

Stabilization of Dredged Mud

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1 Introduction

Traditional disposal alternatives of dredged material are subaqueous (open-water) disposal, application to intertidal sites and upland deposition. More recently, coastal marine disposal in capped mound deposits above the prevailing seafloor, disposal in subaqueous depressions and capping deposits in depressions have been proposed for contaminated sediments (Kester et al. 1983). These categories differ primarily in the biological population exposed to the contaminated sediments, physico-chemical conditions and transport processes potentially capable of removing contaminants from dredged material at the disposal site (Gambrell et al. 1978).

The ecological effects of heavy metals in contaminated sediments are determined more by the chemical form and reactivity than by the level of accumulation. Land deposition of dredged mud is mainly concerned with the following factors:

1. Change of pH;
2. Change of redox conditions;
3. Formation of soluble, complexing organic compounds;
4. Microbial interactions.

These factors affect the chemical forms and bonding strength of heavy metals in sediment particles and thus mobility and availability. For the deposition of freshwater sediments in intertidal and coastal marine environments, the effect of salinity is of great importance. Remobilization of certain metals, e.g. Cd, is due to increased ion concentrations and formation of soluble chloro-complexes (Ahlf 1983, Calmano et al. 1985).

In order to minimize potential adverse effects upon disposal of dredged material, chemical and mechanical stabilization techniques, especially for upland disposal alternatives, are proposed and discussed in the following sections.

2 Factors Affecting Chemical Stability of Sludges

The most effective physico-chemical environment for immobilizing the most potentially toxic metals in dredged materials is:

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1. Near-neutral pH;
2. Strongly reduced;
3. Non-saline; and
4. Especially, where sulphides are present (Gambrell et al. 1978).

For many metal examples a clear relationship has been found between pH values and dissolved metal concentrations. With decreasing pH, the metal concentration in solution increases. Figure 1 shows the dissolution of Cd in soil as a function of pH (Alloway and Morgan 1986).

Acidity not only imposes problems in increased availability and toxicity of metals, but also in other aspects of pollutant enrichment, ranging from the toxification of groundwater to problems concerning growth and reproduction of organisms, increased leaching of nutrients, the ensuing reduction of soil fertility and finally to the undesirable acceleration of mercury methylation in the sediments (Fagerström and Jernelöv 1972).

Therefore, the content of buffer substances in the sediments is of prime importance. Calcium carbonate and aluminium silicates are the predominant factors affecting buffer capacity which controls the magnitude of shifts in the pH after formation of acid in or addition to the system. Sediments with carbonate contents >10% are protected against acidification over a wide range. This is shown in Fig. 2 with titration curves for dredged material suspensions from the Neckar River and Elbe River (Hamburg harbour).

While the Neckar River sediment belongs to this category, the dredged mud from Hamburg harbour exhibits a very low buffer capacity as evidenced by the immediate decrease of pH after addition of acid. Such acidification effects became evident, when harbour sludge was used in agriculture and led to elevated concentrations of heavy metals in crops and vegetables (Herms and Tent 1982).

The buffer intensity of a sludge can be tested by a simple procedure. Ten percent sludge suspensions in distilled water (pH_0) and in 0.1 N acid (pH_x) are shaken for 1 h and the difference for the obtained pH values is calculated:

$$\Delta\text{pH} = \text{pH}_0 - \text{pH}_x.$$

Three categories of pH values can be established, ranging from $\Delta\text{pH} < 2$ (strongly buffered), $\Delta\text{pH} = 2-4$ (intermediate) to $\Delta\text{pH} > 4$ (poorly buffered). These

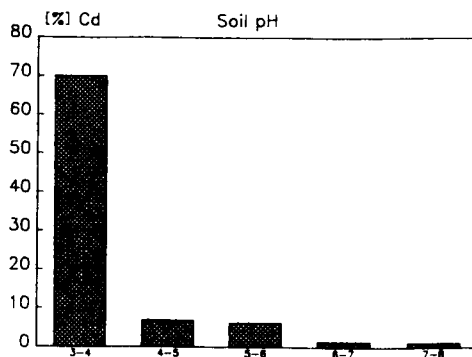


Fig. 1. Relationship between cadmium in the soil solution and pH (After Alloway and Morgan 1986)

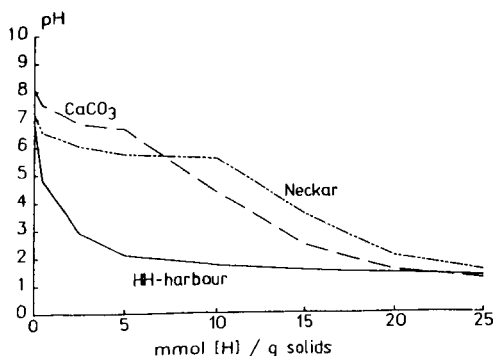


Fig. 2 pH changes in suspensions of calcium carbonate and river sediments after addition of acid (After Calmano et al. 1986)

criteria can help to decide if a dredged mud has to be stabilized, e.g. by addition of lime or limestone, before final deposition, although this procedure does not consider slowly reacting buffer substances.

