610 SW Mudd Building, New York, NY 10027 Phone (212) 854-3143 / Fax (212) 854-6267, internet: www.civil.columbia.edu/meyer
K. Millrath, S. Kozlova, S. Shimanovich, and C. Meyer December 2001
Second Progress Report
Beneficial Use of Dredged Material 2
Department of Civil Engineering and Engineering Mechanics
Columbia University in the City of New York

Summarv

Executive Summary

Dredging is a necessary process to maintain harbors and navigational channels and to deepen them to accommodate larger shipping vessels. Because the dredged material is typically contaminated, its disposal poses environmental hazards and is at present achieved in specially designed confined disposal facilities at high costs. It was the objective of a two-year research project at Columbia University to develop a practical and economically feasible method to decontaminate New York Harbor dredged material, thereby beneficiating it for further use.

The research of the first year focused primarily on the use of dredged material as an aggregate in concrete applications. The results and findings of that research phase were documented in an earlier progress report [1]. During the second year, research efforts concentrated on the use of dredged material as a filler, which is useful for other applications aside cement composites. Fillers are widely used in construction or other industries. Because of their small average particle size, the almost inert quartz portion and the chemically active silt/clay fraction dredged material suggest the use of the material as a filler. The detoxification method developed during this research project was described in some detail in Reference [1], and at present, a patent application is being prepared. It was shown that the treatment procedure is preventing contaminants from leaching out, whether the dredged material is converted into a filler or used as a component in cement composites. Initial studies give rise to the hope that it will likewise encapsulate organic compounds such as PCBs. The treatment procedure lends itself to implementation on the dredging barge, which would reduce transportation costs and in particular avoid the politically sensitive issue of finding a suitable on-shore site for treatment. The estimated costs of the proposed solution promise to be relatively low compared with those of presently available alternatives and fall will within the range that is considered feasible for port operators such as the Port Authority of New York and New Jersey. However, a full-scale pilot study would be required to substantiate this claims.

olun	bia University Beneficial Use Of Dredged Material 2	Content
CON	TENT	
1	Introduction	1
2	Evaluation Of Dredged Material Products As Filler	3
2.1	Filler Characteristics And Uses	3
2.2	Comparative Analysis Of Dredged Material And Other Mineral Filler	s 4
2.3	Organic Components In Dredged Material	7
2.4	Decontamination Or Treatment	9
2.5	Economic Aspects	11
2.6	Projected Technical Data Sheet	12
2.7	Prospective Beneficial Uses	13
3	Fillers From Dredged Material In Concrete Compositions	15
3.1	Mechanical Properties	16
3.2	Plasticity	18
3.3	Workability	20
3.4	Durability	21
3.5	Environmental Aspects	23
4	Conclusions and Outlook	28
5	References	31

1 Introduction

Dredging is absolutely necessary to maintain the Port of New York and New Jersey operational. The navigational access to ports and shipping channels is one of the main tasks for this important harbor on the East Coast. Decreasing storage capacities for disposal of potentially hazardous dredged material urge authorities to search for beneficial uses of such material. Especially, the silt/clay fraction of dredged material is difficult to place because it tends to attract pollutants. Worldwide, major ports need environmentally acceptable yet economical solutions for the same problem.

The previous report, *Beneficial Use of Dredge Material* [1] summarized the first phase of research at Columbia sponsored by Echo Environmental, Inc. Treatment methods were introduced to prepare dredged material to be beneficiated as aggregate replacement in concrete. In comparison to existing treatment approaches, a simple and inexpensive yet comprehensive procedure was proposed with the Columbia University Treatment (CUT). This method changes the microstructure of dredged material by destroying network-like conglomerates of clays, silts and salts around oil products. Leaching tests showed that it is suitable to prepare dredged material for further uses. A replacement of 10% sand in mortar compositions was suggested as a compromise between workability and mechanical properties.

The particle size range of dredged material rather suggests the usage as filler, e.g., in concrete products. Thus, research in the second phase of this project, focused on the conversion of dredged material as a waste product into a valuable resource as filler material. Since a new type of filler needs to be evaluated by itself or as a component of established applications. It was decided to study the effects of dredged material as filler in cement composites. The goal was to design a mortar with desirable mechanical properties and workability yet consuming relatively large quantities of the (treated) material.

An appropriate prior treatment for specific contaminants is necessary. This report introduces approaches to such detoxification and the beneficial use as filler in concrete production. The successful establishment of a new concrete component will be the starting point for the development of a more universal utilization as filler that is not only limited to concrete but also to other applications such as plaster, plastics or tires. The technical implications of in-situ treatment is discussed, but the design of a pilot demonstration test requires further work.

