ABSTRACT

INTEGRATION OF SURFACTANTS AND TIME RELEASE NUTRIENTS WITH PNEUMATIC FRACTURING PROCESS

by
Atiqur Md. Rahman

The objective of this laboratory study was the development of two novel improvements to the pneumatic fracturing process which would extend its present application. The first involved use of surfactant during pneumatic injection, and the second was subsurface injection of "time-release" dry nutrient pellets for enhancement of in situ biodegradation.

Bench scale tests demonstrated that pneumatic fracturing can be successfully performed with air containing a surfactant solution (foam fracturing). The results showed that foam fracturing followed by increased the rate of surrogate contaminant removal from 8% to 10% compared with regular pneumatic fracturing. These increases were attributed to enlarged fracture networks and increased airflow. Commercially available anionic surfactants, which are biodegradable, were used for the process. Recommendations for field scale applications were also developed.

It was also shown that injection of time release nutrient pellets into subsoil during pneumatic fracturing is feasible. Bench scale equipment for this process was developed and tested. Mechanical damage of the nutrient pellets during pneumatic injection was evaluated by different methods, and it was determined that serious damage was sustained above 75 psi. These results suggest pellets with higher mechanical strength characteristics are necessary for successful field integration with pneumatic fracturing process.

INTEGRATION OF SURFACTANTS AND TIME RELEASE NUTRIENTS WITH PNEUMATIC FRACTURING PROCESS

by

Atiqur Md. Rahman

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 in Environmental Engineering

Department of Civil and Environmental Engineering

October 1994

APPROVAL PAGE

INTEGRATION OF SURFACTANTS AND TIME RELEASE NUTRIENTS WITH PNEUMATIC FRACTURING PROCESS

Atiqur Md. Rahman

Dr. John R. Schuring, Thesis Advisor — Date
Associate Professor of Civil and Environmental Engineering, NJIT

Dr. Paul C. Chan, Committee Member — Date
Professor of Civil and Environmental Engineering, NJIT

Dr. Victor Ososkov, Committee Member — Date
Research Professor, Center for Environmental Engineering and Science, NJIT

BIOGRAPHICAL SKETCH

Author: Atiqur Md. Rahman

Degree: Master of Science in Environmental Engineering

Date: October, 1994

Undergraduate and Graduate Education:

- Master of Science in Environmental Engineering
  New Jersey Institute of Technology, Newark, NJ, 1994
- Bachelor of Science in Civil Engineering
  Bangladesh Institute of Technology, Bangladesh, 1991

Major: Environmental Engineering

This thesis is dedicated to
my parents
Abdur Rahman and Noorjahan Begum

ACKNOWLEDGMENT

I wish to express my sincere gratitude to my supervisor, Dr. John Schuring, for his guidance, encouragement, and friendship throughout this research.

I thank Dr. Victor Ososkov for serving as a member of the committee and for his careful review and helpful suggestions.

Special thanks goes to Dr. Paul Chan for serving as a member of the committee and for his careful review and helpful suggestions.

I also wish my acknowledge my colleagues and friends, Trevor King, Thomas Boland, Firoz Ahmed, Suresh Puppala, Conan Fitzgerald, Deepak Nautiyal, Yuan Ding, Heather Hall, Sean McGonigal, Ozzie Rodriguez for their constant cooperation, useful suggestions throughout this study.

This research was supported in part as a project of the Hazardous Substance Management Research Center at New Jersey Institute of Technology; a National Science Foundation Industry/University Cooperative Research Center and an Advanced Technology Center of the New Jersey Commission on Science and Technology.

TABLE OF CONTENTS

Chapter Page

TABLE OF CONTENTS
(Continued)

TABLE OF CONTENTS
(Continued)

LIST OF TABLES

LIST OF FIGURES

CHAPTER 1

INTRODUCTION

1.1 General

Contamination of soil and groundwater is presently one of the major environmental concerns in the United States and other industrialized countries. Subsurface contamination has reached a level and extent which poses a serious threat to human health and environment. Clean up of these contaminated sites is both difficult and expensive. In recent years, a number of in-situ and ex-situ treatment technologies have emerged to accomplish the clean ups. Considering their lower cost and minimal site disruption, in situ technologies are usually preferred.

An important limitation of any in situ remediation technology is they are affected by the pore fluid exchange rate of the soil or rock being treated, and their success is significantly impaired in soils with low permeability ($K < 10^{-5}$ cm/sec). Therefore all in situ technologies require some type of enhancement in low permeability formations; otherwise treatment rates would be unacceptable slow, and in most cases satisfactory regulatory requirements could not be achieved.

Pneumatic fracturing is a technology which has the potential to overcome the permeability limitations of available in situ technologies, especially in the removing volatile organic compounds (VOCs)[1]. The primary function of pneumatic fracturing is to increase vapor flow rates in low permeability formations, but it also has the potential to deliver liquid or granular supplements into the fracture network. For example, recent research[2], has demonstrated that pneumatic fracturing can be successfully integrated with in situ bioremediation, since it can overcome many of the limiting factors inherent with in situ bioremediation including available oxygen, nutrient supply and moisture level. In addition, pneumatic fracturing can permit the extension of in situ bioremediation into low permeability formations which cannot be effectively treated with standard bioremediation methods.

1.2 Purpose and Scope

The objective of this study is to integrate surfactants and time release nutrients with the pneumatic fracturing process in order to improve the efficiency of the process, and to extend its present applications.

