxide particles

The FTIR has also been used in monitoring a peak reduction at 1620-1645 (cm^{-1}) of treated cellulose (Oh, Sang Youn 2005). Based on this work, a ratio change in peaks from samples before and after treatment may be useful in characterizing the chemical changes in the cordage.

4. **Scanning Electron Microscopy**

A Scanning Electron Microscope (SEM), Hitachi 3400N, at UA Spectroscopy and Imaging Facilities (USIF) was used for imaging of the $Ca(OH)_2$ nano-particles. All of the sample mounts were sonicated in methanol for five minutes, and then allowed to dry. For samples of calcium hydroxide the calcium hydroxide was placed directly on the mount and allowed to dry. The mounts were then coated for 2 minutes at 10mAmps with platinum.

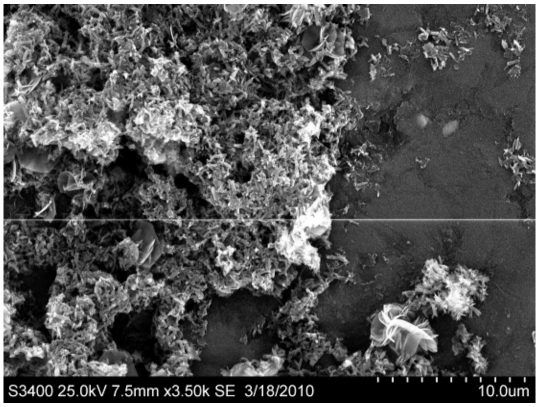

Figure 4. This image, from the third round of synthesis of nano-particles**, shows an agglomeration of particles that occurs upon drying. The SEM image was taken at a working distance of about 7.5mm, 25keV, about 45 mA and 3.50k magnification. Agglomerated particles do not easily dissociate from one another and it becomes difficult to disperse these in cordage. This concentration issue requires that the concentration of the calcium hydroxide in the dispersion is low.**

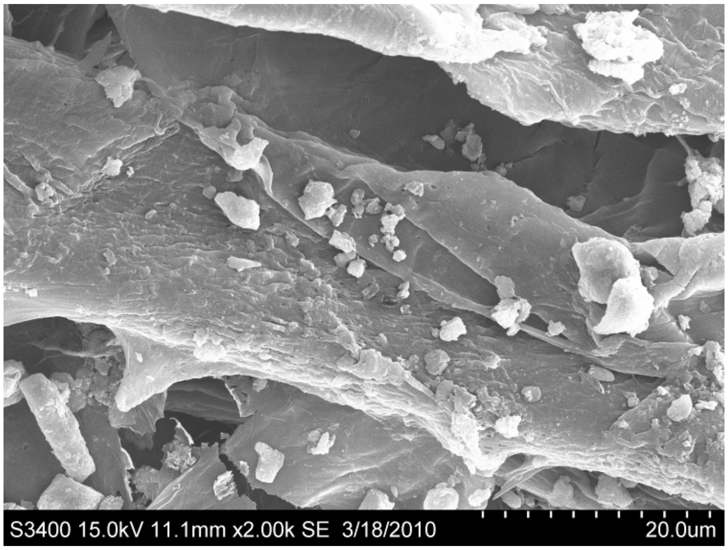

Figure 5. This image, taken at a working distance of approximately 11.1mm, 15keV, t 30 mA and 2.00k magnification, depicts deposits of inorganic particles of commercially available calcium hydroxide on paper. The surface of the paper shows large deposits of calcium. When viewed in cross-section it is evident that these large particles do not penetrate into the interior of the paper (see below).