2 Evaluation Of Dredged Material Products As Filler

2.1 Filler Characteristics And Uses

Fillers are widely used for the formulations of composites to modify properties, such as hardness, permeability, durability, corrosion, chemical resistance, flammability, texture, or electrical characteristics. They can either fill out voids between "regular" particles or actively react with the other components or both. Therefore, fillers are integrated into the composite structure either mechanically or through chemical bonds.

Most of the fillers currently in use are inorganic and derived from naturally occurring minerals. Clay minerals or finely ground sands are the most common type of fillers. Others are synthetic and usually manufactured by precipitation of a solution with soluble salts. Fillers can be found in numerous applications, for example, in the production of polymers, tires, plaster, mortar, concrete, or even dental fillings.

2.2 Comparative Analysis Of Dredged Material And Other Mineral Fillers

The chemical composition of a filler depends strongly on its mineralogy. Main components are various clay minerals, silt, or sand. Pozzolanic properties and chemical behavior are dominated by the crystalline phases of metal oxides. The chemical compositions of fillers selected for this study are given in Table 1.

Table 1: Chemical compositions of selected mineral fillers

Туре	Base	SiO ₂	Al_2O_3	Fe ₂ O ₃	CaO / MgO	Na ₂ O / K ₂ 0
Clay/Sand	Dredged material	58-42%	8-13%	4-6%	3-23%	3-4.5%
Clay	Bentonite [2]	45-66%	16.4-22%	2.5-16.5%	0.8-2%	2-4%
Clay	Kaolin [3]	52%	41%	4.3%	0.3%	0.9%
Sand	Quartz (fines)	90-95 %				

Physical properties and particle size distribution are determined by the production method. Particle size distributions can range from relatively coarse to very fine with median sizes well below 1 micron. Expensive precipitated fillers such as silica fume usually have a finer and narrower particle size distribution than ground fillers. Table 2 shows mineralogy and particle size ranges of dredged material and inorganic fillers with similar mineralogical compositions.

Sand filler

Beneficial Use Of Dredged Material 2

Columbia University

0.075-2 mm

Type of Filler Base	Mineralogical nature	Particles Size Range
Dredged Material	Clay minerals: Illite, Chlorite Silt minerals: Mica & Feldspars Sand: finely grained Quartz	0.8-40µm
Bentonite	Montmorillonite and other clay minerals	0.6-1.2µm
Kaolin clay/China clay	Kaolinite Alumino-silicates	0.5µm

Quartz

Table 2:	Mineralogy and	particle size range o	f selected mineral fillers

Clayey fillers contain specific natural minerals such as kaolinite (Figure 1a), montmorillonite, illite and others. These minerals usually have very active surface properties and thus can be identified as active components in water-based systems such as concrete. 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 able to swell with considerable increase of their volume. When used in cement-based compositions the high water absorption of clays may cause a significant decrease in workability of the fresh mix and increase the permeability of the hardened product.

Columbia University

Beneficial Use Of Dredged Material 2

Sand fillers typically have quartz-crystal structures and non-active surfaces (Figure 1b). Fine-grained sand is a passive filler with high strength properties and low water absorption. When added to cement based material, sand filler can increase the permeability.





a) Kaolinite (500x)	b) Regular sand (100x)
c) Dredged material (500x)	d) Quartz crystal in dredged material (500x)

6

Fillers derived from dredged material combine the properties of clay and sand fillers. They consist of colloid clay minerals and very fine sand particles (Figure 1c). 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 than sand (compare Figures 1b and 1d). Thus, the sand present in dredged material is more active than regular sand filler.

The present study indicates that the behavior of clay minerals in dredged material may govern the performance as active filler. Manipulation of their properties during prior treatment may lead to fillers specially designed for certain purposes with a wide range of applications.

2.3 Organic Components In Dredged Material

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 is now being ordered to dredge the riverbed [4]. The disposal of dredged material will be difficult due to the nature of the contaminants. Especially the placement of the clay/silt fraction of dredged material, which tends to attract pollutants [5], will be very problematic. The effective treatment of organics is one of the biggest challenges in the beneficiation process.

Beneficial Use Of Dredged Material 2

Ground soils at the riverbed or bottom of the sea are covered by sediments and by water. In this anaerobic condition 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, 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, the treatment needs 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 inorganic toxic elements) [6]. Adsorption and absorption properties are altered during the treatment process. Monitoring of the pH level is recommended because chemical reactions with organic substances may be affected in alkaline environments. For effective treatment of various organics present in dredged material a combined treatment method is now under development that addresses the problems introduced above. Unfortunately, the dredged material samples used in the present study so far exhibited very low levels of organic contamination and hence our research was mostly restricted to theoretical considerations.

2.4 Decontamination Or Treatment

The successful development of fillers from dredged material requires an appropriate treatment of the contaminants that may be present. The methods to detoxify the material may be part of a technological cycle. Effective treatment should prevent the trace contaminants from leaching out or at least decrease the leachate concentrations below applicable regulatory limits. It also should improve the filler performance.

