

An evaluation of technologies for the heavy metal remediation of dredged sediments

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Abstract

Sediments dewatering is frequently necessary after dredging to remediate and treat contaminants. Methods include draining of the water in lagoons with or without coagulants and flocculants, or using presses or centrifuges. Treatment methods are similar to those used for soil and include pretreatment, physical separation, thermal processes, biological decontamination, stabilization/solidification and washing. However, compared to soil treatment, few remediation techniques have been commercially used for sediments. In this paper, a review of the methods that have been used and an evaluation of developed and developing technologies is made. Sequential extraction technique can be a useful tool for determining metal speciation before and after washing. Solidification/stabilization techniques are successful but significant monitoring is required, since the solidification process can be reversible. In addition, the presence of organics can reduce treatment efficiency. Vitriification is applicable for sediments but expensive. Only if a useful glass product can be sold will this process be economically viable. Thermal processes are only applicable for removal of volatile metals, such as mercury and costs are high. Biological processes are under development and have the potential to be low cost. Since few low cost metal treatment processes for sediments are available, there exists significant demand for further development. Pretreatment may be one of the methods that can reduce costs by reducing the volumes of sediments that need to be treated. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Pollutants from various sources (industrial, mining, municipal sewage, agricultural and other activities) have entered water ways over time. The sediments then become a sink and source of toxic components due to their resuspension and can, thus be one of the largest potential sources of risk to water quality [1]. Approximately 300 million/m³ of sediments are dredged to deepen harbors and shipping lanes in US and of which 3–12 million/m³ are highly contaminated [2]. Approximately 10% of the sediments in underlying waters in US are contaminated. More than 100 superfund sites will require removal or remediation of sediments that are contaminated within 10 years [3]. This has implications on human health, the ecosystem, the economy and politics.

The contaminants in the sediments can pose threats to small organisms including worms, crustaceans and insect larvae that live on the bottom of water column. The contaminants can be ingested, absorbed by dermal contact or resuspended and dissolved into the overlying water. The small organisms are consumed by fish which in turn are eaten by humans and larger animals. There has been particular evidence of bioaccumulation in the food chain in the Great Lakes due to the contaminated sediments [4]. In 1998, National Quality Survey indicated that mercury, among other organic contaminants was the most frequently found.

Sediments are soil particles found at the bottom of lakes, estuaries, rivers and oceans that are of mineral and organic origin [5]. Most of the particles have been transported by wind, ice or water. The sediments are comprised of organic matter, iron oxides, carbonates, sulfides and interstitial water. Organic matter is derived from humus, decomposed plant and animal residues and other organic matter, such as algae, worms, amphipods that settle to the bottom of the body of water. Other woody or plant material, garbage, dead organisms and other debris can also become components of sediments. Sediments are heterogeneous and can be characterized by grain size distribution and density, water and organic matter contents. Contaminants tend to adsorb the smaller particle sizes due to higher surface area to volume ratios and higher organic matter contents [5]. Metals also have been shown to associate with sulfides.

Although much is known about technologies for the remediation of heavy metal contaminated soil much less is known about sediment treatment. The properties of sediments can differ significantly from soils, and therefore, technologies that work for soils may not be as efficient for sediments. The higher percentage of clay, silt and organic matter of sediments are the most notable. Since we will concentrate on dredged sediments here, only ex situ treatment methods will be discussed here. Dredging is often necessary for navigational purposes. Characterization, analysis and assessment of sediments are required before transport, treatment and disposal. In this paper, a review and analysis of the various technologies available for treatment of dredged sediments will be made.

2. Sequential extraction techniques

The term speciation is related to the distribution of an element among chemical forms or species. The heavy metal distribution in soils and sediments can indicate the potential harm to the environment through the chemical associations. Heavy metals can occur in several forms in water and soils. Interest has increased in these techniques to relate the degree of

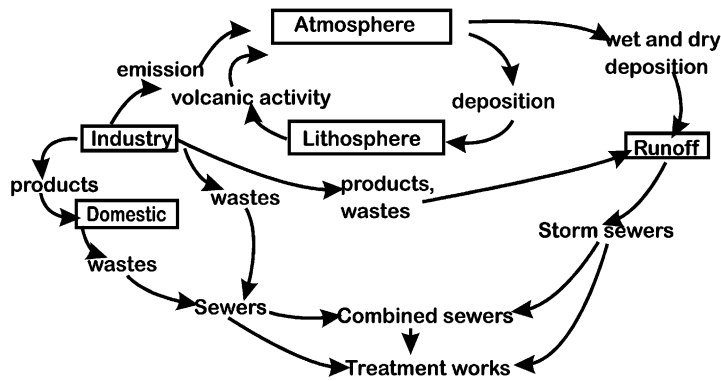


Fig. 1. Transport of metals in the environment.

mobility with risk assessment (i.e. the more mobile the metal is, the more risk associated with it) [6]. Not only is total metal concentration of interest, but it is now accepted that understanding the environmental behavior by determining its speciation is of paramount importance.

