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The B.E.S.T.® Solvent Extraction Process Applications with Hazardous Sludges, Soils and Sediments

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INTRODUCTION

During the 1960's, the Boeing Aerospace Co. invented and patented the B.E.S.T. ® process for use aboard the manned space station. Subsequent to this early development, Resources Conservation Company's (RCC), focus was on the dewatering of municipal water treatment sludges. The process was successfully demonstrated several times and its ability to consistently produce dry, oil free solids was confirmed with a seven ton per day truck mounted pilot unit.

Further development of the B.E.S.T.® process for treating hazardous oily wastes began in in 1984 following the re-authorization of the Resources Conservation and Recovery Act (RCRA). Laboratory work by RCC demonstrated that the process can separate RCRA listed petroleum refining oily sludges into three fractions; oil free water, recycleable oil and dry, oil free solids. A second generation pilot plant was designed, constructed and operated to demonstrate the feasibility of the process for treating oily sludges.

Based on data from the operation of this second generation pilot unit, RCC constructed a commercial scale B.E.S.T.® unit designed to treat petroleum refining sludges (pumpable sludges). In 1987, this transportable B.E.S.T.® unit completed the clean up of 3700 cubic yards of acidic, oily, PCB-contaminated sludges at the General Refining Superfund Site near Savannah, GA.

Recently, RCC has constructed a third generation pilot unit to develop data for a B.E.S.T.® process to treat non-pumpable wastes, such as soils and sediments. This unit is currently being operated at RCC's Laboratory in Bellevue, WA.

During the last five years, RCC's Laboratory has evaluated many different oily sludges and contaminated soils. These bench scale treatability test results have demonstrated that the B.E.S.T.® process is applicable for treating a wide range of wastes contaminated with volatile organics (VOC), polynuclear aromatics (PNA), polychlorinated biphenyls (PCBs) and pesticides.

The main objective of the B.E.S.T.® process is to separate oily sludges, soils and sediments into a water phase that can be treated by conventional treatment and discharged, a dry treated solid phase that can be used as back fill on site and an oil phase containing the organic contaminants that can be destroyed or recycled cost effectively.

THE B.E.S.T.® PROCESS

The B.E.S.T.® process is a patented solvent extraction technology utilizing triethylamine (TEA) as the solvent. TEA is an aliphatic amine that is produced by reacting ethyl alcohol and ammonia.

The key to the success of the B.E.S.T.® process is TEA's property of inverse miscibility. At temperatures below 65°F, TEA is completely soluble with water. Above this temperature, TEA and water are only partially miscible. Figure 1 shows a graphic representation of this phenomenon. The property of inverse miscibility can be utilized since cold TEA can simultaneously solvate oil and water. B.E.S.T. ® produces a single phase extraction solution which is a homogeneous mixture of TEA and the water and oil (containing the organic contaminants, such as PCBs, PNAs and VOCs) present in the feed material. In cases where extraction efficiencies of other solvent extraction systems are hindered by emulsions, which have the effect of partially occluding the solute (oil containing the organic contaminants), TEA can achieve intimate contact at nearly ambient temperatures and pressures. This allows the B.E.S.T.® process to handle feed mixtures with high water content without penalty in extraction efficiency.

TEA is an excellent solvent for treating hazardous wastes because it exhibits several characteristics that enhance its use in a solvent extraction system. These characteristics include:

- A high vapor pressure, therefore the solvent can be easily recovered from the extract (oil, water and solvent) via simple steam stripping.
- Formation of a low-boiling azeotrope with water, therefore the solvent can be recovered from the extract to very low residual levels (typically less than 100 ppm).
- A low heat of vaporization (1/7 of water), therefore solvent can be recovered from the treated solids by simple heat with a very low energy input.
- TEA is alkaline (pH=10), therefore some heavy metals are converted to the hydroxide form, which precipitate and exit the process with the treated solids.
- TEA is only moderately toxic and readily biodegrades. Data available in EPA document EPA-600/2-82-001a shows that a level of 200 ppm TEA in water was degraded completely in 11 hours by Aerobacter, a common soil bacteria.

A fact sheet for triethylamine is presented as Figure 2.

A block diagram for the B.E.S.T.® process is presented as Figure 3. First extraction of the contaminated material is conducted at low temperatures, below 40 °F. At this temperature, the triethylamine (TEA) is soluble with water. Therefore, the extract solution from the first extraction stage contains most of the water in the feed material. If the first stage extract contains sufficient water to allow a phase separation of the TEA and water, the extract is heated to a temperature above the miscibility limit (130 °F). At this temperature, the extract separates into two distinct phases, a TEA/oil phase and a water phase. The two phases are separated by gravity and decanted.

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FIGURE 1
U.S. PATENT (JAN. 11, 1977) 4,002,562

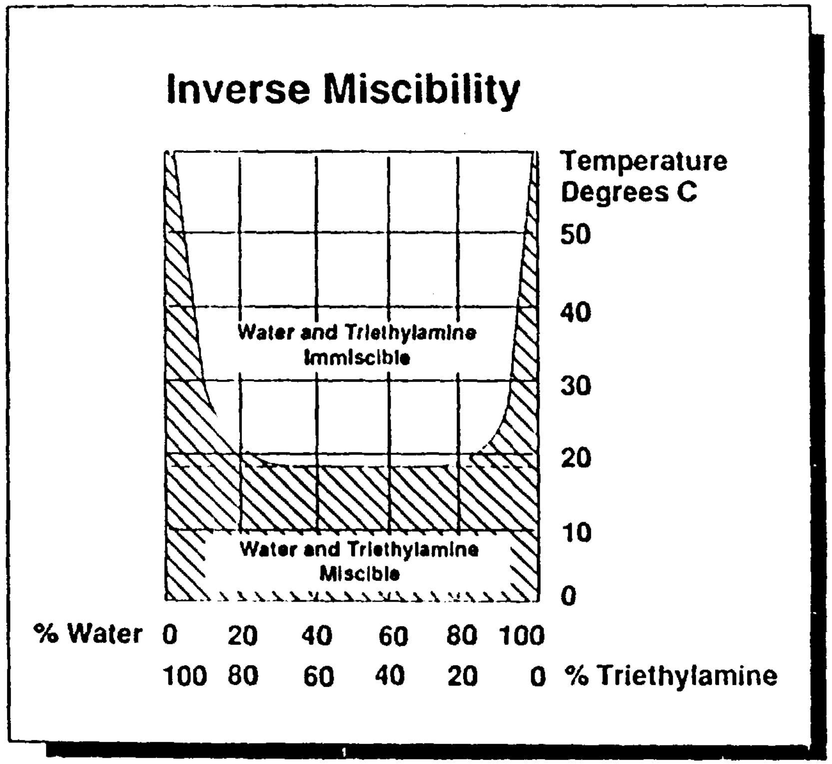

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FIGURE 2
TRIETHYLAMINE
$(C_2H_5)_3N$

