Bioremediation of Petroleum and Radiological Contaminated Soil Using an *Ex Situ* Bioreactor

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Bioremediation of Petroleum and Radiological Contaminated Soil Using an *Ex Situ* Bioreactor

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LIST OF ACRONYMS

ACS	American Chemical Society
BTEX	benzene, toluene, ethyl-benzene and Xylene
C/N/P	Carbon/Nitrogen/Phosphorus
CAP	corrective action plan
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CFR	Code of Federal Regulations
DOE	Department of Energy
DOE EM-50	Department of Energy Environmental Management 50
DRO	Diesel range organics
EEC	environmental evaluation checklist
EPA	Environmental Protection Agency
EPD	Environmental Protection Department
GC/MS	gas chromatograph/mass spectrometer
GRO	Gasoline range organics
HEPA	High efficiency particulate arrestor
HPLC	high-pressure liquid chromatograph
HSWA	Hazardous and Solid Waste Amendments
IETU	Institute for Ecology of Industrial Areas
IH	Industrial Hygiene
JCCES	Joint Coordinating Committee for Environmental Systems
LAW	low-activity waste
LDR	Land Disposal Restrictions
LEL	lower explosive limit
NEPA	National Environmental Policy Act
NIH	National Institute of Health
NIST	National Institute of Standards and Technology
NPT	National Pipe Thread
PAH	polycyclic aromatic hydrocarbon
PCB	polychlorinated biphenyls
PCS	Petroleum Contaminated Soil
PRCS	Petroleum and Radiological Contaminated Soil
PTYG	peptone, tryptone, yeast, and glucose
PVC	polyvinyl chloride
R&D	Research and Development
RBA	Radiological Buffer Area
RCRA	Resource Conservation and Recovery Act
RPD	Radiological Protection Department
SCDHEC	South Carolina Department of Heath and Environmental Control
SRNL	Savannah River National Laboratory
SRS	Savannah River Site
SWD	Solid Waste Department

TEP	Triethylphosphate
TPH	total petroleum hydrocarbon
USEPA	United States Environmental Protection Agency
USQ	Unresolved Safety Question
V	Volt

ABBREVIATIONS

ppm	parts per million
spp.	Species
ID	inner diameter
μm	Micrometer
mN	milliNormal
DC	direct current
SCFH	standard cubic feet per hour

SUMMARY

The Savannah River Site (SRS), a Department of Energy facility located in Aiken, South Carolina, generated non-hazardous petroleum and radiological co-contaminated soils that did not have a disposal pathway (SCDHEC, 2001). These co-contaminated soils were being stored in low-activity vaults at the SRS. The Savannah River National Laboratory (SRNL) proposed clean up of the petroleum portion of the soils, *ex situ*, using simple, inexpensive, bioreactor technology to the South Carolina Department of Health and Environmental Control (SCDHEC). SCDHEC regulations allow for burial of petroleum contaminated soils in sanitary landfills with Total Petroleum Hydrocarbon (TPH) concentrations below 100 mg/kg. Treatment of the petroleum portion of the contaminated soils would allow the soils to be disposed as low-level radiological materials. Therefore, the purpose of this project was to generate treatment data and test the hypothesis that an engineered biological process could safely and efficiently remove co-contamination from radiological contaminated soil.

Biostimulation and bioaugmentation were discussed as effective alternatives for clean up of petroleum contaminated soils. Although radiation and radiological contamination may, depending on the type and level, impact microbial activity and growth, the impact of low levels of radiation were not expected to impact the biodegradation of petroleum contaminated soils. Important parameters identified for successful biological treatment included oxygen mass transfer, bioavailability, temperature, microbiological capabilities, nutrients, and moisture. System design was based on a bioventing approach to control the

supply of oxygen (air) based on petroleum contamination levels and type of soil being treated.

Before bioremediation of the co-contaminated soil began, a bioreactor system was permitted, designed, constructed, and tested. An operating permit was obtained from SCDHEC, as were approvals required by the SRS. The design was based on bioventing principles and used a modified prefabricated skid-pan, which was constructed by SRNL. Once the system was fabricated, system inspections and testing were performed followed by operational testing with clean soils. Testing identified some minor modifications to the system. Once the modifications were complete and SRS approvals were obtained, the system was ready for treatment of the co-contaminated soils.

System operation included formulating a test plan, developing and using system sampling and monitoring methods, loading the system, starting up operations, obtaining results, modifying operation, and final disposal of the soil after the bioremediation goal was achieved.

A general testing plan was developed to guide operation and testing of the PRCS bioreactor that covered general operating ranges, system monitoring, microbial amendments, moisture control, and nutrient addition. System monitoring included taking soil and gas samples to monitor the nutrients, moisture, pH, hydrocarbon, volatile organic

compound, oxygen, and carbon dioxide concentrations. Process gauges and flow meters were used to monitor system soil temperature, system pressure, and airflow rates.

The PRCS system was loaded with three and two thirds ton of petroleum and radiological contaminated soil. While loading, the waste soil was amended with weathered compost, ammonium nitrate, fertilizer, and water. In addition, the soil appeared to have petroleum concentrations that were higher than expected (i.e., oil-soaked soils) based on previous characterization. Pre-characterization of soils from the same source indicated the soil was contaminated with a maximum of 10,000 mg/kg TPH. However, initial TPH contamination in the system, with both boxes loaded, was estimated to be 25,000 mg/kg TPH, based on subsequent analyses.

The PRCS bioreactor operated for 22 months in various configurations treating the contaminated soil to a final TPH concentration of 45 mg/kg. During operation, degradation of over 20,000 mg/kg of waste was accounted for through monitoring of carbon dioxide levels in the effluent. System operation worked best when soil temperatures were above 15 ºC and the pumps were operated continuously. The low level radiological contaminated soil was disposed in an engineered trench at SRS that accepts this type of waste. The project demonstrated that co-contaminated soils could be treated biologically to remove petroleum contamination to levels below 100 mg/kg while protecting workers and the environment from radiological contamination.

CHAPTER 1

PETROLEUM AND RADIOLOGICAL CONTAMINATED SOIL BIOREACTOR REQUIREMENTS AND BACKGROUND INFORMATION

Introduction

The Savannah River Site (SRS) a Department of Energy (DOE) facility located in Aiken, South Carolina, has generated non-hazardous petroleum and radiological contaminated soils from spills and process disposal practices (Lombard and Hazen, 1994). The South Carolina Department of Health and Environmental Control (SCDHEC) regulations allow for burial of petroleum contaminated soils in sanitary land fills with total petroleum hydrocarbon concentrations below 100 ppm, but no allowances were made for radiological and petroleum contaminated soil (SCDHEC, 2001). Therefore, these co-contaminated soils did not have an immediate disposal route and were being stored in low-activity vaults at the SRS. The vaults have a finite amount of storage space, and the material would require storage for an indefinite period of time. SRS submitted a corrective action plan (CAP) to SCDHEC proposing clean up of the petroleum portion of the soils, *ex situ,* using simple, inexpensive, bioreactor technology (Kastner et al., 1998). Treatment in a bioreactor would remove the petroleum contamination from the soil without spreading radiological contamination to the environment. Final disposal of the treated soil after treatment of the petroleum contamination would be to bury the material in trenches that accept low-level radiological wastes. SRS has active waste trenches that accept these types of low-level waste operated by the Solid Waste Department (SWD) at SRS (Mamatey, 2003). The SWD is responsible for accelerating disposition of legacy

Cold War era waste including radioactive, hazardous, and industrial wastes and disposition of newly generated waste from on-going site missions. Providing and demonstrating an efficient treatment pathway for this material would benefit SRS in a number of ways. First, this would open up valuable vault space for other non-hazardous low-level waste. Second, operating costs associated with the indefinite storage of the material would be avoided. Finally, future wastes could be treated directly, possibly at the spill site, which would reduce transportation, handling, storage, and monitoring costs for SRS operations. In 1998, SCDHEC granted approval of the CAP for the Savannah River National Laboratory (SRNL) to pursue testing of the treatment technology.

Purpose

The purpose of this project was to test the hypothesis that petroleum and radiological contaminated soils could be treated to meet disposal criteria using microbiological treatment technology. To test this hypothesis, a Petroleum and Radiological Contaminated Soil (PRCS) bioreactor was built, tested, and demonstrated using contaminated soils at the SRS. Successful treatment of the soils would reduce the petroleum contamination to levels acceptable to SCDHEC (<100 mg/kg Total Petroleum Hydrocarbon), which would allow final disposition of the soil by the SWD at the SRS.

Organization

This thesis is organized into three chapters. The first chapter introduces the purpose of this thesis, provides background information on the location of the treatment, describes the regulatory requirements of a successful project, and introduces background information about bioreactor design and operational parameters. Chapter two describes

the design and construction of the bioreactor system and summarizes the work requirements to meet the site, regulatory, and permitting for operational testing with contaminated soil. The third chapter describes the PRCS testing and operation of the unit and final disposal of the soil.

Requirements

Radiological and petroleum contaminated soils are currently being stored at SRS and more may be generated in future remedial and process activities at SRS. Responding to SRS needs, the SRNL worked with SWD and Environmental Protection Department (EPD) personnel to develop an effective treatment strategy for the remediation of this type of co-contaminated soil. This strategy resulted in the approval of a CAP by SCDHEC. Once the strategy was in place, SRNL and EPD personnel reached an agreement with SWD personnel to coordinate testing of the technology. Funding was provided by the U.S. Department of Energy/EM-50 (DOE EM-50) Office of Science and Technology. With this funding, the SRNL supported the Institute for Ecology of Industrial Areas (IETU), in Katowice, Poland on pilot designs on the PRCS (Altman et al., 1997). SRNL was able to use experiences and operational data from the IETU projects to help develop and operate the SRS bioreactor. Treatment design and construction requirements were based on the strategy proposed in the CAP and included using a bioventing process in an *ex situ* system. The bioreactor design addressed site specific requirements that included issues for transportation of low-level radioactivity materials, worker health, and environmental concerns. SWD requirements included preparing a test plan and a quality assurance plan, performing various risk assessments,

and performing pre-operational testing of the system with clean soils. SWD and SRNL required a rationale for system testing and soil disposal criteria verification.

In order to successfully demonstrate the bioreactor technology, it was necessary to design the PRCS bioreactor to treat soils in remote locations with minimal required infrastructure. The PRCS design included radiological protection for operational personnel and the environment. Flexibility was built-in for required soil and gas monitoring and sampling. A cost effective design was chosen that was substantial enough for loading and unloading activities of 4 cubic yards of material. Finally, the design allowed air circulation and liquid addition to the unit for optimal biological activity and biodegradation performance.

Site Description

The SRS is a Department of Energy (DOE) industrial complex responsible for stewardship of the environment, the enduring nuclear weapons stockpile and nuclear materials, the SRS stores and processes nuclear materials in support of national defense and U.S. nuclear non-proliferation efforts. The site also develops and deploys technologies to improve the environment and treat nuclear and hazardous wastes remaining from the Cold War. The SRS complex covers 198,344 acres, or 310 square miles, encompassing parts of Aiken, Barnwell and Allendale counties in South Carolina, bordering the Savannah River.

SWD and Existing Soils Description

The SWD of SRS manages the storage and disposal of all waste at SRS. At the onset of this project, SWD was storing twelve radiological containers, known as B-12 boxes, filled with radiological and petroleum contaminated soils. Figure 1 illustrates B-12 boxes containing contaminated soils that were tested in this demonstration. The contaminated soils were generated near a tree kill area in the F and H separations areas at SRS. The soils were potentially contaminated with spilled diesel oil, hydraulic fluids, lubricating oils, and alpha or beta/gamma radiological material. The B-12 boxes were stored in the low-level waste vault facility for four years prior to treatment. Four soil samples were taken from the B-12 box in 1998 for analyses and one soil sample was taken from a B-12 prior to bioremediation efforts using the PRCS. Table 1 lists the total petroleum hydrocarbon (TPH) characterization data from these soils.

Figure 1. Petroleum and Radiological Contaminated Soils at SRS

Since the B-12 boxes were taking up valuable storage space and demonstration of the technology would provide a treatment path for these types of materials, the SWD agreed to house the testing of the bioreactor technology in its low-level waste facility. The SWD agreed to provide infrastructure to support transportation, operation, monitoring, and disposition of the test soils. Once the bioreactor technology was demonstrated successfully, SWD would be able to use this technology to treat the remaining, and any future, petroleum and radiological co-contaminated soils.

Table 1. Total Petroleum Hydrocarbon (TPH) Pre-characterization of Radiological and Petroleum Contaminated Soils at SRS

Sample ID	TPH (mg/kg)
B-12-1-98[1]	416
B-12-2-98[1]	581
B-12-3-98[1]	201
B-12-4-98[1]	3,410
B-12-1-2002[2]	9,068

[1] Analyzed by EPA 8015A. [2] Analyzed by EPA 1664.

Funding

Initial funding for this project was received through DOE EM-50 Office of Science and Technology. With this funding, the SRNL supported the IETU, in Katowice, Poland, by providing technical support to IETU and serving as the IETU's customer. All parties cooperated under DOE EM-50 Joint Coordinating Committee for Environmental Systems (JCCES, http://iicer.fsu.edu/ourwork_jcces.cfm). Through this funding, SRNL has provided reactor designs to IETU for small-scale petroleum and chlorinated solvent

bioreactor construction and supported the characterization and clean up of the Czechowice-Dziedzice oil refinery in Poland (Institute for Ecology of Industrial Areas, 1999). A Petroleum Contaminated Soil (PCS) bioreactor was constructed and operated in 2000, in Poland (Kuperberg et al., 2001). Issues pertaining to operational data and system construction were evaluated and led to modifications incorporated into the design of the PRSC at SRS. Some of these issues included: nutrient addition, spot welding during fabrication, leachate recirculation system design, system operating platform, monitoring equipment, drain valve placement, materials of construction, and the operation of process gauges. Petroleum and polycyclic aromatic hydrocarbon (PAH) degrading bacterial isolates from the Polish refinery were also obtained for characterization by SRNL, and were subsequently used in this SRS project.

Disposal Criteria

Disposal criteria were prescribed by SCDHEC and administered by the SRS EPD. SCDHEC regulations require that the soil must be cleaned up to less than 100 mg/kg total TPH before disposal in a landfill. TPH should be measured using Benzene, Toluene, Ethyl-Benzene, and Xylene (BTEX) - analytical method 8260B, PAHs - analytical method 8270C or 8100 or 8310 for (Benzo(a)anthracene, Benzo(b)fluoranthene, Benzo(k)fluoranthene, Chrysene and Dibenz(a,h)anthracene), diesel range organics (DRO), and gasoline range organics (GRO). Analyses were performed at a SCDHEC-registered lab, as required. SCDHEC was contacted when treatment of PRCS began and prior to any soil disposal in low-activity trenches.

Pre-Operational Test Summary

Once the bioreactor design and construction were completed pre-operational testing was performed. This testing documented the operation, safety, and loading of the system. Operational testing was completed before adding soil to the system and safety reviews examined potential radiological, chemical, fire, and physical hazards. Although the PRCS was not operated with soil during this phase, the system loading and unloading protocols were established. The working PRCS ranges and conditions were documented in the form of operating procedures. The airflow system and liquid addition system were operated and tested. This testing demonstrated that the major systems on the bioreactor could be operated as designed safely and efficiently. After adding High Efficiency Particulate Arrestor (HEPA) filters to the system and modifying the operating pressure of the system, the SRS Radiological Protection Department (RPD) was satisfied the system operated in a manner that was safer for personnel and did not pose a risk for a radiological release to the environment. It was also shown that operation of the system did not pose a threat for the release of chemicals. Engineering calculations and operating data were used to further demonstrate through gaseous or liquid emissions that system operation did not pose a fire hazard. Testing also proved that the system would not pose a physical hazard and little or no biological risk to employees. This pre-operational testing demonstrated that the system could operate under its design parameters and should be able to safely treat radiological and petroleum contaminated soils.

System Operational Summary

System testing included operation with non-contaminated and contaminated petroleum and radiological soils. Non-contaminated soil testing was performed to ensure all systems

were operating, all safeguards were working, loading and unloading the reactor with the specified quantity of soil was feasible, and all gauges were operational. This testing provided evidence to SWD Operations that loading the unit with contaminated soil was safe. Contaminated soil testing generated operational guidelines and developed monitoring techniques for petroleum degradation. The testing protocol allowed sampling of the contaminated material, soil, and gas to document progress and monitor key operational parameters. Biodegradation rates were quantified to determine treatment times for this and other contaminated soils. The key operational parameters included moisture content, air flow rates, carbon content, nutrient levels (nitrogen, phosphorus, and potassium), temperature, and operating pressure/vacuum. The impact of these parameters on the operation of the PRCS was evaluated.

Background on Biotreatment of Petroleum Contaminated Soils

General Bioremediation

Biostimulation or bioaugmentation are effective alternatives to traditional physicochemical techniques for clean up or bioremediation of petroleum contaminated soils (Dua et al., 2002). Current physiochemical techniques being employed for disposal or decontamination of hydrocarbon contaminated soils include landfill disposal, incineration, vapor extraction, detergent washing, and chemical oxidation (Riser-Roberts, 1998) Biodegradation of petroleum hydrocarbons by stimulation of indigenous soil microorganisms, also known as biostimulation, is a proven remediation technology. Biostimulation involves the addition of electron acceptors, electron donors or nutrients to increase the numbers or stimulate the activity of indigenous microorganisms (Widada et al., 2002). Bioaugmentation involves the addition of (indigenous or non-indigenous)

laboratory-grown microorganisms capable of biodegrading the target contaminant (Widada et al., 2002; Vogel, 1996) or serving as donors of catabolic genes (Top et al., 2002). Bioremediation of hydrocarbon contaminated soils, which uses the ability of microorganisms to degrade and/or detoxify organic compounds, has been established as an efficient, economic, versatile, and environmentally sound treatment, and on-site, off-site, and *in situ* systems may be used.

The bioavailability of contaminants is an important factor in bioremediation. The bioavailability of a chemical may be described by its mass transfer rate relative to its uptake and degradation rates by microorganisms (Bosma et al., 1997*)*. The efficiency of hydrocarbon degradation will also depend on the characteristics of contaminated material, environmental conditions, and abilities of the microbial population (Van Hamme et al., 2003). If the capacity for hydrocarbon degradation is present and environmental conditions are amenable, the microorganisms must have access to the contaminants for degradation (Villemur et al., 2000). Reduced bioavailability could be caused by low aqueous solubility and a strong sorption to soils or sediments (Harms and Borsma, 1997) and it has been shown that the water-dissolved fraction of chemicals is more available to microorganisms (Thomas et al., 1986). The use of surfactants has been shown to increase biodegradation of hydrocarbon contaminants (Bruheim et al., 1997). The general sequence of biodegradation of petroleum components in decreasing order can be represented as follows (Huesemann, 1995): *n*-alkanes , branched-chain alkanes, branched alkenes, low-molecular-weight *n*-alkyl aromatics, monoaromatics, cyclic

alkanes, polynuclear aromatics, and asphaltenes. It is important to understand bioavailability especially when treating complex hydrocarbons contaminants.

Decontamination by petroleum land farming has been used in the oil industry for decades to degrade large quantities of oil sludges (Atlas, 1984; King et al., 1997 and Norris et al., 1994). Refineries have practiced this technology since 1954 as a disposal method for their oily sludges (API, 1983). Due to concerns with uncontrolled disposal in the 1970s, landfarming gained popularity, and it became the most common method used by major oil companies in the United States to dispose of their generated oily sludge (Dibble and Bartha, 1979). In 1984, the United States Environmental Protection Agency (USEPA) issued a Land Disposal Restriction (LDR) as part of the Hazardous and Solid Waste Amendments (HSWA) to the Resource Conservation and Recovery Act (RCRA). Today, modifications to the old landfarming techniques have been made to meet the LDR requirements in terms of concentrations, treatment technologies, environmental protection, and hazardous chemical removal.

If adequate amounts of moisture, oxygen, and nutrients are available, and contaminants are bioavailable, complete degradation of petroleum hydrocarbons can occur. Biological treatments are less expensive than alternatives such as incineration, storage, or soil washing (Cookson, 1995). Clean-up technologies such as incineration and burial of sludge in secure landfills are expensive. Land treatment disposal of oil refinery sludge generally gives good results (Bartha, 1986). Controlled land treatment, i.e., land farming, is cheaper and also environmentally safe (Bonnier et al., 1980). Current bioremediation

technologies are well-established techniques that can be used for the cleanup of chemically contaminated soils (Boopathy, 2000; Jorgensen et al., 2000). Advantages to using bioremediation technology include simplicity, positive public perception, the flexibility of being coupled with other physical or chemical treatment methods, cost-effectiveness, and complete destruction of the pollutants. Bioremediation can be carried out both *in situ* (without removing the soil) as well as *ex situ* (by excavating the contaminated soil). Contaminated groundwater, sediment, and soil can be treated if necessary. In both the cases, pollutant degradation is carried out in a bioreactor (the ground itself for *in situ* treatment), where operating parameters are optimized to reduce costs and increase efficiency (Hyman and Bagaasen, 1993; Riser-Roberts, 1998).

Radiological Impact on Microorganisms

The impact of radiation fields on microbial activity and survival has been studied but the impact of low level waste microbial survival and activity has not. Although treatment of radiological and petroleum contaminated soils has not been reported in the literature, microbial survival in radiation fields has been reported. *Bacillus* spores and *Kineococcus radiotolerans* have withstood radiation fields up to 350,000 rad (3.5 kGy), and a ten percent survival of *Escherichia coli* was reported after a dose of 50,000 rad (500 Gy) (Phillips et al., 2002). *Deinococcus radiodurans* (Anderson et al., 1956) has survived a chronic dose of 2.0 Mrad (20kGy) and acute dose of 1 Mrad (10kGy). The lethal dose, or dose that would be expected to cause immediate incapacitation and death of a human within one week, is 5,000 rem (50 Gy) (Charpak and Garwin, 2002) Background radiation in the US averages 360 mrem (0.0036 Gy) with levels approaching 2 rem in areas with high radon levels (National Council on Radiation Protection and

Measurement, 1987). In general, bacteria are much more resistant to radiation fields than humans. Although strict dose rate levels are not used to define low-level radioactive waste, the petroleum contaminated soils stored in the low-level vaults at the SRS do not generate dose rates greater than 100 mrem per year. Smith et al. (2003) used risk-based modeling to assess the disposal of radioactive petroleum waste in nonhazardous landfills and found that disposal of technologically-enhanced, naturally-occurring, radiological materials presented a negligible risk to most potential receptors evaluated in their study. Since low-level waste storage is characterized based on risks to humans any impact on microorganisms should be minimal.

Soil Treatment and Bioventing

Bioventing refers to enhancing bioremediation through the addition of oxygen (DuPont, 1993). Enhanced bioremediation using bioventing to treat petroleum contaminated soils requires an understanding of the basic principles of system design and microbial processes. When possible, contaminated soil is usually more efficiently treated if the biological treatment can be done *ex situ* (Alexander, 1999), since the addition of necessary nutrients (i.e. nitrogen and phosphorus), bulking agents, bacteria, and oxygen can be applied more easily than *in situ*. The process utilizes the ability of indigenous soil microorganisms to completely metabolize petroleum hydrocarbons as a carbon and energy source to generate new biomass and produce carbon dioxide. Biostimulation, or the addition of nutrients, can be applied both above ground, in prepared beds or reactors, and below ground (i.e., *in situ*) via bioventing. Bioventing is a method of increasing the amount of available oxygen by air injection or vacuum extraction and is appropriate for relatively porous soil (USEPA, 1995). However, contrary to soil vapor vacuum

extraction, flow rates are relatively low to prevent stripping, but high enough to enhance microbial metabolism (Hinchee et al., 1991). Bioventing has been used to remediate gasoline, diesel, and PAH contaminated soils (Miller and Poindexter, 1994). In any treatment situation it is imperative to identify the potential rate limiting steps, such as low oxygen concentration, low soil temperature, low microbial numbers, low moisture content, bioavailability, or nutrient limitation and design the system to reduce these limitations.

Oxygen

Oxygen mass transfer is one of the rate limiting steps in the degradation of petroleum hydrocarbons. Aerobic conditions and appropriate microorganisms are necessary for an optimal rate of bioremediation of soils contaminated with petroleum hydrocarbons (USEPA, 1995). In soils, the oxygen content depends on microbial activity, soil texture, water content, and depth. Low oxygen content/availability in soils has been shown to limit bioremediation of soils contaminated with petroleum hydrocarbons (von Wedel et al., 1988). In a laboratory batch microcosm experiments using soils acclimated to gasoline vapors for 1.5 months, mineralization of hydrocarbons from soil was severely limited when the oxygen content was below 10% (Freijer, 1986).

Temperature

Temperature is an important parameter for most bioremediation sites because of its impact on the availability of contaminants and the activity of the microorganisms. Although especially true in northern latitudes, seasonal variation in medium latitudes can also impact bioremediation sites (Ward and Brock 1975, Pierce et al. 1976, and Bartha

1986). For optimal contaminant removal, biological treatment of organic pollutants such as petroleum based hydrocarbons, are performed at moderate temperatures (20° to 37°C) in order to increase metabolic activity, diffusion, and mass transfer. Higher degradation rates are usually obtained at moderate compared to lower temperatures (Leahy and Colwell, 1990; Zhou and Crawford 1995). Long chained alkanes (>C10) are generally more insoluble or exist as solids at lower temperatures, which affects the bioavailability of the contaminants (Whyte et al., 1999). Field site groundwater and soil temperatures also play a significant role in controlling the nature and extent of microbiological activity. Mesophilic bacteria have an optimum temperature of 37°C. Psychrophiles have an optimum growth temperature of 15°C and do not grow above 20°C, whereas psychrophiles (or psychrotolerant organisms) have optimum and maximum growth temperatures above 15 and 20°C, respectively (Morita, 1975). Adaptation of psychrotrophs or pychrophiles to lower temperatures takes time and the overall activities of these organisms are less than mesophilic organisms. Erickson et al (2003) showed a decrease in degradation of polyaromatic hydrocarbons under aerobic and anaerobic conditions at 7° and 20° C using arctic soils. Temperature changes and control are important variables associated with bioremediation of petroleum contaminated soils and can be controlled with engineering controls.

Nutrients

Microbial processes require chemicals for cellular process and cellular growth and reproduction. For aerobic bacteria, oxygen acts as an electron acceptor and is required to for cellular processes to occur (Brock et al., 1994). However, if oxygen is available, the addition of other nutrients has been shown to increase biodegradation rates. In general,

air (oxygen) is the only nutrient injected during a bioventing process (USEPA, 1995). It has been reported that additional nutrients are not required in most field bioventing sites (Miller and Poindexter, 1994). However, in many cases biodegradation can be limited or stalled by nutrient availability, once oxygen limitations have been overcome, so nutrient feed systems may have to be combined with the bioventing process (Breedveld et al., 1995; Brockman et al., 1995). Many different nutrients have been used successfully to enhance bioremediation at other sites (Riser-Roberts, 1998). Nitrogen has been successfully introduced into the terrestrial subsurface for biostimulation using ammonia, nitrate, urea, and nitrous oxide (USEPA, 1989). Researchers have shown that wheat straw mineralization may be retarded at by low nitrogen concentrations, and that effects of nitrogen availability should be taken into account when modeling carbon and nitrogen turnover in soils (Henriksen and Breland, 1999). Phosphorus is naturally quite low in most environments and when found it is often tied up in minerals, e.g. apatite, and is biologically unavailable. Several inorganic and organic forms of phosphate have been successfully used to biostimulate contaminated environments (USEPA, 1989). The SRNL demonstrated that tri-ethylphosphate (TEP) can be added in a gaseous form to stimulate bioremediation (Looney et al., 1996; Looney et al., 1998; and Lawrence et al., 1994). Thus, nutrients can be added as gases using injection wells (i.e., nitrous oxide, ammonia, and TEP) or in liquid form via infiltration galleries or sprinkler systems. Liquid nutrients such as ammonium nitrate have been added to contaminated soil via surface irrigation in biosparging processes (Lord et al., 1995) and are transported to the contaminated zone by percolation. In general, the addition of inorganic fertilizers in the ratio of 600 to 9:1 carbon to nitrogen, potassium, and phosphorus has been reported to decrease the

remediation time of petroleum contaminated soils (Riser-Roberts, 1998). The content of microbial cells is generally accepted to be 100 parts carbon to 42 parts nitrogen to 6 parts phosphorus (Nester et al., 1983). Complex organic sources of nutrients, e.g. compost, have also been shown to increase microbial activity (Shimp and Pfaender, 1985) and diversity (Zhou et al., 2002).

Moisture

Moisture level considerations are also important for microbial enzymatic activity and proper operation of bioventing processes. Experience with bioremediation sites has shown that the optimum moisture level for enzymatic reactions is soil saturation or field capacity (Dick and Tabatabai, 1999). In general, enzymatic reaction rates increase with increased moisture, although enzymatic reactions have been shown to decrease when specific metal ions were mobilized with increased soil moisture (Acosta-Martinez and Tabatabai, 2001). However, in a bioventing system, the presence of saturated soils would limit airflow, permeability, or conductivity, through the soil bed and would impact oxygen distribution. Operation of the system with unsaturated soil would improve bioreactor efficiency. The optimal level of moisture depends on many factors and is considered to be soil and contamination specific. Alexander (1977) reported that the optimal soil moisture for microbial activity in bioventing systems is considered to be between 50% and 75% of the soil moisture holding capacity. Huddleston et al., (1986) indicated that a wide range of soil water holding capacity (25-85%) had little effect on biodegradation in soil. In any case, too little water will reduce enzymatic activity and reduce the region where solubilization and biodegradation can occur. Biosurfactant

production is related to soil moisture. Atlas (1981) found biosurfactants hydrocarbon degrading bacteria at the soil/water interface.

Amending/Amendments

Modifying soil contents and structure through mechanical means or through additions can significantly influence bioremediation activities. Tillage is a mechanical manipulation of soil to improve soil conditions (Hillel, 1980). It alters physical and chemical properties of soil in such a way that it stimulates nutrient availability (Melope et al., 1987). Tillage redistributes carbon, nitrogen, and water and reduces spatial distribution within the soil (Rhykerd et al., 1999). Bulking agents are materials of low density that lower soil bulk density, increase porosity and oxygen diffusion, and can help to form water-stable aggregates. These activities increase aeration and microbial activity (Hillel, 1980). Solid phase bioreactors showed an important improvement in performance using sand as soil additive by improving soil porosity (Nano et al., 2003). Aguilera-Vázquez and coworkers (2001) showed that moisture and the porosity of the bulk medium, sugar-cane were directly related to increased biodegradation of hydrocarbons in soil contaminated with oil sludge. Research performed on the bioremediation of oil sludge-contaminated soil in the presence of a bacterial consortium, inorganic nutrients, compost and a bulking agent (wheat bran) showed that bulked soil degraded ten percent more hydrocarbons as compared to test soils amended with inorganic nutrients (Vasudevan and Rajaram, 2001). Compost, peat, wood, and sphagnum moss have been used as both structural support and nutrient source for microorganisms in biofiltration systems (Saberiyan et al., 1994). In general, amendments or amending activities can be used to physically modify soils,

change water activity, impact nutrient transport, contaminants, and provide a complex nutrient source for the microbes.

Bacteria

Indigenous microbes, those growing naturally in site soil, sediment, or groundwater, and non-indigenous microbes, those added from an external source, have been used in bioremediation of petroleum hydrocarbons. It is generally believed that indigenous microorganisms can be used to degrade and clean up soil contaminated with gasoline and diesel fuel hydrocarbons (mainly aliphatics) as long as there are no major limitations of bioavailability, oxygen, and temperature (Alexander, 1999; Atlas, 1981; and Leahy and Colwell, 1990). However, refining of petrochemicals results in the generation of oil sludge consisting of hydrophobic substances and substances resistant to biodegradation (El-Nawawy et al., 1992). The addition of surfactant producing non-indigenous microbes or synthetic surfactants has been used in soil treatment to help treat these recalcitrant substances (Zhang and Miller 1992; and Roane et al., 2001). Moreover, the production and presence of biosurfactants has been shown to have many of the benefits of synthetic surfactants as well as being biodegradable and nontoxic (Makkar and Rockne, 2003). Although non-indigenous organisms must be able to survive in their new environment by actively competing for nutrients and retaining their ability to produce or degrade compounds of interest, bioaugmentation has been shown to work in field conditions for a variety of compounds (Barbeau et al., 1997; Newby et al., 2000; and Zhang et al., 2000). Ward and coworkers (2003) used a defined mixed culture to increase degradation rates of refinery sludges and as a de-emulsifier. The application of indigenous and non-indigenous microorganisms for the degradation of petroleum hydrocarbons has been

demonstrated and the use of biosurfactants producing microorganisms to degrade more hydrophobic compounds may be warranted.

