Evaluation of Treatment Technologies for Listed Petroleum Refinery Wastes

HEALTH AND ENVIRONMENTAL SCIENCES DEPARTMENT
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Final Report

Health and Environmental Sciences Department

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FIELD STUDIES CONDUCTED BY
THE API WASTE TECHNOLOGY TASK FORCE

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PREFACE

Provisions for the land disposal ban of the 1984 RCRA Amendments, require EPA to develop best-demonstrated available technology (BDAT) treatment standards for selected hazardous wastes including listed refinery wastes. The treatment standards in the proposed ruling of April 8, 1988 are based on incineration treatment efficiencies derived from test burns of listed refinery wastes. Land treatment units must comply with the proposed rule unless they fulfill the requirements of a "no migration petition". Refineries without permitted land treatment units will be forced to arrange for incineration of their wastes prior to land disposal unless other technologies become commercially available which can meet the proposed BDAT standards. Due to limited incinerator capacity in the United States, the cost and difficulties in permitting incinerators, and recent emphasis on source reduction and recycling, alternatives to incineration which recycle the toxic constituents of the wastes are of interest to the petroleum industry.

The petroleum refining industry utilizes many different treatment/disposal schemes to manage listed hazardous wastes. The decision as to which scheme to use at a particular site, on a particular waste is a function of many factors, such as waste characteristics, available land, local environmental regulations, permitting, and public opinion. Clearly, there is no one treatment scheme which is applicable for all petroleum refining wastes, at all locations. Currently, the most widely used treatment technology within the industry for oily wastes is land treatment. However, Congress has included land treatment as a form of disposal under the land disposal bans. This study was undertaken in order to determine how effective other treatment technologies could be.

API has previously submitted comments (September 1986) to the EPA regarding technical problems associated with the Toxicity Characteristic Leaching Procedure (TCLP) and its application to oily wastes. The submission of TCLP data in this report should not be construed as a deviation from API's original position regarding TCLP. These data are submitted in an attempt to demonstrate the treatment efficiency of several technologies by applying the same TCLP criteria which were used by EPA in developing the solvents/dioxin rule (Federal Register November 6, 1986).

To provide a more comprehensive waste treatment study, technology vendors who were not API contractors were invited to submit data to the API for review and evaluation. In order to qualify for inclusion in the final report, these vendors had to treat listed refinery wastes, adhere to the API sampling and analytical protocols, and submit operating and test data by February 15, 1987. The only noncontracted vendor who met these criteria was one offering a pyrolysis treatment process. These data are included in this report.

API gratefully acknowledges the efforts of the Rocky Mountain Analytical Laboratory, which supplied all of the analytical data; the participating refineries, which provided listed wastes and treatment process data; the participating equipment vendors; Risk Science International, for writing the interim report; and members of the API Waste Technology Task Force, who planned the project and brought it to fruition. Special recognition is given to Hugh Dickey (Chevron) for the study design, Frank Prince, Ph.D., the API project manager, Piyush Shah, Ph.D. (Exxon) for structuring the analytical data tables, Richard Stalzer (Sohio) and Bill Deever, Ph.D. (Texaco) for the mechanical drawings, and Re'Naye Williams of API for typing the manuscript.

CHAPTER 1. EXECUTIVE SUMMARY

A number of technologies for the treatment of listed petroleum refinery oily wastes were evaluated in this study. The technologies studied were mechanical treatment (filtration), solvent extraction, thermal treatment (drying), chemical fixation and pyrolysis. In several cases the application of two treatment technologies in series was studied, e.g. filtration followed by drying, drying followed by fixation. No attempts were made to develop limits of operability for the subject treatment technologies nor was consideration given to the cost of various technologies. As evaluation tools, the reductions in mass from feed to product residues and the reductions in constituent leachate concentrations from feed to product residues were evaluated.

All of the technologies tested produced a residue of substantially reduced hazard, as measured by leachable concentrations (using TCLP) of hazardous constituents in the product solids. Four of the technologies also reduced the total constituent concentrations.

Table 1-1 allows a comparison of treatment efficiency among these technologies. It shows average residual concentrations (mg/kg) of ten indicator compounds in the product solids from four of the five treatment technologies which were evaluated. The order of decreasing efficiency, based on residual levels of organics, was: pyrolysis > solvent extraction > mechanical/thermal drying > mechanical treatment. The percent reduction for the eight organic compounds was 97-99%, for three of the four treatment technologies, based on average raw feed constituent data. Percent reduction values were lower for mechanical treatment. Metal levels were not changed significantly by any of the treatment processes. Actual percent reductions for each technology are shown in the summary tables of Chapter 8.

TABLE 1-1

AVERAGE CONCENTRATIONS OF TOTAL RESIDUE, mg/kg

	Mechanical Treatment Total Residue Concentration	Solvent Extraction Total Residue Concentration	Mechanical Plus Thermal Total Residue Concentration	Pyrolysis Total Residue Concentration
Benzene	46.5	1.3	0.55	ND
Toluene	304	5.0	3.0	0.01
Xylenes	568	4.4	2.4	ND
Anthracene	10.1	ND	53	ND
Chrysene	125	ND	62	ND
Naphthalene	144	0.005	46	ND
Phenanthrene	109	0.005	364	0.02
Phenols	4.1	ND	17	0.2
Chromium	654	1250	2450	44
Lead	128	260	275	6

ND : Not detected.

Table 1-2 allows a comparison of treatment efficiency among these technologies, based on the leachability of the product residues. It shows average concentrations (mg/L) of ten indicator compounds in the TCLP leachate from the product solids from the five evaluated treatment technologies. The order of decreasing efficiency based on the leachate concentrations of the eight organics was: pyrolysis > solvent extraction > mechanical/thermal drying > chemical fixation/thermal drying > chemical fixation > mechanical treatment. Drying the product solids prior to chemical fixation was more effective in reducing the leachability of the eight organic compounds. Chemical fixation was clearly the most effective in decreasing the leachability of the metals.

Figure 1-1 shows the percent average reduction in constituent weight and reduction in leachate concentrations of the raw feeds following treatment (mechanical, solvent extraction, mechanical plus thermal treatment, and chemical fixation or pyrolysis) for the three classes of compounds.

Results from the land treatment of refinery wastes are presented in another API report entitled, "Land Treatability of Appendix VIII Constituents Present in Petroleum Refinery Wastes" (API Pub. No. 4455). This study demonstrated the suitability of land treatment units to biodegrade organics and immobilize metals present in refinery wastes. Results of this land treatment study are compared to results from the treatment technologies in Chapter 8.

We believe that these two API reports provide technical support for the consideration of technologies other than incineration as best-demonstrated available technology (BDAT) for the treatment of refinery wastes.

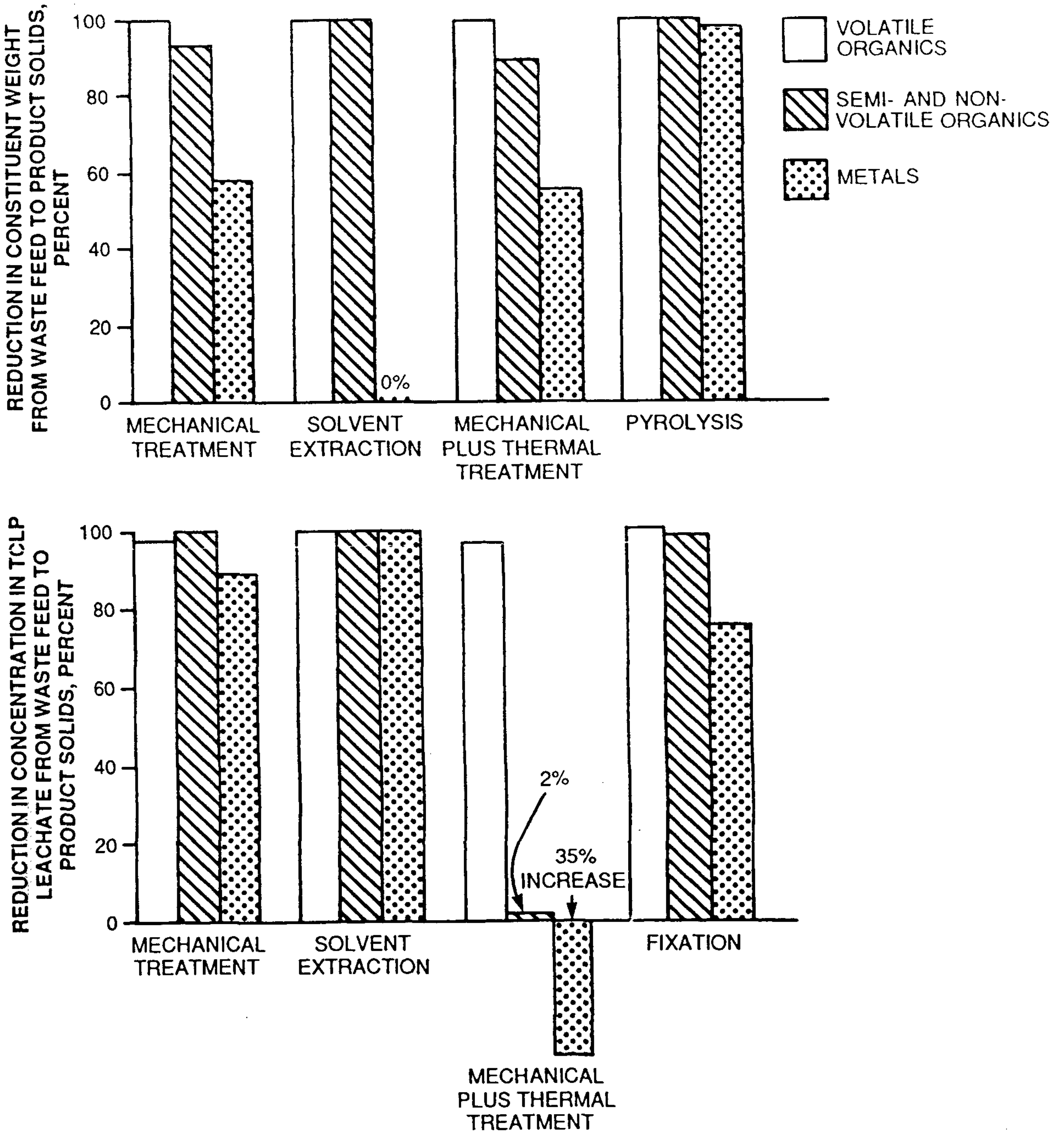
TABLE 1-2

AVERAGE CONCENTRATIONS OF TCLP LEACHATE, mg/L

	Mechanical Treatment TCLP Concentrations	Solvent Extraction TCLP Concentration	Mechanical Plus Thermal TCLP Concentration	Fixation Product			Pyrolysis Residue TCLP Concentration
				Raw Feed TCLP	Cake Feed TCLP	Dried Cake TCLP	
Benzene	1.4	0.005	0.02	0.10	0.22	0.004	ND
Toluene	2.2	0.008	0.04	0.45	0.90	0.01	ND
Xylenes	1.5	0.01	0.07	0.60	0.82	0.02	ND
Anthracene	0.009	ND	0.01	ND	ND	ND	ND
Chrysene	0.024	ND	0.01	ND	ND	ND	ND
Naphthalene	0.17	0.007	0.06	0.19	0.10	ND	ND
Phenanthrene	0.009	ND	0.015	0.01	0.01	ND	0.004
Phenols	0.66	ND	0.27	0.53	ND	ND	ND
Chromium	0.045	0.11	0.05	ND	ND	ND	1.3
Lead	0.08	0.05	0.07	ND	ND	ND	ND

ND : Not detected.

FIGURE 1-1 REDUCTIONS IN CONSTITUENT WEIGHTS AND TCLP LEACHATE CONCENTRATIONS



CHAPTER 2. SCOPE OF STUDY

This report presents the results of a study sponsored by the American Petroleum Institute (API) to evaluate the effectiveness of five technologies which were used to treat petroleum refinery wastes. Technologies specifically excluded from this study were incineration, which has been tested extensively by the U.S. Environmental Protection Agency (EPA), and land treatment, which has been studied and reported on separately by API (API Publ. 4455).

Feed and product samples were collected at various test sites where waste treatment was applied. These samples were subjected to physical/chemical analyses to determine the effectiveness of various treatment processes.

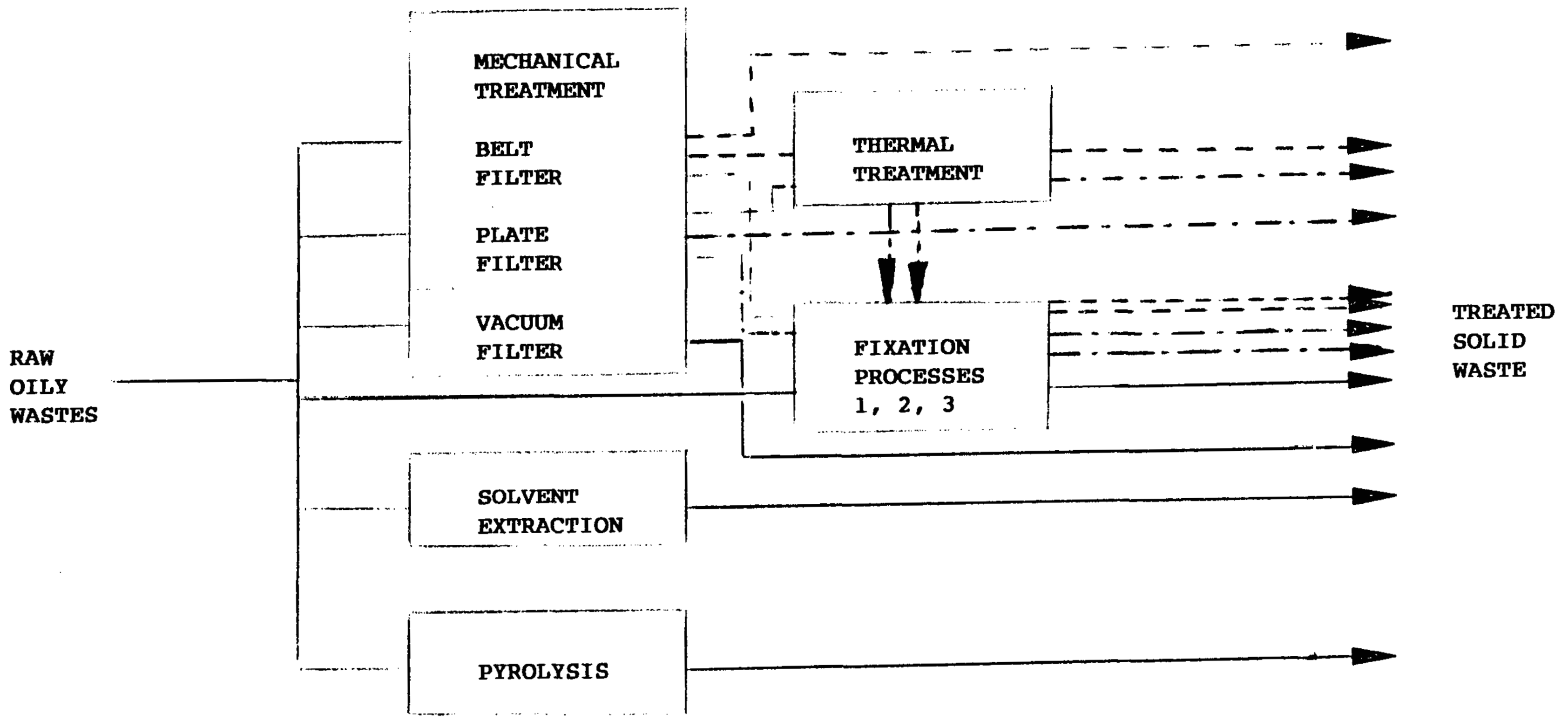
This chapter (2) of the report describes the scope of the study, the technologies, the analytical scheme and the methods of data correlation and interpretation. The approach regarding the test site selection and the scale of treatment operation (commercial, pilot or laboratory), the analyses performed and the quality assurance/quality control methods used are also described in this chapter.

Chapters 3 through 7, provide information on each of the five treatment technologies tested. Chapter 8 provides a comparison of the effectiveness of all of the technologies tested in this study.

A schematic of the study, the treatment processes and the sequences of processes tested, are shown in Figure 2-1.

FIGURE 2-1

SCHEMATIC OF WASTE TREATMENT TECHNOLOGIES EVALUATED



TECHNOLOGIES EVALUATED

Mechanical Treatment

Belt filters were tested at refineries C1 and C2, using listed oily wastes generated at those refineries. Operating conditions of each test were documented. Representative samples of waste feed, filtrates and filter cakes were transmitted to Rocky Mountain Analytical Laboratory (RMAL) for analysis according to EPA-prescribed protocols.

Plate filters were tested in a similar manner at refineries B1, B2, and B3. A rotary vacuum filter was tested at refinery V1.

Centrifuges are currently being used at a number of refineries but were not tested in this study for reasons of location plus the need to limit study costs.

Solvent Extraction

A solvent extraction process was tested which was thought to be representative of the general class of solvent extraction technologies. Tests were conducted on a 50-50 mixture of two listed wastes from refinery D. A batch pilot plant unit was used for this demonstration.

Thermal Treatment

A screw flight dryer was tested to represent this class of treatment technologies. Tests were conducted on belt filter cake from refinery C1, and on plate filter cake from refinery B1. Samples of each cake were treated at two temperatures--400°F (low temperature) and 650°F (high temperature). Tests were conducted in batch at a vendor's pilot-scale facility.

Pyrolysis

A rotary pyrolysis process was tested--in this case by the process vendor following protocols established by the API task force--to represent this class of treatment technologies. The tested feed was a mixture of three listed wastes from refinery E.

Fixation

Three different fixation processes were tested on samples at three different levels of pretreatment. Untreated oily wastes (API separator bottoms and slop oil emulsion solids from refinery A) were treated with fixation process 1. Belt filter cake from refinery C1 and plate filter cake from refinery B1 were treated using all three fixation processes: 1, 2 and 3. Thermally dried belt and plate filter cakes were treated using fixation process 2.

DATA AND CORRELATIONS

Figure 2-2 summarizes the types of analytical data obtained from the technology testing and the correlations of the data that were used to assist in interpreting the test results. The general approach to data analyses is discussed by category below.

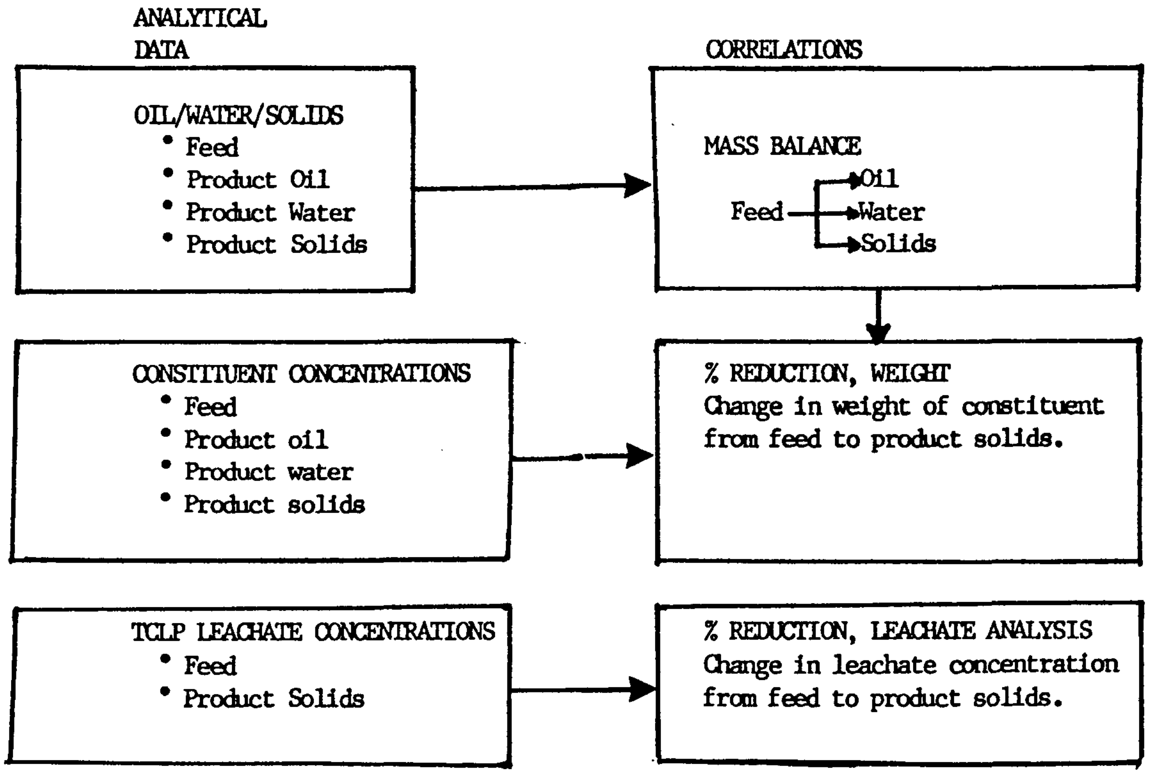
Analytical Data

As shown graphically in Figure 2-2, analytical data were of three types:

1. oil/water/solids analyses of the feed and products of each treatment technology;
2. analyses for Appendix VIII constituents in feed and products; and
3. Toxicity Characteristic Leaching Procedure (TCLP) analyses on feed and product solids.

FIGURE 2-2

ANALYTICAL DATA AND CORRELATIONS



More specific information on the analytical procedures used is given in a later section of this chapter.

Correlations

The analytical data listed above give a large measure of the effectiveness of the various treatment technologies: the concentration of Appendix VIII constituents in the product solids, and the TCLP analyses on product solids. Two additional measures of treatment efficiency were developed: reduction of constituents by weight, and percent reduction in leachable concentrations. The first of these, Percent Reduction (Weight) is derived from a combination of the mass balance (for the most part calculated from oil/water solids analyses) and the constituent concentrations in feed and product solids. When combined, these data allowed the reduction in weight of constituents from feed to product solids to be calculated.

Each process was evaluated using this mass balance approach to determine the bulk amount of hydrocarbons or toxic constituents physically removed from the waste and recycled. The main objective was to generate data which would provide a relative scale of the removal efficiencies of the generic processes, whether or not they could be considered viable BDAT technologies.

The wastes varied substantially in composition from very low to very high oil content. This was desirable because it gave a good range of wastes that would be expected to be processed through these units. However, this variation discourages absolute comparisons within a generic technology (e.g. plate versus belt filters) because some wastes were inherently easier to separate than others.

The second measure of treatment efficiency, Percent Reduction (Leachate Analysis), is derived from TCLP analyses on feed and product solids. The reduction in leachable concentrations of constituents from the feed to the product solids was determined.

LOCATION/SCALE/TECHNOLOGY SELECTION

A goal of this study was to test commercial-scale technologies, where possible, to demonstrate industrial application, availability and treatment performance. All tests on mechanical treatment equipment were conducted on commercial equipment operating at petroleum refineries. The solvent extraction process was tested on a pilot unit using a mixture of refinery sludges. A possible alternative choice would have been to test the commercial scale unit which was operating at a Superfund site. The decision was made that the testing on refinery wastes on a pilot scale was preferable to testing non-refinery wastes on a commercial scale since the two wastes had only a few constituents in common.

Thermal treatment was tested using refinery wastes on a pilot unit from an equipment vendor. Industrial operations other than petroleum use thermal driers on a commercial scale but no such operation exists treating refinery sludges. Feeds which were thermally treated were filter cakes. These were product solids derived from filtration of raw refinery wastes. Use of filter cake was based on a most probable scenario, but does not indicate any technical reason against feed of raw wastes to this equipment.

Pyrolysis and fixation tests were conducted at the laboratories of the process vendors. The process vendors were confident of their ability to scale up the tests based on experience with other feedstocks. For fixation, no advantage was seen in larger scale tests--all were at lab scale.

Selection had to be made among a wide array of process and equipment vendors based on a limited budget and time schedule. Results of the five technologies which were evaluated by API are likely to be indicative of generic classes or groups of processes and equipment.

ANALYTICAL PROCEDURES

The following sections give more information on the analytical tests and techniques and also summarize the quality assurance/ quality control methods of the study.

Analytical Techniques

The oil/water/solids analysis employed a method developed by Chevron Corporation (Modified Oven Drying Technique or MOD-T.). The method is based on a low temperature distillation of the sample to generate a volatile oil and water fraction which is subsequently condensed. The remaining material is extracted with methylene chloride to generate a nonvolatile fraction, with solids defined as the solvent insoluble residue. This was the method of choice over EPA methods (i.e. 418.1, 3540 or 3550) specifically because of the potential for loss of volatile hydrocarbons by the EPA procedures. Consequently, results may differ among the test procedures, with the MOD-T reflecting somewhat higher oil recovery levels. A copy of this procedure is in the appendix.

Table 2-1 shows Appendix VIII constituents of refinery wastes which were analyzed in feeds, products and TCLP leachates. Analytical methods were derived from three sources of EPA methods:
1) the methods promulgated in 40 CFR 136 for priority pollutants;
2) the methods published in SW-846; and
3) methods published by EPA for Superfund investigations.

A subset of the Table 2-1 lists is shown in Table 2-2. This list was developed to allow a screening test as an economy measure. These compounds termed "indicator" or "screening" compounds were measured by alternative techniques.

TABLE 2-1

APPENDIX VIII CONSTITUENTS ANALYZED

Volatile Organics

- Benzene
- Carbon disulfide
- Chlorobenzene
- Chloroform
- 1,2-Dibromoethane
- 1,2-Dichloroethane
- 1,4-Dioxane
- Methyl ethyl ketone
- Styrene
- Ethylbenzene
- Toluene
- Xylene, m
- Xylenes, o & p

Acid Organics

- Benzenethiol
- o-Cresol
- p & m-Cresol
- 2,4-Dimethylphenol
- 2,4-Dinitrophenol
- Phenol

Metals

- Antimony
- Arsenic
- Barium
- Beryllium
- Cadmium
- Chromium
- Cobalt
- Lead
- Mercury
- Nickel
- Selenium
- Silver

Base/Neutral Organics

- Anthracene
- Benzo(a)anthracene
- Benzo(b)fluoranthene
- Benzo(j)fluoranthene
- Benzo(k)fluoranthene
- Benzo(a)pyrene
- Bis(2-ethylhexyl)phthalate
- Butyl benzyl phthalate
- Chrysene
- Dibenz(a,h)acridine
- Dibenz(a,h)anthracene
- Di-n-butyl phthalate
- o-Dichlorobenzene
- m-Dichlorobenzene
- p-Dichlorobenzene
- Diethyl phthalate
- 7,12-Dimethylbenz(a)anthracene
- Dimethyl phthalate
- Di-n-octyl phthalate
- Fluoranthene
- Indene
- Methyl chrysene
- 1-Methylnaphthalene
- Naphthalene
- Phenanthrene
- Pyrene
- Pyridine
- Quinoline

TABLE 2-2

CONSTITUENTS ANALYZED AS INDICATOR OR SCREENING COMPOUNDS

Volatile Aromatics

Benzene
Ethylbenzene
Toluene
Xylenes*

PNAs/Phenols

Anthracene
Chrysene
Naphthalene
Phenanthrene
Phenols*

Metals

Chromium
Lead

---

* Indicator TCLP measures total xylenes and total phenols (sum of phenol, cresols, and 2,4-dimethylphenol).

TCLP leachates were prepared using the method in Appendix I to 40 CFR Part 264. Simply stated, the TCLP procedure is designed to generate an aqueous leachate of a waste. Leachates were prepared at a 20 to 1 ratio relative to the solid material in the sample. The leachate was then analyzed for the various target parameters. Results are reported in mg/L in the leachate.

The initial leaching procedure requires two separate laboratory preparations (extractions), one for volatile organics and one for the remaining parameters. The preparation for volatile organics requires the use of a specially designed device, termed the zero headspace extractor (ZHE).

The initial step in performing a TCLP extraction is the pressure filtration (50 psi) of the sample through a 0.8 micron filter. The solid phase remaining after this filtration is then mixed with the aqueous TCLP extraction fluid using a 20 to 1 ratio. After 18 hours of "extraction" the solid/leachate mixture is filtered a second time. The filtered leachate from this step is then combined with any filtrate from the initial filtration.

For wastes containing "oil," the initial filtration often results in a two-phase filtrate containing oil and water. According to the TCLP protocol, the oil phase must be analyzed separately, and the results mathematically combined with those from the extract. Analyses of the various leachate solutions were performed according to EPA procedures described in Appendix I (40 CFR Part 264).

Samples of fixed waste materials were ground to pass a 5.55 mm (0.375-inch) standard sieve prior to conducting either the Total TCLP or the Indicator TCLP test as required by the EPA protocol (51 FR 40643).

Quality Assurance/Quality Control

All laboratory analyses were performed according to specifications in a Quality Assurance Project Plan (QAPP), as specified in EPAAR 1552.246-71. The QA/QC plan of the laboratory (RMAL) for this project followed the elements of their generic laboratory-wide quality insurance procedures for sample preparation and analyses. A separate QC Data Summary Report has been prepared by RMAL, which presented the QC results that were directly related to the performance of the methods on these samples. Other QC activities such as calibration, mass tuning checks and activities related to the general performance of the instruments have not been reported, but are archived in the report files at RMAL.

Quality control analyses consist of the following activities which are included in the QC Data Summary Report:

- multipoint standard calibration;
- analysis of blanks;
- analysis of spiked and duplicate samples;
- analysis of standard reference materials;
- daily calibration, including mass spectrometer tuning checks (BFB and DFTPP), where appropriate; and
- addition of surrogate spikes into each sample for GC/MS analyses.

Sufficient amounts of representative samples were sent to the laboratory with the following history:

- All samples were collected in glass sample bottles;
- No chemical preservation was used, and the samples were stored at 4°C until analyzed;

- Samples for volatile organics were collected with minimal headspace; and
- Analysis was performed in an expeditious fashion, applying 40 CFR 136 water holding times where appropriate.

A chain of custody record was established for each sample except as noted in the QA/QC report.

CHAPTER 3. **MECHANICAL TREATMENT**

INTRODUCTION

Petroleum refinery wastes are generally oil-in-water emulsions stabilized by the presence of finely divided solids. By removing the solids, the emulsion is often broken, allowing recovery of two distinct liquid phases, an oil-rich phase and a water-rich phase, as well as a concentrated-in-solids cake. Mechanical treatment is a well-demonstrated method to accomplish this phase separation.

The toxic components of the waste, organic compounds and metals (Table 3-1), will partition into these three phases according to whether they are solid or liquid; their solubility in water and organics; and the efficiency of the separation device in separating solids and liquids.

The mechanical treatment methods evaluated in this study were all filtration methods. Filtration is the process of separating suspended solid material from a liquid by forcing the liquid through the voids of a porous mass called the filtering medium. Two important variables in filtration are the material that forms the separating medium and the method used for forcing the liquid through this medium. The filtration methods used in this study--the belt filter, the recessed plate filter and the rotary vacuum filter--demonstrate a wide range of these two variables.

In the belt-filter, the filtering medium can range from a screen to a cloth, and driving force for liquid movement is first gravity and then mechanical pressure of a screen or cloth pressing against the solids. In a recessed plate filter, the medium is a cloth, sometimes with a porous granular solid or precoat deposited on the cloth, and the driving force is the discharge pressure of a pump. In a rotary vacuum filter, the medium is usually a pre-

TABLE 3-1

CONSTITUENTS OF REFINERY WASTES

Volatile Organics

Benzene
1,4-Dioxane
Methyl ethyl ketone
Styrene
Ethylbenzene
Toluene
m-Xylene
o- & p- Xylenes

Acid Organics

o-Cresol
p- & m-Cresol
2,4-Dimethylphenol
Phenol

Metals

Arsenic
Barium
Cadmium
Chromium
Lead
Mercury
Selenium
Silver

Base/Neutral Organics

Anthracene
Benzo(a)anthracene
Benzo(b)fluoranthene
Benzo(a)pyrene
Bis(2-ethylhexyl)phthalate
Chrysene
Dibenz(a,h)anthracene
Fluoranthene
Indene
1-Methylnaphthalene
Naphthalene
Phenanthrene
Pyrene

coated cloth while the driving force is provided by drawing a vacuum on the product liquid side of the cloth.

Depending on the feed waste characteristics and the filtration process chosen, a filter cake results which may vary from 20 to 60 percent solids. A product filtrate stream is produced also which, in all the study cases, separated into an oil phase and a water phase.

OVERVIEW

The data gathered in this program demonstrate the potential effectiveness of mechanical treatment of wastes at petroleum refineries for both economic and environmental reasons.

From an economic standpoint, the most important factors are recovery of oil, which would otherwise be lost, and reduction of the quantity of waste to be disposed.

Oil recovery from the oily sludges tested ranged from 80 to 99%. To put this in perspective, if a refinery produces 50 tons per day of oily sludge with an oil content of 10%, mechanical treatment would recover about 10,000 barrels (42 gal/barrel) of oil per year.

The mass reduction accomplished by mechanical treatment ranged from 85-96%. The actual reduction varies almost inversely with the solids content of the feed waste. Again solely for illustration: if a refinery produces 50 tons per day of waste and can reduce the weight by 90%, only 5 tons of cake is disposed.

The environmental benefits of mechanical treatment are reflected in the mass reduction of Appendix VIII constituents between feed and cake and the reduced concentration of these same Appendix VIII components in the TCLP leachates of feed and cake. For the organic components, both of these reductions--mass balance reduction and TCLP leachate concentration reduction--range from 90 to more than 99%, with only a small number of exceptions. For the volatile organics, average reductions in both mass and leachate analysis are from 97 to 99%. For the metals, the reductions are not so great, but perhaps this is not as significant, since metals can be "fixed" chemically in an added treatment step, or can be immobilized by cation exchange on soil.

Overall, mechanical treatment of refinery wastes yields a much reduced weight of waste which is less toxic and less mobile than the original waste.

Integration of mechanical treatment into an operating refinery would be quite straight forward. Product water can be included readily into the refinery's wastewater treatment system. Product oil can be recycled into the oil processing operation.

DISCUSSION--EQUIPMENT DESCRIPTION AND OPERATION

In this section the three different types of filters are described and the principles of operation and important operating parameters for each are reviewed.

Belt Filter

Applicability: Belt filters have been widely used for many years in the dewatering of sludges from the pulp and paper industry and from municipal sewage treatment plants. Usage for other industrial sludges has increased dramatically over the past 10 years because of the large reduction in volume of residues that is accomplished. Many petroleum refineries have found that belt filter press treatment provides the added benefit of oil recovery from the separated liquid phase.

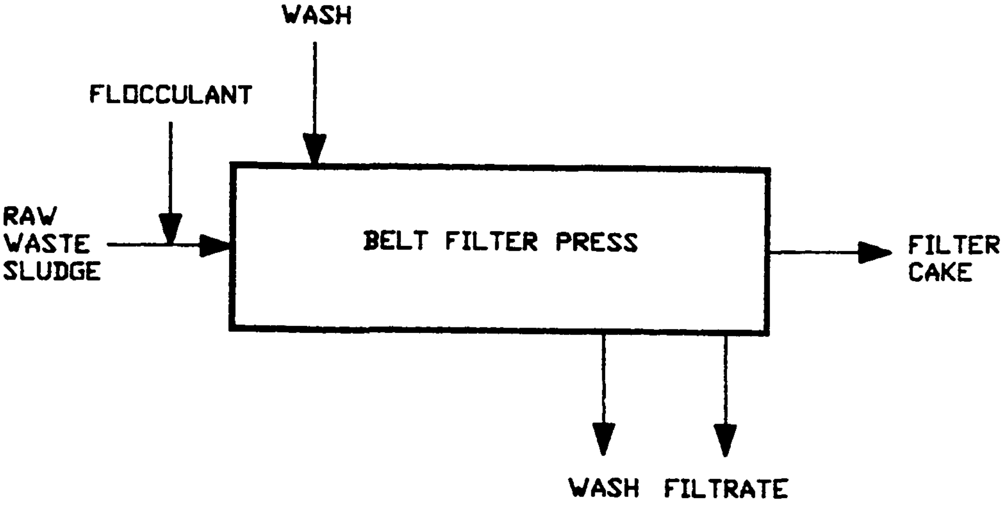
The product streams generated from the belt filter press are filter cake and filtrate, and the filtrate may separate into oil and water phases.

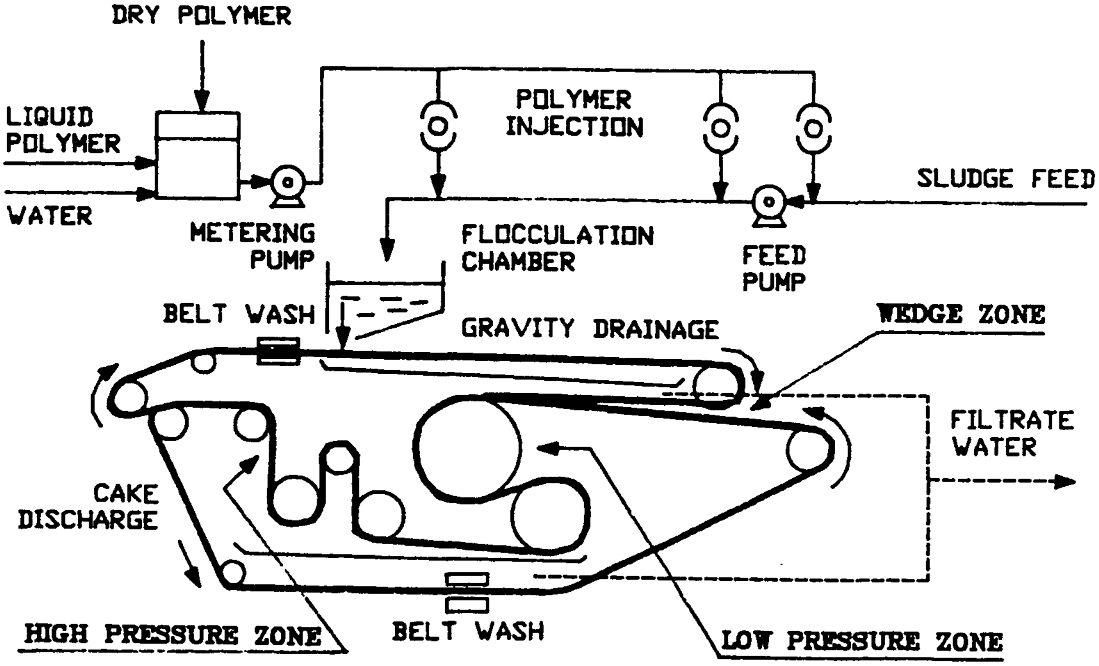
Underlying principles of operation: Belt filtration processes include three basic operational stages: chemical conditioning of the feed slurry, gravity drainage to a nonfluid consistency, and compaction of the predrained sludge. A schematic diagram of the belt filter process is shown in Figure 3-1. After addition of a polymer (polyelectrolyte) and subsequent flocculation, the feed material is applied to a solids retaining membrane or filter cloth. As the feed moves through the filter, liquid flows into filtrate collection pans, and solids are retained on the filter cloth. A cake is produced for disposal.

