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K Basin Sludge Polychlorinated Biphenyl Removal Technology Assessment

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K BASIN SLUDGE POLYCHLORINATED BIPHENYLS REMOVAL TECHNOLOGY ASSESSMENT

HNF-3095
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August 1998

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SUMMARY

The current baseline for the K basin Sludge Treatment process assumes that the polychlorinated biphenyls (PCB) will be split between the solid phase (insoluble residue), the liquid phase (acid liquor) and the gas phase (off gas from the dissolver) during the dissolution step. It is assumed that the quantity in the liquid phase will be limited by the low solubility of PCBs in aqueous solution. So by an adequate design of the solid / liquid separation step(s), the quantities of PCB directed to TWRS can be almost limited to the PCB existing in the liquid phase.

This strategy is based on several assumptions and tests which have been designed to check the validity of these assumptions. In parallel to that experimental approach, it was decided to perform an engineering study to review the technologies that were existing to remove or destroy PCBs from the following phases:

- acidic liquor at the exit of the dissolver
- Off gas produced in the dissolver
- sludge before the dissolution step or solids entrained to TWRS

The process will be designed to remove PCBs to meet appropriate standards: 2 ppm in the solids (non-thermal) and 0.5 ppb in the aqueous phase for material destined for Tank Waste Remediation System (TWRS).

Processing Technologies for removing K Basin sludge PCBs were evaluated. Many new technologies were evaluated to destroy or remove PCBs from the sludge prior to or coinciding with acid dissolution and in acidic dissolver product. Technologies amenable to treating PCBs in solids (sludge), aqueous (dissolver product), and gases were in the scope of this evaluation.

Some of the new technologies that were examined have good potential but have not been developed far enough (e.g., ultrasound). Some of the others have been proven for non-radioactive sludges but not for nuclear type facilities where the high pressures involved might be troublesome from a safety /contamination perspective. (e.g. supercritical water). The following technologies are our recommendation:

Sludges/Solids

Direct Chemical Oxidation (DCO) seems to be the process which is more fitted to the removal/destruction of PCBs from the sludge. However, even if the DCO process is the preferred option, it is necessary to point out that the final demonstration of the efficiency of that process to remove the PCBs remains to be done. This step will only be implemented if it is not possible to meet the PCB content in the solid sent to TWRS.

Aqueous (dissolver product)

Our recommendation is to use cartridge filters with an organic filtering media. The implementation of that solution will require the following series of actions will be necessary:

- review of the organic media available for cartridge filter and fulfilling requirements for PCBs removal and filtration efficiency.
- measurement of PCB adsorption (if not available from the manufacturer)

Gases

The expected offgas PCB concentration is expected to be low. Since granulated activated carbon (GAC) normally is used as a polish for PCB removal, the recommended option is the removal of PCBs from the off-gas.

1.0 INTRODUCTION

The two Hanford K Basins are water-filled concrete pools that contain over 2,100 metric tons of N Reactor fuel elements stored in aluminum or stainless steel canisters. During the time the fuel has been stored, approximately 50 m^3 of heterogeneous solid material have accumulated in the basins. This material, referred to as "sludge", is a mixture of fuel corrosion products, metallic bits of spent fuel and zirconium cladding, iron and aluminum metal corrosion products and silica from migrating sands (Pearce 1998). Some of the sludges also contain PCB. The congener group of PCBs was identified as Aroclor 1254. The maximum concentration of sludge PCBs was found to be 140 ppm (as settled wet basis). However, the distribution of the PCBs is non-uniform throughout the sludge (i.e., there are regions of high and low concentrations and places where no PCBs are present). Higher concentrations could be present at various locations. Aroclors 1016/1242, 1221, 1248, 1254, and 1260 were identified and quantified in K West (KW) Canister sludge. In some of these samples, the concentration of 1260 was higher than 1254. The PCB work done on K East (KE) Floor and Weasel pit was screening in nature, and other Aroclors may exist in KE as well. The sludge requires pre-treatment to meet tank farm waste acceptance criteria. Among the numerous requirements, the sludge should be retreated so that it does not contain regulated levels of Toxic Substances Control Act (TSCA) compounds.

Because of their stable chemistry and relative insolubility in water, PCBs are difficult to treat. They also resist degradation from heat and electrical charges. This stability has resulted in environmental persistence which has prompted the development of a variety of new cleanup processes including supercritical processes, advanced oxidation, dehalogenation and others. Hopefully, most of the new processes are discussed herein. Information on new processes are being received and will be evaluated in a future revision.

1.1 Process Flowsheet

The planned flowsheet for processing K Basin sludges includes solids separations, sludge dissolution, PCB removal/destruction, and precipitation as discussed in the system description (Westra 1998). A block diagram of the baseline system is shown if Figure 1-1.

After separation of ion exchange resins, the sludge will be processed in a dissolver where uranium, iron and other compounds will be dissolved in nitric acid. The dissolution process is inherently a batch process although some of the other processes could be operated continuous or semi-continuous. Insolubles such as silica and graphitic materials will exist in solution as an undissolved species. Resins and insolubles from the dissolver will be leached out with an acidic solution to remove residual amounts of transuranic (TRU). Then resins and insolubles will be solidified/stabilized (e.g., grout) and sent to environmental remediation disposal facility (ERDF). Offgases and ventilation systems will include a condenser, an absorption column for NOX, a mist eliminator and High Efficiency Particulate Air filter (HEPA).

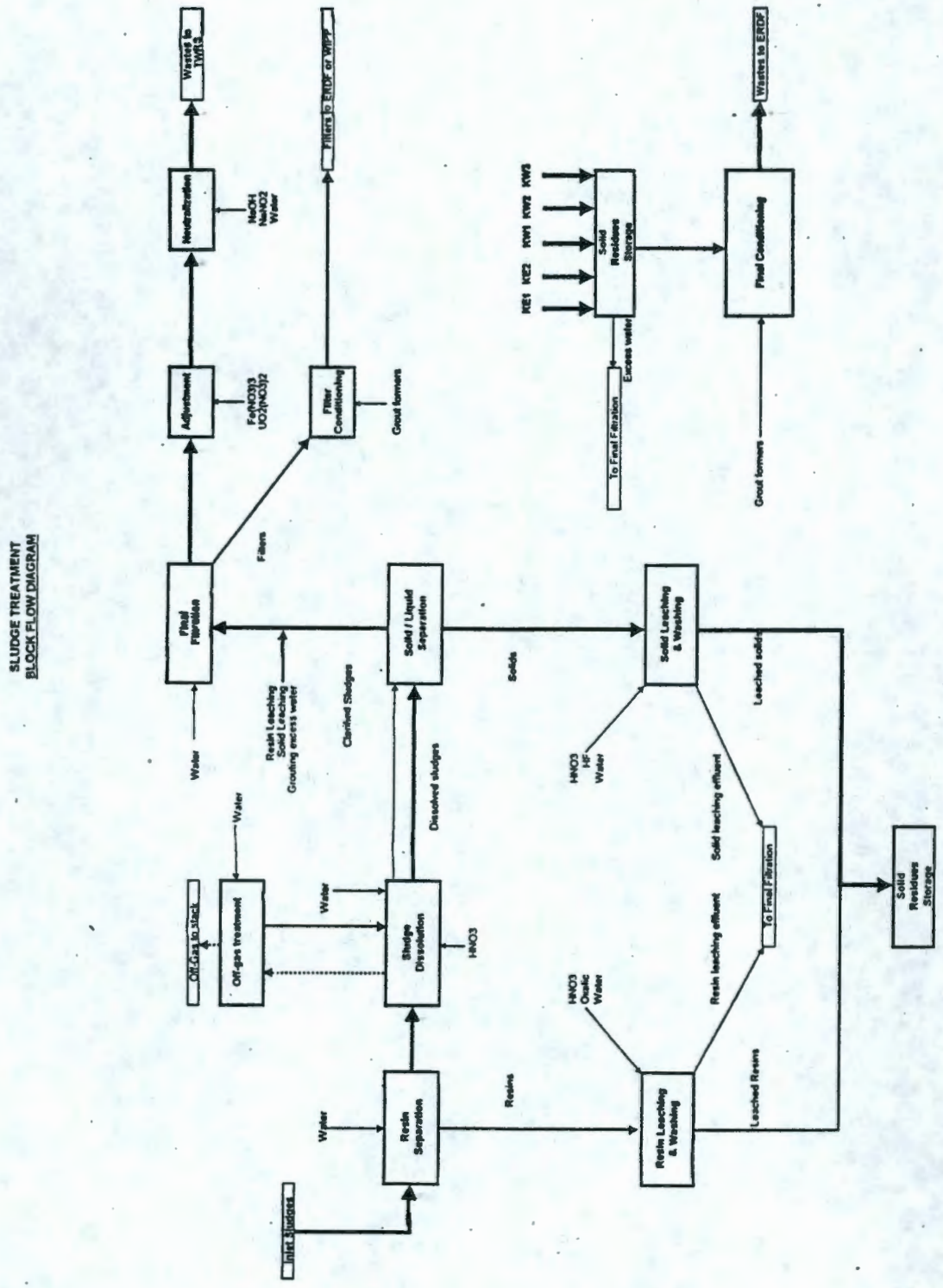


Fig 1.1 Block Flow Diagram

2.0 SCOPE

The current baseline for the K Basin Sludge Treatment process assumes that the PCB will be split between the solid phase (insoluble residue), the liquid phase (acid liquor) and the gas phase (off gas from the dissolver) during the dissolution step. It is assumed that the quantity in the liquid phase will be limited by the low solubility of PCBs in aqueous solution. So by an adequate design of the solid / liquid separation step(s), the quantities of PCB directed to TWRS can be almost limited to the PCB existing in the liquid phase.

This strategy is based on several assumptions and tests have been designed in order to check the validity of these assumptions. In parallel to that experimental approach, it was decided to perform an engineering study to review the technologies that were existing to remove or destroy PCBs from the following phases:

- acidic liquor at the exit of the dissolver
- Off gas produced in the dissolver
- solids entrained to TWRS

The process will be designed to remove PCBs to meet appropriate standards: 2 ppm in the solids (non-thermal) and 0.5 ppb in the aqueous phase for material destined for Tank Waste Remediation System (TWRS).

There was a PCB limit (500 ppm) for the disposal of waste to ERDF but that limit has been suppressed from the new Hanford Site Solid Waste Acceptance Criteria.

2.1 Treatment Standards

TSCA establishes a permitting and demonstration process for PCB treatment systems and treatment requirements. For liquid PCBs (presumably transformer oils) at concentrations of 50 ppm or greater but less than 500 ppm (50 ppm ≤ PCB ≤ 500 ppm), TSCA requires the liquid to be disposed in an incinerator, a chemical waste landfill, or a high efficiency boiler (40 CFR 761.60(3)). TSCA also states that PCB materials can be treated by an alternate technology that provides a level of performance equivalent to incineration and does not present an unreasonable risk of injury to human health or the environment (40 CFR 761.60(e)). For thermal destruction technologies, Environmental Protection Agency (EPA) considers equivalent performance to be a destruction and removal efficiency (DRE) of PCBs equivalent to 99.9999% (EPA 1988f) as determined by PCB concentrations in the offgas. For non-thermal technologies (including thermal desorption), EPA considers equivalent performance to be removal or destruction of the PCBs such that PCBs cannot be quantified in the residual waste or in releases to the air, water, or land. This requirement means that solid matrices or organic liquids must contain less than 2 ppm PCBs per resolvable gas chromatograph peak; aqueous waste must contain 0.5 ppb or less of PCBs; and air emissions must contain less that 10 $\mu g/m^3$ of PCBs. Any stream that does not meet these standards is still regulated under TSCA.

2.2 Design Input Basis

• Sludge Volume	50 m^3
• Maximum PCB Concentration (as settled wet sludge)	140 ppm (Schmidt 1997)
• Process Rate:	52 m^3/10 months (0.17 m^3/day)
• Aroclor 1254 Water Solubility	12 ppb (Erickson 1991)

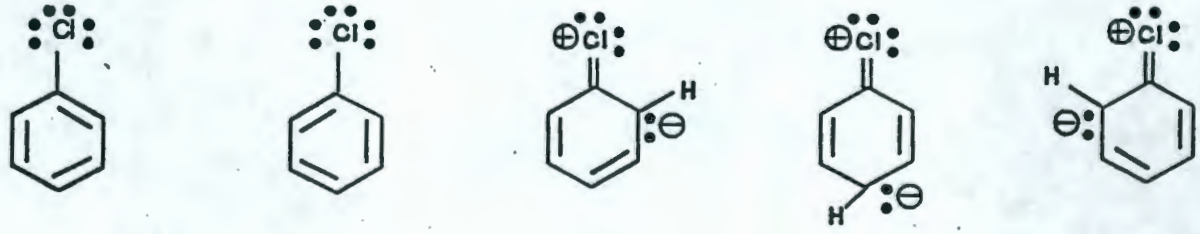
3.0 TECHNOLOGY PRE-SCREENING

3.1 Properties

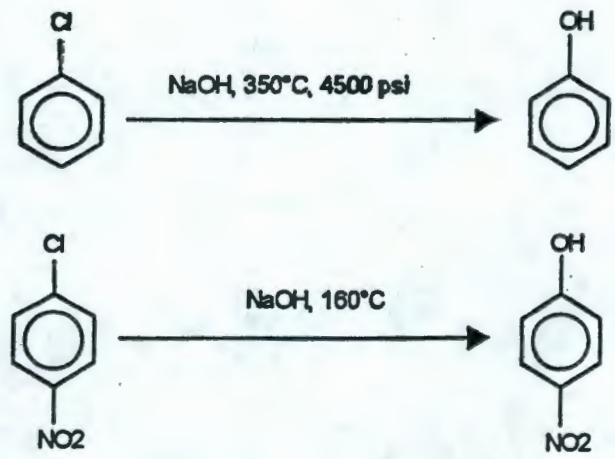
During the process of dissolution, some of the PCBs will be released into solution. The released PCBs will then exist in several phases. Some of the PCB will be absorbed on the remaining undissolved solids and possibly walls of tanks and piping. There will be the water soluble portion of PCBs that ranges from 0.00011 ppm for 2,2', 3,3', 4,4', 5,5', 6 Nonachlorobiphenyl to 5.9 ppm for 2 Monochlorobiphenyl (Erickson 1991). As a point of reference, the drinking water standard is 0.0005 mg/L. If the quantity of PCBs is sufficient, another liquid phase can form which would sink being a dense, non-aqueous phase liquid (DNAPL). This organic liquid phase would be a thin film of pure PCBs. However, based on the small quantities involved, a separate organic phase is not expected. In addition, there will be complex equilibria between these phases and the vapor above it. Therefore, a PCB removal process requires consideration of this distribution to quantify a treatment process(es).