Summary of Background Information

Biostimulation and bioaugmentation are effective alternatives to physical and chemical approaches for clean up of petroleum contaminated soils. Microbiological methods have been used for decades to remediate large petroleum contaminated sites. Although radiation and radiological contamination may impact microbial activity and growth, depending on the type and level, the impact of low levels of radiation are not expected to significantly impact biodegradation of petroleum contaminated soils. Identifying the important parameters in treating petroleum contaminated soil is essential for successful treatment. Oxygen mass transfer is usually the initial rate-limiting step in the biodegradation of petroleum hydrocarbon. Bioavailability of contaminants to microbial activity is also critical for treatment. Bioventing can be used to control the supply of oxygen (air) based on petroleum contamination levels and type of soil being treated. Control and monitoring of nutrient and moisture levels is also important for optimal activity during treatment. The use of bulking agents and complex organic carbons sources have been found to enhance biodegradation and the addition of surfactant producing microorganisms may help degrade hydrophobic or other recalcitrant chemicals by increasing bioavailability. Both, indigenous (soil) and non-indigenous microorganisms have been used successfully to degrade petroleum hydrocarbons. The act of modifying soil structure through mechanical means or through material additions can play a role in bioremediation activities. Temperature is an important parameter for most bioremediation

sites because of its impact on the availability of contaminants and the activity of the microorganisms.

The treatment of petroleum and radiological contaminated soil at SRS was performed using an *ex situ* reactor using the bioventing process. A bioreactor was system designed for bioventing that allowed control of the supply of oxygen (air) based on petroleum contamination levels and type of soil being treated. Nutrient, moisture levels, and temperature were monitored and controlled during treatment. The selection of bulking agents and complex organic carbons sources were designed to enhance biodegradation. Addition of surfactant producing microorganisms will enhance breakdown of hydrophobic or other recalcitrant chemicals including weathered soils present at SRS. PRCS treatment of soils used bulking agents and surfactant producing organisms to improve biodegradation. Due to limitations associated with low-level waste handling, soil modification using mechanical means was difficult at SRS. However, some modifications of the soils were accomplished, included hand mixing using a hoe, addition of compost and nutrients, and adding water for moisture control.

CHAPTER 2

PRCS BIOREACTOR SYSTEM APPROVALS, DESIGN, CONSTRUCTION AND TESTING

Introduction

In order to perform bioremediation of petroleum and radiological contaminated soils a bioreactor system was permitted, designed, constructed, and tested during this investigation. An operating permit was obtained from SCDHEC based on a submitted CAP that outlined the strategy for treating petroleum and radiological contaminated soils (Kastner et al., 1998). Additional approvals required by the SRS were also obtained. The design was based on bioventing principles and used a modified prefabricated skid-pan. The system was then constructed by SRNL using commercially available materials. System inspections and testing included leak tests, smoke tests, loading and unloading, and operation with clean soils. Based on the system inspection and testing results, modifications were made to the system prior to operating the system using contaminated soils.

PRCS System Approvals

Prior to testing and operating the PRCS bioreactor on co-contaminated soils, regulatory approvals from the SCDHEC and SRS were required. The SCDHEC agency reviewed and accepted a corrective action plan for the biological treatment of petroleum and radiological contaminated soil at the SRS. An acceptance letter, see Appendix A, was received specifying a treatment site identification number (ID #01241) for the

biotreatment of non-hazardous petroleum and radiological contaminated soil. SRS approvals were obtained for an environmental evaluation checklist (EEC) and specific SWD department requirements. The SWD approvals included two risk assessments and an Unresolved Safety Question analysis of the PRCS system.

An EEC was required to be submitted, evaluated, and approved prior to construction for the PRSC system. All proposed site actions and projects with the potential to result in a change in emissions, generation rates, or new discharge of hazardous, mixed, radioactive, asbestos, PCB, sanitary/industrial (solid or liquid waste, petroleum substance, wastewater, or any other pollutants from a facility or process are required to have and approved EEC. The EEC is a National Environmental Policy Act (NEPA) evaluation document that demonstrates compliance with Code of Federal Regulations (CFR) 1021.410. The PCRS system was granted a categorical exclusion from the requirements of the above regulations. This exclusion was based on the PRCS biotreatment system meeting the following requirements: 1) The project did not threaten a violation of applicable statutory, regulatory, or permit requirements for environment, safety, and health, including DOE and/or Executive Orders; 2) There was no required siting, construction, or major expansion of waste storage, disposal, recovery, or treatment facilities; 3) The operation of the PRCS would not disturb hazardous substances, pollutants, contaminants, or CERCLA-excluded petroleum and natural gas products that pre-exist in the environment such that there would be uncontrolled or un-permitted releases; and 4) The project would not adversely affect environmentally sensitive

resources (including, but not limited to, those listed in 10 CFR 1021.410 paragraph B. (4)). A copy of the EEC is located in Appendix B.

Two risk assessments were completed to meet SWD department requirements prior to PRCS operations with contaminated soil. The first risk assessment evaluated risks associated with operating the bioreactor in Cell 10 of the Low-Activity Waste (LAW) vault, and the second evaluated the risks associated with loading and unloading the PRCS. The first risk assessment, operation of the bioreactor in the low-activity waste vault, was rated as a category two probability with slightly harmful consequences and a category D risk. A category two probability indicates the activity has a moderate chance of impacting safety, health or operational equipment and infrastructure. A slightly harmful consequence is the lowest consequence rating as is the category D risk rating. The rating specified that approval from the SRS-SWD shift manager before system operation began. A number of probability controls were identified from the first risk assessment. These controls included: 1) performing a functional checkout and writing an operating procedure for the system; 2) coordinating all bioreactor operations with ongoing operations in Cell 10; and 3) operating the system so the vacuum pump operated prior to starting the air pump in order to purge any radiological contaminated gasses through the HEPA filters.

The second assessment evaluated the risks associated with loading and unloading the PRCS bioreactor with soil. This assessment resulted in a slightly harmful consequence and a category one probability. A category one probability is the lowest probability rating and the slightly harmful is the lowest consequence rating. Some probability controls

identified in this assessment included: 1) holding pre-job briefings; 2) ensuring all workers have current heat stress training; 3) using a spotter when moving or loading the PRCS; 4) performing an engineering evaluation of the rigging used when loading and unloading the PRCS; 5) using water when loading and unloading the system to wet the soil and reduce dust; and 6) using Herculite® to prevent contamination of the environment during loading and unloading of the system. The category D risk rating required approval from the shift manager before any work or activity was initiated associated with loading or unloading the PRCS bioreactor.

Unreviewed Safety Question (USQ) analyses are required at SRS for any proposed activity to preserve the safety basis for each DOE nuclear facility, while allowing for operational flexibility. The USQ process uses two steps to determine if a proposed activity involves a USQ. First, a job screening step is used to identify activities that require a USQ evaluation and then a formal USQ evaluation is performed. Both steps were completed prior to operation of the PRCS system. Action items identified in the USQ process included writing a conduct of Research and Development (R&D) task technical plan, performing a lower explosive limit calculation on potential methane production from the system, and writing a Bioreactor Functional Test Check procedure for the system.

A conduct of R&D task technical plan was required by SRS procedures since data used from this investigation could be used in a technical baseline and/or submitted to SCDHEC or other outside agencies. The task technical plan was prepared by the

researcher to document that SRNL personnel and the operation of the PRCS system met SRS safety requirements, worked within established guidelines for personnel exposure and environmental releases, produced high quality results, worked economically and efficiently, communicated effectively, and met the needs of customers and programs. Approval of the task technical plan was obtained from SRNL and SWD management at the SRS.

To meet the requirements of the USQ, a flammability calculation was completed to meet the requirement of the SWD. The purpose of the calculation was to determine if theoretical methane generation in the PRCS Bioreactor could exceed the Lower Explosive Limit (LEL) for methane (5.54%) in the Burial Ground Expansion LAW vault cell 10 assuming the bioreactor stopped operating and anaerobic production of methane occurred. The flammability calculation determined that theoretical methane generation from a uniform mixture of characterized soil would not exceed the LEL for methane when treated in 98 ft^3 quantities in the PRCS system. This calculation was conservative in that it did not account for source reduction by aerobic biodegradation, microbial mass formation, and dispersion in the atmosphere. The theoretical methane concentration calculated was 4.8%. The calculation was approved by SWD engineering.

To complete the requirements of the USQ, a functional test plan procedure was written by SRNL and approved by a low-level waste cognizant engineer, operations specialist, test engineer, and the low-level waste operations manager in SWD. The purpose of the test procedure was to specify and verify functional operation of the PRCS system. System

verification included loading the system with uncontaminated soil, operating all of the pumps, ensuring all gauges and flow meters worked, leak testing, and demonstrating the system could be operated continuously and safely without operator intervention.

Facility and Bioreactor Design

Description of Work

For this project a packed bed reactor was designed for continuous air flow, constructed, tested, and used to remediate petroleum contaminated soil. The design strategy was to collect petroleum contaminated soil, mix it with fertilizer and bulking agents and then load it into a bioreactor of the in-vessel type, skid-pan. Air would then be injected through the soil to stimulate microbial hydrocarbon degradation and liquid would be added, as necessary, to control moisture and nutrient levels. Radiological contamination was kept from the environment and workers using engineering controls. A batch reactor design equation was used to estimate oxygen requirements and hydrocarbon degradation rates. Using this approach, kinetics obtained from the scientific literature and SRNL testing were used to determine oxygen requirements based on different reactor sizes and soil types. The oxygen requirements were then used to determine necessary air flow rates, pump sizes, potential pressure drops, calculate emissions, and estimate treatment times.

Design of the PRCS was based on modifying an existing skid-pan of the appropriate size to create an in-vessel bioreactor system. To support bioreactor operation a pump housing unit was also fabricated. Modification of an existing skid-pan provided the following advantages: skid-pans were readily available and relatively low cost, approximately $1,200 US (2001) for a 6 yd^3 pan; skid-pans have built in components that facilitate

waste handling and movement, as there are lifting lugs attached to the units that work with existing waste handling equipment; and the structural design of skid-pans were adequate to account for the loads that would be involved with the treatment of contaminated soils. The advantages of the in-vessel design included: 1) shortening of the biodegradation process because the internal environment could be controlled and was more uniform; 2) protection from inadvertent mobilization of contaminants from the soil being treated; 3) easier control of the process; and 4) protection of the environment and workers from the release of radiological contamination.

Operational capabilities incorporated into the bioreactor design included the ability to add nutrients, control the moisture content, control oxygen addition, access the system for sampling, and protect the environment from radiological contamination. A liquid feed system was included so that moisture and/or nutrients could be added to the system as necessary using a low-flow liquid pump and industrial sprayers. This provided a method to control moisture and nutrient conditions in the PRCS, which is important for optimizing the rate of microbial waste degradation. To facilitate access to the system a large hinged sampling port was constructed on the lid of the unit. The access port was used to sample the soil to determine TPH levels and moisture content of the soil. Air addition into the system was controlled with pump sizing and control valves. Air flow was designed to flow upwards through the soil matrix. To protect workers and the environment from potential radiological contamination the skid-pan was equipped with a sealable lid with a nuclear-grade HEPA filter system.

The pump housing was enclosed to protect equipment from the environment and included support structures for attachment of process lines and gauges. The pump unit was constructed of aluminum and enclosed on three sides to protect the machinery from the weather. The housing unit was constructed so there was room for three 110Volt (V) pumps. The pumps housed in the unit include a vacuum pump; for pulling air through the reactor vessel and a nuclear grade HEPA filter; a separate blower used for the addition of fresh air, and a third pump used to add liquids and nutrient-containing liquids. The pump housing unit also had built-in gauge holders for flow meters, pressure gauges, and tee points for sampling valves.

Kinetics and Design Equations

A chemical engineering batch reactor design approach was used to configure the bioventing system used in this project (Tchobanoglous and Burton, 1991, Levenspiel, 1972, and Fogler, 1986). The reactor volume was defined as the volume of contaminated soil undergoing biological treatment and the heterogeneous batch reactor design equation was used to determine treatment parameters. Then, the overall degradation rate, including the rate constant, k, and the reaction order, were estimated using the integrated form of the design equation.

First, a degradation rate was estimated based on pilot scale experiments and literature values. This constant was estimated by assuming first or zero order reaction rates and inserting the reaction rate into the heterogeneous batch equation for a batch reactor, equation 1.

Equation 1

$$\frac{dNj}{dt} = r_j W$$

Where W is the weight of the soil, N_j is the mole of hydrocarbon, r_j is the overall rate of hydrocarbon degradation, and t is the time. The oxidation reaction for a straight-chained aliphatic hydrocarbon, a representative total petroleum hydrocarbon (TPH), is shown below, equation 2, and used as the standard reaction, see equations 3 and 4. This equation only accounts for the oxidized portion of the hydrocarbon and does not account for hydrocarbons that are incorporated into biomass. Thus, the oxygen demand calculated below overestimates the oxygen required for hydrocarbon oxidation when biomass is also being created. Equations 5 and 6 show the reaction rates specific for oxygen utilization and carbon dioxide generation.

Equation 2

$$C_nH_{2n+2} + \left(n + \frac{(n+1)}{2}\right)O_2 \rightarrow nCO_2 + (n+1)H_2O$$

Equation 3

$$aA + bB \rightarrow cC + dD$$

Equation 4

$$-r_A = \frac{a}{b} -r_B \text{ or } -r_{tph} = \frac{1}{\left(n + \frac{n+1}{2}\right)} \ -r_B$$

Equation 5

$$-r_B = \frac{b}{a} -r_A \text{ or } -r_{O2} = \left(n + \frac{(n+1)}{2} \right) -r_{tph}$$

Equation 6

$$-r_A = \frac{a}{c} r_C \text{ or } r_{CO2} = (n) -r_{tph}$$

To determine mass equivalency the ratio of the molecular weights of oxygen, carbon dioxide and straight chained aliphatic hydrocarbons were substituted into the rate equations, assuming n>8, see equation 7 through 9. Using this assumption, the mass ratio of hydrocarbon consumed per mole of oxygen does not vary significantly for other hydrocarbons associated with diesel, motor oil, and lubricating oil.

Equation 7

$$-r_{tph} = 0.29 \text{ (mg TPH/mg } O_2) -r_{O2}$$

Thus,

Equation 8

$$-r_{tph} = 0.29 -r_{O2} = 0.29 \frac{dN_j}{dt} \frac{1}{W}$$

and

Equation 9

$$-r_{tph} = 0.31 \text{ (mgTPH/mg } CO_2) r_{CO2} = 0.32 \frac{dN_j}{dt} \frac{1}{W}$$

Assuming zero order reaction and using Monod kinetics (assuming oxygen is the rate limiting nutrient) and assuming a constant reactor volume the petroleum degradation rate

and oxygen utilization rate can be expressed based on reactor flow parameters see equation 10 through 16.

Equation 10

$$-r_{O2} = (\mu_{max}.\frac{X}{Y_{O_2}})\ O_2/(K_{O2}+O_2)$$

$$\text{if } O_2 \gg K_{O2} \text{ then}$$

Equation 11

$$-r_{O2} = \mu_{max}\ \frac{X}{Y_{O_2}} = k_{O2}$$

Equation 12

$$-\ r_{O2} = \frac{dN_j}{dt}\frac{1}{W}$$

Equation 13

$$C_{O2} = \frac{N_{O_2}}{V}$$

Assuming a constant volume reactor

Equation 14

$$-r_{O2} = \frac{dC_{O_2}}{dt}\frac{V}{W}$$

where,

μ_{max} = maximum growth rate of the microbial population, hr-1

X = dry biomass, g

Y_{O2} = grams of biomass produced per g O_2 consumed

K_{O2} = the Monod half constant for oxygen limited growth, mass/l.

k_{O2} = the rate of oxygen consumption, g O_2 / kg soil / hour.

C_{O2} = oxygen concentration in the air, gram/l.

V = reactor volume or volume of contaminated soil, l.

W = {(l–ϕ) V}, kg. Where ϕ = void volume / total bed volume (total porosity)

ρ = soil density, kg/l

Equation 15

$$-r_{O2} = k_{O2} = \frac{dC_{O_2}}{dt}\frac{1}{(1-\phi)\rho}$$

Equation 16

$$-r_{tph} = (0.29)-r_{O2} = 0.29\ \frac{dC_{O_2}}{dt}\frac{1}{(1-\phi)\rho}$$

Once the rate constant, k_{O2}, was calculated, the air flow rate required to maintain excess oxygen was estimated using a plug flow design. The microbial oxygen consumption rates were also used to estimate the time required to reach regulatory thresholds and to obtain samples for confirmation that the target clean-up levels have been reached.

Required Air Flow Rate

The rate law, $r_j = k$ (for zero order) was used with oxygen utilization data from the literature, see Table 2, to estimate the required air flow rate necessary to maintain excess oxygen in the reactor. Equation 17 was used to estimate the required airflow rate based on the PRCS design. It was assumed the system was a plug flow, homogenous reactor with isothermal conditions and pressure will be controlled so it will not affect reaction kinetics.

Equation 17

$$\frac{V_R}{F_{A0}} = \int_0^X \frac{dX}{-r_i}, C_i = \frac{F_{A0}}{FR} * (1 - X)$$

Where, V_R is the reactor volume, F_{A0} is the air molar flow rate, X is the desired fractional conversion of oxygen, and FR is the volumetric flowrate. Equation 17 was solved for the desired air flowrate to maintain an outlet oxygen concentration that did not inhibit or terminate hydrocarbon oxidation (e.g., 15-20%).

Bioreactor Design

The data used to calculate oxygen utilization rates in the design of the petroleum and radiological soil bioreactor were chosen based on SRS investigations, historical evidence, comparative studies in the scientific literature, and SRS specific petroleum contamination events. Historically, the predominant petroleum contamination in SRS soils was diesel fuel as the result of leaks and overflows from emergency power generators. SRS has numerous generators on-line for backup power to support nuclear missions at the site. Although most of the generators have been removed from service at SRS, diesel contamination in radiological areas is still likely. While soils contaminated with gasoline or motor oil were possible, these types of soils were believed to make up a smaller fraction of the radiological contaminated soils at SRS. In an actual field treatment campaign, Kastner et al., 1987, measured oxygen utilization rates of 19-28 mg/kg/hr at a weathered SRS spill site associated with old emergency generators. Soils treated in the PRCS unit were also expected to be highly weathered material from diesel spills. This is due to long term storage of older contaminated materials in the low activity vaults

without treatment (Walker, 2001). Based on these factors, a range of 15 to 100 mg/kg/hr was selected as the peak oxygen demand rate for SRS soils. This range encompasses weathered and freshly spilled diesel contaminated soils. Table 2 lists example environmental restoration data used to estimate oxygen utilization rate range. Most of SRS is located on coastal plain sediment (DOE/EIS-0120, 1987) with low organic content. Therefore, a range of bulk soil densities values similar to sand were selected for modeling purposes. A value of 80-120 lb/ ft^3 was used based on typical SRS soil type. Values of typical soil densities are listed in Table 3 (Walker, 2005).

Table 2. Biological Oxygen Utilization Rates

Petroleum Contamination	Peak Oxygen Demand	References
Diesel Contaminated Sand	14 mg/kg/hr*	(Traux et al. 1995)
Weathered Diesel Fuel	19-28 mg/kg/hr	(Kastner et al. 1997)
Oily Sludge	119-274 mg/kg/hr*	(Vasudevan and
Crude Oil Cocomposting	300 mg/kg/hr*	(L. Aguilera-V´azquez et al.
Landfarmed Waste Oils	1.8 mg/kg/hr*	(Line et al. 1996)
Coal Tar Waste Products	10.1-70 mg/kg/hr	(Harkness et al. 1995)
Diesel Oil	68-120 mg/kg/hr	(Morrison et al. 1996)

*calculated from representative data

Table 3. Typical Bulk Soil Densities

Soil Type	Estimated Bulk Density, lb/ft3
Bentonite	35-60 lb/ft^3
Fuller's earth	40 lb/ft^3
Earth, loam dry	77 lb/ft^3
Earth, dense moist to wet	90-125 lb/ft^3
Kaolin crushed to pulverize.	20-65 lb/ft^3
Sand, silica, dry	90-105 lb/ft^3
Sand, silica, wet	120-130 lb/ft^3
Sand with Gravel, wet and dry	100-130 lb/ft^3

Excess Air Calculation

Excess air requirements were determined based on probable oxygen utilization rates and bulk soil densities. The excess air requirements were then used with pressure drop calculations and known skid-pan volumes to determine pump/compressor requirements. Table 4 shows the results of an example calculation for excess air required based on a soil bulk density of 100 lb/ft^3, an oxygen utilization rate of 50 mg/kg/hr, and oxygen conversion of three percent. This calculation was repeated for the range of physical parameters listed above and for a variety of reactor volumes. Assuming three percent oxygen consumption the required air flow rate for a 100 ft^3 system ranged from 20 to 210 L/h based on the oxygen utilization rates and bulk densities chosen to represent the PRCS operation. In general, the amount of required air increases with higher oxygen utilization rate, reactor volume, and bulk density. Once a reactor volume was determined this calculation was used to estimate the size of the pumps required for the system.

Table 4. Excess Air Flow Rate Calculations for SRS Soil

Vr (ft^3)	FR, Air (L/hr)	FR, Air (ft^3/hr)
10.0	569.2	20.1
50.0	2846.2	100.5
75.0	4269.2	150.8
100.0	**5692.3**	**201.0**
125.0	7115.4	251.3
150.0	8538.5	301.5
200.0	11384.6	402.0

Pressure Drop

The pressure drop across the soil bed was evaluated to determine if this parameter would impact air flow distribution in the PRCS bioreactor. Iterative calculations were performed using estimated soil parameters, bed heights, and known pump flow rates to determine pressure drops. This information was used to determine the placement of the false floor and the inlet and outlet ports for the PRCS system. Pressure drop equations have been used with bioventing designs in a variety of configurations (Riser-Roberts, 1998). For this system, the pressure drop per height was assumed from the Ergun equation (Denn, 1980), equation 18, and calculated at different flow rates. Assumptions for the calculation included laminar flow, equal distribution of particle sizes, isothermal conditions, and constant volume.

Equation 18

$$\frac{dp}{dh} = 150\mu \frac{(1-\varepsilon)^2 U_g}{\varepsilon^3 d_p{}^2} + 1.75\rho \frac{(1-\varepsilon) U_g{}^2}{\varepsilon^3 d_p{}^2} = \frac{\Delta P}{H}$$

Where,

ΔP = pressure drop, lb/in^2, or psi.

H = depth of the packed bed, ft.

U_g = superficial linear velocity, ft/hr.

ρ = fluid density, lb/ft^3.

μ = fluid viscosity, lb/hr-ft

d = effective particle diameter, ft.

ε = interparticle void fraction, dimensionless

The data required for the pressure drop calculation included superficial gas velocity, void volume, and the average particle size of the soil. The reactor height and surface area were taken from actual skid-pan dimensions. Flow rates of typical pumps that require 110V power or less and were available at SRS were used in the calculations. The pressure drops calculated for the reactor bed loaded with 100 ft^3 of soil was less than 1 psi per foot of soil. Typically, surface loads up to 300 $m^3/m^2/hr$ (450 L per minute equivalent in the PRCS) have been applied to biopiles without excessive back pressure. Surface loads up to 500 $m^3/m^2/hr$ have been applied using an optimized matrix (Leson and Warner, 1991). Backpressure concerns were considered neglectable since the pressure drop calculation showed a change of less than 1 psi and pressure drops were not previously reported as a concern at the required air flow rates for the PRCS system (Miller, 1994).

Emissions Calculations

An emissions calculation was completed based on potential methane production by the PRCS system to meet SWD requirements, however, a specific emissions calculation for BTEX was not completed based on low concentrations in SRS petroleum contaminated soils, long period storage times, and low BTEX levels measured in past SRS spill events (Table 5).

Table 5. BTEX and TPH concentrations in soil from different SRS spills during 1993 to 1996 (Kastner, 1998)

Spill Type	Spill Size	BTEX Concentration (mg/kg)	TPH Concentration (mg/kg)
Diesel	30 yd	BQL	100-8000
Diesel	135 yd^3	BQL	8.3-9800
Diesel	135 yd^3	BQL	313-11,250
Gasoline	1 yd^3	1.1	550
Gasoline	0.5 yd^3	BQL	5000
Gasoline	5 lb	1.3	48.2-6340
Diesel	225 yd^3	4-34	4800
Diesel	20 yd^3	1.9	120
Diesel	50 yd^3	6-24	504-4100
Diesel	10 yd^3	6	122
Diesel	40 yd^3	0.4	105-132,000
Diesel	300 yd^3	32	5000
Mean/Typical	**16.4 yd^3**	**1.3**	**12,600**

BQL = Below Quantitation Limit

Treatment Duration

Treatment times were estimated using hydrocarbon degradation rates coupled with the batch reactor design equation, see equations 19 through 23. Data from SRS spills were used to estimate initial contamination levels for use in these calculations (see Table 5).

Hydrocarbon degradation rates from experiments at SRS and other investigations were also used to estimate treatment times, see Table 6 for examples of some first order reaction rates.

Table 6. First Order Reaction Kinetics.

Petroleum Contamination	Reaction rate, k	Reference
#2 Diesel Contaminated Sand	4.01E-02	(Traux et al 1995)
Weathered Diesel Fuel	9.37E-03	(Kastner et al. 1997)
Oily Sludge	3.65E-03 - 1.42E-	(Vasudevan and Rajaram
Crude oil cocomposting	7.80E-02	(L. Aguilera-V´azquez et al. 2001)
Landfarmed mixed Oils	1.07E-02	(Line et al. 1996)
Weathered Crude C<44 and	5.21E-03 and	(Heusemann, 1995)

Assumptions to the design equation used to determine hydrocarbon degradation times included using a constant volume reactor, constant temperature, and using either zero order or first order rate law. It was also assumed that all of the hydrocarbons were degraded at the same rate and contributed equally to oxygen utilization. Example calculations are shown in Table 7 and Table 8 using zero order and first order rate equations. The forms of the batch equation used for treatment time calculations are described below.

Equation 19

$$-r_A = -\frac{dC_A}{dt}$$

Equation 20

$$-r_A = kC_A^n = k \text{ and } -\frac{dC_A}{dt} = k \text{ for zero order}$$

Equation 21

$$-k = \int_{C_{A0}}^{C_{A(t)}} \frac{dC_A}{dt}$$

Equation 22

$$k = \frac{C_{A0} - C_{A(t)}}{t} \text{ or } t = \frac{C_{A0} - C_{A(t)}}{k}$$

Where,

n = reaction order

t = time, days

C_A, $C_{A(t)}$ = hydrocarbon concentration in the soil at any time t, mg/kg

C_{A0} = the initial hydrocarbon concentration, mg/kg

R_A = the rate of hydrocarbon degradation, mg/kg/day

k = the reaction rate constant, mg/kg/day or day^{-1}

To determine the first order rate kinetics for petroleum contamination removal equation a materials balance approach was used. Equation 19 integrated between C = C_{A0} and C = C_A and t=0 and t=t to yield equation 23.

Equation 23

$$\frac{C_A}{C_{Ao}} = e^{-kt} \text{ and } k = -\frac{\ln\left(\frac{C_A}{C_{A0}}\right)}{t}$$

The resulting kinetic parameter, k, is a first order rate constant with units of inverse days. The other approach is to assume zero order kinetics and simply divide the amount degraded or produced by the amount of time. This approach will yield a rate constant with units of mass per unit mass or volume per unit time. Summary calculations of biodegradation rates base on SRS TPH numbers using both approaches are reported below in Table 7 and 8.

Table 7. Estimated Treatment Times Based on Zero Order Kinetics and Initial TPH Concentrations.

Initial TPH (mg/kg)	Final TPH (mg/kg)	TPH Degradation Rate, -ra, (mg/kg/day)	Treatment Time (Day)
200	100	100	1
500	100	100	4
1,000	100	100	9
5,000	100	100	49
10,000	100	100	99
20,000	100	100	199
30,000	100	100	299
10,000	100	10	990
10,000	100	25	396
10,000	100	50	198
10,000	100	125	79.2
10,000	100	150	66
10,000	100	200	49.5
10,000	100	300	33

Table 8. Estimated Treatment Times Based on First Order Kinetics and Initial TPH Concentrations.

Initial TPH Level (mg/kg)	Final TPH Level (mg/kg)	TPH Degradation Rate, -ra, (Day^{-1})	Treatment Time (Day)
200	100	1.60 E-02	43.3
500	100	1.60 E-02	100
1,000	100	1.60 E-02	144
5,000	100	1.60 E-02	244
10,000	100	1.60 E-02	288
20,000	100	1.60 E-02	331
30,000	100	1.60 E-02	356
10,000	100	4.61E-01	10
10,000	100	9.21E-02	50
10,000	100	4.61E-02	100
10,000	100	2.30E-02	200
10,000	100	1.54E-02	300
10,000	100	9.21E-03	500
10,000	100	4.61E-03	1000

PRCS System Construction and Reactor Fabrication

Construction

Construction modifications were performed on a pre-fabricated skid-pan for treatment of petroleum contaminated soil. All modifications were completed by the SRNL fabrications shop. All materials were procured and installed as specified using plot drawings and specification sheets, see Appendix C for details.

Modification of the skid-pan included the addition of a false floor, addition of sample ports, gauge ports, and the construction of a lid and pump housing unit. A perforated false floor was added to the skid-pan to promote oxygen mass transfer. Galvanized carbon steel grating material was bolted to carbon steel angle iron which was welded to the side of the skid-pan, see Figure 2. Data acquisition couplings and nipples, an influent air couple, and influent and effluent water couplings were welded into one side of the skidpan, Figures 3 through 6. An air distribution system was installed below the grating using ½ inch schedule 80 polyvinyl chloride (PVC) piping. Slots in the piping were manually cut to evenly distribute air-flow across the entire bioreactor floor (Figure 7). Figure 8 shows the aluminum lid that was constructed for the system with an air effluent port, an access door, a slot for the HEPA filter, and lifting supports. Neoprene gasket material, ½ inch, was attached between the lid and the top portion of the skid-pan as sealant (Figure 9). The lid was then secured to the unit using 6 inch C-clamps. The HEPA filter is a nuclear grade filter capable of handling 15 cubic feet of air per minute (Flanders Filter #0-007, D-0X-00-NU-12-00-Z98084B). An air compressor, a vacuum pump, and a

liquid pump used to control the air and liquid flows in the system were placed in a separate pump housing unit (Figure 10). After welding was complete, a corrosion resistant liner was painted, using Tile Clad® (Sherman Williams, http://www2.sherwin-williams.com) on the inside of the unit and the outside of the unit and weld locations were painted to help with corrosion control (see Figure 11).

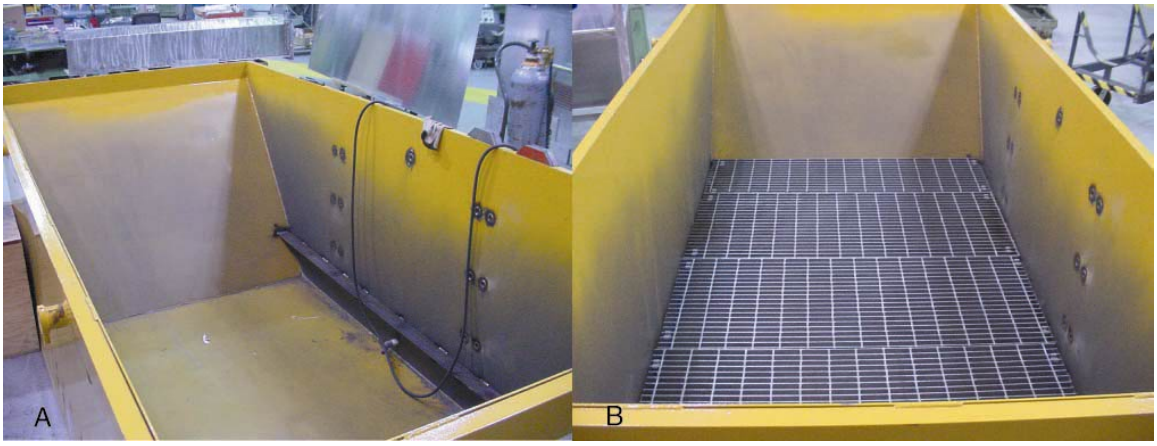


Figure 2. Inside View of Grating Supports and Installed Grating

Grating material consisted of galvanized 1inch x 3/16 inch x 2 feet wide carbon steel grating set on 3 inch x 3 inch x ¼ inch angle iron and clipped together using saddle clips.

