

## 4.0 RESULTS

Table 2 gives an overview of the technologies reviewed in this study and the challenges associated with them. This literature review identified five (5) broad treatment categories encompassing nine (9) treatment technologies and three (3) separation technology categories. These are discussed in more detail in the Subsections referenced in Table 2.

### CATEGORY A: DESTRUCTION TECHNOLOGY

#### 4.1 Biological Methods<sup>2</sup>

Background: Microbial bioremediation uses naturally occurring or genetically engineered microbes, to metabolize specific contaminants in soil, sediments or water to less toxic or non-toxic products. This microbial treatment can be anaerobic (without air), aerobic (with air) or sequential anaerobic-aerobic in which an anaerobic step is followed by an aerobic step. For maximum effectiveness, a consortium or co-culture of microorganisms is grown to enhance chemical degradation in a site specific environment. In the case of New Bedford, the consortium would be required to chemically destroy PCBs under expected temperature and moisture conditions and to withstand the high salt and heavy metals content of the sediments.

Studies have shown that stimulation of indigenous microbial populations to dechlorinate PCBs can be achieved by the addition of nutrients.<sup>3,4</sup> Available literature indicates that, at a minimum, surfactants would need to be added to, and mixed with, the sediments to improve bioavailability of the PCBs. The possible addition of carbon supplements, and/or oxygen, in the case of aerobic treatment, may further maximize the effectiveness of the microbial consortium. The addition of surfactants and nutrients are relatively easy to carry out under controlled laboratory or even under pilot scale conditions, but it is much more difficult to evenly distribute nutrients throughout the contaminated material at a large remediation site. High clay content in the sediments can create additional logistical difficulty for the bacteria to access the PCB molecules. The presence of oil and grease can also inhibit dechlorination of PCBs.<sup>4</sup>

##### 4.1.1 Anaerobic Treatment

Description: Anaerobic treatment utilizes a consortium of anaerobic bacteria and requires that strict anaerobic conditions be maintained. Chang *et al*<sup>5</sup> have observed that under anaerobic conditions PCBs in the sewage sludge samples tested were fully dechlorinated within 40 days. These experiments were carried out under strict laboratory controlled conditions. However, Klimm *et al*.<sup>3</sup> has shown that semi anaerobic digestion of PCBs, which can occur under less well controlled conditions can result in formation of dioxins. Thus, anaerobic treatment requires that the site must be tightly capped to exclude air.

##### 4.1.2 Aerobic Treatment

Description: Aerobic treatment utilizes a consortium of aerobic bacteria and requires that aerobic conditions be maintained. Addition of oxygen is required to maintain aerobic conditions, which is often accomplished by air sparging in which air is pumped in to the soil. Volatile organic compounds (VOCs) with foul odors can be released during this process. Vapor recovery in general is required to capture the VOCs and to maintain odor control, which can be difficult in a large site.

**Table 2**  
**Alternative Technologies**

**CATEGORY A: DESTRUCTION TECHNOLOGIES**

Method	Comments	Challenges
<b>Biological Methods (Section 4.1)</b>		
Bioremediation	Treatment Technology used on soil or on PCB product (oil) after use of a separation technology	Some unknowns; metabolite formation; volatile emissions; toxicity of metabolites (potential for dioxin production in some cases); effectiveness in a high salt environment.
<b>Chemical Reductive and Base Catalytic Methods (Section 4.2)</b>		
Base Catalyzed Decomposition	Destruction Technology used on soil or PCBs after use of a separation technology	Some unknowns; potential for byproduct formation; toxicity of byproducts; requires expensive equipment.
Solvated Electron Technology (SET)/Active Metal Treatment	Destruction Technology on PCBs after a separation technology	Safety issues associated with the use of active metals; requires expensive equipment; Technology has failed to receive community acceptance in the past.
<b>Chemical Oxidative Methods (Section 4.3)</b>		
Peroxide, O <sub>3</sub> , Fenton's chemistry, UV-Oxidation etc.	Destruction Technology used on soil or PCBs after a separation technology	Safety issues associated with the use of oxidizing agents; in some applications requires expensive equipment; Partial treatment could lead to toxic byproducts; Byproduct formation a potential problem; Has been shown to have cost and reliability problems; potential for toxic byproduct production.
Supercritical Water Oxidation	Destruction Technology used on soil or PCBs after a separation technology	Byproduct formation a potential problem; requires expensive equipment.
<b>Thermal Methods (Section 4.4)</b>		
Incineration and Combustion	Destruction Technology used on soil or PCBs after a separation technology	Problems with emission; potential for dioxin production. Technology has failed to receive community acceptance in the past.
Thermal Treatment	Destruction Technology	Emissions control major issue. Technology has failed to receive community acceptance in the past.
<b>Other Treatment Technologies (Section 4.5)</b>		
Plasma	Destruction Technology used on soil or PCBs after a separation technology	Emissions control major issue; requires expensive equipment.
High Energy Decomposition Processes	Destruction Technology used on soil or PCBs after a separation technology	Primarily bench scale work, some implementation problems; requires expensive equipment. Some unknowns: byproduct formation.

**CATEGORY B: SEPARATION METHODS**

Method	Comments	Challenges
Solvent Extraction (Section 4.6)	Separation Technology; requires a second step to carry out destruction or off site removal	Uses large amounts of solvents. Emissions control major issue; requires expensive equipment. Requires follow up with a destruction technology or off site disposal. Technology has failed to receive community acceptance in the past.
Thermal Desorption (Section 4.7)	Separation Technology; requires a second step to carry out destruction or off site removal	Emissions control major issue. Requires follow up with a destruction technology or off site disposal. Technology has failed to receive community acceptance in the past.
Adsorption (Section 4.8)	Separation Technology; requires a second step to carry out destruction or off site removal	Requires follow up with a destruction technology or off site disposal. Not applicable to sediments.

#### 4.1.3 Sequential Anaerobic-Aerobic Treatment

Description: Sequential anaerobic-aerobic treatment appears to be the most successful bioremediation strategy explored to date for the remediation of PCB contaminated soils. In the anaerobic step, anaerobic bacteria reductively dechlorinates PCBs to give less chlorinated biphenyls. In a subsequent step aerobic bacteria oxidizes the partially dechlorinated PCB metabolites. The destruction process can be completed by aerobic microbial ring cleavage and mineralization. Sequential anaerobic-aerobic treatment has been used in the remediation of moist sediments in small holding areas, treatment of sludges in tanks or columns or treatment of sediments with added composting material.

Anaerobic Microbial Granules<sup>4</sup> containing self-immobilized anaerobic microorganisms have been used to dechlorinate PCBs to metabolites which were subsequently further degraded by ring cleavage and complete mineralization. Oxygen has been added to assist aerobic digestion using either the addition of OCR, a patented formulation of magnesium peroxide sold by Regenesis,<sup>6</sup> which gives a slow sustained release of molecular oxygen, for up to a year, when in contact with soil moisture, or air sparging with vapor recovery.

Micro-Bac International offers M-1000PCB for the bioremediation of PCBs. In addition, Micro-Bac provides specially formulated nutrients that augment the activity of their product.<sup>7</sup> Other variations of the sequential anaerobic-aerobic treatment, such as composting, have not been commercialized for PCBs at this point but have been tested at lab and pilot scale.

Owner of Treatment Alternative: Microbial based bioremediation in general is in the public domain. However, a number of proprietary variations have been developed. Anaerobic Microbial Granules is a product of the Natarajan Laboratory at the University of Michigan. Micro-Bac International provides bioremediation technology for PCBs utilizing their M-1000PCB product. ORC is a patented product from Regenesis.<sup>6</sup> Caldwell Environmental provides a microbial treatment of PCB contaminated materials.<sup>8</sup> Other vendors offer bioremediation products.

Level of Implementability: Sequential anaerobic-aerobic PCB treatment has been carried out at both the laboratory and pilot scale.

Cost Range of Implementation: \$32-50/m<sup>3</sup> (1996)<sup>9</sup>

#### List of Projects Where It has Been Implemented:

1. Remediation of oil samples from oil refineries in the cities of Tao-Yuan and Kao-Shiung, Taiwan.<sup>5</sup>
2. Remediation of a high (500 mg TEQ/kg dry weight) content sewage sludge from municipal sewage treatment plant in Sachsen-Anhalt, Germany.<sup>3</sup>
3. Bench scale dechlorination of PCBs in Raisin River sediments using Anaerobic Microbial Granules.<sup>4</sup>
4. Micro-Bac International successfully utilized their M-1000H product to treat 5,000 gallons of PCB-contaminated water collected from an excavation site.<sup>7</sup>
5. Tiedje et al<sup>10</sup> have carried out *in-situ* bioremediation of PCBs and are currently developing a field ready technology for sequential anaerobic-aerobic treatment. This work utilizes recombinant organisms.
6. PCB contaminated soils (100 cubic yards) in Michigan have been treated by composting.<sup>11</sup>

Advantages:

1. Has the potential to destroy the PCBs in the CDFs.
2. Does not require expensive hardware.

Disadvantages:

1. Requires two steps.
2. Potential for the generation of toxic metabolites if strict anaerobic conditions are not maintained in the anaerobic step.
3. A high clay content in the sediment can make it difficult for the bacteria to access the PCBs.
4. It can prove very difficult to monitor the degree of dechlorination and degradation over a large treatment volume.
5. Feasibility had not been established in a high salt environment.
6. Time required to carry out remediation.

Data Gaps/Outstanding Issues and Possible Steps for Resolution: The effectiveness of sequential anaerobic-aerobic treatment has not been established in high salt, high heavy metal, sediments as are found in marine environments. The ability to capture and treat the VOCs occurring during the aerobic step at a large site has not been established.

Conclusions and Recommendations: Most studies have been carried out on sewage sludge or samples from river/lake regions and the effect of high salt and high heavy metal concentrations such as those found in the NBH marine environment has not been established. It may be necessary to utilize microorganisms native to marine environments, which are tolerant to the high salt concentrations, to carry out the biodegradation of PCBs. Future work may also utilize constructed strains of microorganisms for maximal PCB degradation. More studies are required to evaluate the performance of the technology on marine sediments. The development of this technology should be followed in subsequent literature reviews.

## **4.2 Chemical Reductive and Base Catalytic Methods**

### **4.2.1 Base-catalyzed Decomposition (BCD)<sup>12,13,14</sup>**

**Background:** The base-catalyzed decomposition (BCD) process was developed by the USEPA's Risk Reduction Engineering Laboratory in conjunction with the Naval Facilities Engineering Services Center (NFESC). BCD is used to remediate soils and sediments contaminated with chlorinated organic compounds, especially PCBs. Contaminated soil is screened, crushed, and mixed with sodium bicarbonate. The mixture is heated to 300-350° C to decompose and volatilize the contaminants. The volatilized contaminants are captured and treated separately. A number of variations of the BCD process have been developed utilizing other bases such as calcium hydroxide. Base-catalyzed Decomposition is a destruction method. However, some volatiles can be produced in the process that may need to be captured and treated separately.