Initially, the raw feed is mixed with a polymer to cause flocculation of solids and enhance separation of the liquid phase. The preconditioned feed is then distributed to a porous, woven belt where the gravity phase of liquids/solids separation occurs. Free liquid flows through the porous belt by gravity and into filtrate collection pans. Up to 60% of the liquid phase of the feed can be removed in the "gravity zone." The porous belt with the gravity-separated solids on it is then enveloped by another belt as it leaves the gravity zone and enters the low pressure or "wedge zone." Further phase separation is achieved here using mechanical pressure. In the third zone, the belts pass through a series of large rollers that squeeze the belts together, forcing additional liquid through the porous belt into filtrate collection pans. Manufacturers report that pressures can reach 14.2 pounds per square inch or more in the high pressure zone as the belts travel through a series of rollers. The final liquids separation occurs here due to the high pressure and shear forces between the two belts as they travel over the rollers. Pressures in the second and third zones are generally adjustable. The deliquified sludge is scraped off the belt into a container for disposal. A high pressure water wash is usually applied to the belt at this point to clean it and to unplug clogged belt pores.

The polymer used to flocculate solid materials in the feed is mixed with water and can be injected into the feed at several injection points. Often a cationic polymer is used. Oil refiners who have experience in deliquifying oily wastes are able to produce a solids cake with 20-40% oil, depending on feed characteristics.

FIGURE 3-1
DIAGRAM OF BELT FILTER PROCESS





Operating parameters affecting performance: Adjustment of the process variables for "optimum" operation of a belt filter within a refinery is dependent on feed characteristics which change often, sometimes constantly. Within a modern, complex refinery, feed characteristics (e.g. oil and solids content, flocculation characteristics) are always changing and re-optimization of operating parameters must be done frequently.

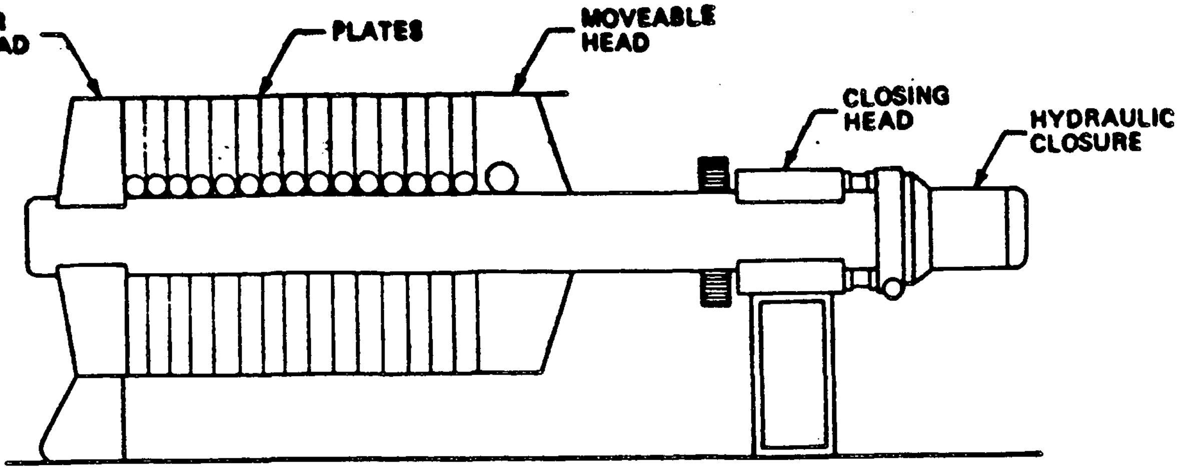
The important process variables for proper operation of the belt filter are as follows:

- waste composition and characteristics
- flocculation efficiency depending on choice and rate of polymer, point and energy of mixing
- belt material, pore size, weave
- feed rate and belt speed (these are interdependent.)
- pressure exerted on the sludge

Plate Filter

Applicability: The recessed plate filter (a modification of the plate and frame filter) has been used for many years in both product processing and sludge treatment. Industries that have used plate filters include petroleum refining, chemical, pharmaceutical, metal finishing, aviation, steel manufacturing, transportation (oily sludges from railroad and motor oil), food (used oils), and paint. Plate filters are very effective at breaking emulsions, if the feed is properly conditioned.

Underlying principles of operation: A plate filter press is a batch filtration process used to separate solids or particulate material from a liquid stream. Figure 3-2 is a schematic process diagram. The recessed plates are connected to form a series of chambers. The filter medium is supported on the plates; the recessed chambers provide a cavity for the collection of solids filtered out of the influent.



SCHEMATIC SIDE VIEW OF A RECESSED PLATE PRESSURE FILTER

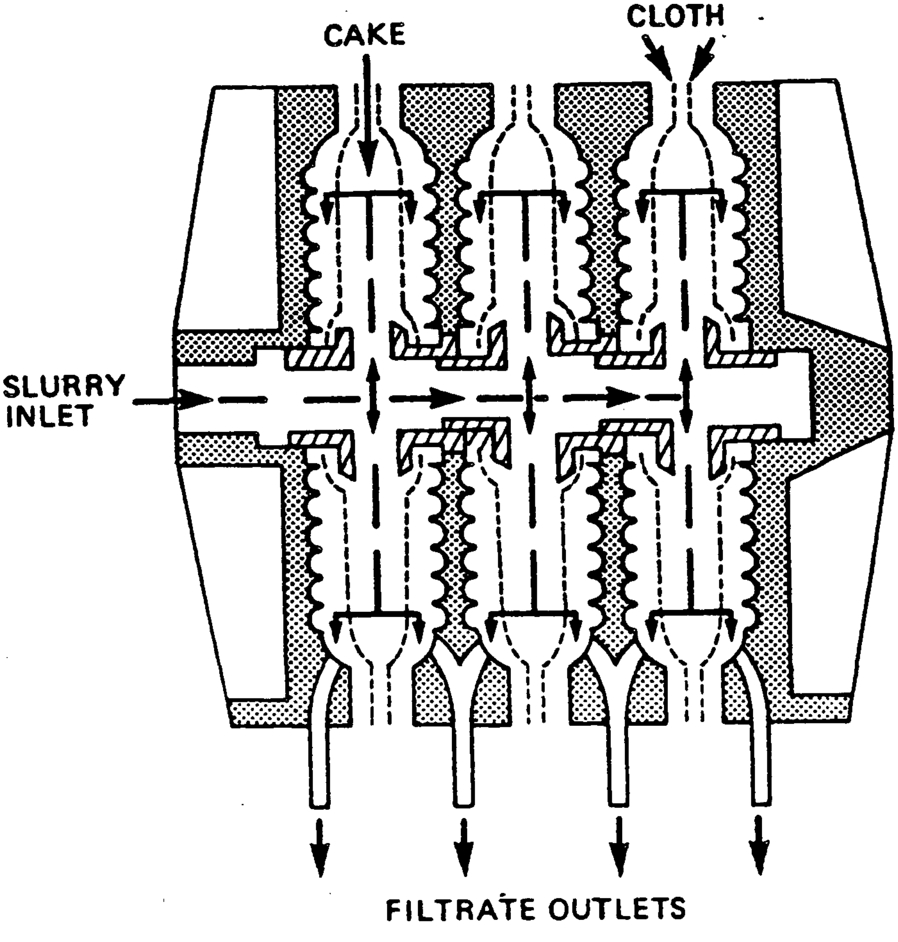


FIGURE 3-2

CROSS SECTION OF A FIXED-VOLUME RECESSED PLATE FILTER ASSEMBLY

Feed sludge is normally conditioned externally by addition of lime and sometimes iron salts (e.g. ferric chloride). The conditioned feed enters through a feed port, typically in the center of the plate, and is fed in parallel to each filter chamber. Feed pressures are 100-250 psig. The plates are pushed together by a piston on the moveable head and held together at 2,000-10,000 psig. The liquids pass through the filter media and are collected through outlet ports on each plate. The most frequently used filter media for refinery sludges are filter cloths of woven synthetic materials, such as nylon or polypropylene. Quite often the filters are precoated with diatomaceous earth to reduce cloth blinding, enhance solids/liquids separation and emulsion breaking and to ensure quick cake release when the filter is opened. The cake collects in the chambers formed by the two plates coming together. When the chambers are full, a wash stream can be injected. The cake is removed by moving the plates apart and dislodging the cake into a container. Any cake remaining on the plate may be scraped off. Air can be introduced behind the media cloth on both sides of each plate to assist in cake removal. Other variations to ease operations are also available.

Operating parameters affecting performance: The important process variables for proper operation of a plate filter press include:

- waste composition and characteristics
- pressure (usually up to 100 to 250 psig)
- type of filter cloth (usually nylon or polypropylene) and weave
- media precoat (usually diatomaceous earth) and thickness
- cycle time (fill time, filtration time, and cake release time)
- influent conditioning (e.g., dosage of lime and/or iron salts)

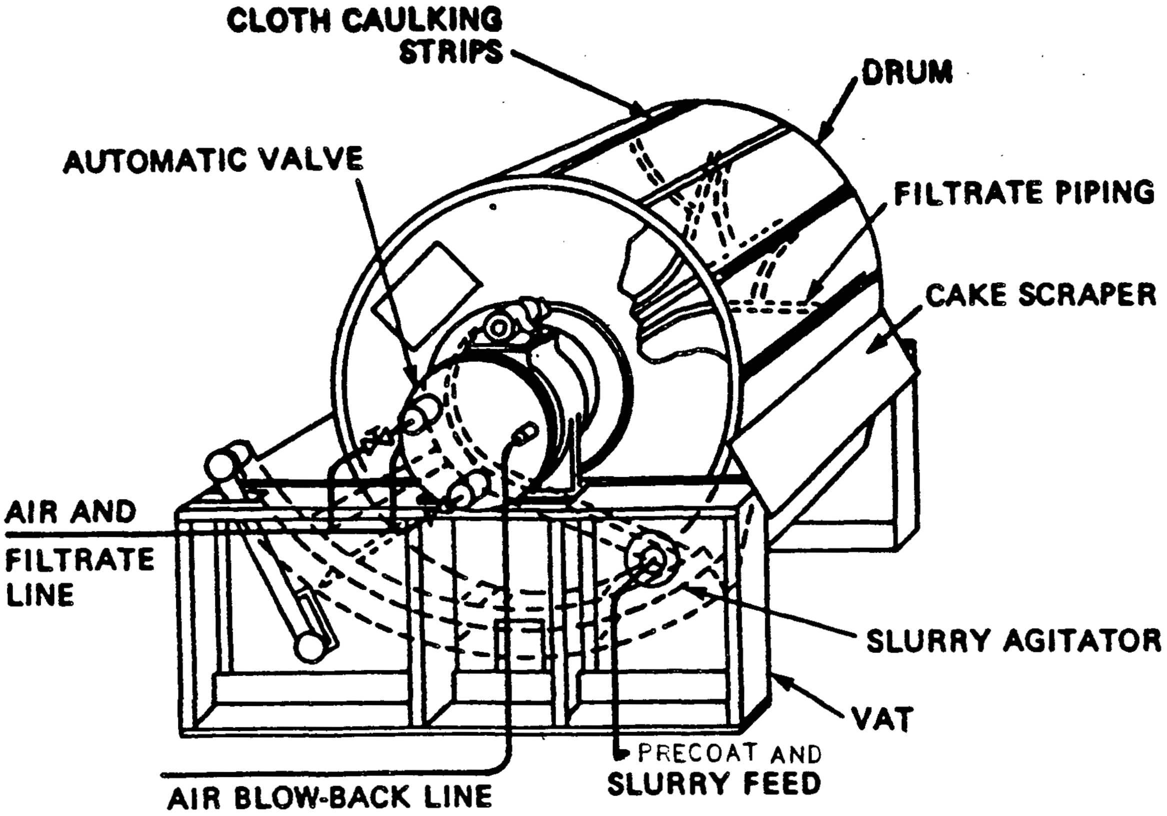
- influent temperature
- cake thickness
- initial flow rate (gal/hr-ft^2) and solids loading (lb/hr-ft^2)

Rotary Drum Vacuum Filter

Applicability: The rotary drum vacuum filter has been used in industry for many years in both product processing and dewatering of sludges. Industries that have used rotary drum vacuum filters include sugar refining, metallurgical industry, petroleum refining, and municipal sewage treatment plants. Product streams generated from the vacuum filter are filter cake and filtrate.

Principles of operation: The rotary drum filter (Figure 3-3) consists essentially of a cylindrical drum supported by an open-tank system. The axial rod of the rotary drum is placed on the open tank to allow rotation of the drum. The placement of the drum is such that its lower portion is confined within the tank walls, while the upper portion is exposed to the atmosphere. The drum shell is composed of a number of shallow compartments covered with a drainage grid and a filter screen which is held in place by lateral caulking. The interior of the compartment is connected to a valve mechanism which, during operation, automatically applies either negative (vacuum) or positive pressure to the several conduits in rotation. The automatic valve is connected to a vacuum system and to a source of compressed air.

A slurry agitator is suspended at the bottom of the tank to mix the feed. The filter cake is discharged from the drum surface by a scraper blade containing a detachable rubber tip. Normally a precoat is applied to the drum before sludge feed is started. Some filters are enclosed to reduce heat loss and control air emissions.



CUTAWAY VIEW OF A DRUM OR SCRAPER-TYPE ROTARY VACUUM FILTER

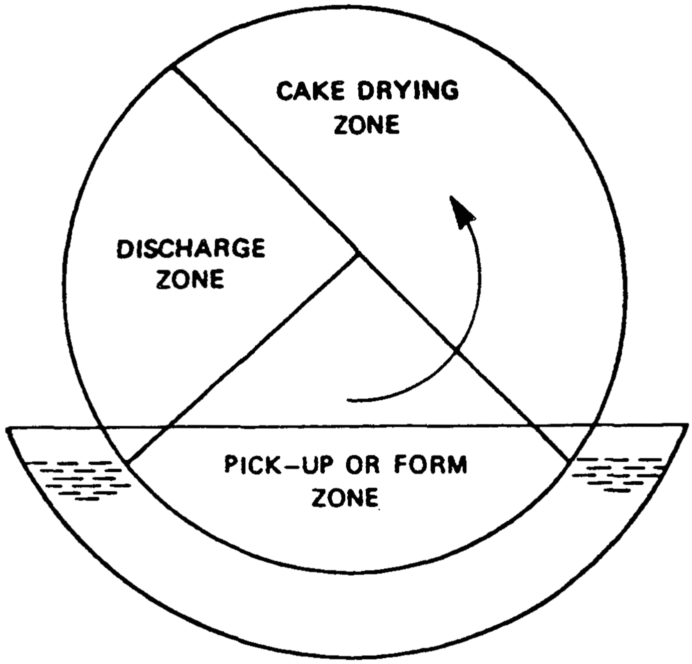


FIGURE 3-3

OPERATING ZONES OF A ROTARY VACUUM FILTER

The drum rotates slowly while the tank is constantly fed with the sludge. The level in the lower tank is maintained at a constant depth. The valve is set for the timing required in each operation. Through the action of the valve, vacuum is applied to those compartments of the drum passing through the sludge. The vacuum created within the compartments causes a flow of filtrate through the filtering medium. This will allow a layer of solids (cake) to deposit upon the filter screen. As the drum rotates, the vacuum in the compartments is maintained. Finally, the cake is scraped from the precoated filter medium. The scraper is slowly advanced into the precoat layer so that a fresh face of unblinded precoat is exposed each rotation. The filtering cycle is complete when most of the precoat has been removed and a new deposit of precoat is required.

Operating parameters affecting performance: The important operating parameters for the vacuum filter press are as follows:

- Sludge composition and characteristics
- Rotation cycle of the drum in ft/min
- Media precoat and thickness
- Influent conditioning
- Temperature of the feed
- Cake thickness
- Hydraulic and solids loading
- Viscosity of the filtrate
- Precoat layer removal rate (knife advance or cut rate)

TEST PROCEDURES

Belt Filter

Two belt filters currently in use at two operating refineries were evaluated in this study. The processes differ slightly as described below.

Refinery C2 At refinery C2, API separator sludges (K051) were treated with a belt filter in two separate tests. The equipment has separate belts for the gravity and pressure filtration sections. The gravity section is 84 inches wide and 11.1 feet long, with an effective area of 74 square feet. The pressure section consists of 14 rollers, the first 36 inches in diameter, the second 18 inches in diameter and the others 12 inches in diameter. The effective area is 39 square feet, and the overall dimensions of the pressure section are 44 inches wide by 80 feet long.

Test sludges were collected from API separators using vacuum trucks, and transferred to a 500 bbl portable tank. Operating parameters for the tests were as follows:

Polymer (cationic)	1.3% solution; mixed with sludge prior to gravity section of press
Total feed rate	26 gpm (1.5 gpm polymer solution, 3 gpm dilution water, 21.5 gpm sludge)
Polymer concentration in feed	750 ppm
Belts	63.5 x 30.5 mesh 0.0748 open area
Belt tension	200 psi (10 lb/linear inch)
Belt speed	20 ft/min in gravity section 35 ft/min in pressure section

The gravity and pressure filtrates were collected in separate portable tanks prior to backwashing the belts.

Refinery C1: At refinery C1, operating parameters for the belt filter test were as follows:

Sludge feed rate	61 gpm (0930 hr); 75 gpm (1300 hr)
Washwater	100 gpm, 96 psig (constant)
Feed Temperature	85°F

Polymer	1.5% solution 230 gph (0930 hr); 225 (1300 hr)
Belt tension	
Top belt	11 psig
Bottom belt	12 psig
Belt speed	12 ft./min.

The operating conditions shown for the two belt filter presses tested are within the ranges typically used at refineries for these types of oily waste feeds.

Plate Filter

Three plate filters currently in use at three operating refineries were evaluated in this study. The processes differ slightly as described below.

Refinery B2: At refinery B2, a mixture of listed refinery wastes was treated in a plate filter. The waste feed was drawn directly into the press from a holding tank. The tank typically contains a mixture of dissolved air flotation (DAF) sludge (K048), API separator sludge (K051), slop oil emulsion solids (K049), and miscellaneous oily materials such as tank bottoms. This mixture was conditioned with lime, at a dosage of about 2.5% of total sludge feed. For the tests reported here, the filter cloth in the press was a satin weave nylon. No precoat was used.

The filtration cycle began with 12 minutes of "fast fill" at 565 gpm, after which the flow rate was halved. Total filtration time was 3 hours and 45 minutes at a final pressure of about 210 psig. This was followed by a 23-minute hot water wash and 20 minutes to allow lines to drain before the filter chambers were opened. Release of the filter cakes took an additional 20 minutes. Throughout the filtration cycle, the temperature was approximately 145°F. At the end of the hot water wash, the filtrate temperature reached about 195°F.

Feed samples were drawn from the holding tank before the run and about 30 minutes, 2 hours and 3 hours after the run had started. At the end of the cycle, cakes were released to a conveyor system which transported the entire cake volume to a clean dumpster. This cake volume was core sampled in 20 locations on a 4 x 5 point grid. These samples were composited in a clean plastic-lined bucket from which sample containers were filled. The sampling procedure was completed within 20 minutes after all cakes had been released.

Refinery B1: At refinery B1, a mixture of about 99% API separator sludge (K051) and 1% tank bottoms (leaded and unleaded) were tested in a plate filter. The filter consists of 99 epoxy-coated recessed chamber plates. A synthetic fabric is used as the filter medium and typically, the sludge is pressurized to 225 psi by hydraulic force. The filter cakes fall into a dumpster located directly below the filter.

Feed solids are initially reduced in size with a comminutor, after which the feed is pumped to decant tanks for solids settling and sludge thickening. The thickened sludge is then pumped to the plate filter press for solids/liquids separation. A 50/50 mixture of silica and alumina is used as a precoat. The feed is conditioned by addition of lime to obtain about 15% solids in the feed and to enhance filterability of the cake. Plant experience on this waste has shown that 15% solids is optimal; a lower solids content would require a longer cycle time.

The precoat is applied to the filter medium by first filling the filter with water. Precoat slurry is then pumped into the filter, and the filtrate is released allowing the precoat to coat the filter medium to about 1/16" thickness. The lime conditioned sludge is then pumped into the filter from both ends, forcing the liquid in the precoat slurry out of the filter. The dual feed entry prevents the plates from warping and more evenly distributes the sludge on the press. When the filtrate flow falls below 32 gpm, the filter cycle is complete and the filter is ready to be opened. The accumulated cake falls from the opened plates through a hole in the floor to an awaiting truck or dumpster. The filter is then backwashed with water; when necessary the filter medium is washed with a high-pressure spray gun.

A typical cycle time for the filter is 3 to 4 hours, depending on the feed characteristics. On an average day, about 28,000 gallons of sludge are processed, generating about 40 tons of filter cake. The average solids content in the cake is about 55 percent.

Refinery B3: At refinery B3 mixed sludges are pumped to a mixed conditioning tank. Lime plus a proprietary agent are added at a rate of 0.7-1.0 pounds per pound of feed solids.

The plate filter has a capacity of 96 cubic feet in 100 chambers, 1" thick, formed by polypropylene plates. The filter is precoated with diatomaceous earth to a thickness of 1/16 inch.

Filter feed rate starts at 135 gpm with rate decreasing over a cycle of 90 to 120 minutes until a filter inlet pressure of 225 psig is reached.

Rotary Drum Vacuum Filter

One vacuum filter, currently in use at an operating refinery, was evaluated in this study.

Refinery V1: At refinery V1 slop oil emulsion sludges (K-049) were treated with a vacuum filter in two separate tests. The rotary drum is 8-feet in diameter and 12-feet long. It is operated by a 40 HP vacuum pump which has a capacity of 850 SCFM. The vacuum rotary drum has a speed of 2-12 minutes/revolution and is driven by a 3 HP drive. The vacuum filter has an adjustable knife to provide effective scraping of filter cake.

Test sludges were collected from the filter and samples were taken for analysis. Operating parameters for the test were as follows:

Feed Temperature = 130°F
Feed Rate = 6 gal/min
Drum speed = 4.3 min./rev.
Conditioning of feed None
Knife advance = 0.0005 inches/sec
Precoat about 2 inches thick when sampled
Vacuum level = 17-18 in. Hg
Feed tank = 2,000 bbl, with two mixers

TEST RESULTS AND DISCUSSION

The types of data obtained from the mechanical treatment tests include:

- Percentage of oil, water and solids in the waste feed
- Percentage of oil, water and solids in each of the three product streams (i.e., "oil", "water", and filter cake)
- Concentrations of specific volatile organics, base neutral organics, phenols and cresols, and metals in the waste feed and product streams
- Concentrations of specific volatile organics, base neutral organics, phenols and cresols, and metals in the TCLP leachate derived from the waste feed and product filter cakes

For each of the filters tested, measurements were made of a subset of the data listed above. The results for each individual test are presented.

The results have been presented in several ways to allow evaluation of how effectively the various treatment processes reduce environmental hazards. Three methods of evaluation have been used, where sufficient data are available.

1. Concentration of selected constituents in the waste feed and the filter cake have been presented.

2. Using the concentration data discussed in 1., and a mass balance defining weight of filter cake as a fraction of weight of raw feed, "percent reduction, weight" has been calculated and presented. The "percent reduction, weight" shows what percentage of a constituent present in the feed has been removed, and is not present in the filter cake.

3. The concentrations of specific constituents in the TCLP leachate from the waste feed and the filter cake is given and the "percent reduction, leachate analysis" has been calculated.

In order to arrive at the mass balance required to complete 2. above, development of a calculated material balance was required. Since all of the mechanical treatment work was done in continuous operation, on industrial scale equipment and within the refineries, mass balance by weight was not possible; the equipment required was not in place. The balances were calculated from the oil/solids/water analyses on filter feed and filter products. It should be appreciated that these are calculated balances and not measured balances.

As a first step toward the material balances, the oil/water/solids analyses were normalized to add up to 100%.

$$\text{Normalized Analysis} = \frac{100}{\text{Sum of oil \& water \& solids analyses}} \times \text{Analysis for Oil, Water, or Solids}$$

As an example, the waste feed to Refinery C2 was normalized as follows:

Parameter	Measured Analysis		Normalized Analysis (Rounded)
Oil	17.4	$\frac{100}{98.6} \times 17.4 =$	18
Water	74.3	$\frac{100}{98.6} \times 74.3 =$	75
Solids	6.9	$\frac{100}{98.6} \times 6.9 =$	7.0
	98.6		

Using the normalized analyses, mass balances were calculated by setting up and solving a set of simultaneous equations for oil, water and total mass balances.

Using the analytical data and the material balances, two additional tabulations were made. The first of these is "Percent Reduction, Weight", and the second is "Percent Reduction, Leachate Analysis."

"Percent Reduction, Weight" compares weight of a compound in the cake to weight in the feed. Arithmetically this is as follows:

% Reduction, Weight =

$$100\% \times \left[\frac{\begin{bmatrix}\text{ppm compound}\\ \text{in feed}\end{bmatrix} - \begin{bmatrix}\text{ppm compound}\\ \text{in cake}\end{bmatrix}\begin{bmatrix}\text{weight cake as a}\\ \text{fraction of feed}\end{bmatrix}}{\text{ppm of compound in feed}} \right]$$

"Percent Reduction, Leachate Analysis" compares the TCLP analyses of cake and feed without modification for weight. Arithmetically this is as follows:

% Reduction, Leachate Analysis =

$$100\% \times \left[\frac{\begin{bmatrix}\text{ppm of compound}\\ \text{in TCLP of feed}\end{bmatrix} - \begin{bmatrix}\text{ppm of compound}\\ \text{in TCLP of cake}\end{bmatrix}}{\text{ppm of compound in TCLP of feed}} \right]$$

When the analysis of feed showed a compound below detection limits (BDL), no calculation could be made, and the percent reduction column is blank. When analysis of the cake was BDL, the detection limit was used in the calculation and the answer given as "more than" (>). When both analyses, feed and cake, were real numbers, the "percent reductions" were rounded to the nearest percent, except, when the calculation gave more than 99.5%, this was reported as >99% rather than round up to 100%.

Belt Filter Results

<u>Refinery C2:</u> Two separate tests were carried out. Results for the first test are presented in Tables 3-2, 3-3, 3-4, and 3-5. Results for the duplicate test are presented in Tables 3-6, 3-7, 3-8, and 3-9.

Table 3-2 includes oil/water/solids data for the waste feed

TABLE 3-2

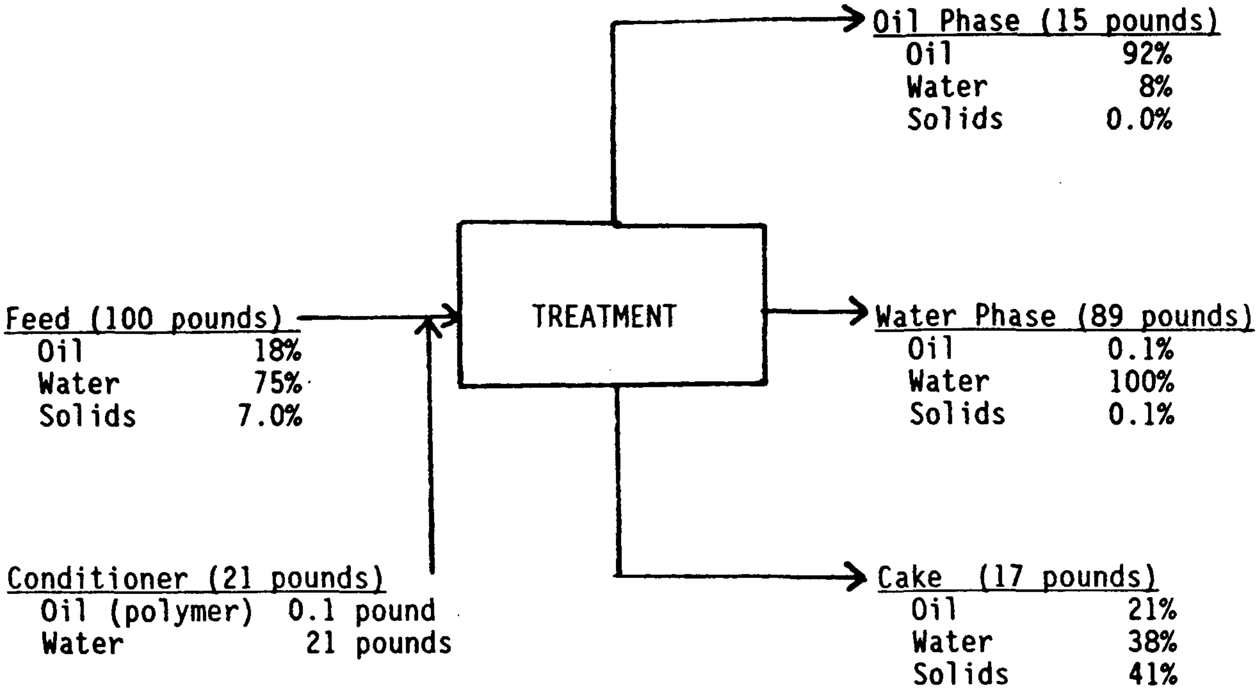
OIL/WATER/SOLIDS CONCENTRATIONS OF BELT FILTER FEED AND PRODUCTS - REFINERY C2

Parameter	Waste Feed	Products		
		Oil	Water	Solids
Lab I.D.	62525-01	62525-04	62525-05	62525-06
Oil, %	18	92	0.1	21
Water, %	75	8.0	100	38
Solids, %	7.0	BDL	0.1	41
Total, %	100	100	100	100

BDL = Below detection limit.

TABLE 3-3

CALCULATED MASS BALANCE
BASED ON OIL/WATER/SOLIDS ANALYSES
BELT FILTER - REFINERY C2



- Weight of Cake as a Fraction of Feed = 0.17
- Oil Recovery = 80%

TABLE 3-4

CONSTITUENT CONCENTRATIONS OF WASTE FEED AND BELT FILTER CAKE, AND CALCULATED % REDUCTION (WEIGHT) - REFINERY C2

	Constituent Concentrations, mg/kg		
Parameter	Waste Feed	Belt Filter Cake	% Reduction, (Weight)*
Lab I.D.	62525-01	62525-06	
Volatile Organics			
Benzene	74	10	98
Ethyl benzene	120	BDL (30)	>95
Toluene	450	83	97
Xylene, m	360	78	96
Xylenes, o&p	360	80	96
PNA's and Phenols			
Anthracene	13	BDL (2)	>97
Benzo(a)anthracene	13	15	81
Benzo(b)fluoranthene	BDL (2)	6	--
Benzo(a)pyrene	7	BDL (2)	>95
Chrysene	23	24	83
7,12-Dimethylbenz(a)anthracene	BDL (2)	17	--
Indene	4	3	87
1-Methylnaphthalene	640	560	85
Naphthalene	200	220	82
Phenanthrene	110	170	74
Pyrene	27	42	74
Acid/organics			
o-Cresols	BDL (2)	BDL (2)	--
p & m-Cresol	BDL (2)	BDL (2)	--
2,4-Dimethylphenol	BDL (2)	BDL (2)	--
Phenol	BDL (2)	BDL (2)	--
Metals			
Arsenic	5.6	21	37
Barium	68	260	36
Cadmium	ND (0.5)	1.5	--
Chromium	80	350	27
Lead	64	240	37
Mercury	4.4	14	47
Selenium	1.6	5	48
Silver	ND (0.3)	ND (0.3)	--

BDL : Below detection limit.
ND : Not detected.
Detection limit in parentheses.

* % Reduction (Weight): See text for calculation

TABLE 3-5

TCLP Leachate Concentrations of Waste Feed and Belt Filter Cake - Refinery C2

	TCLP Levels, mg/L		
Parameter	Waste Feed	Belt Filter Cake	% Reduction, Leachate Analysis*
Lab. I.D.	62525-01	62525-06	
Volatile Organics			
Benzene	15	0.62	96
Methyl ethyl ketone	BDL (460)	BDL (0.7)	
Styrene	BDL (5.5)	BDL (0.07)	
Ethylbenzene	23	0.18	99
Toluene	66	1.5	98
Xylene, m	61	0.55	99
Xylenes, o & p	66	0.65	99
Base/Neutral Organics			
Anthracene	1.0	BDL (0.015)	>98
Benzo(a)anthracene	0.61	BDL (0.015)	>97
Benzo(b)fluoranthene	BDL (0.15)	BDL (0.015)	
Benzo(a)pyrene	0.3-<0.4	BDL (0.015)	>95
Bis(2-ethylhexyl)phthalate	BDL (0.15)	BDL (0.015)	
Chrysene	1.0	BDL (0.015)	>98
Dibenz(a,h)anthracene	BDL (0.15)	BDL (0.015)	
7,12-Dimethylbenz(a) anthracene	BDL (0.15)	BDL (0.015)	
Fluoranthene	0.36-<0.40	BDL (0.015)	>95
Indene	BDL (0.15)	BDL (0.015)	
1-Methylnaphthalene	2.5	0.15	94
Naphthalene	4.6	0.14	97
Phenanthrene	7.3	BDL (0.015)	>99
Pyrene	1.6	BDL (0.015)	>99
Acid Organics			
o-Cresol	BDL (0.15)	BDL (0.015)	
p & m-Cresol	BDL (0.15)	BDL (0.015)	
2,4-Dimethylphenol	BDL (0.15)	0.03	
Phenol	BDL (0.15)	BDL (0.015)	
Metals			
Arsenic	0.02	0.02	0
Barium	1.2	0.26	78
Cadmium	ND (0.015)	ND (0.008)	
Chromium	0.15	0.01	93
Lead	0.13	ND (0.04)	>69
Mercury	ND (0.002)	ND (0.001)	
Selenium	0.02-<0.06	ND (0.04)	
Silver	ND (0.01)	ND (0.006)	

BDL: Below detection limit. Detection limit in parentheses.
ND : Not detected.
* % Reduction, Leachate Analysis; See text for calculation

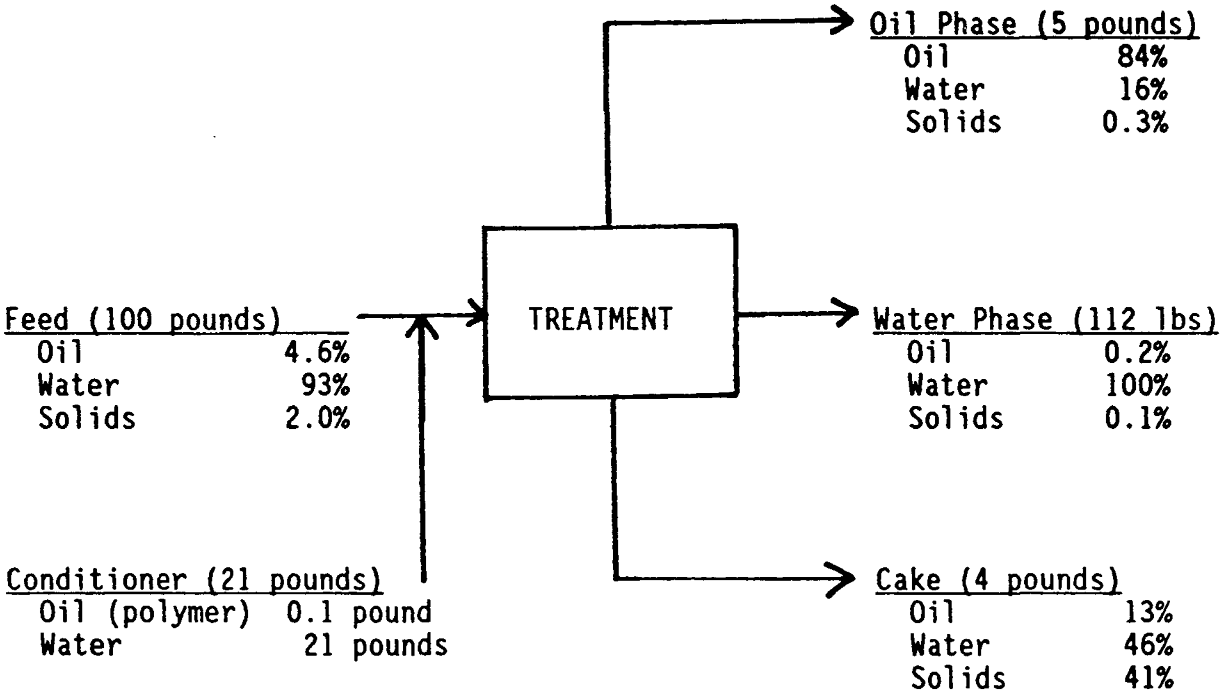
TABLE 3-6

OIL/WATER/SOLIDS CONCENTRATIONS OF BELT FILTER FEED AND PRODUCTS - REFINERY C2 (DUPLICATE RUN)

Parameter	Waste Feed	Products		
		Oil	Water	Solids
Lab I.D.	62525-10	62525-13	62525-14	62525-15
Oil, %	4.6	84	0.2	13
Water, %	93	16	100	46
Solids, %	2	0.3	0.1	41
Total, %	100	100	100	100

TABLE 3-7

CALCULATED MASS BALANCE
BASED ON OIL/WATER/SOLIDS ANALYSES
BELT FILTER - REFINERY C2 (DUPLICATE RUN)



- Weight of Cake as a Fraction of Feed = 0.043
- Oil Recovery = 87%

TABLE 3-8

CONSTITUENT CONCENTRATIONS OF WASTE FEED AND BELT FILTER CAKE, AND CALCULATED % REDUCTION (WEIGHT) - REFINERY C2 (DUPLICATE RUN)

	Constituent Concentrations, mg/kg**		
Parameter	Waste Feed	Belt Filter Cake	% Reduction, (Weight)*
Lab I.D.	62525-10	62525-15	
Volatile Organics			
Benzene	170	59	99
Toluene	650	330	98
Xylenes	1070	580	98
PNA's and Phenols			
Anthracene	ND (83)	ND (13	
Chrysene	ND (250)	ND (670)	
Naphthalene	130	230	92
Phenanthrene	90	170	92
Phenols	ND (1700)	ND (6600)	
Metals			
Chromium	40	360	61
Lead	31	240	67

ND : Not detected.
Detection limit in parentheses.

