# DON'T LET YOUR DISPOSAL SITE GO SOUR ON YOU

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## ABSTRACT

Estuarine sediment when placed in confined upland sites and allowed to dewater can result in the formation of acid soils and low pH runoff. This condition is due to changes in the chemistry of the soils. The potential environmental impact of sediment-associated metals is influenced as much or more by the internal and external physical, chemical, and biological conditions of the sediment as the concentration and extractability of the metals. The potential mobility, bioavailability, and toxicity of metals in sediments are strongly dependent on redox (reducing and oxidizing) and pH conditions. As a result, when dredged material is dewatered and allowed to oxidize, the potential exists for the runoff and leachate to impact surface and ground water quality and violate site discharge permits.

Several methods are available to control environmental conditions (Eh, pH,  $O_2$ ) affecting the formation of acid soils in confined upland sites. Some examples of such methods include; direct incorporation of soil amendments such as liming materials, and organic matter, to reduce Eh and to capture metals; surface ponds and overland flow to maintain saturated, reduced soil conditions; and establishment of healthy vegetation soil covers with or without a low permeable subsurface layer to isolate the final layer of dredged material from the environment. Although synthetics have been used in landfill covers they are generally too expensive for use at dredged material placement sites.

The practical considerations of using solid amendments are generally based upon the economics of the method. Factors such as how much alkalinity (acid neutralization) is needed, the cost of the amendment, costs for transportation to the site of application, and the cost of applying/mixing of the amendment into the soil will varying from site to site.

This paper describes the theory of acid formation in estuarine dredged materials and presents several management considerations for confined disposal of potentially acidic dredged materials as they pertain to the management of potentially acid forming dredged materials.

Keywords: Dredged Material, Acid Sediments, Confined Disposal, Upland Disposal, and Dredged Material Management.

#### **INTRODUCTION**

Estuarine sediment when placed in confined upland sites and allowed to dewater can result in the formation of acid soils and low pH runoff. This condition is due to changes in the chemistry of the soils. As a result, the potential exists for the runoff water to impact surface water quality and violate site discharge permits. The purpose of this paper is to present the theory of acid formation in upland confinement of estuarine dredged material and to discuss various options that could be used to properly manage these materials. The authors will also present suggested steps to develop an acid control plan.

#### **Review of Acid Formation and Leaching of Metals**

The potential environmental impact of sediment-associated metals is influenced as much, or more, by the internal and external physical, chemical, and biological conditions of the sediment as the concentration and extractability of the metals. Total metal concentrations in sediments do not give a good estimation of the "free" or leachable fraction. Metal concentrations in the leachate from different sediments with similar metal contents can vary greatly.

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The potential mobility, bioavailability, and toxicity of metals in sediments are strongly dependent on redox (reducing and oxidizing) and pH conditions.

A dominant role in controlling metal leachability from sediments is played by sulfides. Sulfides are stable only in the absence of oxygen, and in-place, water-saturated, marine sediment. In the sulfidic anoxic environment, even if metals heavily contaminate the sediment, organisms are considered to still be safe due to the strong role of sulfides  $(S^{2-})$  and hydrogen sulfide (HS<sup>-</sup>) in binding the metals in environmentally stable and biologically unavailable forms. The ability of sulfides and authigenic iron sulfide minerals to complex many transition and heavy metals ions is well known (Khalid et. al. 1977) and accounts for the lack of metal leachability from saturated, anoxic sediments or dredged material.

Sulfides in the sediments are generally characterized into two types: acid volatile sulfides (AVS), those forms that react to form hydrogen sulfide ( $H_2S$ ) in cold acid, and the more stable pyritic sulfur [cubic FeS<sub>2</sub>]. AVS reactions tend to be relatively rapid and appear to be a key factor in controlling the release of most metals from anoxic sediments in the short term. Very little metal release or bioavailability is noted when, on a molar basis, the concentration of AVS is greater than the sum of the molar concentrations of metals that bind with sulfides. When the ratio of the AVS to concentration of these metals drops below 1.0, these metals will usually become soluble.

Criteria for the estimation of the middle- and long-term behavior of metals must include the ability of the sediment matrices for producing acidity (Acid Producing Capacity, APC) as well as for forming acid-neutralizing or buffering constituents (Acid Consuming Capacity, ACC). The major acid-producing oxidation reactions (reaction with oxygen) leading to a decrease in pH in low-buffered sediments (low ACC) are listed in Figure 1.

Inorganic sulfur driven:	$H_2S + 2 O_2 = SO_4^{2-} + 2 H^+$
	$S^{-} + 3/2 O_2 + H_2 O = SO_4^{2-} + 2 H^+$
Iron/sulfide driven:	$FeS + 9/4 O_2 + 3/2 H_2O = FeOOH + SO_4^{2-} + 2 H^+$
Iron driven:	$Fe^{2+} + \frac{1}{4}O_2 + \frac{5}{2}H_2O = Fe(OH)_3 + 2H^+$
Nitrogen driven	$NH_4^+ + 2 O_2 = H_2O + NO_3^- + 2H^+$
Organic nitrogen driven:	$R-NH_2 + 2 O_2 = R-OH + NO_3^- + H^+$
Organic sulfur driven:	$R-SH + H_2O + 2 O_2 = R-OH + SO_4^{2-} + 2 H^+$

## Figure 1. Acid-Producing Oxidation Reactions in Sediments

Of these, the sulfide and sulfur reactions are of primary importance to the solubility of most metals as these reactions remove the binding sulfide from the system as well as lower the pH of the system.