3 Stabilization Techniques

In order to maintain ports and channels accessible to shipping, and also if they are polluted with contaminants, sediments have to be removed regularly. Once the potential impacts of contaminants 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 (Rulkens et al. 1985) may also be considered for strongly polluted sediments:

1. Construction of mechanical barriers (encapsulation);
2. Fixation of water by addition of chemicals;
3. Formation of sparingly soluble compounds by chemical reactions (chemical immobilization);
4. 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 aim of these techniques is a stronger encapsulation of contaminants to reduce the emission rate to the biosphere and to retard exchange processes respectively (Wiedemann 1982). Two steps can be differentiated:

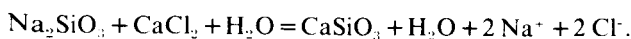
1. At best, a material is produced which can be used for earth or landscape building like road construction, dike construction or building of walls for noise reduction, so that disposal sites are not necessary;
2. In other cases the material could be improved by a stabilization process so that it could be deposited safely and cheaply.

Most techniques used for the immobilization of metal-containing wastes are based on solidification/stabilization with cement, water glass (alkali silicate), coal fly ash, lime or gypsum. A detailed representation and discussion of stabilization techniques of hazardous wastes and remedial actions for redevelopment of contaminated soils is given by Wiedemann (1982). Some typical characteristics, compatibilities, disadvantages and advantages of these methods are given below (Wiedemann 1982; Rulkens et al. 1985) and in Table 1 (Malone et al. 1982).

Cement is mainly a mixture of oxidic calcium, aluminium, silicon and iron compounds which were activated in the kiln and set at contact with water by formation of hydrous aluminates and silicates. After corroboration these compounds are water resistant. It is known that many wastes can be stabilized by cement. For sludges with solid contents of 25%–60%, dewatering is not necessary since cement needs water for consolidation. Other absorbing materials like clays may be added. Bentonite, for example, has a large specific surface and is negatively charged with a corresponding cation exchange capacity. In addition, many inorganic and organic compounds are bound by sorption.

The solidity and permeability of the product may be controlled by the amount of added cement. The immobilization of metals by the formation of less soluble hydroxides or basic carbonates is advanced by the high pH value of cement mixtures. On the other hand, it can be expected that high pH values will have unfavourable effects on the mobility of certain toxic metals, like lead, chromium, copper and nickel which form hydroxy-complexes and show an increased solubility at $\text{pH} > 12$. Also, the dissolution of natural organic substances (humic acids), together with complexed or adsorbed contaminants, may be enhanced.

Water glass (alkali silicate) is another useful solidification reagent for sludges. The reaction with multivalent metal ions leads to a hydrous gel, e.g.:



Most transition metals form practically insoluble silicates. The metals are immobilized in the polymerized structure, just as organic molecules and other pollutants.

Chemically unfixed are, e.g. chloride ions and monovalent cations. This follows from the nature of the water glass reaction which leads to a release of alkali ions and anions as shown above, so that leaching of additional amounts of these ions is only reduced by a decrease in the water permeability of the solidified product.

The American CHEMFIx process is based on the immobilization of hazardous wastes with water glass and is applied above all for inorganic contaminants; the Belgian SOLIROC process uses as yet unknown additives and is also recommended for solidification of organic wastes.

The *pozzolane* effect is based on the settling behaviour of coal fly ashes, cement or kiln dusts and on the reaction of these materials with lime. Similar to cement or water glass, the solidification and immobilization of contaminants with pozzolanes mainly consist in the encapsulation and low water permeability of the product. Also, the high pH values contribute to a certain stabilization of heavy metals by the formation of less soluble compounds. Pozzolanes normally show a good long-term stability, but a slow solidification.

Table 1. Compatibility of selected waste categories with waste solidification/stabilization techniques. (After Malone et al. 1982)

Waste component	S/S treatment type			
	Cement-based	Lime-based	Thermoplastic solidification	Organic polymer (UF) ^a
Organics				
Organic solvents and oils	Many impede setting, may escape as vapor	Many impede setting, may escape as vapor	Organics may vaporize on heating	May retard set of polymers
Solid organics (e.g., plastics, resins, tars)	Good -- often increases durability	Good -- often increases durability	Possible use as binding agent	May retard set of polymers
Inorganics				
Acid wastes	Cement will neutralize acids	Compatible	Can be neutralized before incorporation	Compatible
Oxidizers	Compatible	Compatible	May cause matrix breakdown, fire	May cause matrix breakdown
Sulfates	May retard setting and cause spalling unless special cement is used	Compatible	May dehydrate and rehydrate causing splitting	Compatible
Halides	Easily leached from cement, may retard setting	May retard set, most are easily leached	May dehydrate	Compatible
Heavy metals	Compatible	Compatible	Compatible	Acid pH solubilize metal hydroxides
Radioactive materials	Compatible	Compatible	Compatible	Compatible