**Commercial Technology:** There appear to be no commercial applications of BCD as developed by the EPA/NFESC, however a number of companies have patented technologies that appear to be a variation on the basic method.

Owner of Treatment Alternative: Base-catalyzed Decomposition (BCD) has been developed and patented by the USEPA. Related patents were issued to Sumitomo Metal Industries Ltd; and Elson K. K.

Level of Implementability: A successful run with 15 tons of PCB contaminated soil was conducted in 1994 at the Guam site.<sup>15</sup>

Cost Range of Implementation: The cost has been estimated to be \$220-550/ton not including the cost of excavation.<sup>15</sup>

List of Projects Where It has Been Implemented:

1. Koppers Superfund site in North Carolina (results were inconclusive due to analytical difficulties encountered).
2. A contaminated site in Guam (Pilot scale).

Advantages:

1. Destruction method which works well on halogenated semi volatile organic compounds.
2. Short treatment time and relatively low operational and maintenance costs.

Disadvantages:

1. Requires expensive equipment.
2. High clay and/or high moisture contents increase costs.
3. By-products may require further treatment.

Data Gaps/Outstanding Issues and Possible Steps for Resolution: The impact of a high salt content in the soil from a marine environment on destruction efficiency is unknown.

Conclusions and Recommendations: Several researchers are continuing to work in the area of base-catalyzed decomposition (BCD) of PCBs. The area of research needs to be monitored in the future as it develops.

#### 4.2.2 Alkaline Polyethylene Glycol (APEG)<sup>12,13,14</sup>

Background: Alkaline polyethylene glycol (APEG) treatment, also known as glycolate dehalogenation, is a process in which alkaline polyethylene glycol is used to dehalogenate halogenated aromatic compounds in a batch reactor to give a glycol ether and/or a hydroxylated compound and an alkali metal salt. The most commonly used APEG system is based upon potassium polyethylene glycol (KPEG). Contaminated soils and the reagent are mixed and heated in a treatment vessel to destroy the PCBs. APEG/KPEG dehalogenation is generally considered a stand-alone technology; however, in some cases it is used in combination with other technologies. The wastewater generated by the process may be treated by chemical oxidation, carbon adsorption, biodegradation, precipitation, or some combination of these methods. A number of variations of APEG process have been developed utilizing other bases such as calcium hydroxide and sodium ethoxide. Alkaline Polyethylene Glycol (APEG) is a destruction method. However, some volatiles can be produced in the process that may need to be captured and treated separately.

Commercial Technology: APEG and KPEG have been implemented by several vendors.

Owner of Treatment Alternative: APEG and KPEG technologies are in the public domain, however a number of proprietary variants have been developed such as the DeChlor/KGME process of Chemical Waste Management, Inc.<sup>16</sup>

Level of Implementability: APEG had been utilized for full-scale remediation projects.

Cost Range of Implementation: The cost has been estimated to be \$200-500/ton not including the cost of excavation.<sup>15</sup>

List of Projects Where It has Been Implemented:

1. Wide Beach Development Superfund Site, Brant, N.Y. in conjunction with thermal desorption.<sup>16</sup>

Advantages:

1. Destruction method which works well on halogenated semi volatile organic compounds.

Disadvantages:

1. Process generates washwater, which will require oxidative treatment prior to discharge.
2. Process generates air emissions, which will need to be captured by condensation or adsorbed on granulated activated carbon (GAC).
3. High clay and/or high moisture contents will increase costs.

Data Gaps/Outstanding Issues and Possible Steps for Resolution: The impact of a high salt content in the soil from a marine environment on destruction efficiency is unknown.

Conclusions and Recommendations: APEG and KPEG are variants on the base catalyzed decomposition of PCBs. APEG and KPEG lead to a reduction in toxicity but are unlikely to meet treatment goals in a cost effective manner at NBH, because of additional separation, drying and off-gas treatments needed.

#### 4.2.3 Solvated Electron Technology (SET)/Active Metal Treatment<sup>17,18</sup>

Background: The Solvated Electron Technology (SET) utilizes solvated electrons to neutralize halogenated compounds such as PCBs. Solutions of solvated electrons are produced when an active metal such as sodium, lithium or calcium is dissolved in anhydrous liquid ammonia. The SET process often strips chlorine from the PCB, exchanging it with hydrogen, without further degrading the hydrocarbon skeleton. Thus, while the PCB is destroyed the total petroleum hydrocarbons (TPH) in the soil typically increase during the SET treatment. The SET process achieves high levels of contaminant destruction. No air emissions are generated if all of the ammonia used in the process is recycled. Other active metal treatments with solvents other than ammonia have been examined at the laboratory scale. These destruction technologies can be utilized after another technology has been utilized to separate the PCB from the sediments. In some cases they can also be utilized to treat soils and sediments directly.

Owner of Treatment Alternative: Several technologies have been reported in the open literature and in patents. However, the technology does not appear to have reached the stage for the treatment of soils and sediments on a large scale.

Level of Implementability: Solvated Electron Technology (SET), an active metal treatment of PCBs, has been widely studied at the bench scale and to a lesser extent at the pilot scale for the destruction of PCBs. However, SET has not yet achieved acceptance for full scale implementation.

Advantages:

1. Technology achieves high destruction efficiency (99.9+ %) for PCBs.

Disadvantages:

1. Ammonia emissions can be a problem.
2. Destruction of the PCBs leads to the formations of petroleum hydrocarbons.
3. Active metals utilized in the process can be difficult to handle.

Data Gaps/Outstanding Issues and Possible Steps for Resolution: Effect of high moisture and salt found in marine sediments is unknown.

Conclusions and Recommendations: When SET is applied to soils and sediments PCBs can be destroyed with high efficiency, however this treatment converts the PCBs to hydrocarbons which results in the soils or sediments increasing in total petroleum hydrocarbon (TPH) contamination, which then needs to be treated with another technology. The formation of TPH is less of a problem when these technologies are used on PCBs that have been separated from the soil or sediments using a technology such as solvent extraction or thermal desorption. More studies are required to evaluate the performance of these technologies on marine sediments. This technology has previously been rejected at the NBH site by the public because of the highly dangerous nature of the reagents used in the process.

### 4.3 Chemical Oxidation Methods<sup>19</sup>

Background: Oxidation chemically converts hazardous contaminants to non-hazardous or less toxic compounds that are more stable, less mobile, and/or inert. The oxidizing agents most commonly used are ozone, hydrogen peroxide (with or without metal salts), hypochlorites, chlorine, and chlorine dioxide. This is a destructive technology that has the potential to be implemented either *in situ* (in this case *in situ* would be applied to soils or sediments that have already been dredged, it does not apply to sediments that are still in place in the harbor etc.) or *ex situ*. Chemical Oxidation is reviewed in categories as follows: 1) Classic Fenton Chemistry, 2) Electrochemical peroxidation (ECP), 3) Ozonation, 4) UV/Hydrogen Peroxide, and 5) Supercritical water oxidation (SCWO). These technologies have generally been applied to contaminants such as PCB after they have been separated from soils by some type of separation technology. Chemical Oxidation Technologies are reviewed below.

#### 4.3.1 Classic Fenton's Chemistry

Summary Description: The Enviro-Sciences system<sup>20</sup> uses hydrogen peroxide and an iron catalyst to destroy contaminants either *in situ* or *ex situ*. Ferrous sulfate and hydrogen peroxide are used to form

free radicals that degrade organic contaminants including PCBs, BTEX, chlorinated solvents and volatile organic compounds (VOC). The process has been applied both *ex situ* and *in situ*.

*Ex Situ*: The target contaminants are VOCs, PCBs, and other organic contaminants. The technology appears to be effective in reducing most of the target molecules in an aqueous stream. Some of the factors to consider in this approach are pH adjustment (pH 3–5 is the optimum range), adding the iron catalyst in an aqueous solution, and adding the peroxide slowly to control the reaction.

*In Situ*: Fenton chemistry has been used to chemically destroy contaminants dissolved in groundwater and sorbed onto soil particles in an aquifer matrix. The sorbed phase must be remediated or it will be a continual source of groundwater contamination. In the context of the New Bedford Harbor site *in situ* would correspond to treating material that had already been placed in a CDF.

Owner of Treatment Technology: Classic Fenton chemistry is in the public domain, however many vendors have developed systems for application to groundwater and aquifer matrix.

Level of Implementability: The classic Fenton's chemistry process was employed *in situ* to destroy 600 pounds of a dense non-aqueous phase liquid (DNAPL) of unknown composition. The period of time involved was 6 days with a 94 % destruction efficiency being achieved.

Cost Range of Implementation: The cost of implementing classic Fenton's chemistry varies widely depending on the site's contamination depth and the amount of contamination.

List of Projects Where It has Been Implemented:

Pilot Scale Demonstration at M-Area of the Savannah River Site by the U.S. Department of Energy and the Westinghouse Savannah River Company. In 1997, the process treated 600 pounds DNAPL in a 6-day operating period, achieving 94 % destruction efficiency.

Advantages:

*Ex Situ*

1. Better control over the reaction, which is very important with an exothermic reaction. The reaction rate increases with increasing temperature and is most pronounced between 5 and 20° C. At temperatures above 40° C hydrogen peroxide decomposes leading to waste of active reagents.
2. Better control over the chemicals added with respect to mixing and minimizing wasted chemicals.
3. The ability to recycle the iron catalyst by redissolving and filtering the iron hydroxide sludge after neutralization.
4. The ability to use the effluent of the reaction vessel to preheat the feed.

*In Situ*

1. No clear advantages at the present time. This technology is not applicable *in situ* (i.e. underwater) at the NBH site. It has not been studied in this context.

Disadvantages:

*Ex Situ:*

1. The ability to use identical units at different sites is limited due to different contaminants and stream flow rates.
2. A sharp and sudden increase in pressure and/or temperature can occur particularly in a closed vessel. Constant monitoring of temperature and pressure are required for safety purposes.

Conclusions and Recommendations: The Classic Fenton's chemistry does not appear to be applicable for the remediation of the New Bedford Site sediments. The technology is restricted by its inability to treat solid samples, which tend to adsorb PCBs and minimize the effects of the technologies. The technologies can be applied as either an *in situ* or as an *ex situ* process on the aqueous media. However, the sediments must first be removed from the harbor. The number of treatment cycles required to clean PCBs-containing sediments is not known and further studies are required in this area. More studies are also required to evaluate the performance of the technology on marine sediments.

