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Environmental Protection
Agency

Engineering Issue

# Technology Alternatives for the Remediation of PCB Contaminated Soils and Sediments

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## 1.0 PURPOSE

The U.S. Environmental Protection Agency (EPA) Engineering Issue papers are a series of documents that summarize the available information on specific contaminants, selected treatment and site remediation technologies, and related issues. This Engineering Issue paper is intended to provide remedial project managers (RPMs), on-scene coordinators (OSCs), contractors, and other state or private remediation managers with information to facilitate the selection of appropriate treatment and disposal alternatives for soil and dredged sediment contaminated with polychlorinated biphenyls (PCBs). This information includes the type of data and site characteristics needed by site cleanup managers to evaluate *ex-situ* technologies for potential applicability to their hazardous waste sites. This Engineering Issue paper does not address in situ alternatives for sediment (e.g. monitored natural recovery or capping). For a more comprehensive guidance concerning remedial alternatives specifically for sediments see the “Contaminated Sediment Remediation Guidance for Hazardous Waste Sites,” EPA-540-R-05-012, U.S. Environmental Protection Agency, December 2005 [01]; “A Risk-Management Strategy for PCB-Contaminated Sediments National Research Council,” National Academies Press., May 2001 [02]; and “Reference Guide to Non-Combustion Technologies for Remediation of Persistent Organic Pollutants (POPs) in Stockpiles and Soil,” EPA-542-R-05-006, U.S. Environmental Protection Agency (EPA), 2005 [03].

This Engineering Issue paper provides an overview of PCB contamination and remediation, and was developed from peer reviewed literature, scientific documents, EPA reports, web site sources, input from experts in the field, and other pertinent information. It should be noted that some remediation technologies covered in this paper, while documented to be effective in PCB waste remediation, may not be commercially available or widely used at this time. Also, emerging and innovative technologies discussed herein, while not currently widely used, may see continued growth and use.

The Table of Contents shows the type of information covered in this paper. Important information has been summarized, while references and web site links are provided for readers interested in additional information. The web site links, verified as accurate at the time of publication, are subject to change.

## 2.0 INTRODUCTION

PCBs are now considered the most widespread pollutant on the planet. In industrial countries, the contamination originates from inadequate disposal and leaks from equipment. In remote areas where PCBs were not used, the contamination resulted from atmospheric transport [04]. PCBs are comprised of a class of synthesized organic compounds of up to 209 chlorinated biphenyls, with different physical and chemical characteristics [05, 06]. A biphenyl is a structure comprised of two benzene rings linked by a single carbon-carbon bond. The PCBs are prepared by direct chlorination of the biphenyl ring. Isomers are compounds having the same number of chlorine atoms, and congeners are compounds which bear different number of chlorine atoms. The congeners are designated by describing the position of the chlorine atoms on the biphenyl ring or, more simply, by the IUPAC (International Union of Pure & Applied Chemistry) numbering system. The congeners differ in their physical properties according to the number and the position of chlorine atoms [04, 07]. The high-chlorinated biphenyls are less water-soluble and less volatile than the low-chlorinated ones. The degree of chlorine substitution influences their biodegradability that decreases with increasing chlorination. The toxicity for the biota is related to the number of chlorines but prime importance is their position on the biphenyl ring. The congeners that take a co-planar configuration, such as congener 77 (3,3',4,4'-tetrachlorobiphenyl), are the more toxic ones [04, 08]. Commercially produced PCB mixtures were marketed in the U.S. primarily under the trade name "Aroclor". The various Aroclor formulations contain approximately 175 of the possible 209 identified PCB congeners. For example, Aroclor 1242 contains 42% of chlorine with a predominance of congeners bearing three and four chlorine atoms; Aroclor 1260 has 60% chlorine content with a predominance of six- and seven-chlorinated congeners. These mixtures typically contain more than 70 different congeners and were sold under different names (Aroclor, Phenoclor, Clophen, Delor and Kanechlor), depending on the manufacturer [04]. Due in part to mounting evidence that PCBs persist in the environment and pose a variety of environmental and health hazards, Congress enacted the Toxic Substance Control Act (TSCA) in 1976, which directed the EPA to regulate the disposal, storage, spill response, cleanup, and labeling of PCB containing substances. Domestic manufacturing, processing, and distribution of commercial mixtures and uses of PCBs were banned in the U.S. in 1979. These chemicals are now only manufactured in the U.S. for analytical standards and scientific research [08].

Of the 209 PCB congeners, 12 have dioxin-like effects on humans. Most PCBs are oily liquids, the color of which darkens and the viscosity increases with a corresponding increase in the number of chlorine atoms. PCBs with fewer chlorine atoms are more soluble, amenable to chemical and biological degradation, and less persistent in the environment. However, as a chemical class, PCBs are chemically and biologically stable, hydrophobic, do not conduct electricity, possess a low volatility at ambient temperatures and have no known taste or smell. PCBs are soluble in organic or hydrocarbon solvents, oils, fats, and slightly soluble in water.

The specific properties that made PCBs valuable for industrial applications include extreme stability, chemical inertness, resistance to heat, and high electrical resistivity or a high dielectric constant [09]. These same properties also contributed to the environmental legacy of PCBs. Due to their widespread use in industry, large amounts of PCBs have been released into the environment. It has been estimated that 31% of the total world production of PCBs (370,000 tons) have already been released to the environment. More than 60% remain in use or in storage. Only 4% have been destroyed [10]. PCBs have been found at 410 out of 1290 National Priority List (NPL) sites identified by EPA [11]. PCBs enter the environment as mixtures containing a variety of individual chlorinated biphenyl components, known as congeners. Environmental transport processes such as vaporization, dissolution, and sorption do not act on all congeners equally, resulting in environmental concentrations of individual PCB congeners that may differ substantially from those present in the original commercial mixture. This process is known as weathering. Some congeners are more efficiently biotransformed by microbial action in soil than others [12, 13]. The extent of biotransformation can be dependent on environmental conditions (i.e. aerobic versus anaerobic) and the microorganisms present. These biotic and abiotic changes in congener composition may alter the toxicity of the mixture, making it more or less toxic than the commercial product. Because the PCB mixtures are lipophilic, they accumulate in the adipose tissue of organisms. The extent of chlorine substitution affects biotransformation. PCBs with higher chlorine contents are less biodegradable, making them a greater bioaccumulation risk [14].

PCBs readily adsorb to organic materials, sediments, and soils. Consequently, PCBs are widespread in the environment, whereby humans are exposed through multiple pathways. Levels in air, water, sediment, soil, and foods can vary over several orders of magnitude, often depending on proximity to a source of release into the environment. Through a process known as biomagnification, PCBs pass up the food chain at ever intensifying levels, accumulating in the tissues of the organisms that consume affected fauna [15]. Certain soil and sediment properties including soil density, particle size distribution, moisture content, and permeability are known to affect the mobility of PCBs.

In addition, climatological and chemical characteristics such as rainfall, organic carbon content and the presence of organic colloids can affect PCB mobility [16]. If the PCB contamination is associated with an organic solvent, facilitated transport could occur, whereby the PCBs would exhibit increased mobility above which is typically expected.

PCBs have been shown to cause a number of cancerous and non-cancerous health effects in animals, including effects on the immune, reproductive, nervous, and endocrine systems [17]. Studies in humans provide supportive evidence for potential carcinogenic and non-carcinogenic effects of PCBs [18, 19]. Another adverse health impact may result from the incomplete combustion of PCBs from thermal treatment processes. Incomplete oxidation of PCBs may form polychlorinated dibenzodioxin (PCDD) and polychlorinated dibenzofuran (PCDF) emissions [20].

## 2.1 Regulations Governing PCB Cleanups

### *2.1.1 Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA)*

The National Contingency Plan, instituted by CERCLA of 1980, established a framework for identifying and remediating the nation's most contaminated and hazardous sites (Superfund sites). Section 121(d)(2)(A) of CERCLA requires adherence to other Federal and State laws through the identification of and compliance with applicable or relevant and appropriate requirements (ARARs). These ARARs must be complied with or waived for all Superfund remedial actions and for removal actions, to the extent practicable. Primary Federal ARARs for PCB-contaminated sites are derived from the Toxic Substances Control Act (TSCA) and the Resource Conservation and Recovery Act (RCRA). Other regulations derived from the Clean Water Act (CWA) and the Clean Air Act (CAA) may be implemented when remediation of the site potentially affects water or air quality. Regulations under the Occupational Safety and Health Act (OSHA) may also be ARARs for Superfund PCB sites. These Federal regulations are described below.

To-be-considered material (TBCs) are non-promulgated advisories or guidance (issued by Federal, State, or Tribal governments), that are not legally binding and do not have the status of potential ARARs. However, in many circumstances TBCs are considered along with ARARs during the cleanup decision process. Guidance on conducting risk assessments at Superfund sites, including PCB sites, can be found at "U.S. Environmental Protection Agency (EPA), Waste and Cleanup Risk Assessment, Superfund Risk Assessment." Available at: http://www.epa.gov/oswer/riskassessment/risk_superfund.htm [21]. Guidance on remedy selection (including PCB sites) can be found at "U.S. Environmental Protection Agency (EPA), Superfund, Superfund Remedy Decisions." Available at: http://www.epa.gov/superfund/policy/remedy/sfremedy/index.htm [22].

TBC materials are found in mixtures when cleaning up PCBs at Superfund sites. These include TBCs for dioxin and dioxin-like compounds like polychlorinated dibenzop-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD), along with the dioxin-like PCBs. Information on dioxin, including dioxin toxicity values which serve as TBCs, can be found at "U.S. Environmental Protection Agency (EPA), Environmental Assessment, Dioxin." Available at: http://cfpub.epa.gov/ncea/CFM/nceaQFind.cfm?keyword=Dioxin [23]. To-be-considered material for cleaning up dioxin, including dioxin-like PCBs, at Superfund sites can be found at: "U.S. Environmental Protection Agency (EPA), EPA Non-Cancer Toxicity Value for Dioxin and CERCLA/RCRA Cleanups." Available at: http://www.epa.gov/superfund/health/contaminants/dioxin/dioxinsoil.html [24].

### *2.1.2 Toxic Substances Control Act (TSCA)*

In 1976, Congress passed TSCA, which banned the production, use, distribution in commerce, import, and export of PCBs. The EPA TSCA regulations for PCBs at 40 CFR 761 include requirements for the cleanup, disposal, and storage of PCB-contaminated materials. The TSCA PCB regulations are implemented by EPA, as they cannot be delegated to the states. For this reason, any decisions regarding PCB approvals must be made by the EPA regions or Headquarters, even if a state program, authorized under RCRA or CERCLA, is in charge of a cleanup. Some states regulate PCBs under their RCRA program, but the state PCB requirements do not supplant EPA's TSCA regulations. The TSCA PCB regulations refer to approvals rather than permits, but the terms are essentially synonymous.

PCB-contaminated soil and sediments are regulated for cleanup and disposal under TSCA based on the date they were contaminated, the concentration of the source of PCBs, and the current PCB concentration. Any soil or sediments containing PCBs ≥ 50 mg/kg are regulated for cleanup and disposal as TSCA PCB remediation waste. Additionally, soil or sediments containing between 2 and 50 mg/kg that were spilled after 1978 from a source ≥ 50 mg/kg or a source unauthorized for use, are regulated as PCB remediation waste. The cleanup and disposal options for PCB remediation waste are found at 40 CFR 761.61. There are three options under 761.61. Option (a), the self-implementing option, is very proscriptive (i.e., includes conditions under which this option cannot be used, sampling requirements, cleanup levels, and treatment options); this option is better suited for small to medium size sites. The self-implementing option cannot be used for PCB-contaminated sediments. Option (b), the performance-based option, requires all TSCA material to be sent to a TSCA chemical waste landfill, TSCA incinerator, or a facility approved under TSCA as being equivalent to incineration. Option (c) is a risk-based option under which cleanup and/or disposal methods may be proposed. Approval under the risk-based option requires a finding of no unreasonable risk to human health or the environment by the EPA. Option (c) is often preferred for large, complex sites, such as many Superfund sites.

When disposal technologies other than incineration are used for PCB-contaminated soil or sediments, an approval is required. The approval might be a risk-based cleanup approval under 761.61(c) or an approval under 761.60(e) for disposal technologies demonstrated to be equivalent to incineration. The standard for approvals under 761.61(c) is no unreasonable risk to human health or the environment, and the approval is site-specific. Approvals under 761.60(e) are given to an operator of a specific technology who demonstrates destruction of PCBs to below 2 mg/kg and generally 99.9999% PCB destruction efficiency.

Other TSCA requirements that might apply at sites with PCB-contaminated soil or sediments include, but are not limited to, storage (761.65), record keeping (Subpart J), and manifesting (Subpart K). PCB waste must be disposed of within one year from the date it was determined to be a PCB waste and the decision was made to dispose, unless an extension is granted by the EPA.

### *2.1.3 Resource Conservation and Recovery Act (RCRA)*

PCBs are not regulated as a hazardous waste under RCRA. However, if PCBs are mixed with hazardous wastes listed in 40 CFR 261.31 to 261.33 (e.g., spent trichloroethylene that was used to clean electrical equipment), the mixture is subject to the RCRA hazardous waste regulations. Similarly, if PCBs are mixed with other wastes, and the resulting mixture exhibits one or more of the hazardous characteristics discussed in 40 CFR 261.21 to 261.24 (i.e., ignitability, corrosivity, reactivity, or toxicity), the mixture must be managed as hazardous waste until the waste no longer exhibits the characteristic. PCB-contaminated soil or sediment that is also contaminated with listed waste or exhibits a hazardous characteristic, must be managed as hazardous waste until the contaminated medium no longer contains the listed waste (the site-specific decision for listed wastes must be made by the EPA regional office or the authorized state) or no longer exhibits the hazardous characteristic.

The 1984 Hazardous and Solid Waste Amendments to RCRA specified additional requirements for treatment and disposal of hazardous waste. Solid waste management units (SWMUs) at hazardous waste treatment, storage, and disposal (TSD) facilities became subject to more stringent corrective action requirements. Also, land disposal of hazardous waste without prior treatment by a specified technology, or to a specified constituent concentration, became prohibited under the land disposal restrictions (LDRs).

The California List of the LDRs states that liquid hazardous waste containing greater than 50 mg/kg of PCBs must either be incinerated in a TSCA incinerator or a high-efficiency boiler.

The California List also regulates the disposal of hazardous waste containing halogenated organic compounds (HOCs) when present in concentrations greater than 1,000 mg/kg. The HOC list includes seven specific Aroclors, as well as "PCBs not otherwise specified." Incineration is the specified remedial technology. The presence of other restricted hazardous waste in PCB-contaminated soil and sediments also subjects the media to the applicable LDRs.

### *2.1.4 Other Federal Regulations*

Remediation of PCB-contaminated sediments may affect local and downstream water quality during activities such as dredging and dewatering. The Clean Water Act establishes requirements and discharge limits for actions that affect surface water quality. Accordingly, the technical requirements of permits, such as the National Pollutant Discharge Elimination System (NPDES) permit, may have to be met.

