BEHAVIOUR OF DREDGED MUD AFTER STABILIZATION WITH DIFFERENT ADDITIVES

W. CALMANO, U. FORSTNER, M. KERSTEN and D. KRAUSE

1. ABSTRACT
Mechanical stabilization methods for improving chemical stability of contaminated dredged material used for upland disposal are presented. Assessments of long term environmental consequences involving effects on heavy metal immobilization, TCC, COD, BOD, anion release, gas production and composition after addition of lime, calcium carbonate, cement, coal fly ash and gypsum to fine grained Hamburg harbour sediments have been studied. Best results are attained with CaCO₃ due to in situ pH conditions and sufficient buffer capacity, which is of prime importance for metal immobilization and gas production.

2. INTRODUCTION
2.1. Dredged material disposal
Sediments are increasingly recognized as both a carrier and a possible source of contaminants in aquatic and terrestrial ecosystems. This is especially valid for "dredged materials". As shipping demands minimal water-action or current within the harbour basins, this means that optimal conditions have been created for the sedimentation of river or sea-borne material. In order to maintain these ports and channels accessible to marine shipping, this material has to be removed regularly by dredging (1). Material dredged from waterways and harbours of the United States amounts approx. 250 million m³ annually (2). In the river mouths to the southern coast of the North Sea, approx. 20 million m³ have to be dredged from Rhine/Meuse (Rotterdam Harbour) and approx. 10 million m³ from the rivers Scheld (Antwerp), Weser (Bremen/Bremerhaven) and Elbe (Hamburg) (3). The total quantity of sediment which is dredged in the Netherlands, Belgium, and West Germany amounts to about twelve times the total suspended matter supply from the Rhine (1). The possibilities of disposal of these enormous quantities of material are severely limited because of the pollution present in the dredged material.

The major disposal alternatives are subaqueous (open-water) disposal, application to intertidal sites, and upland deposition. These categories differ primarily in the biological population exposed to the contaminated sediments, oxidation-reduction conditions, and transport processes potentially capable of removing contaminants from dredged material at the disposal site (4).

In discussions of environmental problems associated with contaminated sediments it is now widely accepted that the ecologi
cal significance of pollutant inputs is determined by the specific form and reactivity of the compound rather than by its rate of accumulation. This effect typically refers to adsorbed metal pollutants which may become partly mobilized in the aquatic milieu by changes in pH and redox conditions. While the first two factors typically relate to upland disposal of dredged materials, the effect of salinity is more important for the deposition of freshwater sediments in intertidal and coastal marine environments.

2.2. Stabilization techniques

Once the potential impacts of pollutants are determined, a management plan can be formulated in order to minimize the environmental pollution upon disposal of dredged material. Stabilization techniques proposed for solid waste materials and contaminated soils (5) may be considered for in-situ measures on polluted sediments:

(i) construction of mechanical barriers (encapsulation);

(ii) fixation of water by addition of chemicals;

(iii) formation of sparingly soluble compounds by chemical reactions (chemical immobilization); and

(iv) reduction of mobility of critical compounds by changes of pH/redox conditions.

In general solidification-stabilization technology is considered a ‘last approach’ to the management of hazardous wastes. The process mostly adopted world-wide for the immobilization of metal containing wastes is that of solidification-stabilization with a silicate based admixture using, e.g., cement, waste kiln dust, or power station fly ash (6). This solidified product can be designed to have excellent leachate quality - i.e., capacity to retain the toxic pollutants.

Remedial measures for toxic organic chemicals are not yet available on a larger scale, but should probably be based on the affinity of these compounds to solid organic matter. Several strategies were proposed for mercury contaminated sediments (7, 8, 9):

(i) conversion of mercury to mercury sulphide with a low methylation rate (anaerobic conditions);

(ii) binding of mercury to silica or co-precipitation with hydrous Fe- and Mn-oxides (aerobic condition);

(iii) increasing the pH to form volatile dimethyl mercury rather than monomethylmercury; and

(iv) isolating the polluted sediments from the waterbody by means of physical barriers, such as polymer film overlays, blanket plugs of waste wool, sand and gravel overlays (10).
3. PROCEDURE

3.1. Characterization of dredged material

Pollutant transfer to organisms predominantly takes place via dissolved species. However, with regard to the selection of disposal options for dredged material, the study of the water phase only would not be fully satisfying. While most of the actual situation would be reflected in these data, potential harmful effects in the future as well as that of possible measures for reducing such hazards cannot be predicted. Two major concepts of assessing the environmental implications of pollutants for different disposal alternatives are: (i) Chemical characterization of critical phases, including elutriate test methods and sequential leaching techniques, and (ii) bioassays, in which organisms are used to detect or measure the presence or effect of one or more substances or conditions (11).