The first improvement involves use of surfactant in aqueous solution during pneumatic fracturing, either as a low density foam or in a liquid form. It is believed that surfactants will act as a lubricating agents and enhance the fracture network under certain geologic conditions, thereby accelerating in situ treatment. Surfactants will also achieve some desorption of VOC's from the soil matrix, thereby enhancing their biodegradation.

The second improvement is subsurface injection of time-release nutrient pellets for enhancement of in situ bioremediation. The time-release pellets have advantages over the liquid nutrients presently being injected with the pneumatic fracturing equipment, since they reduce the potential for nitrate overloading, microorganism toxicity and groundwater leaching.

In accordance with the dual objectives, present study is divided into two parts. The first involves bench-scale laboratory studies of surfactant fracturing (foam fracturing) using Plexiglas test cells. Kinematics of contaminant removal from the soil after foam fracturing is compared with removal after regular pneumatic fracturing under the same experiment conditions. The second part of the study involves development, calibration, and testing of a prototype pneumatic dry injection system for time-release pellets. The focus for this part of the study is mechanical degradation of the nutrient pellets as a result of their delivery to subsurface by pneumatic fracturing process.

CHAPTER 2

BACKGROUND INFORMATION

2.1 Pneumatic Fracturing

Pneumatic fracturing is a patented process developed at Hazardous Substance Management Research Center (HSMRC) which enhances the removal and treatment of volatile organic contaminants from contaminated geologic formations. This new technology is now receiving considerable industrial attention since it addresses a problem which has plagued environmental clean up efforts to date: remediation of low permeability geologic formation. The pneumatic fracturing project has been underway since July 1988, and the basic process has been successfully demonstrated at the field pilot scale at fourteen sites including twelve contaminated sites[1].

The purposes of pneumatic fracturing are to reduce treatment time of contaminated formations, and extend available technologies to more difficult geologic condition. Figure 2.1 shows a schematic of the pneumatic fracturing system. The first step of the process involves drilling boreholes at locations and depths determined by the hydrogeology of the site, as well as the distribution of the contaminant. Next, a pneumatic device known as an "HQ injector" is inserted into the borehole to a predetermined elevation. The nozzle can be positioned at any elevation within the hole depending on the number of fractures, and degree of aeration required. The fracturing process involves injecting short bursts of compressed air (up to 500 psi) into the formation, causing the formation to fracture at weak points. These fractures, which are oriented predominantly in a horizontal direction, enlarge and extend existing fissures and/or generate new fissures. Where

