

Characterization of Exploration and Production Associated Waste

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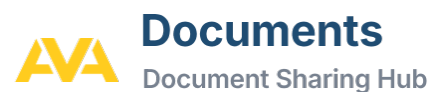
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**AMERICAN PETROLEUM INSTITUTE
PRODUCTION WASTE ISSUE GROUP**

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EXECUTIVE SUMMARY

During the exploration and production of crude oil and natural gas, the oil and gas industry generates a number of wastes that are uniquely associated with its operations. These include produced water, drilling wastes, and so-called "associated wastes." Associated wastes, which include crude oil impacted soil, tank bottoms, and workover fluids, comprise approximately 11 million barrels, or 0.1 percent of the total volume of exploration and production (E&P) wastes generated annually (API, 1988). The 1980 amendments to the Resource Conservation and Recovery Act (RCRA) exempted associated wastes from regulation by EPA under its Subtitle C hazardous waste requirements. Currently, associated wastes are regulated by state agencies under state laws.

The industry aggressively advocates the use of cost-effective waste management options that are protective of human health and the environment. In 1989, the American Petroleum Institute's (API) Production Waste Issue Group (PWIG) of the Executive Committee on Environmental Conservation, initiated a waste characterization and groundwater modeling study to gain a better understanding of the fate and effects of E&P waste in the environment.

A limited composition and constituent concentration database for different categories of associated wastes was developed and the data were then used as input to a soil and groundwater model developed by API that simulates the effects of a variety of land-based waste management practices. It should be stressed that the results presented in this report must be considered with an understanding of how each waste is managed and the probable transport and fate of waste constituents in order to evaluate any potential effects on human health and the environment.

Concurrent with API's study, the Gas Research Institute (GRI) conducted a complementary study to develop characterization data for wastes associated with natural gas industry operations (Myerski *et al.*, 1993).

The products expected from API's study were:

1. An initial constituent database for associated wastes;
2. Sampling and analytical experience;
3. An assessment of potential impacts to groundwater posed by land-managed associated wastes; and
4. Recommendations for future studies.

SAMPLING AND ANALYSIS

Sample collection and analysis were conducted in two phases. In Phase I (1989), 31 samples were collected and analyzed for a comprehensive list of organic and inorganic constituents. During Phase II (1990-1991), 89 additional samples were collected and analyzed for a more narrowly focused set of constituents and characteristics. In all, samples representing 12 different associated waste categories were collected from on-shore E&P sites in seven states. Samples of oil-based drill cuttings and used oil, neither of which are considered associated wastes by EPA, were also collected. However, for simplicity, all analyses of materials sampled during both phases are presented in this report. Oil-based drill cuttings are exempt from regulation under RCRA Subtitle C. Used oil is considered non-exempt from RCRA Subtitle C regulation; however, under existing EPA regulations, used oil may be reintroduced into the crude stream for recycling if the used oils are from normal operations and are to be refined with normal process streams at a petroleum refinery facility (see 40 CFR Section 279).

A conservative approach was taken when collecting samples. A conscious effort was made to sample materials in a manner to capture the highest concentrations of constituents of potential environmental concern. Materials sampled ranged from freshly contaminated soil to a host of potential wastes from various process streams. Care was taken to address all significant wastes and potential wastes, obtain representative samples, and employ appropriate quality assurance/quality control (QA/QC). Some of the sampling difficulties encountered could be minimized in future efforts by following an established plan for associated waste sampling.

Many associated waste samples contained percent levels of oil and parts per million (ppm) levels of volatile organic compounds (benzene, toluene, ethyl benzene, and xylenes; "BTEX"). A few samples were found to contain ppm levels of the semi-volatile compounds 1-methyl naphthalene and phenanthrene. A number of metals were detected: ppm levels of lead,

chromium, copper, nickel, vanadium and zinc were found in many samples. Calcium, sodium, and potassium were found along with barium, a common drilling fluid additive. Since BTEX and semi-volatile compounds are naturally occurring constituents of crude oil and natural gas liquids, and the metals detected are ubiquitous in the environment, these results are not unexpected. Therefore, the transport and fate of these constituents in various media, such as soil and groundwater, must be evaluated before any significance can be placed upon the magnitude of the concentrations found.

This study revealed several practical problems with the sampling and analysis of associated wastes. The two primary, and often related, sampling problems were: 1) obtaining a representative sample, and 2) scheduling the sampling event. For example, sampling methods must be carefully selected to obtain samples that are representative of much larger volumes of generated materials that are typically quite heterogeneous. Care must be taken to schedule sampling so that a true waste can be captured during an actual maintenance procedure (e.g., cleaning out a storage tank or removing waste glycol from a gas plant). The infrequency of certain maintenance events sometimes necessitated the sampling of materials which were still part of the process stream and would not normally be considered wastes.

Many of the samples caused severe matrix interference problems with the EPA SW-846 methods used in this study. Matrix interference issues have been previously addressed in SW-846 and in comments on SW-846 in regard to petroleum matrices (USEPA, 1986). Low concentrations of organic constituents within an organic matrix would not have been detected, if present. These findings clearly show that associated wastes, especially those containing high levels of organic materials, require specialized analytical methods.

This study generated a useful set of analytical data to serve as an initial, but limited, database describing the characteristics of associated wastes. When comparing the data in this study with data in future studies, the data quality elements of precision and accuracy should be evaluated. The RCRA Characteristics data collected in this study should be compared to other predictive tools (i.e., alternative leaching protocols and fate and transport modeling) to determine the validity of continuing to use the EPA methods, such as the Toxicity Characteristic Leaching Procedure (TCLP), for associated wastes.

FATE AND TRANSPORT MODELING

The composition and constituent concentration data generated in the sampling and analysis phase of this study were used to assess the potential impact on groundwater posed by land-managed associated waste. These data were entered into the API-developed Vadose and Saturated Zone Exposure (VADSAT) model which simulates the fate and transport of constituents from a land-management unit to a user-designated drinking water well, directly downgradient. VADSAT accounts for most of the major processes that affect organic constituents moving through the shallow subsurface including: adsorption, dilution and biodegradation.

Industry practices of land spreading, road spreading, and burial were modeled with VADSAT. The modeling investigation considered six associated waste types, four chemical species, two infiltration scenarios, eleven hydrogeological environments, and two hypothetical receptor locations. A total of 1,144 VADSAT Monte Carlo simulations were performed, each simulation involving iteration of 1,000 sets of parameter values. This analysis produced a statistical distribution of possible receptor well concentrations for a wide range of hydrogeologic conditions.

Associated waste management scenarios were converted to input understood by VADSAT using data from a range of sources. Physical and chemical properties data not available from the sampling and analysis portion of this study were obtained from reference works. Hydrogeological settings were described by statistics compiled by API (Newell *et al.*, 1989). Representative volumes of associated waste managed per disposal incident were compiled from information provided by API member companies.

SUMMARY OF RESULTS AND FINDINGS

1. An initial constituent database for associated wastes was established.

The data presented throughout this report indicate that the sampled associated wastes contain few Petroleum Refinery List semi-volatile organic compounds, varying types and concentrations of metals, and a number of volatile organic compounds (VOCs), primarily benzene, toluene, ethylbenzene, and xylene (BTEX). These analytical results were not unexpected because BTEX and semi-volatile compounds are naturally occurring constituents of crude oil and natural gas, and the metals detected are ubiquitous in the environment.

2. Sampling and analytical difficulties were identified.

- Proper scheduling of sampling is a key component.

Due to scheduling problems, it was often extremely difficult to collect actual waste samples. All of the categories sampled, except pit/sump waste, crude oil impacted soil, and dehydration condensate water, are generated intermittently from specific operations such as workovers or tank cleaning. These operations or maintenance procedures are infrequent and are usually scheduled only a few days in advance. They are subject to cancellation due to higher priority work, making it difficult for a sampling team to be present when an actual waste is generated. For some samples, such as tank bottoms and waste glycol, process fluids were the bulk of the sample collected since true wastes were not available. In all cases, the collected sample was expected to contain equivalent or higher concentrations of constituents of possible environmental concern than contained in a true waste.

- Obtaining representative samples was difficult.

Adding to scheduling problems is the extreme difficulty of obtaining representative samples. The sampling team collected samples of up to one liter from waste volumes ranging from one barrel (208 liters) to a maximum of 14,000 barrels. The materials were sometimes stratified and, in some cases, the composition changed from hour to hour. It is very difficult to obtain a representative sample from large volume heterogeneous materials.

- The EPA analytical methods were ineffective with many of the samples which contained high levels of organic constituents. Matrix interferences frequently interfered with test results.

