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Reactive Capping for Coal Tar-Impacted Sediments

An In-Situ Evaluation of Effectiveness and Implementability
(Phase I–Predesign Evaluations and Conceptual Design)

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Technical Update, January 2008

EPRI Project Manager

A. Coleman

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ELECTRIC POWER RESEARCH INSTITUTE
3420 Hillview Avenue, Palo Alto, California 94304-1338 ▪ PO Box 10412, Palo Alto, California 94303-0813 ▪ USA
800.313.3774 ▪ 650.855.2121 ▪ askepri@epri.com ▪ www.epri.com

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This document was prepared by

ARCADIS U.S., Inc.
30 West Monroe, Suite 1710
Chicago, IL 60603

Principal Investigators
N. Gensky
D. Bessingpas

University of Texas at Austin
Department of Civil Engineering
1 University Station C1786
Austin, TX 78712

Principal Investigator
D. Reible

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PRODUCT DESCRIPTION

Many former manufactured gas plant (MGP) sites are located adjacent to rivers and streams, and MGP-related impacts—including the presence of coal tar, a nonaqueous phase liquid (NAPL)—have been observed in the sediments of those adjacent water bodies. Unfortunately, there are only a limited number of remedial alternatives that currently exist to reduce the exposure potential of human and ecological receptors to contaminated sediments. The most common remedial alternatives generally considered are sediment removal, for example by dredging: in-place containment, for example by capping; and monitored natural recovery (MNR), each having advantages and limitations that must be considered on a site-by-site basis. Sediment removal, the predominant remedy chosen for sites with NAPL-impacted sediments, has shown mixed results in achieving remedial goals. Reactive capping (also known as active capping) has shown promise as a potentially viable alternative to sediment removal for remediating NAPL-impacted sediments.

This project seeks to assess the effectiveness and implementability of reactive sediment capping alternatives by designing, implementing and monitoring a field-scale demonstration of an organoclay sediment cap placed over coal tar-impacted sediments adjacent to a former MGP site. The project consists of two phases:

- Phase I involves conducting predesign evaluations and developing a conceptual cap design and monitoring approach.
- Phase II involves designing the cap, installation and performance monitoring.

This Tech Update summarizes Phase I activities.

Results & Findings

This Tech Update is organized as follows:

- **Section 1** discusses the project objectives and provides an overview of the report.
- **Section 2** summarizes available remedial alternatives for sediments; summarizes reactive capping materials and applications previously used, tested or considered at other sites; and identifies and summarizes existing conditions at the site selected for the reactive sediment capping field demonstration.
- **Section 3** summarizes the predesign evaluations that have been completed.
- **Section 4** presents the conceptual cap design.
- **Section 5** discusses potential cap monitoring options.
- **Section 6** summarizes conclusions of the Phase I activities and presents the anticipated scope of work for Phase II.
- **Section 7** lists documents referenced in this Tech Update.

Challenges & Objectives

Reactive capping may be a viable and cost-effective alternative to dredging for remediating coal tar-impacted sediments at MGP sites. This project will provide useful information for designing and implementing reactive sediment capping projects for sites with coal tar-impacted sediments.

Applications, Values & Use

The Phase I results presented in this Tech Update will be used by the project team to complete Phase II of the project, which will include design, installation and monitoring of the reactive sediment cap. A final Tech Update will be prepared after the cap is installed and monitored for a predetermined period of time.

EPRI Perspective

This project provides an in-situ evaluation of the effectiveness and implementability of a reactive sediment cap at a former MGP site. Many former MGP sites are located adjacent to rivers and streams with coal tar-impacted sediments. To abate these impacts, environmental regulators favor the dredging of impacted sediments. While some regulators do consider capping alternatives, the options considered are limited to below grade capping alternatives, which necessitate some level of sediment removal to accommodate the thickness of the designed cap. The EPA's Sediment Guidance, as clarified in June 2007 by the National Academy of Sciences, has suggested that alternatives to dredging should be considered when appropriate. This project provides utility site managers with viable alternatives to sediment dredging by evaluating the use of a reactive sediment cap to manage residual coal tar in areas where infrastructures such as utility crossings and bridge abutments rule out sediment removal.

Approach

The project team developed a conceptual design for a demonstration of a reactive cap to control and/or contain coal tar-impacted sediments adjacent to a former MGP site.

Keywords

Manufactured gas plant (MGP)
Dredge
Active cap
Reactive cap
Organoclay

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- Public Service Electric and Gas Company
- We Energies

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PROJECT OVERVIEW AND OBJECTIVES

Many former manufactured gas plant (MGP) sites are located adjacent to rivers and streams, and MGP-related impacts – including the presence of coal tar nonaqueous phase liquids (NAPLs) – have been observed in the sediments of those adjacent water bodies. Unfortunately, there are only a limited number of remedial alternatives that currently exist to reduce the exposure potential of human and ecological receptors to contaminated sediments. The most common remedial alternatives generally considered are sediment removal (e.g., dredging), in-place containment (e.g., capping) and monitored natural recovery (MNR), each having advantages and limitations that must be considered on a site-by-site basis. As discussed in detail in *Sediment Dredging at Superfund Megasites: Assessing the Effectiveness* (National Academy of Sciences [NAS], 2007), sediment removal has been the predominant remedy chosen for sites with NAPL-impacted sediments, with mixed results for achieving remedial goals. Reactive capping (also known as active capping) has shown promise as a potentially viable alternative to sediment removal for remediating NAPL-impacted sediments (Hart Crowser, 2006).

The objectives of this project are to assess the effectiveness and implementability of reactive sediment capping alternatives by designing, implementing and monitoring a field-scale demonstration of an organoclay sediment cap placed specifically over coal tar NAPL-impacted sediments adjacent to a former MGP site. This project consists of two phases:

- Phase I involves conducting predesign evaluations and developing a conceptual cap design and monitoring approach.
- Phase II involves designing the cap, installation and performance monitoring.

This Tech Update summarizes the Phase I findings and is organized as follows:

- Section 2 summarizes available remedial alternatives for sediments; summarizes reactive capping materials and applications previously used, tested or considered at other sites; and identifies and summarizes existing conditions at the site selected for the reactive sediment capping field demonstration.
- Section 3 summarizes the predesign evaluations that have been completed.
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2
BACKGROUND

Summary of Available Sediment Remedial Alternatives

In general, engineered remedial technologies for MGP-related coal tar NAPL-impacted sediments can be separated into two categories: capping and removal. Sediment capping and sediment removal can also be used in various combinations, where a portion of the coal tar NAPL -impacted sediments is removed and then the remaining NAPL-impacted sediments are capped. Other technologies such as MNR and enhanced natural recovery (ENR), which have been proven to address polycyclic aromatic hydrocarbon- (PAH-) impacted sediments, are not as effective in addressing NAPL-impacted sediments (the critical factor is whether the NAPL is potentially migrating – in general natural recovery and enhanced natural recovery are not as effective in sediments with upwelling of either NAPL or dissolved contaminants, but if the NAPL is largely immobile, they could work well). In-situ technologies such as biological treatment, chemical treatment and immobilization are under development and may be applicable for addressing PAH-impacted sediments, but not likely NAPL-impacted sediments. The *Contaminated Sediment Remediation Guidance for Hazardous Waste Sites* (United States Environmental Protection Agency [USEPA], 2005), *Handbook of Remedial Engineering for MGP Sites with Contaminated Sediments* (Electric Power Research Institute [EPRI], 2007a) and *Sediment Dredging at Superfund Megasites: Assessing the Effectiveness* (NAS, 2007) provide an overview of available remedial alternatives for addressing impacted sediments. The remainder of this section describes remedial design and implementation considerations for capping and removal of coal tar NAPL-impacted sediments.