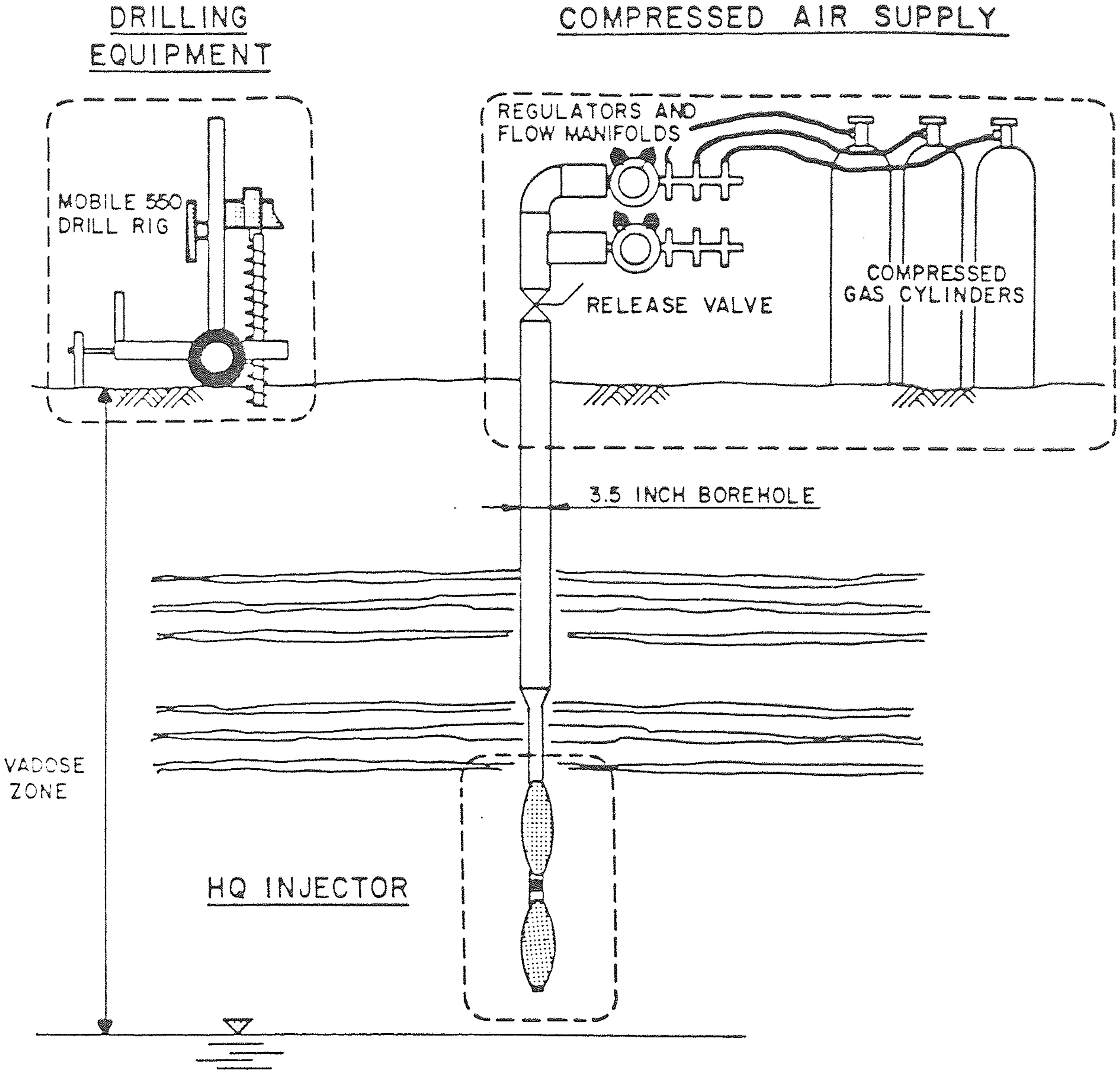


Figure 2.1: Prototype Pneumatic Fracturing System

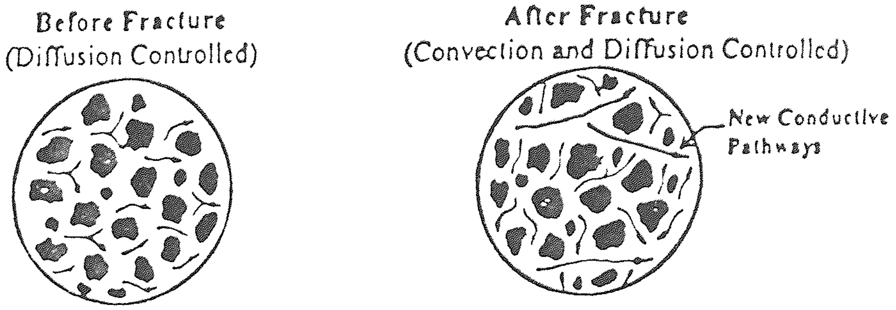
these fractures connect an extraction well with an air injection well or other source of air, they allow increased flow of air through the formation and, in effect, increase the permeability of the formation. In addition, the generation or extension of fractures can provide access to areas of the formation that were simply not accessible to extraction before fracturing. Figure 2.2 shows the concept of pneumatic fracturing for fine-grained soils, coarse-grained soils and rock formations, respectively.

2.1.1 Integration of Pneumatic Fracturing With Other In-situ Technologies

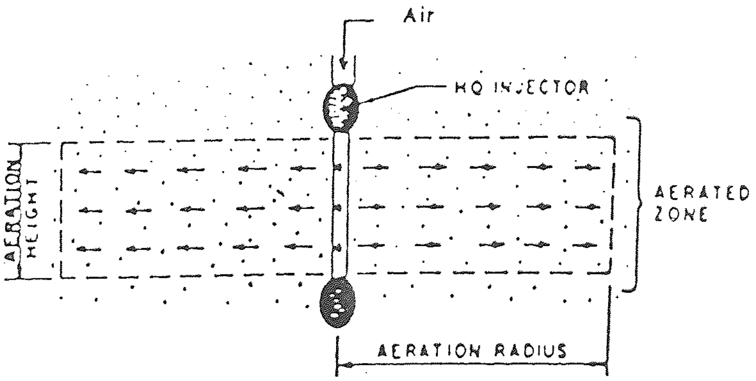
There are a number of existing and emerging technologies for cleaning up contaminated soils in-situ. This section will discuss the most promising in situ technologies that can be integrated with pneumatic fracturing process for enhancement and fast removal of the contaminants from the subsurface.

Vapor extraction was the first in-situ technology that the pneumatic fracturing process was demonstrated to enhance[5]. It includes the extraction of VOCs from the subsurface using an air vacuum pump. To be effective vapor extraction has to provide a large air flowrate through the soil, which is only possible in formations 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. This difficulty can be overcome by integrating pneumatic fracturing with vapor extraction technology. Pneumatic fracturing does increase the permeability of the formation, thereby enhancing vapor extraction of the contaminants[2].

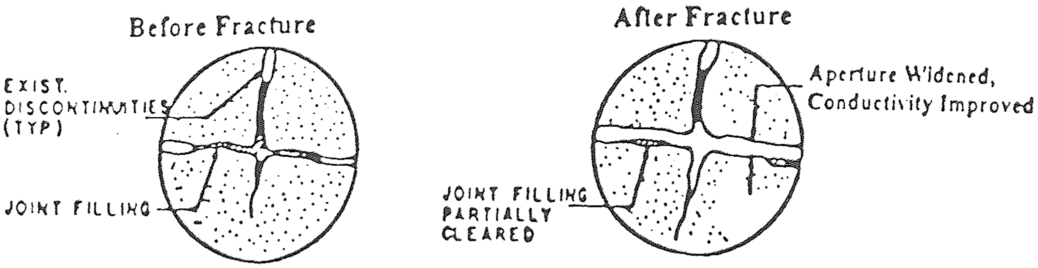
Bioremediation is very promising technology which may be integrated with the pneumatic fracturing to achieve efficient and fast on site removal of contaminants[3]. The process involves biological or chemical transformation of contaminants into a simpler, nontoxic form using microorganisms. The success of in



(a) Fine Grained Soils



(b) Coarse Grained Soils



(c) Rock Formations

Figure 2.2 Pneumatic fracturing concept for soil and rock formations situ bioremediation depends on control of subsurface conditions to enhance microbial growth. Proper control is possible only if the zone of contamination is accessible. In low permeability formations, bioremediation will be ineffective unless action is taken to enhance microbial growth. Pneumatic fracturing is a technology which has potential to provide this enhancement and which can modify some of the influential factors governing bioremediation like oxygen, water content, and temperature[3].