Matrix interference problems were frequently encountered when trying to analyze certain samples by EPA analytical methods (e.g., the TCLP method). Matrix interference involves problems created from substances in the samples that cause either a chemical or physical interference during the analysis of the sample. Approximately 60 percent of the samples in this study indicated a matrix interference problem with at least one constituent analyzed. The large concentrations of n-alkanes can mask the presence of other hydrocarbons and raise the detection limits for compounds of interest.

- Comparison of analytical results from two different laboratories was limited due to the number of "non-detect" results. Where positive analytical results could be compared, the agreement was limited.

The analytical results for four duplicate samples collected by API and the Gas Research Institute (GRI) were comparable for those analyses which did not experience matrix interference problems. API and GRI agreed to collect and analyze four split samples to better understand the variance in analytical results from two different labs, ENSECO and ENSR. The four samples used for this comparison were molecular sieve from a dehydrator, spent molecular sieve from an isobutane sweetener, waste glycol, and glycol dehydrator condensate water. Whereas some differences were encountered in sulfide measurements, the TCLP constituent data were similar. Matrix interference problems created high

detection limits which made it difficult to compare the majority of the TCLP volatile organics data.

3. E&P associated waste management practices were modeled to assess their potential impact to groundwater.

The VADSAT model was run in a Monte Carlo mode to calculate the peak concentration over time of a chemical species corresponding to the 85 percent cumulative probability of non-exceedence at hypothetical downgradient receptor wells. In other words, there is only a 15 percent probability of generating higher peak concentrations. The VADSAT-predicted concentrations were far below the standard analytical detection limits for the compounds benzene, toluene, ethylbenzene, and xylenes (BTEX) at receptor wells located 500 and 1500 feet downgradient. Of the three waste management practices modeled, burial produced the highest predicted concentrations due to greater waste thicknesses.

Modeling results showed that a number of subsurface processes combine to naturally attenuate organic components of associated wastes that may leach to groundwater. Water filtering through the waste management unit carries soluble organic constituents to the water table, where it mixes with a larger body of groundwater and is diluted. Further dilution occurs due to the longitudinal and transverse dispersion. Biodecay lowers the aqueous phase concentrations. Adsorption results in constituent retardation and allows more time for biodecay to occur. These processes collectively result in reduced concentrations at downgradient receptor wells.

VADSAT simulations of the subsurface fate and transport of BTEX leaching from associated wastes in the API database suggest that these wastes do not pose a threat to groundwater when managed in accordance with API guidance on landspreading, roadspreading and burial.

RECOMMENDATIONS

1. The data presented in this report should be used in modeling studies to predict the environmental impact of various land-based waste management techniques.

The objective of this study was to establish a composition and constituent concentration database for different categories of associated wastes. No conclusions regarding the environmental impact of these wastes can be drawn from this data without an understanding of how each waste is managed and the probable transport and fate of the waste constituents. An understanding of the potential impact on soil and groundwater can best be achieved through modeling studies of the type described in this report.

2. The data provided in this study should be supplemented with data from API member companies, from studies performed outside of API, and from additional API studies, where appropriate.

The sampling effort completed in this study resulted in the collection of 120 samples from 12 different categories of associated waste and two waste categories not typically considered to be associated wastes. Although this effort provides a substantial amount of information on the concentrations of constituents that may be present in associated wastes, more data would improve the statistical reliability of the data set.

3. Future studies of associated wastes should sample only waste streams prior to treatment or disposal and avoid sampling process streams.

The scheduling difficulties encountered by the sampling teams are well documented in this report. It is important to design any additional sampling programs so that samples taken are of true wastes. Sampling procedures must be designed to assure collection of a representative material.

4. Laboratories performing analyses of associated waste must use appropriate techniques to reduce matrix interference problems. Where possible, API should support efforts to develop new analytical methods that address complex oily matrices.

For example, laboratories should be required to perform sample cleanup procedures, such as Method 3611 and Method 3650 or techniques supported by user-prescribed QA/QC criteria (i.e., EPA "Performance Based Methods") to achieve improved data quality for semivolatile organic analyses.

5. The RCRA Characteristics data collected in this study should be evaluated only by comparison with other predictive tools and techniques developed specifically for oil and gas waste management practices.

The RCRA Characteristic data (particularly TCLP data) from this study were collected for comparative purposes only. The RCRA TCLP analytical technique is intended to estimate the possible impact a particular waste may have in a domestic landfill environment. With the information from this study, and the information to be generated from soil and groundwater modeling, the oil and gas industry can evaluate the applicability of RCRA Characteristics analytical techniques to its wastes and waste management practices. Any new protocols deemed more appropriate for predicting the leachability of oily wastes should be compared to the TCLP to understand under which conditions, if any, the TCLP is appropriate. Also, because most associated wastes contain significant amounts of solids and water, the appropriateness of RCRA ignitability testing should be evaluated prior to requesting the test.

6. Based on the extensive list of constituents examined in this study, future associated waste studies should analyze for the following constituents.

Arsenic, Barium, Cadmium, Chromium, Copper, Lead, Mercury, Nickel, Potassium, Sodium, Vanadium, Zinc, Polynuclear Aromatics (PNAs), Benzene, Ethyl Benzene, Toluene, Xylenes; general chemical constituents such as pH, reactive sulfide, oil/water/solids, oil and grease/total petroleum hydrocarbons (TPH) and chloride. Other site specific constituents known to be present should also be analyzed.

Section 1 BACKGROUND

The oil and gas industry generates a number of wastes that are uniquely associated with its operations. These wastes include produced water, drilling wastes, and "associated wastes." Associated wastes, which include crude oil impacted soil, tank bottoms, and workover fluids, comprise approximately 0.1 percent of the total volume of E&P wastes generated annually (API, 1987).

The 1980 amendments to the Resource Conservation and Recovery Act (RCRA) exempted E&P wastes from the law's hazardous waste requirements. At the same time, Congress directed EPA to study E&P wastes and recommend appropriate regulatory action.

EPA completed its study of E&P wastes and issued a Regulatory Determination in June 1988 (EPA, 1988). EPA concluded that E&P wastes do not pose a significant threat to human health and the environment when properly managed and, for the most part, these wastes were being adequately regulated under existing state and federal programs. EPA determined that E&P wastes should continue to be exempt from the hazardous waste regulation of RCRA and should continue to be regulated by state agencies using existing state and federal authorities.

Since the Regulatory Determination, the EPA, states, and industry have continued to work to improve the management of E&P wastes. In January 1989, API issued a comprehensive guidance document on E&P waste management practices (API, 1989). The document describes recommended waste management procedures which are believed to be protective of human health and the environment.

In 1989, the API initiated a multi-year waste characterization and groundwater modeling study to improve its knowledge of the fate and effects of E&P wastes in the environment.

Different categories of associated wastes were characterized through a sampling and analysis program that produced an initial composition and constituent concentration database. The characterization data was then used as input for a fate and transport model (VADSAT), developed subsequently by API, to simulate E&P waste management practices.

In all, samples representing 12 different associated waste categories were collected from onshore E&P sites in seven states. Samples of oil-based mud drill cuttings and used oil, neither of which are typically considered associated wastes, were also collected. For simplicity, all samples collected are referred to as associated wastes for the purpose of this report.

Section 2

METHODS

SAMPLING INFORMATION

Sample Collection

The sampling program was designed to obtain a wide cross section of associated wastes generated at onshore E&P facilities, over a wide geographic area, and capture samples expected to contain the highest levels of constituents of potential environmental concern. In some cases, budget and time constraints necessitated the collection of samples of process streams. This was a compromise since, in many cases, samples collected do not represent wastes in E&P operations. In addition, many samples represent material that normally would be subject to further processing to recover hydrocarbon for sale. Collection of these process and intermediate materials did create samples that would be expected to contain constituents of potential environmental concern similar to the wastes they represented.

Sampling was conducted in two phases. Phase I was initiated on August 24, 1989 and ended December 19, 1989. A total of 31 samples were collected. The experience gained in arranging for, collecting, and transporting the Phase I samples led to modifications in the program and additional streams were identified for sampling. Phase II sample collection began on September 4, 1990 and concluded on April 1, 1991, with 89 samples collected. Because the study was conducted in two parts, there was some inconsistency in the sample types collected and the analyses performed during Phase I and Phase II.

A total of 120 samples were collected from E&P sites in distinct geographical regions over seven states: Texas, Oklahoma, New Mexico, Michigan, California, West Virginia and Louisiana. Fourteen categories of wastes were sampled, including 12 associated wastes, and used oil and oil-based mud cuttings. Table 2-1 summarizes the number of samples collected in each category, while Appendix A provides more detailed sample information.

