PERFORMANCE OF HEAVY METALS DECONTAMINATION FOR MARINE SEDIMENTS

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ABSTRACT
The problems created by contaminated marine sediments can pose risks to human health and the environment. Marine sediments are contaminated by heavy metals, among other contaminant types. A number of existing ex situ and in situ treatment technologies can be applied successfully to treating contaminated sediments, but full scale demonstrations are needed to determine their effectiveness and performance. This paper presents a brief discussion on the performance of some of these decontamination methods.

RÉSUMÉ
Les problèmes causés par la contamination des sédiments marins peuvent induire des risques sur la santé humaine et l'environnement. Les sédiments marins sont contaminés par des métaux lourds, à travers d'autres types de contaminant. Différentes technologies existantes (ex-situ et in-situ) peuvent être efficaces pour le traitement de cette contamination, mais l'efficacité et la performance de chacune d'entres elles nécessitent d'être déterminées. Cet article présente ainsi une brève description de la performance de quelques-unes de ces méthodes de traitement.

1. INTRODUCTION

The problem of marine sediment contamination is widespread in coastal waters in many parts of the world. Contamination of marine sediments poses a potential threat to marine resources and human health, e.g. through consumption of seafood. Marine sediments are exposed to a wide range of potential contamination by chemicals that tend to sorb to fine-grained particles, such as heavy metals, hydrophobic organics and ployaromatic hydrocarbons.. Heavy metal contamination primarily originates from industries. The predominant mode of heavy metal retention in sediments can be significantly influenced by the level of sediments contamination by the metal, in addition to geochemical factors and behaviours of the metal itself.

Metal particles frequently bind with the sediments and do not easily dissolve or migrate with water. Dredged sediments can be contaminated with heavy metals because of recent industrial development along the coastal regions of the world. In acidic conditions metals such as cadmium, copper, iron, magnesium and lead can dissolve. Other chemical reactions can also change the state of metals, allowing them to attach to other sediments. The remediation of heavy metals in marine sediments is complicated by the dynamic nature of the aquatic environments, and the possibility of sediment mobilization, resuspension, transport, and deposition. Various management approaches have been proposed and practiced which may be grouped into risk-based measures, interim control, and long-term control strategies. The latter may be further divided into in-situ remediation or ex-situ treatment.

In this paper, the potential environmental and health impacts of metal-contaminated sediments are briefly presented, along with the transport and fate mechanisms of contaminated sediments. The various remediation and treatment strategies for heavy metals are presented, and their performance is evaluated. Various in situ and ex situ heavy metal remediation and treatment techniques have been investigated.

2. ENVIRONMENTAL AND HEALTH IMPACTS OF CONTAMINATED MARINE SEDIMENTS

As with any project, the potential positive and negative environmental consequences of any project which may impact the marine sediment should be assessed. Chemical contaminants associated with sediments can be considered toxic when they adversely affect living organisms. Submerged contaminated sediments may be in intimate contact with aquatic biota that may be affected adversely by, or serve as carriers of, contamination. In this way, contaminants pose a potential risk to coastal ecosystems and, primarily through consumption of fish and shellfish, to human health. Metals are commonly found in the environment. However, adverse health effects may be produced in people or environmental receptors when they are exposed to metals at certain concentrations and under certain exposure conditions. Some metals, such as arsenic, cadmium, chromium, and nickel, have been shown to produce cancer in people under some exposure conditions. Some metals have been shown to produce adverse reproductive and/or other types of health effects in people (e.g., lead, cadmium, mercury) and other animals (e.g., mercury, selenium). As such, metals are often considered chemicals of concern for environmental site assessments.