Hot gas injection is another technology that can be integrated with pneumatic fracturing process[31]. Hot gas injection technology consists of utilizing the energy generated during process operation to aid the remediation effort. Conceptually, by injecting a hot gas into the contaminated subsurface fracture network, the thermal energy of the gas would be transfered to the subsurface rock material surface and any contaminant contained thereon. The resulting rise in contaminant temperature would substantially increase its vapor pressure, which results in directly increasing the mass transport rate of the material to any gas flow through the region. Utilization of conventional hot gas injection technology is impractical in the remediation of most geologic formations due to the inability of the process to develop subsurface thermal effects. By integrating pneumatic fracturing with hot gas injection technology, the limitation of formation permeability can be overcome since the subsurface air flow in a pneumatically fractured formation will be substantially higher than in natural formations.

In Situ Vitrification (ISV) is also be integrated with pneumatic fracturing process. During the ISV process, the soil is heated upto 3000° C for melting waste material. The ISV process introduces generation of heat (up to 3000°C) for melting waste material, pyrolizing organic compounds, vaporizing metals by passing electric current through the electrodes inserted into the contaminated soils[13]. A starter path of graphite and glass frit is placed between the electrodes to allow initiation of the process in typically non-conductive soil. Although in situ vitrification approach seems to be promising in soil decontamination, the difficulty lies in melting the soil at greater depths, and in distributing the graphite in the subsurface. By integrating pneumatic fracturing with ISV process, the limitation of formation permeability can be overcome and dry injection of graphite can be performed at greater depth of soil.

Air sparging is a relatively new in situ technology that enhances desorption, volatilization and bioremediation of volatile compounds from the saturated soil by forcing air under pressure below the water table[14]. The present technology of air sparging is not appropriate for every site. Soils with hydraulic conductivities less than 0.0001 cm/sec are not good candidates for air sparging, since the low permeability of the formation retards air movement. In order to overcome the conductivity limitations of air sparging, pneumatic fracturing can be used to enhance the process. Pneumatic fracturing creates a network of fractures in low to moderate permeability formations which improves access to the contaminants. It is believed that after a formation has been fractured, the sparged air will penetrate the soil more effectively, thereby stripping VOC's which otherwise would not be accessed. This will result in a more rapid in situ clean up of the contaminated site.

2.2 Surfactants and Their Application for Soil Treatment

Surfactant is a substance that, when present at low concentration in a system, has the property of adsorbing onto the surfaces or interfaces of the system and of altering to a marked degree the surface or interfacial free energies of those surfaces (or interfaces). Surfactants are surface active because they concentrate at interfacial regions: air-water, oil-water, and solid-liquid interfaces, for example. A surfactant molecule is amphiphlic, having two distinct structural moieties, one polar and other nonpolar, referred to as head and tail groups respectively (Figure 2.3). The polar moiety of the molecule has an affinity for water and other polar substances, while the nonpolar moiety is hydrophobic. As a result of its amiphilic nature, a surfactant molecule may dissolve in water as a monomer, adsorb at an interface, or be incorporated with other surfactant molecules as part of a micelle.

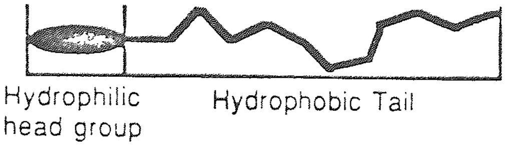


Figure 2.3 Basic molecular structure of surface active materials

The basic properties of surfactants[6,7] and their industrial applications[18,19] are reviewed in the literature. However because the course of colloid chemistry is not offered in NJIT and this work is the first attempt to integrate surfactants with pneumatic fracturing process it is relevant to describe some properties of surfactants and their application in environmental engineering.

2.2.1 Classification of Surfactants

Surfactants may be classified in several ways[7]. One of the more common schemes relies on classification by the application under consideration, so that surfactants may be classified as emulsifiers, foaming agents, wetting agents, dispersants, etc. Surfactants may also be generally classified according to some physical characteristics such as water or oil solubility or stability in harsh environments. Perhaps the most useful scheme from a general point of view, however, is that based upon the overall chemical structure of the materials in question. In such a classification system, it is easier to correlate chemical structures with interfacial activity, and thereby develop some general rules of surfactant structure-performance relationships.

In aqueous systems, which constitute by far the largest number of surfactant applications, the hydrophobic group generally includes a long-chain hydrocarbon radical, although there are examples using halogenated or oxygenated hydrocarbon or siloxane chains. The hydrophilic group will be an ionic or highly polar group that can impart some water solubility to the molecule. The most useful chemical classification of surface-active agents is based on the nature or the hydrophobe. The four general groups are defined as follows:

1. **Anionic**, with the hydrophilic group carrying a negative charge such as carboxyl ($RCOO^-$), sulfonate (RSO_3^-), or sulfate ($ROSO_3^-$), where R is hydrophobic radical.
2. **Cationic**, with the hydrophile bearing a positive charge, as for example, the quaternary ammonium halides ($R_4N^+Cl^-$).
3. **Nonionic**, where the hydrophile has no charge but derives its water solubility from highly polar groups such as polyuoxethylene (---OCH_2CH_2O---) or polyol groups.
4. **Amphoteric** (and zwitterionic), in which the molecule contains, or can potentially contain, both a negative and a positive charge, such as the sulfobetaines, $RN^+(CH_3)_2 CH_2 CH_2 SO_3^-$.

