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Economical Treatment of Dredged Material to Facilitate Beneficial Use

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August 2014

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Abstract

Growing constraints on conventional dredged material disposal are motivating movement toward more sustainable alternatives. Given the lack of universal beneficial use criteria, even the low levels of contaminants typically found in navigation channel sediments may limit or preclude their beneficial use. Intensive treatment to remove or destroy contaminants in such sediments is typically too costly to be a viable alternative within the context of navigation dredging; economical, low-tech sediment and water treatment processes are needed. Recent developments in the area of sediment treatment were assessed through an extensive literature search, and promising technologies were identified. Potentially high value research areas were also identified, to inform subsequent bench and pilot testing. Geochemical contaminant controls and modeling, passive water treatment methods for colloid and ammonia removal, H_2S controls, in-CDF biodegradation, aerobic/anaerobic composting, phase-specific physical separation, low temperature thermal treatment, reactive geobags, and coupled geochemical/stabilization process modeling were areas identified as deserving of additional research investment.

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Preface

This study was funded by the Dredging Operations and Environmental Research (DOER) program. This report was prepared by Dr. Trudy Estes of the Environmental Engineering Branch (EP-E) and Christian McGrath of the Environmental Processes Branch (EP-P), Environmental Laboratory (EL), U.S. Army Corps Engineer Research and Development Center (ERDC). This report was prepared under the direct supervision of Dr. W. Andy Martin, Branch Chief of EP-E, and Mark Farr, Branch Chief of EP-P. Warren P. Lorentz was Chief of The Environmental Processes and Engineering Division, and Dr. Beth Fleming was Director of the EL.

COL Jeffrey Eckstein was Commander of ERDC and Dr. Jeffery P. Holland was Director of ERDC.

1 Introduction

Growing constraints on conventional dredged material disposal are motivating movement toward more sustainable alternatives. In a recent study by the U.S. Army Corps of Engineers (USACE), beneficial use was identified as the management alternative with the greatest potential for extending the useful life of confined disposal facilities in the United States (Bailey et al. 2010). However, given the lack of universal beneficial use criteria, even the low levels of contaminants typically found in navigation channel sediments may limit or preclude the beneficial use of dredged material. Intensive treatment to remove or destroy contaminants in such sediments is typically too costly to be a viable alternative; additionally, sediments have proven to be a very challenging matrix to treat effectively.

Wetlands restoration projects utilizing dredged material in the San Francisco area are required to be maintained in a ponded condition to minimize contaminant releases associated with oxidation of the dredged material. Consequently, the contouring that can be done with the material after placement is limited; yet the contouring is necessary to maximize its environmental benefit as habitat. There is a cost associated with keeping these areas inundated as well. Treatment of the material to “direct” the geochemical processes and sequester target contaminants in one or more immobile phases could eliminate this requirement. Sand recovery efforts at the Erie Pier CDF in Duluth, MN are limited by low levels of mercury in ponded water, which prevents discharge to the surrounding water body. Low-tech, passive water treatment processes capable of polishing low levels of colloids and dissolved organic carbon (DOC) are needed. Concern regarding potential release of metals and salts from marine sediments precludes their use in maintaining flood control levees in California. Effective treatment or stabilization measures could potentially broaden the acceptable uses of these materials and alleviate concerns related to groundwater and surface water impacts.

While some progress has been made toward commercialization of effective sediment treatment technologies for highly contaminated sediments (Estes et al. 2011), these are generally too costly for management of navigation sediments. Further, less aggressive treatment technologies may provide a sufficient level of risk reduction to facilitate use of moderately

contaminated sediments in beneficial use applications. Potentially cost-effective treatment technologies were identified through a review of the literature on previously demonstrated and newly emerging sediment treatment processes and high value research areas were identified. Both *in situ* and *ex situ* treatments were considered, as treatment opportunities exist at multiple points in the dredging, disposal, and beneficial use placement operations.

2 Objective

The preliminary objectives of this work included:

- building on past investment: assessing progress and potential of relevant treatment technologies previously demonstrated on sediments in a technology development program;
- identifying new treatments that have promise for cost-effective management of contaminated sediments in beneficial use applications;
- developing new management approaches exploiting the natural chemical, geochemical and biochemical processes of sediments in a specific beneficial use application; and
- identifying high value research needs and opportunities to advance the application of the most promising technologies and management approaches.

3 Approach

A synopsis of previous research in the area of sediment treatment was prepared in order to assess the current status of previously demonstrated technologies and to determine the best direction for future efforts in the economical treatment or management of sediments intended for beneficial use. An extensive literature search was conducted to locate case studies, identify promising new technologies, and capture relevant geochemical processes that might be exploited to manage contaminant speciation and mobility in sediments utilized in beneficial use applications. Due to the breadth of these topics, this document will focus on the synopsis of treatment technology development to date, relevant case studies pertaining to biological and geochemical processes, and potentially fruitful research areas to advance sediment treatment in a direction more competitive with conventional dredged material disposal alternatives. A companion document (in preparation) will delve deeper into the bio- and geo-chemical mechanisms responsible for contaminant fate in sediments. That publication will also explore the potential to control these processes using sediment amendments or management protocols to minimize contaminant releases. High value research needs will be identified in both documents.

4 A Brief History of Sediment Treatment Development

Sediment treatment was considered as early as the 1970s by the USACE to minimize impacts of contaminated dredged material (USACE 1978) open water disposal. However, that study focused primarily on removal of particulate-associated contaminants in effluent and in the water column, and on oxygen deficits resulting from chemical reactions taking place in reduced sediments during disposal. Direct injection of chemical oxidants into the dredged material discharge line to reduce BOD/COD was considered but ruled out as having limited benefit and potentially significant adverse effects due to the nature of the chemicals. Containment was determined to be the management mode of choice for highly contaminated sediments. Multiple treatment technologies were later evaluated under a variety of technology development programs, however. These are discussed briefly here. Note that some technologies are listed more than once. This reflects the fact that — in some cases — processes were demonstrated under one technology development program, and funding or additional monitoring was done by another.

Assessment and Remediation of Contaminated Sediment (ARCS)

Further studies were conducted under the Assessment and Remediation of Contaminated Sediment (ARCS) program, however, beginning with a screening level assessment of potentially applicable technologies (Averett et al. 1990). Based on this assessment, 27 technologies were recommended for further evaluation and/or demonstration. Although some of these technologies had been tested at pilot scale for treatment of contaminated soils, almost none had been demonstrated on sediments at that time. Nine technologies were reportedly evaluated at bench scale and four at pilot scale (USEPA 1994a) (Table 1). The piloted technologies are more fully described in the literature summary, which follows later in this document.

The overall findings of the ARCS program treatment evaluation were the following:

- The technologies piloted were found to have potential and further development was expected to take place as these technologies were fielded in conjunction with subsequent remediation projects and their utility in treating different sediment types and effectiveness in full-scale operations demonstrated.

- No single technology was found to be effective for all contaminants – typically treatments were designed to address either organic contaminants or metals, although some treatments (such as particle separation and solidification) could be effective for both types of contaminants in some cases. A multistep treatment process was considered likely to be necessary for some sediment.
- Sediment washing was found to be technically feasible and potentially the lowest cost of the effective technologies tested

Table 1. Technologies demonstrated under the ARCS program at bench or pilot scale.

Technology	Scale	
	Bench	Pilot
Solidification/Stabilization[1]	X	
Inorganic Treatment Recovery	X	
Bioremediation[1,3,8]	X	X
Base Catalyzed Decomposition (BCD) (Formerly KPEG Nucleophilic Substitution)[1]	X	
Basic Extraction Sludge Technology (BEST) Extraction Process[1,3,4]	X	X
Low Temperature Thermal Stripping (ReTech)[1,3,5,6]	X	X
Wet Air Oxidation (Zimpro)[1, 3]	X	
Low Energy Extraction	X	
Thermal Reduction (Eco-Logic Destruction Process)[1]	X	
In Situ Stabilization[1]	X	
Acetone Extraction (Rem-Tech)	X	
Aqueous Surfactant Extraction	X	
Sediment Dewatering Methods	X	
Particle Separation[1,3,7,9]	X	X
Soil Tech Anaerobic Thermal Process[3]	X	

[1] Assessment and Remediation of Contaminated Sediments (ARCS) Program Final Summary Report http://epa.gov/greatlakes/arcs/EPA-905-S94-001/EPA-905-S94-001.html#Bench-Scale%20Testing (USEPA 1994a)

[2] "Bench-Scale Evaluation of Sediment Treatment Technologies Summary Report," http://www.epa.gov/greatlakes/arcs/EPA-905-R94-011/EPA-905-R94-011.html (USEPA 1994b)

[3] http://epa.gov/greatlakes/arcs/EPA-905-S94-001/index.html. (USEPA 1994a)

[4]USEPA (1994c) EPA 905-R94-003

[5] USEPA (1993a) EPA 905-R93-005

[6] USEPA (1994d) EPA 905-R94-021

[7] USEPA (1994e) EPA 905-R94-019

[8] USEPA (1996) EPA/625/K-96/001

[9] USEPA (1994f) EPA 905-R94-022

Other programs under which treatment technology development took place included the Superfund Innovative Technology Evaluation (SITE) program, the Contaminated Sediment Treatment Technology Program (CoSTTEP), the Water Resources Development Act (WRDA) Sediment Decontamination Demonstrations, and the New Jersey Department of Transportation's Office of Maritime Resources Sediment Technology Decontamination Demonstration Program. These programs spanned a period of almost two decades, from approximately 1986 through 2007 (Estes et al. 2011).

Superfund Innovative Technology Evaluation (SITE)

The SITE program was established in response to the Superfund Amendments and Reauthorization Act of 1986; SITE was focused on innovative treatment technologies for hazardous waste site remediation[1], and included the following key components: (i) Demonstrations Program (120 technologies evaluated, 16 used in ongoing projects); (ii) Emerging Technology Program (70 technologies evaluated, 7 used in ongoing projects); (iii) Monitoring and Measurement Technologies (45 technologies evaluated); and (iv) Information Transfer Activities (USEPA 2003a,b,c). Additional information can be obtained from the following link: http://www.epa.gov/nrmrl/lrpcd/site/index.html. Treatment technologies demonstrated on sediments under the SITE program are given in Table 2. Summaries and findings of the SITE demonstrations listed in Table 2 are included in the literature summary which follows later in this document.

Table 2. Treatment technologies demonstrated on sediments under the SITE program.

Technology	Scale			Developer
	Bench	Pilot	Full	
In situ Thermal		X		Terra Therm, LLC
Sediment Soil Washing		X		Bergmann, USA[1]
Electrochemical Oxidation		X		Weiss Associates
Glass Furnace Technology		X		Minergy
Sediment Capping		X		AquaBlock
Bioremediation/Composting		X		USACE - Jones Island

[1]Independent evaluation of the same particle separation demonstration conducted under ARCS (Table 1).

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[1] http://www.epa.gov/nrmrl/lrpcd/site/index.html

Contaminated Sediment Treatment Technology Program (CoSSTEP)

CoSTTEP was focused on development and demonstration of *ex situ* technologies for treatment of contaminated sediments, as part of a cooperative effort between the U.S. and Canada to develop remedial action plans for Areas of Concern in the Great Lakes. Technology demonstrations were funded under the Environment Canada Great Lakes 2000 Cleanup Fund. Under the Great Lakes Binational Toxics Strategy, Canada documented the "evaluation and assessment of 250 innovative technologies developed …. for the safe handling and treatment of contaminated sediments" and promoted "the application and use of a computerized, searchable and user-friendly Sediment Technology Directory (SEDTEC)…" Twenty-nine of the technologies in SEDTEC were demonstrated and audited by the Great Lakes 2000 Cleanup Fund and partners (Environment Canada 1997). Twenty-four sediment treatment technologies were selected for bench-scale demonstrations, and eight of these were selected for pilot testing. Sediment remediation technologies evaluated under the umbrella of CoSTTEP/Environment Canada Cleanup Fund (Environment Canada 1997) are listed in Table 3.

Water Resources Development Act (WRDA) Sediment Decontamination Demonstrations

The WRDA of 1992 authorized the USEPA, with the cooperation of USACE, to review the decontamination technologies recommended pursuant to the 1990 Act and select the best technologies to treat dredged material. The USEPA Region 2, USACE New York District, and U.S. Department of Energy Brookhaven National Laboratory (USEPA 1999) interim report to Congress sets forth the major accomplishments under WRDA. Technologies evaluated under the WRDA program are listed in Table 4. Additional information is available at the following link: http://www.bnl.gov/wrdadcon/wrda/wrda.htm.

Table 3. Technologies evaluated under CoSTTEP/Environment Canada Great Lakes 2000 Cleanup Fund.

Technology	Scale			Developer
	Bench	Pilot	Full	
Bioremediation	X	X		Hobbs-Miller, Grade Dearborn, Limnofox, A-TAR [6], Institute of Gas Technology Biotreatment [1], Biogenesis [2], Itorics [3], Waste Stream Bioremediation
Gas phase thermal destruction	X	X		EcoLogic Thermal Destructor [6]

Technology	Scale			Developer
	Bench	Pilot	Full	
Thermal desorption	X			EcoLogic Thermal Desorber, Alberta Oil Sands Technology, X*Trax
Soil washing	X			THC Soil Recycling, Altech, Bergmann, Biogenesis [2]
Separation (pre-treatment)	X	X		Acres/Derrick [6]
Flotation	X			Alberta Research Council (ARC) Coal Agglomeration, Stefan, Robertson and Kirston [4]
Chemical stabilization	X	X		Ensotech Fixation Process, HRT Fixation [6], Reactive Silicate Technologies (SIALLON)
Solvent extraction (metals)	X			Beak Consultants Sequential Leaching, Cognis, Davy In-Pulp Extraction, Itorics [3], Vitrokele Technology (TALLON) [5]
Solvent extraction (organics)	X			Best Process
Chemical oxidation	X			Biogenesis [2]
Magnetic removal	X			Stefan, Robertson and Kirsten [4]
Classification	X			Vitrokele Technology [5]

[1] Solvent washing/bioaugmentation/oxidation

[2] Physico-chemical separation plus amendments to facilitate biodegradation

[3] Acid washing metals biological treatment of organics

[4] Magnetic removal of metals and flotation

[5] Solids classification, acid metal extraction and chelation

[6] Pilot-scale testing reported in Environment Canada (1997)

Table 4. Technologies demonstrated under the WRDA program.

Technology	Scale			Developer/Tester
	Bench	Pilot	Full	
Thermal destruction	X	X	X	Institute of Gas Technology (Rotary Kiln), ENDESCO (Cement-Lock®)
Sediment washing	X	X	X	Biogenesis^{SM}
Plasma torch vitrification	X	X		Westinghouse
Solvent extraction	X	X		Metcalf and Eddy
Thermal desorption	X			International Technology Corporation
Base catalyzed decomposition (BCD)/thermal desorption	X			Batelle
Fluidized bed thermal treatment	X			Biosafe
Manufactured soil	X	X		USACE – WES
Solidification/stabilization	X			Marcor/USACE - WES

The New Jersey Department of Transportation (NJDOT) Office of Maritime Resources Sediment Technology Decontamination Demonstration Program

The New Jersey Department of Transportation's Office of Maritime Resources Sediment Technology Decontamination Demonstration program was a companion program to the WRDA program, and was focused on the NY/NJ harbor. The NJDOT program evaluated sediment treating using several different decontamination technologies as one alternative to ocean disposal of dredged material. Summaries of technologies demonstrated under this program can be found on the NJDOT website[1]; the technologies demonstrated are listed in Table 5.

Table 5. Technologies demonstrated under the NJ DOT Technology Development Program.

Technology	Scale			Developer
	Bench	Pilot	Full	
Thermal destruction		X	X	Upcycle Associates, LLC (Rotary Kiln)[1], ENDESCO Clean Harbors, LLC (Cement Lock®)[2]
Sediment washing/chemical destruction		X	X	Biogenesis℠[3], LLC and NUI Environmental Group
Enhanced mineralization/chemical destruction	X	X		BEM Systems, Inc.
Chemical oxidation/cement stabilization		X		Harbor Resource Environmental Group
In situ stabilization/deep soil mixing		X		CAIT, Raito, Inc.

[1] Approximately 4 cubic yards sediment processed

[2] Approximately 100 cubic yards sediment processed (100 tons reported)(Mensinger 2008)

[3] Approximately 15K cubic yards sediment processed

USACE Dredging Operations and Engineering Research Program (DOER)

While not a technology development program per se, sediment treatment has been the focus of multiple work units executed under the DOER program, with the objective of identifying potentially applicable or adaptable technologies, assessing their developmental status, and identifying remaining obstacles to implementation as well as research needs. To that end, of the technologies demonstrated on sediments, four deemed closest to commercialization were evaluated in a report produced

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[1] http://www.state.nj.us/transportation/airwater/maritime/dresediment.shtm

by the USACE and EPA (Estes et al. 2011). The data from the NJ DOT demonstrations of the rotary kiln (JC Upcycle and Cement Lock) and soil washing (Biogenesis) were evaluated, along with data from subsequent demonstrations of the Biogenesis technology and a glass furnace technology (Minergy). Mass balances for these technologies were reconstructed to facilitate a comparative evaluation of effectiveness and cost. The technologies themselves are more fully described in the sections following. The general findings from this analysis are summarized here.

Estes et al. (2011) concluded that some degree of contaminant reduction was achieved with all four treatment technologies, though only the thermal technologies were highly efficient in terms of contaminant destruction. However, the maximum scale and duration of demonstrations was still relatively limited, as indicated by the following:

- 11,000 m^3 (15,000 yd^3) maximum total sediment volume processed
- 2,000 m^3 (2,700 yd^3) maximum volume processed on continuous basis
- Three days was the longest continuous operating time at maximum rate with validation data
- 30 m^3/hr (40 yd^3/hr) maximum demonstrated processing rate

Though thermal treatment was effective in immobilizing metals, some metals remained leachable at low concentrations following treatment. Multiple contaminant loss and treatment mechanisms were evident with all four technologies evaluated: thermal and chemical destruction, volatilization, immobilization, particle separation, solubilization, dilution, and even incidental losses played a role in contaminant reduction. Chemical oxidation was not shown to be very effective in treatment of organic compounds, however; this was attributed to the affinity of these compounds for natural organic matter and the competition of organic matter for the oxidizing agents. Most contaminant reduction achieved by the BioGenesis^{SM} Sediment Washing technology appeared to have been attributable to solubilization of contaminants (transfer to the aqueous phase), separation of fine solids, and volatilization, rather than destruction due to cavitation/oxidation. Subsequent bench testing on Housatonic and Passaic River sediments suggests that recycling material through the process and flotation for removal of organics-contaminated detritus could improve overall treatment efficiency for organic contaminants, albeit at the cost of additional processing time and operational cost. Technically, combining treatments could offer some promise in terms of increasing overall treatment efficiency. Physical separation could be followed by thermal treatment of a highly contaminated sub-fraction of the sediment, for example. However, the aggregate cost would likely further tighten the economic constraints associated with treatment of navigation sediments. Moreover, high treatment efficiency may not be necessary to achieve treatment objectives for beneficial use of sediments with low to moderate levels of contamination; the most appropriate technology should be determined on a case-by-case basis, taking into account processing goals, technical feasibility and cost, among other factors.

The basis of cost estimates provided by the vendors conducting demonstrations under the NJ DOT demonstration program differed significantly in terms of total volume treated, capital recovery period, profit, land acquisition cost, and other factors. However, the goal of the NJDOT program was to demonstrate "…the feasibility of technologies that can provide long-term decontamination services for the Port at full-scale costs of no more than $35/yd^3 exclusive of dredging." As originally structured, all of the cost estimates fell within the target range, but there were significant differences in the cost basis assumptions for each technology. Further, these costs were predicated on a fixed facility operating continuously for 10 to 20 years; some estimates also reflected net cost after revenue from the sale of the beneficial use product was taken into account. When placed on an equivalent cost basis based on best available information (Estes et al. 2011), unit treatment costs ranged from approximately $52/cy to $101/cy *in situ* (exclusive of dredging and transport cost), not taking into account any potential revenue from sale of beneficial use products produced (US$, 2009 cost basis). Including estimated product value, and assuming a supporting market demand, net treatment costs ranged from approximately $40/cy to $71/cy *in situ* (exclusive of dredging and transport cost).

It is a testament to the technical and logistical challenges of sediment treatment that — despite a significant level of investment in technology development over the last two decades — commercialization is still a goal rather than an accomplishment. Even the simplest treatment seems to be costly enough to discourage its use for management of most navigation sediments at this time. The cost of more sophisticated treatment technologies, such as the thermal and physico-chemical processes developed under some of the previously mentioned technology development programs, is generally prohibitive when other less costly disposal alternatives are available. The economic balance point may change as disposal alternatives become more limited and costly; for the present time, there is a need for cost-effective treatment technologies that are capable of sufficiently removing or immobilizing contaminants in sediments that are not highly contaminated, and that might otherwise be good candidates for beneficial use. To this end, highly efficient contaminant destruction may not be necessary to achieve sufficient risk reduction. This potentially broadens the types of processes that might be considered as “treatment.” An extensive literature search was performed to identify technologies that might fit into this category, as well as to ascertain whether any further work has been published for the technologies previously mentioned here that would suggest they merit further consideration in the treatment of navigation sediments in preparation for beneficial use.