#### 4.3.2 Electrochemical Peroxidation

Summary Description: In waters which have pH < 5, steel electrodes and an oscillating electric current are used to generate hydroxyl radicals from hydrogen peroxide. The hydroxyl radicals are then used to destroy PCBs and VOCs in groundwater and slurries. The process is known as Electrochemical Peroxidation Process (ECP) and no iron salts are added. Results from water samples contaminated with PCBs and VOCs ranged from good to impressive. Incremental treatments led to successive destructions of all components, with most eventually going to below detection limits after three treatments. Destruction of PCBs and VOCs from slurries which came from a subsurface storage tank had poor performance relative to the water samples from the same site. Results from the pilot scale (400 times larger scale than lab scale experiments) showed some loss in efficiency (> 96% for lab scale vs 88% for pilot scale). This is probably more of an engineering issue than a chemistry issue, with variables such as electrode size and distance of separation needing to be optimized.<sup>21</sup>

Owner of Treatment Alternative: Electrochemical Peroxidation was developed by researchers at State University of New York at Oswego and currently a patent is pending on this technology. It is not known whether the other technologies mentioned here are owned and/or protected by patents for individual companies.

Level of Implementability: A pilot study (200 L of subsurface storage tank) utilizing ECP technology resulted in the destruction of 88 % of contaminants. The system was not optimized for this size system.

List of Projects Where It has Been Implemented:

Pilot Scale Demonstration at a New York State Superfund Site in Oswego, NY by the State University of New York at Oswego.<sup>22</sup>

Advantages:

1. Short treatment periods, on the order of minutes.
2. No violent or exothermic reactions.
3. Reagent, energy and capital requirements are minimal.
4. Chemical degradation efficiencies are good to excellent.

### Disadvantages:

1. Medium to be treated must be acidic.
2. Scale up appears results in a loss in efficiency.

Conclusions and Recommendations: The electrochemical peroxidation has limited potential for application for the remediation of the New Bedford Site sediments. The technology is restricted by its inability to treat solid samples, which tend to adsorb PCBs and minimize the effects of the technologies. The number of treatment cycles required to clean PCBs-containing sediments is not known and further studies are required in this area. More studies are also required to evaluate the performance of the technology on marine sediments.

#### 4.3.3 Ozonation

Summary Description: This technology uses three methods of water treatment.<sup>23</sup> They are 1) Ozonation followed by filtration through quartz sand, 2) Adsorption on a newly developed powdered sorbent, and 3) Adsorption on a newly developed granular sorbent. The three were compared with respect to cost and speed of contaminant removal. The cheapest/most efficient is in use currently in Ufa, Russia in the removal of polychlorinated dioxins and dibenzofurans. Solutions for these tests were prepared, which contained 6 to 12 organic contaminants (hydrocarbons, aromatic substances and their chlorinated analogs) at concentrations 10 to 300 times the maximum allowable concentration for each pollutant.

Results: Three different test solutions were prepared. The first solution was tap water spiked with polychlorinated dioxins. The second solution was factory wastewater and contained polychlorinated dioxins and dibenzofurans. The third solution contained higher amounts of polychlorinated dioxins. In all cases, ozonation alone was not successful in treating the sample solutions. The powdered sorbents worked fairly well and the granular sorbent worked the best. Ozonation and the powdered sorbent worked equally well on di- through penta-substituted polychlorinated dioxins, effectively removing most of the contaminants. However, they only removed 30 – 60 % of the higher substituted analogs. The granular sorbent removed 90 – 95 % of all polychlorinated dioxins. The same pattern is observed for polychlorinated dibenzofurans. This technology appears to be effective in reducing most of the target molecules in an aqueous stream when the granulated sorbents are used.

Applicability: Some of the factors to consider in this approach are the life of the sorbent, the sorbent regenerability, disposal of the spent sorbent, and the cost of the sorbent. Regenerability is an issue to keep cost down, as well as disposal of the sorbent. Although this technology is mature for water treatment, there is little data on the removal of PCBs from soils and sediments using ozonation.

#### 4.3.4 UV/Hydrogen Peroxide Process

Some researchers have investigated the use of light and hydrogen peroxide to produce similar results to those reported above. Limitations include the fact that the wavelengths needed to make the process efficient are low. Turbid waters and UV absorbers require higher amounts of light, increasing the costs. Although this technology is mature for water treatment, there is no data on the removal of PCBs from soils and sediments using UV/hydrogen peroxide.

#### 4.3.5 Supercritical Water Oxidation (SCWO)<sup>24</sup>

Summary Description: This is a promising thermal treatment method that has been under development since 1980. It involves the oxidation of organics, with air or oxygen, in the presence of a high concentration of water under temperatures and pressures above the critical points of water (374° C and 22 MPa; 705° F and 218 atm). Organic substances are completely soluble/miscible in water under some supercritical conditions while salts are almost insoluble under others. As an oxidation process, the efficiency of SCWO can be measured as the destruction removal efficiency (DRE) of organic feed materials or as the degree of conversion of organic carbon to carbon dioxide (i.e. destruction efficiency, DE). The DEs and DREs of SCWO range from 99.9 % to 99.9999 %. During SCWO heteroatoms such as chlorine are oxidized to acids, which are precipitated out as salts by adding a base to the feed. The SCWO process generally produces aqueous, solid, and gaseous effluents. The aqueous effluent is primarily water with dissolved alkali salts. The gas is primarily CO<sub>2</sub> and the solid is primarily oxides and insoluble salts of metals (if present in the feed).

Ten abstracts were reviewed. The full papers that were requested, were unfortunately review papers or pilot scale studies in either Japanese or Slovak that could not be translated and reviewed within the scope of this project. Although there are various applications of the SCWO process under research and development in the U.S. no significant and mature recent literature information or data in English was found during this review.

To date, there does not appear to be any commercial SCWO units that have been built.

##### Potential advantages:

1. Potentially less expensive than incineration for treating aqueous wastes.
2. The process can be rapidly bottled up by emergency shutdown procedures so as to avoid discharge of contaminated effluents during an upset or off-specification operation.
3. Gaseous effluents can be virtually eliminated through condensation of the carbon dioxide off gas.

##### Potential disadvantages:

1. Mainly applicable to aqueous or pumpable streams.
2. High temperature and pressure operation.

Conclusions and recommendations: SCWO is mainly applicable to aqueous organic wastes and any pumpable streams including slurries of biomass or soil that can be fed into the reactor. Bench scale applicability to New Bedford Harbor (NBH) sediments cannot be determined at this time. It is recommended that ongoing developments in this area be monitored and evaluated in the future. Future reviews should focus on possible vendors in the U.S., applications to PCBs and any potential formation of dioxins.

## 4.4 Thermal Methods

### 4.4.1 Incineration and Combustion<sup>25</sup>

Background: Incineration/combustion is a mature technology for remediation of hazardous waste. Although the technology is mature and efficient, most communities such as New Bedford Harbor (NBH) are vehemently opposed to it. This stems mainly from the potential formation of dioxins/furans during the incineration process. In spite of the vehement opposition at NBH to combustion/incineration, the few technologies briefly described below are provided because they either include stack control and/or result in extremely high removal efficiencies of dioxins/furans. These are the technologies that should be evaluated if incineration should ever be considered in the future.

#### 4.4.1.1 Combustion Technology

Summary Description: In a paper by Tejima *et al*<sup>26</sup> the method for polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) reduction in exhaust gases from municipal solid waste (MSW) incineration plants is discussed and two plants are compared. Both plants use fabric filters for stack gas treatment. The efficiency of fabric filter (FF, glass fiber type) for PCDDs and PCDFs removal was evaluated. It was reported that a fabric filter removes not only particles and acid gases but also heavy metals. The concentration of PCDDs/PCDFs was reduced to 0.1 ng/m<sup>3</sup>-TEQ. Two different plants were chosen because of the differences in the characteristics of their exhaust gases; particularly with decreasing temperature. Slaked lime and additives were injected into the duct upstream to the fabric filter so that the acid gases would be removed. Those additives (minerals obtained by grinding natural ore) were used to protect the filter cloth and minimize the pressure drop. For the adsorbent they used activated carbon powder. To achieve a high efficiency, exhaust gases from an incinerator must be cooled down and be processed by injecting slake lime, additives and activated carbons.

The test results indicated that the lower the processing or raw exhaust gas temperature in the FF step, the higher the removal efficiency of PCDDs/PCDFs. Thus, the FF inlet temperature was suggested to be maintained at 190° C or less. At this temperature or less, the injection of a small amount of activated carbon into the duct allowed removal efficiency of 97-99% of PCDDs/PCDFs to be obtained. Provided the gas temperature is no higher than 190° C and the PCDD/PCDF concentration in the inlet is less than 5 ng/m<sup>3</sup>-TEQ, the injection of activated carbon enabled the concentration at the FF outlet to be maintained at less than 0.1 ng/m<sup>3</sup>-TEQ.

Owner of Treatment Alternative: Takuma Co., LTD, Japan

Level of Implementability: Plant Test

List of Projects Where It Has Been Implemented:

1. Tested at two plants with gas flow rates of 14,000 and 440,000 m<sup>3</sup>/hr.

Advantages:

1. PCDD/PCDF <0.1 ng/m<sup>3</sup> obtained.
2. Heavy metals removal capability (sediments in estuary and harbor are also contaminated with heavy metals i.e., cadmium, copper, lead, and chromium from past industrial plating and textile dyeing discharges).

Disadvantages:

1. Incineration method and despite improvement in overall removal of PCDD/PCDF, it does not completely eliminate formation and emission of PCDD/PCDF.
2. Incineration is not expected to meet significantly different reception from local community.
3. Disposal of waste adsorbents and filters is an environmental impact problem and the pre-treatment of exhaust gases from incinerator is required.

Conclusions and Recommendations: The FF process in its current stage of development is not expected to offer sufficient improvements in incineration to overcome previous concerns with technology within the NBH community.

4.4.1.2 Rotary Kiln Incinerator

Summary Description: Measurements of chlorinated dioxins and furans were previously performed as part of three test programs at EPA's Incineration Research Facility (IRF).<sup>27</sup> All three tests were performed in a rotary kiln incineration system (RKS). Two of the programs were evaluations of the implementability of incineration for PCB contaminated materials from Superfund sites (New Bedford Harbor and Scientific Chemical Process). The IRF RKS consists of a primary combustion chamber, a transition section, and a fired afterburner chamber. After exiting the afterburner, flue gas flows through a quench section followed by a primary air pollution control system (APCS) consisting of a venturi scrubber followed by a packed-column scrubber. Downstream of the primary APCS, a backup secondary APCS, comprised of a demister, an activated-carbon adsorber, and a high-efficiency particulate air (HEPA) filter, was in place.

PCB-contaminated marine sediments from the hot spot of the New Bedford Harbor (NBH) Superfund site in New Bedford, Massachusetts, were incinerated in the first of the three-test programs performed. The hot spot of the harbor contained about 9,000 m<sup>3</sup> of sediments contaminated with PCBs at levels from 4,000 to over 200,000 mg/kg. PCB-contaminated soil from the Scientific Chemical Processing (SCP) Superfund site in Carlstadt, New Jersey, were incinerated in the second test program. The soil excavated for testing at the IRF contained 1,300 mg/kg PCBs. The third test program incinerated a simulated waste representing typical low-level mixed waste at the Department of Energy's Savannah Plant. All tests resulted in effective organic contaminant destruction. Destruction and removal efficiency for PCB ranged from 99.999938 % to greater than 99.99999%. PCDD/PCDF emissions levels measured in all tests reported were substantially less than the EPA guidance level, and were just at or below the European Community (EC) directive.