- Inversely Miscible In Water
- Heat of Vaporization - 130 BTU/lb (BP - 194°F)
- Forms 90/10 Azeotrope With Water (BP - 170 °F)

- Olfactory Detection Level in Air - 0.1 ppm (OSHA Standard - 15ppm)

- Regulatory Status
  - CERCLA Spill Reporting Level - 5000 lbs. (max.)
  - No TSCA, RCRA, or EPCRA status
  - Clean Water Act Discharge Limits - None

- Mutagenicity - None

- Biodegradation - 200 ppm in water, 100% in 11 hours

- Other Properties
  - Flammable
  - Alkaline. pH 11
  - "Fishy", Ammonia-like Odor

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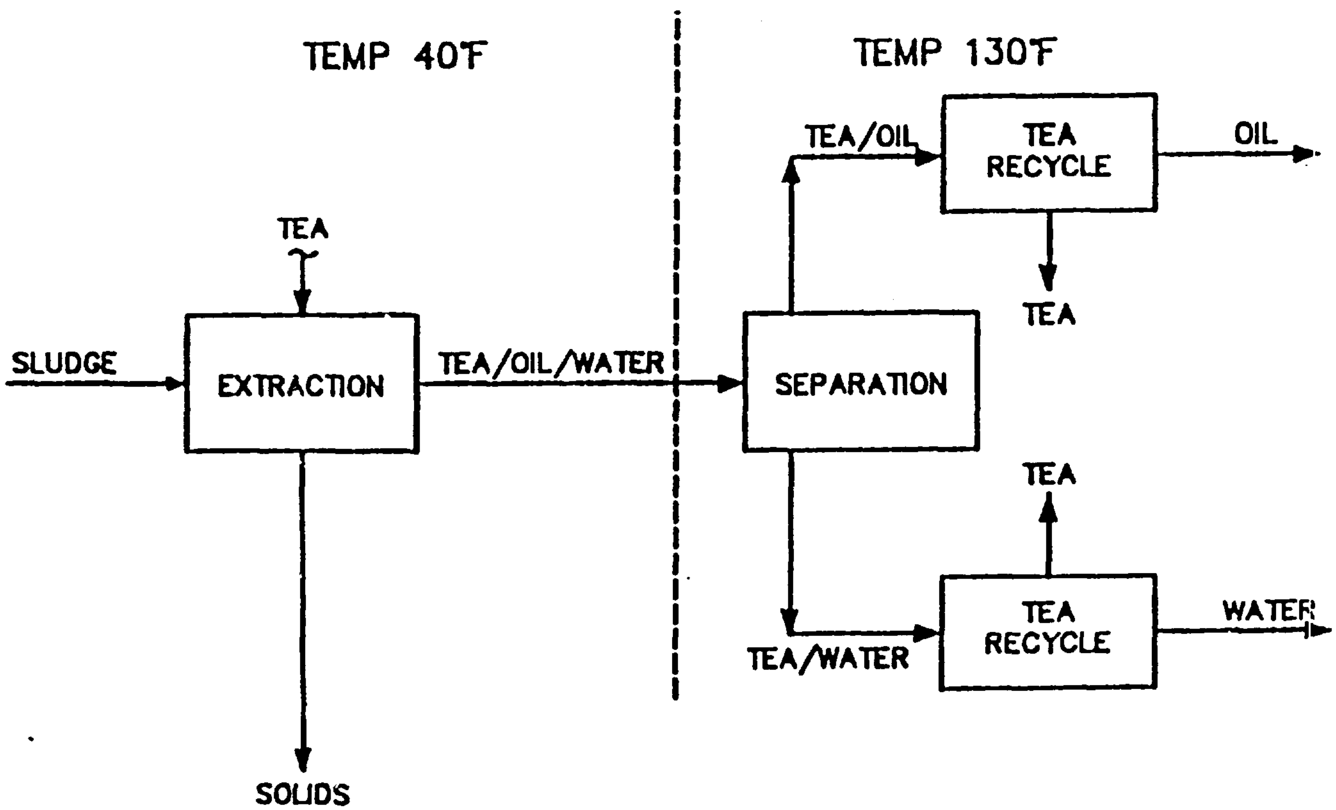
FIGURE 3
B.E.S.T. - USING INVERSE MISCIBILITY



Subsequent extraction stages are conducted at about 130 °F. At this temperature, solubility of oil (organic contaminants) in TEA increases which enhances removal of the oil from the contaminated solids. Extract from these stages are combined with the decanted TEA/oil phase from the first extraction stage. The solvent is recovered from the from the two phases via steam stripping. Residual TEA in the water and oil products is quite low, typically less than 100 ppm. The recovered solvent is recycled to extraction vessels. directly to the solvent recovery portion of the process.

TEA is removed from the treated solids by indirect heating with steam. A small amount of steam may be added directly to the dryer vessel to provide the water required to form the low boiling azeotrope. Typically the residual TEA remaining with the treated solids is less than 500 ppm. The residual TEA in the treated solids biodegrades readily. Typically, the dry treated solids can be used as back fill at the site.

The B.E.S.T.® process operates near ambient pressure and temperature and at a mildly alkaline pH. Temperatures of liquid streams within the unit vary from about 40 - 170 degrees F and high pressures are not required. The system runs at virtually atmospheric pressure. An advantage of this type system is that it uses standard off-the-shelf processing equipment. A low pressure nitrogen blanket creates a small positive pressure of tanks and vessels. Since the process operates in a closed loop, with one small vent for removal of non-condensible gases, there are virtually no air emissions.

COMMERCIAL SCALE OPERATIONAL EXPERIENCE WITH THE B.E.S.T.® PROCESS

The General Refining Superfund Site located near Savannah, GA, was operated as a waste oil re-refining facility from the early 1950's until 1975. The operation collected used crankcase oil from local gas stations and recovered the oil by adding acid and heating followed by filtration to remove suspended material. The treated oil was then re-packaged and sold. The sludge produced in the process was placed in un-lined pits. The acidic, oily sludge contained high levels of lead because the sulfuric acid added to the used oil during the recovery process was supplemented by spent battery acid.

Analysis of the impounded sludges detected heavy metals including lead (up to 10,000 ppm) and copper (83-190 ppm). PCB's were detected in all samples at low concentrations (5-15 ppm). The acidic, oily sludges had a pH of less than 2. Composition of the sludges and soils at the site varied widely from point to point laterally and vertically within the lagoons. Nominal composition was about 10% oil, 70% water and 20% solids. During actual operation at the site, oil concentrations ranged from 0-40%, solids from 2-30% and water from 60-100%.

US EPA investigated several treatment alternatives for clean up of the site including; incineration (on-site and off-site), excavation and transportation to a commercial landfill, and on-site processing with the B.E.S.T.® unit. Decision criteria included; economics, schedule and performance. The B.E.S.T.® process was selected as the most cost effective and suitable treatment alternative for this site.