5 Treatment Literature

Biological

Biological treatment continues to be an attractive treatment alternative that suffers from various limitations when implemented *in situ* and *ex situ* at full scale. Numerous studies can be found in the literature exploring the effectiveness of various organisms, nutrient delivery systems, and management. Although biodegradation does take place naturally, it proceeds very slowly for some contaminants. Recognized limitations to natural degradation of polynuclear aromatic hydrocarbons (PAHs) and polychlorinated biphynels (PCBs) in the environment include (Bishop 1996):

- contaminant toxicity to the microorganisms;
- preferential feeding on other substrates or inability of microorganisms to utilize the target compound as an energy or carbon source;
- unfavorable conditions for propagation of capable microorganisms and enzymatic production; and
- limited contaminant bioavailability due to affinity for sediment constituents.

Bioremediation – Sheboygan River (EPA 1994a, EPA 1996)

A bioremediation pilot was conducted under the ARCS program at Sheboygan River[1], where remedial action was being taken under Superfund. The pilot involved amendment of approximately 2500 cy of PCB-contaminated sediment (Aroclors 1248 and 1254) stored in a confined treatment facility to enhance naturally occurring biodegradation. Bishop (1996) describes the bacterial degradation of PCBs and PAHs as follows. “PCBs are typically degraded under sequential aerobic and anaerobic conditions. Appropriate anaerobic conditions dehalogenate more highly chlorinated PCBs, usually the meta- and para-chlorines on the biphenyl structure. Aerobic conditions usually degrade the resulting lightly chlorinated PCBs with the chlorine atoms at the ortho position.” PAHs are degraded under aerobic conditions.

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[1] http://epa.gov/greatlakes/arcs/EPA-905-S94-001/EPA-905-S94-001.html#Pilot-Scale%20Demonstrations

The Sheboygan study took place in a 14000 s.f. confined treatment facility, constructed of steel sheet piling, and divided into two control cells and two treatment cells (Cells 1, 2, 3, and 4). An under drain system was used to add nutrients, oxygen, and other amendments. Two approaches were tested to add oxygen to the sediments in Cell 4; oxygenated (saturated) water and dilute hydrogen peroxide solution. Mineral nutrients were added to the treatment cells.

Based on average chlorine concentration, only a limited amount of highly chlorinated PCBs remained in the sediment at the inception of treatment (evidence of prior, natural, anaerobic dechlorination). High sediment oxygen demand in Cell 4 prevented establishment of aerobic conditions for further dechlorination of less chlorinated PCBs, even with the oxygen delivery methods tested. Further anaerobic dechlorination was also not observed in the other cells. Heterogeneity of the material placed in the cells (from different locations and at different times) may have prevented meaningful interpretation of the processes taking place, however.

In concurrent laboratory studies, octachlorobiphenyl (octa-CB) was added to induce degradation of more highly chlorinated PCBs. Major increases of mono- and di- homologs were observed in the amended sediment; these increases were indicative of biological degradation. Bishop (1996) concluded that while there was evidence of microbial degradation even in unamended sediments, complete degradation did not occur even with amended sediments. Limited bioavailability of PCBs in sediments appeared to reduce the effectiveness of aerobic/anaerobic sequencing demonstrated to be effective in treatment of aqueous suspension. Bishop (1996) also recommended that treatment endpoints be based on toxicity rather than concentration.

Cost estimates for the technology were not developed pending further research.

Bioremediation – Hudson River (Bishop 1996)

An *in situ* bioremediation study was conducted on Hudson River sediments; six caisson slurry reactors were driven into the PCB-contaminated sediment to isolate the natural bacteria and sediment from the river. The experimental design, taken from Bishop (1996) was as follows: “The experimental design…featured a low-mix caisson and a high-mix caisson as unamended controls: two duplicate low-mix caissons (3 rpm rakes) with indigenous organisms amended with ammonium and phosphate nutrients, biphenyl, and hydrogen peroxide; and one high-mix (40 rpm turbine) and one low-mix caisson with indigenous organisms, both amended with ammonium phosphate nutrients, biphenyl, hydrogen peroxide, and a culture of PCB degraders, *A.eutrophus* H850." Dissolved oxygen was maintained between 6.0 and 6.5 mg/l through addition of hydrogen peroxide in 4 cells; the high-mix and low-mix controls were allowed to become anaerobic.

Changes in PCB concentration and distribution were evaluated by direct concentration measurement and also by normalization to a recalcitrant congener and to sediment TOC; the normalization procedure was effective in facilitating interpretation of the data in otherwise heterogeneous sediments. After 73 days of treatment, there were "…statistically significant PCB losses of 38 to 55 percent in all amended caissons. The addition of the H850 culture produced no impact on the PCB changes, and the H850 cultures were not competitive. Congener homolog group analysis revealed significant biodegradation of the mono- and di- congeners."

Bishop (1996) cites the following challenges and opportunities associated with effective biological treatment of contaminated sediments:

- Combining appropriate microbial pathways, biochemistry, and function of natural microbial communities
- Overcoming contaminant recalcitrance to biodegradation
- Developing in situ biotreatment without reactors (noting limited effectiveness to date)
- Developing in situ treatment of dredged sediments
- Developing in situ biotreatment with slurry reactors

No full-scale cost estimates were provided for the technology in this report.

Composting – Jones Island and Bayport CDF (Myers and Bowman 1999; Myers, Bowman and Myers 2003)

Sediment composting was evaluated by USACE on sediments contaminated with PAHs and PCBs in two studies taking place from 1999 to 2002; at the Bayport confined disposal facility (CDF) in Green Bay, WI (Myers, Bowman, and Myers 2003) and at the Jones Island CDF in Milwaukee, WI (Myers and Bowman 1999; Myers, Bowman, and Myers 2003). These field demonstrations were conducted with the objective of enabling safe beneficial use of dredged material containing various contaminants of concern.

The amount of degradation observed in PAH and PCB concentrations in these two studies was less than hoped. No distinct decreases in PAH concentrations could be seen in the Jones Island sediments; PAH concentrations decreased by 30 to 35 percent in Bayport sediments, but these differences were not statistically significant. Results obtained for PCBs were just the opposite, with a decreasing concentration trend observed for the Jones Island sediments, but no significant trend in the Bayport sediments. Further, the Jones Island sediments evidences minimum PCB concentrations at 1 month, with increasing concentrations as composting continued. High variability was observed in all of the results, complicating interpretation of the data.

Each of the composting studies did reveal processing challenges and parameters requiring optimization in order for composting to be effective in achieving biodegradation of organic contaminants. In particular, heap size and the level and frequency of biosolids addition were identified as critical factors to maintain optimum temperatures within the composting heaps and to assure a balance of nutrient sources for the bacterial consortium. Moisture management was another process parameter identified as critical but potentially difficult to control under field conditions; degradation is limited at moisture content below approximately 40%, while handling properties deteriorate at moisture contents of approximately 50%. Contaminants were found to reside in the amendments themselves. Further, the amendments may be preferred as an energy source over the contaminants, limiting the degradation of the contaminants. The bioavailability of the contaminants is also a factor that needs to be evaluated in treatability studies; a significant fraction of the PAHs in the Jones Island dredged material was found to be associated with a condensed carbon phase. Limited bioavailability may have been a significant factor in the small contaminant reductions observed in these studies.

A-TAR – Autoheating Thermophilic Aerobic Reactor (Environment Canada 1997)

Of the sediment treatment technologies evaluated under the Great Lakes 2000 Cleanup Fund, the A-TAR Technology (autoheating thermophilic aerobic reactor) is particularly interesting in terms of potentially fitting in with an economical treatment process for navigation sediments, and addressing some issues associated with composting (Environment Canada 1997). The process takes place at temperatures ranging from approximately 45-65 degrees C without external heating (temperature ranges reported in the literature vary) and was demonstrated at pilot scale on sediments from Hamilton Harbor. Reportedly the process achieved 95% removal of PAHs, 80% removal of total petroleum hydrocarbons and 70% removal of oil and grease with an 8-day retention time in the reactor. The demonstration was initiated in 1993, and the point of contact was Deo Phagoo, Water Technology International Corporation. The National Biotechnology Strategy Fund was also supporting the effort. This technology is interesting for several reasons:

- Maintaining adequate temperatures to achieve biodegradation was one control variable that proved problematic in previous sediment composting studies (Myers and Bowman 1999; Myers, Bowman and Myers 2003).
- The technology has been applied to digestion of wastewater sludges, which have also been used to amend sediments for composting and soil manufacture. This suggests a possible treatment synergy that could be exploited to achieve higher sediment treatment levels. By combing contaminated dredged material with wastewater sludge, a reusable product would be produced from materials that would otherwise be managed as wastes.
- During wastewater sludge testing, the technology was observed to destroy pathogens, reduce oxygen requirements for aerobic digestion (due to elimination of nitrification), and destroy weed seeds (Jewell and Kabrick 1980). Weed seeds are an acknowledged impediment to beneficial use of sediments in some areas of the country. Pathogens, while not regulated in sediments at this time, could potentially still be of concern in some beneficial use applications.

In the study conducted by Jewell and Kabrick (1980), autoheated aerobic thermophilic digestion was demonstrated at pilot scale on primary and secondary wastewater sludges. They identify requirements for treatment, including:

- a minimum biodegradable organic concentration;
- insulated reactors; and
- efficient aerators (capable of >10% oxygen transfer efficiency in sludge).

Total solids concentration of the thickened primary and secondary sludge ranged from approximately 30% to 63%, but it is likely that this was diluted before being fed to the reactors; the highest rate of organic removal was reportedly for a 3-day retention time at 5% solids. Oxygen transfer utilizing two highly efficient self-aspirating aerators ranged from 12% to 23%. Hydraulic retention time tested ranged from approximately 3 to 8 days. Maximum temperature development occurred with approximately 50% destruction of biodegradable organics, at an effective rate of 4 kg COD/m^3/d. The potential for adaptation to treatment of slurried sediments in a CDF is unknown; it's possible that with smaller cell divisions to prevent decanting, and with the simultaneous mixing of wastewater solids with the discharging dredge material, favorable conditions could be established for biodegradation of organic contaminants. Preferential degradation of the supplied organics rather than the contaminants could be problematic; maintaining sufficient oxygen levels to support aerobic respiration could also pose challenges. Proof of concept testing would be needed to determine whether some of the issues related to composting dredged material could be overcome with this approach. Certainly the pilot testing conducted by Water Technology International Corporation on Hamilton Harbour sediments (Environment Canada 1997) suggests that there is potential. No further studies on sediment were found, but thermophilic digestion has been extensively studied for treatment of wastewater, and various agricultural and food processing waste streams (manure, potato slop, olive oil processing). These studies suggest that there may be a variety of waste streams that could potentially be incorporated with dredged material to enhance degradation by providing nutrients necessary to sustain biological populations. This could enhance the economics of the process and provide for more sustainable waste management for multiple regional industries. It is also interesting to note that the destruction of pathogens and weed seeds occurring in thermophilic processes has been studied, and would be a desirable secondary benefit to contaminant reduction in sediment treatment.

Phytodegradation – Jones Island (USEPA 2003b)

The Jones Island phytoremediation pilot consisted of four 12 ft x 20 ft cells established by excavating dredged material from the facility (143 yd^3), mixing it with appropriate amendments, placing the material in test cells, and vegetating with one of three species (hybrid corn, indigenous willow, and various grasses). One cell was retained as an unplanted control. The plots were monitored for a period of two years and results evaluated through analysis of sediments and plant uptake.

Plant species for phytoremediation are selected based on (USEPA 2003b):

- Growth rate and yield
- Evapotranspiration potential
- Production of degradative enzymes
- Depth of root zone
- Contaminant tolerance
- Ability to “take up” contaminants

Factors influencing the success of phytoremediation include (USEPA 2003b) the following:

- Site water – groundwater depth, seasonal variation, plumes
- Physical and chemical soil properties
- Contaminant magnitude and distribution
- Climate
- Other site conditions (traffic, usage, topography)

Indigenous microorganisms capable of degrading PAHs and PCBs were identified in the Jones Island sediment (Myers and Bowman 1999). Greenhouse studies suggested that selected plants could enhance microbial action in the dredged material; due to their high affinity for sediment solids and relative insolubility, PAHs and PCBs are not considered to be good candidates for plant uptake. Six different plant processes were identified in USEPA 2003b with the potential to affect phytoremediation. These processes include the following:

- Phytoaccumulation (uptake to above ground biomass)
- Rhizostabilization (sorption to plant roots – typically metals)
- Rhizodegradation (interaction of roots, root exudates, soil and microbes to achieve contaminant degradation)
- Phytodegradation (within plant degradation of contaminants)
- Phytovolatilization (transfer of contaminants to atmosphere through evapotranspiration)
- Phytostabilization (exploits high water usage of select plants to contain groundwater flow)

Rhizodegradation was identified as the most likely destruction mechanism for the Jones Island demonstration. The rhizosphere is defined as the area within 1-3 mm of the plant root; carbohydrate-containing plant exudates released in the rhizosphere have the effect of nourishing indigenous bacteria and stimulating bacterial oxidation of contaminants. The two components of rhizodegradation are biodegradation, the process of converting contaminants to a food source for the plants; and co-metabolism, the process in which biological organisms degrade the contaminants without creating a food source for the plant. Maximizing root mass is obviously critical to maximizing removal; therefore, relatively dense plantings are desirable. In this case, corn was seeded as thickly as possible and willows planted on 1 ft spacings.

The primary objective of the demonstration was to attain a specified residual contaminant level for PAHs, PCBs and DRO (diesel range organics) after two growing seasons. Results were mixed. Although vegetation was well established (corn required two plantings, however), no soil samples taken after the requisite treatment period attained target PCB and DRO residual concentrations (1mg/kg and 100 mg/kg, respectively). There was some evidence of DRO increases over the treatment period that could not be fully explained. TOC degradation and production of biogenic hydrocarbons in the corn plot could partially explain this but the degradation was not equivalent in magnitude to the DRO increases. PAH concentrations were largely already below target concentrations prior to treatment. No statistically significant differences were observed between the different treatments, but the magnitude of PAH removal was reportedly greatest for natural vegetation followed by willow and then corn. This may have been attributable in part due to the delayed establishment of the corn, however.

Though they differ in terms of the relative cost to install and maintain, with installation costs lower and maintenance higher for corn, overall costs for full-scale corn and willow treatments were estimated to be in the range of \$20/ton of soil treated (for a treatment volume of approximately 1613 yd^3) (US\$ 2003), with a 30% reduction if irrigation were not needed. This cost is scalable up to the point that similar equipment could be utilized and the initial cost assumptions pertain.

Bioleaching – (Vestola et al. 2010)

Vestola et al. (2010) evaluated the feasibility of bioleaching for the solubilization of metals from solid waste streams and by-products of copper, steel, and recycling industries. The approach is potentially applicable to the leaching of metals from sediments. Bioleaching is an indirect process for leaching metals from sulphide minerals; ferric iron (Fe^{3+}) and oxygen (O_2) in acid solutions act as oxidizing agents (Equations 1 and 4). Ferrous iron (Fe^{2+}), elemental sulphur (S^0), and other reduced sulphur species are oxidized to Fe3$^+$ and sulphate (SO_4^{2-}), respectively (Equations 2 and 3).

$$MS + 2Fe^{3+} \rightarrow M^{2+} + 2Fe^{2+} + S^0 \qquad (1)$$

$$2Fe^{2+} + 0.5O_2 + 2H \rightarrow 2Fe^{3+} + H_2O \qquad (2)$$

$$S^0 + 1.5O_2 + H_2O \rightarrow SO_4^{2-} + 2H^+ \qquad (3)$$

$$MS + 2O_2 \rightarrow M^{2+} + SO_4^{2-} \qquad (4)$$

Where metals are present as oxides, carbonates, or silicates, ferric iron leaching (Equation 1) is not feasible but S-oxidizing acidophiles may be used to leach metals through sulphuric acid production (Equation 3).

Three different types of bacteria (iron and sulphur oxidizing acidophiles) generally resistant to high heavy metal concentrations were identified in this work: Acidithiobacilli, Leptospirilli and A. ferrooxidans. On average, 30-80% of metals were mobilized (dissolved) by acid produced by the bacteria; highest yields were obtained with S^0 supplementation at pH 1.0 and 0.5. Note that at this pH, significant solubilization would be expected, but the bacterial cultures did show higher mobilization than chemical controls — DDI adjusted to pH 0.5 — perhaps because acid is continually produced by the bacteria but finite in a chemical process unless supplemented as consumed. Cu and Ni were almost completely dissolved. Fe^{2+} and NaCl supplementation has been shown to increase metal solubilization but this was not the case here because metals in these materials were present as oxides. Fe^{2+} supplementation did result in faster oxidation rates, however, for two of the materials tested. Metals solubilization was lower for higher pulp densities (10% vs. 1%); this may be a significant finding with respect to sediment treatment, for which solids concentrations will be much higher. Moreover, plant uptake would seem to be the primary means of removing mobilized metals from the sediment unless the sediment were maintained in a slurry for the requisite period of time, followed by dewatering and flushing of any remaining pore water containing extracted metals. This study may be more important in terms of identifying factors which must be controlled to limit metals mobilization due to acidification in beneficial use placements.

Reductive Dechlorination – (Payne et al. 2011)

Payne et al. (2011) evaluated enhanced reductive dechlorination by anaerobic dehalorespiring bacterium in the conversion of highly chlorinated PCB congeners to less chlorinated congeners amenable to aerobic degradation. "Dehalococcoides spp. and related species within the Chloroflexi have been identified that are capable of reductively dechlorinating PCBs by utilizing PCBs as terminal electron acceptors, a process termed dehalorespiration, and several strains with specific dechlorinating capabilities have been reported" (Payne et al. 2011). Further, while substantial attenuation of PCBs is rarely seen in the environment, this may be attributable to low indigenous populations of such bacterium.

Bench scale testing was conducted on sediment containing weathered Arochor 1260 at 1.3 ppm; 2L mesocosms simulating *in situ* conditions were augmented with D. chlorocoercia DF-1 and PCB degradation occurring over a period of 120 days was measured. The effect of activated carbon present at concentrations used in situ to sequester PCBs from benthic organisms (used here as a delivery mechanism for the organisms), and the sustainability of the dehalorespiring in the presence of low PCB concentrations and indigenous bacteria was also evaluated. After a period of 120 days, the mass of penta- and higher chlorinated PCBs decreased by 56%, while no activity was observed in the unamended controls. The rate of dechlorination after bioaugmentation with GAC was roughly 60% higher than the rate observed for direct injection of the bacterium, and this difference was statistically significant. The authors concluded that the DF1 bacterium must have some mechanism that allows them to utilize PCBs sorbed to the carbon. They also noted that "Although the less chlorinated PCBs generated by bioaugmentation are more bioavailable to benthic organisms, they are generally less toxic because they are non-coplanar or have at least two adjacent unsubstituted carbon atoms that would make them subject to rapid metabolic degradation." The population of DF-1 was found to be sustainable in the presence of indigenous bacteria; although numbers had declined to about half after 90 days, no further decline was noted, even though no additional electron donors were provided. There was also evidence that the augmentation of the system with DF-1 stimulated PCB degradation by indigenous dehalorespiring bacteria, in effect “priming” the system with PCB breakdown products. Field studies of the effectiveness of bioaugmentation for *in situ* treatment of PCB contaminated sediments are needed to validate the findings of this and other bench testing under environmental conditions.

In Situ Bioremediation for Reduction of Odors Attributable to H_2S (Chan and Babin 2008 approximate publication date)

Chan and Babin (2008 approximate publication date) reported the results of pilot and full-scale applications of *in situ* bioremediation of sediments highly contaminated by sewage discharges and — in some cases — industrial outfalls, to reduce odor problems associated with the oxidation of sulfides. The technique is potentially interesting for management of H_2S emissions from sediments in confined disposal facilities and at beneficial use placement sites. Concurrent degradation of organic contaminants is also possible, but was not the central focus of this study.

In the presence of oxygen, the preferred degradation pathway for organics is aerobic bacterial oxidation (Chan and Babin unknown publication date):

$$Carbon\,matter + O_s \rightarrow CO_2 + H_2O \tag{5}$$

Nitrate is the next preferred oxidant:

$$Carbon\,matter + NO_3^{2-} \rightarrow CO_2 + N_2 \tag{6}$$

When oxygen and nitrate are exhausted, the following reaction prevails:

$$Carbon\,matter + SO_4^{2-} \rightarrow CO_2 + H_2S \tag{7}$$

Liquid calcium nitrate was injected into the sediments to provide a preferential oxidant for degradation of organic material; the procedure stimulates bio-oxidation of hydrogen sulfide (H_2S) and long term biological breakdown of organics, as per the following mechanisms:

$$HS^- + Ca(NO_3)_2 \rightarrow CaSO_4 + H_2O + N_2 \tag{8}$$

$$Carbon\, matter + NO_3^- \rightarrow CO_2 + H_2O + N_2 \tag{9}$$

A 48-hectare area of the Shin Mun River in Hong Kong was treated with $CaNO_3$ injection between 2001 and 2006. An average odor removal rate of between 95 and 99 percent was reported, in addition to a reduction in sediment organic matter content of approximately 16.5 percent. A second project was executed on an 18,000 m^2 area in the Sam Ka Tsuen Typhoon Shelter in Lei Yue Mun in 2004, achieving an acid volatile sulfide reduction of over 95 percent and a dissolved oxygen (DO) level increase in the water column of approximately 2 mg/l. Both of these sites were predominantly impacted by sewage outfalls. A third site, Kai Tak Approach Channel, in Kowloon Bay was also impacted by industrial discharges. A 1-hectare pilot was first initiated at this site in 2006; over 99 percent of acid volatile sulfide (AVS – a solid phase sulfide – mainly FeS, which is soluble in cold acid; Choi et al. 2006) was removed, polynucleararomatic hydrocarbons (PAHS) were reduced by approximately 30%, and odor was reduced by over 97%. As of the time of this report, treatment of a 3.5 hectare area of deeper sediments was also underway.