3.1.1. Elutriate Test. To estimate short term chemical transformations, the interrelations between solid phases and water has been increasingly subjected to laboratory experimentation. The advantage of such experiments is that especially important parameters can be directly observed and particularly unfavourable conditions simulated. The Army Corps of Engineers and the US Environmental Protection Agency have developed an elutriate test that is designed to detect any significant release of chemical contaminants from dredged material (12). This test involves the mixing of one volume of the sediment with four volumes of the disposal site water for a 30-min shaking period. If the soluble chemical constituent in the water exceeds 1.5 times the ambient concentration in the disposal site water, special conditions will govern the disposal of the dredged material.

A study conducted on the factors influencing the results of the Elutriate Test has shown that the test as originally developed cannot yield a reliable estimate of the potential release of contaminants at the dredged material disposal site, since it did not define the conditions of mixing to enable a well defined, reproducible oxygen status to exist during the test period (13). The result was that a modified Elutriate Test has been proposed in which compressed air agitation is utilized during the mixing period. A sequential leaching study conducted on originally anoxic sediments, which has been treated with the modified Elutriate Test, showed recently that sediment components controlling metal solubilities change drastically during the short aeration period (14, see Fig. 2).

3.1.2. Estimation of buffer capacity. On a regional scale acid precipitation is probably the most important single factor affecting metal mobility in surface water, particularly for Al, Cd, Mn, and Zn. Acidity of surface water imposes problems in all aspects of metal enrichment, ranging from the toxification of drinking water to problems concerning the growth and reproduction of aquatic organisms, the increased leaching of nutrients from the soil and the ensuing reduction of soil fertility, the increased availability and toxicity of metals, and finally to the undesirable acceleration of Hg methylation in sediments (15). During land disposal of anoxic sludges, acid
solutions can result from the oxidation of sulfidic compounds; kinetics of these transformations are typically affected by bacteria (16). In fact, the capability of certain bacteria - e.g., Thiobacillus thi oxidans and T. ferrooxidans - to oxidize sulfur and ferrous iron, while decreasing the pH-values from 4.5 to approx. pH 2 can be utilized for enhancing dissolution of metals from dredged materials (17).

For many metal examples, a linear relationship has been found between pH-values and dissolved metal concentrations. Therefore with regard to the mobility of metals, the buffer capacity of the sediment sample is of prime importance. It is shown in Figure 2 with 'titration curves' for suspensions of dredged material from Neckar river and Hamburg harbour that the content of calcium carbonate is the predominant factor affecting the buffer capacity. For quantifying these properties and for better comparison of samples it is proposed to use the term ΔpH, which is characterized by the difference of ΔpH-values of 10 percent sludge suspensions in distilled water (pH0) and in 0.1 N sulfuric acid after 1 h shaking time (pHx). Three categories of ΔpH-values can be established, ranging from ΔpH < 2 (strongly buffered), ΔpH 2-4 (intermediate) to ΔpH > 4 (poorly buffered). While the sediment from Neckar river belongs obviously to the first category, the dredged sludge from Hamburg harbour exhibits very low buffer capacity, as evidenced by the immediate lowering of pH-values upon addition of sulfuric acid.

3.1.3. Sequential chemical extraction. Since adsorption of pollutants onto particles is a primary factor in determining the transport, deposition, reactivity, and potential toxicity of these materials, analytical methods should be related to the chemistry of the particle's surface and/or to the metal species highly enriched on the surface. Apart from direct analysis on the solid surfaces, solvent leaching techniques can provide

![Figure 1](image-url)
information on the behaviour of metal pollutants under typical environmental conditions. Common single reagent leaching tests, e.g., USEPA, ASTM, IAEA, and ICES use either distilled water or dilute acetic acid (19). In connection with the problems arising from classifying dredged spoils, e.g., for ocean dumping, upland disposal or storage in confined water bodies (20), sequential extraction procedures have been developed, which include the successive leaching of metals from ion exchangeable, carbonatic, reducible, sulfidic/organic and residual sediment fractions (21). One of the more widely used techniques, which are still posing many pitfalls (14, 22), has been described by Tessier et al. (23). Previous studies conducted on anoxic sediments in our laboratory showed that any aeration and drying of the samples prior to sequential leaching experiments leads to characteristic changes of the initial fractionation pattern of heavy metals (see Fig. 2). Thus all handling of fresh samples, including sample preparation and the first (four) steps of the leaching procedure, has to be accomplished in a glove box under an inert atmosphere with de-oxygenated media.