* % Reduction (Weight) : See text for calculation.
** Indicator Compound Screening Analysis : It measures total xylenes and total phenols (sum of phenol, cresols and 2,4 dimethylphenol).

TABLE 3-9

Indicator TCLP Leachate Concentrations of Waste Feed and Belt Filter Cake - Refinery C2 (Duplicate Run)

Parameter	TCLP Levels, mg/L Waste Feed	TCLP Levels, mg/L Belt Filter Cake	% Reduction, Leachate Analysis ***
Lab. I.D.	62525-10	62525-15	
Volatile Organics			
Benzene	20	0.75	96
Toluene	79	2.1	97
Xylenes*	130	1.1	99
PNA's and Phenols			
Anthracene	2.1	ND (0.015)	>99
Chrysene	1.7	ND (0.015)	>99
Naphthalene	15	0.13	99
Phenanthrene	10	ND (0.015)	>99
Phenols*	0.09-<0.44**	ND (0.15)	
Metals			
Chromium	0.23	0.03	87
Lead	0.15-<0.19**	ND (0.04)	>73

BDL: Below detection limit.
ND : Not detected.
Detection limit in parentheses.

* Indicator TCLP measures total xylenes, and total phenols (sum of phenol, cresols, and 2,4-dimethylphenol).
** Parameter was detected in only one phase of a two phase sample.
*** % Reduction, Leachate Analysis: See text for calculations.

and three product streams. These data were used to generate the mass balance information in Table 3-3. The results show that:

- The quantity of waste for disposal (filter cake vs. feed) was reduced by 83%
- 80% of the oil in the feed was recovered in the oil phase.
- The recovered oil contained 8.2% water and no solids
- The recovered water contained 0.1% oil and 0.1% solids

Table 3-4 compares concentrations of volatile organics, base/neutral organics, acid organics and metals in the waste feed and belt filter cake. The third column, "percent reduction, weight" represents the reduction in weight of individual compounds from feed to cake. Thus a benzene reduction of 98% indicates that 2% of the benzene present in the feed is in the filter cake. These reductions are from 74% to 98% for the organic components and 27 to 46% for the metals.

Reductions in leachate concentrations shown in Table 3-5 are even more striking. The data in Table 3-5 are concentrations in the TCLP leachate from the raw waste feed and the belt filter cake. Leachate concentrations from the filter cake were much lower than the leachate from the feed except for 2,4-dimethylphenol and arsenic. The leachate composition of arsenic showed no change. Arsenic concentration, like all of the other metal concentrations, has increased in the solid phase (see Table 3-4).

The concentration of other organic materials in the leachate has decreased by 94 to 99%. This results from a combination of lowered concentrations and leachability for the volatile organics and lowered leachability despite similar or higher concentration for the PNA's and phenols.

It should be noted that this comparison is of leachate compositions, without correction or manipulation based on the weight decrease from feed to filter cake.

Table 3-6 includes oil/water/solids data for the duplicate* test at Refinery C2. These data were used to generate the mass balance information in Table 3-7. The results of the mass balance are:

- The quantity of waste for disposal (filter cake vs. feed) was reduced by 95.7%
- 87% of the oil in the feed was recovered

Table 3-8 compares the concentrations of the indicator components in the waste feed and belt filter cake of these duplicate feed and cake samples. The weight of the organic components has been reduced from 92 to 99%; the chromium and lead reductions are 61% and 67% respectively.

Table 3-9 compares concentrations of indicator parameters in the TCLP leachate from the duplicate waste feed and corresponding filter cake. Reductions in organics in the leachates range from 96% to more than 99%. Chromium concentration in the leachate has been reduced by 87%. Again it should be noted that Table 3-9 is a comparison of TCLP analyses on raw feed and filter cake, with no correction made for decrease in weight from raw feed to belt filter cake. If the two were combined as "Leachate Concentration x Weight Reduction", all reductions would be greater than 99%.

Refinery C1: Two separate tests were carried out. Results for the first test are presented in Table 3-10, 3-11, 3-12, and 3-13.

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* The "duplicate test sampling was done hours after the original test.

TABLE 3-10

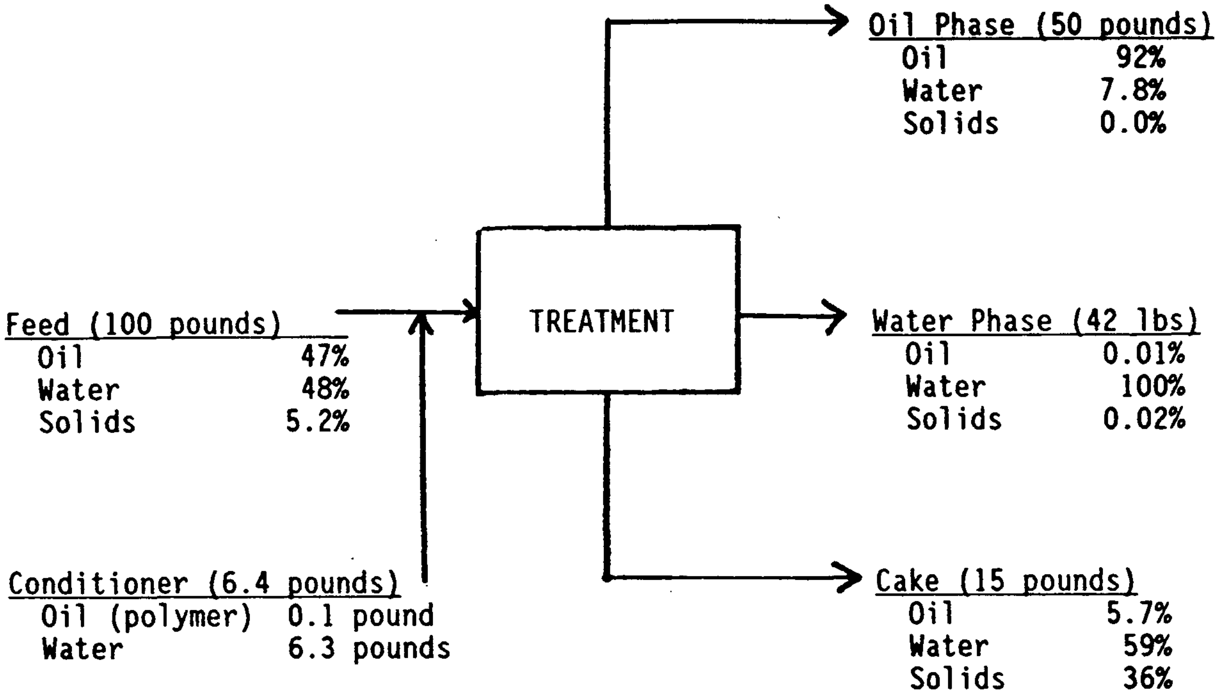
OIL/WATER/SOLIDS CONCENTRATIONS OF BELT FILTER FEED AND PRODUCTS - REFINERY C1

Parameter	Waste Feed	Products Oil	 Water	 Solids
Lab I.D.	62409-06	62409-12	62409-14	62409-10
Oil, %	47	92	0.01	5.7
Water, %	48	7.8	100	59
Solids, %	5.2	BDL	0.02	36
Total, %	100	100	100	100

BDL = Below detection limit.

TABLE 3-11

CALCULATED MASS BALANCE
BASED ON OIL/WATER/SOLIDS ANALYSES
BELT FILTER - REFINERY C1



- Weight of Cake as a Fraction of Feed = 0.15
- Oil Recovery = 98%

TABLE 3-12

CONSTITUENT CONCENTRATIONS OF WASTE FEED AND BELT FILTER CAKE, AND CALCULATED % REDUCTION (WEIGHT) - REFINERY C1

	Constituent Concentrations, mg/kg		
Parameter	Waste Feed	Belt Filter Cake	% Reduction, (Weight)*
Lab I.D.	62409-06	62409-10	
Volatile Organics			
Benzene	2100	41	99
Methyl ethyl ketone	BDL (390)	BDL (12)	--
Styrene	BDL (38)	BDL (12)	--
Ethylbenzene	1300	33	>99
Toluene	6300	190	>99
Xylene, m	2900	89	>99
Xylenes, o&p	3000	130	99
Base/Neutral Organics			
Anthracene	22	18	88
Benzo(a)anthracene	17	BDL (8)	>93
Benzo(b)fluoranthene	6.3	BDL (8)	>81
Benzo(a)pyrene	9.4	BDL (8)	>87
Bis(2-ethylhexyl)phthalate	4.2	BDL (8)	>71
Chrysene	19	10	92
Dibenz(a,h)anthracene	3.9	BDL (8)	>70
7,12-Dimethylbenz(a)anthracene	BDL (2)	BDL (8)	--
Fluoranthene	9.2	BDL (8)	>87
Indene	3.6	BDL (8)	>67
1-Methylnaphthalene	300	250	88
Naphthalene	180	94	92
Phenanthrene	240	120	93
Pyrene	59	30	92
Acid Organics			
o-Cresols	BDL (2)	0.40	--
p & m-Cresol	BDL (2)	1.30	--
2,4-Dimethylphenol	BDL (10)	0.70	--
Phenol	BDL (2)	0.90	--
Metals			
Arsenic	ND (0.2)	ND (10)	--
Barium	120	110	86
Cadmium	ND (0.5)	ND (2)	--
Chromium	150	320	68
Lead	30	37	82
Mercury	0.09	NA	--
Nickel	7	6	87
Selenium	ND (0.4)	ND (30)	--
Vanadium	2.7	2	89

BDL : Below detection limit; detection limit in parentheses.
ND : Not detected.
NA : Not analyzed.
* % Reduction (Weight) : See text for calculation.

TABLE 3-13

TCLP Leachate Concentrations of Waste Feed and Belt Filter Cake - Refinery C1

	TCLP Levels, mg/L			
Parameter	Waste Feed 1	Belt Filter Cake 1		% Reduction, Leachate Analysis**
Lab. I.D.	62409-06	62409-10		
		(***)	(****)	
Volatile Organics				
Benzene	91	1.1	1.5	99
Methyl ethyl ketone	BDL(290)	BDL(0.12)		
Styrene	BDL(29)	BDL(0.06)		
Ethylbenzene	100	BDL(0.06)		>99
Toluene	460	1.8	2.5	99
Xylene, m	205	0.85	1.8	99
Xylenes, o & p	195	0.97		99
Base/Neutral Organics				
Anthracene	13.4	BDL(0.01)	ND(0.0004)	>99
Benzo(a)anthracene	5.4	BDL(0.01)		>99
Benzo(b)fluoranthene	BDL(2.5)	BDL(0.01)		
Benzo(a)pyrene	4.4	BDL(0.01)		>99
Bis(2-ethylhexyl)phthalate	BDL(2.5)	BDL(0.01)	ND(0.002)	
Chrysene	8.6	BDL(0.01)		>99
Dibenz(a,h)anthracene	2.8	BDL(0.01)		>99
7,12-Dimethylbenz(a) anthracene	BDL(2.5)	BDL(0.01)		
Fluoranthene	4.9	BDL(0.01)		>99
Indene	BDL(2.5)	BDL(0.01)		
1-Methylnaphthalene	190	0.10		>99
Naphthalene	77	0.15	0.1	>99
Phenanthrene	102	BDL(0.01)	ND(0.01)	>99
Pyrene	17	BDL(0.01)		>99
Acid Organics				
o-Cresol	0.03-<2.5*	0.017		>94
p & m-Cresol	0.48-<2.7*	0.015		>96
2,4-Dimethylphenol	BDL(2.5)	0.04		
Phenol	BDL(2.5)	BDL(2.5)	ND(2)	
Metals				
Arsenic	0.02-<0.07*	ND(0.1)		
Barium	7.7	1.0		87
Cadmium	ND(0.06)	ND(0.02)		
Chromium	3.9	ND(0.025)	ND(0.025)	>99
Lead	1.1	ND(0.1)	ND(0.1)	>90
Mercury	ND(0.02)	NA		
Selenium	ND(0.2)	ND(0.3)		
Silver	ND(0.04)	ND(0.02)		

BDL: Below detection limit. ND: Not detected. NA: Not analyzed.
Detection limit in parentheses.

* Sample had separate oil phase; component was detected in only one phase.

** Percent reduction based on total TCLP results; see text for calculation.

*** Total TCLP characterization.

**** Indicator TCLP: It measures total xylenes and total phenols (sum of phenol, cresols, and 2,4-dimethylphenol)

Results for the duplicate test are presented in Tables 3-14, 3-15, 3-16, and 3-17.

Table 3-10 includes oil/water/solids data for the waste feed and the three product streams. These data were used to generate the mass balance information in Table 3-11. The results show that:

- The quantity of waste for disposal (filter cake vs. feed) was reduced by 85%
- 98% of the oil in the feed was recovered*
- The recovered oil contained 7.8% water and no solids

Table 3-12 compares, in the first two columns, the concentrations of organic materials and metals in the waste feed and belt filter cake. The third column, "percent reduction, weight" is calculated from the concentrations and the reduction in weight from feed to cake and represents the reduction in weight of individual compounds from feed to cake. Thus a percent reduction of >99% for benzene indicates that less than 1% of the weight of benzene present in the feed is in the filter cake. Of the volatile organics within detection limits, all were reduced by at least 99%. Somewhat lower reductions were achieved for the base/neutral organics. Metal reductions were 68 to 89%.

Table 3-13 compares the TCLP concentrations for leachate on waste feed and belt filter cake. For virtually all of the contained organic materials the leachate concentration has been reduced by 99% or more. The exception is the cresols, where detection limits leave us unsure of how much higher than 94 to 96% the reductions were. Reductions of metals in the TCLP leachate varied from 87% to over 99%.

Table 3-14 includes oil/water/solids data for the duplicate test at Refinery C1. These data were used to generate the mass

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* Oil recovery is very high, likely due to the high oil content and high oil to solids ratio in the feed.

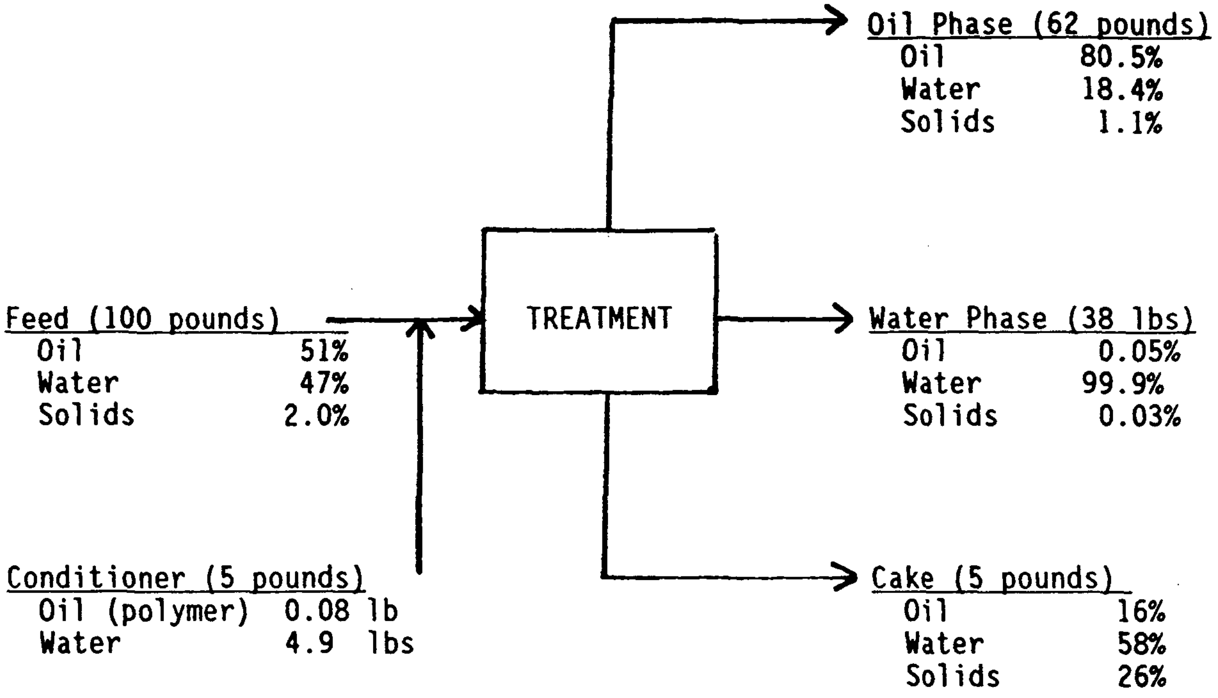
TABLE 3-14

OIL/WATER/SOLIDS CONCENTRATIONS OF BELT FILTER FEED AND PRODUCTS - REFINERY C1 (DUPLICATE RUN)

Parameter	Waste Feed	Products Oil	 Water	 Solids
Lab I.D.	62409-07	62409-13	62409-15	62409-11
Oil, %	51	81	0.05	16
Water, %	47	18	100	58
Solids, %	2.0	1.1	0.03	26
Total, %	100	100	100	100

TABLE 3-15

CALCULATED MASS BALANCE
BASED ON OIL/WATER/SOLIDS ANALYSES
BELT FILTER - REFINERY C1 (DUPLICATE RUN)



- Weight of Cake as a Fraction of Feed = 0.051
- Oil Recovery = 99%

TABLE 3-16

CONSTITUENT CONCENTRATIONS OF WASTE FEED AND BELT FILTER CAKE, AND CALCULATED % REDUCTION (WEIGHT) - REFINERY C1 (DUPLICATE RUN)

Parameter	Constituent Concentrations, mg/kg Waste Feed	 Belt Filter Cake	% Reduction, (Weight)*
Lab I.D.	62409-07**	62409-11***	
Volatile Organics			
Benzene	2200	120	>99
Toluene	7200	490	>99
Xylenes	7100	640	>99
PNA's and Phenols			
Anthracene	ND (149)	8.7	
Chrysene	ND (1500)	8.8	
Naphthalene	270	70	99
Phenanthrene	ND (590)	98	
Phenols	ND (9900)	BDL (1)	
Metals			
Chromium	5.2	360	Increase
Lead	ND (2)	42	

ND : Not detected
BDL : Below detection limits
Detection limit in parentheses.

* % Reduction (Weight) : See text for calculation.
** Indicator Compound Screening Analysis : It measures total xylenes and total phenols (sum of phenol, cresols and 2,4 dimethylphenol).
*** Total characterization.

TABLE 3-17

TCLP Leachate Concentrations of Waste Feed and Belt Filter Cake - Refinery C1 (Duplicate)

	TCLP Levels, mg/L		
Parameter	Waste Feed 2	Belt Filter Cake 2	% Reduction, Leachate Analysis***
Lab. I.D.	62409-07*	62409-11**	
Volatile Organics			
Benzene	220	1.2	99
Methyl ethyl ketone		BDL (0.65)	
Styrene		BDL (0.065)	
Ethylbenzene		0.36	
Toluene	710	3.3	>99
Xylene, m	730	0.68	>99
Xylenes, o & p		0.71	
Base/Neutral Organics			
Anthracene	ND (22)	BDL (0.012)	
Benzo(a)anthracene		BDL (0.012)	
Benzo(b)fluoranthene		BDL (0.012)	
Benzo(a)pyrene		BDL (0.012)	
Bis(2-ethylhexyl)phthalate		BDL (0.012)	
Chrysene	ND (220)	BDL (0.012)	
Dibenz(a,h)anthracene		BDL (0.012)	
7,12-Dimethylbenz(a) anthracene		BDL (0.012)	
Fluoranthene		BDL (0.012)	
Indene		BDL (0.012)	
1-Methylnaphthalene		0.12	
Naphthalene	140	0.16	>99
Phenanthrene	ND (220)	BDL (0.012)	
Pyrene		BDL (0.012)	
Acid Organics			
o-Cresol		0.042	
p & m-Cresol		0.15	
2,4-Dimethylphenol		0.06	
Phenol	ND (570)	0.068	
Metals			
Arsenic		ND (0.004)	
Barium		1.0	
Cadmium		ND (0.02)	
Chromium	1.8	ND (0.025)	>98
Lead	ND (0.5)	ND (0.1)	
Mercury		ND (0.001)	
Selenium		ND (0.04)	
Silver		ND (0.015)	

BDL: Below detection limit. ND: Not detected. Detection limit in parentheses.

* Indicator TCLP: It measures total xylenes and total phenols (sum of phenol, cresols, and 2,4-dimethylphenol)

** Total TCLP characterization.

*** % Reduction, Leachate Analysis: See text for calculation.

balance information in Table 3-15. The results are:

- The quantity of waste for disposal (filter cake vs. feed) was reduced by 94.9%
- 99% of the oil in the feed was recovered*
- The recovered oil contained 18% water and 1.1% solids
- The recovered water contained less than 0.1% oil and solids

At this point in the previous cases the constituent concentrations in the waste feed and belt filter cake were compared and the percent reduction in weight was calculated. For this case, however, equivalent analyses were not done on the two samples; a screening analysis was done on the feed (duplicate) and Appendix VIII analyses done on the cake (duplicate.) Nevertheless, Table 3-16 does compare the analyses we have and shows the calculated weight reduction. The organic compounds have been reduced by 98% to more than 99%. Weight of chromium has increased, almost assuredly an analytical artifact (the filtration equipment could be losing chromium, but that's unlikely.)

Table 3-17 compares concentration of indicator parameters in the TCLP leachate for the duplicate waste feed and corresponding filter cake. The number of comparisons that can be made is limited by the analyses available. The improvements in leachate concentrations are high, from more than 98% for chromium to 99% and more for the organics.

Plate Filter Results

Refinery B2: Table 3-18 contains the oil/water/solids data in feed and product phases.

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* Oil recovery is very high, likely due to the high oil content and high oil to solids ratio in the feed.

TABLE 3-18

OIL/WATER/SOLIDS CONCENTRATIONS OF PLATE FILTER FEED (CONDITIONED) AND PRODUCTS - REFINERY B2

Parameter	Waste Feed (Conditioned)	Products		
		Oil	Water	Solids
Lab I.D.	62493-05	62493-04	62493-03	62493-06
Oil, %	28	88	0.1	9.1
Water, %	67	12	100	43
Solids, %	4.7	0.5*	0.0	48
Total, %	100	100	100	100

---

* Actual <u>reported</u> analysis of solids in the oil phase was 11.8%. Skilled refinery personnel examined the sample, and, based on their long term experience, agreed that there was a maximum of 0.5% solids in the sample (as was usually found). It was not possible to reanalyze the sample -- it was lost.

There was, apparently, an analytical problem with the data from this test at Refinery B2. As noted on Table 3-18, the reported analysis of solids in the oil phase was 11.8%. Examination of the sample made it obvious the analysis was in error (an oil rich sample with 11.8% solids in it would be a viscous sludge; the sample was clearly not that) rather it appeared, as do the usual samples of the filtrate oil phase at Refinery B2, to have less than 0.5% solids. No re-analysis was possible, the sample was lost, and using best engineering judgement 0.5% was assumed. A mass balance was calculated, Table 3-19, based on this assumed solids concentration in the oil phase of 0.5%. The conclusion drawn from the mass balance are as follows:

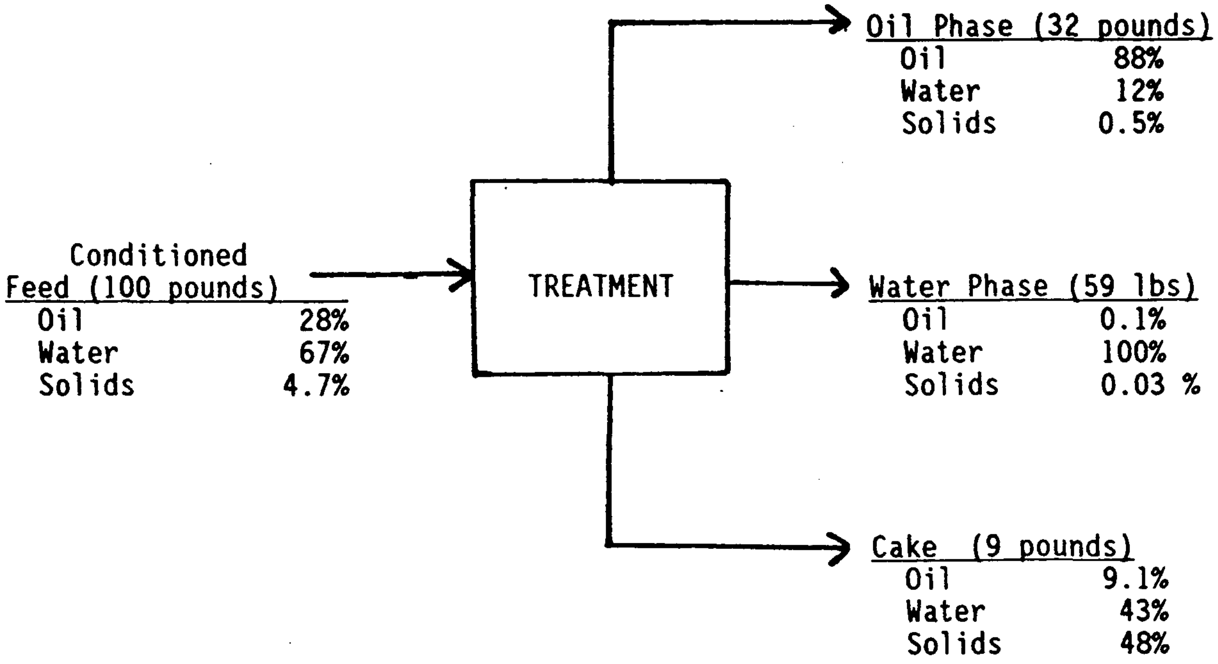
- The quantity of waste for disposal (filter cake vs. feed) was reduced by 90.5%
- 97% of the oil in the feed was recovered

Table 3-20 compares the constituent concentrations in the conditioned feed and the filter cake and the calculated percent reduction by weight of these constituents from feed to filter cake. The reduction of organics is from 96 to 98%. The reduction in metals is low, 3 to 32% where there is a reduction, and an increase, small enough to be within analytical accuracy, for barium and cadmium. The metals results reflect "fixation" of the metals with lime addition and their strong recovery in the solid phase.

Table 3-21 includes TCLP leachate compositions of organics and metals from the conditioned feed and plate filter cake. The reduction in leachate concentrations for volatile, and base/neutral organics are at or above 99%. Acid organics are strongly reduced, but the calculated reduction is limited by detection limits. Metals leachate comparison varies. Due to the use of lime as a conditioner, one expects most of the metals to remain in the filter cake while, at the same time becoming less mobile due to the increased pH.

TABLE 3-19

CALCULATED MASS BALANCE
BASED ON OIL/WATER/SOLIDS ANALYSES
PLATE FILTER - REFINERY B2



- Weight of Cake as a Fraction of Conditioned Feed = 0.095
- Oil Recovery = 97%

TABLE 3-20

CONSTITUENT CONCENTRATIONS OF WASTE FEED AND PLATE FILTER CAKE, AND CALCULATED % REDUCTION (WEIGHT) - REFINERY B2

Parameter	Constituent Concentrations, mg/kg Conditioned Waste Feed	 Plate Filter Cake	% Reduction, (Weight)*
Lab I.D.	62493-05	62493-06	
Volatile Organics			
Benzene	530	89	98
Methyl ethyl ketone	BDL (1500)	BDL (850)	
Styrene	250	BDL (85)	>96
Ethylbenzene	1100	340	97
Toluene	1500	370	98
Xylene, m	1900	520	97
Xylenes, o&p	2100	600	97
Base/Neutral Organics			
Anthracene	29	9.4	97
Benzo(a)anthracene	18	7.7	96
Benzo(b)fluoranthene	8	2.6	97
Benzo(a)pyrene	11	3.8	97
Bis(2-ethylhexyl)phthalate	BDL (2)	BDL (1)	--
Chrysene	30	12	96
Dibenz(a,h)anthracene	BDL (2)	1.2	
Fluoranthene	10	BDL (1)	
Indene	BDL (2)	BDL (1)	
1-Methylnaphthalene	1200	410	97
Naphthalene	490	160	97
Phenanthrene	210	51	98
Pyrene	95	27	97
Acid Organics			
o-Cresols	BDL (2)	BDL (1)	--
p & m-Cresol	BDL (2)	BDL (1)	--
2,4-Dimethylphenol	BDL (2)	BDL (1)	--
Phenol	BDL (2)	BDL (1)	--
Metals			
Arsenic	1.2	8.6	32
Barium	21	260	**
Cadmium	ND (0.5)	ND (2.5)	--
Chromium	150	1700	**
Cobalt	2.0	19	10
Lead	8.2	84	3
Mercury	ND (0.05)	0.74	--
Selenium	ND (1)	ND (4)	--

BDL : Below detection limit.
ND : Not detected.
Detection limit in parentheses.

* % Reduction (Weight) : See text for calculation .
** Percent Increase.

TABLE 3-21

TCLP Leachate Concentrations of Waste Feed and Plate Filter Cake - Refinery B2

Parameter	TCLP Levels, mg/L		% Reduction, Leachate Analysis**
	Waste Conditoned Feed	Plate Filter Cake	
Lab. I.D.	62493-05	62493-06	
Volatile Organics			
Benzene	130	1.9	99
Methyl ethyl ketone	BDL (1300)	BDL (2.5)	
Styrene	43	0.3	99
Ethylbenzene	240	1.2	99
Toluene	360	4.1	99
Xylene, m	340	1.5	>99
Xylenes, o & p	410	2.1	99
Base/Neutral Organics			
Anthracene	BDL (17)	BDL (0.01)	
Benzo(a)anthracene	BDL (17)	BDL (0.01)	
Benzo(b)fluoranthene	BDL (17)	BDL (0.01)	
Benzo(a)pyrene	BDL (17)	BDL (0.01)	
Bis(2-ethylhexyl)phthalate	BDL (17)	BDL (0.01)	
Chrysene	20	BDL (0.01)	>99
Dibenz(a,h)anthracene	BDL (17)	BDL (0.01)	
7,12-Dimethylbenz(a) anthracene	BDL (17)	BDL (0.01)	
Fluoranthene	BDL (17)	BDL (0.01)	
Indene	170	0.02	>99
1-Methylnaphthalene	800	0.20	>99
Naphthalene	310	0.25	>99
Phenanthrene	23	BDL (0.01)	>99
Pyrene	42	BDL (0.01)	>99
Acid Organics			
o-Cresol	0.04-<17*	BDL (0.01)	>75
p & m-Cresol	0.18-<17*	0.025	>86
2,4-Dimethylphenol	0.12-<17*	BDL (0.01)	>91
Phenol	BDL	BDL (0.01)	
Metals			
Arsenic	0.01-<0.07*	0.008	
Barium	1.5	0.82	45
Cadmium	ND (0.08)	ND (0.02)	
Chromium	1.1	ND (0.025)	>97
Lead	0.45-<0.55	ND (0.1)	>77
Mercury	ND (0.009)	ND (0.001)	
Selenium	ND (0.2)	ND (0.004)	
Silver	ND (0.06)	ND (0.01)	

BDL: Below detection limit. Detection limit in parentheses.
ND : Not detected.

* Sample has separate oil phase; component was detected in only one phase.
** % Reduction, leachate analysis; See text for calculation.

<u>Refinery B1*:</u> Table 3-22 includes oil/water/solids data for the raw feed, the duplicate raw feed sample and the three product phases that result from the original raw feed. These data are of particular interest in demonstrating the variability of petroleum refinery wastes. As pointed out earlier in this chapter, the plate filter press feed at refinery B1 is normally a mixture of 99% API separator sludge and 1% tank bottoms. It would be expected, therefore, that a raw feed sample would be virtually API separator sludge which normally has an oil plus solids content of about 20%, the mixture somewhat variable with refinery. An analysis for API separator sludge at refinery B2 was 8.2% oil and 12.9% solids. Contrary to expectation, the raw feed at refinery B1 contained 1.5% oil and 1.7% solids. As shown in Table 3-22, a duplicate sample contained 6.1% oil and 6.6% solids.

Product stream samples--oil phase, water phase and filter cake--were taken only with the original lean raw feed. Therefore, the mass balance was calculated using oil, water and solids analyses for the raw feed and is shown in Table 3-23.

- The quantity of waste for disposal was reduced by 96.3%
- 82% of the oil in the feed was recovered.

Table 3-24 lists the constituent concentrations in the waste feed and the filter cake and gives the calculated reduction by weight of these constituents from feed to filter cake. These reductions vary from 75 to 80% for the volatile organics to impossibly negative, an increase for the heavier organics. Reduction in volatile organics was consistent with percent oil recovery but this was not true for the PNA's and phenols. A probable explanation is that feed composition was changing during sample collection and that the product samples represent a feed much richer in oil and solids than the feed sample.

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* There was no established chain of custody for these samples.

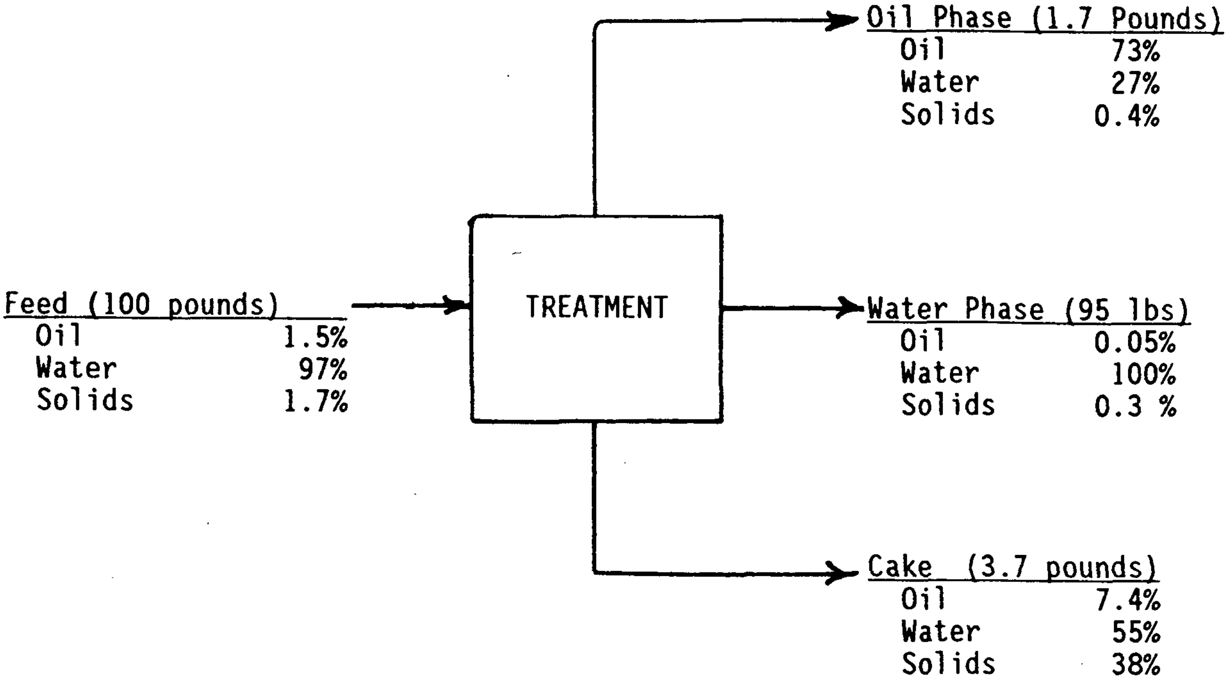
TABLE 3-22

OIL/WATER/SOLIDS CONCENTRATIONS OF PLATE FILTER FEEDS AND PRODUCTS - REFINERY B1

Parameter	Raw Feed	Duplicate Raw Feed	Products OIL	Products Water	Products Solids
Lab I.D.	62291-01	62291-11	62291-08	62291-09	62291-06
Oil, %	1.5	6.1	73	0.05	7.4
Water, %	97	87	27	100	55
Solids, %	1.7	6.6	0.4	0.3	38
Total, %	100	100	100	100	100

TABLE 3-23

CALCULATED MASS BALANCE
BASED ON OIL/WATER/SOLIDS ANALYSES
PLATE FILTER - REFINERY B1



- Weight of Cake as a Fraction of Feed = 0.037
- Oil Recovery = 82%

TABLE 3-24

CONSTITUENT CONCENTRATIONS OF WASTE FEED AND PLATE FILTER CAKE, AND CALCULATED % REDUCTION (WEIGHT) - REFINERY B1

Parameter	Constituent Concentrations, mg/kg Conditioned Waste Feed	 Plate Filter Cake	% Reduction, (Weight)*
Lab I.D.	62291-02	62291-06	
Volatile Organics			
Benzene	9.8	60	77
Ethyl benzene	17	110	76
Methyl ethyl ketone	BDL (43)	BDL (300)	
Styrene	BDL (4.3)	BDL (30)	
Toluene	68	360	80
Xylene, m	55	350	76
Xylenes, o&p	51	340	75
PNA's and Phenols			
Anthracene	0.069	9.4	**
Benzo(a)anthracene	0.14	20	**
Benzo(b)fluoranthene	0.041	6.2	**
Benzo(a)pyrene	0.071	9.9	**
Bis(2-ethylhexyl)phthalate	BDL (0.009)	BDL (1)	
Chrysene	0.24	26	**
Dibenz(a,h)anthracene	BDL (0.009)	BDL (1)	
Fluoranthene	0.055	5.9	**
Indene	0.085	BDL (1)	
1-Methylnaphthalene	2.1	260	**
Naphthalene	1.1	90	**
Phenanthrene	0.53	47	**
Pyrene	0.25	22	**
Acid/organics			
o-Cresol	0.33	BDL (1)	
p & m-Cresols	0.42	BDL (1)	
2,4-Dimethylphenol	BDL (0.009)	BDL (1)	
Phenol	1.7	BDL (1)	
Metals			
Arsenic	0.8	7.0	68
Barium	54	142	90
Cadmium	ND (0.5)	1	
Chromium	328	835	91
Cobalt	3.2	9.3	89
Lead	48	126	90
Mercury	0.13	2.9	17
Selenium	ND (0.4)	ND (4)	

ND : Not detected.
BDL : Below detection limit
Detection limit in parentheses.
* % Reduction (Weight); See text for calculation.
** Increase

Table 3-25 compares composition of TCLP leachate of the raw feed, the conditioned feed and the plate filter cake. The final column shows the Percent Reduction, Leachate analysis. The Analytical information varied; for the raw feed only the indicator analysis of a limited number of materials had been done. A total TCLP characterization had been done on the conditioned feed and the plate filter cake. As noted on the table, the Percent Reduction was calculated from raw feed to cake when the raw feed analysis was available, otherwise from the conditioned feed. Organic compound reductions ranged from an increase (within analytical accuracy) on indene through 95% on total xylenes, and from 33 to more than 92% on the metals. Again, probably feed composition was changing during the test.