In order to evaluate the potential environmental risk and health threat, it is instructive to compare results of leaching tests of dredged material with those of dental filling materials (Table 3). Dental composites and sealants include cement, polymers, organic monomers and heavy metals. All these materials are industrial products and are also present in dredged material as contaminants. Heavy metals and toxic organics present in dental materials can leach out directly into the saliva and from there into the human body.

In the case of dredged material used as filler, the potential of toxin migration into the human body seems to be comparatively low because of the lack of contact points with saliva. This comparison may prove useful in increasing public acceptance of products that contain treated dredged material. The relatively high concentrations of cyanides in dredged material were identified as an unsolved problem, partly because existing leaching procedures are of limited suitability for dredged material fillers. The results of chemical analyses may be incorrect in the presence of ferric materials or salts [7]. Both are available in dredged material. Changes of the pH level influence the detection sensitivity [8]. These conditions limit the reliability of results from cyanide leaching tests. However, all concentrations found in this study are far below those detected in cigarette smoke, 5–70 ppm [9] (see also Table 3). When dredged material was used as filler in mortar compositions no cyanide was leached out in the "rain chamber test" (Section 2.5).

Table 3: Leaching test results for fillers in dentistry and from dredged material

	Concentrations			
Leachable Analyt	Dental filler	Natural dredged	Dredged	
	materials	material (hot spots)	material filler	
Heavy metals				
Arsenic	Detected	Up to 48 ppm	ND <0.1 ppm	
Cadmium	NA	Up to 27 ppm	ND <0.02 ppm	
Chromium	Detected	Up to 300 ppm	ND <0.5 ppm	
Lead	Detected	Up to 610 ppm	ND <0.1 ppm	
Total Mercury	Detected [10]	Up to 3 ppm [11]	ND <0.002 ppm	
Polychlorinated biphenyls (PCBs)	Detected [10]	38-148 ppb [11]	NA	
Semivolatile organics, including	1150-6100 ppm	ND-1100 ppb	NA	
phenols and phthalates	[9]	[11]	INA	
Cyanides	NA	NA	0.27-2.74 ppm	

ND – not detected ppm – parts per million NA – no data available ppb – parts per billion

A more comprehensive overview of dredged material decontamination methods is provided in Reference [1]. Current research focuses on the treatment of organic contaminants. Due to the lack of appropriate samples, mostly theoretical approaches to decontamination are being pursued at present. The low levels of organics concentrations in the samples studied herein suggest that the treatment methods proposed so far are sufficiently effective for such dredged material for which the samples are representative [1] (see also Section 3.5 and Table 14).

2.5 Economic Aspects

The economic evaluation of prospective fillers produced from dredged material has to compare the production costs with those of inexpensive (mass) clay fillers. The main cost factors are comparable as can be seen in Table 4. The most important factor, however, is not shown in Table 4. This is the potentially very large negative value associated with dredged material, if it has to be disposed of in special confined facilities.

Table 4: Cost factors: fillers from natural clays and from dredged material

Clay filler	DM filler
Excavation	Dredging
Preparation of aqueous slurry	Removal of large objects
Pipeline transportation	
Centrifugal separation	Mixing with reagents
Filtration	
Drying	Drying
Grinding	Grinding

2.6 Projected Technical Data Sheet

The classification of (treated) dredged material as filler is necessary to establish it as a "regular" raw material. A possible technical data sheet for the new material is represented in Table 5.

Table 5: Projection of a technical data sheet for fillers from dredged material

Material identification	
Common Name:	Clay/sand modified filler
Physical Form:	Powder, Granules, Chips
Ingredient	Approximate Weight
Clay minerals (predominantly illite and kaolinite)	30-60%
Sand (Si02, quartz)	30-60%
Mica, field spat	>4%
Water	>2%
Physical properties	
Particles < 10 microns	Powder: 70-75%
Median particle size	8-11 microns
Color	Gray/light brown
Fire and Explosion Data	
Flash point	None
Nonflammable, non-explosive	
Reactivity Data	
Condition contributing to instability	None, non-reactive
Incompatibility	None, inert and non-reactive
Hazardous decomposition products	Currently under research
Contribution to hazardous polymerization	None
Spill, Leak, and Disposal procedures	
Aquatic toxicity	Currently under research
Waste disposal method	Landfill
Emergency steps for material release or spill	Vacuum dust or sweep using dust suppressant.
Neutralizing chemicals	None required.
Special Protection Information	
Ventilation requirements	Same as for any nuisance dust
Specific Personal Protective Equipments	Currently under research
Special precautions and comments	
	Aqueous slurry is slippery. Special care is recommended for spills on floors or concrete pads

2.7 Prospective Beneficial Uses

Dredged material fillers may find a very 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. Using a waste product for beneficiation, which otherwise would be of large negative value, fillers derived from dredged material constitute a comprehensive approach to solving an environmentally pressing problem.