Remedial technologies that have the potential to emit PCBs or other contaminants into the air may need to include control measures in accordance with the Clean Air Act. Regulated units could include baghouses, exhaust stacks, and pressure release devices on treatment tanks.

The Occupational Safety and Health Act is the primary Federal law that governs occupational health and safety in the private sector and Federal government. Its main goal is to ensure that employers provide employees with an environment free from recognized hazards, such as exposure to toxic chemicals, excessive noise levels, mechanical dangers, heat or cold stress, or unsanitary conditions.

### *2.1.5 State Regulations*

The TSCA PCB regulations are implemented by EPA, as they cannot be delegated to the states. However, at least 18 states currently regulate various aspects of PCB disposal under their own RCRA regulations. The state PCB requirements do not supplant EPA's TSCA regulations. Therefore, applicable state regulations in addition to TSCA regulations must be included as ARARs or waived, when appropriate, at Superfund sites.

## 2.2 Alternative Remedial Selection Criteria

Prescreening of remedial options begins with a preliminary site investigation prior to the development of a conceptual site model. A carefully designed and implemented site characterization should be conducted to resolve any data gaps identified during the project scoping phase [25]. Table 1 presents a minimum set of soil and sediment characteristics needed for screening the remedial technologies covered in this paper. [25].

Physical characteristics and logistical considerations could impact the installation and operation of any remedial alternative selected. For land based (non-aquatic) sites, these items include:

- Site layout
- Activities conducted at the site
- Site access
- Terrain features and topography
- Drainage patterns
- Facility footprint and traffic patterns
- Security considerations including:
    - Utility connections and locations
    - Buffer zones
    - Community setting (rural, urban), including proximity to residential areas.

**Table 1.** Soil and Dredged Sediments Characteristics for Candidate PCB Treatment and Disposal Technologies

| Characteristics | Incineration | Landfill | Thermal Desorption | Chemical Dehalo-genation | Solvent Extraction | Soil Washing | S/S | Bioremediation* | Vitrification |
|---|---|---|---|---|---|---|---|---|---|
| Particle Size | ▼ | NA | ▼ | O | ▼ | ▼ | ▼ | O | ▼ |
| Bulk Density | ▼ | NA | ▼ | NA | O | O | NA | NA | NA |
| Permeability | NA | NA | NA | NA | ▼ | ▼ | NA | ▼ | NA |
| Moisture Content | ▮ | ▮ | ▮ | NA | O | O | ▮ | ▼ | ▮ |
| pH and Eh | O | NA | O | O | NA | NA | O | O | NA |
| Humic Content | O | NA | O | ▮ | ▮ | ▮ | ▮ | ▮ | ▮ |
| Total Organic Carbon (TOC) | ▼ | NA | ▼ | O | NA | NA | O | ▮ | O |
| Biochemical Oxygen Demand (BOD) | NA | NA | NA | NA | NA | NA | NA | ▮ | NA |
| Chemical Oxygen Demand (COD) | NA | NA | NA | ▼ | NA | NA | NA | ▮ | NA |
| Oil and Grease | NA | NA | NA | ▼ | O | O | ▮ | NA | ▮ |
| Volatile Metals | ▮ | NA | ▮ | ▮ | ▼ | ▮ | ▼ | ▮ | ▮ |
| Nonvolatile Metals | ▮ | NA | ▮ | ▮ | ▼ | ▼ | ▼ | ▮ | ▼ |

▼ Higher values support selection of particular technology group
▮ Lower values support selection of particular technology group
O Effect is variable among systems within technology group
NA Tecnology selection generally not impacted by this characteristic
* Aerobic bioremediation. High values of BOD and COD can be favorable to anaerobic bioremediation process

Soil characteristics and properties that factor into the applicability determination for candidate PCB remedial options are listed in Table 1:

Particle size separation treatment involves separation of the fine materials from the course larger material by physical screening. Particle size separation may serve as a pretreatment step prior to implementation of a treatment alternative. Organic compounds absorb to the finer fractions (e.g. clay or silt); therefore, particle size separation may also be considered a treatment technology distinguishing between hazardous and non-hazardous disposal options [1]. Many treatment processes require particle size of one centimeter or less for optimal operation. Heterogeneities in solid and waste compositions produce non uniform feed streams resulting in inconsistent removal rates [26, 27]. Soils with a high proportion of coarse gravel or cobbles affect performance of vitrification, chemical extraction, *ex-situ* bioremediation, thermal desorption, and incineration systems. Soil with large amounts of fines would generate potentially harmful particulate dust for technologies that require excavation and the use of heavy construction equipment. Fine particles result in high particulate loading in flue gases due to the turbulence in rotary kilns but bioremediation processes, such as slurry reactors, are generally facilitated by finer particles that increase the contact area between the contaminant and microorganisms [27, 28].

Bulk density is the weight of the soil per unit volume including interstitial and absorbed water. Bulk density is used for converting weight to volume in materials handling calculations [30] and is interrelated with PSD in determining mixing and heat transfer in fluidized bed reactors. To allow good circulation and removal of solid residues within the fluidized bed all solids require screening or crushing to a size less than 2 inches in diameter [31].

Permeability (hydraulic conductivity) in soils and sediments controls infiltration of nutrient solutions for some bioremediation technologies [26] and can induce preferential flow pathways in the subsurface.

High moisture content may cause excavation and materials transport problems and may negatively impact processing material feed [29, 30, 31, 32]. High moisture content increases energy requirements for thermal technologies, but favors slurry phase bioremediation systems.

High pH can improve feasibility of applying chemical extraction and alkaline dehalogenation processes [31].

The pH and Eh may negatively influence ion exchange and flocculation processes, applied after solvent extraction [26].

Extreme pH ranges can reduce microbial diversity and activity in bioremediation processes. Eh is generally not a factor for most PCB remedial alternatives.

Humic content consists of decomposed plant and animal residues and offers binding sites for accumulation of both organics and metals. High humic content in the contaminated soil/sediment has increasing energy requirements for thermal technologies. Solvent extraction, S/S and soil washing may be negatively affected due to strong absorption of the contaminants by the organic material. High humic content may also exert an excessive oxygen demand adversely affecting bioremediation.

Total organic carbon (TOC) provides an indication of the total organic material present, which is used as an indicator of the amount of waste available for biodegradation [31]. TOC includes carbon from both naturally occurring organic material and organic chemical contaminants. Natural organic carbon in soil may compete in redox reactions requiring more chemical reduction/oxidation reagents [31].

In situ bioremediation can be negatively influenced by the impeding effects of clay zones [29]. *Ex-situ* solid phase bioremediation requires tight controls on soil moisture content and the periodic addition of amendments would be impaired by soils with high clay content.

Biochemical Oxygen Demand (BOD) provides an estimate of the biological treatability of the soil contaminants [31]. Chemical oxygen demand (COD) is a measure of the oxygen equivalent of organic content that can be oxidized by a strong chemical oxidant. Sometimes BOD and COD can be correlated, and COD can give another indication of biological treatability or treatability by chemical oxidation [31].

Oil and Grease (O&G) coating of soil particles tends to weaken the bond between soil and cement in cement based solidification [27]. O&G can also interfere with reactant-to-waste contact in chemical reduction/oxidation reactions, thus reducing the efficiency of those reactions [31].

These considerations pertain to contaminated sediments, specifically excavated sediments treated *ex-situ* [01]. Certain PCB remediation technologies are space limiting, requiring waste preparation equipment, heavy construction equipment, stockpile areas, equipment staging areas, residual treatment systems and large process units. Technologies that typically require more space to operate include incineration, thermal desorption and soil washing systems [35].

Many of these systems require direct access to the area of contamination to maneuver and hook up trailer mounted treatment equipment.

When selecting a remedial alternative, it is important to assess potential impacts to the surrounding community. Plans may need to be put in place to control fugitive emissions (off gases), dust, noise, and the extra traffic that accompany many remedial activities. Special care should be taken, and management systems put in place to control/capture PCB contaminated dust that might be generated during the excavation, processing, and staging of contaminated soil. Measures also should be considered to control contaminant leaching and runoff. Systems should be put in place to control fugitive emissions from thermal treatment systems [35].

Analytical and spatial variability in PCB concentrations can be significant. Current characterization data, combined with data from previous site investigations, should provide accurate mapping of PCB contamination across the site. Issues related to the different methods of PCB analysis include which methods are appropriate for a specific site and remedial objectives. PCB analyses can be congener, homolog, or Aroclor specific; or for total PCBs with congener specific providing more valuable information. It is important to note that light and dense non aqueous phase liquids (LNAPLs and DNAPLs) are often present in PCB contaminated soil and sediment. NAPL co-contamination can greatly impact the effectiveness of the approaches for site characterization and remedial activities. Volume, distribution, concentration, and the predominant PCB species found at a site are critical aspects in the overall technology selection process as well as for appropriate sizing of treatment unit processes.

Treatability testing is important because characterization of the waste alone may be insufficient to predict treatment performance or to estimate the size and cost of appropriate treatment units. Treatability studies, which can include a combination of bench- and pilot-scale tests, provide data to assess whether the technology can meet the cleanup goals, as well as establish design and operating parameters for optimization of technology performance [36]. Treatability studies may also help identify any matrix interferences or pretreatment requirements and appropriate residual treatment options. The presence of PCBs with other contaminants in soil often creates site-specific treatment problems. In addition, many advantages and limitations should be considered in the tradeoffs of dredging versus leaving PCB contaminated sediment in place. Current information on remedial approaches for contaminated sediment can be found at the following reference: U.S. Environmental Protection Agency, Contaminated Sediments in Superfund web site: http://www.epa.gov/superfund/health/conmedia/sediment [37].

## 3.0 TECHNOLOGY DESCRIPTIONS

This section presents technologies used to remediate PCB contaminated soils and sediments by containment, treatment, or destruction of the PCB waste material. The technologies are classified under the heading of Established or Alternative Technology. Established technologies are those that have been used at the full scale level to successfully meet PCB cleanup goals at multiple sites and are commercially available.

Specific treatment and destruction technologies are allowed by U.S. regulations for certain types of PCB wastes. Alternative technologies are considered if the performances of these technologies meet site specific clean-up requirements. Table 2 lists the advantages of several PCB treatment/destruction technologies, and Table 3 lists the limitations associated with these same technologies. These technologies are discussed in more detail below.

According to information from “Treatment Technologies for Site Cleanup; Annual Status Report (Twelfth Edition).” [38], “Superfund Remedy Report, thirteenth Edition” [39], and CERCLIS [40] when exculding landfilling, Incineration, Solidification, and Thermal Desorption have been the predominante remediation technologies.

### 3.1 Incineration

#### *3.1.1 Technology Description*

Incineration treats organic contaminants in solids and liquids by subjecting them to temperatures typically greater than 760°C (1,400°F) in the presence of oxygen, which causes volatilization, combustion, and destruction of these compounds [41, 42]. The primary factors affecting the design and performance of the system are the furnace temperature, residence time, and turbulence required to expose the combustible material to oxygen in order to obtain complete combustion [31]. The U.S. EPA has approved high efficiency incinerators to destroy PCBs with concentrations above 50 mg/kg. Incinerators destroying PCB liquids must meet technical requirements of 2 second residence time at 1200°C (2192°F) and 3% of excess oxygen, or 1.5 second residence time at 1600°C (2912°F) and 2% of excess oxygen in the stack gases. The destruction and removal efficiency (DRE) for non-liquid PCBs must be equivalent to 99.9999% (less than 1 mg/kg).

**Table 2.** Advantages of Technology Alternatives for Remediating PCB Contaminated Soil and Sediment

| Advantages | Incineration | Landfill | Thermal Desorption* | Chemical Dehalogenation | Solvent Extraction | Soil Washing | S/S | Bioremediation** | Vitrification |
|---|---|---|---|---|---|---|---|---|---|
| Reduces high concentrations to cleanup goals | ▼ | | ▼ | ▼ | ▼ | | | | |
| Destroys PCBs | ▼ | | | ▼ | | | ▼ | ▼ | ▼ |
| Separates PCBs | | | ▼ | ▼ | ▼ | ▼ | | | |
| Immobilizes PCBs | | | | | | | ▼ | | ▼ |
| Can be implemented *in-situ* | | | | | | | ▼ | | ▼ |
| Effective across wide range of soil/sediment characteristics | ▼ | ▼ | | | | | | | ▼ |
| Effective on inorganic co-contaminants | | ▼ | | | | ▼ | ▼ | | ▼ |

* *In-situ* thermal desorption systems have been demonstrated to be effective.

** *Ex-situ* bioremediation systems. In situ systems are innovative and have not been demonstrated to be effective.

Notes: Technologies for which a specific advantage is applicable are identified by a "▼".

1—After destruction residual PCBs are encapsulated in vitrified mass.

Source: Ref [39]. Derived from technology experts and EPA Engineering Bulletins.

The primary stages for incineration are: waste preparation, waste feed, combustion, and off gas treatment. Waste preparation includes excavating and/or transporting the waste to the incinerator. Depending on the feed requirements of the incinerator, classification equipment may be needed to remove oversized particles and obtain the necessary feed size for soil and sediment. Blending of the soil or sediment and size reduction are sometimes required to achieve a uniform feed size, moisture content, thermal value, and contaminant concentration [43, 44, 46, 48]. The waste feed mechanism, which varies with the type of incinerator, introduces the waste into the combustion system. The feed mechanism sets the requirements for waste preparation. Bulk solids are usually shredded; contaminated media are usually ram or gravity fed [47, 48].

In the combustion stage, the four major systems are: rotary kiln, circulating bed combustor (CBC), circulating fluidized bed (CFB), and infrared combustion [46, 48]:

Rotary Kilns operate at temperatures up to 982°C (1,800°F). A refractory lined, slightly inclined, rotation cylinder serves as the combustion chamber. There are many commercial designs most commonly equipped with an afterburner, a quench, and an air pollution control system to remove particulates and neutralize acid gases (HCI, NOx, and SOx) [47]. Baghouses, venturi scrubbers, and wet electrostatic precipitators remove particulates. Packed bed scrubbers and spray dryers remove acid gases [46, 48].

A Circulating Bed Combustor (CBC) operates at lower temperatures than conventional incinerators 788°C (1,450°F) to 872°C (1600°F). It uses high velocity air resulting in a high turbulence that produces a uniform temperature zone around the combustion chamber and hot cyclone. This completely mixes the waste material in the combustion zone destroying toxic hydrocarbons. The effective mixing and low combustion temperature reduce potential emissions of such gases as nitrogen oxide (NOx) and carbon monoxide (CO) [46, 48].

- A Circulating Fluidized Bed (CFB) operates at temperatures up to 872°C (1,600°F). It uses high velocity air to circulate and suspend the waste particles in a combustion loop [46, 48].
- Infrared Combustion (IC) operates at up to 1010°C (1,850°F) using electrically powered silicon carbide rods to heat organic wastes to combustion temperatures. Waste is fed into the primary chamber and exposed to infrared radiant heat provided by silicon carbide rods above the conveyor belt. Blowers deliver air to selected locations to control oxidation

rate of the waste feed with remaining combustibles incinerated in an afterburner [46, 48, 49].