B.E.S.T.® process equipment was moved to the site and set up during 1986. Processing of sludges and soils at the site proceeded through early 1987 and was completed in March, 1987. About 3700 cubic yards of sludges were processed at the site.

Water recovered by the B.E.S.T.® process was transported to a nearby industrial waste treatment plant and discharged. Recovered oil was heavy (API gravity = 15), but was suitable for recycle as fuel oil. The B.E.S.T.® process isolated the PCB's in the oil fraction. Residual PCB levels in the solids were quite low (<0.1 ppm). PCB's were not detected in the water. (Detection limit = 10 ppb).

Near the end of the project at the General Refining site, RCC and EPA cooperated in a comprehensive sampling program. Over 160 samples of input and output streams were collected during a 24 hour period with the B.E.S.T.® unit operating at capacity. These samples were shipped to a CLP laboratory for analysis. Results of these analyses are presented in Figure 4. US EPA has published a report detailing all the results, entitled, "Evaluation of the B.E.S.T.tm Solvent Extraction Process - Twenty-Four Test". The report is available through NTIS.

During the final months of the General Refining cleanup, the system operated twenty four hours per day, achieving a 70 ton per day capacity. A photograph of this unit is presented as Figure 5.

B.E.S.T.® PROCESS TREATMENT OF SOILS AND SEDIMENTS

A B.E.S.T.® system configured for soils and sediments uses washer/dryer vessels for extraction, solids separation and solids drying. The use of the washer/dryer vessel allows the contaminated soil to be handled only once. The soil is not moved from the vessel until the treatment level is reached. Extraction and drying of soil is accomplished in the vessel "batch wise" which provides process flexibility and increases overall system reliability.

Following excavation, contaminated soil is screened to remove material larger than 1/2 inch in diameter. The screened material is loaded into the specially designed hoppers that hold about three cubic yards of soil. As illustrated in Figure 6, each hopper is transported to the B.E.S.T.® unit and lifted by crane to the feeding port on the washer dryer vessel. After the hopper is secured, a bottom gate is opened and the material flows into the vessel. The hopper is then removed and the feeding port is sealed.

Figure 7 shows a schematic diagram of a three stage wash soil cleanup unit. After extracting the feed material with TEA, the solids are allowed to settle and the solvent mixture and particulates are separated. This is accomplished by simple decantation of the liquid contents of the washer dryer vessel. Carryover of particulates from this process can be controlled by backwash filters or disc centrifuges if necessary.

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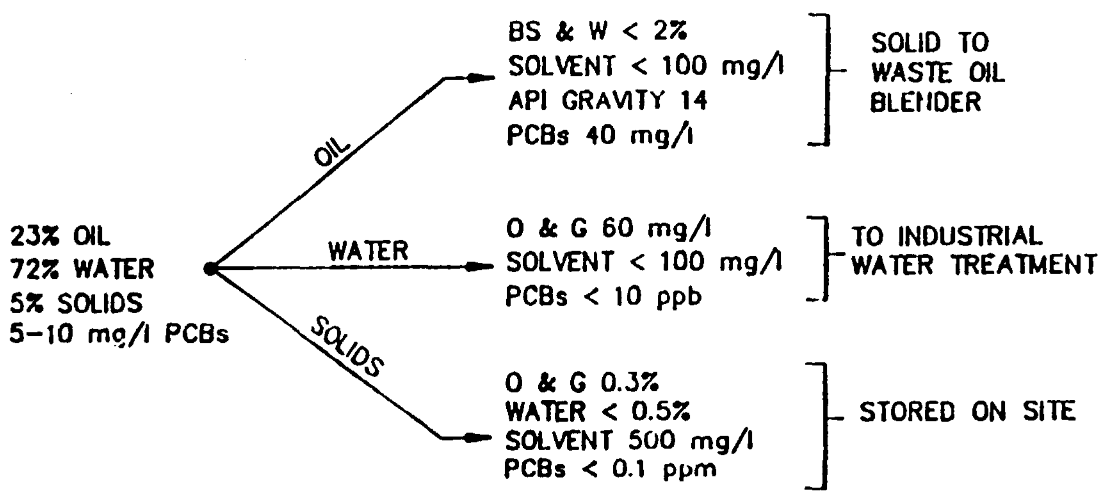
FIGURE 4
TYPICAL GRI OPERATION - EPA DATA



PRODUCT SOLIDS

TOTAL METALS

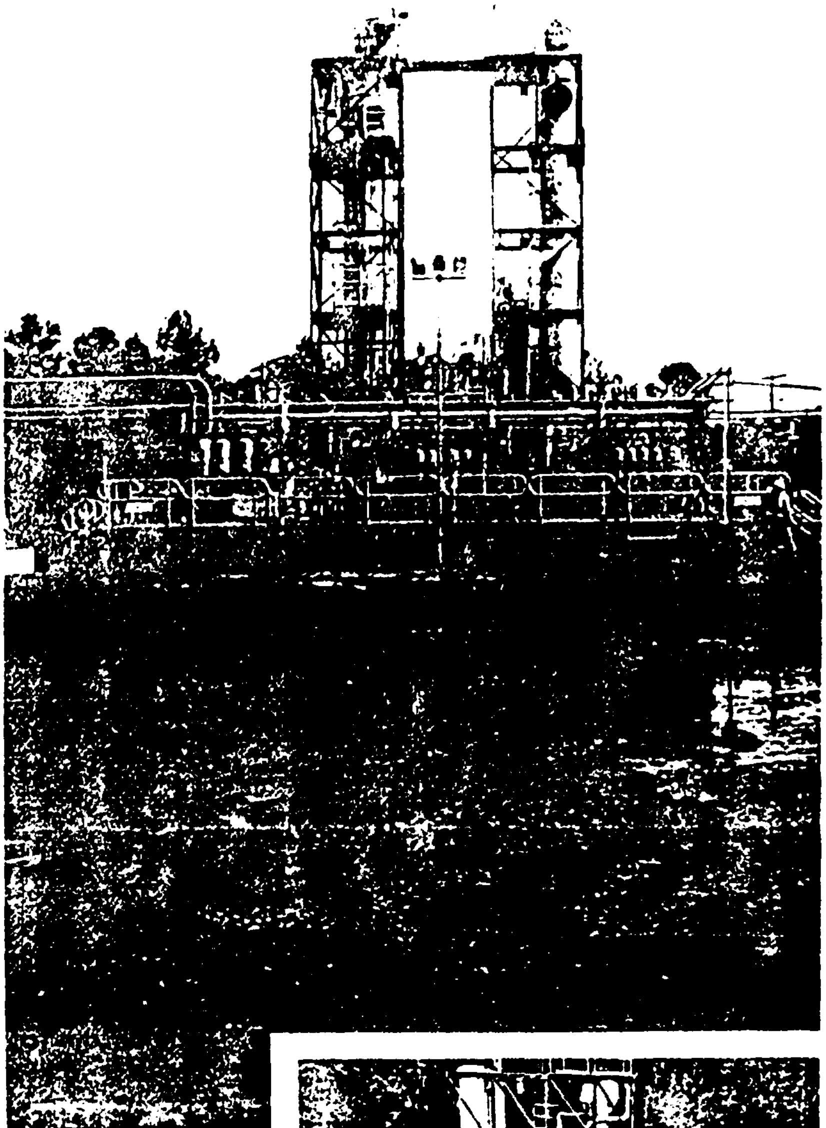
As	< 5.0 ppm
Ba	410
Cd	3.4
Cr	21
Pb	23,000
Zn	1000
Se	< 5.0