Table 2-1. Summary of Associated Waste Samples Collected

<u>Waste Type</u>	<u>No. of Samples Collected</u>
Crude Oil Impacted Soil	32
Natural Gas Dehydration & Sweetening	17
• Dehydration Condensate Water	(3)
• Waste Glycol Solution	(8)
• Molecular Sieve	(3)
• Used Amine Solution	(1)
• Spent Iron Sponge	(2)
Oil-Based Mud Cuttings	5
Produced Sand	1
Pigging Wastes	5
Skimming Pit and Sump Wastes	4
Rig Wash	5
Tank Bottoms	18
Used Oil (Natural Gas & Diesel Crankcase)	12
Workover Fluids & Stimulation Flowback	21

Drilling fluids, produced waters, and so-called "associated wastes" are exempt from hazardous waste regulation under Section 3001 (b)(2)(A) of RCRA. Used Oil is not an exempt "associated waste." For simplicity, all sampled wastes are referred to as "associated wastes" for the purpose of this report.

Sampling Procedures - General

General sampling procedures were designed to maximize sampling efficiency and capture samples containing constituents of potential environmental concern. This was done with the understanding that, on occasion, the samples collected would not necessarily be representative of actual wastes. Of necessity, some samples were collected from process streams, and were obviously not wastes. Subsequently, results have shown the pitfalls of such sampling as explained in the Executive Summary of this report and in Table 2-2. Waste sampling should follow protocols outlined in SW-846 and ASTM Vol 11.04.

Table 2-2. Representative Sampling

Collection of tank bottoms samples via a thieving device provides an example of how a sampling method could impact a waste's chemical composition. Obtaining tank bottom samples through a tank roof hatch with a thieving device unquestionably results in a non-representative sample for a number of reasons.

- **Sample is not exposed to the tank cleaning process.**
Normal procedures require that the tank be drained, then opened to the atmosphere until the oxygen and hydrocarbon levels in the tank are safe for human entry. Once safe, the tank bottoms may be removed by shoveling, washing with a high pressure water hose, or a combination of both methods. Thieved samples would not have this kind of exposure to volatilization and oxidation. In addition, the thieved samples may be pulled through crude oil and emulsion layers adding additional chemical components in the process and possibly altering the sample.
- **Stratification.**
Tank bottoms are generated when solids settle to the bottom of the tank. Often, the solids are laid down in layers. The sample device may not be able to collect from all layers: it may only be able to collect the top layer consisting of mostly crude oil.
- **Lack of tank bottoms.**
The pumper or operator may routinely take thieved samples of tank bottoms to monitor solids buildup. Because this action cleans the area below the tank hatch, it may be impossible to collect a sample of tank bottoms.
- **"Striker plates."**
Striker plates, or other devices placed in the crude oil storage tank to prevent tank gauging devices from hitting the tank bottom, may prevent the same buildup of bottoms material present throughout the remainder of the tank. These samples could contain unrepresentative levels of organic compounds and/or metals.

Therefore, in the case of tank bottoms, it has been determined that valid samples may be collected only during actual cleanout when the tank bottoms are being prepared for handling subsequent to removal of overlying materials.

Sampling Techniques - General

Samples were collected according to standard EPA protocols contained in SW-846, stored and transported at a temperature of 4°C and shipped via overnight carrier to the analytical laboratory. Exceptions to the preceding are noted in the discussion of individual sample types. Actual sampling techniques varied according to the sample matrix. For example, crude oil bearing soils and oily cuttings were generally collected using a stainless steel trowel. Some dehydration and workover fluids were collected directly from equipment valves. Tank bottoms and other samples were collected by a bailer, oil thief or stainless steel trowel.

Sample Jars and Containers were provided by the contract laboratory (ENSECO) as follows:

• TCLP -	Volatile organic compounds	4 oz. glass
	All other analytes	32 oz. glass
• SOLIDS -	Organics, metals	16 oz. glass
	RCRA Characteristics	8 oz. glass
• AQUEOUS -	Volatile organic compounds	3 X 40 ml glass, HCl preservative
	Semivolatile organic compounds	2 X 1 L glass,
	Metals	16 oz. polyethylene bottle, HNO ₃ preservative
	Cyanide	8 oz. polyethylene bottle, 50% NaOH preservative
	Sulfide	8 oz. polyethylene bottle, Zn Acetate/NaOH preservative
	pH, chloride	32 oz. polyethylene bottle

Sampling Considerations

A sampling program of this magnitude presents a host of challenges — scheduling, budget, consistency in collection, and of course, what, where, and how to sample. The objective of the sampling was to obtain random waste samples, collected in a consistent manner, and to ensure the samples were as "fresh" as possible to assure the highest concentration of constituents of potential environmental concern.

The sampling difficulties encountered during this project could be minimized in future efforts by following a formal sampling plan. Budget and time constraints necessitated the collection of samples of process streams. This was a compromise since, in many cases, samples collected do not represent wastes in E&P operations. In addition to process streams, many samples represent material that would be subject to further processing to recover hydrocarbon for sale. But collection of these process and intermediate materials did represent samples that would be expected to contain concentrations of constituents of potential environmental concern that were as high or higher than the wastes they represented.

Timing a sampling trip can be difficult. Collecting tank bottom samples is one example of how scheduling can be a problem. The only time tank bottoms become a priority is when buildup

causes carryover of sediments or water into the crude oil sales line. Generally, crude oil stock tanks only require removal of oil/water/solids sludge buildup (tank bottoms) every three to five years. Therefore, as long as the quality of the crude oil being sold is unaffected, bottoms cleanout is a low priority and subject to cancellation for higher priority work.

To overcome these time and budget constraints, the sampling team found it more efficient to arrange sampling events with several companies targeting all categories of waste in broad geographic locations such as Kansas or East Texas. This approach worked well for unpredictable sampling events such as workovers and crude oil impacted soil sampling. With the sampling team in a particular area, the team could sample an event within a few minutes or hours of a call. At times, it was necessary to sample process streams or intermediate waste streams. This occurred when waste generation was infrequent and the work was subject to cancellation or delay. These categories included tank bottoms, waste glycol and amine, spent mol sieve, and spent iron sponge.

Each category of waste required different approaches to sampling. The following are general examples:

Crude Impacted Soils - sample at active or recent crude oil spill sites.

Natural Gas Dehydration & Sweetening

- Dehydration Condensate Water - collects in sumps or vessels downstream of the glycol reboiler prior to disposal. Samples were collected from the holding sumps or vessels or piping valves connecting the sumps or vessels.
- Molecular Sieve - Waste is generated infrequently and there is usually no method of obtaining a process sample. The intent was to be present for sampling when a vessel was opened for cleanout.
- Spent Iron Sponge - Waste is generated infrequently and there is usually no method of obtaining a process sample. The intent was to be present for sampling when a vessel was opened for cleanout.
- Used Amine Solution - Infrequent waste generation of spent amine waste required the team to sample process streams of active sour gas treaters. The rich amine stream upstream of the reboiler was expected to contain the highest concentration of volatile organics, so samples were collected at that point. Refer to the Amine Sampling Section of this report for more detail.
- Used Glycol Solution - Infrequent waste generation of spent glycol required the team to sample process streams of active dehydrators. The rich glycol stream upstream of the reboiler was expected to contain the highest concentration of volatile organics, so samples were collected at that point. Refer to the Glycol Sampling Section of this report for more detail.

Oil-Based Mud Cuttings - Waste samples were taken either from the shale shaker as they were generated or removed from the interior of mounds of cuttings awaiting disposal.

Pigging Wastes - Waste samples were taken from crude oil gathering line sumps or removed from ball receivers as they were opened at the inlet of natural gas processing plants.

Produced Sand - The single sample of waste was removed from a settling tank specifically placed in the production stream to remove produced sand from the produced fluids. The waste sand was being removed at the time of sampling.

Skimming Pit and Sump Wastes - These vessels are generally exposed to air; therefore, sampling was accomplished by skimming emulsion and hydrocarbon from the surface and/or if solids were present, thiefing solids from the bottom of the vessel.

Rig Wash - Samples were collected in the sump to ensure the highest expected level of constituents of potential environmental concern would be present.

Tank Bottoms - Tank bottom samples were thiefed from tanks still in service. Samples were collected in this manner for two reasons: to ensure that the highest expected level of constituents of potential environmental concern would be present and, principally, because it was very difficult to schedule tank cleanouts and sample collection to coincide. Refer to the Tank Bottoms Sampling Section of this report for more detail.

Used Engine Lube Oil - Samples were taken directly from the engine crankcase or engine oil cooler piping of engines in service.

Workover Wastes - Samples were taken at the wellhead through valves, or from pits or holding tanks where the waste was held prior to disposal.

ANALYTICAL METHODS

This section discusses the general analytical test procedures used, and their limitations for E&P waste characterization. All analyses followed standard EPA methodologies and protocols and full quality assurance/quality control (QA/QC) procedures. Appendix B contains additional details on the analytical methods utilized, QA/QC, and constituents analyzed.