To determine the speciation of metals in soils, specific extractants are used. The different extractants solubilize different phases of metals as shown in Figs. 1 and 2. By sequentially

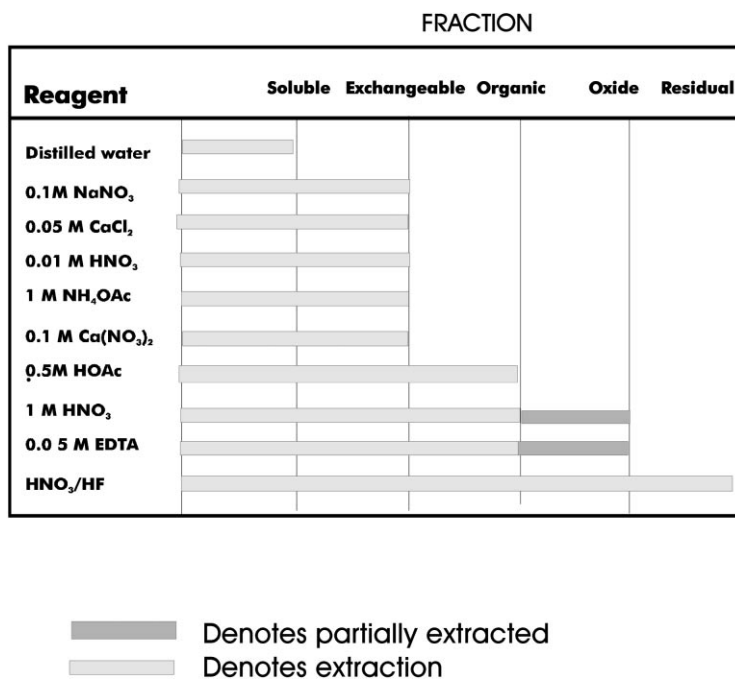


Fig. 2. Extractants used for different metal fractions, Ac denotes acetate, EDTA denotes ethylene diaminetetraacetic acid.

extracting with solutions of increasing strengths, a more precise evaluation of the different fractions can be obtained from sediments [7]. A sediment sample is shaken over time with a weak extractant, centrifuged and the supernatant is removed by decantation. The pellet is washed in water and the supernatant removed and combined with the previous supernatant. A sequence of reagents are used following the same procedure until finally, mineral acid is used to extract the residual fraction. Heavy metal concentrations are then determined in the various extracts by atomic absorption or other means. Numerous techniques and reagents have been developed and have been applied to soils [8], sediments [9], sludge-treated soils [10] and sludges [11]. These methods are not standardized and even the results can vary with the same reagents, pH, temperature, extractant strength and solid to volume of extractant ratio. None of the extractions is completely specific, however, the extractants chosen attempt to minimize solubilization of other fractions.

Kabata-Pendias [12] demonstrated that the speciation of trace metals in natural soils depends on the physical and chemical characteristics of the soil. Soil pH, redox, organic, carbonate, clay and oxide contents all influence metal speciation and mobility. Patrick and Verloo [13] studied the effects of pH and redox on heavy metal speciation in sediments. Mercury and lead were not affected by pH and redox, since they were associated with larger molecular weight organic fractions. Even though iron was associated with large and small molecular weight organic fractions, those associated with the small fractions were affected by pH. Manganese is highly mobile under all redox and pH conditions, resulting in its depletion in Gulf Coast sediments.

Simple and complex cations are the most mobile, exchangeable cations in organic and inorganic complexes are of medium mobility and, chelated cations are slightly mobile. Metals in organic or mineral particles are only mobile after decomposition or weathering and precipitated metals are mobile under dissolution conditions (e.g. change in pH). Kabata-Pendias [12] also showed the speciation of trace metals, such as zinc, copper, cadmium and lead. Zinc and cadmium are mostly organically bound, exchangeable and water soluble. Copper is mainly organically bound and exchangeable, whereas, lead is slightly mobile and bound to the residual fraction. Chlopecka [14] showed, however, that the cadmium and zinc speciation of the soils depended significantly on the application of sewage sludge on the soil. Fertilizer addition, water and air pollution can also effect speciation.

Recently, sequential extraction techniques have been studied as a tool in various applications. Yong et al. [15] examined sequential extraction to obtain a better appreciation of the ability of clay soil barriers to contain contaminants in landfill barriers. The effect of soil pH, constituents and heavy metal types were evaluated. In a study by Ramos et al. [16], sequential extraction techniques were used to evaluate the mobility of cadmium, zinc, lead and copper in contaminated soil in a national park. Cadmium was found to be the most mobile and would likely be the most bioavailable.

A potential method to determine if the heavy metals can be removed by remediation techniques or predict removal efficiencies is to determine speciation with selective extractive techniques. It is believed that exchangeable, carbonate and reducible oxide fractions may be amenable to soil washing techniques [17]. Removal of organically and residually bound fractions may not be economical to recover or necessary due to lack of bioavailability. Papadopoulos et al. [18] indicated that HCl is not effective in removing residual metals from sediments. Reducible and organic forms which can become mobile can be removed

efficiently by HCl. Gombert et al. [19] used sequential extraction to determine if cesium, cobalt and chromium could be removed by soil washing. Since less than 20% was extracted after dissolving 20% of the soil mass, soil washing was abandoned as an option. Mulligan et al. [20] showed that the carbonate and oxide fractions accounted for over 90% of the zinc present in the sediments. The organic fraction constituted over 70% of the copper. Sequential extraction of the sediments after washing with the various surfactants indicated that the biosurfactants, rhamnolipid and surfactin could remove the organically-bound copper and that the sophorolipid could remove the carbonate and oxide-bound zinc. Clearly, more work is needed in this field to be able to predict soil washing efficiencies based on metal speciation.

3. Pretreatment

Pretreatment is usually required to remove debris and dewater the dredged sediments. The debris can include tires, concrete blocks, automobile parts, and rocks. After dredging large debris is removed by backhoes or clamshells while smaller debris is removed by trommel screens or grizzlies.