Some of the other important properties are included in Appendix A. PCBs exhibit relatively low vapor pressures. The vapor pressures range up to 1.12 Pa (0.0084 mm Hg) for 2-chlorobiphenyl, the most volatile congener. Vapor pressures are higher for less chlorinated PCBs similar to solubilities. The partition coefficients (K_{ow}'s) are also high indicating an affinity for solid and organic phases. A chemical with a large K_{ow} ($>10^4$) is considered hydrophobic and tends to accumulate at organic surfaces, such as on humic soil.

Appendix D includes structures of some of the organics treated by reference processes in this study. It is difficult to infer treatability of a particular organic compound from a knowledge of a different one. For example, if a process successfully destroys pentachloro phenol the likelihood of also destroying PCB is not as great as the converse situation. The stability of PCBs stems from the de-localized π electrons, i.e., the entire PCB structure is in resonance. This is shown below by considering the resonance structure of chlorobenzene, a closely related structure to PCB.



The Cl-C bonds are unusually short and strong (Morrison and Boyd 1973) which owes to this structures stability. The same is true for PCB a very similar structure. If one of the other positions on the ring are occupied by something like nitrate (NO_2), it is far easier to treat chemically as electron withdrawing groups activate toward nucleophilic substitution. The converse is also true, electron releasing groups (-OH, -NH_2, -R) deactivate towards nucleophilic substitution. The following two reactions indicate nucleophilic substitutions and the much higher energy required to substitute unactivated chlorobenzene.



For regular dissolver operations, treatment of offgas for PCBs is probably not required. Table 1-1 is based on Raoults Law (a very limited approximation), which states that the vapor pressure of a component is the vapor pressure of the pure component times the mole fraction of that component

$$y_i P = P_v x_i$$

where y_i = vapor mole fraction of I
x_i = liquid mole fraction of I
P = system pressure
P_v = I's pure component vapor pressure

Table 3-1: Vapor pressure of Aroclor 1254 and 2-monochloro-biphenyl as a function of temperature

T, °C	$_v$[1], mm H	Sol., ppb[2]	Vap. Conc.,	Sol., ppb[2]	Vap. Conc.,
		Aroclor 1254	ug/m^3	Congener 2	ug/m^3
25	0.008	12	9.19E-05	5600	0.04
89.3	1	12	0.01	5600	4.41
100	1.8	12	0.02	5600	7.71
109.8	5	12	0.04	5600	20.87
1. To convert to Pascals, divide by 0.0075					
2. Assumes no change as temperature increases					

This is highly simplified and Henry's Law would be more appropriate if the constants were available but provides an approximate magnitude of what type of treatment will be required. The values are considered conservative as they are based on the vapor pressure of the most volatile congener,2-monochloro biphenyl (labeled as congener 2) and thermodynamic equilibrium. This table show that just by cooling down the gas temperature (it is achieved in our processed in the condenser where gas are cooled below 40 C), it is probably possible to keep the PCBs concentration below 10 μg/m^3 even for volatile species such as 2-monochloro biphenyl.

Although offgas may not require any treatment for PCB removal, it may be prudent to include a backup based on the uncertainties involved.

3.2 Technology Summary Descriptions

The following sections contain process descriptions, a reference process (or case history/examples including research), applicability and whether the process/technology is screened out or retained for further analysis. Pre-screening criteria are based on feasibility, maturity and sludge-specific applicability

3.2.1 Advanced Oxidation Technologies

Advanced Oxidation Technologies (AOT) is a subset of high energy chemistry that uses free radicals or photons to oxidize the target compound. Most of these processes work by generation of free radicals followed by attack on the targets bonds by the free radicals. All of these processes are commercially available. However, some of them have certain restrictions in their use (e.g., nitrates, liquid only, etc.). The following are some of the processes comprising AOT.

3.2.1.1 Ultra Violet/Hydrogen Peroxide

3.2.1.1.1 Process Description

This process consists of a chemical reactor (batch or flow-through) that uses internal ultra violet (UV) light to produce free-radical hydroxyls $H_2O_2 + h\nu \rightarrow 2OH\cdot$.

The free radicals extract electrons from the target creating a free radical target product. The ensuing mechanism is a chain reaction eventually degrading the target to CO_2 and H_2O and other simple, less-regulated compounds. The overall reaction can usually be modeled by first order kinetics. The design relation used for this type of reactor is the electrical energy per order (EE/o), the electrical energy per volume per order of magnitude in J/m^3/order (kwh/1000 gal/order). This relationship provides all of the information required to determine efficiency (i.e., once known, any efficiency can be obtained by adjusting the power).

3.2.1.1.2 Reference Process

A groundwater treatment process treating PCBs via H_2O_2/UV is in operation in Grand Rapids, Michigan (Calgon 1998). There are design data available for destroying PCB via H_2O_2/UV. The EE/o, a design relation similar to a first-order reaction constant, is 1.7×10^7 J/m^3/order (18 kwh/1000 gal/order) which is high relative to other organics but indicates feasibility. This is a 10 g.p.m. unit with a 90 kW lamp treating PCBs from 18 ppb to 2 ppt. Calgon also has another unit at Bedford Ma treating PCB from 320 ppb to 1 ppb. There is a unit at Hanford treating low-level, non-PCB wastes at the Effluent Treatment Facility (ETF). The ETF unit is a Peroxypure UV/peroxide system treating approximately 150 g.p.m.. The compounds being treated are chlorinated alkenes (e.g., trichlorocthylone).

3.2.1.1.3 Applicability

3.2.1.1.3.1 Aqueous

This processing technology was developed for and applies to aqueous liquids. There are several facilities treating water containing organics with UV/peroxide throughout the United States. This process will not work for dissolver product as the required UV is strongly absorbed by nitrates which are expected to be much higher than normal limits (100 ppm) for this type of process.

3.2.1.1.3.2 Solids

This process will not work on solids or liquids containing significant undissolved solids. The process depends on the transmittance of UV light that solids interfere with and is not applicable to solids except possibly in thin films of feed.

3.2.1.1.3.3 Gases

This process is not designed for gases.

3.2.1.1.4 Screening Status

The UV/peroxide process described above is a well-developed, commercial process that has been used or is currently used for the destruction of hazardous organic compounds. However, high nitrates in the feed will preclude any process requiring UV as UV is strongly absorbed by nitrate. It is believed that the mechanism for destroying PCBs is synergistic, i.e., UV is required to activate PCB followed by attack from the hydroxyl free radical:

$$PCB + h\nu \rightarrow PCB^{\ddagger}$$

$$PCB + OH^{\cdot} \rightarrow \text{organic free radicals}$$

Therefore, UV peroxide processes are not carried forward as viable processes for further evaluation.

3.2.1.2 Ozone/Ultra Violet

3.2.1.2.1 Process Description

This is similar to UV/peroxide but ozone is used. The ozone reacts with UV as

$$O_3 + h\nu \rightarrow O_2 + O:$$

The superoxygen then reacts with water to form the hydroxyl free radical. So, this is virtually the same as UV/H_2O_2 but is sometimes used where ozone/UV synergism is beneficial.

3.2.1.2.2 Reference Process

A Superfund site at Arvin, California, treats pesticide contaminated soil wash water was used to destroy Dinoseb, DDT, and dichloro phenol (DCP) using an 18,000 J/s (18 kW) system and a 7.4×10^{-5} kg/s (14 lbm/d) ozone generator in a batch reactor. The Dinoseb was reduced from 600 ppm to < 100 ppb. There is some structural similarity between DCP and PCBs as they both contain chlorinated benzene rings. However, DCP should be easier to treat based on previous discussion. Some structural comparisons are made in Appendix D for PCBs and other compounds in the reference processes.

3.2.1.2.3 Applicability

3.2.1.2.3.1 Aqueous

This processing technology was developed and applies to aqueous liquids. This is a very similar process to UV/peroxide and therefore not applicable to dissolver product.

3.2.1.2.3.2 Solids

This process will not work on solids or liquids containing significant undissolved solids. The process depends on the transmittance of UV light that solids interfere with and is not applicable to solids.

3.2.1.2.3.3 Gases

This process is not designed for gases although it may be feasible but not likely efficient as gases would need to be absorbed through the reactor. The absorption represents interphase mass transfer which is not likely to be very fast for PCBs in water. Also, it is not considered a practical application.

3.2.1.3 Non-Ultra Violet Hydroxyl Radical Processes

3.2.1.3.1 Process Description

Ozone/Peroxide. In this one, ozone reacts directly with peroxide

$$O_3 + H_2O_2 \rightarrow OH^- + O_2 + HO_2^{\cdot}$$

and no UV light is required. Since no UV is required, this process is beneficial in murky waters.

Ozone/base. Similarly, ozone in high pH water

$$2O_3 + H_2O \rightarrow OH^- + O_2 + HO_2$$

Fentons Reagent. Iron II (ferrous) is oxidized by peroxide in this AOT technology

$$Fe^{+2} + H_2O_2 \rightarrow Fe^{+3} + OH^- + OH^{\cdot}$$

Pacific Northwest National Laboratory (PNNL) has done various testing using Fentons reagent. The consensus from this testing is that no reaction is occurring with the hydroxyl free radical. Data results tend to confirm this (Hoppe 1998).

Another similar catalytic system has been developed by AEA Technology. AEA Technology began development of the ModuleOx™ process for the treatment of organic wastes in 1987. The basic chemistry of the process involves mixing hydrogen peroxide with organic waste at a controlled rate in the presence of a homogeneous catalyst. The destruction of the organics proceeds by a free radical mechanism initiated by the presence of hydroxyl radicals. For PCB destruction, derivatization pre-treatment is required for this process.

JGC Corporation (TODO, et al 1995) have developed a similar process to AEA's using copper or iron as a catalyst (the WetOx Process). This process, like AEA's, was developed to oxidize ion exchange resins and other organic compounds.

3.2.1.3.2 Reference Process

Wood treatment plant in Missouri. UV/Fenton and a proprietary catalyst (ENOX 510, by Calgon) were used to reduce pentachlorophenol (PCP) from 1000 ppb to < 10 ppb. However, A 60,000 J/s (60 kW) UV system was also used in this process. There is some similarity between PCPs and PCBs as shown in Appendix E. However, based on previous discussion concerning nucleophilic substitution, PCP should be easier to treat. A full-scale peroxide/catalyst demonstration plant was constructed by JGC in 1987 for treating ion exchange resins and chelating agents (e.g., ethylenediaminetetraacetic acid (EDTA)) which are not very similar to PCBs with respect to reactivity. This fully operating system was moved to a nuclear plant in 1994 in Japan.

3.2.1.3.3 Applicability

3.2.1.3.3.1 Aqueous

These processing technologies were developed and apply to aqueous liquids. These processes have potential applicability to dissolver product as no UV is required. All of these processes involve hydroxyl free radicals which destroy organic compounds via the same mechanisms. However, PNNL testing indicates Fentons reagent is not effective for PCBs. Therefore, these processes are not applicable to dissolver product.

3.2.1.3.3.2 Solids

These processes will work on solids or liquids containing significant undissolved solids and K Basin sludges as no UV is required. However, PNNL testing indicates Fentons reagent is not effective for PCBs. Therefore, these processes are not applicable to sludges.

3.2.1.3.3.3 Gases

These processes are not designed for gases although it may be feasible but not likely efficient as gases would need to be absorbed through the reactor. The absorption represents interphase mass transfer which is not likely to be very fast for PCBs in water. Also, it is not considered a practical application.

3.2.1.3.4 Screening Status

Non-UV peroxide processes are not carried forward as viable processes for further evaluation.

3.2.1.4 Direct Ultra Violet

3.2.1.4.1 Process Description

Direct irradiation of organic micro pollutants by high-intensity UV light provides a significant destruction pathway. The target compounds degrade after absorbing UV light. The target must strongly absorb UV as in N-nitrosodimethylamine (NDMA).

NDMA + UV → Non-regulated fragments

3.2.1.4.2 Reference Process

Regional water authority (largest NDMA treatment system in the world). This 0.038 m^3/s (600 g.p.m.) unit treats NDMA from 20 ppb to < 14 ppt.

3.2.1.4.3 Applicability

3.2.1.4.3.1 Aqueous

This processing technology was developed and applies to aqueous liquids. This process does not apply to dissolver product as UV is strongly absorbed by nitrates.

3.2.1.4.3.2 Solids

This process will not work on solids or liquids containing significant undissolved solids. The process depends on the transmittance of UV light that solids interfere with and is not applicable to solids.

3.2.1.4.3.3 Gases

This process is not designed for gases although it may be feasible to place a UV system in the process ventilation system.

3.2.1.4.4 Screening Status

UV processes are not carried forward as viable processes for further evaluation.

3.2.1.5 Ultra Violet/Visible/Peroxide.

3.2.1.5.1 Process Description

This is normally used where other components absorb large quantities of the UV transmitted. The lamp has a much larger spectrum which reduces the energy cost compared to UV alone. The process uses a proprietary catalyst which is regenerated

$$\text{Catalyst} + h\nu \rightarrow \text{Cat}^{\ddagger}$$

$$\text{Cat}^{\ddagger} + H_2O_2 \rightarrow \text{Catalyst} + 2OH^{\cdot}$$

3.2.1.5.2 Reference Process

No installation identified.

3.2.1.5.3 Applicability

3.2.1.5.3.1 Aqueous

This processing technology was developed for aqueous liquids. However, based on previous discussions, the PCB probably requires high UV absorbance in addition to hydroxyl free radicals to decompose. Therefore this process is not applicable to dissolver product.

3.2.1.5.3.2 Solids

This process will not work on solids or liquids containing significant undissolved solids. The process depends on the transmittance of light that solids interfere with and is not applicable to solids.

3.2.1.5.3.3 Gases

This process is not designed for gases although it may be feasible but not likely efficient as gases would need to be absorbed through the reactor. The absorption represents interphase mass transfer which is not likely to be very fast for PCBs in water. Also, it is not considered a practical application.

3.2.1.3.4 Screening Status

Visible/UV/peroxide processes are not carried forward as viable processes for further evaluation.

