Site: WCS- Corwin
ID # KSD984990507
Break: 17.8
Other:
0762 Milde ST

United States
Environmental Protection
Agency

Office of Emergency and
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Washington, DC 20460

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Cincinnati, OH 45268

Superfund

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Engineering Bulletin
Solvent Extraction Treatment

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SUPERFUND RECORDS

Purpose

Section 121(b) of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) mandates the Environmental Protection Agency (EPA) to select remedies that "utilize permanent solutions and alternative treatment technologies or resource recovery technologies to the maximum extent practicable" and to prefer remedial actions in which treatment "permanently and significantly reduces the volume, toxicity, or mobility of hazardous substances, pollutants and contaminants as a principal element." The Engineering Bulletins are a series of documents that summarize the latest information available on selected treatment and site remediation technologies and related issues. They provide summaries of and references for the latest information to help remedial project managers, on-scene coordinators, contractors, and other site cleanup managers understand the type of data and site characteristics needed to evaluate a technology for potential applicability to their Superfund or other hazardous waste site. Those documents that describe individual treatment technologies focus on remedial investigation scoping needs. Addenda will be issued periodically to update the original bulletins.

Abstract

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. Generally it is used as one in a series of unit operations, and can reduce the overall cost for managing a particular site. It is applicable to organic wastes and is generally not used for treating inorganics and metals [15, p.64].* The technology uses an organic chemical as a solvent [14, p. 30], and differs from soil washing, which generally uses water or water with wash improving additives. During 1989, the technology was one of the selected remedies at six Superfund sites. Commercial-scale units are in operation. There is no clear solvent extraction technology leader by virtue of the solvent employed, type of equipment used, or mode of operation. The final determination of the lowest cost alternative will be more site specific than process equipment dominated. Vendors should be contacted to determine the availability of a unit for a particular site. This bulletin provides information on the technology applicability, the types of residuals produced, the latest performance data, site requirements, the status of the technology, and sources for further information.

Technology Applicability

Solvent extraction has been shown to be effective in treating sediments, sludges, and soils containing primarily organic contaminants such as polychlorinated biphenyls (PCB), volatile organic compounds (VOC), halogenated solvents, and petroleum wastes. The technology is generally not used for extracting inorganics (i.e., acids, bases, salts, heavy metals). Inorganics usually do not have a detrimental effect on the extraction of the organic components, and sometimes metals that pass through the process experience a beneficial effect by changing the chemical compound to a less toxic or leachable form. 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 [3].

Table 1 lists the codes for the specific Resource Conservation and Recovery Act (RCRA) wastes that have been treated by this technology [3][1, p.11]. The effectiveness of solvent extraction on general contaminant groups for various matrices is shown in Table 2 [13, p.1] [15, p.10]. Examples of constituents within contaminant groups are provided in Reference 15, "Technology Screening Guide for Treatment of CERCLA Soils and Sludges." This table is based on the current available information or professional judgment where no information was available. The proven effectiveness of the technology for a particular site or waste does not ensure that it will be effective at all sites or that the treatment efficiencies achieved will be acceptable at other sites. For the ratings used for this table, demonstrated effectiveness means that, at some scale treatability was tested to show the technology was effective for that particular contaminant and matrix. The ratings of potential effectiveness, or no expected effectiveness are both based upon expert judgment. Where potential effectiveness is indicated, the technology is believed capable of successfully treating the contaminant group in a particular matrix. When the technology is not applicable or will probably not work for a particular combination of contaminant group and matrix, a no-expected-effectiveness rating is given.

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* [reference number, page number]

Limitations

Organically bound metals can co-extract with the target organic pollutants and become a constituent of the concentrated organic waste stream. This is an unfavorable occurrence because the presence of metals can restrict both disposal and recycle options.

Table 1
RCRA Codes for Wastes Treated by Solvent Extraction

Wood Treating Wastes	K001
Water Treatment Sludges	K044
Dissolved Air Flotation (DAF) Float	K048
Slop Oil Emulsion Solids	K049
Heat Exchanger Bundles Cleaning Sludge	K050
American Petroleum Institute (API) Separator Sludge	K051
Tank Bottoms (leaded)	K052
Ammonia Still Sludge	K060
Pharmaceutical Sludge	K084
Decanter Tar Sludge	K089
Distillation Residues	K101

Table 2
Effectiveness of Solvent Extraction on General Contaminant Groups for Soil, Sludge, and Sediments