The amount of dewatering will depend on the type of dredging used and the technology to be used for treatment. Mechanically dredged sediments typically contains more than 50% water, whereas, hydraulically dredged sediments contain about 20% water. Water contents of up to 40% are required for many processes. Centrifuges, filter presses, plate or diaphragm-plate filter or gravity thickening can be used for dewatering purposes. These methods are not suitable for silt or clay [21].

In a demonstration project in collaboration with Environment Canada [22], metal contaminated sediments were removed at the Port of Sorel in the St. Lawrence River. The sediment was dewatered and treated. A rotary press with additives was used for dewatering. This process removed 30% of the metals which was sufficient for sediment disposal. The dewatering added 30% to the cost of dredging and disposal. There have been various pilot and full scale demonstration and commercial treatment processes. These will be discussed in the following sections.

4. Physical separation processes

Physical separation processes are used to remove smaller, more contaminated particles. These processes include centrifugation, flocculation, hydrocyclones, screening, and sedimentation. Hydrocyclones can be used for sediments with less than 20% solids to separate coarse or fine grain fractions. They include: hydrocyclones which separate the larger particles greater than 10–20 μm by centrifugal force from the smaller particles, fluidized bed separation which remove smaller particles at the top (less than 50 μm) in the countercurrent overflow in a vertical column by gravimetric settling and flotation which is based on the different surface characteristics of contaminated particles. Addition of special chemicals and aeration in the latter case causes these contaminated particles to float. Screening is most applicable for particles larger than 1 mm. Magnetic extraction has not been successful for sediments. If the solids content is high, mechanical screening can be used. Gravity separation or sedimentation is applicable if the contaminated fraction has a higher specific gravity

that the rest of the sediment fraction. According to the US Army Engineer Detroit District [23], costs are in the range of US\$ 30–72/m³ for quantities in the range of 7600–76,000 m³ and for sediments with 75% sand and 25% contaminated silt or clay. The expense is only justified if the sediment contains more than 25% sand which is rare [24]. Physical techniques only concentrate the contaminants in smaller volumes and are, thus useful before thermal, chemical or other processes.

5. Containment

Containment of dredged material is done in confined disposal facilities in diked near the shore, island or on the land facilities. The facilities must be designed for dredging purposes and to contain the contaminants. Potential mechanisms for contaminant release are due to leachates, runoff, effluents, volatilization, uptake by plants, and ingestion by animals. Oxygenation of sediments by the rain can lead to metal contamination of the groundwater. The cost is in the range of US\$ 20–66/m³ [25]. These costs are usually less than those for landfill. The containment facilities can be used for storage, dewatering and pretreatment for other processes.

Contained aquatic disposal is the placement of material in a confined aquatic area. These areas can be strategically placed in depressions. This technique can be used for disposal of contaminated sediments. Clean material can be placed above and at the edges. Another approach is to place the material in woven or non-woven permeable synthetic fabric bags, geotextile tubing or containers [24]. Costs at the demonstration in California were approximately US\$ 66/m³ [26]. The contaminants must not seep through the fabric into the water and these uncertainties must be further investigated.

The US Corps of Engineers have used geocontainers to store dredged sediments. The geocontainers are made of geosynthetic material and assembled by a seaming technique. Large quantities of dredged material are contained in the geocontainers after filling by hydraulic or mechanical filling equipment. The geocontainers are dropped from barges in to open water to form underwater berms, dikes or other structures. They are designed to resist degradation under environmental conditions.

In the Mississippi River near Baton Rouge, the Red Eye Crossing Soft Dikes Demonstration Project [27] used polypropylene bags filled with coarse river sand as soft dikes. Millions of dollars can be saved since less dredging is required. The soft dikes are placed lower than the nearby sandbar where the bags are filled. Both small geobags of 3 m³ and large geocontainers of 200–300 m³ are used. The project has gone well for over 4 years.

Landfill disposal of contaminated sediments can be used for small volumes. The sediments must be previously dewatered, such as in a contained disposal facility, since landfill facilities cannot handle slurries. Large volumes cannot usually be accommodated, since landfills do not have the capacity.

6. Washing

Sediment washing involves the addition of a solution with the contaminated sediments to transfer the contaminants from the sediments to the wash solution. It is most appropriate

for weaker bound metals in the form of hydroxides, oxides and carbonates. Mercury, lead, cadmium, copper, nickel, zinc and chromium can be removed and can be recovered by electro-chemical processes if organic compounds are not significant. Metals can also be removed from precipitation or ion exchange [21]. Precipitation is not applicable for metal sulfides. Pretreatment to remove uncontaminated coarser fractions can be used. Various additives can be employed, such as bases, surfactants, acids, or chelating agents. Nitric, hydrochloric and sulfuric acids can be used. However, if sulfuric acid is used, 50% of the amount is required compared to hydrochloric acid [18]. The treated sediment can then be washed to remove any residual wash solution prior to disposal. Ideally the wash solution should be reused. Costs of sediment washing are usually in the order of US\$ 40–250/t [28]. Washing is usually most applicable for coarser particles. Therefore, fine grain sediments can be difficult to decontaminate through washing solutions. Extraction tests should be conducted to determine optimal conditions (chemical type and dosage, contact time, agitation, temperature and extraction steps to meet regulatory requirements).

