TOXICITY REDUCTION OF REFINERY SLUDGES USING PENTANE EXTRACTION

By

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NOMENCLATURE

API	American Petroleum Institute
ASTM	American Society for Testing and Materials
BDAT	Best Demonstrated Available Technology
EC50	Concentration that caused an effect in 50% of the tested organisms
EPA	Environmental Protection Agency
LC50	Lethal concentration to kill 50% of the tested organisms
RCRA	Resource Conservation and Recovery Act
TEA	Triethylamine
TCLP	Toxicity Characteristic Leaching Procedure
ZHE	Zero Head-Space Extractor

CHAPTER I

INTRODUCTION

On May 19th, 1980, The Environmental Protection Agency (EPA) published a list of hazardous wastes that included five wastes from the petroleum refining industry. These wastes were classified based on the type of unit that produced the waste. The classifications and their respective descriptions for the petroleum refining industry are shown in Table 1 (Code of Federal Regulations, 1991). Each of these sludges were shown to contain high levels of chromium and lead which formed the basis for the listing.

TABLE 1

CLASSIFICATION AND DESCRIPTION OF
REFINERY SOLID WASTES

Type	Description
KO48	Dissolved Air Flotation Float
KO49	Slop Oil Emulsions
KO50	Heat Exchanger Bundle Cleaning Sludge
KO51	API Separator Sludge
KO52	Leaded Tank Bottoms

In November 1980, the EPA was petitioned to expand the listing to include other wastes that were similar in composition but were not listed as hazardous. As a result, the EPA proposed to include all oily separation sludges generated, regardless of the process or type of equipment. This proposal was generally viewed with confusion as to whether it included biologically treated wastes.

The EPA spent the next ten years studying the hazardous constituents in refinery sludges. The goal was to generate an unambiguous listing of hazardous wastes that would exclude biologically treated sludges. Phenol removal and oil content were considered as indicators of biological activity to distinguish primary and secondary (biological) treated sludges. Both of these approaches were abandoned because neither could adequately prevent some primary sludges from escaping the hazardous listing while allowing secondary sludges to be classified as nonhazardous. Finally the EPA decided upon a comprehensive listing based on the process and the unit that produced the waste.

On November 2, 1990, the EPA created two new categories, FO37 and FO38, to complete the listing (Federal Register, 1990). Both listings include all sludges generated in the separation of oil, water and solids during the storage or treatment of process waste waters and oily cooling waters. Type F037 applies to sludges generated in gravitational separations, whereas, type F038 applies to sludges generated in the physical or chemical separation of emulsions. The new categories include all units in which oil, water, and solids are separated but specifically exclude storm water impoundments and aggressive biological treatment units. By the new rule, a sludge is considered generated when "at least a temporary cessation of lateral particle movement occurs" or "the moment they are formed in the top of the unit" (Federal Register, 1990).

Type F wastes were shown to contain concentrations in excess of regulatory levels of benzene, benzo(a)pryene, chrysene, lead and chromium. The EPA cited these results as the basis for creating the new listing. The effective date of the new listing was May 2,

1991. Until that time, these wastes were disposed of as non hazardous. After May 2, 1991, land disposal was allowed only in permitted hazardous waste units. The final land disposal restrictions for type F wastes were similar to those for the K wastes.

Refineries must reconfigure to comply with more restrictive regulations on the disposal of solid waste. Treatment of solid waste can either involve degradation or reclamation of the organic contaminants. Degradation of organics occurs during incineration or in biological treatment. Reclamation is achieved by solvent extraction or thermal desorption. These treatments can be operated on site by permitted refineries, or the wastes can be shipped to other treatment facilities. Refineries must choose the most economical treatment alternative unique to their situation.

The purpose of this research was to study the technical and economic feasibility of solvent extraction in a typical refinery. Solvent extraction was chosen over destruction technologies because of its potential to recover product. Also, recent legislation in the Clean Air Act Amendments has shown a trend toward more stringent air emission standards that increase the cost of incineration. All of the published articles on solvent extraction were developed by companies that reveal only the final results of solvent extraction. Information concerning the process was not provided because of its proprietary nature. The goal of this research was to develop possible processing alternatives and to evaluate the economic feasibility of solvent extraction processes.

CHAPTER II

LITERATURE REVIEW

In this chapter, different methods of solid waste treatment and the regulations affecting solvent extraction are presented. Methods of monitoring extraction efficiency and theoretical applications of the results are also reviewed.

Solid Waste Treatment Processes

Traditionally, refineries have dewatered wastes to reduce the amount of material and shipped them offsite to incinerators or cement kilns. As alternatives, this subsection will present three currently operating solvent extraction processes. Bacterial degradation and thermal desorption are also described.

Solvent Extraction Processes

C.F. systems, a Morrison Knudsen company, has operated a full scale propane extraction unit to process 1,000 barrels/day of hazardous waste since March 17, 1991 (Filippi and Markiewicz, 1991). The process has claimed to remove typically 99% of the organic contaminants. Liquified propane at temperatures of 90-120 ^{o}F and pressure

approximately 300 psig is contacted in a multistage extractor/decanter system with a sludge/water slurry. The propane extract is removed by gravity separation and the propane is recovered in a low pressure still. The propane is then recompressed with make-up propane and recycled to the extractor. The extracted solids are dewatered by a filter press and the solid meets Best Demonstrated Available Technology (BDAT) standards for land disposal.

British Petroleum Oil Company is currently operating a commercial scale extraction unit at the Alliance refinery in Belle Chasse, Louisiana (Poche et al., 1991). Similar to the CF systems plant, this unit uses propane in the first extraction stage, reformate to remove heavy aromatics in the second stage and a final polishing extraction with propane. The sludge feed is deliquified prior to extraction to eliminate a separate wastewater stream downstream from the extraction unit. This process and the preceeding process have been shown to be economically feasible by the operating company.

A process that has been independently evaluated by EPA testing is the B.E.S.T.™ solvent extraction treatment technology (Sudell, 1988). This process uses triethylamine (TEA) as the extraction solvent and is capable of reducing organic contaminants by 98%. Triethylamine is completely miscible with water below 20 ^{o}C but becomes immiscible above 20 ^{o}C. This property allows TEA to separate emulsions of solid/water/organics into three distinct phases. The organic contaminants preferentially separate into the organic phase.

Bacterial Degradation

Aerobic bacterial degradation was shown to effectively reduce organic contaminants below regulated limits in a full scale reactor (Vail, 1990). Active microbes

were combined with optimum levels of nutrients to achieve maximum destruction of organic contaminants. The process did not meet BDAT regulated limits unless the 4, 5 and 6 ring polynuclear aromatics were maintained at specified levels in the feed. The process was also strongly temperature dependent. Studies have shown that the process failed to meet BDAT regulated limits at 77 ^{o}F but succeeded at 104 ^{o}F.

Thermal Desorption

Thermal desorption is a process where sludge is fed to a heated conveyor and dried in an oxygen deficient atmosphere at temperatures approaching 1000 ^{o}F (Abrishamian et al., 1992). The volatile organics are collected, condensed and recycled back to the refinery. The dried solids are cooled and stored for subsequent disposal. The process has been shown to effectively reduce solid waste organic concentrations below regulated limits.

Heavy metal concentration in the solid phase is a problem with all of the previously mentioned extraction processes. As a result, all require some type of metal fixation or removal step. Commonly, pozzalonic material (e.g. cement kiln, fly ash) is used to immobilize the metals in a solid matrix (Vail, 1990).

EPA Regulations Affecting Refinery Wastes

The "mixture" rule and the "derived from" rule are two regulations that affect the treatment of hazardous wastes. The "mixture" rule states that any mixture of a listed hazardous waste remains a hazardous waste (Code of Federal Regulations, 1991). The "derived from" rule states that any waste derived from the treatment, storage, or disposal of

a listed waste is a hazardous waste subject to RCRA regulations (Code of Federal Regulations, 1991). This rule includes the ash deposited during incineration of hazardous wastes . These two regulations limit a refineries ability to treat hazardous material. By these two rules, any treatment method, including solvent extraction, would result in a hazardous solid waste regardless of its composition. The resulting solid must be disposed of in a permitted facility. The only mechanism for excluding a waste from regulation is by the delisting procedure.

Delisting requires that a refinery prove that the waste does not contain any of the contaminants that caused the waste to be listed. Type KO48-KO52 wastes were listed based on high levels of chromium and lead. Type FO37 and FO38 wastes were listed based on high levels of chromium, lead, benzene, benzo(a)pyrene and chrysene. In addition, it must be proven that a waste does not exhibit any of the characteristics of ignitability, corrosivity, reactivity, or toxicity (Code of Federal Regulations, 1991). Ignitability is characteristic of any waste which has a flash point less than 140 ^{o}F. Corrosivity is characteristic of any waste which has a pH less than 2 or greater than 12.5. A waste has the characteristic of reactivity if it exhibits any one of eight properties, however, most refinery wastes do not exhibit reactivity. The toxicity characteristic is exhibited by all listed petroleum refining wastes (Code of Federal Regulations, 1991). A waste is considered toxic if the extract from the Toxicity Characteristic Leaching Procedure (TCLP) contains any one of forty listed contaminants in excess of regulatory levels. Because of all the requirements, delisting is a very expensive and time consuming procedure.

Solvent extraction and incineration are recognized BDAT treatments for KO48-KO52 solid wastes. Prior to land disposal, hazardous organic contaminants and metals must be reduced below BDAT limits. The BDAT standards for refinery wastes are shown on the following page in Table 2. Land disposal restrictions are already in effect for type K

wastes and will be in effect for type F wastes within two years. The treatment standards for the F wastes are similar to those for the K wastes. Treatment of a solid to BDAT standards is less expensive and more time efficient than delisting.

TABLE 2

BDAT STANDARDS FOR PETROLEUM REFINING WASTES

Compound	1990 BDAT standard (mg/kg)
Benzene	14
Ethylbenzene	14
Toluene	14
Xylene	22
Anthracene	28
Benzo(a)anthracene	20
Benzo(a)pyrene	12
Bis-(2-ethylhexyl)phthalate	7.3
Chrysene	15
Di-n-butylphtalate	3.6
Naphthalene	42
Phenanthrene	34
Pyrene	36
Phenol	3.6
o-cresol	6.2
m,p-cresol	6.2
Total cyanide	1.8
Chromium *	1.7
Nickel *	0.2

* Determined by the Toxicity Characteristic Leaching Procedure

Methods of Monitoring Organics Removal

The distribution of components between the solvent and solid phase can be monitored by an overall material balance. In addition, reduction in toxicity of treated sludges can indicate the extractive capability of a solvent.

The Environmental Protection Agency has published numerous analytical methods for determining the composition of sludges and wastewaters (Test Methods for Evaluating Solid Wastes, 1986). The sludge feed, solid raffinate and solvent extract can all be analyzed for organics using standards methods and gas chromatographic/mass spectrophotometric analysis. These methods require analytical equipment not available for this project. As a result, ASTM standard methods were substituted when applicable.

The overall material balance and component material balances for total organics, inert solids, water, and solvent can be solved to determine the distribution of components between the different phases. A representation of the system is shown in Figure 1. The following material balance equations must be satisfied.

Overall Mass Balance: $F + S = F' + S'$ (1)

Organic Mass Balance: $(Xo,f)F = (Xo,s')S' + (Xo,f')F'$ (2)

Inert Solids Mass Balance: $(Xi,f)F = (Xi,s')S' + (Xi,f')F'$ (3)

Solvent Mass Balance: $S + (Xs,f)F = (Xs,s')S' + (Xs,f')F'$ (4)

Water Mass Balance: $(X_{H2O,f})F = (X_{H2O,s}')S' + (X_{H2O,f}')F'$ (5)

where F = sludge feed into extractor ; S = solvent feed; F ' = mass of extracted solids; S ' = mass of solvent extract; X = component mass fraction. The subscripts o, i, s and H2O refer to organics, inert solids, solvent and water respectively.

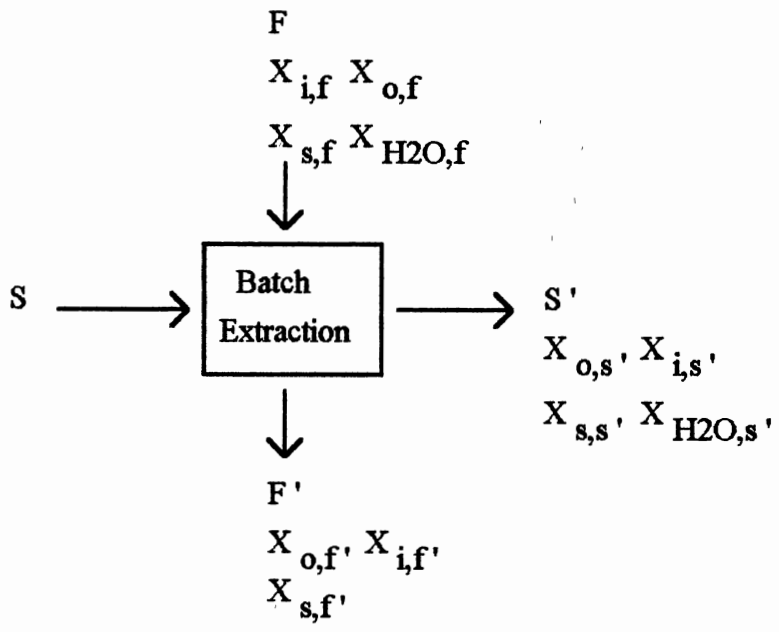

Figure 1. Diagram of overall material balance

If the total mass of the solvent, sludge, and extract are known, then the mass of the raffinate can be obtained from the overall mass balance. In addition, if the composition of the sludge and raffinate are known, then the composition of the extract can be obtained.

Toxicity testing is a second method of determining the effectiveness of the solvent extraction process. Numerous authors have shown a relationship between the nonpolar organic contaminants in process wastewaters and the toxic effects upon aquatic organisms (Dorris et al., 1972). As a result, monitoring aquatic toxicity before and after extraction indicates toxicity reduction due to removal of organic contaminants.

Aquatic toxicity testing methods are well established for process wastewater streams (Peltier and Weber, 1985). Toxicity can be either acute (lethality within 24 or 48 hours) or chronic (cumulative toxicity over 7 days). The measured variable (LC50) is the lethal concentration to kill 50 % of the organisms tested. The test organisms are typically either Ceriodaphnia dubia (water fleas) or Pimephales promelas (fathead minnows).

Other parameters such as pH, ammonia concentration, heavy metals concentration, and temperature can interfere with toxicity results. Toxicity screening tests can be performed to determine which variable contributes the majority to toxicity (Norberg-King et al., 1991). Since solvent extraction is not likely to remove heavy metals, these tests will be helpful in interpreting toxicity results.

Theoretical Application

The material balance distribution data can be applied to solid-liquid equilibrium theory to develop a predictive model for this process. This section presents a discussion of thermodynamic theory and simplifying assumptions that are necessary to reduce the equations to usable forms. The equations are presented to provide background for future extension of this project to theoretical modeling.

In order to obtain thermodynamic equilibrium at constant temperature and pressure for a multicomponent mixture, the fugacities of each component must be equal in the solid and liquid phases. In mathematical form,

$$f_i^S = f_i^L \tag{6}$$

where f is the fugacity of component i and the subscripts S and L refer to the solid and liquid phase, respectively. The fugacity of each component in the liquid is defined as

$$f_i^L = \gamma_i x_i f_i^o \tag{7}$$

where γ_i is the activity coefficient, x_i is the mass fraction and $f^o{}_i$ is the standard state fugacity. Substituting Equation 7 into Equation 6 gives an expression for the solubility of each component in the liquid phase.

$$x_i^L = \frac{f_i^S}{\gamma_i^L f_i^o} \tag{8}$$

where the subscripts L and S have been added to denote liquid and solid phase. The fugacity in the solid phase can be deduced by assuming that the solid is a pure component. This is a valid assumption since the components are physically mixed and do not exist as a thermodynamic mixture. Assuming negligible solubility of the solvent in the solid phase and defining the standard state as pure, subcooled liquid, the fugacity ratio can be obtained by

$$\ln \frac{f_i^o}{f_i^S} = \frac{\Delta h_t^f}{RT}\left(\frac{T_t}{T} - 1\right) - \frac{\Delta cp}{R}\left(\frac{T_t}{T} - 1\right) + \frac{\Delta cp}{R}\ln\left(\frac{T_t}{T}\right) \tag{9}$$

where c_p is the heat capacity, Δh_f is the enthalpy of fusion, T_t is the triple point temperature, T is the system temperature and R is the gas law constant. The only

remaining term to be determined is the activity coefficient for each component in the liquid phase.

