NAVFAC Technology Transfer Review
Sediment Reactive Capping

ENTER

Naval Facilities Engineering Command

Introduction

Contaminated sediment sites represent some of the most complex challenges within the Naval Facilities Engineering Command (NAVFAC) Environmental Restoration (ER) program. Compared to terrestrial sites, sediment sites tend to be large in size, more dynamic, and involve multiple sources and complex ecology. The types of contaminants at Navy sediment sites are wide-ranging such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), pesticides, dioxins/furans, petroleum hydrocarbons, and metals. In addition, radiological and munitions impacts may be present from historical defense operations. The Navy is interested in technological innovations to remediate contaminated sediments in a sustainable and cost-effective manner. This fact sheet was prepared to provide an overview of reactive capping as an emerging contaminated sediment remediation approach.

Typical remedies for contaminated sediments include: monitored natural recovery (MNR); dredging; and capping. MNR involves monitoring natural processes such as the deposition of clean sediment, which acts to reduce the surficial contaminant concentration over time. Dredging involves the physical removal of contaminated sediment material using mechanical or hydraulic equipment. Traditional capping involves the application of a passive barrier to the contaminated sediment surface to contain contamination in place. Reactive capping is an emerging remedial approach that incorporates materials capable of directly sequestering and/or degrading contaminants to reduce the environmental risks posed by the impacted sediments.

Figure 1. Reactive Capping for Contaminated Sediments

Capping Approaches

It is important to understand variations in capping approaches including: traditional capping, thin-layer capping, and reactive capping as described below.

Traditional Capping. Traditional capping approaches at contaminated sediment sites include the controlled application of a layer of clean geologic material (e.g., sand or silt) or synthetic material (e.g., a geotextile or geomembrane) over contaminated sediments. Some traditional sediment caps are constructed in layers of varying composition (i.e., a multilayer cap) and/or as a combination of natural geologic and synthetic materials, depending on site-specific characteristics and objectives (Figure 2). Traditional sediment caps are designed to physically isolate contamination from potential receptors, to prevent or mitigate the flux of contamination from sediments to overlying surface water, and/or to provide stability to contaminated sediments to prevent or mitigate the transport of contamination. Traditional sediment caps are commonly up to several feet thick to provide adequate containment and to prevent exposure to potential receptors, including burrowing benthos.

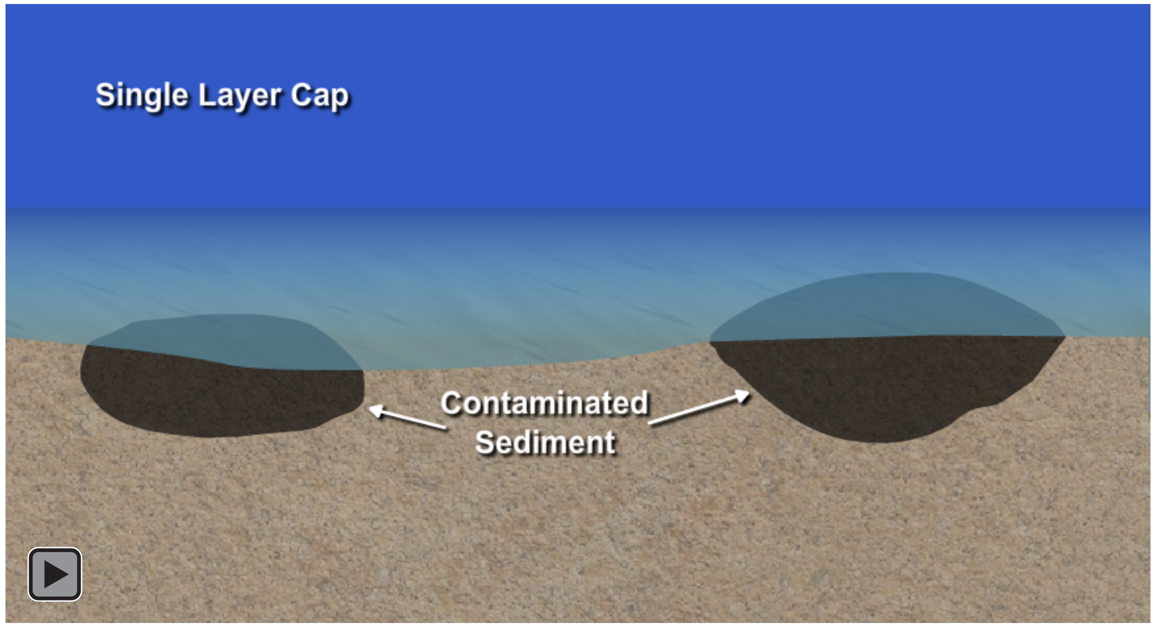

Figure 2. Representations of Traditional Capping Approaches (Courtesy of Battelle)

Thin-Layer Capping. Depending on the severity of risks and other considerations such as local ecological value, thin-layer caps can be used to provide adequate containment and minimize exposure, while simultaneously minimizing ecological disruption through habitat destruction or alteration from cap placement. Thin-layer capping, otherwise known as enhanced natural recovery (ENR), is a modified traditional capping approach. It involves the use of similar capping materials, but at a lesser thickness to provide an immediate reduction in exposure potential. The thinner layer also minimizes potentially significant ecological disruption from placement of the cap. ENR takes advantage of natural processes such as ongoing sedimentation to provide longer-term protection.