The acid-neutralizing (consuming) capacity (ACC) of sediments is determined by the amount of exchangeable bases and by the contents of carbonates and easily weatherable silicate minerals. Most marine heavy clay sediments have appreciable amounts of smectite clays and their exchange complex. When fully saturated with bases smectite clays are capable of neutralizing most of the acidity released by the oxidation of up to about 0.5 percent pyrite-S, so that the pH will not drop below 4.0.

If the clay fraction is predominantly kaolinitic, or if clay contents are low (i.e., less that 0.5 percent) pyrite-S may potentially make the soil very acid. The acidity from 1 percent of pyrite-S is approximately balanced by 3 percent

calcium carbonate. Carbonates are often produced during the reduction of sulfate by anaerobic bacteria and may be sufficient to offset the subsequent acidification under oxidizing conditions.

Under dewatered, moist aerated (oxidized) conditions, the iron sulfides in sediments/dredged material oxidize rapidly to ferric iron and sulfuric acid similar to that of iron sulfide rich soils described by Bloomfield and Coulter (1973) and Singer and Stumm (1970). Although there is disagreement as to the order, speed, and source (chemical or biological) for each reaction, the general consensus is that oxidation of pyrite is brought about by one or more of the reactions in Figure 2.

1. $2\text{FeS}_2 + 2\text{H}_2\text{O} + 7\text{O}_2 \Rightarrow 2\text{FeSO}_4 + 2\text{H}_2\text{SO}_4$	(Chemical)
2. $4\text{FeSO}_4 + \text{O}_2 + \text{H}_2\text{SO}_4 \Rightarrow 2\text{Fe}_2(\text{SO}_4)_3 + 2\text{H}_2\text{O}$	(Biological)
3. $\operatorname{FeS}_2 + \operatorname{Fe}_2(\operatorname{SO}_4)_3 \twoheadrightarrow \operatorname{3FeSO}_4 + 2S$	(Chemical)
4. $2S + 6Fe_2(SO_4)_3 + 8H_2O \rightarrow 12FeSO_4 + 8H_2SO_4$	(Chemical)
5. $\operatorname{FeS}_2 + 7\operatorname{Fe}_2(\operatorname{SO}_4)_3 + 8\operatorname{H}_2\operatorname{O} \implies 15\operatorname{FeSO}_4 + 8\operatorname{H}_2\operatorname{SO}_4$	(Combines 3 & 4)
6. $2S + O_2 + H_2O \rightarrow 2H_2SO_4$	(Biological)

#### Figure 2. Reactions Oxidizing Pyrites

In the overall reactions, microrganisms *Thiobacillus* ferrooxidans (Equation 2) and *Thiobacillus* thiooxidans (Equation 6) are primarily responsible for oxidizing Fe+2 to Fe+3. (*Thiobacillus ferrooxidans* is a chemoautotrophic bacteria that grows at pH 2.0 - 4.5 and oxidizes both iron and sulfide. *Thiobacillus thiooxidans* is a chemoautotrophic bacteria that grows at pH 2.0 and oxidizes S or sulfide. Both bacteria are ubiquitous in soils and sediments that are aerated and oxidized. (Martin and Focht 1977) The Fe+3 is then chemically reduced by pyrite,  $Fe_2(SO_4)_3$ , producing acidity and additional Fe+2, which in turn is oxidized to Fe+3 by the microrganisms. Under moist, aerated (oxidized) conditions, the reactions are self-catalytic.

The rate of oxidation of iron sulfides could be decreased by controlling the levels of *Thiobacillus* ferrooxidans or soluble Fe+3 in the soil. Bactericides such as lauryl sulfate have been used to reduce microbial activity and both lime and organic matter decrease the levels of available Fe+3 (Singer and Stumm, 1970). Organic matter is thought to complex Fe+3 and also reduce it to Fe+2, while lime, by raising soil pH, causes Fe+3 to precitate as  $Fe(OH)_3$ .

Calculating the acid producing capacity (APC) and acid consuming capacity (ACC) for sulfidic mining residues have been estimated by analysis of the total pyritic sulfur. Potential acidity is then subtracted from the neutralizing potential. This is obtained by adding a known amount of HCl, heating the sample and titrating with standardized NaOH to pH 7. However, the APC-relationships of sediments are more complex than that of sulfidic ores because the APC from organic matter in the sediment must be considered. Time-scale plays a major role in sediments because any organic matter in the sediment will also require oxidation during sediment drying and can prolong the oxidation of sediment pyrite for a longer period of time. Generally, sediments with very little organic matter will have sediment pyrite oxidized quicker than sediments containing large amounts of organic matter. One soil treatment to counteract the effects of sediment pyrite oxidation is the addition of large amounts of organic matter.

