New Approach To Treating The Soft Clay / Silt Fraction Of Dredged Material

K. Millrath[1)], S. Kozlova[2)], C. Meyer[2)], S. Shimanovich[2)]

Abstract: Maintenance and capital dredging is absolutely necessary to keep shipping lanes open and harbors accessible. Since the early 1970s the ecological impact of dredging processes and disposal techniques has been studied carefully. Facing strict environmental regulations, ports worldwide are currently changing their dredged material management plans to stay economically viable. Restrictions and exclusion of traditional disposal techniques require a multifaceted approach to dispose of, recycle, decontaminate and reuse the material. For clean dredged material several strategies of beneficial use have been established successfully throughout the last decades. However, contaminated sediments are more difficult to place. Especially the productive use of the soft clay / silt fraction poses many unsolved problems because it tends to attract the pollutants. Existing technologies are often energy-consuming and expensive, treat only certain fractions of dredged material, raise issues of secondary pollution, or lack community acceptance.

At Columbia University, research has been conducted on the beneficiation of dredged material from the Port of New York and New Jersey. Annually about 4.5 million cubic yards have been dredged to maintain and improve its waterways. The bulk of the dredged material is contaminated and not suitable for unrestricted use or disposal. Investigations of physical and chemical properties suggest a beneficial use as filler material in various applications. Prior treatment and detoxification is necessary. A method to prepare dredged material, and especially the fine fraction thereof, for further use was developed. Being able to engineer certain properties according to specific needs, one can obtain dredged material that functions as a valuable semi-product or end product competing ecologically and economically with existing materials. Herein, the approach, findings and results of the search at Columbia University for beneficial use of dredged material are introduced. Beneficiation is the transformation of a waste material into a valuable resource, which requires the adaptation, modification and engineering of properties according to specific needs.

1) Department of Civil Engineering and Engineering Mechanics
Columbia University, 632A S.W. Mudd Building MC 4709, 500 W 120th Street,
New York, NY 10027, USA
millrath@civil.columbia.edu

2) Department of Civil Engineering and Engineering Mechanics
Columbia University, 610 S.W. Mudd Building MC 4709, 500 W 120th Street,
New York, NY 10027, USA

INTRODUCTION

The detrimental environmental impact of dredging and the disposal of dredged material has led to the introduction and tightening of national and international laws. With the prohibition of open-water disposal, the traditionally most common and least expensive placement was no longer an option, and the costs for sediment disposal increased tremendously. Ports worldwide try to use a multifaceted approach including disposal, recycling, separation, dewatering, stabilization, decontamination and reuse of dredged material. For clean dredged material several beneficial uses such as beach nourishment, topsoil, landfill cover, habitats or reclamation have been established successfully throughout the last decades (Millrath et al. 2001a). However, restrictions apply as soon as the sediments are contaminated and hence more difficult to place.

Dredged material consists mainly of clays, silts and sand mingled with rocks, debris, larger obstacles, and to some extent organic matter. The fine particles, i.e. clays and silts, attract contaminants. Thus, the level of concentrations of pollutants can be 10 to 100 times higher than in the other portions. Most of the existing technologies to effectively treat contaminated sediments are either energy-consuming, expensive, deal only with the coarse fraction of dredged material, aim only at volume reduction, may cause secondary pollution, or simply lack community acceptance. Another issue is the standardization of any new product. An appropriate standard for beneficiated dredged material does not exist.

At Columbia University, research has been conducted on the beneficial use of dredged material as a filler in various applications. Its source is the Port of New York and New Jersey. Here alone about 4 million cubic meters are dredged annually, most of which are contaminated to some degree (Wakeman 2001). The research focused on the beneficiation of the clay / silt fraction, because the physical and chemical behavior and level of contamination of very fine particles prevent the successful application of effective yet inexpensive treatments. First investigations of the material properties suggest a beneficial use as filler.

Mineral fillers are widely used in concrete and mortar production, for tires, paints, and plaster, just to name a few applications. Dredged sediments have similar properties as existing mineral fillers and should be able to replace or complement such materials after modification and re-organization of its structure, if treated and detoxified. This re-structuring is essential and the key to successful treatment. When used in cement-bound materials dredged material fillers exhibited promising results.