Reactive Capping. A reactive cap is designed with amendments intended to actively sequester or promote the chemical or biological degradation of contaminants in underlying sediments and/or in porewater fluxing from contaminated sediments to the overlying water column. Reactive sediment caps are often physically thinner compared to traditional caps because their purpose is not just solely for isolation as the reactive material is actively reducing the contaminant mass or mass flux. Reactive capping is an emerging remedial technology with applications primarily at the bench-scale and pilot-scale with limited full-scale applications to date.

Both traditional and reactive caps are most effective in areas that do not have significant erosional forces, although caps can be armored with stone or other materials to provide erosion resistance. All sediment capping techniques require appropriate site conditions, including compatible existing and future uses and required water depths, geotechnical characteristics, and ecological function and value. For all sediment caps, contaminant source control is a critical requirement to ensure that the cap surface itself does not become re-contaminated.

Reactive Cap Materials

Reactive sediment cap amendments take several forms. Table 1 summarizes several reactive amendments and the target contaminant classes treated. Typical organic contaminants targeted include dioxins/furans, PAHs, PCBs, and pesticides. Typical inorganic contaminants targeted include metals, such as arsenic, cadmium, chromium, copper, lead, mercury, nickel, and zinc. Specific cap materials are selected based on the remedial objectives, the characteristics of the site, the nature of the contaminated sediments, and the type(s) of contamination present. Reactive capping amendments generally fall into two primary categories: amendments that sequester contaminants (i.e., physically bind and reduce the mobility or availability of contaminants); and amendments that degrade contaminants (i.e., directly alter contaminants into less toxic forms).

Amendment	Contaminants Targeted
	Sequestering Amendments
activated carbon	organics (dioxins/furans, PAHs, PCBs, pesticides)
apatite	metals (lead)
bauxite	metals (arsenic, cadmium, chromium, lead, mercury, nickel, zinc)
barite	metals
biochars	organics
coal	organics
coke	organics (PAHs, PCBs)
engineered polymers	inorganics, organics
limestone	metals
organoclays	metals, NAPLs, organics (PAHs, PCBs)
zeolites	metals (copper, lead, zinc)
	Degrading Amendments
bioremediation agents	organics (dioxins/furans, PCBs)
palladium	organics (chlorinated hydrocarbons, PCBs)
ZVI	organics (chlorinated hydrocarbons, PCBs)

Table 1. Reactive Amendments for Sediment Capping

Sequestering Amendments. Carbon-based amendments including organic-rich soils, coal, and thermally-altered carbonaceous materials (activated carbon, coke, and biochars) can effectively sequester organic contaminants. Phosphate-rich earth minerals (e.g., apatite) can effectively sequester metals through sorption, exchange, substitution, and precipitation. Other minerals and geologic materials, including sulfate-rich barite, aluminum-rich bauxite, limestone, aluminosilicate zeolites, and other silica forms, are similarly capable of sequestering metals. Organoclays are organophilic clays (typically bentonite) in which host cations are replaced by cationic organic compounds (e.g., quaternary amines), and are effective at sequestering metals and organic contaminants, including non-aqueous phase liquids (NAPLs). Engineered polymers are also capable of sequestering organic and inorganic contaminants. Numerous sequestering agents have been evaluated at bench scale, and some have been deployed at pilot scale. Generally, activated carbon and organoclays are the most well studied of the sequestering amendments for sediment contamination, having been deployed in full-scale applications to address contaminated sediments.

Degrading Amendments. Degradation of sediment contaminants using amendments in a reactive cap has been evaluated using zero-valent iron (ZVI), which has been demonstrated extensively for other applications (i.e., groundwater) to dechlorinate chlorinated hydrocarbons and PCBs. Similarly, elemental palladium has been assessed for its potential to degrade organics in contaminated sediments. Degradation of organic contaminants could also be accomplished through enhanced bioremediation promoted through the addition of specific microbes, electron donors, primers, and/or accelerants. Largely, the evaluation of direct degradation of sediment contaminants using reactive cap amendments has been performed at proof of concept and bench scale.