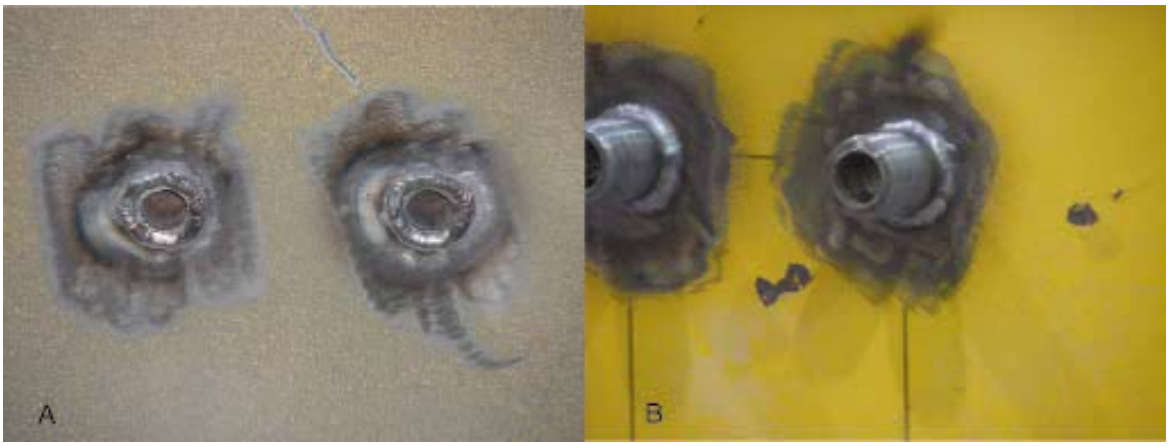


Figure 3. Interior (A) and Exterior (B) Views of Typical Nipple Type Data Acquisition Ports.

The ports were ½ inch National Pipe Thread (NPT) male nipples. The ports were welded flush to the inside of the skid-pan to allow the grating to be removed. The stainless steel nipples were welded to the carbon steel pan body.

Figure 4. Exterior (A) and Interior (B) View of Influent Liquid Coupling.

Couplings consisted of ½ inch NPT Female with 2 inch SS welded to the carbon steel surface.

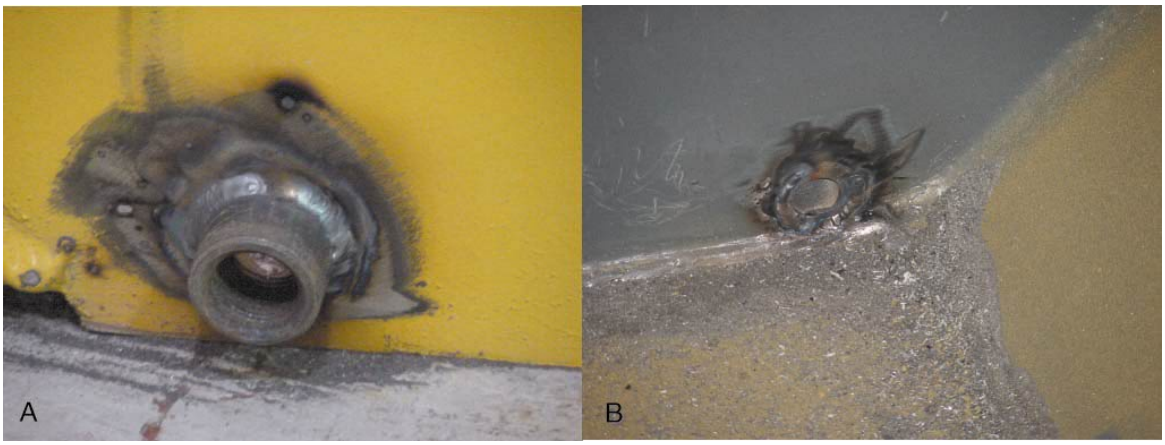


Figure 5. Exterior (A) and Interior (B) Views of the Effluent Water Coupling.

The ports were ½ inch NPT Female threaded SS coupling ports. The ports were welded flush to the inside of the skid-pans carbon steel body to allow for drainage.

Figure 6. Interior View of Air Inlet Coupling with Attachments (A) and Exterior View of Air Inlet (B)

(A) Shows a PVC adapter screwed into ½ inch coupling and glued to ½ inch PVC elbow and piping. (B) Shows a ½ inch NPT Coupling.

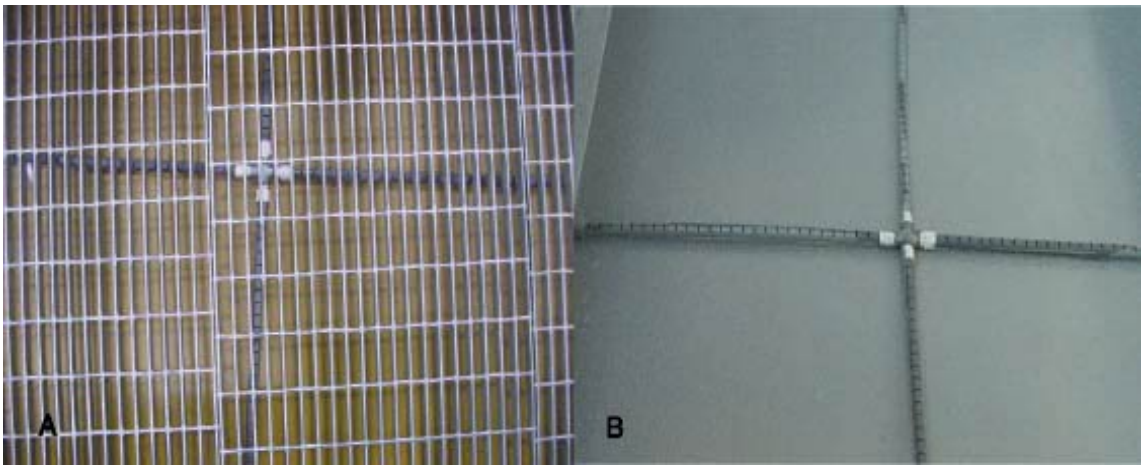


Figure 7. Interior view of the Air Distribution System

The grating was attached to the angle iron with clips that allowed the grating to be removed for access to the air distribution system (A). The distribution system consisted of slotted ½ inch PVC tubing capped at each end (B).

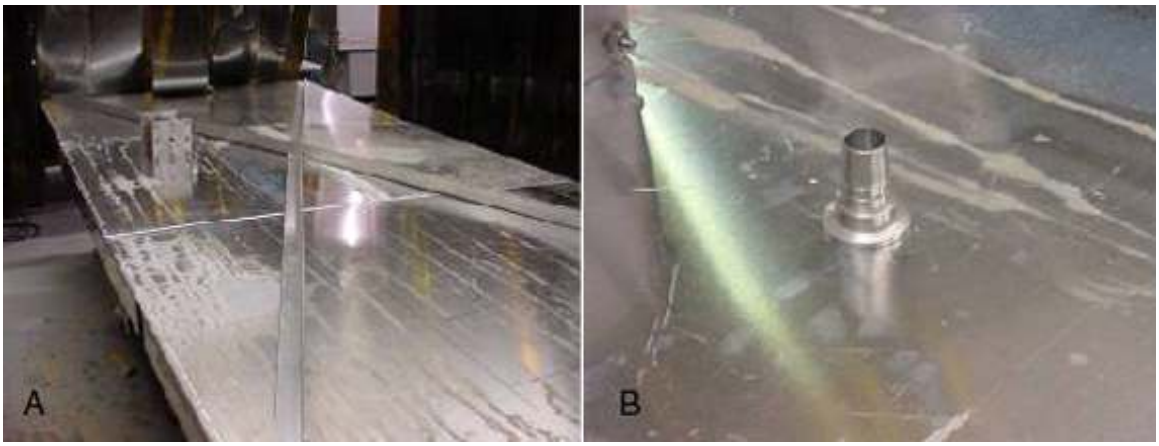


Figure 8. View of Partially Constructed Lid

(A) The lid was constructed of 0.125 inch thick aluminum with aluminum cross braces, 3/8 inch x 2 inch, for support, an access door, shown here as incomplete, and (B) an effluent port connection for the outlet air line.

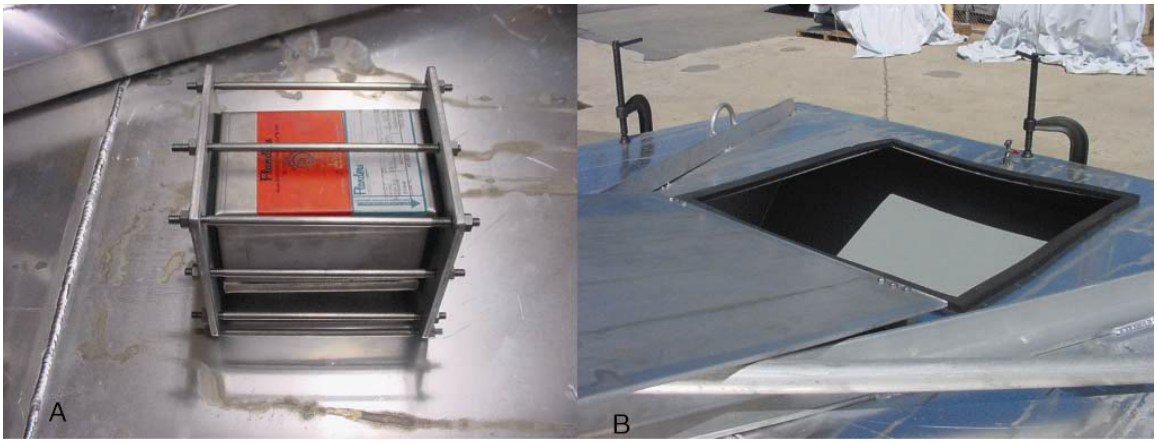


Figure 9. HEPA Filter Assembly and Access Port Showing Gasket Material

Neoprene gasket material was placed between the manifolds and the HEPA filter (A). The stainless steel manifolds house a ¾ inch to 1 inch nipple, as shown in Figure 8, for tubing connection to the vacuum pump. The same gasket material was used around the access port and between the lid and the skid-pan (B).

Figure 10. Pump Housing Unit

The pump unit housed three pumps one liquid pump, one vacuum pump, and one air compressor. The unit had a removable lid and access ports for tubing and/or electrical connections, as needed. The unit was mounted on rollers for transport and was equipped with vertical metal strips for flow meter placement.

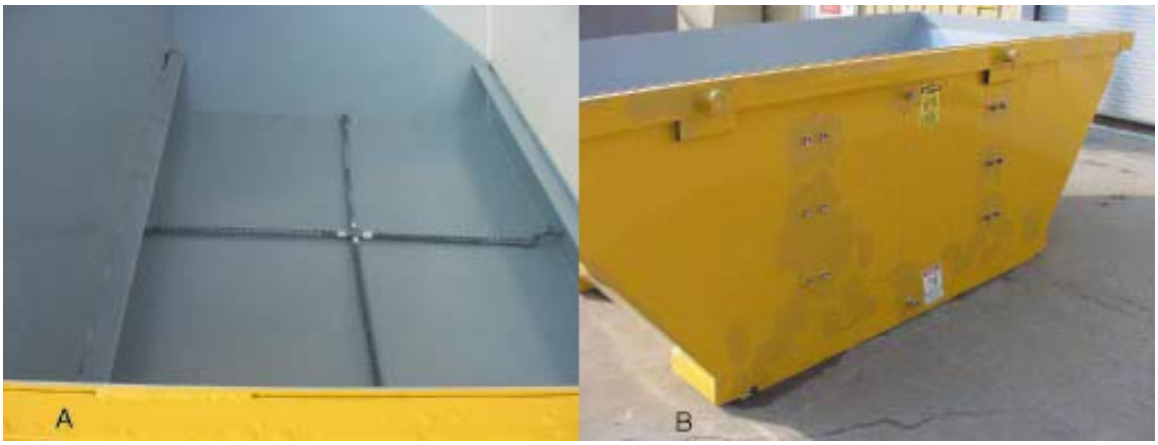


Figure 11. Anti-Corrosion Lining and Spot Painting Around Welds

The inside of the system (A) was painted with three coats of shale gray TileClad and the weld locations (B) were painted with two coats of gold paint.

Site Selection

Once the construction of the PRCS system was complete, the unit was moved to the SRS E-Area Burial Ground for testing. The SWD at the SRS has the responsibility to adhere to DOE order 435.1 (US DOE, 1999). The objective of this Order is to ensure that all DOE radioactive waste is managed in a manner that is protective of worker, public health and safety, and the environment. Soils co-contaminated with radiological material and petroleum products were found to be present in the inventory of the SWD at SRS. Twelve B-12 boxes were “mined”, or removed from the low-level waste storage vaults for treatment. Various locations were investigated at SRS for housing the unit. Original bioreactor design used 110 V pumps to add and remove air from the system and to supply and nutrients to the system. To meet this requirement a vault, Cell 10, in the low-level radiological waste storage facility was selected to house the unit. The vault provided protection from the weather and had access to 110-V power. The unit was staged in this

vault where clean soil testing was performed. Figure 12 shows the setup of the bioreactor in cell 10.

Figure 12. Bioreactor Setup in Cell 10 at SRS.

PRCS Functional Leak Test

Once the system was located in the SRS E-Area Burial Ground facility and process gauges were attached to the system, a functional leak test was performed. Functional leak testing of the system included leak testing, smoke testing, loading with uncontaminated soils, and operational testing. The entire test, including optimal operating parameters, was documented in a SWD functional leak test procedure. During the first test, water was added to the reactor until it was filled (see Figure 13). Water was observed leaking from the reactor around the couplings used for process gauges and from the top of skid-pan just below cover. The couplings were tightened to stop the leaks. However, the leaking area around the top of the reactor was not fixed. It was decided to run a smoke test with the lid in place to verify the location of the leaks. During the smoke test, smoke was observed exiting the system from all four sides of the bioreactor and from the access panel door.

Figure 13. Leak testing of the PRCS System
Image of the system being drained at the completion of the initial leak test.

The skid-pan was returned to the SRNL fabrications shop for continuous welding of the channel at top of the unit. While the unit was located at the shop, it was decided to add structural support to the lid to help form a smooth seal with the gasket. Since this structural support would add weight to the lid, channels were also added to the top of the lid so that it could be easily removed with a fork lift rather than by hand, (Figure 14). Since leaks were also observed coming from the screw holes used to fasten the handle on the access panel and from the screw holes fastening the external clamps on the lid, a new access panel was designed and fabricated using a double sheet of aluminum with inset screw holes rather than through bore holes (see Figure 15).

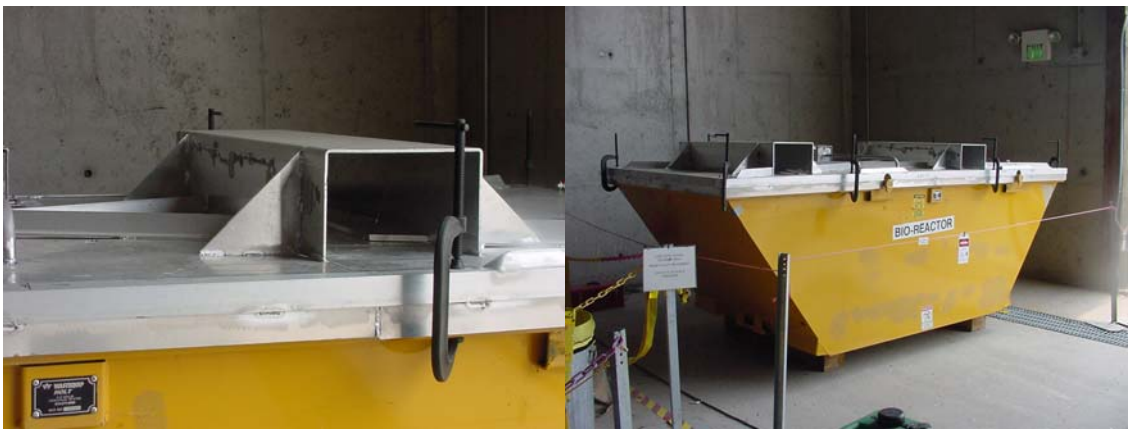


Figure 14. Modified PRCS Lid

Finally, it was observed that the configuration of the HEPA filter was a liability during transport. The piping leading to the HEPA filter unit was replaced with 1 inch aluminum tubing and the HEPA filter unit was screwed directly to the new lid (see Figure 15). The new arrangement made allowances for HEPA filter replacement.

Figure 15. Modified HEPA Filter Housing and Access Port

After final modifications to the reactor were complete, the system was returned to the Burial Ground to complete functional testing. However, before testing could continue, two gauges were replaced due to broken glass faces that occurred during transport. Gauges with smaller faces were then attached to the unit and the piping connections to the unit were shortened so the gauges were closer to the reactor. Once the gauges were replaced, the functional leak test was repeated and no leaks were observed. Then, clean, uncontaminated soil was placed in the reactor. The soil was dumped into the reactor onto geotextile cloth placed on the grating material inside the PRCS. Once the soil was loaded the inlet and outlet tubing were attached to the unit so operational vacuum testing could be completed. After adjusting the clamps holding the lid on the skid-pan, the pumps were started and a vacuum was observed on the pressure gauges. However, after a few minutes of operation the vacuum inside the system began to draw down on the lid. The vacuum pump was shut off and clamps removed to avoid damage to the unit. Since the system was unable to control excessive vacuum conditions SWD and SRNL personnel decided to modify the bioreactor configuration and operating parameters in order to meet the requirement of maintaining negative pressure in the bioreactor. Based on this assessment, it was decided to install two vacuum relief valves and reduce the size of the air and vacuum pumps. Two vacuum check/relief valves and one manual check valve were added to unused access ports on the side of the PRCS system. The manual check valve was added to the system to allow air to enter the system to help control the system vacuum. The pressure check/relief valves were added to the system to control vacuum and pressure fluctuations and as a fail safe to protect the system if one of the pumps stopped operating. All check/relief and manual valves were fitted with nuclear grade

HEPA filters, rated to 1.5 CFM. As an additional control, the air pumps, vacuum and blower, were replaced with smaller units. The units were still able to provide excess oxygen to the system and made control of the system easier. Once the vacuum relief gauges were installed and the pumps were replaced, testing continued.

The vacuum test continued with the manually operated check valve in the open position. This allowed the air to enter the system when vacuum conditions, (<1.5 inch H_2O), existed in the bioreactor. In this configuration the operation of the system was maintained and verified over a 4-hour operating period. Flow upstream of the inlet air pump was 15 standard cubic feet per hour (SCFH), the flow rate upstream of the Bioreactor Vacuum Pump was 20 CFH, and the pressure gauge on the system read -4 inch water column (WC). The system was then tested with all of the pumps operating. The system was continuously operated with the inlet air pump flow rate set to 15 CFH, the vacuum pump flow rate set to 20 CFH, and water pump setting 100%, 18.3 gallons per hour. Operational testing continued with the manual operated check valve closed and the sample port in the open position. System flow rates varied 5-10 SCFH depending on the system configuration.

The relief/check valves were then tested to determine their opening pressure. Larger pumps, 10X flow, were attached to the system to facilitate testing. The two vacuum relief valves opened at 5.5 inch and 3.5 inch water column. While the manual operated check valve opened at 1.5 inch water column. All operational parameters and settings were documented in the SWD leak test procedure.

During the final phase of testing all system pumps were turned on for IH personnel to test the sound level intensity. When all the pumps and a continuous air monitoring device, used to measure radiological particles, were operating, the noise level reached 75 decibels, less than the 85 decibels limit requiring hearing protection. IH determined that hearing protection would not be necessary to operate or take readings on the bioreactor.

After testing the PRCS for leaks using water and smoke testing, repairs and modifications were completed on the system. Once all leaks were repaired, operational testing with clean soils was completed. Again modifications and changes to the PRCS system were required. Once additional controls, relief valves, and pump sizes were modified, functional system testing was completed. Final verification of the system was performed by IH and SWD signed off on the functional leak test procedure qualifying the system to begin treatment of SRS radiological and petroleum contaminated soils in Cell 10 of the LAW vault.

CHAPTER 3

PRCS SYSTEM OPERATION

Introduction

The Savannah River Site (SRS) has generated non-hazardous petroleum and radiological contaminated soils. Although the burial of petroleum contaminated soils in sanitary landfills with total petroleum hydrocarbon concentrations below 100 ppm is permitted, there are no allowances for disposal of co-contaminated petroleum and radiological soil. Therefore, the purpose of this project was to generate treatment data and test the hypothesis that an engineered biological process could safely and efficiently remove petroleum co-contamination from radiological contaminated soil. SRS submitted a CAP to SCDHEC that proposed bioremediation of the petroleum portion of the soils, *ex situ,* using simple, inexpensive, bioreactor technology. The proposed treatment would efficiently and safely remove the petroleum component from the soil without spreading radiological contamination to the environment. Final disposal of the treated soil would be to bury the material in trenches that accept low-level radiological wastes at SRS. This would free vault space for other non-hazardous, low-level wastes, reduce operating costs associated with the indefinite storage of the material, and provide a mechanism for treating similar waste streams. This would provide a safe *ex situ* remediation option to help reduce transportation, storage, and monitoring costs for SRS.

Before testing of the process could begin, a bioreactor design was completed, the system constructed, and work performed to meet the South Carolina state regulatory and SRS requirements. The system was leak tested, modified for operation, and operated with non-radiological and non-petroleum contaminated soil. This chapter will describe the system operation including, testing plan, sampling and monitoring methods, loading, start-up, results, and final disposal of the soil after bioremediation goals were achieved.

Testing Plan

Prior to operation, a general testing plan was developed to guide operation and testing of the PRCS bioreactor. The test plan was developed by SRNL personnel in cooperation with SWE. The plan covered general operating ranges, system monitoring, microbial amendments, moisture control, and nutrient addition.

A summary of the operating parameters and monitoring methods used with this system are shown in Table 9. System performance was monitored throughout testing using readings from instrumentation installed in a number of locations in and around the PRCS bioreactor and through examination of gas and soil samples. The general operating parameters for system oxygen concentration, soil moisture level, nutrient level, soil pH, and soil temperature were determined based on experiences and methodology as described in Chapter 1. Information on the microbial amendments is described below.

Table 9. PRCS Operating Parameters

Parameter	Range	Method of Addition	Monitoring
Oxygen concentration	10-21% in Air	Blowers / Compressors	Take effluent gas samples for GC analysis or use portable measuring instruments.
Soil Moisture	30-80% of Field Capacity or roughly 8-20% by weight	Liquid Feed system Nozzles	Periodically pull soil samples for oven drying gravimetric analyses. Temperature probes may be used to estimate moisture levels across the soil profile.
Carbon:Nitrogen: Phosphorus (C/N/P) ratio	100:10:2	During loading of system or using liquid feed system	Periodically measure nitrogen and phosphorous concentrations in soil samples using Ion Chromatography or alternative methods.
Soil pH	4 to 7	Buffer solutions using liquid feed system	Periodically measure pH in sub-samples.
Soil Temperature	15-35°C	Air and Liquid system	Use process gauges.

A consortium of microbes isolated at SRNL from a petroleum-contaminated site was added to the PRCS system. The organisms were isolated from sludge samples obtained from a 100-year-old oil refinery near Czechowice-Dziedzice, Poland (Altman et al., 1997). The aged sludge was acidic (pH 2) and composed of asphaltics that were highly contaminated with polycyclic aromatic hydrocarbons (PAHs). A total of 45 bacteria, 68

fungi, and 7 yeast species were isolated from the sludge on an acidic minimum medium exposed to naphthalene vapor (Brigmon, 2001). A subset of isolates was characterized by classical taxonomic criteria, BIOLOG©, and analysis of ribosomal ribosomal ribonucleic acid genes. A number of bacteria grouped within the Proteobacteria and were related to *Ralstonia*, *Pseudomonas*, *Stenotrophomonas*, and *Achromobacter species (*Brigmon, 2001). The organisms added for bioaugmentation are listed in Table 10. *Alcaligenes-piechaudii SRS*; *Ralstonia pickettii SRS;* and *Psuedomonas-putida* Biotype B *SRS*, all demonstrate the ability to produce biosurfactants in the presence of pertroleum compounds, the formation of which was noted during culturing conditions (Brigmon, 2003).

Table 10. Bacteria Cultures Used for Bioaugmentation of PCRS

Isolate	**Identification**
CZOR-L1B (KN-1)	*Alcaligenes-piechaudii SRS*
BP-20 (KN-2)	*Ralstonia pickettii SRS.*
CZOR-L1Bsm(KN-3)	*Pseudomonas-putida* Biotype B *SRS*
BPB	*Flexibacter cf. sancti* SRS
BPC	*Pseudomonas fredriksbergensis* SRS
BPE	*Staphylococcus warneri. LMG 19417* SRS
BPF	*Sphingomonas* SRS
BPH	*Sphingomonas Sp. S37* SRS
BPI	*Phylobacterium* SRS
CZOR-L1B (KN-1)	*Alcaligenes-piechaudii SRS* - (α Proteobacterium TA-A1)

In preparation for addition to the bioreactor, microbial isolates were grown in a complex media containing peptone, tryptone, yeast, and glucose (PTYG) media. The PTYG media consisted of 1g/L of peptone, 1g/L of tryptone, 2g/L of yeast, 1 g/L of glucose, 0.45 g/L

of $MgSO_4$, and 0.07 g of $CaCl_2$ (All reagents from Fisher Scientific or Difco – Becton, Dickenson and Company). Isolates were grown at 28 ºC on a shaker flask until bacterial densities were greater than 1 E+07 cell/ml. Active cultures were in log phase growth when added to the bioreactor.

Sampling/Monitoring Methods

Soil and gas samples were taken from the reactor. Approximately 50 grams per sample of soil was taken directly from the reactor access port during week three, month four, month fourteen, month nineteen, and month twenty two. These samples were used to monitor the nutrient, moisture, pH, and hydrocarbon concentrations in the PRCS system. Gas samples were pulled in 1 liter Tedlar® bags downstream of the HEPA filter. These gas samples were used to monitor the volatile organic compound, oxygen, and carbon dioxide concentrations. Process gauges were used to monitor system soil temperature and system vacuum conditions, and flow meters were used to chart airflow rates. The sampling and accessibility schedule depended on Radiological Control Operator (RCO) requirements, industrial hygiene (IH) controls, transportation issues, and SWE schedules. Collecting reactor gas samples and reading flow meters and gauges did not require additional radiological monitoring. However, collecting soil samples did require radiological monitoring transportation support. This additional monitoring and support was costly, approximately $660 per sample, so soil sampling was limited during this investigation. A monitoring schedule for the system is listed with the reactor instrumentation details in Table 11.

Table 11. PRCS Process Measurement Summary

Instrumentation/ Measurement	Location	Description	Data Description
Hydrocarbons	PRCS Soil	Lab Analysis	TPH Degradation
Nutrients	PRCS Soil	Lab Analysis	PRCS Operation
pH	PRCS Soil	Lab Analysis	PRCS Operation
Temperature	Side Port, air and liquid lines	Internal and External sensor	PRCS Operation
Vacuum	Side Port, air and liquid lines	Internal sensors	PRCS Operation
Carbon Dioxide	Air effluent line	External Sensor	TPH Degradation and PRCS Operation
Organic Sensor	Effluent line	External Sensor	TPH Degradation
Flow Meter	Air influent and effluent line.	Flow Meters	PRCS Operation
Oxygen	Air Effluent Line	Lab Analysis	PRCS Operation

Soil Sampling Techniques

Soil samples were periodically taken from the PRCS system to evaluate system performance. Soil hydrocarbon, nutrient concentrations, soil pH, and moisture levels were determined from these samples. Soil sampling required radiological protection of the soil handling personnel and monitoring by RCO. Samplers wore multiple sets of gloves for radiological protection; one pair of Pylox®-vinyl as the inner glove (Pioneer Glove Style V-5) and an outer latex glove (North Hand # ATCP-1815). RCO personnel used hand-held radiological monitoring equipment and atomic swipes to monitor for alpha contamination (Eberline AC-3, Thermo Electron Corporation), beta/gamma contamination (Ludlum model 12 with an HP 110 probe), and radiation (RO-20, Thermo

Electron Corporation). Before sampling began, all system pumps were turned off and all relief valves were opened. Once the pressure/vacuum gauges on the PRCS read zero the access port was opened. Soil samples were taken by hand using a three foot carbon steel sampling rod with a cross handle connected to a stainless steel sampling probe, 7/8 in by 12 in (AMS Inc #424.46). Multiple 50 gram samples were taken from single, randomly selected holes to sample the entire vertical soil profile of the PRCS system. The soil from each hole was immediately placed in a sterile, 50 ml, polypropylene, centrifuge tube (Corning #05526B). Once sampling was complete, the samples were overpacked in a plastic cooler (Colman type-16 quart capacity) on ice and transported in a SRS radiological material transport vehicle to a Radiological Buffer Area (RBA). Collected soils were stored at room temperature, and analyses were performed within 7 days of sampling. All analytical work was performed in radiological protected labs.

Hydrocarbon Concentrations

Hydrocarbon concentrations were determined on soils taken from the PRCS using a gravimetric method and a gas chromatographic-mass spectrophotometer (GC/MS) method. The gravimetric method was used to determine relative concentrations of TPH when the contamination levels were higher than 1,000 mg/kg (Greenberg et al., 1992). The GC/MS method was used to quantitate specific hydrocarbon, including diesel range organics and semivolatile compounds in the standards described below, and qualitatively identify specific contaminants and groups of contaminants in the samples. Both methods were performed in a chemical hood rated for handling low-level radiological materials.

In the gravimetric method, soils ranging from 1g to 10 g were weighed using a Mettler Ae 240-S analytical balance (Mettler Instrument Inc.) into 40 ml, pre-cleaned, screw-top glass vials with Teflon resin silicon septum discs (Fisher Scientific #06-412-37). Sodium sulfate (Fisher Scientific #S419-500) was added to the vial and mixed until the soil ran free, indicating the sodium sulfate had bound the free water. Then 10 ml of methylene chloride, high-pressure liquid chromatographic (HPLC) grade, (J. T. Baker #50-101-088) was added to the vial. The vial was then capped and sonicated using a Bransonic® sonicator (Fisher Scientific) for 10 minutes. After sonication the supernate was transferred through a silanized glass wool filter (Supelco #20410) using pre-cleaned glass pipettes into a pre-weighed 40 ml glass vial. The methylene chloride addition, sonication, and transfer were repeated twice. The vial with the extracted material was then placed under a stream of gaseous nitrogen to remove the methylene chloride. Once the methylene chloride was removed, the vial was weighed and the weight of the residual material recorded.

To determine TPH and specific hydrocarbon concentrations a GC/MS method was used. Samples ranging from 1g to 20 g were weighed in 40 ml, screw top, glass vials and sodium sulfate was added until the soil ran free. Methylene chloride was added to cover the soil with at least 5 ml of freestanding liquid. The vial was then capped and sonicated for 10 minutes. All liquid was transferred to a 20 ml glass vial through a silanized glass wool filter using pre-cleaned glass pipettes. The methylene chloride addition, sonication, and transfer were completed a total of three times. Then 20 ml of an internal standard, Semivolatile Internal Standards Mix (Supelco 4-8902), was added to the vial, and the

contents were placed under gentle nitrogen breeze until 1-2 ml of material remained in the vial. The contents were then analyzed using an Agilent 6890 GC equipped with a 5973 MS system and an Agilent 7683 series injector. The GC/MS system was equipped with a J&W DB-5 analytical column, 30 m, 0.25 mm inner diameter (ID), 0.25 micrometer (μm) film thickness (Agilent #122-5532). Samples from 0.2 to 2.0 μl were injected using a 50:1 injection split with helium as the carrier gas. The temperature program started at 50 ºC and increased at 10 ºC per minute to 300 ºC with a five-minute hold time. External standards, commercially available diesel and a semivolatile Diesel Range Organic Compounds (DRO) standard (Supelco #48166) were used to quantitate samples. The 5973 MS was operated in scan mode between atomic mass 50 and 500. Quantification and qualification were determined using Agilent CHEMSTATION software with a National Institute of Scientific Technology (NIST)/Environmental Protection Agency (EPA)/National Institute of Health (NIH) Mass Spectral Library with Search Program: (Data Version: NIST '02, Software Version 2.0) and EXCEL workbooks.