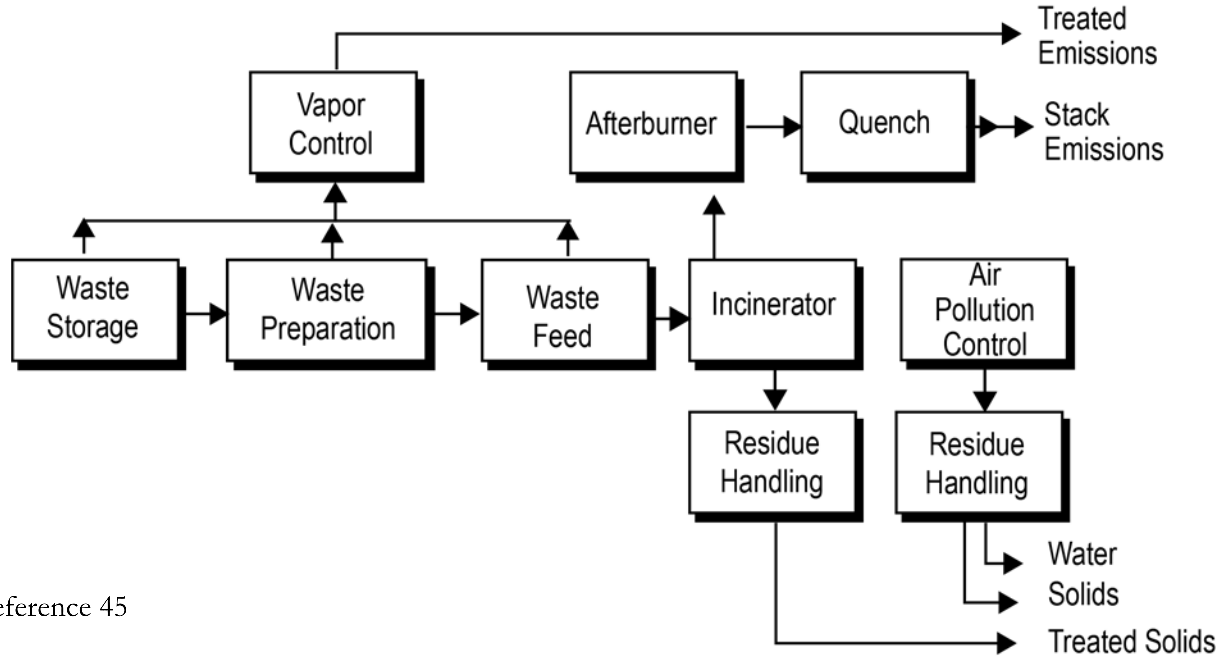
Off gases from the incinerator require treatment by air pollution control (APC) equipment to remove particulates, capture and neutralize acid gases, and capture dioxins if present. A process schematic of a typical mobile incineration unit is depicted in Figure 1. The major waste streams generated by incineration are: solids from the incinerator and APC system, water from the APC system, and emissions from the incinerator. Ash is either air cooled or quenched with water after discharge from the combustion chamber. In the case of water quenched ash, dewatering may be required before additional handling or treatment occurs. Solidification/stabilization (S/S) may also be necessary if the ash contains leachable metals at concentrations above the regulatory limits. The alkalinity of the matrix may influence the leachability of the ash [50]. The flue gases from the incinerator are treated by APC systems, such as cyclones, venturi scrubbers, wet electrostatic precipitators, baghouses, packed scrubbers, and chiller condensers before discharge through a stack. A low pH (acidic) liquid waste can be generated by the APC system. This waste may contain high concentrations of chlorides, volatile metals, trace organics, metal particulates, and other inorganic particulates. Wastewater requiring treatment may be subjected to neutralization, chemical precipitation, reverse osmosis, settling, evaporation, filtration, or carbon adsorption before discharge [34].

In order to properly design an on-site incineration unit, additional information is needed on the PCB contaminated matrix. This information includes soil moisture content, particle size distribution (PSD), soil fusion temperature and soil heating value. A sieve analysis is required to account for the dust loading in the system for proper design of the air pollution control equipment [51, 52].

### *3.1.2 Applications*

Economic reasons are often a key factor in determining whether mobile, transportable, fixed, or off site commercial incineration will be used at a given site [33]. Many companies have built incinerators that are actively used in the remediation of Superfund sites. Scaled down versions are portable. Portable incinerators are trailer mounted versions of conventional rotary kiln or fluidized bed incinerators with thermal capacities of 10 to 20 million British thermal units per hour (Btu/hr). However, portable units as large as 80 million BTU/hr are available. At large sites where the cleanup times are expected to be of several years' duration, it is often more feasible to construct an incinerator on site. Standard 440 V, three-phase electrical service is generally needed. A continuous water supply must be available at the site. Auxiliary fuel for feed Btu enhancement may also be required. Incinerators must be designed and operated to meet the 99.9999% Destruction and Removal Efficiency (DRE) required for PCBs. The potentially toxic residuals (ash) that are generated require further processing and disposal. Cost is generally sensitive to the volume of soil being treated [43, 45, 49]. A comparison of the advantages of incineration to other PCB remediation systems is depicted in Table 2.

**Figure 1.** Typical Mobile/Transportable Incineration Process



Reference 45

**Table 3.** Limitations of Technology Alternatives for Remediating PCB Contaminated Soil and Sediment

| Limitations | Incineration | Landfill | Thermal Desorption | Chemical Dehalogenation | Solvent Extraction | Soil Washing | S/S | Bioremediation | Vitrification |
|---|---|---|---|---|---|---|---|---|---|
| High moisture content adversely affects treatment | | | | ▼ | | | ▼ | | ▼ |
| PCBs must be destroyed by another technology | | | ▼ | | ▼ | | | | |
| Produces other residuals that must be treated and/or disposed | ▼ | | | ▼ | ▼ | | | | ● |
| Sensitive to media particle size, clay content, and/or pH | | | | ▼ | ▼ | ▼ | ▼ | ▼ | |
| Not proven to treat all PCB congeners | | | | ▼ | | | ▼ | ▼ | |
| Sensitive to co-contaminants | ▼ | | ▼ | ▼ | | | ▼ | ▼ | |
| Off gases must be treated prior to release | ▼ | | ▼ | ▼ | | | | | ▼ |
| Volume and/or characteristic changes to treated media | | | | | | ▼ | ▼ | | ▼ |
| Potentially affected by ambient temperature extremes | | | | | | ▼ | ▼ | ▼ | |
| Difficult to measure effectiveness of treatment | | ▼ | | | | | ▼ | ▼ | ▼ |
| Long term monitoring required | | ▼ | | | | | ▼ | | |

- Notes: Technologies for which a specific limitation is applicable are identified by a " ▼ ".
- Limitations that only apply the *ex-situ* subgroup of a technology are identified by a "●"
- Source: Ref. [37, 38]

### *3.1.3 Performance*

Incinerator performance is most often measured by comparing initial PCB concentrations in feed materials with both final concentrations in ash (i.e. destruction and removal efficiency DRE) and concentrations present in off gas emissions. Incinerators burning non-liquid PCB wastes must meet the performance and monitoring requirements. A substantial body of trial burn results and other quality assured data exist to verify that incinerator operations remove and destroy organic contaminants from a variety of waste matrices to parts per billion or even parts per trillion levels, while meeting stringent stack emission and water discharge requirements.

### *3.1.4 Limitations*

The applicability of incineration to the remediation of PCB contaminated soil or sediment may be limited by the types and concentrations of metals present in the medium [53]. When soil or sediment containing metals are incinerated, the metals vaporize, react to form other metal compounds, or remain with the soil residuals. Metals in ash, scrubber sludge, or stack emissions, if improperly managed, can result in potential exposures and adverse health effects [54]. Metals commonly found in association with PCB contamination volatilize at most incinerator operating temperatures and must be captured before process off gases are released into the atmosphere. Therefore, it is important to adequately characterize the metal content of the soil or sediment when considering incineration systems for PCB treatment [54]. Metals can also react with chlorine and sulfur in the feed stream, forming other volatile and toxic compounds. High levels of potassium and sodium in the waste stream can form low melting point particulates that can attack the refractory tile lining and form particulates that foul the gas ducts [43, 45, 49].

A comparison of the limitations of incineration systems to those of other PCB remediation systems is depicted in Table 3.

### 3.1.5 Case Studies

Some examples of recent commercial applications of incineration systems are presented in Table 4. Incineration technologies have been selected as the remedial action for at least 36 Superfund sites with PCB contaminated soils or sediments [11, 42, 57, 58].

## 3.2 Landfill Disposal

### 3.2.1 Technology Description

Landfill disposal is one of the most common methods for disposal of PCB contaminated media. Landfills are tightly compacted and generally anaerobic, where little degradation occurs. It is used to cover buried waste materials to prevent contact with the environment and to effectively manage the human and ecological risks associated with those wastes. For most wastes, especially persistent substances like PCBs, burial in landfills is not considered a destruction technology; rather, a method of disposal and containment. Confined disposal facilities (CDFs) are also used at some sites to contain PCB contaminated sediments, but these are not discussed in detail in this paper. In general, CDFs are designed to physically contain a volume of dredged sediment; to provide management and removal of water associated with the sediment; and to provide environmental protection from contaminants [57]. Dredged sediments may be temporarily stored in a CDF, dewatered, and then transported to an off-site landfill for permanent disposal.

Commercial, private, or municipal solid waste landfills, with potentially reduced costs and increased throughput, may provide another option for RPMs. However these landfills must be authorized to accept PCB contaminated wastes. Private landfills may provide an option other than the 10 TSCA approved commercial landfills. A comparison of the advantages of landfill disposal to those of other PCB remediation systems is depicted in Table 2.

### 3.2.2 Applications

Landfill disposal of PCB contaminated soil and sediment is relatively inexpensive compared to other available treatment technologies. Landfill disposal costs are mostly those of transportation and disposal rather than treatment, and disposal is often the most economical choice for waste remediation. TSCA landfills capable of taking more than or equal to 50 mg/kg PCB soil/sediment have yearly tonnage acceptance limits. These limits are determined by the state in which they are located and are specified in the landfill's operating permit. These landfills are set up to receive large quantities of materials, often by rail shipment, thereby further reducing the overall costs of disposal by lowering the material handling costs. Residuals from other PCB treatment technologies may require landfill disposal.

### 3.2.3 Performance

There are specific design and operating criteria for chemical waste landfills in the United States. Landfill site soils should be of sufficient depth and relatively impermeable (i.e. large area clay pans). If this is not possible, soil should have high clay and silt content, or a synthetic membrane liner with a minimum thickness of 30 mils should be used to meet the permeability criteria. The location of the bottom of the landfill must be at least 50 feet above the historically high groundwater table. Floodplains, shore lands, groundwater recharge areas, and standing or flowing water should be avoided. The site should have monitoring wells and leachate collection [08]. Disposal steps include excavation of the waste material, thorough containment and transport of the material to a licensed landfill, and placement in the landfill according to specified procedures.

### 3.2.4 Limitations

Landfill disposal of PCB contaminated soil and sediment does not provide waste reduction or destruction, only containment. Persistent substances like PCB wastes will remain in landfills for long periods of time with little degradation.

For disposal in municipal/industrial or TSCA landfills, it is necessary that no free liquid is present in the disposal materials. Therefore, it is typical that the material must pass the RCRA paint filter test to be accepted (Method 9095 to

**Table 4.** Commercial Application of Incineration Systems at PCB Contaminated Soil/Sediment Superfund Sites

| Site | Media Treated | Status | Results |
|---|---|---|---|
| **On-Site Mobile Incineration System** | | | |
| New Brighton/Arden HillsNew Brighton, MN | 1,400 yd$^3$ soil | | Initial: 71 mg/kg<br>Final: <2 mg/kg<br>Standard: <2 mg/kg |
| Rose Township Dump<br>Holly, MI | 24,300 yd$^3$ soil | Infrared Incinerator with silicon carbon rods-dual chamber<br>Operational from 9/1992 to 10/1993 | Initial: 980 mg/kg<br>Final: <1 mg/kg<br>Standard: <1 mg/kg |
| Rose Disposal Pit<br>Lanesborough, MA | 36,428 yd$^3$ soil | Rotary kiln with secondary chamber<br>Operational from 3/1994 to 6/1994 | Initial: 500 mg/kg<br>Final: 0.062 mg/kg (9.99987% DRE)<br>Standard: 13 mg/kg (99.9999% DRE) |
| Coal Creek<br>Chehalis, WA | 6477 yd$^3$ soil | Rotary kiln with secondary chamber<br>Operational from 1/1994 to 5/1994 | Initial: 21,000 mg/kg<br>Final: 99.9997% DRE<br>Standard: 99.9999% DRE |
| Bridgeport Rental & Oil Services<br>Logan Township, NJ | 3,035 yd$^3$ soil<br>9,285 yd$^3$ sediment | Rotary kiln with secondary chamber<br>Operational from 12/1991 to 1/1996 | Initial: > 500 mg/kg<br>Final: 99.9997% DRE<br>Standard: 99.9999% DRE |
| Sangamo Electric Dump/ Crab Orchard National Wildlife Refuge<br>Caterville, IL | 117,145 yd$^3$ soil | Rotary kiln. Operational from 6/1996 to 6/1997 | Initial: 980 mg/kg<br>Final: <1 mg/kg<br>Standard: <1mg/kg |
| **Off-Site Incineration** | | | |
| Industrial Latex Corp.<br>Wallington Borough, NJ | 12,048 gallons of flammable PCB solids | 1986 | |
| Northwest Transformer<br>Everson, WA | 265 tons soil | Aptus Incinerator, Utah | Initial: 5,000 mg/kg<br>Final: 99.9999% DRE<br>Standard: 99.9999% DRE |
| MW Manufacturing<br>Valley Township, PA | 875 yd$^3$ carbon black and 800 drums of PCB contaminated wastes | Rotary kiln. Operational from 1990 to 1992 | Additional treatability testing indicated incineration of fluff caused dioxin problems |
| FAA Technical Center<br>Atlantic County, NJ | 930 yd$^3$ soil | Rotary Kiln | Initial: 9 - 836 mg/kg<br>Final: <1 mg/kg<br>Standard: 5.0 mg/kg |

Reference 11, 40, 55, 56

**Table 5.** PCB and Chemical Waste Landfills

| Company | Address | Phone |
|---|---|---|
| Republic Waste Services of Texas Limited (a.k.a. Republic CSC Landfill) | 101 Republic Way, P.O. Box 236<br>Avalon, TX 76623 | 800-256-9278 |
| Waste Control Specialists, LLC | 9998 West Hwy 176, P.O. Box 1129, Andrews, TX 79714 | 888-789-2783 |
| Chemical Waste Management Chemical Services | 1550 Balmer Road, Model City, NY 14107 | 716-754-8231 |
| Waste Management Inc | Alabama Inc. , Box 55, Emelle, AL 35459 | 205-652-9721 |
| Wayne Disposal Inc. | 1349 Huron St., South Belleville, MI 48197 | 313-480-8085 |
| Clean Harbors Grassy Mountains, LLC | P.O. Box 22750, Salt Lake City, UT 84122 | 435-884-8900 |
| Chemical Waste Management | Box 471, Kettleman City, CA 93239 | 559-386-9711 |
| U.S. Ecology, Inc. | Box 578 , Beatty, NV 89003 | |
| Chemical Waste Management of the Northwest | 17639 Cedar Spring Land, Box 9, Arlington, OR 97812 | 503-454-2643 |
| US Ecology Idaho | PO Box 400, 20400 Lemley Road, Grand View, ID 83624 | 208-834-2275 |

Reference [58]

determine free liquids in waste). This may require pretreatment by processes such as thermal desorption to dewater the contaminated waste prior to landfill disposal. Disposal in private landfills creates a continuing liability issue for the owner, also monitoring at the waste site must be performed indefinitely to meet clean closure requirements. There may be some public opposition to the use of landfills. A comparison of the limitations of landfill disposal to those of other PCB remediation systems is depicted in Table 3.