# POTENTIAL FOR ENVIRONMENTAL IMPACTS FROMUPLAND CONFINEMENT OF ESTUARINE DREDGED MATERIALS

#### **Environmental Impacts of Estuarine Pyrites in Dredged Materials**

Ohimain (2004) presents a discussion of the environmental impacts of oilfield infrastructure in the mangrove areas of the Niger Delta due to dredging for navigation and clearance of vegetation. Excavated materials are cast on land along a right of way and piled up as bare heaps of acidic dredged material that can impact the surrounding environment. The estuarine sediment heaps or stockpiles of soils with pH's as low as 2.3 have been reported to kill vegetation and fish, and cause significant changes in water quality with increases in heavy metals (Ohimain, 2003). Ohimain attributes the acidification to reduced iron sulfides, particularly pyrite, and presents an illustration of the formation of the acid sulfate soil from pyrite in Figure 3.

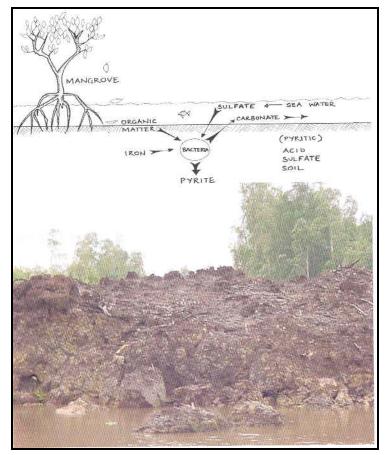


Figure 3. Acid Sulfate Pyrite Soil – Niger Delta Mangrove (Ohimain 2004)

The photograph in Figure 3 also shows one of these abandoned heaps of acid sediment deposits along a channel bank in the Niger Delta. Ohimain states,

"that after several cycles of natural weathering, the dredged materials often become relatively lower in salinity and acidity, and are then colonized by acid and metal tolerant invading species.....Grasses are usually the first to colonize the sites, followed by shrubs mostly Alchornia cordifolia and the Siam weed (Chromolaena odoranta) and as conditions becomes more favorable other non-mangrove plants become established. Woody trees such as Alstronica boonei (stool wool), Musanga cecropioides (umbrella trees) and Anthoclesta vogelii (cabbage tree) are now common on abandoned/weathered dredged material heaps in the delta." What Ohimain has described is the natural succession of vegetation if nature is left to deal with the existing disposal practice.

Ohimain (2003) further suggests methods to prevent or control acidification by using techniques that selectively prevent either air or water from reaching the materials, neutralize acidity, or inhibit acid-forming bacteria. However, he emphasizes that prior to dredging, the sediment should be analyzed for acid production and resulting potential for metals leaching, and that the relocation method and areas for placement of the dredged material be chosen to have the least impact on the delta. He makes a case for beneficial uses of the dredged material such as construction of coastal habitat to reduce coastal erosion, backfilling of abandoned canals (channels) that once provided access to the oil wells, thin layer nourishment of subsiding wetlands, and use of open water natural depressions by raising sediment bottoms to encourage recolonization of wetland habitat.

Finally, Ohimain recommends the development of an acid sulfate soil management plan to mitigate potential impacts from acid-forming dredged materials. Briefly stated,

"The management plan should contain strategies to manage the potential impacts of activities that are likely to disturb the acid sulphate soils. The ASSMP should specify all potential environmental impacts, performance criteria, and mitigation strategies together with relevant monitoring and reporting requirements, and where an undesirable impact or unforeseen level of impact occurs, the appropriate corrective action. The ASSMP should be structured to address the key elements of environmental management onsite and the performance criteria for all elements determined."

## **Environmental Pathways of Concern in Upland CDF's**

As long as the sediments remain anoxic, the metal sulfide compounds are very stable and largely insoluble. However, with the introduction of oxygen or oxygenated seawater, the sulfide compounds will rapidly oxidize to sulfate, acidifying the medium and solubilizing the metals. This reaction is well documented by published literature (Khalid et. al. 1977) and by comprehensive bench-scale testing (Folsom et. al. 1981). These research findings were the basis for the evaluation of disposal alternatives for contaminated dredged material as a management tool to minimize adverse environmental effects by Gambrell et. al. (1978).

The principal pathways of concern associated with the upland placement of estuarine dredged materials are effluent discharges during placement, runoff from rainfall events, and potential discharges to surface water and groundwater via seepage through dikes; and, leachate into fill material and foundation soils. Food web impacts through plants and animals colonizing the site can also become a potential contaminant loss pathway during and after closure.

## Effluent During Placement

Effluent discharges during placement can be controlled with appropriate sized ponded area and spillway weir boards. Acidity should not be a concern during placement because the sediment will not oxidize to any appreciable extent as long as the site does not dewater sufficiently to provide significant changes in redox status. Also, as long as the suspended solids are contained within the CDF, water quality should be acceptable.

#### Groundwater

Impacts of acid soils on groundwater are very site and material specific. Dissolved concentrations of some metals in the leachate might increase if the pH of the soils and groundwater decreases. Leachate from dredged material placed in a CDF is produced by three potential sources: gravity drainage of the original pore water, inflow of groundwater, and infiltration of precipitation. Immediately after placement, dredged material is saturated, begins to dewater, and consolidate resulting in seepage remove water from the voids. Because the amount of water stored and available for gravity drainage decreases, the generation and transport of leachate in a CDF is highly dependent on site-specific conditions at the disposal site such as dredged material hydraulic conductivity, initial water content, and nature of any contaminants in the dredged material. All these factors must be evaluated to predict time-varying leachate flow and quality (USACE 2003).