Refinery B3: A third set of plate filter tests were run at refinery B3 when two samples each of raw feed and filter cake were taken. Only a limited set of analyses was done: oil/water/solids (O/W/S) and TCLP leachate concentrations of screening parameters on each feed and cake sample. Table 3-26 shows the O/W/S analyses. Tables 3-27 and 3-28 show the TCLP data and the calculated percent reduction in leachate concentration from feed to cake.

An interesting comparison is possible since the two feed samples were very different. As seen in Table 3-27 Raw Feed 1 was quite low in oil and solids, 1.3% and 0.6% respectively, while Feed 2 had 5.7% oil and 2.5% solids. The cake concentrations are fairly similar: 26.5% and 21.0% oil, and 42.1 and 40.3% solids. A much bigger difference is seen in the reductions in leachate analysis. The first set, from the dilute feed (Table 3-27) show low percent reductions: 18 to 47%, with chromium concentration increasing. Leachate on the feed was low in concentration and so limited reduction is seen. For the second data set, from the more

TABLE 3-25

TCLP Leachate Concentrations of Waste Feed and Plate Filter Cake - Refinery B1

Parameter	TCLP Levels, mg/L			% Reduction, Leachate Analysis***
	Raw Feed	Waste Conditioned Feed	Plate Filter Cake	
Lab. I.D.	62291-01*	62291-02**	62291-06**	
Volatile Organics				
Benzene	3.2	2.7	0.80	75
Methyl ethyl ketone		BDL(0.5)	BDL(1.2)	
Styrene		BDL(0.05)	BDL(0.12)	
Ethylbenzene		0.29	0.22	24
Toluene	22	3.5	2.2	90
Xylene, m		0.83	0.69	17
Xylenes, o & p	31	0.88	0.73	95
Base/Neutral Organics				
Anthracene	ND(0.02)	BDL(0.002)	BDL(0.002)	
Benzo(a)anthracene		BDL(0.002)	BDL(0.002)	
Benzo(b)fluoranthene		BDL(0.002)	BDL(0.002)	
Benzo(a)pyrene		BDL(0.002)	BDL(0.002)	
Bis(2-ethylhexyl)phthalate		BDL(0.002)	BDL(0.002)	
Chrysene	ND(0.1)	BDL(0.002)	BDL(0.002)	
Dibenz(a,h)anthracene		BDL(0.002)	BDL(0.002)	
7,12-Dimethylbenz(a) anthracene		BDL(0.002)	BDL(0.002)	
Fluoranthene		BDL(0.002)	BDL(0.002)	
Indene		0.014	0.015	((7))
1-Methylnaphthalene		0.13	0.13	0
Naphthalene	2.6	0.16	0.16	77
Phenanthrene	ND(1.3)	0.007	0.004	43
Pyrene		BDL(0.002)	BDL(0.002)	
Acid Organics				
o-Cresol		0.33	0.02	94
p & m-Cresol		0.30	0.03	90
2,4-Dimethylphenol		0.10	0.01	90
Phenol	ND(10)	0.85	0.10	88
Metals				
Arsenic		0.006	0.004	33
Barium		0.95	0.57	40
Cadmium		ND(0.02)	ND(0.02)	
Chromium	0.34	ND(0.025)	ND(0.025)	>92
Lead	ND(0.1)	ND(0.1)	ND(0.1)	
Mercury		0.001	ND(0.001)	
Selenium		ND(0.004)	ND(0.004)	
Silver		ND(0.015)	ND(0.015)	

BDL: Below detection limit.
Detection limit in parentheses.

ND: Not detected.
Percent increase in double parentheses.

* Indicator TCLP: It measures total xylenes and total phenols (sum of phenol, cresols, and 2,4-dimethylphenol).

** Total TCLP characterization.

*** % Reduction is based on Raw Feed and Plate Filter Cake when raw feed analysis is available; otherwise on conditioned feed and filter cake.

TABLE 3-26

OIL/WATER/SOLIDS CONCENTRATIONS OF PLATE FILTER FEEDS AND CAKES - REFINERY B3

Parameter	Raw Feed #1	Plate Filter Cake #1	Raw Feed #2	Plate Filter Cake #2
Lab I.D.	63043-01	63043-02	63043-03	63043-04
Oil, %	1.3	27	5.7	21
Water, %	98	31	92	39
Solids, %	0.6	42.2	2.5	40
Total, %	100	100	100	100

TABLE 3-27

INDICATOR TCLP LEACHATE CONCENTRATIONS OF WASTE FEED AND PLATE FILTER CAKE - REFINERY B3 (FIRST TEST)

Parameter	Indicator TCLP Levels, mg/L** Raw Feed #1	Plate Filter Cake #1	% Reduction, Leachate Analysis*
Lab I.D.	63043-01	63043-02	
Volatile Organics			
Benzene	3.3	2.7	18
Toluene	2.4	1.9	21
Xylenes	0.82	0.74	10
PNA's and Phenols			
Anthracene	ND (0.015)	ND (0.001)	
Chrysene	ND (0.51)	ND (0.002)	
Naphthalene	0.77	0.041	47
Phenanthrene	ND (0.32)	ND (0.016)	
Phenols	ND (5.8)	ND (0.59)	
Metals			
Chromium	0.05	0.15	((200))
Lead	ND (0.01)	ND (0.1)	

ND : Not detected.
Detection limit in parentheses.
Percent increase in parentheses.

* % Reduction, Leachate Analysis; See text for calculation.

** Indicator TCLP measures total xylenes, and total phenols (sum of phenol, cresols and 2,4-dimethylphenol).

concentrated feed (Table 3-28), the data show 88 to 97% reduction, much more in line with data on other equipment.

Rotary Drum Vacuum Filter Results

Refinery V1: The vacuum filter press tests were run at refinery V1. Two sets of feed and cake samples were taken (four samples). Analyses done were oil/water/solids on each sample and TCLP for indicator compounds for each sample. Analyses on the filtrate phase (or phases) were not done, therefore no material balances can be made. Also, constituent analyses on feed and cake were not done, so that weight reduction from feed to cake can not be presented.

Table 3-29 presents the oil/water/solids data for the samples. Tables 3-30 and 3-31 compare concentration of constituents in the TCLP leachates from feed and cake and the calculated percent reduction in the leachate analyses from feed to cake. All of the organic compound comparisons show leachate concentration reductions of more than 99%. The metals concentration reduction in the leachate is quite strong, limited by analytical detection limits.

TABLE 3-28

INDICATOR TCLP LEACHATE CONCENTRATIONS OF WASTE FEED AND PLATE FILTER CAKE - REFINERY B3 (SECOND TEST)

	Indicator TCLP Levels, mg/L**		
Parameter	Raw Feed #2	Plate Filter Cake #2	% Reduction Leachate Analysis *
Lab I.D	63043-03	63043-04	
Volatile Organics			
Benzene	37	4.5	88
Toluene	42	2.5	94
Xylenes	63	1.6	97
PNA's and Phenols			
Anthracene	ND	ND (0.001)	
Chrysene	ND	ND (0.001)	
Naphthalene	8.0	0.12	98
Phenanthrene	ND	ND (0.014)	
Phenols	ND	ND (0.56)	
Metals			
Chromium	4.1	0.12	97
Lead	0.01-<0.11	ND (0.1)	

ND : Not detected.
Detection limit in parentheses.

* % Reduction, Leachate Analysis; See text for calculation.

** Indicator TCLP measures total xylenes, and total phenols (sum of phenol, cresols and 2,4 dimethylphenol).

*** Detection limits for all parameters were not available at this time.

TABLE 3-29

OIL/WATER/SOLIDS CONCENTRATIONS OF VACUUM FILTER FEEDS AND CAKES - REFINERY VI

Parameter	Waste Feed #1	Cake #1	Waste Feed #2	Cake #2
Lab I.D.	63223-01	63223-03	63223-02	63223-04
Oil, %	63	37	57	38
Water, %	34	29	39	30
Solids, %	3.1	33	3.5	33
Total, %	100	99	100	101

TABLE 3-30

INDICATOR TCLP LEACHATE CONCENTRATIONS OF WASTE FEED AND VACUUM FILTER CAKE - REFINERY VI (FIRST TEST)

Parameter	Indicator TCLP Levels, mg/L** Raw Feed #1	Indicator TCLP Levels, mg/L** Vacuum Filter Cake #1	% Reduction, Leachate Analysis***
Lab I.D.	63223-01	63223-03	
Volatile Organics			
Benzene	78	0.27	>99
Toluene	570	1.5	>99
Xylenes	700	0.77	>99
PNA's and Phenols			
Anthracene	ND (20)	ND (0.015)	
Chrysene	ND (180)	ND (0.045)	
Naphthalene	0.13-<33*	0.25	
Phenanthrene	240	ND (0.13)	>99
Phenols	ND (1600)	ND (0.62)	
Metals			
Chromium	1.54	ND (0.02)	>98
Lead	0.34-<1.14*	ND (0.04)	>88

ND : Not detected.
Detection limit in parentheses.

* Parameter was detected in only one phase of a two phase sample.

** Indicator TCLP measures total xylenes, and total phenols (sum of phenol, cresols and 2,4 dimethylphenol).

*** % Reduction, Leachate Analysis; See text for calculation.

TABLE 3-31

INDICATOR TCLP LEACHATE CONCENTRATIONS OF WASTE FEED AND VACUUM FILTER CAKE - REFINERY VI (SECOND TEST)

Parameter	Indicator TCLP Levels, mg/L** Raw Feed #2	Indicator TCLP Levels, mg/L** Vacuum Filter Cake #2	% Reduction, Leachate Analysis*
Lab I.D.	63223-02	63223-04	
Volatile Organics			
Benzene	71	0.2	>99
Toluene	500	0.98	>99
Xylenes	680	0.58	>99
PNA's and Phenols			
Anthracene	ND (24)	ND (0.009)	
Chrysene	ND (260)	ND (0.13)	
Naphthalene	180	0.33	>99
Phenanthrene	320	ND (0.15)	>99
Phenols	ND (2000)	ND (1.6)	
Metals			
Chromium	0.05-<0.2***	ND (0.02)	>60
Lead	1.3	ND (0.4)	>69

ND : Not detected.
Detection limit in parentheses.

* % Reduction, Leachate Analysis : See text for calculation.

** Indicator Compound Screening Analysis : It measures total xylenes and total phenols (sum of phenol, cresols and 2,4 dimethylphenol).

*** Parameter was detected in only one phase of a two phase sample.

CHAPTER 4. SOLVENT EXTRACTION

INTRODUCTION

In Chapter 3, it was demonstrated that the oil-water-solids emulsions of petroleum refinery wastes could be eliminated by filtering the solids. Such an emulsion can also be broken by extracting the oil or water or both from the solids by mixing the waste with a solvent.

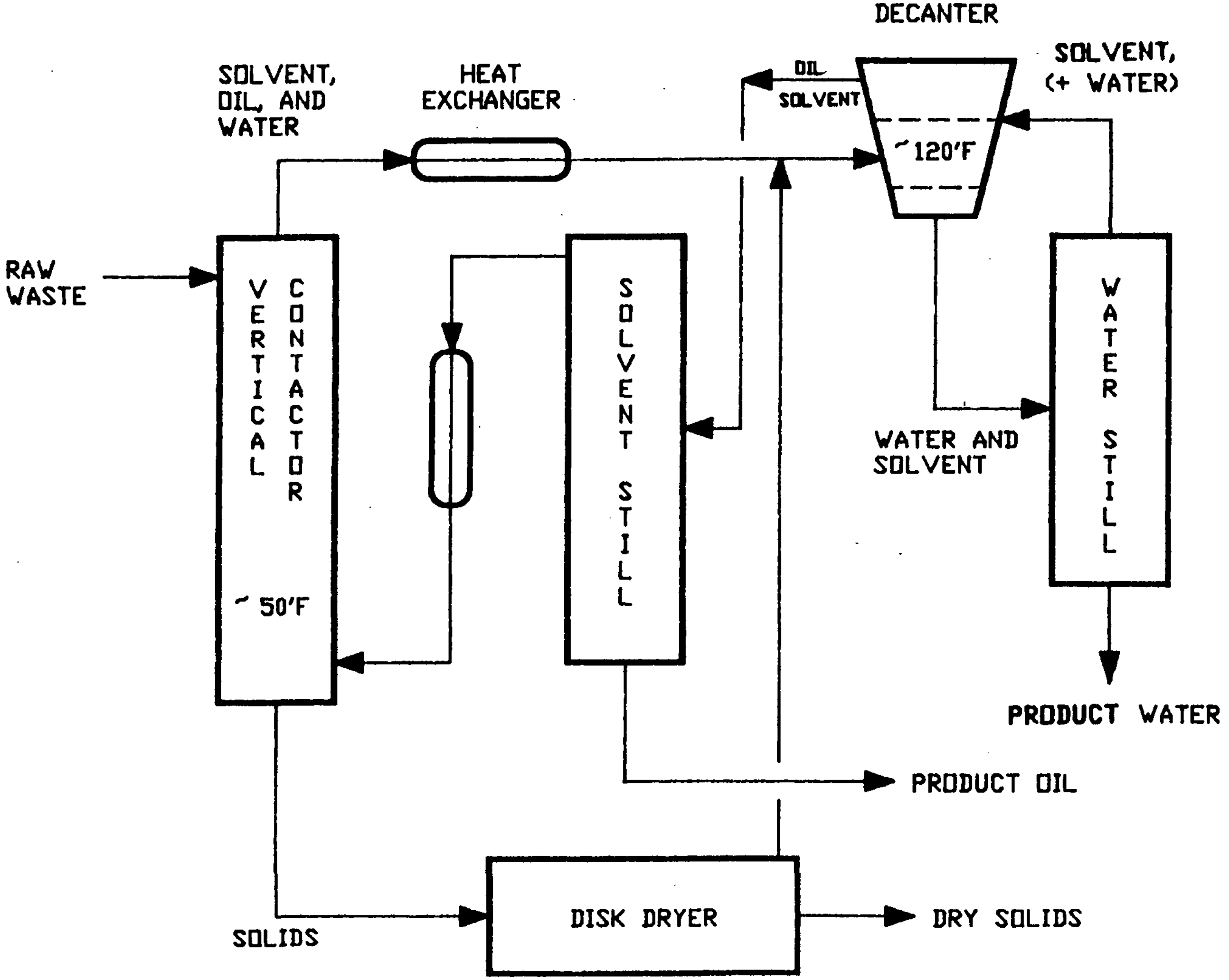
Figure 4-1 shows a simplified diagram of a general solvent extraction process as it could be used to treat refinery oily sludges. The solvent, in the case shown, extracts both oil and water, allowing the solids to be separated by gravity from the oil-water-solvent solution. A phase separation then divides the extract into oil/solvent and water/solvent phases. Recovery of solvent (which is recycled) from each phase leaves "product oil" and "product water".

OVERVIEW

The data gathered in this test demonstrate the potential effectiveness of solvent extraction of wastes at petroleum refineries. Advantages of the process are a high level of oil recovery; compatibility and integration into refinery operation; and isolation of product solids and wastewater streams with substantially reduced levels of hazardous constituents in the product solids. Pilot scale tests resulted in 98% oil recovery from the feed. The extracted oil phase had a solids content of less than 1% and about 3% water.

Integration of the solvent extraction process into an operating refinery has not been demonstrated but would be quite straightforward. Product water contains 58 ppm oil and grease and

FIGURE 4-1
SIMPLIFIED STEPS OF SOLVENT EXTRACTION PROCESS



263 ppm total suspended solids, allowing inclusion in the refinery's wastewater treatment system. The product oil stream is low enough in both water and solids to fit readily into the oil processing operation.

Due to a very efficient separation, the weight of the product solids was little more than the solids content in the waste feed. Concentrations of all the indicator organics present in the feed were reduced by more than 99%, as were the concentrations in the TCLP leachates.

Total metal concentrations were increased from waste feed to product solids since the metals are primarily in the solids. TCLP leachate concentrations for metals in the product solids were quite low--0.11 mg/L for chromium and 0.05 mg/L for lead, greatly reduced from levels in the feed.

DISCUSSION--EQUIPMENT DESCRIPTION AND OPERATION

In this section, the solvent extraction process used to collect test data is described, and the principles of operation and important operating parameters are presented.

The process has been demonstrated on a commercial scale by a single unit which has operated at a Superfund site under the Superfund Innovative Technology Evaluation (SITE) program. The waste at that site was a mixture of acidic oily sludges containing up to 20% oil and 20% solids.

Underlying Principles of Operation

The process tested employs the inverse miscibility properties of its solvent to break down emulsions in feed sludges. At about 40-50^{O}F, both oil and water dissolve in this solvent to form a single-phase liquid from which solvent-wet solids are readily separated, When the single liquid phase is heated to

120-130°F, phase separation of two liquids occurs, one of oil and solvent, the other of water with some dissolved solvent.

The basic steps in the process, shown in Figure 4-1 are:

1. extraction of oil and water from the solids at approximately 50°F;
2. drying of the solids to remove residual solvent and water;
3. heating of the single-phase-liquid effluent from the contractor to about 120°F to bring about separation into two liquid phases;
4. distillation of the decanted water phase to remove solvent for recycle; and
5. distillation of the decanted solvent/oil mixture to recover solvent for recycle.

While not demonstrated as yet by operation within a petroleum refinery, it is anticipated that oil, water and solids products can fit readily into the operation of a petroleum refinery. "Product Oil" from the solvent extraction unit can be recycled to the refinery oil processing units with precise location of the recycle depending on the oil quality and the refinery processing scheme. The "product water" stream can be recycled to the refinery's wastewater treatment system. Solids could be disposed of in a variety of ways, depending on whether they can be delisted, solids could be land disposed as either pre-treated hazardous waste or as delisted non-hazardous waste.

Operating Parameters Affecting Performance: The key process elements of the solvent extraction process are the following:

- Sludge composition and characteristics
- Sludge preparation
- Solvent mixing/extraction
- Solids separation

- Solids drying
- Solvent/water decanting
- Solvent recovery
- Water stripping

Specific process parameters or conditions that were used in the test are discussed in the next section.

TEST PROCEDURES

The testing of the solvent extraction process was done at the process vendor's pilot unit. The single largest difference between pilot and commercial operation is that the pilot process is a series of batch processes. Each process step was performed in sequence as process streams were moved from one piece of equipment to the next. Pilot operation was the only way possible to test the process on refinery waste, since the only existing commercial unit was at a Superfund site rather than at a refinery.

Drum size samples of API separator sludge (KO51) and slop oil emulsion solids (K049) were received, from Refinery D, at the pilot unit. After separately mixing each drum, equal parts of each waste were blended to form the feed sample for this test.

Table 4-1 can be used to compare the test conditions used in the pilot unit to treat the mixture of refinery wastes to the process conditions of the commercial unit used for sludge treatment at the Superfund site. The parameters compared are those which the process developer considers "the key process elements".

Sludge Preparation

This involves two steps, screening and neutralization. In full scale operation, the feed material is screened to separate

TABLE 4-1

TEST PARAMETERS FOR PILOT AND COMMERCIAL SOLVENT EXTRACTION UNITS

KEY STEPS	PARAMETERS	PILOT TEST ON API SAMPLE	COMMERCIAL OPERATION	COMMENTS
• Screening	Screen Size	1/16 inch	1/8 inch	Pilot scale required smaller particles
• Neutralization	pH	10 with NaOH	10 with NaOH	--
• Solvent Mixing/ Extraction	Solvent/Sludge	3/1	3/1, Over 20% Oil	API Feed 20.1% Oil
	Mixing Residence	1 hour/stage	1 hour/stage	
	Number of Stages	3 stages	2 or 3 Stages	Third pilot stage extraneous
• Solids Separation-Centrifuge	g-force	Similar to comercial	Varied to achieve less than 1% solids carryover	--
	Residence Time	Similar to comercial		
• Solids Drying	Residence Time	Oven Overnight	Continuous drier	Differences considered non-critical
	Temperature	220°F	250°F	
• Solvent/Water Decanting	Residence Time	1 hour	1 hour	--
	Temperature	140°F	140°F	
• Solvent Recovery	Equipment	Single unit 2 stages	Stripping/Polishing Towers	No critical change
	Temperature	170°F each stage	170°F each stage	
• Water Stripping	Feed/Steam	2.8/1.0	Same as pilot	--
	Overhead Temperature	210°F	Same as pilot	
	Sump Temperature	215°F-220°F	Same as pilot	

particles larger than 1/8 inch (to avoid damage to the downstream centrifuge) and caustic soda is used to adjust feed pH to about 10. Screening for the API test sample was to 1/16 inch (to accommodate smaller, pilot scale equipment) and the feed was neutralized to the same pH in the same way. The screening size difference was judged to have no scaleup importance.

Solvent Mixing/Extraction

The important process parameters have been found to be: 1) solvent/sludge ratio; 2) residence time; and 3) number of extraction stages. For the commercial unit, a solvent/sludge ratio of 3:1 by weight was used for sludges containing more than 20 wt.% oil, and the same ratio was used for the API pilot study.

Residence time, at both the full scale and pilot units, was about one hour in each extraction stage. In the full scale plant, two or three extraction stages were used depending on feed character and product requirements. Three stages were used for the API sample pilot test. Analytical data indicated that the third stage was extraneous.

Solids Separation

The phase separation following extraction is accomplished, in the full scale plant, in a solid bowl, decanter-type centrifuge. Operating conditions in the plant are adjusted to optimize liquid phase quality, with a readily achieved target of less than 1% solids carry over. The pilot solid bowl centrifuge operated with comparable g-force and residence time and less than 1% solids carry over.

Solids Drying

In the full scale unit, solids are dried in an externally heated, torus-disc-type, continuous flow drier, operating at 250°F with a target of less than 500mg/kg of residual solvent. For the pilot test, the wet solids were held overnight in an oven at 220°F. The target level of residual solvent was reached and the process difference is considered negligible based on vendor experience.

Solvent/Water Decanting

The two key variables affecting performance are residence time and temperature. In both full scale and pilot scale systems, these parameters were one hour and 140°F respectively.

Solvent Recovery

In the full scale plant, this is accomplished in two steps; gross recovery solvent stripping, followed by a solvent evaporation polishing step. Both steps run at about 170°F, the boiling point of the solvent/water azeotrope. In the pilot unit, both steps occur in sequence in a single distillation unit, first operated as a reboiled stripper and then as a steam stripper. Overhead temperature for both steps was 170°F.

Water Stripping

The water stripper in the full scale system is a steam stripping column. Key variables are steam rate, overhead temperature and sump temperature. Control of these variables are at: 2.8:1 feed/steam (lb/lb), 210°F overhead and 215-220°F bottoms. A small version of the same system was used for the pilot test.

TEST RESULTS AND DISCUSSION

The following data were obtained from the solvent extraction test:

- Oil, water and solids concentrations in the waste feed, product oil, product water and product solids.
- Indicator compound screening analyses on the feed and products.
- Indicator compound screening analyses on the TCLP leachate from the feed and product solids.

The results were correlated and presented to allow evaluation of the effectiveness of the solvent extraction process in reducing environmental hazards. The following methods of evaluation are available:

1. The concentrations of the indicator compounds in the waste feed and product solids are presented.

2. Using a calculated mass balance (based on oil/water/solids analyses) and the constituent concentrations in feed and product solids, "Percent Reduction, Weight" was calculated. A Percent Reduction, Weight of >99% shows that the product solids contain less than 1% of the weight of compound in the waste feed.

3. The concentrations of indicator compounds in the TCLP leachate from the waste feed and the product solids are given.

4. Percent Reduction, Leachate Analysis has been calculated.

Table 4-2 presents oil, water and solids concentrations for the waste feed and the three treatment products, the product oil stream, the product water stream and the product solids. The oil, water and solids analyses were normalized to add up to 100%. Notable in this table are the relative purities of the respective streams. This purity in the oil and solids streams is much higher

TABLE 4-2

OIL/WATER/SOLIDS CONCENTRATIONS OF SOLVENT EXTRACTION FEED AND PRODUCTS

Parameter	Waste Feed	Products Oil	 Water	 Solids
Lab I.D.	62587-01	62686-03	62686-01	62686-02
Oil, %	20	97	0.006	1.4
Water, %	60	2.2	100	0.1
Solids, %	20	0.4	0.030	98
Total, %	100	100	100	100

than that which was achieved by mechanical treatment as documented in Chapter 3.

Using oil, water and solids concentrations in Table 4-2, the material balance in Table 4-3 was calculated.

Table 4-3 was put to use in developing Table 4-4. In Table 4-4, the first columns show the concentrations in waste feed and product solids of the screening analysis indicator compounds. The last column is the calculated, "Percent Reduction, Weight," which gives the <u>weight</u> reduction of each compound from feed to product solids. Arithmetically this is as follows:

$$\text{\% Reduction, Weight of benzene} = 100\% \times \left[\frac{\begin{bmatrix}\text{ppm of compound}\\ \text{in feed} = 600\end{bmatrix} - \begin{bmatrix}\text{ppm of compound}\\ \text{in cake} = 1.3\end{bmatrix}\begin{bmatrix}\text{weight of cake as a}\\ \text{fraction of feed} = 0.21\end{bmatrix}}{\text{ppm of compound in feed} = 600} \right]$$

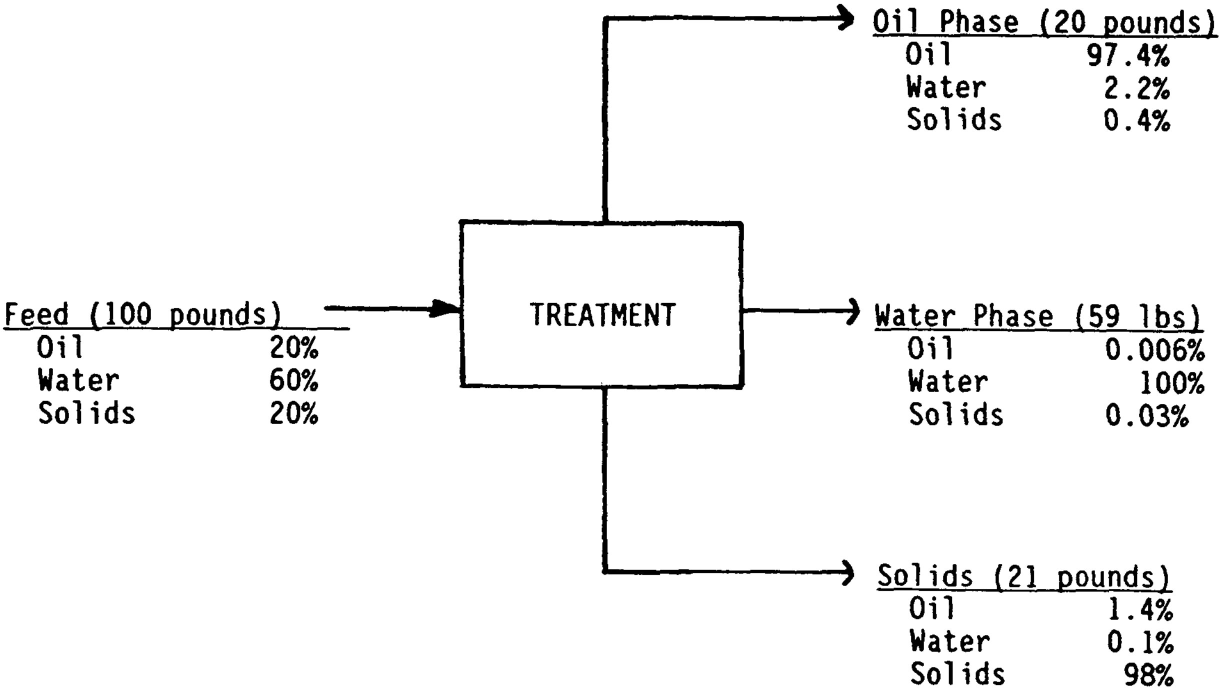
$$= >99\%$$

Inspection of Table 4-4 shows that all of the organic compounds which were present in the feed in detectable quantities have been drastically reduced in concentration--while not shown, the reduction in concentration is more than 99%--and reduced in weight by more than 99%.

The indicator metals concentrations move quite differently. As shown in Table 4-1, the feed is brought to a pH of 10 before extraction effectively placing most metals in the solid phase. The relatively high concentration levels in the product solids can be anticipated--the fact that there is a weight increase shown is an indication of sampling and analysis discrepancies.

TABLE 4-3

CALCULATED MASS BALANCE
BASED ON OIL/WATER/SOLIDS ANALYSES
SOLVENT EXTRACTION



- Weight of Cake as a Fraction of Feed = 0.21
- Oil Recovery = 98%

TABLE 4-4

CONSTITUENT CONCENTRATIONS IN FEED AND PRODUCT SOLIDS AND CALCULATED % REDUCTION (WEIGHT) -- SOLVENT EXTRACTION

Parameter	Constituent Concentrations, mg/kg*** Waste Feed	Constituent Concentrations, mg/kg*** Product Solids	% Reduction, Weight*
Lab I.D.	62587-01	62686-02	
Volatile Organics			
Benzene	600	1.3	>99
Toluene	6600	5.0	>99
Xylenes	8880	4.4	>99
PNA's and Phenols			
Anthracene	ND (46)	ND (0.001)	
Chrysene	ND (19)	ND (0.001)	
Naphthalene	560	0.005	>99
Phenanthrene	740	0.005	>99
Phenols	ND (1900)	ND (0.10)	
Metals			
Chromium	220	1250	**
Lead	27	260	**

ND : Not detected.
Detection limit in parentheses.

* % Reduction (Weight) : See text for calculation.
** Increase.
*** Indicator Compound Screening Analysis : It measures total xylenes and total phenols (sum of phenol, cresols and 2,4 dimethylphenol).

The final data table is Table 4-5. The first columns show the concentrations of indicator compounds in the TCLP leachate produced from the waste feed and product solids. The final column is the calculated, "Percent Reduction, Leachate Analysis," which is derived arithmetically as follows:

% Reduction, Weight of chromium =

$$100\% \times \left[\frac{\begin{bmatrix}\text{ppm compound in TCLP}\\ \text{of feed} = 0.39\end{bmatrix} - \begin{bmatrix}\text{ppm compound in TCLP of}\\ \text{product solids} = 0.11\end{bmatrix}}{\text{ppm of compound in TCLP of feed} = 0.39}\right]$$

$$= 71.79\% \cong 72\%$$

The concentrations of organic compounds in the leachate have been reduced by more than 99%, a reflection of the drastically lowered organic concentrations in the solids, plus a tendency for sorption on the solids.

The concentrations of chromium and lead in the leachate are reduced by 72% and 89%, a reflection of the lowered solubility of the metals.

TABLE 4-5

TCLP LEACHATE CONCENTRATIONS OF WASTE FEED AND PRODUCT SOLIDS -- SOLVENT EXTRACTION

	TCLP Levels, mg/L**		% Reduction, Leachate Analysis*
Parameter	Waste Feed	Product Solids	
Lab I.D.	62587-01	62686-02	
Volatile Organics			
Benzene	42	0.005	>99
Toluene	240	0.008	>99
Xylenes	320	0.01	>99
PNA's and Phenols			
Anthracene	ND (0.84)	ND (0.005)	
Chrysene	ND (4.2)	ND (0.005)	
Naphthalene	59	0.007	>99
Phenanthrene	75	ND (0.005)	>99
Phenols	ND (420)	ND (0.05)	
Metals			
Chromium	0.39	0.11	72
Lead	0.47	0.05	89

ND : Not detected.
Detection limit in parentheses.

* % Reduction, Leachate Analysis; See text for calculation.

** Indicator Compound Screening Analysis : It measures total xylenes and total phenols (sum of phenol, cresols and 2,4 dimethylphenol).

CHAPTER 5. **THERMAL TREATMENT**

INTRODUCTION

Thermal treatment of petroleum refinery wastes removes water and volatile organics from oil-water-solids mixtures by heating the mixture and causing vaporization. The feed stock for a thermal treatment unit could be a raw waste or a filter cake from a mechanical treatment process.

Figure 5-1 shows a simplified diagram of a general thermal treatment process as might be used in the treatment of refinery oily sludges. Heat introduced to the thermal processor vaporizes volatile organics and water, so that the discharged product solids have a reduced content of these vaporized materials. The vaporized materials are condensed and then gravity separated in a condensate/decanter drum from which the product water and product oil phases are withdrawn.

OVERVIEW

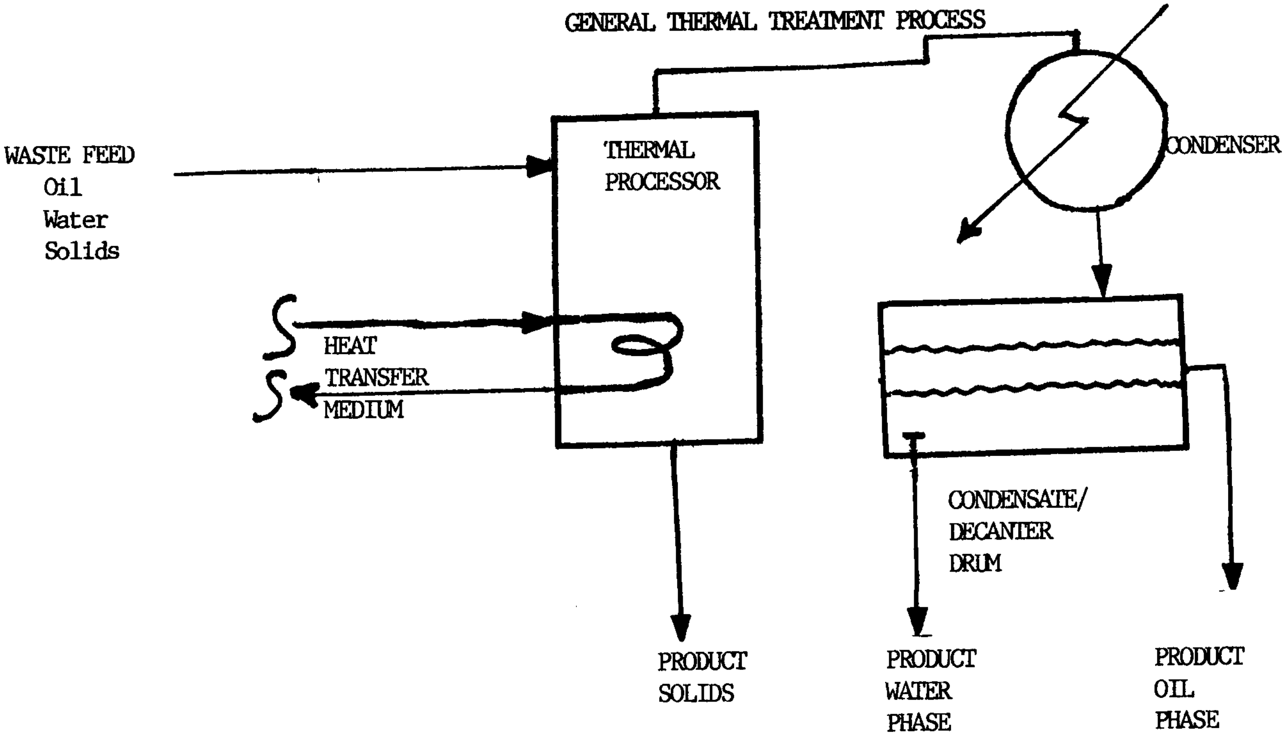
Thermal treatment is demonstrated to be highly effective in removing the volatile organics from the process feed and in accomplishing an overall reduction of waste volume by also reducing water content of the waste.

API's thermal treatment tests used two types of filter cake as feed to the thermal processor. Raw wastes can also be used as feed to thermal treatment. The choice of feedstock would be based on economic evaluation, and would very much depend on the specific site for which the choice was being made.

Integration of thermal treatment into a petroleum refinery should be no problem. Oil and water product streams are readily

FIGURE 5-1

GENERAL THERMAL TREATMENT PROCESS



integrated into the normal oil recycle system and the wastewater treatment system. Product solids are particularly suited to land disposal since the volatile organic materials have been almost completely removed.

DISCUSSION--EQUIPMENT DESCRIPTION AND OPERATION

The screw-flight drier was tested in this program as an example of thermal treatment. This equipment is useful to transfer heat to viscous and solids-containing materials. These units have been used for mineral processing, food processing, and drying of pulp/paper and municipal sludges.

Underlying Principles of Operation

The processor consists of a jacketed trough within which are a hollow screw (or screws) driven by a hollow shaft. Heat transfer fluid circulates through the screw flights, screw shaft and trough jacket. The screw, besides providing heat transfer surface, moves the feed sludge through the processor and provides good contacting between the sludge and the heat transfer surfaces. The unit can include breaker bars to enhance the mixing action and minimize fouling of the screws and hot surfaces.