Based on nearly six years of monitoring data at Shing Mun River, average AVS levels remained below the established threshold for “revival” of 100 mg/kg for over 3 years. Individual exceedances were noted beginning as early as 1.7 years, but only 18 of 135 data sets exceeded the AVS threshold over the six year period. Monitoring data at Sam Ka Tsuen was more limited, but based on the available data, the authors projected suppressed AVS levels for at least 2 years. For the pilot treatment plot in the Kai Tak Approach Channel, effective odor suppression appears to have been sustained over a period of a year, with the only exceptions being low dosage plots where treatment was clearly inadequate and nitrate depleted during this time period.

Nitrate dosages ranged from 2,900 to 4,000 mg $NO_3 \ - N/L$ at Shing Mun River, 5,000 to 6,250 at Sam Ka Tsuen Typhoon Shelter, and 5,200 to 8,400 at Kai Tak Approach Channel. Potential concerns with this technology include eutrophication associated with nitrate additions to a natural system and mobilization of sulfide-associated metals.

Limnofix (NAVFAC 2002)

NAVFAC (2002) reported on the results of a pilot study using Limnofix™, a proprietary process utilizing nitrate addition for oxidation of organic contaminants. Reportedly, Limnofix™ reduced PAHs by 64% and TPH by 57% after 2 years. A subsequent white paper by Golder Associates (Golder 2003) reports that the technology had been demonstrated on 5000 m^3 of sediments to enhance biodegradation of organic compounds, compounds, at Hamilton Harbor, St. Mary's River, Ontario, and the previously mentioned Hong Kong sites, to address sulfide associated odors. Bench testing was also reportedly conducted on oil refinery-impacted pond sediments in Michigan to reduce AVS. The technology saw full-scale application at a coal tar contaminated intertidal zone site in Massachusetts in 1998; 50% reduction of total petroleum hydrocarbons (TPH), and 90% reduction of PAHs was reported after a period of approximately one year (Golder 2003). Results of the pilot in Hamilton Harbor were: 79% reduction of benzene, toluene, ethylbenzene and xylene (BTEX) compounds; 57% reduction of TPH; and 64% reduction of PAHs, after a period of approximately two years.

Surface Aeration - InStreem™ (NAVFAC 2002)

An *in situ* aquatic aeration technology -InStreem™ – utilizes surface aerators to achieve oxidation of sediment organic loads (NAVFAC (2002)). No other information was found regarding demonstration of this technology for treatment of contaminated sediments. However, another interesting application that was demonstrated in the removal of heavy metals from mine effluent was the use of the InStreem™ aeration unit in combination with the Self-Assembled Monolayers on Mesoporous Support (SAMMS™) technology developed at Battelle. The SAMMS™ was integrated into the InStreem™ system to create a floating plant for passive treatment (sorption) of mercury and other heavy metals (Mattigod et al. 2008). Depending on the effect of dissolved organics on sorption capacity, this technology may have potential for effective treatment of ponded water in CDFs prior to discharge.

Chemical Oxidation

In Situ Oxidation of Soils and Groundwater (Interstate Technology and Regulatory Council (ITRC) 2005)

The fundamentals of *in situ* oxidation of soils and groundwater are extensively detailed in a comprehensive document produced by the ITRC (2005). While there are differences between *in situ* treatment of soils and sediments, the reagent choices and primary chemical reactions are the same. Differences in sediment composition and environment will obviously influence some of the secondary reactions that will occur. Chemical oxidants can also react with water, resulting in non-productive depletion of reagents. According to the ITRC (2005), there are four primary chemical oxidants in use for chemical oxidation of contaminants in soils and groundwater:

- Permanganate
    - $KMnO_4$
    - $NaMnO_4$
    - Strong agents
    - Affinity for oxidizing compounds containing carbon-carbon double bonds, aldehyde groups, hydroxyl groups
    - Complex stoichiometry and kinetics due to multiple Mn reactions *in situ*
- Persulfate
    - $Na_2S_2O_8$
    - $(NH_4)_2S_2O_8$
    - $K_2S_2O_8$
    - Persulfate anion – ($S_2O_82^-$) - more powerful than hydrogen peroxide
    - Heat, ferrous salt (Iron II) or high pH (lime addition) increases strength through production of sulfate free radicals ($SO_4^{-\cdot}$)
- Peroxide/Fenton’s Reagent
    - H_2O_2
    - Ca_2O_2 (Modified Fenton’s Reagent)
    - Kinetically slow – addition of Iron II dramatically increases strength due to production of hydroxyl radicals (Fenton’s Reagent)
- Ozone
    - Gas phase reagent
    - Liquid phases – Ozonated water, ozone plus peroxide (peroxone)
    - Two forms – vadose zone and below water table
    - Elevated pH increases hydroxyl radical production
    - Mass transfer limitations leads to more sustained oxidation than for other reagents

Hydroxyl radical formation may also be promoted by the presence of common soil/sediment constituents, including:

- Alcohols
- Carboxylic acids
- Humics

However, certain soil constituents are also potentially problematic to *in situ* oxidation, including bacterial biomass, total organic carbon, iron, manganese, hydrogen sulfide and carbonates (ITRC 2005). Natural organic matter, carbonates, humic acids, by-products of oxidation and reagents themselves (in peroxide overdosing) can all act as scavengers resulting in higher required reagent dosages. Carbonates may also provide significant buffering. Although competition from natural organics for reagents is often cited as a major factor limiting the success of chemical oxidation, the majority of organic contaminants will reside in the organic materials. Destruction of the natural organics may be necessary to access the associated contaminants, rather than being a secondary and undesirable reaction. In any case, reagent dosing must take into account competition from soil constituents in addition to the target contaminants.

The following contaminants are amenable to treatment by chemical oxidation (ITRC 2005):

- Benzene, toluene, ethylbenzene and xylene (BTEX)
- Methyl *tert*-butyl ether (MTBE)
- Total petroleum hydrocarbons (TPH)
- Chlorinated solvents (ethenes and ethanes)
- Polyaromatic hydrocarbons (PAHs)
- Polychlorinated biphenyls (PCBs)
- Chlorinated benzenes (CBs)
- Phenols
- Organic pesticides, insecticides, and herbicides
- Munitions constituents

The strength of a chemical oxidant is given as “standard oxidation potential,” expressed in volts, which is determined using chlorine as a reference. A number of variables will influence the effectiveness of a given oxidant when used in the field, with the major ones being:

- stoichiometry;
- thermodynamics;
- kinetics (reaction and contaminant desorption/dissolution kinetics); and
- contact (delivery).

The rate and completion of reactions are also influenced by pH, temperature, concentration, catalysts, oxygen levels/redox, reaction by-products and system constituents (which may favor radical production and enhance oxidation or act as scavengers and increase reagent requirements). Stronger oxidants are capable of degrading more recalcitrant compounds but are also more difficult to disseminate over long distances; due to their high reactivity, they are consumed by competing constituents within the soil matrix.

BEM System (NJDOT 2004)

The BEM system piloted under the NJDOT technology demonstration program (NJDOT 2004) utilizes a proprietary mixture to incorporate metals into a mineral matrix and oxidize organic contaminants. Bench scale tests on dredged material produced inconsistent results with respect to destruction of organic contaminants and leaching of some metals actually increased; geotechnical properties of the treated dredged material did not meet specifications for either transportation fill or landfill liner or cap (NJ DOT 2004). As a result, the technology was not taken to pilot scale. Without further specifics on the process and the sediments being treated, it is difficult to conjecture about the failure of the technology in this application.

Harbor Resources Technology (NUI Environmental Group Inc. 2002 and Harbor Resources Environmental Group 2005)

The Harbor Resource technology fielded by the NJDOT employed potassium permanganate for oxidation of organic contaminants, followed by blending with Portland cement to create a stabilized material. Pilot (650 gallons) and larger scale (300 yd^3) demonstrations were conducted (NUI *Environmental* Group Inc. 2002 and Harbor Resources Environmental Group 2005). Although the final reports indicate the demonstrations were successful, based on the data report for the field demonstration, the contaminant reduction achieved was relatively low (10 and12%, respectively, for SVOCS and PCB). Contaminant concentrations in the feed were near MDLs, contributing to the difficulty in distinguishing treatment from material variation. As for the BEM technology (NJDOT 2004), further analysis of the data — including sediment composition — is needed to better understand these demonstration outcomes.

Chemical Oxidation of PAH Contaminated Sediments (Andreottola et al. 2010)

A recent study by Andreottola et al. (2010) reported the results of bench scale testing of chemical oxidation for treatment of contaminated sediments containing PAHs. The study largely confirms the already recognized limitations of oxidation processes in sediments attributable to competition for the reagents from organic matter and non-target contaminants. The study does provide some comparative performance values for the technologies, however.

The performance of modified Fenton's reagents in oxidizing PAHs was compared to that of chemically and thermally activated persulfate catalyzed by ferrous ions. Fenton-like reagents included peroxide alone (OX1), peroxide with phosphoric acid (OX2), peroxide with acetic acid (OX3), peroxide with HCL and buffer acetate (OX4 and OX5), peroxide with ferrous sulfate (OX6), ferrous sulfate with peroxodisulfate (OX7), and ferrous sulfate with peroxodisulfate following pretreatment with peroxide (OX8). The peroxide alone achieved the highest removal of the Fenton-like reagents, achieving 45% removal of total PAHs from the sediments; the activated persulfate achieved 72% removal of total PAHs. Kinetics were reportedly rapid, with consumption of Fenton's reagent at 24 hours comparable to that observed at 6 hours, and consumption of persulfate at 24 hours comparable to that observed at 3 hours.

Note that the addition of $CaNO_3$ to sediments to stimulate biological oxidation and reduce production of hydrogen sulfide was discussed previously under biological treatment (Chan and Babin approximate publication date 2008); this was done because the mechanism for contaminant degradation is bacterial, even though mediated through the artificial introduction of a chemical oxidant, which acts as an electron acceptor utilized in bacterial respiration.

Chemical Extraction

BEST Pilot-Scale Demonstration of Solvent Extraction for the Treatment of Grand Calumet River Sediments (EPA 1994c)

Extraction of PCBs, PAHs, and oil and grease (O&G) using the solvent triethylamine was tested at bench and pilot scale on two different sediment types, with a range of PCB concentrations. Solubility of triethylamine is temperature dependent, a property that can be exploited to separate solubilized contaminants from the aqueous solution. Extractions are carried out at a pH greater than 10; this also promotes precipitation of heavy metals as hydroxides. Precipitated metals are not separated from the sediment matrix as part of this treatment. The BEST pilot system incorporated four operations: extraction, solvent recovery and oil polishing, solid drying and water stripping. Two temperature ranges can be utilized for "cold" (chilled) or "warm/hot" (>38 deg C and approximately 43 deg C, respectively) extractions; cold extractions precede warm extractions and serve to dewater the solids prior to extraction and drying. Residual solvent was removed first by indirect heating, followed by direct injection of steam to the clean sediment. The scale of the demonstration was 40 liters of low solids feed material to 120 liters of chilled solvent, with a capacity of 0.03 m3 sediment/day; 5 batches were processed in the pilot-scale testing. Washer/dryer operations are batch in both pilot- and full-scale operations.

The process reportedly removed more than 99 percent of PCBs and PAHs, and more than 98 percent of O&G. Residual solvent concentrations were relatively low (<150 ppm); biological degradation of solvent residuals was tested but was not successful under the conditions tested. Full-scale treatment cost estimates ranged from \$139/yd^3 to \$361/ yd^3, for total treatment volumes of 5,000 and 100,000 cubic yards of sediment, respectively, processed at a rate of 184 yd^3 /day.

Electrokinetic

The first commercial use of electrokinetics (EK) was for dewatering of soils and sediments for structural applications, primarily for construction of railway beds and forced consolidation of soils for building construction (Gent and Estes in preparation). Electroosmotic dewatering of dredged material was evaluated by O'Bannon and USAE District, Mobile (1977) and Haliburton et al. (1978); the Haliburton pilot revealed a number of operational issues requiring resolution for successful field application. Rapid corrosion of electrodes was one significant issue; surface water management was also problematic, preventing effective dewatering of the material. Newer, corrosion-resistant electrodes are now available and horizontally oriented electrode placements would likely minimize issues with undesirable annular flow. The technology continues to be of interest because of the low energy requirements and potential for *in situ* application, and this is evidenced by the number of subsequent studies found in the literature.

Weiss Associates – ElectroChemical Remediation Technologies (ECRTs) (EPA 2007a)

The ECRT technology utilizes an AC/DC current passed between an electrode pair in soil, sediment, or water (*in situ* or *ex situ*) to achieve electrochemical oxidation of organic contaminants and/or complexation, mobilization, or removal of metals through induced complexation. The system reportedly operates at lower power than conventional electrokinetic systems. A field demonstration was conducted at the Georgia-Pacific (G-P) Log Pond in Bellingham, WA (EPA 2007). Nine steel plate anodes and nine graphite plate cathodes were installed in two parallel rows, 30 ft long, in a 50 ft x 50 ft area in sediments in the G-P Log Pond. The Log Pond is a marine embayment previously used for log storage and handling. Sediments here were contaminated with mercury, PAHs, and phenolic compounds; the primary objective of the demonstration was to determine whether there was a “significant trend in the reduction of sediment mercury over the period of the demonstration.” (Metals are mobilized toward both anode and cathode with ECRT, plating out on the electrodes, which may then be removed and regenerated or disposed of.) Other contaminants were also monitored, however, with the following secondary objectives:

- Determine rate of organic compound mineralization
- Assess potential vertical migration of contaminants
- Determine zone of influence of the process
- Track natural changes in contaminant concentrations in reference area
- Evaluate possible environmental effects of ECRTs
- Evaluate potential contaminant flux across water-sediment interface (as indicated by cap chemistry)
- Evaluate mercury migration through mass collected on electrodes
- Determine field scale costs

Equipment problems, including steady degradation of system performance due to corrosion of connections between the electrical supply and the anodes, resulted in early termination of the test. The equipment was in place for six months but actual operating time was much less (perhaps four months of discontinuous operation) due to the operational issues; only two of three sampling events were completed. Statistical analysis of the sediment contaminant concentrations failed to show a statistically significant decrease over the period of the test. One outcome of the demonstration was the determination that a monitoring protocol is needed to identify and rectify operational problems. In this case, it could not be determined how long the system was fully operational; the failure to meet the primary and secondary project objectives (decreasing mercury trends and mineralization of organic contaminants) could have been due to inherent limitations in the technology, or simply the failure to operate as designed. Heterogeneity of the sediment concentrations also contributed to the difficulty in demonstrating statistically significant changes. Although some elevation in mercury was detected on 12 of 13 cathodes, this may have been attributable to direct contact with the sediment rather than mobilization of mercury throughout the test plot. In short, few conclusions regarding the effectiveness or the environmental impact of a properly operating system could be made on the basis of this demonstration.

Order of magnitude cost (+50%/-30%) for a hypothetical full-scale application, involving *in situ* treatment of approximately 460 yd^3 sediment in a 50 ft^2 area over a period of six months, was estimated to be $388,500.00 or approximately $845/ yd^3 (2002 US$). Actual cost will be influence by the depth and areal distribution of contamination to be treated, initial contaminant concentrations and treatment targets, and monitoring requirements, among other factors. Given that the cost is depth and area dependent, potential economies of scale to be derived from treating larger volumes of sediment may be less for this technology than for those in which larger treatment volumes do not involve a proportionate increase in equipment.

EK Bio (Andreottola et al. 2010)

Beginning in the early 1990s, EK application expanded to research in *in situ* removal of heavy metals and organic contaminants. Electrokinetic-enhanced bioremediation (EK-Bio) involves the transport of electron donors through a heterogeneous soil medium through application of direct current (DC) at opposing electrodes. DC electric fields will induce transport of constituents by ion migration and electroosmosis. EK-Bio has been shown to be capable of achieving uniform distribution of amendments in soils with low permeability lenses for biodegradation of organic solvents, while avoiding the contaminant displacement associated with hydraulic delivery methods; since the transport occurs in the form of ion migration, soil pore size and porosity have little effect on transport rates. The electroosmotic coefficient of permeability has been shown to be independent of the size of the soil capillaries, as compared to the hydraulic coefficient of permeability, which is proportional to the first power of the cross-sectional area of the individual capillaries (Mitchell, 1993 and cited in Gent et al. 2001). Where the hydraulic permeability is orders of magnitude smaller than the electroosmotic permeability, significant increases in flow can be achieved.

ERDC EL studies have demonstrated transport rates of 3.4 cm/day for lactate, 2.2 cm/day for citrate, and 2.1 cm/day for acetate in clay with a hydraulic conductivity of less than 10^{-6} cm/s (0.086 cm/day) under current densities ranging from 0.5 to 2.0 A/m^2 (Wu et al. 2007; Gent et al. 2001; SERDP ER-1204). Under similar conditions, EK-Bio can potentially improve the *in situ* amendment migration rate by an order of magnitude as compared to typical advection-based delivery techniques Gent and Estes (in preparation).

EK-BIO is potentially of interest for application to treatment of organic contaminants such as PAHs and PCBs in sediments and dredged material. Andreottola et al. (2010) conducted bench tests of electrochemical oxidation for treatment of PAH-contaminated sediments, as well as of electrokinetic treatment of heavy metal contaminants in the same sediments.

Metals removal was evaluated using electrokinetics in a 30 cm long by 6.2 cm diameter Plexiglas cell. Tests were conducted using only water as an extractant (unenhanced tests – EK1), and 0.2M ethylenediaminetetraacetic acid (EDTA) as a conditioning agent at the cathode, or at the cathode (EK2) and the anode (EK3). TWEEN 80 surfactant was used as conditioning agent at the anode for PAH removal. An applied voltage gradient of 2V/cm was used in tests EK1, EK2 and EK3, and 1 V/cm in EK4 over a period of 23-30 days. Given the high buffer capacity of the sediment, little pH variation was seen across the specimen in the unenhanced test (EK1) with the results that little metal mobilization occurred (3.7 percent (Cu) to 31 percent (Cr) removal). Declining current intensity was also observed over the 27-day test. Metals removal was also minimal (a maximum of 8 percent was observed) for the EDTA-enhanced EK2 test; highest removals were achieved by conditioning both anode and cathode, with removals ranging from 22 percent (Zn) to 81 percent (As). The electric field was also more consistently maintained during this test. PAH mobilization was limited; this was attributed to the low liquid/solid ratio (1.65 l/kg dry weight), as compared to preliminary batch tests conducted at 10 l/kg dry weight.

Electrochemical oxidation was evaluated on a 10 cm x 10 cm x 10-20 cm sediment sample placed in a rectangular PVC cell and subjected to a voltage gradient of 0.7 V/cm (14.5 cm long sample) over periods of 4 weeks (EO1) and 8 weeks (EO2). A third test was conducted on a 20 cm-long sample at a voltage gradient of 1.5 V/cm, over a period of 4 weeks (EO3). No conditioning fluids were used to control electrical conductivity, pH, or improve contaminant migration. For all of the electrochemical tests, electric currents initially increased to a peak value of 1.8 to 3.8 A, and then rapidly decreased to steady state levels of 3-14 mA. PAHs with 3 rings were most effectively reduced, with a maximum removal of 85 percent for anthracene in test EO2. Average removal efficiencies for test EO1 were 54 percent for light PAHs and 29 percent for heavy PAHs. Degradation was attributed to indirect oxidation through “production of hydrogen peroxide and hydroxyl radicals through Fenton-like reactions, catalyzed by natural iron minerals in the sediments” (Rahner et al. 2002 as cited in Andreottola et al. (2010). Little or no increase in removals was seen with increasing the voltage gradient (test EO3) or running the test for a longer period at the lower voltage gradient (EO2).

The authors (Andreottola et al. 2010) recommended further evaluation of PAH removal by electrokinetics, focusing on the influence of the liquid/solid ratio and other surfactant types with lower viscosities and higher dielectric constants. Evaluation of the use of EDTA as the catholyte and an inorganic salt solution as the anolyte was recommended for metals removal by EK, to prevent EDTA oxidation in the anodic zone. The authors proposed possible enhancements to PAH removal by electrooxidation, including the addition of Fenton’s catalysts to the sediments and the combined use of electrooxidation and electrokinetically enhanced chemical oxidation.