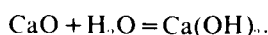
^aUrea-Formaldehyde resin

Note: "Compatible" indicates that the S/S process can generally be successfully applied to the indicated waste component. Exceptions to this may arise dependant upon regulatory and specific situation factors.

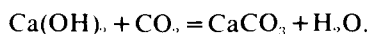
The advantage of common handling of both sludges and pozzolanic ashes or dusts is that disposal capacity is not reduced if both wastes have to be removed by deposition.

Lime, in the form of calcium oxide or calcium hydroxide, is often used for chemical stabilization of soils. Most natural soils contain larger amounts of silicic acid or colloidal aluminium silicates in a strongly hydrous state. If such soils are mixed with lime, pozzolanic reactions occur and calcium silicates and aluminates are formed which show the known effects for heavy metals. Also, in the absence of these reactive substances a certain solidification can be obtained by a mixture of sludges with calcium oxide. It has been used especially for the treatment of oil-contaminated sludges.

Calcium oxide reacts with water to calcium hydroxide which has an increased surface:



Calcium hydroxide shows a relatively good water solubility and does not represent a stable end product. On the other hand, at contact with carbon dioxide in the air, the more stable calcium carbonate is formed under natural conditions:



This reaction may be accelerated by artificial treatment with carbon dioxide gas.

The solidification of *gypsum* by addition of water is a known process in which water is included in the crystal structure and calcium sulphate dihydrate results. This process can be used to solidify sludges because the strong resorption of water by the gypsum dries up the waste, and the crystals form a strong and stable frame in which other pollutants and contaminants may be included.

In contrast to calcium hydroxide, gypsum is a stable end product, although the solubility in water is relatively high.

At present, it does not seem possible for the gypsum and cement industries to absorb the expected quantities of flue gas gypsum arising from coal-fired and lignite-fired power stations. New applications for these quantities must be developed, and one possibility may be the stabilization of heavy metal contaminated sludges.

4 Implementation Strategies

Francingues (1985) indicates three basic on-site implementation strategies according to the manner in which the chemical reagents are added to and mixed with the materials being treated:

1. In situ mixing;
2. Plant mixing;
3. Area mixing.

In situ mixing is suitable primarily for dredged slurries that have been initially dewatered. It is best applicable for the addition of large volumes of low reactivity solid chemicals. This strategy incorporates the use of construction machinery, typically a backhoe, to accomplish the mixing process. Where large containment areas are being treated, clamshells and/or draglines may be used. Major modifications to the *in situ* mixing strategy include the development of the reagent addition and mixing equipment that allows better control of the process.

Plant mixing strategies can be adapted for applications to slurries and solids. It is most suitable for application at sites with relatively large quantities of contaminated materials to be treated. In the plant mixing process the materials are physically removed from their location, mechanically mixed with the immobilization reagents and redeposited in a prepared disposal site. Special equipment adaptations have been utilized to handle sludges with high solid contents and contaminated soils.

Area mixing is applicable to those confined disposal sites, where high solids content slurries must be treated. The term "area mixing" is used to denote those strategies that use horizontal construction techniques to add and mix the stabilization reagents with the dredged material. Area mixing is land intensive, requiring a relatively large land area to carry out the process. Area mixing strategies present the greatest possibility for fugitive dust, organic vapour and odour generation. The typical area mixing strategy will require that the dredged material be sufficiently dewatered to support construction equipment.

The three basic implementation strategies can be incorporated into confined disposal operations in a variety of ways to improve contaminant containment. In most cases, the same immobilization reagents and equipment can be employed.

Figure 3 (Francingues 1985) shows three concepts in the application of immobilization technology at confined disposal sites.

Concept A involves alternating layers (thin lifts) of relatively clean dredged material and contaminated dredged material that is stabilized. The initial lift of clean, fine-grained sediments would be dewatered to promote densification and consolidation to provide a low permeable soil layer or natural liner for the containment area. Once this layer has achieved the desired degree of consolidation and permeability, the contaminated material would be placed on top, dewatered and stabilized *in situ*. This layering process would continue until the containment area was filled. A final soil cover would be added, shaped and vegetated.