DREDGED MATERIAL PROPERTIES

Dredged material properties vary with space and time. Geology, mineralogy, morphology, and composition strongly depend on the geographic location. Physical and chemical behavior can differ greatly. Also the type, level of concentration, and chemical activity of contaminants are variable. Any treatment method has to address these great uncertainties. The most important task of the dredged material beneficiation is the detoxification of the sediments, because restrictions on further uses and public acceptance strongly depend on successfully rendering the material harmless. For that purpose prior modification of the structure has been found necessary.

Sediments found in the Port of New York / New Jersey are generally fine silts and clays mixed with coarser particles, mainly sand. The fine-particle content changes with location and time. Typical values quoted in the literature are 51% (US ACE 1999) and 80-95% (US EPA et al. 1999). The mean particle diameter is of the order of 10 µm. The main mineral components are quartz, mica, albite and feldspar (Millrath et al. 2001a).

Clays are generally able of swelling and water absorption. Their specific surfaces can be 100 times greater than those of sand, which, in combination with the surface charge and ion-exchange ability (Holtz/Kovacs 1981), leads to the sorption of contaminants. Oil products and salts cover the fine particles. As a result, fine particles attract each other and conglomerate (Figure 1). The microstructure consists of networks, which form layers of agglomerates with water intrusions. Dredged material samples have the consistency of "black mayonnaise", with water contents of 55-60% and around 9% organic compounds (Millrath et al. 2001a).

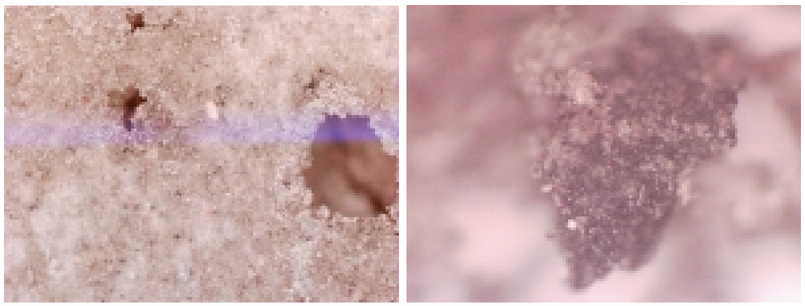

Figure 1: Light microscope observation (100x): Dry dredged material from Newtown Creek, salts on the surface (left) and conglomeration around oil products (Millrath et al. 2001a).

Samples used in this study contained negligible bacteriological contamination and exhibited only relatively low concentrations of hazardous organic components. Because the concentrations of heavy metals were unexpectedly low, samples were "doped" with cadmium and lead to evaluate the effectiveness of our treatment methods in worst-case scenarios. However, any treatment is effective if it can decrease even low concentrations, because the higher the level of contamination the more likely a system seeks a state of equilibrium at a lower concentration and the easier initial "clean-up" becomes. Therefore, one can conclude that detoxification methods, which are successful at low levels, work also if applied on highly contaminated dredged material.

DREDGED MATERIAL TREATMENT

It was found that a preliminary modification of the structure is necessary before decontamination of dredged material. In cooperation with Echo Environmental, Inc., New York, a chelating agent (hereafter referred to as Echo chemical) was evaluated for its capacity to bind heavy metals. Such chemicals are able to integrate heavy metals into stable macromolecules and thus render the material harmless. The agglomerate structure of untreated dredged material prevents the successful penetration of detoxification agents into the sediments. A method to break up the conglomerates was developed to create a much finer, i.e. widespread microstructure of dredged material leading to increased accessibility (Figure 2). This so-called Columbia University Treatment (CUT) prepares the material such that it drastically improves the effectiveness of detoxification agents.

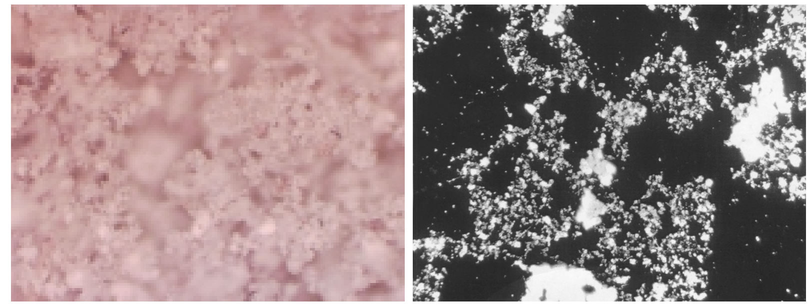

Figure 2: Light microscope observation: Widespread structure of dredged material after treatment, before (left, 100x) and after ultrasonic separation (right, 200x). Note: Small dark spots are "purified" oil products (Millrath et al. 2001a)

Conglomerates are destroyed during this treatment, and the individual components are separated from each other, which eases the access and thus success of detoxification agents. The microstructure of the resulting material might be comparable to that of available clay or mineral fillers (Figure 3). Clayey fillers contain specific natural minerals such as kaolinite (Figure 3a), montmorillonite, or illite. Those minerals usually have very active surface properties and thus, can be identified as active components in water-based systems. The main benefits of clayey fillers are their ability to absorb certain materials and exchange surface charges. Due to the fineness of the individual particles clay minerals tend to conglomerate and are capable of swelling.