4. CHEMICAL STABILIZATION OF SEDIMENTS

Figure 3 shows acid titration curves for Hamburg harbour mud without and after addition of limestone and cement/fly ash stabilizers. Best results are attained with calcium carbonate, since the pH-conditions are not changed significantly upon addition of CaCO₃. Generally, maintenance of a pH of neutrality or slightly beyond favours adsorption or precipitation of soluble metals (20, 24). On the other hand it can be expected, that both low and high pH-values will have unfavourable effects on the mobility of heavy metals. Table 1 shows the initial pH-values of Hamburg harbour dredged material stabilized with lime limestone, cement, and power plant fly ash.

![Diagram](image)

**FIGURE 2.** Sample aeration as an important methodological error of the sequential extraction procedure. (A) original sediment extracted under oxygen-free conditions, (B) subsample extracted upon Elutriate Test with air bubbling, (C) oven-dried (60°C).
Table 1. Fixation formulations for 100g material (dry weight)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sediment</th>
<th>Lime</th>
<th>Limestone</th>
<th>Cement</th>
<th>Fly Ash</th>
<th>Initial pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>E-0</td>
<td>100g</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>7.74</td>
</tr>
<tr>
<td>E-4</td>
<td>80g</td>
<td>10g</td>
<td>10g</td>
<td>-</td>
<td>-</td>
<td>11.76</td>
</tr>
<tr>
<td>E-8</td>
<td>80g</td>
<td>-</td>
<td>20g</td>
<td>-</td>
<td>-</td>
<td>8.66</td>
</tr>
<tr>
<td>E-9</td>
<td>80g</td>
<td>10g</td>
<td>-</td>
<td>10g</td>
<td>-</td>
<td>11.43</td>
</tr>
<tr>
<td>E-11</td>
<td>80g</td>
<td>-</td>
<td>-</td>
<td>10g</td>
<td>10g</td>
<td>11.44</td>
</tr>
</tbody>
</table>

![Graph showing pH vs. mmol [H] / g solids]

FIGURE 3. Effect of calcium carbonate and cement/fly ash additives on chemical stabilization of fine grained sediment from Hamburg harbour.

Table 2. Bulk heavy metal and metalloid concentrations of the harbour sediments samples with and without stabilizer

<table>
<thead>
<tr>
<th>Sample</th>
<th>As</th>
<th>Cd</th>
<th>Co</th>
<th>Cr</th>
<th>Cu</th>
<th>Hg</th>
<th>Ni</th>
<th>Pb</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>E-0</td>
<td>10.3</td>
<td>9.6</td>
<td>58.6</td>
<td>117</td>
<td>228</td>
<td>42.2</td>
<td>53.2</td>
<td>162</td>
<td>1023</td>
</tr>
<tr>
<td>E-4</td>
<td>6.5</td>
<td>5.7</td>
<td>25.4</td>
<td>63.7</td>
<td>157</td>
<td>25.7</td>
<td>30.2</td>
<td>92</td>
<td>570</td>
</tr>
<tr>
<td>E-8</td>
<td>5.1</td>
<td>5.7</td>
<td>23.3</td>
<td>62.1</td>
<td>147</td>
<td>20.2</td>
<td>31.2</td>
<td>99</td>
<td>592</td>
</tr>
<tr>
<td>E-9</td>
<td>6.1</td>
<td>6.6</td>
<td>26.5</td>
<td>74.2</td>
<td>167</td>
<td>27.9</td>
<td>36.8</td>
<td>112</td>
<td>651</td>
</tr>
<tr>
<td>E-11</td>
<td>7.2</td>
<td>6.7</td>
<td>30.1</td>
<td>77.1</td>
<td>176</td>
<td>35.3</td>
<td>45.6</td>
<td>122</td>
<td>626</td>
</tr>
</tbody>
</table>
The stabilized but not solidified sediments were subjected to a leaching procedure using reagent water. In these tests a sample of a fine grained, final sludge material mix was shaken mechanically at initial pH for 15 hours in a 10 to 1 reagent water to solids ratio. Subsequent to the extraction the resultant leachate was filtered (0.45 μm). Following the separation, the resultant leachates were examined by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) for dissolved elements. The TOC content of the leachates was determined with the aid of a Dohrmann TOC-Analyzer. COD and BOD determinations were conducted as recommended by German Standard Methods for the Examination of Water, Waste Water and Sludges (25). Bulk metal concentrations were determined upon hot acid digestion with HNO₃/H₂O₂ (2:1). The results of the leachate extraction are shown in Tables 3 and 4.

