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ABSTRACT

Integration of Pneumatic Fracturing to Enhance In Situ Bioremediation

by
Conan Dante Fitzgerald

The purpose of this thesis was to study the anticipated benefits of integrating pneumatic fracturing with in situ bioremediation. Since pneumatic fracturing increases subsurface air flow in low permeability formations, it has the potential to overcome many of the major limiting factors of microbial growth and activity. A new innovation called pneumatic bio-injection can further enhance in situ bioremediation by efficiently dispersing biological solutions, including microorganisms, into a formation.

Bench scale experiments were conducted to examine the ability of microorganisms to survive the pressures and stresses associated with pneumatic injection. Tests conducted at pressures ranging from 60 to 500 psi showed consistent survivability under varied conditions. In fact, many tests showed an increase in microbial growth following pressurization, which was found to be a result of the superior dispersion produced by the injection system. Full scale tests indicated that the prototype pneumatic bio-injection system will disperse a finely-textured mist into the fracture network at flow rates up to 4.5 GPM.

A full field pilot demonstration was implemented for an industrial site underlain by petroleum contaminated clayey silt. The characterization and preparation phases are described including the initial pneumatic fracturing activities. Subsurface permeabilites increased 35 times as result of fracturing, and mass removal through vapor extraction for the target contaminants increased 50 to 75 times.

INTEGRATION OF PNEUMATIC FRACTURING TO ENHANCE IN SITU BIOREMEDIATION

by

Conan Dante Fitzgerald

A Thesis
Submitted to the Faculty of
New Jersey Institute of Technology
in Partial Fulfillment of the Requirements for the Degree of
Master of Science

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APPROVAL PAGE

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This thesis is dedicated to
my parents
James and Jean Fitzgerald

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CHAPTER 1
INTRODUCTION

1.1 General Information

It is estimated that there are over 10,000 sites in the United States which are contaminated with some kind or combination of hazardous wastes. To date, the Superfund National Priority List (NPL) already contains 1255 locations. Of these sites, most include contamination of the soil and almost all have produced some sort of groundwater pollution. The United States Government, as well as both state and local governments, have passed laws and developed programs during the 1970's and 1980's in order to deal with these problems. However, very few hazardous waste clean-ups have actually been completed.

One of the major reasons for the sluggish rate of contaminated site remediation is a lack of technology. Soil pollution is a problem that is relatively new to our society, and cleaning contaminants out of the ground is both difficult and expensive.

There are presently a number of treatment technologies available to remediation consultants when dealing with soil contamination problems. Of these, the least favored is removal and disposal, since it only displaces the problem and is usually the most costly alternative. Most government agencies favor some sort of permanent, in-situ treatment method, where the soil is treated on site and in place.

Technologies in this realm include vapor extraction and bioremediation. Although these treatment methods have had their successes, they have been until recently limited to very permeable soils.[1] A new technology is now available that can extend these forms of remediation to all types of soils.

1.2 Purpose and Scope

The objective of this study is to show that pneumatic fracturing can enhance the current technology of bioremediation. Pneumatic fracturing has been demonstrated to increase soil permeability for vacuum extraction[2] and it is theorized that the same process can increase permeability for bioremediation.

Pneumatic fracturing injects air into the soil at high pressures in order to create horizontal cracks or "fractures" in the soil. This process has been demonstrated at both "clean" or uncontaminated sites, as well as at contaminated sites. At all locations where pneumatic fracturing has been applied, it has increased permeability of the geologic formation as measured by subsurface air flowrates. On contaminated sites, substantial increases in the removal rate of volatile contaminants have been measured after pneumatic fracturing.[2] The types of geologic formations where pneumatic fracturing has been demonstrated include silts, clays, and sedimentary rock.

Although bioremediation has been demonstrated as an effective way to destroy soil contaminants in-situ, it has generally been limited to very permeable soils. Pneumatic fracturing has the potential to expand the range of soil types which can be treated with in-situ biological treatment. The increased permeability provided by pneumatic fracturing can improve many of the key parameters for biological activity such as subsurface oxygen control. In addition, a modification to the pneumatic fracturing process known as pneumatic bio-injection can inject fluids containing nitrates or lime for pH control horizontally into a contaminated formation to more efficiently aid microbial activity. This same system can also inject microorganisms into the formation.

The study will begin with a general review of the status and methods of pneumatic fracturing and bioremediation as separate technologies. Next the advantages of integrating the technologies will be explained. The results of the interrelated studies of this technology integration will then be presented.

The first is a bench-scale laboratory study which examines whether microorganisms can survive the pressures and stresses associated with pneumatic injection. The second study involves development, calibration, and testing of the prototype pneumatic bio-injection system. The final study is a field demonstration of pneumatic fracturing combined with in situ bioremediation at an actual contaminated site which is typical of those facing industry today. The thesis concludes with recommendations for further study.

CHAPTER 2

BACKGROUND INFORMATION

2.1 Pneumatic Fracturing

Engineers, contractors, and regulators involved with site remediation are faced with a new and difficult problem. With the number of identified hazardous waste sites consistently growing and the costs associated with cleaning up those sites escalating as well, cost effective solutions to these contamination problems must be found. Technologies which treat contamination in place or "in situ" are viewed as the most efficient method of cleaning sites, and therefore have the potential to reduce remediation costs. For this reason, methods of treatment which can be performed in situ are usually preferred if the site conditions will allow them to be used.

A major limiting factor for in situ technologies is soil permeability. The efficiency and success of any of these treatment methods will be governed by the pore fluid (liquid or gas) exchange rate of the formation being treated. Pneumatic fracturing was conceived of as a method of artificially increasing the permeability of a formation with the minimum possible impact to the natural formation.

2.1.1 Concept of Pneumatic Fracturing

The original objective of pneumatic fracturing was to enhance the removal and treatment of volatile organic compounds (VOCs) from the vadose zone with vapor extraction. Figure 2.1 shows the concept of pneumatic fracturing as it is applied in clay and silt formations. Compressed air (or another gas) is injected into the formation at a pressure that exceeds the in situ stresses that are present. The burst of air cracks the formation and creates horizontal fracture planes

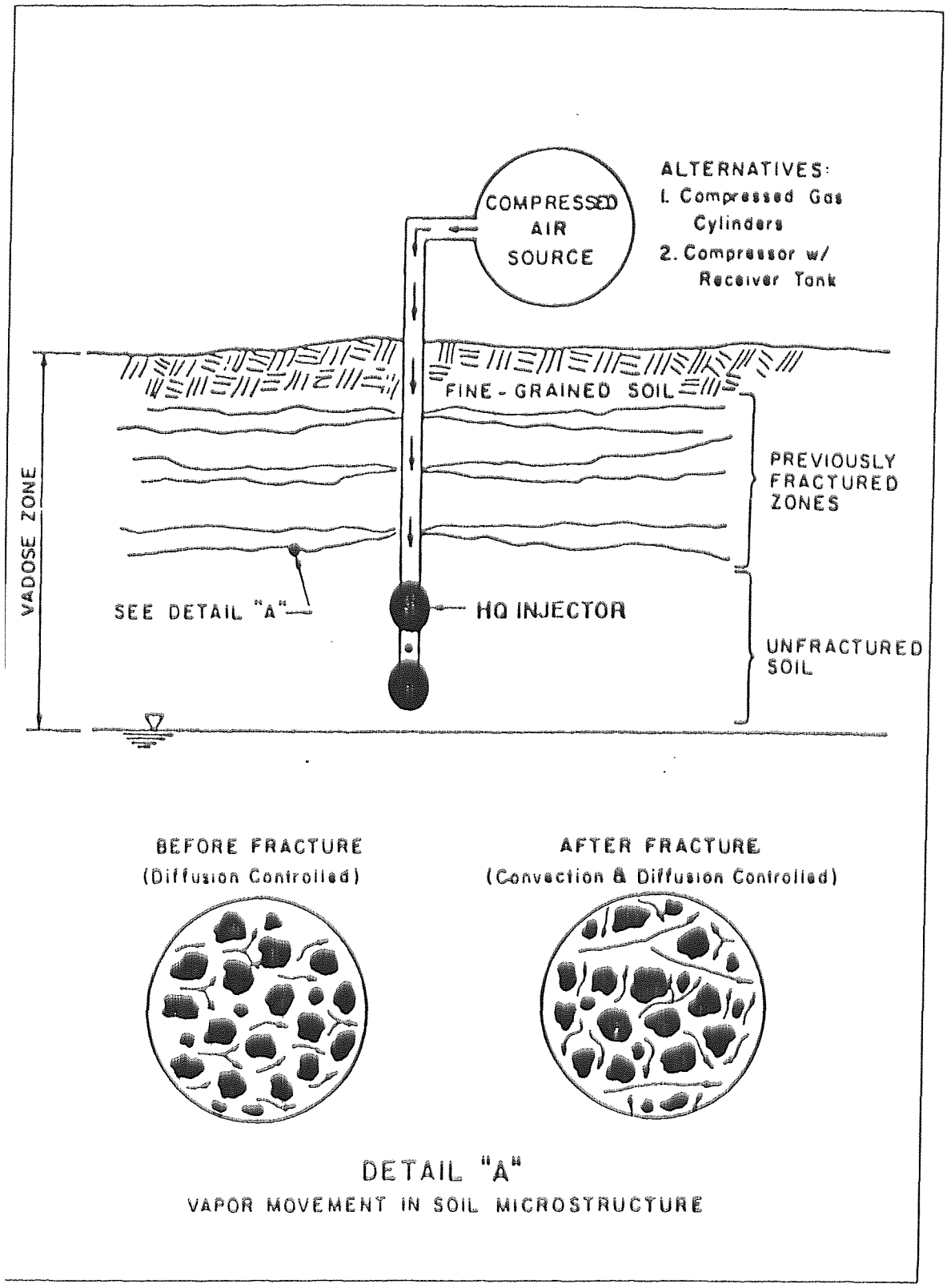


Figure 2.1 Schematic diagram of pneumatic fracturing.

which extend out radially from the point of injection. Upon completion of the pneumatic fracturing process, both the permeability and the exposed surface area of the formation is greatly increased. This allows for greater access to contaminated locations, thereby accelerating removal and/or treatment of contaminants in situ.

2.1.2 Mechanics of Fracture

An understanding of the mechanics of fracture is essential in applying pneumatic fracturing to geologic formations. Since pneumatic fracturing is a new technology, specific information is not available in the literature to explain its mechanisms. The theory of pneumatic fracturing which is presently under development relies on a combination of soil mechanics, rock mechanics, and observations during early field tests.

Compressed air, when injected into an isolated section of a borehole, will stress the geologic formation and will eventually cause failure when the "breakdown" pressure is reached. Upon failure, fractures will propagate perpendicular to the least principal stress in the formation. More simply, the fluid (air) will take the path of least resistance. Low permeability soils tend to be overconsolidated, which means that the least principal stress is in the vertical direction. Fractures in overconsolidated conditions would therefore tend to extend horizontally from the injection point. This correlates with field observations to date, which have shown that fractures are predominately horizontal.

Pressure, however, is not the most important factor in determining the size of a fracture. Downhole pressure measurements have indicated that high initiation pressures are not required to initiate shallow fractures. Field

measurements show that fracture initiation pressures at depths less of than 20 feet are less than 200 psi for rock and 100 psi for soil.

More important than injection pressure is the injection flow rate. The greater the volume of air per unit time injected into the formation, the further the fracture will propagate, since the fracture initiation pressure is maintained over a greater area of soil. Therefore, a fracturing system must not only be capable of high pressures, but it must also be able to produce high flow rates. Field observations have supported this analysis in Schuring and Chan.[1] To date, pneumatic fractures have attained radii in excess of 25 feet in radius.

2.1.3 Pneumatic Fracturing to Enhance Vapor Extraction

Vapor extraction was the first in situ technology that the pneumatic fracturing process was demonstrated to enhance. This technology consists of extracting volatile organic compounds (VOCs) from the subsurface using an air vacuum pump. For vapor extraction to be effective, it must move large volumes of air through the soil, which is only possible in a formation with substantial permeability. In geologic formations containing a significant amount of silt, clay, and/or shale, vapor extraction has been found to be ineffective without some type of enhancement.

Originally, laboratory studies were performed in soil vats to determine the predicted effectiveness of integrating pneumatic fracturing and vapor extraction. These experiments consistently showed that pneumatically fractured soil provided faster contaminant removal rates than unfractured soil. Further discussion of these studies is available in Schuring and Chan.[1] Based upon the success of the laboratory studies, a full-scale prototype pneumatic fracturing system was built and field demonstrations were begun.

In the field demonstrations, permeability increases in soil and rock formations were verified in the following manner. Before fracturing, a vacuum was applied to an extraction well as shown in Figure 2.2, using a vacuum blower pump. Flow readings, measured in volume per unit time (i.e. standard cubic feet per minute), were recorded at constant vacuum to establish the pre-fracture behavior of the formation. After pneumatically fracturing the formation, the flow readings were again measured at the same vacuum level and compared with the pre-fracture reading. This procedure permitted direct comparison of formation permeabilities before and after fracturing activities, which is the primary tool for evaluating the effects of pneumatic fracturing.

Permeability test results from a recent field test conducted in the Brunswick Shale Formation in Newark, New Jersey, are presented in Figure 2.3. The figure is a subsurface flow profile conducted at two foot intervals in the test borehole. By comparing the white bar chart sections (pre-fracture flow), with the cross-hatched sections (post-fracture flow), it is clear that pneumatic fracturing has substantially increased the formation permeability. Table 2.1 shows a summary of flow rate increases observed during recent demonstrations of pneumatic fracturing.

A secondary measurement of formation permeability enhancement through pneumatic fracturing is radius of influence. By measuring the vacuum induced at monitoring wells located at various distances from a vapor extraction point, the radius of influence of the system can be determined. This radius of influence is directly proportional to the permeability of the formation. By increasing formation permeability, pneumatic fracturing has consistently demonstrated the ability to increase the effective radius of influence for vapor extraction systems. An example of this is shown in Figure 2.4.

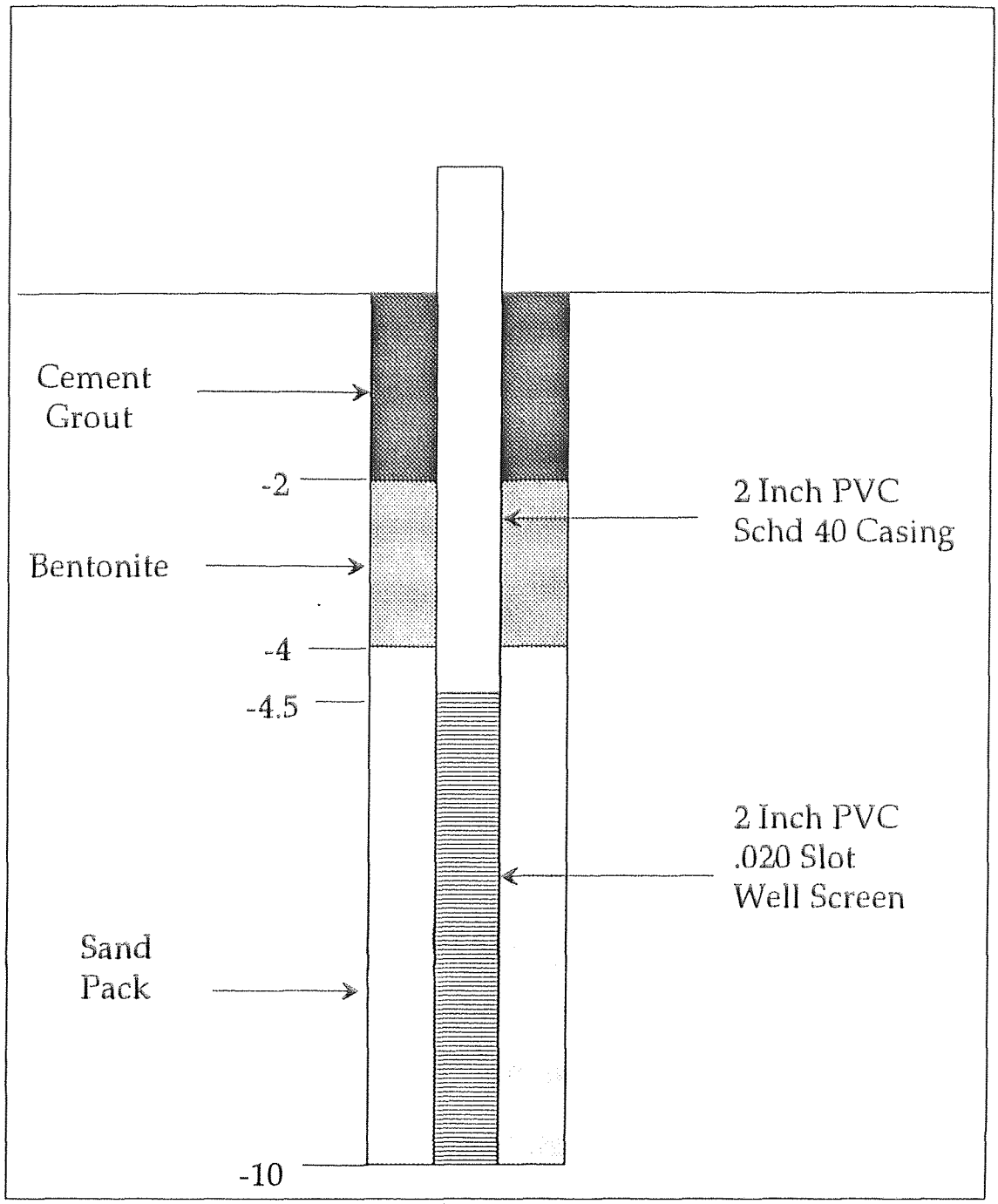


Figure 2.2 Typical extraction well.

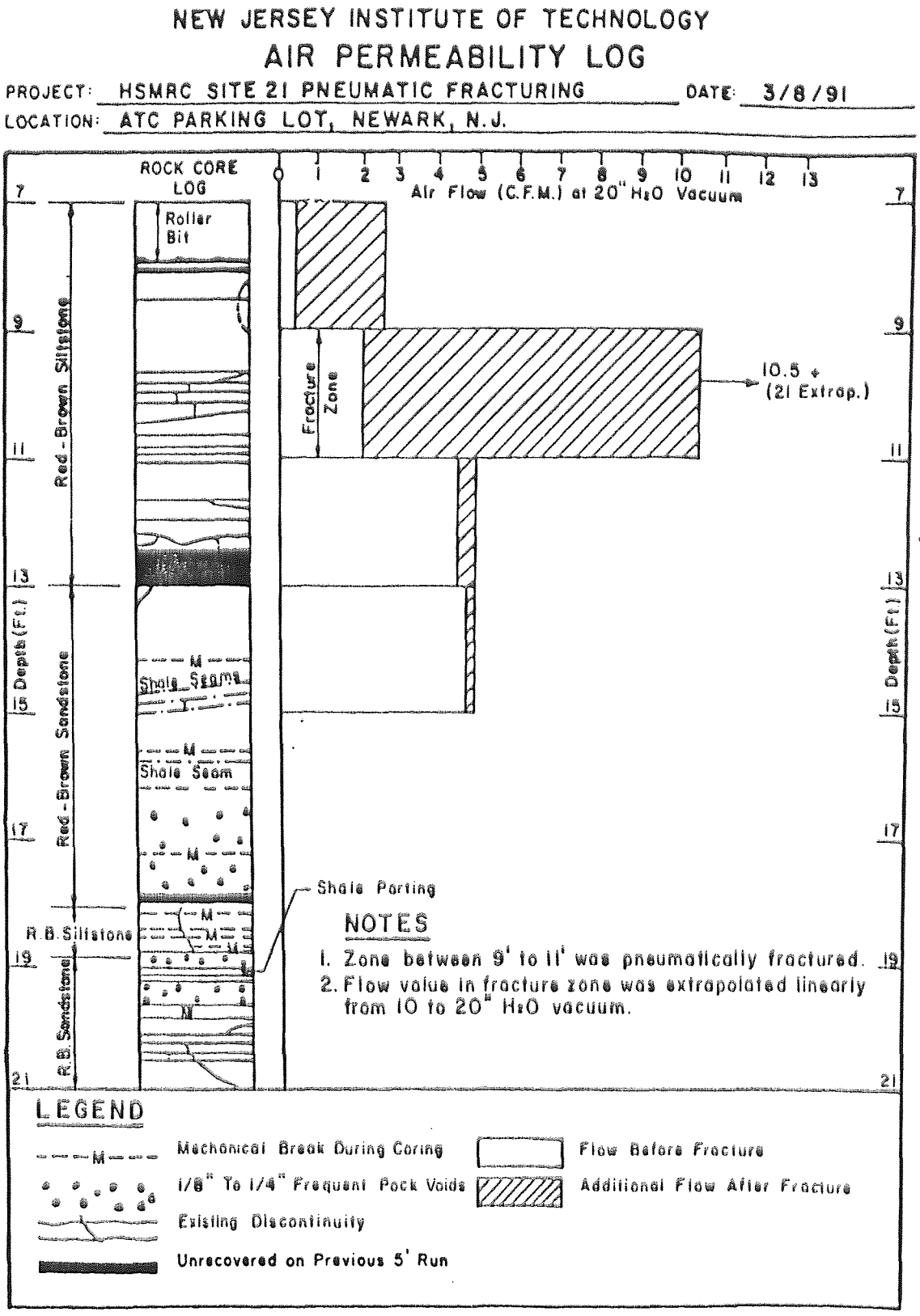


Figure 2.3 Air permeability log from ATC parking lot Newark, NJ.

Table 2.1 Summary of permeability increases for pneumatic fracturing projects

Site Location	Geology	Well/ Zone	Pre-fract. Flowrate (SCFM)	Post-fract. Flowrate (SCFM)	Vacuum Inches H2O	Percent Increase
Frelinghysen, New Jersey	Clayey Silt	Well VW-1	0.12	5	30	4067
Frelinghysen, New Jersey	Clayey Silt	Well VW-4	0.2	10	30	4900
Newark, ATC New Jersey	Sand-stone	Zone 9'-11'	0.2	21	20	10400
Newark, ATC New Jersey	Sand-stone	Zone 15'-17'	0.5	7	20	1300
Richmond, Virginia	Silty Clay	Well	0.001	3.5	27	349900
Somerville, New Jersey	Silt-Stone	Well	0.5	5	110	900
Newark, (CF) New Jersey	Clay, Silt, Sand	Well	5	15	110	200
Roseland, New Jersey	Silty Sand	RW-1	5	10+	59 (24)	100+

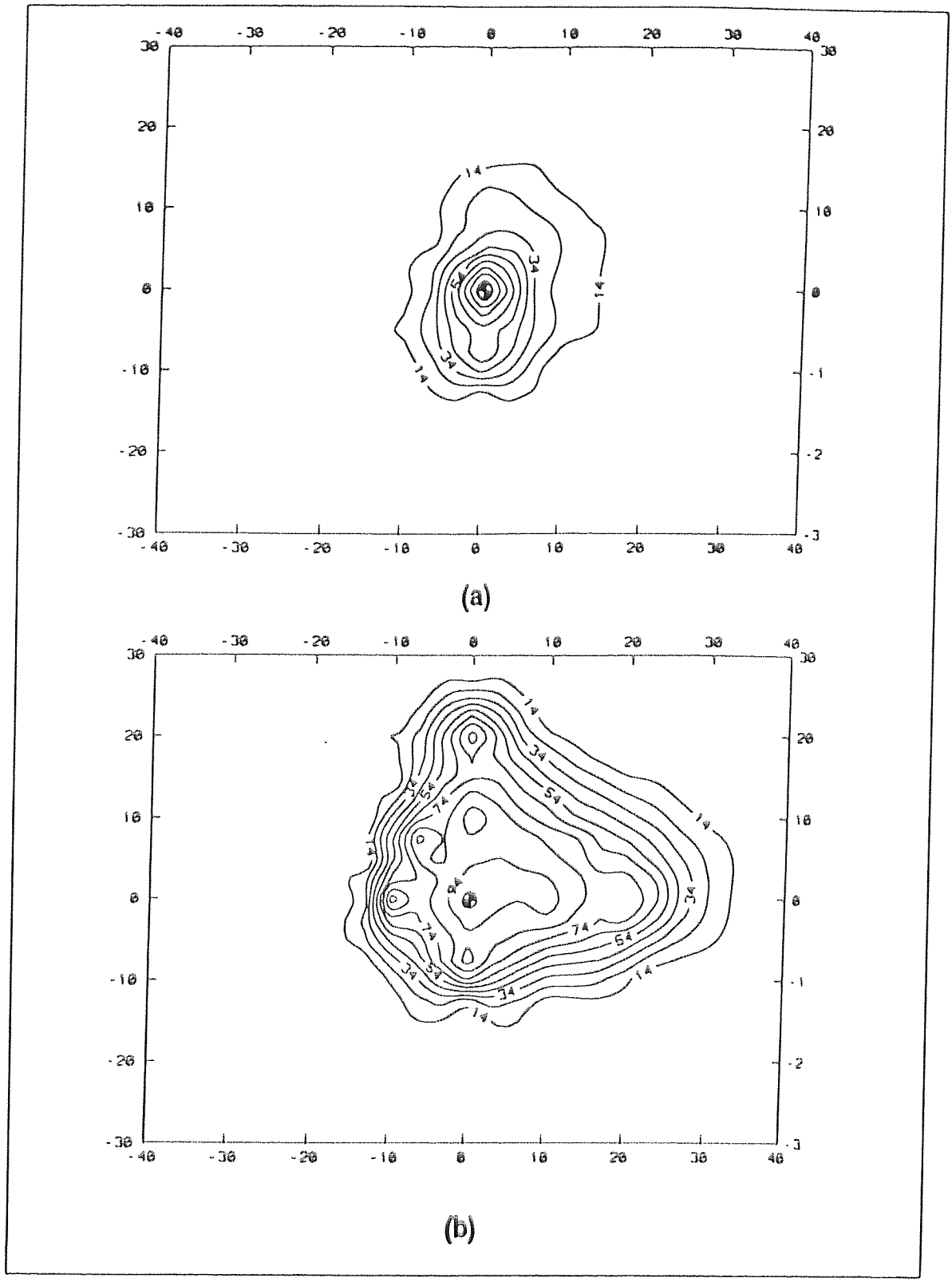


Figure 2.4 Vacuum radius of influence increase from site in Somerville, NJ. Pre fracture vacuum radius of influence is shown in part a, while the post fracture vacuum radius of influence is shown in part b. Distance is measured in feet, and vacuum is measured in inches of water.