Two EPA approved analytical laboratories were also used to analyze samples for this investigation, Accura Analytical Laboratories, Inc., Norcross, GA and General Engineering Laboratories, Charleston, SC. Both laboratories used standard USEPA test methods for analyzing samples (USEPA, 2005). General Engineering Laboratories was used by SWD to characterize four of eleven B-12 containers for TPH levels using EPA method 8015A. Prior to shipment to the burial ground LAW vault, a PRCS soil samples was sent to General Engineering for analyses. The analyses included DRO using SW 846

8015B, Gasoline Range Organics (GRO) using SW 846 8015B, BTEX using SW 846 8260B, and PAHs using SW 846 8270. Accura Analytical Laboratories was used to quantitate TPH using the SW846 8015 modified analytical method and the SW846 3545 analytical preparation method for final waste acceptance by SCDHEC.

Soil Nutrients

Soil nutrient levels were monitored by quantitating the water-soluble inorganic forms of nitrate, nitrite, ammonia, potassium, and phosphate. To prepare samples for analyses, approximately 10 g of fresh soil were weighed on a Mettler balance in pre-cleaned, 40 ml glass vials. Then 10 ml of nanopure-deionized water, which was greater than 17.5 megohms-centimeter and was used for all eluents and standards, was added to the vial. The vial was sonicated for 10 minutes and then allowed to settle. The sample was then transferred to 0.5 ml polyvials with filtercaps (Dionex #038142) for analyses.

Cation and anion analyses were performed using a Dionex DX-500 ion chromatograph with a Dionex GP50 gradient pump, a Dionex ED40 electrochemical detector, and a Dionex AS40 automated sampler. Anion analyses were performed using an IonPac® AS14 4-mm analytical column (Dionex #046124) in combination with an IonPac® AG14 4-mm guard column (Dionex #046134) and an anion self-regenerating suppressor ULTRA (Dionex #061561). Samples were analyzed using 3.5 mM Na_2CO_3/1 mM $NaHCO_3$ eluent, prepared from American Chemical Society (ACS) grade salts (Fisher Scientific) at 1.2 ml per minute. Standards were prepared from ACS certified grade salts (Fisher Scientific) for chloride, bromide, nitrite, nitrate, phosphate, and sulfate between 0.5 mg/L and 100 mg/L.

Cation analyses were performed using an IonPac® CS12 4-mm (Dionex #04401) analytical column in combination with an IonPac® CG12 4-mm guard column (Dionex #04402) and a cation self-regenerating suppressor ULTRA 4-mm (Dionex #053948). Samples were analyzed using 31 mN H_2SO_4 eluent from ACS grade salts (Fisher Scientific) at 0.9 ml per minute. Standards were prepared from ACS certified grade salts (Fisher Scientific) for lithium, sodium, potassium, ammonium, cesium, manganese, calcium, and strontium between 0.5 mg/L and 100 mg/L.

Soil Moisture

Moisture level determinations on soils taken from the PRCS system were performed in the radiological hood. Soil samples were added to pre-weighed, 40 ml, pre-cleaned vials, weighed, and allowed to air-dry in the hood for a total of seven days. The samples were reweighed at intervals of 72 hours and 7 days, at which point the soil moisture content was determined.

Water level readings were also taken on the outside of the system to determine if free water was present in the reactor. This was an indirect measurement of available water in the system. A Zircon® Studsensor™ pro SL (Zircon #58052) was used to measure water level in the PRCS bioreactor.

pH

Soil pH levels were determined on samples using a 1:1 ratio of soil to water (20 grams of soil and 20 grams of water), 17.5 megohms-centimeter or greater. After calibration with pH 7 buffer (Fisher Scientific, SB107-500), an Orion 520A pH meter with a glass automatic temperature compensating pH probe (Orion #615600) was used to measure pH.

Gas Phase Organic Carbon, Oxygen, Methane, and Carbon Dioxide Analyses

Gas samples were taken from a sampling valve downstream of the PRCS HEPA filter and the vacuum pump; therefore, these samples could be analyzed in a non-radiological laboratory. Gas samples were taken in 1 liter Tedlar® sampling bags (Supelco, 2-4633), and then 250 µl were manually injected into an Agilent 6890 GC for analyses of volatile organic compounds (VOC), carbon dioxide, methane, and oxygen. VOC analyses were performed using an HP-5 trace column, 50 m, 0.32 mm ID, 0.25 µm film thickness (Agilent #19091M-105), to separate the compounds. Helium carrier flow was 1.0 ml/min with the temperature program starting at 40 °C, holding for 5 minutes, and then increasing 10 °C per minute to 250 °C. Data analysis and peak identification was performed using an Agilent 5972 MS system. Calibration standards for EPA method 524.2 (Supelco #47932) were used to create a single ion mode method for detection of VOCs. Oxygen, carbon dioxide, and methane analyses were performed using a carboxen-1010 PLOT column, 30m, 0.32 mm ID, (Supelco, Bellefonte, PA) connected to a thermal conductivity detector. Five hundred microliter samples were injected into an Agilent 6890 GC operating in split mode, 10:1, initial temperature 35 °C for three minutes ramping at 40 °C per minute to 160 °C. Data analysis was done with the Agilent 6890

software. Certified compressed gases from Air Liquide were used to calibrate the instruments.

Carbon dioxide generation rates were also determined on weathered compost. Compost weathered for approximately 15 months was obtained from the same source (C. J. Berry) as was added to the PRCS system. 1000 ml of compost was added to a 2400 ml glass vacuum flask (Fisher Science) with a solid rubber stopper (Fisher Science) and crimped Tygon® tubing (Cole Palmer, Vernon Hills, Illinois) amended with 15 % deionized water by total weight of soil. The Flask was stored at 28 °C and sampled in triplicate every 30 minutes for three separate, four hour periods, using a gas tight syringe (Hamilton # 81343) for analyses, as described above, of carbon dioxide concentrations. Between each four hour sampling event the flask was connected to a compressed air line to recharge the flask with oxygen and remove residual carbon dioxide.

System Readings

Carbon dioxide, methane, temperature, pressure/vacuum, and flowrate readings were taken from the PRCS system during operation. No radiological monitoring or protection was required to take these readings.

Carbon dioxide and methane readings were taken directly from PRCS sampling ports using a LFG10 landfill gas analyzer (CEA Instruments) equipped with a sampling pump. Carbon dioxide levels were calibrated using a gas certified gas mixture containing 0.693 % CO2, 20.7% oxygen, and 78.607 % nitrogen (Air Liquide, custom mixture). Methane

calibration was completed using a certified gas mixture, 4.5% methane and 95.5% nitrogen, calibration gas (Air Liquide, custom mixture).

Temperature readings were taken from three 316 stainless steel, 4" stem, 1/2" Male Pipe thread (MPT), 3" dial w/ dual scale, 20°F to 120°F thermometers (Miljoco Corporation), through an access port on the side of the PRCS with stems extending into the soil or headspace of the PRCS. Ambient temperature data was obtained from the Atmospheric Technologies Department at SRS (Hunter, 2003, 2004, and 2005).

Vacuum readings were taken with either an Ascroft compound vacuum gauge, which had a range of 30 in WC vacuum - 15 psi, ¼ in. MPT (Ashcroft Dresser Instrument #25-1009SW-02L), or a McDaniel 4" dial compound gauge, which had a range of 10 in. WC vacuum - 30 in.WC, 1/2 in. MPT (McDaniels Controls, # M10-1-30).

Air flow rates were measured on the inlet and outlet lines on the PRCS system. Two sets of flow meters were used during the investigation, one set measured flow rates between 20 and 250 SCFH (Dwyer-Instruments, VFA-9-SSV) and the other measured flows between 0 and 68 SCFH (Fischer and Porter Company, 10A6131Na2CX).

Reactor loading

Two B-12 boxes containing 7,340 lb. of petroleum and radiological contaminated soil were loaded into the PRCS bioreactor. Prior to loading, a Mylar® sheet was laid under and around the PRCS system to catch any contaminated material spilled during the transfer process. During all phases of the transfer, personnel and environmental

radiological monitoring was performed by SRS RCO personnel. Once the Mylar was in place, a Typar® -style (Tri-State Stone ® & Building Supply, Inc., Style 3201) geotextile fabric was placed on top of the grating inside the bioreactor. Loading was done using a forklift with modified lifting forks to pour the contaminated soil from the B-12 boxes into the bioreactor with minimal waste handling. While loading, the waste soil in the PRCS was amended by mixing in 6 ft^3 of compost (weathered domestic waste, C. J. Berry), 1.36 pounds of ammonium nitrate (Fisher Scientific, A676-212) and 0.54 pounds of 10-10-10 fertilizer (Lowe's®, USA). Bags of mixed compost and fertilizer were manually added to the reactor system toward the end of each B-12 transfer. Once the bioreactor was filled, the soil inside the reactor was leveled using a hoe. When level, the soil covered the lower two rows of temperature and pressure gauges. The upper third row of gauges, vacuum relief valve, and pressure relief valve were not in contact with the soil. After leveling, water was added to the system. Water was evenly distributed to the top of the soil layer and allowed to sink into the soil bed. This was repeated once, and an estimated total of 80 gallons of water was added to the system. Approximately sixteen inches of headspace was in the system after soil loading and wetting. The PRCS bioreactor was then capped with the bioreactor lid and left in the field pending transfer into cell 10 of the LAW vault.

Two B-12 boxes, LLWIN99015 and LLWIN99016 were placed in the PRCS. While being loaded, it was noted that LLWIN99016 had considerably more petroleum contamination, oil-soaked soils, than LLWIN99015. This box had not been characterized for TPH contamination prior to loading. The original characterization assayed four of eleven boxes collected from the same spill site. The results from General Engineering

showed the four boxes had TPH levels of 67, 69, 68, and 656 mg/kg. Initial characterization obtained prior to loading box LLWIN99015 indicated the soil was contaminated with approximately 10,000 mg/kg of TPH, based on gravimetric analysis at SRNL. The initial contamination in the system, with both boxes loaded, was estimated to be 25,000 mg/kg TPH, based on subsequent analyses.

Gas readings were taken while the bioreactor was still in the field. A carbon dioxide/methane analyzer was used to detect gasses coming from the HEPA filter outlet line and the pressure relief valve. Carbon dioxide was detected emerging from the pressure relief valve with the HEPA filter, therefore, it was determined that pressure was not building up in the system. After four days the system was moved into cell 10 of the LAW vault facility and connected to the process piping. The vacuum, inlet-air, and water pumps were operationally tested. During testing, carbon dioxide levels of 9.4% were detected in the effluent air stream. Samples for VOCs and methane were taken but none were detected exiting the system. After the water pump was tested, 18 liters of densely grown microbial cultures, two liters each, consisting of two types of *Burkholdera,* four types of *Ralsotonia*, two *Achromobacter*, and one *Stenotrophomonas,* in logarithmic growth phase were directly added to the PRCS system. Once the pumps were tested, they were placed in the off position for the night. Testing was repeated for two days during normal working hours. During this time the system outlet flow rate varied from 35 to 45 SCFH. The measured flow rate into the system fluctuated between 5 and 15 SCFH. Carbon dioxide production varied from 1-2 ft^3 per hour, and temperatures readings were higher in the soil than the PRCS headspace. After three days of flow testing and monitoring, the system was determined ready for full-time operation.

Operation of the reactor

The PRCS bioreactor operated for 22 months in various configurations treating the contaminated soil. Table 12 lists the chronological order of the PRCS operations. Initial soil TPH concentration was greater than 20,000 mg/kg and final TPH concentration was 45 mg/kg (see Appendix D). This section will summarize the general operation of the PRCS bioreactor, changes made to the system during operation, data obtained from monitoring the system, and results obtained from the system. A discussion of system results and operations will then be presented followed by conclusions.

General Operation

Ten days after loading and staging the PRCS system in cell 10 of the LAW vault the system began continuous operation. System parameters were initially adjusted so that there was a slight vacuum, less than –0.6 inch water, on all of the pressure gauges. Over the next few weeks the pumps were run continuously with small adjustments being made to the air flow streams to keep a small vacuum on the system. Temperature, vacuum/pressure, and carbon dioxide readings were taken daily during the five-day work week. After three weeks of operation the system vacuum pump was turned off for soil sampling. Two random sample cores were taken from the entire height of the soil bed. The system was restarted and the samples were transported to SRNL for analyses. See Figure 16 for photographs of system sampling. After system restart, adjustments were made until a vacuum was obtained in the system.

Figure 16. Bioreactor Pictures During Soil Sampling.

A- Core sampling tool in PRCS soil, B- Interior of PRCS with arrow pointing to a temperature probe, C- Interior PRCS picture of the general soil distribution, and D- an image of the access port, access port gasket material, radiological sampling gloves and carbon dioxide meter (red instrument).

During the second month of operation, gas bag samples were taken to determine oxygen and hydrocarbon levels, and a leak test was performed. No hydrocarbons were detected exiting the system. The leak test was performed using the portable carbon dioxide meter to account for the differences between inlet and outlet air flow rates. A leak was found around the HEPA filter and was repaired by tightening the bolts holding the filter to the top of the bioreactor and by applying caulk around the HEPA filter gasket.

During the third month of operation the carbon dioxide gas analyzer battery failed and gas bag samples were taken to determine carbon dioxide levels. An alternating current converter was attached to the instrument and a new battery was ordered. Power was lost once during the month over a four day weekend.

During the fourth month of operation the system was shut down for four days while the liquid inlet pump was repaired. After repairing the liquid pump, 58 gallons of tap water, which was open to the atmosphere for 5 days, was pumped into the system to adjust soil moisture levels. To allow the water to settle evenly over the soil bed, the air and vacuum pumps were turned off overnight. During the fifth month of operation three soil samples were pulled from the reactor as previously described. While pulling samples condensate was observed in the effluent line. This line was drained with RCO present. The pressure fluctuation was determined to be related to changes in soil moisture.

During the sixth month of operation, temperature and carbon dioxide production levels were low, and the inlet and outlet air pumps were turned off. The system was checked biweekly to operate the pumps and check carbon dioxide levels. The system pumps were turned back on for eight days in month seven. In month eight through ten the pumps were operated periodically to purge carbon dioxide from the system and provide oxygen.

During the tenth month of operation, the system was moved from cell 10 of the LAW vault facility to an outside radiological material storage area. The system was moved at

the request of SWD to provide room for other activities in the LAW vault facility. A cover was constructed to provide protection from the sun and rain, but power was no longer available. Therefore the system was operated using a portable generator while being located in the outdoor storage area. During month eleven, it was noted that the inlet air line check valve had failed in the closed position. At that time SWD was unable to provide operational and RCO support to change the valve. Obtaining SWD operational approval and support and RCO support necessary to repair the valve took 42 days.

Table 12. PRCS Operating Events

Time (Day)	Event Description
0	Bioreactor Loading
6	Continuous Operation Began
24	PRCS Soil Sampling
39	Leak Test Performed
45	Gas Bag Sampling
66	Gas Analyzer Battery Failed
120	Added 58 Gallons of Water
128	PRCS Soil Sampling
172	Pumps turned off
289	System Moved Outside
305	Check Valve Found Failed
347	Check Valve Replaced
354	Large Pumps Added to System
403	Solar Pumps Added to System
424	PRCS Soil Sample
571	Samples Shipped for Analyses
625	No CO2 Measured exiting System
661	Samples Pulled for Final Analysis
733	Ceased Operations
743	Soil Disposal

After the check valve was replaced, system pumps were operated for two to four hours. During operation system readings showed that carbon dioxide was not completely purged

from the system and oxygen concentrations were not fully recharged. During month twelve, the inlet pumps were replaced with larger flow pumps to facilitate oxygen input into the system and carbon dioxide removal. Carbon dioxide removal was achieved by operating the system for approximately 90 minutes on a weekly basis. The larger pumps were left connected to the PRCS so the systems oxygen levels could be recharged quickly. In addition, a flow meter, Dwyer-Instruments, was added to the inlet air line to accurately monitor inlet flow rates.

In the thirteenth month of operation, SWD was contacted to help evaluate options for increasing the amount of oxygen being added to the system since the system was consuming all of the oxygen between pump operations. Three options were evaluated to enhance the oxygen (air) supply. The first would keep the original configuration and operate two to three times a week for short periods of time, less than four hours. The second would install replacement pumps that operate with solar powered cells, and the third option would move the system to a location with a constant power supply, and would use the smaller pumps. It was decided to test a solar powered pump system. The system consisted of two solar panels, 1000 Wm^2 (Solarex http://www.oksolar.com/panels/solarex.html), connected to controllers, two 12 V (Morningstar Sunsaver #SS-6L), which supplied two 1.0 Amp, 12.0 V DC, air pumps, (ColePalmer #L-79200-10), and two 12 V, 24 Amp hour rechargeable batteries (YUASA, #NP24-12T). One panel, pump, controller, and pump were connected to the inlet and outlet gas flow ports.

During month fourteen the system was checked, solar pumps were installed, and soil samples were pulled. Flow rate through the system was approximately 15 SCFH. Soil analyses showed that hydrocarbon degradation was not complete but that soil moisture, pH, and nutrient levels were acceptable. During month nineteen a soil sample was taken for analyses by General Engineering laboratories to see if the system met the 100 mg/kg disposal criteria. Carbon dioxide was still being measured at the system when the sample was pulled. Analyses of PRCS soil showed TPH concentrations of 279 mg/kg. This was above the 100 mg/kg, required by SCDHEC for disposal. Carbon dioxide was not measured exiting the system in month twenty two. The system was again sampled in month twenty two for external analyses. Results were obtained in month twenty two and confirmed successful treatment of the soil to less than 100 mg/kg. A summary of these operating events is listed in Table 12.

Operational Data

Operational data obtained from the PRCS bioreactor included information obtained from soil samples and from system monitoring. Soil sample analyses examined pH, moisture, nutrients and hydrocarbon concentrations. System monitoring included gas concentrations, system temperatures, system pressures and vacuums, and air flow rates entering and exiting the system.

Soil Analyses

Soil samples were taken from one of the B-12 boxes prior to loading the system and from the PRCS five times during operation. Samples were taken at three weeks, four months,

fourteen months, nineteen months, and twenty-one months. Soil hydrocarbon concentrations were measured for all of the sample events. Soil moisture levels were measured at months four and fourteen, and soil pHs were measured on the B-12 box in the three week soil sample. Soil nutrient levels were obtained from the B-12 box prior to loading the system, at three weeks and fourteen months.

Soil moisture analysis was performed on samples pulled during months four and fourteen. In month four, the average soil moisture level from 5 samples was 10.6%, which was just above, but close to, the lower operating limit of 10%, as listed in Table 9. Additional water was added to the system. Soil moisture was also analyzed during month fourteen and the results from three samples averaged 12.4%. Soil moisture levels were indirectly monitored by measuring the level of water in the bottom of the PRCS system using a stud finder. Greater than one inch of water was detected in the bottom of the reactor until month nineteen.

Soil pH levels were measured on soils pulled from the B-12 box prior to system startup and at three weeks into operation. Soil pH was 5.9 in the B-12 box sample and 6.2 in the three week or sample. Soil pH was in the range of the values listed in Table 9 and was not measured again during PRCS operation.

Soil nutrients that were measured included nitrate, nitrite, ammonia, phosphate, and potassium and were analyzed using an ion chromatograph. Analyses were performed on the B-12 box prior to loading and on the three week soil samples. The results are shown

below in Table 13. Although total nitrogen was not determined due to the high levels of ammonium present, available nitrogen, potassium and phosphate concentrations were greater than the ratio, 100:10:1, listed in Table 9. No further sampling for nutrient content was performed.

Table 13. Nutrient Levels as measured by Ion Chromatograph

Sample ID	Nitrite (mg/kg)	Nitrate (mg/kg)	Phosphate (mg/kg)	Ammonium (mg/kg)	Potassium (mg/kg)
B-12 Box	1.2	11	3.9	<1.0	<1.0
3 Week	540	3,140	710	>5,000	400

Analysis of soil samples for TPH values was performed at SRNL and two outside labs. The outside labs analyzed the nineteen and twenty-one month samples. SRNL analyzed the remainder of the samples. Table 13 shows a summary of the results.

Table 14. TPH Values

Sample ID	TPH (mg/kg)	Laboratory
B-12 Box	9,068	SRNL
3 Week	18,200 ± 9,000	SRNL
4 Month	13,111	SRNL
14 Month	4, 875	SRNL
19 Month	279	General Engineering
22 Month	45	Accura Analytical

Due to the heterogeneity of the sampling taken in the third week, all sampled material was combined, mixed by hand, and separated into four samples. The uncertainty reported

in Table 14 is the standard deviation obtained from the results of the four samples. The samples analyzed by the outside laboratories were analyzed once. Results from month four and fourteen are averages of duplicate samples. Results for the SRNL analyses of the B-12 box, 4 month and 14 month samples are from gravimetric analyses. Results from GC/MS analyses were not used to quantitate the TPH levels.

General Engineering Laboratories also analyzed soils samples for BTEX using SW 846 8260B; PAHs using SW 846 8270; and GRO using SW 846 8015B. No detectable BTEX, PAH or GRO were measured. Final analyses by Accura Analytical demonstrated TPH, as measured by DRO, was 45 mg/kg, which was less than the 100 mg/kg maximum disposal level required by SCDHEC at month twenty-two.

System Monitoring

System monitoring included PRCS pressure and vacuum readings, system flow rates, system temperature readings on the three ports, and methane, VOC, oxygen, and carbon dioxide concentrations measured in the effluent gas line.

Figure 13, located in Chapter 2, shows the locations of the pressure gauges used to take readings normal operational surveillance of the PRCS. Three gauges were screwed in to ports located on the face of the PRCS system. Pressure readings ranged widely depending the operating status, soil temperatures, ambient temperatures, and ambient pressures in relation to the system. During operation with the pumps, system vacuum was kept at 0.5 in H_2O or less. System pressures of -5.0 in. H_2O were observed on the system gauges. Pressures greater than 1.0 in water were not observed on the system, even when the

system had lost power or the system pumps did not operate for extended periods. Figure 17 shows the averages of the three readings taken at each observation point during PRCS operation.

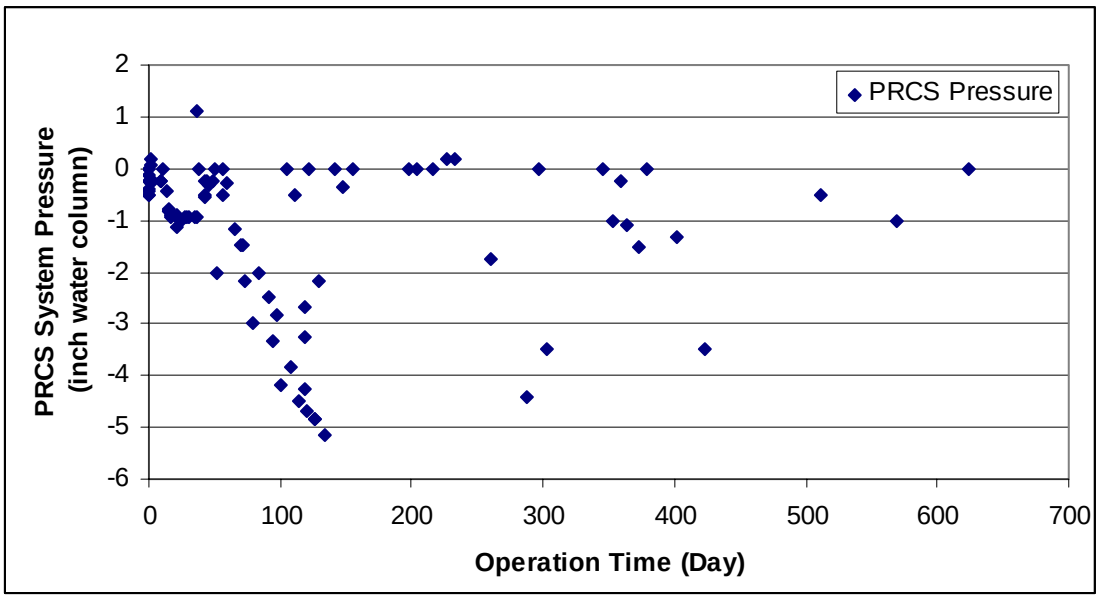


Figure 17. PRCS System Pressure Readings.

Flow rates entering and exiting the system were primarily determined by the pump type being used. Three sets of pumps were used to operate the system. During the first twelve months of operation, two medium flow vacuum pumps were used, 115 V 3.74 Amp, (KNF, Neuberger, NJ, MUNO35TTP). During months twelve through fourteen, while the system was located outside at the E-Area facility and the pumps were powered using a portable generator, large flow pumps were used, 110 V 1.5-5.5 Amp., (GAST Pumps, #0523-1010). Solar powered pumps were added to the system during month fourteen. Flow rates using the medium size pumps ranged from 30 to over 75 SCFH with an average flow rate of 48 SCFH (Figure 18). Outlet flow rates using the medium flow

pumps were consistently higher than the influent flow rates which average 16 SCFH. Inlet and Outlet flow rates using the larger pumps averaged 225 SCFH. Inlet and outlet flow rates using the smaller pumps ranged from 10 to 20 SCFH with an average flow rate of 17.5 SCFH for inlet and outlet flows. Figure 18 shows a chart of maximum outlet flow rates, as measured on the PRCS, and a chart of calculated averaged system flow rates that accounted for system downtimes.

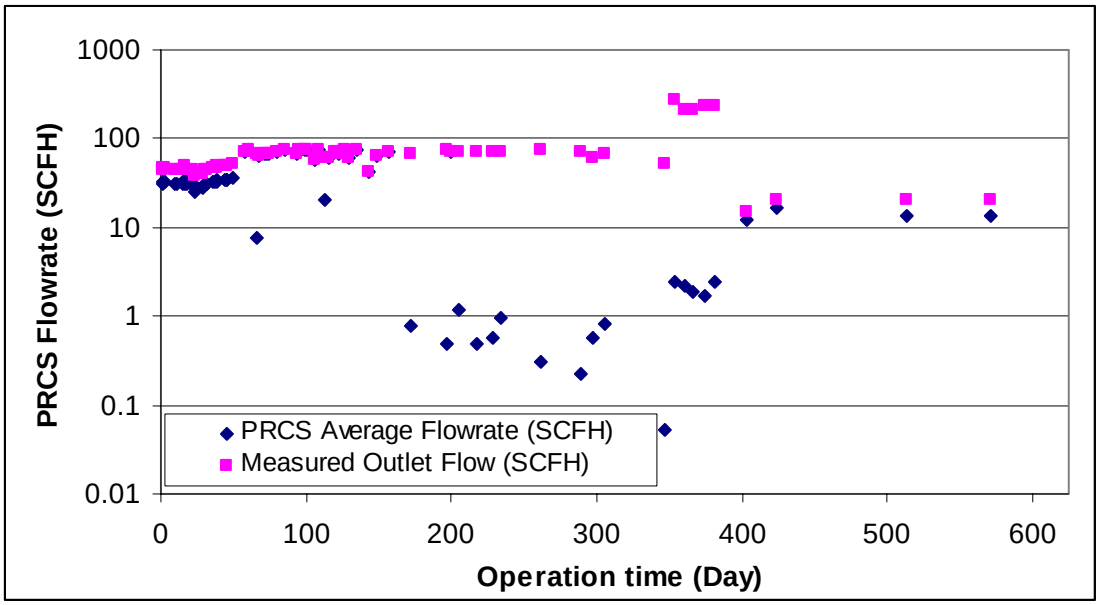


Figure 18. PRCS Measured and Averaged Flow Rates

PRCS temperatures were taken using stem gauge thermometers screwed into the side of the PRCS system (see Figure 13). PRCS temperatures were taken at three points, one in the headspace of the system and two in the soil profile of the unit. Figure 19 shows the soil, averaged, and headspace temperature during operation. Maximum soil temperatures, above 25 ºC, were measured during the first four months of operation and during months

eleven through fifteen. Minimum temperatures, which were below 15 ºC, were measured at the end of the fifth month of operation through the ninth month and in months seventeen through twenty-one. Soil temperatures changed with the median outdoor temperatures as the cell was sheltered from rain but open to the outside (see Figure 12).

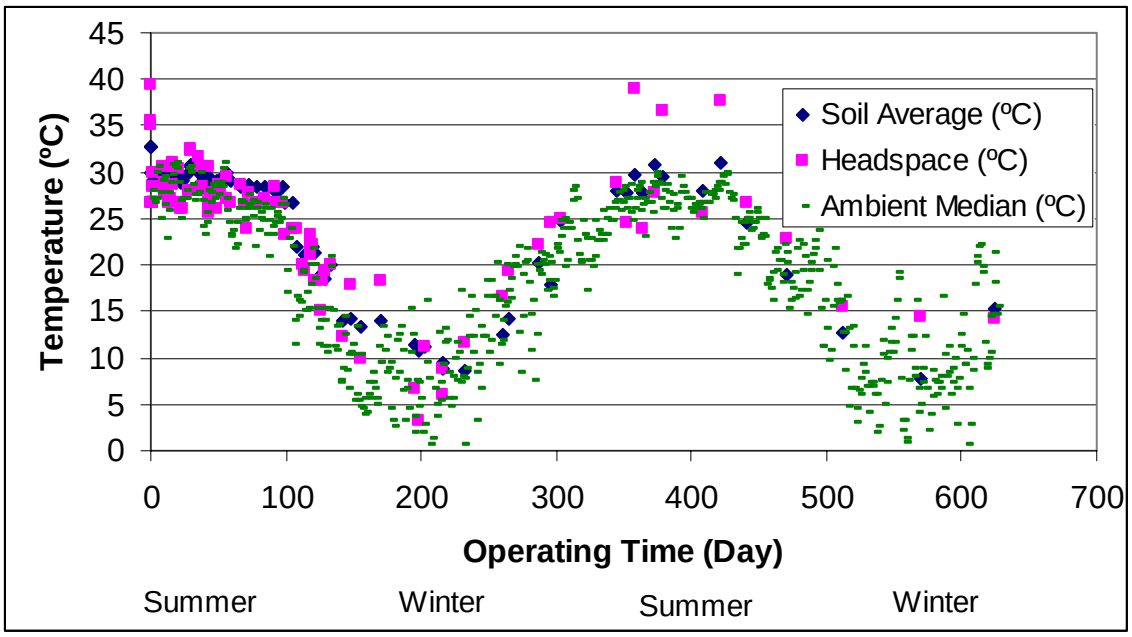


Figure 19. PRCS Temperature (ºC) vs. Time

Several analyses were performed on effluent stream samples. Carbon dioxide and methane were analyzed using a portable gas analyzer, while VOC and oxygen levels were measured using gas bags and GC analyses. Methane was not detected in any sampling of the system using the portable analyzer or in any gas bag samples. VOCs also were not detected in any gas bag samples. Oxygen concentrations were measured during the second month of operation to determine if the oxygen utilization rates were reducing

concentrations below the operating parameters. The measured oxygen concentration was measured to be 17.12 %, which was well within the range of 10-21% listed in Table 9.

Carbon dioxide analyses formed the bulk of the operational data obtained from the system. Carbon dioxide measurements were used to monitor hydrocarbon degradation, microbial activity, and to indicate when the system had completed bioremediation of the contaminated soil (Figures 20-21). Figure 20 demonstrates carbon dioxide concentrations taken from the carbon dioxide analyzer during system pump operation. The chart does not account for system outages, volumetric flow rate changes, the system headspace, or pump configurations.

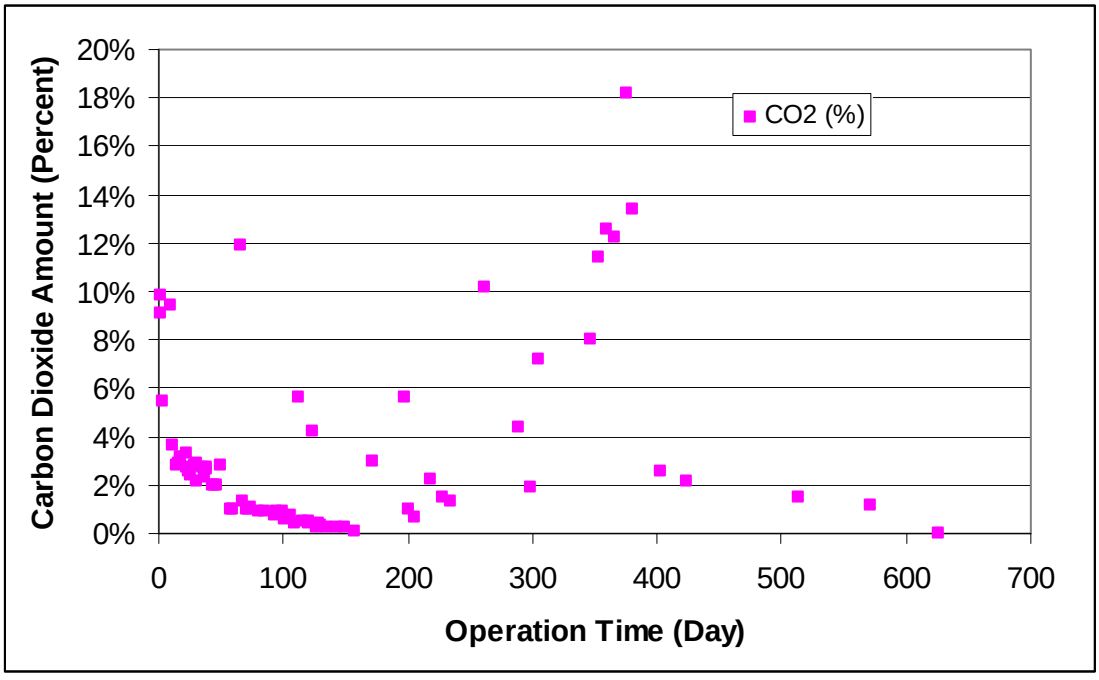


Figure 20. Carbon Dioxide Concentration in the PRCS Effluent Stream

Based on the carbon dioxide effluent concentrations (see Figure 20), the system flow rates, pump operation, the amount of material loaded into the reactor, and equation 9, Figure 21 was developed to show a conservative monitoring tool for total hydrocarbon degradation.