#### *3.2.5 Case Studies*

Currently, there are 10 commercial TSCA approved landfills in the USA, not including private TSCA approved landfills (Table 6).

General Electric (GE) sited two landfills on property they own near the Housatonic River site. One landfill was built to TSCA standards to receive material >50 mg/kg, and the other for material <50 mg/kg. Because of proximity to the removal area the transportation costs are minimal, although there are costs associated with permitting, building, and maintaining the landfills [59].

Excavation and disposal in an offsite TSCA permitted landfill is another commonly used option as was demonstrated for dredged PCB contaminated sediments at the Ashtabula River clean up. The river was dredged of 500,000 cubic yards of PCB contaminated sediment that was pumped to a polishing bag field with effluent water treated with clarification followed by sand and carbon treatment [60].

### 3.3 Thermal Desorption

#### *3.3.1 Technology Description*

Thermal desorption is an *ex-situ* and in situ technology that physically separates volatile and semi-volatile contaminants from soil, sediment, sludge, and filter cake by heating the matrices at temperatures high enough to volatilize the organic contaminants. It is a physical separation process and is not designed to destroy organics [51]. Air, combusted flue gas, or an inert gas is used to transfer vaporized contaminants from the medium. The chamber temperatures, usually between 93°C (200°F) and 538°C (1,000°F) and residence times (site-specific) used by thermal desorption systems will volatilize but typically neither oxidize nor destroy organic contaminants, [34, 52]. Thermal desorption utilizes either a direct or indirect heat exchange [31].

The primary stages of a typical thermal desorption system are materials preparation, desorption, particulate removal, and off gas treatment. Most *ex-situ* soil thermal desorption systems use similar feed systems consisting of a screening device to separate and remove materials greater than 2 inches, a belt conveyor to move the screened soil from the screen to the desorption chamber, and a weight belt to

**Table 6.** Commercial Application of Ex-situ Thermal Desorption Systems at PCB Contaminated Soil/Sediment Superfund Sites

| Site | Media Treated | Status | Results |
|---|---|---|---|
| Fields Brook<br>Ashtabula, OH | 21,855 yd$^3$ soil and sediment | Operational from 6/2002 to 12/2002 | Initial: 41,000 mg/kg<br>Final: 2 mg/kg<br>Standard: 1.3 mg/kg sediment & 3.1 mg/kg soil |
| Universal Oil Products (Chemical Division)<br>East Rutherford, NJ | 8,200 tons soil | Process proved inefficient to achieve clean up goals. Remedy change to off-site disposal | Initial: 2,000 mg/kg<br>Final: 2 mg/kg<br>Standard: 2 mg/kg |
| Industrial Latex Corp.<br>Wallington Borough, NJ | 53,600 yd$^3$ soil | Operational from 9/1997 to 9/2001 | Initial: 4,000 mg/kg<br>Final: 1 mg/kg<br>Standard: 1mg/kg |
| Acme Solvent Reclaiming, Inc.<br>Morristown, IL | 6,000 yd$^3$ soil | Operational from 6/1994 to 9/1994 | Initial: 290 ppb<br>Final: 1 ppb<br>Standard: 10 ppb |
| Re-Solve, Inc. | 36,000 yd$^3$ soil | Operational from 4/1995 to 3/1996 | Initial: 247 mg/kg<br>Final: 0.13 mg/kg<br>Standard: 25 mg/kg |
| Sangamo/Twelve-Mile/Hartwell PCB, Pickens, SC | 40,700 yd$^3$ soil<br>7,500 yd$^3$ sediment | Operational from 12/1995 to 5/1997 | Initial: 40,000 mg/kg<br>Final: <2 mg/kg<br>Standard: <2 mg/kg |
| Smith's Farm<br>Brooks, KY | 21,000 yd$^3$ soil and sediment | Anaerobic low temperature desorber. Completed 9/1995 | Initial: 300-500 mg/kg<br>Final: 3-25 mg/kg<br>Standard: 2 mg/kg |

Reference 11, 38, 53, 54

measure soil mass. Augers are occasionally used in place of belt conveyors, but either type of system requires regular maintenance and is subject to system failure. Soil conveyors in large systems seem more prone to failure than those in smaller systems. Size reduction equipment can be incorporated into the feed system, but its installation into a continuous feed system is usually avoided to minimize shutdown as a result of frequent equipment failure and jamming [34, 52]. Directly heated thermal desorption units primarily transfer heat through radiation and convection from the carrier gas to the contaminated soil/sediment. In a direct heat unit, the burner exhaust gases are mixed with the waste and volatilized contaminants. Contaminants are volatized and swept with the burner combustion products to the emission control system for treatment, typically more energy/cost effective than indirectly heated units [51].

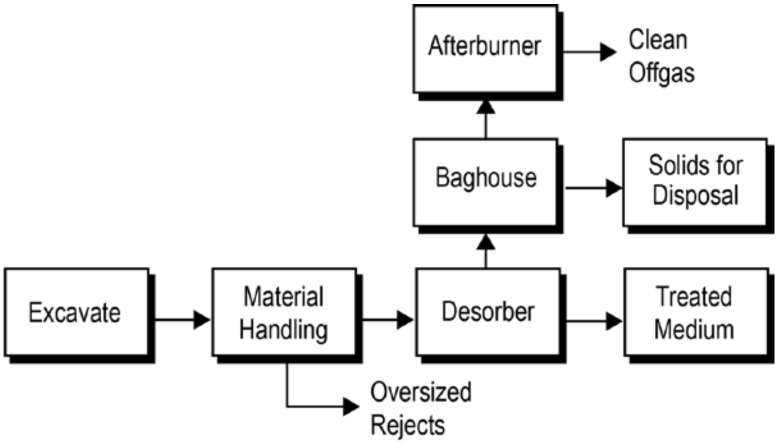
Indirectly heated thermal desorption units usually transfer heat by conduction, or by electrical resistance heaters to the contaminated soil/sediment, or by convection through an indirectly heated gas stream. In either case burner exhaust gases never come into contact with the contaminated matrix. Contaminants are volatilized and exhausted to the emission control system for treatment. Burner combustion products do not mix with volatilized contaminants and are exhausted to separate stacks, reducing the volume of contaminated gas and size of emission control equipment required. Indirectly heated thermal desorption units typically are less sensitive to waste heating values and potential heat releases than directly heated units. Thermal screws are well suited for treating high moisture content sediments. The principal differences between direct and indirect units are the extent to which air emissions can be controlled and the treatment capacity (which directly impacts operational costs) [51].

Two common thermal desorption designs are the rotary dryer and thermal screw. Rotary dryers are horizontal cylinders that can be directly or indirectly heated. The dryer is normally inclined and rotated. For the thermal screw units, screw conveyors or hollow augers are used to transport the medium through an enclosed trough. Hot oil or steam circulates through the auger to indirectly heat the medium. The thermal screw design has been found to require more waste pretreatment than the rotary dryer design, and may be more costly to use [36]. All thermal desorption systems require treatment of the off gas to remove particulate and other contaminant emissions and vapors. Most of these units are transportable [52].

Based upon the operating temperature of the desorber, thermal processes can be further categorized into two groups: high temperature thermal desorption (HTTD) and low temperature thermal desorption (LTTD) [45, 52]. HTTD is a full scale technology in which wastes are heated to 316°C (600°F) to 538°C (1,000°F). HTTD is frequently used in conjunction with incineration, S/S, and/or dechlorination, depending on site-specific conditions [45, 52] (see Table 1). For LTTD processes, wastes are heated to between 93°C (200°F) and 316°C (600°F). LTTD is a full scale technology that has been successful for remediating petroleum hydrocarbon contamination in all types of soil. Contaminant destruction efficiencies in the afterburners of these units are reportedly greater than 95%. Desorbed soil retains its physical properties. Unless heated to the higher end of the LTTD temperature range, organic components in the soil are not damaged, which enables treated soil to retain the ability to be used and support biological activity [45, 52]. Process diagrams of a typical low and high temperature thermal desorption unit are shown in Figures 2 and 3, respectively.

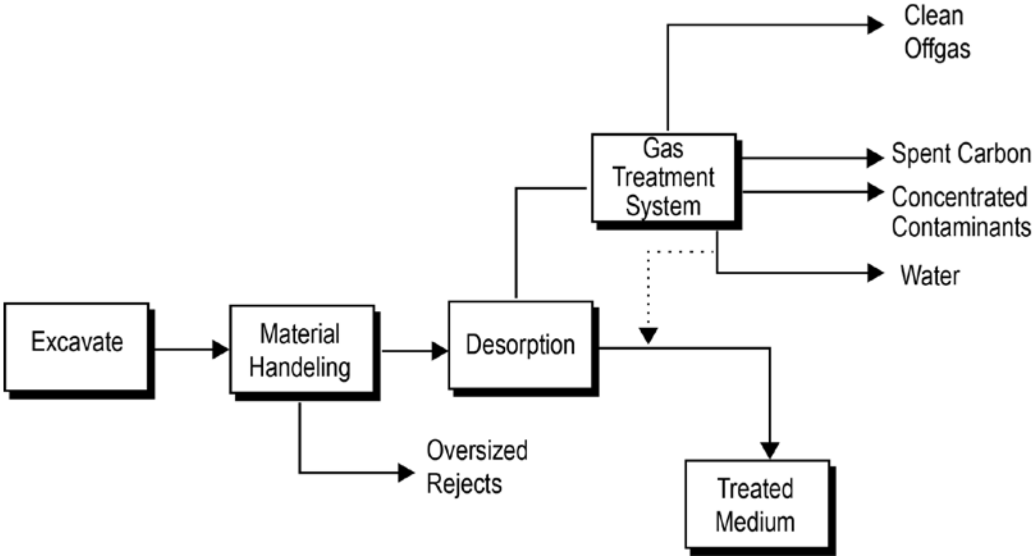
Operation of *ex-situ* thermal desorption systems can create up to eight process residual streams: treated medium, oversized medium and debris rejects, condensed contaminants, water, particulate control system dust, clean off gas, spent carbon, and aqueous phase activated carbon. Treated medium, debris, and oversized rejects may be suitable for replacement on site or require off-site disposal. Particulates

**Figure 2.** Typical Thermal Desorption Process with an Afterburner



Reference 45

**Figure 3.** Typical Thermal Desorption Process with Noncombustion Gas Treatment



Reference 45

are removed by conventional particulate removal equipment, such as wet scrubbers, cyclones and baghouses. Baghouses may become contaminated with dioxins if operated above 232°C (450°F) and require further decontamination. Collected particulates may still be contaminated, and may be recycled into the feed stream for retreatment or treated as a separate waste stream. In situations where PCB contaminants must be recovered from the system exhaust, emission control can be achieved using a secondary combustion chamber (afterburner), a catalytic oxidizer, chiller condenser, or activated carbon adsorption. The selection of the gas treatment system will depend on the concentrations and types of contaminants, air emission standards, and the economics of the off gas treatment system(s) used [61]. When a combustion process destroys off gas, compliance with incineration emission standards may be required [61]. In addition to the required monitoring and assessment of PCBs in thermal desorption waste streams, the possibility of dioxin/furan formation during thermal treatment of contaminated media should be considered [61]. In order to design an *ex-situ* thermal desorption system for a specific site, gathering characteristic information on the PCB contaminated matrix is essential. This information will include soil moisture content and particle size classification, determination of boiling points for various compounds to be removed, and treatability testing to determine the efficiency of the thermal desorption unit on a particular waste stream. A sieve analysis is required to account for the dust loading in the system for proper design of the air pollution control equipment [51, 52].

### 3.3.2 Applications

LTTD systems are more applicable to treatment matrices contaminated by nonhalogenated volatile organic compounds (VOCs) and fuels. LTTD systems experience reduced effectiveness when used to treat semi-volatile organic compounds (SVOCs). HTTD systems are more applicable to the treatment of PCB contaminated matrices, as well as soil, sediment and sludge contaminated by SVOCs, polycyclic aromatic hydrocarbons (PAHs), and pesticides. VOCs and fuels can also be treated by HTTD systems, but treatment by LTTD systems is generally more cost effective [51].

*Ex-situ* thermal desorption has been proven effective in treating organic contaminated (including PCBs) soil, sediment, sludge, and various filter cakes. *Ex-situ* thermal desorption is applicable to sites where the following conditions exist: the target matrix can be excavated or dredged readily for processing or the organic contaminants are amenable to desorption at kiln temperatures between 315°C (600°F) and 590°C (1,100°F). Within each solid waste type, the technology can accept a range of particle sizes, from granular to silty clays. Oversize material (e.g. debris) requires separation or size reduction prior to processing [45, 52].

*In-situ* processes have also been demonstrated for the thermal desorption of PCBs from contaminated soils. Thermal conductive heating (TCH) also called *in-situ* thermal desorption (ISTD), simultaneously applies heat and vacuum to the soil. Heat is applied through thermal wells, which operate at temperatures as high as 900°C (1650°F). Heat is conducted from the wells into the soil, reaching treatment temperatures of 300°C (572°F) or greater. Desorbed and volatilized contaminants are collected and treated above ground using thermal oxidization and/or carbon cannisters.

ISTD has the advantage of eliminating the need for excavation and materials processing, which can be a significant advantage when other infrastructures are present or for clay like soils that tend to cake during *ex-situ* thermal desorption. Because treatment temperatures of approximately 300°C (572°F) are required to effectively desorb PCBs, ISTD can only be applied above the water table or where the influx of water can be controlled. Thermal wells (ISTD) have been successfully demonstrated at pilot-scale at three sites and full scale at one site for the treatment of PCB contaminated soils and has been used at full scale at a large number of sites to treat other VOCs and SVOCs [1, 52]. For the treatment of shallow soils, the soils are excavated and treated ex situ in piles using horizontal heater wells installed in the soil pile. In this process, the soils to be treated are placed in a bermed area on an impervious surface, and heater elements, air injection, vapor extraction wells, and thermocouples are built into each pile. The soil pile is then covered by a vapor cap and insulation. Advantages of this approach over the customary *ex-situ* thermal desorption process include the fact that this system can treat larger debris and rock up to approximately one foot in diameter, it can handle materials such as ash, clinkers, brick, glass, etc., and it can be operated to reduce noise impacts without increasing the overall time of treatment.

Using thermal wells, a treatment time on the order of 40 days with well spacings of 5 feet and a depth of 12 feet reduced soil concentrations in tight clay from as high as 20,000 mg/kg to less than 1 mg/kg, with most post-treatment soil samples being below the detection limit of 0.033 mg/kg PCBs [62-65)].