The chemical species of a metal is important in determining a metal's toxicity. For example, the inorganic form of arsenic is believed to be the carcinogenic form, while the organic forms are not. Also, hexavalent chromium is carcinogenic, while trivalent and elemental chromium are not. Therefore, knowledge of the specific form of metal in an environmental sample is important for accurate risk evaluation. Although it is well known that different chemical forms of the same metal have different toxicities, and there is a need for speciation of metals, the analytical methodologies commonly employed do not readily distinguish these forms. Risk evaluations for metals then are usually based on the very conservative assumption that any metal detected in a sample is in a form that may produce toxicity. This then often results in an overestimation of the potential risks posed by metals in environmental samples (c.f. Hamed, 1997, Hamed, 2000).

3. SEDIMENT MOVEMENT IN COASTAL WATERS AND ITS EFFECT ON MARINE SEDIMENT CONTAMINATION

What exacerbates the potential environmental impacts of contaminated sediments is that they move in coastal waters in different modes according to location. The most common type of such movement is the longshore sediment transport (Van Rijn, L., 1998) where sediments move parallel to the coastline, carried by the longshore current resulting from wave breaking. If the longshore sediment transport is interrupted by any obstacle (e.g coastal structure), or entered an area with reduced current velocity (e.g. shadow area of a detached breakwater) it will start to deposit causing an accretion area where contamination is concentrated (Frihy and Lotfy, 1995). Another important type of coastal sediment movement is that surrounding a tidal inlet. In such situations governed by tidal motion, sea water carrying sediments enters the inlet at high tide forming the so called flood-tidal current. During low tide, the situation is reversed, as sea water carrying sediment leaves the inlet to the sea forming the ebb-tidal current. Such movement result in sediment deposition on both sides of the inlet (lake and sea sides) known as flood and ebb tidal deltas. Such deltas are characterized by their fine sediments which are locations of concentrated contamination if the bed sediment are originally contaminated. This situation is usually encountered as most of coastal lakes are used for fishing purposed which makes them subjected to contamination due to navigation and fishing activities. This situation is almost similar to that of estuaries.

Sediment movement in harbour basins is different, as sediment tend to circulate with water existing in the basin, portions of it may also leave or enter the basin with the outgoing/incoming flow. Sediments may also move as a result of ship propeller induced currents. Sediments tend to deposit in the deeper parts of the harbour basin, the entrance channel and the stagnant areas where weak or no water circulation exists. As harbour sediments are generally subjected to contamination as a result of navigational activities (ship refuse, fuel,.. etc) and some kinds of cargo (i.e. oil, coal, cement, …etc) such locations of sediment deposition can be considered as concentration areas of contaminants.

4. REMEDIATION OF CONTAMINATED MARINE SEDIMENT

4.1 Ex-Situ Techniques

Ex-situ treatment of contaminated marine sediment requires transportation of such sediments to treatment location. Thus environmental dredging should be carried out using proper equipment to limit the spread of contaminants by sediment resuspension, or extra dredging of clean sediment as this will increase the quantity to be treated thus increasing costs. Various techniques are available for such purposes as can be found in National Academy of Science (1997).

Delai Sun et. al (2001) used a combination of ex-situ decontamination techniques to treat two industrial solid wastes produced by oil refiners in Singapore.