The system studied in this project consisted primarily of hydrocarbons dissolved in an organic solvent. In addition, the liquid phase is a dilute solution which minimizes the interaction effects between molecules. Therefore, the Scatchard-Hildebrand (1964) relation for the solubility parameter should be a valid model for the distribution of hydrocarbons. The relation for a multicomponent mixture is given by the following equation

$$\ln \gamma_i = \frac{v_i \left(\delta_i - \bar{\delta} \right)^2}{RT} \tag{10}$$

where v_i is the molar volume of the subcooled liquid, δ_i is the solubility parameter for the component of interest and δ is the volume-fraction average of the solubility parameters of all components in the solution. Both the molar volume and the solubility parameters must be obtained at the subcooled liquid reference state. The volume-fraction average solubility parameter is given by

$$\bar{\delta} = \sum_{i}^{m} \phi_i \delta_i \tag{11}$$

where ϕ_i is the volume fraction of component i given by

$$\phi_i = \frac{x_i v_i}{\sum_j^m x_j v_j} \tag{12}$$

where the summation is taken over all components other than the *i*th component. Equation 11 can be modified with an interaction parameter to maximize agreement between the predicted values and experimental results.

The water phase and the distribution of metals into the aqueous phase are more difficult to model due to the strong molecular interactions. In addition, the metal ions exhibit an effect on the activity coefficients of the organic solutes known as the salting effect. Due to these difficulties, the current status of mathematical modeling in this area is incomplete. As an approximation, the water phase distribution can be determined with the same equations as the hydrocarbon mixture resulting in approximately 20% error. The metal ions distribution and effect on the hydrocarbon solutes can be estimated by procedures given by Gordon (1975).

Ideally, this project could provide distribution coefficients for each component that would be compared to distribution data calculated from the model equations. This approach, however, is not possible due to the complexities associated with characterizing the raw sludge. Without analysis techniques to accurately quantify every component in the solid matrix, model development for predictive purposes is premature. As a result, the focus of this project is to characterize the overall distribution of components and determine the technical feasibility of solvent extraction as a process to meet BDAT standards.

CHAPTER III

METHODS AND MATERIALS

In this chapter, the experimental procedures are presented. The chapter contains three subsections; preliminary evaluation, batch extractions and analytical methods.

Preliminary Evaluation

A preliminary evaluation of solvent extraction of sludge was performed. Type FO37 wastes were used in both the preliminary evaluation and the batch extractions. Type KO51 waste was used in the batch extraction phase and the determination of maximum extractable organics. The preliminary evaluations can be divided into three categories; physical characterization of the sludge, determination of an effective solvent and determination of maximum extractable organics.

Physical Characterization

Two types of FO37 sludge, raw and dewatered, were used in the physical characterization stage. Each was examined for color, number of distinct phases, odor, sedimentation properties and presence of an emulsion.

The raw sludge was dark black in color and appeared to contain a large quantity of liquid. There was not a distinct solid phase but the sludge appeared to contain suspended solids. A strong hydrocarbon odor was prevalent with this sludge, and the existence of hydrocarbons was further substantiated by the oily film left on all glassware used to handle the sludge.

A sedimentation test was conducted on the raw sludge to determine the number of phases that resulting from gravity separation. Fifty milliliters of sludge were added to a graduated 50 ml cylinder. The sludge was allowed to separate for 24 hours. A thin layer, approximately 1 ml, of tan liquid had appeared on the surface. The remaining sludge did not settled into distinct layers. From these observations, it was apparent that the sludge was a suspension of hydrocarbons, water and solids that did not separate by gravity.

The dewatered sludge was dark black in color and appeared to be a solid coated with liquid. This sludge also emitted a strong hydrocarbon odor. This sludge was not used for sedimentation tests because it was essentially solid.

A preliminary extraction was performed after qualitatively examining both sludges. In a 10 milliliter bottle with a teflon lined screw cap, three 0.5 milliliter drops of the raw sludge were combined with 10 milliliters of pentane. Similarly, three 0.5 milliliter clumps of the dewatered sludge were added to 10 milliliters of pentane. Each was shaken for 30 minutes and allowed to sit overnight. After 24 hours, the samples had changed from black oily globules to light tan solids. This indicated that a change had occured in the sludge and that further investigation was warranted.

Solvent Selection

Appropriate solvents for the experimental procedure were selected based on toxicity, cost and volatility. Extensive research has been performed on propane and other proprietary solvents as presented earlier in this paper. Propane exists as a gas at ambient temperatures and pressures and must be compressed prior to extraction. Hydrocarbons with aromatic rings were not considered because of their toxic nature. Normal hydrocarbons with larger carbon numbers overcome the toxicity problems but lose economic advantages with increased value of solvent. Pentane, hexane and mixtures of these, however, have been economically utilized to clean offshore oily cuttings (Menton, 1991). In addition, pentane and hexane couple high solvation power with low boiling points for solvent recovery. As a result, pentane and hexane were compared for extraction efficiency.

Each solvent was used in a single stage batch extraction of the dewatered sludge. In a Millipore Zero Head-Space Extractor (Model # YT30090HW), 400 milliliters of pentane were combined with 98.9 grams of sludge. The sample was pressurized to 10 psig to minimize the formation of a vapor phase. The extractor was then tumbled in a Millipore Rotary Agitator (Model # YT310RAHW) for 24 hours at 28 rotations per minute. At intervals of 1, 2, 4, 8, 16 and 24 hours, a 10 milliliter sample of extract was collected to monitor the approach to equilibrium. Although only qualitative, the sample color was used to determine the time when maximum extraction was achieved. After collection of all six samples, each was placed side by side in front of a white background. The colors ranged from a light yellow to a dark brown progressing from the shortest contact time to the longest. There were definite differences in color of all samples but the 16 and 24 hour samples. As a result, 24 hours was chosen as the target time for all subsequent extractions.

Similar to the pentane extraction, 400 milliliters of hexane were combined with 100.5 grams of sludge. The extractor was tumbled for 24 hours and two 10 milliliter samples of the extract were collected.

Each 24 hour extract was analyzed for total organics by gas chromatography. Neither sample showed detectable peaks other than the solvent so each sample was concentrated to 1 milliliter using a nitrogen purge. The concentrated samples were then used for gas chromatographic analysis. Each sample was combined with 10 microliters of toluene as a standard. Assuming that the response factor was constant, the seven major peaks that existed in both the pentane and hexane extracts were summed. This "total peak area" was divided by the standard peak area and used as a basis of comparison. The gas chromatographic results are shown in Table 3. There was no difference in extractive ability between pentane and hexane. As result, pentane was selected for the batch extraction studies because it exists as a liquid at ambient temperatures and pressures and it has lower cost than hexane. In addition, pentane has a lower boiling point that enables better separation from recovered organics.

Maximum Extractable Organics

The maximum extractable organics and the mass percent solids and water were determined by a modified soxhlet extraction. A sample of sludge was placed in a Whatman cellulose extraction thimble (cat. no. 2810258). The thimble was then placed in a Kimax 24005 Soxhlet Extraction Apparatus that drained into a Dean & Stark Moisture Test Receiver. The overflow from the moisture receiver was collected in a 500 milliliter round bottom flask that was heated to vaporize the solvent. The solvent vapor passed up through the apparatus where it was condensed above the soxhlet by a water condenser. The

TABLE 3

COMPARISON OF PENTANE AND HEXANE
EXTRACTION CAPABILITIES

Observation	Total Organic Area / Standard Area	
	Pentane	Hexane
1	1.628	1.753
2	1.733	1.677
3	1.690	1.656
4	1.826	1.673
Mean	1.719	1.690
95 % C.I.	0.115	0.060

condensed solvent washed the solids in the extraction thimble and drained into the moisture trap. In this cycle, the extractable organics were removed from the solids and collected in the round bottom flask. Any water that was contained in the solids was washed with the solvent and collected in the moisture trap. Following extraction for more than 16 hours, the thimble was removed and dried to determine the mass percentage of solids. The collected volume of water was multiplied by the density to determine the mass percentage of water. The mass percentage of extractable organics was determined by difference (subtraction of the mass percentages of water and solids from one hundred).

Batch Extractions

Single-stage and two-stage batch extractions of the FO37 dewatered sludge and

the KO51 sludge with pentane were the primary focus of the experimental procedure. These sludges were chosen because they are commonly found in many refineries, and they offer a comparison between a sludge that contains water (KO51) and one that does not (FO37). With these different treatments, it was desired to determine the effect of multiple stages of extraction and the presence of water in the feed on the overall organic removal. A diagram of the experimental procedure is shown in Figure 2.

The extractions were performed in a Millipore Zero Head-Space Extractor (ZHE) with approximately 100 grams of sludge feed and 400 milliters of pentane solvent. Figure 3 is an illustration of the extraction vessel. The ZHE was chosen as an extractor to minimize the formation of vapor inside the extractor which simplified the model of the system. As a result, liquid-vapor equilibrium was not considered. One hundred grams of sludge was used because that amount resulted in the minimum residual solids required for characterization and toxicity testing. The volume of solvent was restricted by the capacity of the ZHE (approximately 500 milliliters). All extractions were performed with these nominal parameters.

Weights of the sludge feed and the solvent feed were measured and recorded. The solvent was added fifty milliliters at a time using a 50 milliliter gas tight syringe. Each stage of extraction was pressurized to 10 psig and tumbled for 24 hours, the time required to reach equilibrium. Following the extractions, the extract was collected under 50 psig of pressure and weighed. The extract was then concentrated with a nitrogen purge until detection by gas chromatography was possible. The mass of the raffinate solids was calculated by the overall material balance and three small samples (1-2 grams) of the raffinate were collected in small tared crucibles. The samples were weighed and dried overnight at 105 ^{o}C to determine the mass percentage of solvent remaining in the raffinate. The remaining solids were collected for soxhlet extraction, ash testing and toxicity testing.

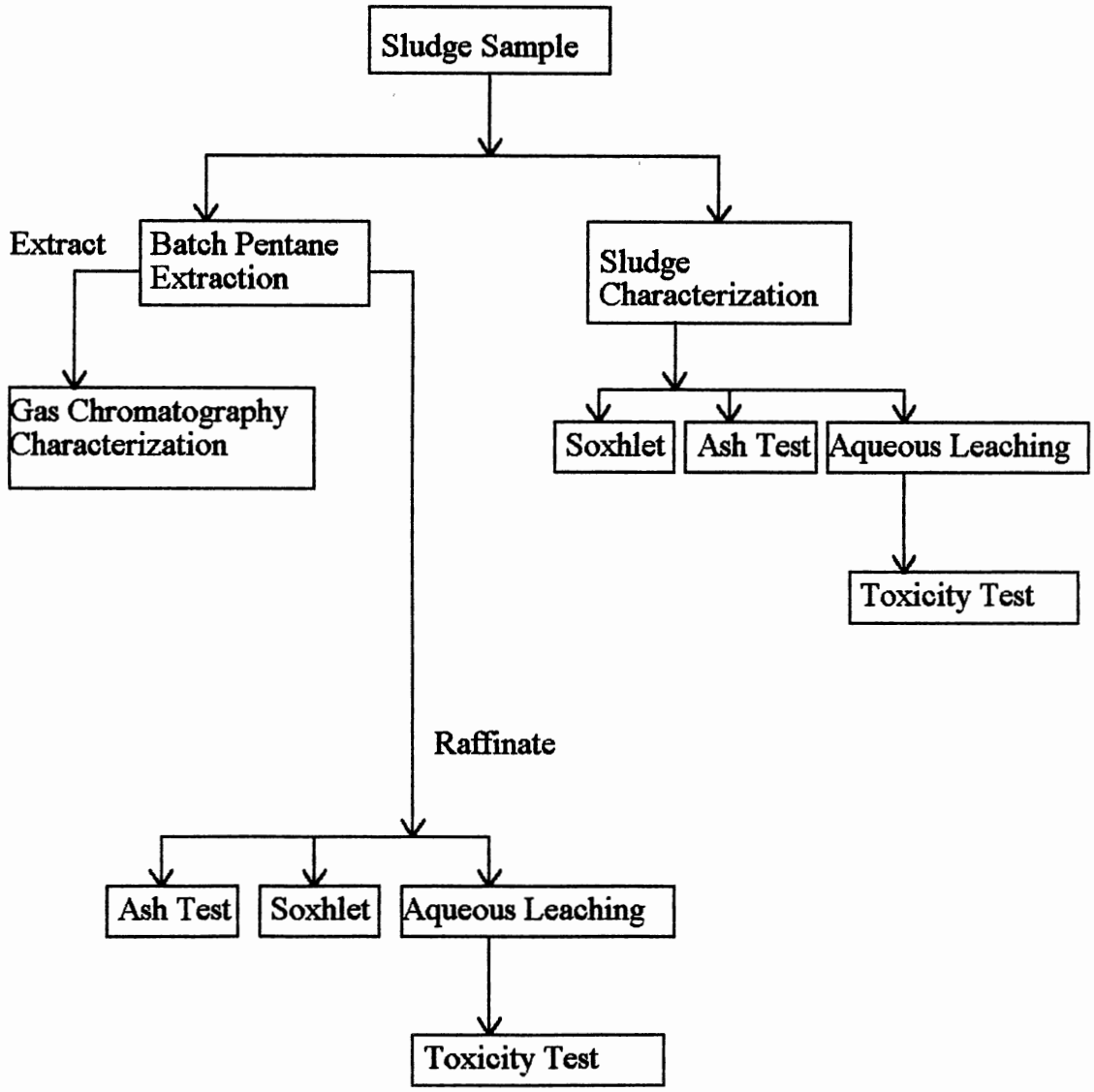

Figure 2. Diagram of Experimental Plan

For the second stage extractions, the ZHE was not opened after the first stage to determine the mass percentage of solvent in the solids. This was done to minimize the loss of solvent that occurs when the ZHE is opened. Instead, the ZHE was immediately loaded with 400 milliliters of fresh pentane and extracted a second time by the same procedure.

The second stage solids and extract were characterized using the same procedures as the first stage.