2.1.4 Fracture Endurance: The Effect of Moisture

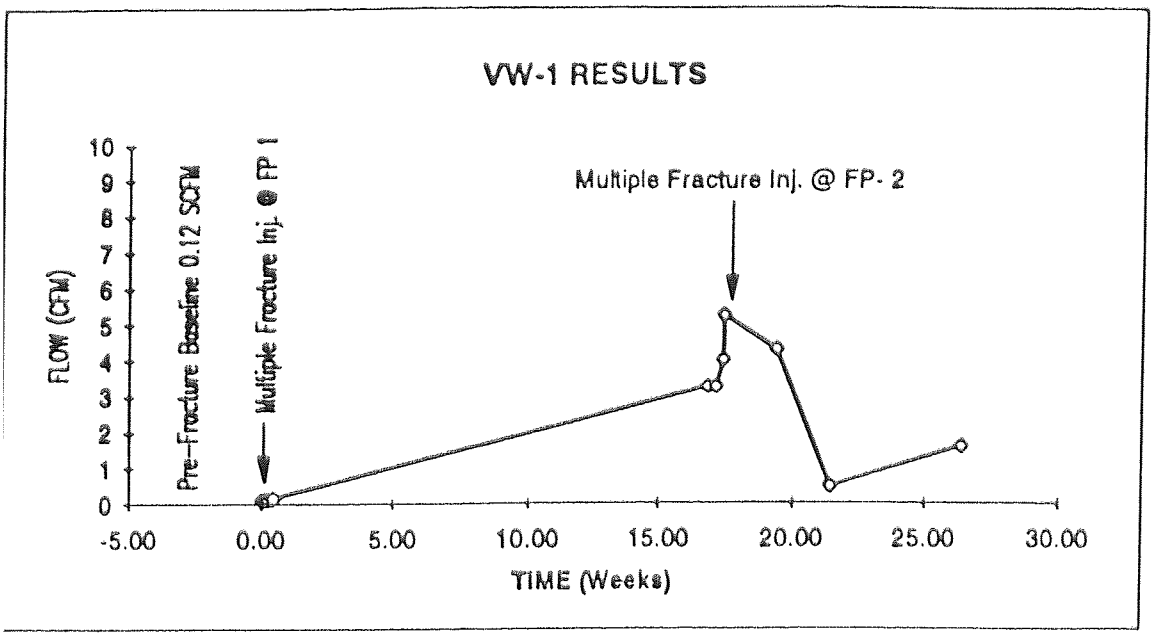
An important aspect of pneumatic fracturing is the endurance of the fractures in soil. That is, how long will the fractures remain viable, and will reinjections be necessary to re-open the formation? This aspect was studied at a demonstration site in Frelinghuysen, New Jersey over a six month period.

The study involved two site visits during which the formation was fractured, and four intermittent visits for monitoring and data collection. During the tests, vacuum flow rates were correlated with soil moisture and water table readings. Moisture levels were also correlated with precipitation. The data from this study are summarized in Figures 2.5 to 2.7.

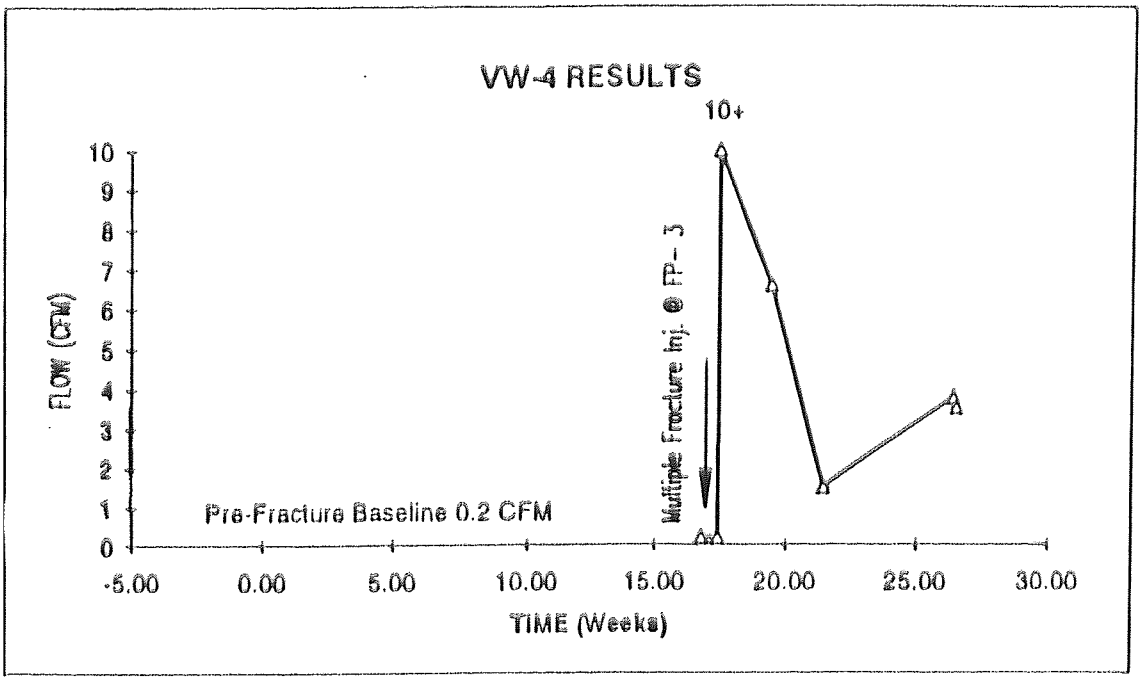
As indicated in the figures, flow behaviors for the extraction wells VW-1 and VW-4 varied inversely with the soil moisture content. During periods of high water table and elevated soil moisture, vacuum air flow rates were observed to decrease. The greatest air flow rates occurred when the soil was dry and the water table was below the fracture zones. In all cases, however, post-fracture air flow rates were greater than pre-fracture levels.

Three observations about the long term effects of soil moisture on pneumatic fracturing were made based on this data. First, despite the periods of heavy moisture and successive dry spells, the soil fractures remained open and viable, as evidenced by the flow rates measured at the end of the test. In all cases, the flow rate at the end of the study period was at least one order of magnitude higher than the pre-fracture condition. The greatest flow rate readings were observed during the driest periods.

Second, soil can be effectively fractured despite heavy moisture as shown in the flow rate/time history of VW-1. The initial fracture occurred in wet soil and did not show the typical flow increase which had been observed elsewhere

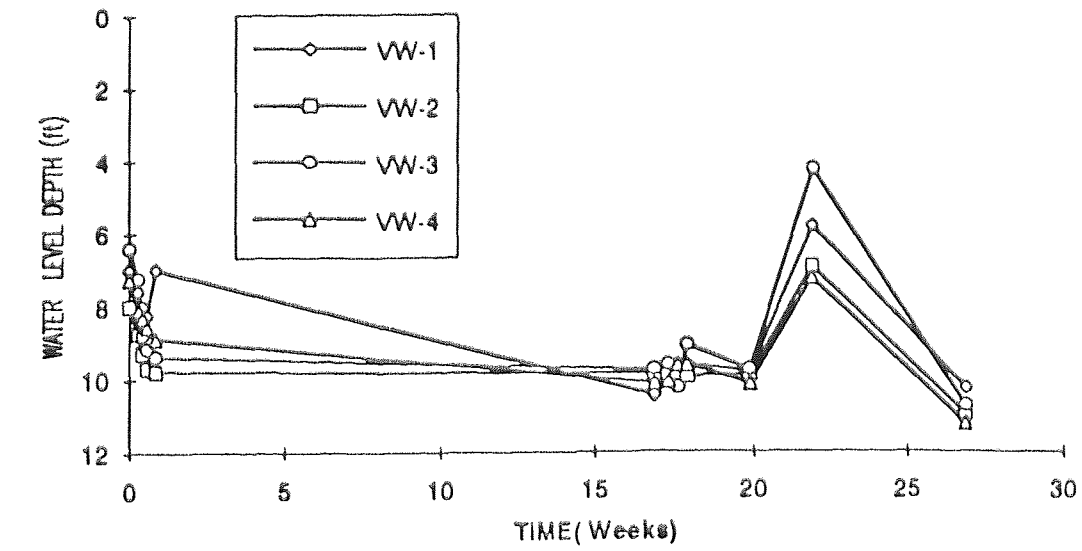


(a)



(b)

Figure 2.5 Long term behavior of fractures, Frelinghuysen Township, NJ. The long term permeability of VW-1 is shown in part a, and part b shows the permeability over time of VW-4.



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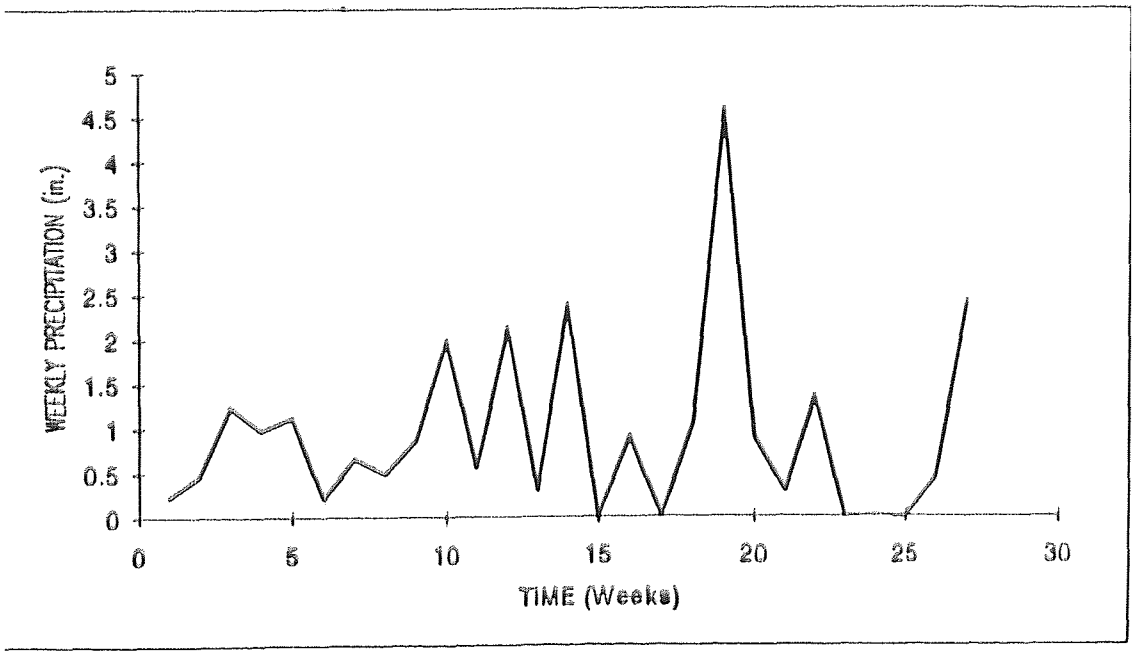
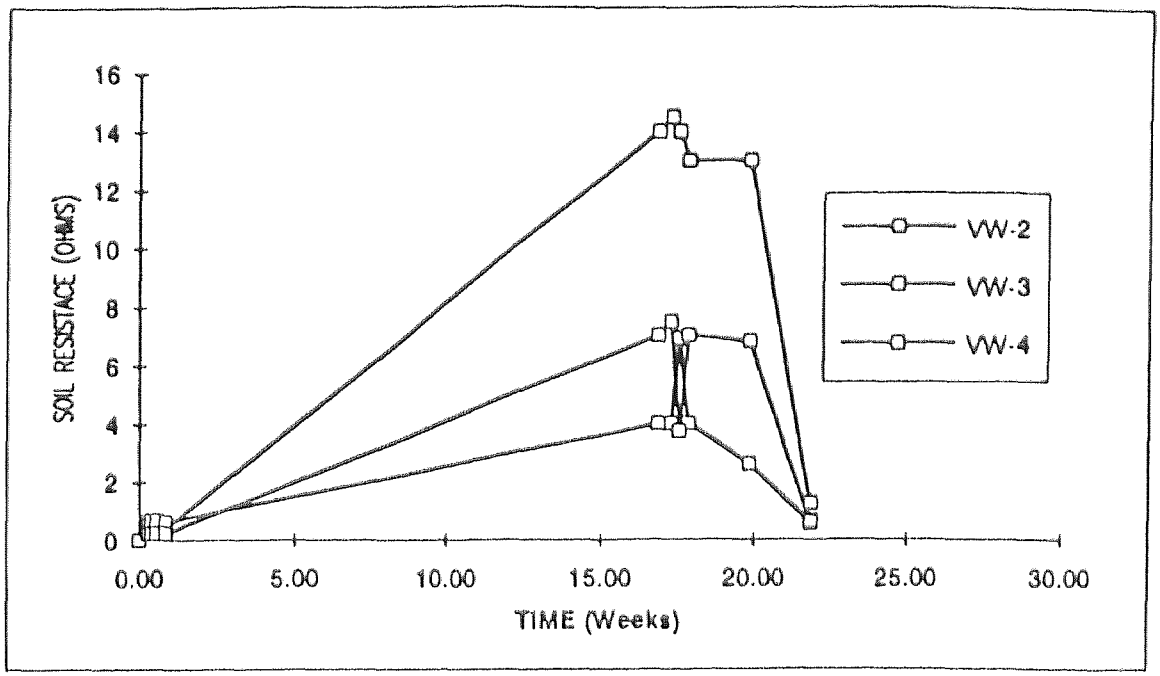


(b)

Figure 2.6 Water level and precipitation, Frelinghuysen Township, NJ. Part a shows the depth to the water table over time, and part b shows the corresponding weekly precipitation.



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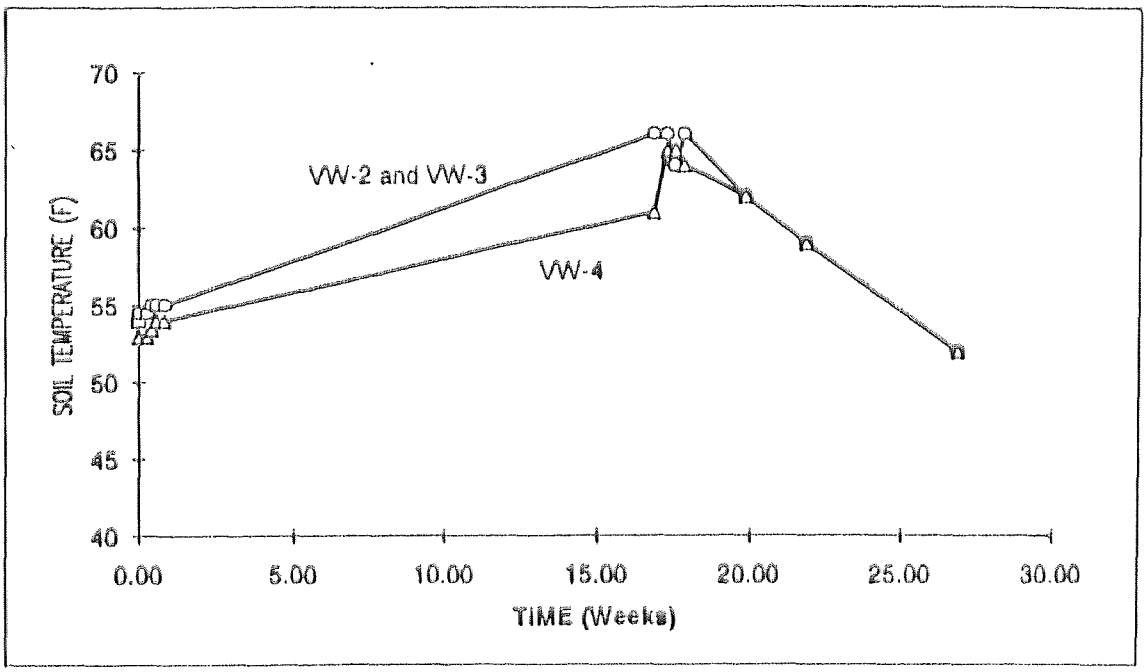


(b)

Figure 2.7 Soil resistance and temperature, Frelinghuysen Township, NJ. Soil moisture as measured through resistance is shown in part a, and the corresponding soil temperature is shown in part b.

in the formation. However, after the soil had dried over the course of 17 weeks, it was discovered that the flow rate had increased substantially. When compared to the low permeabilities of nearby sections of the formation which had not been fractured, it was concluded that the flow increase was a delayed reaction to the fracturing.

Third, it can be concluded that soil moisture can have a retarding effect on air flow in a formation after it has been pneumatically fractured. However, a high vacuum, high flow rate vapor extraction system, will volatilize and extract the water from the formation. The retarding effects of soil moisture should therefore not be a major factor in sites under active remediation by vapor extraction.

2.1.5 Status of Pneumatic Fracturing

To date, pneumatic fracturing has successfully enhanced subsurface air flow at three clean sites and five contaminated sites. These demonstrations have included a USEPA SITE demonstration in Hillsborough, NJ. Transfer of the technology to commercial development partners for continued vapor extraction projects is currently underway. As the work with vapor extraction continues, research has also begun to integrate pneumatic fracturing with bioremediation.

2.2 Bioremediation

Bioremediation is a solution to many soil pollution problems. By stimulating subsurface activity of microorganisms, dangerous chemicals can be degraded into harmless minerals. Because it is a natural occurring process, bioremediation can be performed in situ if critical parameters can be controlled. Before discussing the ways in which pneumatic fracturing can enhance in situ

bioremediation, it is important to explain the manner in which chemicals are biologically degraded in soil.

2.2.1 Concept of Bioremediation

Most organic wastes found in contaminated soils will eventually naturally degrade biologically into harmless compounds. For example, benzene, which is a suspected carcinogen, will degrade as follows:

$$2C_6H_6 + 15O_2 \Rightarrow 12CO_2 + 6H_2O \qquad (2.1)$$

Thus the chemical is converted to basic carbon dioxide and water, and thereby rendered harmless.

A process like the one shown above is called mineralization or ultimate degradation, which refers to a complete breakdown of a chemical to inorganic compounds.[3] Besides water and carbon dioxide, ammonia, sulfate, nitrate, or chloride may be the end products of mineralization. Biodegradation rates which are reported in terms of BOD, COD, oxygen uptake, methane production, or loss of dissolved organic carbon refer to ultimate degradation.[4] Less than complete mineralization of a chemical would indicate partial degradation.

Primary degradation, is used to describe a biologically induced structural change in an organic chemical. For example, primary degradation of tetrachloromethane would indicate the replacement of one chlorine atom by a hydrogen atom, which would yield trichloromethane. Organic chemical biodegradation rates reported in terms of removal, disappearance, or loss of a particular chemical refer to primary degradation.[4]

2.2.2 Metabolic Considerations

There are two major types of microorganisms involved with in situ bioremediation. Bacteria are the most numerous, although they are smaller. Fungi are larger and often account for the majority of the microbial mass present in the soil, although they usually would have the smallest population count.[5] Algae are also commonly present in the soil environment, but have very limited effects on in situ bioremediation.

Bacteria can be defined as any of a group of diverse and ubiquitous single celled microorganisms.[6] The variety of bacterial species that are commonly found in the soil reflects their diversity. Much of the work in bioremediation is believed to be accomplished by bacteria.

Actinomycetes are a special group of gram-positive bacteria that are characterized by their formation of branching filaments. They tend to be more predominant in warm, dry soils.[6] Importantly for bioremediation, they have shown the capability to degrade complex organic compounds, as they play an important role in building soil fertility.

Fungi typically require oxygen and therefore stay within the first few layers of the surface. Their normal activity in the soil is to degrade the major constituents of plant tissue.[6] Algae are photosynthetic organisms and therefore must stay on or close enough to the surface in order to receive sunlight. In fertile soils the activity of algae is dwarfed by that of the fungi and bacteria.[6] They are more dominant in barren situations.

Microorganisms require a carbon source and an energy source in order to survive and reproduce.[3] Based on their means of satisfying these requirements, microorganisms are either classified as heterotrophs or autotrophs. Heterotrophs are organisms which utilize an organic compound as the carbon source and the oxidation of the organic compound as the energy source.

Autotrophs use carbon dioxide as the carbon source and obtain energy from the oxidation of inorganic compounds. For degradation of petroleum contaminated soils, heterotrophic microorganisms are more common.[5]

Microorganisms also require a terminal electron acceptor for electrons which are transferred during energy reactions.[3] Oxygen usually serves as the receptor for electrons. Without an adequate supply of molecular oxygen, an inorganic compound such as nitrate or sulfate may accept the electrons.

The ability to grow in the presence or absence of oxygen is another method of classifying microorganisms. Those that require oxygen for growth and activity are aerobic. Microorganisms that survive only in an environment completely void of oxygen are anaerobic. Facultative anaerobes can survive under both aerobic and anaerobic conditions. This means that they can switch electron acceptors between oxygen and other compounds.

Another important substrate required of soil microorganisms are inorganic nutrients.[7] Any substance that is required for growth is referred to as a nutrient. There are two categories for nutrients: Macronutrients and micronutrients. Some nutrients form the building blocks of the cell while others are only used for energy generation or in a certain enzyme.[8] In some instances a particular nutrient may serve both roles.

The two major macronutrients required by microorganisms are carbon and nitrogen. Carbon can be supplied by a variety of sources, and serves as the basic building block for the cell. After carbon, nitrogen is the most abundant nutrient found in cells. A typical bacterial cell will contain 12-15% nitrogen.[8] Natural sources of nitrogen are ammonia (NH_3) and nitrate (NO_3^-). In addition, certain microorganisms, through a process called nitrogen fixing, can use molecular nitrogen from the air (N_2).[6] Nitrogen is a major component of the various

proteins and nucleic acids found in the cell, as well as being an important constituent of the material that makes up the cell wall.

The third most abundant macronutrient found in microorganisms is phosphorus, and the fourth is sulfur.[8] Phosphorus is a prime constituent of many nucleic acids, as well as certain lipids. Sulfur is present in the cell as a part of certain key amino acids and many important vitamins. Other common macronutrients include potassium, magnesium, calcium, sodium, and iron.[7]

Micronutrients, which are typically trace metals, are required only in small amounts. They are found in different amino acids, vitamins, or enzymes. Although only small amounts are necessary, a lack of trace metals can stop cell activity. Typical micronutrients include copper, cobalt, nickel, manganese, and tungsten.[8]

The actual degradation of compounds by microorganisms is performed by enzymes. Enzymes, of course, are very specific in the reaction that they will catalyze. A compound that has a complicated degradation path may require a host of enzymes to complete the process. These enzymes may all come from a single microorganism or be produced by a group consisting of various species. Constitutive enzymes are the types of enzymes that are present inside of a microorganism during its normal metabolic processes. Inducible enzymes are produced in response to the presence of a certain substrate.[5]

2.2.3 Reaction Rates

Most of the available biodegradation rate equations are for aquatic environments and not for soil systems.[5] Modeling the rates of degradation in a soil is difficult because of the numerous impurities that are encountered. Some general equations have been established, however. Valentine and Schnoor expressed the following first order equation based on contaminant removal[5]

$$\ln (S/S_0) = -k_1 t \qquad (2.2)$$

where S is the substrate concentration at time t, S_0 is the initial substrate concentration, and k_1 reaction rate constant. Substrate half life could then be measured using

$$k_1 = \ln(2)/t_{1/2} = 0.693/t_{1/2} \qquad (2.3)$$

In cases where the maximum growth rate of the microorganisms, as well as the concentration are known, the following equation could be used to predict specific growth rates.

$$V = V_{max} C/(K + C) \qquad (2.4)$$

Where:

V = Specific growth rate of microorganisms.

V_{max} = Maximum growth rate of microorganisms.

C = Concentration of organic chemical.

K = Organic chemical concentration supporting a growth rate which would equal one half of the maximum ($V_{max}/2$).

This is known as the Monad Kinetics rate equation and is designed to illustrate the relationship of a single or mixed species population of microorganisms which are using a single organic chemical as a source of energy.[4]

An empirical approach was taken by Bradford and Krishnamoorthy.[3]

$$WDR = K_2 C_w C_O C_P C_N \qquad (2.5)$$

In their equation, WDR is the aerobic waste destruction rate, while the C coefficients are the concentrations of the waste, oxygen, phosphorus, and, nitrogen, respectively. K_2 is the reaction rate constant and is based on the following parameters.

Type of Waste
Toxicity of Waste
Acclimation
pH
Temperature
Moisture Content

These are key parameters for bioremediation, and several will be discussed in the following sections. Under ideal conditions, in which an ample supply of oxygen and nutrients are available, this equation reduces to

$$WDR = K_3 C_w \tag{2.6}$$

Usually the rates for natural degradation are too slow to be considered as an effective remediation alternative. If, however, the important parameters for biological growth and activity are properly controlled, the rates of degradation can be greatly increased. In this manner, contaminants present in soil and groundwater can be efficiently, and cost effectively destroyed. The most crucial aspect of this in situ bioremediation is gaining control of the subsurface environment in which the degradation is to take place. All parameters must be considered.

2.3 Key Parameters of In Situ Bioremediation

There are a host of factors involved in biological treatment of contaminated soils. Tables 2.2 and 2.3 lists the most important parameters for successful bioremediation. Attempts at in situ bioremediation which do not properly account for these parameters will fail, resulting in excavation of the soil for ex-situ biological treatment[7] or other soil treatment technology. As stated previously, in situ technologies are usually more favored, although they are also more challenging. The remainder of this thesis will focus on the use of in situ bioremediation to solve soil contamination problems by controlling the key parameters of the process.

2.3.1 Soil Moisture

All microorganisms require some degree of soil moisture for growth and activity. The optimum soil moisture content in the vadose zone is between 50% and 75% of the soil moisture holding capacity.[5] In clean soils, the soil moisture is often the major limiting growth factor in the vadose zone.[8]

Moisture content in the soil will affect degradation of contaminants in a variety of ways. An increase in soil water may allow more contaminant to be present in the aqueous phase or dilute the chemical concentration, both of which would tend to increase degradation rates. Decreasing the moisture content may allow for more of the contaminant to sorb onto soil particles and reduce accessibility to degradation.[5] Too much water, however, can limit the amount of oxygen available by reducing the pore gas exchange rate in the soil.