During Phase I, conducted in 1989, it was requested that all samples be analyzed for oil/water/solids [MODT: modified oven drying technique (API, 1987)] Appendix IX volatile organic compounds, Petroleum Refinery List semi-volatile organic compounds, Appendix IX metals and RCRA Characteristics — ignitability, corrosivity and reactivity, TCLP volatile organic compounds, TCLP semi-volatile organic compounds, and TCLP metals (USEPA, 1986). (See Appendix B.)

The Petroleum Refinery List, a subset of the Appendix IX list, contains compounds of concern to the petroleum industry, such as PNAs and phenols. To improve the reliability of the

analysis of these compounds, cleanup procedures (Methods 3650 and 3611) are used to remove interfering aliphatic hydrocarbons.

Analytical methods contained in EPA document SW-846 (*Test Methods for Evaluating Solid Waste*) were employed to identify both organic and inorganic constituent types and concentrations in the wastes. The RCRA Characteristic data (including TCLP data) were collected for comparative purposes only. The RCRA TCLP test is the only approved EPA leaching method for waste evaluation. It is intended to estimate the possible impact that a particular waste may have in a municipal landfill environment. It does not apply to exempt E&P wastes. Further, EPA has recognized that predicting a material's leachability requires consideration of the disposal conditions and the use of fate and transport models that reasonably simulate how constituents would be released from a source and move through the subsurface. They also recognize that no universal test procedure (including TCLP) is likely to be developed that will accurately replicate all disposal conditions (Freidman, 1992).

RCRA ignitability testing (EPA Method 1010) was conducted on all waste types except spent amine. The test is considered reliable when performed on non-aqueous liquids, but unreliable for aqueous, solid and semi-solid samples (Hanson and Freidman, pers. comm.). Therefore, ignitability results from aqueous, solid and semi-solid samples tested in this study should be considered unreliable. For each waste type discussed in Section 3 of this report, results of ignitability testing on appropriate matrices will be noted. All ignitability results are reported in Appendix C.

Based on Phase I results, the sampling plan for Phase II (conducted in 1990-91) called for a reduced suite of analyses including: oil/water/solids (MODT), Appendix IX volatile organic compounds, RCRA ignitability, RCRA corrosivity, RCRA reactivity, TCLP volatile organic compounds, and TCLP metals. The Petroleum Refinery List semi-volatile organic compounds and metals, and the TCLP semi-volatile organic compound tests were not performed. The oil/water/solids contents were not determined for used oil, glycol, or amine because the sample consisted primarily of the known process fluid. In other cases, tests were not performed because only limited sample volumes were available. These decisions allowed a greater number of samples to be analyzed for parameters of concern and eliminate tests which were less informative.

While samples were analyzed for a broad range of constituents (See Tables 1-6, Appendix B), very few were detected. For clarity, constituents which were not detected in any sample are not included in the analytical results in the body of the report, or in the table in Appendix C.

In cases where matrix interferences caused high detection limits, it is possible that some constituents were present in the samples but were not detected. The analytical results summary tables for each waste type (presented in Section 3 of this report) state the range of detection limits experienced for each constituent (e.g., benzene) in that group of samples. By examining the range of detection limits, the reader can evaluate the bias associated with mean constituent concentration values calculated using only samples where the constituent was detected.

Section 3

ANALYTICAL RESULTS

This section summarizes sampling, testing, and analytical results for each category of samples evaluated. It includes information on sampling, and laboratory and matrix interference issues which influenced the results. Summary tables of total analysis test information is included for each waste category. Appendix C contains more detailed results for total analysis testing, as well as the results for RCRA ignitability, corrosivity and reactivity and TCLP analyses. Quality Assurance/Quality Control information is indicated by footnotes in the Appendix C data tables.

Finally, a discussion of the overall data is made, along with a limited comparison of these data with results obtained in the Gas Research Institute's study on associated wastes in the natural gas production industry (Myerski *et al.*, 1993).

CRUDE OIL IMPACTED SOILS

Crude oil impacted soils in E&P operations typically result from equipment leaks and spills. Leaks and spills come from such equipment as valves, stuffing boxes, tanks, ruptured flow lines, gas plants, workover equipment, etc. Crude oil impacted soils can also contain a variety of other contaminants, ranging from glycol to workover completion fluids. Crude oil impacted soils are often exposed to weathering before they are discovered. Generally, when discovered, excess fluid is removed from the soil surface and returned to the production process, if possible.

Sampling and Analysis

Thirty-two crude oil impacted soil samples were taken from East Texas (5), West Texas (16), Oklahoma (8), California (1), West Virginia (1), and New Mexico (1). Four were Phase I samples and twenty-eight were Phase II samples. Samples were collected from fifteen facilities. Sampling locations included, but were not limited to: stock tank loading valves, stuffing boxes on wells being pumped by beam pumping units, centrifugal pumps, workovers, crude oil flow line and gas gathering systems leaks, and spills from overfilling of storage tanks. Collection was made by excavating the top three inches of soil with a stainless steel trowel.

Twenty-nine of the soil samples were analyzed for oil, water, and solids content. All thirty-two samples were analyzed for total Appendix IX volatile organic compounds. Four samples were analyzed for total Appendix IX metals and Petroleum Refinery List semi-volatile organic compounds.

All samples were analyzed for RCRA ignitability, corrosivity and reactivity. All samples were evaluated for some TCLP volatile organic constituents. One sample was analyzed for TCLP semi-volatile organic compounds, and 30 samples were analyzed for TCLP metals.

Results

Crude oil impacted soil samples were typically solid (30-85 percent solids) with variable amounts of oil (2-55 percent oil) and water (2-25 percent water).

Five volatile organic compounds were found at measurable levels: benzene, carbon disulfide, ethyl benzene, toluene, and xylene (Table 3-1). Acetone and dichloromethane were also detected, but these results are considered qualitatively unreliable due to the occurrence of these compounds as lab contaminants (see Appendix B).

Table 3-1. Total Appendix IX Volatile Components Detected in Crude Oil Impacted Soil

Compound	Number of Samples Analyzed	Number of Detections	Number of Non-Detections [Range of Reporting Limits for Non-Detections (mg/kg)] ^a	Mean Concentration of Detected Constituents ^b (mg/kg)	Range of Detected Concentrations (mg/kg)
Acetone	32	7	25 (1-1000)	65	3 - 260
Benzene	32	7	25 (0.5-500)	60	2.8 - 270
Carbon Disulfide	32	1	31 (0.5-500)	54 ^c	N/A
Dichloro Methane	32	1	31 (0.5-500)	120 ^c	N/A
Ethyl Benzene	32	16	16 (0.5-500)	109	3.5 - 930
MethylEthyl Ketone	32	0	32 (1-1000)	N/A	N/A
Toluene	32	17	15 (0.5-500)	148	1.2 - 1200
Xylenes	32	27	5 (0.5-2.5)	188	0.6 - 1100

^a The "Range of Reporting Limits for Non-Detections" qualitatively reflects the bias associated with the reported mean, due to excluding non-detected concentrations.

^b Non-detected concentrations were not used in calculating the mean.

^c Represents one value.

N/A Not Applicable

Two semi-volatile compounds were detected: 1-methyl naphthalene and phenanthrene (Table 3-2).

Table 3-2. Petroleum Refinery List Semi-Volatile Organic Compounds Detected in Crude Oil Impacted Soil

Compounds	Number of Samples Analyzed	Number of Detections	Number of Non-Detections [Range of Reporting Limits for Non-Detections (mg/kg)] ^a	Mean Concentration of Detected Constituents ^b (mg/kg)	Range of Detected Concentrations (mg/kg)
Chrysene	4	0	4 (5-100)	N/A	N/A
1-Methyl Naphthalene	4	2	2 (5-100)	43	21 - 45
Naphthalene	4	0	4 (5-100)	N/A	N/A
Phenanthrene	4	1	3 (5-100)	10 ^c	N/A

^a The "Range of Reporting Limits for Non-Detections" qualitatively reflects the bias associated with the reported mean, due to excluding non-detected concentrations.

^b Non-detected concentrations were not used in calculating the mean.

^c Represents one value.

N/A Not Applicable

Sixteen different metals were detected: aluminum, arsenic, barium, beryllium, cadmium, calcium, chromium, cobalt, copper, lead, mercury, nickel, potassium, sodium, vanadium, and zinc (Table 3-3).

RCRA Characteristics data showed: pH ranged from 4.1 to 8.8; reactive sulfide was detected in four out of thirty-two samples, reactive cyanide in one out of thirty-two. Six samples had a flash point of less than 140°F; however, the results are unreliable because the sample matrices were not non-aqueous liquids.