Combined Amendments. Specific proprietary formulations of sequestering and degrading amendments have been developed by vendors under various product names, including some that incorporate activating agents to enhance reactivity and degradation capacity. In addition, formulations combining multiple sequestering amendments or both sequestering and degrading amendments also exist at various stages of research and development. For instance, products are available or are being researched that combine activated carbon with engineered polymers, activated carbon with ZVI and palladium, and organoclays with specific degrading amendments. Other reactive amendment technologies come in the form of geotextiles impregnated with amendments and various reactive amendments embedded in a permeable concrete matrix.

Reactive Cap Deployment

Reactive cap amendments are typically available in powdered, granular, or other solid forms, or can be delivered as aqueous solutions or slurries. Methods of deploying a reactive cap include:

Cap Deployment via Surface Release from a Barge. Utilizing a reactive amendment in granular or other solid form as a discrete layer, either placed alone as a cap or as a component of a multilayer cap system. Typical cap placement methods would be employed to install such a cap, including gravitational settling (Figure 3) following broadcast or focused surface release from a barge, crane, or pipeline, subaqueous placement using a crane, tremie, spreader, or diffuser, or subaqueous placement using a hydraulic pipeline following slurrying**.**

Cap Deployment via Subsurface Tremie Placement. Mixing a reactive amendment with some other capping material (e.g., sand) depending on the distributed effectiveness of the amendment, and then placed alone as a sediment cap or as a component of a multilayer cap system. Typical placement methods as above would be used to install such a cap (Figure 4).

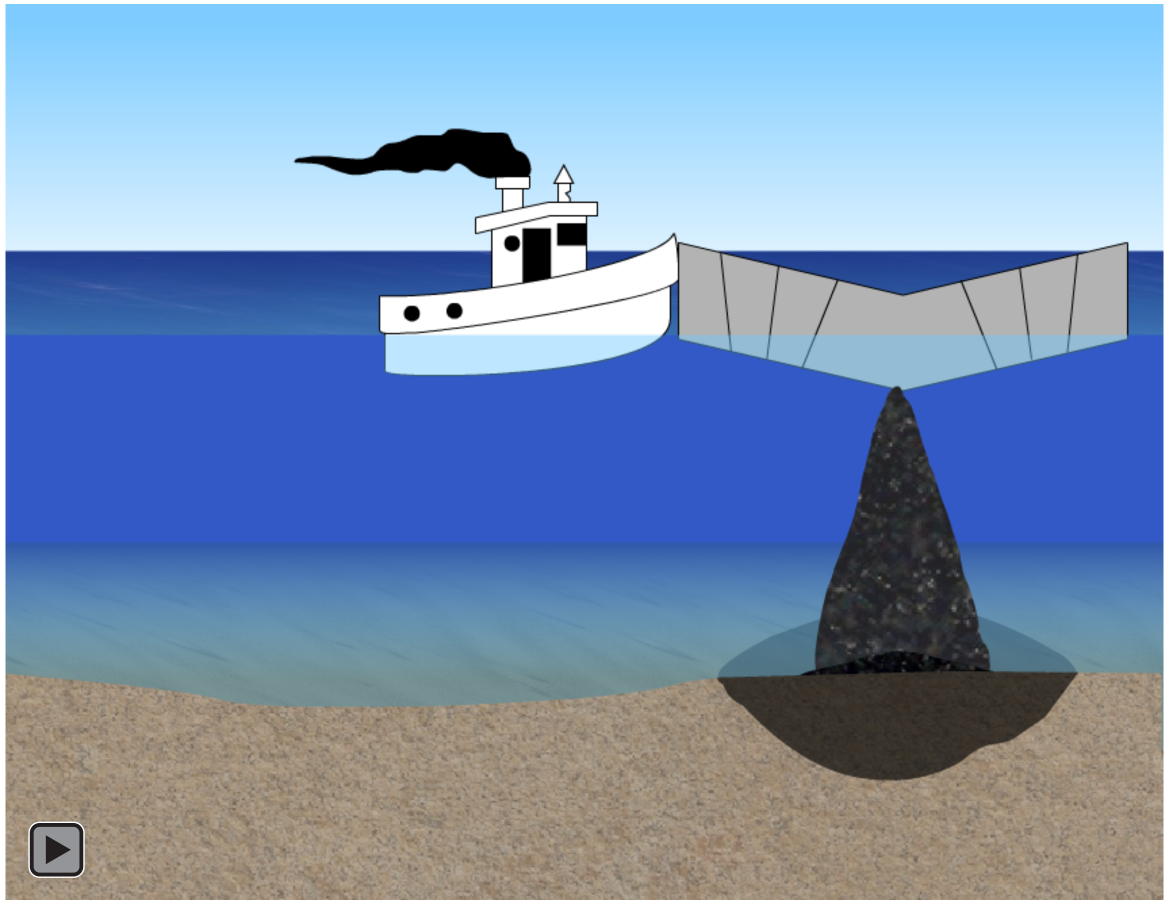

Figure 3. Cap Deployment via Surface Release from a Barge (Courtesy of Battelle)