Advantages:

1. Efficiency >99.9999%

Disadvantages:

1. Incineration method and hence vehement public debate and opposition expected.

Conclusions and Recommendations: Although the test results indicated that PCBs, dioxins, and furans were successfully removed from soils/sediments from the Superfund sites, public/community objection to the use of incineration effectively still makes this technique not appropriate at New Bedford Harbor.

#### 4.4.1.3 Circulating Fluidized Bed Combustion (CFBC)

Summary Description: Circulating fluidized bed combustion (CFBC) is an alternative incineration technology that offers a solution to remediate PCB contaminated soils in an environmentally acceptable way. It provides good mixing and gas-solid contact, and long solid residence times necessary for effective incineration. In addition, its low temperature combustion reduces emissions of other pollutants like NO<sub>x</sub>. Incineration tests were conducted in CANMET's 0.8 MWt CFBC pilot plant in Canada.<sup>28</sup> The combustor was 0.405 m in diameter and 6.6 m high. Normal process required a steady state where combustor temperature was maintained at about 870° C. The combustor temperature was controlled by using up to four water-cooled bayonet tubes. An 1,800 MJ/h startup burner fired with natural gas or propane preheated the combustor to the ignition temperature of the test fuel. The combustor and return leg were charged with sand at the beginning of each test. Sufficient air was supplied to mildly fluidize the solids in the combustor. After contaminated soils were fed into the combustion chamber, a circulating process occurred by using a forced draft fan. The exhaust gas exiting the cyclone was cooled to about 190° C and then passed to the baghouse and fine ash particles were collected. The flue gas from the baghouse was then fed into a dry scrubber using hydrated lime where acid compounds were removed. The natural gas ignition burner was fired at a low rate and the refractory and solids in the combustor were heated gradually by increasing the firing rate. When the temperature reached about 600° C, No. 2 fuel oil was fed at a low flow rate. The sand feed was started and gradually increased to about 300 kg/h. The combustor was maintained at about 871° C.

Results showed that the destruction and removal efficiency (DRE) of dichlorobenzene (DBC, the test surrogate material) ranged from 99.99994% to 99.99999%. With a CaCO<sub>3</sub>:HCl ratio of 3:1 and combustion efficiency of 99.92%, the CO levels dropped significantly to about 21 ppm, whereas NO<sub>x</sub> emission was reduced to 29-38 ppm and the SO<sub>2</sub> was 43 ppm. It was shown that proper operation include the use of appropriate liquid waste feed pumps and interlock system to stop waste incineration occurring under undesirable process conditions. CFBC will not require supplemental limestone for CO emission control if the waste contains enough Ca components such as wastes treated in the Quebec project.

##### Advantages:

1. High efficiency for removal of high concentrations of PCB surrogates.
2. Low CO, NO<sub>x</sub> and SO<sub>x</sub> emission with good combustion efficiency.
3. Good mixing, gas-solid contact, long solid residence time.
4. low temperature combustion, and high heat transfer rate achievable.

##### Disadvantages:

1. Incineration method and hence anticipated public debate and objection/opposition; Lower treatment capacity (~300 kg/h)

Conclusions and Recommendations: When 1,3 dichlorobenzene (DCB) was used as a PCB surrogate, a DRE in excess of 99.9999 % was achieved and dioxin/furan emissions were lower than the Quebec regulatory limit of 1 ng/g when a dry scrubbing system was utilized. The unit was not tested on PCBs and the emission of dioxin/furans, although within regulatory limits with a scrubbing system, makes that process inappropriate at NBH based upon the previous community concerns/objections.

#### 4.4.2 Thermal Treatment/Destruction<sup>29</sup>

**Background:** This is an ex-situ process that thermally destroys organic contaminants. It is a mature technology that employs a variety of combustion chambers but in waste-site remediation rotary kilns are most common. Many of the thermal-based innovations have been developed for purposes other than destruction. Those classified as removal are referred to as desorption processes (see Section 4.7) and those classified as immobilization are referred to as vitrification processes. While some destruction of organic contaminants does occur with such systems, destruction is not their primary goal except in thermal treatment/destruction processes. Thermal destruction technologies judged to be sufficiently developed include catalytic oxidation, rotary cascading bed incineration system, and the ECO LOGIC process.

The challenge in the thermal treatment area is to systematically evaluate the various methods in order to select the right technically and economically viable process. Actual field testing and evaluation of the selected thermal treatment method would then need to be undertaken on the New Bedford Harbor soil matrix. The evaluation has to consider the waste matrix, soil carry-over, volatile metal emissions, materials handling and the potential formation of dioxins. The relevant commercial operations employing thermal destruction technologies are summarized below.

##### 4.4.2.1 Flameless Thermal Oxidation (FTO)

**Summary Description:** Thermatrix's flameless thermal oxidation (FTO)<sup>30</sup> process is a patented technology that carries out oxidation of organic vapors without flame. The core design is the flameless thermal oxidizer where a high temperature (lower than flame limit of fuel) reaction zone provides a bed for oxidizing hazardous compounds into H<sub>2</sub>O, CO<sub>2</sub> and acid gases. The treatment processes include pre-treatment, oxidation, wet scrub and filtration. In FTO process, organic compounds are oxidized in an inert ceramic bed, without a flame or catalyst, into carbon dioxide and water vapor. Although the process uses a fixed bed, it is non-catalytic and problems associated with deactivation or poisoning of catalysts are avoided. A pre-treatment step is required where contaminants are vaporized and mixed with air before feeding into the oxidizer so that gases containing organic vapors can be processed in the oxidizer unit and in further treatment steps. Very low concentrations of thermal NO<sub>x</sub> are produced (i.e., typically less than 2 ppmv). During the startup of the unit, the matrix or bed is pre-heated until it reaches a minimum temperature of approximately 760° C, which is necessary for reliable oxidation of natural gas. Once the bed is preheated, a fuel-air mixture is introduced into the reactor and a stable reaction zone is established. When the temperature profile in the bed is satisfactory for complete oxidation, the fume stream is introduced.

A commercial size 5,100 m<sup>3</sup>/hr (3,000 scfm) oxidizer was constructed and tested at the Thermatrix fabrication facility in Knoxville, TN. The unit was operated for over 1,000 hours. Performance tests with gas treatment capacity of from 850 m<sup>3</sup>/hr to 5,575 m<sup>3</sup>/hr and on halogenated and non-halogenated organic liquids demonstrated >99.99% destruction and removal efficiencies, CO concentrations of less than 10 ppmv, and NO<sub>x</sub> concentrations of less than 10 ppmv. The acid gas removal system achieved a removal efficiency of 99.99%. Coupled with a steam reformer on the front end, the FTO technology was extended into the thermal treatment of hazardous liquids, sludges, solids, and mixed wastes with a destruction and removal efficiency of 99.99% guarantee.

Owner of Treatment Alternative: Thermatrix Inc.

Level of Implementability: Commercial Demonstration

Advantages:

1. Classified by worldwide regulatory agencies as a non-incineration technology for treating hazardous and toxic organic compounds.
2. Non flame-base technology.
3. Cost effective; high performance.
4. May be used for liquid, solid, sludge; Low combustibles (hydrocarbons), CO, and NOx emissions.
5. Commercialized with over 70 applications in North America, Europe and Asia.
6. Lower treatment temperature with high efficiency.
7. Coupling with steam reforming extends application into the treatment of hazardous sludges, solids and mixed waste.

Disadvantages:

1. Mainly demonstrated for the treatment of soils contaminated with low to middle distilled organic compounds; the paper of DeCicco<sup>30</sup> however mentions successful use of this technology to treat gas phase contaminants including benzene, toluene, acetone, PCBs, carbon tetrachloride, phosgene, methylene chloride, dimethyl sulfide, freon and formaldehyde.

Conclusions and Recommendations: Flameless thermal oxidation is a non-incineration technology with wide commercial application. While it has the potential for the treatment of PCBs, extensive bench or pilot testing and evaluation would be needed as part of any consideration for its use at NBH. These studies will have to address issues relating to applicability to PCBs and sludges/solids (with a steam reformer on the front end), emissions (especially of dioxins and furans) and cost.

#### 4.4.2.2 In-situ Remediation by Thermal Blanket

Summary Description: The thermal blanket is a cost-effective in-situ technology for remediation of soils with surficial organic contamination.<sup>31</sup> Pilot thermal blanket systems include heater, thermal oxidizer, and HCl scrubber containing  $\beta$ -sodium aluminate following a granular activated carbon (GAC) drum. The ground is heated using a 3.1 m x 3.1 m thermal blanket consisting of a 1-cm-thick steel furnace belt containing 39 resistive tubular heaters (chromalox) spaced at 8-cm intervals. Power is supplied by a 480 V/3Ø 120 kVA power supply (Cooperheat). Thermal insulation measuring 3.7 m x 3.7 m is placed on top of the heater. A 9.1 m x 9.1 m impermeable sheet of fiberglass reinforced silicon rubber is placed on top of the insulation. The sheet serves to trap effluent gases emanating from the heated soil. The heaters are operated at 800-900° C, and heat diffuses down into the soil, heating and mobilizing contaminants. The blower draws air and vaporized contaminants through the system. The contaminants are oxidized in the thermal oxidizer and are further trapped by GAC heated slightly above 100° C so produced water vapor will not condense.

The post heating soil sampling of contaminated areas showed PCBs thoroughly removed at all depth and no evident migration of PCBs was observed after sampling around the thermal blanket. It was reported that downward migration of PCBs was not significant. In the heated region, all the soil hydrocarbons were oxidized and removed to a depth of 7.5 cm. All but one of 18 test runs achieved post-heating PCB concentrations well below the cleanup target of 2 mg/kg. Initial PCB concentration on some of the more contaminated areas averaged 700 mg/kg from 0 to 7.5 cm deep and 100 mg/kg from 7.5 to 15 cm, with maximum concentrations as high as 2,000 mg/kg at the surface. PCB concentrations were reduced from up to 2,000 ppm to less than 2 ppm in 24 h of heating. The full-scale system based on remediating a total area of approximately 6 ha (15 acres) would remediate 297 m<sup>2</sup> of soil/day and would require a total power input of 1.8 MW for a 20-blanket assembly. Agreement between model and measurement was good. Water content and water table level is of primary concern when using thermal blanket remediation due to the major power consumption of water evaporation and the limit of heater temperature. A properly sized flameless thermal oxidizer used with the thermal blanket commercial system guarantees 99.99% destruction and removal efficiency. The pilot test clearly showed that PCBs could be removed to less than 2 mg/kg.

Owners of Treatment Alternative: GE and Shell<sup>31</sup>

Level of Implementability: Pilot Test by GE Corporate Research and Development<sup>31</sup>

Cost Range of Implementation: Commercial soil treatment at a large (> 6 ha) site to a depth of 15 cm is estimated to cost from approximately \$45 to \$60/m<sup>2</sup> (\$150-200/t of soil), excluding profit and royalties.