3.2.1.7 Direct Chemical Oxidation (sulfate free radical)

3.2.1.7.1 Process Description

DCO is a non-thermal, ambient pressure, aqueous based technology for the oxidative destruction of the organic components of hazardous or mixed waste streams (Lawrence Livermore National Laboratories (LLNL) 1998b). The process uses solutions of peroxydisulfate salts (typically sodium or ammonium) to completely mineralize the

organics to carbon dioxide and water, and the expended oxidant may be electrolytically regenerated to minimize secondary waste. The net waste treatment reaction for non-refractories is

$$S_2O_8^{-2} + \{\text{organics}\} \rightarrow 2HSO_4^{-} + (CO_2, H_2O, \text{inorganic residues})$$

Mild thermal activation (80-100°C) of peroxydisulfate solutions results in the generation of the sulfate free radical, which is the active oxidizing agent required for recalcitrant, highly stable compounds like PCBs:

$$S_2O_8^{-2} \Rightarrow 2SO_4^{\cdot-}$$

Alternatively, this radical-generation process may be effected at near ambient temperatures (30 to 50°C) through the use of a catalyst such as platinum, silver or copper. The reaction of the sulfate free radical with the organic and with water results in a cascade of active oxidants including organic free radical fragments, hydroxyl free radicals, peroxymonosulfate (a strong industrial bleach), hydrogen peroxide, etc.

The general problem solved by DCO technology is the total oxidative destruction (by non-thermal, ambient pressure, low temperature means) of nearly any organic solid or liquid. This includes solvents, detergents, pesticides, water-insoluble oils and greases, charcoal filter media, incinerator chars and graphite, paper, plastics (excepting perfluorinated polymers), highly chlorinated and nitrated wastes, and organics immobilized in organic/inorganic matrices such as soils, sands or sludges. Solutions of the oxidant can be used to treat inaccessible wastes (such as radioactively-contaminated organics within metal machinery, glove boxes, or weapons components), as a surface etching agent for contaminated metal or plastic equipment, and in decontamination or destruction of chemical warfare agents, explosives and propellants. Potentially important applications include destruction of any organic materials in a medium containing free chloride, nitrate, phosphate, sulfate, or carbonate ions, with a reduction in secondary waste: chloride is converted to free chlorine, which is segregated from the waste and converted to NaCl, carbonate is liberated as carbon dioxide, amino nitrogen is converted to ammonium ion, and nitrite ion is converted to nitrate. Since ammonium peroxydisulfate can be stored almost indefinitely at room temperature, the process of waste destruction can be decoupled in time and place from the generation of peroxydisulfate oxidant.

3.2.1.7.2 Reference Process

Existing industrial basis: Thousands of tons of ammonium peroxydisulfate are used annually to destroy hydraulic fluids used to fracture rock in enhanced petroleum recovery; massive amounts are used as industrial bleaches, etchants, reaction initiators, etc. Peroxydisulfate has also been used to oxidize recalcitrant structures found in coal, as part of a coal-depolarized electrolytic production of hydrogen gas. Because of these industrial uses, large scale sulfate-to-peroxydisulfate electrolysis equipment is available for lease or purchase.

Personnel at LLNL have indicated that DCO does destroy the PCBs but further testing is required to quantify results and obtain kinetic data (LLNL 1998c). Results are available from the LLNL testing program (LLNL 1997). Appendix C presents the results of testing at LLNL (used with permission from Bryan Balazs of LLNL). However these results are preliminary and there is a lack of control experiments in order to clearly understand if the PCBs have been destroyed or are simply on the surface of the experimental vessel.

3.2.1.7.3 Applicability

3.2.1.7.3.1 Aqueous

This processing technology was developed and applies to aqueous liquids (research funded under mixed waste focus area (LMITCO 1998)). This process is very applicable to nuclear waste liquids and sludges as it involves only adding a chemical to a reactor and heating and agitating.

3.2.1.7.3.2 Solids

This process may work on solids or liquids containing significant undissolved solids. The DCO process is likely effective for PCBs on K Basin sludges but testing is required to verify effectiveness for this particular form of a solid.

3.2.1.7.3.3 Gases

This process is not designed for gases although it may be feasible but not likely efficient as gases would need to be absorbed through a reactor. The absorption represents interphase mass transfer which is not likely to be very fast for PCBs in water. A special reactor based on simultaneous mass transfer and chemical reactions could be designed as part of a scrubber system but is not considered practical for this application.

3.2.1.8 Screening Status

The DCO process is evaluated further in Section 4.

3.2.2 Reduction by Aqueous Electron

The hydrated electron is a very strong reducing agent that can react with halogenated alkanes and alkenes. The hydrated electron interacts with the chlorine-carbon bonding electrons providing energy to break the bond and demineralize the target. There are several commercially available processes involving reduction via aqueous electrons. The aqueous electron is produced by several mechanisms including nuclear and high energy processes, photochemistry, and chemically. Some processes require transfer of high energy electrons through thin films of water as the free path or linear energy transfer is small for electrons (high voltage process).

3.2.2.1 Calgon Ultra Violet Catalyzed Process

3.2.2.1.1 Process Description

The Calgon process is a UV catalyzed process. The chemical added is a proprietary catalyst (ENOX 710). The catalyst interacts with UV light produces the aqueous electron ($e^- \cdot xH_2O$ or e^-_{aq}). An example of this production reaction is:

$$Fe(CN)_6^{-4} + h\nu \rightarrow Fe(CN)_6^{-3} + e^-_{aq}$$

The aqueous electron then interacts with the chlorine-carbon bond producing chloride ion and a free radical chlorinated aromatic.

$$e^-_{aq} + C_{12}H_5Cl_5 \rightarrow C_{12}H_5Cl_4\cdot + Cl^-$$

The free radical goes on to extract electrons from another molecule and a chain reaction usually occurs. The rate constants for reductions are normally quite large. This process is particularly well suited to compounds not amenable to advanced oxidations, e.g., CCl_4. The UV induced process is commercially available (e.g., Calgon Advanced Oxidation Technologies).

3.2.2.1.2 Applicability

3.2.2.1.2.1 Aqueous

This processing technology was developed and applies to aqueous liquids including organic liquids. The process is not applicable to dissolver product which will have high nitrates that interact with the aqueous electron. Nitrates are a well know scavenger of hydrated electrons. The G value for water radiolysis is significantly decreased by nitrates in solution. This scavening reaction is (Bugaenko et al, 1993):

$$NO^-_3 + e^-_{aq} \rightarrow NO^{-2}_3$$

3.2.2.1.2.2 *Solids*

This process will not work on solids or liquids containing significant undissolved solids. The process depends on the transmittance of UV light that solids interfere with and is not applicable to solids.

3.2.2.1.2.3 Gases

This process is not designed for gases although it may be feasible to place a UV system in the process ventilation system.

3.2.2.1.3 Screening Status

The aqueous electron interacts with NO_3^- which will be abundant in dissolver product. This virtually eliminates this process as a candidate technology in the aqueous phase dissolver product.

3.2.2.2 High Voltage Electron

3.2.2.2.1 Process Description

High-energy electron irradiation of water produces a large number of very reactive chemical species, including the aqueous electron (e^-_{aq}), the hydrogen radical ($H_2\cdot$), and the hydroxyl radical ($OH\cdot$). These short-lived intermediates break down organic contaminants in aqueous wastes.

In the principal reaction, the aqueous electron transfers to halogen-containing compounds, breaking the halogen-carbon bond and liberating halogen anions such as chloride (Cl^-) or bromide (Br^-). The hydroxyl radical can undergo addition or hydrogen abstraction reactions, producing organic free radicals that decompose in the presence of other hydroxyl radicals and water. In most cases, organics are converted to carbon dioxide, water, and salts. Lower molecular weight aldehydes, haloacetic acids, and carboxylic acids form at low concentrations in some cases.

During the high-energy electron irradiation process, electricity generates high voltage electrons. The electrons are accelerated by the voltage to approximately 95% of the speed of light. They are then directed into a thin stream of water or sludge. All reactions are complete in less than 0.1 second. The electron beam and waste flow are adjusted to deliver the necessary dose of electrons. Although this is a form of ionizing radiation, there is no residual radioactivity.

High Voltage Environmental Applications, Inc. (High Voltage), has developed a mobile facility to demonstrate the treatment process (High Voltage 1998). This treatment process can effectively treat more than 100 common organic compounds. These compounds include the following:

- Trihalomethanes (such as chloroform), which are found in chlorinated drinking water
- Chlorinated solvents, including carbon tetrachloride, trichloroethane, tetra chloroethene, trichloroethene, ethylene dibromide, dibromo-chloropropane, hexachlorobutadiene, and hexachloroethane
- Aromatics found in gasoline, including benzene, toluene, ethylbenzene, and xylene (BTEX)
- Chlorobenzene and dichlorobenzenes
- Phenol
- Dieldrin, a persistent pesticide
- PCB
- A variety of other organic compounds

The treatment process is appropriate for removing various hazardous organic compounds from aqueous waste streams and sludges.

3.2.2.2.2 Reference Process

The high-energy electron irradiation process was accepted into the SITE Emerging Technology Program in June 1990. Based on results from the Emerging Technology Program, the process was invited to participate in the Demonstration Program.

The treatment process was demonstrated at the U.S. Department of Energy's (DOE) Savannah River site in Aiken, South Carolina during two different periods totaling 3 weeks in September and November 1994. The demonstration of a trailer-mounted treatment system took place on a portion of the Savannah River site known as M Area. During the demonstration, the system treated about 70,000 gallons of M-Area groundwater contaminated with volatile organic compounds (VOC). The principal groundwater contaminants were trichloroethylene (TCE), and PCE, which were present at concentrations of about 27,000 and 11,000 micrograms per liter (μg/L), respectively. The groundwater also contained low levels of cis-1,2-dichloroethene (40 μg/L). The following compounds were also spiked into the influent stream at approximately 500 μg/L: 1,2-dichloroethane, carbon tetrachloride, 1,1,1-trichloroethane, chloroform, and BTEX. The highest VOC

removal efficiencies were observed for TCE (99.5%), PCE (99.0%), and dichloroethene (greater than 99%). Removal efficiencies for chlorinated spiking compounds ranged from 68 to 98%, and removal efficiencies for BTEX ranged from 88 to 99.5%.

3.2.2.2.3 Applicability

3.2.2.2.3.1 Aqueous

This processing technology was developed and applies to aqueous liquids including organic liquids. The process is not applicable to dissolver product which will have high nitrates that interact with the aqueous electron.

3.2.2.2.3.2 Solids

Apparently, this process will work on solids in the form of sludge. This process is applicable to sludges prior to dissolver operations.

3.2.2.2.3.3 Gases

No reference has been found on the use of that process for gas phases.

3.2.2.2.4 Screening Status

This process is retained as a potential method as it is possible to use it on solids. It can also be used as a secondary process that would follow a potentially applicable primary process (e.g., solvent extraction).

3.2.2.3 Gamma Radiolysis

3.2.2.3.1 Process Description

In this process, PCBs in polar solvents or water are radiated with gamma radiation. The laboratory studies completed indicate the mechanism is the solvated electron or electron capture similar to the discussion on reduction via the aqueous electron. The most thoroughly studied solvent has been alkaline isopropanol. It is well known that in alkaline isopropanol decomposition proceeds rapidly via reductive, chain-reaction dechlorination to produce lesser chlorinated, "daughter" PCBs (Mincher 1996). Upon continued irradiation, non-chlorinated biphenyl is produced. G values in excess of 1000 molecules/electron volt/gram have been previously reported (Singh, et al 1985). The perceived process is similar to UV, i.e., a batch or plug flow reactor with an internal gamma source irradiates the process fluid. The reaction follow first order kinetics. Plotting log concentration versus dose results in a straight line.

3.2.2.3.2 Reference Process

Aroclor 1260 was destroyed at Idaho National Engineering Laboratory (INEL) (Mincher et al, 1996 and Mincher et al, 1991) using gamma sources from Advanced Test Reactor spent nuclear fuel in laboratory studies. The radiolysis was conducted in organic media, principally alkaline isopropanol but also isooctane and transformer oils (Mincher et al, 1996). A sealed tube containing the PCB and solvent was lowered down into a spent fuel rack. Absorbed doses were measured using FWT-60 radiochromic film. Dose rates varied from 30

kGy/hr. to 1 kGy/hr. The average gamma energy was 700 keV. The laboratory work completed indicates a first order-type behavior similar to UV, i.e., plotting the log of concentration versus dose results in a straight line. However, as the radiolysis is much more effective in an organic medium, solvent extraction may first be required. While low doses (0.5 kGy) achieved significant decomposition in deaerated alkaline isopropanol, fairly high doses (43 kGy) were required in aerated aqueous solutions (Mincher et al, 1991).

3.2.2.3.3 Applicability

3.2.2.3.3.1 Aqueous

This process is possible for aqueous liquids although it requires more energy than in organic solvents. It would be more effective in aqueous if the aqueous is deaerated as oxygen is also a scavenger. This process is not applicable to dissolver product because the nitrate scavenges the hydrated electron produced during radiolysis.

3.2.2.3.3.2 Solids

The same problem exists for treating sludges as in water; it requires much higher doses and dissolved oxygen is a scavenger. An additional problem is that the solids attenuate gamma reducing it's effectiveness. This process was designed chiefly for organic liquids. For sludge, the PCBs would be extracted first then fed to this process. the There are no known facilities using a system similar to this for treating mixed waste and is considered experimental at this stage.

3.2.2.3.3.3 Gases

Gamma radiolysis does not apply to the gas phase.

3.2.2.3.4 Screening Status

Gamma Radiolysis is retained for further analysis in Section 4 as a secondary process.

3.2.2.4 Commodore Process

3.2.2.4.1 Process Description

The Commodore Solvated Electron Technology (SET) is a patented, EPA permitted, non-thermal, mobile, and scalable process which has proven ability to destroy toxic organic contaminants, including PCBs. This process uses a solution of solvated electrons formed by dissolving elemental sodium in anhydrous liquid ammonia:

$$2Na^{\circ} \xrightarrow{\text{Liquid } NH_3} 2Na^{+} + 2e^{-}_{aq}$$

The hydrated electron dechlorinates the PCBs as described previously.

3.2.2.4.2 Reference Process

The SET process is being used for an on-site treatability study at DOE Comprehensive Environmental Response Compensation and Liability Act of 1980 (CERCLA) managed Weldon Spring Site Remedial Action Project in St. Charles, MO. The purpose of the treatability study is to convert Resource Conservation and Recovery Act of 1976 (RCRA)/TSCA organic mixed waste streams to low-level wastes for on-site disposal. The PCBs and other chlorinated hydrocarbons are absorbed on a variety of matrices including soils, rubble, liquids and corn cobs. The process treats between 450 and 1350 kg/d (0.5 and 1.5 ton/day). The process has met the treatment goals of 2 and 50 ppm on solids matrices.

3.2.2.4.3 Applicability

3.2.2.4.3.1 Aqueous

This process is not applicable to aqueous liquids. The sodium metal is too energetic for aqueous liquids.