Calcinations at 500^o C was effective in removing Carbon and Sulfur in both wastes followed by generation of heavy metal oxides. A two stage leaching process followed, which removed a great portion of Nickel, Cobalt and Molybdenum. Samples of spent and fresh Catalysts ($Co/Mo/\gamma AL_2O_3$ and Ni, Mo, γAL_2O_3) was used for such experiments. The toxicity characteristic leaching procedure (TCLP) test method was carried out to evaluate the leachable portion of heavy metals from the spent catalysts and enhanced stabilization samples. The leachate fluid used was acetate/acetic acid buffer solution having a pH of 4.93. Samples of 100 gm of Catalyst were put into a standard plastic container and 2,00 ml of Leachate was added. The container was then rotated at 30 rpm for 24 h. The volume of leachate was equal to 20 times the sample weight in grams. A powder x-ray diffraction analyzer was used to determine the crystalline structure of material. A bench-scale leaching recovery apparatus consisted of a conical flask to hold the mixture of leachate, spent catalyst and a stirrer. The recovery of heavy metals was carried out in two stages, first an ammonia solution was used to recover Mo while Sulfuric acid was used to recover Ni and Co in a second stage. The leachate sample was filtered and analyzed by AAS, and the percentage of removal of metals calculated. The percentage of removal was 44% for Nickel, 77% for Cobalt and 83% for Molybdenum. The resulting residues were then stabilized in a vitrification process with marine clay. The two materials were mixed together in a homogenize. The mixture was then cast as a brick at a constant pressure of 0.9 bar. The bricks were dried at 35^oC and 105^oC for 4 days and 2 days, respectively before being fired. Such process proved that the leach liquor contains a mixture of metals that may be easily separated and have commercial value. Sub-sequent enhanced binder stabilization treatment using marine clay generated a commercially valuable brick with up to 30% by weight of spent γAL_2O_3 Catalyst in wet marine clay and proved to be an effective method of heavy metal stabilization.

Lim et. al. (2001) investigated the influence of metal loading on the mode of metal retention in a natural clay. Although their study was carried out on an experimental scale, but they arrived at rather interesting results. In such experiments, samples of natural clay were subjected to various levels of contamination by the heavy metal Zn, in a series of batch sorption experiments conducted at pHs of 3–7. The air-dry clay sample used for the sorption experiments with a moisture content of < 2.5%, was ground to pass through a 150 µm sieve. Heavy metal sorption by the clay was determined using a batch sorption technique, with a soil to solution ratio of 1:20. The pH values selected for the sorption experiments were 3, 3.5, 4, 4.5, 5, 5.5, 6 and 7. The pH stabilized soil samples were used according to the method suggested by Lim et. al. (1997). For each pH stabilized 2 g air-dry soil sample in a 60 ml polypropylene centrifuge bottle, 40 mL of a solution containing a known initial concentration of $ZnCl_2$ and 0.05 M NaCL background electrolyte was added. The pH of soil suspensions was controlled at the predetermined values by adding HCL and NaOH. The initial Zn concentrations were 10, 16, 33, 65, 130, 195, 325 and 650 mg/L, which resulted in Zn loadings of 3, 5, 10, 20, 40, 60, 100 and 200 mmol/kg soil respectively. A 24-h contact period with continuous agitation was used in room temperatures of 23±2 °C. At the end of sorption equilibration, the pH of each equilibrated suspension was measured. The suspensions were then centrifuged, filtered through 0.45 µm membrane filters, and the filtrates were acidified. The concentrations of Zn in the filtrates and the soilless blanks were then analyzed using inductivity coupled plasma emission spectrometry, and the total amount of Zn sorption by soil was calculated.

Zinc speciation in the soil was subsequently analyzed using a sequential extraction technique, which fractioned the retained Zn into its various physico-chemical forms or sorbed phases. Each extraction step was designed to extract a particular fraction of the retained metal as suggested by (Tessier et. al., 1979) after applying a minor modification to it. The modification applied is that 1 M $NH_2OH.HCL$ at 70°C was used as a reagent instead of 0.04 M $NH_2OH.HCL$ at 96°C as proposed by (Tessier et. al., 1979). Such changes was proposed by Lim et. al (1998) and proved to increase the metal extraction portion and decrease the volatilization of $NH_2OH.HCL$, HOAc and water during the extraction. Zinc sorbed in the exchangeable, carbonate, reducible, organic and residual fractions of the clay were extracted. The exchangeable was extracted at equilibrium pH measured at the end of sorption tests, in order to prevent redistribution of sorbed phases due to pH change during this extraction stage. The chemical reagents used, the conditions applied are summarized in Table (1).