A bench-scale test (Dec 2011) conducted at Northeastern University, Boston, evaluated electrokinetic-enhanced bioremediation (EK-Bio) for potential application at Hot Spot IV, Skuldelev, Denmark (Gent and Estes in preparation). The site contained chlorinated solvent contamination at depths between 3 and 10 meters in a glacial till. A summary of the conclusions are as follows:

- A current density of 5 A/m^2 was adequate to establish the desired electric field across the soil matrix.
- EK with an electrolyte cross-circulation component can be engineered to maintain neutral pH during EK operation.
- Effective lactate transport (approximately 3.2 cm/day) was achieved for the tested conditions.
- The Site soils were effectively bioaugmented with KB-1 microorganisms, and the microorganisms effectively transported through the soils.
- EK-Bio could be engineered to establish the desired microbial reductive dechlorination capacity in low permeability materials at the Site.
- Biological transformation rates of PCE in clay ranges from 1.5 to 5.0 mgL-1d-1. These rates are approximately half of those in sand under similar conditions.

EK-Bio (Aug 2011-Dec 2011) was pilot tested by ERDC EL, GeoSystec Consultants, and NIRAS at Hot Spot IV, Skuldelev, Denmark, where elevated concentrations of tetrachloroethene (PCE) have impacted the subsurface (GeoSystec 2011). The pilot demonstration consisted of 3 anode and cathode pairs with 3 injection wells located in the center of the test area. Lactate was injected in each electrode and injection well. After 3 weeks of lactate injections, the system was turned off and each well was bioaugmented with KB-1® dechlorinating *Dehalococcoides* microbes. The system was restarted one week after bioaugmentation. Results from soil samples taken at the end of the test (60 days) showed that significant reductive dechlorination of PCE to cis-1,2-DCE was achieved within the short pilot test duration. By the end of the pilot test, further dechlorination of cis-1,2-DCE to vinyl chloride (VC) and ethene was observed, suggesting that PCE dechlorination to ethene can be achieved by EK-Bio with KB-1 bioaugmentation. The pilot test demonstrated that EK-BIO is an effective method for enhancing PCE dechlorination. Electricity consumption for the full-scale pilot demonstration in Denmark was equivalent to operating 10 100-watt incandescent bulbs over the operating time period. While there are still several cost parameters to be validated, the preliminary estimate of the EK-Bio technology for a full-scale application is approximately \$45 to \$68/yd^3 (Gent and Estes in preparation).

In an electrokinetic field pilot study conducted in a chromium- and cadmium-contaminated marine sediment at Point Mugu, citric acid was added to the cathode wells for pH control. The spacing between anodes and cathodes was 4.6 m. Half of the anode well samples contained citric acid in less than 15 days after citrate was added to cathode wells (Gent and Estes in preparation). After 7 months, the citric acid concentration increased in four wells and acetate was detected in all but one anode well. From these results, a citrate migration rate of approximately 30 cm/day was calculated. This migration rate was achieved in the field with a voltage gradient of 0.15 V/cm. Biofouling was not observed over 12 months of continuous operation.

Corrosive surface water (attributed to salinity of the dredged material and production of Cl and HCL), undesirable annular flow (which interferes with dewatering, and which would recontaminate the material in an extraction process), and electrode corrosion were all significant problems in the dewatering demonstration by Haliburton (1978). The Point Magu demonstration utilized dimensionally stable anodes (DSA) that do not corrode; these anodes consist of a titanium substrate tube with a mixed metal oxide coating that protects the substrate from corrosion. After three years of operation, these anodes showed little to no signs of corrosion. Vertical flow configurations could address the issues with annular flow encountered by Haliburton (1978), which would be important where EK was being used as an extractive process, as in metals treatment. Surface water quality impacts are a potential concern; this can be addressed to some extent by optimizing the operation (electrode type and current intensity). Conditioning of anolyte and catholyte may also be feasible to prevent extreme excursions of pH during treatment for organics degradation; low pH is a desirable condition for the extraction of metals, however.

Soil Washing

Mineral Processing Pretreatment of Contaminated Sediments (EPA 1994f)

Under the ARCS program, bench scale testing was conducted by the U.S. Bureau of Mines on six sediment samples (from Ashtabula River, Buffalo

River, Grand Calument/Indiana Harbor and Saginaw River areas of concern) to assess the use of mineral processing techniques as a treatment, or pretreatment, alternative for contaminated sediments. Processes evaluated included:

- Froth flotation
- Magnetic separation
- Grain size separation
- Gravity separation

Initially, samples being tested for removal of metals were deoiled by soxlet extraction to prevent fouling of the process equipment and clumping of the material. The researchers assumed that this would not affect the metals distribution in the sediment (probably not an entirely viable assumption). Later samples tested for removal of organic contaminants were not deoiled prior to testing.

Sediment that was neither dried or deoiled was used for the froth flotation in a 1.2 L Denver flotation machine. Flotation can be designed to remove a target particulate fraction, or to remove hydrophobic fractions such as oil and grease from the mineral particulates (analogous to a detergent wash). In either case, the goal is to achieve a high contaminant distribution and low mass distribution in the “concentrate.”

Three reagent schemes were utilized for metals recovery by froth flotation:

- Flotation without a collector
- Flotation with a fatty acid collector
- Flotation with potassium amyl xanthate (an anionic collector) and copper sulfate (to enhance flotability of metal sulphides)

For concentration of organic contaminants by froth flotation, surfactants are used to reduce the oil phase’s hydrophobicity, resulting in release to the water phase. “The strength of surfactant attachment to an oil phase is approximately by the hydrophile-lipophile balance (HLB) of the surfactant” (USEPA 1994f). The HLB is a measure of the degree to which different portions of the surfactant molecule are hydrophilic or lipophilic, and is calculated using one of the available empirical formulas based on the ratio of the molecular mass of the hydrophilic portion of the molecule and the molecular mass of the entire molecule. Equipment and procedures for removal of organic contaminants by froth flotation were the same as those used for the removal of metals, except that no frothing agent was added (surfactants tend to create a froth). Multiple surfactants were tested, including:

- Rhodafac PL (phosphate ester),
- Nacconol (alkyl aryl sulfonate),
- Hamposyl (lauroyl sarcosinate),
- Fatty acid sulfates,
- Igepal CO and Triton X (ethoxylated alcohols), and
- Triton RW (amine ethoxylates).

Seven flotation parameters were evaluated in the flotation testing for removal of organic contaminants: surfactant composition, dosage (0.01 and 0.1 percent), pulp density (10 and 20 percent solids), aeration rate (1.0-3.5 L/min), pH (4 and 7), agitation intensity (900 and 1700 RPM) and conditioning time (5 and 20 min). For the amine ethoxylate surfactants, slurry density, agitation intensity, and surfactant composition were found to be significant to oil and grease levels in the tailings; the same parameters were found to be significant to the weight distribution of the concentrate. Best results were obtained at lower pH and slurry density and higher reagent concentration. For the ethoxylated alcohol (nonionic) surfactant, similar results were obtained, except that there was no apparent pH dependence. In both cases, higher agitation intensity produced higher material losses to the concentrate. There appears to have been an error in the oil and grease analysis, however, creating some uncertainty in the results obtained.

The benefit of attrition scrubbing was also evaluated, in conjunction with pH adjustment using hydrochloric, nitric and sulfuric acids, depending upon the target metal. The sediment was agitated in a modified Denver flotation machine for 10 minutes at 1700 RPM. The sediment was then filtered, washed, dried, and analyzed for metals. Solubilized metals were recovered from the solution by pH adjustment with NaOH.

Magnetic concentration of metals was evaluated in raw sediments (not deoiled), which were separated into four size fractions for testing on a Carpco-induced roll magnetic separator and a wet high intensity magnetic separator, respectively. Fractions tested were +100 mesh, 100x400 mesh, 400 mesh x 12 um, and -12 um. Before passing through the separators, a hand-held magnet was passed through the sediment to recover as much magnetic material as possible and prevent plugging of the separator; some samples appear to have also have been run through a Davis tube separator to remove highly magnetic material prior to separation in the higher intensity separators.

Samples were separated for metals analysis into different grain sizes by wet sieving at 9 different cut points, with the largest being +20 mesh and the smallest -400 mesh. Size fractions were analyzed for As, Cd, Cr, Cu, Fe, Pb, Hg, Ni and Zn. Samples were separated into 5 size fractions for organics analysis; samples were analyzed for oil and grease and Total PCBs.

Density separations for metals concentration were conducted on deoiled sediments separated into working size fractions, using two different densities of heavy media (bromochloromethane, specific gravity 1.9, and tetrabromoethane 2.9). A water elutriation density separation was also conducted as a polishing step to remove PCBs associated with detritus from the sand fraction of some samples.

Although contaminant distribution with grain size differed from sediment to sediment, grain size separation was found to be feasible for one sediment, with limited application for two additional sediments, and was found to be unlikely to be successful for a fourth sediment. The same trend was mirrored for density separations. There was little correlation between metal contaminants and the magnetic fractions of the sediments; magnetic separation was found to be unlikely to be feasible for three of four sediments, with potentially limited applications for a fourth sediment subject to further study. Results for attrition scrubbing were the same as for magnetic separations, although the sediments with potentially limited application differed. The flotation process was difficult to control, and was not particularly selective in most cases; flotation was determined to have limited potential application for all sediments, although further study was recommended.

Bergmann Particle Separation/Soil Washing – Pilot-scale Demonstration of Sediment Washing for the Treatment of Saginaw River Sediments (EPA 1994e)

The processing plant, with a nominal capacity of 5 tons/hr, was assembled on the COE barge Michigan and moored adjacent to an 80 x 300 ft staging and processing area outside the perimeter of the Saginaw Bay CDF. Feed was transported to the plant from the CDF by conveyors, as was washed material from the plant to the staging area. A 140 gpm trailer mounted plate clarifier was utilized initially; this was replaced with a barge-mounted unit with approximately 4 times the settling area of the initial unit. Approximately 800 yd^3 of partially dewatered mechanically dredged material was barged to the site and used as plant feed. The plant operations included:

- conveyors for transport and manual debris removal, later replaced with a 2-in grizzly with attritioning;
- a rotary trammel;
- 9-in Linatex separators (hydrocylones);
- a Linatex hydrosizer or dense media separator;
- an attrition scrubber (surfactant sand washing step);
- a second set of hydrocyclones;
- Sand recovery and dewatering screens; and
- a clarifier with flocculent treatment.

The plant was operated in co-current and counter-current modes and with and without the clarifier, one hydrocyclone, and the attrition scrubber, to evaluate the importance of these unit operations. Operational observations from the Saginaw demonstration:

- Hydrocyclones were not optimized for removal of particles in the 38- to 75-um range due to the feed limitations of the plant; this affected the efficiency of some separations.
- A significant amount of fines and sand reported with the >6mm oversize separated at the trommel. Between 5 and 15% of the feed reported to the trommel overs; only 18% of the trommel discharge was >430 um. A log washer might be needed in a full-scale plant to break up agglomerated sand and clay balls to prevent this.
- A fairly large amount of sand also reported with the particulate organic stream.
- Relatively small differences resulted from changes in the operation of the dense media separator.
- There was little difference between feed and product from the attrition separator, likely due to the nature of this sediment; tested surfactants produced no noticeable improvement in product.

- Use of recycled water introduced fines contamination at the 2nd hydrocyclone; this would be reduced with use of larger hydrocyclones (24-in) in a full-scale plant.
- In attempting to capture fine sands reporting with the dense material separator overflow on the sand recovery screen, fines may have been reintroduced to the sand separated at the 1st hydrocyclone and the dense material separator.
- The rotary screen appeared to remove only a small amount of large particulate organics.
- Even the larger clarifier was only capable of processing smaller system discharges but ultimately produced an effluent clean enough for recycle in the system.
- The process could also be slurry fed successfully at solids concentrations of 15 to 25% solids.
- Enrichment of contaminants in concentrated sediment fractions could reach TSCA or RCRA regulated levels.
- Bioavailability of residual contaminants in the sand may be enhanced due to the low levels of residual organics and should be evaluated.

Numerous other considerations and recommendations pertaining to feasibility testing and process optimization were made but were too detailed for inclusion here. Overall, the plant was effective in removing most fines and organics from the sand; approximately 80 percent of the feed solids were recovered as washed sand. The remainder was recovered as oversized material, particulate organics, and fines. PCBs were reduced by 82 percent in the washed sand. TOC was reduced by 79 percent, metals from 55 to 88 percent, and fines <75µm by 77 percent. Cost for a 50 ton/hr plant to process 10,000 cubic yards was estimated to be approximately \$54/ yd^3; treatment of 100,000 yd^3 was estimated to cost \$23/ yd^3. Although the authors note that, under certain circumstances, costs could be as much as an order of magnitude lower, the cost of recent state-of-the-art projects suggests that this is highly unlikely. Costs could be significantly reduced with elimination of the clarifier, which could be done if operating in a co-current mode and with sufficient storage to accept all fine and organic particulate slurries; this would also eliminate the reintroduction of fines to the sand product during processing.

MetPro Maximum Density Separator and Dry Screening Demonstration, Green Bay, WI (Olin-Estes et al. 2002)

Simple physical separation processes were evaluated by the Corps of Engineers in a one-day demonstration conducted at the Bayport confined disposal facility (CDF) in Green Bay, WI (Olin-Estes et al. 2002). A portable shaking screen with attritioner and a 24-in hydrocyclone with integrated sump were piloted in a one-day demonstration to evaluate the utility of these respective pieces of equipment in recovering clean sand from a CDF.

The primary objectives of this demonstration were twofold:

- To evaluate the practicality and effectiveness of relatively simple and potentially inexpensive separation equipment in recovery and processing of dewatered sediment previously disposed in a confined disposal facility
- To determine the ability of a simplified separation process to recover a sand fraction with PCB levels below the allowable threshold for beneficial use

Approximately 1 yd^3 of sediment was excavated from the CDF with a crane-mounted edductor pump fed from the site pond, and processed through a 24-in mobile MetPro maximum density separator (a hydrocyclone with restricted outlet to improve separation of fines and sand). Approximately 1 yd^3 of sediment with low levels of PCBs was processed through the MDS in the one-day demonstration. A similar volume of dry, stockpiled material was processed through the shaking screen.

PCB levels in the recovered sand were reduced as compared to concentrations in the bulk sediment, and were below the target threshold of 1 mg/kg for beneficial use. However, based on lessons learned from subsequent projects, this outcome is unlikely to be consistently achievable. The presence of a coarse organic fraction can result in higher-than-anticipated contaminant carryover into the sand fraction, as has been observed in subsequent full-scale operations. For sediment that has been carefully characterized to assess suitability, and found to have low levels of contamination, it may be feasible, however.

Biogenesis^{SM} (Wardlaw unknown publication date; CoSTEPP 2000; BioGenesis Washing BGW, LLC, and MHW Americas, Inc. 2009; BioGenesis Enterprises, Inc. 2008; Biogenesis Italia, LLC, MHW Americas, Inc., and Jan de Nul, N.V. 2005; Biogenesis Enterprises, Inc., and Roy F. Weston, Inc. 1999; Estes et al. 2011)

Several demonstrations have been conducted on the Biogenesis technology for treatment of contaminated sediment. Biogenesis was evaluated under the NJDOT technology demonstration program as a soil washing technology (Biogenesis Enterprises, Inc., and Roy F. Weston, Inc. 1999), and was evaluated for treatment of contaminated sediments in Italy (Biogenesis Italia, LLC, MHW Americas, Inc., and Jan de Nul, N.V. 2005). Biogenesis was more recently evaluated for treatment of Housatonic River sediments (BioGenesis Enterprises, Inc. 2008) and Passaic River sediments (BioGenesis Washing BGW, LLC, and MHW Americas, Inc. 2009), and was one of four technologies evaluated in Estes et al. (2011) that was deemed nearing commercialization.

The Biogenesis process incorporates physical separation and chemical oxidation components for treatment of both sand and fine fractions of the sediment. The demonstration conducted under the NJDOT program was an earlier configuration, and was deemed successful according to their processing objectives site, although some issues were encountered with recalcitrant organic contaminants. Further testing was recommended to evaluate suitability for treating highly contaminated materials. The configuration of the technology has been refined with each subsequent demonstration with some improvements to one of the principal issues related to soil washing technologies: that of the associated large volume waste stream that requires further treatment. Reportedly, the process has been modified to incorporate water treatment, enabling the recycling of process water within the treatment train and minimizing or eliminating external water treatment requirements (Estes et al. 2011).

Subsequent tests have demonstrated the relative role of various physico-chemical mechanisms in achieving contaminant reduction with this technology. Successful chemical oxidation of organic contaminants continues to be somewhat elusive; although the process is certainly capable of achieving a significant level of contaminant reduction in sediment, there is little evidence to suggest that chemical oxidation contributes significantly to that. Solubilization, separation of fine solids, and volatilization appear to be the operative contaminant removal mechanisms, based on the available data (Estes et al. 2011). Recycling of sediment through the process appears to show some promise for further reduction of organic contaminants in the treated sediments, as was demonstrated in bench-scale testing on Housatonic sediment (BioGenesis Enterprises, Inc. 2008) and flotation was evaluated at bench scale for improved removal of organic detritus (BioGenesis Washing BGW, LLC, and MHW Americas, Inc. 2009).

Biogenesis treatment cost was estimated in Estes et al. (2011) to be approximately $52/*in situ* cubic yard (Dec 2009 US$), for the project magnitude and duration assumed (561K yd^3 and 10-year, straight-line depreciation). Net cost, assuming a marketable value for the treated sediment of $11/ yd^3, was estimated to be approximately $41/*in situ* cubic yard.

Physical Separation – Los Angeles, Miami River and Fox River (Averett and Estes 2011)

Soil separation was further evaluated in a recent demonstration conducted by the Los Angeles District of the Army Corps of Engineers; the project was reviewed by ERDC for lessons learned (Averett and Estes 2011). Material handling problems were encountered that were attributable to equipment selection; consolidation of separated fines in holding tanks downstream of the treatment plan was greater than anticipated and the sludge could not be pumped out of the tanks as originally planned. These issues could be readily addressed with more appropriate equipment selection. Ultimately, concentrations of pesticides and heavy metals in the processed sand precluded the intended beneficial use placement. In this case, a better understanding of the location and association of the contaminants within the sediment would have facilitated more appropriate equipment choices capable of meeting treatment objectives in the target fraction.

Soil separation has been used successfully in full-scale projects, however, including the recently completed Miami River project (Averett and Estes 2011) and the ongoing Fox River project. The Miami River plant was a containerized plant that could potentially be relocated for short term projects; the Fox River plant is a permanent facility. The Fox River plant in particular incorporated unit operations to address removal of coarse organics from the sand fraction that can lead to unacceptably high residual contaminant concentrations, as was seen in the Los Angeles demonstration. The question remains whether a more simple and economical plant can be effective in achieving similar treatment objectives at lower cost, such that separation would be economically feasible for management of navigation sediments.

Soil Washing EDTA and Citric Acid Extraction (Oh et al. 2011)

Oh et al. (2011) evaluated soil washing in bench scale testing for treatment of contaminated sediments. EDTA, citric acid (a weak acid that acts as a chelating agent) and NaOH were used as washing agents. NaOH was used to target As extraction, as reported in other studies, and was found to remove 75% of the As, but was not effective in extracting other metals. EDTA was effective for Cu, Pb and Zn, and has been used effectively in other studies for removal of As, but complete removal of metals was not achieved, even at 100 mM concentrations of the reagents.

Solidification/Stabilization

Solidification and stabilization are probably the most mature technologies of those presented here. EPA defines solidification as "a process that encapsulates waste to form a solid material" (USEPA 1997, as cited in Oh et al. 2011); the process reduces the surface area of the solidified materials and coats them with low-permeability materials, thus reducing contaminant mobility (Oh et al. 2011). Stabilization is similar to solidification, reducing the leachability of contaminants through the addition of chemical binders. "Portland cement and pozzolanic binders, including fly ash and cement kiln dust, are the most popular additives for stabilization/solidification" (LaGrega et al. 2000, as cited in Oh et al. 2011). Solidification/stabilization (S/S) is typically used to immobilize metals; although S/S may be effective for low levels of organic contaminants. High concentrations of petroleum hydrocarbons or other oily substances will inhibit the hydration of cement and reduce the effectiveness of the treatment. As noted by Oh et al. (2011) and others, S/S offers several advantages over other treatment technologies, including the following:

- Cost – S/S is comparatively inexpensive, making use of industrial wastes such as fly ash and cement kiln dust
- Implementability - High water content sediments can be readily treated without further dewatering; amendments can be mixed in barges, eliminating the need for large staging areas and multiple unit operations

- Synergistic processes – The commonly used binding materials are alkaline in nature, further reducing the mobility of metals

A notable disadvantage of S/S is that contaminants are immobilized, but not destroyed. There is thus potential for future release. Further, oily sediments may not be as readily treated due to the effects of oil on the hydration of cement. Despite these limitations, according to Singh & Pant (2006, as cited in Oh et al. 2011) S/S is recognized as the best demonstrated, available technology for land-based disposal of toxic elements. According to Oh et al. (2011), "among 515 Superfund sites, solidification/stabilization and soil washing were used to remediate 173 sites from 1982 to 2005. Six sites were used as ex situ source control technologies for real field application. Solidification/stabilization was also used for 248 sites out of 462 sites for in situ source control technology (US EPA 2007b)." Stabilized New York harbor sediments were utilized for construction fill at an old municipal landfill in Port Newark, NJ; the 20-acre site was subsequently transitioned to another use as a shopping mall (Wilk white paper (a), unpublished white paper). More than 1.5M cubic yards of treated sediment were used to remediate the 160-acre site of a coal gasification plant, known as the Seaboard site. Another 3M cubic yards was slated for use at the Bayonne, NJ golf course (Wilk white paper (b), unpublished white paper).