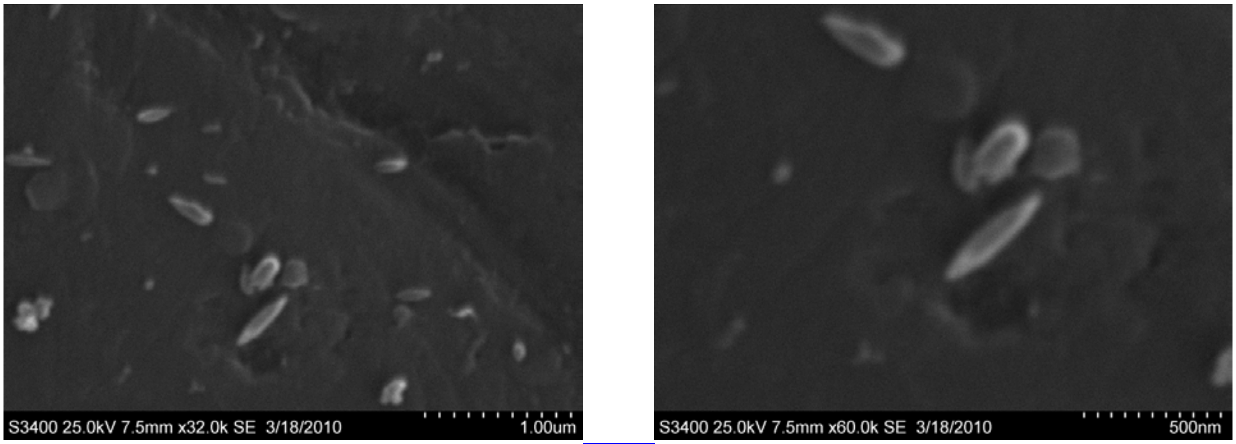

Figure 6. These images illustrate the hexagonal appearance of particles oriented edge on. The image on the left was taken at a working distance of 7.5mm, 25keV, 45 mA and 32.0k magnification. The right SEM image was taken at a working distance of about 7.5mm, 25keV, 45 mA and 60.0k magnification.

To increase the efficiency of analysis of particles, image processing characterization was used. The use of image processing to identify and characterize particles has many limitations. While instinctively the human eye has can recognize the edges of fibers versus edges of spheroids or hexagons instinctively, and can perceive the differences in these shapes easily, the software of a computer does not inherently have this built in. Thus, either a sort of recognition software must be available or there have to be adjustments made to the image to circumvent this problem. Beyond using image processing for data analysis, Image J is serving to add additional usefulness in producing quality images. (Rasband, W.S. 1997-2011) For instance, the 3D surface plot function is useful in showing particle dispersion in a 3D material, even if it is using a 2D image to do this. There are many applications for image processing in this course of research.

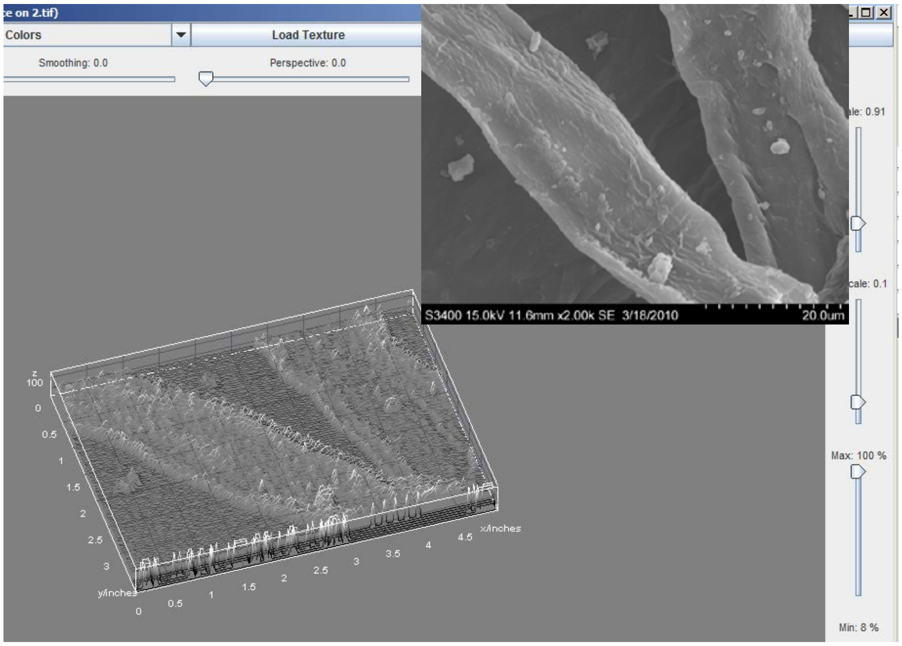

Figure 7. 3D Imaging of Screen Capture of from 2D source, (insert is original SEM Image)

5. **Accelerated Aging Experiments using Elevated Temperature**

To observe the effect of $Ca(OH)_2$ nano-particles treatment on cordage it was necessary to treat and age cordage samples at an accelerated rate in order to determine the effects over time. Tests using aging at elevated temperature were conducted on three types of ethnographic cordage samples: (A) Control samples of un-aged cordage, (B) Samples aged in an oven (Fisher Scientific Isotemp® Vacuum oven #285A) for 2 weeks at 60-70°C, (C) Samples were treated with $Ca(OH)_2$ nano-particles and then aged in the oven for 72 hours at 100° C. (Assuming the normal rate increase of a factor of 2 got every 10^o C, 72 hours, 72 hours at $100^{o \text{ is substantialle}}$ more severe than 2 weeks at 60 – 70^o.) Multiple samples were used due to their heterogeneity and a goal to obtain reliable statistics. After removal from the oven, the cordage was left to cool for 24 hours before tensile strength testing.