Advantages:

1. Commercialized technique that is effective for PCB contaminated soil treatment.
2. *In-situ* cost effective method.
3. High efficiency removal from 2,000 ppm to 2 ppm.
4. Offers complete on-site destruction of contaminants.
5. Eliminates the need for transporting waste.

Disadvantages:

1. Needs thermal oxidizer for destroying emission from blanket.
2. High power requirement (1.8 MW).
3. The ability of the heaters in the blanket to deliver energy to the soil is limited by the maximum allowed heater temperature.
4. Suitable only for shallow depth soil treatment and preferably drier soil.

Conclusions and Recommendations: The technology, as reported, appears attractive especially when operated with a flameless thermal oxidizer to remove organic emissions from the blanket. However, extensive testing and evaluation would need to be undertaken before serious consideration can be given to its application at NBH, given the disadvantages described above.

#### 4.4.2.3 Thermochemical Technique (Reactive Exothermic Liquid-Inorganic Solid Hybrid Process)

Summary Description: The paper of Bhat<sup>32</sup> discusses the efficacy of a patented thermochemical technique of PCB destruction, the Reactive Exothermic Liquid-Inorganic Solid Hybrid (RELISH) process. The tests have shown that PCBs are not volatilized but destroyed and hazardous heavy metals are converted to stable, non-leaching, non-hazardous materials. In the RELISH process, exothermic or self-generated reaction heat that gives rise to temperatures up to 750° F is utilized for breaking down PCBs. According to Bhat<sup>32</sup>, the process does not produce harmful derivatives of PCBs such as furans or dioxins, nor does it change PCBs to short-chained or substituted chlorinated compounds or phenols. The process reagents of water and alkasol (a solid mixture comprising at least 70 wt % quicklime, 0.1-10 wt % products of reaction between an aliphatic acids, 0.1-10 wt % NaOH and or sodium alkoxide, and 0-25 wt % sulfonated alkali phosphates and sulfites) need to be prepared in size of -60 mesh to -325 mesh. The thermochemical treatment process includes: 1) PCB contaminated waste that is thoroughly mixed with alkasol; 2) the ratio of alkasol and water is controlled above 3.2:1 in order to achieve PCB destruction efficiency greater than 87.9%; 3) wet scrubbing and activated carbon adsorption systems were employed to control emissions; and 4) the pH of processed sludge was adjusted to an accepted level by using acid reagents. The final products are clay, limestone and sand.

Pilot tests indicated that the higher the alkasol-to-sludge moisture ratios, the better the efficiency of PCB destruction. Ratios above 3.9:1 are suggested for efficiency of greater than 97.7%. Analysis of phenolics indicated that the degradation products of the process were not simple or substituted phenol compounds. Test results also indicated that VOCs, dibenzofurans and dioxins analyzed were below detection limits. In this process the organophilic component of the reagents plays the distinctive role of absorbing and trapping PCBs before exothermic reaction starts, thus precluding the possibility of PCB volatilization. PCB contaminated waste such as soil, sludge, or sediment is thoroughly mixed with alkasol on-site in a mixing unit such as a muller, a continuous mixing screw, or a pugmill fitted with an air scrubbing system consisting of a high-efficiency particulate air (HEPA) organic filter, a wet scrubbing system, an activated carbon adsorption system and a blower. An exothermic reaction initiates within a few minutes of mixing, resulting in a sudden volume expansion of reaction product. The product temperature begins to rise and optimally within 15 min it reaches 400° F and within 90 min it climbs to 600° F. Then the temperatures begin to drop over the next 4-6 h until the ambient temperature is reached. The thermal milling that occurs during exothermic reaction converts the reaction product into an extremely fine, off-white, water-impermeable powder. The final powder product, which is essentially clay, limestone and sand, can be used as a cement additive or as a roadbed material; it can also be pelletized and/or used for backfill. The sludge PCB concentrations ranged from 35 to 3,000 ppm. PCB destruction in the sludge ranged from 83.6 % to greater than 99.9%. There was no apparent relationship between the level of PCB destruction and the amount of PCB materials in the sludge.

Level of Implementability: On-site tests on approximately 300 lb foundry wastewater sludge pilot unit (20 lb/batch) were conducted.

##### Advantages:

1. Organophilic component of the reagents coats the quicklime and plays the distinctive role of absorbing and trapping PCBs before exothermic reaction starts that breaks down the trapped PCB.
2. Self-generated reaction heat for the waste treatment process.

Disadvantages:

1. No pilot study on soil or sediment was undertaken, all tests were conducted on sludge.
2. Massive reagents were induced into the system.
3. Requires high efficiency particulate air (HEPA) filter and a scrubbing/adsorption system to control emissions.

Conclusions and Recommendations: The claims summarized above are reported in a single paper by the inventor in the open literature. Independent evaluation of the technology needs to be undertaken and/or future developments on the technology should be monitored and reviewed.

## **4.5 Other Treatment Technologies**

### **4.5.1 Plasma Arc Technology<sup>33</sup>**

Background: Plasma heating systems were developed by NASA in the mid 1990s for use in testing spacecraft heat shields. Plasma torches convert electrical energy into thermal energy, generating plasma that is a highly ionized gas. The typical plasma torch generates a “flame” with temperatures ranging from 4,000 to 12,000° C. Due to the extremely high operating temperatures, a plasma heated furnace breaks down most complex organic waste into simple gases. Both *in situ* and *ex situ* plasma remediation technologies have been demonstrated at a pilot scale.<sup>34</sup> In *ex situ* plasma remediation the soil or sediment is placed in a large furnace with a plasma torch and the vitrified soil can be periodically drained off. An off-gas system is needed to treat gases generated during the processes. In pilot studies of *in situ* plasma remediation a 8-10 inch hole is bored in to the ground and the plasma torch is lowered into the hole and ignited. The torch is then slowly raised to leave a vitrified column leaving the material between the columns untreated. The off-gases need to be captured and treated. As the plasma torch requires a constant gas flow to maintain the plasma, the gas treatment system needs to be large enough to treat both the plasma gas and any VOC or acid gases generated during processing.

Level of Implementability: Bench and small pilot scale studies have been carried out.

Advantages:

1. Destruction efficiencies up to 99.9999 % have been reported for organic and chlorinated organic compounds.
2. Less off gases generated than from conventional incineration.

Disadvantages:

1. Has not been demonstrated on a large scale.
2. High moisture content soil would require drying prior to treatment.
3. Soil would be in a vitrified form after treatment.
4. Off-gasses would be produced that would need to be captured and treated.

Data Gaps/Outstanding Issues and Possible Steps for Resolution: Effects of high water content and high chloride content from a marine environment are unknown.

Conclusions and Recommendations: At present, the process has been tested at pilot scale with some promise in low moisture soils. Pilot test would need to be carried out on marine sediments. Gases capturing and treatment systems are not currently sufficiently advanced for *in situ* field level application.

#### 4.5.2 High Energy Decomposition Processes<sup>35</sup>

##### 4.5.2.1 Radiolysis-Induced Decomposition of PCBs

Background: The degradation of PCBs by radiolysis is commonly induced using either direct e<sup>-</sup>-beam injection of electrons from an accelerator, or using γ-radiation from a source such as spent nuclear fuel as an indirect electron source. This is a treatment technology and needs to be used in conjunction with a separation technology.

No known commercial operations employ radiolysis for the destruction of PCBs, although a patent for the destruction of PCBs in transformer oils using this technology has been issued.<sup>36</sup> Simulations using spiked soil samples, involving solubilization of the PCBs, followed by flotation of the PCB-containing solvent, followed by radiolysis, have been carried out, and show effective and complete decomposition of the PCBs.

Summary Description: An extensive body of work by Sawai<sup>37</sup> and others in the 1970s showed that the radiolytic decomposition of PCBs proceeds via a stepwise dechlorination process that involves a solvated electron in the sequential removal of chlorine atoms from the PCBs, ultimately resulting in the formation of inorganic chlorine compounds and biphenyl. The process can be used for the dechlorination of any of a variety of organochlorine compounds. A 1999 review<sup>38</sup> gives a good description of the process, its possible applications and shortcomings.

Radiolytic decomposition of PCBs has been shown to be effective for the decomposition of PCBs in transformer oils,<sup>39</sup> in organic solvents,<sup>40</sup> and even in aqueous solution and suspensions, destroying the PCBs to the point that the solutions are no longer considered PCB-contaminated (less than 50 ppb PCB concentrations).<sup>41</sup> The process, however, is much less efficient (a factor of 40) for *in situ* decomposition of PCBs in soils, evidently because the soil does not provide the necessary solution chemistry or act as an appropriate medium for the electron scavenging processes that have been shown to be important in the decomposition mechanism.<sup>38</sup> Simulations using spiked soil samples, involving solubilization of the PCBs, followed by flotation of the PCB-containing solvent, followed by radiolysis, have been carried out, and show effective and complete decomposition of the PCBs.<sup>38</sup>

Owner of Treatment Alternative: Lockheed Martin Idaho Technologies Company, Idaho Falls, ID, has a patent for the removal of PCBs in transformer oil using radiolysis.

Level of Implementability: It is suggested in the literature that the technology can be applied effectively in a cost-effective manner (less than one-third the cost of incineration) but no firm cost estimates are available.<sup>38</sup>

#### Advantages:

1. The process is a reductive rather than oxidative method for the decomposition of PCBs.
2. The process produces inorganic chlorine and biphenyl as byproducts of the decomposition, both relatively benign.

3. The system is transportable.
4. Waste reduction can be accomplished on sites where combustion is not permissible.

Disadvantages:

1. Requires the use of a portable accelerator or a source of  $\gamma$ -rays such as spent nuclear fuel.
2. Cannot be used as an *in situ* technique. The PCBs must first be extracted from the soil into an appropriate solvent.
3. The technology has not yet been shown to be applicable to a large-scale application.

Conclusions and Recommendations: The technique of radiolytic decomposition of PCBs has not been applied to a large-scale effort. Significant scale-up work is necessary to demonstrate its effectiveness and whether or not it is possible to be used for such a large application. Serious logistical issues with necessary reagents exist.

#### 4.5.2.2 *In Situ* Decomposition of PCBs in Soils Using Microwave Energy

Background: The degradation of PCBs in soil using microwave energy can be carried out *in situ*.<sup>42</sup> The soil is mixed with either graphite fibers or powder, and irradiated with microwave energy. Alternatively, graphite rods (e.g., pencil leads) can be used to conduct the microwave energy into the soil.

The PCBs are decomposed by being heated to high temperature in the neighborhood of the carbon fibers or graphite rods, which are themselves heated by direct interaction with the microwave energy, and the fragments apparently permanently bind to soil species such as clay. Some provision should be made for volatilizing a small fraction of the polychlorinated species, but the yield of these species is typically small.<sup>42</sup> Simulations using spiked soil samples, have been carried out, and show effective and complete decomposition of the PCBs. This is an *in situ* technology and does not need to be used with another separation or treatment technology.

