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Special Remediation of Contaminated Soils and Groundwaters issue
Robert W. Peters, Guest Editor

Contents

Critical Evaluation of PCB Remediation Technologies

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Polychlorinated biphenyls (PCBs) are a family of aromatic compounds consisting of a biphenyl molecule which has been chlorinated to form a large number of possible congeners. The number of chlorine atoms they can contain (from 1 to 10) varies, as does the placement of the chlorine atoms on the biphenyl molecule. Thus, a polychlorinated biphenyl is one of 209 compounds having the formula: $C_{12}H_{10-n}Cl_n$. *Due to their excellent heat stability, fire retardance and electrical insulating properties, they gained widespread use as dielectric fluid incorporated in electrical transformers and capacitors. They were also incorporated in products as various as plastics, hydraulic fluids, surface coatings, inks, paints, pesticides, lubricants, and carbonless copy paper.*

INTRODUCTION

From 1929 through 1980, the world production of PCBs was about 2.4 billion pounds. It is estimated that in the United States, about 404 million pounds of PCBs are still in use and accessible, about 262 million pounds are still in use and generally not accessible, and about 585 million pounds have been destroyed or are in storage, landfills, or the environment. The PCBs still in use and accessible are in transformers, capacitors, and other electrical equipment. Within the last category are PCBs in sediments, soil, vegetation and animals, the atmosphere, and fresh water totalling about 24 million pounds, another 13 million pounds are in the oceans, about 385 million pounds are in landfills and other storage, and an estimated 162 million pounds have been degraded.

In the mid 1960's, concerns regarding the toxicity and persistence of PCBs in the environment led to their eventual control in the United States under the Toxic Substances Control Act of 1976 (TSCA). TSCA regulates the manufacturing, processing, distribution in commerce and use of PCBs (40 CFR 761 et seq.). Subpart G of 40 CFR 761, the PCB Spill Cleanup Policy, specifies "how clean is clean" for spills of PCBs which occur after the effective date of the policy (May 4, 1987). The PCB Spill Cleanup Policy does not apply to several categories of spill situations, including historic spills (those which occurred prior to the policy's effective date), spills which directly contaminate or migrate into surface waters, sewers or sewer treatment systems, private or public drinking water sources or distribution systems, and spills which contaminate animal grazing lands or vegetable gardens. For spills which fall in any of these categories, a cleanup standard must be negotiated with the cognizant regulatory agency(s). Determination of an acceptable residual concentration is imperative prior to selecting a remedial technology for treatment of the specific waste stream(s).

The primary basis of establishing a cleanup standard is the protection of public health and the environment. However, the ability to reach a cleanup level in a given situation is also considered. Thus, current knowledge of the capabilities of remedial technologies is vital. Development of PCB treatment technologies continues due to the ubiquitous nature of the chemical. This paper discusses the current state of development of the available technologies.

INCINERATION

Incineration is a recognized technique of PCB destruction. TSCA requires a "six-nines" (99.9999%) destruction and removal efficiency (DRE) of PCBs for thermal treatment systems. Therefore, for an incineration system to be permitted to destroy PCB containing wastes, it must be able to demonstrate conformance with this strict standard. The high temperatures and long residence times usually required to conform to this standard generally destroy all other organic components of the waste as well.

There are less than ten TSCA permitted commercial PCB incinerators currently operating in the United States. These vendors indicate that PCB destruction costs range from approximately \$500 to \$800 per ton for solid waste and \$3.25 to \$5.00 per gallon for liquid waste. Costs are dependent upon waste characteristics such as heating value and burn characteristic of the waste, PCB concentration, waste matrix, and total amount of waste treated, among other factors.

In some instances, it may be more economically feasible to bring a TSCA permitted incinerator to the waste, rather than transport the waste to a commercial incinerator. However, public acceptance of on-site incineration may be limited. Early regulatory agency and public involvement prior to selection of this remedial alternative may help alleviate the historical "NIMBY" (not in my backyard) attitude against thermal destruction units.