The end product of the treatment methods introduced herein can be processed into various shapes and forms, depending on the specific needs or preferences of customers. It is possible to develop dredged material fillers as granules, droplets, powders, slurries or "cookies" (Figure 2). Depending on the respective processing technology, the behavior of the product may differ. Additional adjustment of certain properties is possible.

The production of construction materials offers a broad range for applications of dredged material fillers. When added to concrete, they can improve its mechanical properties and reduce cost. If modified, they may increase chemical resistance, corrosion behavior, and dynamic stability. They may also be used to adjust setting properties of mortars or concrete compositions. It may be easier to

remove formwork when concrete products contain dredged material fillers. The recommended dosage is up to 30% with respect to cement weight.



Figure 2: Processing options – dredged material fillers in form of powders, droplets, slurries or "cookies"

Polymer composites based on resins and classified as insulators have been formulated with regular siliceous sand. They may benefit significantly from the addition of clay/sand filler from dredged material. Also the beneficiation of dredged material as a filler in tire production seems to be possible. The development of various products is ongoing or planned.

3 Fillers From Dredged Material In Concrete Compositions

Because of the quantitative dominance of sand in dredged material, research had been conducted to replace parts of regular aggregate in mortar compositions. The results are given in the previous report, *Beneficial Use of Dredged Material* [1]. Sand replacement of up to 10% was shown to be a valid option. However, because the clay/silt fraction in dredged material is chemically prevalent, it seems to be at least an equally important component to address. Clays, silts and defect quartz crystals (see Section 2.2) have much smaller mean particle sizes than fine sand. Thus, replacement of regular aggregate with dredged material would exchange two quite different components, both in chemical nature and size.

A dredged material filler seems to be suitable for applications such as plaster, paint, mortar, or concrete. Its particle size distribution and expected adhesive properties are expected to be the main benefits. But to qualify for such uses it is necessary to evaluate its strength, (chemical) stability, durability, mechanical / physical properties, and leaching performance. That can be done either with a known application of the filler or using the filler alone, which may lead to difficulties due to the fine size and character of the material. To assess the performance as filler we conducted various experiments with untreated and treated dredged material in concrete applications. The test set-ups and procedures used are summarized in Reference [1].

3.1 Mechanical Properties

Natural wet dredged material as filler decreases workability so drastically that the amount of such material should not exceed 10% of the cement. A drop in strength of 40% accompanied the poor workability of samples containing 10% dredged material with respect to cement or about 3% of all dry components as a filler (Table 6). In conclusion, dredged material should not be used in natural wet condition. It should be but either dried or treated and dried. This report does not include further details on this preliminary study but focuses on dried and/or treated dredged material as filler. Henceforth, the term *dredged material* refers to material that has been dried and/or treated.

Table 6:	Properties of	f mortar with un	treated wet d	lredged ma	terial as filler
----------	---------------	------------------	---------------	------------	------------------

Dredged material content (in M% of cement)	0	5	10
Water-cement ratio	0.42	0.43	0.42
Flow	56 mm	37 mm	28 mm
7d density	2.34 g/cm ³	2.34 g/cm ³	2.32 g/cm ³
7d compressive strength*)	50.2 MPa	43.8 MPa	30.9 MPa

Test specimens: 1 inch * 1 inch cylinders

When used as filler in concrete applications, the amount of dredged material that may be added is limited by the decrease either in mechanical properties or in workability. On the other hand, the large quantities of material that need to be

dredged and disposed of call for applications that can use as much dredged material as possible. In comparison to reference samples without any fillers, mortar specimen containing dredged material exhibit a slight decrease in strength or workability if the water-cement ratio (w/c) is not adjusted. High flow rates can be obtained at relatively low w/c ratios, if superplasticizers are used. In this case, dredged material contents of 20 to 30M% of cement are suggested.

After administering dredged material to fresh mortar the workability decreases significantly. To maintain a sufficient flow of >45mm (small ring) the addition of superplasticizer is required. When the dredged material content is raised above 30M%, the compressive strength decreases drastically, and so does the density (Table 7). Hence, a dosage of 30M% is suggested as an upper limit.