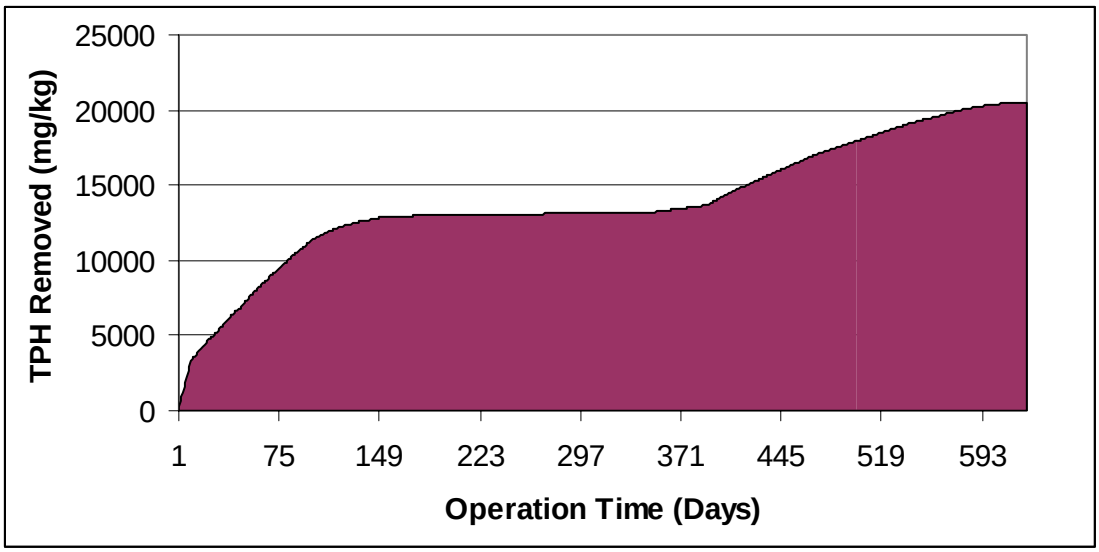


Figure 21. Estimate TPH Treated Based on Carbon Dioxide Data.

Carbon Dioxide production rates were measured on compost material that was similar to the material added to the PRCS system. Calculated carbon dioxide production rates based on concentrations measured during flask studies show that carbon dioxide production from the impact of the added compost would initially contribute less than 0.1 % of the measurable carbon dioxide produced in the PRCS system.

Discussion

The major physical impacts on reactor performance were soil temperature and pump operation. Soil temperatures changed with ambient temperature changes as shown in

Figure 19, (probability > t < 0.0001). TPH degradation and soil temperature also were also somewhat related, (probability > t < 0.0001) (see Figure 22). During the first decrease in temperature, days 123-250, carbon dioxide production dropped below 10 mg/kg/day (Figure 22). Carbon dioxide production also showed a general decrease in degradation rate during the second temperature decrease, days 500-600, although overall degradation rates were higher during the second temperature decrease.

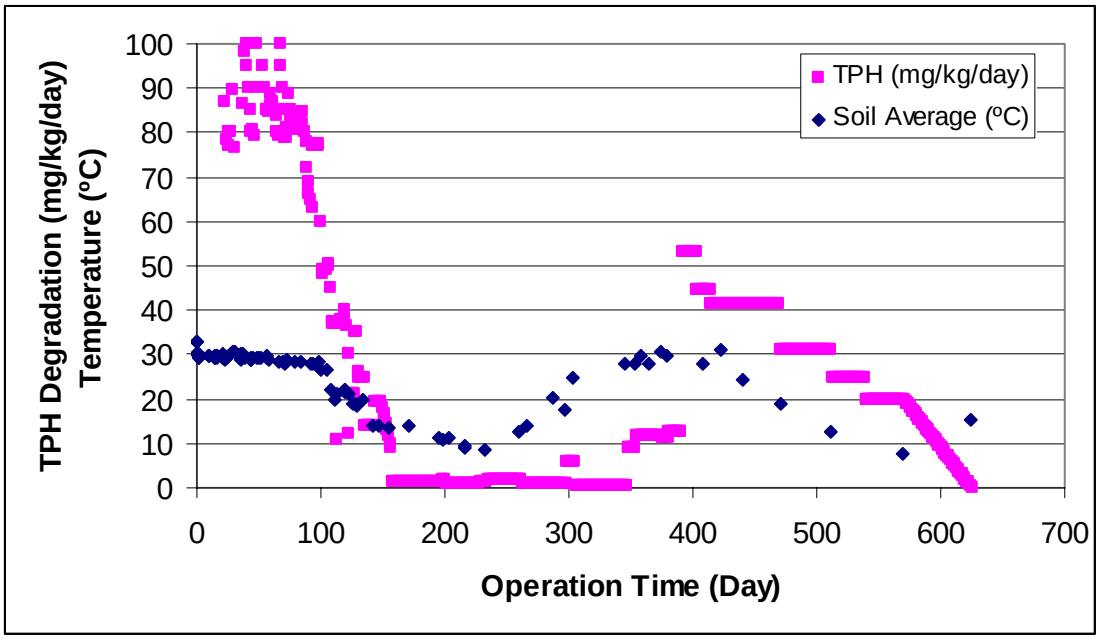


Figure 22. TPH Degradation Rate and PRCS Soil Temperatures

Carbon dioxide production was also reduced during month seven through month fourteen when pump operation was intermittent (Figure 23). During these months, the system was turned off due to low carbon dioxide production, cold soil temperatures, SWD operational directives, and movement of the PRCS system. Low TPH degradation was

observed while soil temperatures were relatively high, above 15 ºC, but flow rate through the system was low. When continuous flow was returned to the system using the solar pumps, TPH degradation increased to over 50 mg/kg/day, but then decreased throughout the remainder of system operation. Overall, pump operation was somewhat related to TPH degradation (probability > t = 0.4), as shown in Figure 23.

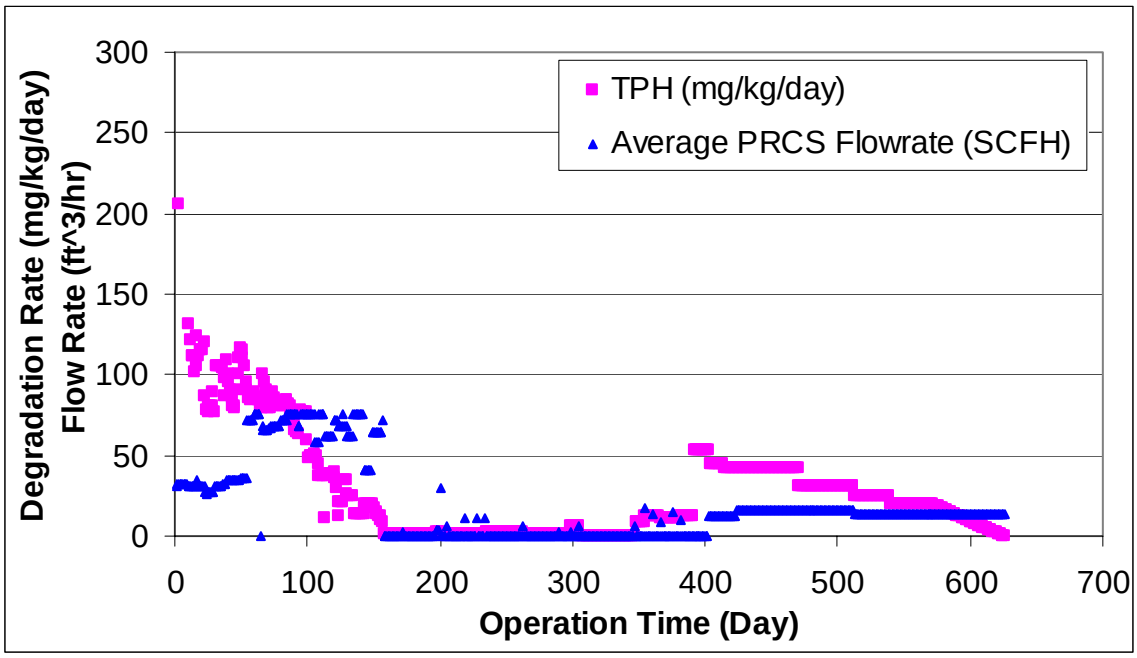


Figure 23. PRCS Flow and TPH Degradation Rates

Using a portable generator reduced the amount of oxygen (air) that was added to the PRCS system (Figure 23) and impacted TPH degradation rates (Figure 20-23) compared to continuous operation in Cell 10 or with solar pumps. On average, the PRCS operated once a week during this period. Carbon dioxide concentrations were measured each time that the system operated, but these measurements probably underestimated the carbon

dioxide volume produced by the system. The system was designed to vent to the atmosphere through the HEPA filters. Therefore, the volume expansion resulting from temperature increases or net gas/vapor production would cause gaseous material to be vented from the system and would change the headspace volume used to calculate TPH degradation (equation 9).

In general, using carbon dioxide concentrations to monitor TPH degradation has uncertainties, but is an easy parameter to use for external monitoring. Additionally, using equation 9 to estimate TPH degradation underestimates the rates when aromatics, PAHs, and olefins are being degraded since the equation assumes that the degraded materials are straight chained alkanes. Using equation 9 to estimate TPH degradation from branched alkanes is relatively accurate. Typical hydrocarbon chain lengths for gasolines consist of 4-8% alkanes, 2-5% alkenes, 25-40% isoalkanes, 3-7% cycloalkanes, l-4% cycloalkenes, and 20-50% aromatics (IARC, 1989), and Huesemann, 1995, showed the general rate of biodegradation of petroleum compounds was *n*-alkanes > branched-chain alkanes > branched alkenes > low-molecular-weight *n*-alkyl aromatics > monoaromatics >cyclic alkanes > polynuclear aromatics > asphaltenes. Equation 9 would accurately estimate TPH degradation during early biodegradation but would overestimate degradation rates as treatment continued.

Factors ignored by equation nine include the impact of the organic carbon content of the soil, external carbon sources added to the system, and the volatilization of breakdown products besides carbon dioxide. As discussed in the Bioreactor Design section of Chapter 2, SRS soils are generally sandy with low organic carbon content so the impact of background organic carbon contributing to carbon dioxide generation should be

minimal. Composted materials were also added to the bioreactor and probably contributed to carbon dioxide production. Although the compost was considered well weathered, as it was composted for two years, the material was predominantly organic so continued degradation of the compost did occur and contributed to carbon dioxide productions. The role of carbon dioxide production originating from the compost added to the system was evaluated using similar material. This evaluation showed that the compost was initially capable of producing an additional 0.1% of carbon dioxide in the effluent gas stream. This evaluation was done using compost that was less weathered than that added to the system, 15 months compared to two years, and at higher temperatures than soil averages, 28 °C compared to 24 °C. Although the compost did impact carbon dioxide measurements, the impact of the compost on the production of carbon dioxide was neglected during the system analyses. Using carbon dioxide to monitor system operation was useful especially since internal system sampling was limited due to radiological protection issues. Although TPH degradation rate estimates are impacted by many factors monitoring carbon dioxide production provided a straightforward monitoring tool during operation of the PRCS.

Examination of GC/MS sample runs on untreated and treated soil showed that most of the petroleum contamination was a complex mixture of hydrocarbons (see Figure 24). The term, “unresolved complex mixture” has been used to describe the raised baseline hump that is often observed in gas chromatograms of petroleum, as seen in Figure 24 (Frysinger et al., 2003). This hump has been described as resulting from the chromatographic overlap of thousands of compounds. The compounds that are present at high

concentrations produce individual peaks on the hump, but these peaks are likely to consist of multiple overlapping compounds (Reddy et al., 2002). Analyses of the total ion chromatograph in Figure 24 did not reveal the presence of distinct chemical compounds but did show a mixture of co-eluting compounds with column residence times after the internal standard, deuterium labeled anthracene (Figure 24). The total ion chromatograph was examined for general trends and specific PAH masses. Generally, mass per charge responses increased by 14 units in the unrefined area indicating an additional carbon group (Prince and Grossman, 2003). Major masses consistent with PAHs were not identified, and NIST library searches, with a probability greater than 50, did not identify any specific compounds. The extended storage period for this material in SWD before processing also contributed to the small number of compounds that were identified using GC/MS analyses. Easily degradable and identifiable compounds were preferentially degraded first, (Huesemann, 1995), probably during storage.

Degradation of this complex hump required microorganisms with specialized enzymatic activities (Atlas, 1981). The phenomenon has been described (Atlas, 1981), and degradation of this complex mixture of peaks is slower than degradation of alkanes. The expected diesel fuel n-alkane peaks do not appear in the chromatogram because of its removal through microbial degradation.

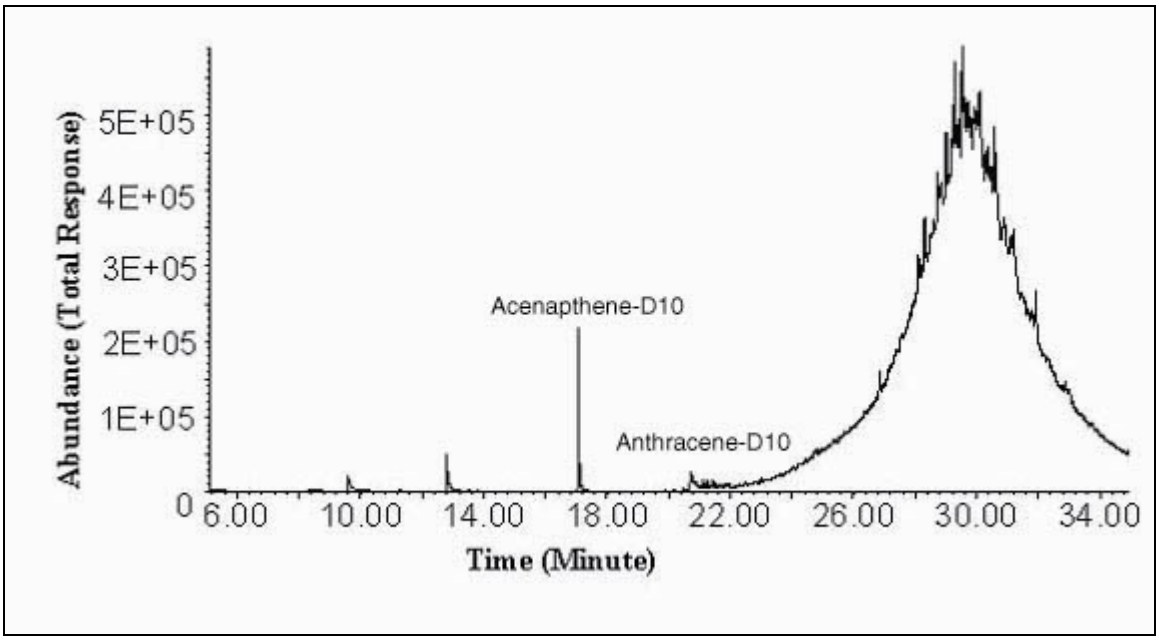


Figure 24. MS Total Ion Chromatograph PRCS Soil Sample – 14 months

The enzyme activity could have been present in the indigenous microorganisms present in the contaminated soil are been added with the addition of active compost or petroleum degrading organisms isolated from Poland. The organisms that were inoculated into the PRCS system were isolated from a refinery site containing asphaltenes and other complex materials. Enzyme systems that were present in this refinery site waste could use these more complex compounds for growth. Although specific organisms and specific enzyme activity were not tracked in this investigation a change in the active microbes during the duration of the PRCS operation is probable. As the less complex compounds were degraded the available food source for many of the microorganisms was removed. Microorganisms with enzyme activity capable of using the more complex compounds as a carbon and energy source would have then increased in number.

Using bioventing to treat petroleum contaminated soil is a well-documented approach (Leeson and Hinchee 1997), but using bioventing to treat co-contaminated radiological and petroleum contaminated soils has not been reported. During this testing it was demonstrated that, assuming proper engineering controls are in place to protect the environment and workers from contamination, co-contaminated soils can be biovented. Since bioventing is designed to maximize the biodegradation of petroleum contaminants with little volatilization and most of the radiological contaminants that would be expected at SRS (i.e. cesium, plutonium, uranium) have low volatility, transfer of the material out of the system would not be expected. To ensure this did not occur, HEPA filters were placed on all process entry and exit points to trap any particulates. In addition the system was operated under slight vacuum conditions so that any leaks that developed in the system would leak inward and not to the environment. Finally, the system was shut down, monitoring was done, and protective clothing was worn at any time that the system was opened. Based on the biodegradation rates and complete treatment of the co-contaminated soil using the PRCS, the impact of the radiological contamination of the treatment was also minimal.

The PRCS reaction rates were examined for periods of extended continuous operation to determine treatment time estimates (see Figure 25).

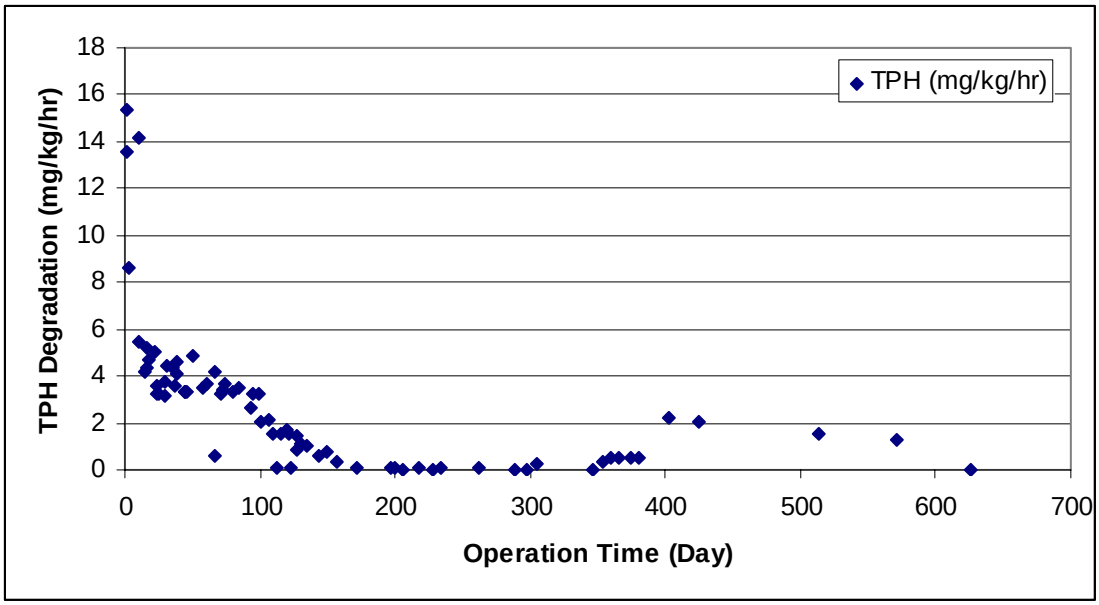


Figure 25. TPH Degradation vs. Operation Time

This estimate disregards temperature effects on reaction rate, but could be used as a tool for estimating treatment times for similarly contaminated soils with similar microbial activity. Based on carbon dioxide production concentrations and final soil sample results, zero-order and first-order rate constants were determined for the following time periods; days three through 100, days three through 157, days 403 through 580, days 402 through 628, and days three through 628. These time periods correspond to the initial operation of the PRCS, initial operation until pumps were turned off due to low carbon dioxide production and low soil temperatures, operation from installation of the solar pumps until carbon dioxide effluent levels were 1%, and operation from installation of the solar pumps until carbon dioxide was no longer measured exiting the PRCS. Table 15 shows calculated zero- and first-order reaction rates using equations 22 and 23.

Table 15. Calculation Reaction Rates and Treatment Times

Operation Period	Zero-Order Reaction Rate, k (mg/kg/day)	First-Order Reaction rate, k (1/day)	Zero-Order Treatment Time, t (day)	First-Order Treatment Time, t (day)
Days 3-100	108	0.00853	172	722
Days 3-157	75	0.0066	240	932
Days 403-580	32	0.01729	629	356
Days 403-628	27	0.02192	768	281
Days 3- 628	32	0.009803	628	628

Initial degradation rates were high and probably followed zero-order kinetics. That is, the rate of reaction was independent of contaminant concentrations. However, as contaminants were degraded, reaction rates slowed, as seen in Table 15 by the zero-order rates and treatment times, when the PRCS operated using the solar pumps. However, the first-order kinetic rates showed a faster reaction rate, k, during the later testing. This is counter intuitive since degradation rates would be expected to be slower after the more easily degraded compounds were removed. This discrepancy may indicate that initial petroleum degradation was not first-order and/or an artifact was introduced by comparing rates over different time periods. Hydrocarbon concentrations changed three orders of magnitude during operation after day 403, > 5,000 mg/kg to 45 mg/kg, but only changed one tenth of an order of magnitude during the first 157 days, > 20,000 mg/kg to >11,000 mg/kg. In addition, the first-order reaction rate for the entire test period, see Table 15, was higher than the rates calculated through day 157. Application of a first-order rate reaction to describe hydrocarbon degradation during the initial 157 days does not appear to be appropriate.

Overall, the calculated treatment times for the selected time intervals show that soil bioremediation could have occurred faster if PRCS maintained optimal conditions. The intervals selected in Table 15 represent time periods when system operation was consistent and soil temperature, for the most part, was above 15 Celsius. Although many factors, both environmental and man-made, influence the biodegradation or remediation rate, major physical-chemical factors clearly impacted the PRCS treatment time. These factors appear to be soil temperature and the mass of oxygen added to the system. Control of these factors through use of external heaters, addition of insulation, and consistent operation of the system pumps could have increased reaction rates and reduced total treatment time.

Soil Disposal

After receipt of the TPH analytical results from soil samples taken in month twenty-two, SRS notified SCDHEC that soil treatment was complete, the soil would be disposed as low-level waste, and SWD disposed of the soil. In accordance with the approved CAP, WSRC notified SCDHEC of the chosen method for disposing of the initial batch of remediated soil. The notification stated that "because of the radiological conditions of this soil, it will be dispositioned in accordance with the SRS radiological waste protocols". The PRCS system containing radiological contaminated soil was disposed in a lined slit trench located on the low level radiological burial ground, E-Area, at SRS.

Conclusions

Based on the results of the study the following conclusions are offered:

1. Biological treatment of co-contaminated soils was successfully completed using an *ex situ* bioreactor system.
2. This demonstration obtained data and technical and operational experience necessary to allow this technology to used to treat future co-contaminated soils at SRS.
3. Carbon dioxide measurements were shown to be a good indicator and monitoring tool for the microbial activity and TPH degradation occurring in the PRCS system.
4. Biodegradation can occur while operating the system under a slight vacuum.
5. Soil temperature and oxygen supply from pump operation were identified as two important parameters that control the rate of biodegradation.
6. Degradation rates were probably a combination of zero and first order kinetics.
7. Total treatment time required twenty-two months of operation and reduced TPH levels from over 20,000 mg/kg to 45 mg/kg.
8. Soil was permanently disposed as low-level waste in engineered trenches at SRS.

Recommendations

Based on the results of the study the following recommendations are offered:

1. Both carbon dioxide and hydrocarbon should be monitored *in situ* to determine the extent and rate of TPH degradation.

2. Co-contaminated soils should be managed so that control of soil temperatures and air flow rates can be maintained.
3. The use of heating strips or the addition of insulation should be considered when treating soil in temperate climates.
4. Recirculation of system liquids is not required for treatment.
5. All local, state, and federal permits, reviews, and analyses should be considered early in the design process when treating co-contaminated soils..
6. When treated co-contaminated soils perform leak testing to identify any system openings.

APPENDIX A

SCDHEC APPROVAL LETTER

Westinghouse
Savannah River Company
Aiken, SC 29808

May 7, 1999

ESH-FSS-99-0135

Ms. Sarah Price
Groundwater Quality Section
Bureau of Water
South Carolina Department of Health
And Environmental Control
2600 Bull Street
Columbia, SC 29201

ADDENDUM FOR CORRECTIVE ACTION PLAN, SITE ID #01241

This Corrective Action Plan (CAP) applies strictly to non-hazardous, petroleum contaminated soil. Treatment of UST petroleum contaminated soil associated with a release from a regulated UST will be managed through the UST program. This plan does not apply to soil derived from RCRA/CERCLA units.

2. WSRC will notify the Department each time a petroleum release to the soil has occurred that will utilize this CAP to treat the soil. Analytical results from soil monitoring will be submitted to the Department at a frequency to be agreed upon on a case-by-case basis.

3.) WSRC will notify the Department of the chosen method of disposal for all petroleum contaminated soil (and associated secondary wastes) treated utilizing this CAP.

If you have any questions, please contact me at (803) 725-2110 or curt.walker@srs.gov.

Sincerely,

Curt Walker
Facility Support Section
Environmental Protection Department
Bldg. 742-A
Savannah River Site
Aiken, SC 29808

cbw/tmj

D H E C
PROMOTE PROTECT PROSPER
2600 Bull Street
Columbia, SC 29201-1708

April 14, 1999

Mr. Curt Walker
Facility Support Section
Building 742-A
Westinghouse Savannah River Company
Aiken, South Carolina 29808

re SRS Soil Bioremediation, Site ID #01241
Corrective Action Plan received September 18, 1998
Aiken County

Dear Mr. Walker

The Department has completed a technical review of the referenced document. The Department requests the submittal of an addendum to the corrective plan which addresses the following concerns:

It is unclear if the referenced corrective action plan applies only to soils contaminated by petroleum sites that would be regulated by the UST program or whether DOE plans to apply this plan to any site that contains petroleum contaminated soils regardless of the sites regulatory status. It should be stated explicitly in the addendum to the corrective action plan that this plan does not apply to any sites that are being addressed by the RCRA Hazardous Waste Permit or the Federal Facility Agreement (RCRA/CERCLA units). Any remediation efforts at RCRA or CERCLA units must be conducted through the program for which the site is regulated.

2 As each release must be tracked separately by the Department, a consistent method of release reporting and frequency of soil condition monitoring in the bioreactor should be developed.

At such time as the soil appears to be reasonably free of petroleum hydrocarbons, SRS-WSRC must notify the Department of the chosen method of disposing of the soil. Copies of any applicable soil disposal manifests must also be provided within thirty days of disposal.

On all future correspondence please reference the Site ID #01241. Should you have any questions, please contact me at pricesw@columb32.dhec.state.sc.us or by calling (803) 898-3796.

Sincerely,

Sarah Price

Sarah Price, Hydrogeologist
Groundwater Quality Section
Bureau of Water

swp/02-01241.lt1

.ower Savannah District EQC

APPENDIX B

SRS ENVIRONMENTAL EVALUATION CHECKLIST

Savannah River Site

Environmental Evaluation Checklist (EEC)

NEPA Review / Environmental Permits

EEC No. SW - E - 2000 - 011

Rev No. 0

Instructions:

- Fill in both the NEPA and Permits portion of the checklist.
- Submit one copy of the completed Checklist with supplemental information to the Department NEPA Coordinator (DNC). The DNC will distribute to the Site NEPA Coordinator for NEPA level approval by DOE.
- Submit one copy of the completed Checklist with supplemental information to the Environmental Compliance Authority (ECA).

Activity Title and Project No. (if any)			Date
Petroleum Contaminated Soils Bioreactor			2/8/2001
Project Contact (Name)	**Phone No.**	**ECA Name**	**Phone No.**
Topher Berry, Environmental	557-7224		

3/15/01	9/30/01	85,000	E-Area
Activity Start	Activity End	Est. Cost	Activity Location

Activity Description: This should be a brief but thorough description of the proposed activity. Be very specific in explaining the purpose and location (a developed/non-developed area, outside/inside/adjacent to existing building no., etc.).

Summary:

Construct, test, and operate a bioreactor system(s) to treat nonhazardous petroleum contaminated soils (PCS) generated at SRS. Specifically, the system will allow the treatment of PCS generated in a radiological area to be treated to remove petroleum constituents and allow disposal to be focused solely on the radiological contaminants. A corrective action plan (CAP) was submitted to South Carolina Department of Health and Environmental Control (SCDHEC) in September 1998. SCDHEC has approved the use of a bioreactor system to treat petroleum contaminated soils generated in a radiological area and given the program a site ID#01241. Soils will be tested prior to treatment by TCLP analyses to ensure the soil is nonhazardous. The soils must not originate in sites being addresses by the RCRA Hazardous Waste Permit of the Federal Facility Agreement (RCRA/CERCLA units). SCDHEC must be notified where the soil will be permanently disposed and how the the soil condition will be monitored during treatment. The system will be operated by the SRS Solid Waste Division.

Reference Documents (e.g., CDR, FDR, Task Plans, etc.) No

Detailed Description:

The system will be designed as a continuous gas-flow packed bed reactor with the capability of operating aerobically or anaerobically. Structurally, the CAP specified two designs, the major design is a nominal 6 yd^3 capacity "skid pan" equipped with a false floor for gas introduction, process monitors, and nutrient injection/recirculation capabilities, with HEPA filter(s) on the outlet gas flow(s). The second design is for a 10ft^3 barrel design with an air blower, a sealable lid and a filter unit for the gas effluent. Utilities required for both systems include 110/120V power, process water, and operating space, preferably, with weather protection.

Process steps for the system include the following: Identifying and analyzing contaminated soil for hazardous constituents, amending, mixing and adding nutrients and water to the soil, loading the bioreactor, adding aqueous nutrients or neat water to the system to account for evaporative losses, adding air or nitrogen to the soil, monitoring and adjusting operating conditions of the system while biodegradation of the petroleum components proceeds, sampling the soil for petroleum concentrations, air drying the soil to remove any residual moisture, and finally, releasing the soil to a slit-trench for final disposal. These steps will be used in a series of treatment campaigns depending upon the amount of material that is generated.

The smaller system will consist of an 10ft^3 container equipped with an air blower, a removable lid, packed gravel bed, an air distribution system, and a gaseous effluent filter for radionuclides. A small scale blower (0-2 ft^3/hr) will be used to provide oxygen to the system and water content and nutrients will be adjusted manually.

The larger system consists of a sealed skid-pan, a HEPA system, one air blower, one liquid pump, sample ports, instrumentation ports, a false floor, a gas distribution system, and gas and liquid introduction ports. Operational conditions within the system will adhere to the following: O_2 concentration 10-21% (not applicable is system is operated anaerobically), soil moisture 30-80% of field capacity, soil pH 4-7, soil temperature 20-45C and nutrient ratio of 100/10/2 carbon/nitrogen/phosphorus. Required gas flow will vary depending on the soil type but is expected to fall between 1 and 20 ft^3/hr. Liquid and nutrient addition will also vary depending on the type of PCS but will be sized to operate from 0.1 to 10 liters/hour. The system will be equipped with a drain to remove any moisture remaining in the system at the end of or between treatment campaigns.

Final analyses of each treatment campaign will require manually sampling for the larger system. All sampling done on the smaller system will be done manually. On-line sensors on the large system will preclude sampling except at treatment end points.

Air emission calculations were performed on typical SRS PCS for benzene, toluene, ethyl-benzene, xylene, (BTEX) and total petroleum hydrocarbons (TPH). Assuming all of the species were transferred to the gas phase the gas phase concentrations of BTEX and TPH was estimated at 6 ppm BTEX and 122 ppm TPH for the large scale system and 1.1 ppm BTEX and 550 ppm TPH for a gasoline spill using the smaller system. The mass of of BTEX emitted will not exceed SCDHEC guidelines. This information was included in the CAP sent to SCDHEC.