2.2.2 Properties of Surfactants Important for their Industrial Applications

Since this project is devoted to the integration of surfactant with pneumatic fracturing system, it is relevant to describe some properties of surfactants and their application for soil treatments.

1. *Micelle formation* is a phenomenon unique to surfactants[6]. It is the self assembly of molecules into dynamic clusters called micelles. Micelle formation, or micellization, is an important phenomenon not only because a number of important interfacial phenomena, such as detergency and solubilization, depend on the existence of micelles in solution, but because it affects other interfacial phenomena, such as surface or interfacial tension reduction, that do not directly involve micelles. Micelle formation occurs above a critical concentration of surfactant monomers,

referred to as the critical micelle concentration (CMC), which is different for every surfactant and typically range between 0.1 and 10 mM. In a micelle, the individual monomers are oriented with their hydrophilic moieties in contact with the aqueous phase and their hydrophobic moieties tucked into the interior of the aggregate. It is generally accepted that most surface active molecules in aqueous solution can aggregate to form micellar structures with an average of from 30 to 200 monomers in such a way that the hydrophobic portions of the molecules are associated and mutually protected from extensive contact with the bulk of the water phase. Changes in temperature, concentration of surfactant, additives in the liquid phase, and the structural groups in the surfactant all may cause change in the size, shape, and aggregation number of the micelle. Figure 2.4 is the example of surfactant micellization.

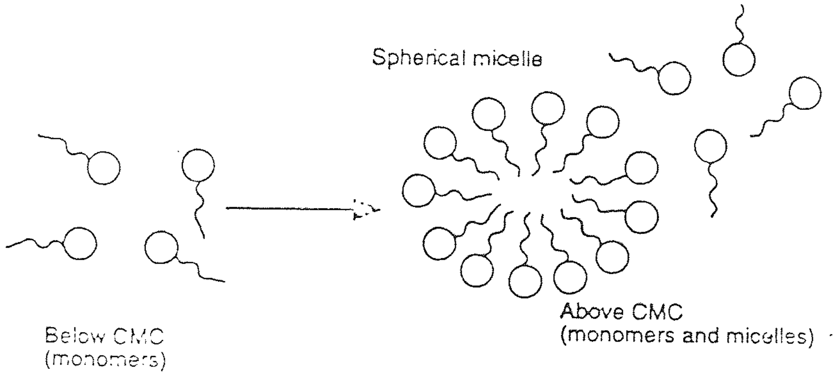


Figure 2.4 Examples of surfactant micellization

2. *Solubilization* is one of the important properties of surfactants related to micelle formation. Solubilization may be defined as the spontaneous dissolving of a substance (solid, liquid, or gas) by reversible interaction with the micelles of a surfactant in a solvent to form a thermodynamically stable isotropic solution with reduced thermodynamic activity of the solubilized material[9]. The importance of the phenomenon from the practical point of view is that it makes possible the dissolving

of substances in solvents in which they are normally insoluble. For example, although ethylbenzene solubility in water is about 300 ppm at 20°C, almost 50 gm of it may be dissolved in one liter of a 0.3 M aqueous solution of potassium hexadecanoate[18].

3. *Surface tension* may be defined as the force per unit length at right angle to the force required to pull apart the surface molecules in order to permit expansion of the surface by movement into it of molecules from the phase underneath it[7]. The interfacial tension between a liquid and its own vapor is also called surface tension[6]. The term interface indicates a boundary between any two immiscible phases; the term surface denotes an interface where one phase is a gas, usually air. When we measure the surface tension of a liquid, we are measuring the interfacial free energy per unit area of the boundary between the liquid and the air above it. Surface tension decreases with increasing temperature and may be affected by pH, surface active agents and gas in solution[6]. Reduction of surface or interfacial tension is one of the most commonly measured properties of surfactants in solution. Since it depends directly on the replacement of molecules of solvent at the interface by molecules of surfactant, and therefore on the surface excess concentration of the surfactant, as shown by the Gibbs equation,

$$d\sigma = - {}_{i}\Sigma\, \Gamma_i \, d\mu i \tag{1}$$

where $d\sigma$ = the change in surface or interfacial tension of the solvent,

Γ_i = the surface excess concentration of any component of the system

$d\mu i$ = the change in chemical potential of any component of the system

Figure 2.5 is a schematic illustration of a typical surface tension - concentration curve for an aqueous surfactant solution. In the figure, A - corresponds approximately to CMC concentration. After micelle formation surface tension is stabilized.

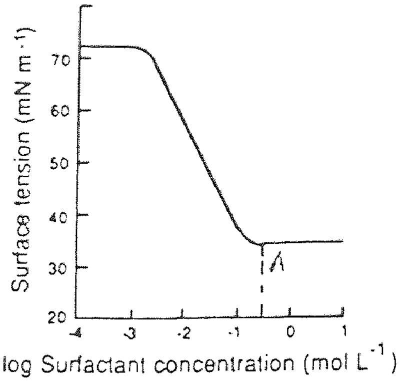


Figure 2.5 Schematic illustration of a typical surface tension concentration curve

If a surface active agent is added to a system of two immiscible phases (e.g., heptane and water), it will orient itself there with the hydrophilic group toward the water and the hydrophobic group toward the heptane. The interaction across the interface is now between the hydrophilic group of the surfactant and water molecules on one side of the interface and between the hydrophobic group of the surfactant and heptane on the other side of the interface. Since these interactions are now much stronger than the original interaction between the highly dissimilar heptane and water molecules, the tension across the interface is significantly reduced by the presence there of the surfactant.