Trichloroethylene, benzene, and toluene were the only organic compounds found in the TCLP leachate. Out of the 32 samples analyzed, trichloroethylene was found in 1, benzene was found in 13, and toluene was found in 20. The following metals were detected in the TCLP leachate: barium, 28 out of 30 samples; cadmium and chromium, 1 out of 30 samples; and lead, 4 out of 30 samples. RCRA Characteristic results are found in Appendix C.

Table 3-3. Total Appendix IX Metals Detected in Crude Oil Impacted Soil

Compound	Number of Samples Analyzed	Number of Detections	Number of Non-Detections [Range of Reporting Limits for Non-Detections (mg/kg)] ^a	Mean Concentration of Detected Constituents ^b (mg/kg)	Range of Detected Concentrations (mg/kg)
Aluminum	4	4	0 (N/A)	2195	480 - 5400
Antimony	4	0	4 (5-50)	N/A	N/A
Arsenic	4	2	2 (0.5-0.8)	72	4.2-140
Barium	4	4	0 (N/A)	285	12 - 940
Beryllium	4	2	2 (0.2-2)	0.5	0.4 - 0.6
Cadmium	4	3	1 (5 ^c)	1.8	0.5 - 3
Calcium	4	4	0 (N/A)	90,438	750 - 273,000
Chromium	4	3	1 (10 ^c)	7	2 - 11
Cobalt	4	1	3 (1-10)	6 ^c	N/A
Copper	4	3	1 (10 ^c)	14	4 - 23
Lead	4	3	1 (50 ^c)	38	7 - 81
Mercury	4	1	3 (0.1)	0.1 ^c	N/A
Nickel	4	3	1 (40 ^c)	14	9 - 24
Potassium	4	1	3 (500-1000)	500 ^c	N/A
Selenium	4	0	4 (0.5-5)	N/A	N/A
Silver	4	0	4 (1-10)	N/A	N/A
Sodium	4	1	3 (500)	1000 ^c	N/A
Thallium	4	0	4 (0.5-10)	N/A	N/A
Tin	4	0	4 (8-50)	N/A	N/A
Vanadium	4	3	1 (10 ^c)	9	3 - 13
Zinc	4	4	0 (N/A)	82	13 - 250

^a The "Range of Reporting Limits for Non-Detections" qualitatively reflects the bias associated with the reported mean, due to excluding non-detected concentrations.

^b Non-detected concentrations were not used in calculating the mean.

^c Represents one value.

N/A - Not applicable

Discussion

A concerted effort was made to find samples at recent spill sites where excess fluids had not yet been removed. This ensured that the highest expected level of constituents of potential environmental concern would be present. Twenty-eight samples were from areas where a leak or spill had occurred within the previous 24 hours. In addition, many of the samples were taken from locations that had been subjected to several spills over the years.

The results for total analysis testing are not unexpected, since the BTEX compounds and semi-volatile compounds are naturally occurring constituents of crude oil, and the metals detected are widespread in the environment. No site-specific background samples were collected to which metal analyses could be compared. Table 3-4 is useful for qualitatively

comparing concentrations of detected metals to concentration ranges of metals in soils in the U.S. Trichloroethylene (TCE), which was detected in the TCLP leachate of a spill from a heater treater drain line, is a questionable result. Although trichloroethylene is a common degreasing agent, it is not associated with this process. The occurrence of TCE in only one of thirteen samples would further support this observation.

Table 3-4. Soil Concentrations for Metals in the U.S.

Metal	Soil Concentrations ¹ Average and (Range)(ppm)
Aluminum	72,000 (700 - >100,000)
Arsenic	7.2 (<0.1 - 97)
Barium	580 (10 - 5,000)
Beryllium	0.92 (<1 - 15)
Cadmium ²	0.27 (0.005 - 2.4)
Calcium	24,000 (100 - 320,000)
Chromium	54 (1 - 2,000)
Cobalt	9.1 (<3 - 70)
Copper	25 (<1 - 700)
Lead	19 (<10 - 700)
Mercury	0.09 (<0.01 - 4.6)
Nickel	19 (<5 - 700)
Potassium	15,000 (50 - 63,000)
Sodium	12,000 (<500 - 100,000)
Vanadium	80 (<7 - 500)
Zinc	60 (<5 - 2,900)

¹ Shacklette, H.T., and Boerngen, J.G. 1984. Element Concentrations in Soils and Other Surficial Material of the Conterminous U.S.: U.S. Geological Survey Professional Paper 1270. USGS. Washington, D.C.

² Holmgren, G.G.S., M.W. Meyer, R.B. Daniels, J. Kubota, and R.L. Chaney. Cadmium, Lead, Zinc, Copper, and Nickel in Agricultural Soils in the United States. Journal of Environmental Quality, Vol. 16, 1986.

TANK BOTTOMS

Tank bottoms describe solids consisting of heavy hydrocarbons, sand, clay, and mineral scale that collect in the bottoms of oil and gas separators, treating vessels, and crude oil stock tanks. Crude oil and natural gas produced from a well generally contain produced water and formation solids that are emulsified with the crude oil. These natural contaminants must be removed in order to sell the crude oil or gas. The removal process begins by separating the produced crude oil into three phases: oil, water, and gas using separators and/or treater vessels. The crude oil and produced water are piped from the separator to a "heater treater" where any oil/water/solids emulsions are broken down and separated. Emulsion breaking chemicals or heat may be used to enhance the separation process.

The crude oil then goes to storage tanks and the water is transferred to produced water storage tanks in preparation for reinjection or disposal. Solids may settle to the bottom of each vessel and tank in the process, and must be removed periodically .

Sampling and Analysis

Eighteen tank bottom samples were collected from West Texas (5), Oklahoma (8), Louisiana (1), West Virginia (2), and California (2). Ten Phase I samples and eight Phase II samples were taken. The samples were collected at nine different facilities from the top/side/bottom hatch or a valve on the tank. Vessels that were sampled included: crude oil storage tanks (13), produced water storage tanks (1), free water knock-out tanks (3), and heater treater vessel bottoms (1).

Samples were "thieved" from vessels that were still in service or troweled from the vessel as it was cleaned.

Eighteen tank bottom samples were analyzed for oil/water/solids and total Appendix IX volatile organic compounds. Ten of the samples were analyzed for total Appendix IX metals and Petroleum Refinery List semi-volatile organic compounds.

All 18 samples were evaluated for RCRA ignitability, corrosivity and reactivity, and TCLP metals. All samples were analyzed for some TCLP volatile organics. Ten samples were analyzed for TCLP semi-volatile organic compounds, and inorganic chlorides by EPA Method 300.0.

Results

Tank bottom samples were extremely variable, consisting of 3-58 percent solids, 5-74 percent water, and 6-92 percent oil.

Four total Appendix IX volatile organic compounds were found at measurable levels: benzene, ethyl benzene, toluene, and xylene (Table 3-5).

Table 3-5. Total Appendix IX Volatile Components Detected in Tank Bottoms

Compound	Number of Samples Analyzed	Number of Detections	Number of Non-Detections [Range of Reporting Limits for Non-Detections (mg/kg)] ^a	Mean Concentration of Detected Constituents ^b (mg/kg)	Range of Detected Concentrations (mg/kg)
Acetone	18	1	17 (1-5000)	60 ^c	N/A
Benzene	18	14	4 (0.5-500)	670	6.3-5500
Carbon Disulfide	18	0	18 (0.5-2500)	N/A	N/A
Dichloro Methane	18	0	18 (0.5-2500)	N/A	N/A
Ethyl Benzene	18	16	2 (13-7400)	722	0.9-7400
MethylEthylKetone	18	0	18 (1-5000)	N/A	N/A
Toluene	18	17	1 (1 ^c)	2661	0.7-32,000
Xylenes	18	18	0 (N/A)	3747	8.8-52,000

^a The "Range of Reporting Limits for Non-Detections" qualitatively reflects the bias associated with the reported mean, due to excluding non-detected concentrations.

^b Non-detected concentrations were not used in calculating the mean.

^c Represents one value.

N/A Not Applicable

Acetone was also detected; however, these results may be qualitatively unreliable due to the common occurrence of this compound as a laboratory contaminant. Three Petroleum Refinery List semi-volatile compounds were detected: 1-methyl naphthalene, naphthalene and phenanthrene (Table 3-6).

Table 3-6. Petroleum Refinery List Semi-Volatile Organic Compounds Detected in Tank Bottoms

Compounds	Number of Samples Analyzed	Number of Detections	Number of Non-Detections [Range of Reporting Limits for Non-Detections (mg/kg)] ^a	Mean Concentration of Detected Constituents ^b (mg/kg)	Range of Detected Concentrations (mg/kg)
Chrysene	10	0	10 (13-70)	N/A	N/A
1-Methyl Naphthalene	10	6	4 (20-200)	150	59-240
Naphthalene	10	6	4 (20-200)	104	40-270
Phenanthrene	10	4	6 (30-200)	32	14-49

^a The "Range of Reporting Limits for Non-Detections" qualitatively reflects the bias associated with the reported mean, due to excluding non-detected concentrations.