3.2.2.4.3.2 Solids

The process was designed for solids, sludges, sediments, and organic liquids. Commodore technical personnel indicate they believe it can be used for K Basin sludges (Timm 1998). However, as there is quite a lot of water in the sludge and taking into account the violent reaction of sodium with water, this process does not seem to be fitted to the K Basin sludge.

3.2.2.4.3.3 Gases

This process is not applicable to gas treatment.

3.2.2.4.4 Screening Status

This process is retained for further analysis.

3.2.3 Supercritical Water Oxidation

3.2.3.1 Process Description

Supercritical Water Oxidation (SCWO), sometimes known as hydrothermal waste processing, uses the solvating traits of water in its supercritical condition to effectively destroy liquid organic wastes. As water is heated beyond its critical temperature (374.1°C) and critical pressure (250 MPa, about 3219 pounds force per square inch (psi), the density of the water drops dramatically (typical operating densities are 0.15-0.2 g/cm^3). With these changes in density and hydrogen bonding, organics become highly soluble while inorganic substances become nearly insoluble. The organic material is dissolved in an oxygen rich environment where conversion occurs rapidly due to the high temperature of the process. Under such high pressure and temperature, organic materials are rapidly decomposed by oxidation with removal efficiencies of 99.9999% or greater.

3.2.3.2 Reference Process

This process is being commercialized and there are several pilot plants operating (EWT 1998). PNNL has performed some testing using supercritical processes.

3.2.3.3 Applicability

3.2.3.3.1 Aqueous

This processing technology was developed and applies to aqueous liquids including organic liquids. Based on the high temperature and pressure required, SCWO is probably not a practical choice for dissolver product. Special containment would likely be required to contain accidental radionuclide emissions. Anything under pressure (3,219 psig for SCWO) can spread radioactivity if breached. This fact leads to negative perceptions for using such devices in nuclear facilities. In addition, uranium metals and hydrides can react with water at high temperatures causing highly energetic reactions. Although toxic materials can be spread by such a breach, radionuclides are controlled at much smaller levels. Reverse osmosis (RO) is used at some nuclear facilities (e.g., Hanford's ETF) that develop high pressure. However, these RO units normally process very low level streams and operate at much lower pressure. SCWO requires many unit processes including compressors, fired heaters, and others that may be costly. Another problem deals with insolubles as nitrates and other salts are no longer soluble during supercritical conditions. Also, there are no known similar systems processing mixed wastes.

3.2.3.3.2 Solids

SCWO has been used for processing solids and slurries but handling of solids in this type of process can be very complicated. Moreover, based on the high temperature and pressure required, SCWO is probably not a practical choice for basin sludge (see 3.2.3.3.1).

3.2.3.3.3 Gases

This process is not designed for gases.

3.2.3.4 Screening Status

This technology is tentatively screened out.

3.2.4 Ultrasonic Destruction

3.2.4.1 Process Description

Ultrasound can induce unusual high-energy chemistry through the process of acoustic cavitation: the formation, growth, and implosive collapse of bubbles in a liquid. Cavitation can occur both in clouds of collapsing bubbles (multi-bubble cavitation) or with high symmetry for isolated bubble (single-bubble cavitation). Multi-bubble cavitational collapse produces localized, transient hot spots with intense local heating (approx>5000°K), high pressures (approx>$2x10^8$ Pa [2000 atm]), and short lifetimes (sub-microsecond) in an otherwise cold liquid. From hydrodynamic modeling of this cavitational collapse, we can estimate that both the heating and cooling rates are in excess of 1,010°K/s, which is faster than splat-cooling of molten metals onto liquid He cooled

surfaces. Acoustic cavitation is a unique means of creating high energy chemistry, easily and inexpensively. Aqueous sonochemistry produces, on a microscopic scale, supercritical water conditions.

In this regime of temperature and pressure, the sonochemistry of water is an extreme limiting case of supercritical phenomena and is closely related to hydrothermal oxidation. For example, the ultrasonic irradiation of water produces a variety of extraordinarily reactive species (including OH·, H·, and HO_2·) capable of decomposing essentially all organic compounds. Furthermore, the temperatures reached in the cavitation hot spots are sufficient to pyrolyze all volatile organic compounds.

3.2.4.2. Reference Process

The applications of cavitation to remediation of toxic organics, however, has only begun to be explored in a convincing fashion. Although ultrasonic destruction is a very promising technology, it has not been developed sufficiently. Interesting results have been obtained for PCBs using this technology (Hua 1998) but sufficient data are not available. Research is in progress as funded by DOE (DOE R&D 1996).

3.2.4.3 Applicability

3.2.4.3.1 Aqueous

This processing technology was developed and applies to aqueous liquids. This process may or may not be applicable to dissolver product as not enough is known about it at this time.

3.2.4.3.2 Solids

Ultrasound can be considered for processing solids and slurries but solids tend to absorb and dispersed the energy making ultrasonic destruction less efficient. The desorption from the solids may be the rate determining step. It is possible that this type of process could be used for sludge from K Basins but would require extensive development.

3.2.4.3.3 Gases

This process is not designed for gases.

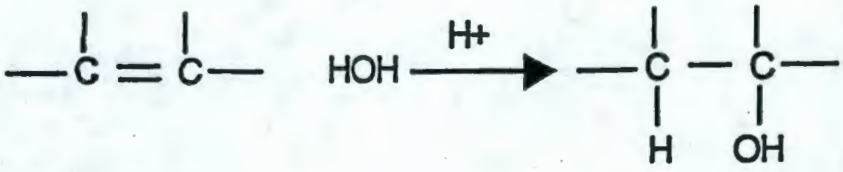
3.2.4.3.4 Screening Status

This technology is not retained for further analysis at this time.

3.2.5 Acid Digestion

3.2.5.1 Process Description

Organic compounds can be hydrated and oxidized under acidic conditions. The reaction below is hydration of a simple alkene.



If this is carried out in hot oxidizing acids, some organic compounds decompose. The DOE has funded the "Mixed Waste Focus Area" at INEL (LMTCO 1998) to use Nitric acid and phosphoric acid in one of these processes. The organics decompose to form CO_2, water and chlorides in the case of chlorinated hydrocarbons. The technology has been commercialized (e.g., Delphi).

3.2.5.2. Reference Process

PNNL has been doing laboratory tests of sludge in nitric acid and hydrogen peroxide mainly in support of sludge dissolution activities (Hoppe 1998). They have also demonstrated that few, if any, PCBs are destroyed by this treatment. Also, no data were available from other researchers in this area (LMTCO 1998).

3.2.5.3 Applicability

3.2.5.3.1 Aqueous

This processing technology was developed and applies to aqueous liquids. Nitric acid processing has been integral to Hanford and other DOE sites since the Manhattan project. Acid digestion would be particularly applicable to dissolver product if feasible as this is the same process used in dissolving sludge (i.e., nitric acid dissolution).

3.2.5.3.2 Solids

Acid digestion is effective for processing solids and slurries. It would be particularly applicable to sludge if feasible as this is the same process used in dissolving sludge (i.e., nitric acid dissolution). Simultaneous dissolving of uranium and PCB destruction would be highly advantageous.

3.2.5.3.3 Gases

This process is not designed for gases.

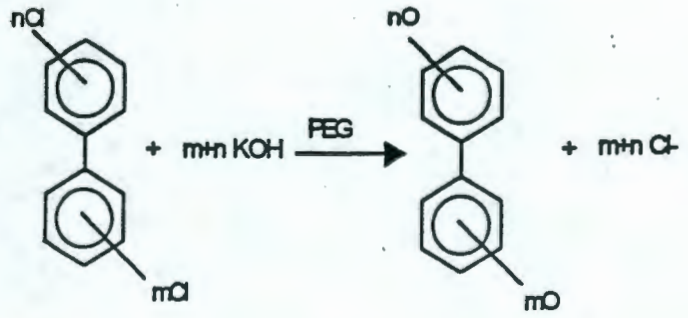
3.2.5.4 Screening Status

As the experiments performed by PNNL have not shown a significant destruction efficiency for PCBs, this process will not be considered further.

3.2.6 Dechlorination

3.2.6.1 Process Description

Chemical reagents prepared from potassium hydroxide and polyethylene glycols (KPEGs) have been demonstrated under mild conditions (25 to 140°C) to dehalogenate chlorinated dibenzo-p-dioxins (PCDDs), PCBs, and chlorinated dibenzofurans (PCDFs) with laboratory destruction efficiencies exceeding 99.9999%. The reaction mechanism is nucleophilic substitution at an aromatic carbon.



Bench-scale studies have already established conditions for PCB destruction to less than 1 ppm and for PCDDs and PCDFs to less than 1 ppb. Toxicological tests have established that arylpolyglycol by-products from KPEG reactions are nontoxic. The non-toxic property of the by-products may allow for delisting and on-site disposal of treated materials.

Dehalogenation (glycolate) is a full-scale technology in which an alkaline polyethylene glycol (APEG) reagent is used to dehalogenate halogenated aromatic compounds in a batch reactor. Potassium polyethylene glycol (KPEG) is the most common APEG reagent. Contaminated soils and the reagent are mixed and heated in a treatment vessel. In the APEG process, the reaction causes the polyethylene glycol to replace halogen molecules and render the compound nonhazardous or less toxic. For example, the reaction between chlorinated organics and KPEG causes replacement of a chlorine molecule and results in a reduction in toxicity. Dehalogenation (APEG/KPEG) is generally considered a standalone technology; however, it can be used in combination with other technologies. Treatment of the wastewater generated by the process may require additional treatment.

The metal hydroxide that has been most widely used for this reagent preparation is potassium hydroxide (KOH) in conjunction with polyethylene glycol (PEG, typically, average molecular weight of 400) to form a polymeric alkoxide referred to as KPEG. Sodium hydroxide has also been used in the past, however, and most likely will find increasing use in the future because of patent applications that have been filed for modification to this technology. This new approach will expand the technology's applicability and efficacy and should reduce chemical costs by facilitating the use of less costly sodium hydroxide. A variation of this reagent is the use of KOH or sodium hydroxide/tetraethylene glycol, referred to as ATEG, that is more effective on halogenated aliphatic compounds. In some KPEG reagent formulations, dimethyl sulfoxide is added to enhance reaction rate kinetics, presumably by improving rates of extraction of the haloaromatic contaminants.

The reagent (APEG) dehalogenates the pollutant to form a glycol ether and/or a hydroxylated compound and an alkali metal salt, which are water-soluble byproducts.

The target contaminant groups for glycolate dehalogenation are halogenated semi-volatile organic carbons (SVOC) and pesticides. The technology can be used but may be less effective against selected halogenated volatile organic carbons (VOC). APEG dehalogenation is one of the few processes available other than incineration that has been successfully field tested in treating PCBs. The technology is amenable to small-scale applications.

3.2.6.2 Reference Process

Dehalogenation (glycolate) has been used to successfully treat contaminant concentrations of PCBs from less than 2 ppm to reportedly as high as 45,000 ppm. This technology has received approval from the EPA's Office of Toxic Substances under the TSCA for PCB treatment. The APEG process has been selected for cleanup of PCB-contaminated soils at three Superfund sites: Wide Beach in Erie County, New York (September 1985); Re-Solve in Massachusetts (September 1987); and Sol Lynn in Texas (March 1988).

This technology uses standard equipment. The reaction vessel must be equipped to mix and heat the soil and reagents. PCDDs and PCDFs have been treated to nondetectable levels at part per trillion sensitivity. The process has successfully destroyed PCDDs and PCDFs contained in contaminated pentachlorophenol oil. For a contaminated activated carbon matrix, direct treatment was less effective, and the reduction of PCDDs/PCDFs to concentrations less than 1 ppb was better achieved by first extracting the carbon matrix with a solvent and then treating the extract.

Site Name	Chemical	Media	Beginning	Attained	DF
Montana Pole Butte, MT	Dioxin, Furans	Oil	<84 ppm	<1 ppb	84
Wide Beach Erie County, NY	PCBs (Aroclor 1254)	Soil	120 ppm	<2 ppm	60
Economy Products Omaha, NE	TCDD,	Liquid	1.3 ppm	Non-detec	
	2, 4-D	17,800 ppm	2,800 ppm	6.3	
	2, 4, 5-T	334 ppm	55 ppm	6.1	

3.2.6.3 Applicability

3.2.6.3.1 Aqueous

This processing technology was developed and applies to organic liquids (e.g., transformer oils) and solids. The process does not apply to aqueous liquids (Freeman 1989). Regarding dissolver product, the PCB would first require extraction into a solvent phase (or other type of removal from the aqueous) in several batches (batch) or stages (continuous). The resulting extract would then be treated via dechlorination. There are no known processes like this treating mixed waste.

3.2.6.3.2 Solids

Dechlorination is effective for processing solids and slurries. This process appears applicable to the basin sludge. However, this would require demonstration and possibly require dewatering. Also, no evidence was found indicating that this has ever been performed or evaluated for use with mixed wastes.

3.2.6.3.3 Gases

This process is not designed for gases.

3.2.6.4 Screening Status

This process is retained for further analysis in Section 4.

3.2.7 Thermal

Thermal processes include a large cadre of technologies used in PCB destruction. Thermal processes would comprise a complete, separate subject by themselves. Some of these include incineration, molten salt and vitrification, thermal desorption and catalysis, wet air oxidation. Thermal processes are an effective and accepted method of destroying PCBs for certain kinds of feeds.

3.2.7.1 High Temperature Thermal Desorption

3.2.7.1.1 Process Description

High Temperature Thermal Desorption (HTTD) is a process in which wastes are heated to 320 to 560°C (600 to 1,000°F) to volatilize water and organic contaminants. A carrier gas or vacuum system transports volatilized water and organics to the gas treatment system. HTTD systems are physical separation processes and are not designed to destroy organics. Bed temperatures and typical residence times will cause selected contaminants to volatilize but not be oxidized. HTTD is frequently used in combination with incineration, solidification/stabilization, or dechlorination, depending upon site-specific conditions. The technology has proven it can produce a final contaminant concentration level below 5 mg/kg (5 ppm) for the target contaminants identified.

The target contaminants are SVOCs, polycyclic aromatic hydrocarbons, PCBs, and pesticides; however, HTTD systems have varying degrees of effectiveness against the full spectrum of organic contaminants. VOCs and fuels also may be treated, but treatment may be less cost-effective. Volatile metals, including some radionuclides (e.g., ^{137}Cs), may be removed by HTTD systems. The presence of chlorine can affect the volatilization of some metals, such as lead. The process is applicable for the separation of organics from refinery wastes, coal tar wastes, wood-treating wastes, creosote-contaminated soils, hydrocarbon -contaminated soils, mixed (radioactive and hazardous) wastes, synthetic rubber processing wastes, and paint wastes.