Overview of Coal Tar NAPL-Impacted Sediment Capping

Key remedial design and implementation considerations for MGP-related coal tar NAPL-impacted sediment capping are as follows:

- **Source Control.** Controlling or eliminating upland NAPL migration into the sediments is particularly important to prevent sediment recontamination, regardless of the remedial approach employed. If NAPL migration continues from upland sources, the areas where sediments have been capped can become recontaminated if the migration occurs above the cap. Conversely, if NAPL migration continues from upland sources below the cap, NAPL loading from the upland sources could result in failure of the cap (i.e., NAPL breaking through the cap materials).
- **NAPL-Impacted Area Delineation.** The extent of NAPL-impacted sediments must be well-defined prior to remediation. Coal tar NAPLs can be challenging to delineate, especially in loose noncohesive sediments, cobbly sediments, as well as in areas with debris, obstructions and submerged structures (e.g., utility lines, piers, bridges). Furthermore, the horizontal and vertical extents of NAPL-impacted sediments can be highly variable. Understanding the mechanism(s) that lead to the distribution and extent of NAPL-impacted sediment (e.g., deposition, direct discharges), and the current level and mechanism(s) of NAPL mobility are

also important for designing an effective remedial approach. Technologies such as TarGOST® (EPRI, 2005; EPRI, 2007b) and Dakota Technologies, Inc.'s DART (EPRI, 2007c) provide additional NAPL-impacted sediment delineation tools in conjunction with conventional sediment coring techniques.

- **NAPL Migration Pathways.** NAPLs can migrate into sediments from upland soils and within sediment beds based on the site-specific geology. NAPLs can migrate as balls and blebs within the water column, and can also sorb onto resuspended sediments. NAPL can also migrate from sediments into the water column via gas ebullition. This is where gas bubbles formed within the sediment are released into the water column and NAPL adheres to and migrates with the bubbles. Understanding the presence, magnitude and importance of the various NAPL migration pathways should be considered in cap design. For example, gas-driven NAPL migration may only occur in high organic carbon sediments or during the warmer seasons. Design considerations could consist of providing an additional layer of sediment to cover the existing sediment and eliminate seasonal contact with warmer surface waters (USEPA, 2005). If NAPL-impacted sediments are at depths below a stable sediment bed, then impacts to surface-water quality may be negligible from groundwater to surface migration pathways. Capping design should focus on mitigating the dominant migration pathways as well as on potential changes to those pathways after capping. For example, placing a low-permeability cap may not prevent potential NAPL migration through time (long-term effectiveness) or space (redirection outside the capped area).
- **Sediment Consolidation.** During cap placement, compression of sediments due to the weight of the cap may result in migration of NAPLs through or around the cap (i.e., an instantaneous migration versus migration through time). To mitigate compression-driven NAPL migration, sediment geotechnical properties such as compression, shear stress, water content and consolidation should be evaluated during cap design. Engineering controls such as silt curtains may help to mitigate NAPL and NAPL-impacted sediment migration within the river during cap installation.
- **Cap Permeability/Capacity.** For caps to be effective in mitigating migration of NAPLs from NAPL-impacted sediments into the water column, they either need to have low permeability or have the capacity to sequester NAPLs. Low-permeability caps may be more effective where gas generation is not a primary pathway and where residual NAPLs are present in the sediments with limited potential to migrate as a separate phase. Alternatively, caps placed over NAPL-impacted sediments should have capacity in the capping materials to sorb, sequester, or otherwise prevent NAPL migration from the sediment into the water column, while allowing groundwater to pass through. These types of caps are called reactive caps. Materials used in reactive caps could include carbon sources such as activated carbon, coke, or other materials such as organoclays (USEPA, 2005). Organoclays have been more effective for coal tar NAPLs than other materials (Hart Crowser, 2006). Organoclays are bentonite clays reacted with organic molecules (typically quaternary amine salts). Organoclays are both hydrophobic and organophillic, resulting in high affinities for coal tar NAPLs. Organoclays maintain permeability, which allows for continued migration of groundwater and gas while NAPLs and dissolved-phase constituents are sequestered (although reduced permeabilities have been observed in organoclays in contact with coal tar NAPLs; Reible, 2005).

- **Cap Monitoring and Maintenance.** The presence of NAPL-impacted sediments may result in more rigorous monitoring and maintenance requirements to prove to regulatory agencies that the cap effectiveness continues through time. NAPL breakthrough at the edges or through sediment caps could require adding additional capping materials.

Overview of Coal Tar NAPL-Impacted Sediment Removal

Key remedial design and implementation considerations for MGP-related coal tar NAPL-impacted sediment removal are as follows:

- **Source Control and NAPL-Impacted Area Delineation.** The considerations for source control and NAPL-impacted area delineation discussed above for capping (see *Overview of Coal Tar NAPL-Impacted Sediment Capping*) are also applicable to removal alternatives.
- **NAPL Releases.** The physical mixing action of dredging stirs up sediments, thereby releasing suspended solids, dissolved constituents and NAPLs to the water column. To reduce the impacts of downstream sediment transport, environmental dredging areas are typically isolated from the rest of the waterway by silt curtains, silt screens, oil booms, portable barriers and other containment barriers (e.g., sheetpile enclosures). All of these barrier systems have limitations based on water depths, sediment foundation stability, water currents, winds, tides, boat wakes and waves. Without these barriers, NAPLs and dissolved-phase constituents may be released to the water column during sediment dredging even with state-of-the-art controls (e.g. environmental buckets). The mass of contaminants released from exposed NAPL during dredging can be considerably more than the 1 to 5 percent of dredged mass normally assumed for solid-associated contaminants (National Research Council, 2001 and NAS, 2007).
- **Sediment Dewatering.** Dewatering of NAPL-impacted sediments requires additional treatment components to remove NAPLs to meet the treated water discharge requirements.

Summary

Remediation of MGP-related coal tar NAPL-impacted sediments is challenging and multiple factors must be considered when designing and implementing NAPL-impacted sediment remedies. The removal of NAPL-impacted sediments may not be feasible in all circumstances due to obstructions and structures, or may result in more releases to the environment during dredging than if the NAPL-impacted sediments were kept intact. Sediment capping (specifically, reactive sediment capping) shows potential as a viable remedial alternative for NAPL-impacted sediments. Of the types of reactive materials available, organoclays are the most effective for coal tar NAPLs.

Summary of Reactive Capping Materials/Applications

Table 6-1 of the *Handbook of Remedial Engineering for MGP Sites with Contaminated Sediments* (EPRI, 2007a) provides an overview of representative sediment capping projects. The first section of that table lists six NAPL-impacted sediment sites where caps have been installed: Pacific Sound Resources in Washington, McCormick and Baxter Superfund Site in Oregon, Head of the Thea Foss Waterway in Washington, East Eagle Harbor/Wyckoff/Bainbridge Island in Washington, Hamilton Harbor in Ontario and Rotterdam Harbor in the Netherlands. Sand caps were used at three sites, a silt/clay cap was used at one site and composite caps (sand and organoclay, sand and high-density polyethylene [HDPE]) were used at two sites. At two of six sites (sand cap only and composite cap of sand and HDPE), sediment recontamination was observed. Organoclay was used as a cap component at one of the six sites (McCormick and Baxter Superfund Site) (EPRI, 2007a). Table 2-1 of this Tech Update provides an overview of additional NAPL-impacted sediment capping projects, as well as an update on the McCormick and Baxter Superfund Site project, with an emphasis on projects with coal tar-type NAPLs and reactive capping materials.

Table 2-1
Summary of Sediment Capping Projects Using Reactive Materials

Project	Site Conditions	Design Thickness	Cap Material(s)	Year Constructed	Performance
McCormick and Baxter Superfund Site Willamette River, Oregon	- 23 acres (9.3 hectares [ha]) - 46+ feet (14+ meters) water depths - Fine to medium sand to silty sand	2 feet (0.6 meters)	- Composite cap including sand, gravel and armoring - Bulk organoclay used in three areas to prevent NAPL seepage	2004	Cap inspection identified additional NAPL seeps, which were addressed by placing organoclay mats in the seep areas.
GASCO Site Willamette River, Oregon	- 35 acres (14.2 ha) pilot study in 1 acre (0.4 ha) - River shoreline - Silts and sands	1.5 feet (0.5 meters)	Sand and armoring with organoclay mat	2006	Performing as designed. Will continue to monitor and evaluate use as permanent remedy.
St. Louis River/Interlake/ Duluth Tar Superfund Site Stryker Bay, Minnesota	- 35 acres (14.2 ha) total - 7 acres (2.8 ha) for capping	4 feet (1.2 meters)	Sand and reactive mat (activated carbon and sand) and a surcharge sand	2006	No long-term performance data are available.