^b Non-detected concentrations were not used in calculating the mean.

N/A Not Applicable

Fourteen total Appendix IX metals were detected: aluminum, arsenic, barium, cadmium, calcium, chromium, cobalt, copper, lead, mercury, nickel, sodium, vanadium, and zinc (Table 3-7).

Table 3-7. Total Appendix IX Metals Detected in Tank Bottoms

Compound	Number of Samples Analyzed	Number of Detections	Number of Non-Detections [Range of Reporting Limits for Non-Detections (mg/kg)] ^a	Mean Concentration of Detected Constituents ^b (mg/kg)	Range of Detected Concentrations (mg/kg)
Aluminum	10	9	1 (10 ^c)	505	13-1200
Antimony	10	0	10 (5-30)	N/A	N/A
Arsenic	10	9	1 (0.5 ^c)	9	0.7-32
Barium	10	10	0 (N/A)	628	3-5400
Beryllium	10	0	10 (0.2-1)	N/A	N/A
Cadmium	10	2	8 (0.5)	3	2.3-3
Calcium	10	9	1 (30 ^c)	18,404	350-114,000
Chromium	10	9	1 (1 ^c)	19	5-54
Cobalt	10	5	5	3	1-5
Copper	10	9	1 (1 ^c)	73	4-210
Lead	10	8	2 (5)	325	12-970
Mercury	10	2	8 (0.1)	0.75	0.1-1.4
Nickel	10	10	0 (N/A)	26	5-100
Potassium	10	0	10 (500-3000)	N/A	N/A
Selenium	10	0	10 (0.5-5)	N/A	N/A
Silver	10	0	10 (1-5)	N/A	N/A
Sodium	10	9	1 (500 ^c)	5492	760-12,000
Thallium	10	0	10 (0.5-50)	N/A	N/A
Tin	10	0	10 (5-30)	N/A	N/A
Vanadium	10	9	1 (5 ^c)	7.1	1-25
Zinc	10	9	1 (1 ^c)	149	10-400

^a The "Range of Reporting Limits for Non-Detections" qualitatively reflects the bias associated with the reported mean, due to excluding non-detected concentrations.

^b Non-detected concentrations were not used in calculating the mean.

^c Represents one value.

N/A Not Applicable

The RCRA Characteristics data showed: pH ranged from 6.1 to 8.9; reactive sulfide was detected in 9 of 18 samples, while reactive cyanide was not detected in any of the 18 samples. Of the 18 samples, 15 exhibited a flash point <140°F. However, due to the water and solids content of these samples, the reliability of these results is questionable. The volatile organic compounds found in the TCLP leachate were: methylene chloride, detected in 1 of 13 samples; benzene, detected in 17 of 18 samples; and toluene, found in 11 of 13 samples analyzed. Of the ten samples analyzed for TCLP semi-volatile organic compounds, one sample contained detected concentrations of phenol, a-cresol, and m & p-cresol. Metals were detected in the TCLP leachate of 18 samples as follows: arsenic (1), barium (17), cadmium (3), chromium (5), lead (6), and mercury (1). The RCRA Characteristic results are found in Appendix C.

The inorganic chloride analyses show the mean salinity as chloride is 1.05%w +/- 0.75 with a range of 0.03 to 2.51%w. These values are low-to-typical for crude oils.

Discussion

Ten of the eighteen tank bottom samples were thieved from tanks still in service while another five samples were collected from taps, hoses or strainers. Samples were collected in this manner principally because it was very difficult to schedule tank cleanouts and sample collection. Ideally, it is best to sample a tank bottom just before it is placed in a waste management unit or disposed. As with the case of many samples collected in this study, this is not always possible or practical. Therefore, samples collected beneath product, produced water or emulsions are likely to contain higher levels of constituents of potential environmental concern. It is expected that the levels of constituents found in these samples may be elevated relative to tank bottoms commonly managed at E&P sites.

WORKOVER FLUIDS

Workover fluids are generated from three general types of workover operations: well control, drilling or milling operations, and stimulation or cleanup of an oil and gas bearing formation. This study focused on sampling the flowback from spent stimulation fluids because they come in contact with crude oil, natural gas condensate, natural gas, saltwater, and minerals comprising the reservoir rock. The drilling/milling and well control type fluids may or may not come into contact with the oil and gas bearing formation and often these fluids are simply produced water. Stimulation fluids are usually more chemically complex. An acid stimulation fluid, for example, may be made using produced saltwater but is more likely to be freshwater mixed with an acid, commonly hydrochloric acid, or a salt such as potassium chloride, sodium chloride, and/or calcium chloride.

Although not totally distinct, stimulation fluids can be broken down into three types: hydraulic fracturing, wellbore cleanup acidizing, and acid stimulation (acid fracturing). Each of these methods is designed to open new pathways for the flow of oil and gas to the wellbore.

Hydraulic fracturing is accomplished when fluid is pumped down the well under pressure sufficient to "fracture" or split the rock formation containing the crude oil and gas. Once opened, sand or some other propping agent such as walnut hulls is pumped into the "fracture" as a slurry to keep the fracture from closing. The slurry of sand is made by mixing a "gel"

such as guar gum (a natural gum produced by plants) or synthetic polymer with fresh or salt water to make the fluid viscous and able to suspend the sand.

Acidizing to stimulate a well is performed when the formation is composed of acid soluble material such as limestone. The acid creates openings by dissolving or etching the limestone until all the acid is consumed. When hydrochloric acid reacts with limestone, it is neutralized, creating a salt (calcium chloride), carbon dioxide gas, and water. Acids used in this type of stimulation work generally contain corrosion inhibitors (typically an amine), friction reducers and buffers such as citric acid.

Acids are also used for wellbore cleanups, where mineral deposits and heavy hydrocarbon accumulations are removed from the formation surface or casing perforations. Accumulations inhibit the ability for oil and gas to flow into the well thereby restricting production until removed. The deposits in the well may include calcium carbonate, calcium sulfate, iron sulfide, and paraffins or other heavy hydrocarbons. Acid fluids for wellbore cleanup typically contain mutual solvents and/or solvents such as xylene to dissolve the hydrocarbon buildup. Workover fluids are generally oil/water/solids mixtures.

Sampling and Analysis

Twenty-one workover fluid samples were collected from East Texas (6), West Texas (10), Oklahoma (3), and New Mexico (2) during Phase II. The samples came from fourteen different facilities and were collected from flowlines or bailed with a stainless steel bailer from collection tanks. Sampling locations included, but were not limited to: the wellhead, swabbing tree, discharge line, flowline, fracture tanks, and valves near the circulation pump. Job sizes varied from 184 barrels to 14,000 barrels of workover fluid injected.

Three samples were analyzed for oil, water, and solids content. All twenty-one samples were analyzed for total Appendix IX volatile organic compounds; RCRA ignitability, corrosivity and reactivity; and TCLP metals. Twenty samples were tested for TCLP volatile organic compounds.

Results

Six total Appendix IX volatile organic compounds were found at measurable levels in the samples analyzed: benzene, carbon disulfide, ethyl benzene, methyl ethyl ketone, toluene,

and xylene (Table 3-8). Acetone was also detected, but these results may be qualitatively unreliable due to the common occurrence of this compound as a laboratory contaminant.

Table 3-8. Total Appendix IX Volatile Components Detected in Workover Fluids

Compound	Number of Samples Analyzed	Number of Detections	Number of Non-Detections [Range of Reporting Limits for Non-Detections (mg/L)] ^a	Mean Concentration of Detected Constituents ^b (mg/L)	Range of Detected Concentrations (mg/L)
Acetone	21	15	6 (0.01-250)	2	0.25-8.7
Benzene	21	17	4 (0.05-10)	35	0.01-540
Carbon Disulfide	21	1	20 (0.005-130)	5.2 ^c	N/A
Dichloro Methane	21	0	21 (0.005-12,000)	N/A	N/A
Ethyl Benzene	21	16	5 (0.005-1.2)	38	0.032-500
Methyl Ethyl Ketone	21	1	20 (0.01-250)	0.18 ^c	N/A
Toluene	21	19	2 (1.2)	107	0.015-1900
Xylenes	21	20	1 (1.2 ^c)	153	0.013-2600

^a The "Range of Reporting Limits for Non-Detections" qualitatively reflects the bias associated with the reported mean, due to excluding non-detected concentrations.

^b Non-detected concentrations were not used in calculating the mean.

^c Represents one value.