Groundwater modeling using the Hydrologic Evaluation of Leachate Production and Quality (HELPQ) model can be used to simulate these processes for selected placement scenarios (USACE 2003). HELPQ may be used to predict impacts on groundwater flow and quality of the deposition of dredged material in the CDF. Important climatic variables needed include precipitation, temperature, wind, and humidity. Important hydrologic processes include infiltration, runoff, and evaporation. Important subsurface processes include evaporation from dredged material voids and flow in unsaturated and saturated zones.

If contaminant migration is deemed a potential problem, barriers might be required to minimize migration. Any barrier design would probably require modeling based on the groundwater database to determine optimum placement and potential effectiveness. Background water quality data of receiving water will be needed to compare with groundwater quality in vicinity of the CDF.

## Surface Runoff

Surface runoff resulting from rainfall events could result in solids becoming resuspended from wet barren dredged material after the ponded water has been drained off the site. Raising the weir boards will control suspended solids and not allow them to be discharged over the weir. This will likely control the release of metals, because the material will still be largely anoxic and reduced keeping the metals bound with the solids.

As the surface of the dredged material is allowed to dry and oxidize, acidity will begin to form as the iron pyrite in the dredged material begins to oxidize. The quality of the surface runoff will become acid and soluble metals will increase. This change in runoff water quality has been well documented at the USACE Field Verification Program (FVP) site (Folsom et al. 1988 and Skogerboe et al. 1987). Under upland conditions, as the surface of the dredged material dried, the amount of suspended solids in the runoff was observed to decrease from 9,247 to 151 mg/l at the FVP site. While the dredged material was wet, unfiltered runoff contained elevated copper, nickel and zinc. But the concentrations of soluble metals were extremely low because the metals were tightly bound with sulfide and the fine particles of dredged material. Therefore, controlling the suspended solids in the early stages of drying should control the discharge of metals.

After drying and oxidizing, surface runoff at the FVP site had lower suspended solids but metals observed in both the unfiltered and filtered runoff exceeded water quality standards and were essentially all in the soluble form. In addition, surface runoff pH decreased from 7.5 to 4.7 after drying (Folsom et al. 1988 and Skogerboe et al. 1987).

Soil amendments have been shown to adjust soil pH and soluble metals in runoff water at the FVP site. Application of lime and manure reduced the soluble metal concentrations in surface runoff water from 0.56 to 0.02 mg/l for cadmium, from 47 to 2.0 mg/l for copper, and from 40 to 2.3 mg/l for zinc. Even these massive decreases in metal concentrations in runoff water did not produce water quality that was acceptable for discharge to the receiving water without a mixing zone. The total metal concentrations in FVP Black Rock Harbor sediments were extremely high in the dredged material (23 mg/kg cadmium, 2,850 mg/kg copper and 1,370 mg/kg zinc, Folsom et al. 1988 and Skogerboe et al. 1987 ).

## **Plants and Animals**

One of the best indications of the environmental effects of placing metal contaminated dredged estuarine materials in both upland and wetland environments was observed at the FVP site (Brandon et al. 1991). The potential for the dredged material to become acid is because of iron pyrite in the dredged material. Consequently, the effects of the soil pH decreasing from pH 7.0 to 3.2 in unamended dredged material at the FVP site will more than likely occur for unamended dredged esturine material at many sites. The surface runoff discussion previously indicated an increase in the solubility of metals under acidic pH conditions; consequently, no plants colonized the control plots of unamended dredged material at the FVP site. Soil pH was 3.2, metals were soluble and everything planted on the unamended plot germinated and quickly died. Conversely, plants did colonize the lime and manure amended dredged material plots. The soil pH was 4.7, but the acid and metal tolerant plants that colonized the plots did not contain any more metals than normal plants. Acid and metal tolerant plant species were planted on the amended plots with soil pH values of 4.7. These plants were studied at the FVP site. The plant species were selected from USACE Report IR-EL-85-2 (Lee et al. 1985). Very few invertebrate animals (32) were collected on the unamended acid dredged material plots. However, lime and/or manure amended plots had more abundance and diversity (from 151 to 223). There was insufficient invertebrate biomass to conduct chemical analyses to determine tissue metal contents. It can be predicted that unamended HMI dredged material with acid pH values will more than likely have relatively few invertebrate animals colonizing the site. Amendments such as liming and organic materials will no doubt increase both abundance and diversity of plants and invertebrate animals on site.

Another good indication of plant persistence on acidic dredged materials is a paper by Palazzo et al. 1995. Organic matter in the form of chicken manure and biosolids improved the establishment and colonization of plants on two different sites, one in Mississippi and the other in Maryland on the C&D Canal. This paper illustrates the importance

of amending pyrite acid dredged material with organic material and liming materials to control acidity and metal solubility.