The study concluded that the total Zn loading in the soil also governed Zn speciation in the clay. It was partly due to the presence of various sorption sites with different electrochemical properties on soil minerals or soil solids. These findings imply that, in qualitative terms, in severely contaminated soils, precipitation is the dominant mechanism in metal retention when favorable soil pH exists. In moderately contaminated soils, the sorbed phase is more persistent, and therefore it is less cost effective to extract the contaminants from the soils.

Table 1: Sequential Extraction Scheme for Determination of Zn Speciation in Clay

Fraction	Extractant	Extraction conditions
Exchangeable	1 M $CaCl_2$	pH varies* 23 °C
Carbonate	1 M NaOAc	pH = 5, 23 °C
Reducible	1M $NH_2OH+HNO_3$ (v/v) HOAc	70°C occasional agitation
Organic	30%H_2O_2+HNO_3 with NH_4OAc	pH = 2 85 °C
Residual	HNO_3(90%), HCL(37%),HF(50%), and H_2O_2(30%)	Microwave digestion

*Soil equilibration pH measured at end of sorption tests

Galvez-Cloutier and El-Herraoui (1998) evaluated various sand/bentonite mixing with field leachate as a landfill liner for heavy metals retention. Although, previous mixing with field leachate decreased final permeability, this factor needs to be closely related to the gain or loss in metal retention. The results showed that heavy metals were retained in a significant way through all sand/bentonite liners. The order of selectivity in the retention of heavy metals was Fe>Zn>Cu>Ni that matched the order of decreasing concentrations in the input leachate. The ability of clay sediments to retain ionic contaminants can be related to its CEC. With respect to pH a very rapid reduction was observed for all liners. Final pH values reached the input leachate pH equal to 5.6. it was noted certain stability of pH for the 10% bentonite liner to pH close to 8. The results showed that the type and sequence of the hydration and compaction steps during the construction of liners have an important impact on final permeability. The durability of a liner in terms of successful retention of an abundant contaminant can be estimated by a number of years required in order to saturate the liner by leachate in the field.

Tsau-Don Tsai and Vesilind (1998) evaluate a new landfill liner to reduce ground-water contamination from heavy metals. Four main materials used in this research are zinc chloride, montmorillonite K10 clay, calcium hydroxide (lime and Ottawa standard sand which was mixed into the lime-clay adsorbent to accelerate the column tests. Clay is a pozzolan in that it is a source of silica and alumina for the pozzolanic reaction. The montmorillonite was treated with nitric acid to wash out most of the adsorbed metal cations. After treatment with nitric acid, protons replace most of the metal cations such as sodium and calcium trapped on the montmorillonite and occupy the adsorption sites once occupied by metal cations. The results clearly indicate that lime changes not only the hydraulic conductivity but also the quantity of Zn(II) immobilized by the clay. The mixture of clay and lime at higher lime concentrations results in more Zn(II) being captured and thereby delaying the Zn(II) breakthrough. With the deionized water, the clay-sand mixtures with 2, 5, and 10 % lime contents had pH values of 8.47, 9.49, and 9.85, respectively. These mixtures do not have a sufficiently high pH to induce a pozzolanic reaction, because the pozzolanic reaction needs a pH higher than 10. The 10% lime could be a transition zone between floctuation and pozzolanic reaction in the clay. With 30 and 50 % lime, the high pHs induce pozzolanic reactions. These reactions change the structure of montmorillonite to form cementitious products such as calcium cilicatehydrate and calcium aluminate hydrate. The adsorbed Zn(II) by montmorillonite becomes a part of Zn-montmorillonite particles, and the increase of the Zn(II) adsorption on the surface of montmorillonite enlarges the volume of Zn-montmorillonite particles.