Table 7:	Properties of mortar with treated dredged material as filler (CL	JT)

Dredged material content (in M% of cement)	20	30	35	40	45
Water-cement ratio	0.50	0.55	0.60	0.65	0.70
Superplasticizer	2%	2%	2%	2%	2%
Flow	63 mm	59 mm	58 mm	60 mm	55 mm
7d density	2.29 g/cm ³	2.28 g/cm ³	2.23 g/cm ³	2.10 g/cm ³	2.02 g/cm^3
28d density	2.17 g/cm ³	2.17 g/cm ³	2.10 g/cm ³	2.01 g/cm ³	1.86 g/cm ³
7d compressive strength*)	43.6 MPa	31.8 MPa	27.7 MPa	20.9 MPa	11.7 MPa
28d compressive strength*)	54.9 MPa	48.8 MPa	37.6 MPa	29.4 MPa	20.3 MPa

*) Test specimens: 1 inch * 1 inch cylinders

In addition to 30M% dredged material, several other fillers were administered to the fresh mix for further improvement of mortar properties. It seems that the two ceramic fillers, *CERA1 and CERA2*, had only little effect, but a clay-based filler, *CLAY*, drastically decreased workability (Table 8). In conclusion, the gap between particle sizes of cement and sand aggregate can be completely closed by addition of dredged material filler. No additional components are required.

Table 8: Properties of mortar with 30M% treated dredged material (CUT) and additional fillers

Additional Filler (Type, M% of cement)	None	CERA1 5.0	CERA2 2.0	CLAY 7.5
Water-cement ratio	0.42	0.42	0.42	0.42
Superplasticizer	2.0%	2.5%	2.5%	2.5%
Flow	86.4%	87.9%	88.1%	17.8%
7d density	2.23 g/cm ³	2.24 g/cm ³	2.23 g/cm ³	2.24 g/cm ³
7d compressive strength*)	49.2 MPa	45.7 MPa	47.9 MPa	48.5 MPa
28d compressive strength*)	64.5 MPa	64.3 MPa	64.2 MPa	62.3MPa

*) Test Specimens: 2-inch cubes

3.2 Plasticity

Tests were conducted to evaluate the plasticity and rheological behavior of cement slurries with or without dredged material. It could be shown that dredged

Beneficial Use Of Dredged Material 2

Columbia Universitv

material fillers increase plasticity of the mortar and substantially improve workability. The "smoothness" of the mix can be compared to the influence of lubricating oil on industrial machinery. This effect may explained with the reduced water absorption. Administering dredged material could prevent segregation.

The rheology of fresh cement-based compositions is controlled by the structure of three-dimensional networks formed by cement particles in water. This network governs the viscoelastic properties of fresh mixes. Initially, cement-based compositions have to be characterized by both, solid and liquid phases simultaneously. Generally, they lose their liquid behavior as soon as the cement starts to set. The rheological properties of fresh mixes have to be adjusted to obtain sufficient workability.

Rheological experiments with a rotational viscometer demonstrated that the addition of dredged material filler significantly alters the viscoelasticity of cement-water slurries with or without superplasticizer. The tests showed that the viscosity increases by about 25-40% after administration of dredged material, while the tendency of segregation diminishes. The flow behavior index changes slightly, leading to the conclusion that the flow can be adjusted easily with regular superplasticizers or other admixtures. Fresh cement-based compositions containing dredged material filler maintain liquid properties for a longer period after mixing. Compaction of mortar samples by means of vibration seems to be easier.

3.3 Workability

Sufficient workability can be indicated by a certain flow rate of fresh mortar. To adjust the flow water can be added to the mix. The resulting increase of the w/c ratio usually leads to undesirable reductions in compressive strength. An alternative to adding water is the administering of admixtures to the mortar composition, such as high-range water reducers or superplasticizers. Because of the clay particles in dredged material a higher dosage than usual is recommended for modified mortars containing such fillers.

However, the addition of superplasticizer in high quantities (up to 4%) alters the (micro-) structure of mortar samples. Thus, its content is limited to avoid the introduction of additional pores to the samples. The recommended dosage is 1.0 to 1.5 M% (with respect to cement). Various superplasticizers were tested, with a proprietary admixture developed at Columbia (SP1 in Table 9) showing the most promising results [1]. The others were based on lignosulfonate (SP2), formaldehyde (SP3), and polyester (SP4). The influence of the superplasticizer type on the flow of fresh mortar was evaluated for one composition containing clayey fillers at constant w/c ratio. Two different methods to determine the flow were used. One uses a small ring, which is filled with mortar. After removal of the ring the diameter is measured in mm. The other method is based on the same principle but uses a cone and the relative change of the area is measured in %. The test results confirm previous findings (Table 9). Table 9: Flow of mortar with different types of superplasticizer

Beneficial Use Of Dredged Material 2

Columbia University

SP amount in M% (of cement)	SP1	SP2	SP3	SP4
0.55	71 mm	46 mm	68 mm	56 mm
1.25	118%	96%	78%	NA

NA – no data available

The setting times of mixes with and without dredged material were determined by means of a Vicat Needle following ASTM C191 [12]. No superplasticizers were used during these tests. The administration of dredged material increased the setting time from 180 min for a mix without dredged material to 205 and 285 min for mixes with treated and with natural dried dredged material, respectively. The effect of accelerating admixtures was studied, but due to poor first results this option was not further pursued.