Transportable incinerators are comprised of the same unit operations as permanent, commercial facilities, namely: primary and secondary combustion chambers, feed systems, bottom and fly ash handling units, air emissions control (filters, electrostatic precipitators, wet scrubbers), heat exchangers, and exhaust stacks. Waste water treatment for cooling/scrubbing water recycle/disposal and a mobile on-site laboratory can be integral supporting operations for transportable incineration systems.

Roy F. Weston, Inc., among others, operates a TSCA permitted Transportable Incineration System (TIS) which utilizes a 23 million BTU/hr rotary kiln as the primary combustion chamber. The kiln is of standard countercurrent cylindrical design which allows retention times of fifteen to ninety minutes. Operating temperatures can be varied below 1200 to 2200°F and the system can process from two to ten tons per hour of contaminated soils. It is also designed to be capable of incinerating fume, hazardous liquids and sludges at rates up to 233 million BTU/hr of heat release. A demonstration test performed in May 1988 indicated that the system could process an average of 13,650 lb/hr of soil spiked with PCB oil to an average concentration of 14,740 parts per million (ppm). The DREs achieved during this demonstration ranged from 99.99983% to 99.999990%, with residual PCB concentrations in the bottom ash of .01 ppm to .15 ppm.

The feed conveyor system requires a maximum particle size of two inches, therefore, materials handling must assure this limit can be met. For loose, sandy soil, simple screening can accomplish this end. Soils with high cohesion will require an operation, such as shredding, which will break down the feed to the appropriate size. As with all incineration systems, inorganic (heavy metal) constituents are not destroyed, but passed through to the ash streams. Stabilization of these streams may be required to immobilize the inorganic components to acceptable levels.

The TSCA permit granted to the TIS eliminates the need to get additional Federal TSCA permits as the unit is moved from site to site. However, National Pollutant Discharge Elimination System (NPDES), Publicly Owned Treatment Works (POTW) discharge, and/or air emissions permits may still be required. Additionally, if the waste feed can also be characterized as Resource Conservation and Recovery Act (RCRA) hazardous waste, a RCRA Treatment Storage and Disposal Facility (TSDF) permit must be gained.

The cost of remediating PCB contaminated soils via the TIS can range from $140 to $600 per ton; and generally fall in the $180 to $200 per ton range. These costs are mainly dependent on the heating value of the waste, the concentration of PCBs to be destroyed, and the total quantity of waste to be remediated.

Ogden Environmental Services owns and operates a transportable 10 million BTU/hr Circulating Bed Combustor (CBC). The CBC can provide DREs of 99.9999%, and is available for on-site operation. Soil feed rates vary based on soil moisture content and heating value of the waste. Solids, liquids and sludges may be treated utilizing this system, however, a maximum particle size of 1″ for solid feed will determine the precombustion material preparation and handling requirements.

The thermal treatment unit of the CBC consists of ceramic lined combustion loop which is comprised of a combustion chamber and cyclone. Waste is fed into the loop along with limestone, which neutralizes acid gases formed during the thermal destruction reactions. The waste contacts hot recirculating soil from the cyclone. As it heats, it is entrained with air and travels upward through the combustor into the cyclone, where the solid fraction is separated from the combustion gases. The hot solids drop down to reenter the combustion chamber, where they will aid in heating new feed being introduced. Remediated solids remaining in the lower portion of the combustion chamber are removed at a controlled rate by an ash conveyor system.

Like the TIS, the CBC is TSCA permitted. However, air emissions, water discharge and RCRA permits must be obtained as required. Treatment costs for remediating soils [illegible] CBC typically range from $100 to $300 per ton, depend[illegible] primarily on soil moisture and quantity of material to be pr[illegible]essed.

Westinghouse Environmental Services has developed [illegible] markets a Pyroplasma plasma arc process which utiliz[illegible] plasma torch to pyrolyze liquid organic materials at temp[illegible]atures up to 15,000°C. Throughput capacities vary from [illegible] to three gallons per minute in single stage units. Waste liqu[illegible] are aspirated into a superheated gas stream, where the mol[illegible]ular bonds of the waste are broken into their component ato[illegible] These atoms recombine in the reaction chamber to form n[illegible] hazardous gases such as carbon monoxide, nitrogen, hydrog[illegible] and some low molecular weight hydrocarbons. Acid gases [illegible] particulate carbon are removed in a wet scrubber. The result[illegible] gaseous stream, primarily hydrogen and carbon monoxide, [illegible] drawn off and flared.