The second disposal method shown in Fig. 3 incorporates soil stabilization as a treatment to produce a low permeable liner and is designated concept B. The stabilized soil layer is used to contain any leachate generated from the dewatering and long-term disposal of the contaminated dredged material. Appropriate chemical reagents are added and mixed with the disposal site soil using either the *in situ* or area mixing methods. Then a layer of coarse material is added above the stabilized layer to facilitate dewatering and collection of leachate. The contaminated dredged material is disposed next and dewatered. A clean layer of dredged material is used as final cover. One modification to this concept would be the additional step of stabilizing the contaminated dredged material to further protect against contaminant escape.

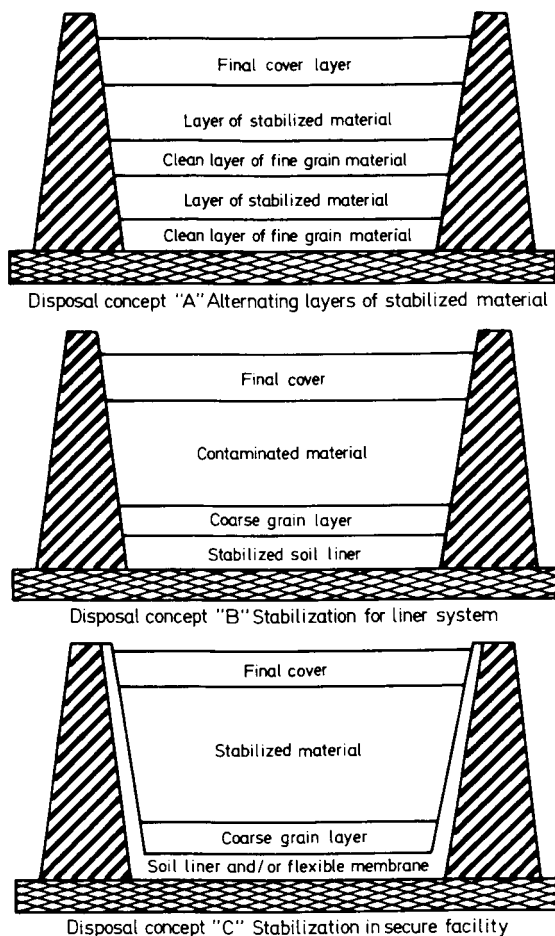


Fig. 3. Immobilization concepts for confined disposal operations (After Francingues 1985)

The final concept illustrated in Fig. 3 provides the highest degree of environmental protection. A soil liner, or flexible membrane, or both, are used to line the bottom and sides of the disposal sites. Then a coarse-grained layer is used to facilitate dewatering and leachate collection. The contaminated sediment is disposed into the lined site, dewatered and stabilized. An alternative would be first to dewater the contaminated sediments in a temporary processing facility, and then to apply the stabilization process prior to placement of the treated material in the confined disposal site. This stabilization operation would be accomplished using the plant mixing strategy (either mobile or field erected) or the area-wide mixing strategy, stockpiling the stabilized material prior to rehandling and disposal in the prepared site. The last operation in concept C would be to finally cover, shape and vegetate the site.

5 Evaluation and Efficiency of Stabilization Processes

Solidification and immobilization processes for chemical and mechanical stabilization of contaminated sludges are designed to prevent hazardous effects for the environment. These processes must include certain qualities of the material, e.g. a better resistance against erosion, a better carrying capacity or a low water permeability. Other qualities like decomposition of organic pollutants or immobilization of persistent pollutants to reduce the leachability and bioavailability are desired.

Processes on the basis of silicates, aluminates, lime and limestone will be preferred, because the chemical reactions and the formed mineral phases are similar to natural conditions. Special attention should be directed to mechanisms which are able to fix pollutants chemically (Wiedemann 1982).

To estimate short- and long-term chemical transformations the interrelations between solid phases and water have been increasingly subjected to laboratory experimentation. From country to country different procedures and tests are used and thus the results are hardly comparable. Unique criteria are rare and often criticized because of their simplicity, e.g. the German standard leaching test "S4", in which one part of a sample is shaken with ten parts distilled water for 24 h (Fachgruppe Wasserchemie 1983).

The chemistry of leaching tests was reviewed by Lowenbach (1978) and Grant et al. (1981). Comparisons of different leaching tests were conducted by Jackson et al. (1981), Ham et al. (1979) and Theis and Padgett (1983).

A critical overview of the most important leaching tests is given by Stegmann (1979, unpubl.), who compares the procedures with the German S4 test. Anderson et al. (1979) presented four factors which should be predicted by an ideal leaching test:

1. The highest concentration of a pollutant in the effluent;
2. The factors which control this concentration;
3. The total amount of a pollutant which may be mobilized from a fixed quantity of the material; and
4. The type of mobilization in the course of time.