### 3.3.3 Performance

Performance objectives must consider the existing site contaminant levels and relative cleanup goals for soil and sediment at the site. System performance is typically measured by the comparison of untreated solid contaminant levels with those of the processed solids. The actual bed temperature and residence time are primary factors affecting performance in thermal desorption. These factors are controlled in the desorption unit by using either a series of increasing temperature zones, multiple passes of the medium through the desorber where the operating temperature is sequentially increased, separate compartments where the heat transfer fluid temperature is higher, or sequential processing into higher temperature zones [66, 67].

### 3.3.4 Limitations

The technology is generally not effective in separating inorganics from the contaminated medium, which could pose a problem at certain sites where PCBs and heavy metals (e.g. lead) coexist. However, the presence of chlorine in the waste enhances the volatilization of some metals, including lead. Generally, as the chlorine content increases, so will the likelihood of metal volatilization [34]. Metals volatilizing may affect the gas treatment system and metals that are not volatilized may produce a treated solid residue that requires stabilization [45, 49, 51].

As the contaminated matrix is heated and passes through the desorber, energy is consumed in heating the moisture contained in the material. The target matrix must possess at least 20 percent solids content to facilitate placement of the waste material into the desorption equipment [68]. High moisture content (greater than 20 per cent) may result in lower contaminant volatilization, and a need to dewater/dry the soil prior to treatment to reduce the energy needed to volatilize the moisture.

Materials handling of soils that are tightly aggregated or plastic can result in poor processing performance due to caking. Clay and silty soils, along with soils with a high humic content, increase desorption time as a result of binding of contaminants. Rock fragments or solids greater than 1 to 2 inches may have to be crushed, screened, or reduced using other unit operations. Size limits depend upon the mechanical clearances in conveyer systems and heat transfer considerations. A highly abrasive feed can potentially damage the processor unit [45, 49, 51].

When a combustion process destroys off gas, compliance with incineration emission standards may be required [61]. Thermal desorption systems can produce dioxin/furans while operating under certain conditions [61. Factors promoting the formation of dioxins/furans include the existence of other chlorinated organic contaminants, addition of ferric chloride to sediments for dewatering, particulates and temperatures above 260°C (500°F) such as in a baghouse and long residence times at 650°C (1202°F) [69].

A comparison of the limitations of thermal desorption systems to those of other PCB remediation systems is depicted in Table 3.

### 3.3.5 Case Studies

*Ex-situ* thermal desorption technologies have been selected as the remedial action for at least 16 Superfund sites with PCB contaminated soils or sediments [11, 40, 55, 56]. Information on the application of thermal desorption for the treatment of PCB contaminated soil and sediment at some of these sites is presented in Table 7.

The U.S. EPA Superfund Innovative Technology Evaluation (SITE) Program, available at: http://www.epa.gov/nrmrl/lrpcd/site/reports.html, lists seven thermal desorption systems reportedly capable of treating PCBs in soil and sediment [70]. The time required to clean up a 20,000 ton site using *ex-situ* thermal desorption is approximately 4 months [70].

## 3.4 Solvent Extraction

### 3.4.1 Technology Description

Solvent extraction processes use solvents to treat contaminated solids in much the same way as they are commonly used by analytical laboratories to extract organic contaminants. Solvent extraction is an *ex-situ* physical process that uses chemical solvents under controlled pressure and temperature conditions to separate contaminants from soil and sediment, thereby reducing the overall volume of the hazardous waste to be treated [71]. The technology is generally applicable to solid matrices contaminated by organic contaminants. Solvent extraction is different from soil washing systems in that it uses an extracting chemical (non-aqueous) instead of water containing additives to separate out contaminants [33]. The chemical formulation of the extractant is often proprietary to the vendor; however, diisopropylamine has been used on PCB contaminated media [72]. Solvent extraction is commonly used in combination with other technologies, such as solidification/stabilization, incineration, and soil washing, depending on site-specific conditions. These systems vary with regard to the solvent employed, type of equipment used, and mode of operation.

Solvent extraction processes can be grouped into three general types: standard, liquified gas (LG), and critical solu-

**Table 7.** Commercial Application of Solvent Extraction Systems at Superfund Sites with PCB Contaminated Soil/Sediment

| Site | Remedy | Lead |
|---|---|---|
| Arctic Surplus - Fairbanks, AK | Solvent Extraction for PCBs >50 mg/kg; off-site disposal of soils <50 mg/kg PCBs. | Federal Lead / Fund Financed |
| Arrowhead Refinery Co. - Hermantown, MN | 7,000 $yd^3$ Soil and 4,600 $yd^3$ Sludge | PRP Lead / Federal Oversight |
| Carolina Transformer Co. - Fayetteville, NC | Excavation and on-site solvent extraction of soil and sediment >1 mg/kg PCBs; solidification of any excavated soil or sediment that does not meet the RCRA toxicity characteristic rule | Federal Lead / Fund Financed |
| Idaho National Engineering Laboratory (USDOE), ID | Solvent extraction, dehalogenation, dechlorination (unspecified) on site. | Federal Lead |

Reference 11, 38, 53, 54

tion temperature (CST) solvents. A schematic of a typical solvent extraction unit is depicted in Figure 4. The standard process uses alkanes, alcohols, ketones, or similar liquid solvents at or near ambient temperature and pressure. They operate in either batch or continuous mode and consist of four basic steps: extraction, separation, desorption, and solvent recovery [73]. The design of the extraction vessel varies from countercurrent, continuous flow systems to batch mixers. The ratio of solvent-to-solids varies, but normally remains within a range from 2:1 to 5:1. Separation of solids from liquids is achieved by allowing solids to settle and pumping the contaminant containing solvent to the solvent recovery system. Filtration or centrifugation can be used if gravity settling is insufficient.

Residual solids are processed with additional solvent washes until cleanup goals are achieved. Settled solids retain some solvent that must be removed usually by thermal desorption. Contaminant laden solvent, along with the solvent vapors removed during the desorption or raffinate stripping stage, are transferred to a distillation system. Condensed solvents are normally recycled to the extractor; this conserves solvent and reduces costs. Captured water may be evaporated or discharged from the system. Still bottoms, which contain high boiling point contaminants, are recovered for the future treatment or disposed of as hazardous waste.

The Liquified Gas (LG) process uses propane, butane, carbon dioxide, or other pressurized gases but still has the same basic steps associated with standard solvent extraction processes with some notable differences in operating conditions. Increased pressure and lower temperature are required for the solvent to take on LG characteristics. The extraction step can involve multiple stages, with feed and solvent moving in countercurrent directions [73]. The slurry in the extractor is vigorously mixed with the solvent by pumps or screw augers which move the contaminated feed through the process.

The solvent/solids slurry is pumped to a decanting tank where phase separation occurs. A reduction in pressure vaporizes the solvent, which is recycled, and the decontaminated slurry is discharged. Contaminated solvent is removed from the top of the decanter and is directed to a solvent recovery unit. The organic contaminants remain in the liquid phase and the solvent is vaporized and removed. The solvent is then compressed and recycled to the extractor.

The Critical Solution Temperature (CST) process uses the unique solubility properties of CST solvents to extract contaminants. CST uses extraction solvents whose solubility characteristics can be manipulated by changing the temperature of the fluid. Contaminants are extracted at one temperature where the solvent and water are miscible. The concentrated contaminants are separated from the decanted liquid fraction at another temperature where the solvent has minimal solubility in water (process referred to as inverse miscibility). The same basic process steps are used for the CST solvent extraction systems; however, the solvent recovery step consists of numerous unit operations [73].

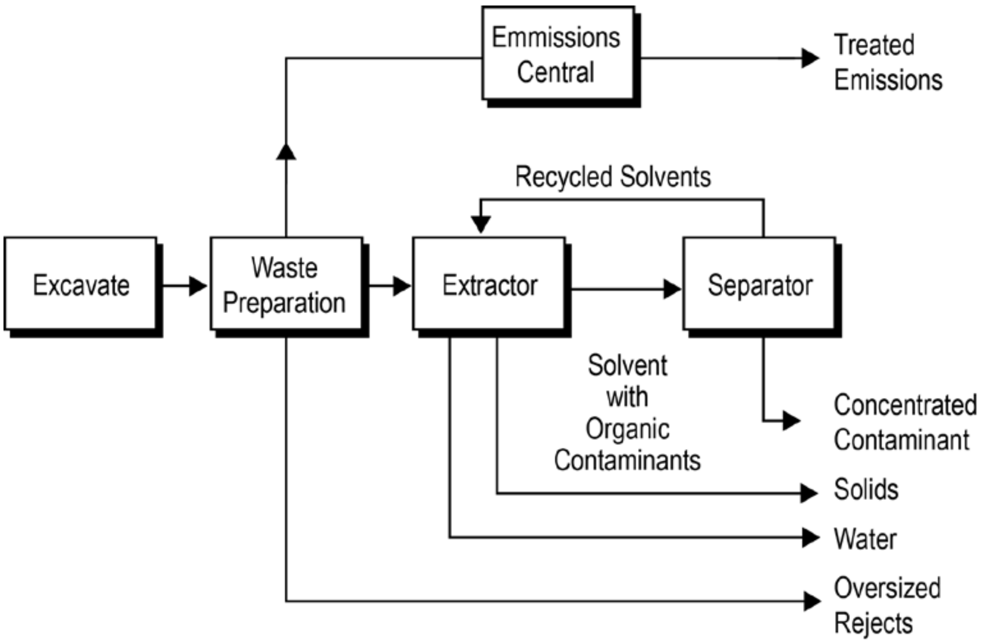
Implementation of the solvent extraction technology includes several stages: media preparation, contaminant extraction, solvent/media separation, contaminant collection, and solvent recycling. Pretreatment of the contaminated media is usually necessary. This may involve physical processing and, if needed, chemical conditioning after the contaminated medium has been excavated. Physical processing starts with excavation and dredging operations. It is followed by a series of material classification processes, which can include any combination of material classifiers, screens/sieves, shredders, and crushers. This phase reduces the size of the particles being fed into a solvent extraction process. Size reduction of particles increases the exposed surface area of the particles, thereby increasing extraction efficiency. Caution must be applied to ensure that an overabundance of fines does not lead to problems with phase separation between the solvent and treated solids. The optimum particle size varies with the type of extraction equipment used [33]. In the next phase, an extractor is used to dissolve the organic contaminant into the solvent. Then the extracted organics are isolated along with the solvent and go into a separator, where the pressure and temperature are optimized to separate the organic contaminant from the solvent phase [30]. The solvent is recycled to the extractor and the concentrated contaminants are removed from the separator [72].

Three main process streams are generated by this technology: the extract containing concentrated contaminants, the treated soil or sediment, and the separated water. The extract contains contaminants concentrated into a smaller volume, which requires further treatment such as incineration, dehalogenation, and/or thermal desorption [33, 73]. Depending on the system used, the treated solids may need to be dewatered, creating both a dry solid and a separate water stream. The water requires analysis to determine whether treatment is necessary prior to discharge. Because the solvent is an organic material, a solvent residue may remain in the soil matrix. This can be mitigated by selection of an appropriate solvent, and if necessary, an additional separation stage. Concentrated contaminants normally include organic contaminants, O&G, naturally occurring organic substances found in the feed solids, and extraction fluid. Concentration factors may reduce the overall volume of contaminated material to 1/10,000 of the original waste volume depending on the volume of the total extractable fraction. The resulting highly concentrated waste stream is either incinerated or collected for reuse. Particular soil properties that should be determined beforehand include: pH, partition coefficient, cation exchange capacity, organic content, toxicity characteristic leaching procedure (TCLP) for leachable metals and volatiles, moisture content, clays, and complex waste mixtures.

### *3.4.2 Applications*

Solvent extraction has been shown to be effective in treating sediment, sludge and soil containing primarily organic contaminants such as PCBs, VOCs, halogenated solvents, and petroleum wastes. It is least effective on very high molecular weight organics and very hydrophilic substances. The process has been shown to be applicable for the separation of the organic contaminants in paint wastes, synthetic rubber process wastes, coal tar wastes, drilling muds, wood treatment wastes, separation sludges, pesticide/insecticide wastes, and petroleum refinery oily wastes [45, 49, 73]. The rate limitations of extraction technology

**Figure 4.** Typical Solvent Extraction Process



Reference 45

are typical of a mass transfer controlled kinetic process, although equilibrium phase partitioning considerations often become limiting factors. It is important to conduct a laboratory scale treatability test to determine whether mass transfer or equilibrium partitioning will be the controlling factor. Often irreversible partitioning into organic rich medium can limit the effectiveness of solvent extraction to PCB remediation. The controlling factor is critical to the design of the unit and to the determination of whether the technology is appropriate for the waste [33, 73].

Inorganics usually do not have a detrimental effect on the extraction of organic components, and may have a beneficial effect by changing the metals to a less toxic or leachable form. When treated solids leave the extraction subsystem, traces of extraction solvents are present [45, 49, 73]. The typical extraction solvents used in currently available systems either volatilize quickly from the treated solids or may biodegrade. Ambient air monitoring can be used to determine if the volatilizing solvents present a problem. Some commercial extraction systems have used solvents that are flammable, toxic or both [45, 49, 73].

### 3.4.3 Performance

The performance of solvent extraction systems is usually determined by comparing initial and final PCB concentrations in the contaminated medium. The most significant factors influencing performance are the waste volume, the number of extraction stages, and operations and maintenance (O&M) parameters. Extraction efficiency can be influenced by process parameters such as solvent used, solvent/waste ratio, throughput rate, extractor residence time, and the number of extraction stages. Performance data have indicated concentration factors of up to 10,000:1. This represents a substantial reduction in the volume of contaminants. Technology vendors have reported a reduction of >98% of polychlorinated biphenyls (PCBs) at levels up to 4,600 mg/kg and reduction of >95% of polyaromatic hydrocarbons (PAHs) at levels up to 2,900 mg/kg. Removal efficiencies >90% are generally reported for many organic contaminants with residual levels in many cases <1 mg/kg. However, performance may require a higher number of extraction stages (6 to 8), especially at higher initial concentrations. The number of times the medium must be recycled through the system (the number of passes) in order to meet the treatment goal is an important criterion of system design and operation [33, 74].

### 3.4.4 Limitations

The technology is generally not used for extracting inorganics (i.e. acids, bases, salts, heavy metals). Organically bound metals can co-extract with the target organic pollutants and become a constituent of the concentrated organic waste stream. The presence of metals can restrict both disposal and recycle options.

Moisture content, the amount of clays, percentage of fines (>15% ), and the amount of naturally occurring organic carbon may each affect the performance of a solvent extraction process depending on the specific system design [75] which can be semi-batch or continuous. The waste may need to be made pumpable by the addition of solvents or water. Other systems may require reduction of the moisture content (<20% moisture) to effectively treat contaminated media. Matrices with higher clay content reduce extraction efficiency and require longer contact times. Many extraction processes can only handle a small particle size, usually less than ¼ inch. Treatment of contaminated material with >15% fines and high organic content affects treatment performance because contaminants can be strongly sorbed to the soil particles. Furthermore, soils with high clay and organic matter may form tight aggregates that are difficult to break. Cold temperatures can affect the efficiency of the extraction solution, which can diminish leaching rates [76, 77].