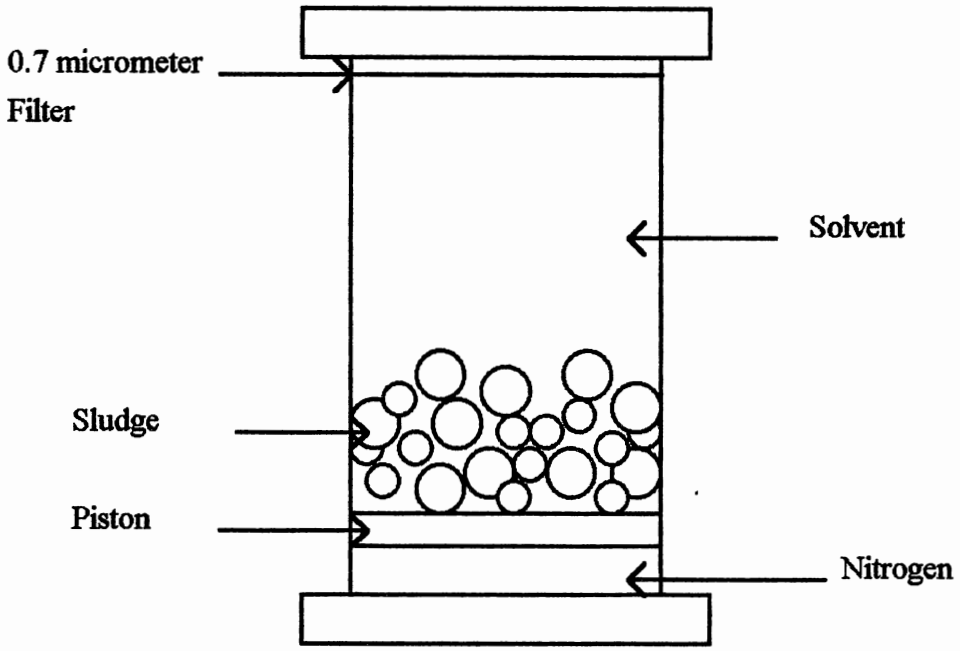

Figure 3. Diagram of Zero Head-Space Extraction Vessel

Quality Control

To minimize the loss of volatiles and increase the homogeniety of the sample, the one gallon bulk waste samples were divided into several smaller subsamples. These subsamples were collected in 120 milliliter bottles with teflon lined screw caps and stored at 4 ^{o}C until used.

The FO37 dewatered waste was nearly 100% solid and heavy oils concentrated at the bottom. The sample did not mix well so several samples were collected from three

different layers (top, middle and bottom) in the bulk sample. Samples from each layer were combined to create the batch extraction sample.

The KO51 bulk sample was very nonhomogenous containing large non-uniform clumps of solid. Most of the non-uniform solids were settled at the bottom and would not suspend with vigorous shaking. As a result, good homogenous samples were removed from above the dense solids. These samples were placed in 120 milliliter bottles and stored at 4 ^{o}C.

Analytical Methods

The analytical methods can be divided into sample preparation procedures and analytical procedures. The sample preparation procedures included concentration of the solvent extracts for gas chromatographic analysis and leaching of the solids for aquatic toxicity testing. The analytical procedures used gas chromatography, ash testing and 48 hour acute toxicity testing using Ceriodaphnia dubia.

Sample Preparation

The solvent extracts from both the soxhlet extractions and the batch extractions required concentration to detect the organic components. The extracts for the FO37 wastes were purged to a fume hood resulting in the loss of any volatiles that were present. The procedure was slightly modified for the KO51 waste. The overhead volatiles were trapped in a cold finger using dry ice and acetone. The condensed volatiles were collected

and analyzed by gas chromatography similar to the nonvolatiles. Different samples were concentrated to different extents depending on the original concentration of the extract. After concentration, the remaining extract was collected in 20 ml vials with screw cap lids with teflon-lined septa and stored at 4 ^{o}C.

Twenty-five grams of the raffinate solids were prepared for toxicity testing. The original proposal was to perform the Toxicity Characteristic Leaching Procedure (TCLP) on the raffinate and test the TCLP leachate for toxicity. The TCLP leachate was shown to result in unacceptable levels of blank toxicity. As a result, the Standard Elutriate Test from the Dredged Material Testing Manual (EPA-503/8-91/001) was substituted. For this leaching procedure, distilled water was combined with sludge in a 4:1 volume/weight ratio. The mixture was stirred for 30 minutes and allowed to settle for 1 hour. The mixture resulted in emulsions that would not separate within 1 hour. As a result, the emulsion was separated by centrifugation for 20 minutes followed by filtration through a 1.2 micrometer glass fiber filter. The leachate was then used for toxicity testing.

Analytical Techniques

The concentrated extracts were analyzed for total peak area of organics using gas chromatography. A measured mass of toluene was added to each sample as an internal standard. A Hewlett-Packard 5890A gas chromatograph and 3392A integrator were used. The gas chromatograph operating parameters are summarized as follows:

Column: 60 meters by 0.32 micrometer DB1 Durabond J&W Capillary Column with 1.0 micrometer thick methyl silicone substrate

Detector: Thermal Conductivity

Carrier Gas: Helium

Injector Temperature: 325 ^{o}C

Detector Temperature: 350 ^{o}C

Column Temperature: 50 ^{o}C - 9 minutes, 15 ^{o}C/min to 150 ^{o}C, 5 ^{o}C/min to 320 ^{o}C, 320 ^{o}C for 35 minutes.

Column Flowrate: 1.0 ml/min

Make-up Gas Flowrate: 11.0 ml/min

Purge Flowrate: 3.6 ml/min

The column was operated using splitless injection and septum purge after 30 seconds. The septum purge was necessary to remove condensed heavy organic contaminants that remained in the injector.

Gas chromatography was used in conjuction with the Standard Test Method for Boiling Range Distribution of Petroleum Fractions by Gas Chromatography (ASTM D2886-89) to characterize the solvent extracts. This method characterized the extract by boiling fractions that were determined from a calibration curve of normal boiling point (^{o}F) as a function of retention time (minutes). The calibration curve was experimentally derived from injections of a standard mixture of normal hydrocarbons (Supelco D-2887 Quantitative Calibration Mix). The method calibration curve is shown in Figure 4. The data were fit with the second order polynomial $Y = -74.92 + (11.06)X + (-.059)X^2$. Typically with this method, the curve is linear at the higher boiling points when a linear temperature program is used to high final temperatures greater than 360 ^{o}C . Because the maximum column temperature is reached at 320 ^{o}C and held for 35 minutes, the plot shows curvature at the upper end of the boiling region. As a result, the curve cannot be used for extrapolation outside of the experimental range. The column resolution was determined using a 1% of each component mixture of C_{16} and C_{18} in n-octane (Supelco D-2887 Column Test Mix). A column resolution of 4.6 was calculated by the ASTM 2887 method equations.

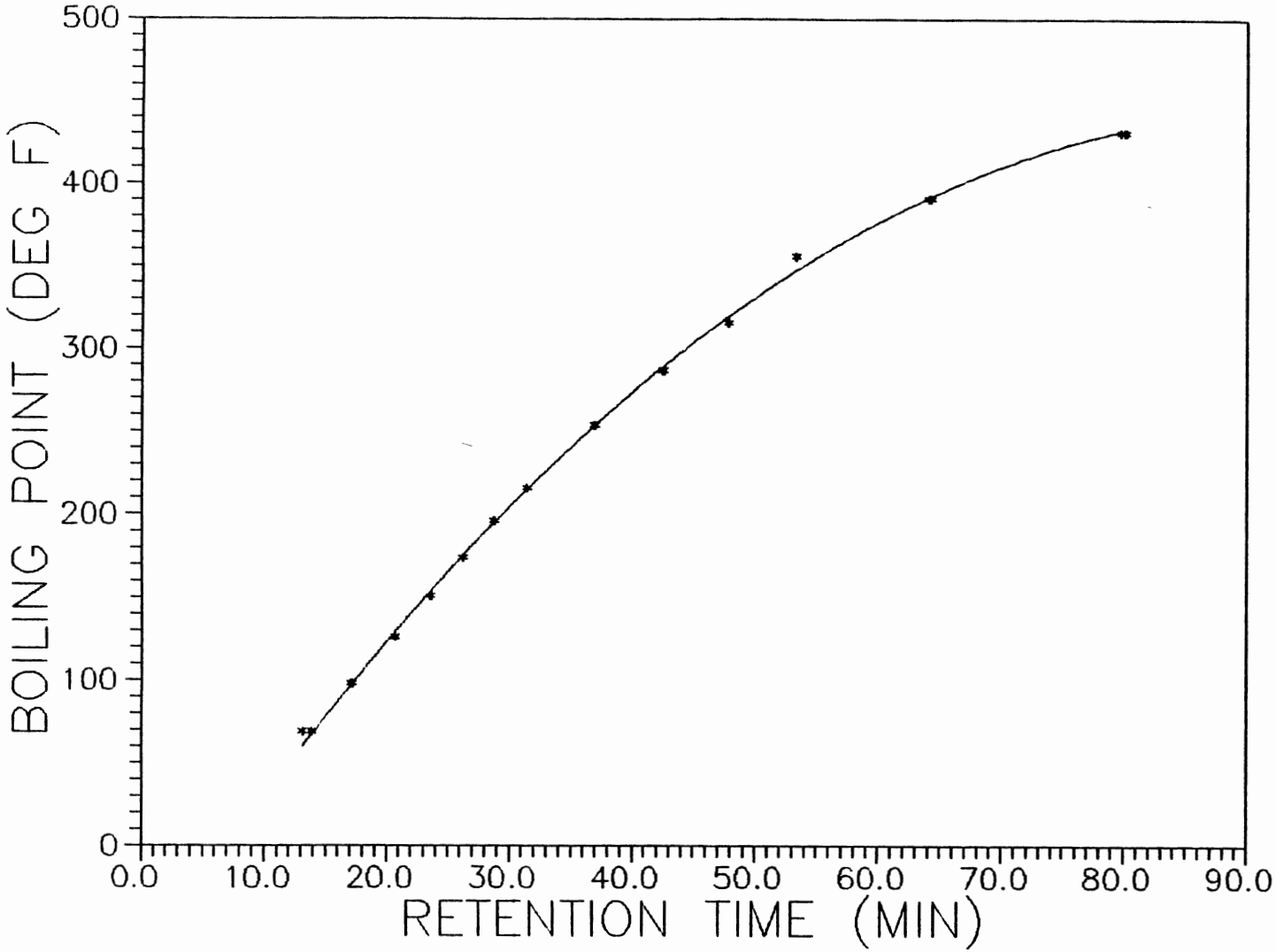

Figure 4. Boiling Point Calibration Curve for ASTM 2887

The sludges and raffinate solids were tested for inert solids by the Standard Test Method for Ash from Petroleum Products (ASTM D482-91). This method was used to give information on the total mass of heavy hydrocarbon material (asphaltenes, oils, etc.) that remained in the solid matrix. The method was altered slightly to prevent the volatilization of inorganic carbonaceous solids. The muffle furnace was only operated at 545 ^{o}C instead of 750 ^{o}C.

The prepared leachates for toxicity testing were used in 48 hour acute toxicity tests using Ceriodaphnia dubia. The procedure followed the method given in the Compendium of ERT Toxicity Testing Procedures (EPA/540/P-91/009). Four dilutions were used of each leachate at 100%, 40%, 15% and 5% by volume. Each test chamber used six organisms in 10 milliliters of leachate. Duplicates were tested for each dilution giving a total of 12 organisms at each dilution. At time intervals of 1, 2, 4, 8, 24 and 48 hours, the number of dead organisms / total organisms was recorded. Death was prescribed when the organism did not move when gently proded with a glass pipet. The LC50 data was calculated from the percent mortalities at each dilution using a computer program written for the Trimmed Spearman-Karber Method (Hamilton et al., 1977). This method calculated the 95% confidence interval for the LC50 when possible. The two dilutions bracketing the LC50 were used when the 95% confidence interval could not be calculated.

CHAPTER IV

RESULTS

This chapter presents the results of the material balances on the batch extractions and toxicity testing for the FO37 and KO51 wastes. The chapter is divided into four sections; extraction results, toxicity tests, BDAT test results and process design and economic considerations. The results for each type of sludge are presented simultaneously.

Extraction Results

This section presents the maximum extractable organics followed by the experimentally determined compositions of the sludge feed. The compositions of the single-stage and two-stage batch products are also presented.

Maximum Extractable Organics

The maximum extractable organics were determined using soxhlet extraction with pentane of the FO37 and KO51 wastes. The results for the FO37 and KO51 wastes are shown in Tables 4 and 5, respectively. The raw and dewatered FO37 sludges were both tested for extractable organics. The mean percent organics values for each sludge

represent the maximum removal with infinite batch extractions. The percent solids included inert solids and nonextractable organics. These values defined the limits on organic removal using pentane.

TABLE 4

MAXIMUM EXTRACTABLE ORGANICS (FO37)

Sludge	% Water	% Solids	% Organics
Raw #1	21.1	13.1	65.8
Raw #2	26.0	13.3	60.7
Raw #3	17.8	12.2	70.0
Mean	21.6	12.9	65.5
σ	2.38	0.34	2.69
95% C.I.	7.6	1.1	8.6
Dewatered #1	0.0	30.9	69.1
Dewatered #2	0.0	28.4	71.6
Mean		29.6	70.4
σ		1.25	1.25
95% C.I.		5.4	5.4

The maximum extractable organics for the raw and dewatered FO37 sludge were not statistically different. This result indicated that the presence of water in the raw sludge did not affect the maximum removal of organics. The results were not used, however, to interpret the affect that the water had on organic removal for a single equilibrium stage.

TABLE 5

MAXIMUM EXTRACTABLE ORGANICS (KO51)

Observation	% Water	% Solids	% Organics
1	9.7	45.6	44.7
2	12.7	45.2	42.1
3	12.0	44.8	43.2
Mean	11.5	45.2	43.3
σ	.911	.220	.754
95% C.I.	2.9	0.7	2.4

The percent relative error of the water in the aqueous sludges was the largest experimental error in these results. The error analysis procedure is contained in Appendix A. The FO37 raw waste exhibited 11.0% relative error in the water percentage. The KO51 waste showed 7.9% relative error. These large deviations were an indication of the nonhomogeneity of the sludges containing water. The calculated values of the percent extractable organics showed large standard deviations as a result of the error in the percent water. The relative error in the maximum extractable organics for the FO37 raw sludge is 4.1% and for the KO51 sludge is 1.7%.

The extracts from both sludges were characterized by gas chromatography. The chromatograms for the FO37 waste and the KO51 wastes are shown in Figures 5 and 6, respectively. The peak at approximately 9.5 minutes is pentane and the peak at about 18.8 minutes is the internal standard. These figures are useful qualitative comparisons to the chromatograms of the batch extracts.