Single reagent extraction tests are useful for defining the release characteristics of contaminants under specific conditions. Liquid/solid ratio, pH value, contact time and complexing capacity of the leachate must be considered a new for any case. The selectivity of extraction reagents can sometimes be enhanced through use of serial extraction procedures, whereby the solid material is sequentially contacted with one extractant at a time. A major advantage of this approach is that the type and sequence of extracting reagents can be altered for application to a specific material (Theis and Padgett 1983).

Column leachate tests on polluted harbour sediments were conducted to determine the types and concentrations of pollutants which might be leached in an upland disposal site (Seeger and Leonard 1984). For these tests a set of three replicate columns was used. Each column was loaded to a depth of 10 in. with sediments. The system was designed to maintain anaerobic conditions which would be expected to persist at an upland disposal site. An artificial rainfall

buffered at pH 4.5 was periodically added to each column to maintain a head of 1.5 to 2.0 ft. above the sediments.

In the Netherlands a working group with participants of research institutions and industry has proposed a standard leaching test for combustion residues consisting of a column leaching test and a series of cascade extractions with renewal of the contact solution up to an ultimate liquid/solid ratio of 100 (van der Sloot et al. 1984). The procedure was operated in an upflow using a peristaltic pump to maintain a constant percolation rate and a series of five subsequent extractions at a liquid/solid ratio of 20 using the same portion of residue repeatedly. The contact time for each extraction was 23 h. Agitation was effectuated by rolling tightly closed polyethylene bottles on a roller table. The obtained cumulative liquid/solid ratio was 100. A material can be solidified in such a way (monolith) that the convectonal transport of contaminants due to movement of the interstitial water becomes negligible, and the diffusive flux is decisive for emission of pollutants. The diffusion process depends on the temperature and composition of the surrounding water.

For simulation of the dynamics of these diffusion processes a stand test has been designed with which it is possible to determine the effective diffusion factor for a number of materials. The test must be carried out over a long period, and for the translation of the data to practical situations very sophisticated descriptions are needed (van der Sloot et al. 1985b).

The US Army Corps of Engineers and the US Environmental Protection Agency have developed an elutriate test which is designed to detect any significant release of contaminants from dredged material (Lee and Plumb 1974). This test involves the mixing of 1 vol of the sediment with 4 vol of the disposal site water for a 30-min shaking period.

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 existing during the test period (Lee et al. 1976). As a result a modified elutriate test has been proposed in which compressed air agitation is utilized during the mixing period.

Recently, a sequential leaching study conducted on originally anoxic sediments, which had been treated with the modified elutriate test, showed that sediment components controlling metal solubilities change drastically during the short aeration period (Kersten and Förstner 1986).

Such sequential leaching techniques, which include the successive leaching of metals from ion exchangeable, carbonatic, reducible, sulphidic/organic and residual sediment fractions, can provide reliable information on the behaviour of metal pollutants before and after the application of stabilizing additives and characterize typical environmental conditions.

Most realistic, but very time-consuming and expensive, are experiments and measures in field studies on disposal sites or on comparable and equivalent models (e.g. lysimeter studies). Such disposal experiments have to be carried out as a rule over several years, must produce an enormous amount of data and can only be justified in cases in which the behaviour of a hazardous waste is mostly uncertain. Even then it is difficult to make long-term predictions over geological periods (Wiedemann 1982).

The majority of stabilization processes leads to an improvement of the physical and mechanical properties of the material. Thus, a decrease in the mobilization of hazardous substances can be obtained, but for all known and studied processes the immobilization effect is nearly exclusively based on physical encapsulation of the contaminants in a solid and low permeable mass. Chemical fixation is insignificant. It can be expected that the reaction with some additives increases the chemical reactivity and water solubility of certain pollutants. Amphoteric metals and some organic contaminants show an enhanced dissolution in an acid and alkaline milieu, thus the best alternative for upland disposal of dredged material seems to be a strongly buffered system with pH values in the range of 7 and 9.

6 Application of Stabilization Techniques for Metal-Polluted Dredged Sediments

In 1985 Battelle carried out a feasibility study on the solidification of dredged mud from Hamburg harbour (West Germany) (Battelle 1985). This study evaluated experimental works done by several firms and institutions and summarized the fundamental results. Three important questions had to be answered:

1. To what degree are the mechanistic properties of the material improved by solidification (improved possibilities to form a hill by upland disposal)?
2. How far is it possible to improve fixation of pollutants in the mud by solidification (improved disposal abilities)?
3. Are there other experiences with solidification of dredged mud, and what about the cost factor?