Many bioremediation efforts to date have used a saturated system in order to better control the other parameters that affect biological growth in the

Table 2.2 Important Geologic Formation Characteristics for Successful In-Situ Treatment

Soil Properties	Hydraulic Properties	Geology and Climate
Location /Topography	Permeability (saturated)	Subsurface geology
Soil type and extent	Permeability (unsaturated)	Groundwater flow patterns
Soil boundary and depth	Water holding capacity	Groundwater characteristics
Structure/Stratification	Infiltration rates	Wind velocity/direction
Clay content	Depth to impermeable layer	Temperature
Clay type	Depth to groundwater	Precipitation
Bulk density	Flooding frequency	
Organic matter content	Runoff potential	
Soil pH and Eh		
Aeration status		

Table 2.3 Major Parameters for Microbial Growth and Activity

Environmental Factor	Optimum Level
Oxygen	Aerobic: More than 0.2 mg/l dissolved oxygen or more than 10% of air space filled with air Anaerobic: Less than 1 % oxygen
Moisture	25% to 85% of water holding capacity
Nutrients	Enough nutrients (nitrogen, phosphorus) To insure that they are not a limiting factor
Soil pH	Neutral, usually between 5.5 to 8.5
Temperature	Mesophilic range (15-45 degrees Celsius)
Contaminant concentration	Varies depending on the compounds present
Microorganism acclimation	Contamination present for over 12 months

soil.[10] These systems operate much like a standard pump and treat system with infiltration trenches or injection wells, combined with recovery wells. The water that is injected into the soil is augmented with oxygen, nutrients, and/or microorganisms in a variety of methods. A general schematic drawing of this type of system is shown in Figure 2.8. For this type of system to be effective, however, the formation must be very permeable.

2.3.2 Available Oxygen

Available oxygen in the soil matrix is often a major limiting factor for in situ bioremediation.[10] The availability of oxygen in soil will determine whether aerobic processes or anaerobic processes are dominant. Aerobic processes are typically favored because an aerobic system will produce a great deal more energy than an anaerobic system.[6] This will tend to accelerate the reaction rates of the degradation process, which is the objective of in situ bioremediation. For this reason, control of available oxygen is crucial to the success of a bioremediation system.

Unfortunately, the intense microbial activity required by this technology will quickly deplete available oxygen before it can be replaced by natural soil diffusion. This makes the contaminated zone anaerobic, which will usually either slow or prevent biological degradation. As the contamination travels further below the surface, the problem is compounded because atmospheric air must diffuse deeper into the soil. Therefore, the deeper the contamination, the lesser the amount of oxygen that will be available for degradation.

Methods for increasing available oxygen in the subsurface have included the addition of the following:

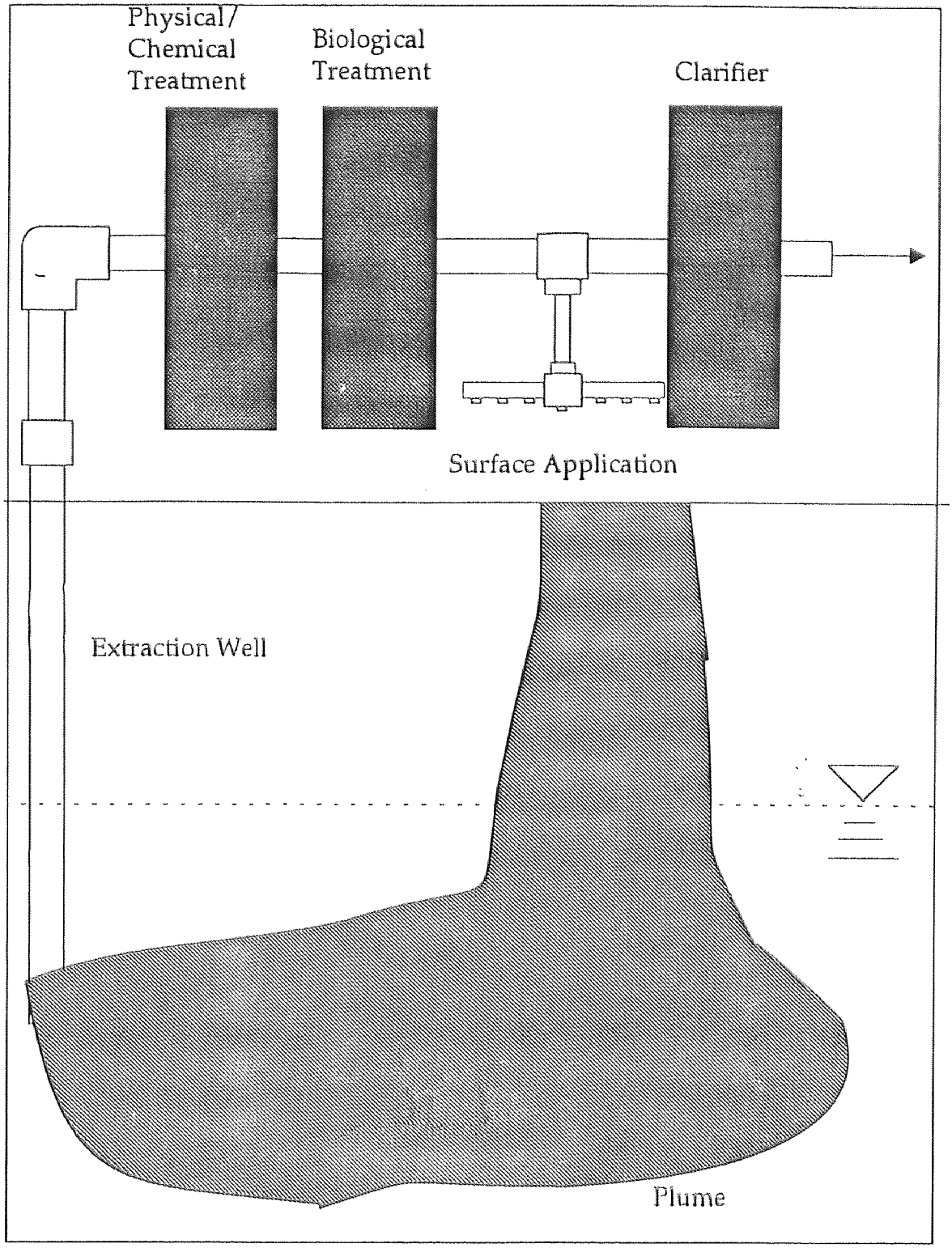


Figure 2.8 In situ bioremediation in a saturated system.

Air (Aeration)	Hydrogen Peroxide
Pure Oxygen	Nitrate/Ozone
Nitrate	

Aeration of the soil is by far the most economical of the alternatives. It is most efficient in bioventing systems operated in the vadose zone. Bioventing is an in situ process of stimulating microbial growth by aerating the soil, either through injection, extraction, or a combination of the two.[11] A schematic diagram of a typical bioventing system is shown in Figure 2.9. It is a popular and relatively new technology for enhancing biodegradation, that is still in the demonstration phase.

In bioremediation systems which involve a saturated condition, however, aeration only produces approximately an 8 mg/l oxygen level under typical groundwater conditions and is therefore not very effective. For systems which use a saturated condition the water may be saturated with pure oxygen rather than air which may allow slightly higher levels of oxygen..

To further improve the concentration of oxygen in the infiltration water, hydrogen peroxide has been used. Its instability allows for good oxygen release throughout a formation. For example, 200 ppm of H_2O_2 will produce a concentration of 94 mg/l of oxygen[10]:

$$2H_2O_2 \Rightarrow O_2 + 2H_2O \qquad (2.7)$$

The concentration of hydrogen peroxide, however, must be limited, as it can be toxic to microorganisms. To overcome this difficulty, hydrogen peroxide application should begin with small doses. Concentrations could then be

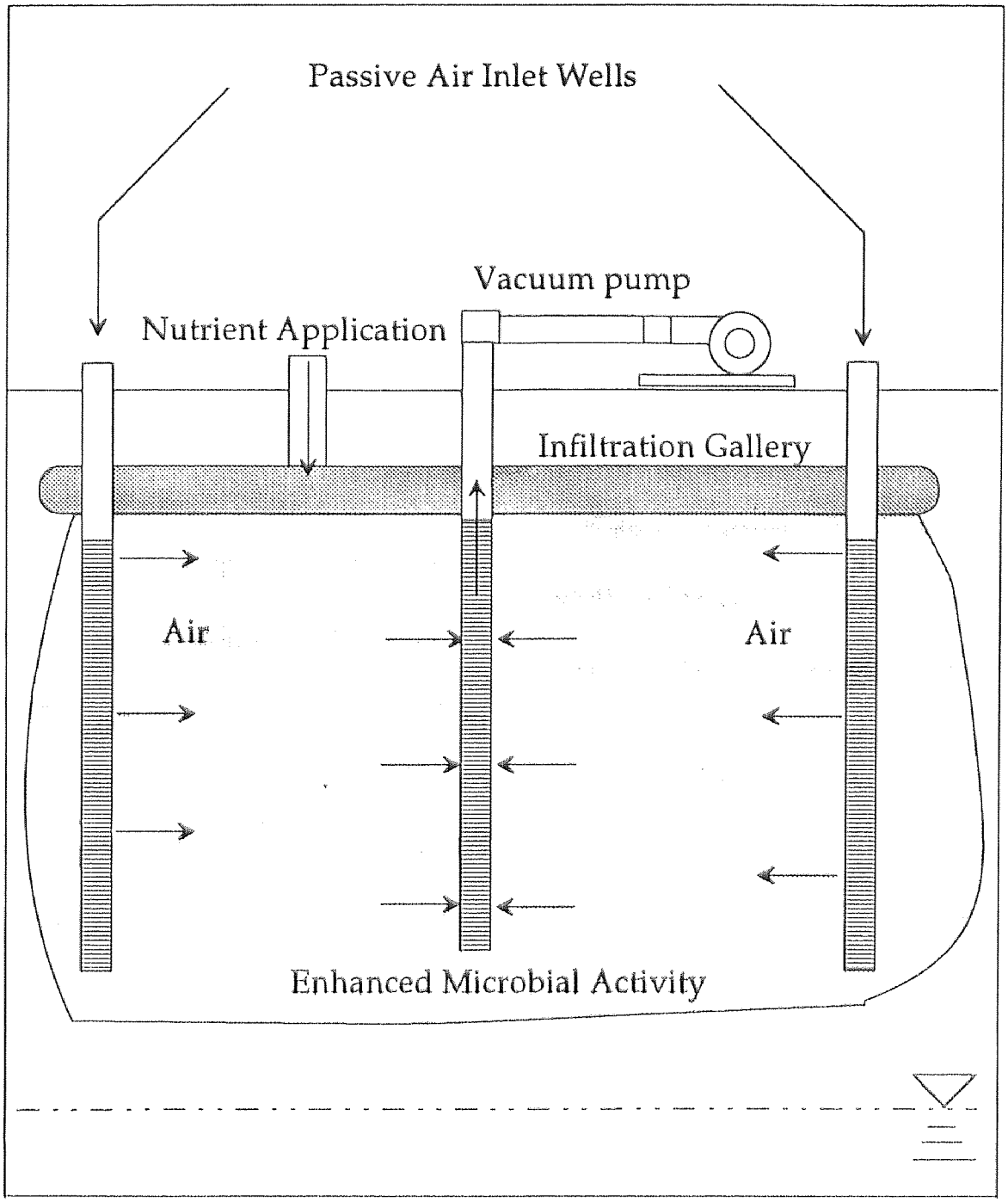


Figure 2.9 Schematic of a bioventing system

increased as the microorganisms became acclimated to the chemical. Using this approach, it has been reported that peroxide can be applied in concentrations of up to 1000 mg/l.[10]

Another disadvantage of hydrogen peroxide is that it sometimes degrades in the soil before reaching the zone where it is needed. The larger the infiltration distance, the more likely this will happen. Certain compounds, such as phosphate, can be added to improve the stability of hydrogen peroxide.[7] Phosphate can also help microbial growth and activity in that it serves as a nutrient.[10]

Under anaerobic conditions, nitrate can serve as the electron acceptor rather than oxygen. A system has also been developed in which ozone is used above ground to treat recirculating water by oxidizing the contaminants, while nitrates are returned to the soil to aid in degradation. Unfortunately, there are very few instances of successfully replacing oxygen with nitrate in a full scale in situ bioremediation system.[10]

In the laboratory, methane and oxygen can be combined together in a process called co-metabolism. This type of reaction occurs when the degradation of the organic substance is done by a microorganism which cannot use the compound for growth and must rely on other compounds for carbon and energy.[7] The degradation, however, is done by an enzyme that the microorganism produces. An example of microorganisms which use cometabolism are methanotrophs. Methanotrophs use methane for their energy source. In an environment which contains methane and oxygen, these organisms will produce the enzyme monooxygenase, which is their first step in utilizing methane. This enzyme is also capable of degrading a host of hydrocarbons. For example, monooxygenase will bring about the conversion of an alkene to an epoxide:

$$CHCl{=}CHCl + H_2O \Rightarrow CHClOCHCl + 2H^+ + 2e^- \quad (2.8)$$

Epoxides are unstable in water and can be further degraded easily by heterotrophic microorganisms.[10] The feasibility of extending cometabolism to the field are still under study.

The major dissatisfaction with these methods of oxygen enhancement is that they are greatly inhibited by the soil permeability. Whether the method uses the liquid or the vapor phase to carry the oxygen throughout the formation, difficulties will arise in fine grained soils.

2.3.3 Available Nutrients

Nutrient requirements for in situ bioremediation projects are site specific, and in some cases, nutrient addition may not be necessary. Most situations will, however, require a certain amount of nutrient application, especially in locations with heavy organic contamination. The difficulty with nutrient control is similar to that of oxygen; microbial activity will use up these compounds faster than they can naturally be replaced.

General techniques of nutrient application have been similar to common agricultural methods for spreading fertilizer. This has included the various tillers and applicators necessary to apply the nutrients.[10] Nutrients have also been added to the formation through injection wells and infiltration galleries. Unfortunately the success of these methods will rely on the diffusion of these materials to the proper depth, which is governed by soil permeability.

2.3.4 Soil pH

In general, the optimum growth rate for microorganisms in the soil will occur at a neutral pH. There are some instances where a certain species will excel under extremely acidic or alkaline conditions. In such situations it may be desirable to radically change the pH of the soil. Most bioremediation situations, however, will require the activity of a group of microorganisms. To satisfy the needs of the majority, a neutral pH is usually recommended.

Most degradation processes will produce organic acids which lower the pH. Nitrogen from nutrient application will also tend to make the soil slightly acidic. To counter this, lime can be added with the fertilizer during nutrient application.[10]

2.3.5 Temperature

Growth and activity of microorganisms are directly associated with the temperature. Based on optimum growth rate temperatures, microorganisms are divided into three groups. Psychophiles exhibit maximum growth rates at temperatures of less than 20 degrees Celsius, and can grow under freezing conditions. Mesophiles grow best in the range of 25 to 40 degrees Celsius, while thermophiles grow best at temperatures above 45 degrees Celsius.[6] Most microorganisms involved with situ bioremediation would be classified as mesophiles.

Soil temperature is mainly influenced by either vegetation or applying a mulch. A well vegetated soil will retain temperatures better than a bare soil, both in summer and in winter. Unfortunately, accurate control of temperatures in soil is very difficult. The soil will absorb a great deal of energy before the temperature will rise significantly.

A bioventing field test underway at Eielson Air Force Base near Fairbanks, Alaska is using warm water to control subsurface temperatures. In this test, water at a temperature of 35 degrees Celsius is added to the formation through surface infiltration. Preliminary results show that the warm water can elevate the soil temperatures sufficiently to allow significant biodegradation.[12]

2.3.6 Availability of the Contaminant

Another important factor that must be considered for in situ bioremediation is the availability of the chemical to the microorganism. The chemical must be accessible, both on the macroscopic level and on the microscopic level, to be effectively degraded. Macroscopically, indigenous microorganisms may be spatially distributed in an irregular manner so that there are zones in which there is no population capable of degrading the compound. This can be remedied by moving microorganisms to the more sparsely populated locations. Problems on the microscopic level are more difficult to solve.

At the microscopic level, situations often occur in which the chemical becomes sorbed onto the soil particles. Although there are cases in which the rates of degradation increased, this phenomenon usually results in repression of chemical degradation.[5] The reasons for this decrease are not fully understood, but there are three major theories given to explain this.

1. Physical barriers of some sort may exist, once a chemical is sorbed onto a particle, that prevent an enzyme from attacking the chemical.
2. The chemical may be sorbed onto the particle in such a manner that the microorganism can only get to it after some agitation.
3. The chemical may be concentrated in an area where the microorganisms cannot grow.

A potential solution to this problem is to desorb the chemical by adding some sort of surfactant to the soil. Some preliminary work along these lines has been performed, but no field data are available to show its feasibility.

2.3.7 Microorganism Augmentation

Most cases of in situ bioremediation focus on using the indigenous microorganisms. Under certain circumstances, however, it is desirable to add a different culture of microorganisms. This may be necessary if the indigenous microorganisms are unable to degrade the compounds, or if natural limiting factors in the soil do not allow a critical microbial species to develop a large enough population that will degrade the compound. Microorganisms that are added to a soil basically fall into two categories: Acclimated or genetically engineered.

Acclimated microorganisms are grown in a laboratory under conditions that require them to degrade certain compound in order to survive. In this manner they become accustomed to using that compound for growth, and when they are added to the soil, the microorganisms can more quickly degrade the contaminant. Often the source for acclimated microorganisms is the contaminated soil which is to be treated.

Genetically engineered microorganisms have shown potential to degrade some of the most hazardous wastes.[7] These microorganisms are genetically altered to degrade certain compounds. Once created in the laboratory, these microorganisms are harvested and acclimated before being added to the soil.

Addition of exogeneously grown microorganisms does have its potential drawbacks, however. There is no guarantee that these microorganisms will not be destroyed by a pathogen or eliminated by competition once in the soil

population. They also may be washed out of the soil by excessive moisture. In addition, particular microorganisms designed to attack one certain compound may unable to tolerate other chemicals that are present in the subsurface environment.

Another difficulty of microorganism augmentation is permeability. Diffusion of a exogeneously grown microorganism population throughout a formation is inhibited by its permeability. Since such a population is usually added to the soil in a solution form, commonly called an inoculum, the solution must be able to permeate through the formation. In a overconsolidated soil formation, this process can be very difficult.

CHAPTER 3
ANTICIPATED BENEFITS OF PNEUMATIC FRACTURING INTEGRATED WITH BIOREMEDIATION

3.1 Concept

The success of in situ bioremediation depends on control of subsurface conditions to enhance microbial growth. Proper control is possible only if the zone of contamination is accessible. As a result , the feasibility of using in situ bioremediation is directly related to the permeability of the soil. In low permeability formations, bioremediation will be ineffective unless action is taken to enhance microbial growth. Pneumatic fracturing is a technology which has the potential to provide this enhancement.

The major goal of integrating pneumatic fracturing to enhance in situ bioremediation is to attain better control over the parameters that affect biological growth in the soil. Some theoretical concepts and benefits of combining pneumatic fracturing with in situ bioremediation will now be described.

3.2 Field Design Options

The pneumatic fracturing process will provide three potential options for enhancing in situ bioremediation. These options may be used individually or they may be combined, according to whichever method will most effectively attack the problem. In full scale production situations, a combination of methods will likely be most effective.

3.2.1 Bioventing

The first option is to install a bioventing system, similar to the one displayed in Figure 2.9. This type of system circulates air from the atmosphere through inlet

wells, and into the formation to enhance levels of available oxygen. The problem of liquid nutrient addition would be overcome using a pneumatic bio-injection system capable of injecting liquid solutions horizontally into the zone of contamination, thereby providing nutrients, microorganisms and anything else that is necessary. Bio-injection is easily accomplished by adding a liquid spray to the same high pressure air stream used to fracture the formation. A schematic diagram of the pneumatic bio-injection system is shown in Figure 3.1. Pneumatic injection of life supporting solutions directly into the biologic activity zone will accelerate degradation rates, and avoid the usual lengthy diffusion times associated with surface or borehole application of nutrients.

3.2.2 Standard Pump and Treat

Another option of in situ bioremediation enhancement by pneumatic fracturing could involve the standard pump and treat system typically found in bioremediation projects. Preliminary data indicates that water has the ability to move through the fractures created by the pneumatic fracturing process. This has been observed in siltstone and clayey silt formations.

In accordance with current standard practice, the effluent water would be treated and then augmented with nutrients, hydrogen peroxide, or whatever else was necessary, before being reinjected into the subsurface. The increased permeability due to pneumatic fracturing would allow for greater fluid movement throughout the soil.

The method of reapplying the treated water will depend on the results of the fracturing process. If the fractures reach the ground surface, then a surface application procedure could be used. In the event the fractures intersect monitoring wells, the liquid could be applied through the well screens.

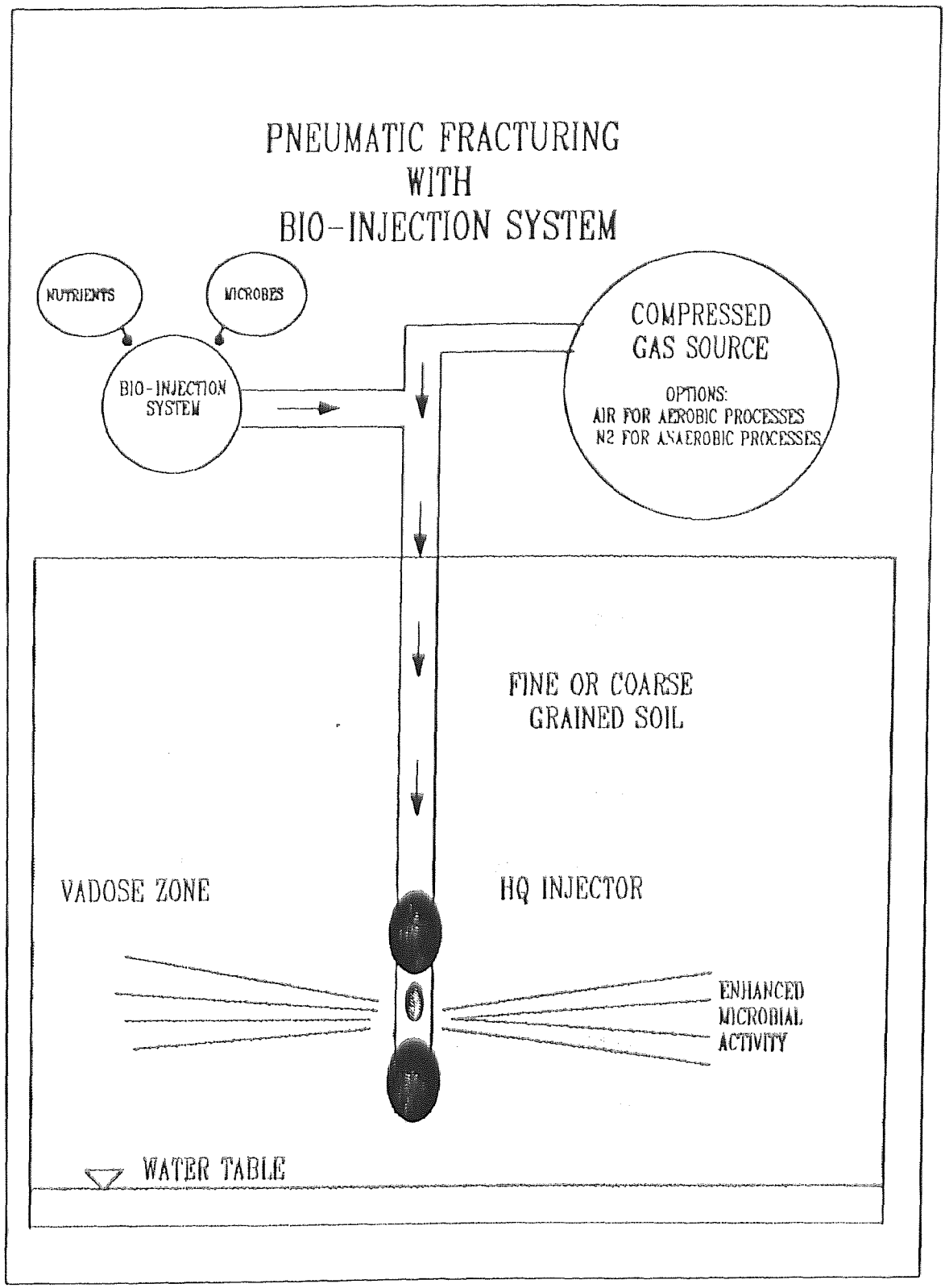


Figure 3.1 Conceptual diagram of pneumatic bio-injection.

3.2.3 Vacuum Pump

A third option would be to use an air vacuum pump rather than a water pump to remove water from the formation. By using a high vacuum, high flow rate vacuum pump, both water and air could be extracted simultaneously from a well. The effluent water would be treated and then reinjected, while oxygen would circulate throughout the formation via the vacuum extraction. Any effluent air would be treated by a method such as activated carbon. By circulating air and water simultaneously, the formation would remain aerobic, as well as moist.

3.2.4 Combinations

A full scale in situ bioremediation clean up utilizing pneumatic fracturing as an enhancement would most likely use a combination of the previously described methods. By supplementing the more common methods of surface application and well infiltration with pneumatic bio-injection of fluids, a given volume of soil could be more effectively treated. The increased formation permeability would allow for greater control of the important parameters crucial to subsurface microbial growth. The anticipated beneficial effects of these crucial parameters will now be described.

3.3 Key Parameters

3.3.1 Soil Moisture

As stated in Section 2.2, moisture content can be a limiting factor for microbial growth in the vadose zone. The increase in formation permeability provided by pneumatic fracturing can aid in soil moisture control in a variety of ways. In fractured formations, it will be easier to add or remove water from the soil. Water can be added either at the surface or through infiltration wells and

trenches, depending on fracture patterns and orientations. Water removal would most likely be done through extraction wells.

Another innovative method to exercise moisture control is the use of the pneumatic bio-injection system. This system permits injection of fluids directly into the zone where microbial activity is desired. In situations where it was necessary to remove water, the bio-injection system can be connected to a vacuum pump. Which can then remove water from a localized section of the formation. The bio-injection system will also be effective for controlling many of the other parameters of subsurface microbial growth.

3.3.2 Oxygen

Increased soil permeability will allow for superior air flow in the soil formation at greater distances from air flow wells. Oxygen could be efficiently circulated through the soil pores directly as a gas instead of being transported by water. Since atmospheric air is the most cost effective method of increasing available oxygen, this method of oxygen enrichment has great potential to reduce bioremediation costs.

Available oxygen could also be enhanced through more standard methods, such as water augmented with low level concentrations of hydrogen peroxide. One of the difficulties in using hydrogen peroxide enriched water is the instability of the chemical. This results in the degradation of the hydrogen peroxide before it covers the entire area of contamination. Since pneumatic fracturing increases formation permeability, the travel time for the hydrogen peroxide to the zone of contamination would be reduced. Water enriched with hydrogen peroxide can also be injected with the bio-injection system, thereby dispersing the oxygen producing chemical more efficiently.

Another way that pneumatic fracturing may be used for oxygen control is to aid in the removal of oxygen. In cases where anaerobic conditions are desired for microbial activity, the formation could be injected with nitrogen or some other gas in order to purge the subsurface of oxygen. The increase in permeability could also allow the formation to be flooded with water which also would tend to make the system anaerobic.