N/A Not Applicable

The RCRA Characteristics data showed: pH ranged from 0.058 to 7.8; reactive sulfide was detected in 6 out of 21 samples; reactive cyanide in 2 out of 21 samples. A flash point <140°F was measured in 7 of the 21 samples; however, the results are thought to be unreliable for produced water or other aqueous fluids or solids.

The volatile organic compounds found in the TCLP leachate of the 20 samples tested were: methyl ethyl ketone (5), carbon disulfide (1), benzene (16), and toluene (18). Metals were detected in the TCLP leachate of 21 samples: barium (20), cadmium (2), chromium (8), lead (5), and mercury (1). The RCRA Characteristics results are found in Appendix C.

Discussion

Sampling was focused on flowback of spent stimulation fluids because they come in contact with crude oil, natural gas condensate, natural gas, saltwater, and minerals comprising the reservoir rock. Workover samples were taken directly from the flowlines or after discharge into a pit or holding vessel. This ensured that the highest expected level of constituents of potential environmental concern would be present.

Samples were collected after one well pipe volume was recovered from the well to ensure the sample collected had been in contact with the oil and gas bearing formation. Workover wastes sampled should be considered representative of actual workover waste from stimulation operations at the stage of flowback for that particular job, except where sampling resulted in capturing free oil such as those samples taken at the wellhead and other valves where oil and water had not had the opportunity to separate prior to sampling. In practice, crude oil returned with the flowback is recovered and sold as product.

PRODUCED SAND

Sand and other formation solids from a petroleum producing formation often build up in the wellbore in both producing and injection wells. In producing wells with high gas and/or fluid production rates, sand is carried to the surface where it builds up in the vessels. In producing wells with low gas and/or fluid flow rates, it may build up in the wellbore to the extent of blocking the inflow of petroleum. It can also cause fouling of the downhole pumps that lift the fluids to the surface facilities. When produced sand becomes a problem, it is removed from the wellbore via a workover operation and removed from surface vessels by washing or by shoveling.

Sampling and Analysis

One produced sand sample was collected from a Louisiana facility during Phase I sampling. The produced sand sample was analyzed for oil, water, and solids content, and for total Appendix IX volatile and Petroleum Refinery List semi-volatile organic compounds and metals. The sample was also tested for RCRA ignitability, corrosivity and reactivity; inorganic chlorides by EPA Method 300.0; TCLP volatile and semi-volatile organic compounds; and TCLP metals.

Results

The sample contained 3 percent oil, 18 percent water, and 79 percent solids. Four total Appendix IX volatile organic compounds were detected: benzene, ethyl benzene, toluene, and xylene (Table 3-9).

Table 3-9. Total Appendix IX Volatile Components Detected in Produced Sand

Compound	Number of Samples Analyzed	Number of Detections	Reporting Limit for Non-Detections (mg/kg)	Detected Concentration (mg/kg)
Acetone	1	0	20	N/A
Benzene	1	1	N/A	20
Carbon Disulfide	1	0	10	N/A
Dichloro Methane	1	0	10	N/A
Ethyl Benzene	1	1	N/A	17
Methyl Ethyl Ketone	1	0	20	N/A
Toluene	1	1	N/A	93
Xylenes	1	1	N/A	130

N/A Not Applicable

No Petroleum Refinery List semi-volatile organic compounds were detected (Table 3-10).

Table 3-10. Petroleum Refinery List Semi-Volatile Organic Compounds Detected in Produced Sand

Compound	Number of Samples Analyzed	Number of Detections	Reporting Limit for Non-Detections (mg/kg)	Detected Concentration (mg/kg)
Chrysene	1	0	28	N/A
1-Methyl Naphthalene	1	0	28	N/A
Naphthalene	1	0	28	N/A
Phenanthrene	1	0	28	N/A

N/A Not Applicable

Ten total Appendix IX metals were detected: aluminum, barium, calcium, chromium, copper, lead, nickel, sodium, vanadium, and zinc (Table 3-11). Chlorides were detected at a level of 13,600 mg/kg.

The RCRA Characteristics data showed a pH of 5 with no reactive sulfide or cyanide detected. The ignitability test resulted in a flash point >160°F; however, it is considered unreliable for this type of material.

Table 3-11. Total Appendix IX Metals Concentrations Detected in Produced Sand

Compound	Number of Samples Analyzed	Number of Detections	Reporting Limit for Non-Detections (mg/kg)	Detected Concentration (mg/kg)
Aluminum	1	1	N/A	977
Antimony	1	0	5	N/A
Arsenic	1	0	1	N/A
Barium	1	1	N/A	140
Beryllium	1	0	2	N/A
Cadmium	1	0	0.5	N/A
Calcium	1	1	N/A	4130
Chromium	1	1	N/A	5
Cobalt	1	0	1	N/A
Copper	1	1	N/A	9
Lead	1	1	N/A	16
Mercury	1	0	0.1	N/A
Nickel	1	1	N/A	4
Potassium	1	0	500	N/A
Selenium	1	0	0.5	N/A
Silver	1	0	1	N/A
Sodium	1	1	N/A	10,100
Thallium	1	0	0.5	N/A
Tin	1	0	5	N/A
Vanadium	1	1	N/A	2
Zinc	1	1	N/A	44

N/A - Not applicable

Two volatile organic compounds were found in the TCLP leachate: benzene and toluene. No semi-volatile organic compounds were detected in the TCLP leachate. Three metals were detected in the TCLP leachate: barium, chromium, and lead. The RCRA Characteristic results are found in Appendix C.

Discussion

The sample was collected from a solids settling tank in service to collect produced sand. The tank was opened for cleaning and the sample was collected as it was shoveled out of the tank. The sample should be representative of the type waste being generated at this facility, but not necessarily indicative of the type material that would be bailed from a wellbore.

USED OIL

Used oil wastes generated at E&P sites include various lubrication oils used in engines, compressors, pumps, and gear boxes of equipment and related machinery. Compressor and

pump lube oils may come in contact with crude oil, natural gas and produced water.

(NOTE: Used oil is not typically considered an associated waste. Because used oil samples were collected along with several true associated waste samples, the results are reported here for convenience.)

Sampling and Analysis

Twelve used oil samples were taken from East Texas (2), West Texas (2), New Mexico (1), Oklahoma (4), Louisiana (1), West Virginia (1), and California (1). Six Phase I and six Phase II samples were taken. Samples were collected directly from the engine crankcase or oil cooling piping at ten different locations. Six samples were taken while the compressor was running.

Two samples were analyzed for oil/water/solids. All twelve samples were analyzed for total Appendix IX volatile organic compounds, while six samples were also analyzed for total Appendix IX metals and Petroleum Refinery List semi-volatile organic compounds. The RCRA ignitability, corrosivity and reactivity and TCLP metals tests were performed on twelve samples. Ten samples were tested for TCLP volatile organic compounds. Of these 10 samples, six were analyzed for 19 organic compounds and six were analyzed for 10 organic compounds. Six samples were evaluated for TCLP semi-volatile organic compounds.

Results

The samples analyzed for oil, water and solids content were 98-100 percent oil, with negligible water or solids. Four total Appendix IX volatile organic compounds were found at measurable levels: benzene, ethyl benzene, toluene, and xylene (Table 3-12). Acetone and dichloromethane were also detected, but the results may be qualitatively unreliable due to the common occurrence of these compounds as laboratory contaminants.

Table 3-12. Total Appendix IX Volatile Components Detected in Used Oil

Compound	Number of Samples Analyzed	Number of Detections	Number of Non-Detections [Range of Reporting Limits for Non-Detections (mg/kg)] ^a	Mean Concentration of Detected Constituents ^b (mg/kg)	Range of Detected Concentrations (mg/kg)
Acetone	12	1	11 (0.5-100)	3 ^c	N/A
Benzene	12	6	6 (0.5)	25	1.4-120
Carbon Disulfide	12	0	12 (0.25-50)	N/A	N/A
Dichloro Methane	12	1	11 (0.25-50)	0.55 ^c	N/A
Ethyl Benzene	12	2	10 (0.25-50)	0.79	0.58-1
Methyl Ethyl Ketone	12	0	12 (0.5-100)	N/A	N/A
Toluene	12	6	6 (0.5)	44	2.1-240
Xylenes	12	6	6 (0.5)	54	1.6-310

^a The "Range of Reporting Limits for Non-Detections" qualitatively reflects the bias associated with the reported mean, due to excluding non-detected concentrations.

^b Non-detected concentrations were not used in calculating the mean.

^c Represents one value.

N/A Not Applicable

Only one Petroleum Refinery List semi-volatile compound was detected: phenanthrene (Table 3-13).