4. *Adsorption* is one of the characteristic features of surfactants and its tendency to adsorb at interfaces in an oriented fashion[9]. At the liquid/solid interface, direct measurement of the concentration of surfactant adsorbed at the interface as a function of concentration in the liquid phase when equilibrium has been reached at a given temperature - the adsorption isotherm - is readily accomplished. The effect of a surfactant on an interfacial phenomenon is a function of the concentration of surfactant at the interface. The effectiveness of adsorption is related to the interfacial area occupied by the surfactant molecule; the smaller the effective cross sectional area of the surfactant at the interface, the greater its effectiveness of adsorption. It depends on the structural grouping in the surfactant molecule and its

orientation at the interface. The efficiency of surfactant adsorption at the solution - vapor interface is dominated by the nature of the hydrophobic group and is relatively little affected by the hydrophilic head group. *Surfactant sorption* on soil particles is a function of the nature of the surfactant (its ionic character and its hydrophobicity) and soil qualities including surface charge and organic carbon content[7]. Since soil minerals are usually negatively charged (e.g., clays), anionic surfactants will tend to sorb less than cationic surfactants. Positively charged minerals like iron oxides, aluminium oxides, and calcium carbonates may result in some anionic surfactant sorption. Soils with significant organic carbon content will tend to sorb more surfactant, regardless of the surfactant's charge.

5. *Wetting* in its most general sense is the displacement from a surface of one fluid by another. Wetting, therefore, always involves three phases, at least two of which are fluids: a gas and two immiscible liquids, or a solid and two immiscible liquids, or a gas, a liquid, and a solid, or even immiscible liquids[9]. Commonly, however, the term wetting is applied to the displacement of air from a liquid or solid surface by water or an aqueous solution. Wettability describes the preferential spreading of one fluid over solid surfaces in a two-fluid system; it depends on interfacial tension. Whereas the wetting fluid will tend to coat the surface of grains and occupy smaller spaces in porous media, the nonwetting fluid will tend to be connected to the largest openings. A measure of wettability is the contact angle at the fluid-solid interface (Fig 2.6).

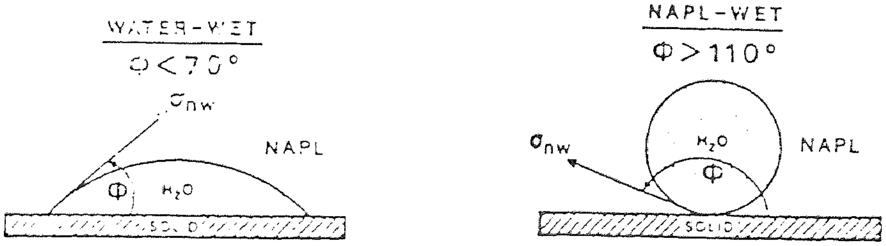


Figure 2.6 Wettability configurations

For two fluids, such as NAPL (Non aqueous phase liquid) and water, in contact with a solid; Young's equation describes the contact angle of the interface:

$\cos\phi = (\sigma_{NS} - \sigma_{WS})/\sigma_{NW}$ (2)

where, σ_{NS} is the interfacial tension between NAPL and solid; σ_{WS} is the interfacial tension between water and solid; σ_{Nw} is the interfacial tension between NAPL and water; and ϕ is the contact angle measured into the water. The contact angle indicates whether the porous medium will be preferentially wetted by NAPL or water and may vary between 0 and 180°. If $\phi \leq 70°$, the system is water-wet; if $\phi > 110°$, it is NAPL-wet; and if $\phi = 70° - 110°$, it is considered neutral[6]. Looking again at Young's equation, one can see that ϕ will decrease if either σ_{WS} or σ_{NW} or both are reduced and σ_{NS} remains essentially unchanged. The effect of such changes will be greater if σ_{NS} is larger, that is, if the second fluid in the system is air. The contact angle will increase with surfactant addition only if the surfactant is adsorbed at the N-S interface.

6. *Capillary pressure* is a property that causes porous media to draw in the wetting fluid and repel the nonwetting fluid[6]. If capillary pressure assumed positive, it is defined as the difference between the nonwetting fluid pressure and the wetting fluid pressure. For a water-NAPL system with water making the wetting phase, capillary pressure, P_C , is defined as:

$$P_C = P_N - P_W \qquad (3)$$

where P_N and P_W are NAPL and water pressure.

Capillary pressure is related to interfacial tension, contact angle, and pore space: by $P_C = (2\sigma \cos \phi)/r$ (4)

where r is the radius of the water filled pore; and σ is the interfacial tension between NAPL and water with the subscripts dropped. Equation (4) is valid only for interfaces that form subsections of a sphere. Capillary pressure increases as r and ϕ decreases and as σ increases.

7. *Foam formation* is the ability of a surfactant to perform as a foaming agent and is dependent primarily on its effectiveness at reducing the surface tension of the solution, its diffusion characteristics, its properties with regarding to disjoining pressures in thin films, and the elastic properties it imparts to interfaces[6]. The amount of foam that can be produced in a solution under given conditions (i.e., for a set amount of work input) will be related to the product of the surface tension and new surface area generated during the foaming process. Obviously, the lower the surface tension of the solution, the greater will be the the surface area that can be expected to be developed by the input of given amount of work.