3.3.3 Available Nutrients

As discussed in Section 2.2, nutrients can be a limiting factor for microbial growth in the subsurface. Influencing nutrient levels, especially deep in low permeability formations, is difficult with existing technology. Pneumatic fracturing has the potential to enhance nutrient application using both conventional methods and new, innovative techniques.

Conventional technology for nutrient application, consists of adding granular fertilizer either on the surface or through monitoring wells. In some cases nutrients are contained in a liquid solution and are added to the subsurface in the same manner. The increased permeability of pneumatically fractured soil would make these methods more effective. Nutrients could move along the fractures, allowing for faster dispersion of the nutrients. Also, the increased surface area of the formation exposed after fracturing would also allow for a greater volume of soil to be effectively treated, resulting in more effective treatment.

Nutrient addition can also be accomplished directly with the pneumatic bio-injection system, which was designed specifically to enhance nutrient application. As mentioned previously, the system can inject a liquid solution a considerable distance into the contaminated formation. Thus, the indigenous microorganisms can get the nutrients they require in a matter of seconds, rather

than waiting for these compounds to diffuse through the soil. For this reason, bio-injection becomes more important when the contamination is located deep in the formation.

In actual field applications, a combination of nutrient application methods would most likely be used. To address contamination in the shallow zones of the formation, surface application could be coupled with bio-injection. This will require that the fractures reach or "daylight" the ground surface, so that the liquid will penetrate into the formation. For situations where the contamination is located deeper, nutrient solutions could be added both through wells and through bio-injection. Once again, in low permeability formations, fractures must intersect the wells in order for well injection to be worthwhile. Bio-injection will be a valuable asset in both application scenarios, since it allows the nutrients to be added to the formation from two or more directions, which reduces the possibility that certain zones of the formation are "missed".

3.3.4 Soil pH

Soil pH is an important biological parameter related to in situ bioremediation. Improper pH can reduce or eliminate biological activity. For most remediation situations, a neutral pH is recommended, although in some cases a radical pH may be desired. The typical method for controlling this parameter is lime addition to the fertilizer during nutrient application.

Adjustment of pH with pneumatic fracturing could be used in both regional and local applications. A buffer could be added to the nutrient solution in order to insure that a region of soil does not turn acidic during biodegradation. The nutrient solution would then be added as described in Section 3.3.3. In situations where the pH of a region of soil needed to be radically changed in order to encourage the growth of a certain microorganism,

the increased permeability provided by pneumatic fracturing would greatly improve the ability to do this.

The second major application of soil pH control would occur in situations where a localized soil zone contained highly acidic or highly basic conditions, while the remainder of the formation was neutral. It would be inefficient to treat the entire subsurface for pH if only one section required the adjustment, and such treatment would risk upsetting the pH balance of the entire formation. Unfortunately, with current technology, this would be the only alternative. Utilization of the bio-injection system, however, will allow for pH control in a specific zones efficiently and safely with minimum impact in other areas.

3.3.5 Temperature

Temperature control of in situ biological systems is difficult since geologic formations are excellent heat sinks and will absorb a great deal of energy before the temperature changes significantly. However, the pathways created by pneumatic fracturing could potentially provide a corridor for warm air to permeate through the soil matrix. Theoretical calculations have shown that thermal injection with pneumatic fracturing is feasible, and field tests are underway to evaluate the concept.

A better method of subsurface temperature may be to percolate warm water through the formation, as mentioned in Section 2.3.5. The heat transfer characteristics of water are much better than that of air. This thermal fluid advantage, combined with an increased formation permeability due to pneumatic fracturing, will result in higher formation temperatures and more microbial activity.

3.3.6 Availability of the Chemical

In order for biodegradation of a chemical compound to occur, it must be accessible to the microorganisms. Very often a proportion of the chemical present in the formation will be sorbed to the soil particles and therefore become unavailable for biodegradation. A method of increasing the availability of the chemical to the microorganisms may be to add some sort of surfactant to the soil. Surfactants could help to break down the microscopic barriers to chemical degradation, making in situ bioremediation more thorough. Unfortunately, there have been no field demonstrations to show that viability of this technology.

Pneumatic fracturing, may make the use of surfactants feasible. Using either standard surface application and well addition, or through bio-injection, a surfactant could be added to the soil in order to increase the availability of the chemical to biodegradation.

3.3.7 Microorganism Augmentation

Pneumatic fracturing can also be used for microorganism augmentation. Addition of exogeneously grown microorganisms to soil is usually a very difficult task, and can be greatly limited by low formation permeability. The increased permeability provided by pneumatic fracturing can make microorganism augmentation much more efficient.

A pneumatically fractured formation will allow for better circulation of microorganism bearing innoculum. Therefore microorganisms, can permeate through the formation at a much faster rate than would be expected in an unfractured soil.

Addition of microorganisms could be accomplished with standard methods (surface or well application), or they could also be injected through the pneumatic bio-injection system. Studies conducted by Graczyk (1991)[13] and

continued by the author (see Section 4.1), have consistently demonstrated that microorganisms can survive the pressures and stresses associated with pneumatic injection and fracturing. By injecting an innoculum bearing solution, a population could be distributed throughout a fracture network in a matter of seconds. Thus, a large volume of soil could be treated from a single borehole.

CHAPTER 4
DESIGN OF EXPERIMENTAL STUDY

The experimental study for this thesis focused on three major areas: (1) Microorganism survivability was explored in order to show that microorganisms could survive the pressures and stresses associated with pneumatic fracturing, and therefore could feasibly be injected into a formation; (2) A full scale bio-injection system was developed in order disperse biological solutions throughout the subsurface; and (3) A field demonstration of in situ bioremediation enhanced by pneumatic fracturing was implemented. The design of each of the these study areas will now be described.

4.1 Study of Microorganism Survivability

Pneumatic fracturing has the potential to inject microorganisms horizontally into a soil formation from a borehole. Before attempting to do this, however, it is important to determine whether the microorganisms can survive the stresses associated with high pressure injection. Since there were no existing studies on the feasibility of high pressure injection of microorganisms, a series of survivability tests were developed.

The key parameters under consideration for this study were: (1) shear stresses on the cell walls that would occur during nozzle passage and atomization of the liquid solution, (2) impact stresses that would take place as the microorganisms contacted the formation, (3) and rapid pressure changes that would transpire during the injection process. To test these aspects of survivability, the "torture chamber" was created.

4.1.1 Equipment Description

The torture chamber was constructed using a 4.5 inch ID, 3/8" plexiglass cylinder which was 20 inches in length. A drainage plate was placed inside of the cylinder, leaving just enough clearance for a collection beaker to be placed underneath. On one side of the cylinder an injection port was installed. Figure 4.1 shows a schematic diagram of the torture chamber, which was designed by James Chang, a former research assistant at NJIT.

During the first series of tests, a siphon spray system was employed to atomize the liquid solution. Two different spray guns were used for these tests. One was capable of spraying 2.3 gallons per hour at an air pressure of 60 psi and an air flow rate of 4.3 cfm. The second was rated for spraying 7.5 gallons per hour at an air pressure of 80 psi and an air flow rate of 11 cfm.

The experiment was then upgraded in the next series of tests to better simulate the pressures and flow rates expected to be used in the field. This series of tests employed an air powered liquid pump which is capable of pressures greater than 1000 psi and flow rates of 6 gallons per minute. More about this system will be discussed in Section 4.2.

4.1.2 Experimental Procedure

The experimental procedure for injecting and analyzing microorganisms was originated by Graczyk.[13] Early in the design of this experiment, Escherichia coli (E. coli) was chosen as the microorganism for analysis. One reason for using E. coli was that it is structurally similar (gram-negative), to other species of bacteria found in petroleum contaminated soils. Additionally, use of E. coli was conservative, in that the cell walls of gram negative microorganisms are thinner and therefore more susceptible to rupture.[13] A third reason for using E coli was that the testing and cultivation methods for

this species of bacteria are relatively safe and simple, and coliform selective Endo agar is commonly available.

E. coli for these tests were grown in batch reactors (500 ml beakers) from nutrient agar slants at 37 degrees Celsius. Optical density was recorded during the first series of runs using a Baush & Lomb Spectronic 70 with the wavelength set at 560 nm. Readings for optical density were then correlated with Standard Plate Count measurements to get an understanding as to the length of time required to grow the E. coli. It was determined that 24 hours was sufficient to produce a biomass large enough for the experiment.

Once a sufficient biomass had been produced, a sample of the solution was taken and set aside as a control. The remaining solution was then placed into the spraying device and injected in an atomized form into the torture chamber at a specified pressure. Once inside the torture chamber, the atomized fluid would condense and collect in a beaker at the bottom of the chamber. This residual liquid was then diluted to various concentrations and placed on petri dishes using a Les Endo agar as the growth medium. Simultaneously, the control liquid which had not been atomized, was diluted to the same concentrations and placed onto Les Endo agar petri dishes.

The plates were then grown in an incubator at 37 degrees Celsius for 24 hours. At the end of the growth period, the colonies were counted using standard plate count method. Count differences in colony forming units between the control and the atomized liquid were used to evaluate survivability.

During the first phase of the tests, dilutions and plate counts were performed according to EPA Standard Plate Count method. However, due to discrepancies found in the results which will be discussed in Section 5.1, glass beads were added to the dilution bottles during the latter series of

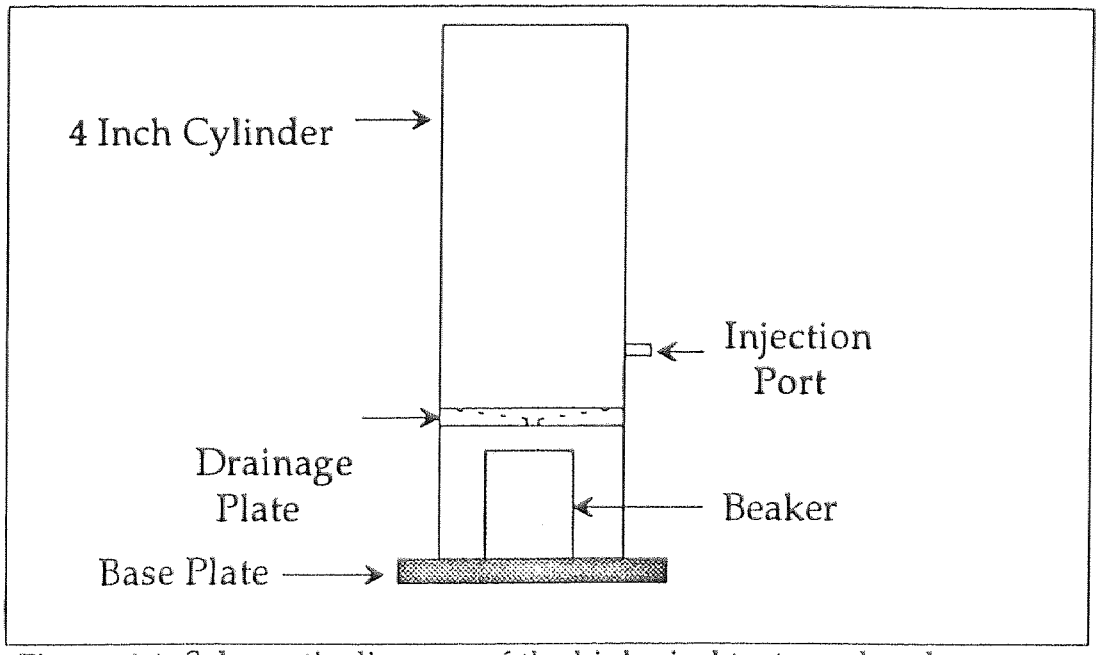


Figure 4.1 Schematic diagram of the biological torture chamber.

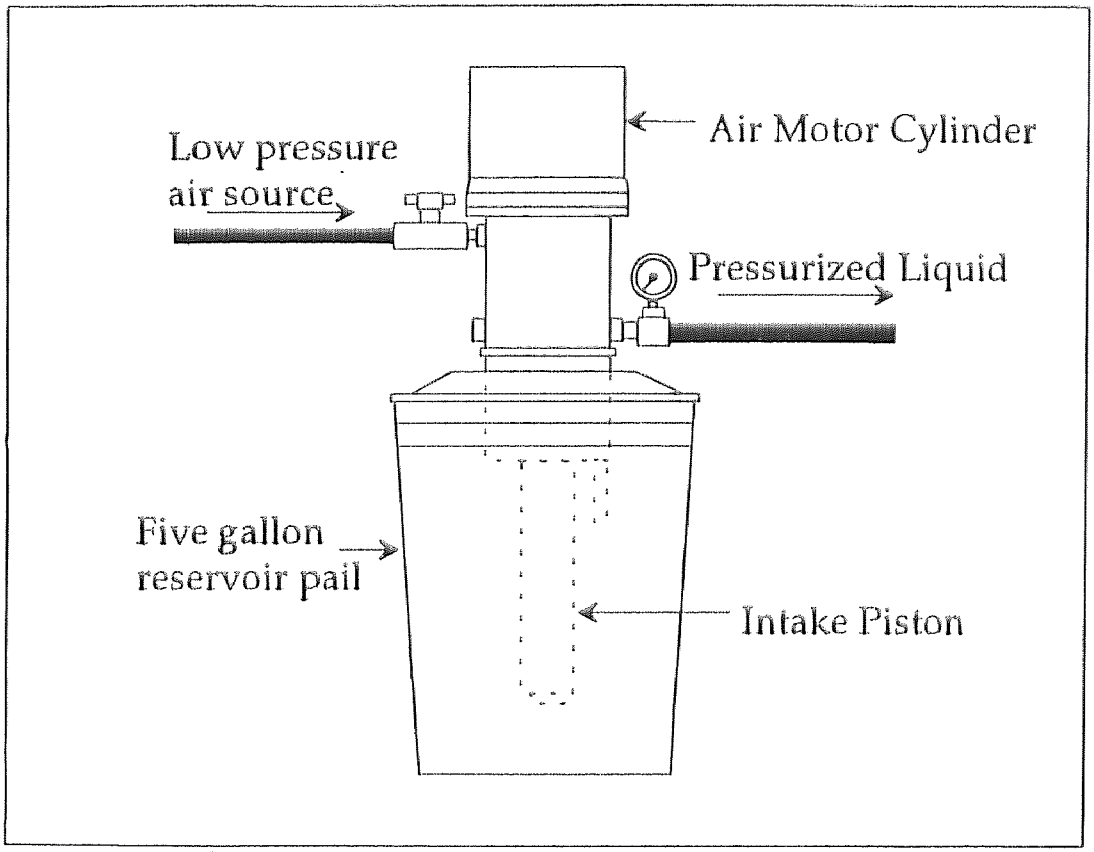


Figure 4.2 The pneumatic bio-pump.

experiments. The purpose of the glass beads was to better disperse the microorganisms in the dilution bottles and reduce the number of clumps. To further help microorganism dispersion, the bottles were shaken more vigorously than in previous tests. Other than these changes, the testing methods remained the same throughout the series of survivability tests.

The specific procedure for the torture chamber testing was as follows:[13]

1) Preparation of E. coli microbial solution (volume varies depending on injection instrument).

2) Incubation of solution for 24 hours.

3) Preparation of torture chamber, including thorough cleansing of all components.

4) Removal of a sample of the solution prior to injection for control purposes.

5) Injection of the remaining liquid into torture chamber at selected pressure for 5 seconds or less.

6) Simultaneous plate count preparation of both control and atomized samples.

7) Incubation of plates for 24 hours.

8) Simultaneous plate count determination of both control and atomized samples.

9) Comparison of control and atomized plate counts to evaluate survivability.

4.2 Development of Bio-Injection System

Providing soil microorganisms with the substances that they need for contaminant degradation is a problem which plagues the field of in situ bioremediation. Standard technology has relied on percolation of nutrients and other substances to percolate down from the ground surface or outward from a borehole. These methods are severely limited by the permeability of

the soil. During the development of pneumatic fracturing, however, a new and more efficient method of liquid addition was envisioned.

The pneumatic fracturing process injects a pressurized gas, (usually compressed air) into a formation to create horizontal fractures ranging up to one inch in thickness.[1] By adding an atomized liquid containing nutrients, microorganisms, and buffer solutions to the injection stream, the necessary substrates for biodegradation can be dispersed throughout the formation via the fractures. In this manner the liquid can reach areas in a matter of seconds, where it would normally require weeks or months to arrive through natural diffusion.

4.2.1 Equipment Description

The main piece of equipment selected for the task of injecting a liquid into the air stream was a Graco, President series 10 : 1 air powered pump which can generate liquid pressures of well over 1000 psi. A schematic diagram of this pump is shown in Figure 4.2. The designation 10 : 1 indicates that an incoming air pressure of 20 psi will theoretically produce an outgoing liquid pressure of 200 psi. To atomize the liquid, a spray nozzle was placed at the connection of the liquid hose and the pneumatic fracturing system. Various sizes of nozzles with design flow rates ranging up to 6 gallons per minute of liquid were obtained.

The other major component of this system is a J.D. Gould model BHP-3/8 in. solenoid valve which opens and closes the liquid injection line electronically. This was placed as close to the pneumatic fracturing injection piping as possible to minimize pressure drops across the hose during injection as is shown in Figure 4.3.

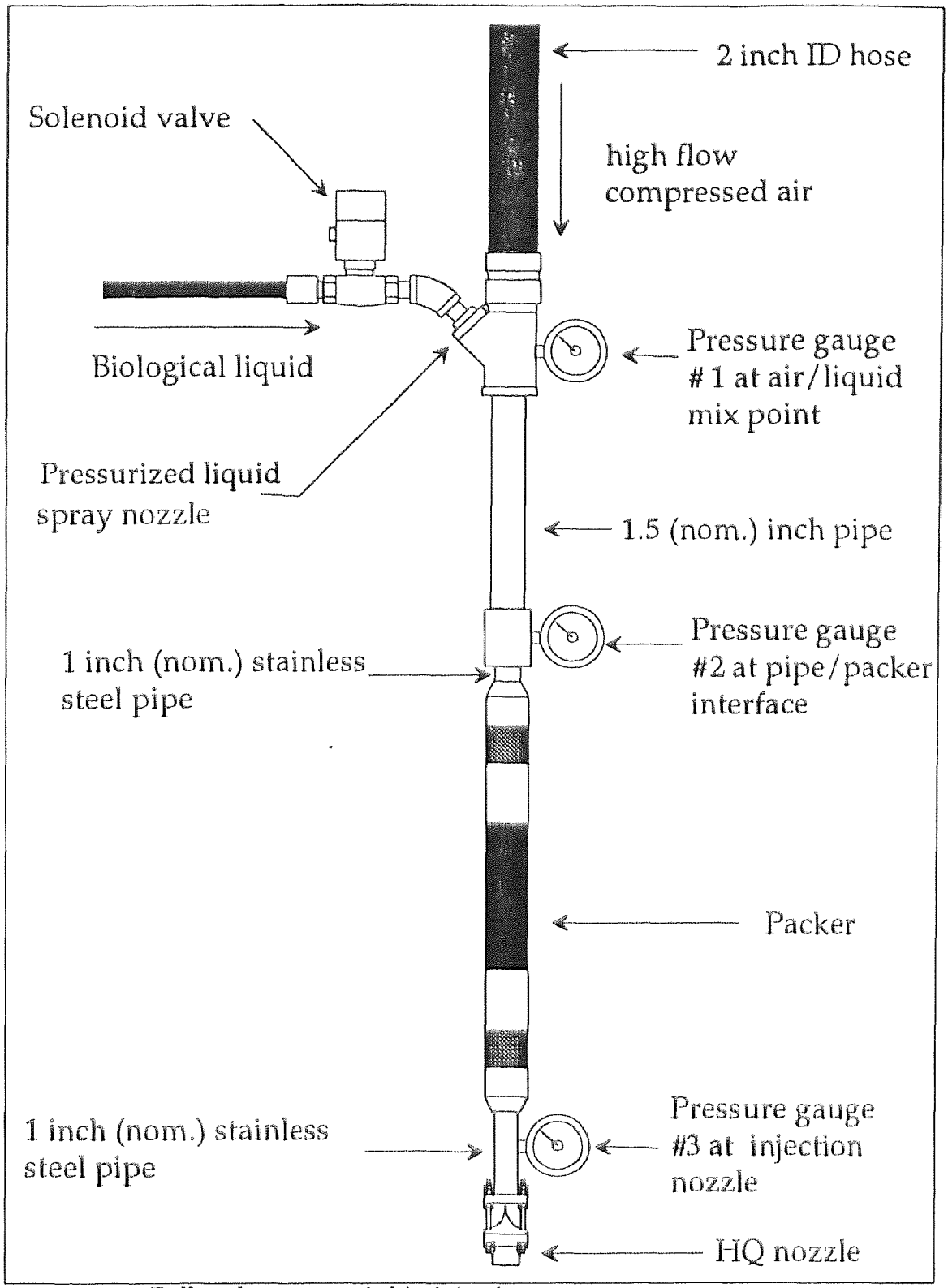


Figure 4.3 Full scale pneumatic bio-injection system.

4.2.2 Experimental Procedure

The first series of tests with the pneumatic bio-injection system focused on optimization of the air powered bio-pump. Experiments consisted of using various air supply pressures and flowrates to collect data on liquid pressures and flowrates produced by the pump. These data were used to develop an air to liquid ratio which can predict the liquid effluent pressure based upon inlet air pressure. Although the pump is designed to have a air to liquid ratio of 0.1, actual measured values indicated that the ratio averaged about 0.3. This disparity can be attributed to head losses in the system.

System flow rates were then measured to find the pump configuration that allowed the greatest flowrate while still maintaining a large liquid pressure. Maximum liquid flowrates for this pump are listed at 3 gallons per minute for continuous duty, or 6 gallons per minute for intermittent duty. Based on the intended use of this pump, it was decided that a flow rate of 4.5 GPM would be a safe target level. The results of these tests are presented and discussed in Section 5.2.

The second part of this study involved combining the bio-pump with the pneumatic fracturing system. There were three major goals of this phase. The first objective was to determine the efficiency of the pneumatic bio-injection system by measuring the percentage of the liquid leaving the injector in an atomized state. These tests were performed above ground which enabled direct visual observation of atomization efficiency. Above ground testing was accomplished by erecting a scaffolding and suspending the packer system (HQ injector) vertically as shown in Figure 4.3.

Second, maximum pressure was measured at three points on the injection system in order to determine the liquid pressure that would be required during full scale injection. It is essential that the pressure of the

injected liquid be higher than that of the injected air to assure a thorough dispersion. The location of the pressure gauges with respect to the pneumatic fracturing system is shown in Figure 4.3.

Third, the flow rate was measured in order to obtain a predictable rate of liquid injection into the formation. These flowrates of liquid injection in the pneumatic fracturing system were compared to previously obtained flowrates of liquid injection into open air from the bio-pump tests in the first phase. This comparison would determine whether the liquid flow would be constricted during a full scale pneumatic injection.

Two sets of experiments were performed using this system configuration. During the first run the measured parameters were air injection pressure, air flow rate, and liquid pressure. A qualitative measurement of the efficiency of atomization was also recorded. Liquid flow rates could not be measured because the solenoid valve was not functioning properly.

The second set of tests was performed with the solenoid valve operational. In these tests the liquid flow rates were measured, in addition to other parameters to check whether they were affected by back pressures from the pneumatic air stream. Results from these tests are presented and discussed in Section 5.2.

4.3 Field Demonstration

The final part of the experimental study involved a field demonstration of the integrated pneumatic fracturing / bio-injection system. This demonstration was performed under the U.S.E.P.A. Emerging Technology SITE Program in cooperation with BP America. This section will now

describe key aspects of the field project including site selection and characterization, project design, field procedure, and project status.

4.3.1 Site Selection and Characterization

The first step in the field demonstration was to select a site which was representative of typical industrial contamination problems, yet one which contained characteristics favorable to pneumatic fracturing. Listed below are the primary criteria used to select the demonstration site. These are based upon past laboratory and field studies, as well as the results of the bio-injection tests described in the previous section.

The primary selection criteria were:

1. Low initial soil permeability ($<10^{-4}$cm/sec).
2. Sufficient contamination levels (between 10 and 1000 ppm of BTX).
3. Moderate depth to the water table (>10 feet).
4. Initial soil moisture levels near the plastic limit.
5. Good security and access.
6. At least 50 foot clearance from active structures and utilities.

After receiving data from several potential sites, the decision was made to proceed with the field demonstration at a refinery located in Marcus Hook, PA. Site characterization work was begun in December 1991 to select the exact location for the demonstration within the refinery facility. Exploratory soil borings and a soil gas survey were conducted over a four month period to further characterize the geology and extent of contamination.

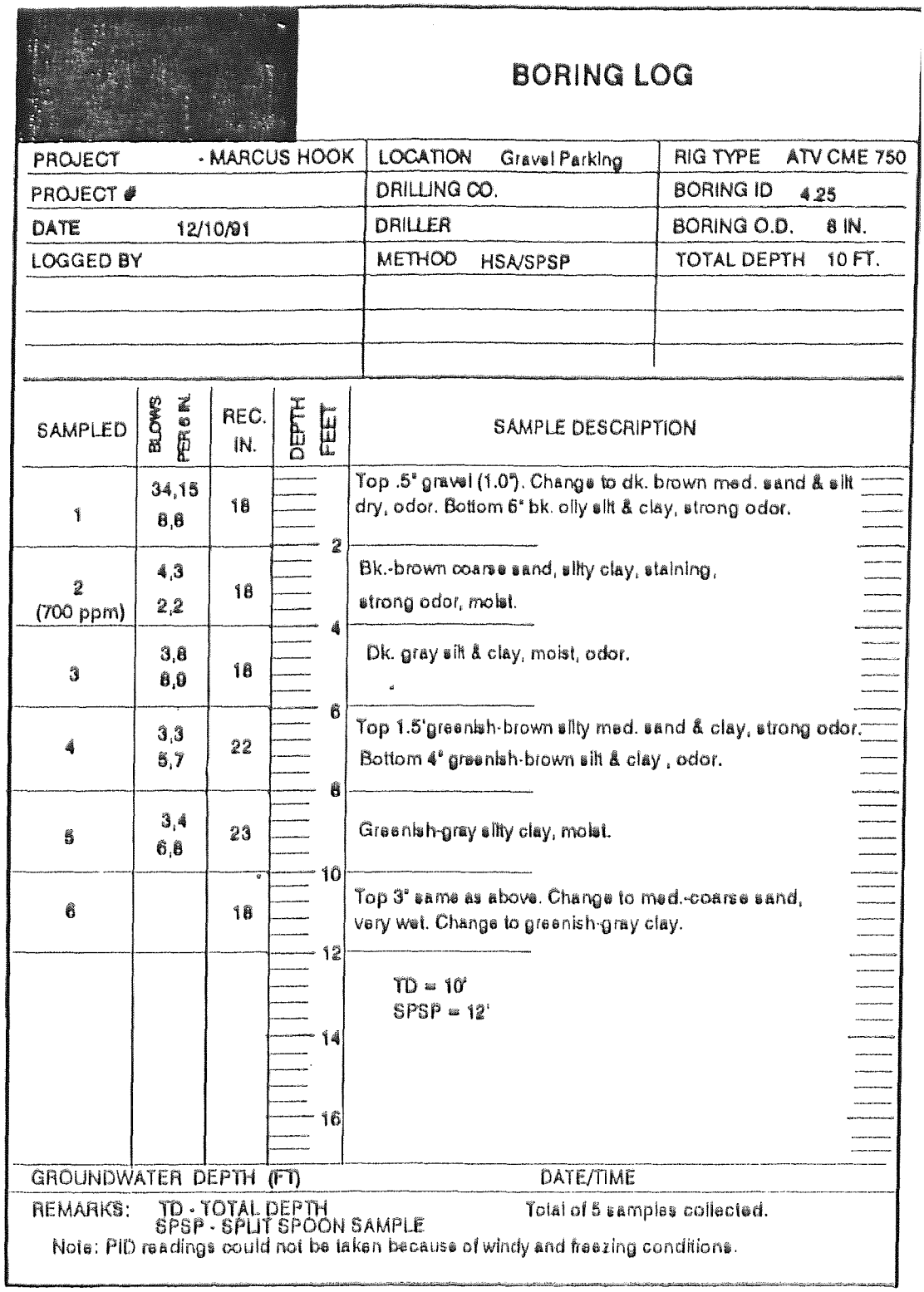
A typical boring log from the exploratory program is shown in Figure 4.4, and additional logs are contained in Appendix A. The major subsurface strata encountered at the site are summarized as follows:

Fill - A surficial layer of fill overlies the site ranging in thickness from one to four feet. The fill is derived predominantly from the clayey silts which occur naturally at the site, mixed with varying amounts of imported sand and gravel. Abandoned concrete foundations are dispersed throughout the site, but do not appear to extend deeper than four feet.