Vandevivere et. al. (2001) investigated the use of metal chelant [S,S]-EDDS (stereoisomer of ethylenediamine disuccinate) for decontamination of soil, harbor sediment and sewage polluted by heavy metals. They carried out bench-scale experiments for simulation of the extraction step that would occur as a part of an overall washing scheme The process for heavy metal extraction from solid substrates using EDDS involves substrate pretreatment, washing extraction of heavy metals, metal recovery and regeneration of the chelant and final rinse(s) with water treatment before disposal or reuse. Three types of metal polluted substrates were used by Vandevivere et. al. (2001) used three types of metal polluted with the metals already present before sampling (i.e authentic pollution). The soil was polluted with fly ashes from a nearby Zn smelter in Balen, Belgium. It is a sandy loam with 15 % organic matter (largely due to a trinitrotoluene pollution) and pH (water) of 7.5. Biosolids were sampled in the mixed liquor of the municipal wastewater treatment plant in Ghent (Belgium). Fresh samples were taken for each experiment and were concentrated by overnight gravity sedimentation to 2.5% suspended solids. Anaerobic sediment was sampled in sea harbor of Zeebrugge (Belgium) and stored anaerobically at their original moisture level (37% solid content) until use. A fractionation analysis was carried out according to the sequential procedure of Tessier et. al (1979). The exchangeable fraction was that released with 1 M $MgCl_2$ at pH 7, carbonate fraction with 0.04 M $NH_2OH.HCl$ in 25% CH_3COOH (95^{o}C), oxidizable fraction with 30% H_2O_2 in 0.02 M HNO_3 (pH 2 and 85^{o}C), and finally, the residual fraction with aqua region. The experimental protocol used to test the extraction efficiency of chelants for metal polluted solids involved placing 60 g (dry matter) of the substrate (6g for biosolids). The chelant solution was added up to a liquid/solid ratio of 5 (50 for biosolids). The chelant solution was 50 mM $CaCl_2$ (control). All chemicals were reagent grade. Extractant pH was adjusted to 7-8 with HCl or NaOH. The flasks were covered to minimize evaporation losses and placed on a rotary shaker (140 rpm) at 28^o C in the dark. Measuring the total metal concentration in the aqueous phase followed the time course of metal extraction. To this end, a 40-ml slurry sample was taken immediately after vigorous agitation and centrifuged, and the total metal concentration. The paper advances that the major problem in achieving the cleanup goal is one of kinetics. Facilitating mass transfer from the solids to the liquid increased the speed and extent of metal extraction

Reed et al (1996) investigate the flushing of Pb(II) contaminated soil using HCL, EDTA, and $CaCl_2$. Batch soil washes and soil column flushing experiments, were conducted using a sandy loam (ph=5.5;CEC=7.6 meq/100g; Hydraulic conductivity – 0.0025 cm/sec. Effluent Pb and pH versus the number of pore volumes of flushing solution passed through the column are presented for 0.1 N HCL, 0.01 m EDTA, and 1 M $CaCl_2$ respectively.

For all flushing solutions, there was significant Pb removal after 1 PV (pore volume) of flushing solution while there was little additional Pb removal after 4 PVs of flow. The effluent Pb concentration peak was highest for HCL followed by EDTA and $CaCl_2$. For HCL, Pb was removed by low pH enhanced desorption and ion exchange (H+ for Pb_2+). For EDTA, lead removal was due to chelation; and for $CaCl_2$, Pb removal was by a combination of ion exchange (Ca_2+ for Pb_2+) and complexation with Cl-. The low soil pH during HCL flushing is of concern because there is a possibility that metals remaining on the soil, as well as metals that may be added to the soil, will be highly mobile given the low soil. The final effluent pH for the EDTA and $CaCl_2$ flushes were approximately 5.2 and 4.85, respectively.