The remainder of the system, water-cooled condenser and condensate/decanter drum, are of conventional design.

While not demonstrated as yet, it is anticipated, that a screw-flight drier can fit readily into the operation of a petroleum refinery.

Operating parameters affecting performance: The critical operating parameters of the screw-flight drier are:

- Sludge composition and characteristics
  - Volatiles and water concentrations
  - Viscosity of both feed and product
  - Tendency to bridge, stick, foul: general, "transportability" of feed and product
  - Foaming tendency
  - Dusting or fines carry over characteristics
- Hot side temperature
- Retention time of sludge in the processor.

TEST PROCEDURES

Testing of the thermal treatment process was done at the equipment vendor's pilot unit. The pilot operation is considered to be suitable for evaluation and design scale up to commercial equipment including drying rates, heat transfer coefficients, handling characteristics, retention time and horsepower requirements. Drum sized quantities of filter cake from the belt filter at refinery C1 and the plate filter at refinery B1 were used in the pilot unit for batch tests. Two tests were performed on each filter cake. In the first test on each feed, the temperature of hot oil entering the processor was held at 400-450^{o}F (nominally 400^{o}F). In the second test, hot oil temperature was maintained at 580-680^{o}F (nominally 650^{o}F). Lower temperature tests ran for about 50 minutes, higher temperature tests for about 40 minutes. Feed charged was 120-150 pounds for each test.

Vaporized hydrocarbons and water were condensed, separated into phases, weighed and sent for analysis. Dried cake was collected, weighed and sent for analysis.

The pilot unit screw-flight drier was about four feet long. Heat transfer oil was heated in an external fired heater and circulated by pump. The vapors from the drier were vented to an eight inch diameter overhead line and then to a water cooled condenser. Condensate was collected in buckets, then the phases were separated and measured.

During the testing it was noted that the product solids from the belt-filter cake feed became a semisolid, pasty material which might be difficult to discharge from the drier. In contrast, the product solids derived from drying plate filter cake were a free flowing solid. The equipment vendor recommended that, for a commercial operation, sand should be mixed with any feed which resulted in a sticky, pasty consistency after thermal treatment.

Table 5-1 shows the oil, water, and solids concentrations in the product solids from the four test runs. The oil to solids ratio column readily explains the difference in product solids characteristics. Belt cake derived material had oil to solids ratios of 0.82 and 0.92 indicative of product with high residual oil content. Plate filter material had oil to solids ratios of 0.13 and 0.08, which indicates a relatively low oil content.

For most effective use of this technology, proper selection of mixed wastes as feed to the drier will be necessary.

TEST RESULTS AND DISCUSSION

The following methods of data correlation and presentation are used to allow evaluation of the effectiveness of thermal treatment in reducing environmental hazards.

1. The concentration of a wide array of Appendix VIII compounds in the thermal treatment feed and product solids are presented.

2. Using a measured mass balance--feed and products were collected and weighed at the pilot unit--and the

TABLE 5-1

OIL/WATER/SOLIDS CONCENTRATIONS OF PRODUCT SOLIDS FROM THERMAL TREATMENT TESTS

THERMAL TREATMENT CAKES	PRODUCTS, %			OIL TO SOLIDS RATIO
	OIL	WATER	SOLIDS	
Dried Belt Filter Cake (Low Temperature)	41.6	10.4	51.0	0.82 *
Dried Belt Filter Cake (High Temperature)	47.5	0.1	51.6	0.92 *
Dried Plate Filter Cake (Low Temperature)	10.2	16.0	77.4	0.13 **
Dried Plate Filter Cake (High Temperature)	7.1	3.8	89.0	0.08 **

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* Belt filter dried product was observed to be "a semi-solid pasty material."

** Plate filter dried product was "a very free flowing solid."

constituent concentrations in feed and product solids, "Percent Reduction (Weight)" was calculated. This parameter measures the fraction of a compound removed from the feed. Thus a Percent Reduction (Weight) of 97% of a compound shows that the product solids contain 3% of the weight of compound in the feed.

3. The concentration of the (same) array of Appendix VIII compounds in the TCLP leachate from the feed and the product solids are given; and

4. The "Percent Reduction, Leachate Analysis" was calculated.

Table 5-2 through 5-5 present constituent concentration data and Tables 5-6 through 5-9 present TCLP data for the four tests--two feeds at two temperatures each. Before examining the data it is useful to consider what would be expected.

The thermal processor should be effective in removing much of the water and most of the volatile organic materials, percent removal varying with the boiling point of the material. Some heavier-than-expected organics will be removed due to steam distillation or stripping in the presence of water. Some of the lighter material may tend to be held by sorption on the solids.

It will also be useful to again record the calculation procedure for "Percent Reduction, Weight" and "Percent Reduction, Leachate Analysis" which are presented in the tables.

Using naphthalene in Table 5-2 as an example:

% Reduction, Weight of naphthalene =

$$100\%\ \text{x} \left[\frac{\begin{bmatrix}\text{ppm compound}\\ \text{in feed} = 82\end{bmatrix} - \begin{bmatrix}\text{ppm compound in}\\ \text{solids} = 120\end{bmatrix} \begin{bmatrix}\text{weight of cake as}\\ \text{fraction of feed} = 0.34\end{bmatrix}}{\text{ppm of compound in feed} = 82} \right]$$

= 50%

Note, weight of cake as a fraction of feed comes from pilot plant data, and is recorded at the bottom of Table 5-2.

Using naphthalene in Table 5-6 as an example:

% Reduction, Leachate Analysis of naphthalene =

$$100\%\ \text{x} \left[\frac{\begin{bmatrix}\text{ppm compound in}\\ \text{TCLP of feed} = 0.15\end{bmatrix} - \begin{bmatrix}\text{ppm compound in TCLP}\\ \text{of product solids} = 0.045\end{bmatrix}}{\text{ppm of compound in TCLP of feed} = 0.15} \right]$$

= 70%

With this introduction, the tables can be reviewed. Tables 5-2 through 5-5 are consistent in showing strong reduction of the concentrations and weights of the volatile organics--from 98 to more than 99% for the weight reductions. No other clear trends are seen. Sampling and analysis inconsistencies in sampling solid materials lead to a mixture of losses and gains in weight for the higher boiling organics and metals.

Tables 5-4 and 5-5 are closest to the theoretical showing; for the most part, there are limited reductions in weight of the heavier organics and little or no change for the metals.

A similar trend can be seen in Tables 5-6 through 5-9. Most of the volatile organics in the product TCLP leachate have been reduced to below detection limits. Where the compounds are found, the concentration is very low and the reductions over 90%.

Most of the other organics are either below detection limits or at low levels, but the removals are not as great, and are not always reductions. As expected, the metals show no trend.

TABLE 5-2

CONSTITUENT CONCENTRATIONS IN FEED AND PRODUCT SOLIDS
LOW TEMPERATURE THERMAL TREATMENT OF BELT FILTER CAKE FEED - REFINERY C1

	Constituent Concentrations, mg/kg		
Parameter	Waste Feed	Product Solids	% Reduction, (Weight)*
Lab I.D.	Average of 62409-10 & 62409-11	62583-30	
Volatile Organics			
Benzene	80	0.5	>99
Methyl ethyl ketone	BDL (12,50)	BDL (5.0)	
Styrene	BDL (12,5)	BDL (0.5)	
Ethylbenzene	86	BDL (0.5)	
Toluene	340	1.5	>99
Xylene, m	195	1.3	>99
Xylenes, o&p	235	1.2	>99
Base/Neutral Organics			
Anthracene	13.3	100	**
Benzo(a)anthracene	3.4	60	**
Benzo(b)fluoranthene	1.2	BDL (48)	
Benzo(a)pyrene	1.8	BDL (48)	
Bis(2-ethylhexyl)phthalate	1.1	BDL (48)	
Chrysene	9.4	81	**
Dibenz(a,h)anthracene	1.1	BDL (48)	
7,12-Dimethylbenz(a)anthracene	BDL (8,1)	BDL (48)	
Fluoranthene	BDL (8,1)	BDL (48)	
Indene	1.3	BDL (48)	
1-Methylnaphthalene	220	670	**
Naphthalene	82	120	50
Phenanthrene	109	720	**
Pyrene	26	200	**
Acid Organics			
o-Cresols	0.4	BDL (7.3)	
p & m-Cresol	1.3	BDL (7.3)	
2,4-Dimethylphenol	0.7	BDL (7.3)	
Phenol	0.9	BDL (7.3)	
Metals			
Arsenic	2.0	20	**
Barium	115	905	**
Cadmium	ND (2,2.5)	1.2	--
Chromium	340	2800	**
Lead	40	260	**
Mercury	0.2	NA	--
Selenium	ND (30,4)	ND (90)	--
Silver	ND (2,1.5)	NA	--

BDL : Below detection limit;
Detection limit in parentheses (one or two samples).
ND : Not detected.
NA : Not analyzed.
* % Reduction (Weight); See text for calculation.
** Increase.
Cake as fraction of feed = 0.34 (pilot unit data)

TABLE 5-3

CONSTITUENT CONCENTRATIONS IN FEED AND PRODUCT SOLIDS
HIGH TEMPERATURE THERMAL TREATMENT OF BELT FILTER CAKE FEED - REFINERY C1

	Constituent Concentrations, mg/kg		
Parameter	**Waste Feed**	**Product Solids**	**% Reduction, (Weight)***
Lab I.D.	Average of 62409-10 & 62409-11	62583-31	
Volatile Organics			
Benzene	80	BDL (0.05)	>99
Methyl ethyl ketone	BDL (12,50)	3.4	
Styrene	BDL (12,5)	0.09	
Ethylbenzene	86	0.12	>99
Toluene	340	1.2	>99
Xylene, m	195	0.17	>99
Xylenes, o&p	235	0.16	>99
Base/Neutral Organics			
Anthracene	13.3	96	**
Benzo(a)anthracene	3.4	70	**
Benzo(b)fluoranthene	1.2	29	**
Benzo(a)pyrene	1.8	44	**
Bis(2-ethylhexyl)phthalate	1.1	14	**
Chrysene	9.4	100	**
Dibenz(a,h)anthracene	1.1	21	**
7,12-Dimethylbenz(a)anthracene	BDL (8,1)	BDL (10)	
Fluoranthene	BDL (8,1)	56	
Indene	1.3	BDL (10)	
1-Methylnaphthalene	220	190	81
Naphthalene	82	15	96
Phenanthrene	109	590	**
Pyrene	26	200	**
Acid Organics			
o-Cresols	0.4	BDL (1)	
p & m-Cresol	1.3	19	**
2,4-Dimethylphenol	0.7	BDL (1)	
Phenol	0.9	12	**
Metals			
Arsenic	2.0	24	**
Barium	115	1100	**
Cadmium	ND (2,2.5)	2	
Chromium	340	3900	**
Lead	40	340	
Mercury	0.2	ND (0.05)	
Selenium	ND (30,4)	12	
Silver	ND (2,1.5)	--	

BDL : Below detection limit;
Detection limit in parentheses (one or two samples).
ND : Not detected.
* % Reduction, Weight; See text for calculation
** Increase.
Cake as fraction of feed = 0.215 (pilot unit data).

TABLE 5-4

CONSTITUENT CONCENTRATIONS OF WASTE FEED AND PRODUCT SOLIDS
LOW TEMPERATURE THERMAL TREATMENT OF PLATE FILTER CAKE FEED - REFINERY B1

	Constituent Concentrations, mg/kg		
Parameter	Waste Feed	Product Solids	% Reduction, (Weight)*
Lab I.D.	62291-06	62583-03	
Volatile Organics			
Benzene	60	BDL (1.5)	99
Methyl ethyl ketone	BDL (300)	BDL (1.5)	
Styrene	BDL (30)	BDL (1.5)	
Ethylbenzene	110	4.3	98
Toluene	360	8.3	99
Xylene, m	350	1.6	>99
Xylenes, o&p	340	1.6	>99
Base/Neutral Organics			
Anthracene	9.4	11	37
Benzo(a)anthracene	20	19	49
Benzo(b)fluoranthene	6.2	10	13
Benzo(a)pyrene	9.9	20	**
Bis(2-ethylhexyl)phthalate	BDL (1)	BDL (6.4)	
Chrysene	26	37	23
Dibenz(a,h)anthracene	BDL (1)	BDL (6.4)	
7,12-Dimethylbenz(a)anthracene	BDL (1)	BDL (6.4)	
Fluoranthene	5.9	13	**
Indene	BDL (1)	BDL (6.4)	
1-Methylnaphthalene	260	210	56
Naphthalene	90	42	75
Phenanthrene	47	120	**
Pyrene	22	92	**
Acid Organics			
o-Cresol	BDL (1)	BDL (0.64)	
p & m-Cresols	BDL (1)	BDL (0.64)	
2,4-Dimethylphenol	BDL (1)	BDL (0.64)	
Phenol	BDL (1)	1.2	
Metals			
Arsenic	7.0	ND (20)	
Barium	142	270	3
Cadmium	1	ND (4)	
Chromium	835	1400	9
Lead	126	240	
Mercury	2.9	NA	**
Selenium	ND (4)	ND (200)	
Silver	ND (0.6)	NA	

BDL : Below detection limit; NA : Not analyzed.
Detection limit in parentheses.
ND : Not detected.
* % Reduction (Weight) : See text for calculation.
** Increase.
Cake as fraction of feed = 0.54 (pilot unit data).

TABLE 5-5

CONSTITUENT CONCENTRATIONS IN FEED AND PRODUCT SOLIDS
HIGH TEMPERATURE THERMAL TREATMENT OF PLATE FILTER CAKE FEED - REFINERY B1

Parameter	Constituent Concentrations, mg/kg		% Reduction, (Weight)*
	Waste Feed	Product Solids	
Lab I.D.	62291-06	62583-04	
Volatile Organics			
Benzene	60	0.17	>99
Methyl ethyl ketone	BDL (300)	BDL (1.3)	
Styrene	BDL (300)	BDL (0.13)	
Ethylbenzene	110	0.51	>99
Toluene	360	1.0	>99
Xylene, m	350	1.7	>99
Xylenes, o&p	340	1.7	>99
Base/Neutral Organics			
Anthracene	9.4	4.1	80
Benzo(a)anthracene	20	17	60
Benzo(b)fluoranthene	6.2	11	17
Benzo(a)pyrene	9.9	16	24
Bis(2-ethylhexyl)phthalate	BDL (1)	BDL (1)	
Chrysene	26	28	49
Dibenz(a,h)anthracene	BDL (1)	BDL (1)	
7,12-Dimethylbenz(a)anthracene	BDL (1)	BDL (1)	
Fluoranthene	5.9	4.6	63
Indene	BDL (1)	BDL (1)	
1-Methylnaphthalene	260	27	95
Naphthalene	90	4.6	98
Phenanthrene	47	2.6	74
Pyrene	22	16	68
Acid Organics			
o-Cresol	BDL (1)	BDL (1)	
p & m-Cresols	BDL (1)	BDL (1)	
2,4-Dimethylphenol	BDL (1)	BDL (1)	
Phenol	BDL (1)	1.0	
Metals			
Arsenic	7.0	16	**
Barium	142	350	**
Cadmium	1	4	**
Chromium	835	1700	4
Lead	126	260	3
Mercury	2.9	0.72	88
Selenium	ND (4)	ND (8)	
Silver	ND (0.6)	NA	

BDL : Below detection limit; Detection limit in parentheses.

NA : Not analyzed.

ND : Not detected.

* % Reduction (Weight); See text for calculation.

** Increase.

Cake as fraction of feed = 0.47 (pilot unit data).

TABLE 5-6

TCLP Leachate Concentrations of Waste Feed and Low Temperature (350°F) Thermally Treated Belt Cake - Refinery C1

Parameter	TCLP Levels, mg/L		% Reduction Leachate Analysis*
	Waste Feed	Thermally Treated Belt Cake (350°F)	
Lab. I.D.	Average of 62409-10 and 62409-11	62583-30	
Volatile Organics			
Benzene	1.1	BDL (0.005)	>99
Methyl ethyl ketone	BDL (0.40)	BDL (0.05)	
Styrene	BDL (0.06)	BDL (0.005)	
Ethylbenzene	0.21	BDL (0.005)	>97
Toluene	2.6	BDL (0.005)	>99
Xylene, m	0.76	BDL (0.005)	>99
Xylenes, o & p	0.84	BDL (0.005)	>99
Base/Neutral Organics			
Anthracene	BDL (0.012)	BDL (0.01)	
Benzo(a)anthracene	BDL (0.012)	BDL (0.01)	
Benzo(b)fluoranthene	BDL (0.012)	BDL (0.01)	
Benzo(a)pyrene	BDL (0.012)	BDL (0.01)	
Bis(2-ethylhexyl)phthalate	BDL (0.012)	BDL (0.01)	
Chrysene	BDL (0.012)	BDL (0.01)	
Dibenz(a,h)anthracene	BDL (0.012)	BDL (0.01)	
7,12-Dimethylbenz(a) anthracene	BDL (0.012)	BDL (0.01)	
Fluoranthene	BDL (0.012)	BDL (0.01)	
Indene	BDL (0.012)	BDL (0.01)	
1-Methylnaphthalene	0.11	0.095	13
Naphthalene	0.15	0.045	70
Phenanthrene	BDL (0.012)	0.013	((8))
Pyrene	BDL (0.012)	BDL (.01)	
Acid Organics			
o-Cresol	0.03	BDL (.01)	>66
p & m-Cresol	0.08	0.044	45
2,4-Dimethylphenol	0.05	0.011	80
Phenol	0.039	0.013	67
Metals			
Arsenic	ND (0.01)	0.005	
Barium	1.0	ND (0.6)	>39
Cadmium	ND (0.02)	ND (0.01)	
Chromium	ND (0.025)	0.1	((300))
Lead	ND (0.1)	ND (0.04)	
Mercury	ND (.001)	ND (.001)	
Selenium	ND (0.3)	0.004	
Silver	ND (0.02)	ND (0.004)	

BDL: Below detection limit.
Detection limit in parentheses.

ND: Not detected.
Percent increase in double parentheses.

* % Reduction, Leachate Analysis; See text for calculation.

TABLE 5-7

TCLP Leachate Concentrations of Waste Feed and High Temperature (550°F) Thermally Treated Belt Cake - Refinery C1

Parameter	TCLP Levels, mg/L Waste Feed	 Thermally Treated Belt Cake (550°F)	% Reduction, Leachate Analysis*
Lab. I.D.	Average of 62409-10 and 62409-11	62583-31	
Volatile Organics			
Benzene	1.1	BDL (0.05)	>95
Methyl ethyl ketone	BDL (0.40)	BDL (0.01)	
Styrene	BDL (0.06)	BDL (0.05)	
Ethylbenzene	0.21	BDL (0.05)	>76
Toluene	2.6	BDL (0.05)	>98
Xylene, m	0.76	BDL (0.05)	>93
Xylenes, o & p	0.84	BDL (0.05)	>94
Base/Neutral Organics			
Anthracene	BDL (0.012)	BDL (0.015)	
Benzo(a)anthracene	BDL (0.012)	BDL (0.015)	
Benzo(b)fluoranthene	BDL (0.012)	BDL (0.015)	
Benzo(a)pyrene	BDL (0.012)	BDL (0.015)	
Bis(2-ethylhexyl)phthalate	BDL (0.012)	BDL (0.015)	
Chrysene	BDL (0.012)	BDL (0.015)	
Dibenz(a,h)anthracene	BDL (0.012)	BDL (0.015)	
7,12-Dimethylbenz(a) anthracene	BDL (0.012)	BDL (0.015)	
Fluoranthene	BDL (0.012)	BDL (0.015)	
Indene	BDL (0.012)	BDL (0.015)	
1-Methylnaphthalene	0.11	0.23	((109))
Naphthalene	0.15	0.13	13
Phenanthrene	BDL (0.012)	0.03	((150))
Pyrene	BDL (0.012)	BDL (0.015)	
Acid Organics			
o-Cresol	0.03	0.089	((197))
p & m-Cresol	0.08	0.24	((200))
2,4-Dimethylphenol	0.05	0.056	((12))
Phenol	0.039	0.045	((15))
Metals			
Arsenic	ND (0.01)	ND (0.04)	
Barium	1.0	0.57	43
Cadmium	ND (0.02)	ND (.008)	
Chromium	ND (0.025)	0.04	((60))
Lead	ND (0.1)	ND (.04)	
Mercury	ND (.001)	NA	
Selenium	ND (0.3)	ND (0.1)	
Silver	ND (0.02)	ND (.006)	

BDL: Below detection limit. Detection limit in parentheses.
ND: Not detected. NA: Not analyzed.
Percent increase in double parentheses.

% Reduction, Leachate Analysis; See text for calculation.

TABLE 5-8

TCLP Leachate Concentrations of Waste Feed and Low Temperature (350°F) Thermally Treated Plate Cake - Refinery B1

	TCLP Levels, mg/L		% Reduction, Leachate Analysis*
Parameter	Waste Feed	Thermally Treated Plate Cake (350°F)	
Lab. I.D.	62291-06	62583-03	
Volatile Organics			
Benzene	0.8	0.014	98
Methyl ethyl ketone	BDL (1.2)	BDL (0.10)	
Styrene	BDL (0.12)	BDL (0.01)	
Ethylbenzene	0.22	0.016	93
Toluene	2.2	0.084	96
Xylene, m	0.69	0.053	92
Xylenes, o & p	0.73	0.057	92
Base/Neutral Organics			
Anthracene	BDL (0.002)	BDL (0.01)	
Benzo(a)anthracene	BDL (0.002)	BDL (0.01)	
Benzo(b)fluoranthene	BDL (0.002)	BDL (0.01)	
Benzo(a)pyrene	BDL (0.002)	BDL (0.01)	
Bis(2-ethylhexyl)phthalate	BDL (0.002)	BDL (0.01)	
Chrysene	BDL (0.002)	BDL (0.01)	
Dibenz(a,h)anthracene	BDL (0.002)	BDL (0.01)	
7,12-Dimethylbenz(a) anthracene	BDL (0.002)	BDL (0.01)	
Fluoranthene	BDL (0.002)	BDL (0.01)	
Indene	0.015	BDL (0.01)	>33
1-Methylnaphthalene	0.13	0.09	31
Naphthalene	0.16	0.06	62
Phenanthrene	0.004	BDL (0.01)	((15))
Pyrene	BDL (0.002)	BDL (0.01)	
Acid Organics			
o-Cresol	0.021	0.018	15
p & m-Cresol	0.032	0.063	((97))
2,4-Dimethylphenol	0.008	0.033	((312))
Phenol	0.095	0.16	((68))
Metals			
Arsenic	0.004	0.01	((150))
Barium	0.57	0.8	((40))
Cadmium	ND (0.02)	ND (0.1)	
Chromium	ND (0.025)	ND (0.025)	
Lead	ND (0.1)	ND (0.1)	
Mercury	ND (.001)	ND (0.001)	
Selenium	ND (0.004)	ND (0.004)	
Silver	ND (0.015)	ND (0.015)	

BDL: Below detection limit.
ND: Not detected.
NA: Not analyzed.

Detection limit in parentheses.
Percent increase in double parentheses.

* % Reduction, Leachate Analysis; See text for calculation.

TABLE 5-9

TCLP Leachate Concentrations of Waste Feed and High Temperature (550°F) Thermally Treated Plate Cake - Refinery B1

Parameter	TCLP Levels, mg/L		% Reduction, Leachate Analysis*
	Waste Feed	Thermally Treated Plate Cake (550°F)	
Lab. I.D.	62291-06	62583-04	
Volatile Organics			
Benzene	0.8	BDL (0.025)	>96
Methyl ethyl ketone	BDL (1.2)	BDL (0.05)	
Styrene	BDL (0.12)	BDL (0.025)	
Ethylbenzene	0.22	BDL (0.025)	>88
Toluene	2.2	0.033	99
Xylene, m	0.69	BDL (0.025)	>96
Xylenes, o & p	0.73	BDL (0.025)	>96
Base/Neutral Organics			
Anthracene	BDL (0.002)	BDL (0.005)	
Benzo(a)anthracene	BDL (0.002)	BDL (0.005)	
Benzo(b)fluoranthene	BDL (0.002)	BDL (0.005)	
Benzo(a)pyrene	BDL (0.002)	BDL (0.005)	
Bis(2-ethylhexyl)phthalate	BDL (0.002)	0.012	
Chrysene	BDL (0.002)	BDL (0.005)	
Dibenz(a,h)anthracene	BDL (0.002)	BDL (0.005)	
7,12-Dimethylbenz(a) anthracene	BDL (0.002)	BDL (0.005)	
Fluoranthene	BDL (0.002)	BDL (0.005)	
Indene	0.015	BDL (0.005)	>66
1-Methylnaphthalene	0.13	0.009	93
Naphthalene	0.16	0.012	93
Phenanthrene	0.004	BDL (0.005)	((25))
Pyrene	BDL (0.002)	BDL (0.005)	
Acid Organics			
o-Cresol	0.021	0.019	9
p & m-Cresol	0.032	0.11	((244))
2,4-Dimethylphenol	0.008	BDL (0.005)	>37
Phenol	0.095	0.084	12
Metals			
Arsenic	0.004	ND (0.1)	
Barium	0.57	1.3	((128))
Cadmium	ND (0.02)	0.02	
Chromium	ND (0.025)	ND (0.025)	
Lead	ND (0.1)	ND (0.1)	
Mercury	ND (.001)	NA	
Selenium	ND (0.004)	ND (0.3)	
Silver	ND (0.015)	ND (0.02)	

BDL: Below detection limit.
ND: Not detected.
NA: Not analyzed.

Detection limit in parentheses.
Percent increase in double parentheses.

% Reduction, Leachate Analysis; See text for calculation.

CHAPTER 6. FIXATION

INTRODUCTION

Fixation processes generally involve the treatment of wastes with cement, silicates and/or lime-based materials to form a solid or semisolid product. The processes are well proven for sludges containing heavy metals, such as electroplating (F006) sludges. These processes have been called stabilization, solidification, or encapsulation. The term "fixation" will be used here for simplicity.

OVERVIEW

Unlike all of the other classes of treatment included in this project, fixation does not remove any of the hazardous materials present in a waste, does not recover any oil that can be reclaimed/recycled into the refinery operation, and does not reduce the volume of waste to be disposed. Rather, fixation changes the physical, and sometimes chemical, characteristics of the waste to reduce leachability. Volume and weight of material requiring disposal typically increases anywhere from 10% to 100%.

Fixation Process Number 1, which claims to be effective in encapsulating/fixing a hazardous wastes containing organics as well as inorganics, shows effectiveness in reducing leachability of the volatile organics. As seen in Tables 6-1, 6-2 and 6-3, except for one reduction of 65%, the reduction in volatile organics in the TCLP leachate was 92-99%. It is uncertain whether the volatiles are actually fixed or lost during fixation.

Effectiveness for other organics and the metals is inconsistent.

The data for Process Number 2 and Process Number 3 are inconsistent and insufficient to allow drawing strong conclusions.

Fixation technologies continue to change and develop and should be considered a tool for use when effectiveness can be demonstrated in meeting required performance standards.

DISCUSSION--PROCESS DESCRIPTION AND OPERATION

Fixation Process Number 1

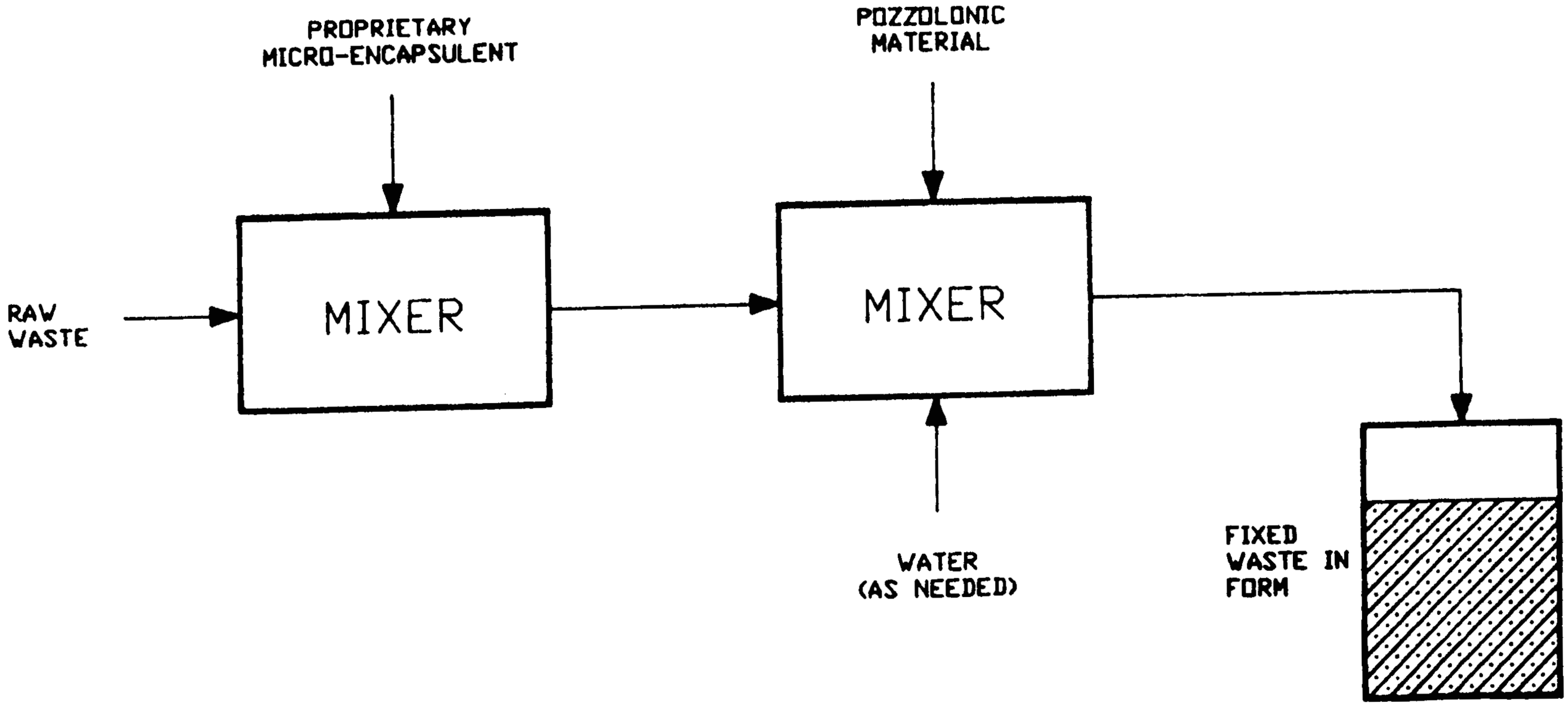
Applicability: This fixation process has potential applicability for stabilizing both the organic and inorganic components of raw petroleum refinery wastes.

Underlying principles of operation: A schematic diagram is shown in Figure 6-1. The first step involves the addition of a proprietary chemical (PC) to disperse and microencapsulate the hydrocarbons in the sludge. The organics are claimed to be surrounded by the PC and entrapped. The second step involves the addition of cementitious material (e.g. fly ash, cement, and kiln dust) to fix and solidify the entire waste. Reportedly, fly ash works best with petroleum refinery wastes. The resultant hardened mass can attain high compressive strengths of 1,000 to 5,000 psi, and can have permeabilities of 10^{-2} to 10^{-9} cm/sec. This process can be applied over a temperature range of -20°F to 200°F.

Fixation Process Number 2

Applicability: This process is one of the oldest fixation processes available commercially. It has been used to treat liquids and solids from a wide variety of industries including primary metals, metal finishing, chemical, petrochemical, and automotive. The process has gained considerable acceptance for fixation of municipal sewage and industrial wastewater treatment plant sludges.

FIGURE 6-1
TWO-STEP SOLIDIFICATION PROCESS



Underlying Principles of Operation: Water soluble silicates are reacted with complex cations in the presence of a silicone setting agent. The proprietor claims at least two general types of reactions occur.

(1) Amorphous, colloidal silicates precipitate. These silicates are extremely complex and the chemical formulae will vary depending at least upon: pH, availability and concentrations of cations, and temperature. All three parameters vary during the process resulting in a variety of silicates being formed. Silicate ions have the form of double, trigonal and tetragonal rings of the $(Si_6O_{15})^{-6}$, $(Si_8O_{20})^{-8}$, and $(Si_8O_{18}(OH)_2)^{-6}$ compositions.

(2) SiO_2 acts as a precipitating agent. The metallic precipitates are generally trapped within the physical structure developed during the formation of the amorphous colloids. The encapsulation of the particles tends to make them impermeable to water.

Fixation Process Number 3

Applicability: This fixation process is a demonstrated technology which claims the capability of reducing the leachability of a wide variety of hazardous industrial sludge wastes. The process has been in commercial use since 1974. This process is generally applied to inorganic sludges with a water content between 20 to 75% and an oil content of less than 10%.

Underlying principles of operation: In this process, hazardous waste sludges are treated with a mixture of cement, fly ash and lime. The proportions of the three reagents and the weight ratios of waste to total reagent are adjusted for each waste to achieve desired setting times, compressive strength and leachability of the final formulation.

Cement is typically prepared by heating a mixture of calcium carbonate and aluminum silicate in a kiln at high temperature to form a complex calcium-aluminum silicate. In the presence of water, the cement particles hydrate with the formation of a gel, and the growth of silica fibrils. As the particles swell and the fibrils interlock, a rigid solid mass is formed.

Adjustment of the ratios of calcium oxide (lime) and aluminum silicate, added in the form of fly ash, in the reaction mixture with water can impart improved properties to the final product. Lime additions aid in the precipitation of heavy metals as their hydroxides. These become entrapped in the cement matrix as it solidifies, with resultant reduced leachability.

The physical-chemical mechanisms which lead to waste fixation in cement-lime-fly ash systems are not easily determined. For each waste, therefore, the appropriate reagent mix must generally be established in bench scale tests, using the leachate characteristics of the end product as a measure of treatment effectiveness.

TEST PROCEDURES, RESULTS AND DISCUSSION

The following methods of data correlation and presentation are used to evaluate the effectiveness of fixation in reducing environmental hazards. The concentration of either an array of Appendix VIII compounds or a limited number of screening compounds in the TCLP leachate from the feed and from the fixed product are given, and the "Percent Reduction, Leachate Analysis" calculated.

Percent Reduction, Leachate Analysis of Naphthalene in Table 6-1 =

$$\left[\frac{\begin{bmatrix}\text{ppm compound in TCLP}\\ \text{of feed} = 10.2\end{bmatrix} - \begin{bmatrix}\text{ppm compound in TCLP}\\ \text{of product} = 0.16\end{bmatrix}}{\text{ppm compound in TCLP of feed} = 10.2}\right]$$

$= 98.4\,\% \cong 98\%$

Fixation process number 1: This treatment process was tested on API separator sludge, slop oil emulsion solids, plate filter cake from refinery B1, and belt filter cake from refinery C1.

To determine the optimum treatment for each waste, 50-g waste samples were mixed with different amounts of proprietary chemical (PC). These tests were conducted in 8-oz plastic cups. Proprietary chemical was first added to the waste in a 1:20 ratio by weight.

Depending on the consistency of the initial mixture of waste and proprietary chemical, a 1:30 or a 1:10 mixture was prepared. The 1:20 sample mixture or the one with the best consistency was then mixed with different cementitious materials. Ratios of waste/PC mixture to cementitious material are typically 1:1, 2:1, and 3:1. The sludge consistency dictates whether these selected ratios need further modification.

An an example, the test procedure for the filter cake from refinery B1 was as follows. A 50 g sample was placed in a plastic cup. Proprietary chemical was added at a 20:1 waste to proprietary chemical ratio. After a few minutes of mixing, a 1:1 ratio of kiln dust was added. Since the resultant blend was too dry, a second ratio was prepared. A 100 g sample was placed in a plastic cup and set on the balance. Liquid proprietary chemical, 5 g (20:1) was added to the sludge, and mixed well. A 2:1 ratio (50 g) of kiln dust was added to the mixture. As the kiln dust is mixed, more can be added to create the desired consistency. The sample was cured for 24 hours then tested for pH and compressive strength, and immersed in water to test the sample's integrity.

Test results are shown in Tables 6-1 and 6-2 for raw waste feeds, and in Tables 6-3 and 6-4 for plate and belt filter cake feeds, respectively.

It should be noted that the sample bottles with fixed raw feeds and fixed filter cakes were broken at the vendor's facilities by the vendor after being witnessed and sealed by an API task force member. This was prior to analysis being conducted by RMAL. The integrity of the samples can therefore not be guaranteed.

Fixation Process Number 2: This commercial fixation process is a continuous flow-through treatment system, but a batch/bench-scale test was used for the API study. In the process a series of chemical reactions takes place which involve the use of soluble sodium silicate and cementitious materials. The oxygen atoms in the silica tetrahedron bind salts and metals into the lattice work. It is claimed that organics are also trapped. The silicates give a high cation exchange capacity (CEC), which can trap polyvalent metal ions to produce stable and insoluble compounds. The exact ratios of the additives is predetermined by an independent laboratory and depends on the type and concentration of contaminants contained in the sludge.

Fixed waste is a soil-like material with an unconfined compressive strength that ranges from 2,000 to 10,000 pounds/square foot, and permeabilities from 1.0×10^{-6} to 1.0×10^{-7} cm/sec. It is resistant to erosion and is good for use as slope stability material; levees, berms, tank farm support material; landfill cover; and backfill material. Volume increase is claimed to be about 10%.