3.2.7.1.2 Reference Process

There are at least five vendors actively promoting the technology, and most of the hardware components for HTTD systems are readily available off the shelf. The time to complete cleanup of the "standard" non-nuclear, 18,200-metric ton (20,000-ton) site using HTTD is just over 4 months.

Site Information:

Site Name	Contact	Summary	Beginning	Attained	DF
Escambia Wood Treating Company Superfund Site, Pensacola, FL	Terri Richardson EPA RREL 26 West M.L. King Dr. Cincinnati, OH	Pilot scale, featuring particle size classification and surfactant addition.	550-1,700 ppm PAHs 48-210 ppm PCP (projected)	45 ppm PAHs, 3 ppm PCPs	12 16

3.2.7.1.3 Applicability

3.2.7.1.3.1 Aqueous

This processing technology is not applicable to liquids.

3.2.7.3.2 Solids

Thermal desorption is effective for processing solids and slurries. The desorption from the solids may be the rate determining step. This process appears compatible with K Basin sludges and is believed to be applicable at this time. However, corrosion reactions producing hydrogen will be accelerated at the higher temperature involved. This could lead to rapid reactions that are hard to control. No known similar processes are being used at DOE facilities but EPA has stated the process is applicable to radioactive sludges.

3.2.7.3.3 Gases

This process is not designed for gases.

3.2.7.4 Screening Status

This technology for K Basin sludges is retained for further analysis in Section 4.

3.2.7.5 Incineration

3.2.7.5.1 Process Description

High temperatures, 870 to 1,200°C (1,400 to 2,200°F), are used to volatilize and combust (in the presence of air) halogenated and other refractory organics in hazardous wastes. The DRE for properly operated incinerators exceeds the 99.99% requirement for hazardous waste and can be operated to meet the 99.9999% requirement for PCBs and dioxins.

Incinerator off-gas requires treatment by an air pollution-control system to remove particulates and neutralize and remove acid gases (HCl, NOX, and SOx). Baghouses, venturi scrubbers, and wet electrostatic precipitators remove particulates; packed-bed scrubbers and spray driers remove acid gases. Incineration is subject to a series of technology-specific regulations, including the following federal requirements: clean air act (air emissions), TSCA (PCB treatment and disposal), RCRA (hazardous waste generation, treatment, storage, and disposal), National Pollution Discharge Elimination System (discharge to surface waters), and Noise Control Act (noise). If an off-site incinerator is used, the potential risk of transporting the hazardous waste through the community must be considered.

3.2.7.5.2 Reference Process

Incineration, primarily off-site, has been selected or used as the remedial action at more than 150 Superfund sites. Approximately 20 commercial RCRA-permitted hazardous waste incinerators and approximately 10 transportable high temperature units are operating. The commercial units are large capacity rotary kilns with afterburners and sophisticated air pollution control systems.

3.2.7.5.3 Applicability

3.2.7.5.3.1 Aqueous

Incineration is applicable to aqueous liquids. The dissolver product is not amenable to incineration based on low organic, high water content and very high radionuclide content (TRU and Beta-gamma). There are no known processes like this in operation at mixed waste facilities.

3.2.7.5.3.2 Solids

Incineration is used to remediate soils contaminated with explosives and hazardous wastes, particularly chlorinated hydrocarbons, PCBs, and dioxins. Incineration may be applicable to sludges. However, the organic content is very low. The incinerator would be required to be permitted for TSCA and high-level waste processing. There are no known systems like this in operation for treating mixed wastes.

3.2.7.5.3.3 Gases

Gases can be burned in incinerators. However, the quantity of gas generated is expected to be small and incineration is not considered practical for this system.

3.2.7.5.4 Screening Status

Incineration is not considered a practical alternative based on best engineering judgement and is not retained for further analysis.

3.2.8 Solvent Extraction

3.2.8.1 Organic Solvent

3.2.8.1.1 Process Description

Solvent extraction would involve contacting the sludge with a suitable solvent to extract the PCBs. This type of operation is normally performed continuous, counter-current but batch processing could also be performed. The solvent would then require another process to destroy the PCBs within the solvent. The solvent would also likely contain traces of radionuclides which could impact the required secondary treatment process. Under some scenarios, the solvent could be recovered (e.g., non-thermal).

Solvent extraction does not destroy wastes but is a means of separating hazardous contaminants from soils, sludges, and sediments, thereby reducing the volume of the hazardous waste that must be treated. The technology uses an organic chemical as a solvent and differs from soil washing, which generally uses water or water with wash-improving additives. Commercial-scale units are in operation; they vary in regard to the solvent employed, type of equipment used, and mode of operation.

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

Solvent extraction has been shown to be effective in treating sediments, sludges, and soils containing primarily organic contaminants such as PCBs, VOCs, halogenated solvents, and petroleum wastes. The technology is generally not used for extracting inorganics (i.e., acids, bases, salts, or heavy metals). Inorganics usually do not have a detrimental effect on the extraction of the organic components. 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-treating wastes, separation sludges, pesticide/insecticide wastes, and petroleum refinery oily wastes. Some soil types and moisture content levels will adversely impact process performance.

3.2.8.1.2 Reference Process

The performance data currently available are mostly from Resource Conservation Company (RCC). The ability of RCC's full-scale B.E.S.T.™ process to separate oily feedstock into product fractions was evaluated by EPA at the General Refining Superfund site near Savannah, Georgia, in February 1987. The treated soils from this unit were backfilled to the site, product oil was recycled as a fuel oil blend, and the recovered water was pH-adjusted and transported to a local industrial wastewater treatment facility.

Site Name	Summary	Beginning	Attained
Port Arthur, TX	Full-scale 50-tpd refinery sludge treatment unit	2,575 ppm	90% PCB reduction--TBD
Conroe, TX	Oil and grease and aromatic priority pollutants	2,879 ppm PAH	122 ppm (DF=24) PAH

3.2.8.1.3 Applicability

3.2.8.1.3.1 Aqueous

Although designed for solids (and considered a solids process by EPA), solvent extraction of an aqueous phase is feasible but not considered practical. It is potentially applicable to dissolver product but no other similar systems are operating as such.

3.2.8.1.3.2 Solids

This process was designed primarily for soils/solids systems. The technology is believed to be applicable to K Basin sludges. However, no other similar sites are known to use this process for mixed wastes.

3.2.8.1.3.3 Gases

Solvent extraction is not applicable to gases.

3.2.8.1.4 Screening Status

Solvent extraction is retained for further analysis in Section 4.

3.2.8.2 Supercritical Carbon Dioxide Extraction

3.2.8.2.1 Process Description

The interest in applications of supercritical extraction in environmental remediation is increasing rapidly (Zimmerman 1958). Contaminated soil, river and lake sediments, and industry sludges are all solid matrices of major environmental concern and supercritical extraction may be a feasible alternative for remediation of these matrices (Erdogan et al, 1993). Water slurries such as basin sludge can be extracted using supercritical fluid extraction (SCFE) (Bruno et al 1991). SCF extraction has been investigated as an alternative clean-up technique to remove organic compounds from soil. SCFE of PCBs from soils have been demonstrated using supercritical CO_2. Greater than 90% of the PCBs were extracted from the solid matrix in less than one minute (Brady et al, 1987). The extraction time is increased by the presence of water which will be the case for basin sludges.

SCFE is similar to the SCWO described previously but differs in a few regards. One is that only extraction occurs whereas in SCWO, oxidation of the organic also occurs. SCFE would require a companion technology to destroy or remove the PCBs after being extracted. The other is that SCFE uses carbon dioxide instead of water. Carbon dioxide requires lower temperature and pressure to become supercritical. The critical point for CO_2 is at T=31°C and P≈ 7.38 Mpa (73 atmospheres).

3.2.8.2.2 Reference Process

SCFE has been developed sufficiently to be considered a viable technology, at least for further testing of K Basin sludges. In fact, the extraction should be less difficult than with soils that have been tested as the sludge has less organics present (excepting, of course, the organic resins which may absorb PCBs disproportionately). There are some cost estimates available that compare SCFE to some of the other technologies (Montero et al, 1996).

3.2.8.2.3 Applicability

3.2.8.2.3.1 Aqueous

This processing technology was developed and applies to aqueous liquids including organic liquids. Based on the high temperature and pressure required, SCFE is probably not a practical choice for dissolver product. Special containment would likely be required to contain accidental radionuclide emissions. Anything under pressure (73 atmospheres for SCFE) can spread radioactivity if breached. This fact leads to negative perceptions for using such devices in nuclear facilities. Although toxic materials can be spread by such a breach, radionuclides are controlled at much smaller levels. RO is used at some nuclear facilities (e.g., Hanford's ETF) that develop high pressure. However, these RO units normally process very low level streams and operate at much lower pressure. Also, there are no known similar systems processing mixed wastes.

3.2.8.2.3.2 Solids

SCFE is effective for processing solids and slurries. Based on the high pressure required, SCFE is probably not a practical choice for basin sludge (see 3.2.13.3.1).

3.2.8.2.3.3 Gases

SCFE is not designed for gaseous treatment.

3.2.8.2.4 Screening Status

SCFE is tentatively screened out based on engineering judgement.

3.2.9 Electrochemical Oxidation

3.2.9.1 Process Description

Electrochemical oxidation has been used to treat hazardous wastes. In one aqueous, room-temperature process referred to as mediated electrochemical oxidation, silver and cobalt ions are generated in an electrochemical cell (LLNL 1998a). These ions are extremely effective at decomposing organic compounds. Organic waste is converted into carbon dioxide gas and water vapor that, after treatment, can be safely vented into the atmosphere. This process is well suited for treating wastewater and for removing toxic organics from contaminated equipment.

3.2.9.2 Reference Process

This process is being developed at LLNL where it was found that PCB polymerizes into a difficult to handle material (Referred to as gunk) under these conditions (LLNL 1998a). The Russians are designing a system like this at Sverodvinsk to treat mixed wastes containing organics but not PCBs.

3.2.9.3 Applicability

3.2.9.3.1 Aqueous

This process is effective for aqueous liquids. The process could be easily configured for dissolver product. Based on the LLNL results, this process is not applicable to dissolver product.

3.2.9.3.2 Solids

Electrochemical oxidation is very effective for slurries and aqueous containing undissolved solids. It is possible that sludge could be treated in an electrochemical unit. The Russian system discussed above included solids/pulps in their system. Based on the LLNL results, this process is not applicable to sludge.

3.2.9.3.3 Gases

Gases are not treated by this method.

3.2.9.4 Screening Status

Based on these observations, electrochemical oxidation is not considered further.

3.2.10 Absorption Processes

3.2.10.1 Granulated Activated Carbon

3.2.10.1.1 Process Description

Effluents containing organics are treated by passing through Granulated Activated Carbon (GAC) beds. The GAC has an extensive pore structure which provides approximately 20,000 m^2/kg internal surface area, depending on the grade. The organic diffuses from the aqueous phase and adsorbs onto the GAC surface via physi-sorption processes. The GAC interior is characterized by macropores (D>10 Å) and micropores (10Å < D

< 1000Å). The absorption properties of GAC result from the high specific surface area of the finished product. Use of granular activated carbon in wastewater treatment systems is a proven process for removal of organic compounds. As a tertiary treatment method, carbon adsorption and regeneration have been used for a number of years to process domestic wastewaters contaminated with industrial wastes of organic origin as well as biologically treated wastewaters.

Activated carbon, when contacted with water containing organic material, will remove these compounds selectively by a combination of adsorption of the less polar molecules, filtration of the larger particles, and partial deposition of colloidal material on the exterior surface of the activated carbon. The extent of removal of soluble organics by adsorption depends on the diffusion of the particle to the external surface of the carbon and diffusion within the porous adsorbent. For colloidal particles, internal diffusion is relatively unimportant because of particle size. Organic substances that pass through the column consist strongly of hydrophilic organic molecules such as carbohydrates and other highly oxygenated organic compounds.

Adsorption is partially the result of forces of attraction at the surface of a particle that cause soluble organic materials to adhere to the particle, and partially attributable to the limited water solubility of many organic substances. Activated carbon has a large and highly active surface area that results from the activation process. This produces numerous pores within the carbon particle and creates active sites on the surface of the pores.

Vapor-phase carbon adsorption is a remediation technology in which pollutants are removed from air by physical adsorption onto activated carbon grains. Commercial grades of activated carbon are available for specific use in vaporphase applications. The granular form of activated carbon is typically used in packed beds through which the contaminated air flows until the concentration of contaminants in the effluent from the carbon bed exceeds an acceptable level. GAC systems typically consist of one or more vessels filled with carbon connected in series and/or parallel operating under atmospheric, negative, or positive pressure. The carbon can then be regenerated in place, regenerated at an off-site regeneration facility, or disposed of, depending upon economic considerations.

3.2.10.1.2 Reference Process

GAC is used in hundreds of applications for both non-radioactive and nuclear facilities. The reference process for liquid effluents discussed is a unit used at the ETF at the Savannah River Plant (SRP 1988). The GAC used at Savannah River Plant removes tri-butyl phosphate and other organic compounds (but not PCBs) upstream of the reverse osmosis unit to prevent fouling of the membrane. The effluent is very low in radionuclides at the ETF. GAC is considered best available technology (BAT) to meet PCB requirements for drinking water (EPA 1991).

3.2.10.1.3 Applicability

3.2.10.1.3.1 Aqueous

The feasibility of GAC for this application is questionable based on pH and TRU uptake. The acidity of dissolver product can attack the GAC matrix structure of Calgons GAC (Calgon 1998b). A rough estimate is that the pH shouldn't be allowed to be less than four (pH≥ 4). However at this pH, uranium uptake is about 10% (1 kg U per 10 kg GAC) and decreases with decreasing pH (Abbasi et al 1994).

3.2.10.1.3.2 Solids

This process cannot handle solids of any significant concentration. The solids plug and block sites used for absorption.

3.2.10.1.3.3 Gases

GAC is considered one of the premier technologies for removing organic compounds, including PCBs, from gaseous effluents. Vapor-phase carbon adsorption is not recommended to remove high contaminant concentrations from the effluent air streams. Economics favor pretreatment of the VOC stream, followed by the use of a vapor-phase GAC system as a polishing step. Based on the low levels of PCBs expected, no pre-treatment is required.

3.2.10.1.4 Screening Status

GAC is not considered feasible for treating aqueous dissolver product based on the current expected flowsheet and is not evaluated further for this. However, it is the only process considered for gases.

3.2.10.2 Other Absorption Processes (e.g., Polyguard)

3.2.10.2.1 Process Description

PolyGuard is one of several commercial absorbents that have potential application for absorbing PCBs from aqueous effluents and gases. PolyGuard is a blend of polymers that work on a principal entirely different than conventional adsorbents such as GAC. PolyGuard's mode of action depends upon the ability of the active material to selectively absorb molecules with suitable solubility characteristics directly into its internal structure to form a stable, solid solution. This mechanism allows absorption of large quantities of molecules which have compatible solubility characteristics.