It is often observed that the amount of foam produced by the members of an homologous series of surfactants will go through a maximum as the chain length of the hydrophobic group increases. This is probably due to the conflicting effects of the structural changes. It has been found in many instances that surfactants with branched hydrophobic groups will lower the surface tension of a solution more rapidly than a straight-chain material of equal carbon number. Nonionic surfactants generally produce less initial foam and less stable foams than ionic in aqueous solution. If the solubility of a surfactant is highly temperature dependent, it will be found that foaming ability will increase in the same direction as its solubility.

8. *Mobilization* is the phenomenon on which surfactant-enhanced oil recovery work was based[18]. Mobilization has greater potential than solubilization to increase the rate of remediation, but can be riskier because of the movement of the free-phase liquid. In the saturated zone, the interface between the water -wet soil surface and non aqueous phase liquid (NAPL) is characterized by NAPL -water interfacial tension (IFT). The forces that trap organic liquids are dominated by capillarity (adhesive-cohesive forces), which is proportional to the IFT at the liquid (water) interface. When the NAPL -ground water IFT is high, a large pressure drop per unit of distance (hydraulic gradient, P/L) between the injection and extraction wells.

Hydraulic gradient is required to push a residual droplet of NAPL out of its pore space.

Organic liquids, such as gasoline and industrial solvents, are major sources of ground water contamination throughout the United States. As an organic liquid moves through the subsurface, a portion of the liquid may become entrapped within the aquifer as immobile globules. Due to the low solubility no most organic liquids in water, the entrapped globules are extremely difficult and costly to remove by conventional pump-and treat remediation technologies. For this reason, surfactant enhanced aquifer remediation has been proposed as an alternative means of restoring aquifers contaminated by organic liquids[18].

9. *Biodegradation* may be defined as the removal or destruction of chemical compounds through the biological action of living organisms[12]. For surfactants, such degradation may be divided into two stages: (1) primary degradation, leading to modification of the chemical structure of the material sufficient to eliminate any surface active properties; and (2) ultimate degradation, in which the material is completely removed from the environment as carbon dioxide, water, inorganic salts, or other materials that are the normal waste byproducts of biological activity[23]. Years of research indicate that it is at the first stage of primary degradation that the chemical structure of a surfactant molecule most heavily impacts biodegradability[24].

2.3.3 Some Applications in Environmental Engineering

Surfactants due to their unique properties have tremendous application in industry. Some of them concerning soil treatment and remediation. Practically nontoxic and biodegradable surfactants are available for application in this area.

1. *SoilDrilling:* Surfactants are widely used as a drilling fluid[17] in wells. In an air-foaming drilling system, surfactant mixed with water is injected into an air stream. Surfactants include anionic soaps, alkyl polyoxythylene nonionic compounds, and

cationic amine derivatives. All of these are available as commercial products. Anionic surfactants are used more frequently because of less adsorption on soil particles that are mostly charged negatively.

Foams are used primarily to enhance the rate of cuttings removal by preventing them from aggregating so they can be lifted more easily to the surface. Surfactant is also added to air when the air stream can no longer lift the water entering the borehole. A surfactant injected into the air stream helps break up the water mass by reducing the surface tension of water droplets.

Surfactants are often mixed with water in large container adjacent to the rig, and then injected slowly into the air stream at a rate sufficient to lift the cuttings. Another mixing method is direct injection of a surfactant through a metered chemical pump into a water stream. The required volume of surfactant will usually range from 1 to 12 l per hour, depending on the type of surfactant, the volume of water entering the borehole, the diameter and depth of the borehole, and the quantity and size of cuttings. The surfactant concentration commonly varies from 0.25 to 2 percent of the injected water. Surfactants used in water wells are usually biodegradable and non toxic.

2. *Soil Washing:* Environmentally adequate disposal and treatment facilities for wastes containing polychlorinated biphenyls (PCBs), or technologies for the cleanup of PCB contaminated soil and ground water systems are still costly to find. On site surfactant washing after excavation have shown good promise to decontaminate nonvolatile and hardly biodegradable organic compounds like PCBs from contaminated soil systems[19]. Aqueous surfactant washing of oils containing dissolved PCBs from porous geologic media could involve several mechanisms. First because of reduced surface tension,

aqueous surfactant solution could displace oil trapped in the soil-pore space that could not be displaced by water[18]. Second, this reduction in surface tension will increase the detergency of the solution to disperse and transport more oil through the soil with the flowing water. Further, surfactants in aqueous solution can form micelles, which are macromolecules having hydrophobic interiors and hydrophilic exteriors (Figure 2.8). The affinity of the oils and PCBs for the hydrophobic interior of micelles could increase the apparent water solubility of these contaminants and enhance their removal from the porous system[17].