Summary Description: While this technology is promising, in that it uses radiation that is non-ionizing, it suffers from the limitation that it can only be used effectively in dry soils. Water in the soil absorbs the microwave energy and converts it to heat of vaporization. So, if this technique were to be used on wet soils, energy input during the initial stages would go into evaporation of water, and only after the water had been evaporated would decomposition occur. If this technology is to be applied to the New Bedford Harbor problem, it would require first drying the soils. This requirement makes the technology impractical as a truly *in situ* remediation technology, but nonetheless offers treatment without the use of chemical solvents. The technology can be thought of as a limited vitrification of the soil using microwaves.

Owner of Treatment Alternative: As far as can be determined, no patent exists on this technology.

Advantages:

1. The technology is an *in situ* technique and does not need to be used with another separation or treatment technology.
2. The process uses relatively low-technology devices for implementation.
3. The process uses no chemical solvents.
4. The system is transportable.

Disadvantages:

1. The process is not effective in wet soils.
2. The technology has not been demonstrated on a large scale.

Data Gaps/Outstanding Issues and Possible Steps for Resolution: Data on the performance of the technology in commercial scale applications is not known. The capability of the technology to clean up high concentration samples needs to be evaluated.

Conclusions and Recommendations: The decomposition of PCBs using microwave energy is promising and has potential for application to New Bedford Harbor sediments, but the technology is still in the research stage and has not been applied to any large-scale efforts.

#### 4.5.2.3 High Energy Corona Destruction of Volatile Organic Compounds

A significant effort has been funded by the US DOE for the development of this and other technologies for the destruction of volatile organic compounds.<sup>43</sup> It is only applicable for the destruction of gas-phase species, and thus could only be used as a treatment step after volatilization of the PCBs in the New Bedford Harbor soils.

Summary Description: This technique is not an in situ technique, and can only be used to destroy gases that have been purged from soils, for example. It is, however, very effective for this use, and has been shown to destroy 99.9% of trichloroethylene (TCE), with one reactor processing up to five cubic feet per minute (5 scfm) of soil off-gas. Several reactors can be run in parallel to treat more off-gas (up to 105 scfm), and the energy requirements are modest, using up to about 50 mA of current at 30 kV (=1.5 kW) per reactor.

Owner of Patent: Pacific Northwest Laboratories has applied for a patent on the technology.

Level of Implementability: It is suggested that the technology is easy to implement, and the whole package, including reactor and analytical support equipment, can be housed in a trailer to make the process easy to transport from site to site.

Cost Range of Implementation: It is estimated that the initial cost for the 105 scfm system would be \$50,000.

Advantages:

1. The process has been shown to be 99.9% effective in destroying trichloroethylene and 90-95% effective in destroying tetrachloroethylene.
2. The process is available in a field prototype system.
3. The system is mobile.

### Disadvantages:

1. Application to higher molecular weight polychlorinated organic species has not been demonstrated, and probably will not be quite as effective.
2. Can only be used to treat gas-phase species. The PCBs must first be volatilized from the soil.

Data Gaps/Outstanding Issues and Possible Steps for Resolution: The technique may have limited applicability to the destruction of PCBs found in the New Bedford Harbor sediments, but may be applicable to clean up of volatile organic carbon in off-gases from other treatment processes, should they be chosen for these sediments.

Conclusions and Recommendations: The technology is potentially very useful for VOC cleanup of the sediments, but probably of limited applicability for the removal or destruction of the PCBs.

## **CATEGORY B: SEPARATION TECHNOLOGY**

### **4.6 Solvent Extraction<sup>44</sup>**

Background: Solvent extraction is a common form of chemical extraction using organic solvent as the extractant. It is commonly used in combination with other technologies, such as solidification/stabilization, incineration, or soil washing, depending upon site-specific conditions. Solvent extraction also can be used, as a stand-alone technology in some instances. Organically bound metals can be extracted along with the target organic contaminants, thereby creating residuals with special handling requirements. Traces of solvent may remain within the treated soil matrix, so the toxicity of the solvent is an important consideration. The treated media are usually returned to the site after having met Best Demonstrated Available Technology (BDAT) and other standards. Commercial operations employing the Solvent Extraction Technology are reviewed below.

#### **4.6.1 The Ionics Basic Extractive Sludge Treatment (BEST) Process<sup>45</sup>**

Summary Description: The BEST process uses organic solvents, usually triethylamine (TEA), to extract organic contaminants from soil, sludge and sediments. Triethylamine is preferred because it has a high vapor pressure and because it exhibits inverse miscibility with respect to water. At temperatures above 55° C, TEA is miscible with water, and immiscible below this temperature. The process is nondestructive, functioning as a separation technology, segregating materials into three fractions: oil, water and solids. The BEST system is a batch process consisting of four basic operations: extraction, solvent recovery, solids drying, and water stripping. Extraction is carried out in two separate vessels, a premix tank and an extractor/dryer. Cold extractions are carried out on high water content materials in a premix tank. The solids to be treated are batch-fed to the tank and chilled. TEA is then added to the tank with mechanical agitation for five minutes. Both water and organic contaminants are removed in this process. The solvent is decanted and pumped to a solvent recovery system and the solid is moved to the Extractor Dryer. The solid is extracted at 77° C in the agitated Extractor/Dryer with additional TEA. No water is removed in this phase. The solvent is recovered from the solvent/oil/water mixture in the solvent recovery evaporator. The solvent is condensed and stored in a solvent storage tank. The solid is dried under agitation in the Extractor/Dryer by steam at 77° C, after which it is discharged through a port at the bottom of the vessel. The number of extraction cycles necessary to decrease the concentration of a specific organic contaminant to a given clean up level varies and is determined by treatability test.

Owner of Treatment Alternative: Ionics Resource Conservation Company (RCC)

Level of Implementability: The process was employed in pilot scale operation to treat river sediments in ten 68 kg batches at RCC. The system is transportable. Full scale operation is mentioned but not referenced.

Cost Range of Implementation: Cost of implementation was \$617/ton. This cost includes the BEST process coupled with the CRTI post extraction, PCB dechlorination process.

List of Projects Where It has Been Implemented:

1. Pilot Scale Demonstration at Resources Conservation Company. The process treated ten 68 Kg batches of PCB and other semivolatiles sediments. PCB concentrations in the sediments ranged from 10 to 427 mg/Kg. Removal efficiency was greater than 99%.
2. Pilot Scale Demonstration on New Bedford Harbor Hot Spot Sediments. The process treated high concentration PCBs containing sediments (average 5,667 mg/Kg) to less than 50 ppm in five to six extraction cycles. With additional extraction cycles (eight to nine), the process appears capable of treating the sediments to concentrations below 10 ppm.

Advantages:

1. The BEST process is effective in removing PCBs or other semivolatiles organic contaminants from high moisture content containing sediments with 99.2% efficiency. Removal efficiency is dependent on sample type.
2. The process reduces toxicity and mobility with removal of soil contaminants.
3. The process is effective in volume reduction.
4. The system is transportable.
5. Waste reduction can be accomplished on-sites where combustion is not permissible.
6. The process is a non-thermal process and does not produce undesirable organic by-products, or an extensive off gas system.

Disadvantages:

1. The process does not eliminate the need to dispose of PCBs, but only concentrates it.
2. Lengthy implementation time for fullscale operation (3 years).
3. The technology suffers from poor community acceptance due to the hazardous nature of the solvent.

Data Gaps/Outstanding Issues and Possible Steps for Resolution: Data on the performance of the technology in commercial scale applications is not known. The fate of residual TEA in the soil needs to be studied. The capability of the technology to clean up high concentration samples needs to be evaluated.

Conclusions and Recommendations: The BEST process has potential for application for remediation of the New Bedford Harbor sediments since the process is effective on high moisture content samples. The technology is an *ex-situ* process, and therefore requires that sediments be first removed from the harbor.

The number of extraction cycles required to clean PCBs-containing samples to defined target levels is not known and further studies are required in this area. The technology shows great potential to remove PCBs from NBH sediment samples but its implementation is limited by poor community acceptance due to the hazardous nature of the solvent. There appears to be no advancement in the technology or its community acceptance since its pilot scale demonstration at the NBH site.

#### 4.6.2 Terra Kleen Solvent Extraction Technology

Summary Description: The Terra Kleen System is a batch process that operates at ambient temperatures and removes semi-volatile organic compounds (SVOCs) from soils using proprietary solvents. The system was largely developed to remove polychlorinated biphenyls (PCBs). After soils are washed with solvent, the contaminated solvent passes through a recovery unit, where contaminants are separated from the solvent and concentrated, reducing the contaminant volume for disposal. The reclaimed solvent is then reused in the process. The PCB-contaminated purification media is transported off site for incineration at a permitted facility.<sup>46</sup>

The system consists of multiple extraction tanks, a sedimentation tank, a microfiltration unit, a solvent purification station, a clean solvent storage tank, a vacuum extraction system and a pneumatic and spark-proof pumping system to circulate the flammable extraction solvent. Excavated soil is loaded into the extraction tanks and clean solvent from the solvent storage tank is pumped into the extraction vessels. Soil and solvent are held in the tank, allowing organic contaminants to dissolve in the solvent, separating them from the soil. The retention time in the extraction tanks is based on the site characteristics and the results of treatability tests. Solvent washing continues until a site-specific soil cleanup level is attained.

The PCB-laden solvent is then transferred from the extraction tanks to the sedimentation tank. Suspended solids are settled and the solvent is regenerated. Residual solvent in the soil is removed using vacuum extraction and biological treatment.

Owner of Treatment Alternative: The Terra Kleen Solvent Extraction Process is owned by Terra Response Group, Inc.

Level of Implementability: The process was employed in commercial operation to treat 250 tons of soil using 19 extraction tanks (each 16- to 17-yd<sup>3</sup> capacity). The system is transportable and can be configured to treat both small and large quantities of soil.

Cost Range of Implementation: Cost of implementation range from \$165 to \$600 per ton of soil and is site specific.

#### List of Projects Where It has Been Implemented:

1. Pilot Scale Demonstration at Naval Air Station, North Island (NASNI) in June 1994 under Naval Environmental Leadership Program.<sup>46</sup> The process treated 5 tons of PCB contaminated soil with concentration ranging from 17 to 640 mg/Kg. Removal efficiency ranged from 95 % to 99% and treated soil was below targeted TSCA incineration equivalency performance guidance level of 2 mg/Kg of PCBs in the soil.
2. Commercial Operation at Cape Canaveral Air Station, Florida.<sup>46</sup> The Terra Kleen process was used to process 10,000 tons of PCB and TCE contaminated soil at this site. PCBs were reduced from levels as high as 500 mg/Kg to less than 1 mg/Kg. Processing cost was reported to be \$120/ton.

3. Fernald Uranium Feed Plant, Ohio: Terra Kleen processed three types of mixed waste at the Fernald, Ohio DOE site; soils, sludges, and debris. Complete performance report was not accessible but significant reduction in PCBs removal rates, in some cases, bringing concentration to below method detection limit was reported.
4. Sparrevohn Long Range Radar System, Sparrevohn Alaska: The solvent extraction system was reported to effectively treat 288 cubic yards of PCB contaminated soil.