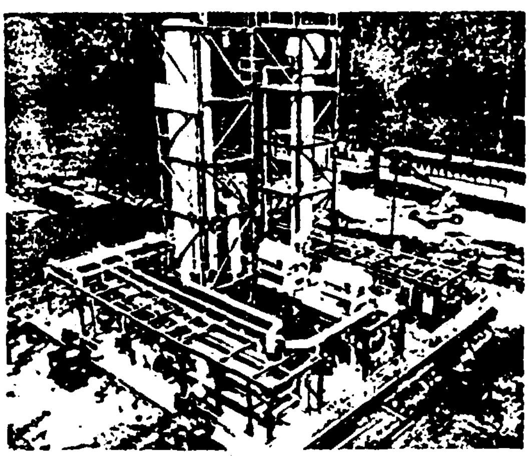
TCLP METALS

As	< 0.03 ppm
Ba	< 0.03
Cd	--
Cr	< 0.05
Pb	5.2
Hg	< 0.001
Se	0.008
Ag	--

FIGURE 5
General Refining Superfund site

Garden City, Georgia





(Top) The B.E.S.T. unit with oily sludge in the foreground. (Right) The B.E.S.T. unit being assembled on the waste site near Savannah, Georgia.

B.E.S.T. is a registered trademark of Resources Conservation Company.

The B.E.S.T.® unit cleaned 3700 tons of contaminated sludge during EPA emergency response action.

Equipment:
Skid-mounted B.E.S.T. unit

Feature:
Uses triethylamine in a patented process to separate toxic sludge into solids, water and oil

Capacity:
Up to 100 tons per day

Input:
Oily sludge of variable consistency: 25% oil, 20% solids, 55% water

Output:
Water to local industrial plant for treatment and discharge
Oil recovered as fuel
Inert solids retained on site

Client:
Environmental Protection Agency

Operational:
August 1986 to February 1987

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FIGURE 6
WASHER / DRYER CHARGING