While treatment has been employed at more contaminated soil sites than contaminated sediment sites, solidification and stabilization is also the most mature treatment technology available for management of contaminated sediments. There have been numerous studies on application of S/S to sediments, including Fleming et al. (1991) and Channell and Averett (1997). The ITRC released a more recent publication (ITRC 2011) consolidating the state of the practice into guidance on "applicable contaminants, effectiveness, comprehensive performance specifications, and long-term performance." The document attempts to address one of the key gaps, that of long term performance, through informed leaching testing, modeling, and data interpretation. No case studies were provided in the ITRC document, however, to demonstrate an established correlation between predicted and actual performance of S/S.

Zeolite and Lime for Stabilization of Cu and Zn (Antoniadis et al. 2012)

Antoniadis et al. (2012) evaluated the availability of Cu and Zn in an acidic sludge-amended soil treated with zeolite and lime. The study has potential relevance for the management of contaminants in dredged material placed in upland locations. The following were the treatments evaluated:

- A1: Acidic control soil (no additions)
- A2: Acidic soil + sewage sludge at 50 Mg ha−1 with no zeolite (Z-0)
- A3: Acidic soil + sewage sludge at 50 Mg ha−1 + zeolite at 2 Mg ha−1 (Z-1)
- A4: Acidic soil + sewage sludge at 50 Mg ha−1 + zeolite at 5 Mg ha−1 (Z-2)
- L1: Limed control soil (no additions other than lime)
- L2: Limed soil + sewage sludge at 50 Mg ha−1 with no zeolite (Z-0)
- L3: Limed soil + sewage sludge at 50 Mg ha−1 + zeolite at 2 Mg ha−1 (Z-2)
- L4: Limed soil + sewage sludge at 50 Mg ha−1 + zeolite at 5 Mg ha−1 (Z-2)

The authors concluded that zeolite hindered metals sorption even in soil limed to increase pH and limit metals mobility. The effect was most pronounced for the highest zeolite dosage (5Mg/ha), as compared to the unamended and low zeolite dosage (0 and 2Mg/ha). Because there was no correlation between extractable Cu and plant uptake of Cu, however, this may have more to do with the zeolite taking up the Nitrogen (ammonia) in the sludge and releasing it to the plants in a more controlled manner, leading to sustained plant growth and continuous (greater overall) uptake than in plots not amended with zeolite. Thus, there is potentially some triangulation of factors involved. Zn uptake did show a correlation between extractable Zn and plant uptake, while DTPA extractable metals were reduced for zeolite treatments. There is some indication that metals sorption in zeolites is reversible, which is consistent with the mechanisms of ion exchange and physical trapping. Zeolite may therefore be less effective than other amendments — such as bentonite — in permanently binding metals from pore water solutions, or may retard the uptake of metals onto permanent binding sites of the soil matrix.

S/S of Contaminated Sediments with Portland Cement and Fly Ash (Oh et al. 2011)

Oh et al. (2011) also evaluated solidification/stabilization in bench-scale testing for treatment of contaminated sediments. Portland cement (1-40%) and power plant fly ash (approximately 20%) were used for stabilization (with a single water to solid ratio of 0.6). The authors report that after S/S, the sediments were no longer classified as hazardous waste, based on the Toxicity Characteristic Leaching Procedure (TCLP) testing. TCLP tests showed that solidified sediments did not release significant amounts of metals. The addition of fly ash to Portland cement for solidification reportedly did reduce unconfined compressive strength of the materials somewhat, but materials still developed sufficient strength to pass the threshold of 0.35 MPa required for disposal of stabilized hazardous waste in landfills. The cited hydraulic conductivity threshold was 10-7 m/s; levels of 10-9 cm/s were achieved. Increasing cement content from 1-20% did not affect the hydraulic conductivity; however, the addition of fly ash increased the hydraulic conductivity by a factor of 3. After completion of the soil washing and S/S testing, S/S was determined to be the treatment method of choice for these sediments.

In Situ Deep Soil Mixing (Maher et al. 2005)

In situ S/S using Cement Deep Soil Mixing technology (CDSM) was evaluated for NY/NJ Harbor sediments and reported in Maher et al. (2005). The effectiveness, optimum dosage of pozzolanic additive, potential dispersion during mixing, and impact of organic content of the sediment were all evaluated in this study. This study targeted highly contaminated sediments; three test cells were treated with cement slurry at dosages ranging from 100 kg/m^3 to 200 kg/m^3, at a water to cement ratio of 80%. Objectives of the treatment were to minimize pulverization and dispersion of sediments while avoiding excessive strength gain, which would make dredging infeasible; based on bench testing, dosages at or below 340 lb cement/yd^3 maintained dredgability of the sediments. Very soft silt sediments developed the consistency of hard silt/clay; standard penetrometer testing (SPT) was conducted before and after treatment. Strength increased from weight of rod to a maximum of 46. Reportedly, environmental buckets cannot penetrate sediments with SPT-N values greater than 2; even the sediments with the lowest cement dosages in this study developed N values well above this.

Immobilization of contaminants present in Passaic River sediments was evaluated in a follow on study. SPLP extract reductions of 90% were reported for PAHs, and 95-99% for dioxins. PCBs stabilization was evaluated by treatment of a synthetic waste, using cement, soluble silicate, and $FeCL_2$ or Na_2S. Cement with soluble silicate gave best results; tests with $FeCL_2$ and Na_2S additives were reportedly unsatisfactory. Other additives that have been reported in the literature for PCB immobilization include:

- Organically modified clays
- Activated carbon
- Ferric hydroxide
- Rubber particulate

Additives evaluated for immobilization of PAHs and PCBs, all of which were found to be effective, included the following:

- Fly ash
- Activated carbon
- OHMAR-8
- STC P-1
- STC P-4

High organic content of sediment did impede the soil/cement reaction; organic content of sediments is therefore an important variable for characterization, and cement dosages must be adjusted to account for this factor. In samples with more than 10% oil by dry weight, cement particles tended to agglomerate and separate; hydration of the cement was also inhibited by the oil. Both of these factors would result in lower strength gains.

Localized increases in TSS were observed during mixing; there was some indication that higher TSS was associated with higher pH (a function of cement dosage). Losses of volatiles and semi-volatiles as a result of mixing and the heat generated as a result of the chemical reaction in the treated materials have been reported by others but were not specifically evaluated here.

Parameters identified as important to S/S include cement type and dosage, soil type, mixing, and curing conditions (mixing time, temperature), organic content, pH and grain size distribution (Niina et al. 1977 and Saitoh 1988 as cited in Maher 2005). Highest strength gain was reported by Saitoh (1988) for soils with higher pH, low organic content, and average sand fraction of 60% in clay. Higher short term strength gain is seen for higher curing temperatures; longer mixing times also produce higher strength. Saitoh (1988) reported that Portland cement was more effective in clay with a high pozzolanic reaction (Hokohama clay), while blast furnace slag was more effective in treatment of soils with low pozzolanic reaction (Osaka clay). Higher cement dosage results in higher strength, though at a diminishing rate as cement dosages increase. For this study, long term strength gain was expected to be two to three times the 28- day strength, a factor that should be considered if stabilized sediments are to be later dredged.

Lime By-Products for Production of Engineering Structural Fill (Beeghly and Schrock 2009)

Beeghly and Schrock (2009) evaluated S/S of dredged material using lime by-products to produce an engineered structural fill meeting the following criteria as "suitable soil":

- Unconfined compressive strength >35 psi
- California Bearing Ratio (CBR) >8
- Liquid limit (LL) <45%
- Plastic index (PI) <20

One aim of the study was to demonstrate successful S/S on dredged material using economical alternatives to Portland cement. Three materials were tested during this study:

- Lime kiln dust (LKD)
- Class F coal fly ash (FA)
- Spray dryer ash (SDA)

LKD is a by-product of quicklime manufacture, and contains some active calcium oxide (typically 15-35% by weight) and some coal fly ash, (where coal is used as a fuel in the production of quicklime), comprised primarily of silica and alumina oxides. Class F FA is a by-product of combustion of Eastern bituminous coal, and is a siliceous or alumino-silicous material that is not in itself pozzolanic but that will react with alkali or alkaline earth hydroxides to form compounds with cementitious properties. SDA is a residue from spray dryer absorbers used for sulfur dioxide gas scrubbing, containing varying proportions of reactive lime (unreacted lime used to capture SO_2 and other acid gases) and significant amounts of calcium sulfite and/or sulfate. Another scrubber material that is a by-product of gas scrubbing but which was not tested here is circulating fluidized bed boiler ash (CFB). CFB ash contains a small amount of reactive lime and anhydrous calcium sulfate, and is used for stabilization of coal waste and abandoned mine land in PA. Further discussion of the relative composition of these materials can be found in Beeghly and Schrock (2009).

Several parameters critical to production of a material suitable for construction fill and achieving immobilization of metals were identified in this study:

- Sufficient lime alkalinity must be added to take advantage of the pozzonlanic and sulfo-pozzolanic cementitious reaction potential.
- The pH must be raised to >9 to sustain the pozzolonic reaction; minimum solubility of metals and pozzonlonic hydration can be achieved at a pH in the range of 9-11; pH must be maintained above 11 to maintain solubility of lime and alumina.
- Sufficient reagent must be added to achieve optimum moisture content for maximum dry density; near optimum moisture content as determined by Proctor test required – 3-5% additional may be advantages to long-term hydration but higher than optimum moisture contents result in lower early strength.
- A “mellowing” period prior to compaction may prevent swelling from Ettringite precipitation (Eqn 4 below) and improve workability.
- Strength of treated material is a function of residual pH, curing conditions, and moisture content.

Stabilization can be done on freshly dredged material, or on material dewatered by gravity in a CDF. There must be sufficient moisture present to fully hydrate the pozzolonic materials, but excess moisture will increase the volume of amendment required. Depending upon fill material specifications, pre-screening of oversize materials may be desirable. Drying is achieved by three mechanisms:

- Bulking by the addition of dry materials
- Hydration of calcium oxide (quicklime) to hydrated lime (calcium hydroxide)
- Heat generated by the hydration process
- Subsequent dissolution of silicates and aluminates by hydrated lime (at high pH), initiating pozzolanic and sulfo-pozzolanic reactions and forming (over time) calcium silicates, calcium aluminates and calcium sulfo-aluminates. These reactions take up additional free water from the sediment.

Beeghly and Schrock (2009) provide a useful summary of the relevant pozzolanic reactions resulting from the dissolution of silicates and aluminates: formation of calcium silicate (Eqn 1); formation of calcium aluminate (Eqn 2); and formation of ferro aluminates (Eqn 3):

$$SiO_2 + Ca(OH)_2 + H_2O \rightarrow CaO - SiO_2 - H_2O \tag{10}$$

$$Al_2O_3 + Ca(OH)_2 + H_2O \rightarrow CaO - Al_2O_3 - H_2O \tag{11}$$

$$Fe_2O_3 + Al_2O_3 + Ca(OH)_2 \rightarrow CaO - Al_2O_3 - Fe_2O_3 - H_2O \tag{12}$$

Where calcium, sulfates (or sulfites) and aluminates are present at high pH, the Ettringite reaction (formation of calcium sulfo-aluminate) may take place (Eqn 4). If this reaction takes place following compaction, undesirable swelling may occur; a “mellowing” period following treatment and prior to compaction may minimize this reaction, which can occur quickly but is also known to occur as a secondary reaction over a period of days or months.

$$2Ca(OH)_2 + 3CaSO_4 \cdot H_2O + CaO \cdot Al_2O_3 + 30H_2O \rightarrow (CaO)_6 - Al_2(SO_4)_3 \cdot 32H_2O \tag{13}$$

Calcium sulfite $CaSO_3 \cdot 0.5H_2O$ can replace gypsum $CaSO_4 \cdot 2H_2O$ in the sulfo-pozzolanic reaction (Eqn 4).

There have been several demonstrations of the use of kiln dust as a substitute for lime for material stabilization. A 1982 study evaluating the use of kiln dust and fly ash to prepare highway base/subbase materials found that “with few exceptions” LKD can be substituted for lime in lime-fly ash-aggregate road base mixtures (Beeghly and Schrock 2009). Reportedly, most LKD-fly ash mixtures achieve maximum strength at a 1:1 ratio, as opposed to a 1:2 lime-fly ash ratio. LKD-fly ash-aggregate mixtures also demonstrated strength gains over time, achieving compressive strengths >2000 psi. In the Bark Camp project, coal fly ash was used to increase solids content of over 250 thousand tons of dredged material from the NY/NJ ports in preparation for transport and placement on abandoned mine lands; LKD and additional fly ash were added at the site to further increase solid content and facilitate compaction.

Cox Creek was one of the materials evaluated in the study by Beeghly and Schrock (2009); Cox Creek was classified as an organic clay with medium to high plasticity, 7.1% organic matter, plasticity index (PI) of 58, and untreated CBR of 1 (without soak, unmeasurable with soak). CBR was evaluated for two admixtures (dry weight basis) with resulting CBRs of 20% and 15% respectively:

- 5% quicklime (QL) plus 15% fly ash
- 10% LKD plus 15% fly ash

The pH after curing varied for the admixtures tested. Values below 9 indicate insufficient lime was added to sustain the pozzolanic reaction; only the mixtures containing quicklime sustained a pH above 10 (10.5 for 4% QL &8% FA, 10.3 for 4% QL & 10% SDA). The pH for 10% LKD dropped to 8.3, and for 10% SDA, dropped to 7.1 (the SDA had only 3% available lime content). Significant swelling (8.4%) was noted for the DM treated with 10% SDA. Approximate unconfined compressive strengths ranged from 51 to 89 psi (lowest for 10% SDA, highest for 4% QL/8% FA). PI was reduced to between 16 and 27 for the tests for which this parameter was reported, with the lowest PI obtained for 4% QL/10% LKD mixture.

A similar study was conducted with Ft Mifflin DM; this material had a solids content of 67%, with 54% passing a #200 sieve. The material was classified as inorganic silt, with a PI of 29%. Three admixtures were tested, with a 7-day mellowing period prior to compaction to minimize swelling:

- 10% SDA
- 8% LKD plus 8% FA
- 4% LKD plus 7% SDA

No swelling was observed in any of the samples over the mellowing period. An abbreviated summary of results is presented in Table 6.

Table 6. Ft. Mifflin DM stabilization results.

Parameter	Untreated DM	10% SDA	8% LKD/8% FA	4% LKD/7% SDA
Plasticity Index	29	18	10	15
CBR	-	11	5	2
UCS (psi)	0	>50	≈50	≈35

A third test was conducted with Craney Island DM; this DM had a water content of 130%, and was thought to be more representative of in-scow water contents than either the Ft Mifflin or the Cox Creek sediments. Craney Island DM contained approximately 92% fines, with a PI of 37, and was classified as an inorganic clay of high plasticity. Nine different reagents were evaluated initially in a “paste study,” to assess the workability and compactability of the treated DM. Five dosages of LKD were tested in the paste study (dry weight basis): 5, 10, 15, 20 and 25%. Four ratios of LKD and FA were tested in a second set of samples (dry weight basis): 5/5, 5/10, 10/5 and 10/10. Based on the results of the paste study demonstrating workability of only admixture dosages of 20% or higher, this was the minimum dosage used in the strength testing, and a 30% dosage was also added. The following mixes were tested: LKD/FA – 10/10, 20/0, 25/0, 30/0 at optimum moisture contents ranging from 27-32%. A second set at 20% LKD was tested at a moisture content of 50% and broken at 7 days, instead of the customary 28 days. Approximate UCS results were as follows: 20% LKD/40 psi, 25% LKD/105 psi, 30% LKD/110 psi. No samples dosed at the 20% reagent rate could be recovered intact from the Proctor cylinders.

Beeghly and Schrock (2009) provide characterization and mix design guidelines for dredged material stabilization. Characterization should include:

- Moisture content, solids content
- Particle size distribution
- Atterburg limits
- Soil type or classification
- Organic matter content
- Eads-Grim test (ASTM D-6276)
- Proctor curve
- California Bearing Ratio (CBR) with Swell Measurement (ASTM D-3668)
- Unconfined Compressive Strength (UCS) (ASTM-D5102)

The Eads-Grim test determines the amount of lime required both to achieve a pH>12, and to solubilize alumina materials. The moisture-density relationship developed by the Proctor Curve is required to determine optimum moisture content for maximum compaction and strength. The CBR test is a relative measure of the strength of the material as compared to a crushed stone base, and is conducted at a selected moisture content based on results of the Proctor test. The UCS is performed on compacted treated and untreated dredged material at representative curing and moisture conditions.

Due to the low solids content of fresh dredged material, bulking agents are needed to increase the solid content and approach the optimum moisture content in the treated material. Class F coal fly ash is often the most economical amendment. The amount of bulking agent needed is based on the optimum moisture content, plus 2-5%, to sustain long term hydration.

Performance Specification for Solidification/Stabilization (ITRC 2011)

Perhaps the most recent and comprehensive reference on S/S is the guidance manual published by ITRC (2011), which contains an overview of the technology, performance of S/S- treated materials, performance specifications as part of process design and implementation, treatability testing, and performance verification, among other topics. Equipment and leaching tests are also included in appendices to this document. The focus of this document is S/S of hazardous waste sites; this is most relevant to use of contaminated sediments as construction fill.

High Performance Solidification/Stabilization (Ferrari 2008)

Ferrari (2008) reported on a study to evaluate a new S/S process with the simultaneous objectives of immobilizing contaminants and imparting good mechanical properties that would facilitate reuse of the stabilized material. The MAPEI HPSS System is described as a high performance S/S system; the first step in the process is to produce a cementitious granular material, utilizing superplasticizers and hydrophobic additives to reduce water content and improve water tightness. The second step involves thermal vacuum distillation of sediments containing organic, volatile and semivolatile contaminants. This is essentially a low temperature thermal desorption (max 250 deg C), conducted under a high vacuum. The process was applied to a marine sediment from Augusta Harbour in Sicily, and was reportedly effective in stabilizing inorganic contaminants, removing VOCs and SVOCs, resulting in an “aggregate-like” product with good mechanical properties for reuse. More rigorous future testing was planned to construct a contaminant mass balance, conduct pH-dependent leaching tests, and undertake more complete testing of physical and mechanical properties and durability under environmental conditions.

In Situ Stabilization – Sedimite™ (ESTCP[1],[2])

As previously mentioned, *in situ* stabilization using amendments to sequester contaminants has been piloted at multiple sites over the last several years; although highly contaminated sites have been targeted to date, sediments with contaminant levels only slightly exceeding specified beneficial use thresholds may be an appropriate application as well. Sedimite™ was utilized as a delivery system for activated carbon at Canal Creek, Aberdeen Proving Ground, a tidal creek contaminated with mercury and other contaminants, and may have potential as a delivery system for other amendments as well. Sedimite™ is "comprised of a treatment agent (typically activated carbon), a weighting agent (to enable it to sink and resist resuspension), and an inert binder[3]." The pelleted delivery system is then mixed into the sediment through bioturbation. Canal Creek implementation and monitoring was originally scheduled for an 8-10 month period in 2009; however, monitoring data was not yet available at the time of this report.

Implementation costs for a pilot-scale effort, based on the project summary provided on the ESTCP website[4], were projected to range from "$100,000 to $500,000 per acre, depending on the nature of the amendment, site-specific characteristics, and the delivery system employed." Whether this technology will prove to be sufficiently economical for *in situ* management of dredged material is uncertain; however, such a delivery system could be advantageous in vegetated areas where injection or mixing in sediments would not be feasible. Wetland restoration sites that have re-vegetated but require ongoing amendment for contaminant control would be an example where this delivery system might be useful.

Biopolymer Sequestration and Stabilization (Knox et al. 2010)

A more natural approach to stabilization of sediments and concurrent sequestration of contaminants involves the addition of biopolymers and amended biopolymers to the sediments. Biopolymers are polymeric

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[1] In Situ Wetland Restoration Demonstration ESTCP Project Number ER-200825

[2] Evaluating the Efficacy of a Low-Impact Delivery System for In Situ Treatment of Sediments Contaminated with Methylmercury and Other Hydrophobic Chemicals ESTCP Project Number ER-200835

[3] http://sedimite.com/

[4] http://serdp-estcp.org/Program-Areas/Environmental-Restoration/Contaminated-Sediments/ER-200825/#factsheet-5182-technology

substances produced by living organisms. They are characterized by repeating functional groups, which makes them highly reactive and subject to cross linking. Physically, they are viscous when wet; when added to sediment, they can significantly alter the cohesiveness of the sediment and increase erosion resistance. Biopolymers are therefore of great interest for cap stabilization. They have also been studied fairly extensively for their ability to immobilize contaminants, and are particularly interesting for their potential to immobilize heavy metals.