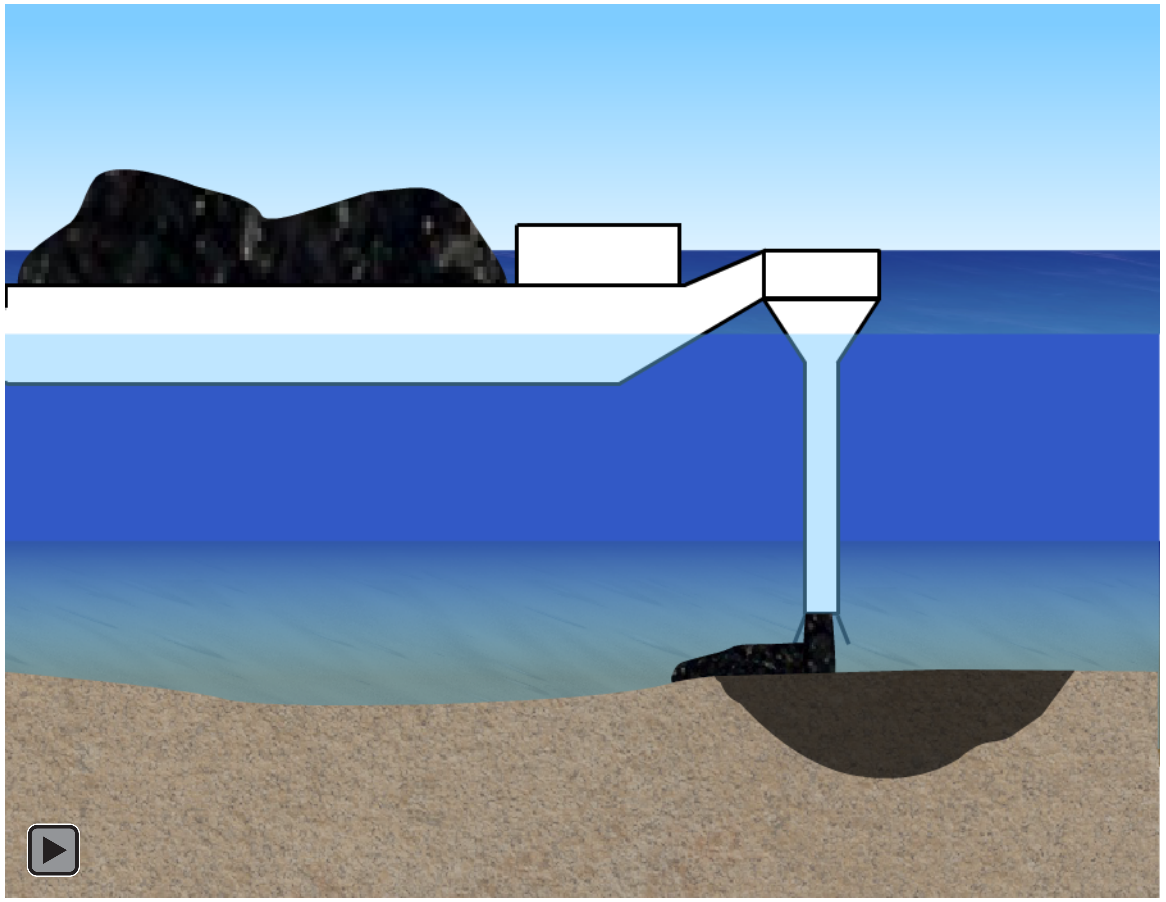

Figure 4. Cap Deployment via Subsurface Tremie Placement (Courtesy of Battelle)

Reactive Cap Deployment (Continued)

Placement in Designed Channels. Placing a reactive amendment in designed channels within an otherwise traditional isolation cap to capture the flux of contamination along induced preferential pathways (Figure 5). Such a system could be placed alone as a sediment cap or as a component of a multilayer cap system, using a combination of typical cap placement methods and focused placement methods such as diver-assisted placement to construct the reactive channels.

Geotextile Placement via Surface Craft. Embedding the reactive amendment in a geotextile or geofabric matrix, placed alone as a sediment cap or as a component of a multilayer cap. Placing a geotextile or geofabric system (or layer) requires specialized deployment methods such as a vessel with the capability to hold and spool out rolls of the geotextile/geofabric material (Figure 6) and a mechanism to ensure the material settles on the sediment surface.