Two companies, Biogenesis and Roy F. Weston, have combined mechanical and chemical processes for the removal of 90% of the organic compounds and 70% of the inorganic contaminants from sediments [29]. High pressure water jets are used with various surfactants, oxidizing and chelating agents. A full scale facility will be built to process 209,000 m³ per year at a cost of US\$ 40–65/m³. Large facilities with capacities greater than 380,000 m³ per year would require large areas for the installation.

The feasibility of using biodegradable biosurfactants to remove heavy metals from an oil contaminated soil was recently demonstrated by batch washes with surfactin, a rhamnolipid and a sophorolipid [30]. The soil contained 890 mg/kg of zinc, 420 mg/kg of copper with a 12.6% oil and grease content. A series of five batch washes removed 70% of the copper with 0.1% surfactin/1% NaOH while 4% sophorolipid/0.7% HCl was able to remove 100% of the zinc. The results clearly indicated the feasibility of removing metals with the anionic biosurfactants tested even though the exchangeable metal fractions were very low. These biosurfactants were also able to remove metals from sediments [20]. Since these agents are biodegradable, they can enhance hydrocarbon removal and can potentially be produced in the sediments.

7. Thermal extraction

Mercury, arsenic and cadmium and its compounds can be evaporated at 800°C with the appropriate air pollution control system. Some of the metals remain in the solid residues and will have to be properly disposed of. Temperature and retention time are the main factors determining decontamination levels. Lower temperatures around 500°C are not sufficient to eliminate most organic compounds and metals [28]. Rotary kilns are the main type of equipment used where the sediments are rotated as the temperature increases. A disadvantage of this process is that waste stream containing hazardous material is produced that requires disposal at a waste treatment facility. Thermal extraction is applicable mainly for mercury, since this metal is highly volatile. Costs are in the order of US\$ 35–1000/t [28]. However, there are numerous problems related to the treatment of sediments. Often the equipment is not appropriate for the feed size and moisture content of sediments. There

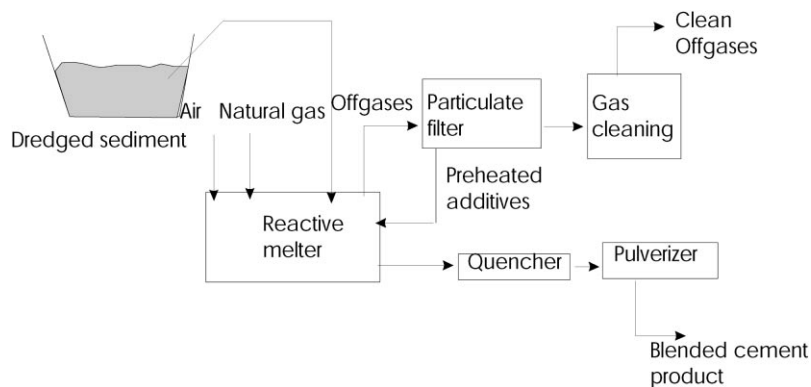


Fig. 3. Schematic diagram of Cement Lock process developed by IGT [28].

are numerous suppliers, however, that claim that their equipment will work for the treatment of sediments. However, it has been proposed that the decontaminated sediment be used as construction fill and in restoration projects.

A thermal chemical process called Cement Lock was developed by the Institute of Gas Technology (IGT) and has been used for dredged sediment in the New York/New Jersey Harbour [31]. The sediment containing metal contamination (33 mg/kg As, 37 mg/kg Cd, 377 mg/kg Cr, 617 mg/kg Pb, 1.3 mg/kg Hg, 3.2 mg/kg Se and 1.8 mg/kg Ag) was fed with lime into a rotary kiln reactor smelter at 1200–1600°C. The soil/lime is then melted, and quenched, forming micrometer fibers (Fig. 3). The mixture is then pulverized with cement to produce a suitable type I Portland cement construction material. The sediment passed the toxicity characteristic leaching procedure (TCLP) for all metals. The offgas must be treated to remove volatilized heavy metals and other combustion products by removing particulates by a filter, acid gas removal and then heavy metal gas removal in an activated carbon filter with affinity for heavy metals. Costs based on pilot tests were estimated at US\$ 20–30/m³ [32]. The pilot facility at Newark Bay, NJ has a capacity of 23,000 m³ per year. This type of process can be used for many types of dredged materials with no pretreatment.

Mercury Recovery Services (MRS) has developed and commercialized process that mixes a proprietary material and the mercury contaminated material at temperatures of 150–650°C [33]. The process can be mobile or fixed, batch, continuous or semicontinuous and has operated, since 1994. Unit capacities range from 0.5 to 10 t/h. The mercury can be as an oxide, chloride and sulfide. No liquid or solid secondary products are generated. The treated material contains less than 1 ppm of mercury. The process consists of two stages, drying of the feed and desorption of the mercury that is then condensed as a 99% pure metallic form from the vapor phase. Air emissions do not contain mercury. Costs are high, in the range of US\$ 650–1000/t.

The X-TraxTM is a relatively low temperature process for removal of organics and mercury in soils, sludges, and sediments that was developed by Chemical Waste Management Inc. and currently marketed by OHM remediation services. The contaminated sediment is fed into a rotary dryer (400–650°C). Mercury is desorbed and forms of oxide and sulfide are

reduced to mercury. Nitrogen transports the vapors to the gas treatment systems. 10–30% of the mercury is removed by the dust scrubber. The liquid from the scrubber is treated to separate water, organic, mercury and sludge components. Nitrogen gas is then sent to a two-stage condenser to condense mercury pure enough to send it to an outside company. The gas passes through a mist eliminator to remove droplets. Approximately 5–10% of the gas is passed through a particulate filter and carbon absorption system before discharge into the atmosphere. The remaining amount is reheated and recycled to the rotary dryer. The system has been used for treatment of soil and sediments with levels from 130–34,000 mg/kg of mercury to reduce levels to 1.3–228 mg/kg. Full scale units are available for treating 10 t/h for sites with 20,000–100,000 t of contaminated soil [34].