		Effectiveness		
	Treatability Groups	Soil	Sludge	Sediments
Organic	Halogenated volatiles	▼	▼	▼
	Halogenated semivolatiles	■	▼	▼
	Nonhalogenated volatiles	■	■	▼
	Nonhalogenated semivolatiles	■	■	▼
	PCBs	■	■	■
	Pesticides	■	▼	▼
	Dioxins/Furans	▼	▼	▼
	Organic cyanides	▼	▼	▼
	Organic corrosives	▼	▼	▼
Inorganic	Volatile metals	❑	❑	❑
	Nonvolatile metals	❑	❑	❑
	Asbestos	❑	❑	❑
	Radioactive materials	❑	❑	❑
	Inorganic corrosives	❑	❑	❑
	Inorganic cyanides	❑	❑	❑
Reactive	Oxidizers	❑	❑	❑

■ Demonstrated Effectiveness: Successful treatability test at some scale completed
▼ Potential Effectiveness: Expert opinion that technology will work
❑ No Expected Effectiveness: Expert opinion that technology will not work

The presence of detergents and emulsifiers can unfavorably influence extraction performance and materials throughput. Water-soluble detergents, found in some raw wastes (particularly municipal), will dissolve and retain organic pollutants in competition with the extraction solvent. This can impede a system's ability to achieve low concentration treatment levels. Detergents and emulsifiers can promote the evolution of foam, which hinders separation and settling characteristics and generally decreases materials throughput. Although methods exist to combat these problems, they will add to the process cost.

When treated solids leave the extraction subsystem, traces of extraction solvent will be present [8, p. 125]. The typical extraction solvents used in currently available systems either volatilize quickly from the treated solids or biodegrade easily. Ambient air monitoring can be employed to determine if the volatilizing solvents present a problem.

The types of organic pollutants that can be extracted successfully depends, in part, on the nature of the extraction solvent. Invariably, treatability tests should be conducted to determine which solvent or combination of solvents is best suited to the site-specific vagaries of a particular parameter/matrix mix. In general, solvent extraction is least effective on very high molecular weight organics and very hydrophilic substances.

Some commercially available extraction systems use solvents that are either flammable or mildly toxic or both [20, p. 2]. However, there are long-standing standard procedures used by chemical companies, gasoline stations, etc., that can be used to greatly reduce the potential for accidents.

Technology Description

Figure 1 is a general schematic of the solvent extraction process [3][15, p. 65][4, p. 3].

Waste preparation (1) includes excavation and/or moving the waste material to the process where it is normally screened to remove debris and large objects. Depending upon the process vendor and whether the process is semibatch or continuous, the waste may need to be made pumpable by the addition of solvent or water.

In the extractor (2), the waste and solvent mix, resulting in the organic contaminant dissolving into the solvent. The extraction behavior exhibited by this technology is typical of a mass transfer controlled process, although equilibrium considerations often become limiting factors. It is important to have a competent source conduct a laboratory-scale treatability test to determine whether mass transfer or equilibrium will be controlling. The controlling factor is critical to the design of the unit and to the determination of whether the technology is appropriate for the waste.

The extracted organics are removed from the extractor with the solvent and go to the separator (3), where the pressure or temperature is changed, causing the organic contaminants to separate from the solvent [9, p. 4-2].

The solvent is recycled (4) to the extractor and the concentrated contaminants (5) are removed from the separator [11, p. 6].

Process Residuals

There are three main product streams generated by this technology: the concentrated contaminants, the treated soil or sludge, and the separated water. The extract contains solvent-free contaminants, concentrated into a smaller volume, for post treatment. The recovered contaminants may require analysis to determine their suitability for recycle, reuse, or further treatment before disposal.

The cleaned soil and solids from treated sludge or sediments may need to be dewatered, forming a dry solid and a separate water stream. The volume of product water depends on the inherent dewatering capability of the individual process, as well as the process-specific requirements for feed slurrying. Since the solvent is an organic material, some residue may remain in the soil matrix. This can be mitigated by solvent selection, and if necessary, an additional separation stage. Depending on the extent of metal or other inorganic contaminants, treatment of the cleaned solids by some other technique (i.e., stabilization) may be necessary. Since the organic component has been separated, additional solids treatment should be simplified. The water produced should be analyzed to determine if treatment is necessary before discharge.

Solvent extraction units are designed to operate without air emissions. However, volatile air emissions could occur during waste preparation.

Site Requirements

Solvent extraction units are transported by trailers. Therefore, adequate access roads are required to get the unit to the site. Typical commercial-scale units, 50-70 tons per day (tpd), require a setup area of up to 3,600 square feet.