3.4 Durability

The durability of concrete materials is determined by numerous factors. Here, only the potential alkali silica reactivity was investigated, as measured by the standard ASTM C1260 test [12] and a new autoclave test [13]. For samples containing 20% dredged material as replacement of aggregate the compressive strength was determined at ages up to 150 days. No drop in strength was experienced for higher ages (Table 10).

Beneficial Use Of Dredged Material 2

In addition, reference specimens were tested at age 150 days both without dredged material and with 5M% and 10M% dredged material as filler. The increase of compressive strength with age was comparable for all samples (Table 10).

Dredged material content (Type, M% of cement)	0	Replacement, 20	Filler, 5	Filler, 10
Water-cement ratio	0.42	0.63	0.42	0.42
Superplasticizer	1.0%	2.0%	2.0%	3.0%
Flow	56 mm	48 mm	37 mm	28 mm
7d density	2.34 g/cm ³	1.93 g/cm ³	2.34 g/cm ³	2.32 g/cm ³
150d density	2.26 g/cm ³	1.95 g/cm ³	2.24 g/cm ³	2.24 g/cm ³
7d compressive strength*)	50.2 MPa	25.9 MPa	43.8 MPa	30.9 MPa
150d compressive strength*)	71.8 MPa	48.0 MPa	66.8 MPa	64.5 MPa
Increase	30%	46%	34%	52%

Table 10: Properties of mortar with dredged material at increased age

*) Test Specimens: 1 inch * 1 inch cylinders

For the ASR tests, three 10x1x1 inch mortar bars were prepared for each of three series containing no, untreated, and treated dredged material. None of the samples exceeded the threshold value of 0.10% length change in the ASTM C1260 test and thus, can be considered non-reactive (Table 11). Additional tests, such as freeze-thaw and chemical resistance tests, are planned.

 Table 11:
 Length changes of mortars without and with dredged material filler

Dredged material content and treatment	None	30M%, dried untreated	30M%, CUT treated
ASTM C1260*)	0.059%	0.038%	0.045%
Autoclave	0.019%	0.026%	0.034%
*) ASTM C1260 limit for innocu	<0.100%,		

>0.200%

ASTM C1260 limit for innocuous behavior: for potentially deleterious expansion:

3.5 Environmental Aspects

Dredged materials and especially the clay/silt fraction thereof accumulate various heavy metals and organic contaminants. Some pollutants might be toxic and leach out when in contact with water, thereby contaminating the local environment. Therefore, a thorough study on the leachability of contaminants is essential to demonstrate that the use of dredged material as filler in cement-based compositions is feasible, while meeting regulatory limits. Testing methods can be assessed by using artificially contaminated dredged material. But such material may not reflect real life conditions (see also Reference [1]).

A new leaching test set-up for extraction of contaminants prior to chemical analysis is suggested below, which is based on those described in References [14] and [15]. Three "rain chambers" were installed using plastic containers (polypropylene) with independent water circulation (Figures 3 and 4).

Columbia University

Beneficial Use Of Dredged Material 2

The flow rate was held constant over the test period. For better comparability, demineralised water was used to extract the pore solution over about 110 days. Sample to water ratio was 1:5 (by volume) as suggested in Reference [15]. The system was somewhat but not completely sealed to keep possible pollutants out. For each rain chamber, three 2-inch mortar cubes were prepared and placed on small pedestals in the containers.





Beneficial Use Of Dredged Material 2

Columbia University



Figure 4: Test set-up for "rain chamber test"

Table 12 contains information on the three sets of specimens tested, and their flow and strength test results are summarized in Table 13. The superplasticizer content was higher than the recommended dosage to determine the effect of this additive on the leaching test results (compare Section 3.3). After extraction during the "raining" period samples of the circulating water in each system were analyzed for any contaminants leached out of the pore solution of the specimens. The specimens themselves were crushed after the rain chamber test and also sent for analysis. The cubes used to determine the 28-day compressive strength were not subjected to the rain chamber test. After the strength test they were stored at regular room conditions, then crushed and sent for chemical analysis at the same age as the other samples.

Beneficial Use Of Dredged Material 2

Table 12: Test plan for rain chamber test

Mix No.	DM amount	Treatment	w/c- ratio	SP *)
1	none	-	0.41	2.5 M%
2	30 M%	none	0.48	2.5 M%
3	30 M%	CUT / Echo	0.42	2.5 M%

*) Superplasticizer dosage (with respect to cement)

Table 13: Test results for rain chamber test specimens

No.	Flow	28d density	28d comp. strength	148d comp. strength *)
1	>150%	2.29 g/cm ³	64 MPa	67 MPa
2	56%	2.19 g/cm ³	52 MPa	54 MPa
3	85%	2.23 g/cm ³	50 MPa	65 MPa

*) After rain chamber test

The three compositions did not differ much in the levels of detectable leachates such as heavy metals and cyanides. Table 14 indicates that the cement matrix prevents the leaching of heavy metals, but cyanides were detected in the mortar. The concentrations are far below the level found in dredged material that was used. Similarly low levels of total cyanides were also found in mix 1, the reference mortar without dredged material. It was shown before that heavy metals are detectable even in "clean" aggregates [16]. This may also be the case for cyanides. However, the leachable cyanide concentrations in the pore solution were below the detection limit. Hence, it can be concluded that no cyanide leached out of mortar samples. None of the samples showed physical damage after having been exposed to "rain" for 16 weeks.