8. Bioremediation

Microorganisms have been effective in treating organic contamination in sediments, such as PAHs. Bioleaching involves *Thiobacillus* sp. bacteria which can reduce sulphur compounds under aerobic and acidic conditions (pH 4) at temperatures between 15 and 55°C, depending on the strain. Leaching can be performed by indirect means, acidification of sulfur compounds to produce sulfuric acid which then can desorb the metals on the soil by substitution of protons. Direct leaching solubilizes metal sulfides by oxidation to metal sulfates. In laboratory tests, *Thiobacilli* were able to remove 70–75% of heavy metals (with the exception of lead and arsenic) from contaminated sediments [36].

Options are available for bioleaching including heap leaching and bioslurry reactors. Sediments require lower pH values to extract the metals, since they have already been exposed to oxidizing conditions. For both heap leaching and reactors, bacteria and sulfur compounds are added. In the reactor, mixing is used and pH can be controlled more easily, leachate is recycled during heap leaching. Copper, zinc, uranium and gold have been removed by *Thiobacillus* sp. in biohydrometallurgical processes [36].

Percolation field tests were run by Seidel et al. [37] as shown in Fig. 4. They found that addition of sulfur as a substrate provided better leaching results than sulfuric acid.

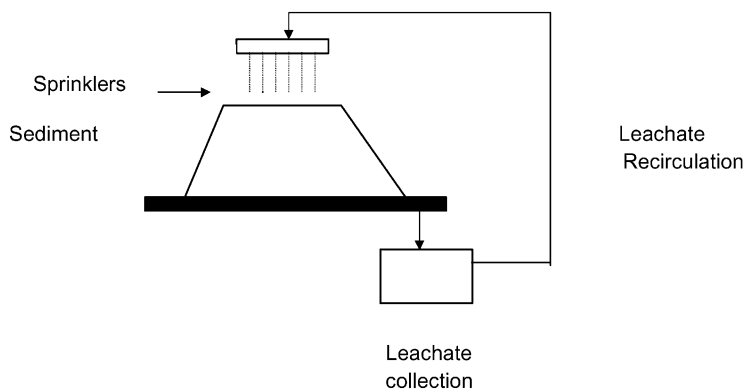


Fig. 4. Biological heap leaching of sediments.

Approximately 62% of the metals were removed by percolation leaching after 120 days for the oxic sediments. Only 9% of the metals were removed from the anoxic sediments. They indicated that anoxic sediments are less suitable for treatment and must be ripened as a pretreatment.

Microorganisms are also known to oxidize and reduce metal contaminants. Mercury and cadmium can be oxidized while arsenic and iron can be reduced by microorganisms. This process (called mercurites) has been developed and tested in Germany at concentrations greater than 100 ppm. Since the mobility is influenced by its oxidation state, these reactions can affect the contaminant mobility.

Metal removal can be accomplished in conjunction with organic removal. For example, Vega has developed a landfarming process that using chelating organic acids with nutrients and soil conditioners to initiate biodegradation. The organic acids can chelate metals, as well as promote organic degradation. Temperature, moisture content and pH need to be controlled as in any microbial process. It has mainly been applied for petroleum contamination. Retention time can be long (30–120 days).

Slurry methods can be used, since dewatering is not required. There are also other limitations as discussed for sediment washing. Bioremediation is a low cost technology, and therefore, has the potential for wide use. However, metal remediation technologies are not as developed as organic treatment. Costs are in the range of US\$ 15–200/t [28]. Some plants have been shown to retain metals in their roots, stems and leaves [38]. This process is called phytoremediation. Vegetative caps consisting of grasses, trees, and shrubs can be established in shallow fresh water. The resulting vegetative mat can hold sediments in place. The construction of wetlands is growing for wastewater treatment and thus the knowledge on wetland configurations is growing. However, vegetative caps have not yet been applied to the remediation of sediments [38]. Genetically engineering plants will need to be developed to enable hyperaccumulation of metals [39]. It is more likely, though, that this technology will be used as an in situ method of reducing large volumes of sediment transport. However, phytoremediation could be implemented where dredged sediments have been placed in contained areas and a wetland is then constructed to remediate and contain the sediments. Efficiency will depend on sediment characteristics and is best if the contamination is low to medium and if the contamination is within the first 100 cm to enable the roots of access the contaminants. Lead is difficult to uptake due to the low pH and nutrient requirements. This area is developing but there is little cost or performance data.