6. **Tensile Testing**:

Tensile tests were conducted at the UA M3 (multi-scale mechanics of materials) Laboratory in the Aerospace and Mechanical Engineering Department. An Instron 1011 instrument was equipped with cordage grips and was used to stretch the sample at 0.06 inches/minute while measuring the load capacity in pounds until breakage. These experiments helped to clarify if $Ca(OH)_2$ nano-particles act as a buffer under accelerated aging and inhibit deterioration of the cordage samples.

On average, the aged samples broke at a lower load (50 lb decrease) when compared to samples of un-aged cordage (A). Treated modern cordage samples (C) were placed into the oven at 100°C for 72 hours. Then they were tested using tensile strength tests to ascertain how the treated aged cordage (C) compared to the untreated cordage (A). The treated (C) and untreated (A) cordage samples did not show a significant difference in load when compared. The results indicate that cordage aged (B) lost significant strength when compared with un-aged cordage (A) and there was not a significant difference between un-aged cordage (A) and cordage treated and aged (C).

Tensile Strength Measurements of Cordage Samples

	Unaged (A)	Aged Untreated (B)	Aged Treated (C)
Sample	load (lbs)	load (lbs)	load (lbs)
1	330.47	175.94	229.68
2	295.79	190.75	231.86
3	209.17	199.27	287.09
4	259.61	199.78	237.56
5	248.70	205.46	269.53
Average load	268.75	194.24	251.14
Standard Deviation	46.31	11.50	25.72

Table 1 Shows the maximum loads for three groups of ethnographic cordage (A) unaged and untreated (B) aged and untreated (C) aged and treated with $Ca(OH)_2$ in isopropanol.

7. **pH Tests:**

Testing for pH was done in the ASM Conservation Chemistry Laboratory using a ECO pH 2 Tester. The pH cold extraction method outlined by TAPPI (T 509 om-06) was used on various cordage samples including: (A) Control samples of un-aged ethnographic cordage, (B) Aged ethnographic cordage, (C) $Ca(OH)_2$ nano-particle treated for (ten minutes) then aged ethnographic samples, (D) untreated archaeological samples, and (E) archaeological samples treated for ten minutes with $Ca(OH)_2$ nano-particles dispersed in isopropanol.

pH measurements of cordage samples

Sample	pH	pH	pH
A	6.5	6.5	6.5
B	5.4	5.4	5.4
C	7	7	6.9
D	6.3	6.3	6.3
E	7.1	7.1	7.1

Table 2 Shows the pH's measured for three groups of ethnographic cordage (A) unaged and untreated (B) aged and untreated (C) aged and treated with $Ca(OH)_2$ in isopropanol; and two groups of archaeological cordage (D) untreated and (E) treated.

The pH testing results indicate an increase in pH on treated and aged ethnographic samples (C) and treated archaeological samples (E) compared to untreated samples (A) and (D). Aging decreased the pH of the untreated ethnographic samples as samples (B) had a lower pH than the treated and aged ethnographic samples (C). Since a decrease in pH has been shown to be associated with increased degradation one can conclude that the treated sample will be more stable on aging. (REF?)

8. Artificial Aging Experiment Using a Shake Table:

To observe the results of $Ca(OH)_2$ nano-particles treatment on cordage for long-term storage stability it was necessary to treat and age cordage samples at an accelerated rate using artificial vibration to determine the effects of handling and housing over time. Untreated cordage samples were aged using a dental vibrator (Ray Foster Dental Supplies). Different container types used for cordage storage at ASM were evaluated. This method was also used to compare untreated (D) and treated (E) archaeological cordage samples under the accelerated handling conditions. The tables below indicate the results.

Archaeological Cordage without and with nano-particle treatment.

After 4 hours of shaking						
Sample	Ave weight (g) Before	Ave weight (g) After	Difference	% Difference	Average % Difference	Standard Deviation
(D) ACST_1	0.10	0.10	0.00	0.68	Untreated cordage	
(D) ACST_2	0.10	0.10	0.00	2.28	1.47	0.80
(D) ACST_3	0.12	0.12	0.00	1.48		
(E) ACST_4	0.11	0.11	0.00	0.20	Treated Cordage	
(E) ACST_5	0.10	0.10	0.00	1.27	0.78	0.54
(E) ACST_6	0.09	0.09	0.00	0.86		

Table 3 Shows the weight lost upon shaking archaeological cordage in plastic boxes. The untreated samples appear to lose more weight than the treated cordage.

