Protecting Archeological Objects Contaminated with Crude Oil

This document was developed as general guidance for the care of archeological materials that have been contaminated from releases of crude oil in the marine environment from oil tankers, drilling rigs, wells, or offshore platforms. It provides guidance on how to clean, preserve, and/or conserve materials that were recovered or collected because it was believed that they would not survive in situ or would suffer accelerated deterioration unless cleaned/decontaminated. An extensive survey of existing literature shows that little to no information exists on either the appropriate methods to clean archeological materials contaminated with crude oil, or the long term effects of decontamination to the materials and collection environment in which they are held. This document uses information from both archeological conservation and materials conservation to make recommendations for treatment of a variety of archeological materials that have been exposed to crude oil.

Composition of Crude Oil

All crude oils include lighter components similar to gasoline as well as heavier tar or wax. The primary elements that make up the oil are carbon and hydrogen with varying amounts of sulfur, nitrogen, oxygen, and trace metals. The lighter, more volatile components tend to evaporate more quickly if they are on the sea surface. Some of the gases and other aromatic components are relatively soluble in water compared to other hydrocarbons, and will disperse more readily in the water leaving the heavier fractions that remain on the surface to be carried to shorelines.

Crude oil contains three primary components: alkanes, hazardous air pollutants (HAPs), and polycyclic aromatic hydrocarbons (PAHs). Alkanes are those compounds that can be decomposed by microbes. HAPs are compounds such as benzene (a known carcinogen), toluene, and xylene that pose significant health threats to humans. PAHs are highly toxic compounds that tend to persist in the environment, particularly once the crude oil has penetrated shorelines and building materials.

Types of crude oil found in the Gulf of Mexico

Mousse: a weathered mixture or emulsion of water and oil, typically appearing orange, reddish brown, or chocolate brown in color.

Tar balls: a product of further weathering of mousse. Patches of mousse are broken into smaller pieces that weather and become sticky as they continue to lose volatile components.

Sheen: a very thin layer of oil floating on the surface.

Potential Threats to Archeological Objects

Contamination and Toxicity

HAPs are acutely toxic components of fresh or emulsified oil and can be a potential inhalation hazard. Acute exposure can lead to drowsiness, dizziness, headaches, or nausea. Though HAPs are volatile, they take time to dissipate. Contamination of archeological objects could require special cleaning and storage arrangements until levels of HAPs are considered safe. PAHs are highly toxic and, if they have penetrated objects, can persist for long periods of time. Some cleaning methods can hasten the volatilization of these toxic substances, increasing the chance of human exposure to them, so care should be taken if cleaning is attempted. The more soluble fraction of oil, made up of some of the gases and other aromatic components, has a greater potential to contaminate objects that are already wet or submerged. Thus, the aromatic fraction of the oil poses a greater exposure risk because aromatics are relatively more soluble than the other components in oil.

Staining and Disfiguration

Staining and disfiguration could range from black or brown staining to subtle darkening of the materials. Even after cleaning, this visual disfiguration can persist. Some cleaning methods have the potential to enhance differences between portions of the materials exposed to oil and unexposed areas, and some methods can force oil farther into the material. It is important to test a cleaning method on a small, inconspicuous area before cleaning the entire object.

Bio-growth and Deterioration

The complex chemical mixture that makes up crude oil has the potential to accelerate decay of cultural materials and archeological objects. In particular, microorganisms that live in oil have the ability to digest components of the oil and produce acidic waste. Nitrifying organisms that produce nitric acid are commonly found around oil. Sulfur-reducing organisms are present that produce sulfuric acid. These microorganisms can be beneficial in the breakdown of the oil, but their acidic byproducts can chemically attack many types of materials.

Clean Up Activities

Far more damage can be done to historic and cultural resources by people and equipment associated with the cleanup than by the oil itself. Archeological sites should be identified early, or an archeologist should be consulted in advance of activities, so that use of equipment such as hot water power washers and boom stakes can be avoided in areas of known archeological sites and cultural resources. An additional concern is that oil can be transported to archeological sites on the boots, gloves, and heavy equipment of the cleanup team.

Personal Safety

When handling oiled artifacts, the most important issue is personal safety. Basic equipment that should be always be used are gloves and safety glasses. Gloves types used by OSHA for oil-spill cleanup that would also be applicable for handling artifacts include PVC 26-40 mil for heavy use and Nitrile 11-26 mil for light use.

For fresh oil spills, full-face respirators should be worn when dealing with oiled materials to protect personnel from off-gassing of volatile components of the oil. OSHA recommends that respirators be equipped with P100 cartridges that filter particulate matter as well as organic vapor. Weathered oil does not off-gas as much as fresh oil that contains more volatile components and respirators are not as critical. However, they are still recommended any time off-gassing is detected, i.e. smells or odors. According to the Centers for Disease Control and Prevention (CDC), the symptoms of over-exposure to oil are listed as: coughing, shortness of breath, headache and upset stomach.