Clayey Silt - The fill is underlain by a layer of orange-tan clayey silt which extends to a depth of nine to ten feet below the ground surface. Occasional sandy zones were noted in this stratum. Based on blow counts recorded during soil sampling, the consistency of the clayey-silt ranges from medium stiff to stiff, which indicates a high degree of overconsolidation. The upper few feet of the clayey silt stratum are stained dark brown to black from infiltration of petroleum residues.

Silty Sand - The clayey silt stratum grades into a gray silty sand at a depth of approximately nine to ten feet below the ground surface. Varying amounts of clay were observed, and increasing moisture contents were noted. The water table is located in this stratum, at a depth ranging from twelve to fifteen feet below the ground surface. Although all site borings terminated in the silty sand, reconnaissance geologic data indicates that mica schist bedrock is present at depths of less than 50 feet.

The phraetic groundwater surface is encountered twelve to fifteen feet below grade. It occurs in a granular silty sand unit and may be classified as an unconfined aquifer. Local groundwater gradients are southward towards the Delaware River.



BORING LOG

PROJECT - MARCUS HOOK	LOCATION Gravel Parking	RIG TYPE ATV CME 750
PROJECT #	DRILLING CO.	BORING ID 4.25
DATE 12/10/91	DRILLER	BORING O.D. 8 IN.
LOGGED BY	METHOD HSA/SPSP	TOTAL DEPTH 10 FT.

SAMPLED	BLOWS PER 6 IN.	REC. IN.	DEPTH FEET	SAMPLE DESCRIPTION
1	34,15 8,8	18		Top .5" gravel (1.0'). Change to dk. brown med. sand & silt dry, odor. Bottom 6" bk. oily silt & clay, strong odor.
2 (700 ppm)	4,3 2,2	18	2	Bk.-brown coarse sand, silty clay, staining, strong odor, moist.
3	3,8 8,9	18	4	Dk. gray silt & clay, moist, odor.
4	3,3 5,7	22	6	Top 1.5'greenish-brown silty med. sand & clay, strong odor. Bottom 4" greenish-brown silt & clay , odor.
5	3,4 6,8	23	8	Greenish-gray silty clay, moist.
6		18	10	Top 3" same as above. Change to med.-coarse sand, very wet. Change to greenish-gray clay.
			12	TD = 10' SPSP = 12'
			14	
			16	

GROUNDWATER DEPTH (FT) DATE/TIME

REMARKS: TD - TOTAL DEPTH Total of 5 samples collected.
SPSP - SPLIT SPOON SAMPLE
Note: PID readings could not be taken because of windy and freezing conditions.

Figure 4.4 Typical boring log from demonstration site.

The field data obtained during the borings indicated a favorable location for pneumatic fracturing. The overconsolidated clayey silts were similar to other formations which have been previously fractured. Laboratory tests also showed that the clayey silt was below the plastic limit, which was also a favorable indicator for fracturing.

Although the geology of the site was satisfactory, the size of the available test area exceeded two acres. Within that area contamination varied greatly from section to section. A soil gas survey was therefore conducted to determine the extent and location of petroleum in the region. Vapor probes were placed on roughly a 50 ft by 50 ft grid. The vapor from these probes was analyzed with both a field portable photoionization detector (PID)and a laboratory gas chromatograph. Based on the results from the soil gas survey, a 40 ft by 40 ft section of the region was selected for the demonstration. Results for the soil gas survey are presented in Appendix B.

Following the selection of the actual location for the demonstration, the level of contamination in this section had to be characterized. Since the major source of contamination in the selected area was gasoline, the major compounds of interest were benzene, toluene, and the xylenes (BTX). Soils containing up to 1000 ppm of BTX were desired in order to demonstrate the effectiveness of this technology in highly contaminated zones. Concentration of BTX above 1500 ppm were considered excessive, as the microorganisms would not be able to flourish in such an environment. Contamination of less than 10 ppm was considered too small to reliably demonstrate destruction of contaminants through biodegradation.

In order to define the levels of BTX in the soil at the selected location, five borings were performed. Continuous split spoon samples were obtained from 1 to 10 feet. Detailed results of soil contamination are presented in

Section 5. Field observations with a field PID, which were later confirmed by chemical analysis of the soil, indicated that most of the contamination occurred in the top 5 feet of the formation. Some petroleum was also detected below a depth of nine feet, which was attributed to contamination in the groundwater.

From the chemical analysis of BTX concentrations in the soil, it was concluded that the site met the required criteria. Although the contamination was concentrated shallower than originally anticipated, the demonstration was altered to accommodate this finding.

4.3.2 Design of Field Demonstration

The goal of the field demonstration is to remove a substantial amount of BTX from the formation and thereby prove the effectiveness of combining pneumatic fracturing and in situ bioremediation. As previously discussed in Section 2.3, key subsurface parameters must be controlled for in situ bioremediation to be effective. This section describes the general plan for controlling those parameters. A site plan of the demonstration showing the actual field set up is presented in Figure 4.5.

Microbial tests conducted on the soil indicated the presence of a number of indigenous, benzene degrading, facultative, bacterial species. These tests indicated that while these microorganisms were capable of surviving under anaerobic conditions, they were most productive at benzene destruction in the presence of oxygen. The tests also indicated that nitrogen concentrations were insufficient to support microbial growth. Therefore, the primary objective of the treatment plan was to provide the indigenous microorganisms with both oxygen and nitrates.

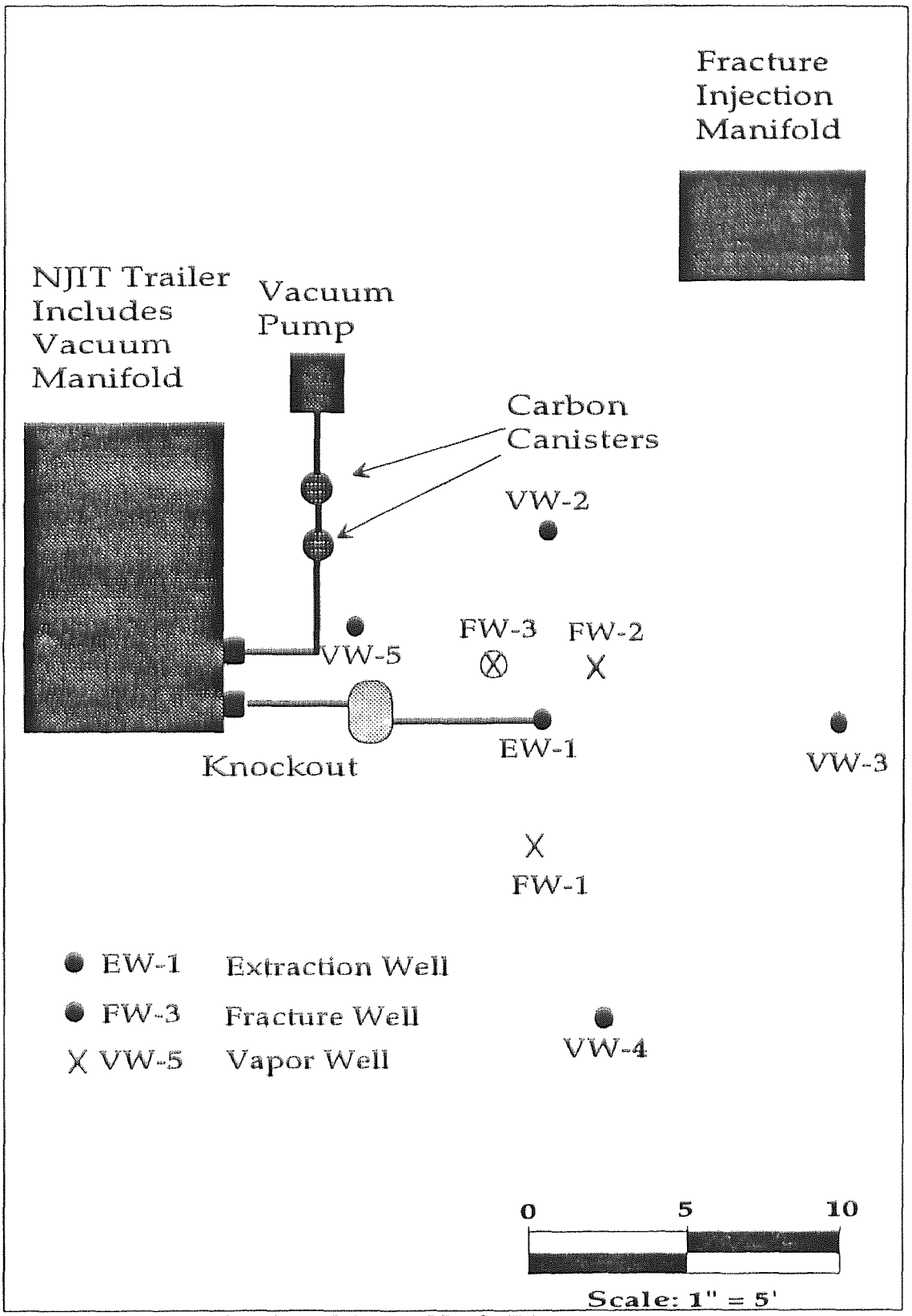


Figure 4.5 Site plan from Marcus Hook, PA.

Aeration is the most efficient method to provide oxygen to microbial populations. Since the BTX was concentrated in the top five feet of the formation, it was decided to create a system of shallow pneumatic fractures to enhance subsurface air flow. To accomplish this, it was envisioned that fracturing should proceed at two levels. The first injection would be made below the highly contaminated zone at a depth of 5 to 7 feet, to establish air communication between the four vapor wells (VWs) and the extraction well (EW). Subsequent fractures would be executed above five feet to open the contaminated zone to greater subsurface control. It was intended that the shallower fractures "daylight" the ground surface to provide direct aeration from the atmosphere. The actual fracture patterns deviated somewhat from this original plan, and the actual results are discussed in Section 5.3.

It was decided to stimulate aeration of the formation with a low level vapor extraction system. A slight vacuum was maintained on the extraction well to produce a slow but constant air flow through the treatment area. Air entered the contaminated zone through both the vapor wells, as well as through the surface cracks.

Nitrate addition was the other major objective of the treatment plan. Because the permeability of the formation was low and it was not known whether water could enter the formation through surface fractures, pneumatic bio-injection was intended to be the primary method of nitrate addition. Bio-injection of nitrates would be accomplished after initial fracturing at the same depth intervals. The concentration of the added nitrates would be large enough to encourage biodegradation, yet small enough to avoid groundwater contamination or microbial inhibition.

4.3.3 Field Demonstration Procedure

The field demonstration procedure involved four distinct phases. These phases are listed below, and each is discussed in the text that follows.

1. Continued site characterization and establishment of baseline conditions.
2. Pneumatic fracturing and post fracture monitoring.
3. Biological injection.
4. Continued monitoring/biological re-injection as required.

Complete and thorough characterization of the site was important to properly assess the baseline conditions. Characterization of the geologic and chemical contamination properties of the formation was conducted through split spoon soil sampling. Detailed methods for sampling and chemical analysis of the soil, as performed by Rutgers University, are contained in Appendix C.

Soil samples were analyzed for standard physical properties such as plastic limit and grain size, as well as contamination levels of organic compounds. The permeability of the formation was measured through vapor extraction tests. Baseline VOC levels in the soil vapor were obtained from each VW and the EW via periodic vapor sampling. Detailed methods for sampling and chemical analysis of the vapor, as performed by Rutgers University, are contained in Appendix C.

The second phase of the project involved the actual pneumatic fracturing of the formation. A major component of the field data collected during this phase was the formation permeability, which was measured before and after fracturing in the manner described in Section 2.1.

Permeability was recorded at the extraction well as well as the four vapor wells which included both flow rate measurements and radius of influence measurements.

Secondary measurements made during the fracture injections included ground surface heave, injection pressures measured at the vapor wells, and fracture initiation pressure at the point of injection. Surface heave was used to determine the radius of fracture and to estimate the fracture aperture. Vapor well injection pressures indicated the extent to which the fractures intersect the vapor wells. By combining these two parameters, the extent and orientation of the fracture network can be determined. The fracture initiation pressures were measured since they are useful for analytical studies. These measurements will be presented in Section 5.

The third phase of the project involved the addition of the necessary biological substrates to enhance biological activity. Originally it was intended to use pneumatic bio-injection as the primary method of adding substrates to the subsurface.

Following initial biologic treatment of the site, a period of long term maintenance will be required to monitor the critical parameters for biological growth as well as the success of the biological treatment. Vapor samples will be obtained and checked for oxygen, carbon dioxide, and methane levels as an indication of biological activity. Organic vapor samples will also be measured to demonstrate contaminant reduction in the soil as the project progresses. Reinjection and reapplication of biological fluids will occur as necessary.

CHAPTER 5
RESULTS OF EXPERIMENTAL STUDY

5.1 Survivability Results

The microorganism survivability tests were conducted in two phases. Phase I utilized a siphon spray system, while Phase II used the pneumatic bio-injection pump. The second phase was further subdivided into part A, which used standard agitation, and part B, which used improved agitation with glass beads.

Results for the survivability tests are summarized in Figures 5.1, 5.2, and 5.3. The control colony forming units (CFU's), as previously described in Section 4.1, represent the number of colonies found in the unsprayed portion of the liquid medium, while the pressurized CFU's characterize colonies counted after spraying. Percent change in growth is calculated to show the increase or decrease in colony counts after pressurized spraying.

5.1.1 Observed Trends

Colony counts for the siphon spray system typically displayed a large increase in CFU's over the control. As indicated in Figure 5.1, the spray count ranged from 2 to 1438 percent greater than the control. This is attributed to the high dispersion potential of this spray system, which had a volumetric liquid to air ratio of 0.0015. The greater dispersion produced by this system resulted in a better distribution of colonies throughout the liquid. Conversely, the control, which had been subjected to pressurized dispersion, was likely plagued by clumping of the microorganisms. For example, ten individual microorganisms together in a clump will appear as a single colony on a petri dish. Therefore, a better dispersed sample will break up any clumping and produce a more accurate representation of the number of microorganisms present.

Survivability results for the system utilizing the pneumatic bio-injection pump also showed an increase in colony counts, although the differences were less dramatic. As shown in Figure 5.2, the pressurized counts ranged from 35 to 135 percent greater than the control. It is noted that the bio-injection pump injects an atomized liquid rather than a mix of air and liquid, so it has a higher liquid to air ratio. Hence, the microorganisms are not dispersed as efficiently as with the siphon spray system.

In order to further investigate the reason for the increased colony counts, a second series of experiments were conducted with the bio-pump. Specifically, the dilution procedure was modified to include agitation with glass beads. stage. The results of these experiments are shown in Figure 5.3, which showed much greater consistency than previous results. Two of the tests actually showed a decrease in CFU's. This confirmed that the reason for the increase in colony counts measured during the initial parts of this study were largely due to the dispersion provided by the injection system. Other possible factors such as aeration and microorganism fatality were considered to be insignificant compared with the dispersion effects.

5.1.2 Survivability Conclusions

The most important result of the survivability test is that microorganisms can endure the pressures and stresses associated with pneumatic fracturing. In almost every trial, an increase of CFU's was measured, which indicates that the microorganisms not only can survive pneumatic biological injection, they also can benefit from the dispersion it provides.

The increase in colony counts observed throughout most of the survivability studies can be attributed to the superior dispersion that occurs during the atomization process. Since the goal of pneumatic biological injection

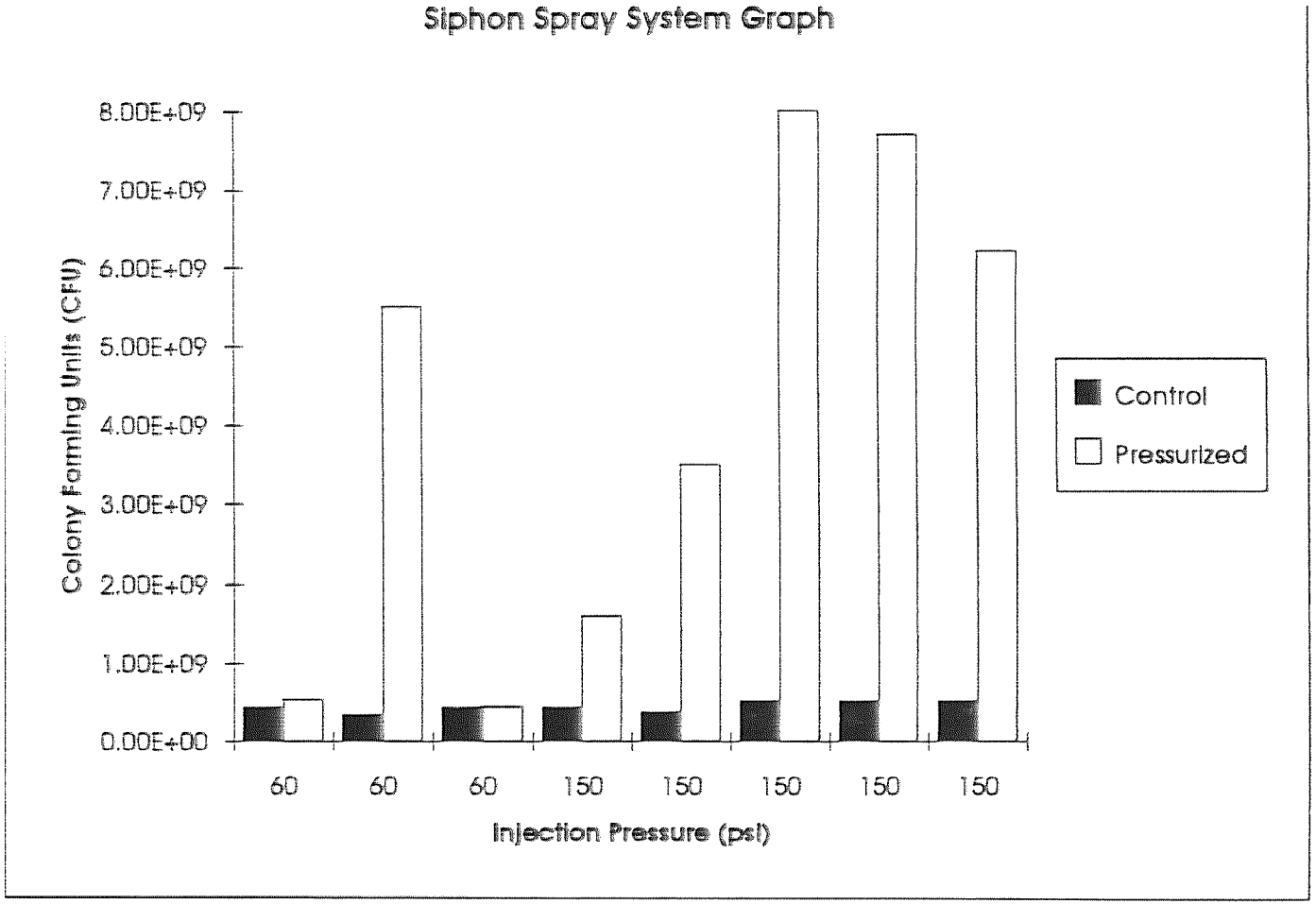


Figure 5.1 Survivability tests, phase I - siphon system.

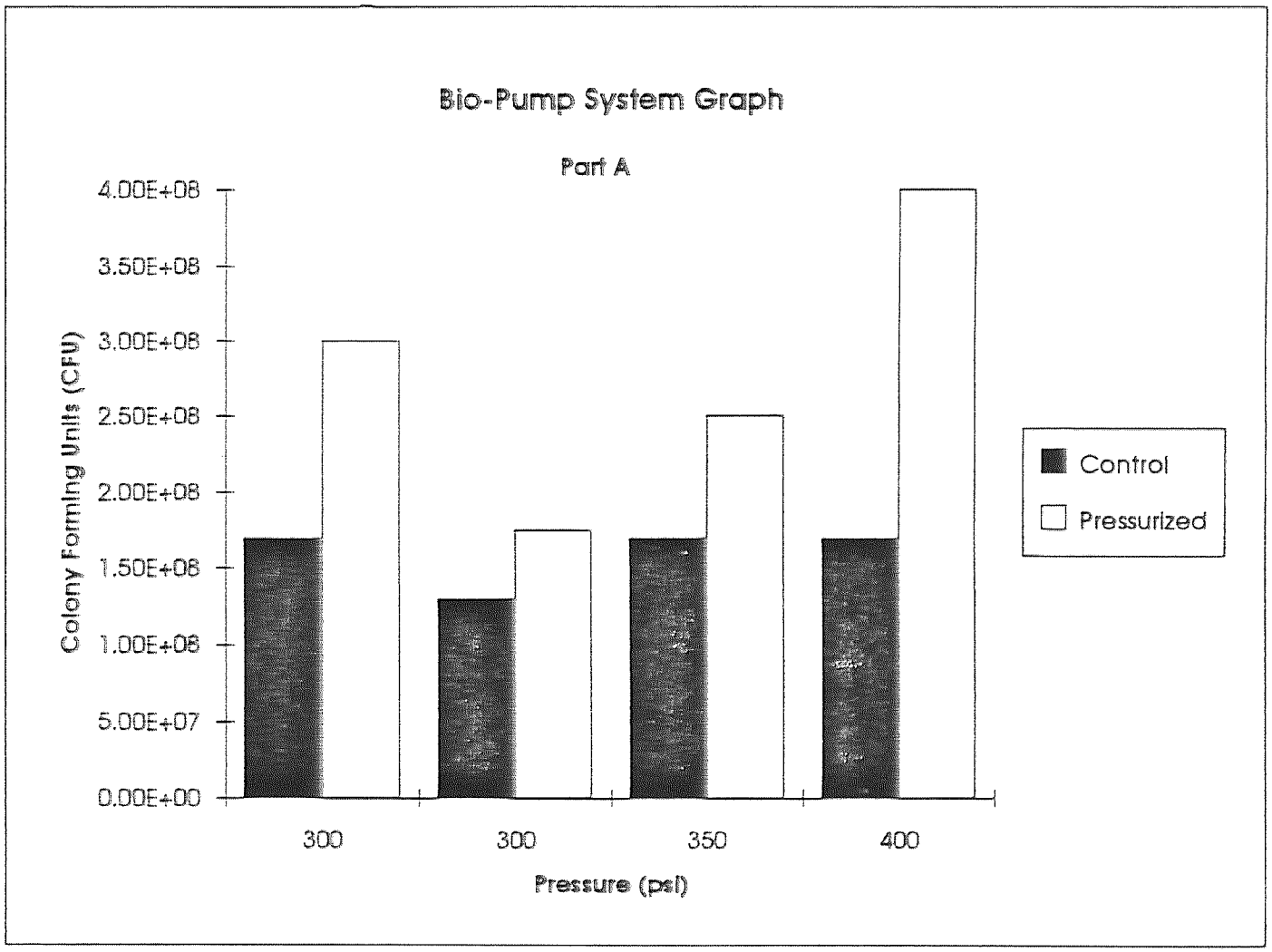


Figure 5.2 Survivability tests, phase II part A - bio-pump system.