The Pyroplasma unit is suitable for liquid wastes only. Un[illegible] a TSCA Research and Development Permit, it has dem[illegible]strated DREs greater than 99.9999% for PCB liquids w[illegible] concentrations of 70–80% PCBs by weight. This technol[illegible] is available in mobile units. Permitting and public accepta[illegible] issues for this treatment system are the same as those for [illegible] TIS and CBC.

A transportable Infrared Incineration System has been [illegible]signed by Shirco Infrared Systems, Inc., which utilizes e[illegible]trically powered silicon carbide rods to provide infrared ene[illegible] that heats organic waste to combustion temperatures. [illegible]maining combustibles are incinerated in an afterburner. [illegible] demonstration of this system in 1987 under the United St[illegible] Environmental Protection Agency's (EPA's) Superfund [illegible]novative Technology Evaluation (SITE) program dem[illegible]strated its ability to destroy PCBs at concentrations ran[illegible] from 10 ppm to 669 ppm in the feed with DREs exceed[illegible] 99.99%. While this demonstration did not meet TSCA's [illegible]quirement for PCB destruction by thermal treatment, o[illegible] tests with the same unit have achieved DREs of 99.999[illegible] Therefore, this incineration system, based on waste spe[illegible] trial burn results, may be granted TSCA approval for re[illegible]diation of PCB contaminated soils.

IN-SITU VITRIFICATION

A variation of traditional thermal treatment systems is [illegible] In-Situ Vitrification (ISV) Technology developed by the Pa[illegible] Northwest Laboratories Division of Battelle Memorial In[illegible]tute and marketed exclusively by Geosafe Corporation. [illegible] is a process which melts inorganic soil for the purpose [illegible] thermally destroying its organic component. This is acco[illegible]plished as follows.

Electrodes are placed in the soil to the desired treatm[illegible] depth. A conductive starter path is placed on the surface [illegible]tween electrodes, and the treatment area is covered by an [illegible] gas collection hood. As a result of the electric potential betw[illegible] the electrodes, current which flows through the starter p[illegible] generates heat which in turn melts the underlying soils. [illegible] molten soils are generally quite electrically conductive, all[illegible]ing the process to continue to depth. The high temperat[illegible] within the molten soil cause organic material (either natur[illegible] occurring or contaminants) to volatilize and pyrolyze. [illegible] resultant gases either become dissolved in the melt or mov[illegible] the surface, where they combust on contact with air. Prod[illegible] of pyrolization and combustion are collected in the off[illegible] collection hood, and are treated prior to emission.

As the soils melt, the void space is removed. A vol[illegible] reduction of 20–40% is typical. When the melt mass reac[illegible] an optimum, power to the electrodes is removed and the [illegible] is allowed to cool naturally. As it cools, it vitrifies int[illegible] monolith which resembles naturally occurring obsidian ([illegible] glass). The surface depression which results from the reduction in volume may be backfilled with clean soils, allowing for unrestricted future use of the area upon approval by the cognizant regulatory agency.

Potentially toxic inorganic contaminants are chemically incorporated in this matrix. Leach, hydration, and weathering tests of vitrified waste indicate that it has excellent long-term stability and can expect a mean life of thousands of years.

The vendor indicates this process exceeds PCB DREs of 99.9999% as required by TSCA, but requires treatability testing on actual waste samples to verify the process is capable of satisfying cleanup requirements. They also indicate this method is applicable to a variety of organic, inorganic and radioactive materials.

The ISV process is an in-situ treatment, and the treated vitrified waste may be left in place. As such, materials handling requirements are minimized. While the process can operate in fully saturated soils, the energy required to vaporize water could more cost effectively be used in vitrifying soils. Organic and inorganic debris may be left in place and treated within the melt volume, dependent on their expected effect on off-gas generation and residual product.