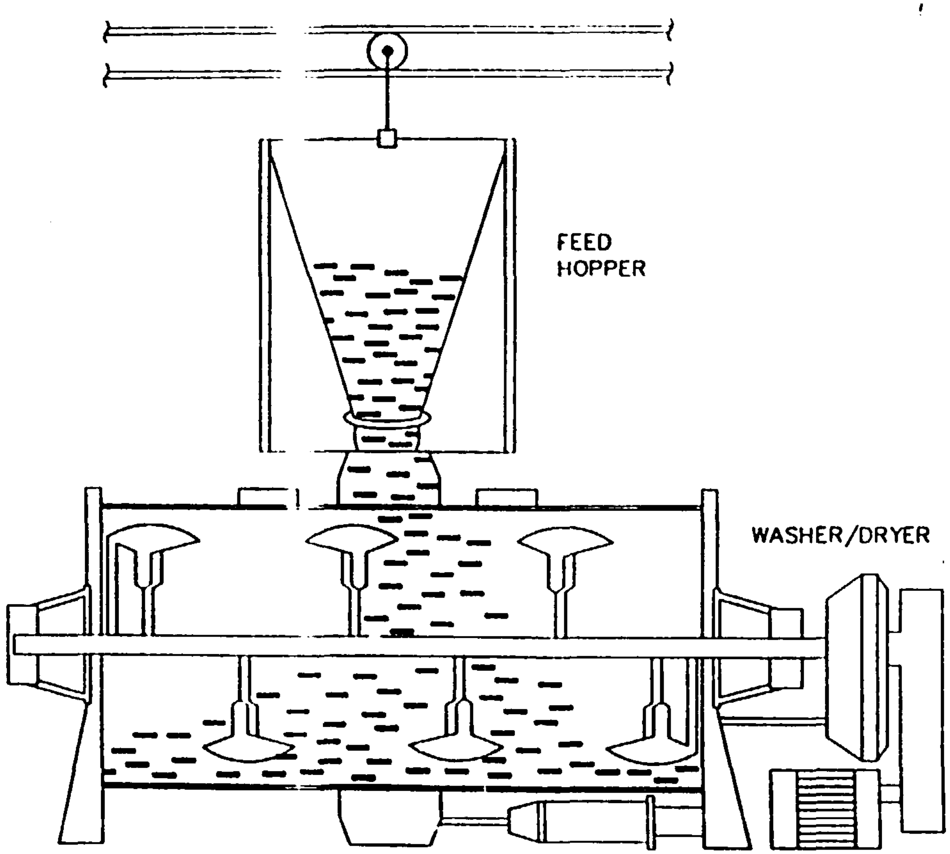

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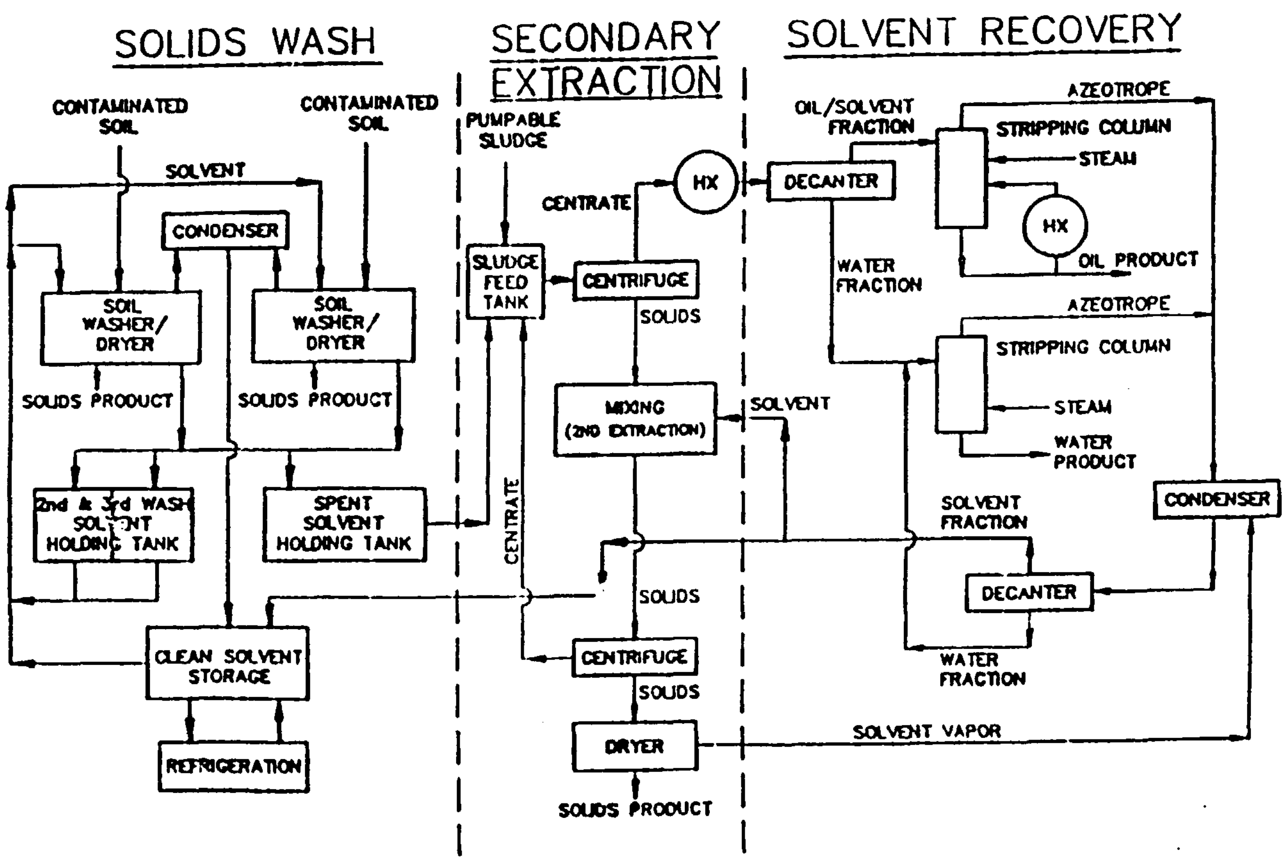
FIGURE 7
HYBRID, SOIL & SLUDGE SYSTEM



After each extraction step, the spent solvent is discharged from the washer/dryer vessel into the spent solvent storage tank. The decanted extraction solution of TEA, water, and oil is then heated to about 140°F to separate water. Because much of the water can be separated without distillation there is an energy savings. In some cases, however, it may be necessary to distill the water if TEA/water separation is adversely affected by matrix interferences such as detergents, surfactants, or some types of synthetic oils. Empirical treatability testing is currently the only means of determining the efficiency of the separation of TEA/oil from water for a given waste sample.

The solvent/oil phase is steam stripped to recover the solvent for recycle to the washer/dryer vessel to extract additional soils. The recovered oil is stored for subsequent treatment or recycle. Water from the steam stripper is treated and may be suitable for direct discharge.

Upon final extraction of the soil, the washer/dryer vessel is heated by direct and indirect addition of steam. The solvent is vaporized and recovered for recycle. The energy required for evaporation of the solvent is low, approximately 1/7th that of water. Upon completion of the drying step the solids are unloaded from the washer/dryer into a 3 cubic yard hopper and sent to final disposition. Some water (about 5% by weight) will be left in the solids to control dusting.

BENCH-SCALE TREATABILITY TESTING

In order to evaluate each potential application for the B.E.S.T.® process, RCC has developed a low cost glassware test protocol that requires only three liters of sample material. A schematic of the glassware test protocol is shown in Figure 8.

A quote from USEPA's report evaluating the B.E.S.T.® process states;

> "Resources Conservation Company has conducted many laboratory tests and developed correlations to which data from full-scale operations, such as the General Refining site can be compared."

Figure 9 presents data from two separate bench-scale treatability tests conducted prior to full scale operation at the General Refining Inc. (GRI) site. These results correlate quite well with full scale performance data collected during the twenty-four hour sampling period.

Initially in the bench-scale treatability test, the waste material is analyzed to characterize its phase composition; oil, water and solids. A 600 gram sample is adjusted to a pH = 10 and mixed with TEA to three extraction stages. Following extraction, the treated solids are separated from the extract (oil, water and solvent) in a floor mounted centrifuge.

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FIGURE 8
SOLVENT EXTRACTION TECHNOLOGY GLASSWARE TESTING APPROACH

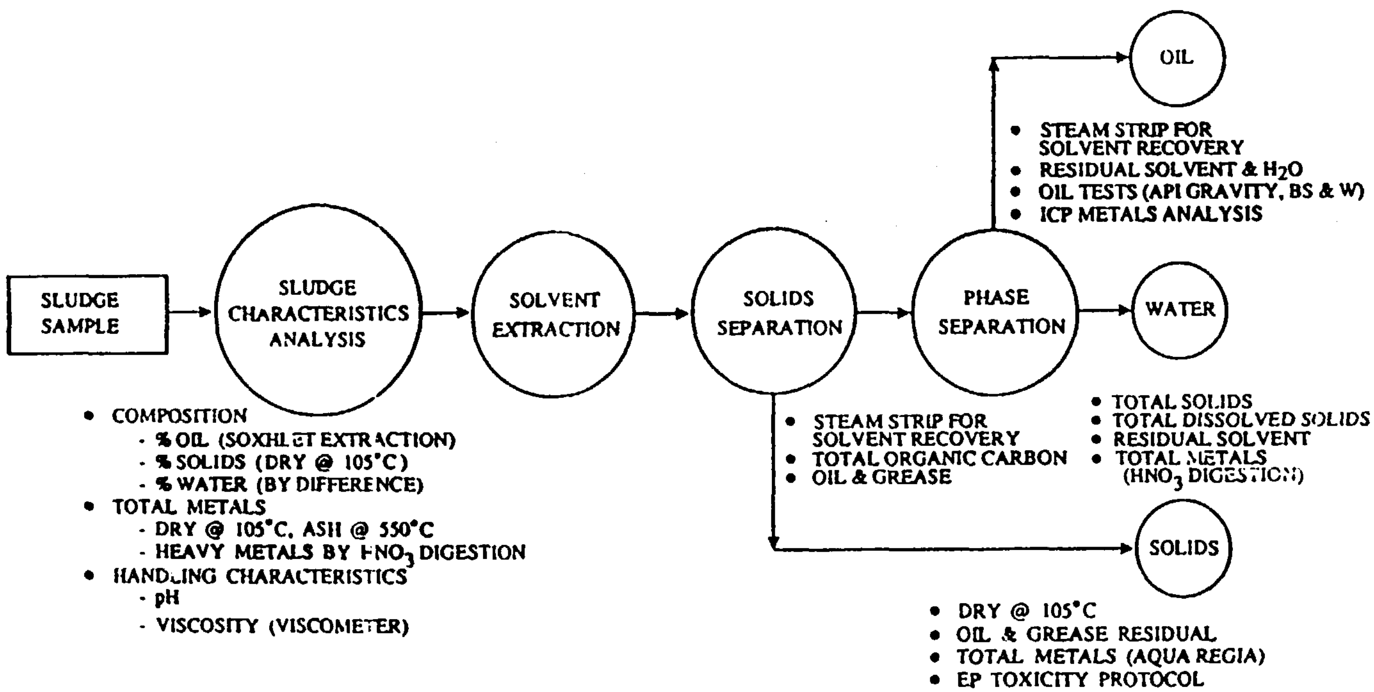

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FIGURE 9

GENERAL REFINING SITE
PCB CONCENTRATIONS IN RAW SLUDGE & PRODUCT FRACTIONS
(ppm)