Advantages:

1. The process can achieve TSCA incineration equivalency limits on selected sample types.
2. The process reduces toxicity and mobility with removal of soil contaminants.
3. The process is effective in volume reduction.
4. The system is transportable.
5. Waste reduction can be accomplished on sites where combustion is not permissible.

Disadvantages:

1. Contaminated soils with greater than 15 % clays or fines are difficult to treat due to strongly sorbed contaminants and difficult to penetrate soil aggregates.
2. High moisture content soil (>20 %) requires drying prior to treatment. The drying process introduces significant cost for energy and for volatile organic compounds (VOCs) emission control and treatment if present. Solvent distillation to reduce water accumulation in the solvent is also costly.
3. The system is designed to operate at ambient temperatures above freezing. Cold solvent reduces solvent mobility.
4. The process does not eliminate the need to dispose of PCBs, but only concentrates it.

Data Gaps/Outstanding Issues and Possible Steps for Resolution: Community acceptance of this technology is unknown, however based upon the lack of acceptance of similar technologies, the community is unlikely to accept this technology.

Conclusions and Recommendations: The Terra Kleen Technology has limited potential for application for remediation of the New Bedford Site sediments. The technology is restricted by its inability to treat samples of high moisture content, which will be the case for NBH sediments. The technology is an *ex-situ* process, and therefore requires that sediments be first removed from the harbor. The number of extraction cycles required to clean PCBs-containing samples defined target levels is not known and further studies are required in this area. More studies are also required to evaluate the performance of the technology on marine sediments. Due to the low tolerance of this process for high percentage moisture in sediments, it is anticipated to be less effective than the BEST process reviewed above. Like the BEST process, the implementation of the technology is expected to be limited by poor community acceptance due to the hazardous nature of the extraction solvent.

#### **4.7 Thermal Desorption<sup>47</sup>**

Background: Thermal desorption is an ex-situ physical separation process to separate contaminants (organics, mercury, cyanide, etc.) from a waste matrix which is typically made of soils, sludges, sediments or filter cakes. The contaminants are typically volatilized in a thermal desorber and swept into

an off gas. The off gas is then treated in an emission control system either by collection of the contaminant for subsequent recovery or off-site treatment/disposal or by destroying the contaminant on-site in an afterburner. Thermal desorbers may be characterized by:

1. Method of heating (direct or indirect).
2. Operating pressure (slight vacuum or high vacuum).
3. Maximum solids treatment temperature (low: 149-315° C; medium: 315-538° C; and high: 538-649° C).

The emission control system may be characterized as a recovery-type or a destructive-type. The selection of the type of emission control system depends on the concentration of the contaminants in the feed, air emission regulations, community relation's considerations, and economic factors. Contaminants for which bench, pilot, and full-scale treatment data are available in the literature include volatile organic compounds, semi-volatile organic compounds, polychlorinated biphenyls, chlorinated phenols, pesticides, herbicides, dioxins/furans, mercury, and cyanide. Thermal desorption has also been extensively applied to soils and sludges contaminated with petroleum products.

Thermal desorption has been in commercial use since the late 1980s. Properly designed and operated, thermal desorption with pre- and post-processing offers a viable means for remediation of contaminated soils, sludges and sediments. Experience has revealed a number of factors that need to be considered in evaluating potential thermal desorption applications. Some of these features include organic material characterization, particulate carryover into downstream emission control devices, fugitive emissions during excavation, screening, crushing, and storage before treatment, materials handling, chlorine and sulfur content of feed material, contaminant treatment criteria, maximum bed temperature effected in the soil media, and selection of appropriate emission control system. From the point of view of cost, it is mainly a function of the solid moisture content, solid characteristics, contaminants volatility, contaminants concentration, vendor equipment limitations, and clean up standards. Regulatory requirements may also be a key contributor to the cost of treatment.

Based on the review of the bench, pilot and full scale studies of thermal desorption for remediation of PCBs, it is concluded that thermal desorption will remove PCBs and other organics from New Bedford Harbor sediment. Pilot scale testing did not provide data that met the criteria for community acceptance. In particular, scaling of the process to a full-scale system, including the use of hazardous materials (hydrogen and/or flammable gas) in the process, the fate of metals and the potential formation of dioxins need to be thoroughly evaluated. The relevant mature operations employing Thermal Treatment technology are summarized below.

#### 4.7.1 Low Temperature Thermal Desorption

Summary Description: The PCB contaminated soil discussed in Norris *et al*<sup>48</sup> arose from a 20 ha (49.4 acres) telecommunications manufacturing facility (capacitor manufacture). Potential remedial alternatives investigated included the use of landfill, soil washing, solvent washing, bioremediation, high temperature incineration and low temperature thermal desorption (LTTD). Following technology evaluation studies, including a number of treatment trials, LTTD was selected. Treatment was undertaken by British Aerospace Royal Ordnance Environmental Services Group (ESG) using a 20 t/h mobile unit. Low temperature thermal desorption at around 400° C is a remediation technology suitable for the treatment of soils contaminated with low and middle distillate organic compounds such as solvent, gasoline, diesel and lubricating oils, and some pesticides.

The soil contaminated by PCB with average concentration of 120 mg/kg and a peak of 1,300 mg/kg was treated by using low temperature thermal desorption technology. Thermal treatment was shown to remove PCBs from a difficult matrix sufficiently to pass stringent residual contamination values, without unacceptable impacts on the environment and at a cost per ton significantly lower than that of high temperature incineration—a saving of 75%. The process of the technology consists of two steps: 1) feeding contaminated material continuously to evaporate the contaminants through a rotary kiln where the temperature is around 400° C; and 2) the exhaust gas from the 1<sup>st</sup> stage is then passed through dust filters into a thermal oxidizer unit where controlled oxidation at a minimum temperature of 850° C ensures extremely high destruction efficiencies of the contaminant vapors. The treatment resulted in output soil PCB concentrations of 0.1 ± 0.1 mg/m<sup>3</sup> relative to a consent target value of 1 ng/m<sup>3</sup> and dioxins of 0.01 ng/m<sup>3</sup>-TEQ compared to a consent value of 1 ng/m<sup>3</sup>-TEQ.

Owner of Treatment Alternative: Nortel Ltd., Golder Associates (UK) Ltd.

Level of Implementability: Bench Scale (20 t/h)

Cost Range of Implementation: Remediation using low temperature desorption presented a saving of 75 % compared to incineration cost of about £770 per ton of soil in 1998 (Equivalent to \$ 1,270 at a 1998 conversion rate of \$ 1.00 = £ 0.6098).

List of Projects Where It Has Been Implemented: British Aerospace Royal Ordnance Environmental Service Group (ESG) using a 20t/h mobile unit.

Advantages:

1. Good for low and middle distillate contaminants; Low cost (saving 75%).
2. Can remove PCBs from a difficult soil matrix.
3. Lower treatment temperature with high efficiency.
4. High destruction efficiencies and very low dioxins emissions.

Disadvantages:

1. Logistical issues in handling of high moisture content sediments.
2. Requires thermal oxidizer or secondary treatment of emissions for high destruction efficiencies and extremely low levels of dioxins.

Conclusions and Recommendations: Thermal desorption was tested at a pilot scale at NBH and found to be effective at removing PCBs from solid matrix. Some logistical issues were identified; in particular, the handling of high moisture content sediments. These would require resolution prior to implementation at full scale but were not considered insurmountable. The process was not accepted by the community, primarily because it did not resolve previously identified issues associated with thermal processes and because disposal/treatment of resulting PCB oil remained a significant concern.

#### 4.7.2 ESMI Thermal Desorption Process

Summary Description: R&D pilot scale treatment was conducted from 1994 to 1997 at Environmental Soil Management Inc. (ESMI) in Loudon, New Hampshire, to demonstrate both pilot and full scale thermal desorption of soils contaminated with various compounds such as manufactured gas plant (MGP)

waste, low level PCBs and chlorinated solvents. Upon demonstration of contaminant treatability in the pilot scale, soils were then treated in full scale thermal desorption units.<sup>49</sup> Full-scale soil treatment was completed at ESMI facilities located in both New Hampshire and New York. Ultimately, the full-scale technology was applied to remediate soils contaminated with chlorinated solvents at the sites. Plant scale remediation entailed heating contaminated soils in a rotary dryer at temperatures between 450 and 900°F. The contaminant was driven from the soil and destroyed in a thermal oxidizer with a hydrocarbon destruction efficiency of greater than 99.6%. Solids were stored and pre-processed in an enclosed storage building. Pre-processing included blending, screening, crushing, and removal of untreatable debris (wood, plastic, metal). Pre-processed soils were fed via conveyors to the thermal desorption plant. Soils were fed to the rotary dryer and tumbled through for a designated residence time. The burner was fired to achieve a desired soil exit temperature. Treated soils exited the burner end of the dryer and were dehydrated in a pugmill. Treated soils were stockpiled, sampled and segregated before post-treatment analytical results were retrieved. Soil contaminants volatilized from the soil in the dryer and exited with the flue gas stream at the feed end of the dryer. Flue gases passed from the dryer to a cyclone where initial particulate removal took place. Particulate matter collected in the cyclone was returned to the burner end of the dryer for treatment and exited the dryer discharge soils. Flue gases exited the cyclone and were treated for contaminants.

The removal efficiencies of total petroleum hydrocarbon (TPH) and polycyclic aromatic hydrocarbon (PAH) ranged from 98.97% to 99.99% and 95.44% to 99.99%, respectively. All soil contaminated with low level PCBs (<50 ppm) were remediated to below 1 ppm. Under existing regulations, only soils with less than 50 ppm PCB were eligible to be remediated at the ESMI fixed facilities. Thermal desorption of PCB contaminated soils required temperatures in excess of 825° F. Soils contaminated with chlorinated solvents were successfully treated with removal efficiencies of 95.8 to 99.98% for trichloroethylene (TCE) and 93.5% to 99.98% for perchloroethylene (PCE).

Level of Implementability: Bench-scale, pilot, and full scale

Advantages: Good efficiency for hydrocarbon destruction.

Disadvantages: Used for low level (<50 ppm) PCB removal only (under existing regulations at the fixed facilities). This method requires temperature in excess of 825° F.

Conclusions and Recommendations: Plant scale tests showed that the overall process was efficient for destruction of TPH and PAH without a wet scrubber. With a wet scrubber, TCE and PCE were removed from soils at high efficiency. Under existing regulations, only soils with <50 ppm PCB were eligible to be remediated at the existing fixed facilities. It is likely to have the same concerns as other thermal processes and will require post treatment of the gases to ensure high efficiency and low dioxin emissions.