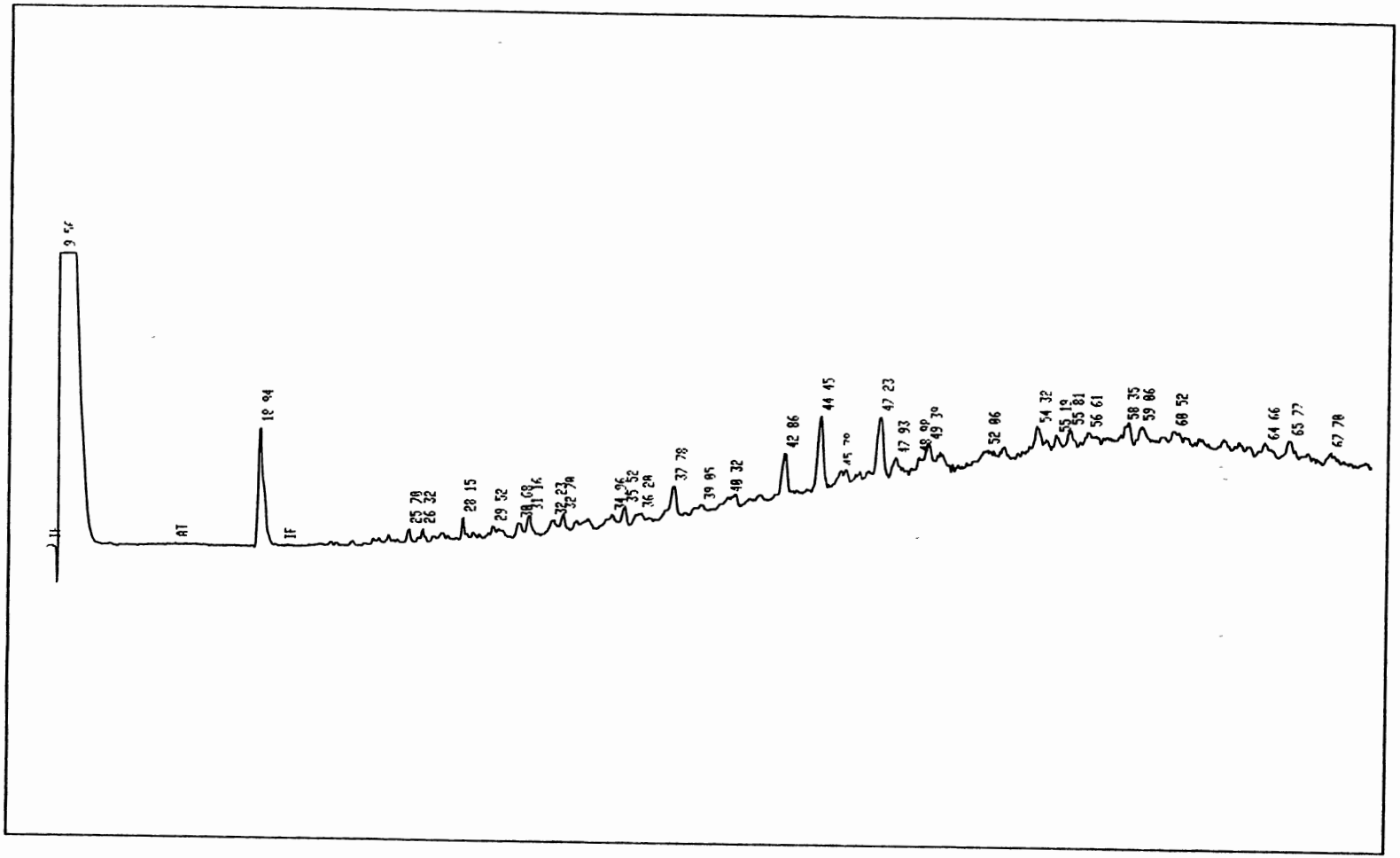

Figure 5. Chromatogram of Maximum Extractable Organics Extract (FO37)

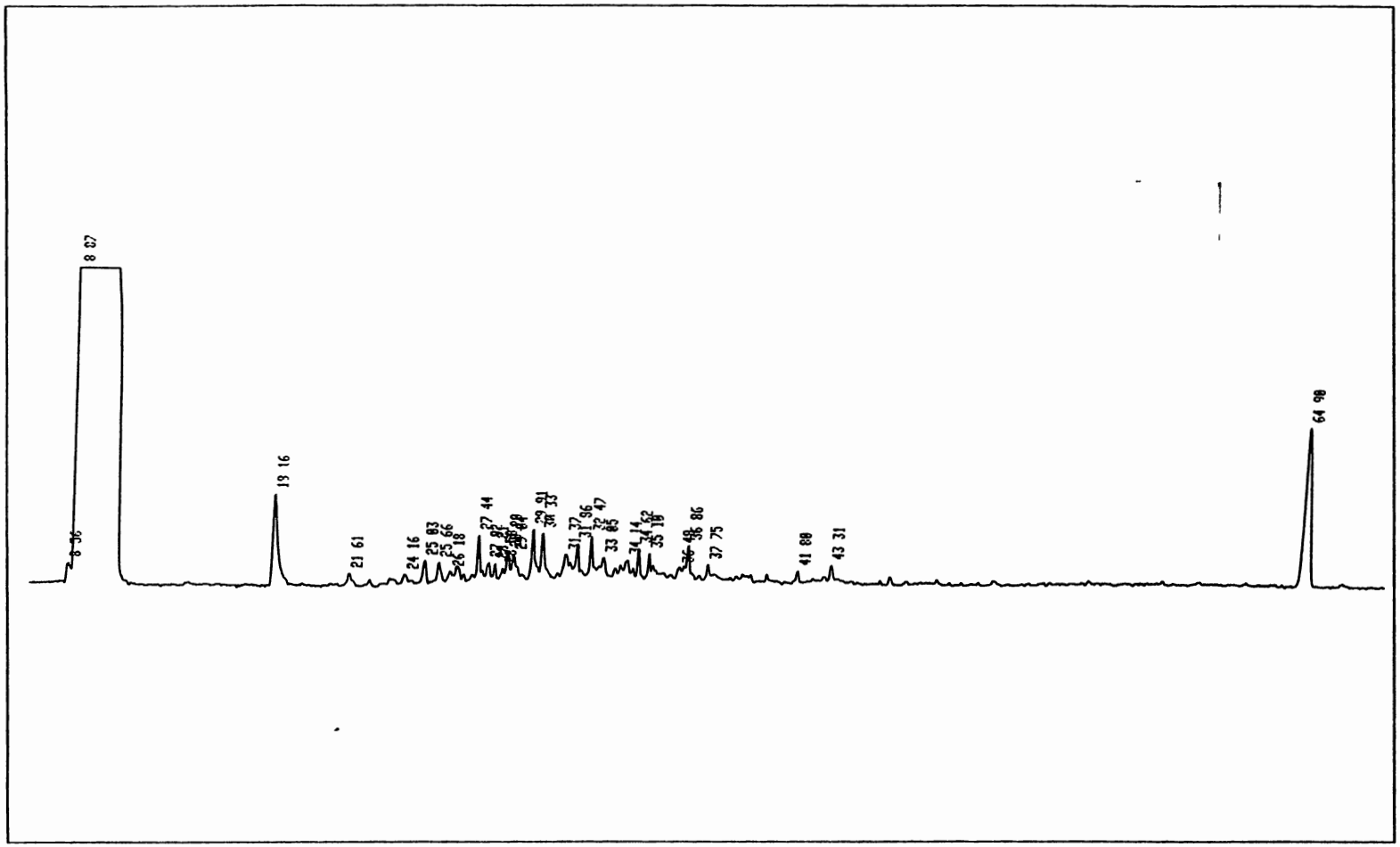

Figure 6. Chromatogram of Maximum Extractable Organics Extract (KO51)

The FO37 chromatogram revealed that the organic contaminants were a very wide boiling point mixture from about 165 ^{o}C to 400 ^{o}C. The slow tailing of the chromatogram toward the original baseline indicated the presence of very heavy components with boiling points greater than 400 ^{o}C.

Figure 6 shows the narrower boiling range of the KO51 extract. The majority of components in the KO51 waste boil between 135 ^{o}C and 320 ^{o}C. The KO51 extract contained one relatively pure component with a boiling point approximately 395 ^{o}C. This corresponds to the normal hydrocarbon, C_{24}.

Composition of Sludge Feeds

The mass fractions of the water, inert solids and total organics in the sludge were determined for the FO37 dewatered sludge and the KO51 sludge. The inert solids in the feed sludges were determined using ash testing procedures described previously. The mass fraction of water was used from the soxhlet extraction results and the mass fraction of organics was calculated by difference. Although fixed by the inert material balance, the single stage raffinate solids were also tested to check agreement with calculated values. The results for the FO37 dewatered sludge are shown in Table 6 and the results for the KO51 sludge are shown in Table 7.

TABLE 6

FO37 DEWATERED SLUDGE FEED COMPOSITION

Observation	Mass Fraction	
	Organics	Inert Solids
1	0.816	0.184
2	0.815	0.185
3	0.816	0.184
4	0.804	0.196
Mean	0.813	0.187
σ	.0029	.0029
95% C.I.	0.008	0.008

TABLE 7

KO51 SLUDGE FEED COMPOSITION

Observation	Mass Fraction		
	Water	Organics	Solids
1	0.115	0.537	0.348
2	0.115	0.552	0.333
3	0.115	0.551	0.334
4	0.115	0.560	0.325
Mean	0.115	0.550	0.335
σ	.0091	.0048	.0048
95% C.I.	0.029	0.032	0.013

Single-Stage Extractions

The single-stage batch extraction of the dewatered FO37 waste was accomplished by combining 100.2 grams of sludge with 400 ml of pentane in the extractor. The mass of the pentane was 248.8 grams corresponding to a solvent ratio of 2.48 (w/w). After 24 hours of agitation, the weight of the extract removed was 251.3 grams. From the overall material balance, the mass of the remaining raffinate was 97.7 grams. The mass balance for the single-stage pentane extraction of the FO37 dewatered sludge is summarized in Table 8.

TABLE 8

SINGLE-STAGE EXTRACTION RESULTS (FO37)

Stream	Organics	Solvent	Inert solids
Sludge Feed	0.8131		0.1870
Solvent Feed		1.0000	
Extract	0.2808	0.7192	
Raffinate	0.1116	0.6966	0.1918

The mass fraction of solvent remaining in the raffinate was determined by removing 3.56 grams and drying at 25 ^{o}C until constant weight was obtained. Assuming that only solvent was removed, the mass fraction of solvent was 0.6966.

From the inert solids material balance, the mass fraction of inerts in the raffinate was 0.1918. Using propagation of error, the population standard deviation on the calculated inert mass fraction was 0.00293 corresponding to a 95% confidence interval of

+/- 0.0083. Ash testing was performed on a sample of the raffinate to verify this value but the results were not valid. Assuming the solids were completely dried of solvent, the mass fraction of inert solids was 0.1081, yielding 0.1953 as the mass fraction of nonextracted organics. These results are significantly different from the calculated values and are consistent with a sample that was not completely dried of solvent prior to testing.

The percent removal of total organics in the single-stage extraction of the FO37 waste was 86.6 +/- 1.8 % and the percent removal of the extractable organics was >98.1%.

The extract from the single stage extraction of the FO37 sludge was characterized by gas chromatography. The chromatogram is shown in Figure 7. The chromatogram appears very similar in shape to the chromatogram of the maximum extractable organics. This indicated that the single-stage pentane extraction effectively removed the entire boiling range of components.

The boiling fractions were characterized by correlating the retention times of individual peaks versus the normal boiling point calibration curve. Peak areas were assigned to the nearest normal hydrocarbon boiling point. Assuming the percentage area of a single peak to the total peak area was equal to the mass percentage of that component, the extract was characterized into normal boiling fractions. The area percentage of each peak multiplied by the mass percentage of organics in the solvent gave the approximate composition of the extract. The composition of the FO37 single-stage extract characterized by normal boiling point fractions is shown in Table 9.

The single-stage batch extraction of the KO51 waste was performed by adding 186.9 grams of pentane to 72.4 grams of sludge. The solvent ratio was 2.92 (weight solvent/weight dry sludge) and the weight of the extract removed was 208.6 grams. The resulting raffinate weighed 50.7 grams by the overall material balance. The mass fractions of the water, inert solids and organics for each stream are shown in Table 10.

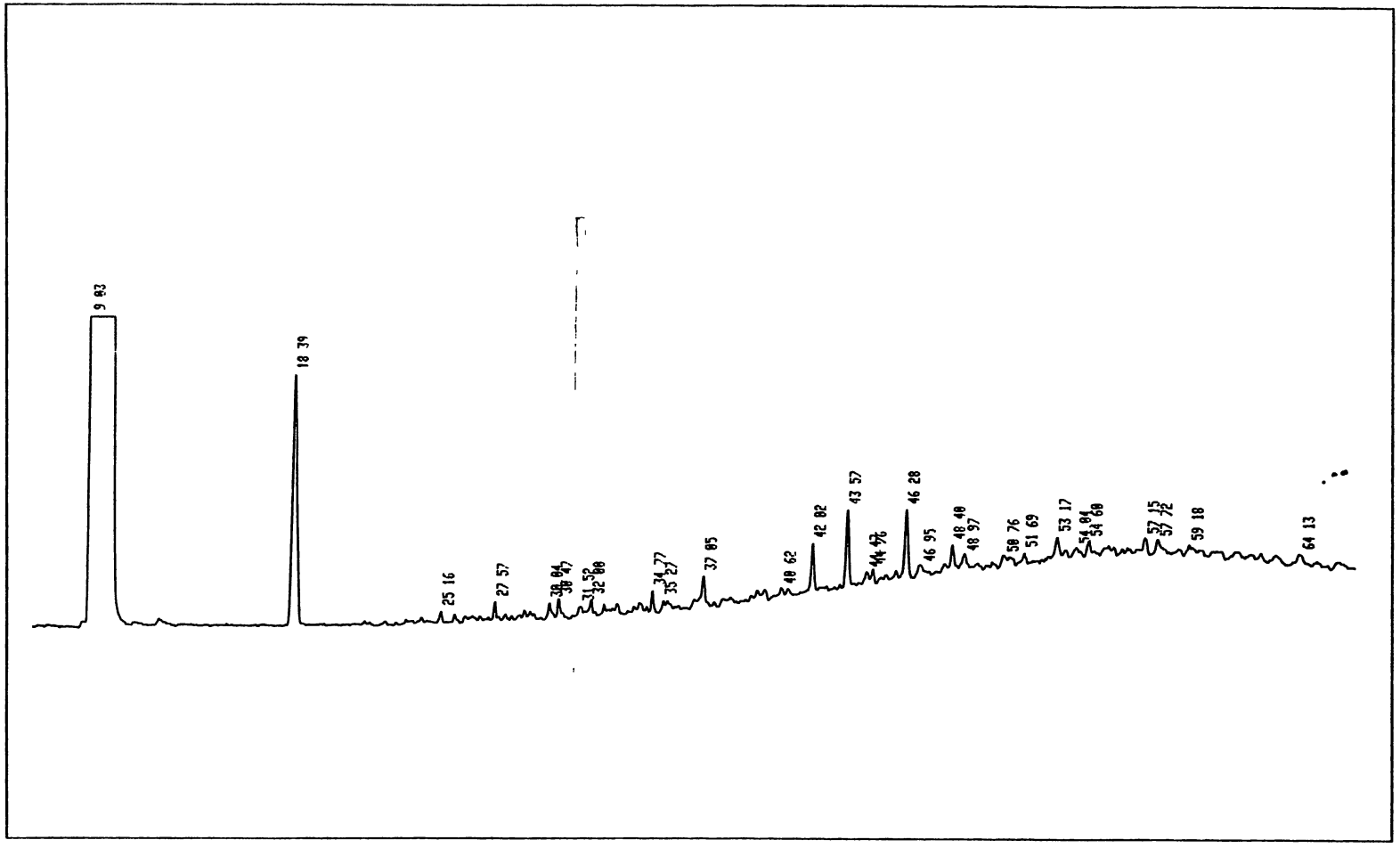

Figure 7. Chromatogram of Single-Stage Extract (FO37)

TABLE 9

NORMAL BOILING FRACTIONS (FO37 EXTRACT)

Normal Hydrocarbon	Mass Fraction
C_5	.7192
C_{10}	.0032
C_{11}	.0117
C_{12}	.0251
C_{13}	.0106
C_{14}	.0207
C_{15}	.0068
C_{16}	.0200
C_{17}	.0431
C_{18}	.0495
C_{19}	.0165
C_{20}	.0158
C_{21}	.0147
C_{22}	.0325
C_{24}	.0106

TABLE 10

SINGLE-STAGE EXTRACTION RESULTS (KO51)

	Mass Fraction			
Stream	Water	Organics	Solvent	Inert Solids
Sludge Feed	0.115	0.550		0.335
Solvent Feed			1.000	
Extract	0.040	0.144	0.816	
Raffinate		0.192	0.330	0.478

The mass fraction of water in the feed was obtained from the maximum extractable organics results. The mass fraction of water in the extract was calculated from the water material balance and by assuming all of the water was removed with the extract. This assumption was verified with a soxhlet extraction of the single-stage KO51 raffinate. After extraction for 24 hours, no water was collected in the moisture trap indicating that essentially all water was removed in the first stage of extraction.

The mass fraction of the solvent remaining in the raffinate was determined by removing three small samples (0.2-0.3 grams) and drying until constant weight was obtained. The remaining mass fractions were calculated by the material balance equations.

The mass fraction of the inert solids in the raffinate was verified by ash testing of the single-stage raffinate. The mass fraction of inert solids in the raffinate was 0.478 by the inert material balance. Using propagation of error, the 95% confidence interval for this value was +/- 0.013. The experimentally determined value of the inert solids using ash testing was 0.5450 +/- 0.082. No significant difference was declared between these values since the 95% confidence intervals overlapped. As a result, 0.478 was accepted as the best estimate for the mass fraction of inert solids.