Important Factors to Consider for Clean-up

All deterioration of cultural materials resulting from exposure to crude oil will be dependent on the rate and types of reactions between the oil and the object. Soiling and staining can be readily observed, but oil also may penetrate porous objects. The resulting growth of microorganisms may cause deterioration only observed at a later date. When planning for clean-up, the following guidelines should be kept in mind:

- Do no harm.
- Human health and safety come first.
- Do not rush decisions.
- If at all possible, do not remove the artifact from its original location.[1]
- Artifacts may be composed of a wide range of materials.

Types of Materials Susceptible to Damage

Shell. Shell is typically calcium carbonate -- either calcite or aragonite. Both are susceptible to degradation by acids.

Bone. Bone has a complex internal and external structure made up of calcareous and organic material. Like shell, the inorganic material can be degraded by acids, but any organic material can be degraded by alkaline materials. The porous structure of bone can absorb and hold molecules of crude oil.

Ceramics. Oil is capable of penetrating the pores of ceramic material and reacting with its components, including some temper or grog materials, leading to long-term contamination. Low-fired ceramics are more porous than porcelains or refined earthenwares such as whiteware and stoneware, and thus are more susceptible to damage over the long term. High-fired ceramics such as porcelain, should be stored in fresh water. Low-fired ceramics must be kept wet, and initially should be stored in clean seawater at salinity similar to that from which they were recovered.

[1] According the Secretary of Interior's Standards for Historic Preservation, "Archeological resources will be protected and preserved in place. If such resources must be disturbed, mitigation measures will be undertaken."

Glass. Submerged glass corrodes over time, making the surface more porous. Oil is capable of penetrating this corroded surface and contributing to breakdown of the glass. It is best to store glass in seawater. Desalination is a task best left to the laboratory.

Metal. Metals are susceptible to acids and biologically induced corrosion resulting from organisms that live in oily environments.

Wood. Depending on the environment, submerged, waterlogged wood can be fragile. Oil is capable of penetrating wood fibers.

Combination objects. Some objects might be made up of a combination of materials. Such objects are likely to require special handling and treatment, depending on their composition.

Collection of Objects

If objects must be collected, the basic steps in archeology should be followed. A professional archeologist and/or conservator should be consulted if these steps are not familiar to those conducting the work.

In the field, segregate contaminated artifacts from uncontaminated artifacts to prevent cross-contamination.

Document the condition of the artifact. Before cleaning or other treatment is undertaken, the general condition of the artifact should be documented. The condition of the artifact will help determine the best approach for handling, cleaning, treatment, and, if necessary, storage. The documented initial conditions also can be used as a reference point during any handling, cleaning, or other treatment. Suggested minimum documentation would be photographic documentation with a color card and a ruler as well as measurement of the object’s mass. If the object’s initial weight is taken when it is wet, later measurements should be made when the object is wet. Keep the artifact in its current conditions. If the material is wet, keep it submerged in clean water. If the artifact is in seawater, use clean, local seawater to maintain exposure to existing salinity levels. If the artifact is in fresh water, use clean fresh water. If artifacts are to be stored in clean water for more than a few days, consider temperature and light conditions. Warmer temperatures and high light levels may enhance biological growth leading to deterioration of the materials. Changing the water on a regular schedule or using a flow-through storage tank can eliminate some, but not all, of the issues with biological growth. If the object has been recovered from a seawater setting and will be transferred to a collection, leaching of the salt should begin as soon as the object is recovered. Place the object in purified fresh water, and use a conductivity meter to monitor the salinity. Change the water every day to continue leaching of salts from the object. Measure and record the amount of water used. If the object must be stored in clean water for some time before cleaning, document the condition periodically to determine whether degradation is occurring. Keep records of recovery time, handling, and any treatment, including the weight of the objects before and after treatment.

Site cleanup usually necessitates collection or recovery of objects. Objects found on the surface are likely to have been moved from their original context. If cleanup of the site was successful and conditions are similar to pre-oiling parameters, such objects can be returned to the site.

Segregate contaminated artifacts from other collections. Even after cleaning, it may be necessary to segregate previously contaminated objects from other collections. It is likely that complete cleaning was not possible or that the condition of the artifacts requires special storage conditions.

Cleaning Archeological Materials

Little to no scientific research has been done on the removal of crude oil from archeological materials. Therefore, these recommendations are based only on current conservation practices as well as information about the materials and probable condition issues. If an object could be expected to yield DNA information or isotopic information, it is best not to attempt to clean the object before these studies are undertaken. Collagen and DNA are damaged by water. It is also possible that oil contamination could be spread over larger portions of the object, rendering it useless for such studies. The oil itself will affect these studies, so if the object is completely contaminated, it cannot be used for DNA or radiometric analyses. It is advisable to consult with a radiocarbon laboratory or other specialist in advance of treatment.