### 3.4.5 Case Studies

Solvent extraction technologies have been selected as the remedial action for PCB contaminated soils or sediments for at least four Superfund sites [11, 40, 55, 56]. Information on the application of solvent extraction for the treatment of PCB contaminated soil and sediment at these sites is presented in Table 7.

There have been several applications of solvent extraction at remediation sites. The EPA SITE Program lists five innovative solvent extraction systems capable of treating PCBs in soil and sediment [70].

## 3.5 Chemical Dehalogenation

### 3.5.1 Introduction

Chemical dehalogenation, as used in this section, refers to the use of chemical reagents and reduction processes to destroy or chemically alter the PCB congeners to a less toxic form. *Ex-situ* chemical dehalogenation systems typically are preferred over incineration alternatives. A comparison of the limitations of chemical dehalogenation systems to those of other PCB remediation systems is depicted in Table 3. Ideally, the goal is to convert or mineralize PCBs to innocuous byproducts such as sodium chloride, carbon dioxide, and water. More realistically, the goal is to reduce the toxicity to a form that will satisfy standards for ultimate disposal or reuse of the contaminated media. One example of this is to replace the chlorine in PCB with an aryl or alkyl functional group such as a sodium naphthalide reagent, polyethylene glycol, or Fenton's reagent. However, long term stability and other environmental constraints may require further treatment depending on the treatment goal [77].

Chemical dehalogenation can be achieved by either the replacement of the halogen molecules or the decomposition and partial volatilization of the contaminants. The contaminant is partially decomposed rather than transferred to another medium. Several processes have been utilized to accomplish chemical dehalogenation: Base Catalyzed Decomposition (BCD), Zero Valent Iron (ZVI), Solvated Electron Technology (SET™), and Gas Phase Chemical Reduction. Each of these applications will be discussed in this section.

BCD is an efficient, relatively inexpensive treatment process for PCBs. BCD treats PCBs directly in transformer oils, or as part of a two stage treatment train scheme for contaminated soils and sediments. PCB contaminated soils or sediments are mixed with sodium bicarbonate and initially treated by a thermal desorption process to completely dechlorinate the soil or sediment. The PCB contaminated vapor condensate is collected in the air treatment system and transferred to a heated stirred tank reactor where proprietary catalyst reagents are mixed with high boiling point hydrocarbon oil and sodium hydroxide [78, 79].

Although proprietary reagents are used in a BCD treatment process, EPA holds the patent rights to this technology in the U.S [80]. A process schematic of a typical BCD dehalogenation unit is depicted in Figure 5.

Zero valent iron (ZVI) offers another chemical dehalogenation treatment application. The use of reactive metal particles have shown great potential for remediating groundwater and sediments contaminated with chlorinated compounds, such as PCBs. For example, zero valent iron (ZVI) particles can be used in constructed reactive walls or barriers intercepting the pathway of PCB contaminated groundwater plumes and sediments. Nanoscale zero valent iron (ZVI) particles are characterized by high surface area to volume ratios with high reactivity rates. Batch studies have demonstrated that these particles can quickly and completely dechlorinate PCB congeners at relatively low metal to solution ratios (2.5 g/100ml). Further studies have shown that the metal particles can be directly injected into the contaminated aquifer creating a reactive zone for treatment [81].

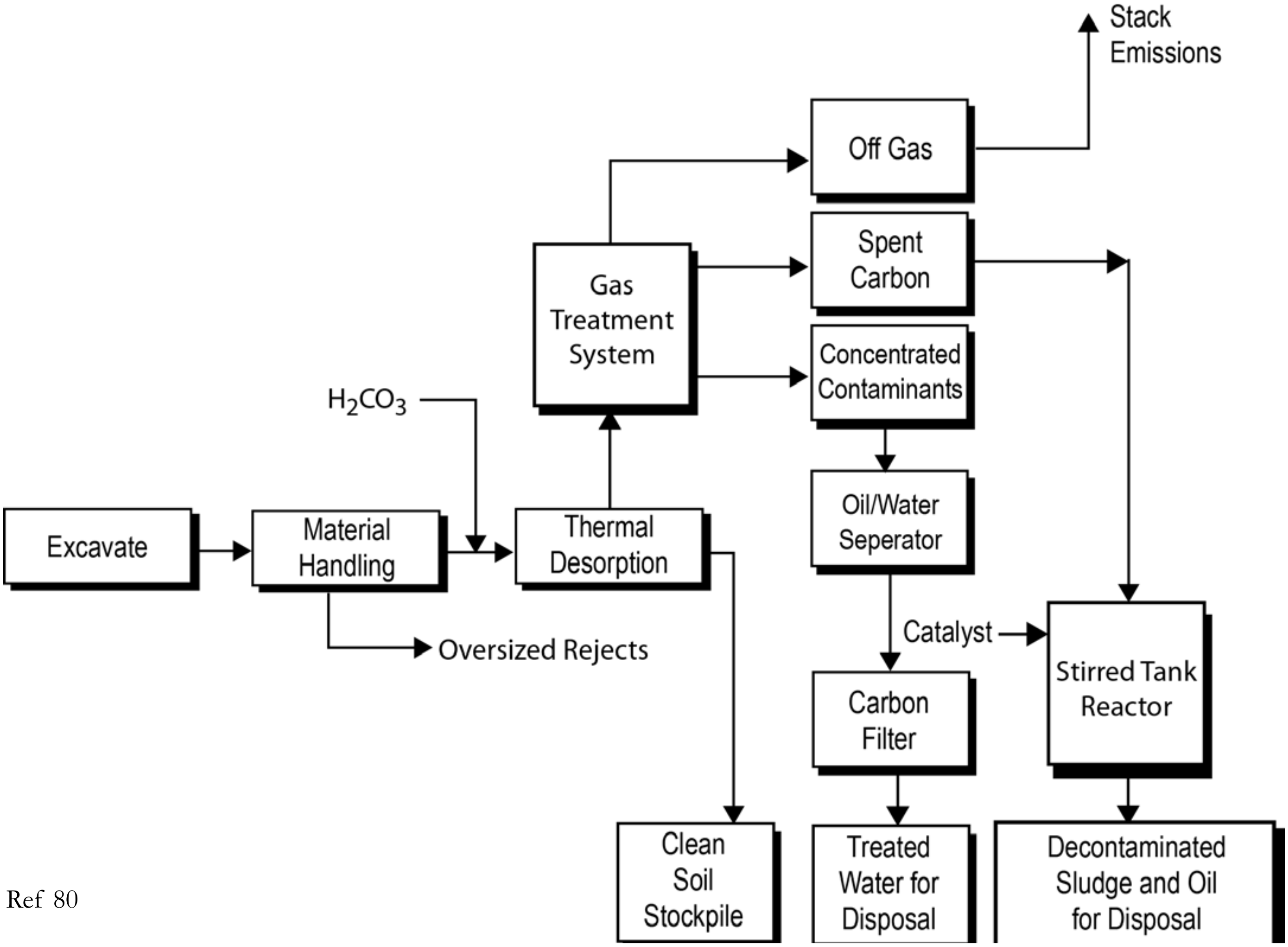
SET™ uses a solution of ammonia and an "active" metal, such as metallic sodium or potassium, to create a reducing agent that can chemically reduce toxic contaminants, such as PCBs and pesticides, into relatively benign substances [72, 82, 83, 84]. Solvated electrons are formed when certain alkaline earth metals (e.g. sodium, calcium, lithium, and potassium) are dissolved from their metallic form into ammonia, resulting in the formation of metal ions (e.g. Na+, Ca2+, Li+, and K+) and free electrons. These free electrons produce a strong reducing agent that removes halogens from organic molecules, breaking the chlorine-carbon bond. This chemical process was initially investigated for the remediation of environmental media contaminated with SVOCs. Typical waste products of SET™ treatment include hydrogen substituted aromatics from the original contaminant, sodium chloride, and sodium amide.

Eco Logic's Gas Phase Chemical Reduction (GPCR™) technology involves the gas phase chemical reduction of organic compounds by hydrogen at a temperature of 850°C (1562°F) or higher. Chlorinated hydrocarbons, such as PCB, polychlorinated dibenzo-p-dioxins (dioxins) and other POPs, are chemically reduced to methane and hydrogen chloride (HCl). Unlike oxidation reactions, the efficiency of these reduction reactions is enhanced by the presence of water, which acts as a heat transfer agent as well as a source of hydrogen. Therefore, dewatering of input waste is unnecessary. The water shift reactions produce hydrogen, carbon monoxide and carbon dioxide from methane and water. These reactions can be used at higher efficiencies to generate hydrogen for reuse in the system by subjecting scrubbed methane rich product gas to high temperatures in the presence of a catalyst. This is particularly useful when a hydrogen source for plant operations is not immediately available. Solid and bulk waste materials are processed in a Thermal Reduction Batch Processor (TRBP). This waste is placed in the TRBP, which is sealed and heated in an oxygen free atmosphere to about 600°C (1112°F). Organic components are volatilized and swept into the GPCR™ reactor, where complete reduction takes place at 850-900°C (1562-1652°F). Gas leaving this reactor is scrubbed to move particulate and acid and then stored for reuse as a fuel [85].

### *3.5.2 Applications*

BCD treats PCBs directly in transformer oils. PCB contaminated soils or sediments are mixed with sodium bicarbonate and initially treated by a thermal desorption process as part of a two stage treatment train to completely dechlorinate the soil or sediment. The PCB contaminated vapor condensate and fines are collected in the air treatment system and transferred to a heated stirred tank reactor containing a caustic (typically sodium bicarbonate [NaHC03]

**Figure 5.** Typical Base Catalyzed Decomposition (BCD)



Ref 80

or sodium hydroxide [NaOH]), catalyst reagents (e.g. carbon, graphite, or iron), a hydrogen donor (e.g. paraffinic or aliphatic oil), a hydrogen transfer agent, and other proprietary reagents [78, 79]. When heated above 300°C (572°F) for a time period that is predetermined after pilot-scale treatability tests, the reagent produces highly reactive atomic hydrogen, which cleaves chemical bonds that confer toxicity to compounds [1].

Following the thermal treatment reaction, inorganic carbonaceous solids are separated from the untreated oil by gravity or denitrification. The oil and catalyst may be recovered for reuse. If desired, the salts and excess base can be removed from carbon residue by rinsing. The carbon residue can be rendered non-toxic for disposal.

Four main waste streams are generated by BCD technology: the treated soil or solids, the wash water, residual decontaminated sludge, and possible air emissions. After treatment, the inorganic sodium salts and carbonaceous solids can be removed from the non-hazardous oils by gravity or centrifugation. If necessary, the salts and excess base can be removed from the solids by water wash-ing. The carbonaceous material left after centrifugation and washing is non-toxic and can be disposed of as non-hazardous material. Latest development in 2004 was that the process has the choice of using low cost heavy fuel oils or refined paraffinic oils as the donor oil in the process. Heavy fuel oils can be used once only, with the used oil being fed to cement kilns after destruction of POP's. Where this option is not used, it is now possible to recover and re-use 90-95% of the donor oil, which greatly improves the economics of the process and reduces the production of wastes virtually to a solids stream of sodium chloride and carbon from the breakdown of the POP molecule. Any wastewater generated by the process should be minimal and can be disposed directly to the sanitary sewer.

However, if prior treatment is required, chemical oxidation, biodegradation, carbon adsorption, or precipitation can be used. The residual decontaminated sludge from the stirred tank reactor must be analyzed to ensure conformance with regulatory requirements before disposal, but can generally be disposed of as municipal sewage sludge [33]. If other contaminants are present in the untreated waste feed material, they should also be evaluated in the residual sludge. If the sludge does not meet disposal standards, it can be retreated through the primary thermal desorption or solvent extraction treatment train process. Air emissions are typically minimal since the process is not pressurized. A reflux condenser is used to keep the oil in the stirred tank reactor while capturing the water vapor. However, if the contaminated material has significant moisture content, capture of the residual volatile fraction may be difficult even with a reflux condenser. Any resulting stream can be treated by activated carbon or catalytic oxidation.

The chemistry of this technology is not just specific to halogenated organics. Based on tests on halogenated organics, the byproduct compounds appear to be non-toxic [33]. The BCD process produces biphenyl and low boiling olefins (which are not water soluble and much less toxic) and sodium chloride. A comparison of the advantages of chemical dehalogenation systems to those of other PCB remediation systems is depicted in Table 2.

The innovative ZVI particle dechlorination technology has potential for in-situ PCB remediation. ZVI oxidizes to Fe (III) and can be applied through direct subsurface injection. A total understanding of the fate and transport of nano-scale ZVI is necessary prior to its commercial use in soils and sediments. Mass balances and PCB dechlorination pathways must be confirmed. The high cost and short reactive life span of nano-scale ZVI is a limitation to field application. The limited (biochemical) availability of PCBs in soils and sediments *in situ* is also a barrier to use of this and other *in-situ* PCB remediation technologies. Comprehensive field scale research is needed to further evaluate and develop this technology [86]. In the SET™ process, contaminated soil is excavated, screened to remove debris, and dewatered. During application, contaminated material is placed into a treatment cell and mixed with the solvated electron solution. Liquid ammonia is added to the vessel at room temperature, where it is mixed into slurry. After mixing, elemental calcium or sodium is added to the slurry, and mixing continues until the reaction is complete. The mixture is then transferred to an ammonia/soil separation vessel where liquid ammonia is separated from the soil. The separator is then rotated, warming the soil and driving off the remaining ammonia as vapor. The vapor is collected, along with the liquid, in the ammonia/water separator. Water is separated from the ammonia for return to the cleaned soil. The ammonia is returned to the main ammonia storage tank for reuse. The SET™ process is a non-thermal destruction process that operates under low pressure. Since the process is low pressure and operates in a closed system, there are no hazardous gases produced and no toxic byproducts (e.g. dioxins/furans), such as those created by some thermal treatments [85].

SET™ is applicable to a wide range of organic contaminants in different media. It is a non-thermal alternative to the destruction of recalcitrant semi-volatile organochlorine contaminants. SET™ systems typically present less risk than incineration for the treatment of mixed low level wastes. Ammonia is commonly used as an agricultural fertilizer and as a refrigerant and is handled and transported by qualified trained personnel. Metallic sodium, the primary reactant in the SET process, is received in 55 gallon drums. Metallic sodium is known to react violently with water to produce hydrogen gas, sodium hydroxide, and considerable heat. After dissolving in ammonia, the reactive properties of sodium are not as extreme as in the metallic form. All of these potential hazards are mitigated by engineering controls. Due to the aggressive reactivity of the solvated electron solution with liquid water, material with high water content must be dewatered prior to treatment.