Knox et al. (2010) coated sand with different biopolymers and evaluated them for metals sorption capacity, stability under shear stress, biological degradation and contaminant release resulting from degradation of the biopolymer. The polymer coatings evaluated included:

- Chitosan/Guar gum, crosslinking agent Borax (Biopolymer/sand ratio 0.05) and with the following additives:
    - CGB1 - 5% HCL and water
    - CGB2 - 5% HCL, glutaraldehyde and water
    - CGB3 - 5% HCL, 1N sodium hydroxide and water
- Guar gum, crosslinking agent Borax (biopolymer/sand ratio 0.005) and with the following additives:
    - GB1 - 5% HCL and water
    - GB2 - 1N sodium hydroxide and water
    - GB3 - Glutaraldehyde, 1N sodium hydroxide and water (polymer/sand ratio 0.025)
- Guar gum, crosslinking agent Xanthan (biopolymer/sand ratio 0.05) and with the following additives:
    - GX1 - 5% HCL and water
    - GX2 - 1N sodium hydroxide and water
    - GX3 - Water
- Xanthan Chitosan, crosslinking agent calcium chloride (biopolymer/sand ratio 0.025)
    - XCc - 5% HCL, glutaraldehyde and water
- Xanthan, crosslinking agent Chitosan and with the following additives:

  - XC - Water

- Xanthan, crosslinking agent Guar Gum and with the following additives:
  - XG - Water

CGB3 and XCc were evaluated in sorption studies with phenanthrene, pyrene and benzo(a)pyrene. XC and XG were evaluated for metals sorption with a spiked solution containing As, Cd, Co, Cr, Cu, Ni, Pb, and Zn. Biodegradability of the biopolymers was evaluated by monitoring CO_2 production in closed test tubes over a period of 10 weeks. Resistance to shear forces, such as would be experienced in the aquatic environment, were evaluated in shake tests and in a SedFlume.

Removal of most metals by XC and XG exceeded 90% at the concentrations tested; removal was generally comparable to that achieved with a North Carolina apatite. Sorption coefficients for phenanthrene ranged from 0.4 to 40.6 L/kg (CGB1 and CGB3, respectively). Sorption coefficients for pyrene ranged from 27 to 127 L/kg (uncoated sand and CGB2, respectively).

Responses varied, but the lowest biodegradability of the biopolymers was observed for CGB and XCc. The authors noted that for all biopolymers — but in particular XG — greater degradation occurred under wet conditions and high temperatures than under dry conditions. Minimal increases were observed in CO2 evolution over a period of 6 months, suggesting that biopolymer-associated bacteria did not contribute significantly to degradation of the biopolymers. Metals containing biopolymers evidenced minimal degradation, with little associated release of sorbed metals.

Efficiency and stability of the sand carbon coating process was evaluated by measuring the carbon content on the coated sand before and after multiple washings. Percent carbon on the unwashed sand ranged from less than 1% to nearly 8%. After multiple washings, the reduction in carbon content appears to have ranged from near zero, to approximately 50%, based on the figures provided.

Increases in the shear resistance of the biopolymer sand varied for the different biopolymers, and the conditions under which they were tested (dried and then rewetted, or tested as viscous slurries). CGB3 and XCc, treated with HCL, did not become viscous on rewetting and performed similarly to plain sand. CGB3 without HCl became very viscous upon rewetting and the top layer of the sand was never suspended, even at maximum mixing intensity. The slurries all performed well in the suspension tests. An interesting finding was that organoclay without biopolymers was not suspension resistant, and would likely undergo erosion similar to a sand cap.

The study suggest that the use of biopolymers for cap stabilization and contaminant sequestration is promising, but longer term and larger scale testing is required to more conclusively evaluate the expected performance in the environment. Potential ecological effects of biopolymer stabilization also need to be evaluated.

Thermal

ReTEC Pilot-Scale Demonstration of Thermal Desorption for the Treatment of Buffalo River Sediments (EPA 1993a) and Ashtabula River Sediments (EPA 1994d)

A pilot-scale thermal desorption unit was tested on 12 yd^3 Buffalo River sediments contaminated with PAHs and PCBs, and 8 m3 (4-55 gal drums/day for 9 days of operation) of Ashtabula River Sediments contaminated with heavy metals, PCBs, hexachlorobenzene, hexachloro-butadiene and other chlorinated compounds. Various contaminant concentrations, water contents, residence times and temperatures were evaluated. Treated sediments from the Buffalo River demonstration were mixed with various proportions of Portland cement to immobilize metal contaminants.

Large debris was removed from Ashtabula sediments (little oversize was present), which were then fed to the pilot system as a slurry (1.8 to 3.6 L/min at 40-50 % solids) and processed through a Holo-FliteTM screw processor (an indirect heat exchanger), capable of producing the temperatures required for volatilization of chlorinated compounds in this sediment (>250 deg C). Some sediments were processed a second time after thermal treatment and drying.

The heat transfer fluid was a molten salt eutectic, heated by electric immersion heaters with one million BTU/hr heating capacity. Pressure inside the processor was maintained at -0.185 to -0.925 mm mercury to prevent intrusion of ambient air, and an inert atmosphere was maintained with Nitrogen. The system was designed to handle an off-gas flow rate of 4.2 cm/min; approximately 1000 m2 were required to stage the thermal processor and support equipment.

For the Ashtabula sediments, residences times of 60, 90, and 120 min resulted in average sediment temperatures of 179 deg C (60 min) and 332 deg C (120 min). Significant mass balance issues were encountered with the semi-volatile compounds and solvent extractable compounds due to sediment heterogeneity. Over 92 percent of all chlorinated volatile compounds were removed for all conditions tested. On average, based on analysis of congeners present in Aroclors 1242, 1248, 1254, and 1260, 86 percent of total PCBs (Aroclor 1248) were removed; mass removal of individual congeners in individual sediment samples varied greatly, however. TOC removal ranged from 2 percent to 35 percent, implying many of the constituents of TOC were not removed at these treatment temperatures. This negated the utility of TOC as a surrogate for contaminant mass balance; removal of solvent extractable residue appeared to have potential as a PCBs surrogate, however. Approximately 74 to 97 percent of mercury was removed by volatilization. Remaining metals were largely unaffected, with less than 10 percent lost due to the treatment based on mass balance calculations. Arsenic, chromium, lead, and zinc tended to distribute between the treated solids and the cyclone fines, reflective of either the size of metal precipitates or the size of particulates with which they are associated. TCLP testing provided inconsistent evidence regarding the effect of thermal treatment on metal leachability; none of the organic compounds exceeded TCLP limits before or after treatment. Processed solids were ultimately dried to a solids content ≥95 percent.

Trace amounts of mercury, dioxins and furans were detected in process off-gases. Based on the data, dioxins and furans appear to have been produced during the thermal processing of the sediment; however, levels were generally below accepted standards for thermal treatment units and whether they derived directly from the sediment or as a result of the thermal processing was not determined.

The intent of concentrating removed contaminants into a smaller mass than the original sediment mass was met, but volume reductions were not as great as expected. The authors noted that thermal desorption is not a destructive technology; desorbed contaminants must be captured in off-gas treatment systems and appropriately disposed; both particulate (carbon) and aqueous (condensate) waste streams were produced. Most pollutants were transferred to the condensate, yielding a volume reduction of approximately 50 percent. The remaining contaminants were transferred to the carbon. Both would require further treatment or appropriate disposal. Further, operating thermal systems to remediate chlorinated compounds in an oxygenated environment can potentially produce products of incomplete combustion, such as dioxins and furans; indirect fired equipment is advantageous in that they operate in an oxygen-free environment and generate a much smaller volume of off-gases than drying or incineration.

Full-scale processing costs based on the Ashtabula pilot testing were estimated to be approximately \$436/ yd^3 for treatment of 10,000 yd^3 of sediment delivered at *in situ* water content, and processed at a rate of 30 yd^3 /day over a period of 12 months (1993 US\$). Costs for a 100,000 yd^3 scenario, at a processing rate of 150 yd^3 /day, was estimated to be \$273/ yd^3. Both of these estimates assumed an off-gas incineration mode. The cost estimate based on the Buffalo River treatment pilot ranged from \$352/ yd^3 to \$535/ yd^3 for 100,000- and 10,000- yd^3 projects, respectively, operated in an off-gas condensation mode. Assumptions regarding delivered sediment solids content were identified as a variable having a significant impact on the comparative cost estimates produced for the Ashtabula and Buffalo demonstrations. A number of process modifications were recommended to improve system performance; these are well detailed in the recommendations in the Ashtabula testing report (EPA 1994d). Although relatively good removal efficiency was achieved for volatiles, due to the inability to adequately close the mass balance for other contaminants, treatment efficiency for other organic contaminants is still mostly a matter of conjecture. Testing of sediments with higher contaminant concentrations could possibly have produced more consistent data, although sediment heterogeneity could still be problematic in this regard.

For residence times ranging from 30-90 min and temperatures ranging from 380 to 480 °F, approximately 44 to 98 percent of total PAHs were removed from the Buffalo River sediments (with approximately 71-74 percent of the incoming PAH mass unaccounted for), and 0 to 100 percent of total PCBs (EPA 1993a). Approximately 17 to 100 percent of mercury was also removed from the sediment, but on average, 70 percent of the incoming mercury was unaccounted for in the mass balance. Remaining metals were largely unaffected by the thermal treatment. Average oil and grease removal was 68 percent, ranging from 17 to 86 percent (with 68 percent of the incoming oil and grease unaccounted for). Correlation of solvent extractable removal to PAH removal suggests that the solvent extractable may be a good surrogate for PAHs, but without better closure of the mass balances this requires verification. As for the Ashtabula sediment, TOC was incompletely removed, with removal ranging from 5 to 35 percent. TOC was also evaluated as a surrogate for PAHs; correlation coefficients suggest this may be possible, but also requires further verification.

The authors note that removal rates did not correlate well with treatment times or temperatures, with the implication that some unmeasured process parameter must have influenced removal efficiency. They postulated that some threshold energy input may be required to achieve complete removal of the target contaminants and that this threshold was not met for the residence times and temperatures tested. Some mass balance issues might have been resolved with analysis of the carbon in the carbon capture system and the air emissions (if possible). Several problems were also encountered with cohesive material caking on the auger in the thermal processor, which had to be disassembled and cleaned during processing of two of the sediment samples.

Treated Buffalo sediments were amended with Portland cement at a cement to treated solids ratio of from 0.1 to 0.6. Based on the mass balance, it appeared that copper, chromium, and lead tended to remain with the treated solids and would be good candidates for stabilization. Solidification resulted in an 89 percent reduction in the TCLP Pb concentration, though this was not correlated to cement/residue ratio. Leachability of Cu and Cr increased with solidification; the cause was not determined. TOC mobility was reduced in two cases and enhanced in two cases, as determined by SBLT.

Additional findings from the Buffalo River thermal pilot included the following:

- Material handling problems were reduced with moisture content >50 percent by weight, though the possible influence of changes in the solids properties was not determined.
- Heat transfer characteristics of the sediment were low, resulting in lower-than-anticipated exit temperatures.

- Residence times of 60 minutes achieved moisture removal and mass reduction.
- Residence times in excess of 90 minutes were required for consistent organic removal.
- Poor separation of aqueous and organic condensates due to the dilute nature of the oil stream – temperature separation was not successful, physical separation may be required.
- Feed material at 44-56 percent solids was successfully pumped with a peristaltic pump, and dried to a solids content >95 percent.
- Removal efficiencies were constituent-specific.
- Process monitoring modifications would be required to improve mass balance closure.
- Analysis of air emissions should include metals analysis.
- Thermal treatment should undergo additional testing with higher initial contaminant concentrations and higher treatment temperatures/longer residence times.

Terratherm, Inc. In Situ Thermal Destruction (EPA 2003a, EPA 2004a)

Terratherm is a conductive heating technology that exploits the thermal conductivity of the soil, which varies little over a wide range of soil types. An array of heater wells are installed at 6 to 7.5 ft spacings in a typical installation for treatment of organic contaminants, with an impermeable layer overlying the soil surface to capture vented gases and volatilized contaminants. The electrically powered heating elements can achieve temperatures of up to 800 deg C. Volatile and semi-volatile contaminants are vaporized and destroyed by multiple mechanisms, including oxidation and pyrolysis. Vacuum wells remove volatilized contaminants, which are then treated with (typically) a thermal oxidizer, heat exchanger, dry scrubber, and carbon absorbers. The technology has reportedly been demonstrated at seven field sites, four of which were full-scale applications.

TerraTherm was demonstrated on a former disposal pit (the Hex Pit) at Rocky Mountain Arsenal in Commerce City, CO. The Hex Pit contains a tar-like waste phase interlayered with soil that was used to cover the waste; the pit was also periodically limed. The demonstration was terminated 12 days after start-up due to destruction of system components attributed to an unexpectedly high level of hydrogen chloride (HCl) production. Although components were constructed of 304 stainless steel, corrosion occurred in both aboveground and belowground piping. Heater cans and well screens were severely corroded; hex material was visualized on and coming through well screens, and accumulated at some depth in at least one heater can. Metallurgical evaluation of the corroded screens confirmed chloride attack. Liquids captured in the knockout pot storage tank, part of the off-gas treatment system, had a measured pH of zero. Blockage of high-temperature rubber hoses also used in the system was also observed; deposits varied in character from “crystalline to or fibrous to tarry, muddy, powdery or cake-like” (USEPA 2004a). The composition of the deposits included “metallic salts and both amorphous and crystalline organic materials containing high concentrations of hex.” It appeared that the pure phase hex may have begun to flow as the soil heated up, rapidly producing HCl, and that unheated connections in the vapor treatment system allowed condensation of vapor in the system to an even more corrosive aqueous form. Although the failure modes were comprehensively evaluated, no recommendations were made in the final report regarding retrofitting the system to operate in such an environment. Sampling was conducted to determine whether any degradation had taken place during the brief period of operation, but results were inconclusive.

Minergy Corporation Glass Furnace Technology Evaluation (USEPA 2004b)

The Minergy glass furnace technology was demonstrated June-August 2001 on sediments dredged from the lower Fox River, WI. System components include a dryer, melter, and air pollution control system. Sediment must be cleaned of debris — including relatively small metallic debris — and dried to approximately 10 percent moisture content prior to treatment in the melter. The furnace is heated with a combination of natural gas and oxygen; use of oxygen instead of atmospheric air reportedly reduces nitrogen oxide emissions and gives a cleaner burn. The process is distinguished from other thermal technologies in that it does not rely on the fuel value of the sediment; flux mixtures are added to control the temperature and final properties of the melt. The process does produce some wastewater in association with capture and management of the off-gases and quenching of the melt; some or all of this wastewater could require treatment prior to disposal. Given the size and weight of the equipment, this is not a mobile technology.

The sediment is heated to a temperature of approximately 1600 deg C over a retention time of six hours, at which point the sediment becomes molten; PCBs and other organic compounds are destroyed or volatilized and metals immobilized in the glassy matrix resulting after the materials are quenched. The resulting glass aggregate is considered suitable for fill or other beneficial uses (aggregate produced from treatment of sewage sludge has since been utilized as trench fill by various municipalities; there were commercial scale plants processing sewage sludge at the time the technology demonstration was reviewed by Estes et al. (2011).

Approximately 27,000 lbs of dried sediment were treated during the demonstration of a pilot-scale melter constructed specifically for the demonstration. A representative, bench-scale test of an indirect heat Holoflite® dryer was demonstrated separately, as no production scale dryers of this type were available. A drum dryer was used to prepare the larger volume of sediment for treatment in the glass furnace. There were some operational problems during the demonstration. The initial melter run was interrupted after processing about 11,000 lbs of sediment because of a failure of the furnace refractory brick, resulting in a leak of molten glass. Reportedly, there were many interruptions of flow during operation due to the lack of fluidity of the molten glass. The remaining 17,000 lbs of sediment were processed without interruption (as long as sediment entered the melter) after the furnace was repaired. Approximately 11,000 lbs of glass aggregate was produced, a mass reduction of 2.5 to 1.

Full-scale costs were estimated to be in the range of $39/ton of dredged and dewatered sediment (at 50 percent moisture), assuming a capacity of 600 tons sediment/day and a 15-year project life. A critical discussion of the economic analysis for this and three other significant technology demonstrations is presented in Estes et al. (2011). The primary objective of the treatment demonstration was to demonstrate the efficiency of the technology in destroying PCBs. Based on the pre- and post-treatment sediment/aggregate PCBs concentrations, the primary objective appears to have been met. Mean pre-treatment sediment concentrations was 28.8 mg/kg; mean post-treatment aggregate concentration was 1.4 X 10^{-4} mg/kg.

Rotary Kiln – JCI Upcycle and Cement Lock (JCI/Upcycle Associates, LLC 2002; Mensinger 2008a, 2008b; Mensinger, M. C., and T. R. Sheng 2006; Estes et al. 2011)

Two rotary kiln technologies were demonstrated under the NJDOT technology development program. The process, demonstrated by JCI Upcycle, consisted of two phases: pretreatment, including size reduction, dewatering and drying; and the treatment (kiln) phase. Debris and solids larger than 1.3 cm (0.5 in.) (gravel, and cobbles) are removed and the sand and fine sediment fraction dewatered. After dewatering, filter cake and shale are dried and ground, then blended. Water is added to optimize moisture content and the blend is then extruded as pelleted feed for the kiln (Estes et al. 2011). Approximately 3 cy of dredged material were processed during the demonstration.

The Cement-Lock® process is also a two-phase process, with pretreatment including removal of debris and solids typically larger than 50 mm (2 in.) (gravel and cobbles), dewatering of the fine fraction, and blending with modifiers to control the properties of the melt. The sediment/modifier blend is then fed to the kiln, or “Ecomelt® Generator.” The Ecomelt® Generator is operated at a temperature of 1,400 to 1,500 °C (2,600 to 2,700 °F), causing the minerals in the sediment and modifier mixture to react together. After a sufficient residence time in the melter, the melt is discharged and then quenched with water to granulate the material (Estes et al. 2011).

During the Cement-Lock® extended duration tests with Passaic River sediments, a total of 28.7 mtons (31.6 tons) of Passaic River sediment and modifiers, which is equivalent to approximately 34 m3 (44 yd^3) of sediment in situ, were processed through the demonstration plant at rates up to 0.8 m3/hr (1 yd^3/hr) (Mensinger 2008b). An estimated total of 21 mtons (23 tons) of Ecomelt® was produced as part of these extended campaigns.

A number of equipment issues were encountered during demonstration of the thermal technologies. Both Cement-Lock® extended duration tests experienced equipment-related problems and operational issues, which led to early termination of the demonstration. Although reliable, sustained operation has not yet been demonstrated, these technologies were largely successful in achieving decontamination of the sediments and producing a material suitable for beneficial use as an aggregate or (partial) cement substitute. Larger scale testing, co-processing of feedstocks, and long-term performance evaluation of products was recommended for subsequent demonstrations of the Cement-Lock® technology.

Total processing costs for Cement-Lock® and rotary kiln treatment were estimated based on the economic analysis conducted by the vendors and other available information (2009 $U.S. basis) and reported in Estes et al. (2011); estimated total cost ranged from approximately $90 to $100/cy for rotary kiln and Cement-Lock®, respectively, excluding any cost recovery from the sale of beneficial use products. The estimated cost were normalized for a full-scale operation based on an annual volume of 380,000 m3 (500,000 yd^3) and continuous operation of the processing plant. Smaller processing volumes typically result in higher unit costs due to the influence of factors, such as capital cost of equipment, that are determined by processing rate rather than volume. Further information on the assumptions of the cost estimate is available in Estes et al. (2011).

Capping

Although capping is typically utilized to isolate highly contaminated sediments, there may be applications to facilitate beneficial use of less contaminated materials, providing isolation from surficial organisms or serving as a distribution medium for reagents or seeds, as further described below.

AquaBlock® - Demonstration of the AquaBlock® Sediment Capping Technology (EPA 2007c)

AquaBlock® is a proprietary clay polymer blend developed as an alternative to natural sediment capping materials such as sand; the material is designed to swell after placement, forming an impermeable barrier between contaminated sediments and the water column. A variety of formulations are available to facilitate use under a variety of conditions (shallow, freshwater, nearshore vs. saline environments). Active reagents or sorbents reportedly can also be incorporated, as can plant seed to promote establishment of desired vegetation. The performance of AquaBlock® was evaluated over a three-year period in a test plot on the Anacostia River; the sediments of the Anacostia are contaminated with PAHs, PCBs, heavy metals, and other compounds. The principal objectives of the study were to evaluate the physical stability of the AquaBlock®, as compared to a sand cap, as well as the ability to prevent seepage through the cap and the impact of the cap on benthic habitat and ecology. The overall results of the demonstration indicate that the AquaBlock® is very stable, and that even under very high shear stresses, it is more impermeable and potentially more effective at controlling contaminant flux than traditional sand capping materials. No significant intrusion of PAHs or PCBs into the AquaBlock® cap was observed; conversely, metals were found throughout the cap profile. Whether these metals were indigenous to the bentonite clay in the cap material or released by the sediment and captured by the AquaBlock® was not definitively determined; the relative performance between the sand cap and the AquaBlock® with respect to metals containment was therefore somewhat unclear. Composition of gas collected above the caps was similar with the single exception of Hydrogen sulfide, which was significantly lower for the AquaBlock® cap. While gas ebullition was lowest for the AquaBlock® cap, there was also some evidence suggesting episodic gas released due to buildup of gas underneath the impermeable cap. Although it cannot be statistically supported by the available data, discharge through the cap appeared to be lower for the AquaBlock® cap than for the sand cap. Environmental impacts appear to be similar to that of a sand cap.