Sand fillers typically have quartz-crystal structures and non-active surfaces (Figure 3b). Fine-grained sand is a passive (inert) filler with high strength properties and cannot absorb water. Fillers from dredged material combine the properties of clay and sand fillers. They consist of clay minerals, which partially are colloids, and tiny sand particles (Figure 3c).

The properties of clay minerals in dredged material can be modified by specific treatment. The water adsorption can be reduced while the surface activity may be improved. Quartz crystals generally have surface defects and are smaller in size (compare Figures 3b and 3d). Thus, sand present in dredged material is more active than regular sand filler (Millrath et al. 2001b).

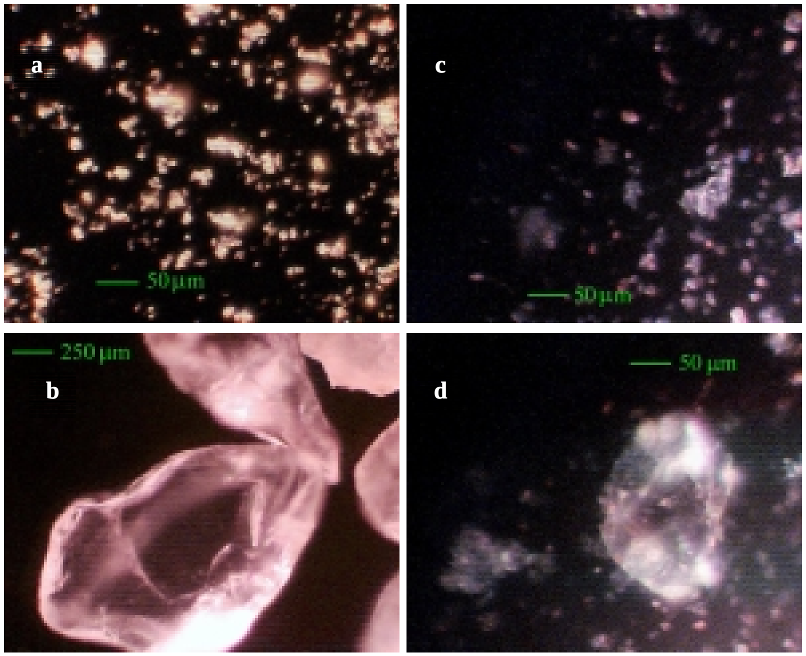

Figure 3: Light microscope observation (Millrath et al. 2001b):
a) Kaolinite (500x) c) Treated dredged material (500x)
b) Regular sand (100x) d) Quartz crystal in treated dredged material (500x)

After successful reorganization of the (micro-) structure a detoxification agent may be applied. The effectiveness of various treatment methods was evaluated following the Toxicity Characteristic Leaching Procedure (TCLP), a standard method described by US EPA (1988). The increased effectiveness of the new approach in decontamination can clearly be seen in Table 1.

Table 1: Influence of treatment methods on leaching of heavy metals in dredged material (Millrath et al. 2001c)

Sample	CUT	Echo	Lead [1)]	Cadmium [1)]
1	no	no	0.38	0.22
2	no	yes	0.53	0.20
3	yes	yes	0.17	ND < 0.02

[1)] Results of chemical analysis in ppm/dry material, ND – not detectable

For regular dredged material the concentration of cadmium was only slightly decreased after the introduction of the Echo chemical without prior modification of the structure (Samples 1 & 2), while after CUT treatment and the subsequent application of the Echo chemical, cadmium could no longer be detected (Samples 1 & 3). It is not clear why the amount of lead leached out from samples treated only with the Echo chemical increases. Possible explanations are secondary contamination or non-homogeneity of the material (Samples 1 & 2). However, the combined treatment more than halved the level of leachable lead (Samples 1 & 3).