The extract from the single-stage extraction of the KO51 waste was characterized in the same manner as the FO37 single-stage extract. The chromatogram of the extract is shown in Figure 8 for qualitative comparison to Figure 6. The figure shows the same general peak structure as the soxhlet extract indicating effective removal of the majority of extractable organics. One difference is the lack of a peak at 64.91 minutes. This observation indicated that single-stage extraction did not effectively remove this particular component. The normal boiling point distribution is shown in Table 11.

Soxhlet extraction was performed on the single-stage raffinate to verify the chromatographic results. After extraction, the extract was collected and analyzed. The chromatogram of the soxhlet extract of the single-stage raffinate is shown in Figure 9. The

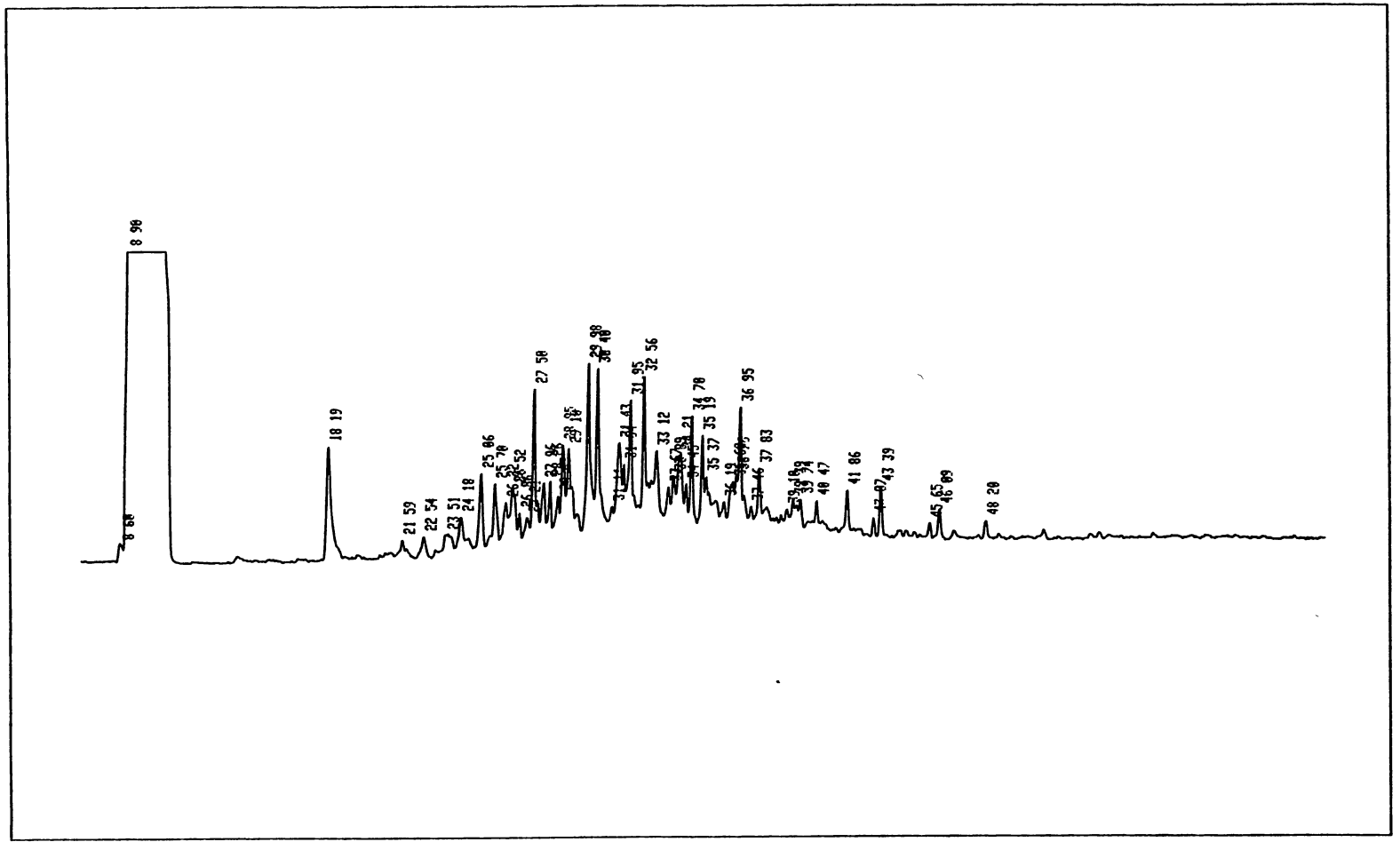

Figure 8. Chromatogram of Single-Stage Extract (KO51)

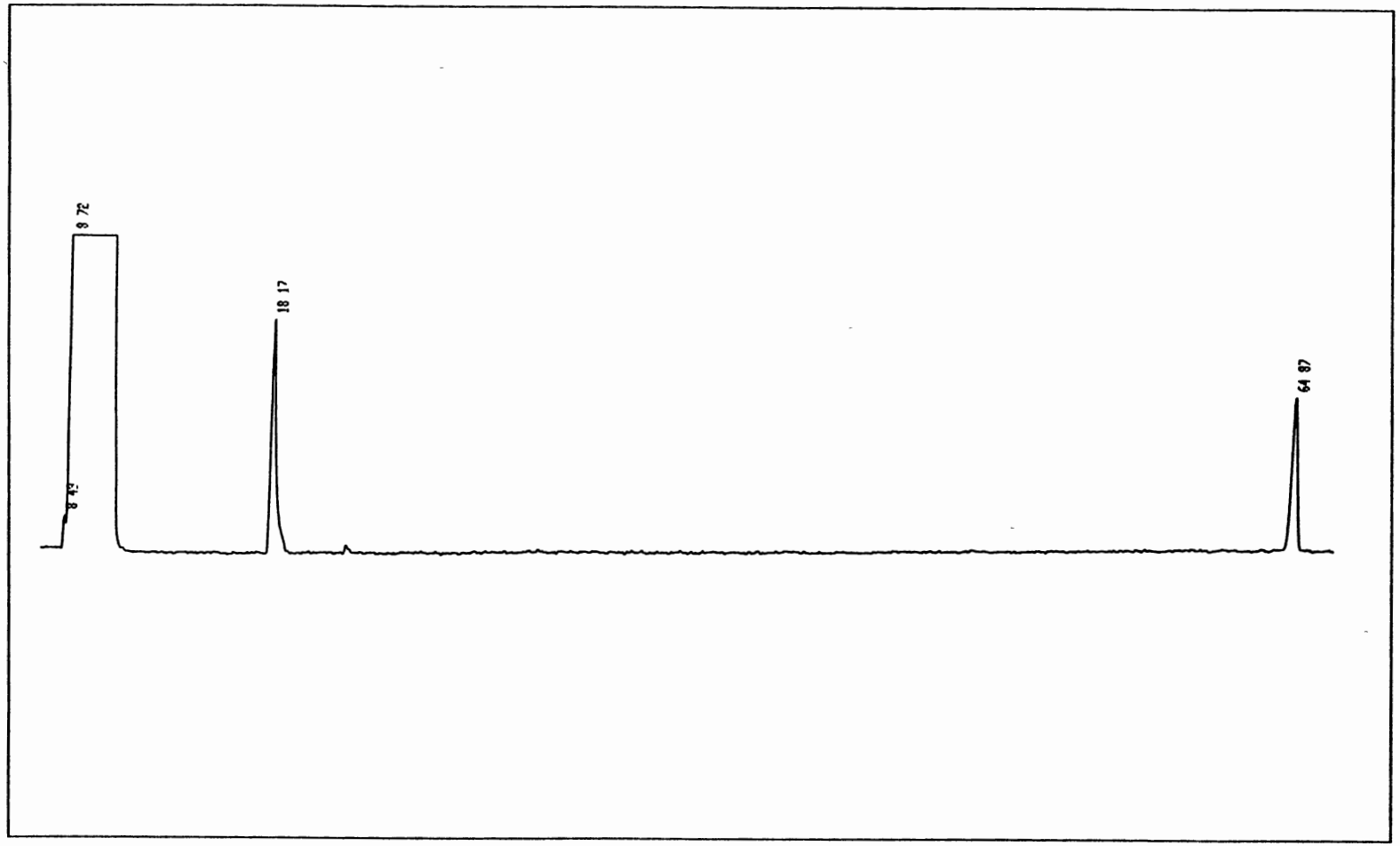

Figure 9. Chromatogram of Single-Stage Soxhlet Extract (KO51)

figure shows a large peak at 64.87 minutes substantiating the previous results that single stage extraction did not remove this contaminant.

From these results, the percent removal of the total organics was 75.4 +/- 4.8% and the percent removal of the extractable organics was > 89.9 %.

TABLE 11

NORMAL BOILING FRACTIONS (KO51 EXTRACT)

Normal Hydrocarbon	Mass Fraction
C_5	.8160
C_8	.0010
C_9	.0070
C_{10}	.0250
C_{11}	.0266
C_{12}	.0306
C_{13}	.0264
C_{14}	.0157
C_{15}	.0044
C_{16}	.0045
C_{17}	.0006
C_{18}	.0015
C_{19}	.0008

Two-Stage Extractions

Two-stage batch extractions were performed on both the FO37 dewatered sludge and the KO51 sludge. The second stage extraction of the FO37 dewatered sludge was

performed on the single-stage raffinate. The two-stage extraction of the KO51 sludge was performed on a fresh sample.

For the FO37 sludge, 249.0 grams of pentane were combined with the remaining 94.1 grams of single-stage raffinate. This was a solvent ratio of 8.72 (weight solvent / weight dry sludge). The extract removed weighed 243.0 grams resulting in 100.1 grams of raffinate. The results for the second stage extraction of the FO37 sludge are shown in Table 12.

TABLE 12

TWO STAGE EXTRACTION RESULTS (FO37)

	Mass Fraction		
Stream	Organics	Solvent	Inert Solids
Sludge Feed	0.1116	0.6966	0.1918
Solvent Feed		1.0000	
Extract	0.0067	0.9933	
Raffinate	0.0943	0.7245	0.1803

For the second stage extraction of the FO37 waste, the organics remaining in the raffinate were experimentally determined instead of the solvent. The raffinate was allowed to air dry until constant weight was achieved. The dried raffinate was tested for organics using ash testing. The inerts in the raffinate were calculated from the inert solids material balance and the solvent in the raffinate was obtained by difference. The mass fraction of inerts in the raffinate was checked by the results of the ash testing.

From the ash testing, the mass fraction of inerts was 0.1841 +/- 0.0006 which was not significantly different from the calculated value of 0.1803 +/- 0.0054. These results also verified the mass fraction of inerts in the single-stage raffinate.

The second-stage extract was a very light yellow color indicating that organics were removed. The gas chromatogram of the second-stage extract is shown in Figure 10. The major components were detectable with similar peak structure. From this it was concluded that single-stage extraction effectively removed the entire range of boiling point fractions.

The percent removal of total organics was 88.6 +/- 2.1 % and the percent removal of extractable organics was > 98.1 %. Although organics were obviously removed in the second stage of extraction, the calculated percent removal of extractable organics for the two-stage process was the same as the single-stage process. This was a result of the propagation of error from the first stage to the second stage calculations. These results indicated that the majority of organics were removed in the first stage.

For the KO51 waste, 134.6 grams of fresh sludge were combined with 254.8 grams of solvent. This was a solvent ratio of 2.14 (weight solvent/weight dry sludge). The weight of the first stage extract was 269.6 grams resulting in 119.8 grams of raffinate. Without opening the extractor, 245.0 grams of fresh solvent were added. The second-stage solvent ratio was not calculated because the composition of the first-stage raffinate was unknown. The results for the two-stage extraction of the KO51 sludge are shown in Table 13.

The extract was concentrated and characterized similar to the FO37 second-stage extract. The chromatogram is shown in Figure 11. The second stage of extraction removed the same range of boiling fractions as the first stage. It also removed a portion of the heavy component that the first stage did not, as shown by the small peak at 65.7 minutes.

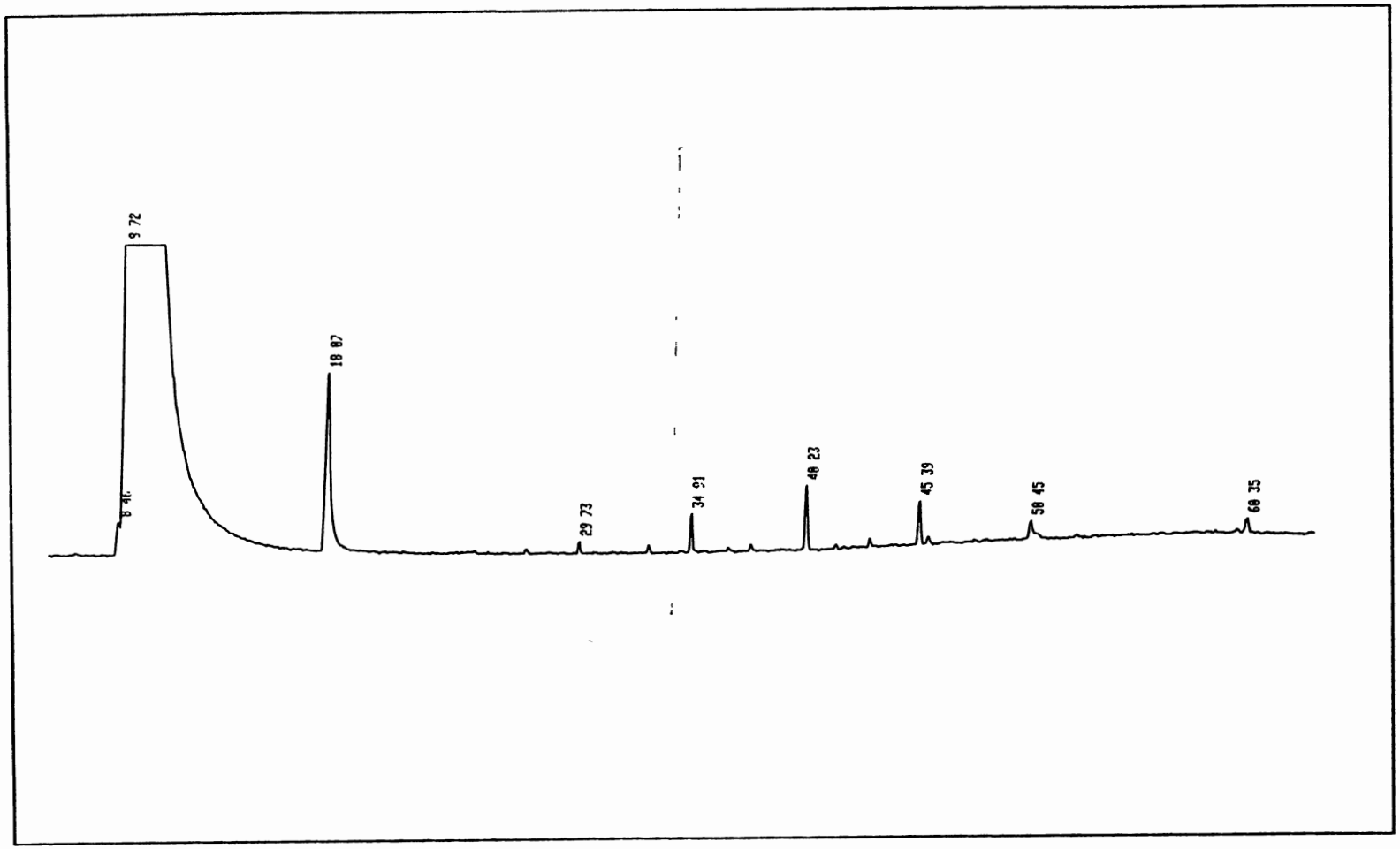

Figure 10. Chromatogram of Two-Stage Extract (FO37)