Standard 440V three-phase electrical service is needed. Water must be available at the site [3]. The quantity of water needed is vendor and site specific.

Contaminated soils or other waste materials are hazardous and their handling requires that a site safety plan be developed to provide for personnel protection and special handling measures. Storage should be provided to hold the process product streams until they have been tested to determine their acceptability for disposal or release. Depending upon the site, a method to store waste that has been prepared for treatment may be necessary. Storage capacity will depend on waste volume.

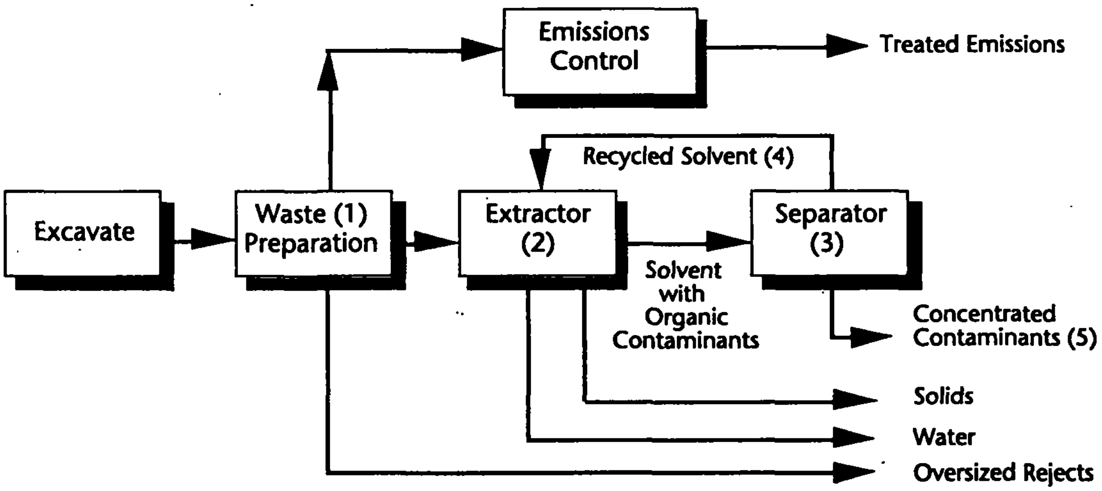
Onsite analytical equipment for conducting oil and grease analyses and a gas chromatograph capable of determining site-specific organic compounds for performance assessment make the operation more efficient and provide better information for process control.

Performance Data

The performance data currently available are mostly from two vendors, CF Systems and Resource Conservation Company (RCC).

CF Systems' full-scale 50-tpd commercial unit (PCU 200), which is treating refinery sludge at Port Arthur, Texas, meets or

Figure 1. Solvent Extraction Process



exceeds the EPA's Best Demonstrated Available Technology (BDAT) standards for a number of organic contaminants (Table 3) [3].

Table 3
API Separator Sludge Results*
(Concentrations in mg/kg)

	Feed Concentrations	*BDAT Target*	*Treated Products for Land Disposal*
Benzene	30.2	9.5	0.18
Toluene	16.6	9.5	0.18
Ethylbenzene	30.4	67.0	0.23
Xylenes (Total)	13.2	Reserved	0.98
Anthracene	28.3	6.2	0.12
Benzo(a)anthracene	BMDL**	1.4	0.18
Benzo(a)pyrene	1.9	0.84	0.33
Bis-(2-ethylhexy)phthalate	4.1	37.0	1.04
Chrysene	6.3	2.2	0.69
Di-n-butyl phthalate	BMDL	4.2	0.11
Naphthalene	42.2	Reserved	0.66
Phenanthrene	28.6	7.7	1.01
Phenol	BMDL	2.7	BMDL
Pyrene	7.7	2.0	1.08

* This information is from vendor-published literature; therefore, quality assurance has not been evaluated.

** Below Minimum Detection Limits (different values in Feed and Treated products).

Source: [3], CF Systems, 50 tpd

Under the Superfund Innovative Technology Evaluation (SITE) program, as shown in Table 4, CF Systems demonstrated an overall PCB reduction of more than 90% for harbor sediments with inlet concentrations up to 2,575 ppm [11, p. 6].

A mobile demonstration unit processed different feed types including clay pit material, ditch skimmer sludge, and drainage basin soil. The wastes were contaminated with oil and grease and aromatic priority pollutants. The oil and grease were separated and their concentrations were reduced to between 89% and 94% of the original amount. For the most part, the aromatic compounds were reduced to nondetectable levels [6, p. 10].