Table 3. Stabilized sediment reagent water leachate results

<table>
<thead>
<tr>
<th>Element</th>
<th>E-D (ug/l)*</th>
<th>E-4 (%)**</th>
<th>E-8 (ug/l) (%)</th>
<th>E-9 (ug/l) (%)</th>
<th>E-11 (ug/l) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td>13.8 1.3</td>
<td>4.0 0.6</td>
<td>25.8 5.1</td>
<td>2.9 0.5</td>
<td>3.0 0.4</td>
</tr>
<tr>
<td>Cd</td>
<td>0.28 &lt;0.1</td>
<td>&lt;0.05 &lt;0.1</td>
<td>0.09 &lt;0.1</td>
<td>&lt;0.05 &lt;0.1</td>
<td>&lt;0.05 &lt;0.1</td>
</tr>
<tr>
<td>Co</td>
<td>5.5 &lt;0.1</td>
<td>54.6 2.1</td>
<td>5.4 0.2</td>
<td>55.4 2.1</td>
<td>42.0 1.4</td>
</tr>
<tr>
<td>Cr</td>
<td>&lt;1 &lt;0.1</td>
<td>11.3 0.2</td>
<td>1.5 0.2</td>
<td>24.4 0.3</td>
<td>18.9 0.2</td>
</tr>
<tr>
<td>Cu</td>
<td>19.1 &lt;0.1</td>
<td>3260 20.8</td>
<td>24.1 0.2</td>
<td>2610 15.6</td>
<td>2900 16.5</td>
</tr>
<tr>
<td>Hg</td>
<td>&lt;0.5 &lt;0.1</td>
<td>&lt;0.5 &lt;0.1</td>
<td>&lt;0.5 &lt;0.1</td>
<td>&lt;0.5 &lt;0.1</td>
<td>&lt;0.5 &lt;0.1</td>
</tr>
<tr>
<td>Ni</td>
<td>18.2 0.3</td>
<td>530 17.5</td>
<td>20.9 0.7</td>
<td>539 14.6</td>
<td>476 10.4</td>
</tr>
<tr>
<td>Pb</td>
<td>2.3 &lt;0.1</td>
<td>8.1 &lt;0.1</td>
<td>3.3 &lt;0.1</td>
<td>2.0 &lt;0.1</td>
<td>2.8 &lt;0.1</td>
</tr>
<tr>
<td>Zn</td>
<td>42.3 &lt;0.1</td>
<td>73.0 0.1</td>
<td>&lt;10 &lt;0.1</td>
<td>&lt;10 &lt;0.1</td>
<td>&lt;10 &lt;0.1</td>
</tr>
</tbody>
</table>

Final pH 7.46 12.26 7.79 11.97 11.98
SO₄²⁻ (mg/l) 750 400
TOC (mg/l) 44 259 46 307 277
BOD*** 24 260 46 362 321
COD*** 132 650 177 781 733

* Leachate concentration
** % mobilized from solids
*** (mg O₂/l)

Leachates show low retention capacity for higher pH mixes introduced by lime and fly ash additives, especially for Cu, through this mixes exhibit a high buffer capacity. The high metal mobilization correlates with high TOC-, BOD-, and COD-values in the leachates. Since natural humic acids become increasingly soluble with higher pH-values, metals complexed strongly with organic matter are likely mobilized at these pH-values from the stabilized dredged materials. In addition, a distinct NH₃-odour was noticed on the samples E-4, E-9 and E-11.
The relatively high $\text{SO}_4^{2-}$-values in the leachates - the Hamburg harbour basins are situated at the freshwater part of the Elbe estuary - indicate initiation of oxidation processes in the dredged sludges. As mentioned above, during disposal of anoxic sludges, acidification can result from the oxidation of the sulfidic compounds. In order to trace the metal remobilization behaviour of the sediment, a dried E-0 subsample was titrated with $\text{HNO}_3$ to pH-values 5 and 3, respectively. Subsamples of E-8 titrated with the same amounts of $\text{HNO}_3$ exhibit higher pH-values of pH 6.8 and 5.9, respectively. The results of the retention capacity for metals are presented in Table 4.