Full-scale costs are projected to be dependent on a number of factors, including:

- Salinity
- Project location
- Project size
- Performance criteria
- Composite cap design
- Regulatory constraints

Material and installation cost for a "typical" AquaBlock® cap installation (as defined in USEPA 2007c) was estimated to be approximately $4.68/sf (year basis was not indicated, but is assumed to be 2006 US$).

Water Treatment

Colloid- and DOC-associated contaminants can be problematic in effluent discharges from CDFs. The volume of material that can be processed and recovered from Erie Pier CDF is limited by the fact that mercury levels in the ponded water exceed water quality criteria; this water cannot be discharged without treatment; currently, evaporation and infiltration is the primary means of reducing pond volume. It is not known in this case whether the mercury is associated with colloids in the water column, or with DOC. Both are potentially problematic, however. While DOC should be relatively easily removed with appropriate sorption processes, the remoteness of many CDFs and lack of infrastructure will dictate technically simple solutions. Further, while treatments do exist for removal of colloids from solution, such as microfiltration and coagulation, these are not likely applicable to the low levels of colloids in clarified pond water. Coagulation relies on particle contact for agglomeration, and this, in turn, typically requires a minimum suspended solids concentration.

Sonic flocculation was reportedly tested at bench scale under the Great Lakes 2000 Cleanup Fund demonstration program; no report could be found summarizing this work, however. The technology (Triton/Sonofloc) utilized sound waves to "drive fine particulate matter towards acoustic nodes, where they agglomerate into flocs and settle out of the water." More recent studies suggest that while acoustic filtration has been successfully demonstrated for removal of small particles in low flow liquids, over a small cross sectional area (Karpul et al. 2010), energy requirements may be excessive on an industrial scale. Further investigation will be required to ascertain the potential application of this technology in colloid removal for relevant volumes and flow rates. Used in conjunction with appropriate coagulants, however, this could comprise a relatively simple water treatment process that could be utilized intermittently as needed for colloid removal. The scale of the equipment required, the associated capital and energy costs, the lifespan of the sonicating equipment and effectiveness at expected colloid concentrations will determine feasibility in this application.

Bench testing was recently completed in the use of carbon-impregnated silt curtains for treatment of dredged material effluent (Acevedo and Estes in preparation). This is potentially a very simple, passive water treatment technology that could be used at Erie Pier and other CDFs where effluent and runoff treatment is needed. The technology could also be applied in small weir structures for passive treatment of flow from beneficial use sites. Contact time at high flow rates was insufficient for significant removal of dissolved metals; greater removal was seen for PCBs in the synthetic effluent tested, however. For controlled, low-flow applications this might not be problematic. Experimentation with different sorbents and ion exchange media might enable improved metals removal. Zeolite-impregnated silt curtains may provide a feasible and cost-effective treatment for removal of ammonia as well, for which effective alternatives to biological treatment are needed. More extensive testing is needed to determine a suitable range of applications for this management approach.

6 Chemical/Geo-Chemical Processes

The literature was reviewed for relevant geo-chemical processes having potential to influence contaminant mobility, organic degradation, and production of nuisance species, such as H_2S. A comprehensive summary of these processes and their potential interactions is beyond the scope of this document; the importance of these processes to contaminant fate in beneficial use applications and the potential to control them as a risk-reduction measure will be explored more fully in a companion document (in preparation). A few of the most relevant studies are summarized here.

Baldwin and Mitchell (2012) studied the effects of sulfate (as sodium sulfate solution) and sulfate plus carbon (as glucose or acetate) addition on the anaerobic biogeochemical cycles in a wetland sediment. The study is of potential interest in the management of dredged material placed in intertidal areas for wetland restoration, where management of sulfide levels might be one approach to limiting metals mobility. In the natural environment, sulfur may be introduced in the form of sulfates, in runoff from agricultural areas. Under the reducing conditions found in wetlands, sulfates cycle back and forth into sulfides (S^{2-}). The sensitivity of plants to sulfide concentrations varies, with the result that the natural plant distribution may shift in favor of more tolerant species. Other potential consequences of sulfate additions to wetland systems identified by the authors include:

- Methylation of mercury associated with sulfur reduction[1]

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[1] "In the presence of the oxidation-reduction reactions between sulfates and sulfides, carried out by sulfate-reducing bacteria, Hg^{2+} is transformed into methyl mercury (HgMe) - Since it is the process of sulfate reduction that stimulates the biological activation of Mercury, methylation takes place when the concentration of sulfates is neither "too low" nor "too high." For example, concentrations of sulfates, normally less than 10 parts per million or ppm for the undisturbed everglades, are too low for methylation to occur. At high concentrations of surface-water sulfate (> 20 ppm) and/or high concentrations of sulfide (> 0.3 ppm), production of methyl mercury becomes curtailed because of immobilization of mercury by sulfide. [24] [25] Thus, peak methylation occurs at sulfate concentrations in surface waters of 10-20 ppm, which coincides with sulfide concentrations of 0.2-0.3 ppm in sediment porewaters." http://www.everglades.org/sulfur-and-mercury/

- Enhanced eutrophication through mobilization of phosphorus
- As a reducing agent, may facilitate the reduction of solid ferric minerals to dissolved ferrous ions with concurrent P release – favored by insolubility of iron sulfide, a reaction product
- S^{2-} may displace P from insoluble Fe^{2+} phases – again favored by insolubility of reaction product FeS
- Impacts to nitrogen dynamics - sulfide inhibition of denitrification and stimulation of dissimilatory nitrate reduction to ammonia
- Impacts to carbon dynamics - diminished production of methane
- Potential to affect other biogeochemical processes

Where mercury is present, sulfide concentrations favorable to limited metals mobility will need to be balanced against sulfate concentrations that would trigger methylation. This and other interdependent geochemical mechanisms require further study within the context of geochemical controls in dredged material, in order to effectively control contaminant releases without unintended adverse consequences.

Wood and Shelley (1999) modeled the mechanisms that influence pore water metal activity and bioavailability in constructed wetland sediments using STELLA II software with complex numerical integration capability. This study also has relevance to the concept of geochemical control of contaminant releases from dredged material in beneficial use placements.

The most interesting findings in Wood and Shelley (1999) were the behavior of metals' pore water concentrations over time, in the presence and/or absence of the acid volatile sulfide (AVS) mechanism and organic carbon (OC) binding. To summarize, the model predicted that pore water concentrations would be low as long as the AVS capacity had not been exhausted. Once AVS assimilative capacity was exhausted, pore water concentrations would begin to rise gradually, controlled by OC sorption. In the absence of AVS, this gradual rise would begin immediately upon introduction of metals containing stormwater to the wetland. If OC is very low, once AVS capacity is exhausted, pore water concentrations would rise quickly. The model indicated that in the pool preceding the wetland, steady state was achieved within a 16-year simulation, but that for the downstream wetland it was not, with pore water concentrations continuing to rise with time.

Wood and Shelley (1999) also noted the influence of organic sediments on pH; while organics provide more binding sites for metals, they also tend to drive down the pH, resulting in H^+ competition for binding sites and metals mobilization. However, this is contradictory to the pH response observed following activated carbon addition to metal containing solutions in batch sorption studies conducted by Acevedo and Estes (in preparation). In that study, pH increased significantly over a 24-hour period following addition of activated carbon; the response was observed to vary significantly for different carbon samples. Potential pH response will require evaluation for any carbon amendments employed to control contaminant releases in dredged material at beneficial use sites.

Wood and Shelley (1999) noted that pore water concentrations were only slightly sensitive to AVS concentrations, but when AVS is controlling until exhausted, then partitioning is defined by OC, and the fraction of OC has a stronger influence on pore water concentration than differences in AVS does. The authors also observed that OC was more important in limiting Pb and Cu concentrations than it was for Cd, for OC increases of 5 to 40% over a period of 7000 days.

Individual metal behavior is reportedly dependent upon sulfide solubility products. Metals released from the sulfide bond are in the following order: Fe>Ni>Zn>Cd>Pb>Cu>Hg. Wood and Shelley (1999) postulate that because Cd is more soluble than Cu or Pb in sulfides, Cd, along with Ni or Zn, will produce the highest pore water concentrations in sediments with multiple metal species present. They conclude that OC in the deep anaerobic sediment appears to have the largest influence on metal bioavailability, even at moderately low pH.

DeSouza et al. (1986) evaluated the geochemical distribution and the bioavailable fraction of metals in sediments under changing conditions. For the purposes of managing contaminated sediment in a beneficial use application, the study primarily highlights the need to understand what sedimentary phases (exchangeable cations, easily and moderately-reducible compounds, organic/sulfidic phases, and residual components) the metals are associated with. In contrast to Calmano (1983), who found that of the major sedimentary phases, the easily-reducible fractions are most important in metals accumulation, DeSouza et al. (1986) found that in highly contaminated systems the oxidizable fraction was more important.

The complexity of the geochemical phases the metals were associated with in this study (DeSouza et al. 1986) increased as sampling locations moved downstream and salinity increased. However, it is not known whether this was due to changes in the inherent sediment composition (becoming more complex in the downstream direction), differing anthropogenic inputs (different metals speciation from sources), or effects of salinity. Had this information been coupled with corresponding sediment characterization, some inferences might have been drawn regarding the influence of the sediment composition, but would not enable differentiation between the effects of salinity and metals source.

DeSouza et al. (1986) conclude that “the more contaminated a system is the more diversified the contaminant forms present”; for sediments with significant organic inputs (such as sewage outfalls) the oxidizable phase may be more important than the reducible phase. This was especially true for Cu and Cr in the system studied. Conversely, uncontaminated sediments were characterized by “a low diversity of geochemical phases containing metals,” with more than 65% of the metals studied found in the residual (lithogeneous) fraction 100% and 80%, respectively for Cd and Cr. The only mobile fraction containing significant amounts of metals in the uncontaminated sediments studied was the reducible phase.

Payan et al. (2012) evaluated the potential for release of trace metals from marine sediment as a result of CO_2 release from a carbon capture storage site. The study is of interest in terms of expected release of metals as a function of changing pH from sediments placed in a marine or estuarine area; the study reflects the benefit of natural buffering in resisting pH change and contaminant release, which may inform treatment of sediments to augment natural buffering capacity. As, Cd, Cr, Cu, Ni, Pb, Zn were studied, as well as conductivity, pH, and DOC, for different pH regimes (pH 5, 6, and 7). Visual MINTEQ was used for modeling the results. The natural pH of seawater is reportedly 7.9 to 8 (Payan et al. 2012. The pH-dependent leaching of metals is a function of the sediment phases with which they are associated and the pH at which those phases become soluble. This underscores the need to characterize the phases in the sediment acting as metals sinks, the major crystalline phases present, and the pH and ionic strength of the site water, in order to assess potential leaching in response to changing conditions, such as would be expected with placement of dredged material in an intertidal area. Other phases may also be important, depending upon the character of the sediment. Payan et al. (2012) also evaluated the effect of different liquid to solid ratios, ranging from 2 to 40; metal leaching decreased with higher liquid solid ratios for seawater as the leaching solution (for all metals except Cr in this case). Differences of an order of magnitude were observed in going from a liquid solid ratio of 2 to 40. Metals mobilization was higher for seawater as the leaching solution than for DDI; final pH for DDI as the leaching solution was around 8, but ranged from about 6.8 to 8 for seawater. This result has interesting implications for the relative mobility of metals at marine and estuarine sites, as compared to freshwater sites. DOC concentrations were also shown to have a slight dependence on pH, which could be important to mobilization of organic contaminants, depending upon the magnitude of the response to pH changes. The authors estimated that compared to pH 8 (normal seawater pH), at pH 7.3, As, Cd, and Zn concentrations could increase by about 45%, and at pH 6.8 by 66-82%.

Emission of H_2S represents an air quality issue near some confined disposal facilities and open water and beach disposal sites. Although at high concentrations H_2S presents an imminent danger, and health problems have been reported after prolonged exposure at low concentrations, issues related to hydrogen sulfide (H_2S) and dredged material are primarily aesthetic. Air monitoring has been conducted at the Santa Cruz harbor since 1997, as a result of community concerns related to emissions from sediments placed on the beach (U.S. Department of Health and Human Services 2007). Effective treatment or management methods are needed to prevent, or minimize, H_2S generation and its release in water and solids produced during dredging, and following disposal.

Sulfate (SO_4^{2-}) is the most oxidized form of sulfur, and is one of the major anions in seawater. H_2S generation is generally more problematic for saline sediments. However, sulfides are present in certain industrial wastewaters, such as those produced from tanning and etching processes. The presence of such industries in the area would certainly suggest the potential for sulfides in freshwater sediments as well.

In situ, H_2S is produced through the dissimilative reduction of sulfate by sulfate-reducing bacteria. The sulfate acts as an electron acceptor in the bacterial respiration process, which occurs under anoxic/reducing conditions (E_0' between approximately 0 and –0.25V) Madigan, Martinko and Parker (1996).

"Degradation of hydrogen sulfide in the atmosphere can occur through oxidation by oxygen (O_2) and ozone (O_3) to give sulfur dioxide (SO_2), and ultimately, sulfate compounds. Residence time in air ranges from hours to days (ATSDR 2006). In water, H_2S is a weak acid, dissociating to the bisulfide ion HS^-, and then to the sulfide ion S^{2-}, although the proportion of sulfide ion is only greater than 50% at very high pH (>12). H_2S is readily oxidized by O_2 in water; wastewater emissions can therefore be readily controlled through the addition of oxidizing reagents, such as hydrogen peroxide. The rate of oxidation and the resulting products are pH dependent. At pH 6-7, chemical oxidation of H_2S produces sulfur; at pH 7-9, sulfur, polysulfides, thiosulfates and sulfate are formed. Therefore, water sprays near the source of atmospheric H_2S can effectively reduce H_2S emissions. The use of oxidants, such as potassium permanganate, hydrogen peroxide, and sodium hypochlorite in the sprayed solutions, enhance the ability of the water sprays to lower emissions (USACE 1976). The solubility is exploited to remove sulfur dioxide from industrial gas streams; once dissolved, sulfur dioxide forms sulfurous acid (H_2SO_3), and oxidizers are used to form inorganic sulfites (SO_3^-) and sulfates (So_4^{2-}) preventing the reverse reaction[1]. The use of ferrous sulfate has been used to form insoluble salts with H_2S (USACE 1976).

A recent paper by Smith and Luna (2011) suggests that aerobic degradation of organic contaminants may be facilitated in wetland soils through selection of plants with high rates of oxygen loss into the rhizosphere (radial oxygen loss). The results of this study were used to select plants for a subsequent study evaluating the degradation of PAHs in saturated sediments. The concept is also important to the biogeochemistry of sulfur species and heavy metal mobility in wetland sediments, as reported by Choi et al. (2006).

There are numerous studies showing that many pollutants are more readily broken down under aerobic conditions, where oxygen serves as the terminal electron acceptor. While saturated soils typically do not provide sufficient oxygen to support aerobic organisms capable of breaking down organic contaminants, plants with structures known as aerenchyma can oxygenate the rhizosphere in a saturated environment. Plants also secrete compounds stimulating further microbial growth, such as amino acids,

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[1] USEPA Module 6: Air Pollutants and Control Techniques - Sulfur Oxides - Control Techniques http://www.epa.gov/apti/bces/module6/sulfur/control/control.htm

sugars, and organic acids. Plant species employed in the study (Smith and Luna 2011) included:

- Cardinal Flower (Lobelia cardinalis),
- Dark-Green Bulrush (Scirpus atrovirens)
- River Bulrush (Scirpus fluviatilis)
- Common Arrowhead (Sagittaria latifolia)
- Prairie Cord Grass (Spartina pectinata)
- Blue Flag Iris (Iris shrevei)
- Monkey Flower (Mimulus ringens)
- Common Rush (Juncus effusus)

The root zone area oxygenated by each species was estimated by one of three methods:

- Visualizing plant roots immersed in redox sensitive methylene blue dye solution, and estimating the oxygenated area by image analysis at 5 and 24 hours
- Immersing plant roots in a titanium (III) redox buffer and calculating O_2 loss based on changes in absorbance of this solution at 6 and 24 hours
- Measuring dissolved oxygen levels in deoxygenated water after 5 and 24 hours of root immersion, using a dissolved oxygen probe

The study confirmed that *S. latifolia, I. shrevei, a*nd *M. ringens h*ad the highest rates of radial oxygen loss of those species studied. *J. effusus* also showed high oxygen loss, but due to the relatively small rhizosphere, affected a smaller area than the other species. Maximum root zone oxygenation area was 56 cm^2 (*S. latifolia*); methylene blue proved to be the most sensitive measurement method of those tested. The findings of this study suggest that selective planting of species with high radial O_2 loss might provide another means of optimizing conditions favoring aerobic degradation of organic contaminants obtained during composting. Tolerance and uptake of metals has also been shown to be related to radial oxygen loss in wetland plants (Li et al., 2011; Mei et al., 2009; Deng et al., 2009 as cited in Smith and Luna 2011), with highest uptake occurring at an optimum (not necessarily highest) root oxygen level.

Another study underscoring the importance of radial oxygen loss to contaminant dynamics in wetland environments was conducted by Choi et al. (2006). This study evaluated the effect of plants on the biogeochemistry of sulfur species and heavy metal mobility in wetland sediments. Elevated sulfate concentrations were reported in the rhizosphere during the growing season in vegetated areas (SO_4^{2-} *and* S^0 are produced from oxidation of sediment sulfide); the oxygen release rate from the plant roots was estimated to be 0.85 g/m^2*day (based on the extent of sulfide oxidation observed). In vegetated areas, evapotranspiration induces an advective flow from the surface water into the sediments, moving dissolved constituents in the surface water into the sediments. There, in the absence of more favorable electron acceptors, organic matter is broken down by sulfate reduction, resulting in accumulation of sulfides in the sediments. Acid volatile sulfides react with dissolved metals in the sediment pore water, immobilizing them in the sediment until the sulfides become re-oxidized. In freshwater wetlands, degradation of organic sulfur from plant residue results in elevated sulfate concentrations in the water column, resulting in higher sulfide concentrations within the sediment than in unvegetated areas. In unvegetated areas, transport is primarily diffusion driven.

Choi et al. (2006) evaluated the effect of plants on the cycling of sulfur and trace metal fate in freshwater sediments through field measurements obtained over a two-year period; the authors noted a maximum observed root depth of 20 cm from sediment surface, with most concentrated at 12 to 17 cm depth. Vertical pore water sulfate profiles were obtained monthly from *in situ* sampling chambers placed at 0.5 cm intervals. The samplers were filled with distilled deoxygenated water and covered by a semi-permeable membrane; samplers were allowed to equilibrate for two weeks and then recovered for sulfate analysis. Acid volatile sulfide (AVS) and simultaneously extractable metals (SEM) were measured in sediment cores obtained adjacent to the pore water sampling locations. Statistical analysis was used to determine whether season, vegetation and sediment depth affected concentrations of AVS and trace metals Cd, Pb and Zn.

Choi et al. (2006) reported SO_4^{2-} in the 10 to 20 cm root zone to be four to 20 times higher in vegetated areas vs. unvegetated in year one of a two-year study. Sulfate concentrations increased during the growing season by approximately a factor of 30 in this zone in the vegetated sites (from 0.2 mmol/L to 6.20 mmol/L), but increased by only 0.25 mmol/L in the non-vegetated sites. Sulfate increases were reduced in the following year; attributed to diminished plant growth and subsequent decreases in oxygen root loss; sulfate increased by a maximum factor of 10 to 0.02 mmol/L in vegetated areas and remained below 0.02 mmol/L in unvegetated areas. Seasonal porewater SO_4^{2-} profiles were shown to increase in vegetated areas during warmer months (May, June, July) with maximum concentrations observed between 15 and 20 cm; AVS concentrations increased with depth in vegetated sediments, and diminished with depth in unvegetated sediments.

Oxygen release rates of 0.85 g/m^2/day were estimated to have been required to account for the degree of AVS oxidation seen in this study; actual release rates may have been even higher if oxidation of other species was taken into account. Laboratory root zone oxygen release rates of 0.52 – 0.72 g/m2/day were reported by Dunbabin et al. (1988, as cited by Choi et al. 2006) and rates of 1.62 g/m^2/day were reported by Armstrong and Armstrong (1990, as cited by Choi et al. 2006), which are in good agreement with the field measurements obtained in this study.