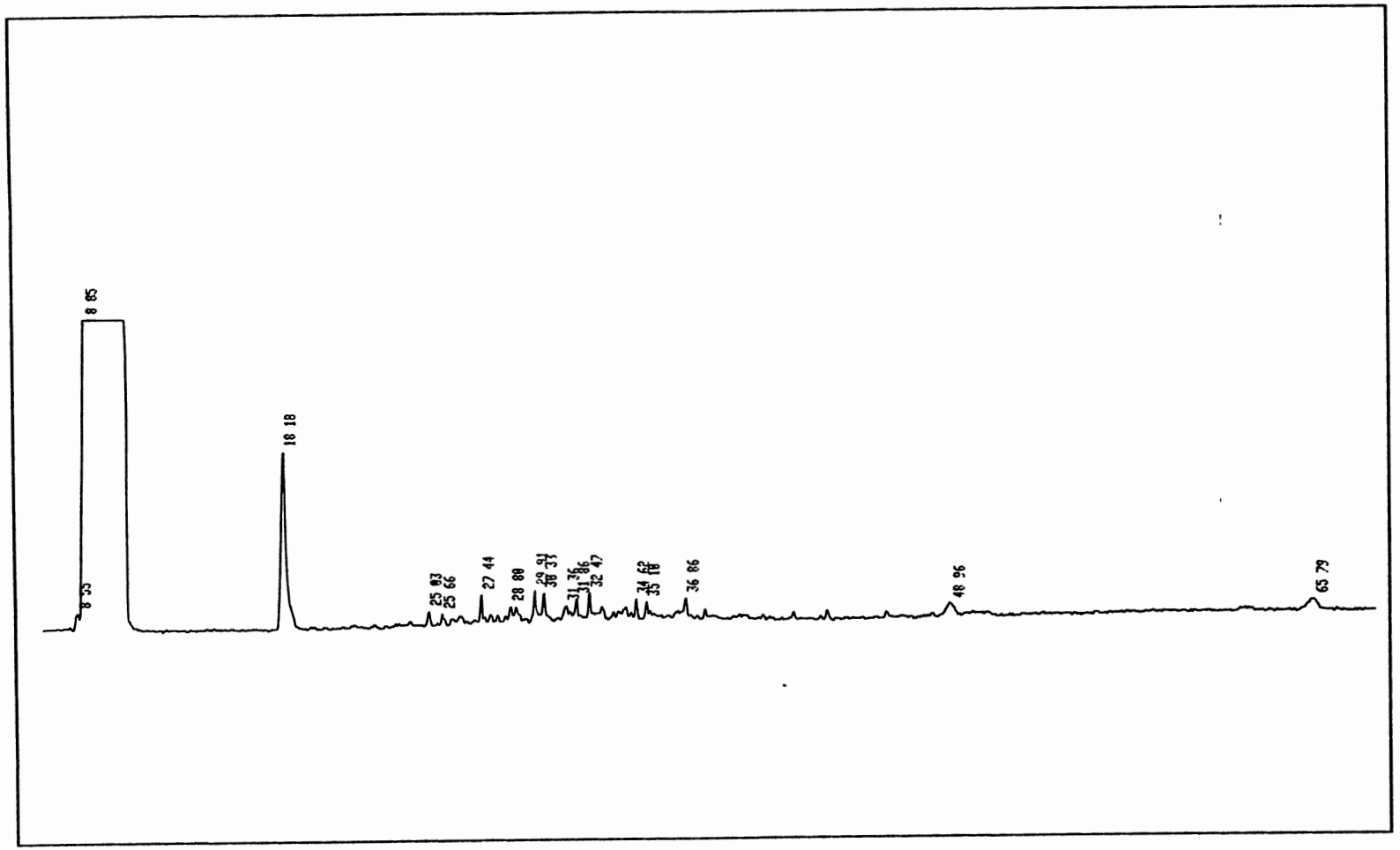

Figure 11. Chromatogram of Two-Stage Extract (KO51)

TABLE 13

TWO-STAGE EXTRACTION RESULTS (KO51)

Stream	Mass Fraction			
	Water	Organics	Solvent	Inert Solids
Sludge Feed	0.115	0.550		0.335
Solvent Feed			1.000	
Second Stage Raffinate		0.142	0.466	0.392

Toxicity Results

Static acute 48 hour toxicity tests were run on aqueous leachates of the dewatered FO37 and KO51 sludges. The leachates were prepared as described in the methods section. The results of the FO37 sludges are presented first followed by the results for the KO51 sludge.

To monitor toxicity reduction in the FO37 dewatered sludge, the tests were run on the raw sludge, single-stage raffinate and two-stage raffinate. The tests on the extracted raffinates were split into two groups, wet and solvent dry. This was done to detect cosolvent effects on toxicity. In addition, a water sample saturated with pentane was tested to detect toxicity contributions from the solvent.

Approximately 25 grams of each solid, except the second-stage dry solids, was leached by 100 milliliters of water. Since all samples were dewatered, this was a 4:1 (v/w) water to dry solid ratio. The second stage dry solids weighed only 10.6 grams, therefore, 42 milliliters of water were used to maintain the leachate ratio. The LC50 data and the

upper and lower limits to the 95% confidence interval are shown in Table 14. The solvent saturated sample and the reconstituted water blank showed no observable effect at 100% concentration indicating no toxicity effects from the solvent or the dilution water.

From these results, no difference existed in acute toxicity between the untreated sludge and the first stage of extraction. In addition, no difference in 48 hour acute toxicity was evident between the solvent dried and wet samples. A significant difference in toxicity did exist between the first stage of extraction and the second stage. As a result, a second stage of extraction is justified by the significant reduction in toxicity.

TABLE 14

LC50 TOXICITY DATA (FO37)

Sample	LC50	95% Confidence Limits	
		Lower Limit	Upper Limit
FO37 Sludge	8.66	5.00	15.00
Single-Stage wet	9.44	8.00	11.15
Single-Stage dry	9.38	7.24	12.15
Two-Stage wet	22.46	19.03	26.52
Two-Stage dry	24.49	15.00	40.00

From the 48 hour results, no toxicity difference was detected between the solvent wet and dried samples. Interaction was present, however, when plots were constructed for the fraction mortality as a function of time. Figures 12 through 16 display the fraction mortality over time with dilution as a parameter. Superposition of Figure 13 over Figure 14 shows a difference in toxicity between the single-stage wet and dry samples. Higher mortality occurs at shorter time periods in the solvent wet single-stage sample. Similarly,

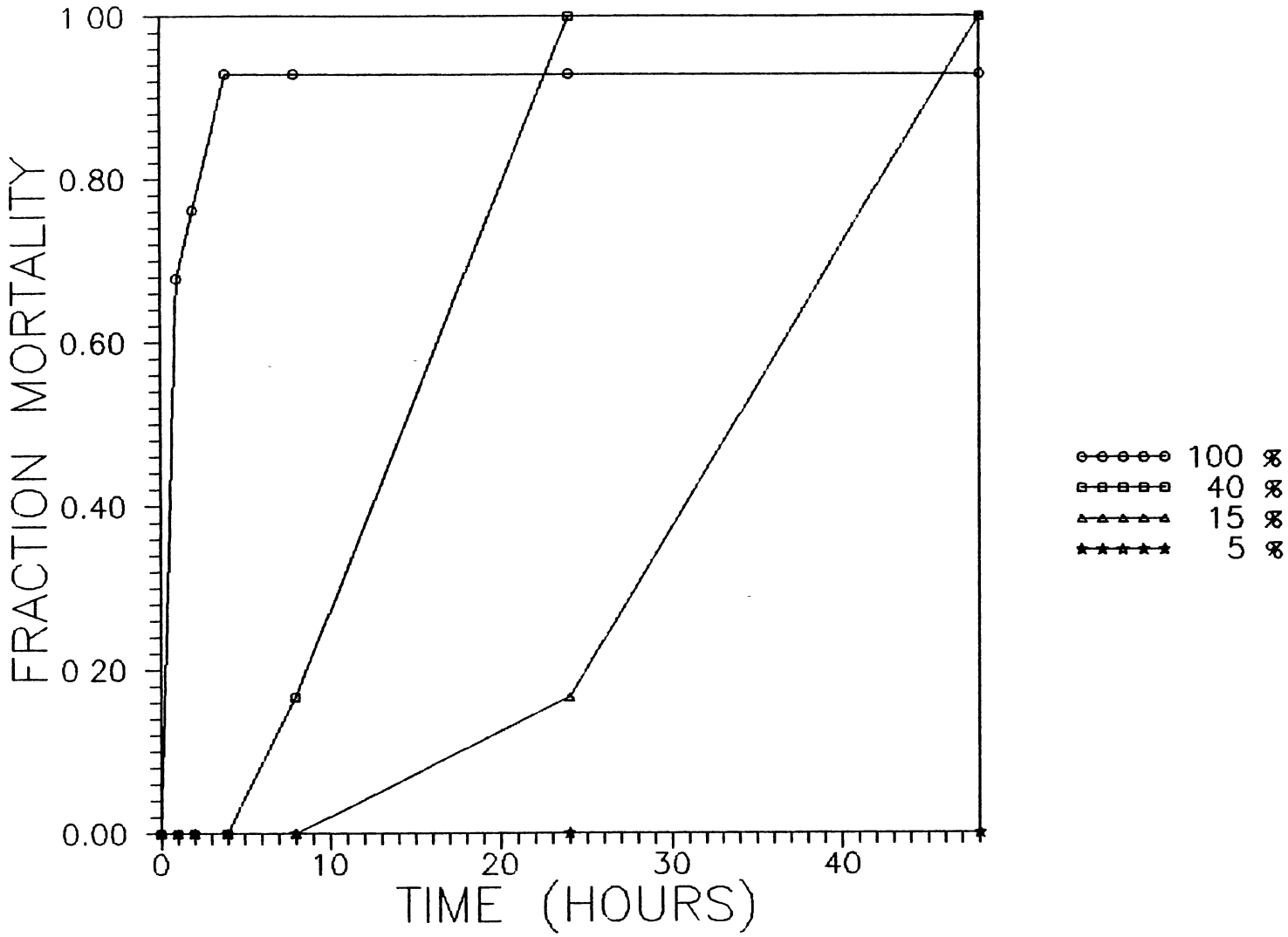

Figure 12. Mortality Rates as a Function of Time (FO37)

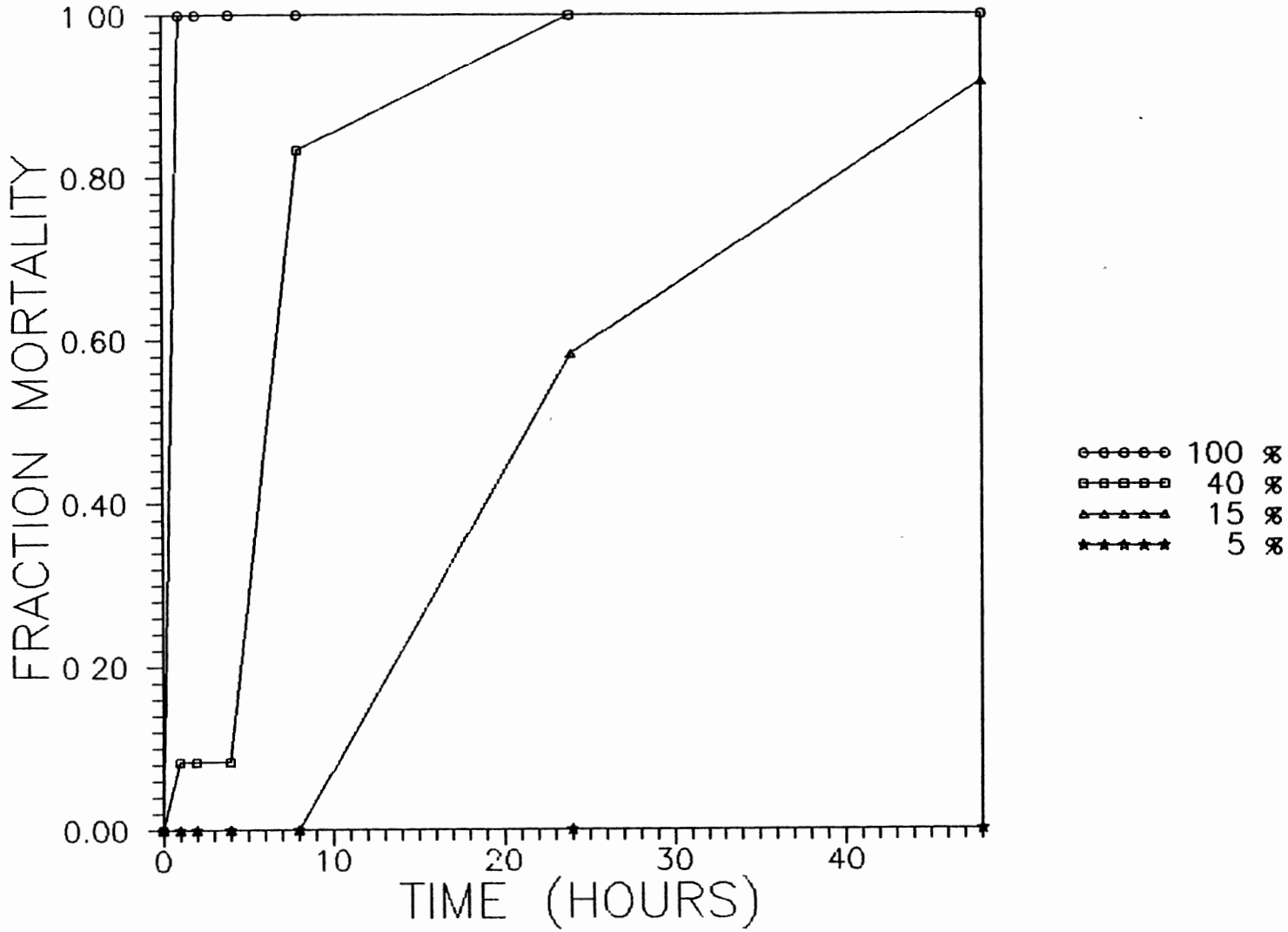

Figure 13. Mortality Rates as a Function of Time (FO37 #1 Wet)