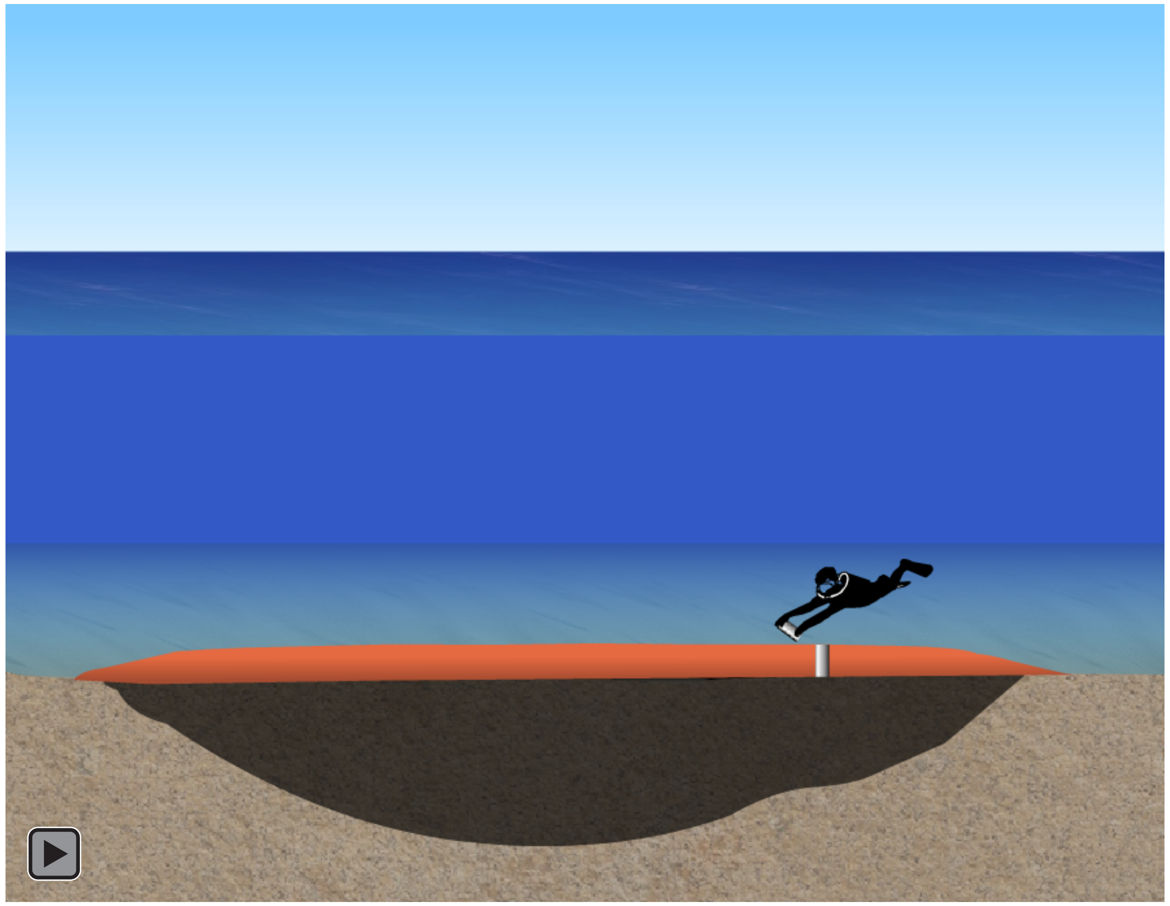

Figure 5. Diver-Assisted Placement of Reactive Channels (Courtesy of Battelle)