# ACID SOILS BUFFERING INVESTIGATIONS

A significant component of acid soils management is the determination of the amount of acid neutralization needed for the acid forming potential in estuarine sediments. An estimate of the amount of acidification the complete oxidation of the sulfur in the sediments would cause can be made. In assays of sulfur content in several Chesapeake Bay CDF's between 0 and 1 ft depth at 20 sampling sites, and at 5 to 6 ft depths at 10 sites, sulfur levels averaged 589 mg/kg ( $\pm 125$  mg/kg), and 403 mg/kg ( $\pm 108$  mg/kg) respectively. A concentration of 600 mg/kg of sulfur is equal to 0.0176 M sulfur in each kg of sediment. If this amount of H<sub>2</sub>S were reacted with O<sub>2</sub>, as in the first equation shown in Figure 1, 0.0176 M of sulfate and 0.035 M of H<sup>+</sup> would be produced. This much hydrogen ion, H<sup>+</sup>, in 1 liter of distilled water at pH 7 would bring its pH down to 1.45 units. This is serious acidification. This rough calculation of course ignores all other materials in the sediments that might offset (buffer), or increase, the effects of the onset of an oxidative atmosphere. It is also doubtful that the acid from each kg of H<sub>2</sub>S would be dissolved in a whole liter of leachate, increasing its effect.

# **MES Test Plots**

The Maryland Environmental Service (MES) (Slatnick 2000) conducted field soil and water-buffering studies at Hart-Miller Island (HMI) dredged material containment facility between 1998-2000. The test plot was divided into four quadrants that received lime and compost, lime only, compost only, and no amendments. In June 1998, sixty to eighty tons of compost was spread by bulldozer onto one-half of each one-acre test plot in the South Cell of HMI. The compost was thoroughly tilled into the top layer of soil. Four tons of agricultural lime was incorporated in the acid soils by a spreader on a tractor. The soil in these plots was sampled and tested. The four plots were subdivided into 8 plots and planted with different short- and tall- species mixes of vegetation. *Phragmites* growth was observed in all plots. A second modified planting was performed in June 1999 after 270 tons of compost and 4 tons of lime was incorporated in Plot Number 1. Native seed mix of tall and short grasses and ornamental species was applied at 12 lbs per acre. In December 1999, MES (Slatnick 1999) reported that *Phragmites* covered about 30% of the test plot.

In January 2000, two soil samples were taken in the test plot near Spillway No.5 of the South Cell. One sample represented the 6-12 inch horizon and the other sample was representative of the 18-24 inch horizon. Table 1 shows

Sample Identification	Sample Location	Buffer pH <sup>1</sup> STD	Neutralization Potential <sup>2</sup> Ton/KT	Soil pH <sup>3</sup> STD	Potential Acidity <sup>4</sup> Ton/KT	Sulfur <sup>5</sup> % / Weight	
South Cell 1	6"-12"	6.95	6.61	3.4	10.9	0.35	
South Cell 2	18"-24"	6.95	0.95	3.6	14.1	0.45	
<i>The results of the individual parameter analysis are used in combination to calculate lime requirements.</i> <sup>1</sup> A measure of soil pH, which takes into account the texture of the soil (i.e. clay, silt) for lime requiremen							

calculations.

<sup>2</sup> A measure of the presence of acid neutralizing minerals in the soil.

<sup>3</sup> A measure of the active acidity of the soil.

<sup>4</sup>An estimation of the lime requirement using the soil pH, buffer pH and oxidizable sulfur content of the soil.

<sup>5</sup>The oxidizable sulfur content of the soil ( $H_2SO_4$ ), which produces soil acidity as a result of the soil weathering processes.

the results for buffer pH, neutralization potential, soil pH, potential acidity and sulfur to determine the approximate lime requirement. The amount of lime needed to raise the soil pH to approximately 7 pH units in the 6-12 inch and 18-24 inch layers is calculated by subtracting the neutralization potential value from the potential acidity value. MES (Slatnick 2000) calculated a lime requirement to be 4.3 and 13 tons/acre, respectively, for each 6-inch layer.

On February 22, 2000, MES (Slatnick 2000) took a water sample to provide a baseline of the test plot water quality prior to soil amendment activities. Results of the analysis are presented in Table 2.

Parameter	Maryland Toxic Substance	Total Metals	Dissolved Metals		
r ai ainetei	Criteria <sup>1</sup>	(mg/l)	(mg/l)		
Antimony	NC	< 0.002	< 0.002		
Arsenic	0.069	0.004	0.003		
Beryllium	NC	0.017	0.015		
Cadmium	0.043	0.005	0.005		
Chromium <sup>2</sup>	1.1	0.008	0.004		
Copper	0.0061	0.076	0.059		
Lead	0.14	0.007	0.003		
Mercury	0.0021	< 0.0002	< 0.0002		
Nickel	0.075	0.716	0.685		
Selenium	0.3	0.009	0.008		
Silver	0.0023	< 0.001	< 0.001		
Thallium	NC	< 0.002	< 0.002		
Zinc	0.095	4.66	4.23		
<b>Bold</b> indicates result e	exceeded criteria				
n the case of copper	ria available. Maryland Tox, , Estuarine) for Ambient Surj ared to the hexavalent chrom	face Waters. Chron	nium was measured		

Table 2. Hart-Miller Island Test Plot – Water Sample Priority Metal Analysis

Copper, nickel, and zinc concentrations each exceeded the Maryland Toxic Substance Criteria. In June 2002, prior to the start of the South Cell Restoration project, MES collected soil samples from 10 locations in the upper 6 inches down to 3 feet. The samples were sent to the University of Maryland for analysis. Soil pH averaged just below pH 4 in 0-6 inches to pH 5.5 at 30-36 inches as shown in Table 3.