Nutrient additions will include standard agricultural fertilizers with adjustments made depending upon the nutrient content of the soil. Surfactants may also be used for heavily aged or weathered samples. If anaerobic degradation is performed a nonhazardous carbon source such as molasses may be used.

NATIONAL ENVIRONMENTAL POLICY ACT (NEPA)
CHECKLIST

EEC No. SW - E - 2000 - 011
Rev No. 0

Questions to Answer: *An EEC is required to be submitted, evaluated, and approved for all proposed site actions and projects that have the potential to:

1. result in a change in emissions, generation rates, or new discharge of hazardous, mixed, radioactive, asbestos, PCB, sanitary/industrial (solid or liquid waste, petroleum substance, wastewater, or any other pollutants from a facility or process. ... ◉ yes ○ no
2. be located outside of a previously developed area ... ○ yes ◉ no
3. involve siting, construction, modification, renovation, closure or D&D of facilities or processes ... ○ yes ◉ no
4. potentially affect environmentally sensitive areas/resources such as floodplain/wetlands, archeologically or historically significant areas, threatened or endangered species, and / or their habitat, special water sources (e.g, aquifers) ... ○ yes ◉ no
5. involve site characterization, environmental monitoring, or R&D programs ... ○ yes ◉ no
6. involve any type of land disturbance, underground storage tank (UST), or subsurface injection/extraction ... ○ yes ◉ no
7. involve a Site Evaluation (SE) area, RCRA/CERCLA area/facility, or associated 200 ft. Buffer Zone ... ○ yes ○ no

***Note:** **- If any unknown, call Department NEPA Coordinator (DNC) or ECA for consultation.**
- Consult with DNC to verify; file with project & complete PERMITS CHECKLIST.
- If any are "Yes", complete rest of NEPA CHECKLIST & the PERMITS CHECKLIST.

Environmental Impacts Evaluation: (Note: If any are "Yes", provide specifics/supplemental information.)

Air
- Will there be a new air emission or a change in the quantity or quality of an existing air emission? ... ◉ yes ○ no

Surface Water
- Will there be a liquid release to streams, swamps, wetlands, seepage basins, storm drains, process sewers, ponds, or lakes? ... ○ yes ◉ no
- Will river or stream water be utilized? ... ○ yes ◉ no

Groundwater
- Will there be a discharge to subsurface/groundwater? ... ○ yes ◉ no
- Will groundwater be utilized? ... ○ yes ◉ no

Safety
- Is there a potential exposure to hazardous substances (e.g., radiological/toxic/chemical materials)? ... ◉ yes ○ no
- Is there a potential for explosion or criticality? ... ○ yes ◉ no
- Does action involve transportation of hazardous materials? ... ○ yes ◉ no

Natural/Cultural Resources
- Is there a potential for impacts on wetlands, swamps, streams, river beds, ponds, set aside areas? ... ○ yes ◉ no
- Is there a potential impact on fish/wildlife resources or habitats? ... ○ yes ◉ no
- Is there a potential impact on protected species (e.g., sensitive, rare, threatened, endangered)? ... ○ yes ◉ no
- Is there a potential for impacting archaeological and historical sites? ... ○ yes ◉ no
- Does this action require a site use/site clearance permit? ... ○ yes ◉ no

For Department NEPA Coordinator and Site NEPA Coordinator Use Only (NEPA Recommendation)
- Are there potential cumulative effects when combined with other actions? ... ○ yes ◉ no
- Is the proposed activity a component of a larger line item project? _____ (doc. title/number) ○ yes ◉ no

☒ CX applied for by DNC (Must meet all requirements of 10 CFR 1021.410(b)): B6.1 (a)

☐ Covered by previous NEPA Documentation (CX, EA, EIS):
EA - State specific EA _____ (document title) _____ (document number)
EIS - State specific section of EIS and ROD

☐ Additional NEPA Documentation Required: ☐ EA ☐ EIS ☐ SA ☐ Revised ROD ☐ Revised FONSI ☐ EE/CA

J. R. Brookshire — 2/13/2001 Date
DNC: J. R. Brookshire 2-2266

Greg Peterson — 2/13/2001 Date
SNC: Greg Peterson 5-5230

For DOE NEPA Compliance Officer Use Only (NEPA Determination)
For categorical exclusions: Based on my review of information conveyed to me and in my possession as NEPA Compliance Officer (as authorized under DOE Order 451.1B), I have determined that the proposed action fits within the specific class of action at 10 CFR 1021. For classes of actions listed in Appendix B, the proposal does not:
A. Threaten a violation of applicable statutory, regulatory, or permit requirements for environment, safety, and health, including DOE and/or Executive Orders;
B. Require siting, construction, or major expansion of waste storage, disposal, recovery, or treatment facilities, but may include such categorically excluded facilities;
C. Disturb hazardous substances, pollutants, contaminants, or CERCLA-excluded petroleum and natural gas products that pre-exist in the environment such that there would be uncontrolled or unpermitted releases; or
D. Adversely affect environmentally sensitive resources (including but not limited to those listed in 10 CFR 1021.410 paragraph B.(4)).

☒ Approved ☐ Approved w/ Comments ☐ Not Approved - Alternate NEPA Action Required: _____

2/14/2001 Date
Andrew R. Grainger, NCO 2-8001

ENVIRONMENTAL PERMITS
CHECKLIST

EEC No. SW - E - 2000 - 011
Rev No. 0

General:

Does this activity involve any land disturbance which may potentially result in erosion or sedimentation? (If "yes", what is the approximate disturbance?) ○ yes ◉ no

☐ Less than 1/2 acre ☐ 1/2 acre to 1 acre ☐ 1 to 2 acres ☐ Greater than 2 acres

Will the proposed activity install, modify, or remove an (including tie-in to) Underground Storage Tank? ○ yes ◉ no

Will the proposed activity consist of a Renovation or Demolition to an existing building/structure? ○ yes ◉ no

(Please specify): ☐ Renovation ☐ Demolition

Is asbestos containing material present? ☐ yes ☐ no

*If "no", inspector signature and license number required:

Inspector Signature: _____ License Number: _____

Date:

Will you import or manufacture a new chemical substance? ○ yes ◉ no

Will the proposed activity impact a Site Evaluation Area or RCRA/CERCLA Area or an associated 200 ft Buffer Zone? ○ yes ◉ no

Will the proposed activity involve construction or modification, or to a facility or process where the potential exists for a radioactive emission? ◉ yes ○ no

Will pesticides / herbicides be applied? ○ yes ○ no

Air:

Will the proposed activity impact a non-radionuclide air emission source? (answer "yes" if any of the following are "yes") ○ yes ◉ no

- Will the project install or modify a piece of equipment which will emit, or have the potential to emit, an air emission?
- Will the project modify (including demolition) an existing permitted facility or process, which emits an air emission?
- Will the project modify (including demolition) an existing facility or process, not already permitted by SCDHEC, which emits, or has the potential to emit an air emission?
- Will the project be a demonstration (short term or long term) of a new technology which will emit an air emission?
- Will the project install or modify a piece of equipment that is used to sample or monitor air emissions?

Air emissions include regulated criteria pollutants (i.e., particulate matter, lead, nitrogen oxides, carbon monoxide, sulfur dioxide, volatile organic compounds (VOC's), etc.) and hazardous and toxic pollutants identified in SCDHEC R.61-62.5 Standard 8 and Section 112(b) of the Clean Air Act.

Examples of typical permitted equipment or process air emission sources include, but are not limited to the following:

- coal or fuel oil fired boilers
- diesel generators
- diesel powered equipment
- process feed chemical storage tanks
- fuel oil storage tanks
- waste combustion incinerators
- paint booths
- lead melters
- air strippers, etc.
- degreasing operations
- HVAC and chiller equipment

Groundwater:

Will the proposed activity: (See "HOW" Manual WSRC-IM-91-69 for permitting guidance)

Install a monitoring well, abandonment of a well, or piezometer(s)? ○ yes ◉ no

Involve subsurface penetration for a hydrogeological investigation, geotechnical data collection, or characterization? ○ yes ◉ no

Involve the injection of a fluid, gas, or air mixture into the subsurface? ○ yes ◉ no

Involve the extraction of a fluid or air mixture from the subsurface? ○ yes ◉ no

Wastewater: (See "HOW" Manual WSRC-IM-91-69 for permitting guidance)

Will the proposed activity install, construct, modify, demolish, or impact:

A sanitary/industrial process wastewater treatment system? ○ yes ◉ no

A sanitary/industrial process wastewater collection system? ○ yes ◉ no

A pump station(s) to transfer sanitary/industrial waste? ○ yes ◉ no

A septic tank/tile field system? ○ yes ◉ no

A stormwater management system? ○ yes ◉ no

Domestic Water:

Will the proposed activity install, construct, modify, or demolish:

A domestic water distribution/treatment system? ○ yes ◉ no

A domestic or process water well? ○ yes ◉ no

ENVIRONMENTAL PERMITS
CHECKLIST (cont.)

EEC No. SW - E - 2000 - 011
Rev No. 0

Wastes:

Will the proposed activity install, construct, modify, demolish, close, or otherwise impact a RCRA permitted facility? ○ yes ◉ no

Will the proposed activity generate a mixed waste? ○ yes ◉ no

If "yes", does a wastestream with similar characteristics currently exist at SRS? (Consult with Facility Environmental Coordinator if assistance is needed) ☐ yes ☐ no

Will the proposed activity generate a hazardous waste? ○ yes ◉ no

Will you be sending hazardous/mixed waste to other on-site Treatment/Storage/Disposal (TSD) facilities? ○ yes ◉ no

Is the TSD permitted to accept this waste? ○ yes ◉ no

(If "yes", provide the following)

- name of receiving facility: _____
- source used to confirm facility can accept waste: _____

Is this activity to take place at an existing TSD (including groundwater unit, vadose zone, process sewer, Carolina Bay, secondary containment system, etc.)? ○ yes ◉ no

Would this activity impact an existing TSD (including changing or improving stormwater runoff/runon drainage, security, communications, electrical, etc.)? ○ yes ◉ no

Does this activity involve Research and Development (R&D)? ◉ yes ○ no

(If "yes", answer the following)

- Does it involve hazardous/mixed waste? ☐ yes ☒ no
- Does it treat more than 1,000 kg of hazardous waste? ☐ yes ☒ no
- Does it involve polychlorinated biphenyls (PCBs)? ☐ yes ☒ no
- Will this activity continue for more than 30 days? ☒ yes ☐ no
- Will more than 250 kg of hazardous waste be introduced into treatment in a single day? ☐ yes ☒ no
- Does it treat more than 500 kg of soil, water, or debris contaminated with acute hazardous or 1kg of acute hazardous waste? ☐ yes ☒ no
- Does it involve the placement of hazardous waste on the land or open burning of hazardous waste? ☐ yes ☒ no

Waste Identification, Generation and Management:

Will the proposed activity include the purchase of lead or lead components? (If "yes", complete OSR 29-6 for each item and submit with Checklist) ○ yes ◉ no

Will the proposed activity disturb soil, sludge or water at or near a RCRA/CERCLA Unit or Site Evaluation Area? ○ yes ◉ no

If "yes", were any listed wastes disposed of at this facility? (Consult with Facility EC if assistance is needed) ○ yes ○ no

If "yes", please contact EPD for guidance regarding the Investigation-Derived Waste Management Plan.

Does this activity result in a new liquid and/or solid waste generation (one-time or continuous), or a change in the quantity or the characteristic of an existing waste stream? If "yes" check all that apply: ◉ yes ○ no

☐ TRU	☐ Hazardous	☐ TSCA (PCB)
☐ Mixed - Covered by LDR FFCA	☐ Suspect Hazardous	☐ Wastewater
☒ Low-Level	☐ Sanitary/Industrial	☐ Acute Hazardous
☐ High-Level	☐ Used/Waste Oil	☐ Other...(specify)

Where will waste be stored/disposed/treated? Slit Trench

Is the facility permitted to manage this waste? ○ yes ◉ no

If "yes", complete the following items and submit with the Checklist

- ☐ Source utilized to confirm facility is permitted to accept the waste.
- ☐ Description of generated waste.
- ☐ Dates generation is to begin/end.
- ☐ Estimate of waste generation rate for each category.
- ☐ Description of activity/process generating waste.
- ☐ Description of waste reduction principles (reducing the volume, mass, or toxicity) for this activity.

Has the proposed activity been evaluated for waste minimization/pollution prevention? ◉ yes ○ no

For Department ECA use only:

J. R. Brookshire
2/13/2001
Date

APPENDIX C

CONSTRUCTION AND DESIGN DOCUMENTS

WESTINGHOUSE SAVANNAH RIVER COMPANY

INTEROFFICE MEMORANDUM

August 20, 2001 SRT-EST-2001-0000148

To: Tom McCoy

From: C. J. (Topher)Berry

Subject: Construction of a Petroleum and Radiological Contaminated Soil Bioreactor

Enclosed is information to be used in estimating construction of a six cubic yard b ioreactor that will be used to treat petroleum-contaminated soil. This system was designed to use easily accessible equipment to treat contaminated soils cheaply. The skid (skip) pan will be provided by EBS. The unit will be shipped from Greenwood, SC on August 23, 2001 and the unit should arrive at SRTC on August 27, 2001. A schematic drawing of this unit is attached. To treat contaminated soil the following skip pan modifications are required.

- The top portion of the skid will require grinding.
- Access ports need to be cut and fitted with bulkhead connections. Three of the ports will require a welded NPT nipple.
- Expanded metal grating needs installed.
- A cover with an access port an effluent air port and clamps needs fabricated
- A corrosion sealant needs to be applied inside the system.
- The air distribution system needs to be constructed and installed
- The leachate distribution system needs to be installed.
- A housing for pumps and flow meters needs to be fabricated

The skip pan needs to be water tight below the grating and the top lid will require grinding so a cover can be placed on top of the unit. I have provided pictures of an existing skip-pan, Figures 1-3, and pictures of a similar system being fabricated in Poland, Figures 4-7. I have also taken pictures of the pumps we will be using with the system, Figure 8. A housing unit with a weather protective, not enclosed, cover needs to be constructed for this equipment. I have also provided, as an attachment, a series of developmental drawings with specifications about system construction. Some of the process flow information included in the drawings is not applicable to construction of the unit and some of the specific construction details are not shown.

For additional questions please do not hesitate to contact me, 7-7224 or beeper 12215, at any time.

Attachments:
- 3 each - Petroleum Contaminated Soil Bioreactor, SRS Development Drawing EST-BT-98-001, Revision E Sheets 1-10.
- 3 each - 6 Cubic Yard Skip Pan Drawing – 3 sheets

C: w/o Att. M. A. Heitkamp, 704-8T
D. J. Altman, 704-8T
J. Malanowski, 773-42A

Figure 1. Wide View of Existing 6 yd³ Skid-Pan

An existing 6-yd³ skip-pan with tape markings for inlet, outlet and data acquisition ports. The system requires an air distribution system placed on the bottom of the skid pan. An expanded metal grating, galvanized carbon or stainless steel, should be placed 9" above the base of the skid with supports. This grating will hold contaminated soil. A liner will be placed on top of the grating for containment. EBS will provide the liner but will need input on grating procurement. The system needs to be water tight below the grating. A one-piece removable cover is required with one access port (2' x 2') and an effluent air connection. The cover will need a gasket and clamping or screws to attach it to the skip-pan. The system will operate at negative pressure so an absolute seal between the lid and skid-pan is not required and standard (cheaper) gasket material can be used. The system cover material needs to be cost effective but still manageable (not too heavy). Aluminum is recommended for fabricating the cover but other cost effective and cheap materials are acceptable. EBS will obtain these materials with input from EES.

Figure 2. Corner Detail of Existing SRS Skip-pan

Close up view of the skid pan lip. Grinding will be required around the top of the unit. The lip could be used to clamp the lid to the unit. The lip is 4" in height.

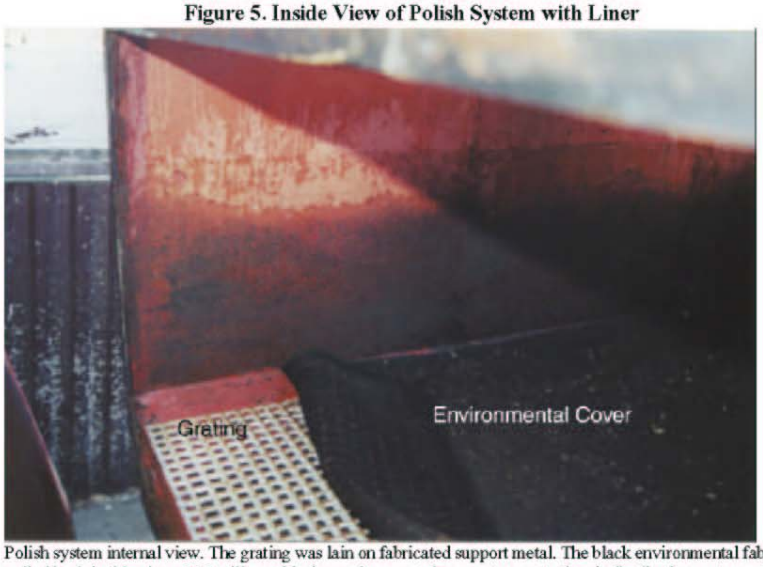
Figure 3. Detail of Required Lifting Nut on SRS Skid Pan

Close up of the lifting lugs and a typical location of a data acquisition port. Exact location of the data acquisition can be changed if to the work area is difficult.

Figure 4. Polish System Grating Installation

Grating was placed on welded metal supports.

Figure 5. Inside View of Polish System with Liner

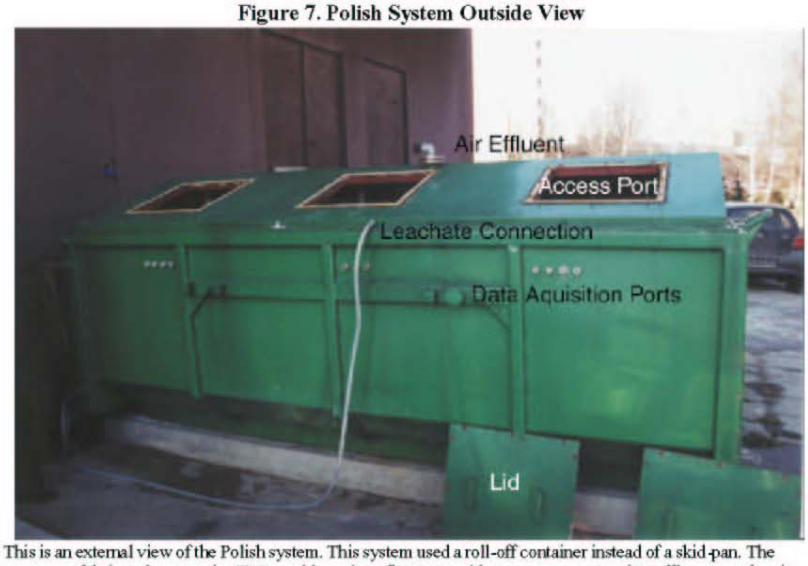


Polish system internal view. The grating was lain on fabricated support metal. The black environmental fabric is pulled back in this view. SRS will provide the environmental cover. Access to the air distribution system, placed below the grating is required for the EBS system. However, the entire unit will be upended when emptied so the grates must also be fastened to the skip pan.

Figure 6. Inside Ceiling View of Polish System

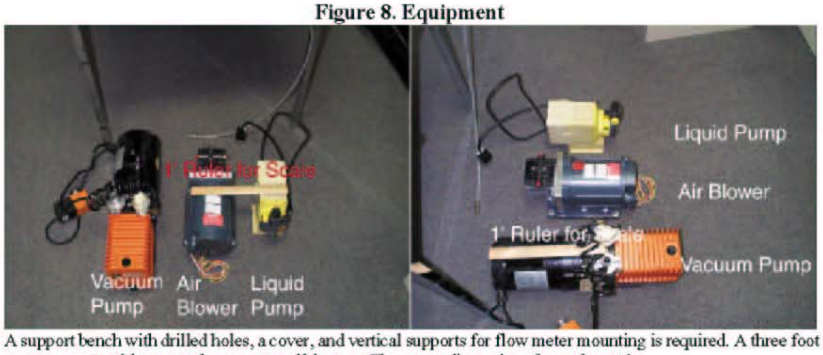
Note the data acquisition ports on the inside wall.

Figure 7. Polish System Outside View



This is an external view of the Polish system. This system used a roll-off container instead of a skid-pan. The cover was fabricated separately. SRS would require a flat cover with one access port and an effluent port for air similar to the one shown. The tubing entering the system is typical of SRS requirements as are the data acquisition ports shown as a group of four in the picture.

Figure 8. Equipment



A support bench with drilled holes, a cover, and vertical supports for flow meter mounting is required. A three foot square area would support the pumps and blowers. The screw dimensions for each part is:

- Air Pump – 4 ½" x 3 ¾"
- Liquid Pump – 8 ¼" x 6"
- Vacuum Pump –9" x 4"
- Flow Meter 2 ½" square by 8" Height.

WESTINGHOUSE SAVANNAH RIVER COMPANY

INTEROFFICE MEMORANDUM

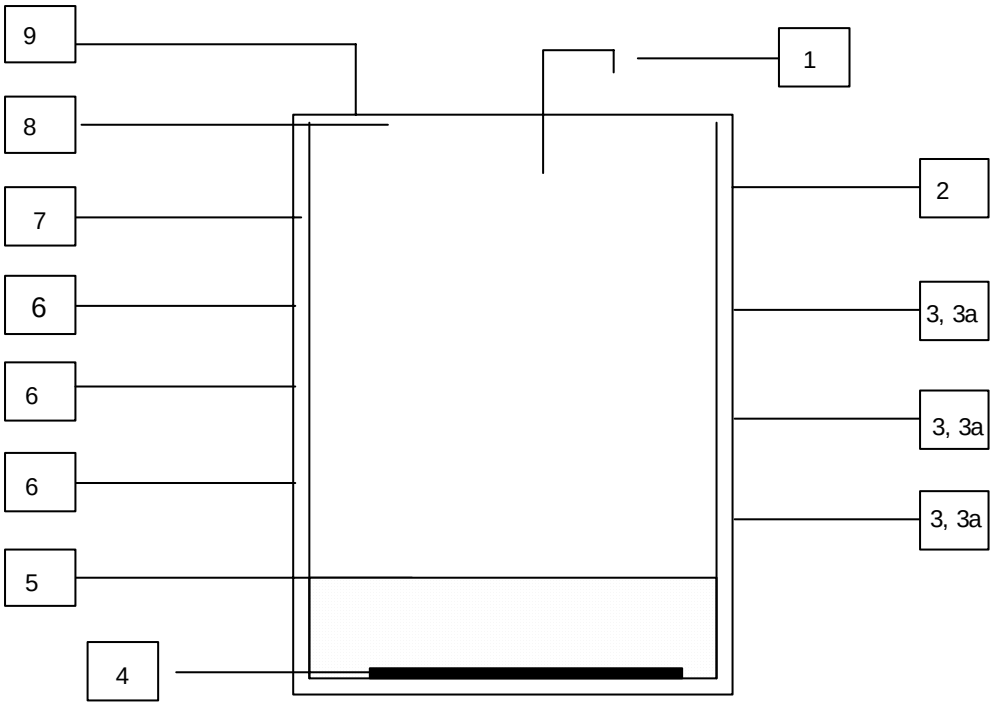
September 3, 2001

From: Topher Berry, 7-7224, Bpr 12215

Subject: PCSB Fabrication Notes.

1. Cut holes for Instrument Ports: Cut or burn holes for nipple liners, see page 7 of design package.
2. Weld nipples to Skip-pan. Requires SS to CS welding rod.
3. Cut carbon steel for grating support. See page 8 for details. Grating support is 9" above skip-pan bottom.
4. Drill holes for grating clamps.
5. Weld carbon steel to system.
6. Fabricate aeration system, see page 8 of design package.
7. Set up PVC tubing in Hatch design, cross cut with hand saw and glue.
8. Install aeration system.
9. Install grating.
10. Fabricate system lid. See Page 10 of design package.
11. Install gasket material around lip of the skid-pan.
12. Fabricate weather cover for three pumps and a flow meter.

6 CU. YD. BIOREACTOR (SYS 1)



UNITED STATES DEPARTMENT OF ENERGY			
SAVANNAH RIVER SITE			
SCALE NTS	SRS DEVELOPMENT DRAWING NO. EST-BT-2001-001	SHEET NO. 1 OF 10	LATEST REVISION E

6 CUBIC YARD BIOREACTOR (SYS 1)

ITEM	QTY	TITLE	DESCRIPTION	NOTE
1	1	HEPA Effluent	HEPA Filter with Connections	1
2	1	Skip Pan, 6 CU. YD.	6 yd^3 or approved equal	2
3, 3a	6	Rear Sensor Ports	3-3/4" &3-1/2" NPT Nipple Welded Ports	3
6				
4	1	Aeration Tube	3/4" PVC, slot cut, glued, T or Hatch design	4
5	1	Grate	Expd metal & TEX-NET Ultra TN3001CN-1260	5, 8
6	6	Front Sensor Ports	1/2" Holes with Plastic bulkhead Ports	10
7	1	Corrosion Protection	Rhino Liner or similiar approved equal	7
8	1	Liquid Distrubution	Drip irrigation garden hose with appropriate connectors	11
9	1	Cover	Aluminum Cover	9

NOTES:

1. Bought fr Flandres Filters Inc. 252-946-8081 EBS will provide HEPA Filter housings, See Sheet 4.
2. EBS will supply.
3. Three elevations used for access ports on front and back of skid pan 3@3/4" and 3@1/2" NPT. See Sheet 7 for location detail.
4. See Sheet 4 and 8 for location detail.
5. EES will provide liner.
6. Carbon Steel Nipple acceptable.
7. Sealant req. for corrosion protection
8. EXpd metal with support and geofabirc liner. See Sheet 9 for detail.
9. Fr Aluminum sheet, Fabricate to fit item 2. Removable using clamps. See One piece with support Nipple required for gas effluent and one access door 2'x 2' required for system access. See sheet 10 for detail
10. 1/2" Holes required to support bulkhead fittings - PVC Bulkhead Fitting FPT x FPT with EPDM Gasket, Loose or approved equal.
11. See Sheets 5 and 6 for detail.

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SAVANNAH RIVER SITE

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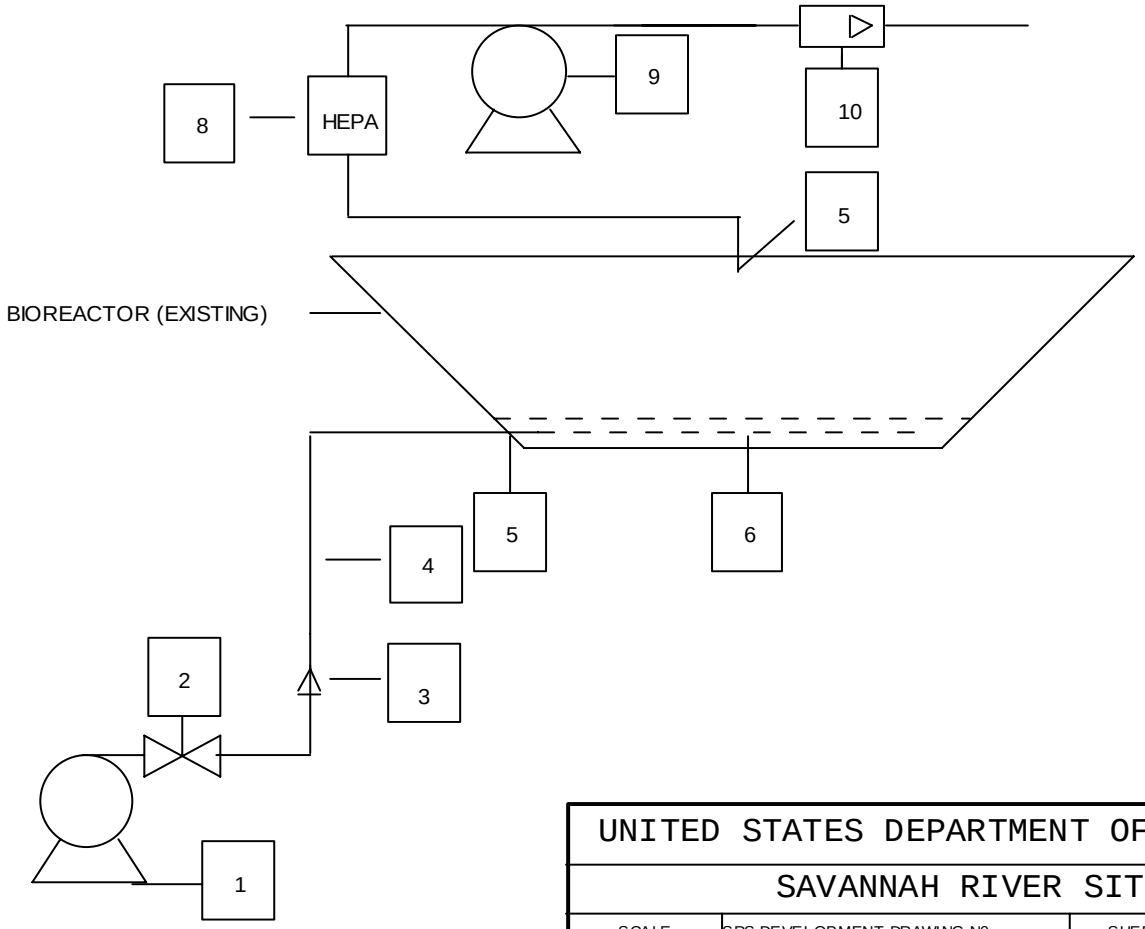
6 CUBIC YARD BIOREACTOR AERATION SYSTEM (SYS 2)



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SAVANNAH RIVER SITE			
SCALE NTS	SRS DEVELOPMENT DRAWING NO. EST-BT-2001-001	SHEET NO. 3 OF 10	LATEST REVISION E

6 CUBIC YARD BIOREACTOR AERATION SYSTEM(SYS 2)

ITEM	QTY	TITLE	DESCRIPTION	NOTE
1	1	Compressor	1/3 hp Rotary Vane , P/ N AQ3 or equivalent	1
2	1	Three way w/Valve	3/4" PVC Ball valve with 3-way T connector or equivalent	1
3	1	Check Valve	3/4 IN., 150 LB., SOCKET ENDS PVC or equal.	1
4	as req.	Tubing	3/4" ID. PVC, Nylobrade, Reinforced.	2, 8
5	2	Bulkhead Connection	3/4" Bulkhead Fitting	3,5
6	1	Aeration Tube	3/4" PVC, slot cut, glued, T or Hatch design	4
7	1	HEPA Filter Unit	Flanders0007D0XN2NU1200Z98084B or Eq.	7
8	1	Vacuum Pump	1/2 HP Vacuum Pump	1, 9
9	1	Flow Meter	Compact Shielded Rotometer, Brooks R-8M-75-1	1, 6

NOTES:

1. Provided by EBS
2. NewAge Industries Phone: 800-506-3924 or 215-526-2300 NewAge P/N 100-0923-100 or equal. EBS will supply.
3. Bulkhead connection detail on sheet 7.
4. PVC sch 40 or 80 piping to fit biorx. base man. cut slotted crosslength facing up with open ends capped. See Detail sheet 8
5. Bulkhead fitting PVC or approved equal. to fit 3/4" tubing for item 4 and 6.
6. Requires vertical mount with 3/4" female NPT connection to 3/4" tubing - Item 4.
7. Low volume HEPA filter housing required to connect to 3/4" tubing. EBS will provide one of the following Flanders filters: 0007D0X00NU1200Z98084B, 007d42N2NU1213Z99086, 0007W0X00NU1300Z92172C, 0007D42N1NU1213Z99086 or 0007D03R2NU1323BU5.
8. Clamps required. SS worm gear clamps or equivalent.
9. Equipped with metal barb type 3/4" connections.