The investigations showed that about 14 firms and institutions were occupied with solidification of river sediments and harbour sludges. Although there have been some experiences with technical solidification of wastes for years, only results from laboratory experiments could be obtained for harbour sludges. These studies clearly showed an improvement of soil-mechanistic data by solidification. Examination of heavy metal leachability on the solidified and original harbour sludge led to the following results:

1. Solidification of harbour sludges from Hamburg and Bremen (West Germany) is practicable in the laboratory with hydraulic additives on the basis of cement and lime.
2. From the results of comparable leaching tests no significant advantage or disadvantage of the studied solidification techniques could be detected.
3. Heavy metal concentrations in the leachates in the solidified and original harbour sludge are comparable, from which can be seen, that solidification did not lead to immobilization in the studied cases.

At present, cost estimations of solidification are accompanied by many uncertainties. Battelle expects for solidification with cement, depending on the use of additives, 10 and 15% cement respectively, between 30 and 55 DM m⁻³ (deutsche marks) dewatered dredged mud. Other estimations for upland disposal of

solidified sludge (15% cement) are in the order of 100 DM m^{-3} (ARGE Schlick-technik 1985, unpubl.).

At the Technical University of Hamburg experiments are being carried out to stabilize dredged mud with lime, limestone, cement and coal fly ash in different mixtures (Calmano et al. 1986). Table 2 shows the mixtures of dredged mud from Hamburg harbour and additives; as can be seen pH values differed strongly.

Acid titration curves of two examples are shown in Fig. 4. At high pH values after addition of lime, cement or coal fly ash, soluble metal bases can be formed and problems with development of ammonia result. More favourable is the addition of limestone, since pH conditions are not changed significantly and maintenance of pH at neutrality or slightly beyond favours adsorption and precipitation of most toxic metals.

The stabilized but not solidified sediments were subjected to a leaching procedure using distilled water. In this test the samples of the fine-grained and stabilized sediments were shaken for 15 h in a 1:10 solid/water ratio. The results are shown in Table 3.

Leachates show lower retention capacity for higher pH mixtures introduced by lime and cement/coal fly ash additives, especially for copper and nickel, although these mixtures exhibit a relatively 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 strongly complexed by organic matter are most likely mobilized at these pH values from the stabilized dredged materials.

Table 2. Mixtures of dredged mud from Hamburg harbour and additives

Sample	Dredged mud (g)	Lime (g)	Limestone (g)	Cement (g)	Coal fly ash (g)	Initial pH
1	100					7.74
2	80	10	10			11.76
3	80		20			8.68
4	80	10		10		11.43
5	80			10	10	11.44

Fig. 4. Effect of calcium carbonate and cement/fly ash additives on chemical stabilization of fine-grained sediment from Hamburg harbour (After Calmano et al. 1986)

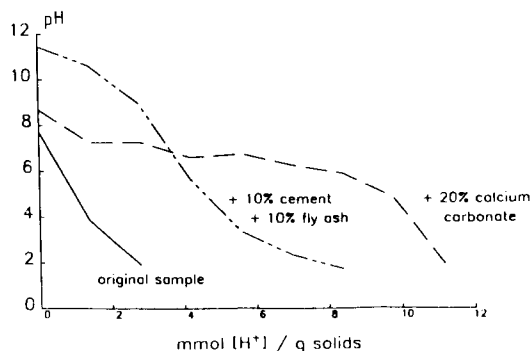


Table 3. Leachable metal portions with dist. water (% of total metal content in the dry sample) and sulphate (mg l^{-1}), total organic carbon (TOC) (mg l^{-1}), biological oxygen demand (BOD) ($\text{mg O}_2 \text{ l}^{-1}$) and chemical oxygen demand (COD) ($\text{mg O}_2 \text{ l}^{-1}$) in the leachates

Element	Dredged mud	Limestone	Lime/limestone	Lime/cement	Cement/coal fly ash
As	1.3	5.1	0.6	0.5	0.4
Cd	—	—	—	—	—
Co	—	0.2	2.1	2.1	1.4
Cr	—	0.2	0.2	0.3	0.2
Cu	—	0.2	20.8	15.6	16.5
Hg	—	—	—	—	—
Ni	0.3	0.7	17.5	14.6	10.4
Pb	—	—	—	—	—
Zn	—	—	—	—	—
Final pH	7.5	7.8	12.3	12.0	12.0
SO_4^{2-}	750	400	n.d.	n.d.	n.d.
TOC	44	46	259	307	277
BOD	24	46	260	362	321
COD	132	177	650	781	733

n.d. = not determined

The relatively high sulphate concentrations in the leachates (the Hamburg harbour basins are situated in the freshwater part of the Elbe estuary) indicate initiation of oxidation processes in the dredged mud. As mentioned above, during disposal of anoxic sediments acidification can result from the oxidation of sulphidic compounds.

In order to trace the metal remobilization behaviour of the sediment, a dried original sludge sample was titrated with nitric acid to pH values of 5 and 3 respectively. Limestone stabilized samples titrated with the same amount of acid exhibited higher pH values of 6.8 and 5.9 respectively. The results of the retention capacity for metals are presented in Table 4.