As shown in appendix A, the partition coefficient (K_{ow}'s) are high. When a chemical has a K_{ow} larger than 10^4, it tends to accumulate on organic surfaces. Recent results obtained by PNNL (Hoppe 1998) have shown that the filtration of an acidic liquor containing PCBs on a filter equipped with an organic membrane was sufficient to remove more than 90% of PCBs initially existing in the solution.

So Absorption of PCBs on organic materials (beads, filters..) Appears really as an interesting alternative.

3.2.10.2.2 Reference Process

A Burton, Ohio site owned by a major petroleum company is treating groundwater containing diesel fuel using PolyGuard that replaced a GAC system. The GAC system could not adapt to slugs of higher concentrations that were occurring. The PolyGuard system was installed in June 1997. Over 150 m^3 (40,000 gallons) have been treated without breakthrough of oil or BTEX that is also present.

3.2.10.2.3 Applicability

3.2.10.2.3.1 Aqueous

PolyGuard was specifically designed for aqueous feeds. It can handle the nitric acid present in dissolver product. Little uptake of TRU is expected but the material needs to be tested to validate this. The organic material may be susceptible to degradation due to radiation fields. However, the total absorbed dose will not be extreme as changeouts will be frequent to limit PCBs to the 500 ppm. No similar system is known to be in use at DOE facilities.

3.2.10.2.3.2 Solids

PolyGuard is not designed or usable for solids or effluents containing significant solids.

3.2.10.2.3.3 Gaseous

Testing has been done indicating PolyGuard is effective in gas treatment for removing organics. No similar system is known to be in use at DOE facilities.

3.2.10.2.4 Screening Status

This technology is retained for consideration in treating dissolver product.

3.2.11 Microwave Technology

3.2.11.1 Process Description

Microwave technology can potentially be used to remove PCBs from the sludge. High power microwaves have been tested to remove DNAPLs from subsurface deposits. The microwaves also increase the permeability of fine grained soils by four orders of magnitude.

3.2.11.2 Screening Status

Although this technology has outstanding potential, it is not developed far enough at this date to consider. Research has been ongoing at Oak Ridge National Laboratory (ORNL 1998).

3.2.12 High Energy Corona

3.2.12.1 Process Description

The High Energy Corona (HEC) technology is being developed by DOE as one of many approaches toward decontaminating soil off-gases prior to atmospheric release. The objective of the HEC technology is to provide a standalone, field-portable means of treating soil off-gases produced during soil treatment operations. The HEC process uses high-voltage electricity to destroy VOCs at room temperature. The equipment consists of the following: an HEC reactor in which the VOCs are destroyed; inlet and outlet piping containing process instrumentation to measure humidity, temperature, pressure, contaminant concentration, and mass flow rate; a

means for controlling inlet flow rates and inlet humidity; and a secondary scrubber.

The HEC reactor is a glass tube filled with glass beads through which the pretreated contaminated off-gas is passed. Each reactor is 5.1 cm (2 inches) in diameter, 1.2 m (4 ft) long, and weighs less than 9 kg (20 pounds). A high-voltage electrode is placed along the centerline of the reactor, and a grounded metal screen is attached to the outer glass surface of the reactor. A high-voltage power supply is connected across the electrodes to provide 0 to 50 mA of 60 Hz electricity at 30 kV. The electrode current and power depend upon the type and concentration of contaminant.

The technology is packaged in a self-contained mobile trailer that includes gas handling equipment and on-line analytical capabilities. Installation consists of connecting inlet and outlet hoses to the HEC process trailer.

3.2.12.2 Reference Process

One reactor processes up to 0.14 m^3/min. (5 scfm) of soil off-gas. The HEC field-scale process demonstrated at Savannah River uses 21 HEC reactors in parallel to treat up to 3 m^3/min. (105 scfm) of contaminated off-gas. A typical application will involve an inlet stream containing 1,800 ppm of TCE in humid air at 10 to 20°C. Power input is typically 1765 to 5300 J/s/m^3/min. (50 to 150 W/scfm) being processed. For dry inlet streams, deionized water is added as steam to produce an inlet humidity (hr.) of 60 to 80%. Less than 20 mL per minute of water is required to humidify a completely dry stream at a flow of 3 m^3/min. (105 scfm). For water-saturated inlet streams, the stream is preheated (using electric heaters) to lower the humidity from 100% to 80%. In many cases, the vapor-extraction blower associated with retrieving the VOCs from soil will sufficiently preheat the soil off-gas to 80% or lower so that no further preheating is required.

Discussions with manufacturers/licensees have been initiated with the belief that HEC is now ready for commercial availability. The 3 m^3/min. (105 scfm) field prototype is available now for commercial testing and evaluation. PNNL is continuing research and development to improve and scale the technology. Scaleup to 1.4 m^3/min. (50 scfm) per reactor seems feasible for extremely large applications.

3.2.12.3 Applicability

3.2.12.3.1 Aqueous

Research is underway at PNNL for potentially treating water-borne organics via a gas corona. It is not developed sufficiently for dissolver product.

3.2.12.3.2 Solids

This is a gas process not designed for solids.

3.2.12.3.3 Gaseous

Contaminants that can be treated include most or all VOCs and SVOCs. The potential also exists for treating inorganic compounds, such as oxides of nitrogen and oxides of sulfur. This technique is specifically useful for destroying organics and chlorinated solvents such as TCE, tetrachloroethylene, carbon tetrachloride, chloroform, diesel fuel, and gasoline.

3.2.12.4 Screening Status

This technology is not retained for consideration in treating dissolver product, based on the small amount of PCBs expected. It may have been considered for the gases but the amount of PCB is so low that it has been judged that this technology cannot be used for the gases.

3.2.13 Membrane Separation

3.2.13.1 Process Description

A high pressure membrane separation system has been designed by DOE to treat feedstreams that contain dilute concentrations of VOCs. The organic vapor/air separation technology involves the preferential transport of organic vapors through a nonporous gas separation membrane (a diffusion process analogous to pumping saline water through a reverse osmosis membrane). In this system, the feedstream is compressed and sent to a condenser where the liquid solvent is recovered. The condenser bleed stream, which contains approximately 5,000 ppm of the VOC, is then sent to the membrane module.

The membrane module is comprised of spiral-wound modules of thin film membranes separated by plastic mesh spacers. The membrane and the spacers are wound spirally around a central collection pipe. In the membrane module the stream is further concentrated to 3% VOC. The concentrated stream is then returned to the compressor for further recovery in the condenser.

3.2.13.2 Reference Process

This technology is being tested at a Hanford site where VOCs will be obtained by vacuum extraction. Carbon tetrachloride and chloroform will preferentially be removed from the gas stream. Based upon a VOC effluent concentration of 1,000 ppm, there is a 95% removal efficiency. The remaining 5% is polished using carbon adsorption. Future work involves sizing the pilot plant to handle fluctuations in the VOC concentrations and fouling of the membrane with other constituents.

3.2.13.3 Applicability

3.2.13.3.1 Aqueous

This process does not apply to aqueous feeds.

3.2.13.3.2 Solids

This is a gas process not designed for solids.

3.2.13.3.3 Gaseous

The targeted contaminants are VOCs, carbon tetrachloride, and chloroform in gas streams. However, that technology is not really adapted to gas flow with a very low organic content.

3.2.13.4 Screening Status

This technology is not retained for consideration.

3.2.14 Gas Oxidation

3.2.14.1 Process Description

Oxidation equipment (thermal or catalytic) is used for destroying contaminants in the exhaust gas from air strippers and soil vapor extraction systems. Thermal oxidation units are typically single chamber, refractory-lined oxidizers equipped with a propane or natural gas burner and a stack. Lightweight ceramic blanket refractory is used because many of these units are mounted on skids or trailers. Flame arrestors are always installed between the vapor source and the thermal oxidizer. Burner capacities in the combustion chamber range from 1.4×10^5 to 5.9×10^5 J/s (0.5 to 2 million Btus per hour). Operating temperatures range from 760 to 870°C (1,400 to 1,600°F), and gas residence times are typically 1 second or less.

Catalytic oxidation is a relatively recently applied alternative for the treatment of VOCs in air streams resulting from remedial operations. The addition of a catalyst accelerates the rate of oxidation by adsorbing the oxygen and the contaminant on the catalyst surface where they react to form carbon dioxide, water, and hydrochloric gas. The catalyst enables the oxidation reaction to occur at much lower temperatures than required by a conventional thermal oxidation. VOCs are thermally destroyed at temperatures typically ranging from 320 to 540°C (600 to 1,000°F) by using a solid catalyst. First, the contaminated air is directly preheated (electrically or, more frequently, using natural gas or propane) to reach a temperature necessary to initiate the catalytic oxidation [310 to 370°C (600 to 700°F)] of the VOCs. Then the preheated VOC-laden air is passed through a bed of solid catalysts where the VOCs are rapidly oxidized. Thermal oxidizers can often be converted to catalytic units after initially high influent contaminant concentrations decrease to less than 1,000 to 5,000 ppm_v.

Catalyst systems used to oxidize VOCs typically use metal oxides such as nickel oxide, copper oxide, manganese dioxide, or chromium oxide. Noble metals such as platinum and palladium may also be used. Most commercially available catalysts are proprietary.

3.2.14.2 Reference Process

Thermal oxidation is effective for site remediation. Its use is increasing among remediation equipment vendors, and several variations in design are being marketed. Growing applications include treatment of air stripper and vacuum extraction gas-phase emissions.

More than 20 firms manufacture catalytic oxidation systems specifically for remedial activities. These firms will generally supply the equipment to remedial action contractors for integration with specific remedial technologies, such as in situ vapor extraction of organics from soil or air stripping of organics from groundwater.

Despite its relatively newer application in remedial activities, catalytic oxidation is a mature technology, and its status as an implementable technology is well established. Nevertheless, the technology continues to evolve with respect to heat recovery techniques, catalysts to increase destruction efficiency and/or to extend the operating life of the catalyst bed, and performance data on a wider range of VOCs.

3.2.14.3 Applicability

3.2.14.3.1 Aqueous

This process does not apply to aqueous feeds.

3.2.14.3.2 Solids

This is a gas process not designed for solids.

3.2.14.3.3 Gaseous

The target contaminant groups for oxidation are nonhalogenated VOCs and SVOCs and fuel hydrocarbons. Both precious metal and base metal catalysts have been developed that are reportedly capable of effectively destroying halogenated (including chlorinated) hydrocarbons. Specific chlorinated hydrocarbons that have been treated include TCE, Trichloroethane, methylene chloride, and 1,1DCA. However that process is not well adapted to off-gas with a very low organic content.

3.2.14.4 Screening Status

This technology is not retained for consideration.

3.3 Technology Pre-Screening Summary

The following Table 3-1 is a summary of the screened technologies and those that will be evaluated further in Section 4.

Table 3-2, Pre-Screening Summary

Technology	Subset	Status	Screening Rationale/Comments
Advanced Oxidation Processes	UV/Peroxide	Out	Nitrate absorbs UV
	Catalyst/peroxide	Out	Need UV and radical
	UV/ozone	Out	Nitrate absorbs UV
	Visible/peroxide	Out	Nitrate absorbs UV
	DCO	In	Dissolver product or sludge
Reduction (Aqueous Electron)	Calgon Aqueous	Out	Nitrate scavenges aqueous electron
	High Voltage	In	Sludge or as secondary to extraction
	Gamma Radiolysis	In	Best in organic phase which requires prior extraction
	Commodore (SET)	In	as secondary to extraction
Ultrasonic Destruction		Out	Feasibility unknown, not developed. Looks promising
Other Absorption	GAC	In	applicable to off-gas only
	PolyGuard or equal	In	can be considered for the dissolution solution or the off-gas treatment.
Thermal	Desorption	In	May not be acceptable based on uranium metal corrosion-sludge only
	Incineration	Out	Unless transported off-site
Extraction	Solvent	In	Applicable to sludge only
	SCFE	Out	High pressure
Acid Digestion		Out	Not effective from PNNL Study
Electromagnetic Radiation		Out	Not developed but looks very promising
SCWO		Out	High temperature and pressure
Dechlorination		In	Sludge or as secondary to extraction
HEC		Out	Gases only, PCBs too low
Membrane		Out	Gases only, PCBs too low
Gas Oxidation		Out	Gases only, PCBs too low
Electrochemical Oxidation		Out	Not developed, lab tests indicate PCB polymerizes under this technology

As shown in Table 3-1, the six remaining technologies are DCO, Reduction (including gamma radiolysis), thermal desorption, solvent extraction, absorption, and dechlorination. Solvent extraction cannot work alone so it is coupled with processes that destroy the PCBs in the organic phase (dechlorination, and gamma radiolysis). Also, thermal desorption must also have a companion process for treating PCBs post-desorption. These are described/evaluated further in Section 4.

4.0 RECOMMENDED TECHNOLOGIES

The following paragraph is dedicated to the selection of what is considered to be the Best Available Technology for the three following streams

- Acidic liquor after the dissolver
- Solids
- Gases

The following criteria have been used qualitatively to screen the technologies:

- Technological Maturity
- Feasibility
- Match Current Flowsheet Objectives
- EPA Concurrence
- Operability (including maintainability)
- Decontaminable
- Logistics/Siting
- Secondary Waste Streams, and
- Need for Ancillary Unit Operations

4.1 Acidic liquor

The processes available to treat aqueous dissolver product are very limited. This limitation is mainly based on the presence of high nitrates which absorb ultraviolet light and scavenge the aqueous electron. The two remaining processes, DCO and absorption, are discussed below.

4.1.1 Absorption (PolyGuard)

This system can potentially provide PCB removal to meet the criteria for dissolver product. However. the system requires process control to ensure that the limit for ERDF criteria is not exceeded for TRU.

The process configuration consists of removable columns containing PolyGuard. The columns are pre-designed requiring only connections for inlet and outlet piping. Upon reaching the 100 nCi/g for TRU, the columns are disconnected and shipped out to ERDF. Each column has a 91% efficiency (vendor information). The number of column has to be adapted to the requirements for the liquid effluent.

Advantages:

- Ease of operations and maintenance
- Can easily fit spacing requirements
- No special regulatory interpretations or requirements

Disadvantages:

- Produces a secondary solid waste that must be disposed
- Possibly degrade under radiation field

4.1.2 Absorption on cartridge filter membranes

It has been shown during the testing program performed by PNNL that organic filtration membrane were able to remove 90 % of the PCBs dissolved in the acidic liquor.