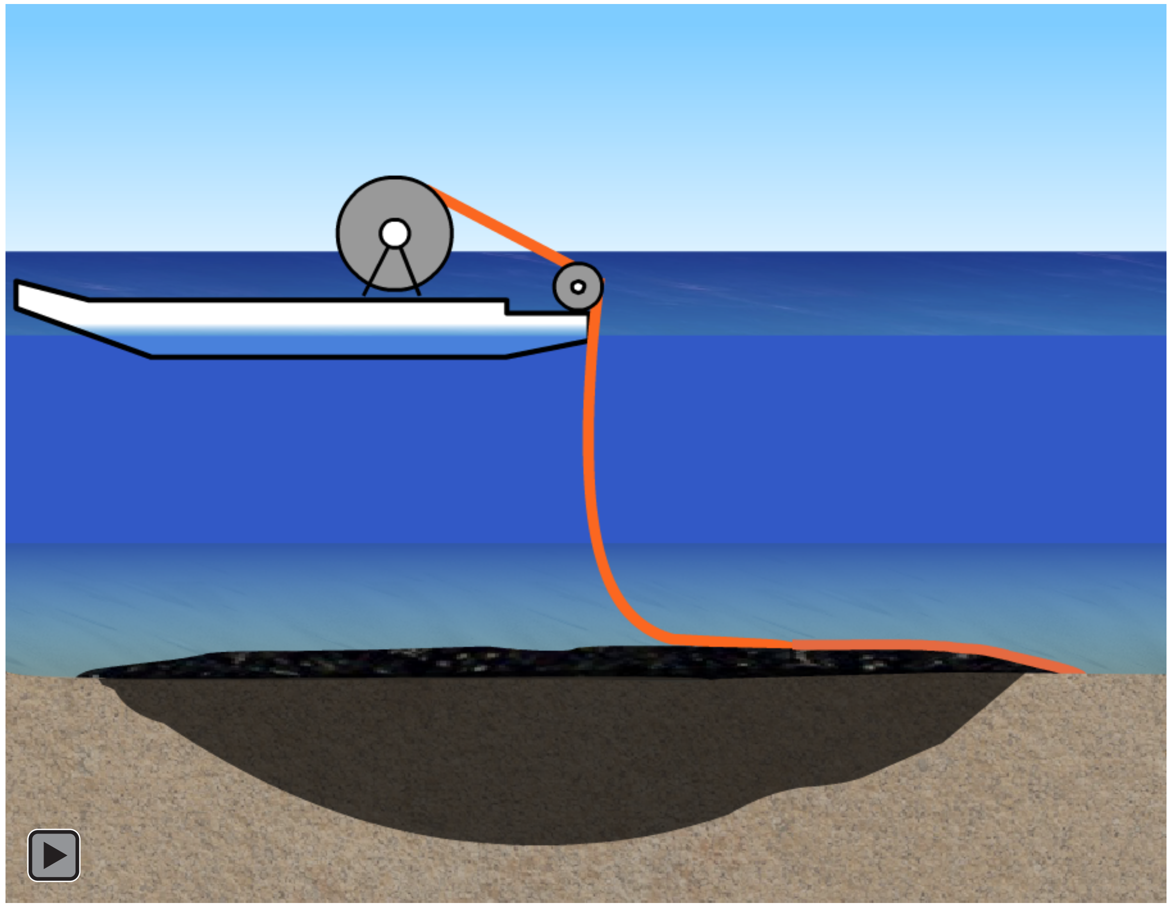

Figure 6. Geotextile Placement via Surface Craft (Courtesy of Battelle)

Reactive Cap Monitoring

Routine monitoring should be performed before, during, and after reactive cap construction to support remedy design, implementation, and performance assessment.

Monitoring Prior to Cap Construction. Prior to reactive cap construction, monitoring should be performed to evaluate the geomorphological and geotechnical characteristics of the existing sediments to understand physical constraints (e.g., slopes), bearing capacity, and the potential for contaminated sediment resuspension. Monitoring should also be completed to establish baseline conditions related to ecological characteristics and chemical concentrations in various media (e.g., sediment, surface water, and porewater) and possibly the flux of contamination between various media. Such monitoring can be conducted by oceanographic surveying, sediment profile imaging (SPI), box, piston, and vibracore samplers (Figure 7), grab samplers, shear testing devices, typical geophysical and analytical laboratory tests, ecological community, toxicity, and bioaccumulation assays, seepage meters, and various passive samplers.

Monitoring During Cap Construction. During reactive cap construction, monitoring should be performed to evaluate contaminated sediment resuspension and cap placement accuracy relative to critical construction tolerances. Methods available to perform such monitoring include oceanographic surveying, in situ water quality sensors, grab samplers, sediment transport and plume tracking tools, and typical analytical laboratory tests.

Figure 7. Vibracorer Deployed from Sampling Vessel (Courtesy of Battelle)

Monitoring Post-Cap Construction. Following reactive cap construction, monitoring should be performed to verify the successful placement of the cap relative to design requirements. Methods available to perform such monitoring typically include oceanographic surveying, coring, SPI (Figure 8), and possibly diver-assisted visualization.

Long-Term Monitoring. Long-term performance monitoring should be conducted to evaluate the continued presence of the reactive cap relative to erosion or other physical disturbance, to assess the potential flux of contamination from the underlying contaminated sediments, and to observe ecological recovery. Methods available to perform such monitoring include oceanographic surveying, SPI, box, piston, and vibracorers, grab samplers, typical analytical laboratory tests, ecological community, toxicity, and bioaccumulation assays, seepage meters, and various passive samplers.