Distinct mobilization after acidification was shown by As, Ni, Zn and especially Cd. Leachates of the limestone stabilized sample show improved immobilization. This property is not only the consequence of the increased buffer intensity, but also other mechanisms seem to retain the metals as evidenced by comparison of the original sample at pH 5 and the limestone stabilized sample at pH 5.9. Somewhat problematic remains the behaviour of As, since it was not immobilized by this chemical stabilization technique. Further studies are necessary.

Kamon (1985) investigated the possibility of using a stabilization treatment by lime and cement mixture for very soft freshwater clay.

Lime alone or cement alone did not cause any hardening in preliminary tests. Hence, a special stabilizing agent which aims at the pozzolanic reaction and can reduce the free water by enclosing it into ettringite crystals was introduced. A lime/cement mixture with aluminium sulphate was used with varying relative proportions of their contents. The proportion of lime to cement was mixed in a weight ratio of 2:1. The combination ratio of the lime/cement mixture to liquid

Table 4. Mobilization of metals after addition of acid (% of total metal content in the dry sample)

Element	Original pH 5	Sample pH 3	Limestone stabilized sample	
			pH 6.8	pH 5.9
As	2.1	12.2	7.6	25.9
Cd	7.4	62.5	< 0.1	0.4
Co	1.8	4.6	1.1	3.0
Cr	< 0.1	0.5	< 0.1	< 0.1
Cu	0.2	3.8	< 0.1	< 0.1
Hg	< 0.1	< 0.1	< 0.1	< 0.1
Ni	10.7	37.6	1.8	5.2
Pb	< 0.1	0.3	< 0.1	< 0.1
Zn	13.4	56.2	0.3	2.0

aluminium sulphate was varied in a weight ratio of 9:1, 8:2, 7:3 and 6:4. These stabilizing agents were added to the soil samples at 5, 10, 15, 20, 30 and 40% of the soil dry weight. The varied water contents of the soil samples were 150 and 200% which corresponded to the in situ water content. The effect of the hardening treatment was examined by the unconfined compressive strength q_u of the treated samples.

Figure 5 shows the unconfined compressive strength of a sample with a water content of 150% after a curing time of 360 days in relation to the combination ratio and added volume of stabilizers. The increasing strength in samples of 9:1 and 8:2 combination ratios and at more than 15% added volume is clearly illustrated in the slope of the figure. The hardening strength increases with the increase in the added volume of stabilizing agents. The optimum combination ratio is 9:1 to 8:2. Beyond these ratios the effect of the ettringite crystals reduces the hardening strength.

By X-ray diffraction analysis and scanning electron microscope study it was clearly seen that the pozzolanic reaction products are directly related to strength increase.

In order to trace the gas production properties of chemically stabilized sludge from Hamburg harbour, we conducted a batch test (Garbers and Krause, pers. commun.). Original and stabilized samples were sealed airtight in 120-l plastic containers equipped with an automatic leachate recycling unit. The containers were kept in temperature stabilized rooms at predefined conditions (30°C). The gas produced within the containers was sampled in aluminium gas balloons. Preliminary results on the gas and leachate production indicate that microbial metabolic reactions in chemically stabilized samples differ from those of the original dredged mud. 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 the original sample a methane proportion of 25% was found after the same time. Long-term incubation experiments with lime, limestone and gypsum stabilized sediments are in progress.

Another possible solution for the solidification of dredged mud is the use as building materials. A feasibility study by Battelle showed the following possibilities (Battelle-Institut 1982):

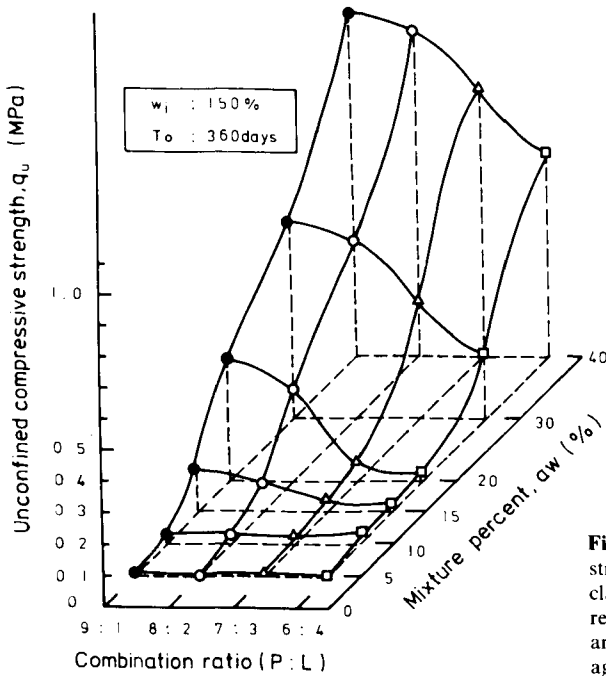


Fig. 5. Unconfined compressive strength q_u of stabilized freshwater clay after curing time of 360 days in relation to the combination ratio and added volume of stabilizing agents (After Kamon 1985)

1. Admixture for production of building stones;
2. Surrogate of raw materials for production of quartz fibre;
3. Admixture for production of cement;
4. Solidification to mudstone.