9. Electrokinetics

Electrolytic processes for metal removal include the use of ac or dc fields. Electrokinetic processes involve passing a low intensity electric current between a cathode and an anode imbedded in the contaminated sediments (Fig. 5). Ions and small charged particles, in addition to water, are transported between the electrodes. Anions move towards the positive electrode and cations towards the negative. An electric gradient initiates movement by electromigration (charged chemicals movement), electro-osmosis (movement of fluid), electrophoresis (charged particle movement) and electrolysis (chemical reactions due to electric field) [32]. Control of the pH and electrolyte conditions within the electrode

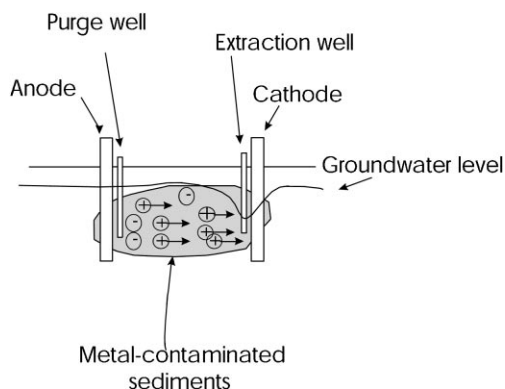


Fig. 5. Electrokinetic treatment of sediments.

casings is essential in the optimization of the process efficiency. Drying near the anode is a problem so recirculating processing fluids are necessary. The process can be used to recover ions from soils, muds, dredgings, and other materials [40]. Dredged material is treated in lagoons between 2 and 7400 m³ with batch time of 8 h to 5 days, depending on current loading and electrode spacing. Spacing can be up to 3 m as long as the potential gradient of 1 V/cm is maintained. Metals as soluble ions and bound to soils as oxides, hydroxides and carbonates are removed by this method. Other non-ionic components can also be transported due to the flow. Unlike soil washing, this process is effective with clay soils.

Demonstrations of this technology have been performed but are limited in North America [41]. In Europe, this technology is currently used for copper, zinc, lead, arsenic, cadmium, chromium and nickel. Other ions, such as cyanide and nitrate and radionuclides, such as uranium and strontium can also be treated by electrokinetics. Heterogeneities, large amounts of oxides, large rocks, large metal objects, gravel submerged foundations, moisture content, temperature and other contaminants can interfere with the process [40]. Recently, new developments at the pilot stage have been made in using electrokinetics for high-level metal containing sediments. Metal recovery will improve the process economics to achieve partial cost-effectiveness.

10. Solidification/stabilization

The purpose of solidification/stabilization processes is to reduce the mobility of the heavy metal contaminants by addition of an agent that solidifies and then immobilizes the metals. Agents include lime, fly ash, cement and/or other chemicals. Solidification/stabilization is effective for metal contamination as there are few destructive techniques available for metals. Some metals, such as arsenic, lead, chromium(VI) and mercury are suitable for this type of treatment. Other metals, such as cadmium, copper and zinc are also commonly stabilized by this process. Reduction must occur from the chromium(VI) to the chromium(III) form either during mixing or in a two step process by addition of reducing agents followed by stabilization. Liquid monomers that polymerize and cement are injected to encapsulate

the soils. Leaching of the contaminants must, however, be carefully monitored as is the case for vitrification, the formation of a glassy solid. Cement- or silicate-based processes are useful for sediments and are economical, particularly if the end product (an aggregate) can be used as for landfill closure or in other applications. Other materials containing iron (red mud, sludge from a water treatment plants, bog iron ore, unused steel shot and steel shot waste) have been evaluated [41] for immobilizing cadmium and arsenic contaminants in sediments. All were effective in reducing the bioavailability of the metals to plants, but the safest was sludge from a drinking water plant with low levels of arsenic. However, if there are different types of metals present, the treatment may not be as effective. Water contents greater than 20% or chlorinated hydrocarbons contents greater than 5% increase the amount of agents required. Moisture contents should be less than 50%, organic contents not more than 10% and metals should not be more than 25 wt.%. Variability in the water content, grain size, and the presence of debris can make handling of the materials difficult and decrease the efficiency of the solidification process. Mixing efficiency is the key to the process. In addition, since immobilization leads to an increase in volume, larger areas of land are required for disposal. The volume increase can be up to 30%. Thus, smaller volumes for treatment are more appropriate. Metal condensation on fine particulates can also limit disposal options. Costs range from US\$ 30 to 250/t [28].

Full scale projects have been performed in US, Canada, Japan, and Belgium. In The Netherlands, a rotating drum was used in a full scale experiment [35]. An amount of 680 t of dewatered sediment were treated at 600°C for 38.5 h for mineral oil, PAHs and mercury. Mercury levels decreased by 80% from 1.5 to 0.3 mg/kg while mineral oil and PAHs decreased by greater than 99.8%. Leaching of arsenic, molybdenum and fluoride increased after thermal treatment which can have implications in the reuse of the treated sediments as road or construction materials.

11. Vitrification

Another immobilization technique is vitrification. Vitrification involves the insertion of electrodes into the soil which must be able to carry a current and then to solidify as it cools. Toxic gases can also be produced during vitrification. Temperatures can reach 3000°C. Some vitrification processes have been tested on sediments. Costs can be high since fuel values are low and moisture contents are high (above 20%). High organic contents can also decrease efficiency. It is applicable for a wide variety of metals.

A technology was developed for the remediation of organic contaminants and immobilization of metals in a glassy matrix and evaluated on the dredged sediments from NY/NJ Harbour [42]. A plasma torch is used to heat the sediments. Feeding of the wet sediments into the plasma reactor and adjustment of residence times can be difficult, however. Cadmium, mercury, and lead levels were reduced efficiently (97, 95 and 82%). The flowsheet of the process is shown in Fig. 6. Glass tiles and fiber glass materials were produced and could be used as valuable end products and to recover costs. Pilot facilities can process 76,000 m³ per year of contaminated material while full scale units can handle 290,000 m³ per year.