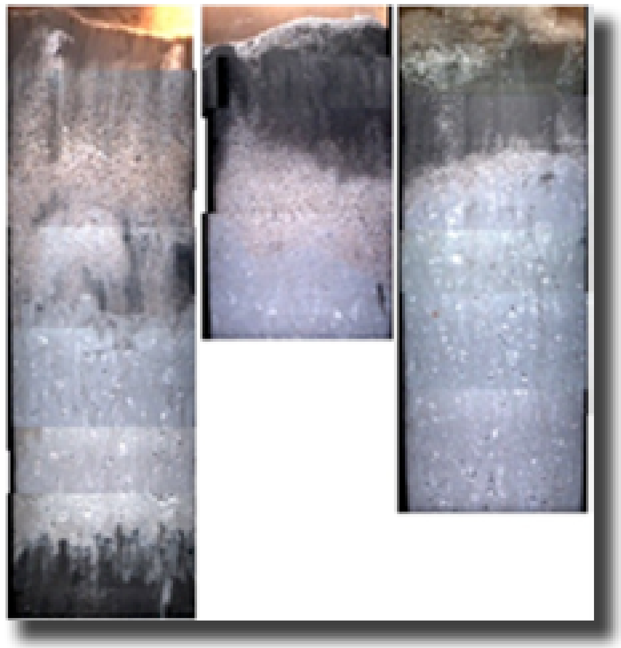

Figure 8. Vertical SPI Profiles Showing Variations in Material Type with Depth (Courtesy of Battelle)

Non-routine monitoring of a sediment cap system can be triggered by specific events, such as storms, elevated flow stages, ice flows, earthquakes, and other high energy events with the potential to cause cap disruption or damage. Provisions for in situ subaqueous capping remedies often include the requirement to perform repairs if the cap system is damaged by a high energy event or is found to not meet design parameters during long-term monitoring.

Reactive Capping Case Studies

Several reactive capping projects have been sponsored by the Department of Defense (DoD) Strategic Environmental Research and Development Program (SERDP) and the Environmental Security Technology Certification Program (ESTCP). References to key studies related to reactive capping are cited in the resources section. Two of these projects are highlighted below.

Evaluation of Reactive Capping Mat Technologies at Cottonwood Bay, Texas

Cottonwood Bay (Figure 9) is situated between the Vought Aircraft Industries facility (formerly the Naval Weapons Industrial Reserve Plant) and Naval Air Station Dallas in Grand Prairie, Texas. Historical investigations revealed that concentrations of metals (chromium, copper, and zinc), PAHs (represented by fluoranthene), and PCBs are elevated in sediments in Cottonwood Bay. SERDP Project Number ER-1493 (Reactive Capping Mat Development and Evaluation for Sequestering Contaminants in Sediment) was implemented by a collaborative team that included the NAVFAC Expeditionary Warfare Center (EXWC). The project objective was to develop a reactive geotextile mat system and deploy the mat system in test plots in Cottonwood Bay.

Figure 9. Cottonwood Bay

Various mixtures of reactive amendments (activated carbon, apatite, and organoclay) were evaluated at bench scale to determine the optimal combination of materials to sequester sediment contaminants. Through isotherm and kinetic testing, organoclay containing bentonite and coconut shell activated carbon were identified as the optimal amendment components for achieving maximum contaminant sequestration. Preloading studies with humic acid on activated carbon generally indicated negligible effects, but similar tests with organoclay showed that preloading with humic acid did change the relative adsorption capacity for individual PAHs. Laboratory testing was also conducted to identify the geotextile most resistant to biofouling and gas uplift. A reactive mat featuring an apparent opening size (AOS) 80 geotextile and a 0.28 pounds per square foot (lb/ft^2) activated carbon, 0.23 lb/ft^2 apatite, and 0.28 lb/ft^2 organoclay amendment mixture was recommended for field deployment (Figure 10).

Figure 10. Reactive Mat Material Prior to Deployment at Cottonwood Bay Study Site (Courtesy of SERDP)

A pilot-scale mat system was deployed in Cottonwood Bay in April 2008 (Figure 11), featuring four 25 foot (ft) by 25 ft test arrangements (single layer reactive mat, single layer reactive mat with overlying sand cap, double layer reactive mat, and sand cap only) and an undisturbed control. After five months of deployment, contaminant sequestration was monitored for the various test arrangements with passive samplers. The passive samplers were strategically placed at specific interfaces of interest in the various mat system treatments. A post-construction geophysical investigation was also conducted to evaluate the geophysical properties of the various treatments. Approximately one year after deployment of the test mats (six months after deployment of the passive samplers), porewater measurements were collected to quantify water flux from sediments through the various treatments and identify any change in contaminant concentrations. Passive sampling at the prototype mat system was repeated in fall 2009 to provide comparative second year results. Sediment cores were also collected from each treatment area at that time.

Figure 11. Small-scale geotextile test mat deployment.