	LAB SCALE TESTING (1986) TEST "A"	TEST "B"	FULL SCALE PROCESSING FEB. 26-27, 1987
RAW SLUDGE (DRY BASIS) mg/kg	14.	12.	13.5
PRODUCT SOLIDS mg/kg	0.02	0.14	<0.13
PRODUCT WATER mg/L	<0.01	<0.01	<0.005
%EXTRACTION EFFICIENCY	99.9	98.8	>99.0

The extract solution is then heated and allowed to decant in a separatory funnel into distinct oil/TEA and water phases. Stripping of the TEA from the oil and water phases is conducted in a rotovap apparatus operating at atmospheric pressure. The recovered fractions are analyzed to determine the partitioning of the contaminants and to determine the quality of the treated solids.

PILOT-SCALE TREATABILITY TESTING

RCC has available a pilot-scale B.E.S.T.® unit configured to demonstrate the full scale performance of the process. The unit has a capacity of 100 pounds per day of treated dry solids. A photograph of the pilot unit is presented in Figure 10.

TREATMENT OF PCB CONTAMINATED WASTES WITH THE B.E.S.T.® PROCESS

The goal of treating PCB contaminated materials is the destruction of the PCBs; however, the logical approach is to destroy the PCBs without handling the entire bulk of the waste with the PCB destruction technology. If this can be done the volume requiring treatment will be greatly reduced. A technology that accomplishes this goal is the B.E.S.T.® Process.

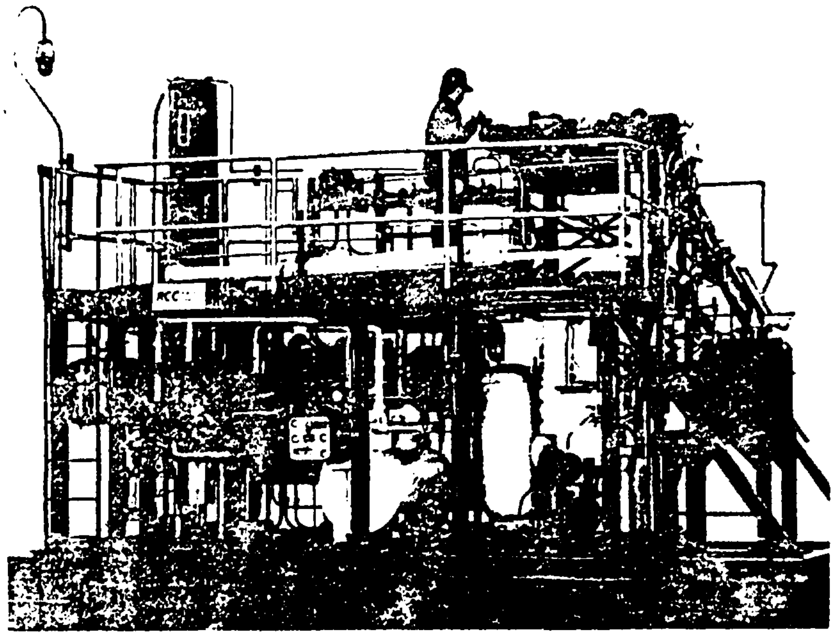
Recent laboratory and full scale work has evaluated the usefulness of the B.E.S.T. ® process for treatment of PCB contaminated soils. Data shows high performance for the extraction of PCB from environmental samples.

Over the past two years several laboratory studies have been conducted on PCB contaminated soils. The soils tested varied from dry sandy soil with low oil content, to clay like soil with high amounts of plant debris present. A summary of PCB data collected from these experiments is shown in Figure 11. Analysis was conducted in accordance with SW846 8080 and Method 608 were applicable.

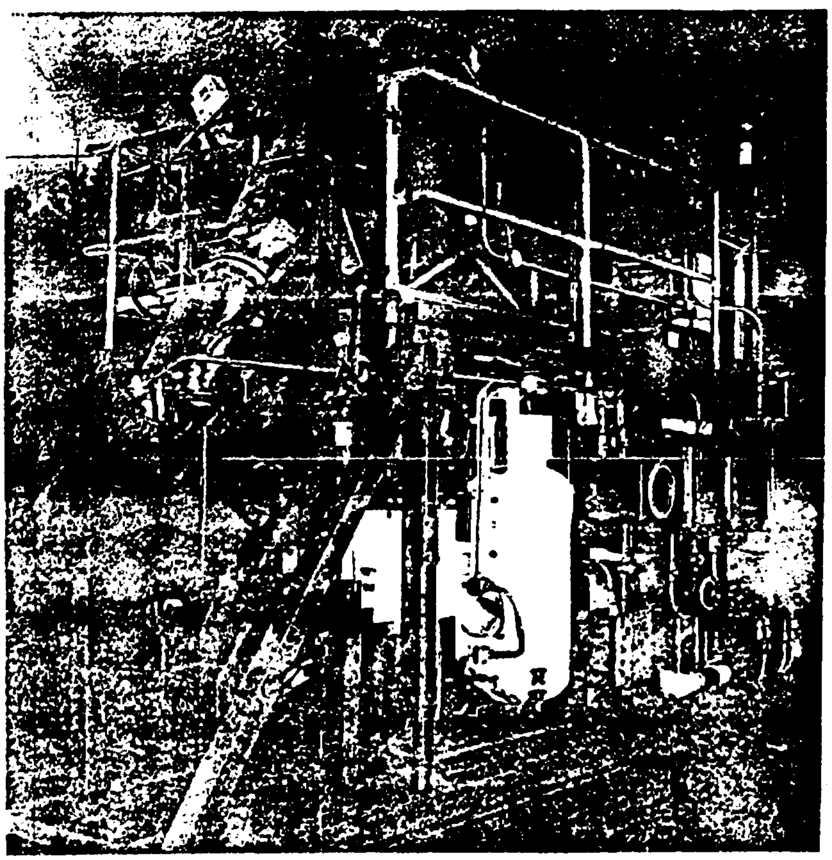
As can be seen from the data in Figure 12, the extraction of PCBs from the soils was accomplished with a high degree of efficiency. Typical extraction efficiency is 99% and substantially higher in some instances. Extraction efficiencies have been calculated here on an absolute weight removal basis. Mass balance calculations for the tests indicate that essentially all of the PCBs are extracted into a small volume oil stream. The oil stream, free of particulates and water, is then ready for destruction or disposal.