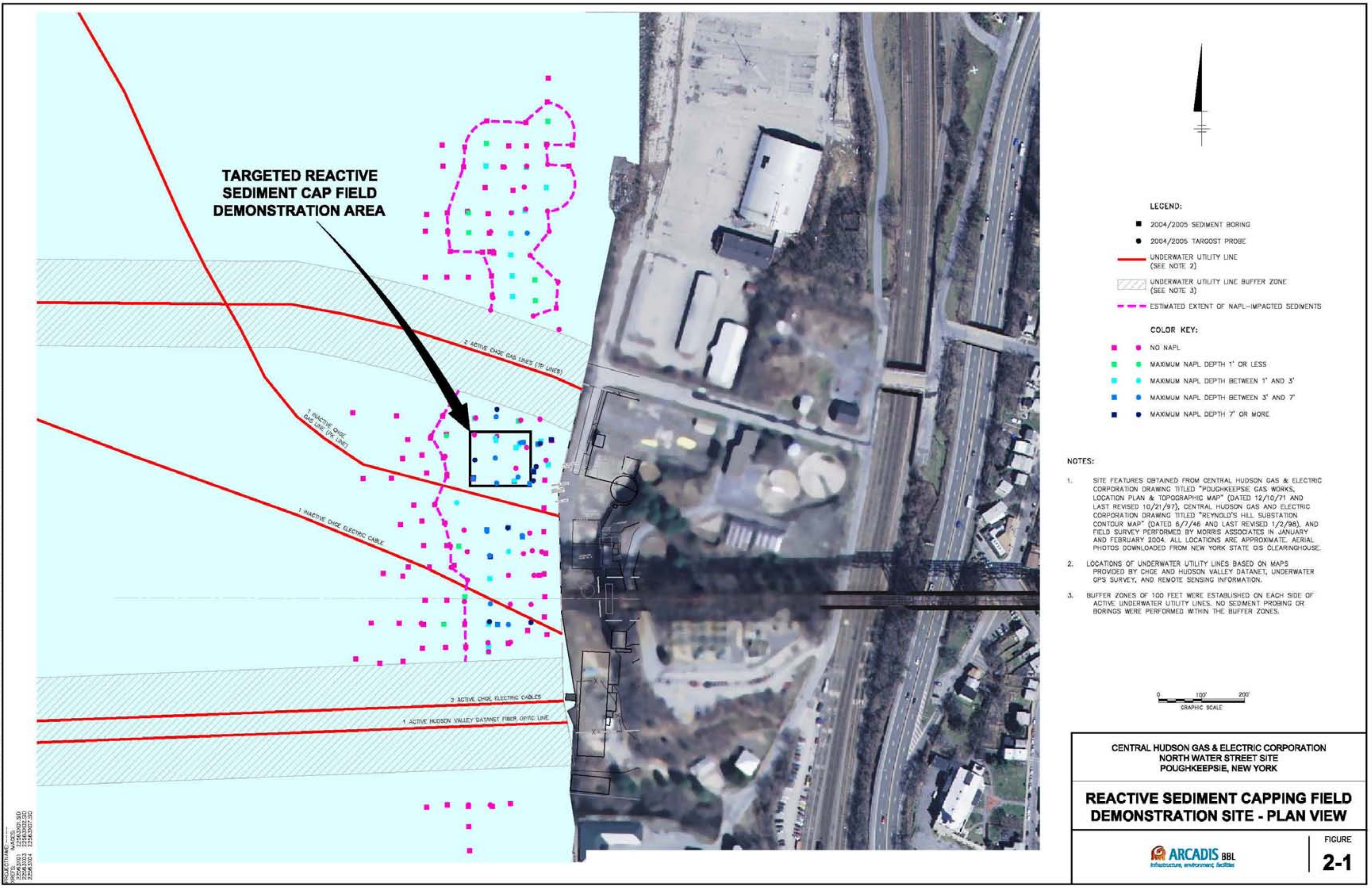
Notes:
1. Data obtained from EPRI, 2007a; Oregon Department of Environmental Quality, 2007a and 2007b; and USEPA, 2007a, 2007b and 2007c.
2. Refer to Table 6-1 in *Handbook of Remedial Engineering for MGP Sites with Contaminated Sediments* (EPRI, 2007a), for a list of additional NAPL-impacted sediment sites where capping has been performed.

Field Demonstration Site

The site selected for the reactive sediment capping field demonstration is the Central Hudson Gas & Electric Corporation North Water Street Former MGP Site in Poughkeepsie, New York (North Water Street Site). Specifically, capping will be performed on NAPL-impacted sediments in the Hudson River adjacent to the North Water Street Site.

The North Water Street MGP operated from approximately 1911 to 1955 and used the carbureted water gas process. Based on the results of field investigations conducted in 2004 and 2005, the extent of NAPL-impacted sediments at the site has generally been delineated (Figure 2-1). As shown on the conceptual cross-section on Figure 2-2, the most concentrated NAPL-impacted sediments are generally located from the bottom edge of the steep slope at the river's eastern shoreline, extending outward approximately 200 to 250 feet (approximately 60 to 75 meters) into the river, at depths of 0.5 to 3 feet (0.15 to 0.9 meters), and generally covered by less-impacted materials. The source of NAPL to the river is from historical seepage and/or discharges from the former MGP operations. Ongoing seepage of NAPL from the overburden or bedrock has not been observed. NAPL does migrate within the river due to erosion/deposition of near-surface NAPL-impacted sediments. NAPLs from near-surface and deeper sediments are also released to the surface water via gas ebullition and groundwater discharge. Sediments are primarily silts, with some fill and shale fragments (from historical on-site bedrock blasting), especially closer to the shoreline.

Conditions at the North Water Street Site that limit the practicability of sediment dredging include 50- to 60-foot (approximately 15- to 18-meter) water depths, tidal flows and the presence of submarine utility lines. Active submarine utility lines include two 8-inch- (20.3 centimeter- [cm-]) diameter gas pipes, two 138-kV electric cables contained in two 8⅝-inch- (21.9-cm-) diameter pipes and one fiber optic cable. The approximate locations of the utility lines are shown on Figure 2-1.