Cleaning should be undertaken with caution, particularly if the objects are fragile or if they are expected to be sensitive to particular conditions, i.e., the pH of the cleaner. In most cases it is best to use a cleaner that has a neutral or slightly basic pH (7 to 10). Cleaning tests should be performed on small, inconspicuous areas, if possible, before undertaking a full-scale cleaning. Removal of crude oil contamination should be the only goal of the initial cleanup efforts. Removal of corrosion or other deterioration or contamination should be deferred until a trained conservator can examine the material.

Objects should be cleaned as thoroughly as possible before storage or reintroduction to their original location. If chemical cleaning is to be done in the field, measures must be taken to prevent contamination of waterways and waste water must be disposed of responsibly. After cleaning take extra care to remove as much of the cleaner as possible. Residues from cleaners may continue to act on the surface of the object and can cause ongoing damage. Again, keep detailed records of any treatment, including dates, cleaning methods, type(s) of cleaner(s), before and after images, and unique/identifying characteristics of the object. If cleaning is done in a laboratory, it is advisable to use a fume hood to avoid exposure to volatile components of the oil that could be toxic.

Chemical Cleaners

The use of any chemical cleaner on cultural materials should be undertaken carefully. This document considers a variety of materials, and no single cleaner is likely to work well and be safe for use on all materials.

Cleaning should be undertaken with the mildest, least abrasive method. Improper cleaning can lead to acceleration of deterioration or loss of original materials. Always begin by reviewing the Materials Data Safety Sheet (MSDS) for any chemical product to be used. The MSDS may be found by searching online or by contacting the manufacturer or distributor. The MSDS contains important chemical information, safety precautions for handling, as well as transport and disposal information needed for use of the product.

Never *use the following cleaning methods*:

- Household bleach or other oxidizing cleaners, or mild cleaners with added bleach or oxidizing agents. These products may chemically react with the surface of the object and leave soluble salts in the pores of the material which will lead to decay. Check the label of the cleaner or the MSDS for active cleaning ingredients. Do not use products for cleaning archeological materials if the products contain sodium hypochlorite (NaClO), sodium perborate, sodium percarbonate, sodium persulfate, tetrasodium pyrophosphate, calcium hypochlorite, or urea peroxide.
- Strong acids, including muriatic acid, hydrochloric acid, or others. These chemicals are too harsh and may etch or dissolve the surface. Because they are corrosive, they can also be hazardous to workers.
- Strong bases, such as concentrated ammonia, sodium hydroxide, calcium hydroxide, potassium hydroxide, or others. These cleaners may be aggressive on the surface of the object, are difficult to rinse thoroughly, and may be hazardous to workers.
- Harsh mechanical devices or power tools such as sanders, drills, high-pressure power washers, or even stiff-bristled brushes can damage the surface of sensitive objects. These techniques remove the original material.

Several types of cleaners can be considered for use on archeological materials:

Detergents

Detergents are surfactant-based cleaners, or cleaners that contain a “surface-active agent.” The detergent decreases the differences between water and oil by providing a “bridge” between the two. One end of the bridge is hydrophobic and will attach to the oil, while the other is hydrophilic and will attach to the water. This allows the oil to be released to the detergent and water. When the hydrophilic end of the detergent carries a charge, the detergent is called an ionic detergent. Non-ionic detergents do not have a charge associated with the head. Non-ionic detergents are usually considered to be most effective at removing oil-based contamination.

Any detergent should be prepared and applied as recommended by the manufacturer. Most detergents should be diluted with clean water before use, as the concentrated solution may be too harsh for sensitive materials. Warming the detergent or diluting with warm water might improve the product’s efficiency and efficacy. Non-abrasive brushes or sponges can be used carefully. Any materials cleaned with detergents must be flushed thoroughly with clean water. If the object will not withstand this type of rinsing, it is best not to use a detergent.

Solvent-based Systems

Solvents such as mineral spirits, white spirit (Stoddard solvent), and xylene combine with and dilute the oil. On surfaces, a solvent might displace the oil rather than removing it by breaking it down as a detergent would. Though solvents can be very effective, this means that solvent-based cleaning systems can require secondary cleaning to remove residual solvent.

Enzymatic Detergents

Some detergents include enzymes that are added to break down specific types of stains. Enzymes are naturally-occurring proteins that catalyze certain types of chemical reactions. Enzymes are used for protein-based stains, carbohydrates and starches, and lipids or fats. Soaking is the usual method for cleaning with enzymatic detergents. Enzymatic detergents probably are not appropriate for most cultural materials.