TABLE 6-1

TCLP Leachate Concentrations of API Separator Sludge and Residue from Fixation Process #1 - Refinery A

Parameter	TCLP Levels, mg/L API Separator Sludge	 Fixed Residue**	% Reduction, Leachate Analysis***
Lab. I.D.	62421-01	62607-02	
Volatile Organics			
Benzene	22	0.04	>99
Methyl ethyl ketone	BDL (30)	BDL (0.15)	
Styrene	BDL (3)	0.02	
Ethylbenzene	8	0.11	99
Toluene	28	0.24	99
Xylene, m	17	0.25	99
Xylenes, o & p	16	0.32	98
Base/Neutral Organics			
Anthracene	3.6	BDL (0.005)	>99
Benzo(a)anthracene	0.49	BDL (0.005)	>98
Benzo(b)fluoranthene	BDL (0.07)	BDL (0.005)	
Benzo(a)pyrene	0.38	BDL (0.005)	>98
Bis(2-ethylhexyl)phthalate	BDL (0.08)	BDL (0.005)	
Chrysene	0.99	BDL (0.005)	>99
Dibenz(a,h)anthracene	BDL (0.07)	BDL (0.005)	
7,12-Dimethylbenz(a) anthracene	BDL (0.07)	BDL (0.005)	
Fluoranthene	BDL (0.07)	BDL (0.005)	
Indene	1.6	0.01	99
1-Methylnaphthalene	18	0.13	99
Naphthalene	10.2	0.16	98
Phenanthrene	0.005-<0.06*	0.01	
Pyrene	1.2	BDL (0.005)	>99
Acid Organics			
o-Cresol	0.25	0.01	96
p & m-Cresol	0.8	0.01	99
2,4-Dimethylphenol	0.25	0.01	96
Phenol	2.4	0.03	98
Metals			
Arsenic	0.01	ND (0.002)	>79
Barium	1.3	1.9	((46))
Cadmium	ND (0.02)	ND (0.02)	
Chromium	0.89	ND (0.025)	>97
Lead	0.29-<0.069*	ND (0.1)	
Mercury	ND (0.001)	ND (0.001)	
Selenium	ND (0.045)	ND (0.02)	
Silver	ND (0.008)	ND (0.015)	

BDL: Below detection limit.
Detection limit in parentheses.

ND: Not detected.
Percent increase in double parentheses.

* Sample had separate oil phase; component was detected only one phase.

** Sample bottle of fixed raw feed was broken by the vendor after being witnessed and sealed by API task force member. This was done prior to analysis by RMAL. Results can, therefore, not be guaranteed.

*** % Reduction, Leachate Analysis; See text for calculation.

TABLE 6-2

TCLP Leachate Concentrations of Slop Oil Emulsion Solids and Residue from Fixation Process #1 - Refinery A

Parameter	TCLP Levels, mg/L Slop Oil Elmulsion Solids	 Fixed Residue*	% Reduction Leachate Analysis**
Lab. I.D.	62421-02	62607-01	
Volatile Organics			
Benzene	26	0.16	99
Methyl ethyl ketone	BDL (70)	BDL (0.35)	
Styrene	BDL (7)	0.06	
Ethylbenzene	27	0.13	99
Toluene	51	0.66	99
Xylene, m	50	0.29	99
Xylenes, o & p	51	0.34	98
Base/Neutral Organics			
Anthracene	BDL (0.003)	BDL (0.005)	
Benzo(a)anthracene	BDL (0.003)	BDL (0.005)	
Benzo(b)fluoranthene	BDL (0.003)	BDL (0.005)	
Benzo(a)pyrene	BDL (0.003)	BDL (0.005)	
Bis(2-ethylhexyl)phthalate	BDL (0.010)	BDL (0.005)	
Chrysene	BDL (0.003)	BDL (0.005)	
Dibenz(a,h)anthracene	BDL (0.003)	BDL (0.005)	
7,12-Dimethylbenz(a) anthracene	BDL (0.003)	BDL (0.005)	
Fluoranthene	BDL (0.003)	BDL (0.005)	
Indene	0.05	0.16	((220))
1-Methylnaphthalene	0.13	0.13	0
Naphthalene	0.27	0.22	19
Phenanthrene	0.01	0.01	0
Pyrene	BDL (0.003)	BDL (0.005)	
Acid Organics			
o-Cresol	0.05	0.07	((140))
p & m-Cresol	0.01	0.32	((3100))
2,4-Dimethylphenol	0.06	0.07	((17))
Phenol	0.02	0.94	((4600))
Metals			
Arsenic	ND (0.004)	0.01	
Barium	1.4	1.4	0
Cadmium	ND (0.008)	ND (0.02)	
Chromium	ND (0.01)	ND (0.025)	
Lead	ND (0.04)	ND (0.1)	
Mercury	ND (0.001)	ND (0.001)	
Selenium	ND (0.04)	ND (0.02)	
Silver	ND (0.006)	ND (0.015)	

BDL : Below detection limit. Detection limit in parentheses. Percent increase in double parentheses.

ND : Not detected.

* Sample bottle of fixed raw feed was broken by the vendor after being witnessed and sealed by API task force member. This was done prior to analysis by RMAL. Results can, therefore, not be guaranteed.

** % Reduction, Leachate Analysis; See text for calculation.

TABLE 6-3

TCLP Leachate Concentrations of Plate Filter Cake and Residue from Fixation Process #1 - Refinery B1

	TCLP Levels, mg/L		% Reduction, Leachate Analysis****
Parameter	Plate Cake	Fixed Residue*	
Lab. I.D.	62291-06**	62607-03***	
Volatile Organics			
Benzene	0.8	0.007	99
Methyl ethyl ketone	BDL (1.2)		
Styrene	BDL (0.12)		
Ethylbenzene	0.22		
Toluene	2.2	0.09	96
Xylene, m	0.69		
Xylenes, o & p	0.73	0.47	67
Base/Neutral Organics			
Anthracene	BDL (0.002)	ND (0.002)	
Benzo(a)anthracene	BDL (0.002)		
Benzo(b)fluoranthene	BDL (0.002)		
Benzo(a)pyrene	BDL (0.002)		
Bis(2-ethylhexyl)phthalate	BDL (0.002)		
Chrysene	BDL (0.002)	ND (0.004)	
Dibenz(a,h)anthracene	BDL (0.002)		
7,12-Dimethylbenz(a) anthracene	BDL (0.002)		
Fluoranthene	BDL (0.002)		
Indene	0.02		
1-Methylnaphthalene	0.13		
Naphthalene	0.16	0.22	((38))
Phenanthrene	0.004	ND (0.001)	>74
Pyrene	BDL (0.002)		
Acid Organics			
o-Cresol	0.02		
p & m-Cresol	0.03		
2,4-Dimethylphenol	0.01		
Phenol	0.1	ND (0.12)	
Metals			
Arsenic	0.004	ND (0.002)	>49
Barium	0.57	2.0	((251))
Cadmium	ND (0.02)	ND (0.02)	
Chromium	ND (0.025)	ND (0.025)	
Lead	ND (0.1)	ND (0.1)	
Mercury	ND (0.001)	ND (0.001)	
Selenium	ND (0.004)	ND (0.02)	
Silver	ND (0.015)	ND (0.015)	

BDL: Below detection limit.
Detection limit in parentheses.

ND: Not detected.
Percent increase in double parentheses.

* Sample bottle of fixed raw feed was broken by the vendor after being witnessed and sealed by API task force member. This was done prior to analysis by RMAL. Results can, therefore, not be guaranteed.

** Total TCLP characterization.

*** Indicator TCLP: It measures total xylenes and total phenols (sum of Phenol, cresols, and 2,4-dimethylphenol).

**** % Reduction Leachate Analysis; See text for calculation.

TABLE 6-4

TCLP Leachate Concentrations of Belt Filter Cake and Residue from Process #1 - Refinery C1

Parameter	TCLP Levels, mg/L* Belt Filter Cake	TCLP Levels, mg/L* Fixed Residue**	% Reduction Leachate Analysis***
Lab. I.D.	62409-10	62671-02	
Volatile Organics			
Benzene	1.5	0.003	>99
Toluene	2.5	0.01	>99
Xylenes	1.8	0.14	92
PNAs and Phenols			
Anthracene	ND (0.0004)	ND (0.002)	
Chrysene	ND (0.002)	ND (0.0001)	
Naphthalene	0.1	ND (0.0004)	>99
Phenanthrene	ND (0.01)	0.01	
Phenols	ND (2)	ND (0.065)	
Metals			
Arsenic	ND (0.1)	ND (0.002)	
Barium	1.0	2.2	((120))
Cadmium	ND (0.02)	ND (0.04)	
Chromium	ND (0.025)	ND (0.05)	
Lead	ND (0.1)	ND (0.2)	
Mercury	NA	ND (0.001)	
Selenium	ND (0.3)	ND (0.004)	
Silver	ND (0.02)	ND (0.03)	

ND: Not detected.
NA: Not analyzed.
Detection limit in parentheses.
Percent increase in double parentheses.

* Indicator TCLP measures total xylenes and total phenols (sum of phenol, cresols, and 2,4-dimethylphenol). Total characterization for metals.

** Sample bottle of fixed raw feed was broken by the vendor after being witnessed and sealed by API task force member. This was done prior to analysis by RMAL. Results can, therefore, not be guaranteed.

*** % Reduction, Leachate Analysis; See text for calculation.

Normal fixation takes four to twelve hours after processing. For API waste sludge, 12 to 24 hours are required for fixation. A total of 72 hours is suggested.

For the initial screening, a waste characterization program is conducted. Once the material is determined to be compatible with the process, chemical reactions are designed for each waste material to produce a chemically stable product. The percent oil, solids, and organics; the water requirement; and the volume increase are determined. After the sample was fixed it was tested for TCLP leachate, metals, and organics.

Some pretreatment may be required for refinery sludges. A sample may not harden if too much oil is present. If a sample does not harden after the fixation, it may first need to be filtered. A sample that contains between 10 to 20% oil can be treated; 5% is preferred.

Waste sludge must be agitated and mixed into a fine slurry. The soluble sodium silicate needs to be in contact with as much of the waste as possible to ensure proper treatment; the better the mix, the better the results. The typical test procedure for a sample of API separator sludge is as follows. Samples are first diluted with water to 30% solids content and homogenized with a blender; Portland cement was added at 22% by weight, homogenized and mixed for a couple of minutes. Liquid (soluble) sodium silicate was added at a 5% by weight ratio and mixed. The mixture was poured into jars and sealed 30 minutes later in the presence of an API member. After 24 hours the hardness is tested with a penetrometer. The penetrometer gives a preliminary indication of the hardness of the material in pounds per square foot.

Test results for Process Number 2 are shown in Tables 6-5 and 6-6 for fixed belt and plate filter cakes and in Tables 6-7 and 6-8 for thermally dried filter cakes from refineries C1 and B1. TCLP leachate concentrations from the feed material were so close

TABLE 6-5

Indicator TCLP Leachate Concentrations of Plate Filter Cake and Residue from Process #2 - Refinery B1

Parameter	TCLP Levels, mg/L* Plate Filter Cake	TCLP Levels, mg/L* Fixed Residue	% Reduction, Leachate Analysis**
Lab. I.D.	62291-06	62657-06	
Volatile Organics			
Benzene	0.80	0.79	1
Toluene	2.2	3.1	((41))
Xylenes	1.42	2.1	((48))
PNAs and Phenols			
Anthracene	BDL (0.002)	ND (0.0002)	
Chrysene	BDL (0.002)	ND (0.0001)	
Naphthalene	0.16	0.17	((6))
Phenanthrene	0.004	ND (0.01)	((150))
Phenols	0.156	ND (0.1)	>35
Metals			
Arsenic	0.004	0.003	25
Barium	0.57	ND (0.5)	>12
Cadmium	ND (0.02)	ND (0.02)	
Chromium	ND (0.025)	ND (0.025)	
Lead	ND (0.1)	ND (0.1)	
Mercury	ND (0.001)	ND (0.001)	
Selenium	ND (0.004)	ND (1.5)	
Silver	ND (0.015)	ND (0.015)	

BDL : Below detection limit.
ND : Not detected.
Detection limit in parentheses.
Percent increase in double parentheses.

* Indicator TCLP measures total xylenes and total phenols (sum of phenol, cresols, and 2,4-dimethylphenol).

** % Reduction, Leachate Analysis; See text for calculation.

TABLE 6-6

Indicator TCLP Leachate Concentrations of Belt Filter Cake and Residue from Process #2 - Refinery C1

Parameter	TCLP Levels, mg/L Belt Filter Cake**	 Fixed Residue*	% Reduction Leachate Analysis***
Lab. I.D.	62409-10	62657-08	
Volatile Organics			
Benzene	1.1	0.48	56
Toluene	1.8	1.8	0
Xylenes	1.82	1.2	34
PNAs and Phenols			
Anthracene	BDL (0.01)	ND (0.0002)	
Chrysene	BDL (0.01)	ND (0.003)	
Naphthalene	0.15	0.18	((20))
Phenanthrene	BDL (0.01)	ND (0.01)	
Phenols	0.072	ND (0.16)	
Metals			
Arsenic	ND (0.1)	0.007	
Barium	1.07	ND (0.5)	>53
Cadmium	ND (0.02)	ND (0.02)	
Chromium	ND (0.025)	ND (0.025)	
Cobalt	ND (0.02)	ND (0.015)	
Lead	ND (0.1)	ND (0.1)	
Mercury	NA	ND (0.001)	
Selenium	ND (0.3)	ND (1.5)	
Silver	ND (0.02)	ND (0.015)	

BDL : Below detection limit.
ND : Not detected.
NA : Not analyzed.
Detection limit in parentheses.
Percent increase in double parentheses.

* Indicator TCLP measures total xylenes and total phenols (sum of phenol, cresols, and 2,4-dimethylphenol). Total characterization for metals.
** Total TCLP characterization.
*** % Reduction, Leachate Analysis; See text for calculation.

TABLE 6-7

Indicator TCLP Leachate Concentrations of Thermally Treated Plate Filter Cake and Residue from Fixation Process # 2 - Refinery B1

Parameter	TCLP Levels, mg/L* Thermally Treated Plate Filter Cake	TCLP Levels, mg/L* Fixed Residue	% Reduction Leachate Analysis**
Lab. I.D.	62583-04	62657-02	
Volatile Organics			
Benzene	0.012	0.003	75
Toluene	0.034	0.01	71
Xylenes	0.039	0.02	49
PNAs and Phenols			
Anthracene	ND (0.001)	ND (0.0002)	
Chrysene	ND (0.005)	ND (0.001)	
Naphthalene	ND (0.020)	ND (0.002)	
Phenanthrene	ND (0.006)	ND (0.01)	
Phenols	ND (1.3)	ND (1.3)	
Metals			
Arsenic	ND (0.1)	ND (0.002)	
Barium	1.3	0.5	62
Cadmium	0.02	ND (0.02)	
Chromium	ND (0.025)	ND (0.025)	
Lead	ND (0.1)	ND (0.1)	
Mercury	NA	ND (0.001)	
Selenium	ND (0.3)	ND (1.5)	
Silver	ND (0.02)	ND (0.015)	

BDL : Below detection limit.
ND : Not detected.
NA : Not analyzed
Detection limit in parentheses.

* Indicator TCLP measures total xylenes and total phenols (sum of phenol, cresols, and 2,4-dimethylphenol).

** % Reduction, Leachate Analysis; See text for calculation.

TABLE 6-8

Indicator TCLP Leachate Concentrations of Thermally Treated Belt Filter Cake and Residue from Fixation Process #2 - Refinery C1

Parameter	TCLP Levels, mg/L* Thermally Treated Belt Filter Cake	Fixed Residue	% Reduction Leachate Analysis**
Lab. I.D.	62583-31	62657-04	
Volatile Organics			
Benzene	0.002	0.005	((150))
Toluene	0.020	0.01	50
Xylenes	0.003	0.02	((566))
PNAs and Phenols			
Anthracene	ND (0.003)	ND (0.002)	
Chrysene	ND (0.10)	ND (0.01)	
Naphthalene	0.17	ND (0.15)	>11
Phenanthrene	0.050	ND (0.1)	
Phenols	ND (0.94)	ND (3.1)	
Metals			
Arsenic	ND (0.04)	0.016	
Barium	0.57	ND (0.5)	>12
Cadmium	ND (0.008)	ND (0.02)	
Chromium	0.04	0.051	((28))
Lead	ND (0.04)	ND (0.1)	
Mercury	NA	ND (0.001)	
Selenium	ND (0.1)	ND (1.5)	
Silver	ND (0.006)	ND (0.015)	

BDL : Below detection limit.
ND : Not detected.
NA : Not analyzed
Detection limit in parentheses.
Percent increase in double parentheses.

* Indicator TCLP measures total xylenes and total phenols (sum of phenol, cresols, and 2,4-dimethylphenol).

** % Reduction, Leachate Analysis; See text for calculation.

to the detection limits that additional reduction, due to fixation could not be measured accurately.

Fixation process number 3: To determine the proper mix of cement, lime and fly ash, a homogenized sample of about 3 kg is used. A reagent formulation is selected, based on prior experience with similar wastes. The wastes and reagents are blended for about 10 minutes at room temperature with a mixer. There is a small temperature rise (around $5^{o}C$) during mixing due to the heat released by hydration. The mixture is then transferred to plastic cylinders, about 3 inches in diameter and 6 inches in height. The filled cylinders are then capped and stored to cure (i.e., harden) for about a month. Finally, a leachate test is done on the hardened materials.

The parameters that are adjusted to optimize performance include:

- pH of the waste;
- redox potential of the waste, (e.g., oxidation of cyanide or reduction of Cr (VI) to Cr (III);
- bulk ratio = weight of product/weight of waste;
- percent water;
- percent cement;
- percent lime;
- percent fly ash; and
- other additions to promote fixation (e.g., activated carbon or filler).

Performance data were obtained on samples of filter cake from a belt filter press operated at refinery C1, and from a plate filter press in operation at refinery B1. The bulking factor (ratio of total reagent to waste) used was 1.5. The reagent mix (cememt:lime:fly ash) is considered proprietary. However, the same fixation formula was used for both types of wastes.

Performance data for fixation Process Number 3 for the belt filter cake is summarized in Table 6-9 and for the plate filter cake in Table 6-10. Incremental reductions in leachate concentrations of benzene, toluene, and xylenes, from 50 to 99+% were observed.

TABLE 6-9

Indicator TCLP Leachate Concentrations of Belt Filter Cake and Residue from Fixation Process # 3 - Refinery C1

Parameter	TCLP Levels, mg/L* Belt Filter Cake	TCLP Levels, mg/L* Fixed Residue	% Reduction, Leachate Analysis**
Lab. I.D.	62409-10	62687-02	
Volatile Organics			
Benzene	1.5	0.01	>99
Toluene	2.5	0.13	95
Xylenes	1.8	0.39	78
PNAs and Phenols			
Anthracene	ND (0.0004)	ND (0.003)	
Chrysene	ND (0.002)	ND (0.003)	
Naphthalene	0.1	0.004	96
Phenanthrene	ND (0.01)	0.01	
Phenols	ND (2.0)	ND (0.37)	
Metals			
Arsenic	ND (0.1)	0.02	
Barium	1.0	1.2	((20))
Cadmium	ND (0.02)	ND (0.025)	
Chromium	ND (0.025)	ND (0.05)	
Lead	ND (0.1)	ND (0.25)	
Mercury	NA	ND (0.001)	
Selenium	ND (0.3)	ND (0.02)	
Silver	ND (0.02)	ND (0.025)	

BDL : Below detection limit.
ND : Not detected.
NA : Not analyzed
Detection limit in parentheses.
Percent increase in double parentheses.

* Indicator TCLP measures total xylenes and total phenols (sum of phenol, cresols, and 2,4-dimethylphenol). Total characterization for metals.

** % Reduction, Leachate Analysis; See text for calculation.

TABLE 6-10

Indicator TCLP Leachate Concentrations of Plate Filter Cake and Residue from Fixation Process # 3 - Refinery B1

Parameter	TCLP Levels, mg/L* Plate Filter Cake	TCLP Levels, mg/L* Fixed Residue	% Reduction Leachate Analyses**
Lab. I.D.	62291-06	62687-01	
Volatile Organics			
Benzene	0.8	0.03	97
Toluene	2.2	0.26	88
Xylenes	1.4	0.59	58
PNAs and Phenols			
Anthracene	BDL (0.002)	ND (0.10)	
Chrysene	BDL (0.002)	ND (0.003)	
Naphthalene	0.16	0.1	38
Phenanthrene	0.004	0.01	((150))
Phenols	0.16	0.07	56
Metals			
Arsenic	0.004	0.01	((150))
Barium	0.57	1.5	((163))
Cadmium	ND (0.06)	ND (0.025)	
Chromium	ND (0.025)	ND (0.05)	
Lead	ND (0.1)	ND (0.25)	
Mercury	ND (0.001)	ND (0.001)	
Selenium	ND (0.004)	ND (0.02)	
Silver	ND (0.015)	ND (0.025)	

BDL : Below detection limit.
ND : Not detected.
Detection limit in parentheses.
Percent increase in double parentheses.

* Indicator TCLP measures total xylenes and total phenols (sum of phenol, cresols, and 2,4-dimethylphenol).

** % Reduction, Leachate Analysis; See text for calculation.

CHAPTER 7. OTHER VENDOR TECHNOLOGIES

INTRODUCTION

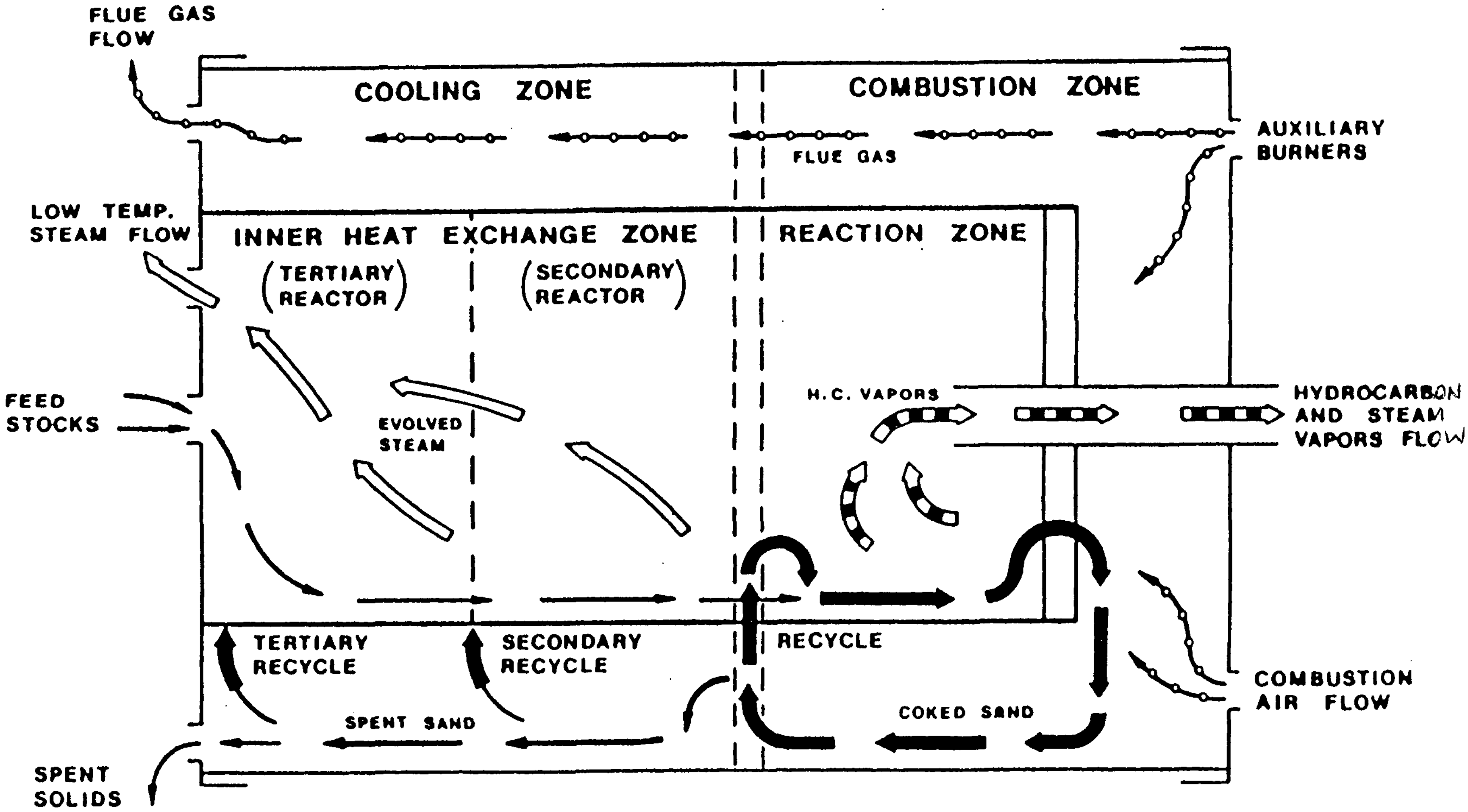
This section of the report was reserved to report data supplied by vendors of other treatment technologies for listed petroleum refinery wastes. Processing, sampling, and analytical protocols were set by the API task force to assure that data included in this chapter could be compared to data in other parts of the report. The protocols were followed for a pyrolysis process and the information provided is summarized below.

Figure 7-1 shows a simplified diagram of the rotary pyrolysis process. The technology was developed for the recovery of bitumen from mineral oil sands in Canada and has been demonstrated in this application in a 5 ton per hour pilot plant since 1978. More recently the technology has been tested on a number of oil-contaminated sludges and solids including listed petroleum refinery wastes.

OVERVIEW

The rotary pyrolysis process is a blend of thermal treatment (to evaporate water and volatile organics) followed by thermal cracking (of heavier oils) along with formation of coke and finally of combustion of the coke to provide heat for the process and to maximize the reduction in hazardous organic material.

As indicated by constituent concentrations and TCLP leachate of the product solids, almost all organic materials have been reduced to below detection limits in the solid residue from the process.



PYROLYSIS PROCESSOR

MAJOR ZONES AND FLOW STREAMS

FIGURE 7-1

No difficulty in integrating this processing system into a petroleum refinery would be expected based on analytical inspections of the products--oil, water and solids.

DISCUSSION--EQUIPMENT DESCRIPTION AND OPERATION

The rotary pyrolysis processor is a horizontal rotating vessel which can accept liquid or solid feeds and perform the following functions (which can be followed on Figure 7-1):

1. Feed enters the center, inner, section of the processor and is preheated by heat exchange with the combusted solids in the annulus of the drum. Most of the contained water and some light organics are evaporated in this heat exchange zone.

2. In the next reaction zone, temperature of the feed is raised further by additional indirect heat transfer and direct contact with recycled combusted solids. The light oils are vaporized and heavier oils are thermally cracked, with coke forming on the inert solids. Vaporized hydrocarbons, the remaining water as steam, and gases formed during cracking flow from the reaction zone to a condensation and gas clean up system external to the processor.

3. The coked inerts flow into the outer annulus of the processor where the coke is burned to provide heat for the process and maximize the removal and destruction of hazardous organics. Part of the solids are recycled into the reaction zone as a direct source of heat.

4. The rest of the solids continue on through the cooling zone, transferring heat to fresh feed.

Typical operation of the reaction zone is at 900°F. to 1100°F while the combustion zone operates over a temperature range of 1200°F. to 1450°F. The processor and its systems can be designed to separate and recover water, oil, gas produced by cracking, flue gas and spent solids.

No problems are anticipated with integrating this system into an operating refinery.

TEST PROCEDURES

Testing was done in small scale batch pyrolysis and combustion equipment at the research laboratory of the process developer. The developer is confident, based on previous experience, that these tests accurately simulate the processes in the various zones of the production-scale processor and can be used for scaleup and design.

DAF Float (K048), slop oil emulsion solids (K049), and API Separator bottoms (K051) were received from Refinery E and blended to form a waste feed. Water, oil, and solids contents of the blend were 62.4% water, 13.5% oil, and 24.1% solids. The developer's standard tests and procedures were then used to simulate the processor.

TEST RESULTS AND DISCUSSION

Table 7-1 provides total constituent data on an array of Appendix VIII compounds in the blended waste feed and in the product solids (or solid residue). Almost all of the organics have been reduced below detectable limits. For most organics the concentration reduction was over 99%. Metals have, as expected, lower reductions.

TABLE 7-1

Total Constituent Concentrations of Waste Feed and Solid Residue from the Pyrolysis Process - Refinery E

Parameter	Total Constituent Levels, mg/kg		% Reduction
	Waste Feed	Solid Residue	
Volatile Organics			
Benzene	180	ND (0.002)	>99
Methyl ethyl ketone			
Styrene			
Ethylbenzene	390	ND (0.003)	>99
Toluene	1300	0.01	>99
Xylene, m	970	ND (0.003)	>99
Xylenes, o & p	920	ND (0.007)	>99
Base/Neutral Organics			
Anthracene	7.6	ND (2)	>73
Benzo(a)anthracene	BDL*	BDL	
Benzo(b)fluoranthene	BDL	BDL	
Benzo(a)pyrene	BDL	BDL	
Bis(2-ethylhexyl)phthalate	BDL	BDL	
Chrysene	15	ND (80)	
Dibenz(a,h)anthracene	BDL	BDL	
7,12-Dimethylbenz(a) anthracene	BDL	BDL	
Fluoranthene	BDL	0.02	
Indene	8.8		
1-Methylnaphthalene	850		
Naphthalene	360	ND (8)	>97
Phenanthrene	70	0.02 (4)	>99
Pyrene	12	BDL	
Acid Organics			
o-Cresol	15.6	0.2	99
2,4-Dimethylphenol	2.3	ND*	
Phenol	7.7	ND	
Metals			
Arsenic	6.8	ND	
Barium	54	20	63
Cadmium	ND (1)	ND (0.04)	
Chromium	420	44	90
Lead	39	6.0	85
Mercury	-	-	
Selenium	ND (0.8)	ND (0.06)	
Silver	-	-	

BDL: Below detection limit.
ND: Not detected

*Detection limits for all parameters were not available at this time.

$$\% \text{ Reduction} = 100\% \times \left[\frac{\left[\begin{array}{c}\text{mg/kg compound}\\ \text{in feed}\end{array}\right] - \left[\begin{array}{c}\text{mg/kg compound}\\ \text{in solid residue}\end{array}\right]}{\text{mg/kg compound in feed}} \right]$$

Table 7-2 gives the results of a partial TCLP leachate analysis of the solid residue from this process. Almost all the components were below detection limits.

TABLE 7-2

Indicator TCLP Leachate Concentrations of Solid Residue from the Pyrolysis Process - Refinery E

Parameter	TCLP Levels, mg/L* Solid Residue
PNAs and Phenols	
Anthracene	ND (0.02)
Chrysene	ND (0.2)
Naphthalene	ND (0.3)
Phenanthrene	0.0004
Phenols	ND (21)
Metals	
Antimony	ND (0.1)
Arsenic	ND (0.1)
Barium	ND (0.6)
Beryllium	ND (0.002)
Cadmium	ND (0.01)
Chromium	1.3
Cobalt	ND (0.006)
Lead	ND (0.04)
Mercury	-
Nickel	0.08
Selenium	ND (0.6)
Silver	ND (0.006)
Vanadium	0.006

ND: Not detected.
Detection limit in parentheses.

*Indicator TCLP measures total xylenes and total phenols (sum of phenol, cresols, and 2,4-dimethylphenol). Total characterization for metals.

CHAPTER 8. SUMMARY AND PERSPECTIVE

In this chapter, the data on the effectiveness of the treatment technologies is summarized and examined. The techologies are compared to each other and, as limited by available data, to other treatment methods. Integration of a waste treatment system into a petroleum refinery and possible secondary environmental effects are also considered.

TREATMENT EFFECTIVENESS

All of the waste treatment technologies tested can provide effective treatment of listed petroleum refinery oily wastes. A series of tables will be used to demonstrate the effectiveness of each technology. Treatment effectiveness is measured by the reduction in weight of constituents from feed to product and the reduction in leachate concentrations of each constituent from feed to product.

Mechanical Treatment

Separate tests, detailed in Chapter 3, were made on two belt filters, three plate filters and one rotary drum vacuum filter, six tests in all. Table 8-1 shows the range and average concentrations of the ten indicator compounds--eight organics and two metals--in both the raw waste feeds and solid products from these tests. In the last two columns are the calculated treatment efficiencies as, 'Percent Reduction, Weight' and 'Percent Reduction, Leachate Analysis.' These two values were calculated as explained in earlier chapters. As shown in a footnote to the table, the average weight of cake as a fraction of feed was 0.090 for the six tests, and this was used to calculate Percent Reduction, Weight.

TABLE 8-1

CONSTITUENT AND TCLP CONCENTRATIONS - WASTE FEED AND PRODUCT SOLIDS -- MECHANICAL TREATMENT

	Raw Feed				Product Solids				% Reduction	
	Constituent Conc., mg/kg		TCLP Conc., mg/L		Constituent Conc., mg/kg		TCLP Conc., mg/L			Leachate
	Avg.	Range	Avg.	Range	Avg.	Range	Avg.	Range	Weight	Analysis
Benzene	850	10-2200	54	3-220	46.5	10-120	1.4	0.2-4.5	>99	97
Toluene	2694	68-7200	281	2.4-710	304	83-490	2.2	0.98-4.1	99	99
Xylenes	3149	106-7100	225	0.8-750	568	158-1120	1.5	0.58-3.6	98	99
Anthracene	49	0.069-149	11	0.015-24	10.1	2-18	0.009	0.001-0.015	98	>99
Chrysene	64**	0.24-1500*	88	0.1-280	125	12-670	0.24	0.001-0.045	82	>99
Naphthalene	212	1.1-490	74	0.13-310	144	70-230	0.17	0.007-0.33	94	>99
Phenanthrene	207	0.53-590	102	0.32-320	109	47-170	0.009	0.004-0.15	95	>99
Phenols	8.6***	2.5-9900*	92***	0.44-2000*	4.1**	1-6600*	0.66*	0.075-2.6*	95	99
Chromium	126	5.2-328	1.32	0.05-3.9	654	320-1700	0.045	0.01-0.15	53	97
Lead	30.5	2-48	0.38	0.01-1.1	128	37-240	0.08**	0.04-0.4*	62	79

Average Weight of Cake as a Fraction of Feed = 0.090 (Range = 0.037-0.167)

* Sample and average strongly influenced by detection limits at high levels.

** Average omits largest of detection limits outliers. When constituents were below detection limits, the detection limits are included in the range and also in the calculation of average and percent reductions except if more than a degree of magnitude above the other values.

*** Average omits two values, largest of detection limits outliers.

The data in Table 8-1 clearly show the effectiveness of mechanical treatment in lowering the environmental hazard level of Appendix VIII constituents in the wastes treated. The weight of organics has been greatly reduced, from 82% to more than 99%; and the weight of metals has been reduced by more than 50%. The mobility of these hazardous constituents as measured by TCLP leachate concentrations, has been reduced by 97% or more for all but one of the constituents. That one constituent, lead, was reduced by 79%.

Solvent Extraction

The solvent extraction test work was done at the vendor's pilot unit and is described in detail in Chapter 4. Table 8-2 summarizes the data from that test. Indicator compound concentrations are given for waste feed, product solids and the TCLP leachates from feed and product solids.

Reductions are more than 99% for all the organics both in weight and in leachate analysis. Metals have been strongly partitioned into the product solids, and concentrations in the solids reflect almost quantitative segregation into the solids phase. Leachate concentrations of the metals are reduced from feed to product--72% and 89% for Cr and Pb, respectively.

Thermal Treatment

Filter cakes from one belt filter and one plate filter were treated in a screw-flight dryer at two different temperature levels. The data for the four tests--two feeds at two temperatures--and background on the process used are given in Chapter 5.

Table 8-3 shows data for: 1) the raw feed to the filters; 2) the product solids from the filters; and 3) the product solids from thermal treatment.

TABLE 8-2

CONSTITUENT AND TCLP CONCENTRATIONS - WASTE FEED AND PRODUCT SOLIDS -- SOLVENT EXTRACTION

	Raw Feed		Product Solids		% Reduction	
	Constituent Concentration mg/kg	TLCP Concentration mg/L	Constituent Concentration mg/kg	TCLP Concentration mg/L	Weight	Leachate Analysis
Benzene	600	42	1.3	0.005	>99	>99
Toluene	6600	240	5.0	0.008	>99	>99
Xylenes	8880	320	4.4	0.01	>99	>99
Anthracene	ND (46)	ND (0.84)	ND (0.001)	ND (0.005)	--	--
Chrysene	ND (19)	ND (4.2)	ND (0.001)	ND (0.005)	--	--
Naphthalene	560	59	0.005	0.007	>99	>99
Phenanthrene	740	75	0.005	ND (0.005)	>99	>99
Phenols	ND (1900)	ND (420)	ND (0.20)	ND (0.05)	--	--
Chromium	220	0.39	1250	0.11	((16))	72
Lead	27	0.47	260	0.05	((97))	89

ND : Not Detected.
Detection limit in parentheses.
Percent increase in double parentheses.

TABLE 8-3

CONSTITUENT AND TCLP CONCENTRATIONS -- MECHANICAL PLUS THERMAL TREATMENT

	Raw Feed to Mechanical Treatment				Product Solids from Mechanical Treatment to Thermal Treatment				Product Solids from Thermal Treatment				Overall % Reduction: Raw Feed to Thermally Treated Product	
	Constituent Conc., mg/kg		TLCP Conc., mg/L		Constituent Conc., mg/kg		TCLP Conc., mg/L		Constituent Conc., mg/kg		TCLP Conc., mg/L			
	Avg.	Range	Avg.	Range	Avg.	Range	Avg.	Range	Avg.	Range	Avg.	Range	Weight	Leachate Analysis
Benzene	1433	10-2200	1.0	0.8-1.2	95	71-120	0.95	0.8-1.1	0.55	0.05-1.5*	0.02	0.005-0.05*	>99	98
Toluene	4522	68-7200	2.1	1.8-3.3	425	350-500	2.4	2.2-2.6	3.0	1.0-8.3	0.04	0.005-0.08	>99	98
Xylenes (Total)	4352	55-7100	1.5	1.4-1.8	835	830-840	1.5	1.4-1.6	2.4	0.33-3.4	0.07	0.01-0.11	>99	95
Anthracene	11**	0.1-149*	0.008	0.002-0.012	5.7	1.4*-10*	0.008	0.002-0.012	53	4.1-100	0.01	0.005-0.015	83	((25))
Chrysene	8.5**	0.2-1500*	0.008	0.002-0.012	254	7.1*-500*	0.008	0.002-0.012	62	28-100	0.01	0.005-0.015	74	((25))
Naphthalene	150	1.1-270	0.16	0.15-0.16	77	14-140	0.15	0.15-0.16	46	4.6-120	0.06	0.012-0.06	99	62
Penanthrene	120**	0.5-590*	0.009	0.004-0.012	54	7.1*-100*	0.008	0.004-0.012	364	26-720	0.015	0.005-0.03	89	((67))
Phenols	9.2**	2.4-9900*	0.83	0.16-2*	600*	500*-700*	0.067	0.039-0.095	17	3-29	0.27	0.08-0.43	94	67
Chromium	161	5.2-328	0.025	0.025	522	73-970	0.025	0.025	2450	1400-3900	0.05	0.025-0.1	47	((100))
Lead	27	2-48	0.1	0.1	90	84-95	0.1	0.1	275	240-340	0.07	0.04-0.1	64	30

Average weight of thermally treated cakes as a fraction of raw feed = (Mech. Treatment fraction) (Thermal Treatment fraction) = (0.09)(0.39) =.0 35

* Sample and average strongly influenced by high level detection limits.