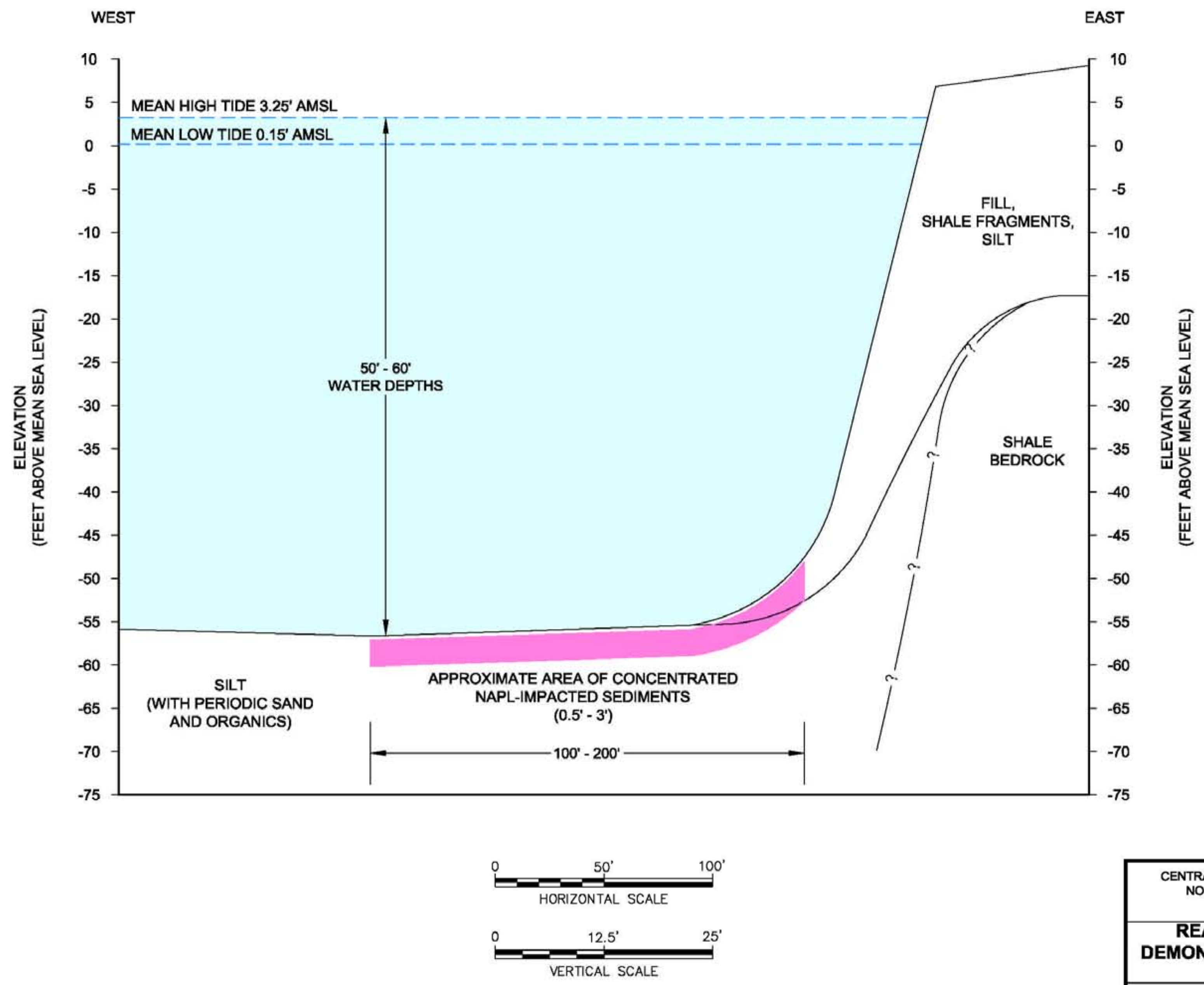
NOTES:

1. SITE FEATURES OBTAINED FROM CENTRAL HUDSON GAS & ELECTRIC CORPORATION DRAWING TITLED "POUGHKEEPSIE GAS WORKS, LOCATION PLAN & TOPOGRAPHIC MAP" (DATED 12/10/71 AND LAST REVISED 10/21/97), CENTRAL HUDSON GAS AND ELECTRIC CORPORATION DRAWING TITLED "REYNOLD'S HILL SUBSTATION CONTOUR MAP" (DATED 6/7/46 AND LAST REVISED 1/2/98), AND FIELD SURVEY PERFORMED BY MORRIS ASSOCIATES IN JANUARY AND FEBRUARY 2004. ALL LOCATIONS ARE APPROXIMATE. AERIAL PHOTOS DOWNLOADED FROM NEW YORK STATE GIS CLEARINGHOUSE.
2. LOCATIONS OF UNDERWATER UTILITY LINES BASED ON MAPS PROVIDED BY CHGE AND HUDSON VALLEY DATANET, UNDERWATER GPS SURVEY, AND REMOTE SENSING INFORMATION.
3. BUFFER ZONES OF 100 FEET WERE ESTABLISHED ON EACH SIDE OF ACTIVE UNDERWATER UTILITY LINES. NO SEDIMENT PROBING OR BORINGS WERE PERFORMED WITHIN THE BUFFER ZONES.

CENTRAL HUDSON GAS & ELECTRIC CORPORATION
NORTH WATER STREET SITE
POUGHKEEPSIE, NEW YORK

REACTIVE SEDIMENT CAPPING FIELD DEMONSTRATION SITE - PLAN VIEW

Figure 2-2-1
Reactive Sediment Capping Field Demonstration Site – Plan View



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NORTH WATER STREET FORMER MGP SITE
POUGHKEEPSIE, NEW YORK

REACTIVE SEDIMENT CAPPING DEMONSTRATION SITE - CONCEPTUAL CROSS SECTION

ARCADIS BBL
infrastructure, environment, facilities

FIGURE
2-2

Figure 2-2
Reactive Sediment Capping Field Demonstration Site – Conceptual Cross Section

3
PREDESIGN EVALUATIONS

This section summarizes various evaluations that were completed in preparation for designing the reactive sediment cap to be installed as part of this field demonstration project, including the following:

- Selection of field demonstration area
- Organoclay laboratory tests
- Submarine utility line considerations
- Identification of other data needs

Each of these topics is discussed in the following subsections.

Selection of Field Demonstration Area

The specific area anticipated to be targeted for capping as part of the field demonstration is an approximately 100- by 100-foot (approximately 30- by 30-meter) area located adjacent to the northern portion of the North Water Street Site (Figure 2-1). This area was selected based on the following considerations:

- Area with near-surface NAPL-impacted sediments (based on sediment borings and TarGOST probes conducted during previous field investigations)
- Area where sheens have been observed on the water surface
- Located off shore from former MGP operation areas/structures thought to be primary historical sources of NAPL in the river (e.g., tar processing area, tar centrifuge house)

Characteristics of the targeted sediment capping area, based on data collected during previous field investigations, are as follows:

- The most concentrated NAPL impacts are located in the upper 3 feet (0.9 meters) of sediment.
- Total PAH concentrations in surficial sediment samples range from 79 to 9,700 milligrams per kilogram (mg/kg).
- Total organic carbon concentrations in surficial sediment samples range from 26,400 to 76,400 mg/kg.
- Sediments are primarily silts with lesser amounts of fill (e.g., slag, cinders, bricks), shale fragments, sand, gravel, clay and organics (e.g., wood).
- Blow counts from split-spoon sediment borings ranged from “weight of hammer/rods” over 2.5 feet (0.76 meters) to 2 blows per 6 inches (15.24 cm) for silts, and up to 12 blows per 6 inches (15.24 cm) for fill materials.

- Geotechnical data for two Shelby tube samples collected from within the targeted sediment capping area are summarized in Table 3-1.

Table 3-1
Summary of Geotechnical Data for Field Demonstration Area

Parameter	SED-121CC 3.5-5.5 feet (1.1-1.7 meter)	SED-128CC 0.0-2.0 feet (0.0-0.6 meter)
Grain Size – Sieve/Hydrometer (ASTM D422 & D1140)		
% Gravel	0	1.6
% Sand	8.7	13.9
% Fines	91.3	84.5
Atterberg Limits (ASTM D4318)		
Plastic Limit	26	Nonplastic
Liquid Limit	32	--
Plasticity Index	6	--
Bulk (Natural) Soil Density (USACE EM-1110-2-2906 Appendix II, Displacement Method)		
Dry Density, lb/ft^3 (g/cm^3)	66.3 (1.1)	69.4 (1.1)
Moist Density, lb/ft^3 (g/cm^3)	102.9 (1.6)	105.3 (1.7)

Notes:
1. lb/ft^3 = pound per cubic foot
2. g/cm^3 = gram per cubic centimeter
3. -- = No data available

Organoclay Laboratory Tests

Based on the results of reactive capping materials used and tested to date at other sites, organoclay has been selected as the reactive capping material to be used as part of this field demonstration project. To provide data to develop the conceptual cap design, various laboratory tests were conducted with organoclay and NAPL obtained from a monitoring well at the North Water Street Site. The tests were conducted at the University of Texas at Austin and included the following:

- Batch tests
  - NAPL sorption capacity
  - dissolved-phase sorption capacity
- Column tests
  - NAPL sorption capacity
  - flow uniformity
  - organoclay layer permeability

The scope and findings of the organoclay laboratory tests is summarized in Appendix A. Based on the test results presented in Appendix A, PM-199 (manufactured by CETCO) was recommended as the organoclay to be used for the reactive sediment capping field demonstration. The expected performance of the PM-199 organoclay is as follows:

- PM-199 organoclay is expected to absorb and retain approximately 1 lb (0.45 kg) dry NAPL per 1 lb (0.45 kg) dry organoclay. Using a mat containing 0.8 lb dry organoclay per square foot (ft^2) (3.9 kilograms per square meter [kg/m^2]), the mat is expected to absorb 0.8 lb NAPL per ft^2 (3.9 kg/m^2). Upwelling of more than 0.8 lb NAPL per ft^2 (3.9 kg/m^2) is expected to penetrate the mat, although the reduction in permeability of the mat layer will lower the likelihood of NAPL migration to the overlying water.
- The intrinsic permeability of the PM-199 organoclay layer after NAPL exposure is expected to be on the order of $1x10^{-3}$ Darcy ($\sim 1x10^{-11}$ square centimeter [cm^2]). Although the intrinsic permeability of NAPL-impacted organoclay is considerably less than fresh organoclay, it is still equivalent to that of silty sand and is, therefore, not atypical of a surficial sediment.
- If an area of the mat is expected to be exposed to dissolved PAH contaminants only, the organoclay will be expected to retard contaminant release for extremely long periods (255 years for phenanthrene, 1,700 years for pyrene) if the upwelling velocity is on the order of 40 inches (100 cm) per year.
- If an organoclay layer is exposed to both trace NAPL and dissolved-phase contaminants, the NAPL will tend to be absorbed in the lowest organoclay layers and the dissolved-phase will be contained in the upper layers of organoclay; the total NAPL absorption and dissolved-phase containment time will be less than if only NAPL or only dissolved-phase contaminants are present.

Submarine Electric Utility Line Considerations

Because waterways adjacent to many MGP sites contain in-service submarine utility lines that may limit the practicability of dredging impacted sediments, evaluating the potential effects of placing sediment cap materials on top of submarine utility lines is also a component of this project. Specifically, Phase I of this reactive sediment capping field demonstration project included identifying data needed to evaluate the potential for cap materials to cause overheating of electric cables. Based on the final cap design, Phase II will include calculations to estimate thermal effects of placing the designed cap over electric cables present at the field demonstration site. However, as shown on Figure 2-1, it is not anticipated that the cap will actually be placed over electric cables as part of this project.

Data needed to evaluate thermal effects of placing a sediment cap over submarine electric cables include:

- Cable specifications and installation details
- Current and planned electrical loading data
- Thickness and thermal conductivity of existing sediment and armor materials above the cable
- Thickness and thermal conductivity of sediment cap materials

Identification of Other Data Needs

The following list of additional data needs identified to design the reactive sediment cap for this field demonstration project:

- **Identification and mapping of NAPL-impacted sediment and sheen generation areas.** The specific area identified for the reactive sediment capping field demonstration was selected because it is an area with near-surface NAPL-impacted sediments and where sheens have been observed on the water surface. Prior to designing the cap, a remote-operated (or diver-operated) underwater camera will be tested to identify areas where NAPL is entering the water column from impacted sediments and to confirm the suitability of (or modify) the area selected for the field demonstration.
- **Hydraulic data.** Hudson River hydraulic data, such as flow rates, tidal fluctuations and currents, will be obtained from the United States Geological Survey (USGS). Specifically, flow rate and tidal fluctuation data are available from a nearby USGS tide monitoring station. In addition, current data is anticipated to be available from a USGS suspended sediment discharge study recently completed in the Hudson River near the field demonstration site (USGS, 2006).
- **Groundwater, NAPL and gas flux rates.** These data are needed to estimate the amount and rate of NAPL transport from sediment into the water column. Groundwater flux rates can be estimated based on existing geologic and hydrogeologic data obtained during previous field investigations. However, existing data are not available to estimate NAPL or gas flux rates. Given the site conditions (e.g., 50- to 60-foot [approximately 15- to 18-meter] water depths, currents, low visibility) and lack of commercially available gas flux measurement devices, it may not be possible to measure gas flux rates as part of this project. Direct measurements of groundwater flux are anticipated to be obtained using seepage meters as part of the cap monitoring program. NAPL flux rates are also anticipated to be estimated as part of the cap monitoring program.
- **Sediment geotechnical data.** Existing site-specific sediment geotechnical data collected during previous field investigations will be used.
- **River-bottom mapping and debris survey.** Remote sensing data (e.g., multibeam bathymetry, sidescan sonar, sub-bottom profiling) collected as part of the NYSDEC’s Hudson River Estuary Benthic Mapping Project were used to evaluate river bottom conditions at the site. Additional higher resolution and site-specific remote sensing work may be conducted as part of the cap design, and depending on visibility at the field demonstration site, a remote-operated (or diver operated) underwater camera may also be used to evaluate river-bottom conditions and the presence of debris within the targeted capping area.

4

CONCEPTUAL CAP DESIGN

This section presents the conceptual design of the cap to be placed as part of the reactive sediment cap field demonstration. The goal was to develop a reactive cap design that:

- Isolates impacted sediments from the water column
- Mitigates transport of NAPL from the impacted sediments into the water column
- Could logistically be placed given conditions at the field demonstration site
- Was flexible to allow for installation of various configurations
- Could potentially be removed for inspection and testing as part of the monitoring program

Based on these considerations, the conceptual cap configuration consists of the following (from top to bottom):

- Triton Marine Mattress
- Reactive Core Mat (RCM)
- Geonet/geogrid

An expanded cross section of the conceptual cap configuration is shown on Figure 4-1. The cap materials are described in this section. The final cap configuration will be designed during Phase II of this project.

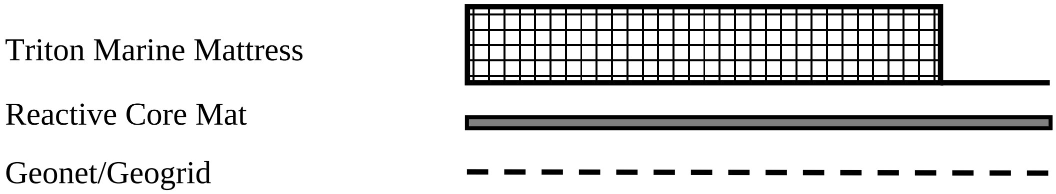


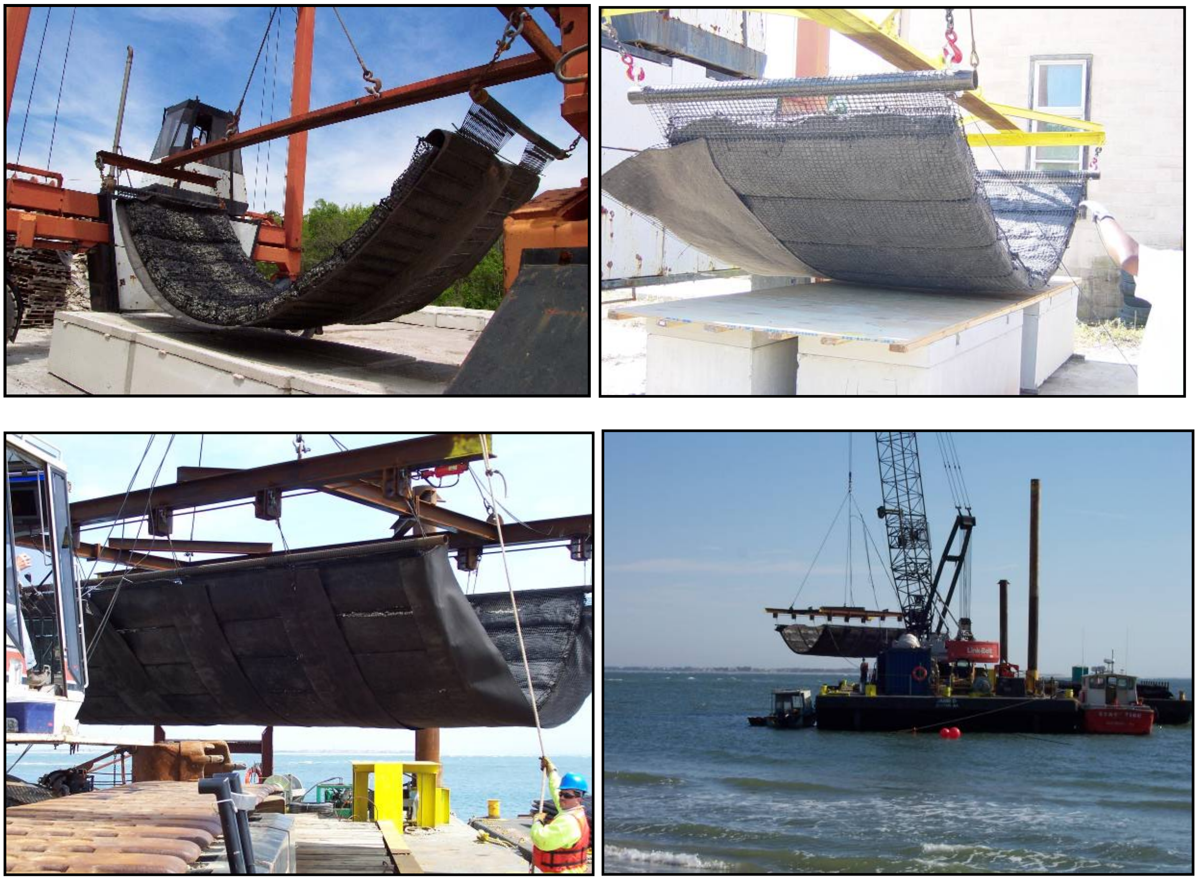
Figure 4-4-1
Expanded Cross Section of Conceptual Cap Configuration