27

Beneficial Use Of Dredged Material 2

Columbia University

Contaminant	Untreated	Mortar composition (see Table 12)						
	dredged material	Mi	Mix 1		Mix 2		Mix 3	
	materiar	M *)	PS *)	M*)	PS *)	M*)	PS*)	
Zinc (Zn)	7.50	0.02	0.01	ND	0.01	ND	0.02	
Nickel (Ni)	0.20	ND	ND	ND	ND	ND	ND	
Copper (Cu)	0.05	ND	0.05	ND	ND	ND	ND	
Total Cyanide (CN)	1.12	0.10		0.12		0.07		
Leachable Cyanide	0.82		ND		ND		ND	
Pesticides / PCBs	ND (below detection limit)							

*) (M) Analysis of mortar specimens (PS)

Analysis of pore solution extracted from samples

The standard for groundwater effluents provides a maximum allowable concentration for cyanides of 400 ppb [17], which is about four times as high as the concentration found in the mortar samples. It is suspected that some cyanides extracted from the test specimens originated from the cement, as specific grinding admixtures are added during cement production. Also superplasticizers and other admixtures may contain low levels of cyanides.

Columbia University

Conclusions And Outlook 4

The research has shown that the suggested treatment methods are effective in detoxification of dredged material. When used as filler in concrete, treated dredged material can improve properties such as plasticity without leaching of contaminants. The costs for such treatment are difficult to estimate at this stage without an indepth economic analysis. However, the treatment process is simple enough so that it may be implemented on a barge immediately after the dredging operation itself. Such in-situ detoxification would reduce logistics problems and the need for temporary storage capacities. Any treatment prior to onshore placement has immense economic and political advantages, because the crucial problem of finding a suitable site and overcoming public resistance to accept potentially hazardous material is thereby eliminated. The barge thus would receive "contaminated" material and deliver basically "clean" material to the user. The economic evaluation of this operation has to await the establishment of a full-scale pilot study.

The goal of the Port Authority of New York and New Jersey to reduce disposal costs below \$25/CY does not seem to be unrealistic. The treatment procedure developed in the present research appears to bring this goal within reach.

rsitv

The decontamination with cementitious material is very promising. A waste product is converted into a valuable resource. At the same time a widely used commodity product such as concrete would benefit from dredged material as filler. Concrete products with dredged material filler exhibited no degradation but rather improvement of certain properties. At this stage, much of the basic research seems to be completed and specific products may be developed. The use in other applications is possible. Still, it has to be shown that applicable standard requirements are met and end products have to satisfy the needs of specific customers. In summary, the following conclusions can be drawn and the following prospects be identified.

- The treatment developed at Columbia University is effective in detoxification of New York Harbor dredged material. The detoxification procedures should be applicable for a variety of contaminants and different levels of contamination.
- 2) Tests with highly contaminated samples have to be conducted to finalize the proposed treatment method and further demonstrate its feasibility. In particular, the evaluation of dredged material with high levels of organic contaminants is needed.

- It seems that the treatment procedure can be implemented onbarge and thus save time and storage space. Dredged material is turned into a valuable resource before it reaches the shore.
- 4) The suggested treatment procedure provides an inexpensive yet effective solution for the disposal problem especially if the high costs of currently alternatives are taken into account. Because the siting problem is avoided high public acceptance is expected to be easier to obtain.
- 5) Dredged material was successfully evaluated as filler in concrete products. Leaching of contaminants was prevented. Filler products according to specific customer needs are currently under development or will be developed in the near future.
- A demonstration-scale project has to be established and evaluated for both technical and economic feasibility.