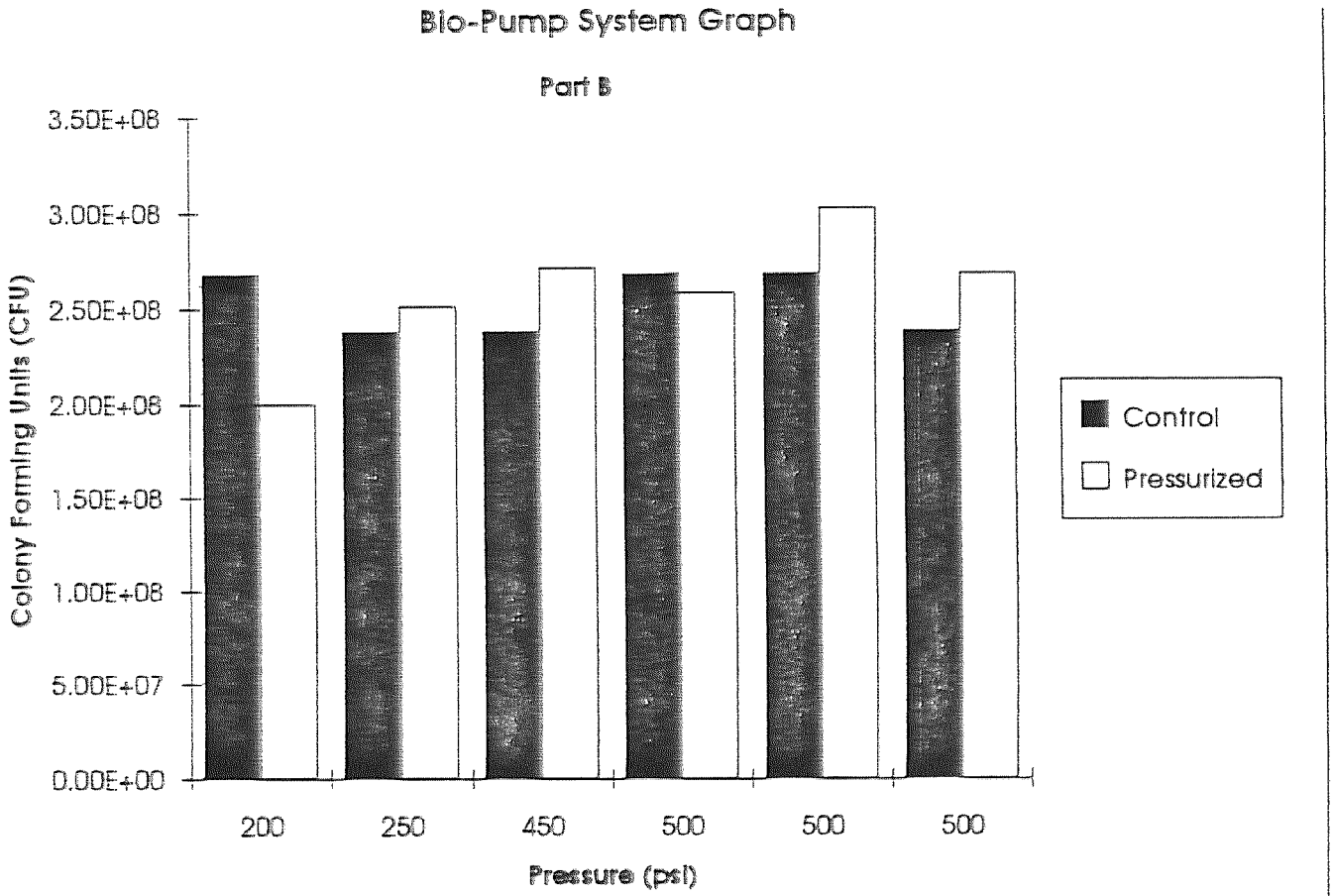


Figure 5.3 Survivability tests, phase II part B, bio-pump system with improved method.

is to disperse microorganisms more efficiently throughout the formation, these tests indicate that this process will achieve its aim.

Comparison of the results between the two phases indicate that the field prototype model will produce less dispersion than the original siphon spray system. It is important to note, however, that the siphon spray system may have more effectively simulated the volumetric liquid to air ratio that will be observed when the full system is used in the field. Bench scale tests of the full scale system, which will be further discussed in Section 5.2, showed a volumetric liquid to air ratio of 0.0005-0.0007, which is the same order of magnitude as the siphon system. Therefore, a similar rate of dispersion should be expected with the full scale bio-injection system.

5.2 Results of Bio-Injection System Tests

The results of the first series of bio-injection tests, which examined the optimization of the bio-pump, are shown in Figures 5.4 and 5.5. These figures show the air to liquid pressure ratio and the liquid flow rates measured during the tests. The results of a second series of tests are displayed in Table 5.1 and Figure 5.6. This part of the study examined the efficiency of operating the full bio-injection system.

5.2.1 Observed Trends of Bio-Pump Tests

During the initial trials, neither the air to liquid pressure ratio nor the liquid flowrate were satisfactory. The air to liquid pressure ratio was not consistent enough to accurately predict liquid effluent pressures, while the effluent flowrates were too small. It was determined that the inlet air flow rate was not large enough for the pump to reach maximum efficiency. To remedy

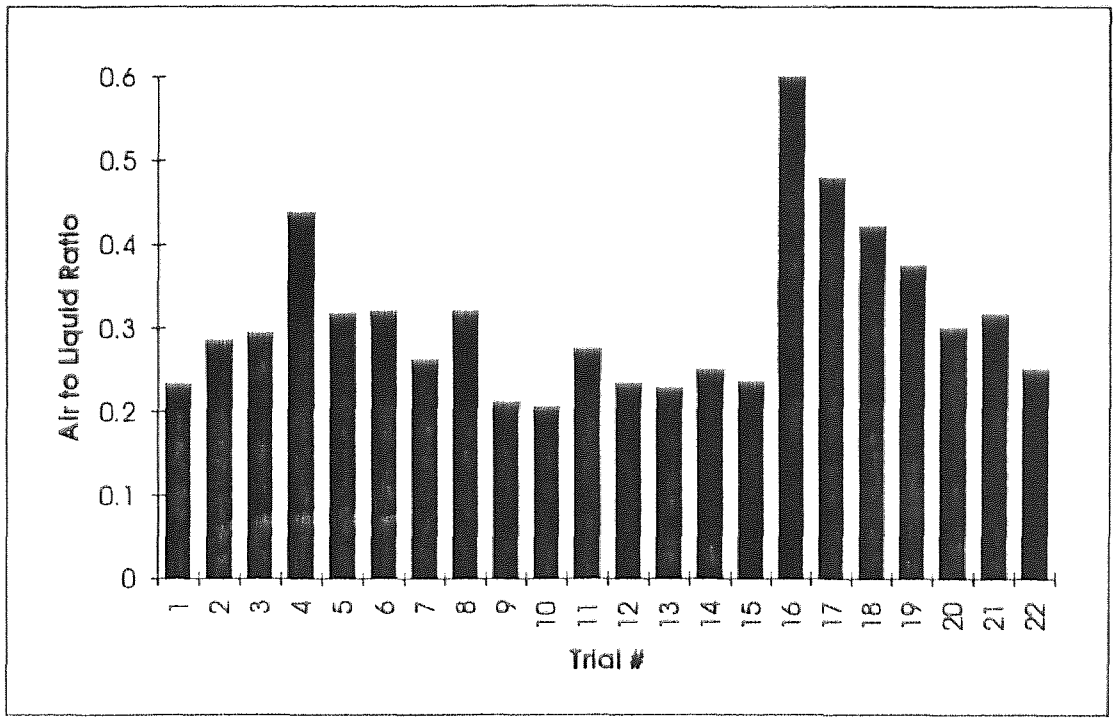


Figure 5.4 Air pressure setting/actual liquid ratio of pneumatic bio-pump.

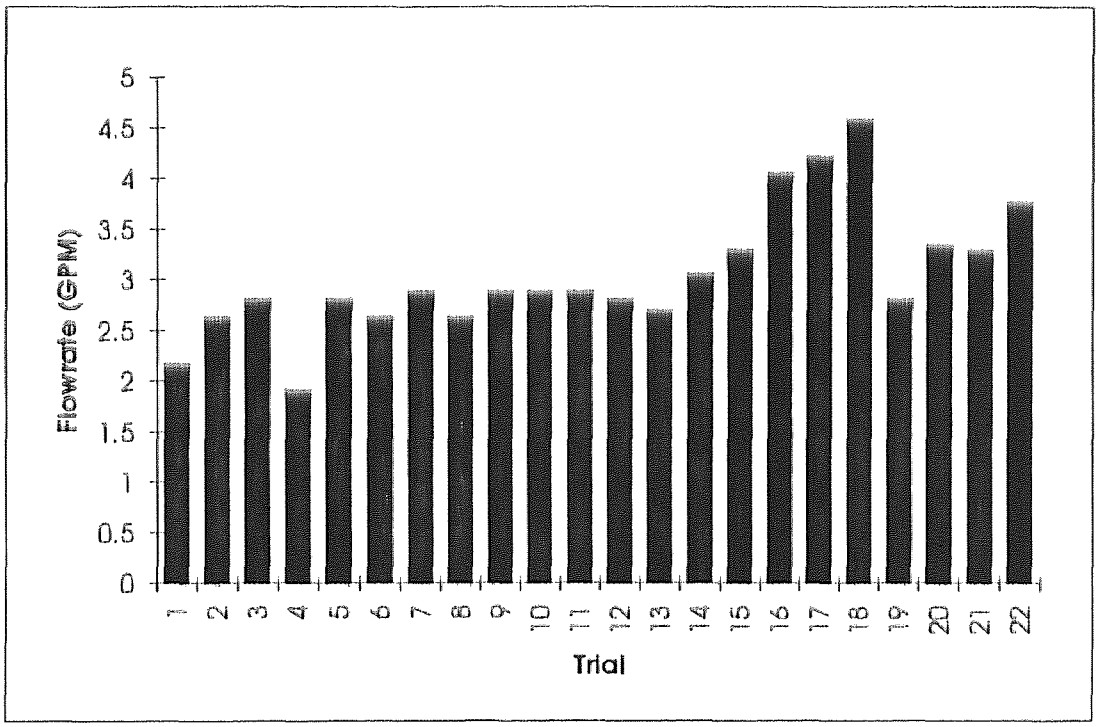


Figure 5.5 Effluent flowrate of pneumatic bio-pump.

Table 5.1 System pressures for the pneumatic bio-injection tests

Trial #	Injection Pressure (psi)	Gauge 1 (psi)	Gauge 2 (psi)	Gauge 3 (psi)	Liquid Flowrate (GPM)	Volumetric Air to Liquid Ratio
1	150	66	64	30	No data	No data
2	150	74	72	29	No data	No data
3	150	66	64	24	No data	No data
4	150	63	61	22	No data	No data
5	120	50	44	0	No data	No data
6	120	44	38	0	3.2	0.00050
7	120	38	32	0	3.2	0.00066

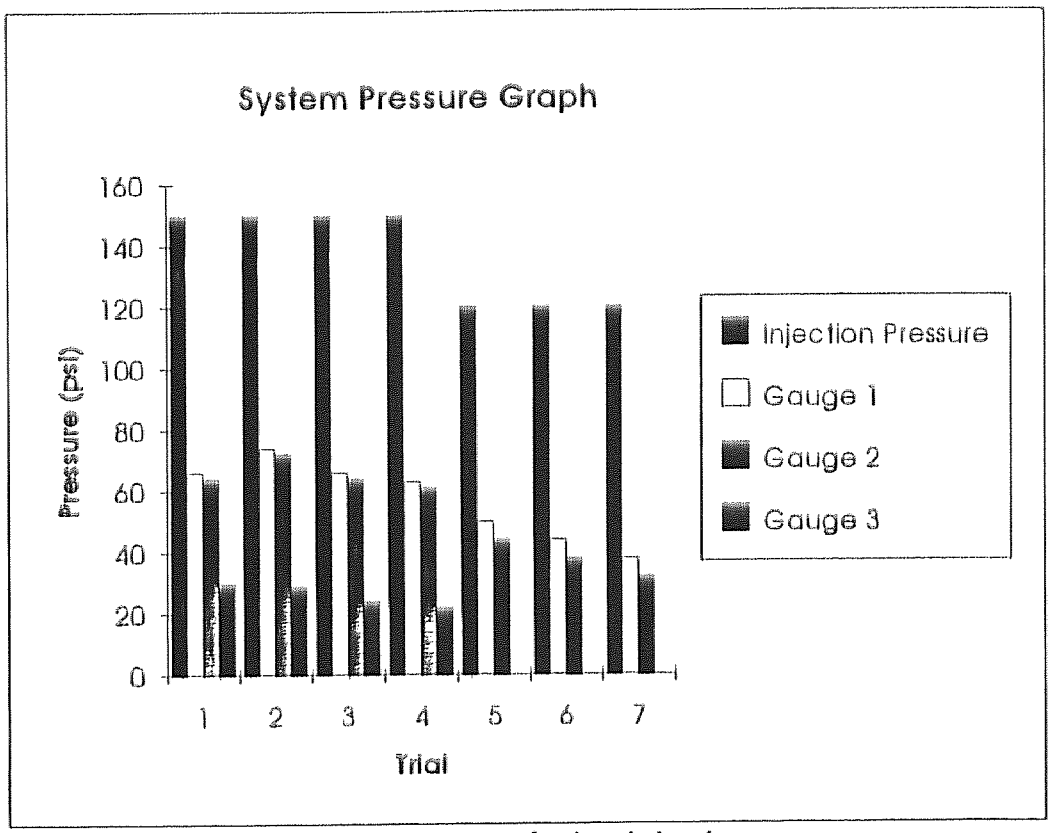


Figure 5.6 Pressure measurements during injection.

the problem, the inlet air piping was enlarged. Following this adjustment, the air to liquid ratio became controllable, which allowed accurate prediction of effluent pressures. Liquid flowrates also increased following these adjustments, to a maximum of 3.5 gallons per minute.

A short series of tests were also performed using a larger size nozzle (trials 16 to 18). During these tests a flowrate of 4.5 gallons per minute was achieved. The increased flow was accompanied by a larger pressure drop, however, as indicated by the sudden change of air to liquid pressure ratios. This indicates that the pump must be set to a higher initial inlet pressure in order to maintain the desired effluent pressure. A series of further bench scale tests using this nozzle should allow accurate prediction of the liquid pressures.

5.2.2 Conclusions of Bio-Pump Tests

As a result of these tests, the capabilities of the bio-pump are fully understood. It can attain a flow rate of 3.5 gallons per minute with the current spray nozzle. The optimum air to liquid ratio for the pump with the current nozzle is 0.25, which means that in order to obtain an effluent liquid pressure of 200 psi, the initial air pressure must be set to one quarter of that pressure or 50 psi. Higher liquid flow rates are possible with the largest size nozzle, but a pressure drop should be expected. Therefore before using this nozzle some additional tests should be performed to obtain an air to liquid pressure ratio for that nozzle. Otherwise it will difficult to select an initial air pressure to operate the pump.

5.2.3 Observed Trends of Full Scale Bio-Injection Tests

The measurement of the efficiency of the liquid injection system was done by visual inspection. Initial fears that only a portion of the liquid would be atomized were allayed as 100 percent of the liquid leaving the system was

observed in an atomized state. This indicates that the pneumatic bio-injection system can very efficiently disperse a liquid into a formation during fracture.

Pressure measurements collected at the three locations of the full scale bio-injection system are shown in Table 5.1. Since the system is open to the atmosphere and does not build up any back pressure, the measured values are much lower than the injection pressure. Pressure measured during an actual fracture injection below ground are slightly higher, although they remain substantially less than the injection pressure.

During the final two runs with the full scale system the liquid flow rate was measured. The results are also shown in Table 5.1. These flowrates correlate well with the bio-pump tests, which indicate that injecting the liquid into a high pressure, high flow air stream does not adversely affect the liquid flowrate. Therefore, liquid can be added to the pneumatic fracturing air stream at the bio-pump's maximum flowrate.

5.2.4 Conclusion of Full Scale Bio-Injection Tests

Visual observations indicate that the bio-injection system will be effective in dispersing a biological fluid into a formation. Pressure measurements on the system indicate that the actual pressures during a fracture injection are much lower than the initial injection pressure of the source supply. This means that the atomized fluid injection may also be lower than the initial air injection pressure, as it must only be greater than the air injection pressure at the mix point. As a rule of thumb, however, it is suggested to set the liquid system at the same pressure as the source injection pressure. Finally, it was observed that the flow rate of the bio-pump was not restricted when combined with the pneumatic fracturing system.

5.3 Field Demonstration Results

At the time of the presentation of this thesis, only the first two stages of the pneumatic fracturing/bioremediation demonstration had been completed. The following section will present the results of the characterization and the pneumatic fracturing stages, and discuss their implications.

5.3.1 Site Characterization

Standard physical analyses of the soil obtained from the site showed that the formation was favorable to pneumatic fracturing. Grain size analysis classified the soil as a clayey silt as shown in Figure 5.7. Clayey silts have been successfully fractured at previous site demonstrations.[11] Atterberg limits testing indicated that the plastic limit of the formation was 20 % and the water content was 18.5 %. This indicated that the soil would behave in a brittle manner, and would therefore respond to fracturing. From a soil characteristic standpoint, the site was highly favorable towards pneumatic fracturing.

Air flow permeability tests were performed on the formation as described in Section 2.1. These tests are summarized in Table 5.2. The initial permeability of the site showed a maximum air flow rate of 4 scfh at a vacuum level of 20 inches of water. The radius of influence from the extraction well was checked at the vapor wells, but no influence could be detected. Due to the exceptionally low pre-fracture permeability of the formation, any in situ treatment method would be ineffective without some form of enhancement.

Vapor samples were obtained from the extraction well and the four vapor wells for chemical analysis prior to fracturing. Results for these tests are shown in Appendix D. Analysis with a gas chromatograph was also performed on samples taken during the vacuum extraction tests. The results of this analysis

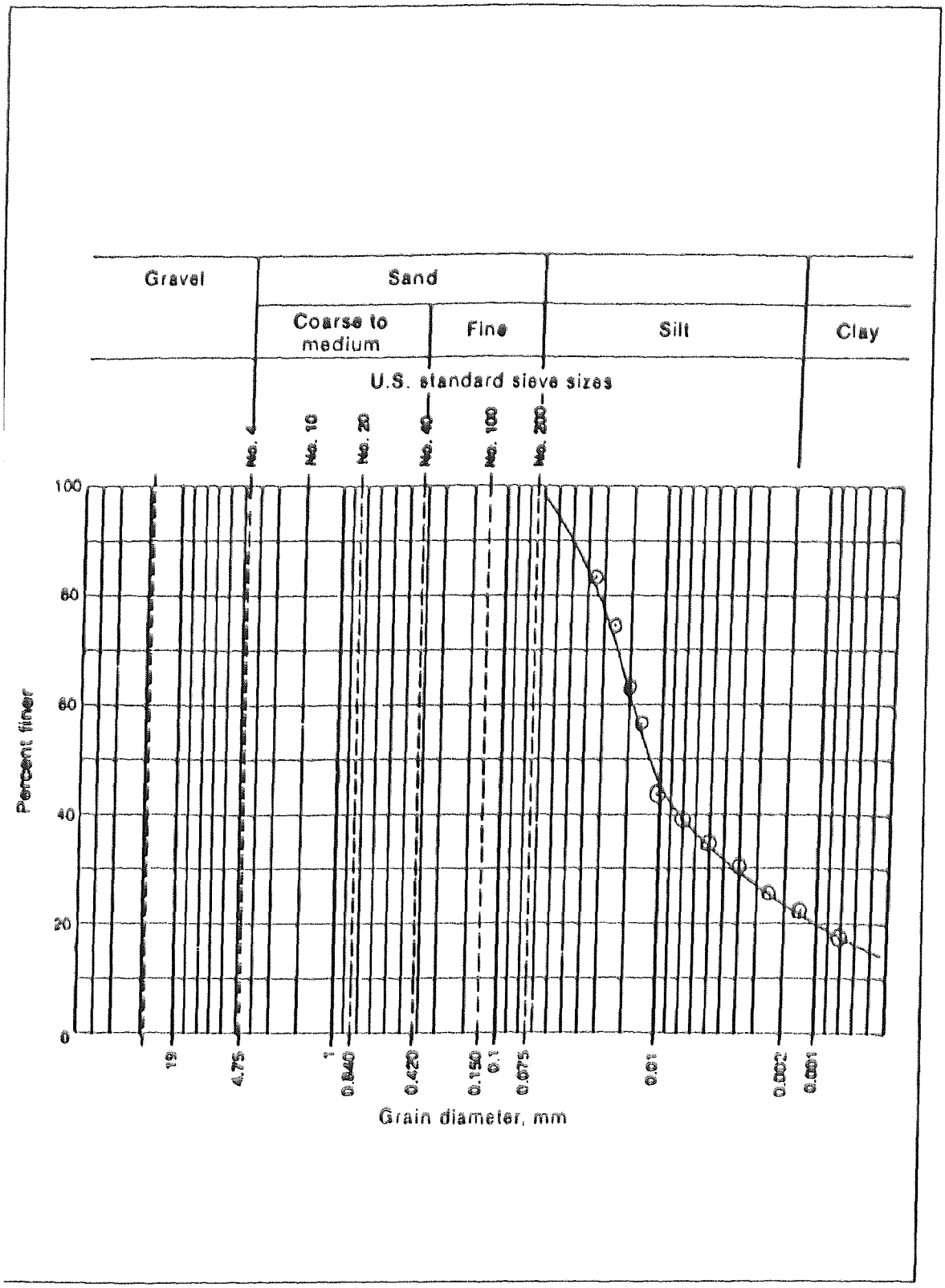


Figure 5.7 Grain size analysis of soil from demonstration site.

Table 5.2 Summary of flow data, Marcus Hook, PA

Baseline Date	Well	Depth	Vacuum Pressure	Condition	Time Min.	VOCs ppm	Flowrate SCFM	Mass Flow* gm/day
10/20/92	EW-1	Total	20" H2O	Plugged	0	180	0.067	0.59
10/20/92	EW-1	Total	20" H2O	Plugged	5	180	0	0
10/20/92	EW-1	Total	20" H2O	Plugged	10	180	0	0
10/20/92	EW-1	Total	20" H2O	Plugged	15	180	0	0
10/20/92	EW-1	Total	20" H2O	Open	0	180	0	0
10/20/92	EW-1	Total	20" H2O	Open	5	180	0	0
10/20/92	EW-1	Total	20" H2O	Open	10	180	0	0
10/20/92	EW-1	Total	20" H2O	Open	15	180	0	0
After first fracture								
Date	Well	Depth	Vacuum	Condition	Time	VOCs	Flowrate	Mass Flow*
10/22/92	EW-1	Total	20" H2O	Plugged	0	330	2.25	36.73
10/22/92	EW-1	Total	20" H2O	Plugged	5	330	2.5	40.81
10/22/92	EW-1	Total	20" H2O	Plugged	10	330	2.5	40.81
10/22/92	EW-1	Total	20" H2O	Plugged	15	330	2.5	40.81
10/22/92	EW-1	Total	20" H2O	Open	0	370	2.3	42.09
10/22/92	EW-1	Total	20" H2O	Open	5	375	2.5	46.38
10/22/92	EW-1	Total	20" H2O	Open	10	375	2	37.1
10/22/92	EW-1	Total	20" H2O	Open	15	375	2.75	51.01
After fourth fracture								
Date	Well	Depth	Vacuum	Condition	Time	VOCs	Flowrate	Mass Flow*
10/22/92	EW-1	Total	20" H2O	Plugged	0	550	1.25	34
10/22/92	EW-1	Total	20" H2O	Plugged	5	550	1.5	40.81
10/22/92	EW-1	Total	20" H2O	Plugged	10	550	1.5	40.81
10/22/92	EW-1	Total	20" H2O	Plugged	15	550	1.5	40.81
10/22/92	EW-1	Total	20" H2O	Open	0	------	1.5	------
10/22/92	EW-1	Total	20" H2O	Open	5	------	1.5	------
10/22/92	EW-1	Total	20" H2O	Open	10	------	1.5	------
10/22/92	EW-1	Total	20" H2O	Open	15	------	1.5	------
Date	Well	Depth	Vacuum	Condition	Time	VOCs	Flowrate	Mass Flow*
10/27/92	EW-1	Total	20" H2O	Plugged	0	450	1.5	33.39
10/27/92	EW-1	Total	20" H2O	Plugged	5	450	1.5	33.39
10/27/92	EW-1	Total	20" H2O	Plugged	10	450	1.75	38.96
10/27/92	EW-1	Total	20" H2O	Plugged	15	450	1.75	38.96
10/27/92	EW-1	Total	20" H2O	Open	0	750	1.8	66.78
10/27/92	EW-1	Total	20" H2O	Open	5	750	1.8	66.78
10/27/92	EW-1	Total	20" H2O	Open	10	750	1.8	66.78
10/27/92	EW-1	Total	20" H2O	Open	15	750	1.8	66.78

* Mass flowrate for this table calculated from field PID measurements

for benzene are shown in Table 5.4 for the date 10/20/92. As indicated, the concentration of benzene in the well was about 500 ppm before any fracturing took place. Inspection of the mass removal rate listed in Figure 5.6 for the same date shows that despite the high concentration of benzene, very little mass was being extracted due to the low formation permeability.

5.3.2 Pneumatic Fracturing - Fracture Information

A total of four fracture injections were made at the site during the period of October 21-22, 1992 as summarized in Table 5.3. The average heave radius for the fractures was about 15 feet. This is based both upon heave data obtained through tiltmeters and visual observations of fracture surface cracking. Figure 5.8 is a heave diagram based on visual surface heave measurements for the first fracture. Subsurface profiles of the formation displaying the estimated paths of the fractures are shown in Figure 5.9 and 5.10. Fracture pathways were estimated through tiltmeter data, pressures measured at the wells during fracture, and locations where the fractures daylighted the surface.

The fractures in this formation were not as horizontal as has been observed at previous sites. Rather than traveling along a horizontal plane, they inclined upwardly at angles of 20 to 30 degrees from the horizontal in most directions. This behavior is attributed to the following factors.