Triton Marine Mattress

Triton Marine Mattresses are manufactured by Tensar International Corporation (Tensar) and are typically used for coastal and waterway erosion protection applications. For this project, the Triton Marine Mattresses will be used to deliver the organoclay-filled RCM (as further discussed below, the RCM will be attached to the bottom of the Triton Marine Mattress) to the sediment surface and will be filled with armor stone to provide stability and keep the RCM in place. Triton Marine Mattresses are constructed with a synthetic geogrid material (specifically, Tensar's BX1500); the grid openings are approximately 1 inch by 1 inch (2.5 cm by 2.5 cm). For this project, dimensions of the Triton Marine Mattress are anticipated to be 6 inches (15.2 cm) thick by 6 feet (1.8 meters) wide by 20 feet (6.1 meters) long, with internal baffles approximately every 2 feet (0.6 meters) along the length of the mattress. The geogrid material extends 2 feet (0.6 meters) out from the mattress on one side and one end, to allow for overlap of materials attached to the bottom of the mattresses (geotextile filter fabric has been used in previous applications; as indicated above, RCM will be used for this project). Although the mattresses would be filled with armor stone during a typical application, the individual compartments created by the baffles could be lined with geotextile and partially filled with other materials (e.g., sand, bulk organoclay). The materials used to fill the mattresses will be determined during design. Multiple configurations may be used.

Attaching the RCM to the Triton Marine Mattresses and filling the mattresses with armor stone and/or other materials will be conducted on shore or on a barge prior to placement in the river. Multiple mattresses may be “ganged” together to expedite the installation process. Triton Marine Mattresses have been installed in water depths similar to those at the field demonstration site. Divers and sonar are typically used to provide proper placement of the mattresses.

Photographs of example Triton Marine Mattress installations are provided on Figure 4-2 below.



Photographs reprinted with permission from Tensar.

Figure 4-2
Triton Marine Mattress Photographs

Reactive Core Mat

RCM is manufactured by CETCO and consists of a reactive/adsorptive material encapsulated within a geotextile. For this project, pure organoclay (specifically, CETCO's PM-199) will be used as the reactive/adsorptive material; other reactive/adsorptive materials that have been used include granular-activated carbon and zero-valent iron. Dissolved organic constituents and NAPLs that are being transported from the impacted sediments to the water column will be adsorbed by the organoclay, while water is allowed to pass through. The total thickness of RCM is approximately 0.2 inches (0.5 cm). RCM has been used for various applications, including in-situ capping of contaminated sediment, embankment seepage control and groundwater remediation.

The RCM will be attached to the bottom of the Triton Marine Mattress. Although the exact means of attaching the RCM to the mattresses will be determined during the design, it is anticipated that metal *hog-rings* will be used. It is possible that more than one layer of RCM may be attached to the mattresses.

Geonet/Geogrid

Geonet is another geosynthetic material manufactured by Tensar. Geonet is similar to the geogrid material used to construct the Triton Marine Mattresses, but is less rigid and has smaller grid openings (approximately 0.5 inches by 0.5 inches [1.25 cm by 1.25 cm]). For this project, geonet (specifically, Tensar's LW240B) will be used to provide support to the RCM(s) being attached to the Triton Marine Mattresses. It is anticipated that metal *hog-rings* will be used to attach the geonet and RCM to the Triton Marine Mattresses.

For sections of the cap that may be removed for monitoring (see Section 5), it is anticipated that Tensar's BX4100 geogrid material (1.3-inch by 1.3-inch [3.3-cm by 3.3-cm] grid openings) will be used to support the RCM in lieu of the geonet. The BX4100 geogrid is better suited than the geonet for the increased stresses that may occur as the cap sections are lifted out of the water.

5

CAP MONITORING OPTIONS

Following installation of the field demonstration reactive sediment cap, a monitoring program will be implemented to monitor the effectiveness of the cap. Given the site conditions (e.g., 50- to 60-foot [approximately 15- to 18-meter] water depths, tidal flows, low visibility), it is unknown what specific monitoring methods and tools will be effective; therefore, various monitoring methods and tools may be used. This section discusses potential options that will be considered for monitoring the effectiveness of the cap. The final monitoring approach (including monitoring methods and tools, frequency, and duration) will be determined during cap design.

Visual Inspections and Material Testing

As indicated in Section 3, prior to designing the cap, a remote-operated (or diver-operated) underwater camera will be tested to identify areas where NAPL is entering the water column from impacted sediments via gas ebullition and groundwater discharge. If successful, the camera will also be used periodically after installing the cap to monitor the condition of the cap and to determine if NAPL is seeping through the cap.

It will be beneficial to periodically retrieve sections of the cap for visual inspection and material testing. To accomplish this, it is anticipated that the cap will be designed and installed such that sections of the cap (e.g., individual Triton Marine Mattresses) can be retrieved with a barge and crane. Once removed, the RCM will be visually inspected for the presence and distribution of NAPL, and samples will be collected for testing. Following inspection and sampling, the RCM will be patched or replaced prior to reinstalling the cap section.

Passive Monitoring

The following passive monitoring tools will be considered to monitor the cap:

- Solid-phase extraction (SPE) tools (e.g., Dakota Technologies, Inc.'s DART) and/or solid-phase microextraction (SPME) tools (Reible et al., 2007) will be considered for determining the presence of PAHs and NAPLs below, within and/or above the RCM as a means of evaluating the effectiveness of the cap at sequestering NAPLs.
- NAPL FLUTe™, developed by Flexible Liner Underground Technologies, Ltd. Co., is a color-reactive material that changes color in the presence of NAPLs. The technology is typically applied in direct-push boreholes, but will be evaluated for use in the cap to detect the presence of NAPLs above the RCM.
- Groundwater seepage meters will be considered to measure groundwater flux rates through the cap. Seepage meters will also be evaluated to determine if they can be deployed outside of the capped area to determine actual "baseline" conditions.
- Sediment traps will be considered to measure rates of sediment deposition on top of the cap.

The passive monitoring tools to be used and the means by which these passive monitoring tools will be installed and retrieved, will be determined during the cap design.

6

PHASE I SUMMARY AND PHASE II SCOPE OF WORK

Phase I Summary

Phase I of this project involved completing predesign evaluations and developing a conceptual cap design and monitoring approach.

Predesign evaluations included selecting the field demonstration area, organoclay laboratory tests, identifying submarine utility line considerations and identifying other data needs.