The recent debate about cleaning up the Hudson River introduced problems of contaminated soils to a broad public. General Electric, Inc. is considered liable for extremely high concentrations of PCBs found in sediments and has been ordered to dredge the riverbed (Johnson 2001). The disposal of dredged material will be difficult due to the nature of the contaminants. An effective treatment of organics is one of the biggest challenges for the beneficiation process.

Ground soils at the riverbed or bottom of the sea are covered by sediments and by water. In these anaerobic conditions organic contaminants such as oil products, pesticides and dioxins remain unaltered. The network structure of clays or conglomerates of other fine particles allows the pollutants to migrate into clay layers and voids and thus provides “shelter” against physical and chemical attacks. In addition, relatively constant cold temperatures have a stabilizing effect on the organics. However, while their chemical activity is diminished to a minimum under water, the contact with air and changes in temperature and pressure may cause evaporation of volatile or semi-volatile components.

The presence of salts strongly influences the chemical activity of possible reactants. To be successful, treatment agents need to have access to the contaminants. Destruction of conglomerates in dredged material is necessary prior to or during detoxification as in the case of heavy metals or other inorganic toxic elements (Millrath et al. 2001c). Adsorption and absorption properties are altered during the treatment process. For effective treatment of various organics present in dredged material a combined treatment method is now under development. Generally, main goals of the detoxification process are the immobilization of organics and the encapsulation of heavy metals.

DREDGED MATERIAL FILLER

The use of mineral fillers such as finely ground limestone or quartz is very common in concrete and mortar production. The clays / silt fraction of dredged material exhibits similar characteristics. Therefore, untreated and treated dredged material was used as filler in cement- or gypsum-bound mortars. It was found that plastic and adhesive properties seem to improve with the administration of dredged material. When compared to reference mixes without additional fillers, samples containing dredged material were more homogenous and less segregation was observed. Because the clay minerals can adsorb and hold back water, the water-to-binder ratio had to be adjusted for sufficient workability.

To simulate worst-case scenarios as can be found in so-called hot spots, soluble salts of cadmium and lead were added to and mixed thoroughly with dredged material. Both metals are widely used in various industrial processes and are of very different chemical nature. Lead is able to change its valency, which results in various stages of reactivity and solubility. Cadmium, typically used in production of electronics or semi-conductors, is far more active than lead and very soluble in various liquids. Therefore, it is extremely hazardous, especially when in contact with blood. If both, cadmium and lead, can be rendered harmless, all other heavy metals can be dealt with as well.

Some mortar samples were prepared with such artificially contaminated material. Samples were tested for compressive strength after 2 days (gypsum-bound) or 7 and 28 days (cement-bound) and afterwards sent for chemical analysis. No clear correlation between compressive strength and artificial contamination or treatment method could be established. However, cement-bound samples with untreated dredged material exhibited significantly lower strength (Table 2).

Table 2: Leaching test and compressive strength test results of mortar compositions with artificially contaminated dredged material (Millrath et al. 2001a)

Sample	CUT	Echo	Binder	Lead [1)]	Cadmium [1)]	Strength [2)]	
						2d	7d
A1	no	no	-	0.85	5.0	-	-
GY1	no	no	Gypsum	0.70	1.15	4.9	-
GY2	no	yes	Gypsum	0.75	0.94	3.3	-
GY3	yes	yes	Gypsum	ND < 0.01	0.05	4.8	-
CE1	no	no	Cement	ND < 0.01	ND < 0.02	-	14.1
CE2	no	yes	Cement	ND < 0.01	ND < 0.02	-	20.8
CE3	yes	yes	Cement	ND < 0.01	ND < 0.02	-	19.0

[1)] Results of chemical analysis in ppm/dry material (after TCLP), ND – not detectable

[2)] Compressive strength in MPa

The results of the leaching tests for mortar samples are summarized in Table 2. They show a drastic drop in the level of leachable cadmium after treatment when dredged material was administered as a filler. Gypsum-bound mortar samples GY1 and GY2 exhibit only partial decontamination. However, after combined treatment the concentrations were below or close to detection limits (GY3). It is obvious that CUT is necessary as a prior treatment. Cement itself seems to be effective in binding metals and in preventing leaching. Thus, neither lead nor cadmium was detected in any case (CE1 to CE3).

Figure 4: Processing options – dredged material fillers in form of powders, droplets, slurries or "cookies" (Millrath et al. 2001b)

Dredged material fillers may find a wide field of applications because they include modified clay as the chemically dominant phase and sand as the largest fraction. Various treatment methods allow adjusting filler properties to suit particular customer needs. For example, it can be processed as granules, droplets or powder (Figure 4). But also mechanical properties can be designed. As an example, the solubility of dredged material fillers in water after 24 hours is illustrated in Figure 5. The modification of porosity and hydrophobic characteristics changes the behavior of treated dredged material in nearly any desired way. It can be stable under water, dissolve, or even float.