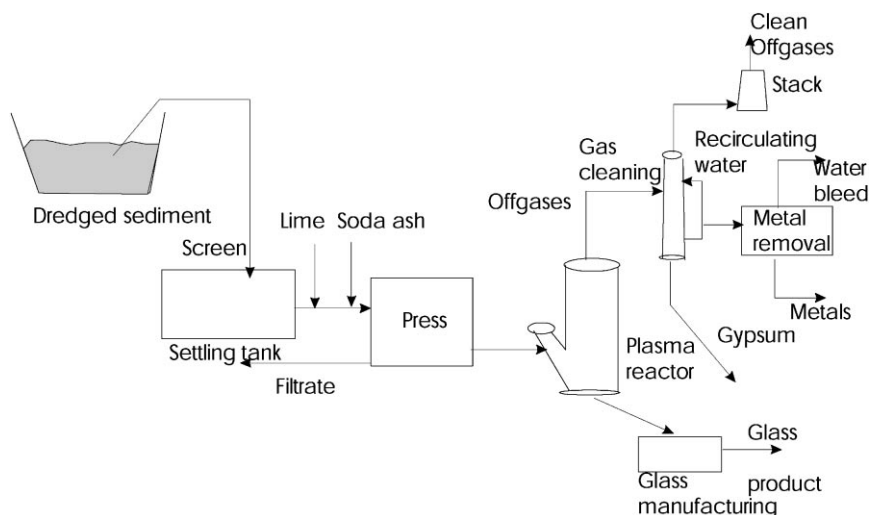


Fig. 6. Vitrification of sediments by the Westinghouse Science and Technology plasma torch melter [42].

12. Chemical oxidation

Oxidation/reduction of heavy metals is another method for remediating *ex situ* sediments. A detoxification technology called TR-DETOX involves the percolation of inorganic and organic reagents to reduce heavy metals to their lowest valence state and form stable organometallic complexes. One of the main chemicals is sodium polythiocarbonate that forms a precipitate that becomes less soluble over time. The treated residue is no longer leachable. Lime, silicates and Portland cement are not added and costs are usually about one-quarter of stabilization/solidification processes. A unique characteristic is electronic addition of reagent. Pilot tests are required to determine the most appropriate formulation [41].

13. Case study comparison of technologies

One of the major problems of comparing treatment technologies is that very few studies are performed using the same samples. Recently, however, the EPA's Great Lakes National Programs Office conducted a study on sediments from Trenton Channel to evaluate technologies [43]. Five technologies were evaluated including solid phase extraction, solidification (Growth Resources), soil washing (Biogenesis), thermal desorption (Cement Lock) and plasma vitrification (Westinghouse). The companies who took part were each given a 208 l drum of sediments that contained PAHs, metals, PCBs and oil and grease. Mercury and lead were the main heavy metals of concern. Solid phase extraction had no significant effect on total metals. Plasma vitrification was greater than 90% effective for all contaminants including the metals. Treatment sediment in the form of glass that can be used as an

aggregate, glass tile or in glass fiber products. Cement Lock was very efficient for all contaminants except for metals where the results varied between 20 and 90% reduction. Heavy metals are locked in the cement matrix while volatile metals, such as mercury and arsenic are volatilized and distributed over a filter element. Advantage of process is that there was a volume reduction. Cement end product can be used in construction, eliminating disposal costs. Soil washing was very effective for leachable metals and only partially effective for total metals. Wastes reduced to reusable oil, treated water and soil for backfill. Overall most technologies could remove mercury to residential levels while none could remove lead to residential requirements. Only industrial and commercial criteria could be achieved.

Costs for the technologies were later estimated [44]. The highest capital costs were US\$ 10–15 million for the vitrification process and US\$ 20 million for Cement Lock while those for soil washing were US\$ 3.5 million and for solidification US\$ 0.7 million. Operating costs were the highest for soil washing (US\$ 118/m³) followed by vitrification (US\$ 110/m³). The lowest operating costs were for the thermal desorption (US\$ 63/m³) and solidification (US\$ 59/m³). Although these tests were performed at bench scale, they are useful in the comparison of technologies. The summary and recommendations included that Cement Lock and vitrification achieved the highest removal efficiencies, produced useful final products and were recommended for further pilot tests. In 1999, it was decided to remove 23,000 m³ of contaminated sediment from Black lagoon and treat a part of it with Cement Lock [45].

14. Conclusions

Although numerous techniques have been tested for contaminated soil, few have been evaluated for sediments at full scale. These are summarized in Tables 1 and 2. Physical treatments enable separation of the more highly contaminated fines from the rest of the sediments, thus reducing the mass to be treated and costs for treatment. Containment has been practiced widely but there are major difficulties in placing these facilities and the public does not favor landfill disposal. The use of geocontainers is developing but there is little information available regarding the risk of contaminant release. The main treatments for metal contaminated sediments include solidification/stabilization and washing. The latter is primarily useful for sands and gravels. Sequential extraction technique can be a useful tool for determining metal speciation before and after washing. Solidification/stabilization techniques are successful but significant monitoring is required, since the solidification process can be reversible. In addition, the presence of organics can reduce treatment efficiency. Vitrification is applicable for sediments but expensive. Only if a useful glass product can be sold will this process be economically viable. Thermal processes are only applicable for removal of volatile metals, such as mercury and costs are high. Highly pure mercury can be obtained and could potentially provide economic benefits to the process. Biological processes are under development and have the potential to be low cost. Since few low cost metal treatment processes for sediments are available, there exists significant demand for further development. It is very difficult to compare technologies, since few technologies are evaluated on the same type of sediment. Conditions vary significantly for each type of sediment. Costs of the various processes need to be reduced. Pretreatment may be one of