Cleaning Metal Artifacts

Manually remove any thick outer coating or build-up of oil using a Teflon or wooden scraper. Depending on the friability of the metal object, it may be cleaned in an ultrasonic bath using a solvent based cleaner. Alternatively, a platform shaker or mixer may be used to move the cleaner around the object more gently. If neither of these is available then a soft nylon brush (such as a child's toothbrush) can be used to scrub the surface gently in conjunction with a solvent-based cleaner. The oil will stick to the bristles of the brush, so the brush should be rinsed in solvent frequently. Possible cleaning agents are acetone, mineral spirits, or diluted Vulpex Liquid Soap. Note that Vulpex may be diluted with either clean water or mineral spirits. For cleaning metals, it is probably best to dilute with mineral spirits, one part soap to 20 parts spirits.

Cleaning Wooden Artifacts

Manually remove any thick outer coating or build-up of oil using a Teflon scraper. Depending on the condition of the material, a sturdy wooden object can be cleaned in an ultrasonic bath using solvent based cleaner. A platform shaker/mixer may be used for more delicate objects. The wooden object should be kept in clean seawater until its future use is decided or further treatment such as polyethylene glycol can be preformed. Possible solvents are acetone and mineral spirits.

Cleaning Glass and Ceramics

Most importantly, be mindful of any broken or jagged edges. If the glass is in stable condition, excess oil can be removed by wiping with non-abrasive wipes or scraping with a non-reactive object, such as a Teflon scraper. The surface of archeological glass that has been exposed to a marine environment typically shows two alteration layers: an outer crust of iridescent lamellae and/or opaque white oxidation crusts and a "gel layer" between this outer crust and any remaining pristine glass. Because these layers form as a result of oxidation of the original glass surface, they are sensitive to pH. Use of a solvent-based cleaner might be less damaging to these alteration products. As with any cleaning method, a trial in a small, inconspicuous area is recommended before large-scale cleaning is attempted.

Cleaning Shell and Bone

Little to no testing has been done on the proper removal of oil from shell and bone. A careful evaluation of the sample must be done before cleaning is undertaken, considering that there are no scientific data on the cleaning of oil-contaminated shell and bone, and that there is the potential to render the sample useless for further studies (DNA or isotopic analyses) if the wrong method is used. If it is determined that the sample should be cleaned, any excess oil should be removed with a soft, non-abrasive wipe or a non-abrasive, non-reactive tool such as a Teflon scraper. Do not use stiff or wire bristled brushes on these objects as these methods are excessively abrasive and likely to cause permanent damage to the object. A solvent poultice (a solvent mixed with powdered clay) should be considered because shell and bone are pH sensitive. Citrus-based solvents should be avoided until further testing determines that they do not enhance biological growth. Limonene and D-limonene are both well-known chemical solvents, but the side-effects of these chemicals on shell and bone are not documented. Any acid-based cleaners should also be avoided, as these would break down the material. Prior to any full-scale cleaning, it is important to test clean a small, inconspicuous patch to guarantee that there is no immediate negative impact on the material.

Storage and Segregation Issues

Artifacts may need to be permanently segregated from other collections.

It might not be possible to thoroughly clean some materials. Even slightly soiled objects may continue to release volatile components of the crude oil over time. These objects may need to be permanently segregated from other collections. This will preserve the contaminated objects under the best possible conditions while eliminating the possibility of tainting objects that were not contaminated.

Artifacts may need to be segregated based on storage conditions.

Some materials are more porous than others, and cleaning may be more effective for some materials. This may dictate special storage conditions for sensitive materials that are not thoroughly cleaned. As mentioned earlier in this document, oil residues can promote biological growth. Conditions that inhibit biological activity and therefore limit degradation of the materials, such as cold storage or storage in a low-oxygen environment (i.e., a sealed container that has been filled with nitrogen), might be required in order to stabilize objects until further cleaning can be carried out. These storage conditions might not be appropriate for all materials. Storage at or below freezing is not recommended because the formation of ice crystals within pore spaces of materials can cause fracturing. In addition, objects should be rinsed thoroughly before cold storage because residues from some cleaning products can crystallize at temperatures above the freezing point of water.

Artifacts may need to be segregated based on material.

Even if the storage conditions are similar for different materials, more porous materials might retain more of the oil residue than others, or some materials may release volatiles more readily than others. Segregation of objects based on their material composition might be required.

Ongoing and Future Studies

Little research has been done on the removal of crude oil from archeological materials. The recommendations included in this document are based on information in existing literature, as well as personal communications with a few archeologists who have experience with crude oil contaminated artifacts. A study is currently underway at the National Center for Preservation Technology and Training in conjunction with Northwestern State University's Heritage Resources program on the removal of crude oil from shell and bone, with final results expected by the end of summer 2011. An additional study on removing crude oil from brick is also underway, with preliminary results expected by the end of summer 2011. Much more research is needed to document the effects of a variety of cleaners and cleaning methods on archeological materials.

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