This technology is commercially available through Geosafe, which holds worldwide exclusive rights to it. Costs for utilizing this technology are on a similar order of magnitude as incineration, but can vary greatly based on variables such as waste-soil properties, volume of material, depth of required vitrification, unit price of electricity, moisture content, and distance of the site from the vendor's base location in Washington.

DESTRUCTION USING QUICKLIME

At several EPA remedial action sites in the recent past, observations by regional staff had suggested that treatment with quicklime (CaO) may achieve destruction of PCB contaminated soils and sludges.

EPA's Risk Reduction Engineering Laboratory (RREL) initiated studies, both in-house and through a contracted laboratory (RMC Environmental and Analytical Laboratories) to verify the results indicated in the field. The initial study conducted by RMC were extremely limited in scope, and indicated that reductions in PCB concentrations, on the order of 90%, were achieved in the waste matrices. The in-house project designed by RREL and conducted by their on-site contractor, Technology Applications Inc., indicated that the reductions detected in the waste matrices were due to evaporation and steam stripping in PCBs during the lime shaking process. Furthermore, only minimal amounts of products of phenyl-phenyl bond cleavage were detected, further supporting the theory that this process is not applicable to the destruction of PCBs.

BIOREMEDIATION

Biological treatment technologies use microorganisms to detoxify or decompose degradable organics. Naturally occurring (native) species may be utilized or specially adapted microorganisms may be introduced into the contaminated media.

Biodegradation of PCBs as a remedial technology is in the developmental stages. Many studies have identified several microbes which exhibit an ability to degrade specific PCB congeners to varying degrees. These microorganisms include several species of Achromobacter, Alcaligenes, and Pseudomonas, as well as a fungus, Phanerochaete chrysosporium. Best results can be obtained in biological reactors which can ensure the necessary aeration, mixing, temperature control and nutrient delivery to optimize the biokinetics.

Biological treatment systems are living systems. Survival of the necessary microbes is vital for this technology to be feasible. It is therefore necessary to conduct treatability testing on actual waste samples to determine if the microorganisms can degrade the specific PCB congeners present or even survive.

While the inherent toxicity of PCBs indicates that their biodegradation would occur only at dilute concentrations, laboratory studies performed by General Electric Company, Corporate Research and Development have indicated degradation of soils spiked with PCBs in concentrations as high as 500 ppm Aroclor 1242.

The extremely limited amount of data on field applications of biological processes to remediate PCB contaminated wastes makes it difficult to specify levels of detoxification possible in nonlaboratory conditions. Likewise, it is not possible to quantify chemical or matrix interferences which may be encountered, or the costs to be expected on a per unit basis. However, bioremediation is gaining favor in hazardous waste remediation in both Europe and the United States. As it is utilized, more data will be made available for assessing the efficiency of the technology for a myriad of contaminants, including PCBs. Specifically, the results of a field study of biodegradation in PCB contaminated Hudson River sediments, being conducted by General Electric, will make field application data available for future bioremediation schemes.

CHEMICAL DECHLORINATION

In 1978 at the Chemistry and Biosciences Laboratory, Franklin Research Center, a chemical reagent was synthesized and found to destroy PCBs by the process of dechlorination. Since that time, a family of alkali metal polyethylene glycolate (APEG) reagents have been developed which effectively dechlorinate PCBs in soils and liquids quickly. These reagents are known as KPEG or NaPEG, dependent on whether the alkali metal utilized is potassium or sodium. Research has shown that KPEG is more effective in destroying PCBs than NaPEG.

In a patented process, the KPEG reagent is prepared by reacting potassium hydroxide with one of several polyethylene glycols. This reaction produces an alkoxide which reacts with one of the chlorines on the aryl ring of the PCB to produce an ether (hydroxyl substituted aryl ring) and potassium chloride. The substitution of the chlorine atom with the ether-linked polyethylene glycol molecule detoxifies the PCB. Additional research indicated this process can also dechlorinate (and thereby detoxify) polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) in either a solid or liquid matrix.