Zagury et. al, (1999) have carried out an ex situ remediation of heavy metals-contaminated industrial sludge (PH=10.35, Zn=3,500 mg/kg) by electroreclamation (I=2.5 A) was studied at pilot scale (42.5 Kg of sludge). Such sludge was obtained from a gas plant located in aquitaine, France. Incinerator sludge is collected in a pond where it is stored prior to landfilling. Sludge samples were stored for a few days in 60-L plastic barrels and kept at 4^{o}C before analysis. The sludge was analyzed for PH (pH meter used was WTW Model pH 320) using French standard method AFNOR, water content, and total volatile solids carbonate content and particle size distribution between medium sand, fine sand, and silt and clay classes. The sludge was digested in HNO_3, HF and $HClO_4$ following the standard method procedure (1992). Heavy metal concentrations (Cu, Cr, Ni, Mn, Zn, and Fe) of the digested sludge were determined by atomic absorption spectrophotometry. Sludge conductivity was determined using AFNOR NF. Buffer capacity gives an indication of the sludge resistance to a pH variation. According to Federer and Hornbeck (1985), it can be expressed as the number of moles of H^+ ions needed to lower the initial pH of 1 Kg of sludge by 1 pH unit. Buffer capacity is determined experimentally by measuring the pH change when a strong acid is added to a sludge suspension. It has been evaluated by titration of the sludge with NHO_3 according to Zagury (1997). A leaching test of sludge in deionized water was performed according to French standard method AFNOR NF x 31-210 (Recueil 1994). In order to evaluate the retention form of metals in sludge prior to electroremediation, a selective sequential extraction (SSE) was performed as suggested (Tessier et. al. 1979).

The pilot scale batch cell used consisted of one main compartment (0.4 m x0.4 m x0.4 m) containing 24.5 Kg (dry weight) of contaminated sludge and two electrode compartments (0.2 m x0.4 m x0.4 m) filled with water (anode) and nitric acid (cathode). Chemically inert platinumplated titanium electrodes were used. Gases produced by electrode reactions were vented from electrode reservoirs using a cover connected to a fuming hood. The cell wall was equipped with seven contacts connected to stainless steal rods inserted into the sludge. These contacts were used to measure the potential drop along the sludge sample.

The results of such study showed the following:
Chemical preacidification allows improvement of sludge initial pH and electrical conductivity, therefore promoting migration of metals. The use of a high current permits a strong acidification of the sludge, which reaches very low pH values. The use of SSE prior to electroremediation can help to predict the efficiency of treatment. High migration or removal of metals could not be expected, since 70 to 90% of metals were partitioned in the residual fraction. However, results have shown that part of Zn found in the residual fraction was dissolved, then mobilized during the treatment, probably because of very severe pH conditions reached. The fraction of toxic metals that was theoretically amenable to migration was mobilized during electroremediation. Concentration of heavy metals near the cathode area may represent a useful treatment technique since it reduces the total volume of sludge to be disposed off. Furthermore, if metals remaining in the treated portion of sludge are in a residual form, they should not be considered hazardous. Such a technique, called electroaccumulation, does not imply treatment of processing fluid and removal of pollutants. The potential of electroreclamation to treat heavy metals contaminated sludge is confirmed. Interesting costs were achieved in the French context. The overall treatment cost could be lowered with a better adjustment of chemical preconditioning, conditioning of catholyte, current intensity, and duration of treatment. A significant percentage of the energy was spent in removing less toxic or nontoxic metals such as manganese, calcium and iron.

4.2 In-Situ Techniques

In-situ treatment involves adding unconfined chemicals or agents to the environment to immobilize or break down contaminants. In situ treatment poses numerous technical problems and has been at very few contaminated sites, including several small sites in North America. Nevertheless, attention must be given to several in situ treatments, including immobilization, and biological treatment. The National Academy of Sciences (1997).

4.2.1 Immobilization

The goal of in situ immobilization is to isolate sediment contaminants from the benthic and aquatic ecosystem. The immobilization techniques considered most often are solidification and stabilization. However, because marine sediments of even moderate organic content are likely to be rich in sulfides, which naturally limit the mobility of metals, the addition of sulfides is not likely to be an appropriate treatment.