32

5 References

- K. MILLRATH, S. KOZLOVA, S. SHIMANOVICH, C. MEYER: Beneficial Use of Dredge Material. Columbia University, New York, February 2001.
- [2] ASHAPURA GROUP: Products Bentonite. http://www.ashapura.com/bent.htm (webpage), India, 1999.
- [3] S. WILD, J.M. KHATIB, A. JONES: Relative Strength, Pozzolanic Activity And Cement Hydration In Superplasticised Metakaolin Concrete. *Cement and Concrete Research*, Vol. 26, No. 10, 1996, pp. 1537-1544.
- [4] KIRK JOHNSON: Whitman To Issue Order To Dredge Hudson For PCB's. The New York Times, August 1, 2001.
- [5] T. WAKEMAN: Finding Productive Uses for Dredged Material and Contaminated Sediments. In: R. E. RANDALL (ED.): Proceedings of the 21st Technical Conference of the Western Dredging Association in Houston, TX, June 24-27, 2001. CDS Report No. 373, Center for Dredging Studies, Texas A&M University, College Station, TX, 2001.
- [6] K. MILLRATH, S. KOZLOVA, S. SHIMANOVICH, C. MEYER: New Approach To Beneficiation Of Dredged Material As A Filler. WORLD DREDGING, Mining & Construction, November 2001, pp. 8-20.
- [7] Y. NAKAGAWA, F.L. COE: A Modified Cyanide-Nitroprusside Method For Quantifying Urinary Cystine Concentration That Corrects For Creatinine Interference. *Clinica Chimica Acta*, Vol. 289, No. 1-2, 1999, Pages 57-68.
- [8] R. PERRY, R. E. BROWNER, R. DUNNE, N. STOITIS: Low pH Cyanidation Of Gold. *Minerals Engineering*, Vol. 12, No. 12, 1999, Pages 1431-1440.

- [9] S. YAMANAKA, S. TAKAKU, Y. TAKAESU, M. NISHIMURA: Validity Of Salivary Thiocyanate As An Indicator Of Cyanide Exposure From Smoking. *The Bulletin of Tokyo Dental College*, Vol. 32, No. 4, pp. 157-163.
- [10] J. JAN, V. VRBIC: Polychlorinated Biphenyls Cause Developmental Enamel Defects In Children. *Caries Research*, Vol.34, No. 6, 2000, pp. 469-473.
- [11] THE PORT AUTHORITY OF NEW YORK AND NEW JERSEY (PANYNJ): The Management and Regulation of Dredging Activities and Dredge materials in New Jersey's Tidal Waters, Draft. PANYNJ, New Jersey, 1996.
- [12] AMERICAN SOCIETY FOR TESTING AND MATERIALS (ASTM): Annual Book Of ASTM Standards, Section 4 Construction, Volume 04.02 Concrete And Aggregates. ASTM, Danvers, MA, 1998.
- [13] S. KOZLOVA, C. MEYER, K. MILLRATH, S. SHIMANOVICH: A Suggested Rapid Autoclave Test For ASR In Cement-Alumino-Silicate Composites with Glass Aggregate. *Cement and Concrete Research*, submitted for publication, 2001.
- [14] S.R. HILLIER, C.M. SANGHA, B.A. PLUNKETT, P.J. WALDEN: Long-Term Leaching Of Toxic Trace Metals From Portland Cement Concrete. *Cement* and Concrete Research, Vol. 29, No. 4, 1999, pp. 515-521.
- [15] I. HOHBERG, G.J. DE GROOT, A.M.H. VAN DER VEEN, W. WASSING: Development Of A Leaching Protocol For Concrete. *Waste Management*, Vol. 20, No. 2-3, 2000, pp. 177-184.
- [16] U.-M. MROEH, P. ESKOLA, J. LAINE-YLIJOKI: Life-Cycle Impacts Of The Use Of Industrial By-Products In Road And Earth Construction. Waste Management, Vol. 21, 2001, pp.271-277.

- [17] NEW YORK STATE DEPARTMENT OF ENVIRONMENTAL CONSERVATION (NYSDEC): New York State Environmental Conservation Law, Part 703: Surface Water And Groundwater Quality Standards And Groundwater Effluent Limitations. NYSDEC, New York, 1999.
- [18] H. LYGRE, E. SOLHEIM, N.R. GJERDET: Leaching From Denture Base Material In Vitro. Acta Odontologica Scandinavica, Vol. 53, No. 2, 1995, pp. 75-80.
- [19] H. LYGRE, K.N. KLEPP, E. SOLHEIM, N.R. GJERDET: Leaching Of Additives And Degradation Products From Cold-Cured Orthodontic Resins. Acta Odontologica Scandinavica, Vol. 52, No. 3, 1994, pp. 150-156.
- [20] R. PULGAR, M.F. OLEA-SERRANO, A. NOVILLO-FERTRELL, A. RIVAS, P. PAZOS, V. PEDRAZA, J.M. NAVAJAS, N. OLEA: Determination Of Bisphenol A And Related Aromatic Compounds Released From Bis-GMA-Based Composites And Sealants By High Performance Liquid Chromatography. *Environmental Heals Perspectives*, Vol. 108, No. 1, 2000, pp. 21-27.
- [21] US ENVIRONMENTAL PROTECTION AGENCY (US EPA): Hazardous Waste Management System; Land Disposal Restrictions; Final Rule (40 CFR Part 260 et al.). *Federal Register, Part II EPA Rules and Regulations*, Vol. 51 No. 218, 1988.