1. Footings, dispersed throughout the site to a depth of 4 feet and covered with fill, may have created a significant non-homogeneity in the formation. The injected air therefore tended to travel upwards through the weakly consolidated fill, rather than horizontally through the overconsolidated formation.
2. The clay in this area is ancient and highly overconsolidated. It is possible that horizontal stratification, which provide natural planes of

Table 5.4 GC concentrations for benzene from vapor extraction analysis

Date	10/20/92	10/22/92	10/27/92	11/4/92
Well	Conc (ppm)	Conc (ppm)	Conc (ppm)	Conc (ppm)
EW-1-A	224.5	613.6	676	392.1
EW-1-B	491.6	1129	891.5	56.09
EW-1-C	550	1076	604.9	21.46
EW-1-D	591.6	784.7	859.8	12.97
EW-1-E	577.1	345.1	864.8	17.37
EW-1-F	No data	914.9	665.4	16.09
Average	486.96	810.55	760.4	86.01
Flowrate (SCFM)	0.07	2.50	1.75	0.07
Mass Removal gm/day	1.62	100.31	65.87	0.29

Table 5.5 GC average concentrations for BTX from vapor extraction analysis

Date	10/20/92	10/22/92	10/27/92	11/4/92
Well	Conc (ppm)	Conc (ppm)	Conc (ppm)	Conc (ppm)
Benzene	486.96	810.55	760.4	86.01
Toluene	56.11	252.04	266.82	41.3
p-Xylene	11.59	66.39	68.13	17.12

Table 5.6 GC mass removal rate during vapor extraction

Date	10/20/92	10/22/92	10/27/92	11/4/92
Well	gm/day	gm/day	gm/day	gm/day
Benzene	1.62	100.31	65.87	0.29
Toluene	0.19	31.19	23.11	0.14
p-Xylene	0.04	8.22	5.9	0.06
Total	1.85	139.72	94.88	0.49

Table 5.3 Pneumatic fracturing data from Marcus Hook, PA

Date	Injection Number	Depth	Injection Pressure (psi)	Injection Flowrate (scfm)	Time of Injection (seconds)	Breakdown Pressure (psi)	Comments
10/21/92	1	5'-7'	150	1200	20	72	Initial formation fracture
10/22/92	2	5'-7'	150	No data	5	38	Aborted refracture
10/22/92	3	5'-7'	150	1276	20	25	Refracture
10/22/92	4	5'-7'	150	1400	20	25	Directional nozzle
10/22/92	5	3'-5'	150	No data	20	No data	Initial fracture in shallow zone

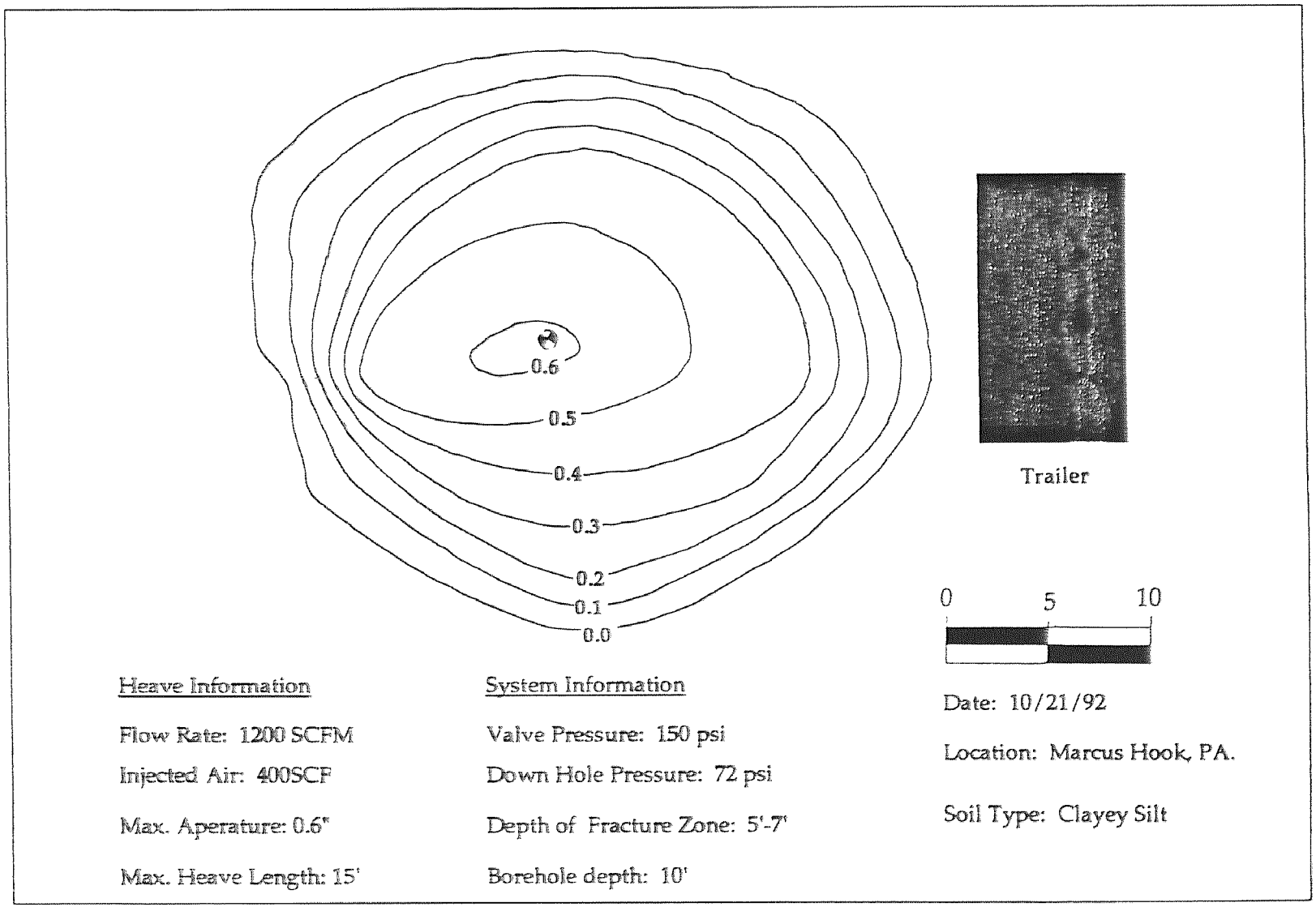


Figure 5.8 Heave diagram, fracture I, Marcus Hook, PA.

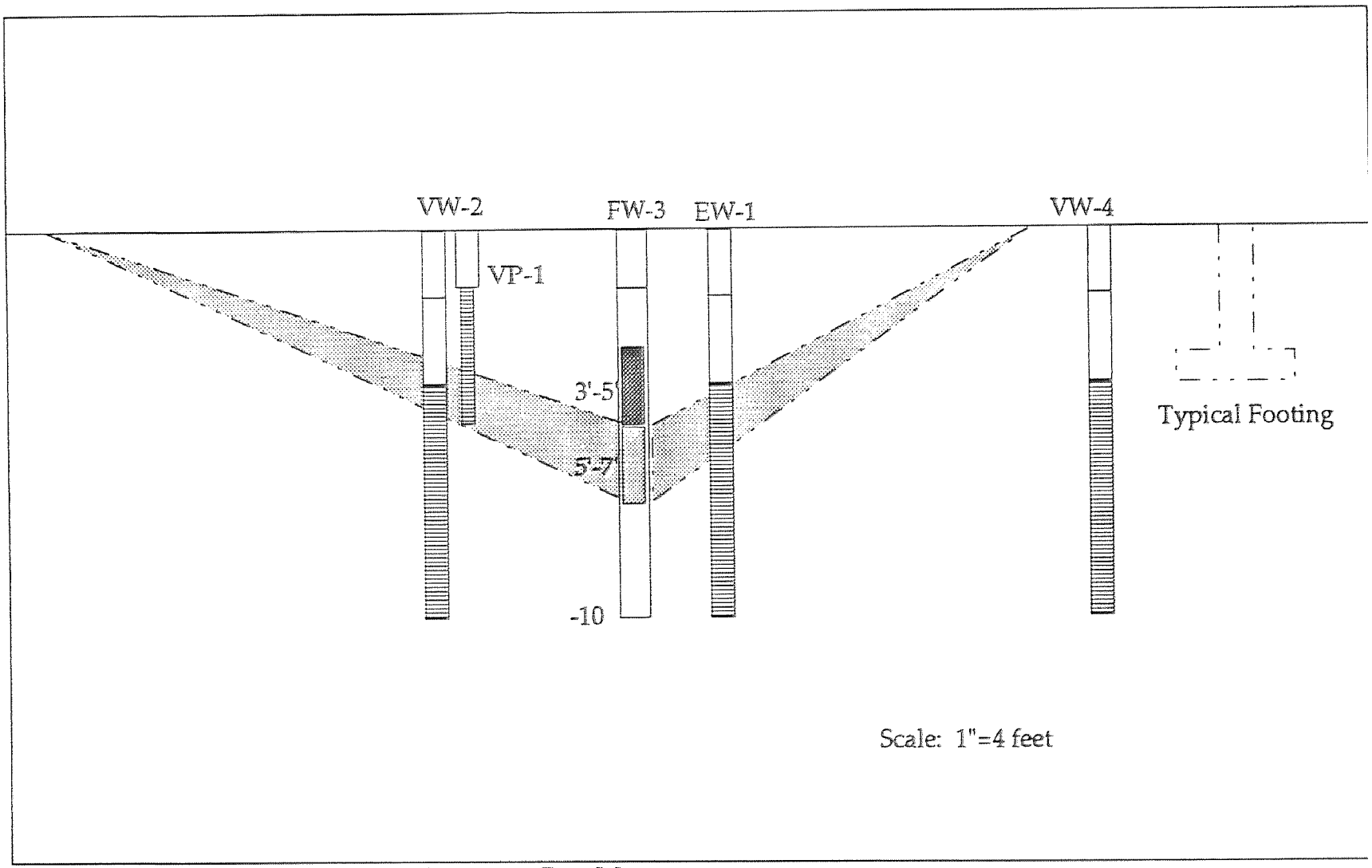


Figure 5.9 Subsurface fracture profile, section East-West.

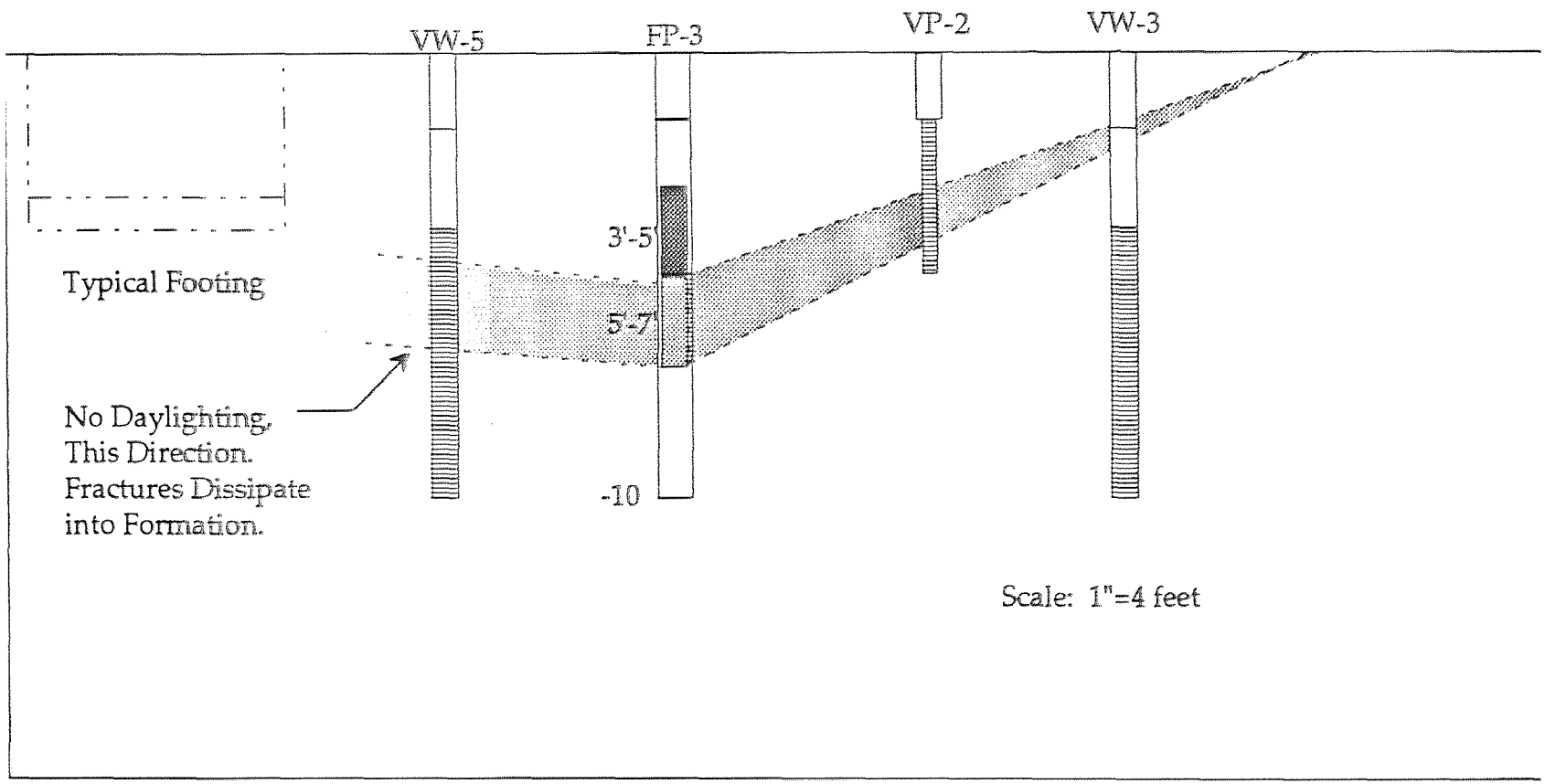


Figure 5.10 Subsurface fracture profile, section North- South..

weakness, was not as distinct as that found in younger sedimentary formations.

3. The depth of the fracture injections was shallower than many previous sites. As a result, the compressed air only had to travel a relatively short distance through the soil to reach the surface.

5.3.3 Post-Fracture Permeability

Following the second fracture injection, the vacuum air flow permeability of the formation was measured. As shown in Table 5.1, an 37 fold increase in flowrate was observed, which demonstrated that the formation was successfully fractured and the permeability had been enhanced. Vacuum influence at outlying vapor wells during extraction from EW-1 was only detected at VW-4 and VW-5, however. Further evidence of low communication between the wells was the minor change in flowrate observed between the open well (passive air) and sealed well conditions.

The results of permeability vacuum tests following the fourth fracture injection were similar to those after the second injection. Flowrates, however, decreased to 1.8 scfm from 2.5 scfm, at a vacuum of 21 inches of water. This was probably due to the fact that the fourth fracture injection was shallower and may have caused some closure of the lower fractures. It is important to note that the flowrate measured after the fourth fracture far exceeded the values obtained during the pre-fracture baseline.

The post-fracture vacuum extraction tests proved that the formation permeability was substantially improved with pneumatic fracturing. They also further verified the approximate fracture pathways, since only certain wells exhibited air communication. Fracturing a borehole progressively deep to

shallow will tend to close previous fractures. In the future, the sequence of fracture injections must be adjusted to site conditions.

5.3.4 Post-Fracture Chemical Analysis

Tables 5.4-5.6 compare the average concentrations of benzene, toluene, and p-xylene in the effluent before and after fracturing. A substantial increase in concentration was found after fracturing for all three compounds. Even more dramatic is the increase found in the mass removal rate during the extraction test. The data shows that the total BTX removal rate increased over 50 times as a result of fracturing. It is interesting to note the decrease in concentration measured during the last test date. This decrease in both flowrate and concentration is due to saturation of the fractures with rain water, which greatly reduced the formation air flow. More detailed information on this aspect of the demonstration is presented in the next section.

5.3.5 Water Data

Water level measurements made during the first six months prior to fracturing consistently showed no standing water in the monitoring wells (EW and the VW's). Water levels remained at zero immediately after fracturing and for one week after the fracture events. During the second week following fracturing, the site was subjected to heavy rain. When the wells were tested for water after this period, EW-1, VW-5, and FP-3, were filled with water to a level of three feet from the surface. The other wells remained dry.

It is noted that the water filled wells were the same ones that had good intercommunication after fracturing. Water had apparently infiltrated into the formation through the apertures produced during pneumatic fracturing. Although this proved to be a short term difficulty since rain water infiltration

must be controlled during this demonstration for quality assurance and quality control purposes, it should prove to be a long term benefit. This condition will allow more flexibility in the nutrient application which will be discussed further in Section 5.4.2.

5.4 Remediation Strategy Adaptations

Based on the results of the pneumatic fracture injections made in October, certain changes were made in the remediation strategy for the site. These adaptations were necessary to best take advantage of the fracturing patterns observed in the formation. The change in strategy underscores the importance of using pilot studies to predict effectiveness and properly plan production applications of pneumatic fracturing at a given site. Adaptations in the form of site improvements were made in basically two areas: well location and subsurface water control. Each of these areas will now be discussed.

5.4.1 Site Improvements

After fracturing, the extraction well was demonstrated to have good communication with only one of the four vapor wells. This occurred because the fractures intersected the grouted portion of the well instead of the screened portion (see Figures 5.9 and 5.10). To remedy this problem, new wells called vapor probes (VP's) were installed. The location of these new wells in relationship to the old ones is shown in Figure 5.11.

In order to control rain water infiltration, a waterproof cover was constructed over the site. First, gravel was placed over the demonstration area and graded to create sufficient pitch for water runoff. Within the gravel, perforated pipe was laid to provide a pathway for the formation to connect with

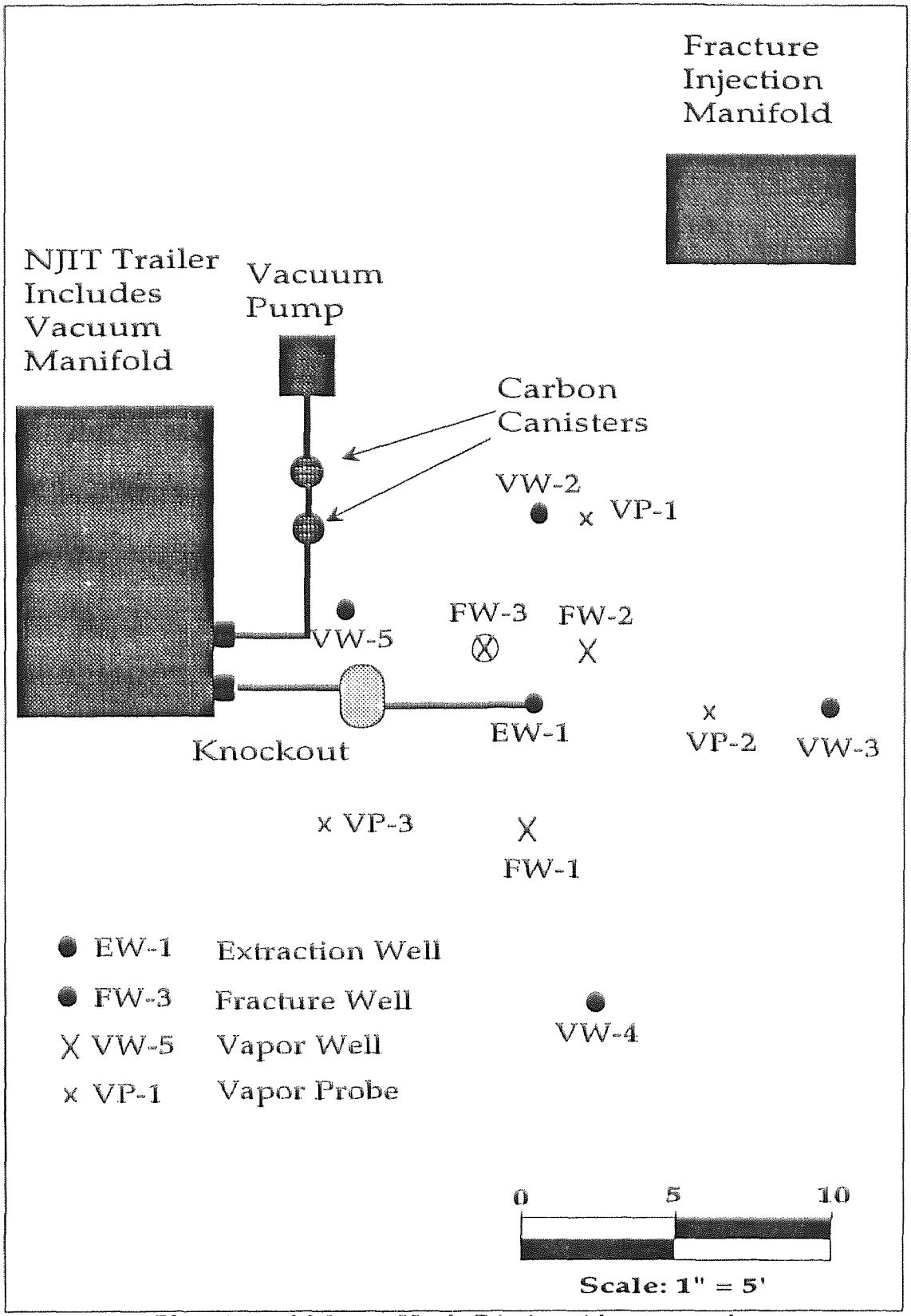


Figure 5.11 Plan view of Marcus Hook, PA site with vapor probes.

the atmosphere. Soaker hoses were laid on top of the gravel to provide a method of adding liquid to the site through surface infiltration.

The gravel was then capped with 6 mil black plastic sheeting to form a waterproof cover. Well penetrations were sealed with duct tape, and a drainage trench was dug around the perimeter of the plastic to divert water away from the demonstration. The plastic was secured by wood timbers, which were placed both around the edges and across its length.

5.4.2 Remediation strategy

The results of the water data discussed in Section 5.3.5 demonstrate that fluid can enter this formation from the surface after fracturing. Water communication between the wells demonstrates that fluid can also travel through fractures between wells. These revelations will allow more flexibility in the future remediation of the site.

Three methods of adding fluid to the subsurface will be recommended:

1. Pneumatic bio-injection is still the best way to guarantee an even distribution of nutrients in the deepest areas of the demonstration.
2. Surface application through the soaker hoses underneath the plastic can also be used. This is the best way to insure that the top layers of the soil, which show the greatest amount of contamination, are treated with an adequate nutrient supply.
3. Well infiltration can be used to treat the lower portions of the formation which are on the outskirts of the fracture zones.

A combination of all three methods should be used to one degree or another. Care should be taken, however, to prevent saturation of the formation for long periods of time, which would hinder the circulation of oxygen.

CHAPTER 6
CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

The following conclusions were drawn from the study:

1. Pneumatic fracturing can be successfully integrated with in situ bioremediation. It has the potential to overcome many of the limiting factors inherent with in situ bioremediation including available oxygen, nutrient supply and moisture level. It is believed that the combination of pneumatic fracturing and bioventing will greatly accelerate the rate at which the biodegradation can occur. In addition, pneumatic fracturing will permit the extension of in situ bioremediation into low permeability formations which cannot be effectively treated with standard bioremediation methods.

2. Bench scale studies have shown that microorganisms will survive the pressures and stresses associated with pneumatic injection. Experiments performed with a pneumatic bio-pump demonstrated that microbial populations in a liquid solution were not significantly affected by pneumatic injection. In fact, most of the tests showed an increase in microbial growth following the pressurization, which was demonstrated to be a result of superior dispersion produced by the injection systems. This result indicates that the microorganisms can benefit from pneumatic injection, while being dispersed more evenly throughout the formation.

3. A pneumatic bio-pump has been designed and fabricated which attaches to the current pneumatic fracturing system. It is capable of injecting biological

fluids into the pneumatic air stream up to 4.5 gallons per minute. The system successfully atomizes the biological liquids into a fine mist which can then follow the air into the formation.

4. Visual observations made during aboveground injection with the bio-injection system confirmed that the liquid mist has a fine texture and is uniformly distributed in a radial pattern. It is expected that fluids injected with this system will receive superior aeration and distribution, which should enhance microbial growth. The estimated volumetric liquid to air ratio of the system range from 0.0005 to 0.0007

5. It is anticipated that pneumatic bio-injection will deliver biological fluids more efficiently and over a larger area than standard application methods such as surface application and well infiltration. Fluid will be injected after the fracture network has been established to attain maximum distribution. Pneumatic bio-injection may also be combined with these other methods of fluid delivery to guarantee thorough treatment of the formation.

6. A full field pilot demonstration of the integrated pneumatic fracturing with the in situ bioremediation system has been designed and implemented for a contaminated site. The project, which is being performed under the EPA Emerging Technology SITE Program, was begun in December of 1991. The target formation for this demonstration is a combination of fill and clayey silt which is contaminated with petroleum hydrocarbons.

7. As part of the site preparation activities, four fracture injections were performed at depths ranging from 3 to 7 feet below the ground surface. Ground

surface observations indicated that the fractures extended up to 16 feet from the injection point. Subsurface air flows increased from 0.067 SCFM to 2.5 SCFM at a vacuum pressure of 20 inches of water. Increases in mass removal of BTX were measured from 1.6 gm/day to 100 gm/day. Following the fracturing, water seeped into the formation through fractures which had reached the surface.

8. As of this writing all site preparation work is complete, and the bio-injection is scheduled for early 1993.

6.2 Recommendations for further study

The following are recommendations for future study.

1. Development of the pneumatic bio-pump should continue. Consideration should be given to upgrade the system to produce higher liquid flowrates at the same pressures. An analytical procedure should be developed to predict the radius of influence of the pneumatic bio-injection system, and field tests should be conducted to verify the results.

2. Further studies are recommended to test survivability of microorganisms through the full pneumatic bio-injection system. Ideally, both above ground and below ground tests should be conducted.

3. Field demonstrations for this technology integration should be continued. Full scale demonstrations can be planned for using pneumatic fracturing to enhance bioventing projects involving simple compounds, such as those found in gasoline. Small scale studies can be performed using pneumatic fracturing to

enhance in situ bioremediation with more persistent compounds such as polyaromatic hydrocarbons (PAHs), polychlorinated bi-phenlys, (PCBs), and trichloroethylene (TCE). These types of compounds are currently difficult to degrade, but as bioremediation technology improves, pneumatic fracturing can help new innovations move into the field faster.

4. More study is needed to understand the effects of pneumatic fracturing in various types of soils under highly moist and/or saturated conditions. Field observations indicate that pneumatic fracturing can also increase the flow rate of water through a formation besides increasing its pore gas exchange rate. If the permeability increase is as great in the saturated zone as it is in the vadose zone is as large, pneumatic fracturing could have a profound influence on bioremediation of ground water.

5. Pneumatic injection of a dry nutrient should be developed. Once this system is constructed, analytical testing should be performed to determine the effective radius of the nutrient, as well as the size and gradation nutrient leaving the HQ nozzle. Analysis should be conducted both above and below ground.