The conceptual cap design includes one or more layers of RCM (with CETCO’s PM-199 organoclay as the reactive/adsorptive material) attached to a Triton Marine Mattress (the mattress will be filled with sand, bulk organoclay and/or armor stone). Potential cap monitoring options include visual inspection, material testing and various passive monitoring tools. Given the site conditions (e.g., 50- to 60-foot water [approximately 15- to 18-meter] depths, tidal flows, low visibility), it is unknown what specific monitoring methods and tools will be effective; therefore, various monitoring methods and tools are anticipated to be used. The final cap configuration and monitoring approach will be developed during Phase II of this project.

Phase II Scope of Work

Phase II of this reactive sediment capping field demonstration project will consist of the following activities:

- Preparing a detailed design of the reactive sediment cap, installation plan and monitoring approach
- Installing the cap (including obtaining any necessary permits)
- Monitoring the performance of the cap
- Preparing a final Tech Update to summarize the final cap design used, installation methods, monitoring results and considerations for full-scale application

7
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A

ORGANOCLAY LABORATORY TESTING SUMMARY

Objectives

As a component of Phase I of the reactive sediment capping project, the University of Texas at Austin conducted laboratory testing with various organoclays and site NAPL to define potential effectiveness and expected as-placed effectiveness, and to identify issues that might influence design, implementation or long-term performance of an organoclay sediment cap. The laboratory testing results and recommendations for the organoclay material to be used as part of this reactive cap design are summarized below.

Summary of Phase I Laboratory Results

Preliminary evaluation of site and contaminant conditions indicated that limited remedial alternatives existed for the demonstration site. Specific problematic conditions at the site included presence of NAPL, tidal currents, relatively deep water and the potential existence of debris. These conditions suggested that placement of organoclay, with high NAPL sorption capacity as well as dissolved contaminant sorption capacity, in a thin layer with armoring would be required. Controlled placement of organoclay at depth requires use of a reactive core mat, in which the active material is confined by geofabric layers. CETCO, the manufacturer of the reactive core mat concept, warrants the ability to place 0.8 lb of organoclay per ft^2 (3.9 kg/m^2) of mat. With a typical bulk density for organoclay of 50 lb/ft^3 (0.8 g/cm^3), this corresponds to an equivalent mat thickness of approximately 0.2 inches (0.5 cm). The goal of the current effort is to evaluate the capacity of such an organoclay for sorption of NAPL and the expected retardation of anticipated dissolved contaminants.

Methods

Table A-1 summarizes the physical properties of NAPL collected from a monitoring well at the reactive sediment capping field demonstration site.

Table A-1
Physical properties of NAPL

Sample ID	Density, lb/ft^3 (g/mL)	Viscosity, cP	Interfacial Tension, mN/m	Water Content, percent
NMW-117S	67.9 (1.087)	151	22.33	25

Notes:
1. lb/ft^3 = pound per cubic foot.
2. g/mL = gram per milliliter.
3. cP = centipose.
4. mN/m = milliNewton per meter.

As indicated in Table A-1, the NAPL is denser than water and considerably more viscous (62.4 lb/ft^3 [1 g/mL] and 1 cP, respectively).

The flow and sorption characteristics of organoclays to this NAPL and to any dissolved constituents that might migrate from this NAPL were evaluated via several tests using selected commercially available organoclays. The organoclays evaluated included CETCO PM-199, CETCO PM-200 and Biomin Clay 750. CETCO PM-199 and CETCO PM-200 organoclays have a bulk density of approximately 46.8 lb/ft^3 (0.75 g/cm^3), while the Biomin Clay 750 has a considerably lower bulk density of about 25 lb/ft^3 (0.4 g/cm^3). The CETCO PM-199 and PM-200 organoclays are identical, except the PM-199 exhibits a finer particle size with essentially all organoclay particles between 0.01 inches (50 mesh) (300 micrometer [µm]) and 0.04 inches (18 mesh) (1 millimeter [mm]).

The dissolved-phase sorption capacity was similar for all three organoclays. Therefore, the lower density of the Biomin product appeared to provide no advantages, but may present potential disadvantages relative to the achievement of full loading of a reactive core mat. As a result, the Biomin product was only included in the dissolved-phase sorption evaluation.

The following flow and sorption tests were conducted on the organoclays:

- Batch capacity tests to determine potential NAPL and dissolved phase-sorption capacity:
  - Dissolved-phase sorption capacity tests were conducted by measuring equilibrium uptake of selected polycyclic aromatic hydrocarbon (PAH) contaminants from prepared standard solutions. Sorbent (7.05×10^{-4} ounces [20 mg]) was added to 3.05-cubic inch (50-mL) centrifuge tubes containing the known stock solution. The samples were tumbled for 48 hours. Following the 2-day tumbling, the tubes were centrifuged for 30 minutes at 3,000 revolutions per minute (rpm). Contaminants in the supernatant were then analyzed with a High Performance Liquid Chromatograph (HPLC) and partition coefficients were estimated by mass balance. Results were reported as $K_d = W_s / C_w$ in liters per kilogram (L/kg), where W_s is estimated solid loading and C_w is measured water concentration at equilibrium.
  - NAPL sorption capacity tests were conducted by adding NAPL to a known mass of organoclay until physical sorption of NAPL was no longer observed. Results were reported on the basis of mass of NAPL absorbed per mass of dry organoclay.
- Column tests were used to determine the NAPL flow characteristics in a 0.5-inch (1.2-cm) layer of organoclay and in a 5-inch (13-cm) layer of organoclay. The potential NAPL sorption capacity was measured by volume of NAPL injected until breakthrough of the organoclay layer. Site NAPL was injected continuously at a rate equivalent to a Darcy (superficial) velocity of 0.4 inches/day (1 cm/day). Sorption capacity at breakthrough was measured by use of this rate and time required until breakthrough. The measured sorption capacity was confirmed by subjecting a post-experiment organoclay sample to a hexane extraction test. The mass of hexane extractible material (HEM) should correspond to the mass of NAPL absorbed. Fresh organoclays contain small amounts (2 to 3 percent) of hexane-extractible material, but this would not significantly alter the expected NAPL sorption. Observations were also made of flow uniformity and layer permeability during the column tests.

Results from these tests were used to project sorption capacity for a NAPL contaminant and the expected retardation and breakthrough times expected for selected dissolved-phase contaminants in the reactive core mat, assuming an organoclay loading of 0.8 lb/ft^2 (3.9 kg/m^2) in a 0.2-inch (0.5-cm) thick layer.

Results

Batch Sorption Capacity

The dissolved-phase sorption capacities of the three organoclays evaluated are summarized in Table A-2. The organoclay sorption coefficient (K_{abs}) is defined as:

$$K_{abs} = \frac{W_s}{C_w} \qquad \frac{(mg/kg)}{(mg/L)} = \frac{L}{kg}$$

The predicted porewater concentration is a theoretical estimate of the reduction in concentration of the dissolved constituent that would be expected when compared to a typical sediment layer containing 5 percent organic carbon and the same bulk (solid-phase) concentration. This reduction is estimated by the relationship:

$$\%\,red = 1 - \frac{K_{oc} f_{oc}}{K_d}$$

Where K_{oc} is the literature estimate of the organic carbon based partition coefficient for the compound (Phenanthrene K_{oc}=20,000, Pyrene K_{oc}=100,000) and f_{oc} is the fraction organic carbon of the sediment layer (here assumed to be 5 percent).

Table A-2
Organoclay Sorption Coefficient, Predicted Porewater Concentration Reduction and Estimated Cap Penetration Time

Organoclay Sample (bulk density)	K_{abs}, L/kg	% pw reduction	τ, years 0.5 cm layer	K_{abs}, L/kg	% pw reduction	τ, years 0.5 cm layer
	Phenanthrene K_{oc}=20,000 L/kg			Pyrene K_{oc}=100,000 L/kg		
Biomin Clay 750 (ρ=0.4g/cm^3)	55,600	98.20%	111	414,000	98.79%	828
CETCO PM-199 (ρ=0.75g/cm^3)	68,000	98.53%	255	454,000	98.90%	1,703
CETCO PM-200 (ρ=0.75g/cm^3)	36,500	97.26%	137	98,700	94.93%	370

Notes:
1. K_{abs} = organoclay sorption coefficient.
2. % pw reduction = predicted percentage of porewater concentration reduction (compared to a 5 percent organic carbon sediment layer with the same bulk phase contaminant loading)
3. τ = estimated cap penetration time (in years) for dissolved PAHs through a 0.2-inch (0.5-cm)-thick organoclay layer subject to a 40 inches/year (100 cm/year) groundwater upwelling velocity

As shown by the results in Table A-2, the PM-199 organoclay provides the greatest dissolved contaminant sorption of the three organoclays tested. The PM-199 also provides the greatest reduction in porewater concentrations compared to a clean 5 percent organic carbon sediment layer and the greatest retardation (and longest breakthrough times) of dissolved contaminants.