The in situ immobilization of sediments is likely to be based on the concepts of solidification and stabilization and to involve the addition of Portland cement, fly ash, or other binding agents to keep contaminated sediments in place and to reduce contaminant mobility. Immobilization has been used on a small scale at Manitowoc Harbor in Wisconsin, where a cement and fly ash slurry was added to the sediment using a proprietary mixing tool and slurry injector (EPA, 1994b). The in situ mixing of cement with sediments for the primary purpose of enhancing compressive strength has not been proved or accepted for treatment of contaminated marine sediments in the United States (EPA,1993a).

4.2.2 Biological Treatment

In situ bioremediation technologies are used in land-based soils to degrade many, but not all, contaminants. With respect to marine sediments, however, bioremediation technologies are experimental. Soil and ground water bioremediation technologies cannot be transferred directly to in situ marine sediments for a number of reasons. Three major barriers are noted here. First, because little is know about the degratative potential of marine microbial consortia, it is not known how well lessons learned in land-based systems will translate to marine systems. Second, the introduction of nutrients and an oxidant source to in-place contaminants is a major challenge in a marine environment. Third, unlike subsurface aquifers and soils, marine sediment biota are linked intimately to the benthic food chain.

In sum, the in situ bioremediation of PCB-contaminated sediment has only recently been recognized as a potential alternative. Although the technology looks promising, given the current level of application and the regulatory focus on total PCBs, it is unclear whether in situ bioremediation can achieve the cleanup levels required at a reasonable cost.

5. CONCLUSION

Delai Sun et.al. (2001) Conclude that optimum removal of the heavy metals was achieved by two stages leaching process. The first stage consists of adsorption through a cation exchange process (internal and external) as well as bond formation between the clay minerals and the complex heavy metal ions through the liberation of OH- ions around 600 ^{o} C. This is then followed by the formation of a new matrix of mullite and eristobalite, in which the heavy metals actually become incorporated. R. Galvez-Cloutier and E El Herraoui (1998) concluded that the liner previous mixing with field leachate and the higher the cation exchange capacity (CEC) increase the metal retention, specially with sand/10 % bentonite mixtures. Tsan-Don Tsai et. al. (1998) concluded that the dual affects of lime and Zn(II) capture delay the appearances of Zn(II) in percolation tests. Liners constructed with clay/lime mixtures would provide superior resistance to leachate percolation with the additional advantage of providing a chemical barrier to ground-water contaminant by heavy metals in acidic leachate. Lim et. al. (2001) concluded that Zn speciation among various sorbed phases in the clay was susceptible to changes in Zn loading on the soil and pH. This phenomenon has been also observed from the interactions between other heavy metals and soil components. Reed et. al. (1996) concluded that Pb removal efficiencies for HCL, EDTA, and $CaCl_2$ were 85%, 100%, and 78%, respectively. EDTA removed all lead, its treatment and reuse and possible adverse health effects make its use difficult. Soil pH for EDTA and $CaCl_2$ was in the slightly acidic range (4.85 – 5.2). Vandervive et. al. (2001) concluded that speed and extent of metal extraction were increased by facilitating mass transfer from the solids to the liquid. Slightly alkaline pH was necessary to eliminate the interference by iron. Zagury et. al. (1999) concluded that the ex situ remediation of heavy metals contaminated industrial sludge by electroreclamation was studied at pilot scale. In the anode region, Zn and Cu concentrations decreased by 33 and 39%, respectively, and increased in the cathode region by 33 and 26%, respectively. These metals were concentrated in the cathode area but were not mobile than other metals.

Experience with immobilization techniques is not extensive enough to provide reliable estimates of the costs of large-scale treatments, their effectiveness, or possible toxic by products. The National Academy of Sciences (1997).

Initial experiments found that microbial degradation of polyaromatic hydrocarbons could be simulated in harbor sediments, but the approach was difficult to monitor and the effectiveness could not be evaluated. Research is now under way on ex situ processes for the removal of ployaromatic hydrocarbons and metals.

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