### Table 4. Leachate results of acidified sediment mixtures

<table>
<thead>
<tr>
<th>Element</th>
<th>Sample No.</th>
<th>E-0 (pH 5) (µg/l)</th>
<th>E-0 (pH 3) (µg/l)</th>
<th>E-8 (pH 6.8) (µg/l)</th>
<th>E-8 (pH 5.9) (µg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td></td>
<td>22 2.1</td>
<td>126 12.2</td>
<td>39 7.6</td>
<td>132 25.9</td>
</tr>
<tr>
<td>Cd</td>
<td></td>
<td>71 7.4</td>
<td>600 62.5</td>
<td>0.5</td>
<td>2.3</td>
</tr>
<tr>
<td>Co</td>
<td></td>
<td>105 1.8</td>
<td>269 4.6</td>
<td>25 1.1</td>
<td>69.4</td>
</tr>
<tr>
<td>Cr</td>
<td></td>
<td>5.7</td>
<td>55 0.5</td>
<td>2.9</td>
<td>3.9</td>
</tr>
<tr>
<td>Cu</td>
<td></td>
<td>37.8 0.2</td>
<td>863 3.8</td>
<td>7.8</td>
<td>8.2</td>
</tr>
<tr>
<td>Hg</td>
<td></td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Ni</td>
<td></td>
<td>568 10.7</td>
<td>2000 37.6</td>
<td>55.6 1.8</td>
<td>163 5.2</td>
</tr>
<tr>
<td>Pb</td>
<td></td>
<td>&lt;5</td>
<td>46 0.3</td>
<td>&lt;5</td>
<td>&lt;5</td>
</tr>
<tr>
<td>Zn</td>
<td></td>
<td>13750 13.4</td>
<td>57500 56.2</td>
<td>187 0.3</td>
<td>1180 2.0</td>
</tr>
</tbody>
</table>

Distinct mobilization upon acidification of oxidized sludge showed As, Ni, Zn, and especially Cd. Leachates of the sample stabilized with 20% limestone addition show improved immobilization. This property is not only the consequence of the buffer capacity, but also other mechanisms seem to retain the metals, as evidenced by comparison of samples E-0 (pH 5) and E-8 (pH 5.9). Somewhat problematic remains the behaviour of As, since it was not immobilized by these chemical stabilization technique. In contrary to the other metals, As mobility seems to be enhanced upon acidification of the limestone stabilized sample.

In order to trace the gas production properties of chemically stabilized harbour sludge, a batch test was conducted. Original and stabilized samples were sealed air-tight in 120-l plastic containers equipped with a automatical leachate recycling unit. The containers are kept in temperature stabilized rooms at pre-defined conditions. The gas produced within the containers is sampled in aluminum gas baloons. Preliminary results on the gas and leachate production indicate that the microbial metabolic reactions in chemically stabilized sludges differ from that of the original samples. The initial microbial degradation of the organic matter in the limestone stabilized samples seems to be inhibited. No methane was detected after 4 weeks of incubation in the gas of the stabilized mixture, whereas in that of the original sample a methane proportion of 25% is found after the same time. Long term incubation experiments are in progress.
4. CONCLUSIONS

With respect to various containment strategies for hazardous dredged sediments, it has been argued that upland containment could provide a more controlled management than, e.g., containment in the marine environment. However, contaminants released either gradually from an imperfect impermeable barrier (also to groundwater) or catastrophically from failure of a barrier could produce substantial damage (26). The best strategy for upland disposal would be to stabilize the wastes chemically prior to containment. Our results suggest that for optimum dredged sediment immobilization, by chemical stabilization, limestone additions are desirable due to the low pH-change. The behaviour of As, gas production, and organic pollutants need to be examined still further.

REFERENCES