All these procedures are objected in view of recycling. Brickwork products, like tiles and clinkers, can be produced by the use of fine-grained dredged materials with high clay contents. Indeed, there are more scruples to use strong polluted sediment, especially if the material is contaminated with mercury, arsenic, cadmium and volatile organic pollutants, because a very sophisticated foul-air purification is required. If these problems are solved technically, parts of solidified dredged mud could be used, e.g. as building materials in disposal sites (in drainage layers), since the leachability of these substances is relatively favourable.

7 Conclusions

The chemistry and microstructure of stabilized dredged material have to be studied more extensively in the future. Previous work on the mechanisms of fixation by the use of scanning electron microscopy (SEM), X-ray diffraction (XRD), polarization microscopy, porosimetry and chemical leaching tests demonstrated the impor-

tance of microstructure in determining the degree of fixation of toxic substances (Kamon 1985, Poon et al. 1985, Khorasani, pers. commun.). Also, the ecological effects of the stabilized material and corresponding bioassays must be included in further investigations.

From a geochemical point of view, another natural stabilization alternative for dredged sediments could be of interest. The deposition in an anoxic and sulphidic milieu seems to be a very efficient method to immobilize most heavy metals because of formation of very stable metal sulphides. Such a milieu is found in the marine environment, and it must be, of course, strictly isolated from the surrounding hydrosphere and biosphere. Especially for mercury-contaminated sediments a typical marine process is of interest (Berman and Bartha 1986; Blum and Bartha 1980): in the anoxic, sulphidic milieu monomethyl mercury, one of the most toxic compounds, is transformed into readily volatile dimethyl mercury and low soluble mercury sulphide (Craig and Moreton 1984).

Besides the example of the harbour sludge depot at Rotterdam, several projects are in progress, in which dredged material is deposited into submarine borrow pits and covered with clean sediments (Bokuniewicz 1982, Morton 1980). On this occasion organic pollutants are increasingly accounted for, the behaviour of which as yet has been little studied in comparison to heavy metals (Brannon et al. 1984; Förstner et al. 1985; Sumeri 1984).

In Hamburg a subsediment deposition for contaminated harbour sludge is planned (Tamminga et al. 1986). The present studies show the following technological concepts (Führböter 1985).

1. The optimal location is an area with a water depth between 2–5 m and a ground consisting of sand at least 25 m thick.
2. The site should be located in an area which is morphologically as stabile as possible with a low erosion potential by current and wave forces.
3. The most suitable technological concept seems to be the deposition into a previously dug hole which is sealed with uncontaminated material after completion of disposal.
4. The site should be enclosed by an annular dam to prevent the transport of contaminants.
5. The dredged material can be placed by spoiling or in partially dewatered form (see Fig. 6). The transport water must be recirculated and cleared off.

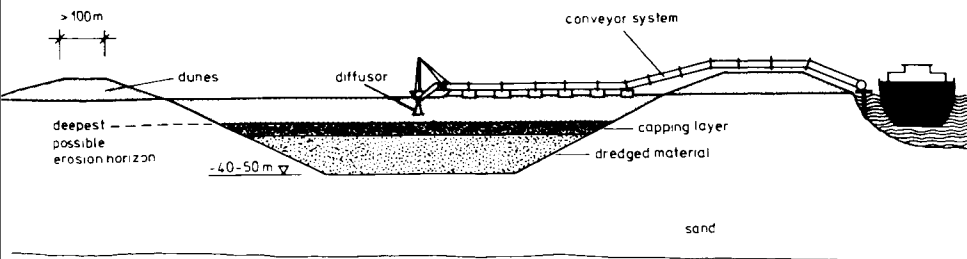


Fig. 6. Model of a planned subsediment deposition for contaminated dredged mud from Hamburg harbour (After Tamminga et al. 1986)

The disposal site is outlined for a period of 20 years. The yearly dredging volume is 600,000 m³ partially dewatered material and 2,500,000 m³ untreated dredged sludge respectively.

From an ecological point of view there are some open questions. Apart from long-term stability, resistance of the capping material and contaminant exchange processes through ground, dam and capping layer, the decomposition of organic material combined with gas development (H₂S) and the formation of metal-complexing compounds have to be studied. The answers to these questions require interdisciplinary efforts in research.

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