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SAVANNAH RIVER SITE

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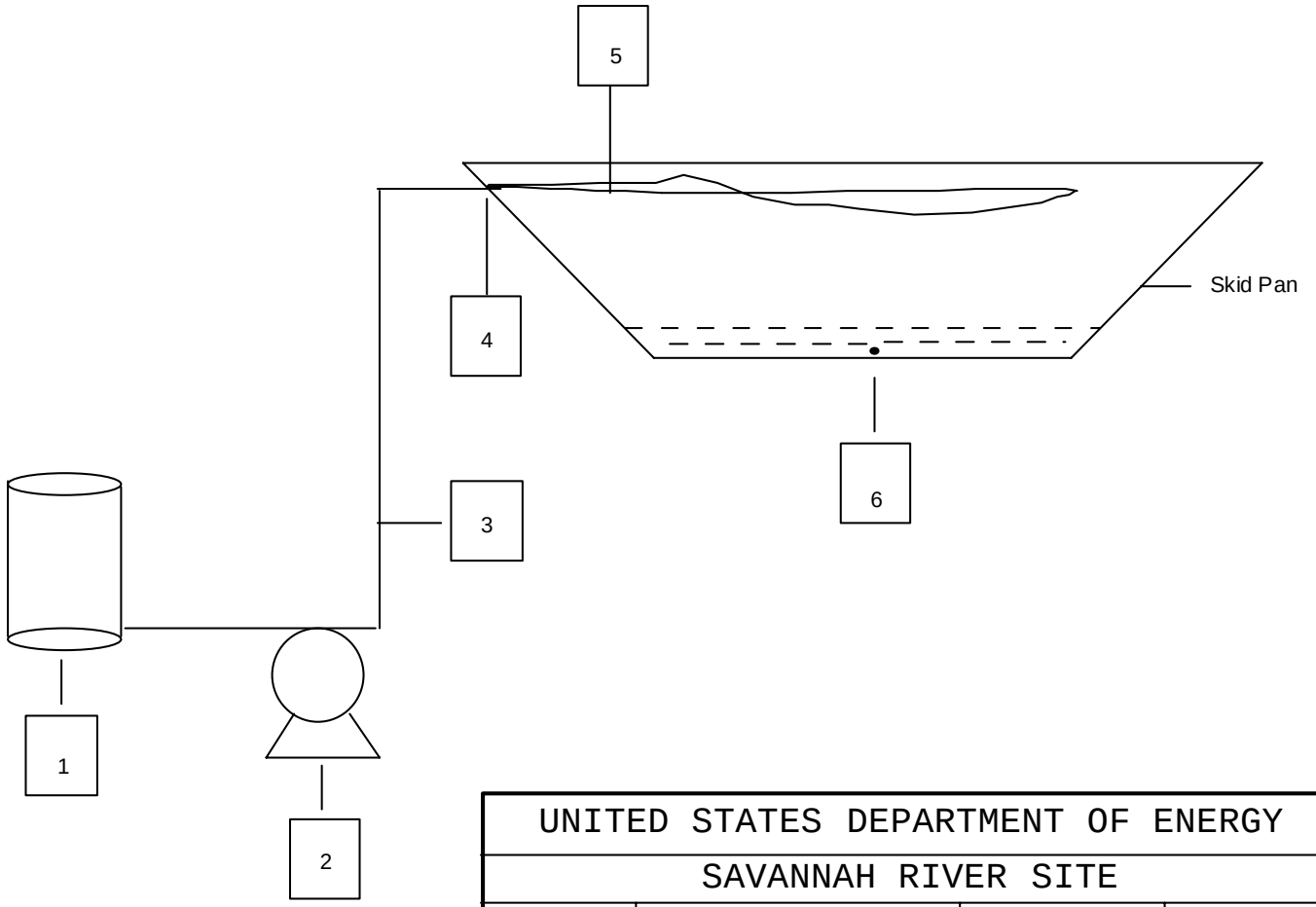
6 CUBIC YARD BIOREACTOR LEACHATE SYSTEM(SYS 3)



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SAVANNAH RIVER SITE			
SCALE NTS	SRS DEVELOPMENT DRAWING NO. EST-BT-2001-001	SHEET NO. 5 OF 10	LATEST REVISION E

6 CUBIC YARD BIOREACTOR (SYS 1)

ITEM	QTY	TITLE	DESCRIPTION	NOTE
1	1	HEPA Filter	0-007-D-43-R1-NU-14-22-B	9
2	1	BIOREACTOR, 6 CU. YD.	Fr Skid Pan CSWE Dwg FDD No. S5094 or eq.	1
3	3	Thermocouple	P/N 1T327 or eq.	6
4	3	Hydrocarbon Sensor	P/N ADS201-25 or eq.	2, 7
5	1	Moisture Sensor	Model GB-1, graphite block type or eq.	3, 5
6	1	Gravel	As required, (optional item)	
7	1	Grate	Expd metal (opt) & TEX-NET Ultra TN3001CN-1260	8, 10
8	3	Oxygen Sensor	P/N Xt253-25 or eq.	2, 4
9	4	Extra Sensor Ports	Additional connections, sealable, for add. sensors	
10	1	Coating	Rhino Guard or eq.	12
11	1	Cover		1, 13

NOTES:

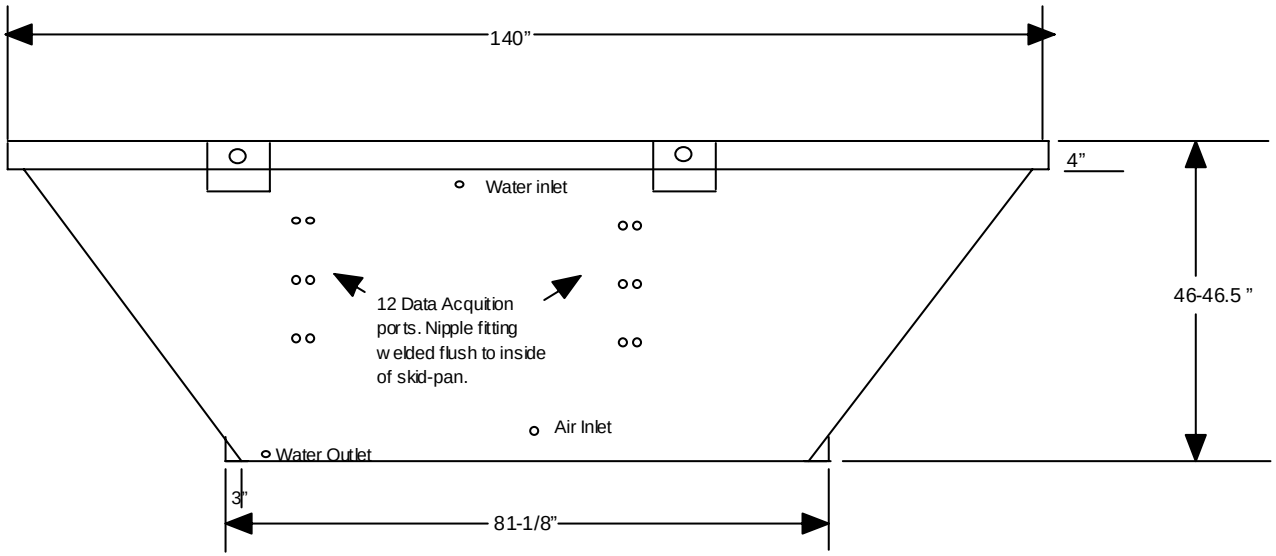
1 Supplied by EBS
2 Bought fr DataWrite Research Co 800-739-1003
3 Bought fr Forestry Supplies Inc. 800-647-5368
4 Requires 02 meter P/N MT200-A or equal
5 Requires Delmhorst KS-DI Digintal Soil Moisture Tester or equal
6 Requires Thermocouple Thermometer p/n 3A025 or equal
7 Requires Hydrocarbon Micrologger p/n EAD100-E or equal
8 EXpd metal supplied at SRS. Cut to fit. Enironmental fabric cover supplied by EBS
9 Bought fr Flandres Filters Inc. 252-946-8081
10 Bought fr Fluid Systems, SC 864-949-2689 or eq cut to fit
11 Fr Aluminum sheet , Fabricate to fit items 1 and 9
12 Sealant req. for corrosion protection
13 Connection clamps required for attachment to skid pan

UNITED STATES DEPARTMENT OF ENERGY

SAVANNAH RIVER SITE

SCALE	SRS DEVELOPMENT DRAWING NO.	SHEET NO.	LATEST REVISION
NTS	EST-BT-2001-001	6 OF 10	E

Inlet and Outlet Port Locations



Notes: Water inlet, outlet and Air Inlet ports are nipple fittings, approximately 3/4” welded flush to skid-pan.
All fittings marked on system with tape.

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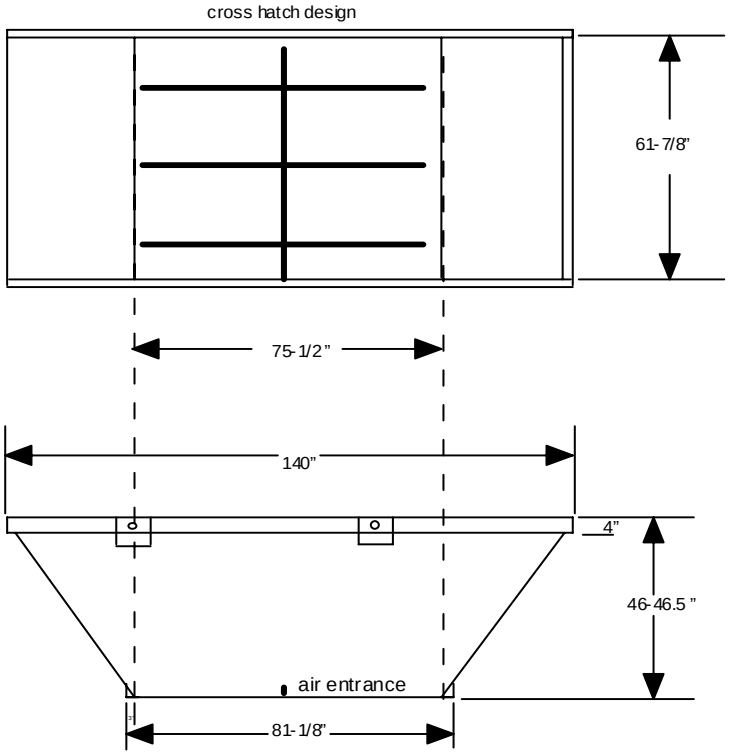
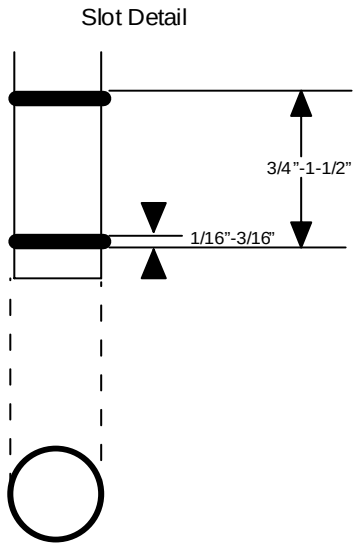
SCALE NTS	SRS DEVELOPMENT DRAWING NO. EST-BT-2001-001	SHEET NO. 7 OF 10	LATEST REVISION E

Aeration System Location and Detail





Notes:

Glued PVC piping arranged as above cut with saw or melted wire. Needs connection through bulkhead.

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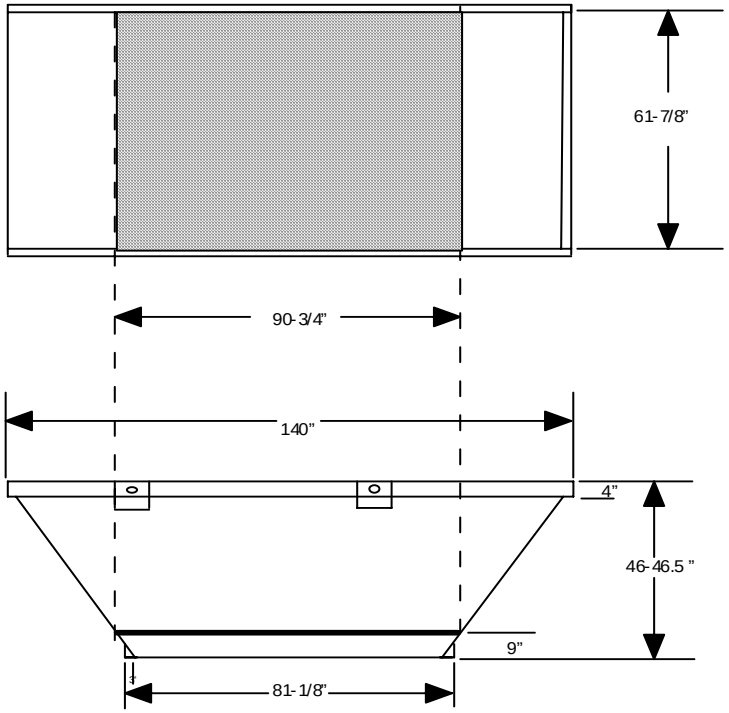
SAVANNAH RIVER SITE			
SCALE NTS	SRS DEVELOPMENT DRAWING NO. EST-BT-2001-001	SHEET NO. 8 OF 10	LATEST REVISION E

Grating Detail



Notes:
The grating will require carbon steel supports running approximately 90-3/4" across the length of the skid-pan and be removable, not welded, to gain access to the aeration system beneath.

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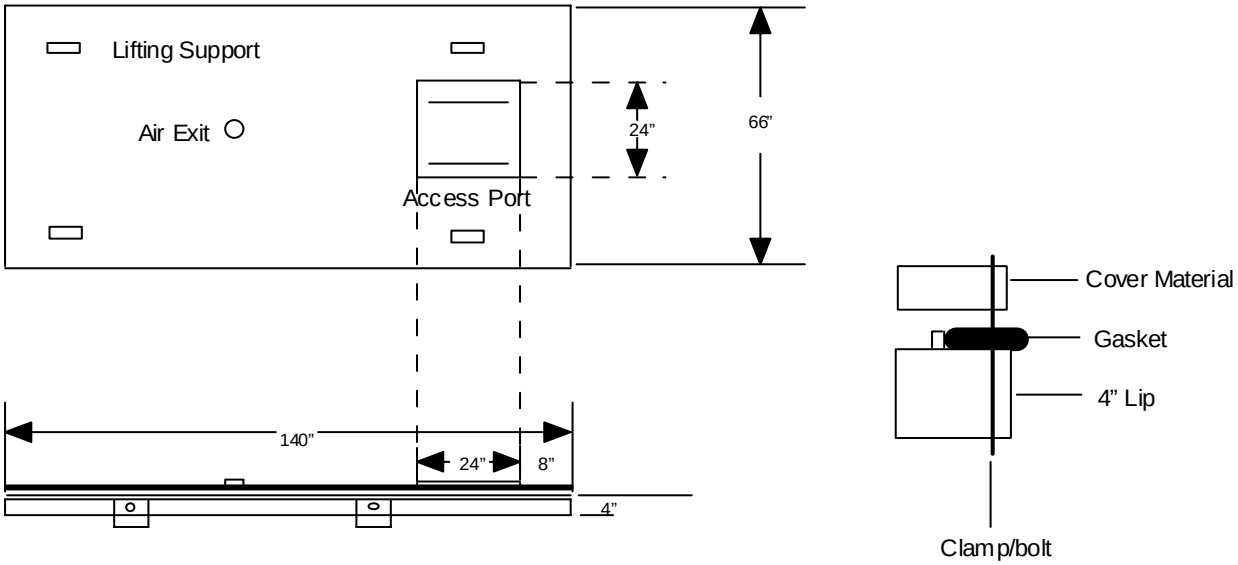
SAVANNAH RIVER SITE			
SCALE NTS	SRS DEVELOPMENT DRAWING NO. EST-BT-2001-001	SHEET NO. 9 OF 10	LATEST REVISION E

Cover Detail



Notes: The cover should be one piece with access port and air exit line. A gasket is required and clamps or bolts are required for closure. Aluminum 0.125” is recommended and may require bracing. Required Air vent 3/4” Aluminum Nipple. Lifting supports, four, are required.

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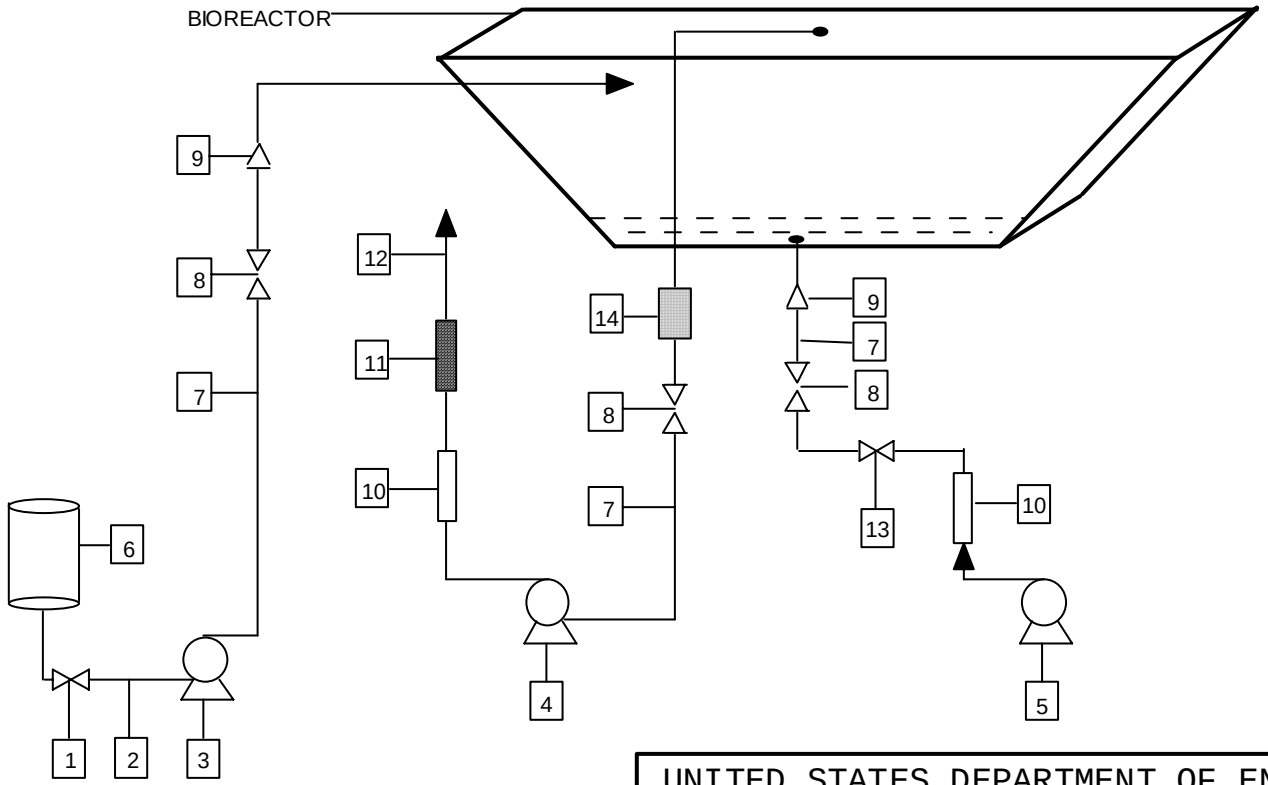
SCALE NTS	SRS DEVELOPMENT DRAWING NO. EST-BT-2001-001	SHEET NO. 10 OF 10	LATEST REVISION E

SRTC/SWD: Petroleum and Radiological Contaminates Soil
Bioreactor Flow Sheet



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SAVANNAH RIVER SITE			
SCALE	SRS DEVELOPMENT DRAWING NO.	SHEET NO.	LATEST REVISION
NTS	EST-BT-2002-001	1 OF 2	A

SRTC/SWD: Petroleum and Radiological Contaminates Soil Bioreactor Flow Sheet - Descriptions

ITEM	QTY	TITLE	DESCRIPTION	NOTE
1	1	Tank Valve	1/4" Swagelok valve connected to the Water/Nutrient Feed Tank	
2	as req.	1/4" SS Tubing	1/4" Swagelok tubing	
3	1	Liquid Pump	Chemcon	
4	1	Vacuum Pump	Oilless diaphram pump/compressor/vacuum 5.5 amps	
5	1	Air Pump/Compressor	Oilless diaphram pump/compressor/vacuum 3.5 amps	
6	1	Liquid Tank	Polyethlyene tank capacity 35 gallons	
7	as req.	Plastic Tubing	1/2" Nalibrated clear PVC tubing	
8	3	Quick Disconnect Valve	3/4" SS quick disconnect with dry ends	
9	2	Check Valve	1/2" check valve activation pressure 1 psi	
10	2	Flowmeter	Verticle mounted 0-5 CFM	
11	1	Carbon Trap	Activated Carbon trap with Thermal desorption tube connnections	
12	as req.	Effluent Tubing	1/2" Nalibrated tubing run to outside of the vault	
13	1	Gas Valve	1/2" needle valve for gas inlet flow control	
14	1	HEPA Filter	Flandres Nuclear grade rated up to 15 CFM	

UNITED STATES DEPARTMENT OF ENERGY

SAVANNAH RIVER SITE

SCALE	SRS DEVELOPMENT DRAWING NO.	SHEET NO.	LATEST REVISION
NTS	EST-BT-2002-001	2 OF 2	A

APPENDIX D

PRCS FINAL ACCEPTANCE SOIL ANALYSIS

CHAIN-OF-CUSTODY

04164

Contract Number AC23324N

Customer Name: Cole, David
Customer Department: SWO
Customer Address: 724-20E
Customer Phone/Beeper: 2-2524 14731

JK

Ship to: Company: Accura Analytical Laboratory
Address: 6017 Financial Drive, Norcross, GA 30071
Attention: David Fuller

Westinghouse Savannah River Company
Aiken, SC 29808

COC creation date. 4/8/04

Environmental Monitoring Section
Environmental Geochemistry Group

Matrix: S=Soil,SO=Solid,SL=Sludge,O=Organic,A=Aqueous, SM=Smear

Sample Analysis Requested

Sample Analysis Requested	Sample ID: 04164BIC-01	Sample ID:	Sample ID:	Sample ID:	Sample ID:	Sample ID:
	Collect Date 4/21/04	Collect Date	Collect Date	Collect Date	Collect Date	Collect Date
	Collect Time 1000	Collect Time	Collect Time	Collect Time	Collect Time	Collect Time
	No. Containers 1	No. Containers	No. Containers	No. Containers	No. Containers	No. Containers
	Matrix Soil	Matrix	Matrix	Matrix	Matrix	Matrix
TPH by GC FID (Diesel Range Organics) (37)	✓					

28 Day TAT

STR Authorization Larry DeWitt

1 Relinquished by:	Date/Time	Received by:	2 Relinquished by:	Date/Time	Received by:
(Print) Tom Arnold	Date 4/21/04	(Print) CJS	(Print) AAA Cooper Transport	Date 04/26/04	(Print) David Fuller
(Sign) Tom Arnold	Time 1300	(Sign) Shipping 4/21/04	(Sign)	Time 14:15	(Sign) David C Fuller
3 Relinquished by:	Date/Time	Received by:	**4** Relinquished by:	Date/Time	Received by:
(Print)		(Print)	(Print)		(Print)
(Sign)	Time	(Sign)	(Sign)	Time	(Sign)

ACCURA ANALYTICAL LABORATORY, INC
A Multi-Service Corporation.
6017 Financial Drive, Norcross, Georgia 30071, 770-449-8800 (ph), 770-449-5477 (fax)

CASE NARRATIVE REPORT
for
Westinghouse Savannah River Site
Subcontract No. AC23324N
WSRC Job #: 04164
AAL WO #: 6039

Date: 05/19/04

Laboratory Identification: Accura Analytical Laboratory, Inc.

Summary:

Sample Receipt:
One Soil sample from the Westinghouse Savannah River Site arrived at Accura Analytical Laboratory, Inc. on April 26, 2004 for analysis. The sample listed on the chain arrived to the laboratory via AAA Cooper Transport. A twenty eight -day turnaround was requested on the chain of custody.

The sample was stored properly according to SW-846 procedures and Laboratory Standard Operating Procedures (SOP).

The laboratory received the following sample:

Description	Sample Number	Matrix
04164B10-01	6039-001	Soil

Case Narrative
Sample analyses were conducted using methodology as outlined in Accura Analytical Laboratory's Standard Operating Procedures. Any technical or administrative problems during analysis, data review, and reduction are written by analytical fraction in the enclosed narratives.

Data Package:
The enclosed data package contains the following sections: Case Narrative, Certificate of Analysis, Surrogate information, Quality Control Results, Sample Receipt Checklist, Chain of Custody, and Nonconformance Reports, if applicable.

The Certificate of Analysis contains the following headings:

Sample ID:	Sample Identification
Lab ID:	This is the laboratory identification number
Matrix:	Sample matrix
Date Collected:	Date of sample collection
Date Received:	Date of sample receipt by the laboratory

Priority:	NA
Collector:	Party responsible for sample collection

The detail on the Certificate includes the following:

Parameter:	Analyte or characteristic tested for in the sample
Qualifier:	Qualifier used for data interpretation
Result:	Final result for each parameter
DL:	Method Detection Limit (adjusted)
RL:	Reporting Limit (adjusted)
Units:	Units of final result
DF:	Dilution Factor
Analyst:	Initials of analyst who performed test
Date:	Date of analysis
Time:	Time of analysis
Batch:	Analytical batch in which the sample was analyzed
Method:	Analytical method used for the analysis of the sample. Identified on the report numerically with a corresponding table.
Surrogate Recovery:	Provided for organic analysis only. Surrogate compound identified.
Test:	Analytical test associated with surrogate compound.
Percent %:	Surrogate percent recovery
Acceptable Limits:	Limits established for surrogate recoveries based upon the method requirements.

The QC Summary Report contains the following headings:

Sample ID:	Analyte or characteristic tested for in the QC sample.
Batch:	Analytical batch in which the QC sample was analyzed
Spike Amt:	Nominal concentration of the spiking compound
Sample Result:	Amount of compound found in the sample associated with the QC sample.
__Result:	Amount of compound found in the QC sample
RPD:	Relative percent difference between LCS/LCS dup, MS/MSD, and/or Sample/Sample duplicate
__Recovery:	Recovery for the control samples
Reference Range:	Acceptance limits for control samples

Types of QC samples that may be found on the QC Summary Report and/or Certificate of Analysis are:

Blank:	Results of the blank analysis for the sample batch
Dup:	Duplicate analysis of sample
LCS:	Lab control sample
LCS dup:	Lab control sample duplicate

MS:	Matrix spike
MSD:	Matrix spike duplicate
PS:	Post-Digestion Spike
PSD:	Post-Digestion Spike Duplicate
SDILT:	Serial Dilution

The following are definitions of reporting limits used at Accura Analytical Laboratory:

DL — Detection Limit: The minimum level of an analyte that can be determined (identified not quantified) with 99% confidence. The values are normally achieved by preparing and analyzing seven aliquots of laboratory water spiked 1 to 5 times the estimated MDL, taking the standard deviation and multiplying it against the one-tailed t-statistic at 99%.

The detection limit is the minimum concentration of a substance that can be identified, measured, and reported with 99% confidence that the analyte concentration is above zero. It answers the question "Is it present".

QL — Quantitation Limit: The lowest concentration that can be reliably achieved within specified limits of precision and accuracy during routine laboratory operating conditions. The QL is generally 5 to 10 times the MDL. However, it may be nominally chosen within these guidelines to simplify data reporting. For many analytes the QL analyte concentration is selected as the slowest non-zero standard in the calibration curve. Sample QL's are highly matrix-dependent. Sample specific preparation and dilution factors are applied to these limits when they are reported.

The QL is always > DL

RL — Reporting Limit: Same as QL except where driven by contract or client specifications. If the sample specific preparation and dilution factors cause the QL to be elevated above the RL, then the QL is used as the RL.

The quantitation limit is the lowest level at which a chemical may be accurately and reproducibly quantitated. It answers the question "How much is present".

Interpretation of RESULT column on the Certificate of Analysis:

If the final concentration in the sample was found to be above the RL, then the value reported is reported without a flag;

If the final concentration in the sample was found to the below the RL but above the DL, then the value reported is flagged with a "J";

If the final concentration in the sample was found to be below the DL, the value reported

is flagged with a "U".

If the final concentration in the sample was found in the corresponding method blank, the value reported is flagged with a "B".

Quality Control Flags

Accura Analytical Laboratory maintains acceptance criteria for QC samples through use of statistical process control (SPC). The SPC limits are used to qualify data usability. The flagging criterion identified in WSRC AN98 Format does not necessarily coincide with the laboratory SPC criteria. There may be instances where the Electronic Data Deliverable (EDD) has flagged data based on the AN98 criteria and the lab has not identified the data to be outside of established control limits.

Those instances where the QC has not met laboratory SPC established criteria will be noted in the section case narratives that are included in this package.

This data package, to the best of my knowledge, is in compliance with technical and administrative requirements.

Larry M. Gwinn Jr.
Project Manager

ACCURA ANALYTICAL LABORATORY, INC
A Multi-Service Corporation.
6017 Financial Drive, Norcross, Georgia 30071, 770-449-8800 (ph), 770-449-5477 (fax)

Case Narrative for WSRC
Work Order # 6039
GC Semivolatile Organics

Sample Analysis

The following field sample and sample quality control analyses associated with this work order were prepared and analyzed for "Diesel Range Organics Compounds", according to the methods referenced in the "Method / Analysis Information" section of this narrative:

Client Sample ID	Laboratory ID
04164B10-01	6039-001

Semivolatile Organic Compounds	
18777 BLK (Blank)	Method Blank (MB)
16551 BKS (Blank Spike)	Laboratory Control Sample (LCS)
Retension Pond MS	Matrix Spike - 6041-001MS
Retension Pond MSD	Matrix Spike Duplicate - 6041-001MSD

Method/Analysis Information:

Analysis Batch:	21851
Prep Batch #:	18777
Procedure:	Diesel Range Organic Compounds (DRO) by Gas Chromatograph
Analytical Method:	SW846 8015 Mod
Prep Method:	SW846 3545

Preparation/Analytical Method Verification:
Procedures for preparation, analysis, and reporting of analytical data are documented by the laboratory as Standard Operating Procedures (SOP).

Calibration Information:
Initial Calibration
All the initial calibration requirements were met.

CVS Requirements
All the calibration verification standard (CVS) requirements were met.

Quality Control (QC) Information

Surrogate Recoveries
Surrogate recoveries, in all samples and quality control samples, were within the acceptance limits.

Blank Acceptance
The method blank(s) analyzed with this work order did not contain analytes of interest at concentrations greater than the reporting limit (RL).

LCS/LCSD Recovery Statement
The laboratory control sample recovery for all the analytes in this work order were within the acceptance limits.

QC Sample Designation
Sample "Retension Pond" from another client project was designated as the quality control samples for DRO batch.

The Batch QC included a laboratory control sample (LCS), matrix spike (MS) and matrix spike duplicate (MSD).

MS and MSD Recovery Statement
The percent recoveries (%R) obtained from the matrix spike (MS) and matrix spike duplicate (MSD) analyses are evaluated when the sample concentration is less than four times (4X) the spike concentration added. All applicable elements in the MS and MSD analyses met the established recovery acceptance.

MS/MSD RPD Statement
The relative percent differences (RPD) between the matrix spike and matrix spike duplicate recoveries were outside the quality control limits.

Client Sample ID	Analysis	Lab Sample ID	Analytes	Reason
Retension Pond	DRO	6041-001 MS/MSD	DRO	Sample heterogeneity.

Technical Information

Holding Time Specifications
All the samples were prepared and/or analyzed within the required holding time period.

Sample Preservation and Integrity
Sample integrity was met for all the samples in this work order.

Preparation/Analytical Method Verification
All procedures were performed as stated in the SOPs.

Sample Dilutions
The sample analysis was completed with the following dilution.

Client Sample ID	*Analysis*	Lab Sample ID	Prep. Dilution	Reason
04164B10-01	DRO	6039-001	10 X	Matrix interference.

Sample Re-prep/Re-analysis
The samples in this work order did not require re-analysis.

Miscellaneous Information
Laboratory Quality Communication Forms (LQCF)
Laboratory Quality Communication Forms (LQCFs) are generated to document procedural anomalies that may deviate from referenced SOPs or Contractual documents.

The following LQCF (SVO0405015) was generated to record the following deviations.

The MS/MSD RPD failed possibly due to sample heterogeneity.

Manual Integration
Data files associated with the initial calibration, continuing calibration check and sample did not require manual integrations.

System Configuration
The laboratory utilizes the following GC/MS configurations:

Chromatographic Columns
Chromatographic separation of semi-volatile components is accomplished through analysis on one of the following columns:

Column ID	I.D. (mm)	Length (m)	Film (um)	Coating
ZB-5	0.25	30	0.50	5% phenyl polysiloxane

Instrument Configuration
Instrument systems are referenced in the raw data and individual form headers by the Instrument ID designation below.

Instrument ID	System Configuration	Chromatographic Column
HP-GCO	HP5890	ZB-5

Additional Comments
The additional comments field is used to address special issues associated with each analysis, clarify method/contractual issues pertaining to the analysis. Additional comments were not necessary for this work order.

ACCURA ANALYTICAL LABORATORY, INC
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Review / Validation

The following data validator verified the data presented in this work order.

