EVALUATION OF BASE-CATALYZED DECOMPOSITION (BCD) PROCESS FOR NEW YORK/NEW JERSEY HARBOR SEDIMENT DECONTAMINATION

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INTRODUCTION

Dredging and disposal of sediments from the New York/New Jersey Harbor (Harbor) are conducted on a regular basis to ensure that shipping channels are maintained for safe navigation. Sediments that accumulate in these areas may contain a variety of contaminants at concentrations that pose a range of potential risks to ecological and human health. Heavy metals (Hg, Cd, Pb, Ni, Cu, Zn, and As), chlorinated pesticides, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and dioxins are the major contaminants of concern in the Harbor.

Most sediments dredged from the Harbor have been disposed at the New York Dredged Material Disposal Site which is located six miles off the New Jersey coast. Such material must pass recently revised tests for ocean disposal of dredged material, however. The updated testing manual contains more stringent chemical and biological testing guidelines for determining the suitability of dredged sediments for ocean disposal. As a result, the volume of contaminated dredged material prohibited from unrestricted ocean disposal may increase dramatically. Although alternatives to ocean disposal have been investigated on a preliminary basis, presently there are no long term non-ocean disposal alternatives in operation in the Harbor region.

The U.S. Army Corps of Engineers, in consultation with the U.S. Environmental Protection Agency, identified existing technologies for the treatment of contaminated dredged material. Screening level bench-scale tests were performed with the most promising technologies. The Base-Catalyzed Decomposition (BCD) process was one of the technologies tested at the bench-scale level which demonstrated high removal efficiencies for dioxin. The fact that the BCD process actually destroyed dioxins rather than merely removing them was a significant advantage.

Based on the promising screening level bench-scale tests, the decision was made to conduct a field demonstration of the BCD process. Prior to conducting the field demonstration, it was necessary to conduct detailed bench-scale tests, the results of which would be used to size equipment and determine operating conditions for the pilot unit. This paper details the results of these bench-scale tests.

METHODOLOGY

BCD is a two-stage chemical process which operates at moderate temperatures to remove organic contaminants and decompose chlorinated hydrocarbons from soils and sediments. In the first stage, sodium bicarbonate is added to the sediment, which is heated to about 340 C. As a result, (a) water is evaporated and separated from the sediment into one waste stream, and (b) organic contaminants are partially decomposed and removed in another waste stream. In the second stage, sodium hydroxide, a hydrogen-donor oil, and a catalyst are added to the organic waste stream at 340 C.

Sediment was collected from three Harbor sites: Newark Bay, Arthur Kill, and Newtown Creek. The plan was to use one of the sediments for initial tests to determine optimum conditions and then to treat all three of the sediments at the optimum conditions. The Newtown Creek sediment was chosen as the sediment for the optimization tests because it had the highest concentration of the higher chlorinated dioxin, furan, and PCB congeners. The untreated sediment had a total dioxin concentration of 18 ppb (10 ppt 2,3,7,8-TCDD), a total furan concentration of 4 ppb, and a total PCB concentration of 1.5 ppm.

RESULTS

Three process variables were evaluated during the Stage 1 optimization tests: contact time, sodium bicarbonate dosage, and water content of the feed. The tests revealed that a contact time of one hour, a sodium bicarbonate dosage of 10%, and the use of a predried feed material resulted in the greatest destruction of dioxins. In addition to the treated sediment, the process also produced an aqueous condensate and an oil condensate.

While some destruction of chlorinated organics occurred in the Stage 1 reaction, the bulk of the chlorinated organics were transferred to the oil condensate. The oil condensate was to be treated by addition of the BCD reagents, but the aqueous condensate required only polishing. Oil extraction, flocculation, and carbon treatment were considered as treatment options. Testing revealed that a combination of flocculation and carbon treatment provided the highest removal efficiencies of chlorinated organics from the aqueous condensate.

Funds did not exist to treat all three sediments as planned, so only the Newtown Creek sediment was run at the optimum conditions. Four runs were performed to collect sufficient sidestream material to allow for characterization. The oil condensate underwent the Stage 2 BCD reaction with the addition of sodium hydroxide, catalyst, and a hydrogen donor. The aqueous condensate was treated with flocculants followed by carbon.

Preliminary results from the bench-scale testing indicate that the percent removals of dioxins, furans, and PCBs from the sediment were >99% with total dioxin and furan concentrations in the treated sediment at non-detect levels and total PCBs at 22 ppb. The aqueous condensate was relatively free of contaminants prior to flocculation and carbon treatment and these contaminants were at non-detect levels after polishing. The bulk of the contaminants ended up in the oil condensate where Stage 2 BCD treatment resulted in destruction efficiencies >99%.