The process configuration consists of cartridge filter with removable organic cartridge. The material used for the cartridge by PNNL was PVDF but more tests need to be performed to optimize the choice of the material. The cartridge have to be changed upon reaching the TRU limit for ERDF.

Advantages:

- Ease of operations and maintenance
- Can easily fit spacing requirements
- No special regulatory interpretations or requirements
- Cartridge filters are already a necessary second step for the solid / liquid separation

Disadvantages:

- Produces a secondary solid waste that must be disposed

4.1.3 Advanced Oxidation

If it is indeed true that the destruction reaction of PCB (for UV/H_2O_2 processes) requires UV and hydroxyl radical as hypothesized in Section 3, the only AOT processes that may work is DCO. For this process, the dissolver product is fed batch-wise to a reactor followed by addition of peroxydisulfate then heated to 80 to 100°C and mixed during the reaction. The treatment proceeds for a duration time that needs to be determined.

Offgas is treated in the same system as the dissolver. The exact composition of the offgas stream will depend on the particular waste stream being processed, but several general predictions can be made. Common to all organic waste streams will be carbon dioxide; oxygen will also be produced from the direct oxidation of water by peroxydisulfate (occurring at a slower rate than oxidation of organics). Chlorine will be present in the offgas as PCBs are treated in an acidic DCO system.

Advantages:

- The process is virtually "omnivorous," derived from three aspects: Peroxydisulfate is among the strongest oxidants known (E = +2.05 V), exceeding Ag(II) (+1.987 V), Co(III) (+1.84 V), H2O2 (+1.8 V), MnO_4^- (+1.7 V), oxygen (+1.2 V); and Fe(III) (+0.8 V).
- With thermal or UV activation, peroxydisulfate spontaneously forms the sulfate free radical ($SO_4^{-\cdot}$) which then generates a cascade of active oxidants including hydroxyl free radical OH·, peroxymonosulfate (a strong industrial bleach), hydrogen peroxide, etc.
- DCO is non-thermal, ambient pressure, and aqueous based: The non-thermal characteristic would seem to eliminate the possibility of dioxin or furan formation.
- In addition, volatilization of metals or of radionuclides present in the original waste stream is drastically reduced, if not altogether eliminated.
- Like all aqueous phase destruction techniques, the treatment occurs in a wetted medium without generation of dust.
- DCO results in products suitable for further recovery or disposal of inorganic residuals by conventional techniques (precipitation, ion exchange or electrolytic recovery, encapsulation for burial).
- DCO is effective on a diverse group of waste matrices: These matrices include liquid organics (either miscible with water or not), organic solids, and contaminated soils, sands or sludges.
- In addition, DCO of organics can be done in either acidic, neutral, or basic solutions, with the latter producing carbon dioxide in the form of carbonate ion.
- No catalyst is required: The process does not require the use of toxic, expensive of degradable catalysts (such as Ag(II) or Co(III) used by Mediated Electrochemical Oxidation, or the dispersed Pt(IV) or Ru(III) catalysts used by DETOX). DCO therefore obviates the loss of catalysts by precipitation (as, e.g., AgCl, Ag_2SO_4, CoF_2, Ag_2S, etc.) or by entrainment in secondary waste streams.
- Solutions of peroxydisulfate are stable almost indefinitely at room temperature, and are activated either through the use of a catalyst or by heating the solution. Thus, peroxydisulfate can be produced and stored until waste treatment is begun.
- No problems with organic heteroatoms: Peroxydisulfate promotes the destruction of nitrated and nitrate-containing wastes. Ammonium nitrate products are decomposed thermally into nitrogen and/or N_2O in the presence of chloride catalysts. The waste treatment system can be configured to treat chlorinated wastes, consuming transient chlorine or oxychloride species by oxidation of organic intermediates, resulting in a final product containing chlorides and sulfates.
- Versatile scaling: An important aspect of this technology is its ability to scale down without loss of efficiency. Bench-top units are useful in future DOE or Department of Defense (DOD) production facilities to destroy undifferentiated wastes produced as a byproduct of routine chemical analyses.
- DCO can be used as a dedicated unit process to destroy wastes produced in small industry production lines. At the 200 kg carbon/day level, the process is fully transportable. The ability to store stable solutions or precipitates of peroxydisulfate salts adapts well to intermittent waste treatment campaigns.

Disadvantages:

- Sulfates may be added to solution
- the efficiency of PCB destruction is not well established

4.1.4 Recommendation for the Aqueous Dissolver Product

The process using cartridge filters equipped with organic membrane is the simplest solution.

- there is no need for additional vessel
- the absorption process is a well known process for PCB removal
  there is no chemical reagents added to the solution that may prevent the acceptance of the end-product by TWRS

For these reasons, our recommendation is to use cartridge filter with an organic filtering media.
The implementation of that solution will require the following series of actions will be necessary:

- review of the organic media available for cartridge filter and fulfilling requirements for PCBs removal and filtration efficiency.
- measurement of PCBs adsorption (if not available from the manufacturer)

4.2 K Basin Sludge

That part compares the processes that can be used to remove/destroy from solids. These solids can be the sludges before the dissolution process or the precipitate sent to TWRS.

4.2.1 Solvent Extraction

Solvent extraction is performed prior to dissolution in this process. The sludge is contacted with several batches of fresh solvent. The solvent is separated and treated further in one of the PCBs destruction processes, gamma radiolysis (or hydrated electron), or dechlorination. The solvent is recycled. Alternatively, the solvent along with the PCBs could be shipped off to another site for incineration or other treatment.

Advantages:

- High affinity for organic compounds
- Removal of most PCBs, few left on solids or aqueous to deal with

Disadvantages:

- Organically bound metals (in this case radionuclides) can be extracted along with the target organic pollutants, which restricts handling of the residuals.
- The presence of detergents and emulsifiers can unfavorably influence the extraction performance.
- Traces of solvent may remain in the treated solids and may create some problem during the dissolution process or influence the acceptance of the end-product by TWRS.
- Solvent extraction is generally least effective on very high molecular weight organic and very hydrophilic substances.
- The separation of the solvent and the slurry phase may be complicated. Some of the solids may be extracted by the solvent phase (organic resins, grafoil....)
- Requires a secondary process to destroy or stabilize the PCBs.
- Likely requires solids size reduction in conjunction with process to be effective if used on solids phase.

4.2.2 Dechlorination

Dechlorination will include chemical treatment with KPEG or equivalent in a batch chemical reactor as shown in Figure 4-4. The dechlorination is done first before other treatment processes as shown. After dechlorination, the acid digestion is conducted without any other treatment for PCBs except the possible treatment of PCBs in the gas phase by GAC.

Advantages:

- APEG dehalogenation is one of the few processes available other than incineration that has been successfully field tested in treating PCBs.
- The technology is amenable to small-scale applications.
- This technology has received approval from the EPA's Office of Toxic Substances under the TSCA for PCB treatment.
- The APEG process has been selected for cleanup of PCB-contaminated soils at three Superfund sites: Wide Beach in Erie County, New York (September 1985); Re-Solve in Massachusetts (September 1987); and Sol Lynn in Texas (March 1988).
- This technology uses standard equipment.

Disadvantages:

- The technology is generally not cost-effective for large waste volumes.
- Media water content above 20% requires excessive reagent volume.

4.2.3 Thermal Desorption

Thermal desorption is used to desorb the PCBs from the sludge. The sludge is heated via propane combustion and hot gases in a rotary dryer as shown. The PCBs and water are volatilized in the rotary drier. The offgas is treated with GAC The model used during the superfund innovative technology evaluation (SITE) demonstration has a nominal feed capacity of 5.2 tons per hour for solids with a 25% moisture content. If used on this sludge, dewatering may be required. The SITE system is fully transportable.

Advantages:

- Commercially available units
- Mobile units available
- EPA familiarity

Disadvantages:

- Dewatering may be necessary to reduce the amount of energy required to heat the soil.
- Highly abrasive feed can potentially damage the processor unit.
- Clay and silty soils and high humic content soils increase reaction time as a result of binding of contaminants.
- May lead to energetic reactions between water vapor and uranium or uranium hydride .

4.2.4 Direct Chemical Oxidation

Direct Chemical Oxidation (DCO) can also be considered for the destruction of PCBs in the sludge before the dissolution process.

For this process, the sludge is fed batch-wise to a reactor followed by addition of peroxydisulfate then heated to 80 to 100°C and mixed during the reaction. The treatment proceeds for a duration time that needs to be determined. It will be better to implement that processing step after the Organic Ion Exchange Resins separation (OIER) in order to avoid to have a lot of reactions occurring with the OIER and the Grafoil (separated concurrently with the OIER) .

Offgas is treated in the same system as the dissolver. The exact composition of the offgas stream will depend on the particular waste stream being processed, but several general predictions can be made. Common to all organic waste streams will be carbon dioxide; oxygen will also be produced from the direct oxidation of water by peroxydisulfate (occurring at a slower rate than oxidation of organics).

Advantages:

- The process is virtually "omnivorous," derived from three aspects: Peroxydisulfate is among the strongest oxidants known (E = +2.05 V), exceeding Ag(II) (+1.987 V), Co(III) (+1.84 V), H2O2 (+1.8 V), MnO_4^- (+1.7 V), oxygen (+1.2 V); and Fe(III) (+0.8 V).
- With thermal or UV activation, peroxydisulfate spontaneously forms the sulfate free radical ($SO_4^{-\cdot}$) which then generates a cascade of active oxidants including hydroxyl free radical OH·, peroxymonosulfate (a strong industrial bleach), hydrogen peroxide, etc.
- DCO is non-thermal, ambient pressure, and aqueous based: The non-thermal characteristic would seem to eliminate the possibility of dioxin or furan formation.
- In addition, volatilization of metals or of radionuclides present in the original waste stream is drastically reduced, if not altogether eliminated.
- Like all aqueous phase destruction techniques, the treatment occurs in a wetted medium without generation of dust.
- DCO results in products suitable for further recovery or disposal of inorganic residuals by conventional techniques (precipitation, ion exchange or electrolytic recovery, encapsulation for burial).
- DCO is effective on a diverse group of waste matrices: These matrices include liquid organics (either miscible with water or not), organic solids, and contaminated soils, sands or sludges.
- In addition, DCO of organics can be done in either acidic, neutral, or basic solutions, with the latter producing carbon dioxide in the form of carbonate ion.
- No catalyst is required: The process does not require the use of toxic, expensive of degradable catalysts (such as Ag(II) or Co(III) used by Mediated Electrochemical Oxidation, or the dispersed Pt(IV) or Ru(III) catalysts used by DETOX). DCO therefore obviates the loss of catalysts by precipitation (as, e.g., AgCl, Ag_2SO_4, CoF_2, Ag_2S, etc.) or by entrainment in secondary waste streams.
- Solutions of peroxydisulfate are stable almost indefinitely at room temperature, and are activated either through the use of a catalyst or by heating the solution. Thus, peroxydisulfate can be produced and stored until waste treatment is begun.

- No problems with organic heteroatoms: Peroxydisulfate promotes the destruction of nitrated and nitrate-containing wastes. Ammonium nitrate products are decomposed thermally into nitrogen and/or N_2O in the presence of chloride catalysts. The waste treatment system can be configured to treat chlorinated wastes, consuming transient chlorine or oxychloride species by oxidation of organic intermediates, resulting in a final product containing chlorides and sulfates.
- Versatile scaling: An important aspect of this technology is its ability to scale down without loss of efficiency. Bench-top units are useful in future DOE or DOD production facilities to destroy undifferentiated wastes produced as a byproduct of routine chemical analyses.
- DCO can be used as a dedicated unit process to destroy wastes produced in small industry production lines. At the 200 kg carbon/day level, the process is fully transportable. The ability to store stable solutions or precipitates of peroxydisulfate salts adapts well to intermittent waste treatment campaigns.

Disadvantages:

- Sludge likely requires particle size reduction or some means to enhance desorption.
- Sulfates may be added to solution
- The efficiency of PCB destruction is not well established

4.2.5 Recommendation for the Sludge Before the Dissolver

DCO seems to be the process which is more easy to implement for the removal/destruction of PCBs from the sludge. The main reasons are:

- there is no need for complex equipment (by opposition to solvent/slurry separation)
- the process does not need any extensive dewatering operation to be efficient
- there is no secondary stream coming out from the process that need an additional process step
- the reactivity risk is more easy to control in a chemical process where you can control the amount and feeding rate of the reactive species (by opposition to a thermal process)

However, even if the DCO process is the preferred option, it is necessary to point out that the final demonstration of the efficiency of that process to remove the PCBs remains to be done.

4.3 Gases

The EPA has provided information on several gas-phase technologies for PCB removal (EPA 1998). Based on expected offgas PCB concentrations, most of the technologies described in Section 3 are more than is required for adequate treatment. Since GAC normally is used as a polish for these processes under heavy organic loading, it is considered the BAT for this system where the PCB concentration in the off gas is very limited.

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Appendix A

Properties of Aroclor 1254 and PCB Congeners (Erickson 1991)

Aroclor 1254

Density, g/mL	1.54
Viscosity, SSU @98.9°C	44-58
Solubility in water (ppb)	12

Properties of selected congeners

IUPAC No.	Congener	Boiling Point, °C	Vapor Pressure @ 25°C, mm Hg	Log K_{ow}
1	2	274	0.0084	4.56
2	3	284-5	0.0015	4.72
3	4	291	0.0046	4.69
4	2,2'		0.001	5.02
5	2,3	172 (30)		
7	2,4		0.0018	5.15
8	2,4'			<5.32
9	2,5	171 (15)	0.0014	5.18
11	3,3'	322-4	0.00068	5.34
12	3,4	195-200 (15)		
14	3,5	166 (10)		
15	4,4'	315-319	1.9×10^{-5}	5.28
18	2,2',5		9×10^{-5}	5.64
33	2',3,4		7.7×10^{-5}	6.1
28	2,4,4'			5.74
29	2,4,5		0.00033	5.77
30	2,4,6		0.00088	
31	2,4',5		0.0003	5.77

47	2,2',4,4'		0.000086	6.44
101	2,2',4,5,5'		0.000009	6.85
118	2,3',4,4',5	195-220 (10)	0.000009	
180	2,2',3,4,4',5,5'	240-280 (20)	0.00000097	
209	Deca			9.6

Estimates based on properties

Determine the equilibrium concentrations of PCBs on solid, in liquids, and in the vapor phase.