** Average omits one value, largest of detection limit outliers.

Percent increase in double parentheses.

Overall percent reductions of the indicator compounds by weight and leachate analysis are given, from the raw feed to the thermally treated filter cake. Weight reductions are more than 99% for the light organics, between 74 and 99% for the heavier organics, and 47 to 64% for the metals. Reductions in leachate concentrations are high, 95 to 98%, for the light organics and much less for the heavier organics and metals.

Fixation

Fixation tests were run using three different feeds, raw waste, filter cake, and thermally treated filter cakes. Three different fixation processes were tested on all or some of the feed stocks. The detailed data and background on these tests are given in Chapter 6.

In presenting and analyzing the data from fixation, only analyses on TCLP of feed and products have been used. Unlike all of the other processes, fixation does not include removal of hazardous materials from the feed. Therefore, there is no change in weight of hazardous components.

Table 8-4 gives the data for fixation of raw, non-treated, feeds: API Separator Sludge and Slop Oil Emulsion Solids. Only one fixation process designed to treat sludges with high oil levels was tested. With this process, the leachability of the organics and metals was strongly reduced, particularly of the most mobile, volatile organics. However the sample containers were opened by the vendor between the fixation step, which was witnessed by API, and arrival at the analytical laboratory.

Table 8-5 gives the data for fixation of two filter cakes by three different fixation processes. Reduction of leachate concentrations of the volatile organics ranged from 49 to 80%. The heavier organics and the metals are at or close to detection

TABLE 8-4

TCLP CONCENTRATIONS
RAW WASTES AND FIXED PRODUCT - FIXATION

	TCLP Levels, mg/L				
	Raw Wastes		Fixed Product		% Reduction
	Avg.	Range	Avg.	Range	Leachate Analysis
Benzene	24	22-26	0.10	0.04-0.16	>99
Toluene	40	28-51	0.45	0.24-0.66	99
Xylenes	67	33-101	0.60	0.57-0.63	99
Anthracene	1.8	<0.003-3.6	BDL	<0.005	>99
Chrysene	0.5	<0.003-0.99	BDL	<0.005	99
Naphthalene	5.2	0.27-10.2	0.19	0.16-0.22	97
Phenanthrene	0.01	<0.06-0.01	0.01	0.01	0
Phenols	1.9	0.14-3.65	0.70	0.06-1.4	63
Chromium	0.45	<0.01-0.89	ND	<0.025	94
Lead	<0.06	<0.04-<0.07	<0.1	<0.1	--

BDL : Below Detection Limit.
ND : Not Detected.

TABLE 8-5

TCLP CONCENTRATIONS
FILTER CAKES AND FIXED PRODUCT - FIXATION

TCLP Levels, mg/L

	Filter Cakes		Fixed Product		% Reduction
	Avg.	Range	Avg.	Range	Leachate Analysis
Benzene	1.1	0.8-1.5	0.22	0.003-0.79	80
Toluene	2.2	1.8-2.5	0.90	0.01-3.1	59
Xylenes	1.6	1.4-1.8	0.82	0.14-2.1	49
Anthracene	BDL		ND		--
Chrysene	BDL		ND		--
Naphthalene	0.14	0.1-0.16	0.10	ND-0.22	--
Phenanthrene	0.004	BDL-0.004	0.01	ND-0.01	--
Phenols	0.11	ND-0.16	ND		--
Chromium	ND		ND		--
Lead	ND		ND		--

BDL : Below Detection Limit.
ND : Not Detected.

limits in both the feed filter cake and in the fixed product. Table 8-6 shows data for fixation of thermally treated filter cakes. Reductions in leachate analysis are limited by the very low level of indicator compounds in both feed and product.

Pyrolysis

A blend of three oily refinery wastes (API Separator Sludge, Dissolved Air Flotation Float, and Slop Oil Emulsion Solids) were treated in a rotary pyrolysis process. The process includes thermal treatment to recover volatiles, followed by coking/ cracking of heavier oils, and then finally combustion of the coke. The test was run in small scale equipment by the process vendor. Details are given in Chapter 7.

Table 8-7 presents the data available on this test. Treatment has reduced almost all of the organic materials in both the product solids and the leachate from the product solids to below detection limits. While not very obvious in the data, one would expect virtually all of the feed metals to be in the product solids.

PERSPECTIVE

Two areas will be examined to view this study in a wider context. First, how do the treatment technologies studied here compare to each other and to others that might be used in the management of refinery oily wastes? Second, how would these systems be integrated into a petroleum refinery and what secondary environmental effects might they cause?

Comparison of Technologies

To compare relative effectiveness of the tested systems, it is first necessary to choose a "measuring stick". For this

TABLE 8-6

TCLP CONCENTRATIONS
THERMALLY TREATED FILTER CAKES AND FIXED PRODUCT - FIXATION

TCLP Levels, mg/L

	Thermally Treated Filter Cakes Avg.	Thermally Treated Filter Cakes Range	Fixed Product Avg.	Fixed Product Range	% Reduction Leachate Analysis
Benzene	0.007	0.002-0.012	0.004	0.003-0.005	43
Toluene	0.027	0.020-0.034	0.01	0.01	63
Xylenes	0.021	0.003-0.039	0.02	0.02	0
Anthracene	ND		ND		
Chrysene	ND		ND		
Naphthalene	0.085	ND-0.17	ND		
Phenanthrene	0.025	ND-0.050	ND		
Phenols	ND		ND		
Chromium	ND		ND		
Lead	ND		ND		

ND : Not Detected.

TABLE 8-7

CONSTITUENT AND TCLP LEACHATE CONCENTRATIONS -- WASTE FEED AND PRODUCT SOLIDS -- PYROLYSIS

	Waste Feed		Product Solids		Percent Reduction	
	Constituent Concentration ppm	TCLP ppm	Constituent Concentration ppm	TCLP ppm	Weight	Leachate Analysis
Benzene	180	No Data	ND (0.002)	ND	>99	
Toluene	1300		0.01	ND	>99	
Xylenes	1890		ND (0.01)	ND	>99	
Anthracene	7.6		ND (2)	ND (0.02)	>92	
Chrysene	15		ND (80)	ND (0.2)	--	
Naphthalene	360		ND (8)	ND (0.3)	>99	
Phenanthrene	70		0.02	0.004	>99	
Phenols	26		0.2	ND (21)	>99	
Chromium	420		44	1.31	97	
Lead	39		6	ND (0.04)	96	

ND : Not detected.
Detection limit in parentheses.

Product Solids as a fraction of feed estimated at 0.27.

comparison, reduction in weight of constituents and constituent concentrations in the residuals from each process are used, along with the average data in tables 8-1, 8-2, 8-3 and 8-7.

Fixation is not included in this comparison since it reduces hazard by immobilizing constituents rather than reducing their concentration.

Using this yardstick, the order of effectiveness varies with the class of compound.

- For volatile organics (benzene, toluene, xylene) the most effective technology is pyrolysis, followed by thermal treatment, solvent extraction and mechanical treatment.
- For base/neutral organics (anthracene, chrysene, naphthalene, phenanthrene) solvent extraction was most effective, followed closely by pyrolysis and then thermal and mechanical treatment.
- The order for phenols was just about the same as for the base/neutrals except that mechanical treatment gave somewhat lower results than thermal treatment.
- For the indicator metals (chromium and lead) none of the processes should be expected to reduced their concentration to a low level. All of the processes tend to move metals into the solids product. Any other indication would be arbitrary.

Data submitted to EPA's Office of Solid Waste by the API Waste Technology Task Force (WTTF) compared TCLP leachate compositions of treatment product solids. WTTF used the data from this study plus incinerator and land treatment data derived and extrapolated from published material to compare the treatment systems as illustrated in Figure 8-1. Figure 8-2 shows a comparison between the technologies which were evaluated based on total residual levels of indicator organics and metals in the product solids.

Integration Into a Refinery

Figure 8-3 is a simplified representation of a petroleum refinery. On the upper left of the figure are typical petroleum processing units. On the right are shown portions of a wastewater treatment system. The lower section of the figure is the oily waste treatment section showing many of the technologies that could be used.

Product solids from the treatment of oily wastes will, after the required level of treatment, finally reach either a land treatment unit or landfill.

The oily phase would normally be recycled to the crude oil distillation system. The water phase from waste treatment will normally be recycled to the wastewater treatment system. The point of water recycle will be varied with the quality of the water and the design of the waste water treatment system. Another API report, "Fate of Selected Trace Metals in the Petroleum Refining Industry (August, 1985)", provides a detailed evaluation of oil recycle options for a refinery.

Treatment of the solid wastes can be quite variable, depending on the character of the waste and the method of final disposal. Figure 8-4 illustrates many treatment options which could be utilized at a refinery.

Comparison to Land Treatment

Land treatment is the most widely used waste treatment process in the petroleum industry today. It uses biodegradation and immobilization to treat waste constituents. Biodegradation is

FIGURE 8-1 COMPARISON OF ALTERNATE TREATMENT TECHNOLOGY RESIDUALS TO INCINERATION

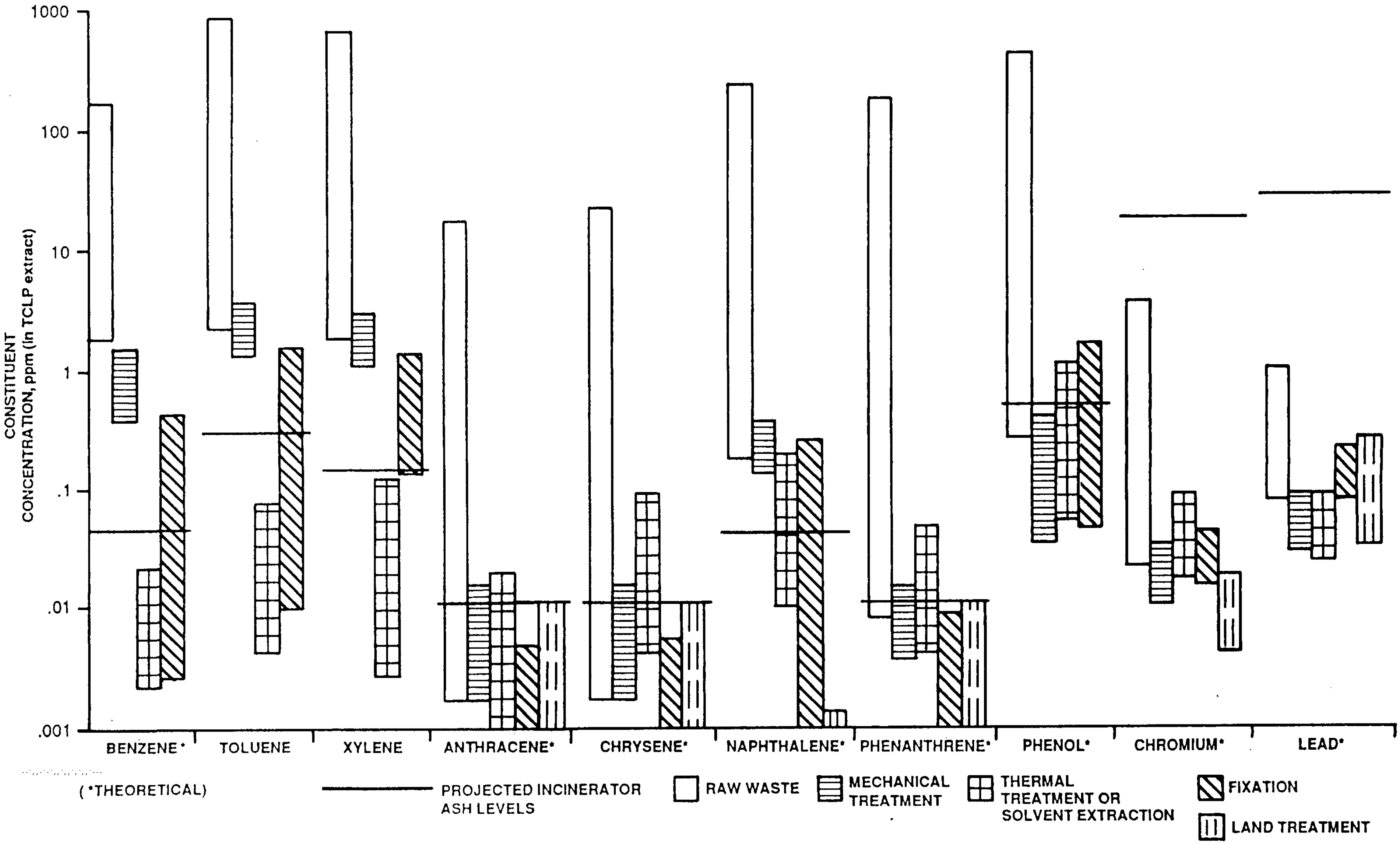


FIGURE 8-2 CONCENTRATIONS IN RAW FEEDS AND RESIDUES

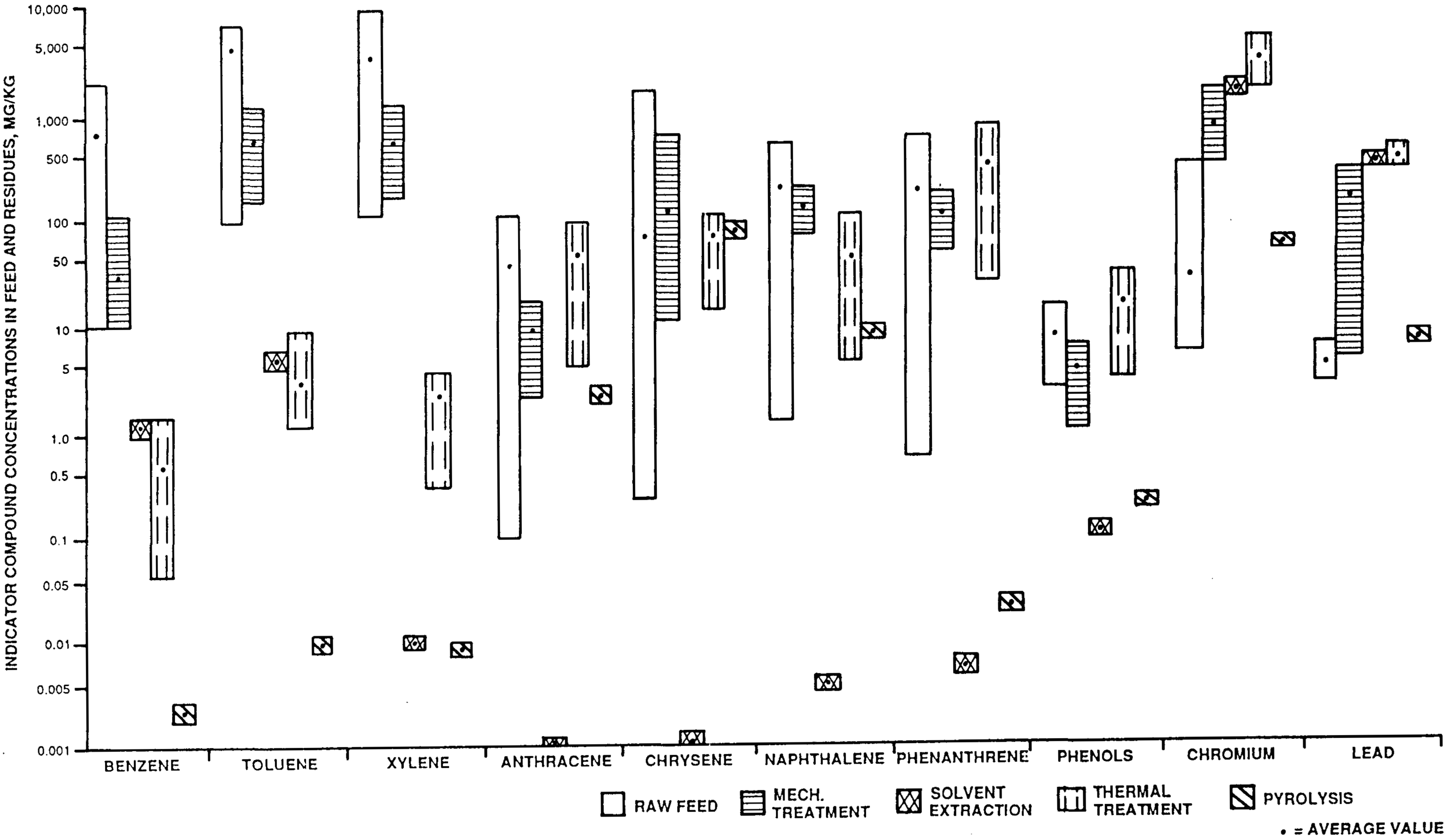


FIGURE 8-3 INTEGRATION OF WASTE TREATMENT INTO A REFINERY

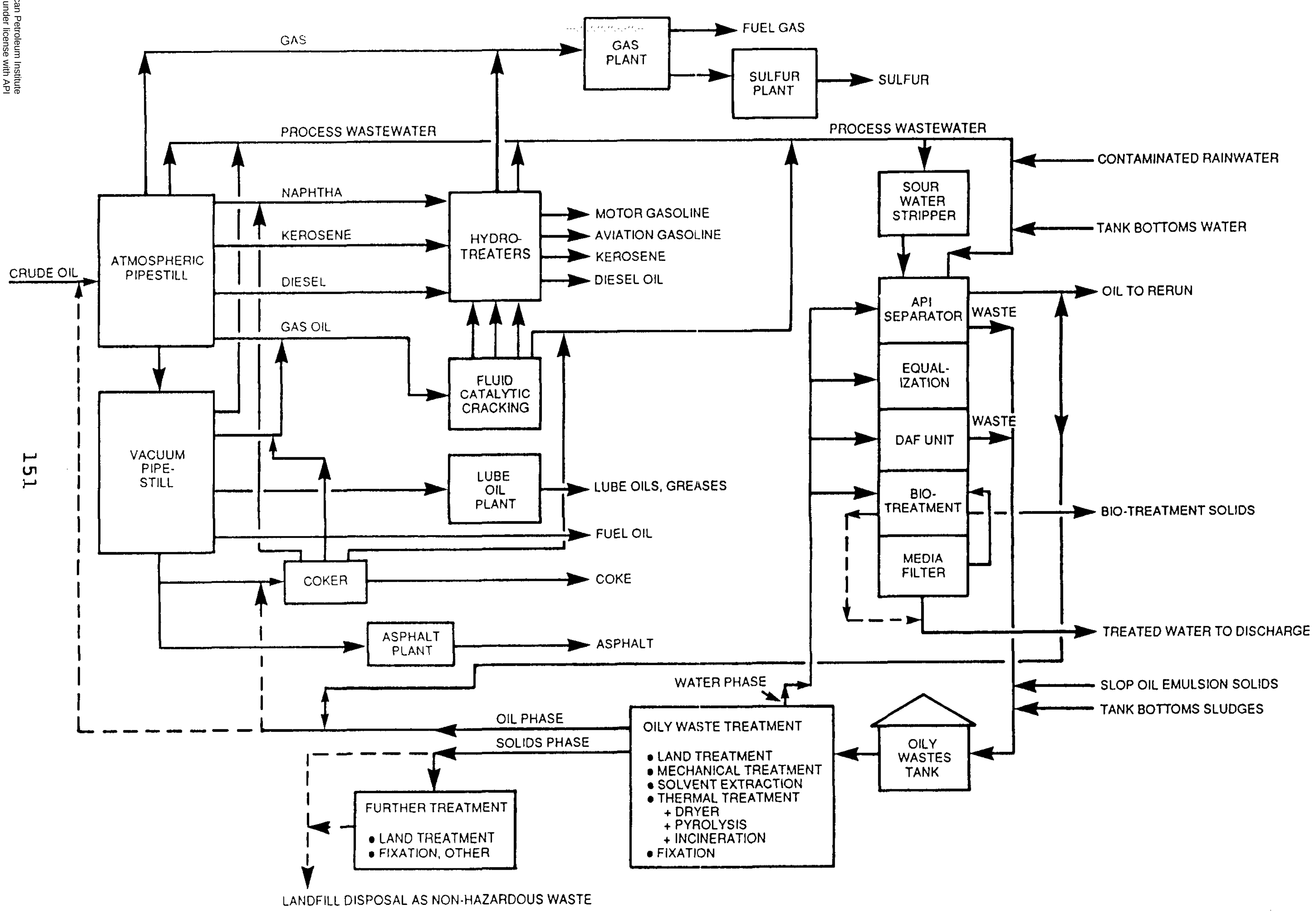


FIGURE 8-4

ALTERNATIVE SEQUENCES FOR TREATMENT OF PETROLEUM WASTES

LEGEND OF TREATMENT STEPS

1. Mechanical treatment
2. Thermal dryer
3. Extraction
4. Fixation
5. Pyrolysis
6. Incineration
7. Land treatment
8. Landfill

ALTERNATIVE SEQUENCES

a. ->7
b. ->1 ->7
c. ->1 ->8
d. ->1 ->2 ->8
e. ->1 ->2 ->7
f. ->1 ->4 ->8
g. ->1 ->2 ->4 ->8
h. ->2 ->7
i. ->2 ->8
j. ->2 ->4 ->8
k. ->3 ->8
l. ->3 ->4 ->8
m. ->4 ->8
n. ->5 ->8
o. ->5 ->4 ->8
p. ->6 ->8
q. ->6 ->4 ->8

similar to incineration in that this process results in the complete oxidation of organic waste constituents to carbon dioxide and water with time. However, since biodegradation is essentially a low temperature, biologically catalyzed process, hazardous by-products (e.g., SO_X, NO_X) are not produced. Biodegradation of refinery wastes does not result in the emission of volatile metal oxides to the atmosphere unlike what occurs when refinery wastes are treated by incineration.

Land treatment units are designed and operated to minimize leaching and, as a result, the leachate quality from a unit is typically excellent. TCLP was developed to predict the quality of leachate from a landfill. Thus, comparing the results of TCLP testing of the solids from various treatment processes with leachate from a land treatment unit provides a good comparison of how these technologies protect the groundwater. Figure 8-2 provides this comparison.

The land treatment levels shown in the figure are those measured in leachate from lab scale studies of land treatment of petroleum wastes. The levels of organic constituents are from an API report entitled, "The Land Treatability of Appendix VIII Constituents Present in Petroleum Refinery Wastes--Laboratory and Modeling Studies" (April 1987.) This study measured leachate concentrations following typically high (4 inches/week) and very high (12 inches instantaneous) rainfall. The soil depth was that of a typical landfarm (6 feet).

Levels shown for inorganic constituents are from AIChE's report, "Treatment of Refinery Oily Wastes by Landfarming" (AIChE's Symposium Series 9190, 1979). This study measured leachate concentrations following 17 to 187 inches of rain. The soil depth was that of a very shallow landfarm (1 foot).

Figure 8-1 shows that land treatment significantly reduces the concentration of waste constituents in the leachate, to levels which are as low as or lower than those from the TCLP extracts of the residual solids from other treatment technologies. The concentration of volatile organics were well below those seen in the TCLP extracts from other processes. The concentration of base neutral semivolatiles and metals were at levels similar to that measured in the TCLP extracts. No data were readily available in the open literature on the acid extractable organics (i.e., phenol) in land treatment leachate.

Unlike downward migration, upward migration or volatile emissions from land treatment has not been extensively studied. Mathematical modeling done by EPA indicates that for some petroleum wastes, volatile emissions may be significant. Preliminary results of lab and field studies being conducted by both API and EPA indicate that emissions may indeed be significant for extremely volatile oily wastes. For extremely volatile wastes, emissions can be controlled in two ways.

- Subsurface injection. This method has been successfully used to control odors from land treatment facilities.

- Pretreatment. Several of the technologies examined in this report can remove the volatiles from oily wastes. Once the volatiles are removed, the remaining waste can be land treated with minimal volatile emissions. Combined treatment processes which can be employed to reduce the quantity of volatiles going to the land are included in Figures 8-3 and 8-4.

Ideally, API would have liked to conduct this study by treating the same waste with all five technologies. This would have allowed for a more scientific comparison of treatment efficiencies. This was not done because of difficulties encountered when attempting to ship hazardous waste from state to state. From an engineering standpoint we find it beneficial that different refinery wastes of varied oil, water, solids composition were tested as this accurately reflects the true nature of wastes from the petroleum industry. A successful treatment technology for refinery wastes would have to be effective over a broad range of compositions.

APPENDIX

CHEVRON RESEARCH COMPANY
RICHMOND, CALIFORNIA

MODIFIED OVEN DRYING TECHNIQUE (MODT)

AUGUST 3, 1984

Participants - A. J. Ricciardelli
C. E. Alderman
T. H. Gouw

Author - T. Leong

SCOPE

This procedure determines the amount of light hydrocarbons, oil, water, and solids in oily waste. Light hydrocarbons are all hydrocarbons which volatilize under the conditions of the test. Oil is defined as those hydrocarbons which are soluble in dichloromethane and do not form solid solutions with water. Solid is defined as material which does not decompose at 250-300°F and is not soluble in dichloromethane.

PRINCIPLE

The MODT is a two-stage process. Light hydrocarbons and water are first separated from heavy oils and solids by heating in vacuum and by the use of a stripping gas. The light hydrocarbons and water are recovered in cold traps and subsequently separated by freezing out the water phase. In the second step, heavy oils are separated from the solids by Soxhlet extraction with dichloromethane.

EQUIPMENT AND REAGENTS

A. Oven (Figure 1)

1. A 50 "O" ring glass oven; two pieces. The top is approximately 3 1/2 in. x 2 1/4 in. OD. The bottom piece is ~7 in. x 2 1/4 in. OD.
2. Size 50 Viton "O" ring.
3. Size 5155 "C" clamp.
4. Whatman cellulose single thickness extraction thimble 43 mm x 123 mm, oven-dried at 105°C overnight.

Encl. - Figures 1-5 (PR 840710-4,
PR 840710-3, PR 840710-2,
PR 840710-1, and RA 843412)
CRR-7900

B. Reflector (Figure 2)

1. 18-in. OD thermocouple, Type J.
2. 14-in. x 1/4-in. OD glass tube.
3. Heat shield reflector, ~17 in. high and 7 in. in diameter.
4. Flowmeter 0-100 ml STP gas/min.
5. 250 watt infrared heat lamp.
6. 10 ft x 0.01 ID SS capillary tubing.

C. Dry Ice Traps (Figure 3)

1. Two 13-in. Dewars; 1000-ml capacity.
2. Dry ice.
3. Isopropyl alcohol.
4. 100-ml Pyrex centrifuge tubes fitted with 29/42 tops.
5. Trap tops containing tangential inlets to induce a rotating flow.
6. Rubber bands for traps.
7. 3/8-in. ID tubing to connect oven to traps.
8. 5/16-in. ID tubing to connect traps together.
9. Rubber caps for trap ends.
10. Copper wire.
11. No. 1005 Hamilton 1-5 ml syringe or equivalent, and 7 in., 16 or 17 gauge needles.
12. GC bottles and septum.

D. Soxhlet

1. 55/50 Soxhlet extractor with H_2O condenser.

2. 500-ml Pyrex 24/40 round bottom flask.

3. 500-ml Glas-Col heating mantle.

4. Dichloromethane FW 84.93 (also known as methylene chloride).

5. Boiling chips.

E. General

1. Balance; capacity 1000 grams accurate to 0.01 grams.

2. Vacuum pump.

3. Hg U-Tube manometer closed.

4. Digital temperature indicator, °F readout.

5. Vacuum oven.

6. Desiccator.

7. Dryer (filled with Drierite or equivalent) for N_2 gas stream.

PROCEDURE

A. Oven Drying (Figures 4 and 5)

1. Make up CO_2 slurry by mixing isopropyl alcohol with dry ice. Consistency should be like a thick mush. Pour mixture into dewars approximately three-fourths full.

2. Record tare weights of glass oven, include Viton "O" ring. Also, record tare weights of traps.

3. Mix sample thoroughly.

4. Remove oven dried thimble from desiccator and record tare weight. Put ~20 grams of thoroughly mixed sample in thimble, weigh, and place in glass oven. If the sample contains more than 50% water and oil, charge about 10 grams. If sample contains less than 10% water and oil, charge 25-30 grams.

5. Put oven assembly together using "C" clamp.

6. Insert thermocouple assembly into oven. Thermocouple should be placed ~1/4 in. above sample.

7. Attach 3/8-in. ID tubing to oven and first trap using copper wire to secure tubing.

8. Attach 5/16-in. ID tubing to connect first and second trap together.

9. Place traps into dewars so that the dry ice mush covers them.

10. Hook up vacuum line to end of second trap.

11. Turn on vacuum pump, set N_2 flow rate at ~16 cc/min., and set pressure at 40 mm Hg.

12. The vacuum and the nitrogen flow rates are best adjusted with the control valve before the flowmeter and the valve above the vacuum pump. Vacuum control by adjusting the air bleed to the vacuum pump is also possible.

13. Plug in heat lamp, heat sample to 230-240°F. The temperature on the unit is adjusted by moving the heat lamp closer or further from the unit. When the trap tops are free of condensation, the sample should be free of light hydrocarbons and water. It should take two to four hours to remove light hydrocarbons and H_2O.

14. Pull heat lamp back from oven and place heat lamp on upper part of oven to volatilize any condensation. Control the temperatures to 150-170°F for approximately one-half hour.

15. Allow oven to cool (until you can handle).

16. Remove traps and plug off with rubber plugs. Refrigerate traps overnight.

17. Remove thermocouple and "C" clamp from oven and weigh oven assembly.

B. Soxhlet Extraction

1. Pour ~350-400 ml of dichloromethane into the 500-ml Pyrex round-bottomed flask.

2. Carefully remove thimble from oven assembly and place into Soxhlet extractor. Rinse out oven assembly with dichloromethane and pour into thimble.

3. Hook up condenser (H_2O) to Soxhlet assembly and reflux overnight, or until clear (Method No. 502C from Standard Methods for the Examination of Water and Waste Water, 14th Edition; APHA; Washington, D.C., 1975.)

4. Remove thimble from Soxhlet extractor. Place thimble containing the solids into a 100-ml beaker and place in hood overnight.

5. Tare a 500-ml beaker and pour the liquid from the 500-ml round bottom flask into tared beaker. Rinse out Soxhlet assembly and flask with dichloromethane and pour into tared beaker. A rotary evaporator with a nitrogen bleed can also be used to evaporate off the solvent.

6. Place 500-ml beaker into fume hood and allow the solvent to evaporate ~24 hours.

7. Record weight of oil in beaker and pour off oil into GC bottle and seal.

8. Place thimble with solids in vacuum oven at 105°F for approximately four hours to dry out any solvent left in solids.

9. Remove thimble from oven and place into a desiccator to cool. After cool, record weight.

C. Hydrocarbon and Water Trap

1. Remove traps from refrigerator, record weights, and place traps into freezer set at 10°F overnight to separate hydrocarbons and water.

2. Remove traps from freezer.

3. If hydrocarbons are present in traps, tare syringe, and needle, remove hydrocarbons using the syringe and record weight. Place hydrocarbons into GC bottle and seal.

4. Any water remaining in the traps should then be placed into a vial and refrigerated. Chemical oxygen demand tests can be run on the remaining liquid to determine the amount of organic matter present.

:mk

FIGURE 1

OVEN

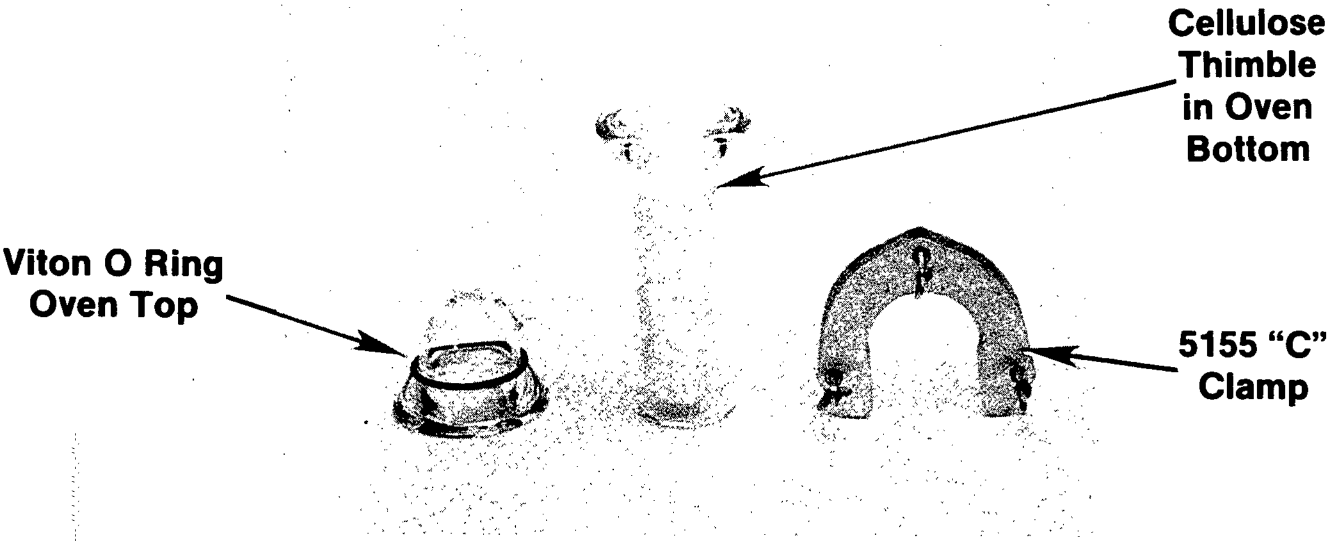
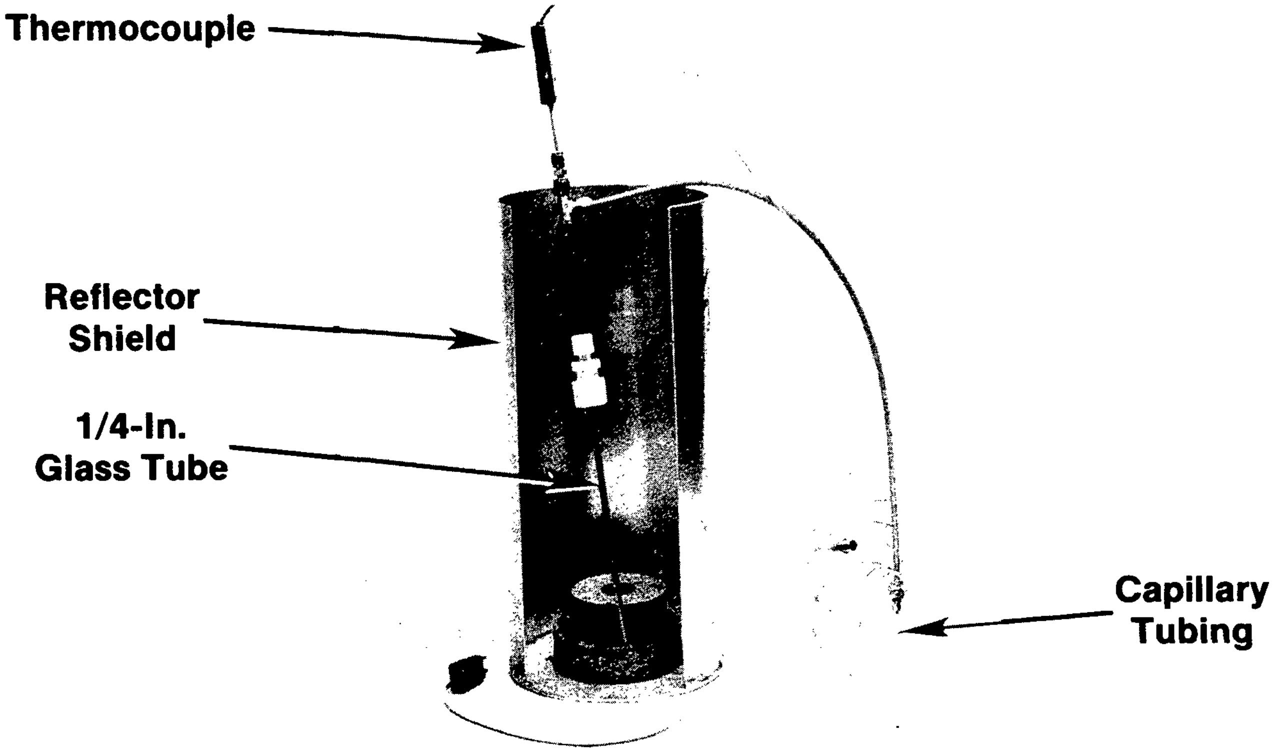