During a site visit in June 2000, Myers and Price (2001) measured soil pH in HMI South Cell using a portable-field pH meter. They concluded that,

"The pH was generally below pH 5.5, tended to increase with depth, and tended to be lower at higher elevations. We noticed a rust color indicating iron oxidation on the banks of a perimeter trench where seepage entered the trench. We were informed that saturated conditions begin about 1 foot beneath the surface in the South Cell. We also noticed extensive coverage of the South Cell with Phragmites, a nuisance plant that MES is attempting to control with herbicides and controlled burns. The North Cell at HMI is an active dredged material disposal area and has not yet developed acid soil conditions."

Depth	Soil pH	Buffer Index	Acidity meq/100g	CEC meq/100g	Organic Matter %	Organic Matter Lbs/Ac.	SO4-S ppm	Zn ppm	Mn ppm	Fe ppm	Cu ppm
0-6"	3.9	5.8	11	20	2.7	74	82	13.6	158	541	6.1
6-12"	3.7	5.5	14.4	26.1	2.1	68	1270	18.6	178	786	8.5
30-36"	5.5	5.7	5.4	31.2	4.2	109	1825	>100	961	1984	11.6

Table 3. Selected Average Soil Analyses for HMI South Cell

Similar acidity and buffering measurements were made at the Cox Creek DMCF (dredged material containment facility) as described in an Interoffice Memo (Slatnick 1999). Slatnick describes results of an analysis of the lime requirement for 12 soil samples by Mr. R. Whittington of McKoy and McKoy Laboratories. Using the neutralization potential and the potential acidity values, a value for the lime dose was determined. This method determined that 8.9 tons of lime/acre were necessary to adjust the pH of the top 6 inches of soil. This result would indicate a very large acid production potential. Similar testing should be conducted on samples that will be representative of any estuarine dredged material to be placed in a CDF and allowed to dewater to assess the potential for acid soils conditions

## **Courthouse Point (USACE Philadelphia District)**

The Courthouse Point Confined Disposal Facility is located in Cecil County, Maryland. The Maryland Department of the Environment (MDE) expressed concern about acid soils formation resulting in low pH- pore water within the site and the subsequent leaching into the underlying aquifer or seeping into the C & D Canal affecting water quality. MDE proposed that the USACE incorporate crushed limestone in the dredged materials to neutralize potential acid soils conditions. In 2001, the Philadelphia District hired Duffield Associates, Inc. to identify a preferred method for applying neutralization materials as a "buffer layer" to be incorporated into the surface and sides of the containment area prior to additional dredged material placement.

As a result, Duffield Associates Inc. (2002a) prepared a work plan to conduct a pilot study. The project objective was to apply a "buffer layer" of crushed limestone to the site prior to the next dredging cycle. This "buffer layer" would be designed to neutralize acid conditions resulting from the maintenance material. Duffield Associates was the Prime Contractor and performed oversight and monitoring. After clearing the vegetation from the site, the limestone was applied at an average application rate of 24.5 tons per acre (10.5 lbs per yd<sup>2</sup>) to the site area of 140 acres on September 16, 2002. Onsite quality control testing showed that the application rates varied from 8.1 to 13.8 lbs per yd<sup>2</sup>. The limestone was disked to depths of 8 to 12 inches and approximately 12 inches up the sides of the dikes of the CDF (Duffield Associates 2002b). Martin Limestone of Blue Bell Pennsylvania supplied the crushed limestone (calcite) and Christiana Excavating of Newark, Delaware incorporated the limestone by making four to six passes with a farm disc (with 18- to 24-inch diameter steel discs). Duffield Associates, Inc. reported a total of 3,430 tons of lime was incorporated into the soils. Figure 4 presents a collage of working photos of the liming operations at the Courthouse Point CDF.

Beginning in mid-October 2002, approximately 400,000 CY of fine-grain maintenance dredged material was pumped into the site in a layer of approximately 2-3 feet. Breakdown of the contract costs resulted in approximately \$250,000 for materials, delivery, disking and A/E oversight for the liming. These costs result in \$1786/acre, for the average 8-10-inch deep soil treatment for the 140 acres (Kelly 2003).



Figure 4. Liming Operations at Courthouse Point CDF

# MANAGEMENT STRATEGIES FOR UPLAND SITES

Few options exist to properly manage estuarine dredged materials placed in upland confined disposal sites to reduce acid formation. Several methods are available to control environmental conditions (Eh, pH,  $O_2$ ) affecting the formation of acid soils in confined placement sites. Examples of such methods include: direct incorporation of soil amendments such as liming materials and organic matter to reduce Eh and to capture metals; surface ponds and overland flow to maintain saturated, reduced soil conditions; and establishment of healthy vegetation soil covers with or without a low permeable subsurface layer to isolate the final layer of dredged material from the environment. Although synthetics have been used in landfill covers they are generally too expensive for use at dredged material placement sites. For purposes of this paper, the following discussion will focus on keeping the fill material saturated, addition of amendments, and use of a vegetation cover to isolate the acid soils from the surface water leaching or runoff.