#### 4.7.3 Ecotechniek Soil Treatment

Summary Description: Soil contaminated with halogenated hydrocarbons like pesticides, PCDD/PCDF and PCB can be treated in an environmentally responsible way with the thermal treatment plant of Ecotechniek BV, The Netherlands.<sup>50</sup> They can be cleaned to values lower than the laboratory detection limit for pesticides and to below the target levels for PCDD/PCDF and PCB. The process includes: 1) removing any iron particles from contaminated soil using a magnetic separator; 2) reducing the coarse rubble into smaller parts when the soil passes through a crusher; 3) preheating the soil to approximately 300° C by the hot exhaust gases and then heating the soil to a maximum of 600° C by a gas burner in a rotary kiln (after evaporating the volatile compounds, the treated soil is discharged and the process gas

further treated); 4) removing dust in the process gas through a series of multi-cyclones and dust filters prior to being fed to an afterburner where contaminants are destructed into CO<sub>2</sub>, H<sub>2</sub>O, and HCl; and 5) removing acid gases and organic components by passing the gas through an adsorbent unit filled with lime and carbon.

The results of soil treatment with rotary kiln temperature of 600° C, afterburner temperature of 1050° C and treatment capacity of 25 tons/hr showed that soil contaminated with halogenated hydrocarbons can be cleaned to values lower than the laboratory detection limit for pesticides and to extremely low end concentrations for PCB and PCDD/PCDF even for heavily contaminated soils. In addition, the emission of dioxins and furans was considerably lower than the target value of 0.1 ng /m<sup>3</sup>-TEQ (recorded values were about 0.01 ng/m<sup>3</sup>-TEQ). Lower values were also measured for other components in the gas flow (CO, SO<sub>2</sub>, HCl, HF, organic carbon and dust).

The destruction efficiency of the afterburner was higher than 99.99% for all tested chlorinated compounds and the removal efficiency for the adsorber unit was at least 95% for any dioxins and furans formed after the afterburner. In total, Ecotechniek has already treated more than 3,000,000 tons of contaminated soils over the past 17 years with one mobile and two stationary thermal treatment plants. (Treatment capacity = 25 tons/hour)

Owner of Treatment Alternative: Ecotechniek , The Netherlands

Level of Implementability: Commercial plant

Cost Range of Implementation: Cost of implementation is £580 (equivalent to \$ 950 using a 1998 conversion rate of \$ 1.00 = £ 0.6098) per ton of soil.

Advantages:

1. Efficiency 99.99%; Soils contaminated with hydrocarbons can be cleaned to values lower than the lab detection limit.
2. 6500 tons of heavily contaminated soils were treated.
3. High efficiency for removal of pesticides, PCB and PCDD/PCDF.
4. Low CO, HCl, and SO<sub>x</sub> emission; High treatment capacity.
5. 17 years operation experience.

Disadvantages:

1. System is complex and potentially costly.
2. Produces products of combustion including PCDD/PCDF.
3. Off-gases require secondary treatment.

Conclusions and Recommendations: Proven technology with the same limitations as other thermal treatment technologies, including production of by-products of incineration that require secondary treatment. Nothing new in this implementation that is likely to mitigate the community's concern for thermal processes at NBH.

#### 4.7.4 *In-situ* thermal desorption (ISTD)

Summary Description: In in-situ thermal desorption (ISTD) heat and vacuum are applied simultaneously to subsurface soils. For shallow contamination (less than 2-ft depth) heat and vacuum are applied by thermal blankets and for deeper contamination thermal wells are used.<sup>51</sup> In the ISTD Thermal Blankets heat is supplied to the soil by downward conduction from a surface heater and vaporized products are collected under an impermeable sheet into a vacuum system. The ISTD-Thermal Blanket is an 8-ft by 20-ft stainless steel box covering 160 square feet. The near surface soil is raised to about 1,600° F by the radiant energy and the heat front then propagates downward into the soil by thermal conduction. As the contaminants in the soil are drawn upwards, the high temperatures in the soil near the heating elements convert the majority of contaminants (98-99%) to CO<sub>2</sub> and H<sub>2</sub>O.

For ISTD-Thermal Wells, an array of heater/vacuum wells is placed vertically in the ground in triangular patterns. The wells are equipped with high temperature electric heaters (1,700° F) and connected to a vacuum blower. As heat is injected and soil temperatures rise, the vaporized products are drawn into the wells by the applied vacuum. Contaminants are converted in the soil near the heater well to CO<sub>2</sub> and H<sub>2</sub>O. For both ISTD-Thermal Blankets and Thermal wells, vapors produced are treated further in a mobile vapor treatment system consisting of a flameless thermal oxidizer with > 99.99 % DRE followed by two carbon beds in series. Both ISTD-Thermal Blanket and Thermal Well technologies were effective in achieving the site remediation goals of <2 ppm at all locations sampled within the treatment zone. The discharge of PCBs and combustion by-products detected during stack testing activities conducted on the mobile vapor treatment system confirmed that the ISTD process did not adversely impact ambient air quality.

The ISTD Thermal Blanket and Wells were shown to remediate high concentration PCB contaminants from shallow and deep clay soils. The demonstrations were conducted at the Missouri Electric Works Superfund site in Cape Girardeau, Missouri. The area chosen had PCB contamination as high as 19,900 ppm near surface and still above 2 ppm at the target depth of 10 ft. The soil was successfully remediated to a depth of 18 inches. The upper one foot of soil was non-detect for PCB (i.e. <33 ppb) and averages at all depths met the remedial objective of < 2 ppm. Sampling after 42 days showed complete clean up of all contaminants to levels below 1 ppm to a depth of 10 ft below ground surface. Sampling down to 15 ft in the center of the treated zone showed that no vertical migration of contamination had occurred. Stack testing of emissions indicated 99.9999998% destruction removal efficiency of PCBs. Post-treatment of soil samples analyzed for PCDD/PCDF exhibited TEQ levels from non-detect to 0.00684 ppb, with an average of 0.003 ppb. This is below the background level of 8 ppt for uncontaminated soil in North America.

Level of Implementability: Full-scale Demonstration

Advantages:

1. ISTD process has a high degree of social acceptance because it is a clean, closed system that is reliable and fast.
2. The operations are low profile, quiet, and cause little disruption of adjoining neighborhoods.
3. There is no odor.
4. High removal efficiency; removal of high concentration PCBs (both methods are highly effective).
5. Commercial remediation services are available; achieves <2 ppm PCB.

6. The discharge of PCBs and combustion by-products conducted on the mobile vapor treatment system showed minimum exposure to the public and caused little disruption of neighborhoods.

Disadvantages:

1. The ISTD process takes a long time to remediate contaminated soils; for example, the test described above took 42 days.
2. Vapors produced need to be treated further with a flameless thermal oxidation followed by carbon bed in order to achieve 99.99 % DRE.

Conclusions and Recommendations: The ISTD technologies volatilized, extracted, and effectively treated high concentrations of the highest boiling point PCBs from dense clay overburden soils without excavation. The discharge of PCBs and combustion byproducts detected during stack testing activities conducted on the mobile vapor treatment system indicated that the ISTD process did not adversely impact ambient air quality. The ISTD wells thermal technique is suitable for remediation of highly contaminated soils in deep ground, preferably small size sites without disturbing the soil. This technology has the same concerns previously identified for thermal processes and offers no new secondary treatment that is likely to meet community acceptance.

#### **4.8 Adsorption<sup>52,53</sup>**

Background: In liquid adsorption, solutes concentrate at the surface of a sorbent, thereby reducing their concentration in the bulk liquid phase. Adsorption mechanisms are generally categorized as physical adsorption, chemisorption, or electrostatic adsorption. Weak molecular forces, such as Van der Waals forces, provide the driving force for physical adsorption, while a chemical reaction forms a chemical bond between the compound and the surface of the solid in chemisorption. Electrostatic adsorption involves the adsorption of ions through Coulombic forces, and is normally referred to as ion exchange, which is addressed separately in the ion exchange modules. In liquids, interactions between the solute and the solvent also play an important role in establishing the degree of adsorption.

The most common adsorbent is granulated activated carbon (GAC). Other natural and synthetic adsorbents including activated alumina, forage sponge, lignin adsorption, sorption clays, and synthetic resins are of limited application and were therefore not reviewed.

##### **4.8.1 Liquid Phase Carbon Adsorption/Granulated Activated Carbon (GAC)**

Description: Ground water is pumped through a series of canisters or columns containing activated carbon to which dissolved organic contaminants adsorb. Periodic replacement or regeneration of saturated carbon is required. When the concentration of contaminants in the effluent from the bed exceeds a certain level, the carbon can be regenerated in place; removed and regenerated at an off-site facility; or removed and disposed. Modification of GAC, such as silicone impregnated carbon, could increase removal efficiency and extend the length of operation. It may also be safer to regenerate. The concepts, theory, and engineering aspects of the technology are well developed. It is a proven technology with documented performance data.

The two most common reactor configurations for carbon adsorption systems are the fixed bed and the pulsed or moving bed. The fixed-bed configuration is the most widely used for adsorption from liquids.

Pretreatment for removal of suspended solids from streams to be treated is an important design consideration. If not removed, suspended solids in a liquid stream may accumulate in the column, causing an increase in pressure drop. When the pressure drop becomes too high, the accumulated solids must be removed, for example, by backwashing. The solids removal process necessitates adsorber downtime and may result in carbon loss and disruption of the mass transfer zone.

Owner of Treatment Technology: Adsorption process using activated carbon is a commonplace technology which is available for general use.

Level of Implementability: Liquid phase carbon adsorption is a full-scale technology. Adsorption by activated carbon has a long history of use in treating municipal, industrial, and hazardous wastes.

Cost Range of Implementation: Estimates on the use of carbon in removal of PCBs from wastestreams are not definitive. However costs associated with GAC are dependent on wastestream flow rates, concentration of contaminant, mass loading, required effluent concentration, and site and timing requirements. Costs are lower with lower concentration levels of a contaminant of a given type. Costs are also lower at higher flow rates. At flow rates of 0.4 million liters per day (0.1 million gallon per day), costs increase from \$0.32 to \$1.70 per 1,000 liters (\$1.20 to \$6.30 per 1,000 gallons) treated.

Advantages:

1. Applicable for the adsorption of PCBs as member of the group of semivolatile organics.
2. Liquid phase carbon adsorption is effective for removing contaminants at low concentrations (less than 10 mg/L) from water at nearly any flow rate, and for removing higher concentrations of contaminants from water at low flow rates (typically 2 to 4 liters per minute or 0.5 to 1 gpm).
3. Carbon adsorption is particularly effective for polishing water discharges from other remedial technologies to attain regulatory compliance.

Disadvantages:

1. Not applicable for the treatment of sediments.
2. The duration of GAC is usually short-term for high concentration wastestreams.
3. The presence of multiple contaminants can impact process performance.
4. Disadvantages arise from the need to transport and decontaminate spent carbon.
5. Costs are high if used as the primary treatment on waste streams with high contaminant concentration levels.

Conclusions and Recommendations: Carbon adsorption is particularly effective for polishing water discharges from other remedial technologies to attain regulatory compliance. However, this technology is not applicable for the direct treatment of sediments from New Bedford Harbor.

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