Figure 5: Solubility in water - effect of different treatment methods (Millrath et al. 2001c)

Depending on the respective processing technology, the behavior of dredged material filler may differ. Additional adjustment of certain properties is possible. Other processing technologies for specific applications have not yet been developed, but the core treatment seems to be established.

CONCLUSIONS

The research has shown that the developed treatment methods are effective in beneficiating dredged material, especially its fine fraction, for further use. New York Harbor dredged material was successfully detoxified, i.e. leaching was prevented. The CUT treatment reorganizes the microstructure, activates mineralogical formations and increases the surface area of sediments.

The clay / silt fraction of the material can be activated and without further separation function as filler in various applications. For clayey fillers or active components a high surface activity is desirable. After modifying of structural properties of treated dredged material it should be possible to engineer certain properties according to specific needs.

Dredged material fillers can function as valuable semi-products or end products that can compete economically with other materials when beneficially used in inorganic and organic composites. Any further use has to be evaluated in terms of economic feasibility and environmental acceptability, in terms of degree of detoxification, and mechanical and chemical properties. It should be possible to redesign the material for specific needs. Different technologies can be developed based on this core treatment.

Dredged material was successfully evaluated as filler in concrete products. Treated dredged material improved plastic properties and decreased segregation (no bleeding). It seems to be suitable to function as mineral filler in cement-based composites without loss of strength and density. However, adjustment of the composition is necessary to achieve sufficient workability. Leaching of contaminants was prevented. Filler products according to specific customer needs are currently under development or will be developed in the near future.

It seems to be possible to implement the treatment process introduced herein on-barge and thus save time and storage space. Dredged material is turned into a valuable resource before it reaches the shore. This treatment provides an inexpensive yet effective solution for the disposal problem especially if the initial negative value of the material is taken into account. By avoiding the siting problem, public acceptance is expected to be easier to obtain.

The proposed treatment can serve as the base for various technologies to beneficiate the clay / silt fraction of dredged material. Tests with highly contaminated samples have to be conducted to finalize the suggested method and further demonstrate its feasibility. In particular, the evaluation of dredged material with high levels of organic contaminants is required. A demonstration-scale project has to be established and evaluated for both technical and economic feasibility.

ACKNOWLEDGEMENT

The work reported herein was sponsored by Echo Environmental, Inc., New York, NY. This support is gratefully acknowledged.

REFERENCES

Kirk Johnson 2001. Whitman To Issue Order To Dredge Hudson For PCB's. *The New York Times*, August 1, 2001.

Robert D. Holtz, William D. Kovacs 1981. An Introduction To Geotechnical Engineering. Prentice Hall, Englewood Cliffs, New Jersey, NJ.

K. Millrath, S. Kozlova, S. Shimanovich, and C. Meyer 2001a. Beneficial Use of Dredge Material, Progress Report. Columbia University, New York, NY.

K. Millrath, S. Kozlova, S. Shimanovich, and C. Meyer 2001b. Beneficial Use of Dredged Material 2, Second Progress Report. Columbia University, New York, NY.

K. Millrath S. Kozlova, S. Shimanovich, and C. Meyer 2001c. New Approach to Beneficiation of Dredged Material as a Filler. *World Dredging (Mining & Construction)*, 37(11): 8-20.

T. Wakeman 2001. Finding Productive Uses for Dredged Material and Contaminated Sediments. In: R. E. Randall (Ed.) 2001. Proceedings of the 21st Technical Conference of the Western Dredging Association in Houston, TX, June 24-27, 2001. Center for Dredging Studies, Texas A&M University, College Station, TX.

US ACE 1999. Dredged Material Management Plan for the Port of New York and New Jersey, DRAFT Implementation Report. USACE, New York, NY.

US EPA 1988. 40 CFR Part 260 et al.: Hazardous Waste Management System; Land Disposal Restrictions; Final Rule. *Federal Register, Part II Environmental Protection Agency: Rules and Regulations*, 51(218).

US EPA, US ACE, US DOE-BNL 1999. Fast Track Dredged Material Decontamination Demonstration for the Port of New York and New Jersey, Report to the Congress. National Technical Information Service, Springfield, VA.