This process and variations of this process have undergone numerous laboratory studies and field demonstrations. A field demonstration conducted by EPA RREL in Guam on PCB contaminated soils utilized a batch reactor equipped with a mixer and an external steam jacket to allow for process heating. The steam jacket was designed to allow it to serve as a process cooling water system as well. A vent from the reactor to a condensate collection system was also provided. Following dechlorination the treated soil was allowed to cool. Sulfuric acid was then added to adjust the pH to the range of 6 to 9. Treated wastes with unacceptable concentrations of PCBs were subsequently re-treated to provide further dechlorination. Soil was discharged from the reactor, sampled and stored pending analytical results. Over several runs, approximately 15 cubic yards of soil with an average concentration of 3,500 ppm PCBs were treated to greater than 99% reduction of PCBs.

Waste soils pretreatment requirements (that is, largest particle size), are highly dependent on the physical configuration of the mixer employed. For the Guam demonstration, a maximum particle size of 1/2 inch was required to prevent fouling of the mixer blades against the reactor wall.

Implementation of this process utilizes commercially available process equipment, therefore is readily available. However, implementation of this process may be slowed by the need to obtain TSCA, RCRA, and potentially air and water discharge permits. Additionally, care must be taken so as not to infringe on the patent holder's legal rights.

The cost to apply this technology will vary greatly depending upon the volume of treated waste and the current reagent prices. Cost estimates for treating soil in plants with a treatment capacity of 25 tons per batch operation have been estimated to range from $242 to $347 per ton of soil, with capital-related and chemical costs accounting for approximately 84 percent of total cost.

Several vendors offer dechlorination of PCB articles (transformers with PCB oil at concentrations greater than 500 ppm) and PCB contaminated equipment (transformers filled with dielectric fluid at concentrations between 50 and 500 ppm). The systems utilized are generally flatbed trailer mounted and operate using a closed loop circulation system. This allows for reclamation of transformer oil on-site, without draining it from the transformers. For a cost premium, the operation can be performed on energized transformers, reducing downtime. Proprietary reagents are utilized to dechlorinate, dewater, degassify and desludge transformer oils.

Properly utilized under the vendors' TSCA permit, these types of procedures allow for declassification of PCB and PCB contaminated electrical equipment. This in turn should reduce future liability for the electrical equipment owners, since equipment with less than 50 ppm PCBs is less likely to release harmful quantities of PCBs to the environment.

The specific nature of the proprietary reagents will determine any potential chemical and/or matrix interferences. Vendors need to be contacted for the costs of these operations. Factors which will affect the cost of treatment include type of unit to be serviced, the volume and concentration of dielectric fluid, access to equipment, and whether it will be energized or deenergized.

SOLVENT EXTRACTION

Solvent extraction of PCBs from soils makes use of PCBs' preferential solubility in oils and various extractants over water. HARBAUER, Sanivan Group, and Resources Conservation Company (RCC) have all developed processes when PCB contaminated oily soils or sludges mixed in an extraction vessel (generally a countercurrent soil washer or mixed reactor) with the appropriate solvent. During this step, the PCBs preferentially enter the oily solvent phase, leaving the soil phase with a greatly reduced PCB concentration. The solvent phase is decanted, and the soil phase is dried if necessary. The oily solvent fraction is then separated using standard separations techniques into oil, water, and solvent fractions. Ideally, solvent can be regenerated or recycled for future use, and all PCBs are concentrated within the oil fraction. These processes do not destroy PCBs, but rather, concentrate them into one phase of the original waste stream with a greatly reduced volume as compared to the original waste. The PCBs in the concentrated stream, generally the oil fraction, must then be either thermally or chemically destroyed as required by regulation.

HARBAUER and RCC have reported removal efficiencies on the order of 98 percent with oily soils contaminated with PCBs in the less than 20 ppm range during actual field scale on-site remediations. Sanivan Group will be conducting a field demonstration of their process under the auspices of EPA's SITE program on soils contaminated with PCBs in the range of 5 to 50 ppm.

Feed preparation requirements for solvent extraction processes are determined, in part, by the physical configuration of the extraction vessel. Maximum particle size and percent fines in the soil/waste matrix will likely be a factor for soil washing techniques, since a higher ratio of fines in the waste results in a greater volume of sludge requiring final disposition.

Potential chemical and matrix interferences will depend on the specific extractant and process equipment utilized. These processes have been designed for treatment of contaminated soils, but modifications may be possible to allow for treatment of liquid phase wastes as well.