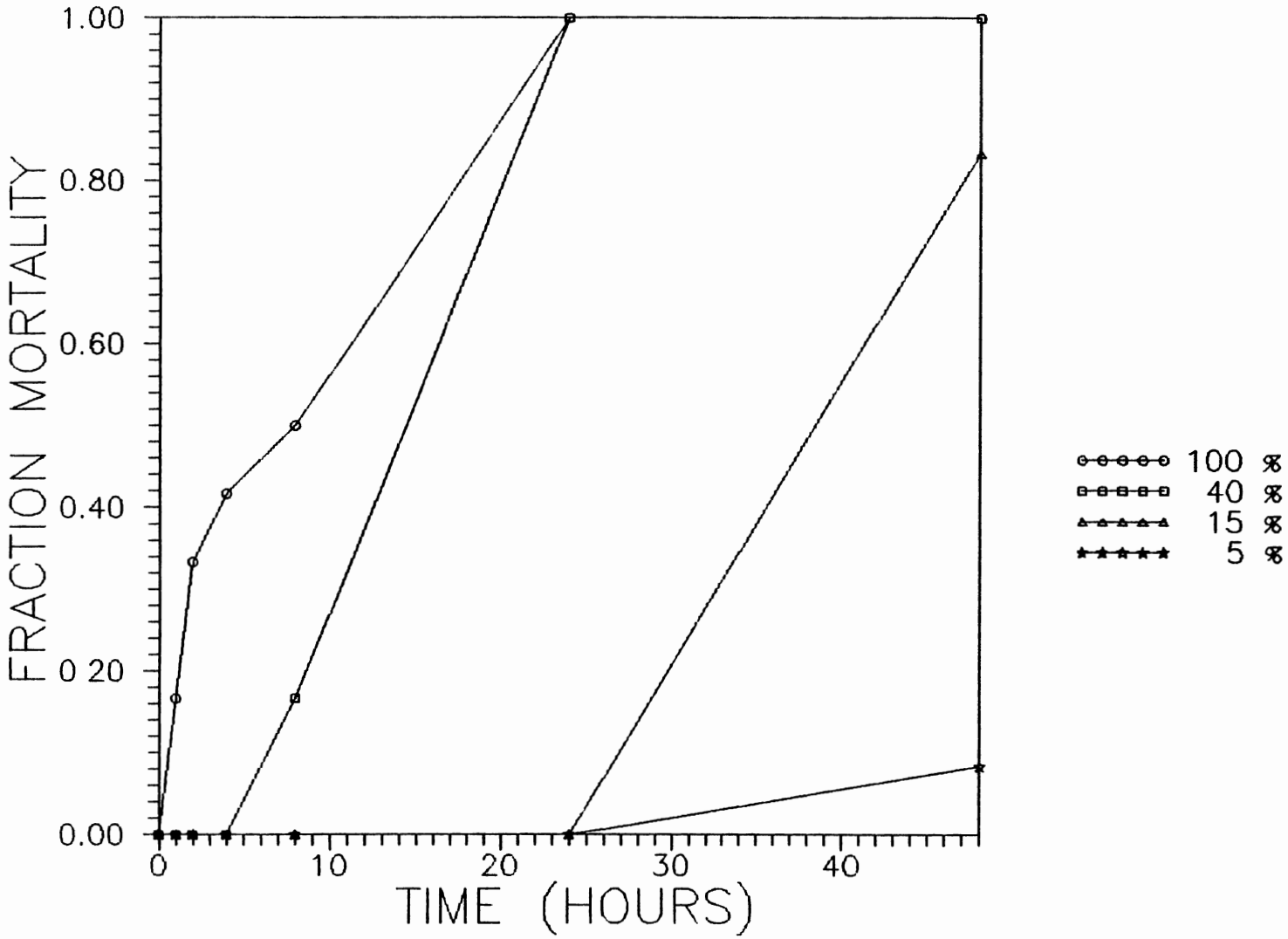

Figure 14. Mortality Rates as a Function of Time (FO37 #1 Dry)

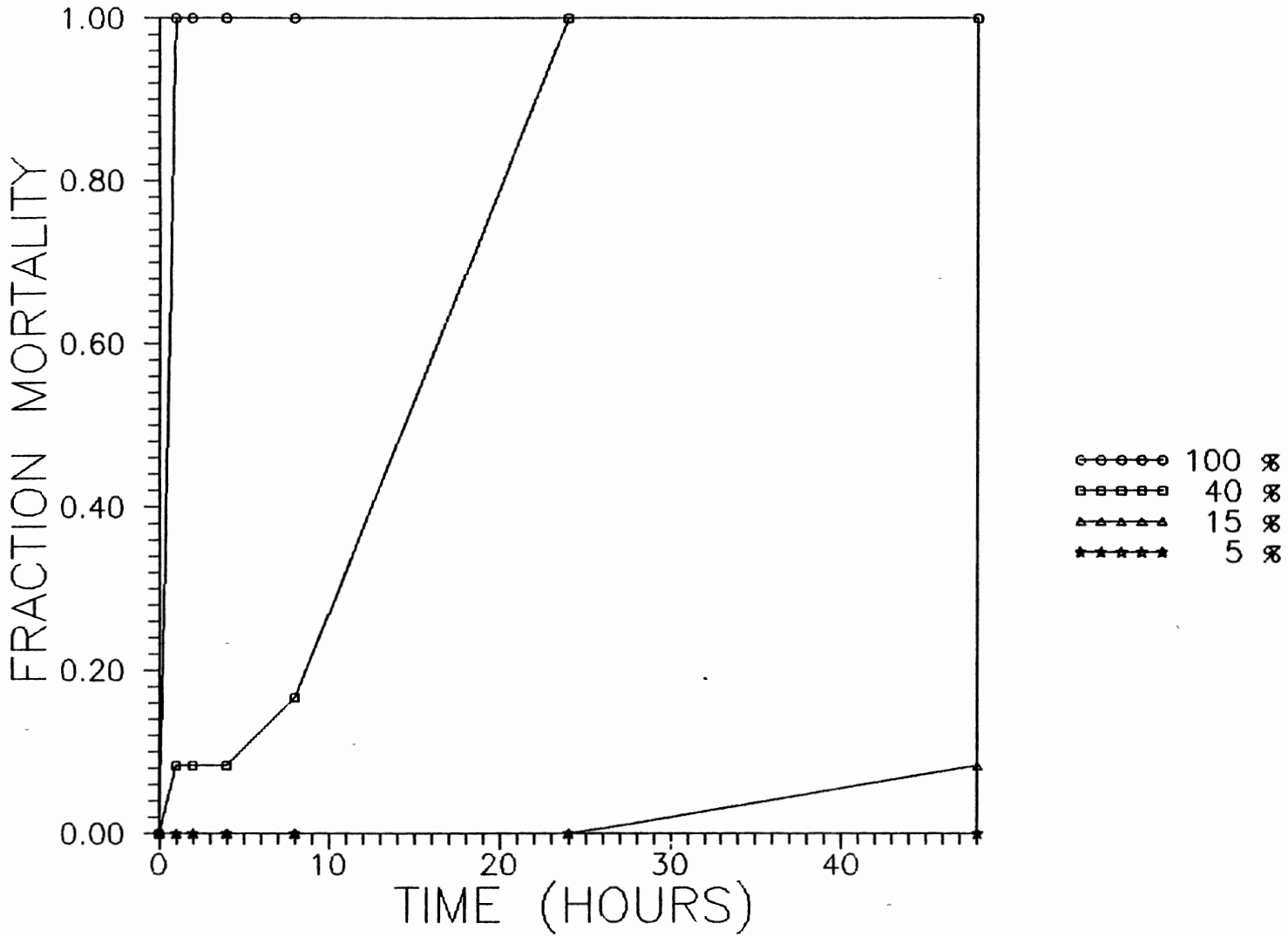

Figure 15. Mortality Rates as a Function of Time (FO37 #2 Wet)

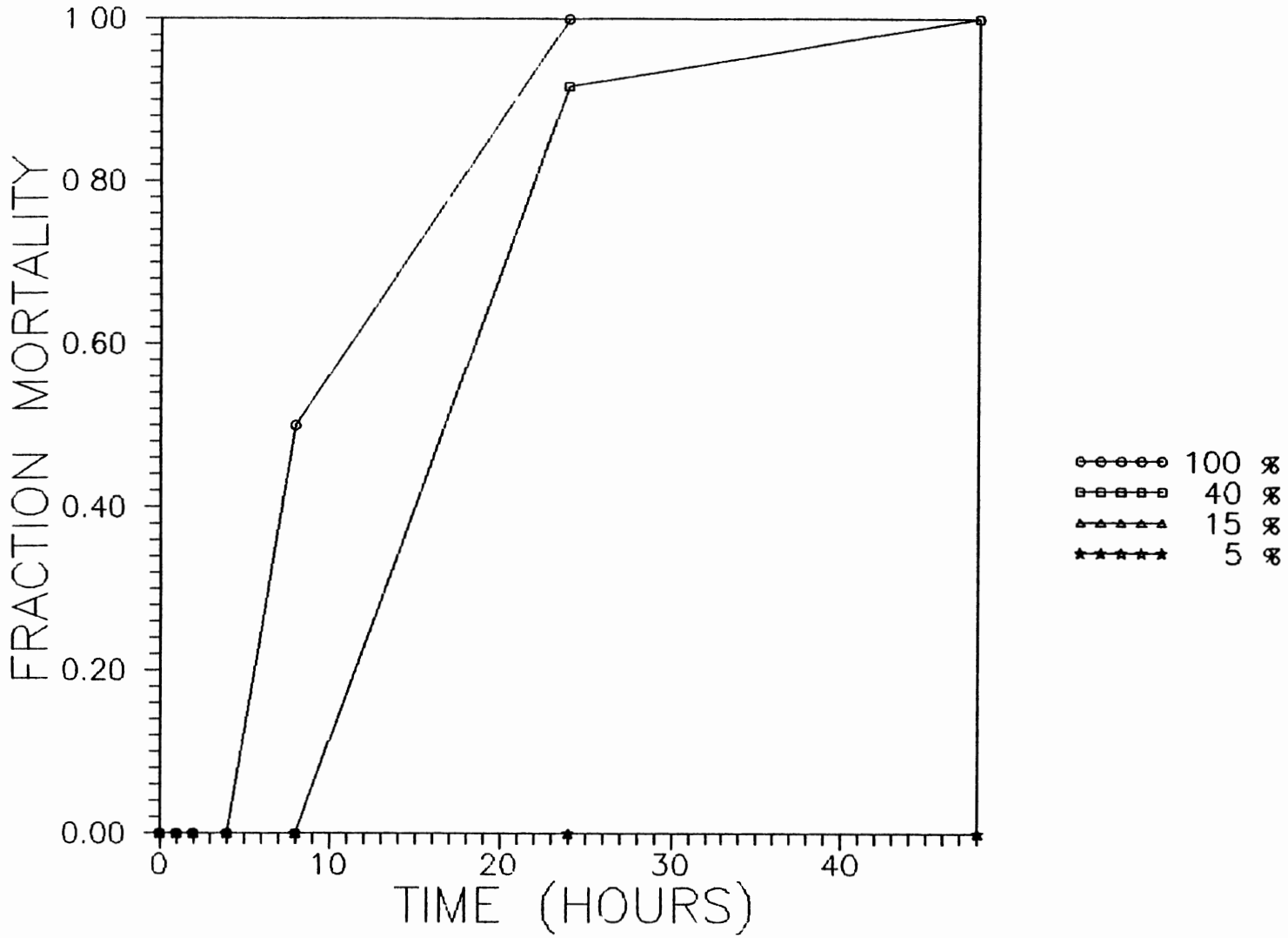

Figure 16. Mortality Rates as a Function of Time (FO37 #2 Dry)

comparison of Figure 15 to Figure 16, reveals higher toxicity rates for the second-stage samples at all dilutions. These results show that solvent removal after extraction can reduce acute toxicity of the raffinate for exposure times less than 24 hours.

Toxicity tests for the KO51 waste were performed on aqueous leachates of the raw sludge, single-stage solid and two-stage solid. Each leachate was divided into two subsamples giving a total of six samples. One subsample was treated by C-18 solid phase extraction to determine the toxicity due to residual organic contaminants. The other was tested directly for aquatic toxicity. This procedural modification was intended to screen out toxicity from metals. If metal toxicity was dominant, toxicity results for the C-18 extracted samples would be statistically similar to the unextracted samples.

For the KO51 raw sludge, 40.5 grams of sludge were leached with 100 milliliters of water. This was a ratio of 2.8 (v/w) milliliters of water to grams of sludge on a dry basis. One hundred milliliters of water were combined with 58.3 and 57.2 grams of single-stage raffinate and two-stage raffinate, respectively. This corresponded to a 1.7 (v/w) water ratio on a dry solid basis.

The toxicity tests on the KO51 wastes presented a problem not encountered in the test on the FO37 waste. The first series of tests showed no toxicity on the single-stage and two-stage raffinate. Differences were apparent, however, in the number of organisms that were able to swim. As a result, a second batch of tests were run in which the EC50 was monitored. The EC50 was calculated in the same manner as the LC50 but an effect was defined instead of death. For these tests, the effect was defined as the organisms inability to swim. The results of the toxicity tests on the KO51 waste are shown in Table 15.

No observable effect was observed in the single stage C-18 extracted sample, two-stage raffinate or two-stage C-18 extracted samples. Toxicity of the KO51 raw sludge, single-stage and two-stage solids were significantly different. The difference in toxicity between the single-stage solids and the C-18 extracted single-stage solids indicated that

residual organics were contributing to the overall toxicity. Removal of the organics in the second stage of extraction decreased toxicity to non-detectable limits.

TABLE 15

EC50 TOXICITY DATA (KO51)

Sample	EC50	95% Confidence Limits	
		Lower Limit	Upper Limit
KO51 Sludge	5.00	0.00	15.00
Single-Stage	70.92	56.35	89.26
Single-Stage (C-18)	100.0	NC*	NC
Two-Stage	100.0	NC	NC
Two-Stage (C-18)	100.0	NC	NC

* NC means value cannot be calculated with statistically reliable methods

BDAT Test Results

The FO37 dewatered sludge, KO51 sludge, FO37 second-stage raffinate and KO51 second-stage raffinate were analyzed for BDAT semi-volatiles, cyanide and metals. The results are shown in Tables 16 and 17 for the FO37 and KO51 wastes respectively. The results do not include contaminants that were not detectable.

The FO37 dewatered sludge did not exceed regulated limits of the BDAT contaminants. The pentane extraction of the FO37 waste was very effective in reducing the BDAT components. Although the original waste met regulated limits, these results indicated that pentane extraction would easily treat dewatered FO37 to BDAT standards.

TABLE 16

FO37 BDAT TEST RESULTS

Contaminant	Concentration (ppm) Regulated Limit	Raw Sludge	Treated Solid	Percent Reduction
Anthracene	28	7.9	<2	>74.7
Benzo(a)anthracene	20	3.0	<2	>33.3
Chrysene	15	14	<4	>71.4
Naphthalene	42	2.8	<2	>40.0
p-Cresol	NA	38	19	50.0
Phenanthrene	34	28	<2	>92.9
Pyrene	36	6.4	2.2	65.6
Total Cyanide	1.8	<0.3	1.5	
Chromium	1.7	0.03	0.15	
Nickel	0.2	0.08	0.09	

The KO51 raw sludge exceeded limits for the naphthalene and phenanthrene. The treated KO51 solids, however, were below limits for all components. These results show that pentane extraction was successful in treating KO51 to BDAT standards. The extraction of the KO51 waste was not as effective as the extraction of the FO37. The presence of water in the KO51 interfered with the extraction. These results support the previous overall organic removal results. The metals concentration in both wastes increased with extraction indicating that metal fixation is required to completely meet the regulated limits.

TABLE 17

KO51 BDAT TEST RESULTS

Contaminant	Concentration (ppm) Regulated Limit	Raw Sludge	Treated Solid	Percent Reduction
Anthracene	28	6.3	2.3	63.5
Benzo(a)anthracene	20	6.8	3.5	48.5
Chrysene	15	13	10	30.0
* Naphthalene	42	53	39	26.4
* Phenanthrene	34	40	13	67.5
Pyrene	36	12	9.8	18.3
Total Cyanide	1.8	<0.3	0.93	
Nickel	0.2	0.11	0.34	

* Raw sludge exceeded regulated limits for this component

Process Design and Economic Considerations

This section specifies potential technical problems with pentane extraction and offers possible process designs. Approximate costs associated with implementing pentane extraction of solid wastes and comparisons to other alternatives are also presented.

Pentane extraction of sludge can be accomplished by one of four schemes. The sludge can be dewatered prior to extraction or the raw sludge can be extracted. The processed solids can be thermally dried to recover more solvent or the solids can be disposed of wet and allowed to air dry. The four options are shown in Figure 17.