#### **Maintaining Saturated Fill Conditions**

Among the operational approaches already contemplated is to keep the dredged material anoxic (reduced) and not allow the oxidation of the metal sulfides. In most fine grain (silts and clays) sediments containing organic matter (1% -5%), dewatering is difficult and favors maintaining reduced conditions. If not managed for dewatering, the material will form desiccation cracks as a top layer of crust about a foot or less (Figure 5) and the underlying dredged material stays saturated. The water is lost vertically as it moves downward as leachate into the foundation or upward into the cracks as it moves horizontally as seepage to surface waters. These water movements in an upland site are illustrated in Figure 6. Unfortunately, in a true upland site where the dikes are raised significantly above the surrounding ground surface, dewatering by gravity will eventually occur but over a very long time due to the nature of the dewatering and consolidation especially if the material is placed in thick lifts, > 5 foot, and not managed. Special management will be required when the site is no longer used and is eventually closed.

#### Amendments

If the CDF site management plan has been to maximize the amount material stored in the site, then the dewatered acid-forming material will need to be managed. One strategy is to provide sufficient organic matter to maintain reducing conditions by allowing the organic matter to be oxidized instead of the metal sulfides. Examples of



Figure 5. Desiccation Cracks in Fine-Grain Dredged Material

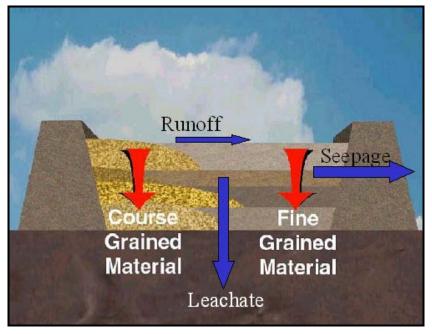


Figure 6. Water Movement in Upland CDF's

organic amendments include cellulose, biosolids (stabilized sewage sludge), and manure. Applications as much as 3000 cy/acre of cellulose and 160 cy/acre of biosolids have been suggested for some Chesapeake Bay sediments (Francingues et al. 2004). Another option is to apply lime as done in agricultural practice and as previously presented in the discussion about Courthouse Point CDF. The amount of lime required per acre-foot of material is determined from the analysis of the acid neutralization requirements of the total amount of acid forming material including the iron pyrite fraction. For highly acid materials, application rates approaching 28 tons per acre-foot may be required. (Francingues, et al. 2004).

The practical considerations of using soil amendments are generally based upon the economics of this method. Factors such as how much alkalinity (lime) is needed, the cost of the amendment, cost for transportation to the site, cost of application, and the cost of applying/mixing of the amendment into the soil will vary from site to site.

## **Surface Cover**

Another approach is to use a vegetated surface cover, which is designed to provide a mass balance of moisture needed to maintain reduced conditions in the dredged material fill. A search of the literature suggests that there are no standard designs or regulatory guidelines for the closure of upland dredged material sites. The U.S.E.P.A. has developed cover systems for landfills but not for dredged material sites. Most states have not developed any specific requirements for closure of upland CDF's, especially those containing estuarine dredged material. Currently, the USACE is preparing a technical note that will discuss various cover systems for confined disposal facilities but it falls short of presenting design criteria (Schroeder 2004).

When considering covers for upland CDF's containing estuarine sediments, there is a basic problem with establishing vegetation directly on top of the dewatered dredged material. If a topsoil layer were placed directly over a very low permeable (almost liner like) dredged material fill, there would be a high probability the vegetation would be highly stressed and could die due to periods of extreme wet and drought conditions because:

- During extreme wet periods the cover would become saturated and the plants could drown.
- Drought would force the plants to send roots deeper into the very tight (highly consolidated) dredged material to obtain moisture but they would probably fail to penetrate.

Eventually, the vegetation would die and the soil surface would become highly susceptible to wind and water erosion. Consequently, the only way a topsoil/vegetation layer would work would be to make it thick enough to provide drainage for shallow root vegetation with enough soil moisture holding capacity to sustain the vegetation during dry periods.

Therefore, the goal that should be selected for a surface cover in this application would be one that can retain precipitation during the wet periods by infiltration into the cover material and to use (reduce) the collected/stored soil moisture during the dry periods by vegetation through evapotranspiration (ET). An assessment should be done to determine the type of cover system needed to keep the top of the dredged material fill near saturation and anaerobic throughout most of the year.

The following the factors should be considered in a cover design:

- Need to infiltrate and evapotranspirate most of the precipitation during a typical wet weather year. Annual meteorological events should be used to forecast this number.
- Topsoil or vegetative support layer having an infiltration capacity of <sup>1</sup>/<sub>4</sub> to <sup>1</sup>/<sub>3</sub> inch of water per inch of soil thickness.
- Cover permeability of  $K = 10^{-4}$  to  $10^{-5}$  cm/sec. (For example, blending of sand with some undetermined percentage of dredged material in HMI could potentially result in an acceptable range of K values but final cover made from sand of desired permeability would be better.)
- Neutralization of acid rain needed to buffer against mobilization of metals in cover and potential for metals toxicity to plants. Derive this value from theory or buffering studies.
- Planting scheme that maximizes water use and stabilizes soil surface. Also, salt tolerant plant species will colonize the site initially if estuarine sediments are used in the cover. A succession of vegetation to freshwater species will occur as the salt is leached from the sediment.
- Site topography to include length of slopes and surface water management needs.