Gas Phase Chemical Reduction (GPCR™) is an *ex-situ* technology that uses a two stage process to treat soil contaminated with POPs. In the first stage, contaminated soil is heated in a thermal reduction batch processor in the absence of oxygen to temperatures around 600°C (1112°F). This causes organic compounds to desorb from the solid matrix and enter the gas phase. The treated soil is non- hazardous and is allowed to cool prior to its disposal on or off site. In the second stage, the desorbed gaseous phase contaminants pass to a GPCR™ reactor, where they react with introduced hydrogen gas at temperatures ranging from 850-900°C (1562-1653°F). This reaction converts organic contaminants into primarily methane and water. Acid gases such as hydrogen chloride may also be produced when chlorinated organic contaminants are present. The gases produced in the second stage are scrubbed by caustic scrubber towers to cool the gases, neutralize acids, and remove fine particulates. The off gas exiting the scrubber is rich in methane and is collected and stored for reuse as fuel. Methane is also used to generate hydrogen for the GPCR™ process in a catalyzed high temperature reaction. Spent scrubber water is treated by granular activated carbon filters prior to its discharge and is available in both fixed and transportable configurations. GPCR™ is applicable to both solids and liquids [85].

**Table 8.** Commercial Application of Dechlorination Systems at Superfund Sites with PCB Contaminated Soil/Sediment

| Site | Media Treated | Status | Results |
|---|---|---|---|
| Wide Beach Development<br>Brant, NY | 30,000 $yd^3$ soil | APEG system. Operational from 9/1990 to 9/1991 | Initial: up to 5,300 mg/kg<br>Final: 2 mg/kg<br>Standard: 2 mg/kg |
| Smith's Farm<br>Brooks, KY | 21,000 $yd^3$ soil and sediment | BCD project completed 9/1995 | Initial: 3-25 mg/kg<br>Final: 300-500 ppb<br>Standard: 2 mg/kg |
| FCX Site<br>Statesville, NC | 15,000 $yd^3$ soil | BCD completed 9/2001 | Initial: up to 830 mg/kg<br>Final: 1 mg/kg<br>Standard: 1 mg/kg |
| Idaho National Engineering Laboratory (USDOE), ID | Not Profiled | Not Profiled | |

References 11, 38, 53, 54

### *3.5.3 Performance*

BCD performance efficiency is typically determined by measuring PCB reduction in soil or sediment before and after treatment. Clean up times are dependent on the type, quantity, and conditions of soils and sediments.

During the chemical dehalogenation process, chemical reactions can result in reactive and ignitable conditions in the reactors. Proper design and operation must be followed to avoid these conditions. If excavation is undertaken, air pollution equipment should be used to control dust and gases. Chemicals are rarely released from the reactor, but air monitoring should be considered to make sure that chemicals are not released in harmful amounts. BCD can be performed on site, which avoids costs associated with transportation of soil to a cleanup facility.

When the two stage BCD process is used to treat solids or sediments with thermal desorption, the capture and treatment of residuals (volatilized contaminants captured, dust, and other condensates) must be considered, especially when the soil contains high levels of fines and moisture, as in other thermal processes. When the BCD process is used with solvent extraction, the capture, treatment, recycling, and disposal of large amounts of liquids will also be necessary.

ZVI performance is best measured with treatment of contaminated groundwater in an aquifer setting whether applied to the vadose or saturated zone. For example, zero valent iron (ZVI) particles can be used in constructed reactive walls or barriers intercepting the pathway of PCB contaminated groundwater plumes and sediments. ZVI has shown less utility in treating soils and sediments *in situ* unless used as a reactive cap.

GPCR™ is non-selective and capable of destroying agents, Schedule 2 compounds, and hazardous intermediates, which ensures organic destruction and eliminates the risk of agent reformation. GPCR™ has been used to treat high strength solid and liquid wastes containing POPs at both full and pilot-scales. The POPs treated include hexachlorobenzene (HCB), DDT, PCBs, dioxins, and furans.

### *3.5.4 Limitations*

For each of the four chemical dehalogenation processes reviewed in this report, all have process limitations in treating residuals generated from front end treatment processes, such as thermal desorption, solvent extraction and soil washing/extraction technologies. For example, various degrees of moisture content, fines, particulates and condensates can affect the efficiency of the process.

When a two stage BCD process is used to treat solids or sediments via thermal desorption, the capture and treatment of residuals (volatilized contaminants captured, dust, and other condensates) must be considered, especially when the soil contains high levels of fines and moisture similar to other thermal processes. Since the BCD process involves stripping chlorine from the waste compound, the treatment process may result in an increased concentration of lower chlorinated species. This may be of potential concern in the treatment of PCDDs and PCDFs, where lower congeners are significantly more toxic than the higher congeners. It is therefore important that the process be appropriately monitored to ensure that the reaction continues to completion. The presence of reducible metals in the PCB contaminated medium can also reduce performance efficiency by scavenging the reactive agent, requiring increased amounts of reagent [33].

When using ZVI, performance is best measured when treating contaminated groundwater in the subsurface or in an aquifer scenario. For example, zero valent iron (ZVI) particles can be used in constructed reactive walls or barriers intercepting the pathway of PCB contaminated groundwater plumes and sediments. ZVI has shown less utility in treating soils and sediments *in situ* unless used as a reactive cap.

In the SET™ process, metallic sodium is the primary reactant. It is known to react violently with water to produce hydrogen gas, sodium hydroxide, and considerable heat. After dissolving in ammonia, the reactive properties of sodium are not as difficult to handle as in the metallic form. However, due to the aggressive reactivity of the solvated electron solution with water, media with high water content should be dewatered prior to treatment.

GPCR™ treatment of arsenic and mercury containing wastes produces volatile elemental metals; although GPCR™ has successfully treated arsenic containing wastes, removal of arsenic and mercury from the air effluent poses a challenge that must be considered in the design of the pollution abatement system. They also noted a concern related to the use of hydrogen in that transportation of large quantities of hydrogen may present a risk of transportation related accidents. However, hydrogen is a standard commercial product, and should be available locally (or generated on-site), minimizing transportation distances [88].

A comparison of the limitations of chemical dehalogenation systems to those of other PCB remediation systems is depicted in Table 3.

### *3.5.5 Case Studies*

Chemical dehalogenation technologies have been selected as the remedial action for at least four Superfund sites with PCB contaminated soils or sediments [11, 40, 55, 56]. Information on the application of chemical dehalogenation for the treatment of PCB contaminated soil and sediment at these sites is presented in Table 9.

The BCD technology has been licensed to environmental firms in Spain, Australia, Japan and Mexico and has been used to treat PCB contaminated oil. Two commercial BCD plants are being constructed in the Czech Republic [89].

Commercially the GPCR™ system has been working more than 5 years at Kiwana in Western Australia, where it has been treating PCBs, HCBs and DDT. Efficiencies of at least 99.9999 % have been achieved [90, 91, 92]. In commercial scale performance tests in Canada, the gas phase reduction process achieved destruction efficiencies (DE) and Destruction and Removal Efficiencies (DRE) with high strength PCB oils and chlorobenzenes. Dioxins that were present as contaminants in the PCB oil were destroyed with efficiencies ranging from 99.999 to 99.9999 percent [93, 94].

The EPA SITE Program listed four innovative chemical dehalogenation systems reportedly capable of treating PCBs in soil and sediment [70].

## 3.6 Solidification/Stabilization (S/S)

### *3.6.1 Technology Description*

Waste solidification involves adding a binding agent, such as Portland cement or asphalt, to the waste to encapsulate the contaminants in a solid matrix [33]. Solidifying waste improves its materials handling characteristics and reduces permeability to leaching agents by reducing waste porosity and exposed surface area.

Waste stabilization involves the addition of a binder, such as Portland cement, cement kiln dust, fly ash, or a combination of the three to a waste to convert contaminants into an insoluble, less mobile, and less toxic form. S/S processes utilize one or both of these techniques and are fundamentally different from other PCB remedial technologies in that they reduce the mobility of PCBs, but do not concentrate or destroy them [95]. Although often considered more appropriate for addressing inorganic contamination, S/S has been used to successfully remediate organics (e.g. PAHs, dioxins) including PCBs at several sites. [96, 97].

*Ex-situ* S/S processes involve: (1) soil or sediment excavation, (2) classification to remove oversized debris, (3) mixing and pouring, and (4) off gas treatment, if necessary. *In-situ* processes generally have only two steps: (1) mixing and (2) off gas treatment, if necessary [98]. Both approaches require that the soil or sediment be mixed with the binding agents and water in a batch or continuous system. In *ex-situ* applications, the resultant slurry can be: (1) poured into containers (e.g. 55 gallon drums) or molds for curing and then disposed of on site or off site, (2) disposed of in on-site waste management cells or trenches, (3) injected into the subsurface environment, or (4) reused as construction material with the appropriate regulatory approvals. Some S/S formulations result in a dryer matrix that can be handled like soil.

*In-situ* applications involve injecting S/S agents into the subsurface environment in the proper proportions and mixing them with the soil or sediment using backhoes for

**Table 9.** Commercial Application of Solidification/Stabilization at Superfund Sites with PCB Contaminated Soil/Sediment

| Site | Media Treated | Status | Results |
|---|---|---|---|
| ***Ex-situ* Applications** | | | |
| Carolina Transformer Co. - Fayetteville, NC | Excavation and on-site solvent extraction of soil and sediment >1 mg/kg PCBs; solidification of any excavated soil or sediment that does not meet the RCRA toxicity characteristic rule | Operational from 3/1984 to 3/1984<br>Operational from 3/1990 to 5/1990 | Initial: 21.000 mg/kg<br>Final: 1 mg/kg<br>Standard: 1 mg/kg |
| White House Oil Pits<br>Jacksonville, FL | 19,000 yd$^3$ soil | Cement based process<br>Operational from 8/1986 to 8/1986<br>Operational from 11/1987 to 2/1988<br>Operational from 9/2001 to 9/2007 | Initial: 5.1 mg/kg<br>Final: 1 mg/kg<br>Standard: 1 mg/kg |
| Pepper Steel & Alloys, Inc<br>Medley, FL | 144,000 yd$^3$ soil | Cement based process<br>Operational from 1987 to 1989 | Initial: 70 mg/l<br>Final: <1mg/l<br>Standard: 1 mg/l in leachate |
| Florida Steel Corporation<br>Indiantown, FL | 53,570 yd$^3$ soil and sediment | Cement based process<br>Operational from 1/1995 to 4/1996 | Initial: 600 mg/kg<br>Final: 0 mg/kg<br>Standard: 25 mg/kg |
| Yellow Water Road Dump<br>Baldwin, FL | 4,472 yd$^3$ soil | Cement based process<br>Operational from 5/1996 to 9/1996 | Initial: 10-600 mg/kg<br>Final: ND<br>Standard: <0.5 ug/l in leachate |
| PSC Resources<br>Palmer, MA | 10,500 yd$^3$ soil and sediment | Cement based process<br>Operational from 3/1997 to 11/1997 | Initial: 1 mg/kg<br>Final: 0 mg/kg<br>Standard: 0 mg/kg |
| Double Eagle Refinery<br>Oklahoma City, OK | 39,970 yd$^3$ soil and sediment | Operational from 5/1998 to 6/1999 | Initial: 50 mg/kg<br>Final: 0 mg/kg<br>Standard: 25 mg/kg |
| Paoli Rail Yard<br>Paoli, PA | 83,000 yd$^3$ soil | Operational from 6/2000 to 2/2006 | Initial: 6,000 mg/kg<br>Final:<br>Standard: 2 mg/kg (R), 25 (I) |
| MW Manufacturing<br>Valley Township, PA | 35,566 yd$^3$ fluff/sediment/soils | Operational from 5/2004 to 12/2004 | Initial: 7.6 mg/kg |

Reference 11, 38, 53, 54

surface mixing or augers for deep mixing [95]. For sediments, recent results from a field scale treatability study have demonstrated the ability of PCB sequestration using an activated carbon amendment to reduce sediment PCB concentrations in the aqueous phase [95].

The type and proportions of the binding agents are adjusted to the specific properties of the waste. This achieves the desired physical and chemical characteristics of the waste suited to the conditions at the site based on bench-scale tests. The most common fixing and binding agents for S/S are cement, lime, natural pozzolans, and fly ash, or mixtures of these [2, 16]. Traditional cement and pozzolanic materials have yet to be shown to be consistently effective in full scale applications treating wastes high in O&G, surfactants, or chelating agents without pretreatment [100].

S/S processes are often divided into the following broad categories: inorganic processes (cement and pozzolanic) and organic processes (thermoplastic and thermosetting). Generic S/S processes involve materials that are well known and readily available. Commercial vendors of this technology have typically developed generic processes into proprietary processes by adding special additives to provide better control of the S/S process or to enhance specific chemical or physical properties of the treated waste. A process diagram of a typical *ex-situ* S/S unit is depicted in Figure 6.

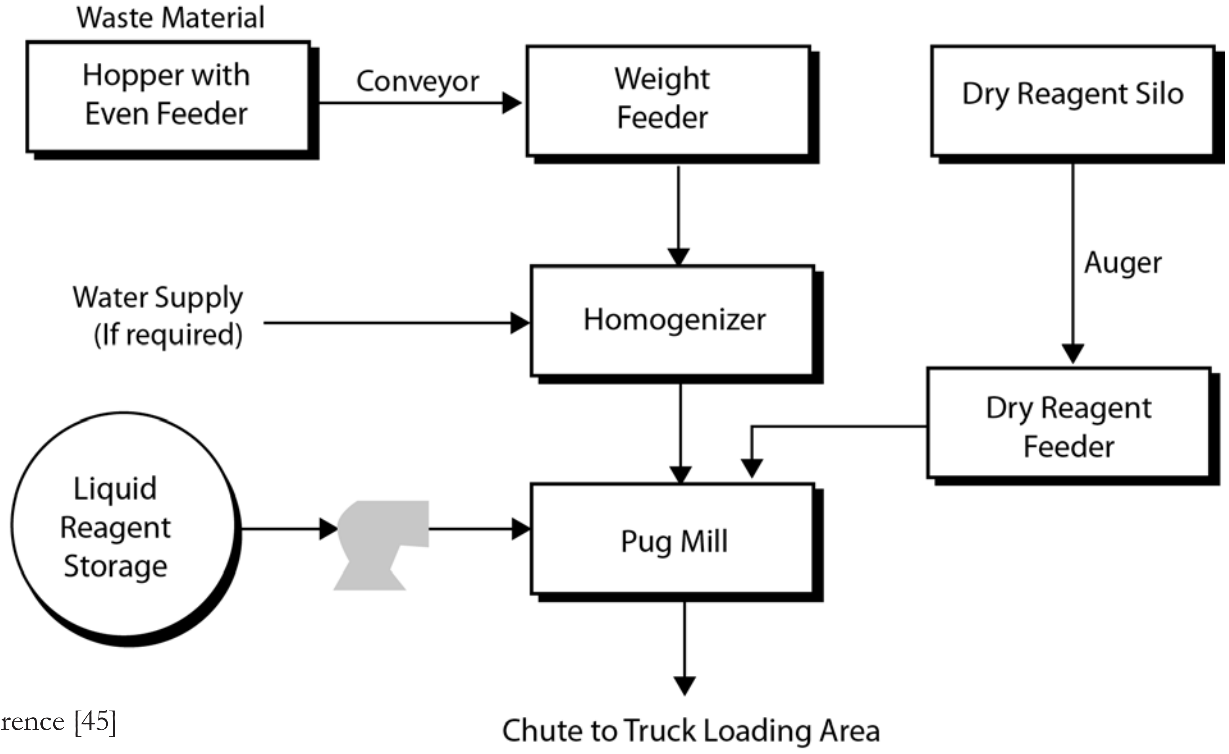
A comparison of the advantages of S/S systems to those of other PCB remediation systems is depicted in Table 2.