A treatability study completed at the Conroe, Texas, Superfund site with the mobile demonstration unit showed that polynuclear aromatic hydrocarbon (PAH) concentrations in the soil were reduced 95% from 2,879 ppm to 122 ppm [12, p. 3-12].

The only available data for the on-line operational availability were from CF Systems, which they estimated to be 85% (corresponding to a treatment process downtime of 15%). This can be verified and possibly improved with increased operating experience.

The ability of RCC's full- scale B.E.S.T.™ process to separate oily feedstock into product fractions was evaluated by the EPA at the General Refining Superfund site near Savannah, Georgia, in February 1987. It is an abandoned waste oil re-refining facility that contained four acidic oily sludge ponds with high levels of heavy metals (Pb=200-10,000 ppm, Cu=83-190 ppm) and detectable PCBs (2.9-5 ppm). The average composition of the sludge from the four lagoons was 10% oil, 20% solids, and 70% water by weight [16, p. 13]. The transportable 70 tons/day B.E.S.T.™ unit processed approximately 3,700 tons of sludge at the General Refining Site. The treated solids from this unit were back filled 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.

Test results (Table 5) showed that the heavy metals were mostly concentrated in the solids product fraction. TCLP test results showed heavy metals to be in stable forms that resisted leaching, illustrating a potential beneficial side effect when metals are treated by the process [1, p. 13].

RCC has bench-scale treatability data on a variety of wastes, including steel mill wastewater treatment sludge and oil refinery sludge (Table 6) [1, p. 12], that will illustrate the degree of separation possible among the oil, water, and solids

Table 4
New Bedford Harbor Sediments Results
(Concentrations in ppm)

Test #	*Initial PCB Concentration*	*Final PCB Concentration*	*Percent Reduction*	*Number of Passes Through Extractor*
1	350	8	98	9
2	288	47	84	1
3	2,575	200	92	6

Source: [11], CF Systems, 1.5 gpm

Table 5
EPA Data from the General Refining Superfund Site, Savannah, GA

Metals	*Initial Concentration (mg/kg)*	*Product Solids Metal (ppm)*	*TCLP Levels (ppm)*
As	<0.6	<5.0	<0.0
Ba	239	410	<0.03
Cr	6.2	21	<0.05
Pb	3,200	23,000	5.2
Se	<4.0	<5.0	0.008

Source: [1], RCC, 100 tpd

components of the waste. The separation of PCBs in contaminated harbor sediments is shown in Table 7 and in a variety of matrices in Table 8. Results of treatment of pesticide-contaminated soils are shown in Table 9.

RCRA Land Disposal Restrictions (LDRs) that require treatment of wastes to BDAT levels prior to land disposal may sometimes be determined to be applicable or relevant and appropriate requirements (ARARs) for CERCLA response actions. The solvent extraction technology can produce a treated waste that meets treatment levels set by BDAT, but may not reach these treatment levels in all cases. The ability to meet required treatment levels is dependent upon the specific waste constituents and the waste matrix. In cases where solvent extraction does not meet these levels, it still may, in certain situations, be selected for use at the site if a treatability variance establishing alternative treatment levels is obtained. EPA has made the treatability variance process available in order to ensure that LDRs do not unnecessarily restrict the use of alternative and innovative treatment technologies. Treatability variances may be justified for handling complex soil and debris matrices. The following guides describe when and how to seek a treatability variance for soil and debris: Superfund LDR Guide #6A, "Obtaining a Soil and Debris Treatability Variance for Remedial Actions" (OSWER Directive 9347.3-06FS) [17], and Superfund LDR Guide #6B, "Obtaining a Soil and Debris Treatability Variance for Removal Actions" (OSWER Directive 9347.3-07FS) [18]. Another approach could be to use other treatment techniques in series with solvent extraction to obtain desired treatment levels.