Although PCBs are readily soluble in TEA, there is a fraction of the total amount that is not extractable during the process. Figure 11 shows the results of multiple extraction stage testing undertaken on a PCB contaminated soil. As can be seen, there is an asymptotic limit on PCB removal. The reason for the limitation is unclear, but may be due to the charge attraction of the PCBs for the surface of the solids particles. This attraction may be greater than the attraction of TEA to PCBs. It is interesting to note that the overall extraction efficiency of PCBs does not appear to be connected to the initial concentration.

FIGURE 10
B.E.S.T.* Pilot Plant



B.E.S.T. Pilot Plant



Reverse side of pilot plant

Mobile field unit demonstrates the effectiveness of the B.E.S.T. process on location with on-site feeds and actual operating conditions.

Equipment:
Skid-mounted module contains all B.E.S.T. unit operations to mix, extract, centrifuge, evaporate, decant, strip and dry. Module is easily transported on highways.

Capacity:
6-10 gallons per batch

Input:
Pumpable and non-pumpable sludges, sediments or soil

Output:
Dewatered oil
Stripped water
Dry solids

Site requirements:
20' x 50' process area.
Industrial air and electricity.
(If needed, all utilities can be supplied by RCC utility skid.)

Operational:
March 1989

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FIGURE 11
SOILS TREATABILITY TEST PCB DATA

	Feed Composition				After Treatment	
Test	PCBs (mg/kg)	%Oil	%Water	%Solids	Solids (mg/kg)	% Removal
A	250.	.06	9.4	91.	2.2	99.2
B	120.	.04	13.	87.	6.4	95.4
C	4,300.	1.0	15.	84.	2.0	>99.9
D	5,300.	1.0	19.	80.	11.	99.8
E	190.	.07	16.	84.	1.6	99.3
F	3,000.	1.5	30.	69.	0.8	>99.9
G	15,000.	1.8	29.	69.	6.9	>99.9
H	760.	2.6	22.	75.	4.1	99.6
I	1,900.	.22	14.	86.	5.5	99.8
J	19.	.09	16.	84.	0.7	96.9
K	1,500.	1.5	11.	88.	19.	98.6
L	820.	0.2	8.	92.	9.4	98.9

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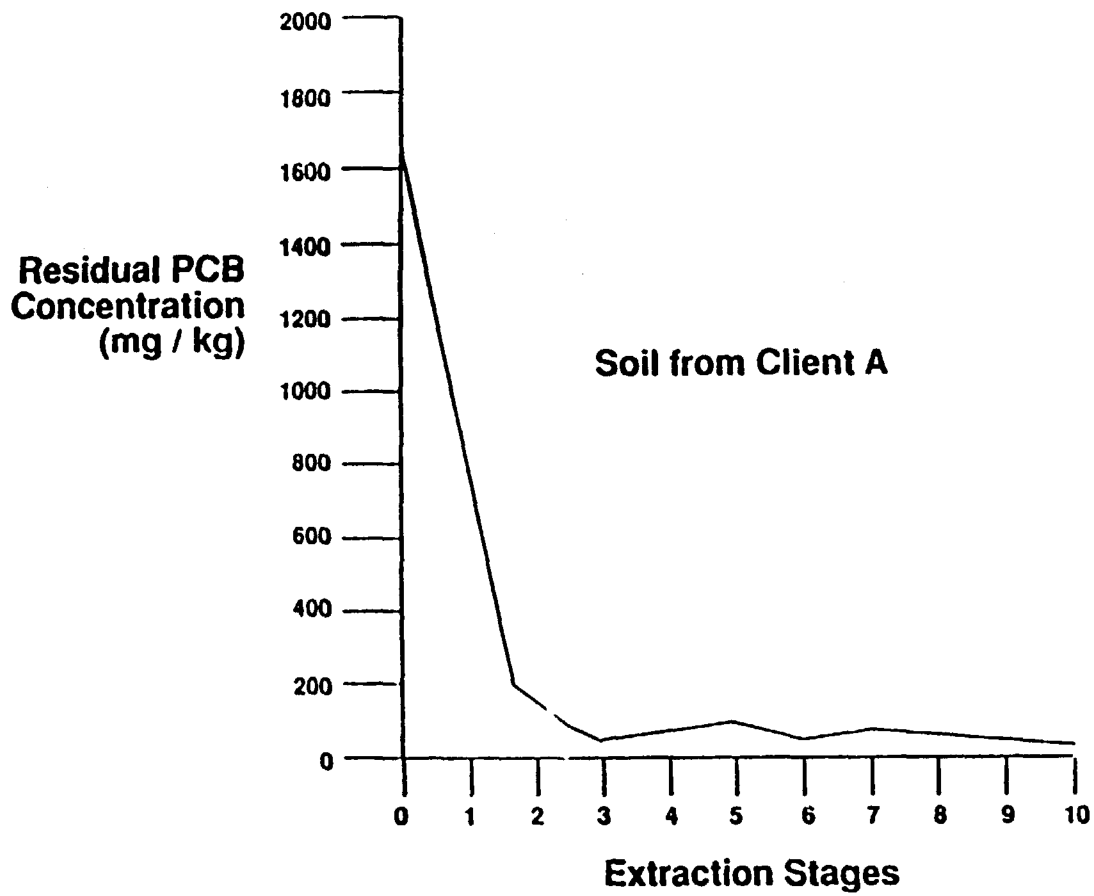
FIGURE 12
MULTIPLE TEA EXTRACTION ANALYSIS



If the phenomenon of PCB adsorption on the surface of the particles was the only reason for extraction inefficiency, the ultimate level of removal would be constant, not the extraction efficiency. More data will have to be collected in order to clarify this phenomenon.

SMALL TRUCK MOUNTED B.E.S.T.® UNIT

RCC has configured a truck mounted B.E.S.T.® unit to economically process small quantities of contaminated soil, sludge or sediment. The unit is capable of processing one cubic yard of material per hour. A flow schematic of the unit is shown in Figure 13. A sketch of the unit is provided in Figure 14.

CONCLUSIONS

- The B.E.S.T.® process is a proven technology for treatment of contaminated sludges, soils and sediments.
- The B.E.S.T.® process is an effective method of concentrating PCB's in the oil fraction, thereby significantly reducing the cost of PCB destruction.
- The B.E.S.T.® process offers a cost effective, viable alternative to land disposal of hazardous wastes.
- The B.E.S.T.® process can be used as an on-site materials handling step which can significantly reduce the amount of hazardous material that is transported off-site for disposal. This reduces the overall cost of site clean up and limits the risks associated with transporting hazardous wastes over public highways.