Using the 3 component box model, the total mass of PCBs is

$$M_{PCB} = x_s S + yV + x_l L$$

The fugacities in each phase are equal such that

$$x_l = \frac{x_s}{K_D}$$

and

$$y = K_v x_l$$

Substituting these into the mass balance

$$x_s = \frac{M_{PCB}}{S + \frac{K_v}{K_D} \bullet V + \frac{L}{K_D}}$$

$$x_l = \frac{K_v M_{PCB}}{K_D S + K_v \bullet V + L}$$

$$y = \frac{K_v M_{PCB}}{K_D S + K_v \bullet V + L}$$

The solid-water distribution coefficient is related to the organic carbon distribution by

$$K_d = K_{oc} f_{oc}$$

The K_{oc} is estimated by

$$\log K_{oc} = 1.00 \log K_{ow} - 0.21$$

S, kg	L, litre	$M_{PCB, kg}$	V, litre					
68000	680000	9.52	1000					
T, °C	K_v	f_{oc}	log K_{ow}	K_{oc}, mL/g	K_d, mL/g	x_s, ppm	x_l, ppb	y, ppb
100	2.26E-10	0.000373	4.56	22387.21	8.35	6.37E+01	7.63E+00	1.73E-09
100	2.26E-10	0.0105	4.56	22387.21	235.07	1.34E+02	5.71E-01	1.29E-10

Using the low end organic carbon (f_{oc}) content of 373 to 10,500 ug/g, estimates can be made for the distribution (this is not to say that K_D is zero if there is no organic carbon). This was done for a rather large dissolver shown below:

Appendix B

Glossary

AOT	Advanced Oxidation Technology
APEG	Alkaline Polyethylene Glycol
Aroclor 1254	Mixture of PCB Congeners (12 is number of carbons, 54 is wt% chlorine)
BTEX	Benzene, Toluene, Ethyl-Benzene, and Xylene
$Cat^{\ddagger}$	Catalyst in the Activated State
CERCLA	Comprehensive Environmental Response, Compensation & Liability Act
Critical Point	The temperature and pressure where a substance exists as a single phase. Above this point (i.e., higher temperatures and pressures), the fluid is supercritical and is single phase.
DCO	Direct Chemical Oxidation
DCP	Dichloro Phenol
DDT	2, 2 - bis (p-chlorophenyl) -1, 1, 1 - trichloroethane
DF	Decontamination Factor = C_i / C_o
DNAPL	Dense, Non-Aqueous Phase Liquid
DOD	Department of Defense
DOE	U.S. Department of Energy
DRE	Destruction and Removal Efficiency
EE/o	The electrical energy per volume per order of magnitude in J/m^3/order (kwh/1000 gal/order.
EPA	Environmental Protection Agency
EDTA	Ethylenediaminetetraacetic Acid
e^-_{aq}	Aqueous or Hydrated or Solvated Electron
ERDF	Environmental Remediation Disposal Facility
ETF	Effluent Treatment Facility
G Value	The number of molecules of material changed for each 100 electron volts of radiation energy absorbed.
GAC	Granulated Activated Carbon
HEC	High Energy Corona
HEPA	High Efficiency Particulate Air
High Energy Chemistry	Where particle (photon, electron, etc) energy is > kT. The mechanisms are non-thermal and are relatively invariant in temperature.
HTTD	High Temperature Thermal Desorption
INEL	Idaho National Engineering Laboratory
k	Boltzmans Constant
K_{ow}	K_{ow} (the octanol/water partition coefficient) is defined as the ratio of a chemical's concentration in the octanol phase to its concentration in the aqueous phase of a two-phase octanol/water system. K_{ow} is a key parameter in describing the fate of organic chemicals in environmental systems. It has been found to be related to the water solubility, soil/sediment adsorption coefficient, and the bioconcentration factors for aquatic species. The physical meaning of K_{ow} is the tendency of a chemical to partition itself between an organic phase [e.g., polycyclic aromatic hydrocarbons (PAHs) in a solvent] and an aqueous phase. Chemicals that have a

	low K_{ow} value (<10) may be considered relatively hydrophilic; they tend to have a high water solubility, small soil/sediment adsorption coefficients, and small bioconcentration factors for aquatic life. Conversely, a chemical with a large K_{ow} (>10^4) is considered hydrophobic and tends to accumulate at organic surfaces, such as on humic soil and aquatic species.
KE	K East
KOH	Potassium Hydroxide
KPEG	Potassium Polyethylene Glycol
KW	K West
LET	Linear Energy Transfer
LLNL	Lawrence Livermore National Laboratory
NDMA	N-nitrosodimethylamine
OIER	Organic Ion Exchange Resins
PAH	Polyaromatic Hydrocarbons
PCB	Polychlorinated Bi-Phenyl
PCB‡	Polychlorinated Bi-Phenyl in the Activated State
PCE	Perchloroethylene
PCDD	Chlorinated Dibenzo-P-Dioxins
PCDF	Chlorinated Dibenzofurans
PCP	Pentachlorophenol
PEG	Polyethylene Glycol
ppb	Parts Per Billion
ppm	Parts Per Million
ppm_v	Parts Per Million by Volume
ppt	Parts Per Trillion
PNNL	Pacific Northwest National Laboratory
RCC	Resource Conservation Company
RCRA	Resource Conservation and Recovery Act of 1976
RO	Reverse Osmosis
SCFE	Supercritical Fluid Extraction
SCWO	Supercritical Water Oxidation
SDWA	Safe Drinking Water Act
SET	Solvated Electron Technology (SET™)
SVOC	Semi-Volatile Organic Carbon
TCE	Trichloroethylene
TRU	Transuranic
TSCA	Toxic Substances Control Act
TWRS	Tank Waste Remediation System
UV	Ultra Violet
VOC	Volatile Organic Carbon

Appendix C

Lawrence Livermore Direct Chemical Oxidation Tests

Laboratory scale tests on the destruction of PCB are preliminary at this point. Previous work by other workers indicated that PCBs are destroyed by peroxydisulfate, and limited experimentation was done by our lab in Fiscal Year 1997 (FY). However, it was not possible to obtain samples of pure PCBs due to California State regulatory restrictions, and thus the work in our laboratory was limited to a PCB concentration of less than 50 ppm in water. Samples of Arochlor 1242 in water were obtained from Centre Analytical, and a surfactant was used to obtain a PCB concentration of 45 ppm (the solubility of arochlors in water is generally much less). Because of this low concentration used for the oxidative tests, a measurement of the amount of PCB destroyed by the IR carbon dioxide analysis described above resulted in measurements that were not sufficiently above background to be conclusive (see Table VII).

Table VII. Summary of results for PCB destruction (45 ppm Arochlor 1242 in water with a surfactant)

Run #	Conditions	Total ml CO2	End TC Analysis*
235	Large Excess Oxidant in 1.0M NaOH, 85-95°C	78	12 ppm
236	""	79	-
247	4.5 hrs. Hydrolysis at 100°C, excess oxidant at 95°C	77	-
249	48 hrs. Hydrolysis at 100°C, excess oxidant at 95°C	67	< 5ppm

Note: 106 mg Triton X-100/liter run as blank. CO_2 expected=68 ml; CO_2 produced=78 ml.
* TC analysis judged inconclusive, as values < 10 ppm are not reliable. Total carbon value at beginning is 25 ppm (from Arochlor 1242) plus 63 ppm (from surfactant), or 88 ppm total.

In addition to the carbon dioxide analyses done for the PCB destruction tests, samples of the final solution treatment with peroxydisulfate at temperature were sent off to an independent laboratory for analysis for PCBs and dioxins/furans. These results are shown in Table VIII, and indicate that no remaining PCBs were found for three out of four samples tested. In addition, exhaustive analyses were done for dibenzo-p-dioxins and dibenzofurans, and none were found within the limits of detection. However, numerous fragments of chlorinated organics were seen, indicating that the destructive breakup of the PCBs by peroxydisulfate was chemically possible. Based on these results, it can be asserted that PCBs are oxidized by peroxydisulfate, but no data is yet available as to mechanisms, rates, or economic costs.

Table VIII. Independent laboratory analysis of final PCB solution after oxidation by peroxydisulfate (235 & 236 are in basic media, 247 & 249 with brief hydrolysis in base, then oxidation). PCB and chloro-organic analysis is by EPA method 608; dibenzo-p-dioxin and dibenzofuran analysis is by EPA method 8280.

Compound	235	236	247	249
PCBs	g/L (ppb)*	g/L (ppb)*	g/L (ppb)*	g/L (ppb)*
monochlorobiphenyl	ND (0.65)	ND (0.5)	ND (0.5)	ND (0.5)
dichlorobiphenyl	N (0.65)	ND (0.5)	ND (0.5)	3.40
trichlorobiphenyl	ND (0.65)	ND (0.5)	ND (0.5)	2.37

tetrachlorobiphenyl	ND (1.3)	ND (1.0)	ND (1.0)	7.08
pentachlorobiphenyl	ND (1.3)	ND (1.0)	ND (1.0)	ND (1.0)
hexachlorobiphenyl	ND (1.3)	ND (1.0)	ND (1.0)	ND (1.0)
heptachlorobiphenyl	ND (1.9)	ND (1.5)	ND (1.5)	ND (1.5)
octachlorobiphenyl	ND (1.9)	ND (1.5)	ND (1.5)	ND (1.5)
decachlorobiphenyl	ND (3.2)	ND (2.5)	ND (2.5)	ND (2.5)
Arochlor 1016	ND (13)	ND (10)	ND (10)	ND (10)
Arochlor 1221	ND (13)	ND (10)	ND (10)	ND (10)
Arochlor 1232	ND (13)	ND (10)	ND (10)	ND (10)
Arochlor 1242	ND (13)	ND (10)	ND (10)	12.9
Arochlor 1248	ND (13)	ND (10)	ND (10)	ND (10)
Arochlor 1254	ND (13)	ND (10)	ND (10)	ND (10)
Arochlor 1260	ND (13)	ND (10)	ND (10)	ND (10)

Chloro-organics:		
2,3-dichloro-2-methylcyclohexane	150	
chlorocyclohexane	96	69
1,1-dichlorocyclopentane	274	
1,1,2,2-tetrachloroethane	108	123
2,3-dichloro-2-methylpropanal	267	506
carbonic acid, methyl phenyl ester	35	
2,3-dichlorocyclopropanecarboxylic acid	241	37
3-chlorocyclohexene	31	
trans-1,2-dichlorocyclohexane	54	
1,1-dichloro-2-ethenylcyclopropane	37	
chloroacetyl chloride	50	50
chloromethoxymethane	61	59
1,1-dichloro-2-methylcyclopropane	594	470
1,4-dichloro-2-butene	84	63
1,1,1,3-tetrachloropropane	61	
5,6-dimethoxyphthalaldehydic acid	50	
2,3-dichlorobutane		311
1,3-dichloro-2-butene		40
cis-1,2-dichlorocyclopentane		894
trans-1,2-dichlorocyclopentane		
2,3-dichlorobutanoic acid, methyl ester		73

7-chloro-3-heptyne		51
Dioxins and Furans	ng/L (ppt)*	ng/L (ppt)*
2,3,7,8-TCDD	ND (0.3)	ND (0.09)
1,2,3,7,8-PeCDD	ND (6.4)	ND (0.2)
1,2,3,4,7,8-HxCDD	ND (4.0)	ND (0.2)
1,2,3,6,7,8-HxCDD	ND (1.4)	ND (0.1)
1,2,3,7,8,9-HxCDD	ND (2.0)	ND (0.2)
1,2,3,4,6,7,8-HpCDD	ND (4.1)	ND (0.2)
1,2,3,4,6,7,8,9-OCDD	ND (4.4)	ND (0.3)
2,3,7,8-TCDF	ND (0.4)	ND (0.07)
1,2,3,7,8-PeCDF	ND (5.6)	ND (0.09)
2,3,4,7,8-PeCDF	ND (8.0)	ND (0.09)
1,2,3,4,7,8-HxCDF	ND (7.0)	ND (0.1)
1,2,3,6,7,8-HxCDF	ND (6.5)	ND (0.1)
2,3,4,6,7,8-HxCDF	ND (4.2)	ND (0.2)
1,2,3,7,8,9-HxCDF	ND (3.8)	ND (0.2)
1,2,3,4,6,7,8-HpCDF	ND (1.4)	ND (0.2)
1,2,3,4,7,8,9-HpCDF	ND (4.3)	ND (0.2)
1,2,3,4,6,7,8,9-OCDF	ND (2.5)	ND (0.3)

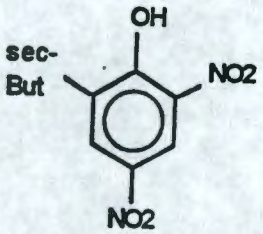
* ND = "Not Detected"; number in parenthesis corresponds to limit of detection

Longer term hydrolysis of PCBs, or at higher temperatures, followed by oxidation (as described for the other chlorosolvents above) remains a viable option, but this work was not completed in FY97. In order to provide more definitive testing, it is suggested that the oxidative destruction tests be performed at a laboratory better equipped to work with higher concentrations of PCBs. Obtaining Environmental Safety &Health and regulatory approval to do the work at our current facilities at LLNL is not believed to be viable due to the time and effort required.

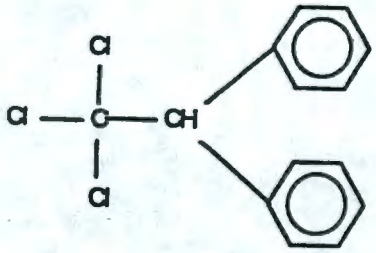
Appendix D

Organic Structural

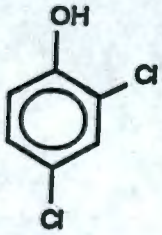
Dinoseb



DDT



2,4 Dichloro Phenol



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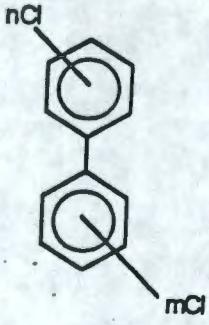
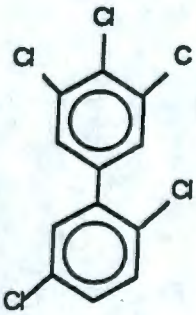


One "Median" Aroclor 1254 Structure



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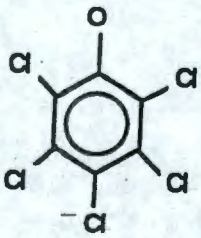

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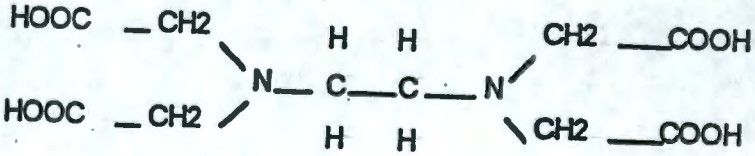

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