Table 6
Oil and Grease Removal
Bench Scale

	Steel Mill Sludge	*Refinery Sludge*
Original Sludge Concentration		
Oil %	11	8
Water %	33	77
Solids %	56	15
Product Stream		
Oil		
Water %	<2	<1
Solvent (ppm)	<100	<150
Water		
Oil & Grease (ppm)	<100	<100
Solvent (ppm)	11	12
Solid		
Oil & Grease (ppm)	0.2	0.9
Solvent (ppm)	34	N/A

Source: RCC, 6 kg Batch

Table 7
Harbor Sediments
PCB Extraction — Bench Scale

Original Sediments	4,500 ppm
Product Stream	
Oil	75,000 ppm
Water	10 ppb
Solid	<1 ppm
% Removal	>99%

Source: RCC, 6 kg Batch

Technology Status

During 1989, solvent extraction technology was selected as the remedial action to clean up 2,000-2,200 cubic yards of soil contaminated with PCBs and organics at the Pinette Salvage Superfund site in Washburn, Maine [13, p. 2]. In 1989, solvent extraction was also selected as the source control remedy in the following Records of Decision: F. O'Connor Superfund site in Augusta, Maine; the Norwood PCBs Superfund site in Norwood, Massachusetts; the Ewan Property Superfund site in Shamong, New Jersey; United Creosoting in Conroe, Texas; and Outboard Marine, State of Illinois [19].

The most significant factors influencing costs are the waste volume, the number of extraction stages, and the operating parameters such as labor, maintenance, setup, decontamination, demobilization, and lost time resulting from equipment operating delays. Extraction efficiency can be influenced by process parameters such as solvent used, solvent/waste ratio, throughput rate, extractor residence time, and number of extraction stages. Thus, variation of these parameters in a particular hardware design and/or configuration will influence the treatment unit cost component, but should not be a significant contributor to the overall site costs.

Cost estimates for this technology range from $100 to $500 per ton.

Solvent Extraction Systems

Solvent extraction systems are at various stages of development. The following is a brief discussion of six systems that have been identified.

CF Systems uses liquefied hydrocarbon gases such as propane and butane as solvents for separating organic contaminants from soils, sludges, and sediments. The extraction units are liquid-filled systems that employ pumps to move the material through the system. As such, the feed material is pretreated, through the addition of water, to ensure the "pumpability" of the material [10, p. 12]. The pH of the feed may be adjusted, through the addition of lime or a similar material, to maintain the metallurgical integrity of the system. Typically, the feed material is screened to remove particles of greater than 1/8" diameter. Depending upon the nature of the

Table 8
PCB Samples Tested in RCC's Laboratory (1/87 through 7/88)

Client	As Received	Raw Sample Phase Composition			PCBs in Product Fraction			
	PCB (mg/kg)	Oil %	Water %	Solids %	Oil (mg/kg)	Water (mg/kg)	Solids (mg/kg)	% Removal
SLUDGES								
GRI	5.9	27	66	7	9.3	<.005	<.01	99.9%
GRI	4.7	10	58	32	N/A	<.01	0.015	99.9%
GRI	5.3	13	57	30	N/A	<.01	0.14	99.2%
Superfund Site Sh	106	35	44	21	270	N/A	1.0	99.8%
Superfund Site CO "A"	51	49	28	23	80	N/A	0.44	99.8%
Superfund Site CO "B"	21	23	24	53	71	N/A	0.08	99.8%
Superfund Site CO "C"	11	15	16	69	52	N/A	0.06	99.6%
SEDIMENTS								
River Sediment "B"	960	26	17	83	N/A	N/A	40	96.5%
Superfund B (#13)	83	44	40	16	N/A	N/A	1.0	99.8%
Harbor Sediment "B"	20,000	3	22	75	970,000	<.006	27	99.9%
Harbor Sediment "C"	30,000	5.6	62	32	550,000	N/A	94	99.9%
Harbor Sediment "D"	430	0.38	47	53	N/A	N/A	32	96.0%
Harbor Sediment NB-A	5,800	1.9	69	29	280,000	<.005	35	99.4%
Harbor Sediment NB-B	16,500	4.3	51.6	44.1	360,000	<.005	75	99.8%
SOILS								
Industrial Soil A	250	0.06	9.4	91	120,000	N/A	2.2	99.1%
Industrial Soil B	120	0.06	13	87	280,000	N/A	6.4	94.7%
Industrial Soil D	5,300	1.0	19	80	370,000	N/A	11	99.8%
Industrial Soil J	19	.09	16	84	10,000	N/A	0.7	96.3%

Source: RCC, .6 kg Batch

oversize material, the large particles may be reduced in size and then returned to the extraction unit for processing.

CF Systems' extraction technology has been demonstrated in the field at two Superfund sites and approximately 10 refineries and treatment, storage, and disposal (TSD) facilities to date.