### 3.6.2 Applications

Solidification/stabilization systems are a viable treatment alternative for material containing inorganics, semi-volatile and/or non-volatile organics. Selection of S/S generally requires the performance of a site-specific treatability study [45, 49, 100].

Factors considered most important in applicability determinations are design, implementation, and performance of S/S processes and products, including the waste characteristics (chemical and physical), processing requirements, S/S product management objectives, regulatory requirements, and economics [95]. These and other site-specific factors (e.g. location, condition, climate, hydrology, etc.) must be taken into account when determining whether, how, where, and to what extent a particular S/S method should be used at a particular site [101].

**Figure 6.** Typical *Ex-situ* Solidification/Stabilization Process Flow Diagram



Reference [45]

### 3.6.3 Performance

The effectiveness of S/S technologies is most often measured using leachability tests: Synthetic Precipitation Leaching Procedure (SPLP) or Toxicity Characteristics Leaching Procedure (TCLP). A wide range of other performance tests may need to be performed in conjunction with S/S treatability studies of the treated material. These include total waste analysis for organics, permeability, unconfined compressive strength (UCS), treated waste and/or leachate toxicity endpoints, and freeze/thaw and wet/dry weathering cycle tests [102, 103]. Treatability studies should be conducted on replicate samples from a representative set of waste batches that span the expected range of physical and chemical properties to be encountered at the site. Due to the hydrophobic properties of PCBs, test results typically do not show significant differences between the leachability of PCBs in the untreated and treated medium. A portion of the PCBs may volatilize during heating and mixing with the S/S agents; the remaining PCBs appear to stay in the solidified mass [33].

Some degree of immobilization of PCBs and related polychlorinated polycyclic compounds appears to occur in cement or pozzolans [104]. Some field observations suggest that PCBs undergo significant levels of dechlorination under the alkaline conditions encountered in pozzolanic processes. EPA directed research into this topic have not confirmed these results, although significant desorption and volatilization of the PCBs were documented [28, 105].

Performance of S/S is also a measure of the ease of operation, processing capacity, frequency of process outages, residuals management, costs and the characteristics of the treated product. These characteristics include weight, density, and volume changes.

### 3.6.4 Limitations

Under normal operating conditions, neither *ex-situ* nor *in-situ* S/S technologies generates significant quantities of contaminated liquids, solid waste, or off gas. Certain S/S applications may require treatment of the off gas. Prescreening collects debris and materials too large for subsequent treatment. In addition, this material may have to be further treated. Treated media that cannot be returned to the original location may have to be disposed off site [33, 95]. If the treated waste meets the specified site cleanup levels, it could be considered for reuse on site as backfill or construction material.

Physical mechanisms that can interfere with the S/S process include: (1) incomplete mixing due to the presence of high moisture or organic chemical content resulting in only partial wetting or coating of the waste particles with the stabilizing and binding agents and, (2) the aggregation of untreated waste into clumps [102]. Wastes with high clay content may aggregate, interfering with uniform mixing of the S/S agents, and/or the clay surface may adsorb key reactants, interrupting the polymerization chemistry of the S/S agents. Wastes with a high hydrophilic organic content may interfere with solidification by disrupting the gel structure of the curing cement or pozzolanic mixture [26, 27, 95]. Chemical mechanisms that can interfere with S/S of cement based systems include chemical adsorption, complexation, precipitation, and nucleation [29]. Known inorganic chemical interference compounds in cement-based S/S processes include the sodium salts of arsenate, borate, phosphate, iodate, and sulfide [32, 49, 102]. Problematic organic interferences include oil & grease (O&G), phenols, surfactants, chelating agents and ethylene glycol [26, 27, 101, 106]. High concentrations of PCBs and other organics may impede the setting of cement, pozzolan, or organic polymer S/S materials. High organic concentrations may decrease long term durability and may result in some release of volatiles during mixing [33]. Organic polymer additives in various stages of development and field testing may significantly improve the performance of the cementitious and pozzolanic S/S agents with respect to immobilization of organic substances. Various polymers are being used to improve reliability, but they have had minimal field application for PCB remediation. Volume increases associated with the addition of S/S agents to the waste are related primarily to the percent volume of S/S reagent added to the waste. While volume increases of 61 percent have been reported by the EPA SITE Program, the majority of volume increases are 5 to 10 percent [70].

Under certain conditions, S/S processes can produce hot gases, including vapors that are potentially toxic, irritating, or noxious. These conditions include: waste containing VOCs, low pH sludge, and when using quicklime as a binding reagent [105].

Environmental conditions must also be considered in determining whether and when to implement an S/S technology. Extremes of heat, cold, and precipitation can adversely affect S/S applications and long term immobilization of contaminants.

A comparison of the limitations of S/S systems to those of other PCB remediation systems is depicted in Table 3. S/S is applicable to remediation of inorganic wastes, and has also been shown to be reliable when treating non-volatile organics such as PCBs.

### *3.6.5 Case Studies*

Solidification/Stabilization technologies have been selected as the remedial action for PCB contaminated soils or sediments for at least 35 Superfund sites [11, 40, 55, 56]. Information on the application of S/S for the treatment of PCB contaminated soil and sediment at some of these sites is presented in Table 10.

The EPA SITE Program listed six innovative S/S systems reportedly capable of treating PCBs in soil and sediment [70].

## 3.7 Additional Technologies

Other technologies have been tested for the remediation of PCB contaminated media. These technologies have been tested at bench- and pilot-scale with minimal field application. These technologies include: bioremediation, vitrification, soil washing, and chemical reduction via Fenton's Reagent.

### *3.7.1 Bioremediation*

Biodegradation of PCBs involves the ability of soil microorganisms to use organic contaminants as an energy source by responders creating a favorable environment for microorganisms to proliferate [107]. Creating a favorable environment involves providing the right balance of oxygen, nutrients, moisture, and controlling temperature and pH. The microorganisms can be indigenous to the impacted soil or exogenously applied, consisting of laboratory cultured strains specifically adapted for the degradation of the contaminants found at a site. In either case, the objective of bioremediation is to degrade (i.e. break down) organic compounds to simpler innocuous forms including carbon dioxide and water [45].

Aerobic bioremediation involves the degradation of contaminants in the presence of oxygen. Conversely, anaerobic bioremediation involves the degradation of contaminants in the absence of oxygen . Aerobic bioremediation typically occurs at a faster rate than anaerobic bioremediation. PCBs may be biodegraded aerobically, anaerobically, or through a combination of the two. Laboratory and field studies indicate that PCBs with fewer chlorine atoms are more amenable to complete aerobic biodegradation [33, 108, 109], whereas those with higher chlorine content require a reductive environment, a process called reductive dechlorination [18, 110].

Bioremediation can be applied *in-situ* or *ex-situ*. The main advantage of *in-situ* treatment is that it allows soil to be treated in place without the need for excavation and transportation, resulting in potentially significant cost savings. The main advantage of *ex-situ* treatment is that it generally requires shorter time periods than *in-situ* processes, and there is more certainty about the uniformity of treatment with the ability to homogenize, screen, and continuously mix the soil.

Bioremediation technologies have been selected as the remedial action for PCB contaminated soils or sediments at two Superfund sites [11, 40, 55, 56]. Although this technology has shown some degree of success in laboratory and pilot-scale applications, comprehensive field scale research is needed to advance bioremediation technology. Innovative technologies are being tested for *in-situ* bioremediation of PCB contamination. Strategies

**Table 10.** Commercial Application of Vitrification Systems at Superfund Sites with PCB Contaminated Soil/Sediment

| Site | Media Treated | Status | Lead | Contact |
|---|---|---|---|---|
| Oak Ridge Reservation (US-DOE) - Oak Ridge, TN | Soil | Predesign Stage | DOE Lead/Federal Oversight | Ken Feely (EPA)<br>404-562-8512 |
| U.S. DOE Idaho National Engineering and Environmental Laboratory, Idaho Falls, ID | 9,260 $yd^3$ Soil | Plasma Arc incineration, ex-situ. Design stage. | DOE Lead/Federal Oversight | Wayne Pierre (EPA)<br>206-553-7261<br>pierre.wayne@epa.gov |

Reference 11, 40, 55, 56

to better utilize the abilities of microorganisms include solubilization of PCBs to allow transport across the cell membrane, regulating the production of PCB degrading enzymes, and genetic engineering of enzymes [112].

Another type of bioremediation technology that offers potential application for treating PCB contamination is phytoremediation. Plants have shown the capacity to withstand organic chemicals without significant toxicity symptoms. Also in some cases they can uptake and transform organic compounds to less phytotoxic metabolites. Several investigations have shown that PCBs can be translocated from soil to various parts of the plants and can accumulate in particular tissues in higher concentrations than in others [04]. The metabolism of PCBs varies between the plant species and is affected by the substitution pattern and the degree of chlorination [112]. Much of the research done with phytoremediation has shown that most of the remediation occurs by the bacteria growing in the rhizosphere, where the root system provides a high surface area for sustaining high populations of degraders. While there exists a large extent of bench- and pilot-scale research on the use of phytoremediation for PCB, much work is necessary to understand the benefits of using plants for full scale remediations [113, 114, 115, 116].

### 3.7.2 Vitrification

Vitrification processes are solidification methods that use heat of up to 1205°C (2,200°F) to melt and convert waste material into glasslike crystalline products [115]. Vitrification can be used to treat soil and sediment containing organic, inorganic, and radioactive contaminants. The destruction mechanism is either pyrolysis (in an oxygen poor environment) or oxidation (in an oxygen rich environment). The volume of the vitrified product is typically 20 to 45% less than the volume of the untreated soil or sediment. Vitrification can either be performed *in-situ* or *ex-situ*. [118].

Vitrification has been selected as the remedial action for PCB contaminated soils or sediments at two Superfund sites [11, 40, 55, 56]. The EPA SITE Program listed three innovative vitrification systems reportedly capable of treating PCBs in soil and sediment [70]. Information on the application of ISV for the treatment of PCB contaminated soil and sediment at these sites is presented in Table 11.

### *3.7.3 Soil Washing*

Soil washing is an *ex-situ*, water-based remedial technology that mechanically mixes, washes, and rinses soil to remove contaminants [33, 117]. *Ex-situ* soil separation processes (often referred to as soil washing) are based on mineral processing techniques commonly used in Northern Europe and the U.S. The process removes contaminants from soil in one of two ways:

- Dissolving or suspending them in the wash water that can be sustained by chemical manipulation of pH for a period of time;
- Concentrating them into a smaller volume of soil through particle size separation, gravity separation, and attrition scrubbing similar to those techniques used in sand and gravel operations.

The technology offers the ability to recover metals and clean a wide range of organic and inorganic contaminants from coarse grained soils [45, 120]. Soil washing is generally considered a media transfer technology. Contaminated soils and sediments, consisting mostly of sand and other coarse material, are better suited for soil washing systems [121].

Hydrophobic contaminants, such as PCBs, can be difficult to separate from soil particles into the aqueous washing fluid. Contaminants with a high partition coefficients log-$K_{ow}$ (e.g. PCB >10,000) are more difficult to wash off soil than a contaminant with a lower partition coefficient (e.g., trichloroethylene = 3). Additives such as surfactants can be used to improve removal efficiencies. However, larger volumes of washing fluid may be needed when additives are used. A high surfactant concentration in the washing fluid can cause foaming problems, which can inhibit the ability to effectively remove contaminants from the soil [119].

Soil washing technology has been selected as the remedial action for PCB contaminated soils at one Superfund site: the Springfield Township Dump in Davisburg, Michigan [11, 40, 55, 56]. The EPA SITE Program also has evaluated soil washing systems [70].

### 3.7.4 Advanced oxidative processes (AOPs)

AOPs involve the use of $O_2$, $H_2O_2$, $TiO_2$, UV light, electrons, iron, or other oxidizing compounds to degrade PCBs and volatile organic compounds (VOCs). AOPs use these oxidizing agents to produce free radicals, which indiscriminately destroy organic matter.

### 3.7.5 Fenton's Reagent

Electrochemical peroxidation (ECP) is an advanced oxidative process developed by researchers at SUNY Oswego. It uses electricity, steel electrodes, and hydrogen peroxide to degrade PCBs and VOCs. The dominant mechanism for this process is Fenton's Reagent enhanced by the input of an electrical current. Fenton's reagent creates free radicals that participate in reactions by indiscriminately oxidizing available organic matter. [122].

The use of catalyzed $H_2O_2$ propagations (CHP or modified Fenton's reagent) has been researched for *in-situ* soil and subsurface treatment. CHP provides the fundamental chemistry for a highly effective *in-situ* chemical oxidation (ISCO) process. Recent research has shown that superoxide generated in CHP reactions destroys highly oxidized, sorbed, and NAPL contaminants that are unreactive with hydroxyl radical. This widespread reactivity is an advantage of CHP ISCO, along with rapid treatment times and relatively low reagent cost. Disadvantages of CHP ISCO include instability of hydrogen peroxide in the subsurface, achieving an optimal pH of 4, generation of oxygen that may volatilize contaminants, generation of excessive heat, and risk of explosion. Hydrogen peroxide can be stabilized through the addition of salts of organic acids such as citrate, malonate, and phytate, minimizing heat and oxygen generation while maintaining effective generation of reactive oxygen species.

Recent research evaluated the feasibility of using CHP to treat PCB contaminated soil samples collected from two Primary Responsible Parties' Superfund sites in the New England region of the United States, Fletcher Paints and Merrimack Industrial Metals. The purpose of this study was to determine the most effective process conditions, including hydrogen peroxide concentration, type of stabilizer, stabilizer concentration, and pH. Soils samples were evaluated for the potential for *in-situ* treatment based on two criteria: temperature (less than 40°C (104°F) after CHP reagent addition) and hydrogen peroxide longevity (greater than 24 hours). Using the highest hydrogen peroxide concentrations appropriate for *in-situ* treatment in each soil, PCB destruction was 94% in the Fletcher soil but only 48% in the Merrimack soil. However, 98% PCB destruction was achieved in the Merrimack soil using conditions more applicable to *ex-situ* treatment (higher hydrogen peroxide concentrations with temperatures > 40°C (104°F)).

Analysis of degradation products by gas chromatography/mass spectrometry (GC/MS) showed no detectable chlorinated degradation products, suggesting that the products of PCB oxidation were rapidly dechlorinated. The results of this research document that the two PCB contaminated soils studied can be effectively treated using aggressive CHP conditions, and that such a detailed bench study provides important information for field implementation [123].

Chemical oxidation using Fenton's reagent or other oxidants has been coupled with bioremediation for PCB remediation. Before this can be done successfully, the pH must be returned to neutral, otherwise the microorganisms won't participate. Examples are chemical and biological treatment (CBT) technology, the CerOx$^{TM}$ process, and the RegenOx$^{TM}$ process. Chemical oxidation technologies are extensively covered in "In-Situ Chemical Oxidation - Engineering Issue." [124].

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