Soil treatment by solvent extraction is currently commercially available. Availability of the concentrated effluent must also be determined to judge overall implementability of these processes. As with all on-site treatment options it is recommended that the appropriate regulatory agency(s) be notified to expedite the approval/permitting process prior to implementation.

Costs are very site/waste specific. A potentially significant portion of the overall cost of treatment is the cost for destruction of the concentrated PCB waste stream. Vendors state that application of this technology is less expensive and more cost effective than incineration, but did not quote figures.

STABILIZATION

Chemical stabilization is a treatment process used to immobilize hazardous waste constituents in a solid matrix through mixing the original waste stream with additives and binders (that is, cement). For treating contaminated soil and sediments, the process generally involves excavation and subsequent conversion of the matrix to a solid mass which immobilizes leachable contaminants. An identical process can be applied to stabilize residual sludge streams with leachable contaminants resulting from various other treatment methods. Stabilized materials are typically sent to permitted landfills for disposal. Stabilization of soils may be applied in situ by adding stabilizing agents via a deep soil mixing auger, although effectiveness may vary. Stabilization reduces the mobility of contaminants, but does not destroy them. Therefore, the risk of exposure to humans or the environment resulting from leaching contaminants at low rates over the long term still exists.

As with all on-site treatment technologies, a determination of the permits required for remediation should be sought from the applicable regulatory agency(s).

Another limitation to stabilization of wastes is the inhibiting effect that organic constituents generally have on the curing process and final quality of the stabilized waste. Several vendors have developed proprietary additives which, when blended with cement, water and the contaminated soils, can overcome the deleterious effect of the organic constituents in the waste.

HAZCON, Inc. has performed a successful field demonstration of immobilizing low level (50 to 80 ppm) PCBs in soil in the presence of up to 25 percent by weight of oil and grease using a cement based process with their proprietary additive Chloranan. Using a 10:10:1 ratio of waste:cement:Chloranan produced a solidified mass in which analysis of leachate could not detect PCBs at a detection limit of 1 ug/L. A volume increase of 120 percent was observed, and cost of $250 per ton for the demonstration was calculated.

International Waste Technologies (IWT) has developed their own proprietary soil stabilization additive, HWT-20. IWT has performed a demonstration of in-situ stabilization of soils contaminated with PCBs in concentrations up to 950 ppm (with most of the samples under 300 ppm) utilizing HWT-20 and a deep soil mixing technique developed by Geo-Con, Inc. Results of this demonstration, conducted as part of EPA RREL's SITE program, indicate that the process may immobilize PCBs. However, due to the low concentrations of PCBs in the treated soils (after dilution resulting from addition of cement and HWT-20), absolute confirmation of this tentative finding could not be proven. Additionally, due to the very limited amount of volatile organics detected in the waste matrix, it is unable to predict if HWT-20 can counteract their effect on the final product. Furthermore, while unconfirmed compressive strength, permeability and wet/dry weathering tests indicate the solidified mass could maintain its integrity over a long period of time, unsatisfactory water loss was observed du the freeze/thaw weathering tests. As compared to HAZCON's process, volume increase (8.5 percent) and cost ($194 per ton) observed in the IWT/Geo-Con process were moderate. However, due to uncertainties in the quality of the final product, further studies should be conducted prior to commercial application of this process.

CONCLUSIONS

When selecting a technology to treat PCB contaminated wastes, it is necessary to take into account the applicability of the technology to the specific waste stream. Availability and reliability of the technology is also of vital importance. As delineated in this paper, there are currently several technologies (for example, incineration, chemical dechlorination and waste water treatment technologies) which have proven their ability to destroy PCBs and for which a significant amount of applications data exists. There are several others which can be considered emerging technologies—they have been proven technically viable, yet limited field applications data reduces the ability to effectively judge the feasibility of utilizing these technologies to treat specific waste streams. These emerging technologies include in-situ vitrification, solvent extraction, surface decontamination, and stabilization. Finally, biodegradation and destruction using quicklime are developmental technologies. A significant amount of study will be required to determine if these technologies will prove effective in destruction of PCBs.

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