There was no evidence of dioxin/furan destruction in the Stage 1 reactor, but there was evidence of partial dechlorination and congener shifting. Essentially all of the dioxins and furans ended up in the oil condensate where Stage 2 destruction efficiencies exceeded 99%. About 50% of the PCBs were completely dechlorinated in the Stage 1 reactor. The remaining 50% showed up in the oil condensate and were completely destroyed during the Stage 2 reaction.

Using the bench-scale data, a mass balance of the BCD process revealed that for every ton (2000 lbs) of wet sediment (67% water content) treated, 0.33 tons (660 lbs) of treated solids, 163 gallons of aqueous condensate, and 1.3 gallons of oil condensate would be generated. Contaminants from one ton of contaminated sediment would be concentrated into the 1.3 gallons of oil condensate where Stage 2 treatment would completely dechlorinate the remaining dioxins, furans, and PCBs.

CONCLUSIONS

The BCD process was successful in destroying chlorinated organic material present in Newtown Creek sediments collected from the New York/New Jersey Harbor. Destruction efficiencies for dioxins, furans, and PCBs were >99% and concentrations in the treated sediment were at or below detection limits.

Having completed the bench-scale testing portion of this study, effort is now being directed towards the pilot-scale field demonstration of the BCD process. The demonstration is being planned for the summer of 1995.

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ELECTROKINETIC SOIL REMEDIATION: IMPACT OF AQUEOUS PHASE PROPERTIES ON SOIL SURFACE CHARGE AND ELECTROOSMOTIC EFFICIENCY

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INTRODUCTION

The *in situ* remediation of a contaminated soil is an exercise in mass transfer limitations. The challenge is to mobilize the contaminant and transport it to a treatment/collection zone or to deliver nutrients, microorganisms, or destruction chemicals to degrade the contaminant where it resides. For soils with high hydraulic permeabilities, mobilization or treatment solutions can be hydraulically delivered to the contaminated zones. Mobilized contaminants and degradation products can be removed in the same manner. However, pressure driven hydraulic delivery/removal in low permeability soils, such as clays, is impractical.

One method of transporting solutions and compounds in low permeability soils is the application of an electric current to the soil in a process called Electrokinetic Soil Remediation (ESR). This form of remediation utilizes the response of charged molecules and particles to an applied voltage gradient to effect the movement of pollutants. Driving the remediation are the electrokinetic phenomena of electroosmosis, ion migration (electromigration), and electrophoresis. As depicted in Figure 1, most soil particles, including clays, carry a negative surface charge. When the soil is immersed in an electrolyte, the particles attract cations, creating a positively charged boundary layer (referred to as the *charged double layer*) next to the surface of the soil particles. Application of a voltage difference across a section of soil causes movement of the ions and associated water within the double layer toward the cathode (electron source). The remainder of the pore fluid moves in the same direction as the double-layer fluid due to viscous drag interactions. This net flow of pore fluid due to an applied voltage gradient is termed "electroosmosis" (EO). EO can be utilized to remediate contaminated soils *in situ* by flushing out the pore fluid and contaminants (or to deliver nonionic nutrients, surfactants, etc.).

The ions in the bulk pore fluid also respond to the applied voltage gradient with the anions being driven to the anode and cations driven to the cathode. This movement of aqueous ions and ion-complexes in response to the voltage gradient is referred to as ion migration or electromigration. Electromigration can be used to recover ionic contaminants from soil even in unsaturated soils (1). Larger charged molecules and particles also move due to an applied voltage gradient (electrophoresis). Substances which fall into this latter category include cationic or anionic surfactant molecules and micelles, clay particles, and polyelectrolytes. The degree to which each electrokinetic phenomenon occurs depends on the properties of the soil/pore fluid matrix including the degree of saturation, ionic strength of pore fluid, types of ions/charged particles present, pH of pore fluid, temperature, porosity of soil, soil composition (% clay, type of clay, etc.), and the surface charge of the soil particles. In this paper, the effect of pore fluid properties on the surface charge of clays and the resultant effect on electroosmosis in saturated clays will be examined.

When a charged particle is suspended in an electrolyte, ions with a charge opposite to that of the particle will concentrate in the charged double layer. The velocity of the particle (v_p) when placed in an electric field is dependent on the viscosity of the fluid (η), the applied voltage gradient (E), and the zeta potential (ζ), or surface charge, of the particle as described by Smoluchowski's classic equation (2):

$$v_p = \frac{\varepsilon \zeta E}{\eta} \qquad (1)$$