Table 1
Commercial full scale systems for treatment of metal contaminated sediments [41]

Type of process	Developer	Applicability	Capacity
Washing			
Water-based washing with additives including feed preparation, attrition scrubbing, size classification, gravity separation, and thickening	Bergmann USA, Gallatin, TN	10 t/h at Toronto Harbour, As, Cr, Pb and radioactive materials	Thirty full scale installations at 5–350 t/h, US\$ 45–125/t
Bescorp — washing including wet screen sizing, density separation, high energy dewatering and water treatment	Brice Environmental Services Corp., Ringoes, NJ	Used for Pb, Hg, Sb, Cu, Zn, Cd and radioactive materials, sediments can be pumped to system,	5–50 t/h with costs of US\$ 25–75/t
Metal recovery and recycling system — acid extraction	Environmental Technologies International, Wyomissing, PA	Used for removal, Hg, Pb, Cr, Cd, Cu, Ni and Zn, metals can be recovered for recycling	7–12 t/h at costs of US\$ 100–250/t
Hydro-sep — washing process physical sizing and gravity separation	Metcalf and Eddy, Atlanta, GA	Treatment of sediments with heavy metals	Capacity of 2–20 t/h at cost of US\$ 50–125/t
Washing with water jets and surfactants to break agglomerate, use of chelating agents and water jet to strip metals	Biogenesis, Springfield, VA	Used for As, Cd, Cr, Cu, Pb, Hg and Zn for low to medium contamination, 93.3% average metal removal for NY/NJ Harbor sediments (853 mg/kg) with PCBs and PAHs	Full scale capacity will be 500,000–1,300,000 m ³ per year
Thermal			
Mercury Recovery Services — thermal desorption	Mercury Recovery Services, New Brighton, PA	Mercury removal at 150–760°C, metallic mercury at 99% purity, solids with less than 1 ppm Hg	US\$ 650–1000/t

Table 1 (Continued)

Type of process	Developer	Applicability	Capacity
Thermatek — thermal desorption	Remediation Technologies, Tuscon, AZ	Temperatures of up to 480°C	2–3 t/h at a cost of US\$ 100–600/t
X-Trax™ — thermal desorption	Chemical Waste Management,	Mercury removal in rotary dryer (40–650°C)	Marketed by OHM Remediation 10 t/h units
Cement Lock — solidification/stabilization	IGT, Des Plains, IL	Addition of mineral compounds for pozzolan production for metal dilution and fixation in cement	US\$ 20–30/m ³
Electrokinetics			
Electrokinetic decontamination — pool process	Geokinetics International Inc., Berkeley, CA	Cu, Cr, Zn, Cd, Ni, Co and radionuclides (U, Sr), applied to high level contaminated sediments	Pilot tests at 0.1–5 m ³ /h costs of US\$ 70–170/t
Solidification/stabilization			
Solfix — solidification/stabilization process	Metcalf and Eddy, Atlanta, GA	0.1–0.2 parts cement per part sediment to reduce leachability of As, Ba, Cd, Cr, Pb, Hg, Se, Ag	US\$ 10/m ³ per 0.1 part of Portland cement added, full scale of more than 500,000 m ³ per year
Vitrification			
Plasma torch for vitrification	Westinghouse Science and Technology Center, Pittsburgh	High levels of metal contamination and production of glass as an end product	Full scale capacity of 380,000 m ³ per year, preliminary costs of US\$ 90–120/t
Chemical			
TR-DETOX — sodium polythiocarbonate reduction and precipitation	ETUS Inc., Sanford, FL	Conversion of heavy metals, such as Cd into stable, non-toxic form	Capacity of 1–500 m ³ /h at cost of US\$ 20–50/t

Table 2
Comparison of remedial technologies

Technology	Description	Applicability	Limitations	Costs
Containment and isolation				
Confined disposal facility and geocontainers	Retention of sediments in a confined area	Wide variety of sediments can be used as pretreatment	Does not destroy contaminants, must control contaminant pathway	US\$ 20–65/m ³
Stabilization/solidification	Creation of an inert waste	Injection of solidifying chemicals	Must contain less than 50% moisture content, organic contaminants can interfere, increases volume greater than 30%	US\$ 60–290/t
Vitrification	Application of electrical energy to vitrify contaminate	Low volatility metals and production of glass materials	High moisture and organic contents require dewatering and vapor recovery	US\$ 90–870/t
Treatment method				
Physical separation	Includes, froth flotation, gravity separation, screening, etc.	For high metal concentrations	Contaminants must be associated with fine grained material	US\$ 30–70/m ³
Washing	Addition of surfactants and other additives to solubilize	For sand and gravel sized sediments	Restricted to weakly bound metals	US\$ 60–245/t
Thermal	Elevated temperature extraction and processing for metal removal	Highly contaminated volatile metal contaminated sediments	Higher water contents increase costs	US\$ 250–9000/t
Biological leaching and phytoremediation	Use of microbes for metal heap leaching or in slurry reactors; use of plants for metal extraction	Applicable for sand and gravel sized sediments and low metal contaminant levels	Not yet demonstrated at large scale	US\$ 15–200/t

the methods that can reduce costs by reducing the volumes of sediments that need to be treated.

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