Table 3-13. Petroleum Refinery List Semi-Volatile Organic Compounds Detected in Used Oil

Compounds	Number of Samples Analyzed	Number of Detections	Number of Non-Detections [Range of Reporting Limits for Non-Detections (mg/kg)] ^a	Mean Concentration of Detected Constituents ^b (mg/kg)	Range of Detected Concentrations (mg/kg)
Chrysene	6	0	6 (40-200)	N/A	N/A
1-Methyl Naphthalene	6	0	6 (40-200)	N/A	N/A
Naphthalene	6	0	6 (40-200)	N/A	N/A
Phenanthrene	6	1	5 (40-200)	57 ^c	N/A

^a The "Range of Reporting Limits for Non-Detections" qualitatively reflects the bias associated with the reported mean, due to excluding non-detected concentrations.

^b Non-detected concentrations were not used in calculating the mean.

^c Represents one value.

N/A Not Applicable

Five total Appendix IX metals were detected: barium, calcium, copper, selenium and zinc (Table 3-14).

Table 3-14. Total Appendix IX Metals Detected in Used Oil

Compound	Number of Samples Analyzed	Number of Detections	Number of Non-Detections [Range of Reporting Limits for Non-Detections (mg/kg)] ^a	Mean Concentration of Detected Constituents ^b (mg/kg)	Range of Detected Concentrations (mg/kg)
Aluminum	6	0	6 (0.1-10)	N/A	N/A
Antimony	6	0	6 (5)	N/A	N/A
Arsenic	6	0	6 (0.5-1)	N/A	N/A
Barium	6	2	4 (1)	550	370-730
Beryllium	6	0	6 (0.2)	N/A	N/A
Cadmium	6	0	6 (0.5)	N/A	N/A
Calcium	6	3	3 (20-30)	391	92-578
Chromium	6	0	6 (1-5)	N/A	N/A
Cobalt	6	0	6 (1)	N/A	N/A
Copper	6	5	1 (1 ^c)	4	1-7
Lead	6	0	6 (5)	N/A	N/A
Mercury	6	0	6 (0.1)	N/A	N/A
Nickel	6	0	6 (4)	N/A	N/A
Potassium	6	0	6 (500)	N/A	N/A
Selenium	6	1	5 (0.5)	1.4 ^c	N/A
Silver	6	0	6 (1)	N/A	N/A
Sodium	6	0	6 (500)	N/A	N/A
Thallium	6	0	6 (0.5-1)	N/A	N/A
Tin	6	0	6 (5-21)	N/A	N/A
Vanadium	6	0	6 (1)	N/A	N/A
Zinc	6	5	1 (4 ^c)	136	4-390

^a The "Range of Reporting Limits for Non-Detections" qualitatively reflects the bias associated with the reported mean, due to excluding non-detected concentrations.

^b Non-detected concentrations were not used in calculating the mean.

^c Represents one value.

N/A Not Applicable

The RCRA Characteristics testing showed: pH ranged from 4.2 to 9.3; reactive sulfide detected in three out of twelve samples; reactive cyanide detected in one out of twelve samples. Ignitability testing, if properly performed, is appropriate for used oil analyses. Ignitability results showed one sample with a flash point of 72°F and another at 154°F; eight samples had results >160°F and two were above 200°F.

The volatile organic compounds found in the TCLP leachate were: benzene, detected in 4 out of 10 samples; and toluene, found in 4 out of 8 samples analyzed. No TCLP semi-volatile

organic compounds were detected. Metals were detected in the TCLP leachate of 12 samples as follows: barium, 11 samples; cadmium, 6 samples; chromium, 4 samples; and lead, 5 samples. The RCRA Characteristic results are found in Appendix C.

Discussion

Used oil samples were collected from natural gas and diesel fired internal combustion engines. These engines are the prime movers for compressors and pumps used at E&P sites and generate the bulk of the used oil stream; gearbox lube oil was not sampled. All of the samples were collected directly from the equipment to ensure the highest expected level of constituents of potential environmental concern.

Sample number 007531-0001 had VOCs that were two orders of magnitude above the rest of the samples and had a flash point of 72°F, less than half of the rest of the samples. From these data, it is possible that this sample was a natural gas liquid. The sample was taken from a compressor. The finfan cooler on the skid generally cools interstage gas, engine jacket water and sometimes the engine lube oil. The piping of this system can be complicated and confusing. It is possible that the sample was inadvertently collected from an interstage gas cooling line and that it consisted of condensed natural gas liquids.

DEHYDRATION AND SWEETENING MATERIALS

Water and hydrogen sulfide gas are impurities in natural gas that must be removed before it can be sold to end users. "Dehydration" and "sweetening" are the terms that describe the treatment processes used to remove these impurities.

GLYCOL WASTE

Glycol waste is generated when a glycol natural gas dehydrator is drained or cleaned. A glycol dehydration unit consists of an absorber tower, a reboiler, heat exchangers, filter, pump and piping (see Figure 3-1). Wet natural gas is placed in contact with glycol in an absorber tower to remove water vapor. Wet gas flows into the bottom of the absorber and upwards where it contacts concentrated glycol being pumped into the top and flowing down over trays contained inside. The concentrated glycol absorbs water vapor from the gas. Dry natural gas flows out the top of the tower, then to a meter where dry natural gas is sold. The dilute glycol and water mixture flows to an energy conserving heat exchanger then to a reboiler where the

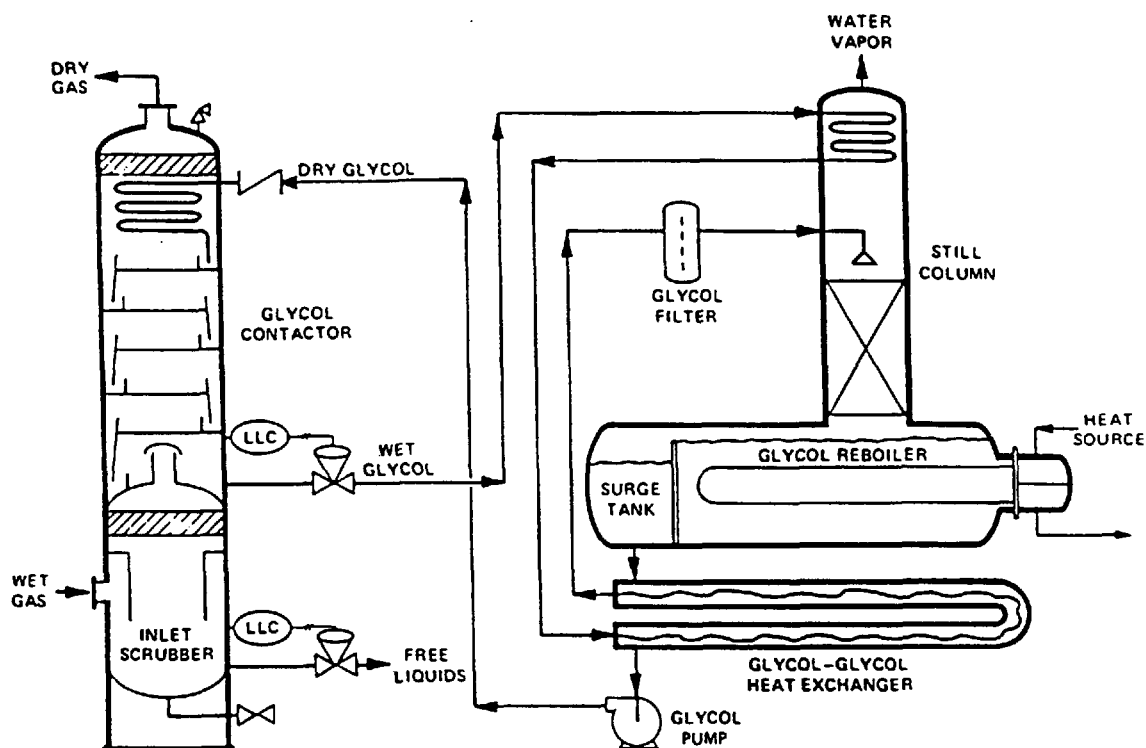


Figure 3-1. Glycol Dehydrator

dilute mixture is heated to 325°F to 350°F. Water is vaporized and passes out of the stack as steam becoming dehydration condensate water. The reconcentrated glycol is recycled (pumped) back to the top of the absorber where the process starts over again. Additional glycol is added to the dehydrator to replace losses due to mechanical carryover, volatilization, and thermal degradation in the reboiler.

Occasionally, glycol in the unit becomes fouled with salt and/or formation solids and cannot be regenerated in the dehydrator unit. If the glycol cannot be regenerated on site, it may be transported to a reclaimer (more sophisticated equipment) or disposed as waste. Waste glycol may contain both hydrocarbon and metal constituents as it comes into contact with produced water, produced hydrocarbon, and formation solids.