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FIGURE 13

B.E.S.T.® SOIL CLEANUP UNIT SCHEMATIC

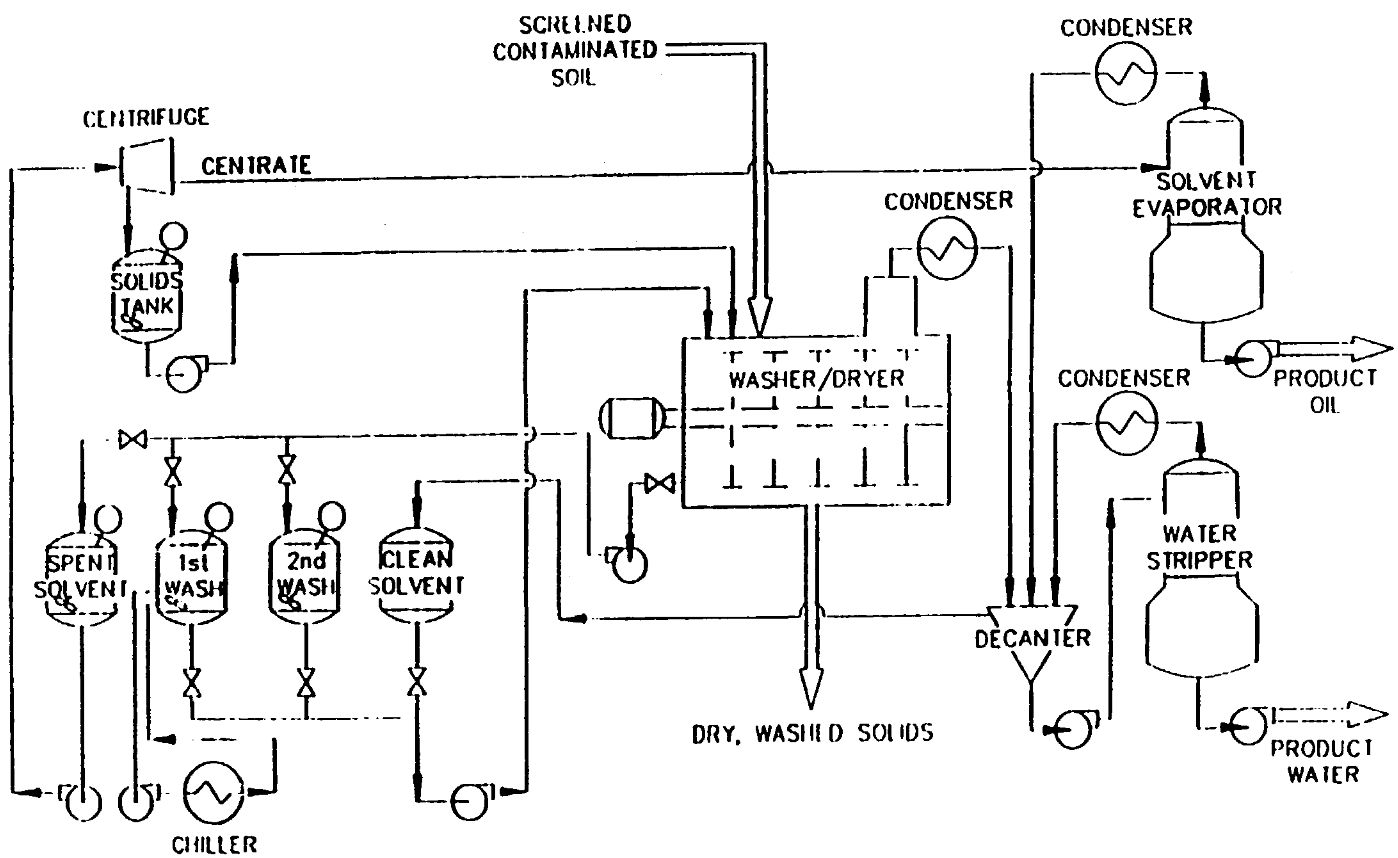

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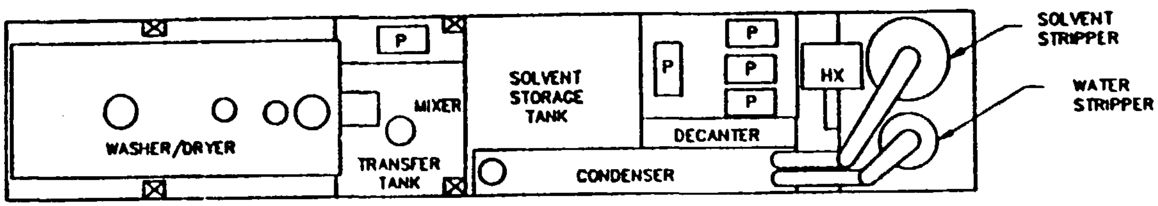
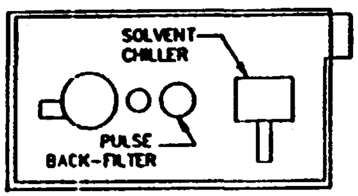
FIGURE 14
INITIAL CONCEPT

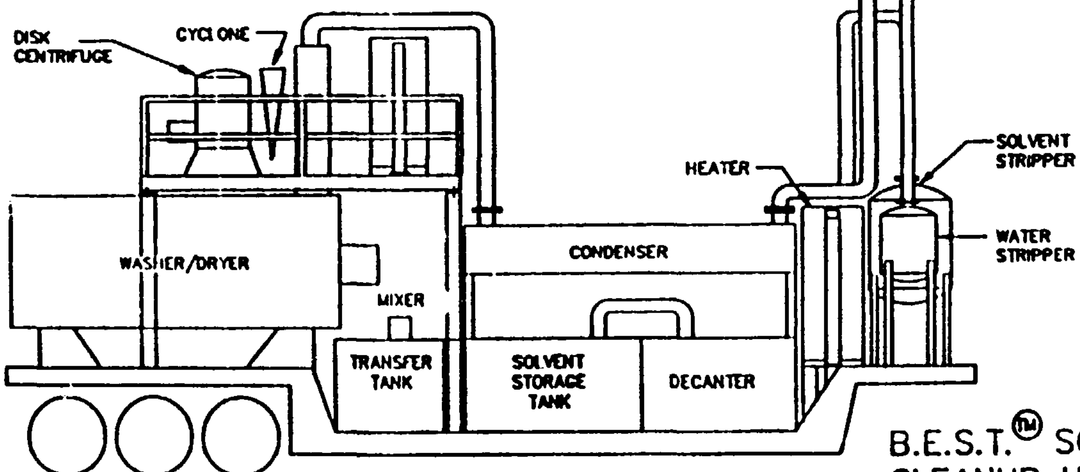


PLAN VIEW

NOTE: UPPER PLATFORM AND UPPER SECTIONS OF STRIPPERS REMOVE FOR SHIPPING.



UPPER PLATFORM



ELEVATION

B.E.S.T.® SOIL CLEANUP UNIT