FIGURE 2
REFLECTOR



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TL/G PR 840710-3

FIGURE 3

COLD TRAPS

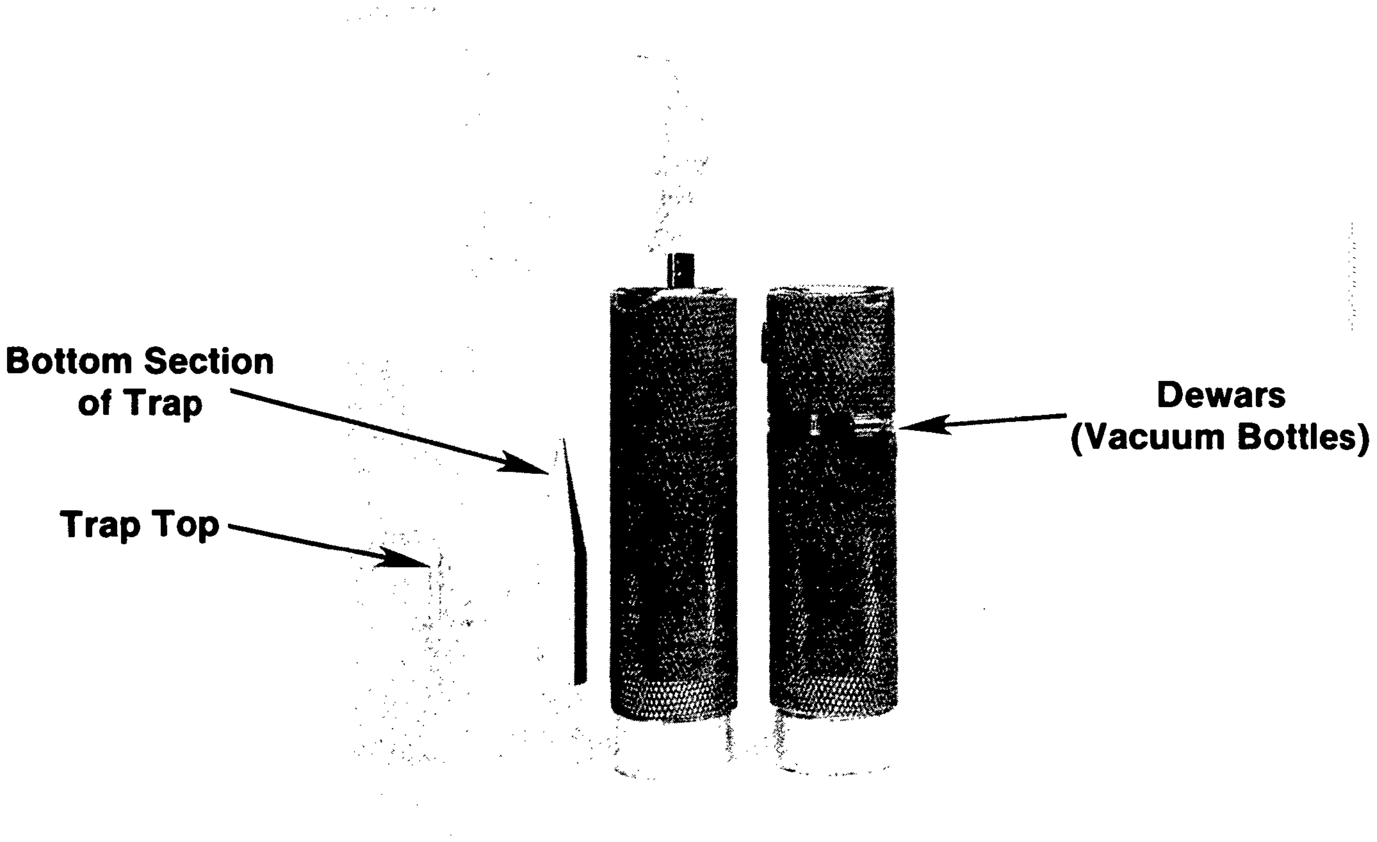


FIGURE 4

UNIT IN OPERATION

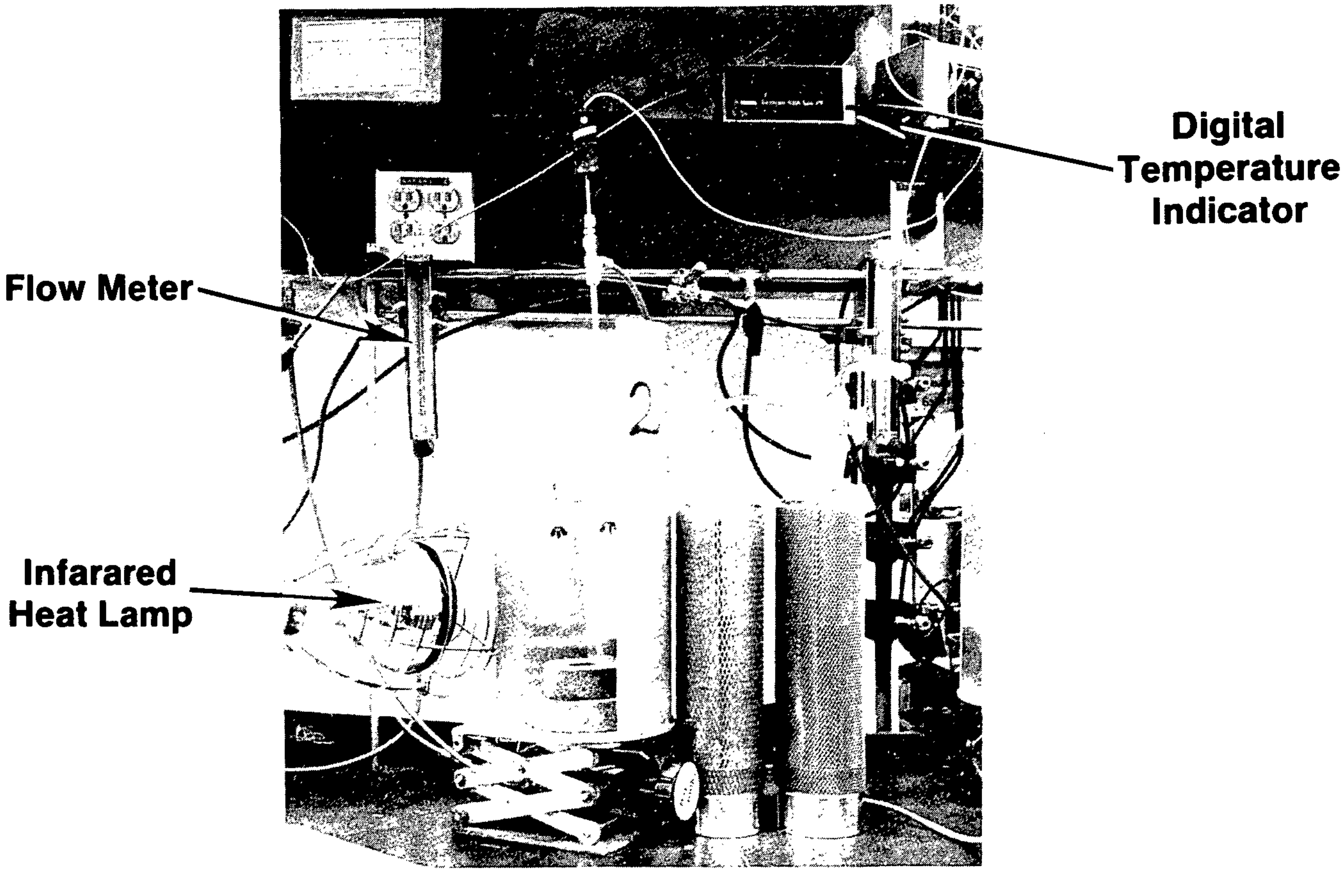
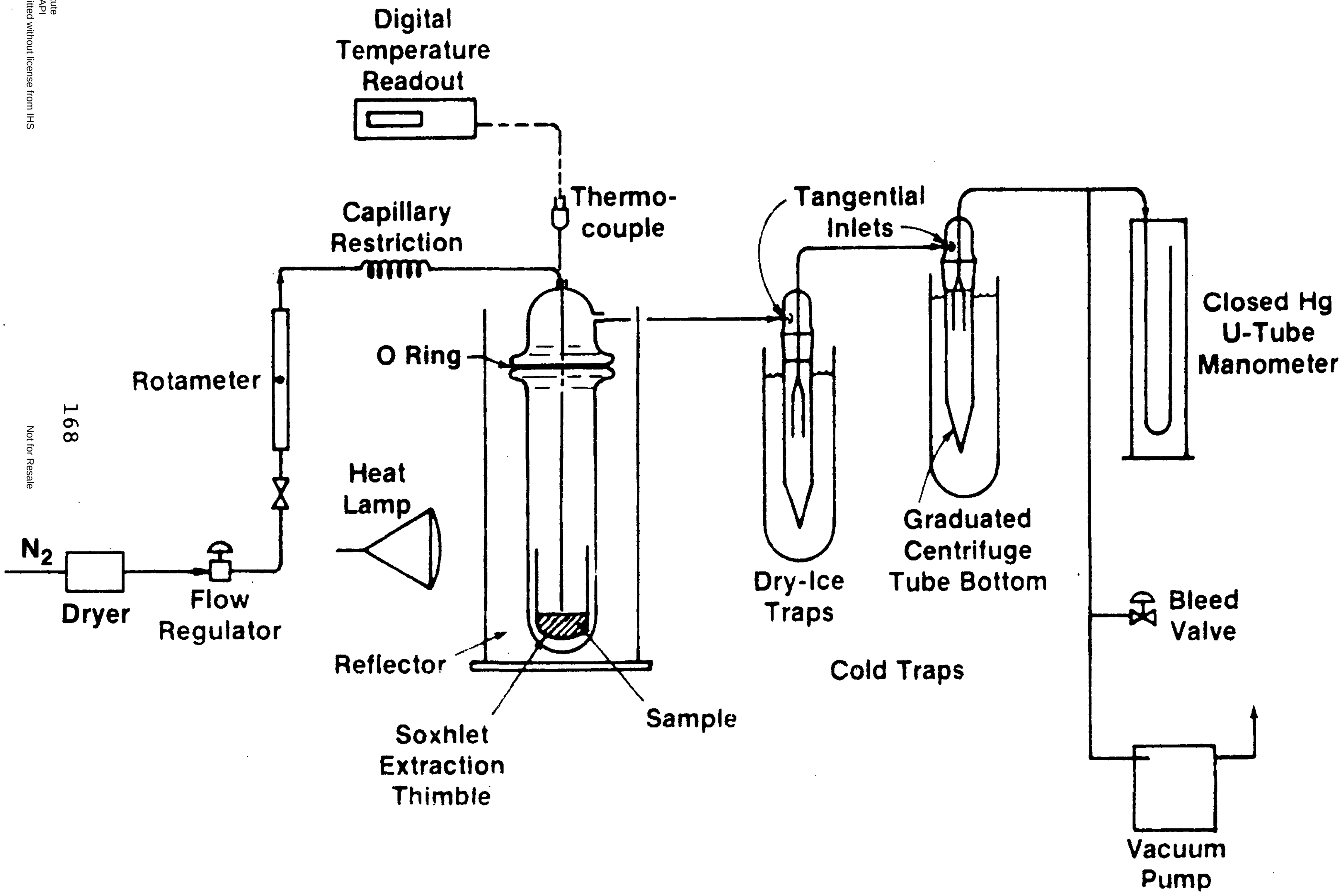


FIGURE 5

MODIFIED OVEN DRYING TECHNIQUE



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CHEVRON RESEARCH COMPANY
OIL, WATER, AND SOLID ANALYSIS
MODIFIED OVEN DRYING TECHNIQUE

Sample I.D. ______________
Customer ______________
Project Number ______________
Date Submitted ____/____/____
Date Completed ____/____/____
Analyst ______________
Vessel ______________

Sample Weight

Thimble Gross: ______________
Thimble Tare: ______________
Net Sample: ______________ (a)

Results Summary

Oil ______________
Water ______________
Solids ______________

Oil Breakdown

Hydrocarbons ______________
Heavy Oil ______________

Vessel Tares

Top: ______________
Bottom: ______________
O Ring: ______________
Thimble: ______________
Total Vessel
Tare: ______________ (b)

Volatilized Weight

Vessel Gross After Drying: ______________ (c)
Total Vessel Tare: ______________ (b)
Net Dried Sample: ______________ (d) = (c) - (b)
Net Sample: ______________ (a)
Weight of Sample Volatilized: ______________ (e) = (a) - (d)

Traps	Weight Full	Weight Empty		Net Liquid	
No. 1			=		(f)
No. 2			=		(g)

Total Liquid In Traps: ______________ (h) = (f) + (g)
Syringe and Hydrocarbons: ______________ (i)
Syringe Tare: ______________ (j)
Hydrocarbons in Traps: ______________ (k) = (i) - (j)
Water in Traps: ______________ (l) = (h) - (k)

Dried Solids

Thimble Gross: ______________
Thimble Tare: ______________
Net Solids: ______________ (m)

Extracted Oils

Beaker Gross: ______________
Beaker Tare: ______________
Recovered Oils: ______________ (n)

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CHEVRON RESEARCH COMPANY
OIL, WATER, AND SOLID ANALYSIS
MODIFIED OVEN DRYING TECHNIQUE

Calculations

1. Sample Loss

Sample Loss = Wt of Sample Volatilized (e) - Total Liquid in Traps (h) = __________

(If the sample loss is >1% of the sample weight, view the results with caution.)

2. Solids

$$\frac{\text{Net Solids (m)}}{\text{Net Sample (a)}} \times 100\% = \_\_\_\_\_\_\_\_ \text{ Wt \% Solids}$$

3. Water

$$\frac{\text{Water in Trap (l)}}{\text{Net Sample (a)}} \times 100\% = \_\_\_\_\_\_\_\_ \text{ Wt \% Water}$$

4. Heavy Oil

Net Heavy Oil = Net Dried Sample (d) - Net Solids (m) = ________ (o)

$$\frac{\text{Net Heavy Oil (o)}}{\text{Net Sample (a)}} \times 100\% = \_\_\_\_\_\_\_\_ \text{ Wt \% Heavy Oil}$$

5. Hydrocarbons

$$\frac{\text{Hydrocarbons in Trap (k)}}{\text{Net Sample (a)}} \times 100\% = \_\_\_\_\_\_\_\_ \text{ Wt \% Hydrocarbons}$$

6. Total Oil

Net Oil = Net Heavy Oil (o) + Hydrocarbons in Trap (k) = _______ (p)

$$\frac{\text{Net Oil (p)}}{\text{Net Sample (a)}} \times 100\% = \_\_\_\_\_\_\_\_ \text{ Wt \% Oil}$$

7. Check for Dichloromethane

Recovered Oil (n) - Net Heavy Oil (o) = __________

(If >0, dichloromethane could be in the recovered oil sample. Dichloromethane will continue to evaporate if the oil sample is uncovered. It could also affect the results of any tests done to characterize the oil.)

ATTACHMENT III

PROPOSED METHOD FOR MEASURING THE VOC CONTENT OF A WASTE RESEARCH TRIANGLE INSTITUTE

VOC Removal and Recovery

Each waste sample will be tested for VOC by two methods: steam distillation and air stripping. A single apparatus will be used for both methods. Figure A-1 is the apparatus setup for steam distillation. The design was chosen for the following reasons. A 1.0-L resin kettle is used because it has a wide mouth opening and samples may be added or removed easily. The 1-L size allows samples of several hundred milliliters to be tested, with room left for foaming and frothing. As an alternative, a three-neck round-bottom flask may be required if leakage around the kettle seal between the bottom and lid cannot be prevented. The large sample size is required to ensure representative sample testing and to provide VOC recovery amounts which can be handled easily and measured with a high degree of certainty. The mechanical stirrer will aid the boiling of liquids and keep solids suspended in solution and multiphase samples well mixed.

A distillation head without a column will be used for the steam distillation. A column will not be used since fractionation of the steam is not required and also to decrease the time required for the distillation. A mercury thermometer placed in the head will monitor the temperature of the vapors entering the condensers.

A two-stage condenser system will be used. First, an ice water-cooled condenser will condense the water and VOC of lower volatility which fall into the cooled receiving flask. The vapors which are not removed go through a cold-finger condenser cooled to -78°C with dry ice and acetone. This will condense most of the VOC remaining. Any remaining vapor then will exit the system into a Tedlar® bag. The condensed water and organics will fall into the ice water-cooled graduated receiving flask. The volume of sample distilled can then be measured and the distillate dispensed into sample vials. Volumes smaller than 5.0 mL will be measured using gas-tight syringes. After the distillation, the dry ice/acetone cold finger will be allowed to warm up and the condensate collected. Both condenser and the receiving flask will be rinsed with

Encl. - Figures A-1 and A-2

carbon tetrachloride to remove any organics condensed or adhering to the surfaces.

For the air stripping tests, the steam distillation apparatus will be modified slightly. Figure A-2 shows the modifications which will need to be made. A purge adapter will be placed in the resin kettle just above the stirrer. It will release a stream of inert gas through a medium-porous frit, forming fine bubbles which will be dispersed by the action of the stirrer. A purge rate of 500 mL/min. will be used. The condenser apparatus will remain the same as in the steam distillation. The Tedlar® bags will be replaced at regular intervals, condensate will be removed, and the dry ice/acetone cold-finger condensate plus glassware rinse will be collected in the same manner as the steam distillation.

Steam Distillation

The steam distillation method will proceed as follows:

1. Five-hundred milliliters waste will be weighed and added to the resin kettle.

2. Check the pH of the solution. If the pH is equal to or greater than 7, add 10N NaOH until the pH is between 12-13. If less than 7, add 50% H_2SO_4 until a pH of between 1 and 2 is reached.

3. The rheostat controlling the heat will be turned to 80% full power and the stirrer set at a moderate rate.

4. The distillation process will be timed, starting the clock at Step 3.

5. The distillate sample will be moved after 5 mL have been collected. The time and temperature will be recorded.

6. Three other distillation samples will be collected at a total of 25 mL, 50 mL, and 100 mL, recording the time and temperature.

7. The kettle will be allowed to cool and the pH adjusted to 1 or 2 if the solution is initially neutral or basic and adjusted to a pH of 12 or 13 if the solution is initially acidic. Reheat and remove distillate fractions at 25 mL and 50 mL.

8. If the distillate separates into two phases, the organic phase will be removed and the volume measured using gas-tight syringes.

Air Stripping

The air stripping test will be performed as follows:

1. Five-hundred milliliters waste added to the kettle.

2. The pH will be adjusted as in Step 2 of the steam distillation.

3. The purge gas will be turned on at a flow rate of 500 mL/min. and the clock started.

4. After five minutes, the purge will be stopped and the bag and condensate samples collected will be removed. This will be repeated at 10 minutes, 20 minutes, and 40 minutes, recording the temperature at each time.

5. Adjust pH as in Step 7 of the steam distillation and purge for 20 minutes.

6. If any phase separation occurs, sample handling will be the same as for the steam distillation procedure.

Analytical

The organic content of each of the aqueous phases should be measured using standard total organic carbon techniques.

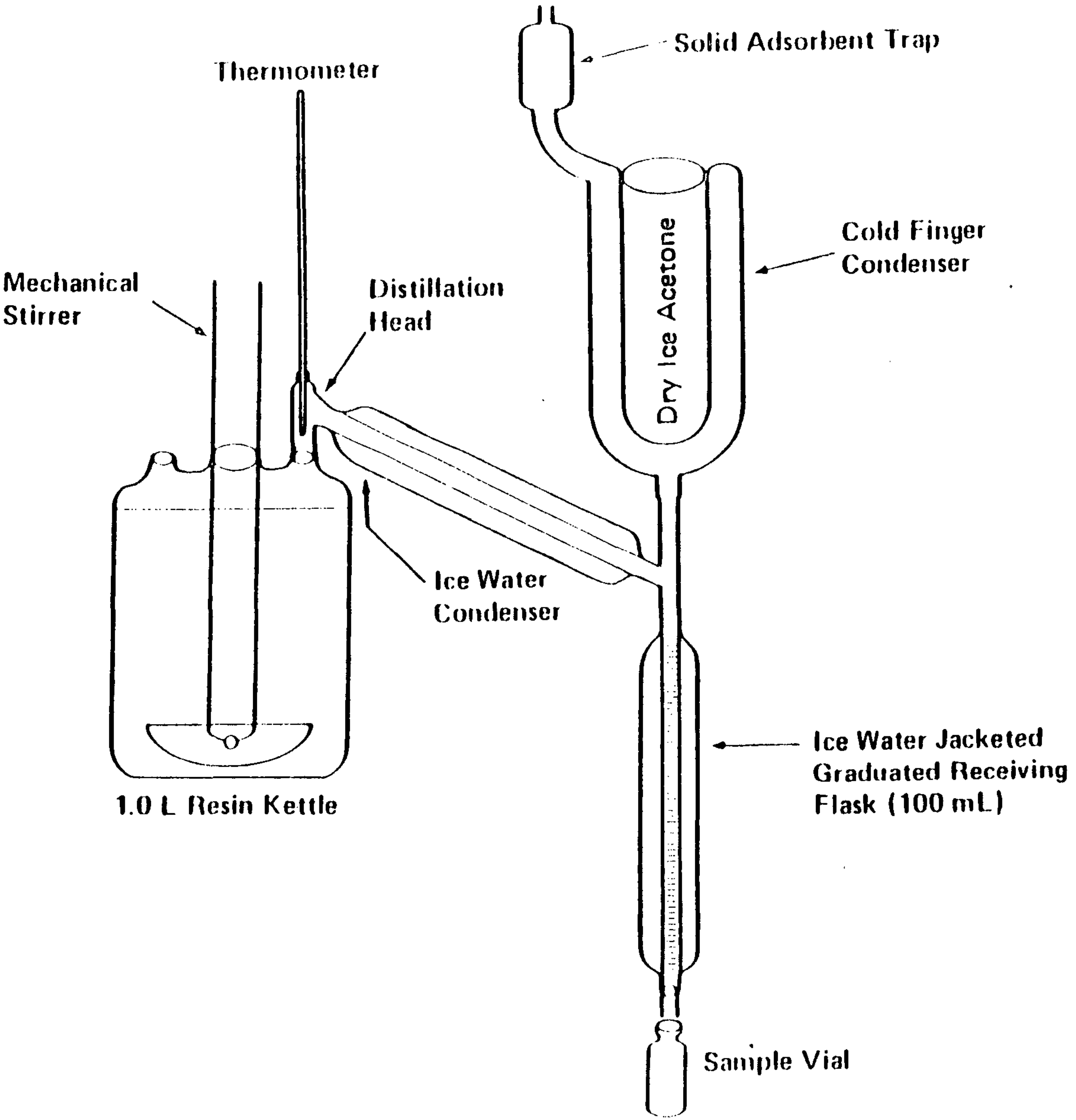

Figure A-1. Steam Distillation Apparatus For Waste Analysis.

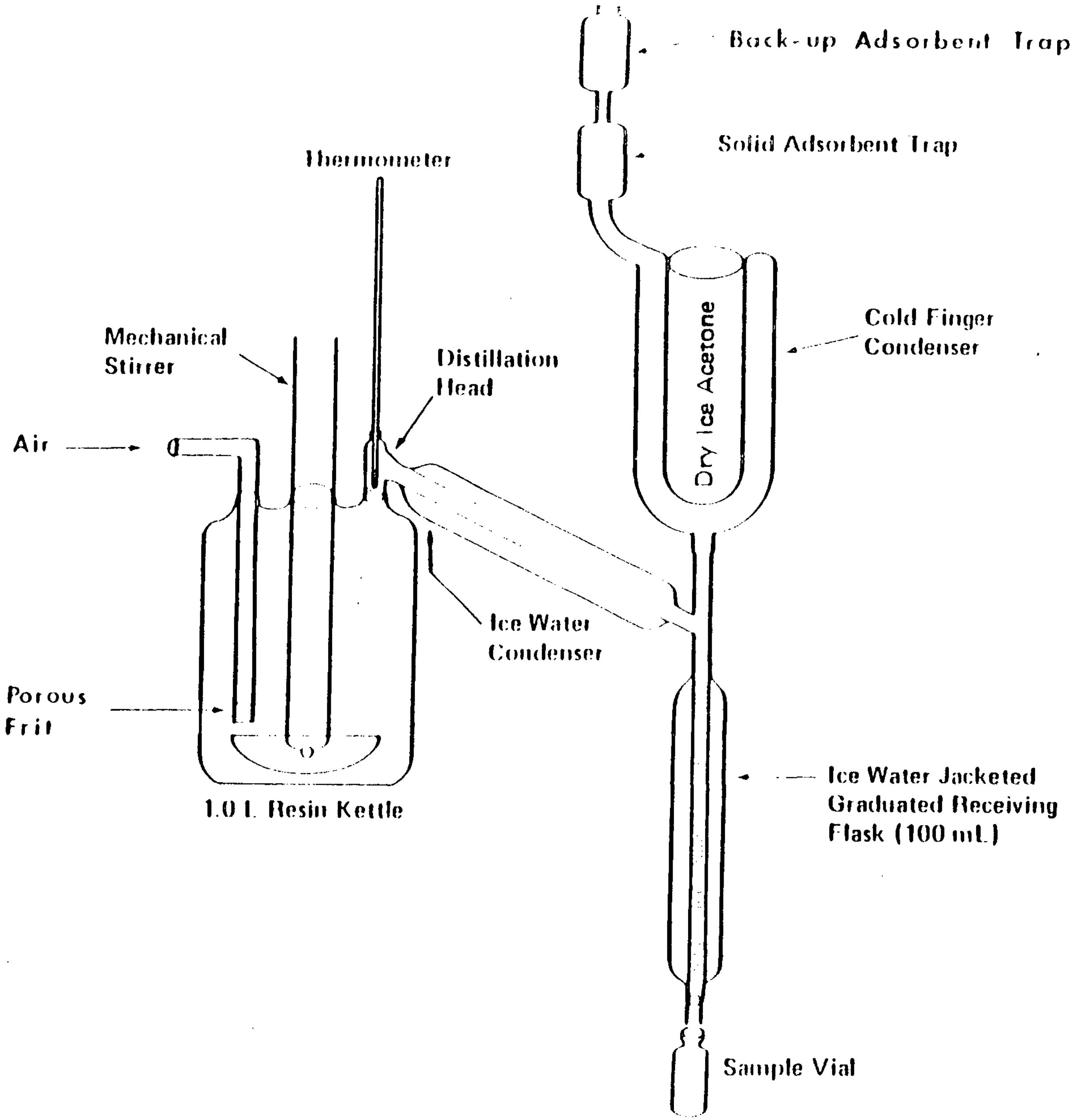

Figure A-2. Air Stripping Apparatus For Waste Analysis.

ATTACHMENT IV

MATHEMATICAL MODEL FOR ESTIMATING VOLATILE EMISSIONS FROM LANDFARMS

I. MODEL DESCRIPTION

This appendix section describes the model that was developed by Clark Allen (termed the RTI model). The assumptions inherent in the derivation of the RTI model are summarized in Table 1.

Using the RTI model, the emission rate, E (g/s), at any time, t (s), is:

$$E = \frac{d\,M_{i\text{-air}}}{dt} = M_{io}\left(\frac{D_{i\text{-soil}}\,A_i}{\pi \ell^2}\right)^{1/2} e^{-t/t_b}\; t^{-1/2} \qquad (1)$$

where $M_{i\text{-air}}$ = grams of pollutant i emitted into the atmosphere/cm^2 surface area, g/cm^2.

M_{io} = grams of pollutant i initially applied to the soil/cm^2 surface area, g/cm^2.

$D_{i\text{-soil}}$ = effective diffusion coefficient of pollutant i in the soil matrix, $cm^2/$.

ℓ = thickness of the initially well mixed soil layer, cm.

A_i = grams of pollutant i in the gas phase per cm^3 soil/ grams of pollutant i in the soil per cm^3 soil, (C_{ig}/C_{isoil}).

t_{bi} = time constant for biological decay of pollutant i, s.

The parameter A can be considered the air/soil partition coefficient, and it determines the amount of pollutant that is available for diffusion and possible emissions. This partition coefficient can be

TABLE 1: LIST OF ASSUMPTIONS

1. The pollutant is applied to the surface of the soil. Soon after this application, it is mixed uniformly within a surface layer of the soil.

2. The applied waste does not flow as a liquid within the soil.

3. The adsorption isotherm of the pollutant is linear within the application surface layer and does not change with time.

4. No bulk flow of gas is induced within the soil.

5. The rate of biological decay/chemical reaction is a first order process.

6. The diffusion coefficient does not vary with either concentration or time.

7. The concentration of pollutants in the gas phase at the surface of the soil is much lower than the concentration of pollutant in the gas phase within the soil.

8. Since the pollutant is expected to be either emitted to the atmosphere or degrade, no diffusion of the pollutant into the depths of the soil is assumed. Although this effect is expected to be insignificant, its inclusion would greatly complicate the solution. The numerical solution includes this effect.

9. Liquid-vapor equilibrium is established at all times within the soil. It is possible to include this effect in the numerical solution.

estimated from the pollutant's Henry's Law constant if the waste is primarily water (is for dilute aqueous solutions) or from the pollutant's vapor pressure assuming Raoult's Law. We assume that the ideal gas law holds for the vapor space within the soil. The appropriate equations are:

A.) Henry's Law

$$A_i = 10^6 \frac{H_{ci}}{RT} \frac{\epsilon_{air}}{\epsilon_{waste}} \qquad (1a)$$

B.) Raoult's Law

$$A_i = P_i^{Vap} \frac{MW_{waste}}{RT} \frac{\epsilon_{air}}{L} \qquad (1b)$$

where H_{ci} = Henry's Law constant for pollutant i, atm-m^3/mol

R = Ideal gas constant = 82.05 cm^3 · atm/(mol · K)

T = temperature of vapor in soil, K

ϵ_{air} = void fraction of soil, cm^3 vapor space/cm^3 soil

ϵ_{waste} = Volume fraction of waste in soil, cm^3 waste/cm^3 soil (Equation 1a assumes that the waste is primarily water and therefore, the waste has a density of 1 g/cm^3 so that ϵ_{waste} [cm^3 waste/cm^3 soil] = L [g waste/cm^3 soil])

L = Waste loading = M_{totalo}/ℓ [g waste/cm^3 soil]

P_i^{Vap} = pure component vapor pressure of pollutant i, atm

MW_{waste} = Average molecular weight of the waste

M_{totalo} = total grams of waste initially added to soil/cm^2 of surface area, g/cm^2.

The time constant, t_B, is simply the reciprocal of the first order biological decay rate constant. If no biological decay rate data are available, this time constant can be used as an adjustable parameter.

Equation 1 can be integrated to yield,

$$\frac{M_{i\text{-air}}}{M_{io}} = F_{i\text{-air}} = \left(\frac{D_{i\text{-soil}}\,A_i}{\pi \ell^2}\right)^{1/2} \int_0^t e^{-t/t_B}\, t^{-1/2}\, dt. \qquad (2)$$

Equation 2 can be numerically integrated to determine the total mass of pollutant i emitted to the atmosphere after any time, t. For small times, specifically when $t/t_B < 0.2$ and $\frac{D_{i\text{-soil}}A_i t}{\ell^2} < 0.2$, an approximate solution for equation 2 is:

$$\frac{M_{i\text{-air}}}{M_{io}} = F_{i\text{-air}} = 1.128 \left(\frac{D_{i\text{-soil}}A_i t}{\ell^2}\right)^{1/2} [1 - 1/3\,(t/t_B)]. \qquad (3)$$

The amount of pollutant left in the soil after any time, t, is simply the difference between the initial amount added and the amount lost by air emissions and biological decay. Mathematically, this is:

$$M_i = M_{io} - M_{i\text{-air}} - M_{i\text{-biol}} \qquad (4)$$

where M_i = grams of pollutant i remaining in soil/cm^2 surface area, g/cm^2
$M_{i\text{-biol}}$ = grams of pollutant i removed by biological destruction/cm^2 surface area, g/cm^2.

We have assumed that the biological decay rate is first order with respect to M_i. That is,

$$\frac{dM_{i\text{-biol}}}{dt} = \frac{M_i}{t_B} \qquad (5)$$

Remember, t_B is the reciprocal of the first order rate constant. Substituting equation 4 into equation 5, the following expression can be written.

$$d\,M_{i\text{-}biol} = (M_{io} - M_{i\text{-}air} - M_{i\text{-}biol})\,(1/t_B)\,dt. \qquad (6)$$

Because $M_{i\text{-}biol}$ is a function of time, equations 2 and 6 must be solved simultaneously.

For very long times, (i.e. t approaching infinity), the fraction of pollutant i that is emitted into the atmosphere (i.e., $M_{i\text{-}air}/M_{io}$) can be estimated using the following correlations.

$$F^{\infty}_{i\text{-}air} = \frac{M_{i\text{-}air}}{M_{io}} = (t_{Bi}\,D_{i\text{-}soil}\,A_i/\ell^2)^{0.5} \qquad \text{for } \frac{t_{Bi}D_{i\text{-}soil}A_i}{\ell^2} < 0.45 \qquad (7)$$

$$F^{\infty}_{i\text{-}air} = \frac{M_{i\text{-}air}}{M_{io}} = 1 - 0.2014\,(t_{Bi}\,D_{i\text{-}soil}\,A_i/\ell^2)^{-0.749} \qquad \text{for } \frac{t_{Bi}D_{i\text{-}soil}A_i}{\ell^2} > 0.45 \qquad (8)$$

where $F^{\infty}_{i\text{-}air}$ = fraction of pollutant i emitted to the atmosphere at infinite time.

Table 2 compares the results of equations 7 and 8 estimates of the fraction emitted to the numerical solution of equation 2.

In order to estimate the fraction of pollutant emitted to the air at smaller times without requiring the numerical solution of equation 2, an exponential decay factor was developed. This expression relates the fraction emitted to the air at any time, t', after tilling

TABLE 2. THE INTEGRATED FLUX FROM LAND TREATMENT OF WASTES AS A FRACTION OF BIOLOGICAL DECAY

Extent of biological decay ($t_B DA/\ell^2$)	Fraction of VOCs emitted to atmosphere	
	Correlation	Calculated
No decay	1.000[a]	1.000
10.0	0.964[a]	0.9679
5.0	0.9397[a]	0.9382
1.0	0.7986[a]	0.7613
0.5	0.661[a]	0.6278
0.2	0.4472[b]	0.4367
0.1	0.3162[b]	0.3147
0.05	0.2236[b]	0.2233
0.01	0.1000[b]	0.0999
0.005	0.0707[b]	0.0706
0.001	0.0316[b]	0.0316

[a] (1-fraction) = 0.2014 $(t_B DA/\ell^2)^{-.74897}$.

[b] fraction = $(t_B DA/\ell^2)^{0.5}$.

of the soil, to the fraction emitted at infinite time (as calculated from equation 7 or 8), as follows:

$$F^{t'}_{i\text{-}air} = F^{\infty}_{i\text{-}air}\,(1 - e^{-t'/t_c}) \qquad (9)$$

where $F^{t'}_{i\text{-}air}$ = fraction of pollutant i emitted into the atmosphere at time, t', after tilling.

t' = time after tilling of soil, s.

t_c = $t_h/0.69315$ = psuedo-first order exponential decay time constant.

t_h = half life assuming no biological decay.

The half life, t_h, assuming no biological decay (i.e. $t_B \rightarrow \infty$) is the time at which $F_{i\text{-}air} = M_{i\text{-}air}/M_{io} = 0.5$. Since, at $t_B \rightarrow \infty$, $e^{-t/t_B} = 1$, equation 2 can be solved analytically to yield.

$$\frac{M_{i\text{-}air}}{M_{io}} = 1.128\left(\frac{D_{i\text{-}soil}\,A_i t}{\ell^2}\right)^{1/2} \qquad (10)$$

This can also be derived from equation 3 assuming $t/t_B = 0$. In any case, setting $\frac{M_{i\text{-}air}}{M_{io}} = 0.5$ and re-arranging yields:

$$t_h = 0.2\left(\frac{\ell^2}{D_{i\text{-}soil}A_i}\right) \qquad (11)$$

or

$$t_c = 0.283\left(\frac{\ell^2}{D_{i\text{-}soil}A_i}\right) \qquad (12)$$

Although the time constant is calculated assuming no biological activity, equation 9 accounts for biological destruction through the infinite time fraction emitted term (i.e. by the dependence of F^{∞}_{i-air} to t_B as given in equations 7 and 8). However, equation 9 is only exact at $t' = t_h$ and $F^{\infty}_{i-air} = 1$ (no biodegradation) and it becomes less accurate as F^{∞}_{i-air} approaches 0. Equation 3 is more accurate than equation 9 for small times independent of F^{∞}_{i-air}. Nonetheless, for many cases, the emission estimates using equations 7,8, and 9 correlate well with the emission estimates from equation 2 while obviating the need to perform numerical integration.

Using similar logic, equation 6 can be simplified as follows:

$$F^{t'}_{i-bio} = (1 - F^{\infty}_{i-air})(1 - e^{-t'/t_s}). \qquad (13)$$

where $F^{t'}_{i-bio}$ = the fraction of pollutant i biodegraded at time t'.

Note that at infinite time, we assumed that $M_i = 0$, so that $\frac{M_{i-air}}{M_{i0}} = F^{\infty}_{i-air}$ (from equation 4). In this instance, the time dependent term $1-e^{-t/t_B})$ is derived directly from equation 6 assuming that there are no air emissions ($M_{i-air} = 0$). Thus, equation 3 is exact for any time t' when $F^{\infty}_{i-air} = 0$. The empirical correlations of equations 7, 8, and 13 allow easy estimations of M_{i-air}, M_{i-bio}, and consequently, M_i. The estimation of Mi is important when we consider what happens after retilling the soil. When the soil is retilled, we can calculate M_i corresponding to the time, t', just prior to retilling denoted M_i'. This mass of pollutant will then be evenly distributed through the soil and the solution becomes analogous to the initial treatment solution except we now have at our new $t' = 0$, $M_{i0} = M_i'$. If additional pollutant is added before retilling (M_i added) our initial pollutant loading is simply $M_{io} = M_i$ added $+ M_i'$. Note that M_i' is the total mass of pollutant i in the soil/cm^2 surface area. That is, M_i includes the mass of pollutant in both the vapor and the liquid.

The equations presented herein allow the calculation of the rates of biodegradation and air emission from landfarms. The exact equations require numerical integration in order to be solved. However, accurate correlations have been developed and presented to estimate these rates. These equations allow easy calculation of the fraction of pollutant lost to the air, the fraction of pollutant lost by biodegradation, and the fraction of pollutant remaining in the soil at any time after the soil is tilled. Method of solution has been outlined for the reapplication of pollutant and retilling of the soil.

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