Ethnographic Cordage in different containers

After 3 hours of Shaking						
Sample	Ave Weight (g) Before	Ave Weight (g) After	Difference	% Difference	% Difference Average	Standard Deviation
MC-1P	0.80	0.79	0.02	2.86	Plastic Boxes	
MC-2P	0.80	0.78	0.02	2.086	2.39	0.41
MC-3P	0.64	0.62	0.01	2.22		
MC-1PB	0.80	0.78	0.01	1.54	Plastic Bags	
MC-2PB	0.90	0.89	0.01	1.16	1.32	0.20
MC-3PB	0.81	0.80	0.01	1.25		
MC-1C	0.82	0.81	0.01	1.63	Archival Cardboard Boxes	
MC-2C	0.80	0.79	0.02	1.91	1.77	0.20
MC-1CA	0.88	0.87	0.01	1.47	Acidic Cardboard Boxes	
MC-2CA	0.84	0.83	0.01	1.21	1.34	0.18

Table 4 Shows the weight lost upon shaking ethnographic cordage in differing containers, the containers with the most confinement: plastic bags and acidic boxes (due to the rougher surface) performed best.

Results and Discussion

The synthesis of nano-particles of calcium hydroxide is a process that requires special equipment and technique. However, with training and the proper laboratory equipment and technique this process can be done in conservation laboratories. The application of nano-particles of calcium hydroxide to cordage has a number of difficulties to consider: (1) penetration of the particles into the interior of the fiber matrix; (2) ensuring a uniform distribution of particles in the matrix; (3) application of a carrier solvent to the matrix must allow for good transfer of particles and not negatively impact the structure of the matrix (by swelling, contracting, or chemically reacting). The evaluation of particle penetration into the matrix may be addressed by measuring the pH of the surface of cordage fibers located near the center of the ply.

The application of carrier solvents to the matrix was addressed by testing a variety of solvents on the matrix and observing changes in the shape of the cordage and changes in the matrix on a chemical level (i.e. measuring pH change). A concern with using non aqueous solvents is the possibility that the solvent may remove bound water and alter structural flexibility. Isopropyl alcohol as a carrier solvent is promising.

The artificial aging study and accelerated aging studies were designed, conducted and gave useful results. The tensile strength data indicates a significant reduction in loss of tensile strength for the treated samples. The data in the artificial aging study using a shake table indicates a difference in loss between the treated and untreated samples; suggests a positive effect of calcium hydroxide nano-particles on archaeological cordage, but the differences are not statistically significant. The artificial aging study using a shake table does identifies the impact of different container types on the cordage's long-term structural stability.

Conclusions

This project has examined the applicability of $Ca(OH)_2$ nano-particles for the treatment of degraded semi-processed cordage from archaeological sites. The treatment has previously found success with cellulosic substrates such as paper and wood. During this project several types of cordage samples were collected, prepared, tested, artificially aged, treated, and evaluated. The project and the data it produced have provided a large volume of information as a basis for further studies. The project has successfully identified reproducible and inexpensive methodology for both treating cordage samples and testing the success of the treatment. Based on our experiments, the use of $Ca(OH)_2$ nano-particles in isopropyl alcohol solvent is a promising conservation treatment for degraded cordage.

Acknowledgements

Charles and Chase Amling; UA Chemistry Department; who created the jacketed filter flask.

Kyle Colavito; UA Multiscale Mechanics of Materials Laboratory (M3 Lab); for the use of the Instron tensile test machine and for feedback for interpreting data.

Dr. Fenella France; Library of Congress; for consultation on deacidification technology and paper testing methods.

Dr. Richard Greenberg; UA Planetary Sciences Department; for use of Image J.

W. Randy Haas; UA Anthropology Department; for instruction and assistance with the creation of modern cordage.

Steven Hernandez and Al Agellon; UA Spectroscopy and Imaging Facilities (USIF); for SEM assistance.

Dave Smith; Raytheon Corp., for consultation on tensile strength methods and use of cordage grips.

Gina Watkinson; Arizona State Museum; for assistance with the creation of a cordage database, laboratory set-up and purchases.

Dr. Ramin Yadegari; Plant Science Department; for consultations on plant structure and swelling studies.

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