Batch NAPL sorption tests were conducted using site NAPL and the two CETCO organoclays. The measured NAPL sorption capacity of the PM-200 was 2.97 g of NAPL per g of organoclay, with a standard deviation of 0.13 g/g. A higher sorption capacity of 4.5 g of NAPL per g of organoclay was measured in PM-199 due to the greater access to the organoclay matrix afforded by the small particle size. The batch NAPL sorption capacity represents a potential capacity under ideal static sorption conditions. It is expected that actual capacity in a layer of organoclay placed in the field would not achieve this capacity.

Column Experiments

Column tests were also conducted with the PM-199 and PM-200 organoclays. Observations during the column experiments indicated that the finer particle size of the PM-199 organoclay gave rise to more uniform NAPL flow and more success at contacting all organoclay, therefore achieving better utilization of the organoclay. This is illustrated on Figure A-1 by flow during the early stages in the thick column (5-inch [13-cm] organoclay layer) experiments. Note that nonuniform fingering would likely be persistent for long periods of exposure because the interfacial tension would likely encourage continued NAPL flow along the same NAPL-wetted flow paths. To maximize organoclay utilization and effectiveness of the organoclay layer in a reactive core mat, the PM-199 organoclay is recommended for inclusion within the mat.

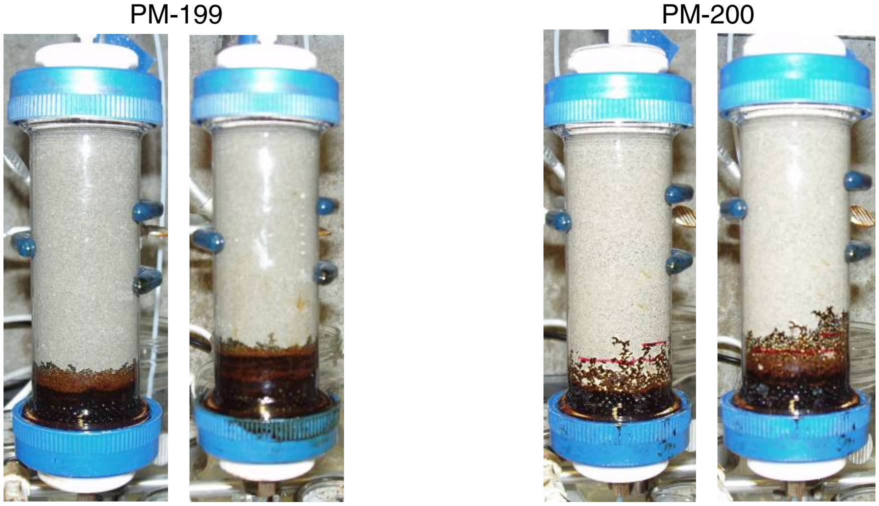

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Figure A-1
Photographs of Flow Maldistribution and Nonaqueous Phase Liquid “Fingering in Layers of PM-200 Organoclay Relative to PM-199 Organoclay

Pressure drop measurements before and after NAPL sorption by the organoclay allows determination of the extent to which the NAPL sorption can reduce the intrinsic permeability of the organoclay layer. The intrinsic permeability of fresh organoclay (i.e., not contacted by NAPL) was on the order of 20 Darcy (~$2x10^{-7}$ cm^2), typical of a coarse sand. The intrinsic permeability of the organoclay layer after NAPL exposure varied from 10 to 3.2 mDarcy (~$1x10^{-10}$ to $3.2x10^{-11}$ cm^2) for PM-200 organoclay and from 6.6 to 3.6 mDarcy (~$6.6x10^{-11}$ to

$3.6\mathrm{x}10^{-11}$ cm^2) for PM-199. Swelling and intrinsic permeability reduction tends to increase with time for the first 72 hours of NAPL exposure, as the NAPL penetrates the organoclay matrix and remains essentially constant thereafter. Although the intrinsic permeability of NAPL-impacted organoclay is considerably less than fresh organoclay, it is still equivalent to the intrinsic permeability of silty sand and therefore is not atypical of surficial sediment.

NAPL Sorption Capacity

NAPL sorption capacity was also measured during the column experiments by determining the rate of NAPL progression in the organoclay columns. The mass fraction of NAPL absorbed (X_{abs} in mass dry NAPL per mass dry organoclay) in a column of NAPL-saturated organoclay of length L depends upon the injection rate (Q_{NAPL}) and dry densities of the NAPL and organoclay (absorbent) by the following relation:

$$X_{abs} = \frac{Q_{NAPL}\rho_{NAPL}\Delta t}{\rho_{abs}AL}$$

Table A-3 summarizes the measured absorption capacities in the PM-200 and PM-199 organoclays, and compares them to the much higher batch measured capacities. The difference between the batch measurements and column measurements are likely the result of flow nonuniformities and column-related limitations on organoclay swelling. Although the NAPL sorption capacity estimated in the PM-199 was only slightly larger than that observed in the PM-200, the significant flow maldistribution in the PM-200 reduces confidence in both the measured sorption capacities and the potential for early failure of a thin PM-200 layer. Therefore, the use of PM-199 in the thin reactive core mat layers is recommended.

Table A-3
NAPL Sorption Capacity (mass dry NAPL per mass dry organoclay) for Batch and Column Tests

Organoclay	Batch Test	Thin-Layer Column Test, 0.5 inch (1.2 cm)	Thick-Layer Column Test, 5 inch (13 cm)
PM-199	4.5±0.11	--	1.07±0.09
PM-200	2.97±0.13	0.81 (0.80±0.07)	0.91±0.05

Notes:
1. (   ) = value based on HEM.
2. ± = standard deviation (where multiple tests where run).
3. -- = thin-layer column test not performed on PM-199.

Predicted Demonstration Performance

The data reported above was used to estimate the performance of PM-199-filled reactive core mat. The mat was assumed to be filled with 0.8 lb/ft^2 (3.9 kg/m^2) PM-199, providing a thickness of approximately 0.2 inches (0.5 cm). The capacity of the mat layer from Table A-3 is approximately 1 lb dry NAPL per lb dry organoclay. Thus, the mat would be expected to contain 0.8 lb NAPL per ft^2 (3.9 kg/m^2) of reactive core mat. Upwelling of more than 0.8 lb NAPL per ft^2 (3.9 kg/m^2) would be expected to penetrate the mat, although the reduction in permeability of the mat layer would lower the likelihood of NAPL migration to the overlying water.

If an area of the mat is expected to be exposed to dissolved-phase PAH contaminants only, the sorption capacities and retardation reported in Table A-2 would be applicable. The organoclay would be expected to retard contaminant release for extremely long periods (255 years for phenanthrene, 1,700 years for pyrene) with an upwelling velocity on the order of 40 inches/year (100 cm/year).

If an organoclay layer is exposed to both trace NAPL and dissolved-phase contaminants, the NAPL would tend to be absorbed in the lowest organoclay layers and the dissolved phase would be contained in the upper layers of organoclay. The total NAPL absorption and dissolved-phase containment time would be less than if only NAPL or only dissolved-phase contaminants were present.

Export Control Restrictions

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Electric Power Research Institute
3420 Hillview Avenue, Palo Alto, California 94304-1338 • PO Box 10412, Palo Alto, California 94303-0813 • USA
800.313.3774 • 650.855.2121 • askepri@epri.com • www.epri.com