Reviewer: [signature]

Date: 5/19/04

Accura Analytical Laboratory Inc.
6017 Financial Drive
Norcross GA. 30071
Tel: 770-449-8800
Fax: 770-449-5477

Certificate of Analysis

		Print Date:	5/19/2004
Company:	Westinghouse Savannah River Co.	Page:	Page 1 of 2
Address:	Building 735-B, Rm 145-A		
	Aiken, SC 29802		
Contact:	Larry Dewitt		
Project No.:	04164		

Client Sample ID:	04164B10-01	Project Name:	04164
Sample ID	6039-001	Client ID:	2321
Matrix:	Soil		
Collect Date:	04/21/2004 10:00		
Receive Date:	04/26/2004 14:15		
Collector:	Westinghouse Savannah River Co.		

Parameter	Qualifier	Result	DL	RL	Units	DF	Analyst	Date	Time	Batch
SW8015-DRO										
TPH-DRO (Diesel Range Organics)	JB	45.0000	15.0000	100.0000	MGKG	10.00	PB	5/6/04	14:19	21851

This data report has been prepared and reviewed in accordance with
standard operating procedures. Please direct any questions to your Project Manager

Reviewed by

DL = Method Detection Limit, RL =Reporting Limit, U= Below DL, J = Greater than DL but less than RL, U = Below DL, B = Detection in Blank

Blank Spike Recovery

Project Name: 04164

Report Date: 05/19/04 16:50

Work Order #: 6039 **Project ID:** 04164

Lab Batch #: 21851 **Sample:** 18777 BKS **Matrix:** S

Reporting Units: mg/kg **Batch #:** 1

TPH DRO by SW8015M Analytes	Blank Result [A]	BLANK /BLANK SPIKE RECOVERY STUDY Spike Added [B]	Blank Spike Result [C]	Blank Spike %R [D]	Control Limits %R	Flags
TPH-DRO (Diesel Range Organics)	3.4	33	33	100	39-114	

Blank Spike Recovery [D] = 100*[C]/[B]
All results are based on MDL and validated for QC purposes.

ND = Not Detected, J = Present Below Reporting Limit, B = Present in Blank, NR = Not Requested, I = Interference, NA = Not ApplicableN = See Narrative, EQL = Estimated Quantitation Limit

Accura Analytical Laboratory Inc.
6017 Financial Drive
Norcross GA. 30071
Tel: 770-449-8800
Fax: 770-449-5477

Certificate of Analysis

		Print Date:	5/19/2004
Company:	Westinghouse Savannah River Co.	Page:	Page 2 of 2
Address:	Building 735-B, Rm 145-A		
	Aiken, SC 29802		
Contact:	Larry Dewitt		
Project No.:			

Client Sample ID:		Project Name:	04164
Sample ID	18777 BLK	Client ID:	2321
Matrix:	Soil		
Collect Date:			
Receive Date:			
Collector:	Westinghouse Savannah River Co.		

Parameter	Qualifier	Result	DL	RL	Units	DF	Analyst	Date	Time	Batch
SW8015-DRO										
TPH-DRO (Diesel Range Organics)		0.0000	1.5000	10.0000	MGKG	1.00	PB	5/6/04	12:23	21851

This data report has been prepared and reviewed in accordance with
standard operating procedures. Please direct any questions to your Project Manager

Reviewed By: _____

DL = Method Detection Limit, RL =Reporting Limit, U= Below DL, J = Greater than DL but less than RL, U = Below DL, B = Detection in Blank

Form 3 - MS / MSD Recoveries

Project Name: 04164

Work Order # : 6039

Lab Batch ID: 21851

Reporting Units: mg/kg

Report Date: 05/19/04 16:50

Project ID: 04164

QC- Sample ID: 6041-001 MS **Batch #:** 1 **Matrix:** S

TPH DRO by SW8015M Analytes	MATRIX SPIKE / MATRIX SPIKE DUPLICATE RECOVERY STUDY										
	Parent Sample Result [A]	Spike Added [B]	Spiked Sample Result [C]	Spiked Sample %R [D]	Spike Added [E]	Duplicate Spiked Sample Result [F]	Spiked Dup. %R [G]	RPD %	Control Limits %R	Control Limits %RPD	Flag
TPH-DRO (Diesel Range Organics)	5.4	33	39	102	33	18	38	91	28-116	20	F

Matrix Spike Percent Recovery [D] = 100*(C-A)/B
Relative Percent Difference RPD = 200*(D-G)/(D+G)

Matrix Spike Duplicate Percent Recovery [G] = 100*(F-A)/E

F = RPD exceeded the laboratory control limits

Version: 1.%

Form 2 - Surrogate Recoveries

Project Name: 04164

Report Date: 05/19/04 16:50

Work Order #: 6039 **Project ID:** 04164

Lab Batch #: 21851 **Sample:** 18777 BKS / BKS **Batch:** 1 **Matrix:** S

Units: mg/kg

TPH DRO by SW8015M Analytes	SURROGATE RECOVERY STUDY Amount Found [A]	True Amount [B]	Recovery %R [D]	Control Limits %R	Flags
o-Terphenyl	44.46	50.00	89	33-124	

Lab Batch #: 21851 **Sample:** 18777 BLK / BLK **Batch:** 1 **Matrix:** S

Units: mg/kg

TPH DRO by SW8015M Analytes	SURROGATE RECOVERY STUDY Amount Found [A]	True Amount [B]	Recovery %R [D]	Control Limits %R	Flags
o-Terphenyl	40.04	50.00	80	33-124	

Lab Batch #: 21851 **Sample:** 6039-001 / SMP **Batch:** 1 **Matrix:** S

Units: mg/kg

TPH DRO by SW8015M Analytes	SURROGATE RECOVERY STUDY Amount Found [A]	True Amount [B]	Recovery %R [D]	Control Limits %R	Flags
o-Terphenyl	3.968	5.000	79	33-124	

Lab Batch #: 21851 **Sample:** 6041-001 MS / MS **Batch:** 1 **Matrix:** S

Units: mg/kg

TPH DRO by SW8015M Analytes	SURROGATE RECOVERY STUDY Amount Found [A]	True Amount [B]	Recovery %R [D]	Control Limits %R	Flags
o-Terphenyl	53.81	50.00	108	33-124	

Lab Batch #: 21851 **Sample:** 6041-001 MSD / MSD **Batch:** 1 **Matrix:** S

Units: mg/kg

TPH DRO by SW8015M Analytes	SURROGATE RECOVERY STUDY Amount Found [A]	True Amount [B]	Recovery %R [D]	Control Limits %R	Flags
o-Terphenyl	19.69	50.00	39	33-124	

* Surrogate outside of Laboratory QC limits
** Surrogates outside limits; data and surrogates confirmed by reanalysis
*** Poor recoveries due to dilution
Surrogate Recovery [D] = 100 * A / B
All results are based on MDL and validated for QC purposes.
Z = Surrogate Recovery exceeded the Labortatory QC limits

Version: 1.5

REFERENCES

1. Acosta-Martinez, V., and M. A. Tabatabai. 2001. Arylamidase Activity In Soils Effect Of Trace Elements And Relationships To Soil Properties And Activities To Amidohydrolases. Soil Biology and Biochemistry. 33:17-23.

2. Aguilera-Vazquez, L., N. O. Soto-Cruz, G. Saucedo-Castañeda, and M.Gutiérrez-Rojas. 2001. A Model System for Cocomposting Hydrocarbon Contaminated Soil by Using Water Activity and Porosity as Response Variables. Chemical Engineering Journal. 81:197–202.

3. Ahn, J. H., and C. F. Forster. 2000. A Comparison of Mesophilic and Thermophilic Anaerobic Upflow Biofilters. Bioresource Technology. 73:201-220.

4. Alexander, M. 1999. Biodegradation and Bioremediation, 2nd ed. Academic Press, San Diego, Calif.

5. Alexander, M. 1977. Introduction to Soil Microbiology, 2nd ed. John Whiley & Sons, New York.

6. Alleman, B. C., R. E. Hinchee, R. C. Brenner, and P. T. McCauley. 1995. Presented at the In Situ Aeration: Air Sparging, Bioventing, and Related Remediation Processes.

7. Altman, D. J., T. C. Hazen, A. J. Tien, A. Worsztynowicz, and U. Krzysztof. 1997. The Czechowice Oil Refinery Bioremediation Demonstration of a Process Waste Lagoon – Czechowice-Dziedzice. Poland. *In* Doe (ed.), vol. EOE/OTD TTP No SR-1-6-pl-21.

8. Anderson, A. W., H. C. Nordan, R. F. Cain, G. Parrish, and D. Duggan. 1956. Studies on a Radioresistant Micrococcus. I. Isolation, Morphology, Cultural Characteristics, and Resistance to Gamma Radiation. Food Technol. 10:575-577.

9. Areas, I. f. E. o. I., W. S. R. C. Savannah River Technology Center, L. B. N. Laboratory, and F. S. U. Institute for International Cooperative Environmental Research. 1999. Bioremediation of Petroleum Hydrocarbon-Contaminated Soils Comprehensive Report vol. Institute for Ecology of Industrial Areas, Katowice, Poland; Savannah River Technology Center, Westinghouse Savannah River Company; Lawrence Berkeley National Laboratory; Institute for International Cooperative Environmental Research, Florida State University

10. Atlas, R. M. 1981. Microbial degradation of petroleum hydrocarbons: an environmental perspective. Microbiological Review. 45:180–209.

11. Atlas, R. M. 1984. Petroleum Microbiology. MacMillan Publishing Company.

12. Baker, K. H., and D. S. Herson. 1994. Bioremediation. McGraw Hill, New York, NY.

13. Barbeau, C., L. Deschenes, D. Karamanev, Y. Comeau, and R. Samson. 1997. Bioremediation of pentachlorophenol-contaminated soil by bioaugmentation using activated soil. Applied and Environmental Microbiology. 48:745-752.

14. Bartha, R. 1986. Biotechnology of petroleum pollutant biodegradation. Microb Ecol. 12:155-172.

15. Bartha, R., and R. M. Atlas. 1977. The microbiology of of aquatic oil spills. Adv apppl Microbiol. 22:225-266.

16. Bonnier, P. D., G. L. Akoun, E. C. Cadron, E. D. Edwards, and H. W. 1980. A technique for the disposal of oily refinery wastes. vol. 3/10. Concawe.The Hague:

17. Boopathy, R. 2000. Factors limiting bioremediation technologies. Bioresour. Technol. 74: 63.

18. Bosma, T. N. P., P. J. M. Middeldorp, G. Schraa, and A. J. B. Zehnder. 1997. Mass transfer limitation of biotransformation: Quantifying bioavailability. Environ. Sci. Technol. 31:248-252.

19. Breedveld, G. D., G. Olstad, T. Briseid, and A. Hauge. 1995. Nutrient demand in bioventing of fuel oil pollution, p. 391-399. *In* R. E. Hinchee, I. N. Miller, and P. C. Johnson (ed.), In Situ Aeration: Air Sparging, Bioventing, and Related Remediation. Battelle Press, Columbus, OH.

20. Brigmon, R. L. 2001. Characterization of Isolates from the Czechowice-Dziedzice Refinery. *In* C. J. Berry (ed.), Aiken.

21. Brigmon, R. L., C. J. Berry, S. Story, D. Altman, R. Upchurch, W. Whitman, D. Singleton, and G. Plaza. 2003. Bioremediation of Mixed Waste at the Savannah River Site: Laboratory to Field Scale Application, The 228th ACS National Meeting. ACS, Philadelphia, PA.

22. Brock, T. D., M. T. Madigan, J. M. Martinko, and J. Parker. 1994. Biology of Microorganisms, Seventh ed. Prentice -Hall, Englewood Cliffs.

23. Brockman, F. J., W. Payne, D. J. Workman, A. Soong, S. Manley, and T. C. Hazen. 1995. Effect of Gaseous Nitrogen and Phosphorus Injection on In Situ Bioremediation of a Trichloroethylene-Contaminated Site. J Haz. Mat. 41:287-298.

24. Bruheim, P., H. Bredholt, and K. Eimhjellen. 1997. Bacterial Degradation of Emulsified Crude Oil and the Effect of Various Surfactants. Can. J. Microbiol. 43:17-22.

25. Charpak, G., R. L. Garwin. 2002. The DARI:A Unit of Measure Suitable to the Practical Appreciation of the Effect of Low Doses of Ionizing Radiation. Europhysics News. 33.

26. Cookson, J. T., Jr. 1995. Bioremediation engineering design and application. McGraw-Hill Inc., New York.

27. Denn, M. M. 1980. Process Fluid Mechanics. Prentice-Hall, Inc., Englewood Cliffs, NJ.

28. Dibble, J. T., and R. Bartha. 1979. Effect of Environmental Parameters on the Biodegradation of Oil Sludge. Applied and Environmental Microbiology. 37:29-739.

29. Dick, W. A., and M. A. Tabatabai. 1999. Use of Immobilized Enzymes for Bioremediation. *In* American Society of Agronomy Inc. (ed.), Bioremediation of Contaminated Soils. American Society of Agronomy Inc., Madison, Wisconsin.

30. DOE, U. S. 1987. Final Environmental Impact Statement Waste Management Activities for Groundwater Protection Savannah River Plant: EIS-0120. Savannah River Plant, Aiken, South Carolina.

31. Dua, M., A. Singh, N. Sethunathan, and A. K. Johri. 2002. Biotechnology and bioremediation: successes and limitations. Appl. Microbiol. Biotechnol. 59:143-152.

32. DuPont, R. R. 1993. Fundamentals of Bioventing Applied to Fuel Contamination Sites. Environmental Progress. 12:45-53.

33. El-Nawawy, A. S., I. H. El-Bagouri, M. Abdal, and M. S. Khalafai. 1992. Bio-degradation of Oily Sludge in Kuwait Soil. World J Microbiol Biotechnol. 8:618-620.

34. Eriksson, M., E. Sodersten, Z. Yu, G. Dalhammar, and W. W. Mohn. 2003. Degradation of Polycyclic Aromatic Hydrocarbons at Low Temperature under Aerobic and Nitrate-Reducing Conditions in Enrichment Cultures from Northern Soils. Applied and Environmental Microbiology. 69:275-284.

35. Felenstein, J. 1989. PHYLIP- Phylogeny inference package (version 3.2). Cladistics. 5.

36. Fogler, H. S. 1986. Elements of Chemcial Reaction Engineering. Prentice Hall, Englewood Cliffs, NJ.

37. Freijer, J. I. 1986. Mineralization of Hydrocarbons in Soil Under Decreasing Oxygen Availability. J Environ Qual. 25:296-304.

38. Frysinger, G. S., R. B. Gaines, L. Xu, and C. M. Reddy. 2003. Resolving the

Unresolved Complex Mixture in Petroleum-Contaminated Sediments. Environ. Sci. Technol. 37:1653-1662.

39. Gentry, a. S. 1995. Experience with Bioventing at Wood Preserving Sites. *In* R. E. Hinchee, I. N. Miller, and P. C. Johnson (ed.), In Situ Aeration: Air Sparging, Bioventing, and Related Remediation Processes. Battelle Press, Columbus, OH.

40. Greenberg, A. E., L. S. Clesceri, and A. D. Eaton. 1992. Standard Methods For The Examination of Water and Wastewater, 18 ed. American Public Health Association, Washington, DC.

41. Harkness, M. A., J. D. Ciampa, and A. A. Bracco. 1995. A Laboratory Assessment of Air Sparging Performance on Oil Contaminated Soil. *In* R. E. Hinchee, I. N. Miller, and P. C. Johnson (ed.), In situ Aeration: Air Sparging, Bioventing and Related Remediation Processes.

42. Harms, H., and T. N. P. Bosma. 1997. Mass transfer limitation of microbial growth and pollutant degradation. J. Ind. Microbiol. Biotechnol. 18:97-105.

43. Hazen, T. C., K. H. Lombard, B. B. Looney, M. V. Enzien, J. M. Dougherty, C. B. Fliermans, J. Wear, and C. A. Eddy-Dilek. 1995. Summary of In Situ Bioremediation Demonstration (Methane Biostimulation) Via Horizontal Wells at the Savannah River Site Integrated Demonstration Project. *In* G. W. Gee, and N. R. Wing (ed.), In Situ Remediation: Scientific Basis for Current and Future Technologies. Battelle Press, Columbus, OH.

44. Henriksen, T. M., and T.A. Breland. 1999. Nitrogen Availability Effects on Carbon Mineralization, Fungal and Bacterial Growth, and Enzyme Activities During Decomposition of Wheat Straw in Soil. Soil Biology and Biochemistry. 31:1121-1134.

45. Hillel, D. 1980. Soil Structure and Aggregation, p. 40- 52, 200-204, Introduction to Soil Physics. Academic Press, London.

46. Hinchee, R. E., D. C. Downey, R. R. Dupont, P. K. Aggarwal, and R. N. Miller. 1991. Enhancing Biodegradation of Petroleum Hydrocarbons Through Soil Venting. J Haz. Mat. 27:315-325.

47. Huddleston, R. L., C. A. Bleckman, and J. R. Wolfe. 1986. Land Treatment - biological degradation processes. *In* R. C. Loehr and J. F. Malina Jr. (ed.), Water Resources Symposium Number 13. Center for Research in Water Resources.

48. Huesemann, M. H. 1995. Predictive Model for Estimating the Extent of Petroleum Hydrocarbon Biodegradation in Contaminated Soils. Environ. Sci. Technol. 29:7-18.

49. Hunter, C. H. 2003. Five-Year Meteorological Data Base for the MACCS Computer Code vol. WSRC-RP-2005-001405. Savannah River Site

50. Hunter, C. H. 2005. Savannah River Site Annual Metrology Report for 2004 vol. WSRC-RP-2005-001405. Savannah River Site

51. Hunter, C. H. S. R. S. A. M. R. f. 2004. Savannah River Site Annual Metrology Report for 2003 vol. WSRC-RP-200-00256. Savannah River Site

52. Hyman, M., and L. Bagaasen. 1997. Select a Site Cleanup Technology. Chem. Eng. Prog. 93:22.

53. IARC. 1989. IARC Monographs on the Evaluation of Carcinogenic Risks to Humans. Diesel and Gasoline Engine Exhausts and Some Nitroarenes vol. 46.Lyon France: International Agency for Research on Cancer.

54. IICR 2005, Joint Coordinating Committee for Environmental Systems (JCCES), Poland-USA. Florida State University, http://iicer.fsu.edu/ourwork_jcces.cfm. http://iicer.fsu.edu/ourwork_jcces.cfm.

55. Institute, A. P. 1983. Land Treatment Practice in the Petroleum Industry vol. Environmental Research and Technology Inc.Washington, DC:

56. Jorgensen, K. S., J. Puustinenn, and A.M. Suortti. 2000. Bioremediation of petroleum hydrocarbon-contaminated soil by composting in biopiles. Environmental Pollution. 107:245.

57. Kastner, J. R., D. J. Altman, and C. B Walker. 1998. Corrective Action Plan - Degradation of Petroleum Contaminated Soils Using Ex-Situ Bioreactors and Bioventing vol. WSRC-RP-97-25. Savannah River Site.Aiken, SC:

58. Kastner, J. R., K. H. Lombard, J. Radway, J. Santo Domingo, T. C. Hazen and G. L. Burbage. 1997. Report on Bioventing of Petroleum Contaminated Soils at 108-3C: Active Extraction and Passive Injection (Barometric Pumping) of a Gaseous Nutrient vol. WSRC-RP-97-25. Savannah River Site.Aiken, SC:

59. King, R. B., G. M. Long, and J. K. Sheldon. 1997. Practical Environmental Bioremediation: The Field Guide, Second ed. CRC Press.

60. Kuperberg, J. M., and M. Khankhasayev, J. Moerlins, and R. Herndon 2001, Overview of International Programs for Identification and Evaluation of Technologies for DOE-EM. Institute for International Cooperative Environmental Research.
http://www.netl.doe.gov/publications/proceedings/01/indpartner/emp.04.pdf.

61. Lawrence. 1994. In Situ Bioventing for Environmental Remediation of Natural Gas Dehydrator Site: A Field Demonstration, Society of Petroleum Engineers 69th Annual Technical Conference, New Orleans.

62. Leahy, J. G., and R. R. Colwell. 1990. Microbial Degradation of Hydrocarbons in the Environment. Microbiol. Rev. 54:305-315.

63. Leson, G., and A. M. Winer. 1991. Biofiltration: An Innovative Air Pollution Control Technology for VOC Emissions. Journal of the Air and Waste Management Association. 41:1045-1054.

64. Levenspiel, O. 1972. Chemical Reaction Engineering, Second ed. John Whiley and Sons.

65. Line, M. A., C. D. Garland, and M. Crowley. 1996. Evaluation of Landfarming Remediation of Hydrocarbon-Contaminated Soil at the Inveresk Railyard, Launceston, Australia. Waste Management. 16:567-570.

66. Lombard, K., and T. C. Hazen. 1994. Test Plan for the Soils Facility Demonstration - A Petroleum Contaminated Soil Bioremediation Facility vol. WSRC-RP-94-0179. Savannah River Site.Aiken, South Carolina:

67. Looney, B. B., K. H. Lombard, T. C. Hazen, S. M. Pfiffner, T. J. Phelps, and J. W. Borthen. 1996. Method for Phosphate-accelerated Bioremediation. U.S. Pat. #5,480,549.

68. Looney, B. B., S. M. Pfiffner, T. J. Phelps, K. H. Lombard, T. C. Hazen, and J. W. Borthen. 1998. Apparatus and Method for Phosphate-accelerated Bioremediation. U.S. Pat. # 5,753,109.

69. Lord, D., J. Lei, M.-C. Chapdelaine, J.-L. Sansregret, and B. Cyr. 1995. In Situ Air Sparging for Bioremediation of Groundwater and Soils, p. 121-126. *In* R. E. Hinchee, I. N. Miller, and P. C. Johnson (ed.), In Situ Aeration: Air Sparging, Bioventing, and Related Remediation Processes. Battelle Press, Columbus, OH.

70. Mamatey, A. E., (ed.). 2003. Savannah River Site Environmental Report for 2003 vol. WSRC-TR-2004-00015

71. Melope, M. B., I. C. Griwe, and E. R. Pege. 1987. Contributions by Fungi and Bacteria to Aggregate Stability of Cultivated Soils. J Soil Sci. 38:71- 77.

72. Miller, R. V., and S. Poindexter. 1994. Strategies and Mechanisms for Field Research in Environmental Bioremediation. American Academy of Microbiology.

73. Morita, R. Y. 1975. Psychrophilic Bacteria. Bacteriol. Rev. 39:144-167.

74. Morrison, I. M., G. T. Eckman, J. G. Stefanoff, J. A. Diaz, and J. H. Herbst. 1996. Evaluation of Aerated Biopile Treatment Options, p. 455-460. *In* B.C. Alleman and A. Leason (ed.), In Situ and On site Bioremediation, vol. Vol. I. Battelle Press, Columbus, OH.

75. Nano, G., A. Borroni, and R. Rota. 2003. Combined Slurry and Solid-phase Bioremediation of Diesel Contaminated Soils. Journal of Hazardous Materials. B100:79-94.

76. NCRPM. 1987. Ionizing Radiation Exposure of the Population of the U.S., vol. Report 93. National Council on Radiation Protection and Measurement.

77. Nester, E. W., E. E. Roberts, M. E. Lidstrom, and M. T. Nester. 1983. Microbiology, 3rd ed. Sanders College Publishing, New York.

78. Newby, D. T., T. J. Gentry, and I. L. Pepper. 2000. Comparison of 2,4-dichlorophenoxyacetic acid degradation and plasmid transfer in soil resulting from bioaugmentation with two different pJP4 donors. Applied and Environmental Microbiology. 66:3399-3407.

79. Norris, R. D., R. E. Hinchee, R. A. Brown, P. L. McCarty, L. Semprirni, J. T. Wilson, D. H. Kambell, M. Reinhard, E. J. Bouwer, R. C. Borden, T. M. Vogel, J. M. Thomas, and C. H. Ward. 1994. Handbook of Bioremediation. CRC Press, Boca Raton.

80. Palis, J. C. 1985. Operation and Monitoring Information for Oily Waste Landfarms vol. Exxon Research and Engineering Company

81. Pearson, W. R., and D. J. Lipman. 1988. Improved tools for biological sequence comparison. PNAS. 85, 2444-2448. PNAS. 85:2444-2448.

82. Phillips, R. W., J. Wiegel, C. J. Berry, C. Fliermans, A.D. Peacock, D. C. White, and L. J. Shimkets. 2002. *Kineococcus radiotolerans* sp. nov., a radiation-resistant, Gram-positive bacterium. Int. J. Syst. Evol. Microbiol. 52:933-938.

83. Pierce, R. H., A. M. Cundell, and R. W. Traxler. 1975. Persitance and Biodegradation of Spilled Residual Fuel Oil on an Estuarine Beach. Applied Microbiology. 29:646-652.

84. Prince, R. C., and M. J. Grossman. 2003. Substrate Preferences in Biodesulfurization of Diesel Range Fuels by Rhodococcus sp. Strain ECRD-1. Applied and Environmental Microbiology. 69:5833–5838.

85. Reddy, C. M., T. I. Eglinton, A. Hounshell, H. K. White, L. Xu, R. B. Gaines, and G. S. Frysinger. 2002. The West Falmouth Oil Spill after Thirty Years: The Persistence of Petroleum Hydrocarbons in Marsh Sediments. Environ. Sci. Technol. 36:4754-4760.

86. Rhykerd, R. L., B. Crews, K. J. McInnes, and R. W. Weaver. 1999. Impact of Bulking Agents, Forced Aeration and Tillage on Remediation of Oil-Contaminated Soil. Biores Technol. 67:279-85.

87. Riser-Roberts, E. 1998. Remediation of Petroleum Contaminated Soils: Biological, Physical, and Chemical Processes. Lewis Publishers CRC Press LLC, Boca Raton.

88. Roane, T. M., K. L. Josephson, and I. L. Pepper. 2001. Dual-Bioaugmentation

Strategy To Enhance Remediation of Cocontaminated Soil. Applied and Environmental Microbiology. 67:3208-3215.

89. Saberiyan, A. G., M. A. Wilson, J. S. Andrilenas, C. T. Esler, G. H. Kite, and Reith. 1994. Removal of Gasoline Volatile Organic Compounds Via Air Biofiltration: A Technique for Treating Secondary Air Emissions from Vapor-extraction and Air-stripping Systems, p. 1-11. *In* R. E. Hinchee, D. C. Downey, R. R. Dupont, P. K. Aggarwal, and R. N. Miller (ed.), Hydrocarbon Bioremediation. CRC Press, Boca Raton, Fl.

90. SCDHEC. 2001. South Carolina Hazardous Waste Management Act, vol. 61-107.18.

91. Shimp, R. J., F. K. Pfaender. 1985. Influence of Naturally Occurring Humic Acids on Biodegradation of Monosubstituted Phenols by Aquatic Bacteria. Appl Environ Microbiol. 49:402-407.

92. Smith, K. P., J. J. Arnish, G. P. Williams, and D. L Blunt. 2003. Assessment of the Disposal of Radioactive Petroleum Industry Waste in Nonhazardous Landfills Using Risk-Based Modeling. Environ. Sci Technol. 37:2060-2066.

93. Tchobanoglous, G., and F. L. Burton. 1991. Wastewater Engineering: Treatment Disposal Reuse, vol. Third. Metcalf and Eddy Inc., McGraw Hill, Inc.

94. Thomas, J. M., J. R. Yordy, J. A. Amador, and M. Alexander. 1986. Rates of Dissolution and Biodegradation of Water-Insoluble Organic Compounds. Appl. Environ. Microbiol. 52:290-296.

95. Top, E. M., D. Springael, and N. Boon. 2002. Catabolic mobile genetic elements and their potential use in bioaugmentation of polluted soils and waters. FEMS Microbiol. Ecol. 42:199-208.

96. Traux, D. D., R. Britto, and J. H. Sherrard. 1995. Bench Scale Studies of Reactor Based Treatment of Fuel-Contaminated Soils. Waste Management. 15:5/6:351-357.

97. USDOE. 1999. Radioactive Waste Management, vol. Order 435.1.

98. USEPA. 1989. Bioremediation of Hazardous Waste Sites workshop, CERI 89-1-1, Washington, DC.

99. USEPA. 1995. Manual: Bioventing Principles and Practive. *In* Epa/ (ed.), vol. 1.

100. USEPA 2005, SW-846 On Line: Test Methods for Evaluating Solid Wastes Physical Chemical Methods. USEPA http://www.epa.gov/epaoswer/hazwaste/test/main.htm. http://www.epa.gov/epaoswer/hazwaste/test/main.htm.

101. Van Hamme, D., A. Singh, and O. P. Ward. 2003. Recent Advances in Petroleum Microbiology. Microbiology and Molecular Biology Reviews. 67(4):503-549.

102. Vasudevan, N., and P. Rajaram. 2001. Bioremediation of Oil Sludge-Contaminated Soil. Environment International. 26:409-411.

103. Viel, M., D. Sayag, A. Peyre, L. Andre. 1987. Optimization of In-Vessel Co-Composting Through Heat Recovery. Biological Wastes. 20:167-185.

104. Villemur, R., R. E. De´ziel, A. Benachenhou, J. Marcoux, E. Gauthier, F. Le´pine, R. Beaudet, and Y. Comeau. 2000. Two-Liquid-Phase Slurry Bioreactors To Enhance the Degradation of High-Molecular-Weight Polycyclic Aromatic Hydrocarbons in Soil. T Biotechnology Progress. 16:966-972.

105. Vogel, T. M. 1996. Bioaugmentation as a soil bioremediation approach. Curr Opin Biotechnol. 7:311-316.

106. von Wedel, R. T., S.F. Mosquera, C.D. Goldsmith, G.R. Hater, A. Wong, T.A. Fox, W.T. Hunt, M.S. Paules, J. M. Quiros, and J.W Wiegand. 1988. Bacterial Biodegradation of Petroleum Hydrocarbons in Ground Water: In Situ Augmented Bioreclaimation with Enrichment Isolates in California. Water Sci Technol. 20:501-503.

107. Walker, C. 2001. Personal Communication.

108. Walker, R. 2005, Simetric.co.uk - Metric Mass of Materials Table. http://www.simetric.co.uk/si_materials.htm. http://www.simetric.co.uk/si_materials.htm.

109. Ward, D. M., and T. D. Brock. 1975. Environmental Factors Influencing the Rate of Hydrocarbon Oxidation in Temperate Lakes. Applied and Environmental Microbiology. 31:764-772.

110. Ward, O., A. Singh, and J. Van Hamme. 2003. Accelerated biodegradation of petroleum hydrocarbon waste. Journal of Industrial Microbiology and Biotechnology. 30(5):260 - 270.

111. Whyte, L. G., S. J. Slagman, F. Pietrantonio, and L. Bourbonnie`re. 1999. Physiological Adaptations Involved in Alkane Assimilation at a Low Temperature by Rhodococcus sp. Strain Q15. Applied and Environmental Microbiology. 65:2961-2968.

112. Widada, J., H. Nojiri, and T. Omori. 2002. Recent developments in molecular techniques for identification and monitoring of xenobiotic-degrading bacteria and their catabolic genes in bioremediation. Appl. Microbiol. Biotechnol. 60:45-59.

113. Zhang, C., J. B. Hughes, S. F. Nishino, and J. C. Spain. 2000. Slurry-Phase Biological Treatment of 2,4-Dinitrotoluene and 2,6-Dinitrotoluene: Role of

Bioaugmentation and Effects of High Dinitrotoluene Concentrations. Environmental Science and Technology. 34:2810-2816.

114. Zhang, Y., and R. M. Miller. 1992. Enhanced Octadecane Dispersion and Biodegradtion by a *Pseudomonas* Rhamnolipid Surfactant (Biosurfactant). Applied and Environmental Microbiology. 58:3276-3282.

115. Zhou, E., and R. L. Crawford. 1995. Effects of oxygen, nitrogen, and temperature on gasoline biodegradation in soil. Biodegradation. 6:127-140.

116. Zhou, J. B., D. S. Xia, Treves, L.Y. Wu, T. L. Marsh, R. V. O'Neill, A. V. Palumbo, and J. M.Tiedje. 2002. Spatial and Resource Factors Influencing High Microbial Diversity in Soil. Appl Environ Microbiol. 68 (1):326-334.

117. Zwick, e. a. 1995. Soil Moisture Effects During Bioventing in Fuel Contaminated Arid Soils. *In* R. E. Hinchee, I. N. Miller, and P. C. Johnson (ed.), In Situ Aeration: Air Sparging, Bioventing, and Related Remediation Processes.