Figure 7 presents a schematic diagram of a typical moisture balancing vegetation cover. This schematic is a generalized design concept. As such, it presents typical design elements that would be incorporated into a final cover. Selection and design of various cover design elements should be based on a calculation of moisture balance (i.e., precipitation, runoff, infiltration, evaporation and transpiration) to establish the multilayer cover thicknesses using a model like HELPQ (USACE 2003).

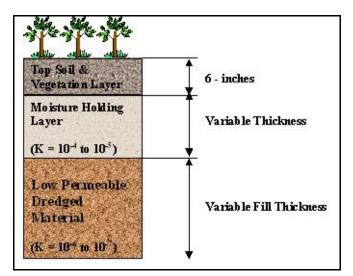


Figure 7. Schematic of Typical Moisture Balance Vegetation Cover

# STEPS TO DESIGN AN ACID CONTROL PLAN

Several steps may be required to design an acid-control plan.

# **Step 1 – Select the End-Use for the CDF**

The first step in the developing a final plan for control of acid forming sediments in upland CDF's is selection of the desired end-use that will dictate the habitat strategy for site. This selection of desirable habitat uses will be critical to the development of an effective and economical acid soil prevention plan. The next step would be to determine how best to close the site. Defining the characteristics of desirable upland habitat in a reference site and developing a list of specific habitat requirements for upland vegetation may achieve this. A sampling program may be needed. For example, take representative samples of the top three ft in various test plots of suitable size and analyze samples for soil pH, nutrients, acid neutralization capacity, vegetation types, infiltration (percolation) rates, and site topography.

## **Step 2 – Select a Closure Option**

A very critical step will be to choose the final closure option that will provide the best opportunity to achieve the goals of maximizing sediment storage capacity while providing the best use of the operating features of the site; and, to achieve minimum production of acid soils and maximum control of any low pH water discharges. The closure option should be selected only after careful consideration of the scheduled project uses of the site and the ability of the closure option to balance both capacity and requirements to control acid soils and low-pH water over the long-term management of site.

## Step 3 – Choose an Acid-Soil Prevention Management Strategy

Select an acid-formation control strategy and begin the process of defining its design features. This task is very site specific and may require several iterations. Assemble physical, chemical, and engineering data on CDF materials potentially available for use as suitable cover materials. If necessary, conduct a geotechnical assessment of the CDF contents for potentially available areas for borrow of course grain material. Review and select potential construction techniques for cover construction on unconsolidated, soft soils. If feasible, demonstrate potentially viable cover construction techniques at the site prior to selection of the final design.

## **Step 4 – Prepare Cost Estimates for a Variety of Alternatives**

Cost estimates will be needed to establish engineering economy of the alternatives that meet the desired management goals. These costs should not only include the capital and operating costs but the annualized costs over project life. At this stage, it may also be wise to conduct an independent review of the engineering and economic analysis of the alternatives developed as part of this process.

#### **Step 5 – Select the Preferred Plan**

The preferred plan is chosen based upon the engineering, environmental, and economic analysis of the potentially feasible options. This choice would normally be made after a public interest review.

#### CONCLUSIONS

Estuarine sediment when placed in confined upland sites and allowed to dewater can result in the formation of acid soils and low pH runoff. This condition is due to changes in the chemistry of the soils. The potential environmental impact of sediment-associated metals is influenced as much or more by the internal and external physical, chemical, and biological conditions of the sediment as the concentration and extractability of the metals. The potential mobility, bioavailability, and toxicity of metals in sediments are strongly dependent on redox (reducing and oxidizing) and pH conditions. As a result, when dredged material is dewatered and allowed to oxidize, the potential exists for the runoff and leachate to impact surface and ground water quality and violate site discharge permits.

Several options exist for the management of acid forming sediments. In practice, the best solution may be simply to keep the dredged material saturated (wet) to avoid oxidation of the metal sulfides. Options such as beneficial uses of the dredged material to restore or nourish wetlands are excellent choices but have limited long-term capacity and are normally viewed as single use options.

Conversely, upland confinement of dredged material can provide for long-term storage capacity (a valuable asset) but these facilities are expensive to build and maintain. Also, location of upland sites is becoming most difficult. By their nature, upland sites that are unmanaged defeat the practice of maximizing storage space by dewatering (drying) the dredged materials but aid in the prevention of acid formation. So, there is a irony with use of upland disposal for the management of estuarine dredged material.

In this paper, the authors have chosen to concentrate on upland management strategies that incorporate either the addition of acid buffering materials as amendments or the use of a vegetated surface cover designed to balance moisture (rainfall and infiltration) within the site. Use of both of these methods together will probably be a logical choice. The amounts and types of amendments and thickness of cover needed are very site and material specific.

A detailed evaluation and design will be needed to choose a preferred management plan. Although, currently there are no standard designs for closing an upland confined disposal site containing estuarine, acid-forming dredged material, the authors suggest several steps to develop a preferred management plan. An obvious conclusion drawn from the discussion is that a management plan to control acid-forming dredged materials will be needed for all upland sites demonstrating this potential.

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