APPENDIX A

WELL LOGS FROM MARCUS HOOK, PA

Table A.1 Summary of boring well logs

Boring #	Well #	Depth	Grout	Bentonite	Sand	Screen
B-1	EW-1	10'	0-2'	2-4'	4-10'	4.5-10'
B-2	VW-2	10'	0-2'	2-4'	4-10'	4.5-10'
B-3	VW-3	10'	0-2'	2-4'	4-10'	4.5-10'
B-4	VW-4	10'	0-2'	2-4'	4-10'	4.5-10'
B-5	VW-5	10'	0-2'	2-4'	4-10'	4.5-10'

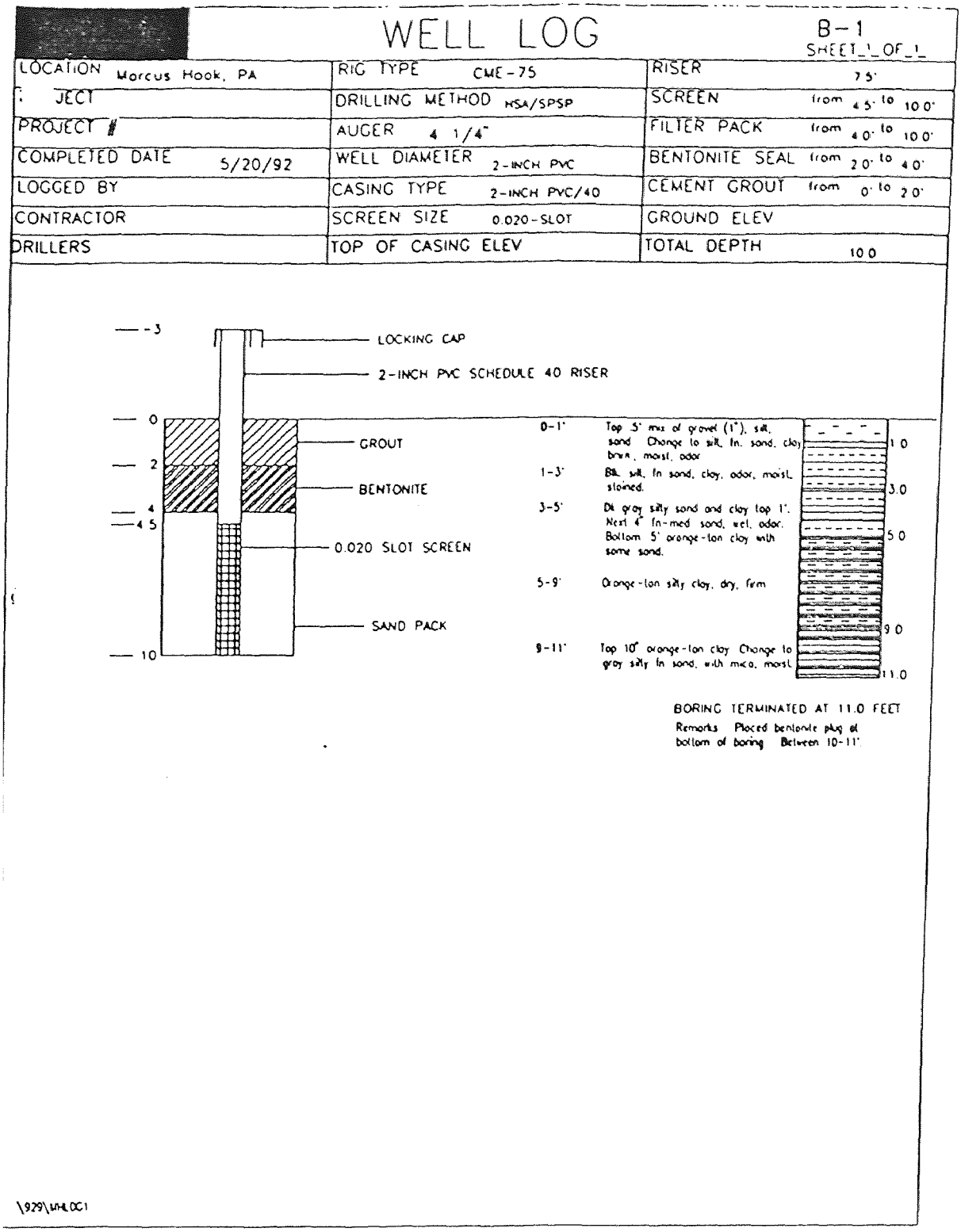


Figure A.1 Well log for EW-1.

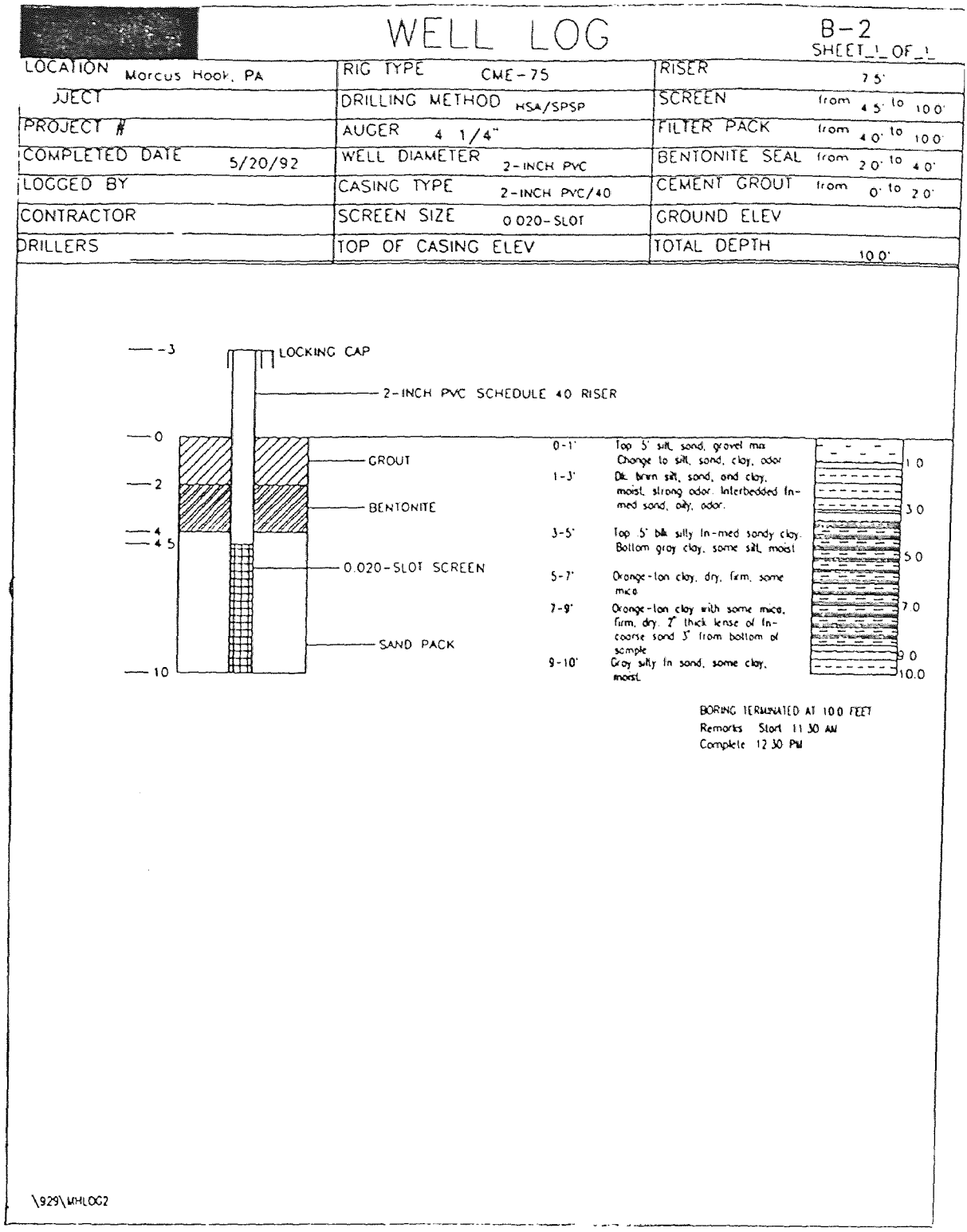


Figure A.2 Well log for VW-2.

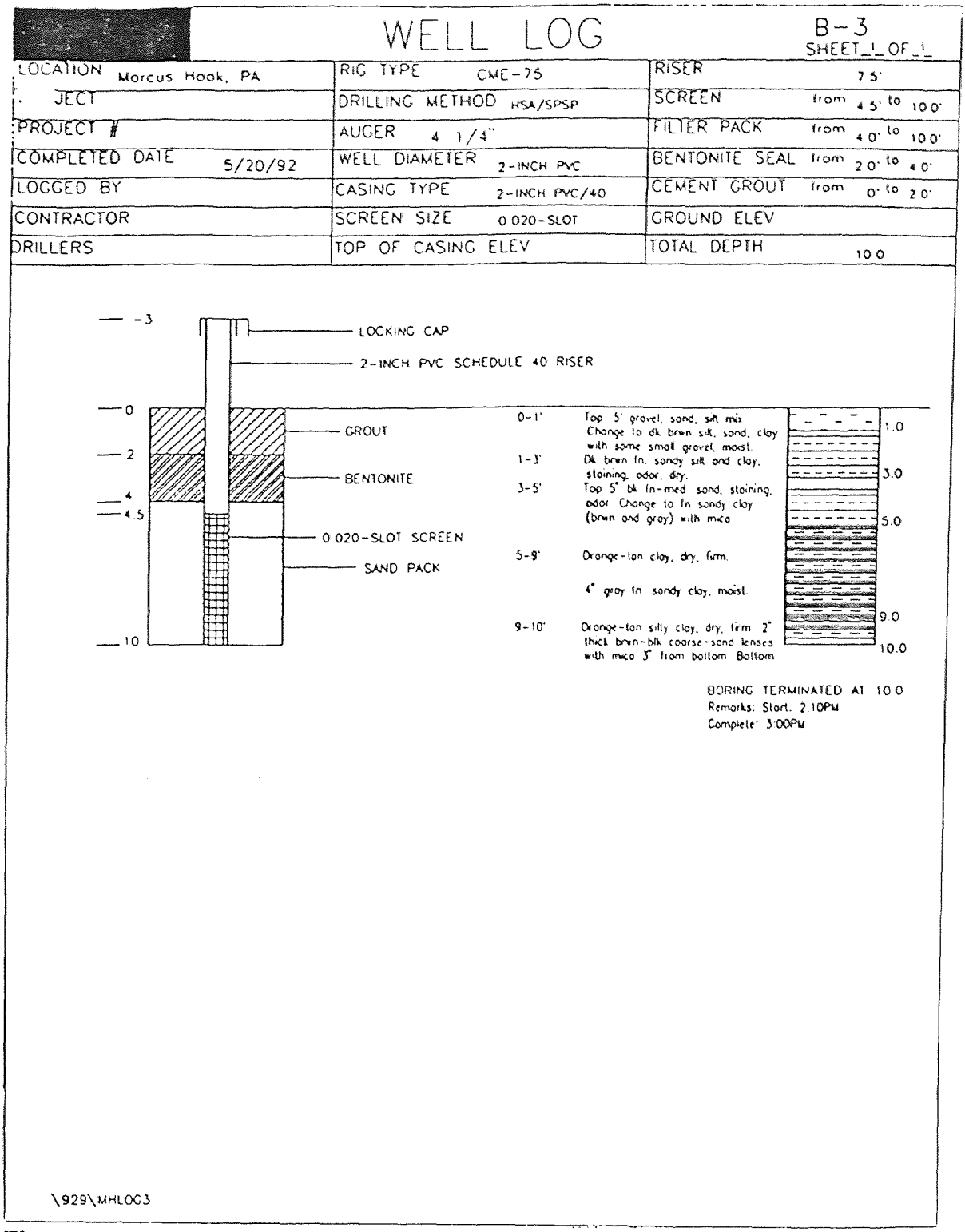


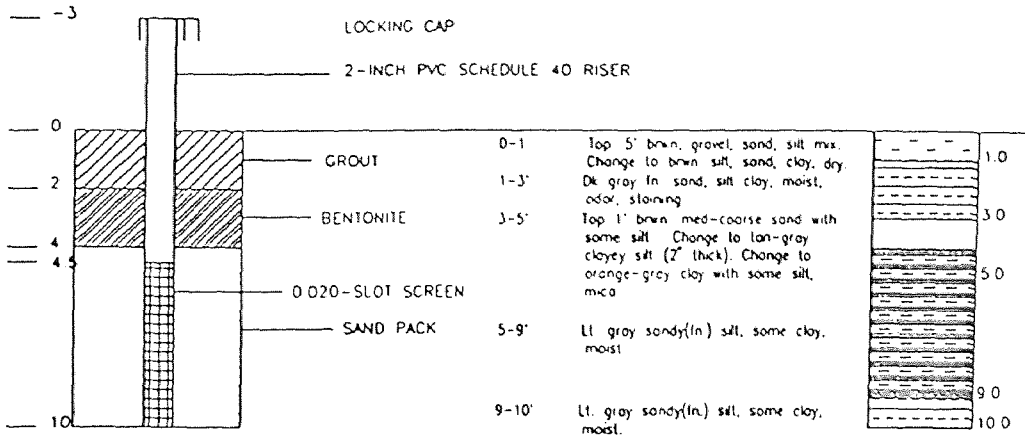
Figure A.3 Well log for VW-3.

[redacted]

WELL LOG

B-4
SHEET 1 OF 1

LOCATION Marcus Hook, PA	RIG TYPE CME-75	RISER 7.5'
JECT	DRILLING METHOD HSA/SPSP	SCREEN from 4.5' to 10.0'
PROJECT #	AUGER 4 1/4"	FILTER PACK from 4.0' to 10.0'
COMPLETED DATE 5/20/92	WELL DIAMETER 2-INCH	BENTONITE SEAL from 2.0' to 4.0'
LOGGED BY	CASING TYPE 2-INCH PVC/40	CEMENT GROUT from 0' to 2.0'
CONTRACTOR	SCREEN SIZE 0.020-SLOT	GROUND ELEV
DRILLERS	TOP OF CASING ELEV	TOTAL DEPTH 10.0'



BORING TERMINATED AT 10 FEET
Remarks: Started 3:40PM
Complete: 4:30PM

\929\MHLOG4

Figure A.4 Well log for VW-4.

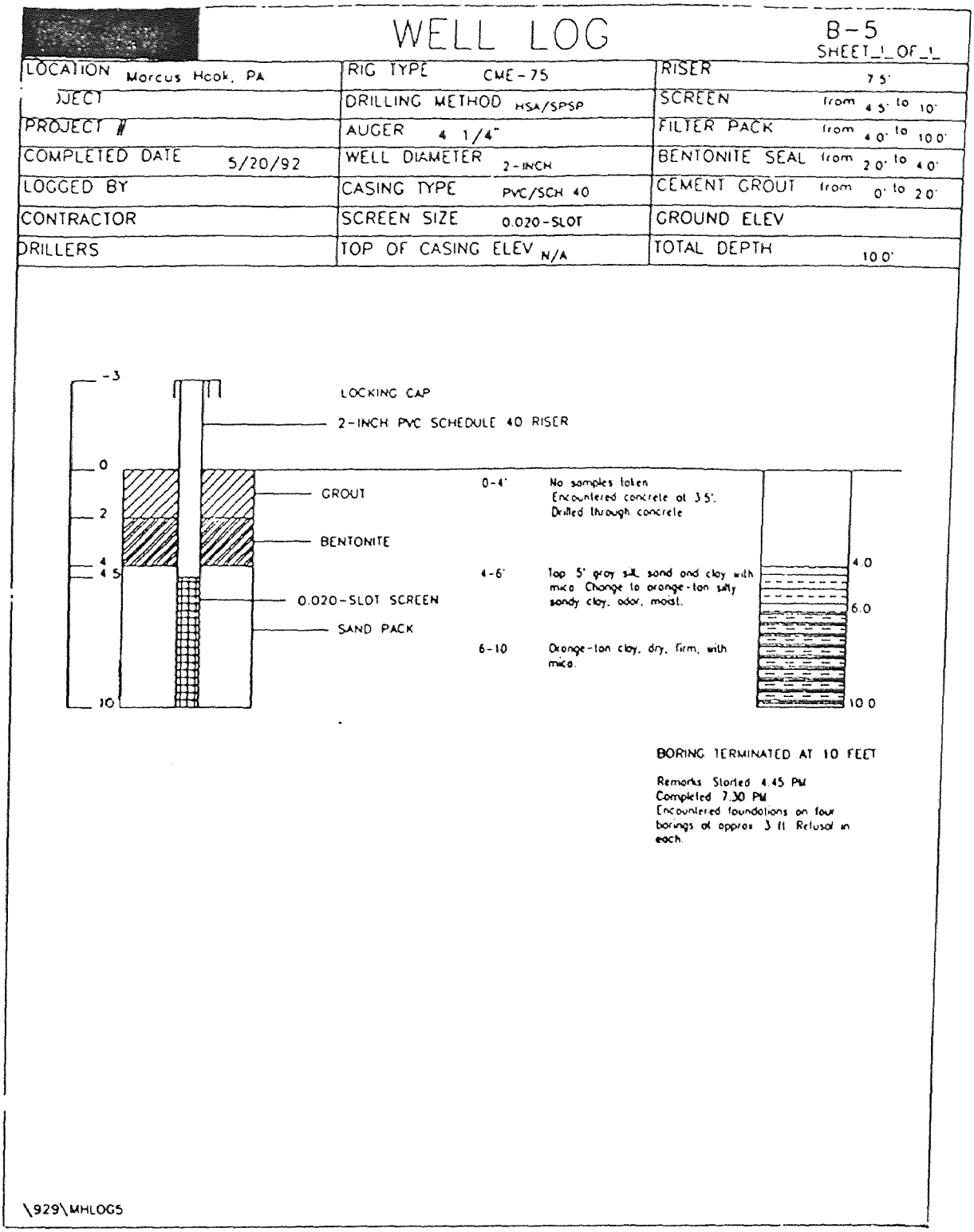


Figure A.5 Well log for VW-5.

APPENDIX B

SOIL GAS SURVEY PROCEDURE

B.1 Procedure

A soil gas survey was performed at the Marcus Hook, PA site to determine a suitable area for the demonstration. The survey consisted of installing vapor probes on a 50 ft by 50 ft grid over two acres of the site. Before installation of the probes, it was necessary to jack-hammer through the surface gravel. Once the gravel had been cleared away, the vapor probes were installed by hammering 1/2" stainless steel rods into the soil to a depth of about 8 ft. The rods were then removed leaving a one half inch diameter well. In order to prevent water infiltration, the wells were cased with 3/8" PVC pipe to a depth of three feet and sealed with bentonite. Tygon tubing was attached at the top of the well. This tubing was then sealed shut with a binder clip.

Vapor samples were taken from the vapor probes and analyzed following the same procedure as described in Appendix C, Section C.2. Field photoionization detector measurements were made on each of the wells following the sampling. The results for this test are shown in Table B.1. Figure B.1 shows the location of the vapor probes on the actual site.

Table B.1 Soil vapor gas survey, Marcus Hook PA

Well	Blows 1'-5'	Blows 5'-8'	Casing Depth	Time of Day	Purge Time(sec)	Extraction Time(sec)	PID peak	PID avg
B	20	68	3 feet	12:20	5 low	28 high	24.5	15
A	15	35	3 feet	12:40	4 low	60 high	7.2	6.5
C	8	70	3 feet	12:58	5 mid	60 low	7	5
4	11	19	3 feet	1:08	3 low	165 high*	50	2
6	42	85	3 feet	12:27	4 low	240 high	30	0
7	32	59	3 feet	12:52	3 low	40 low	10	4.5
8	19	9	3 feet	1:29	3 low	90 high*	7.5	1
11	51	57	3 feet	1:45	3 high	75	2.5	0
12	23	8	3 feet				20	0
17	23	53	3 feet	12:00	5 high	55 high	11.5	7
18	9	42	3 feet	12:15	4 low	120 high	40	0 (-2)
21	13	127	3 feet	1:51	5 low	15 high	11.4	5
22	10	41	3 feet	1:57	3 low	110*	45	1
23	17	70	3 feet	2:15	4 low	60 high	282	6
24	5	34	3 feet	2:22	3 low	34 high	80	10

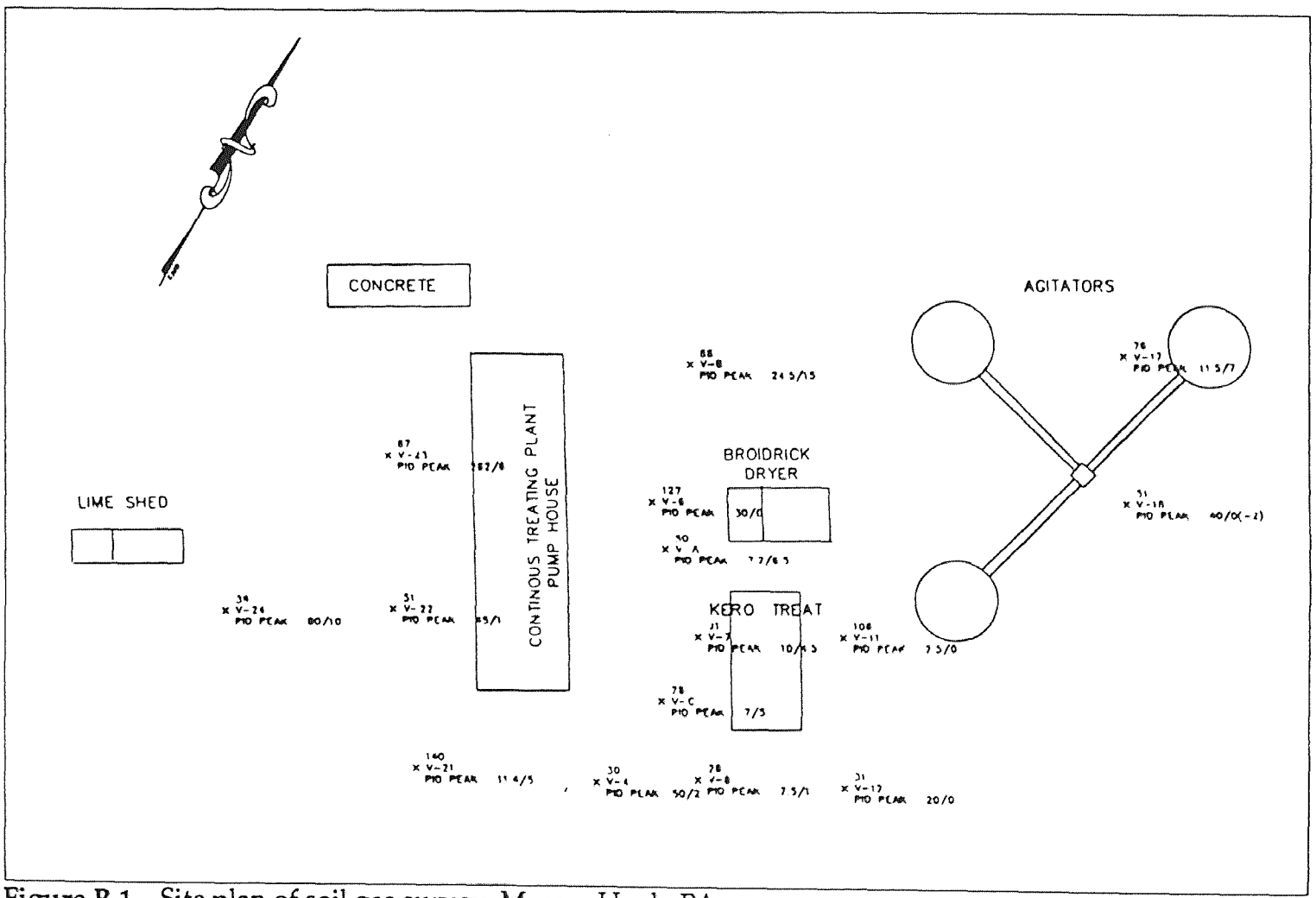


Figure B.1 Site plan of soil gas survey, Marcus Hook, PA.

APPENDIX C

SOIL AND VAPOR CHEMICAL ANALYSIS PROCEDURE

C.1 Soil Analysis

C.1.1 Soil Sampling

Soil samples were taken during the construction of the vent wells (VWs) and the extraction wells (EW). Samples were obtained continuously from a depth of one to ten feet using a split spoon auger. Spoonscan and headspace analysis were performed in the field using a photoionization detector to determine relative concentrations of contamination. The samples were then transported under refrigeration to the Rutgers chemical engineering laboratory for analysis.

C.1.2 Soil Analysis Procedure

Approximately ten grams of the soil sample is mixed with 5 ml of water in a 25 ml vial to disperse the soil sample and enhance the soil-solvent interaction. The remainder of the vial is filled with methylene chloride and the vials are weighed before and after each addition. Two replicates for each soil sample are prepared, sealed with Teflon septa, and crimped. After six days of shaking at room temperature the samples are analyzed for benzene, toluene, and the xylenes (BTX). Two controls are prepared with the exclusion of soil addition. One contains only water and solvent while the other is spiked with 165 mg of each BTX/Kg solvent. An HP5890 GC packed column is used for analysis.

C.2 Vapor Analysis

C.2.1 Vapor Sampling

Vapor samples are obtained from monitoring wells using a small vacuum pump. The samples are collected in stainless steel cylinders which are sealed and transported to the Rutgers chemical engineering laboratory under refrigeration. Sampling can only be done after adequate time is allowed for the vapor in the wells to reach equilibrium. Two sets of controls are used to monitor vapor losses during the handling and transportation. A site blank (surrounding air) and a standard vapor sample (50 ppm BTX from Scott Specialty Gases) are collected on site and transported with the samples to the laboratory.

C.2.2 Vapor Analysis Procedure

Samples are removed from the stainless steel containers using syringes and then injected into an HP5890 GC column. Peak areas and retention times corresponding to each target compound are recorded for each sample. These values are compared to the values obtained from analysis of the standard to determine an accurate concentration level for each compound. The analysis is done in triplicate to obtain a definite initial baseline for the contaminant values.

APPENDIX D

VAPOR SAMPLING DATA-MARCUS HOOK, PA

Table D.1 Vapor sampling data from montoring wells: Benzene

Well #	9/30/92 Conc (ppm)	10/14/92 Conc (ppm)	10/19/92 Conc (ppm)	10/21/92 Conc (ppm)
EW-1	332	84	0	399
VW-2	249	0	192	222
VW-3	61	26	31	37
VW-4	336	62	363	910
VW-5	536	37	0	721

Table D.2 Vapor sampling data from montoring wells: Toluene

Well #	9/30/92 Conc (ppm)	10/14/92 Conc (ppm)	10/19/92 Conc (ppm)	10/21/92 Conc (ppm)
EW-1	19	0	0	31
VW-2	31	40	32	28
VW-3	3	67	51	34
VW-4	0	0	21	0
VW-5	45	0	177	83

Table D.3 Vapor sampling data from montoring wells: p-Xylene

Well #	9/30/92 Conc (ppm)	10/14/92 Conc (ppm)	10/19/92 Conc (ppm)	10/21/92 Conc (ppm)
EW-1	4	9	0	11
VW-2	4	9	18	16
VW-3	0	5	4	8
VW-4	3	0	10	16
VW-5	5	0	11	38

Table D.4 Vapor sampling data from montoring wells: m-Xylene

Well #	9/30/92 Conc (ppm)	10/14/92 Conc (ppm)	10/19/92 Conc (ppm)	10/21/92 Conc (ppm)
EW-1	2	10	0	0
VW-2	3	17	8	0
VW-3	0	0	0	0
VW-4	5	0	9	16
VW-5	3	0	0	23

Table D.5 Vapor sampling data from montoring wells: o-Xylene

	9/30/92	10/14/92	10/19/92	10/21/92
Well #	Conc (ppm)	Conc (ppm)	Conc (ppm)	Conc (ppm)
EW-1	0	0	0	26
VW-2	8	0	27	31
VW-3	4	7	14	22
VW-4	0	0	9	28
VW-5	5	0	0	34

Table D.6 Vapor sampling data from montoring wells: Total BTX

	9/30/92	10/14/92	10/19/92	10/21/92
Well #	Conc (ppm)	Conc (ppm)	Conc (ppm)	Conc (ppm)
EW-1	357	103	0	467
VW-2	295	66	277	297
VW-3	68	105	100	101
VW-4	344	62	412	970
VW-5	594	37	188	899

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