Sediment constituents affecting sorption and complexation of metals include iron and manganese hydroxides in aerated sediments and sulfide and carbonates in anoxic sediments (Bostick et al. 2001, as cited in Choi et al. 2006). AVS is defined as a solid phase sulfide, mainly FeS, soluble in cold acid. Trace metals in porewater exchange with the Fe in FeS, and precipitate out of solution as Me2+ sulfide, according to the following reaction (DiToro et al. 1990 as cited in Choi et al. 2006):

$$Me^{2+} + FeS(s) \rightarrow MeS(s) + Fe^{2+}$$

Divalent metal activity in solution is a good indicator of bioavailability and potential toxicity (Di Toro et al., 1990, 1992; Simpson et al., 1998, as cited in Choi et al. 2006); thus, sulfides can effectively limit bioavailability of metals in anoxic sediments. The cycling of SO_4^{2-} into the pore water as a result of root zone oxygenation, and the conversion of SO_4^{2-} to sulfide as a result of evapotranspiration-induced advection into anoxic sediments, suggests the potential for seasonal changes in bioavailability of metals. This was supported by Simpson et al. (1998, as cited in Choi et al. 2006), who noted that FeS is more reactive and more rapidly oxidized than other metal sulfides, such as CdS, PbS and ZnS; FeS may be preferentially oxidized (due to radial oxygen loss), producing SO_4^{2-} and ferric (hydr)oxides. Once FeS is exhausted, the remaining metal sulfides may be oxidized, releasing metals to pore water. In low AVS sediments, organic carbon and iron and manganese oxides may take up the metals release through sulfide oxidation.

For high AVS to SO_4^{2-} ratios, little release of sulfide- associated metals would be expected, and this was born out in pore water analysis. The average SEM/AVS ratio (a measure of metals toxicity in sediments, with a value less than 1 considered nontoxic), was 0.029 for non-vegetated sediments and 0.022 for vegetated sediments. Unlike the sulfate profiles in the sediment, the AVS (and associated dissolved phase metals) evidenced no seasonal trends in these sediments. Higher metal mass (sediment concentrations) were noted in vegetated vs. unvegetated sites, with the difference attributed to metals transport from the surface water to the sediment due to evapotranspiration.

There are many other papers in the literature documenting chemical and biological mechanisms relevant to the management of dredged material geochemistry for the purposes of minimizing contaminant release.

Conesa et al. 2012, studied the effects of slaked lime and acidic fertilizer amendment of firing range soils, and the uptake of metals in several plant species, as part of a phytomanagement approach to limit metals mobility and exposure through plant ingestion. Some metal concentrations (Pb, Zn and Ni) decreased in drainage water with lime application, while others (Cu) increased along with DOC concentrations. This suggests the mobility of Pb, Zn and Ni have a greater pH dependence, while Cu is likely more influenced by DOC, which also increased with liming. Cu is known to complex strongly with organic ligands, and most dissolved Cu is complexed at pH>6. This is consistent with results reported by other authors indicating that metal affinity to dissolved organic matter decreases according to Cu>Pb>Ni>Zn. Sb showed no DOC solubility dependence here, but there is disagreement in the literature about this. Zn solubility, while reportedly having some DOC dependence, is more greatly influenced by competition from Ca. With liming, soluble metals concentrations increase with increasing DOC for all metals except Sb and Zn. The addition of phosphate in fertilizer may result in competition with the oxyanion $Sb(OH)_6^-$ for anion binding sites. This effect has also been reported for arsenate. Addition of fertilizer increased the $NaNO_3$-extractable concentrations of most of the metals; liming increased the $NaNO_3$ extractable Sb. In soils with high Ca, this may be mitigated by precipitation of $Ca[Sb(OH)_6]_2$. For all metals and Sb, the $NaNO_3$ extractable fraction increased with time. Plant growth was inhibited in unfertilized sites receiving lime treatment, perhaps due to excess Ca in solution and deficit of competing Mg or K, an imbalance resolved with the addition of fertilizer. Plants with higher grain, spike, or shoot uptake may be less desirable from a risk perspective than plants within which root uptake predominates, where harvesting and disposal of the growth is not planned. This work has potential relevance for management of sediments placed in upland beneficial use sites.

Healy et al. (1987) evaluated the relationship between the type of Cu complex in soil solutions and the interaction with Zn sulphide. While the study was motivated by observed copper deficiency in cattle in the presence of adequate soil copper, it has relevance here with respect to the potential for reduced bioavailability of copper as a function of the type of Cu chelate present in solution. The copper-donor atom bond strength reportedly decreases according to: Cu-S>Cu-N>Cu-O; thus O-bonded chelates were projected to be most susceptible to reaction with metal sulphides.

Francios (1987) evaluated possible mechanisms for sulphur enrichment of humic materials marine sediments. These mechanisms are:

- Reaction of HS^- with organic matter through nucleophilic substitution and/or addition within the microaggregates or the sulfidic zones (with the micro-aggregates more likely given the rapid oxidation and/or precipitation of H_2S that would be expected to occur in the sulfidic zone)
- Cleavage of polysulphides formed as intermediates of H_2S oxidation and by the reaction between sulphide and elemental sulfur, producing free radicals that then react with organic matter to form organic polysulphides and (eventually) thiol groups
- Cleavage of the S8 rings of elemental sulfur, producing organic polysulphides, which then produce free radicals that react with organic matter

In some organic-rich marine sediments, organic sulphur may represent up to 50% of the total sedimentary sulphur at the sediment interface, and 15-20% in the sulphidic zone. The implications with respect to formation of metal sulfides require further consideration.

A more complete discussion of the geochemical processes relevant to contaminant fate and transport in dredged material placed at beneficial sites is presently in preparation (McGrath and Estes in preparation). The potential for manipulating the geochemistry with various amendments and management of the ponding regime is explored in that document. Geochemical modeling tools will likely also be critical to anticipating and controlling the many interdependent reactions that may take place at a given site; the capabilities of existing or developmental models to fulfill this requirement also require further exploration.

7 Discussion

The most promising technologies and concepts for treatment or management of navigation sediments are discussed further here.

Solidification/Stabilization

Long-term performance of sediment S/S is difficult to predict because of the wide range of inorganic and organic contaminants in sediment, the complex interactions between contaminants and binding agents, and potential environmental effects on chemical and physical stability of S/S sediment. Contaminant mobility for S/S material is affected by reaction products, speciation effects, pH, redox, solubility, and crystalline development. Evaluation of treatment effectiveness is currently based on laboratory leachability tests for small specimens. Research is needed to identify and describe the important geochemical characteristics and processes for sediments, binders, and their products in order to improve modeling of long-term contaminant mobility and to improve formulations for treatment effectiveness.

However, the fact that S/S has been so extensively utilized for management of contaminated sediments is testament to the effectiveness of the technology in terms of improving the material handling and structural properties of dredged material. Use of S/S to enable the use of dredged material for beneficial use appears to be well demonstrated for construction applications. However, there are potentially some disadvantages to the use of S/S in dredged materials intended for environmental restoration. Depending upon the amendments added to the dredged material, the mixture properties may be significantly different from natural materials after treatment. Radical changes in pH may be incompatible with natural flora and fauna of a beneficial use site. More recent research in the use of *in situ* sorbents in sediments offers the potential for more ecologically compatible amendments for stabilization of contaminants, without solidification of the sediment matrix or major pH adjustments. Demonstrations have been conducted or are underway that utilize activated carbon and other amendments to limit the bioavailability of contaminants in sediments. Biopolymers offer another alternative for stabilization of sediments and sequestration of both metal and organic contaminants; biopolymers may be able to achieve adequate stabilization without altering the sediment characteristics to a degree that normal colonization cannot take place. Further field studies are needed to evaluate the long-term performance of biopolymers under environmental conditions and potential associated ecological effects. The small scale of the most recent demonstrations of *in situ* stabilization and lack of corresponding long-term performance data may limit the opportunities for full-scale application to beneficial use of contaminated sediments in the near term, but the outlook for this technology approach appears promising.

A more dynamic stabilization concept is that of amending sediments to direct the changes in geochemistry that occur naturally as a result of wetting and drying cycles and biological activity. Rather than aggressively and permanently immobilizing contaminants in a single phase through solidification or extreme adjustments to pH, contaminants would be allowed to naturally cycle through different “compartments” with changing conditions. Amendments would be carefully selected to complement the composition of the sediment and the anticipated conditions at the placement site, such that the geochemical processes favor compartments minimizing the solubility of metals and the production of nuisance species such as H_2S. In effect, the geochemistry of the site would be actively managed to achieve an acceptable level of risk reduction. Amendments to simultaneously enhance biological degradation, sorption and phytoremediation could be incorporated if compatible. Electrokinetics might also have a role in facilitating delivery of organisms and nutrients into the sediment or dredged material for *in situ* treatment.

Biological Oxidation

Chemical oxidation has demonstrated little real success for oxidation of contaminants in sediments to date; augmentation of natural biological oxidation through amendment with preferred electron acceptors such as $CaNO_3$ appears much more promising. Ex-situ chemical oxidation might have greater potential given that the contact between the reagents and the contaminants could be better optimized. However, data from technology demonstrations to date (Estes et al. 2011) suggest that even in a slurry reactor, chemical oxidation is of limited effectiveness. Here again, a closer examination of the operating parameters, sediment composition, and reagent dosages might offer information that could be utilized to improve performance. Pre-treating the sediment to remove organic matter would eliminate a significant source of competition for the reagents, although it could also negate the need for oxidation processes to begin with, depending on the character of the residual sediment and the treatment objectives. This suggests that optimized physical separation processes may be just as effective as chemical oxidation, at lower cost, and would avoid concerns regarding environmental impacts of oxidizing reagents. Given that both organics and carbonates can act as reagent scavengers, however, separating the organics from the mineral matrix of the sediment prior to oxidation would eliminate competition for reagents from the carbonates. This may be a better approach than attempting to treat the bulk sediment, and may deserve further exploration, together with the potential for exploiting the synergy of complementary processes. For example, combining *in situ* electrokinetic heating with persulfate addition and nutrient delivery, could encourage production of free radicals and chemical oxidation in addition to enhancing subsequent biological degradation. Liming to stabilize metals may also augment radical production in association with persulfate treatment. These are concepts that could be further explored as a high risk (the potential for success is uncertain), high payoff research area.

There may be potential for amending sediments during beneficial use placement to establish conditions favorable to biological degradation; this could be evaluated on a preliminary basis in bench testing. Use of a carbon-based nutrient delivery system seems promising and would fit well with an engineering-monitored natural attenuation protocol, providing early sequestration of contaminants and rapid risk reduction, followed by enhanced biological degradation of contaminants over time, achieving long-term risk reduction.

Numerous lab-scale studies suggest that biodegradation should be feasible if field conditions can be managed to achieve efficiencies approaching those attained at bench scale. A number of issues were identified in the studies reviewed that could potentially be addressed in an optimized biological treatment “system,” whether land based (such as composting) or ex-situ (biological reactors). Here again, potentially complementary processes to maximize contaminant removal, degradation or stabilization should be evaluated in conjunction with effective system controls for optimized conditions of the target processes. All of the following appear to be deserving of further consideration:

- Planting to maximize root zone oxygenation and/or plant uptake
- Composting or amending sediments (e.g. $CaNO_3$ addition) to augment biological degradation

- Aerobic/anaerobic cycling to achieve degradation of recalcitrant organic compounds
- Bioleaching with sulfur oxidizing bacteria for metals removal
- Thermophilic bacterial treatment
- Electrokinetic nutrient delivery[1]
- Staged biological treatment – organics decomposition, followed by bioleaching of metals
- Co-discharge of thin lifts of sediment and amendments (wood chips, sewage sludge) to establish workable, premixed layers for composting

The Antoniadis et al. (2012) study provides some support for the concept of utilizing a waste product, such as high ammonia feedlot runoff, to load an amendment such as zeolite to provide a dual purpose nitrogen source for bacterial and/or phytotreatment of organic contaminants. The potential for metal binding on the zeolite is also attractive, and could perhaps mitigate the toxicity of metals sometimes encountered in biological treatment. The reversibility of metals uptake by zeolite under environmental conditions would require further study, as would the cost as compared to alternate nitrogen sources, commercial fertilizers, and sorbents or ion exchange media. The potential synergy makes this an attractive concept deserving of further investigation.

Overall, while biological treatment still holds promise, further development is required to establish operational conditions needed to maximize contaminant degradation. Further, performance likely should be evaluated in terms of risk reduction, rather than contaminant concentration thresholds solely, as biologically unavailable fractions cannot be further degraded and also pose little environmental risk. Material handling aspects to facilitate optimum conditions appear to be a key obstacle, particularly when dealing with large volumes of material that may be slow to dewater sufficiently to be trafficable or workable. Moisture and temperature control, oxygen delivery, and other parameters must be optimized and well controlled. Clearly the degradation pathways must be well understood (aerobic, anaerobic), amendments must be well balanced so that they promote the health of the biological community but do not replace the target contaminants as the primary energy source, and intermediate decomposition products, their persistence and toxicity, must be considered.

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[1] The projected cost of EK based on the pilot study conducted in Denmark raises questions regarding the cost effectiveness of this technology in augmenting biological treatment except perhaps for remediation efforts, but the concept merits further study.

Physical Separation

Lessons learned from multiple fractionation studies and physical separation demonstrations suggest that some of the previous failures could be attributed — at least in part — to inadequate characterization of the sediments leading to selection of inappropriate separation processes. In one case in particular, an additional cleaning step designed to remove contaminant rich organic phases from the processed sand may have been all that was necessary to achieve processing objectives. Given the complex relationships between contaminants and different sediment phases, and the sometimes overlapping physical properties of these phases, efficient and selective separation may not always be possible. However, adequate characterization can inform realistic processing objectives and, in many cases, this may make the difference between recovering some decontaminated sediment suitable for beneficial use and complete failure. The key is not necessarily a more complex operation, but selection of processes capable of separating a target fraction that is realistically defined based on appropriate characterization and our understanding of the interaction between contaminants and contaminant-bearing fractions. With such an approach, simplified separation processes may yet have potential to be integrated into a hydraulic dredged material discharge to recover relatively uncontaminated sand fractions. Further bench and small pilot testing would address an existing data gap regarding the relative fate of different sediment fractions under different processing regimes, and the relative efficiency of simple separation processes when appropriately applied.

Passive Water Treatment

Follow-on studies of passive water treatment technologies and delivery systems are needed for treatment of colloid- and DOC-associated contaminants, in addition to low concentrations of ammonia and other contaminants that are occasionally problematic in discharges from CDFs associated with disposal and material processing. The SAMMS™/ InStreem™ floating sorbent plant seems particularly promising. Sonic flocculation of colloids, and colloid removal through addition of oppositely charged colloids, are also potential treatments that could be explored. Further work needs to be done with reactive silt curtains to define their potential applications. While preliminary work shows greater promise for removal of low concentrations of organic contaminants than for metals, testing of silt curtains containing zeolite or other amendments has not yet been undertaken. For all applications, more data is needed to evaluate and understand the value of these passive systems in treating low concentrations of contaminants under different flow regimes, and to develop guidelines for their use. Effective and economical water treatment alternatives will enable processing of greater volumes of dredged material for beneficial use.

Other Treatment Technologies

As an offshoot of the passive water treatment testing, the effective use of geotextile bags to contain dredged material and reduce contaminant releases is another area with potential to facilitate use of moderately contaminated dredged material in beneficial use applications. Modified geotextiles impregnated with various sorbents and/or reactive constituents could be quite effective in preventing unacceptable contaminant releases in appropriate placements. The magnitude and duration of contaminant release over time as compared to unconfined sediments could be studied at relatively small scale under varying conditions to determine whether larger scale demonstrations are warranted. If successful, this could be one of multiple tools that could be used concurrently for an additive reduction in contaminant releases without requiring aggressive extraction or contaminant destruction methods.

H_2S Controls

Identified H_2S controls need to be demonstrated at field scale to assess their effectiveness and implementability for different types of sites (CDF sediments and discharges, open water disposal, beach placement, etc.) and to develop guidelines for dosage and implementation.

Synergistic Treatments – Thermal Treatment and Physical Separation

There are aspects of volume reduction and treatment synergy (staging of treatments such that least costly treatment is applied to the largest sediment volume, and the most costly to a reduced volume) that have not yet been extensively explored. High temperature thermal technologies have been shown to be effective in destruction of organic contaminants and immobilization of metals. Capital and operating costs are prohibitive, however, for treatment and management of navigation sediments. Separation of the organic fraction of a sediment using simplified physical separation processes could potentially produce a sufficiently decontaminated sediment for beneficial use, and allow reduction in the scale of the thermal plant required for treatment of the highly contaminated sediment fractions. Effectiveness of simple separation processes tailored to carefully characterized sediments could undergo preliminary evaluation at bench and small pilot scale. If promising, further testing to couple these processes with smaller scale thermal treatment plants could be considered.

8 Conclusions

Some degree of contaminant reduction was evidenced for all of the treatment technologies identified in the literature search. The subset of treatments that are potentially cost-effective for treatment of dredged material to enable beneficial use is relatively small, however. While treatment technologies resulting in a high degree of contaminant destruction would certainly be desirable, high treatment efficiency is generally too costly for management of navigation dredged material. Further, high treatment efficiency may not be necessary to enable beneficial use of appropriately selected sediments; in some cases, simply reducing contaminant levels to some specified risk-based threshold may be sufficient. Given the inconsistency of results obtained with many of the treatments demonstrated, it may be more reasonable to shift focus from *ex situ* contaminant destruction to *in situ* contaminant management. Reducing the bio-available contaminant fraction not only through sequestration, but also through control of geochemical processes, may be feasible and sufficient for many beneficial use applications. Further, it may be possible to simultaneously integrate enhancements to natural degradation processes such that degradation of residual contaminants also proceeds over time; co-disposal of nutrients and carbon sources is one possible approach. This would achieve both short-term and long-term risk reduction, and could be applicable not only to beneficial use of navigation sediments but potentially to contaminated sediment sites as well. This approach is synergistic with engineered monitored natural recovery (MNR) concepts, and is potentially more sustainable than high energy treatments.

Treatment metrics also deserve re-examination, however. Risk is not always well represented by bulk sediment concentrations, and there are well-established biological testing procedures that were developed to address these inconsistencies for dredged material disposal evaluations. Whether employing *ex situ* or *in situ* treatment, treatment objectives targeting a specified risk reduction level may be more appropriate — and more attainable — than treatment to a specified bulk sediment concentration. As observed in the Jones Island composting demonstration, complete degradation of PAHs in the sediment may have been hindered by a lack of bioavailability, suggesting that perhaps the risk for these sediments was not high to begin with. In cases like this, before concluding that improvements in the treatment process are needed, a re-assessment of bioavailability and toxicity of the residual contaminants would be logical. A well-designed treatment protocol would incorporate periodic assessment of "changes in bioavailability as a result of the treatment," in addition to assessment of bulk sediment concentrations. A successful treatment endpoint might be defined not as a target contaminant concentration, but as a biological metric – such as an acceptable uptake or toxicity threshold. As anecdotal data is developed to support this concept, a new treatment paradigm may emerge.

Future research areas

Little federal research funding has been devoted to basic research for sediment treatment to date; all of the demonstration programs have relied on vendor technologies with rather dismal results. However, the lessons learned from those previous demonstrations can be used to appropriately focus potentially high payoff research. The following are research areas where further investment is needed and having good potential to be fruitful.

- Geochemistry controls coupled with sequestration and facilitation of degradation processes for short- and long-term risk reduction at beneficial use sites
- Geochemical modeling as a tool for designing *in situ* risk reduction treatments
- Development and testing of innovative, passive water treatment methods for colloid and ammonia removal in the CDF setting
- Demonstration of H_2S controls for confined disposal and beneficial use settings
- Enhancements to improve the effectiveness of *ex situ* composting and in-CDF biodegradation
- Integration of geochemical characteristics and processes for sediments, binders, and their products in solidification/stabilization, to improve modeling of long-term contaminant mobility and to improve formulations for treatment effectiveness
- Focused physical separation testing to improve effectiveness through targeted removal of contaminant-bearing phases (hard carbon, amorphous organic carbon, oil and grease) with simplified and economical processes
- Evaluation of contaminant containment achievable with "smart-bags" – geotextile containment systems incorporating reactive materials

- Improved treatment efficiencies attainable through synergistic combinations of *ex situ* treatment technologies targeting past failure points

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14. ABSTRACT

Growing constraints on conventional dredged material disposal are motivating movement toward more sustainable alternatives. Given the lack of universal beneficial use criteria, even the low levels of contaminants typically found in navigation channel sediments may limit or preclude their beneficial use. Intensive treatment to remove or destroy contaminants in such sediments is typically too costly to be a viable alternative within the context of navigation dredging; economical, low tech sediment and water treatment processes are needed. Recent developments in the area of sediment treatment were assessed through an extensive literature search, and promising technologies were identified. Potentially high value research areas were also identified, to inform subsequent bench and pilot testing. Geochemical contaminant controls and modeling, passive water treatment methods for colloid and ammonia removal, H_2S controls, in-CDF biodegradation, aerobic/anaerobic composting, phase specific physical separation, low temperature thermal treatment, reactive geobags, and coupled geochemical/stabilization process modeling were areas identified as deserving of additional research investment.

15. SUBJECT TERMS

Dredged material disposal
Navigation dredging
Sediment treatment
Passive water treatment
Geochemical contaminant control in CDF
biodegradation
Aerobic/anaerobic composting
Physical separation
Thermal treatment
Reactive geobags

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