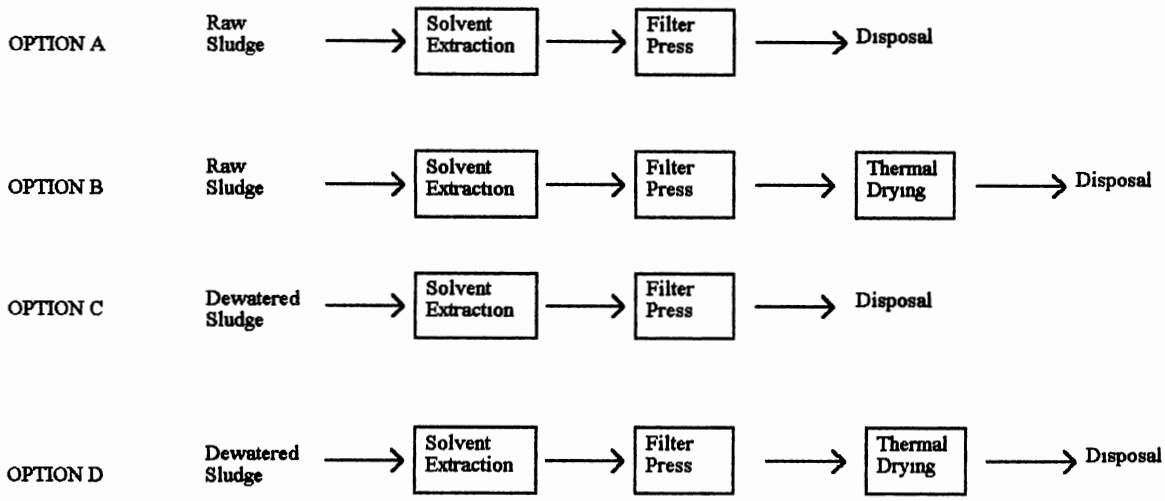

Figure 17. Four Processing Alternatives of Refinery Sludge

Solids handling and efficient contacting of the solvent with the hydrophilic solids were two problems associated with pentane extraction. In bench mixing experiments, difficulties associated with movement of solids and the increased power requirements to suspend solids indicated that dewatering prior to solvent extraction was not feasible. Therefore, options C and D were not considered. Treatment of the raw sludge also offered the advantage of treating the sludge and water simultaneously. As a result, options A and B were considered for preliminary design and costing.

The preliminary process design is shown in Figure 18. The process was designed to treat 10 million pounds per year of KO51 sludge similar to the experimental sludge. The stream compositions and flowrates are shown in Table 18. This corresponded to treating 1200 lbm/hr of sludge in three semi-batch stages. The third stage was added to account for extraction efficiency associated with a real process. The solvent ratio was maintained at approximately 2:1 (w:w), which corresponded to 2500 lbm/hr solvent per stage. This resulted in 7500 lbm/hr of total solvent. Thermal drying was assumed to recover 95% of the solvent in the entering stream and solvent recovery was designed for

98% recovery of pentane with 95% purity. These assumptions resulted in 5.8% solvent losses if the solids were not dried, 2.9% solvent losses in the dried solids and 2.0% solvent losses to the recovered organics. Solvent losses to the water phase were neglected. The solvent was valued at $0.12 per pound.

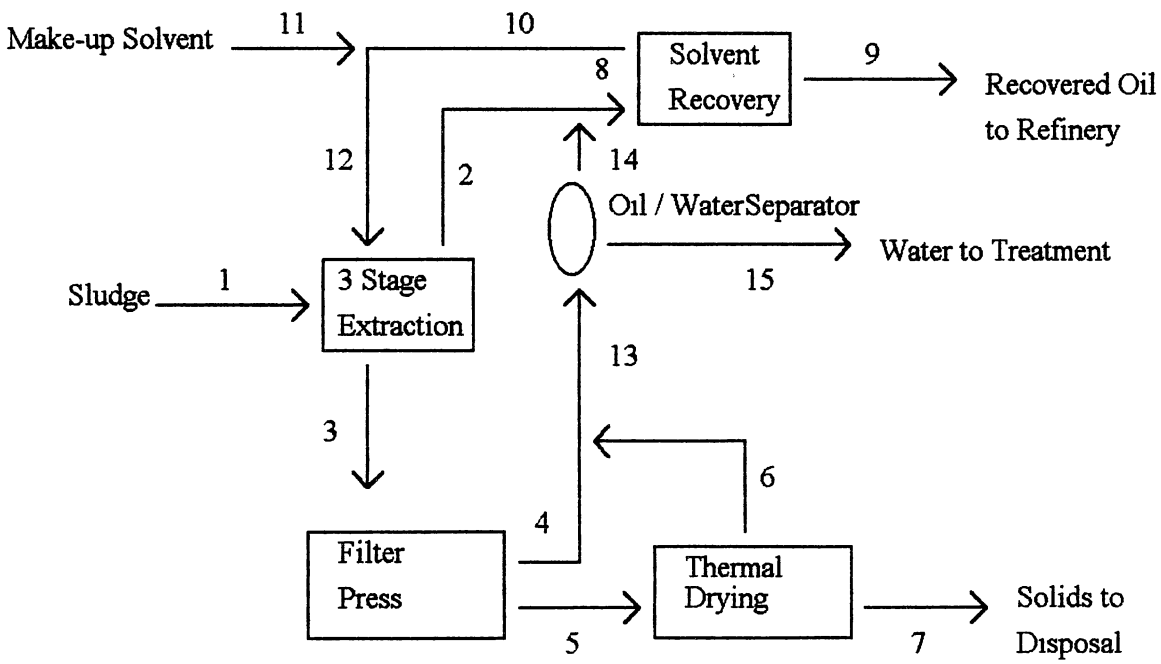

Figure 18. Preliminary Process Design

The total capital costs, operating and labor costs were estimated for the process with and without thermal drying. The costing procedure is described in Appendix B. The results of the preliminary cost analysis for options A and B are shown in Table 19.

TABLE 18

PRELIMINARY STREAM COMPOSITIONS AND FLOWRATES

Stream	Total Flow (lbm/hr)	Mass Fraction Solvent	Organics	Solids	Water
1	1200	.0000	.5500	.3500	.1000
2	4350	.9384	.0616	.0000	.0000
3	4350	.7759	.1000	.0966	.0276
4	3300	.8900	.0918	.0000	.0182
5	1050	.4171	.1257	.4000	.0571
6	416	1.000	.0000	.0000	.0000
7	634	.0345	.2082	.6626	.0947
8	8006	.9287	.0713	.0000	.0000
9	336	.4426	.5574	.0000	.0000
10	7670	.9500	.0500	.0000	.0000
11	170	1.000	.0000	.0000	.0000
12	7500	.9943	.0057	.0000	.0000
13	3716	.9023	.0815	.0000	.0161
14	3656	.9171	.0829	.0000	.0000
15	60	.0000	.0000	.0000	1.000

The alternatives were compared for a ten year service life without taking credit for recovered oil. Assuming a 15% rate of return, the net present value of option B with thermal drying was $2.35 million. The net present value of option A without thermal drying was $4.12 million. The break even solvent cost for option A versus option B was $0.037 per pound. Significant cost savings were realized when the solvent was recovered using thermal drying.

TABLE 19

PRELIMINARY COSTS OF PROCESS (OPTIONS A & B)

Cost	Option B	Option A
Capital	$908,000	$878,000
Operating & Maintenance	$77,200/Yr	$73,900/Yr
Labor	$112,000/Yr	$112,000/Yr
Solvent Loss	$170,000/Yr	$583,000/Yr

The 10 year cost of centrifugal deliquification of sludge followed by thermal desorption were also determined. The estimated cost of thermal desorption was $400 per ton. From the data for the raw sludge and the dewatered sludge, centrifugal deliquification reduced the mass by 58%. Using the same basis of feed, 5000 tons of raw sludge were reduced to 2100 tons of dewatered sludge. Thermal desorption of this mass of sludge over ten years yielded a net present value of $3.67 million. This cost was much lower than option A but significantly higher than option B. The breakeven cost of thermal desorption versus option B was $257 per ton. Deliquification followed by offsite incineration was not considered as an alternative because of the estimated cost of $1000 per ton. Based on this analysis, the payback period for option B versus thermal desorption is 4.5 years.

Since the cost data was estimated with 30% accuracy, sensitivities were tested to determine the effect on the evaluation. The following sensitivities were tested:

1. +30% capital and operating cost of option B versus thermal desorption
2. +30% capital, operating cost and solvent loss cost of option B versus thermal desorption

3. +30% capital and operating cost of thermal drying of option B versus option A.

Sensitivity 1 resulted in net present value cost of option B of $2.59 million. Sensitivity 2 increased the net present value cost of option B to $2.81 million. Both comparisons gave option B the economic advantage over thermal desorption. Sensitivity 3 increased the break even cost of solvent for option A to $0.048 per pound. These results show that increased costs of option B did not affect the economic advantage over other alternatives.

Metal fixation and disposal costs were not included in the evaluation. All processing alternatives include these costs, therefore, the incremental economic comparisons would not be affected.

CHAPTER V

CONCLUSIONS

From the study it was concluded that pentane extraction of FO37 and KO51 sludges significantly reduced the toxicity and levels of organic contaminants in the treated solids. The bulk of removal occurred in the first stage of extraction for both sludges, although the majority of toxicity reduction occurred with the second stage. Solvent removal by thermal drying further reduced the toxicity. The total organics removal based on ashed solids was 86.6 +/- 1.8 % for the FO37 sludge and 75.4 +/- 4.8 % for the KO51 sludge. Pentane extraction treated KO51 to BDAT limits for organic contaminants and reduced BDAT contaminants in the FO37 waste by 33.3% to 92.9%. Based on these results, pentane extraction of FO37 wastes should meet BDAT limits on organic contaminants. Pentane extraction, however, concentrated the metals in the treated solids. A metal fixation step would be required to meet regulated limits on the cyanide, chromium and nickel.

The presence of water in the KO51 waste decreased the overall organic removal but reduced solvent loss to the raffinate. It also reduced the removal of BDAT contaminants. These results suggest that an optimum water/sludge ratio exists to maximize organic removal and minimize solvent loss.

The economic evaluation of a preliminary pentane extraction process showed potential for significant cost savings over thermal desorption. The preliminary process was composed of 3 stages of extraction, followed by filter pressing, thermal drying of solids and

solvent recovery in a batch distillation still. Thermal drying of the solids to increase recovery of pentane was also economically feasible.

Future research should focus on a pilot scale extraction process to verify the bench scale results. Problems with efficient contacting of the solvent and sludge should be addressed. An optimum solvent ratio and water to sludge ratio should also be determined. With this information, a detailed economic analysis of the process could be performed.

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APPENDIXES

APPENDIX A

ERROR ANALYSIS

The experimental errors associated with experimental values were determined using standard statistical practice. For any number of measurements of the same experimental variable, the sample standard deviation was calculated from equation 13.

$$s = \frac{\sum (Y - \bar{Y})}{(n-1)} \tag{13}$$

where s = sample standard deviation

Y = experimental value

Y = mean of sample values

n = number of sample points

The standard deviation of the total population was estimated by the standard error or mean square error. The standard error was calculated by equation 14.

$$\sigma = \frac{s}{\sqrt{n}} \tag{14}$$

where σ = standard error

The standard error was the best estimate of the population standard deviation. The 95% confidence intervals for the experimental variables were calculated from the product of the standard error and the t-value for the given number of experiments.

When calculating the results from experimental variables, the error associated with the calculated value was obtained from propagation of the experimental errors associated with the experimental variables. For the expression,

$$A = B + C \tag{15}$$

the propagated error for A was obtained by equation 16.

$$\sigma_A^2 = \sigma_B^2 (\delta B/\delta A)^2 + \sigma_C^2 (\delta C/\delta A)^2 \tag{16}$$

where σ^2 represented the variance of the subscripted variable and δ represented the partial derivative operator. The 95% confidence interval of the calculated values was estimated by using a t-value of 1.96 for infinite experiments. Using these estimates for σ, the approximate relative errors were calculated from equation 17.

$$\text{Percent Relative Error} = (\sigma / \text{Mean}) \times 100\% \tag{17}$$

The estimated standard errors and the percent relative errors for composition results are shown in Table A-1.

TABLE A-1

RELATIVE ERRORS OF COMPOSITION RESULTS

Sludge	Stage	Component	Value	σ	% error
FO37	Dewatered	Solids	.1870	.00293	1.57
		Oil	.8131	.00293	0.36
	First Extract	Oil	.2808	.00276	0.98
		Solvent	.7192	.00276	0.38
	First Raffinate	Solids	.1918	.00300	1.56
		Oil	.1116	.00583	5.22
		Solvent	.6966	.00500	0.72
	Second Extract	Oil	.0067	.00200	29.8
		Solvent	.9933	.00200	0.20
	Second Raffinate	Solids	.1803	.00275	1.53
		Oil	.0886	.00139	1.57
		Solvent	.7311	.00656	0.90
KO51	Raw	Water	.115	.00906	7.88
		Oil	.550	.01025	1.86
		Solids	.335	.00478	1.43
	First Extract	Water	.040	.00315	7.88
		Oil	.144	.00379	2.63
		Solvent	.816	.00211	0.26
	First Raffinate	Oil	.192	.01103	5.74
		Solvent	.330	.00866	2.62
		Solids	.478	.00683	1.43
	Second Raffinate	Oil	.142	.01549	10.9
		Solvent	.466	.00289	0.62
		Solids	.392	.01520	3.88

APPENDIX B

COSTING PROCEDURE

Before costing the process, a preliminary design was constructed. The design was based on treating 10 million pounds per year of sludge. The sludge was assumed to contain 10% water, 35% solids and 55% oil by weight. This was similar to the KO51 waste treated in the study. The following assumptions about the process were made:

1. 80% of the oil was removed after filter pressing, 70% in the decanted solvent
2. Solid weight percent after filter pressing was 40%
3. Water was reduced by 50% by the filter press
4. Thermal drying at 150-200 ^{o}F recovered 95% of the solvent in the dryer feed
5. Distillation in a batch still at 100-150 ^{o}F recovered 98% of the solvent
6. 50% of the mass in each extractor was decanted.

Using the material balance equations, the stream mass flowrates were calculated and the unit operations were sized and costed. The 3 stages of mixing, filter press, solvent recovery system and thermal drying system were the major equipment items. The total equipment costs and the source of information are shown in Table A-2. The total equipment cost for the filter press included the feed pump and all auxillary equipment.

The operating and maintenance costs were estimated for the filter press from EPA 625/6-85/010. All other operating costs were calculated as 20% of the equipment purchase cost. The operating costs for each unit are shown in Table A-3. Labor costs were

estimated assuming 1 operator per shift, $13.50 per hour salary and 345 days of operation. The total labor costs were $112,000 per year.

TABLE A-2

TOTAL EQUIPMENT COSTS

Unit	Total Equipment Cost	Reference
3 Slurry Mixers	$40,000	Chemical Engineering, 1982
Filter Press	$358,000	EPA 625/6-85/010
Thermal Drying	$14,000	Guthrie, 1970
Solvent Recovery	$59,000	Guthrie, 1970

TABLE A-3

YEARLY OPERATING AND MAINTENANCE COSTS

Unit	Total O&M Cost
3 Slurry Mixers	$8,000 / Yr.
Filter Press	$35,800 / Yr.
Thermal Drying	$2,800 / Yr.
Solvent Recovery	$11,800 / Yr.

The estimated subtotal capital cost was obtained from the summation of the purchased equipment cost multiplied by factors for piping (10%), electrical (8%), instrumentation (5%) and site preparation (5%). The total capital cost was the summation of the subtotal capital cost multiplied by the engineering (15%) and contingency (15%)

factors. The total capital cost for option A was $878,000 and option B was $908,000. The operating and maintenance cost for option A was $73,900 per year and option B was $77,200 per year.

Comparisons of Options A and B with thermal desorption were accomplished by calculating the net present value of all costs associated with each over 10 years. The cost for thermal desorption was $840,000 per year to treat 2100 tons of dewatered sludge. The breakeven cost of solvent for option A was calculated by determining the minimum cost of solvent loss required to give the same net present value cost as option B. The breakeven cost of thermal desorption was calculated similarly. The payback period for option B versus thermal desorption was the number of years required to give equal net present value costs for option B and thermal desorption.

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