Data generated during the pilot study indicated that porewater chemistry in native sediments correlated to surface sediment trends across treatments. Metals concentrations passing through the mats were comparable to those above the mats, indicating that the mats sequestered metals in underlying porewater. Mat uplift due to gas buildup beneath the geotextile was observed in the summer months for the mat only treatments, but these conditions were not found in the mat treatment with an additional sand cap. Passive sampler data showed generally consistent and statistically significant two- to four-fold reductions in contaminant concentrations from below the treatment to above the treatment, primarily for two treatments (mat/sand and double mat) and for several metals (barium, nickel, silver, vanadium, and zinc) and PAHs (anthracene, benzo[a]anthracene, benzo[b]fluoranthene, benzo[g,h,i]perylene, and indeno[1,2,3-c,d]pyrene). Performance for other metals (e.g., copper) was less robust and may have been limited by overall low concentrations relative to detection limits.

SERDP Project ER-1493 concluded that the organoclay, apatite, and activated carbon reactive mat with sand cover would be an effective technology at full scale to sequester contaminants in sediments, while preventing uplift due to gas accumulation.

Evaluation of Activated Carbon Amendment at Bremerton Naval Complex, Washington

ESTCP Project ER-201131 (Short-Term Performance of an Activated Carbon Amendment to Reduce PCB Bioavailability at an Active Naval Shipyard) was implemented as a collaborative team that included the Space and Naval Warfare Systems Center Pacific (SSC Pacific). The project objective was to evaluate the performance of an activated carbon amendment for contaminated sediments at the Bremerton Naval Complex (BNC) Pier 7 complex in Bremerton, Washington (Figure 12). The goals of the study were specifically to assess the placement, distribution, and stability, changes in PCB partitioning and sorption, tissue concentrations and benthic community effects related to an activated carbon amendment introduced to contaminated sediments.

Figure 12. Bremerton Naval Complex.

Laboratory testing was performed using a proprietary formulation of organoclay and powdered activated carbon, which revealed the ability of the amendment to sequester contaminants. Laboratory toxicity testing was also performed, and revealed no adverse survival effects for polychaete worms. The toxicity testing did indicate the potential for reduced polychaete growth with exposure to the amendment, with this effect diminishing over time. The formulation selected for pilot-scale assessment was 2 to 5% (by weight) powdered activated carbon, 5 to 10% clay (calcium bentonite), and 85% aggregate, with a dry bulk density of 85 to 90 pounds per cubic foot (lb/ft^3).

In October 2012, the selected amendment was placed in a 0.5 acre test plot area using broadcast placement methods (Figure 13). Approximately 143 tons of the material was used, and the test area was covered with 2 to 4 inches of amendment.

Figure 13. Reactive Amendment Placement beneath Pier (via Conveyor) at BNC Study Site (Courtesy of ESTCP)

Baseline monitoring was performed prior to cap placement, and again 2 weeks, 3 months, and 10 months after placement (additional monitoring will be reported at a later date under ESTCP). Physical parameters assessed included the distribution, coverage, uniformity, and thicknesses of the amendment immediately after placement, the stability of the amendment and changes in amendment stability over time resulting from natural sedimentation, benthic mixing, and ship and tug activity, sediment cohesiveness over time, and mixing depths. Chemical parameters monitored included surface sediment and sediment porewater concentrations prior to and following amendment delivery. Biological parameters assessed included the reduction of PCBs in the tissues of clams and worms and changes in benthic community richness, abundance, distribution, evenness, and diversity before and after placement. Tools used during monitoring included coring devices, passive samplers, benthic exposure chambers, SPI, diver observations, and benthic community assays.

SPI, sediment core samples, and diver surveys performed two weeks after placement showed that 90% of the target area received the amendment and 70% of the target area received the target thickness or more. The amendment was still found to be present 10 months after placement. The concentration of total PCBs in bioaccumulation test organisms decreased approximately 80% as a result of the activated carbon amendment. The concentration of total freely-dissolved PCBs in surface sediment decreased significantly as a result of the activated carbon amendment, as did the concentration of total PCBs in sediment porewater. Compared to baseline, the average total benthic community abundance decreased by nearly 60% in stations where the amendment was applied, but remained consistent in reference stations. Nematode abundance decreased by 85% from the baseline to the 10-month event; however, the abundance of non-nematode invertebrates at the amended stations was comparable to that of the reference stations. There was no significant difference between average baseline and 10-month post-placement abundance of non-nematodes at the amended stations.

Based on the monitoring data collected through the 10-month post-capping event, ESTCP Project ER-201131 concluded that the organoclay and activated carbon amendment cap was stable. Bioavailability of PCBs to benthic organisms was drastically reduced in response to the addition of the amendment material, and while there was an impact to the nematode population immediately following the addition of the amendment, the addition of amendment also allowed for more diversity among other benthic organisms.

Resources

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