CF Systems' solvent extraction technology is available in several commercial sizes and the Mobile Demonstration Unit is available for onsite treatability studies. To date, CF Systems has supplied three commercial-scale extraction units for the treatment of a variety of wastes [12, p. 3-12]. A 60-tpd treatment system was designed to extract organic liquids from a broad range of hazardous waste feeds at ENSCO's El Dorado, Arkansas, incinerator facility. A commercial-scale extraction unit is being installed at a facility in Baltimore, Maryland, to remove organic contaminants from a 20-gpm wastewater stream. A PCU-200 extraction unit is installed and operating at the Star Enterprise (Texaco) refinery in Port Arthur, Texas. This unit is designed to treat listed refinery wastes to meet or exceed the EPA's BDAT standards. Performance data and the technology status are explained in the body of this bulletin.

RCC's B.E.S.T.™ system uses aliphatic amines (typically triethylamine) as the solvent to separate and recover contaminants [1, p. 2]. It is applicable to soils, sludges, and sediments, and in batch mode of operation does not need a pumpable waste. Before the extraction process is begun, feed materials are screened to remove particles of greater than 1" diameter and pH adjusted to an alkaline condition. The process operates at or near ambient temperature and pressure. Triethylamine can be recycled from the recovered liquid phases via steam stripping because of its high vapor pressure and low boiling point azeotrope formation.

RCC has a transportable B.E.S.T.™ pilot-scale unit available to treat soils and sludges. This pilot-scale equipment has been used at a gulf coast refinery treating various refinery waste streams and has treated PCB-contaminated soils at an industrial site in Ohio in November 1989. A full-scale unit with a nominal capacity of 70 tpd was used to clean up 3,700 tons of PCB-contaminated petroleum sludge at the General Refining Superfund Site in Savannah, Georgia, in 1987. Performance data and the technology status are explained in the body of this bulletin.

ENSR is in the process of developing a mobile solvent extraction unit capable of decontaminating soils and sludges at a rate of 5 to 10 cubic yards/hour [5, p. 1]. The ENSR system uses a proprietary reagent and solvent. The company claims that its solvent extraction system is designed to operate without significant pretreatment of the soil/sludge and without the addition or removal of water. Design of a pilot-scale unit is near completion. Thus far, only performance data from earlier bench-scale tests are available.

The **Extraksol™** process was developed in 1984 by Sanivan Group, Montreal, Canada [7, p. 35]. It is applicable to soils, sludges, and sediments. Performance data on contaminated soils and refinery wastes are available for a 1 ton per hour (tph) mobile unit. The process uses a proprietary solvent that reportedly achieved removal efficiencies up to 99% (depending on the number of extraction cycles and the type of soil) on PCBs, oil, grease, PAHs, and pentachlorophenol [7, p. 45]. The 1-tph unit is suitable for small projects with a maximum of 300 tons of material to be treated. The Sanivan group is planning to build a full-scale unit that can process 6-8 tph of waste [7, p. 41].

Harmon Environmental Services and Acurex Corporation are involved in a cooperative joint venture to develop a solvent soil washer/extraction system appropriate for the onsite remediation of Superfund and RCRA sites. They have completed EPA-sponsored bench-scale studies on different types of soils contaminated with #2 fuel oil. The design of a pilot plant unit is being considered.

Table 9
RCC B.E.S.T.™ Treated Pesticide-Contaminated Soil — Bench Scale

Analyte	*Feedstock (ppm)*	*Product Solids (ppm)*	*Removal Efficiency %*
p,p'-DDT	500	0.2	99.96
p,p'-DDE	84	0.5	99.4
p,p'-DDD	190	0.05	99.97
Endosulfan-I	250	<0.02	>99.99
Endosulfan-II	140	<0.02	>99.99
Endrin	140	0.02	99.99
Dieldrin	37	<0.02	>99.95
Toxaphene	2,600	0.9	99.97
BHC-Beta	<30	<0.13	-
BHC-Gamma (Lindane)	<30	<0.07	-
Pentachlorophenol	150	1.9	98.7

Source: RCC, .6 kg Batch

The **Low Energy Extraction Process (LEEP)** is a patented solvent extraction process that can be used onsite for decontaminating soils, sludges, and sediments. LEEP uses common hydrophilic and hydrophobic organic solvents to extract and further concentrate organic pollutants such as PCBs [2, p. 3]. Bench-scale studies are available. The design of the pilot plant is completed, and the plant is scheduled for operation at the beginning of 1990.

EPA Contact

Technology-specific questions regarding solvent extraction may be directed to:

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FTS 340-6625
(201) 321-6625

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