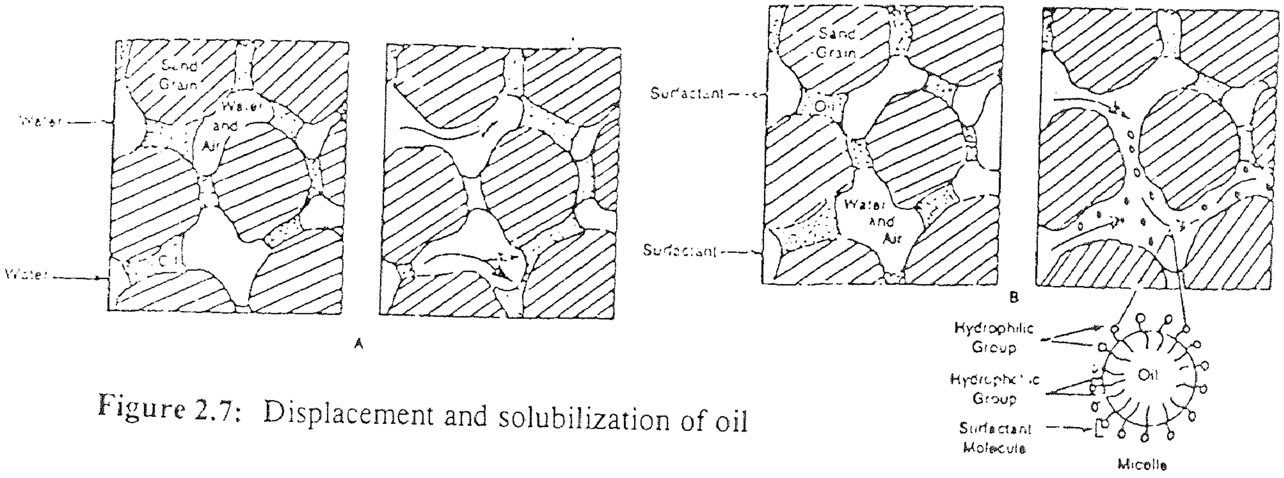


Figure 2.7: Displacement and solubilization of oil

The approach for in-situ surfactant washing is to apply the aqueous surfactant solution on the surface of the test plot to permeate and wash the contaminated zone, and capture the leachate at the depressed water table by pumping from a recovery well installed through the center of the test plot[19]. A nonionic surfactant named ethoxylated alcohol was used for surfactant washing in the test plot.

The major cost component for in-situ surfactant washing of contaminated soil and ground water systems is expected to be the cost of the surfactant. Recovery and reuse of the surfactant would improve any cost advantage of surfactant washing compared to conventional site cleanup technologies. The result of the field test demonstrated that if the surfactant application rate is carefully controlled, permeation and washing of the intended zone can be successfully accomplished without significant lateral spread of the surfactant and leachate. The test results indicate that this in-situ surfactant washing method is a promising candidate for the remediation of compounds with nonvolatile and nonbiodegradable organic soil systems[19,20].

3. *Soil Flushing:* The objectives of surfactant flushing are to remove petroleum-derived hydrocarbon contaminants from the subsurface and to promote desorption of contaminants. Surfactants have the potential to enhance significantly conventional "pump and treat" techniques intended to remove organic contaminants, which are practically unsoluble in water, from the subsurface[21]. When the contaminants are present as a NAPL, surfactants can promote their dissolution by increasing the compound's solubility in the flushing solution or these surface active additives can enable the NAPL's displacement via a reduction of interfacial tension. In addition, when the hydrocarbon is sorbed to aquifer solids, the surfactant can promote the desorpotion of the contaminant by modifying the contaminant's solid/water partition coefficient or, at lower concentrations, it can promote the release of colloids which may be carrying sorbed hydrocarbon contaminants. Successful surfactant flushing is possible only when the surfactant flush has access to the liquid or sorbed hydrocarbon contaminants.

Surfactant-containing solutions could be applied either vertically or horizontally[8]. A vertical flush would be applicable to vadose zone contamination problems where the vertical conductivity is sufficient. One advantage of vertical flushing is that it is relatively easy to apply a large pressure head vertically. Horizontal flushing would be applicable in the saturated zone, under buildings, or perhaps in horizontally stratified, tight soils. Horizontal flushing would require both injection wells and recovery wells. Impermeable walls might be built around the site in order to enhance flushing efficiency and to prevent offsite migration.

The main strength of surfactants is that they have the ability to solubilize or displace extremely hydrophobic chemicals like PCB's or automatic transmission fluid, constituents which are very resistant to remediation by both conventional treatments (e.g., pump and treat) as well as increasing popular techniques such as soil venting and air sparging which are effective only for volatile chemicals. The main weakness of surfactant flushing is that it, like other flushing techniques, is only effective at removing chemicals that it has access to. A surfactant flush might have some unforeseen implications when the contaminants are VOCs. Surfactant will reduce the Henry's law constant of VOC and thereby reduce the offgasing of VOC contaminated water - a positive effect if one is concerned about migrating vapors.

2.3 Bioremediation

Bioremediation technologies involve enhancing biodegradation of contaminants in the saturated and unsaturated zones or the subsurface environment through the artificial stimulation of indigenous soil and ground water microbial populations[12]. Natural biodegradative processes are enhanced by optimizing conditions necessary for subsurface microbes to grow and complete metabolic pathways. By stimulating subsurface activity of microorganisms, dangerous chemicals can be degraded into harmless substances. Because it is a natural occurring process, bioremediation can be performed in situ if critical parameters can be controlled[15].

2.3.1 Key Parameters of In Situ Bioremediation

Environmental variables can also greatly influence the rate and extent of biodegradation. In order to decide whether in-situ bioremediation can be applied at a contaminated site, microbiological, hydrogeological and chemical aspects must be regarded[15]. Tables 2.1 and 2.2 lists the most important parameters for successful bioremediation.

Table 2.1: Important Geologic Formation Chracteristics 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 2.2: 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

The factors that affect bioremediation process fall into three categories: (1) those that affect substrate availability, (2) those that directly affect the microbial population, size, composition and activity, and (3) those that directly control the degradation rates itself (e.g., temperature). Most factors are not independent but are highly interrelated. For example, pH may affect both the availability of a substrate as well as the composition of the microbial community. Following is a brief description of these parameters for successful in situ bioremediation.

Soil moisture is required for microbial growth and activity[15]. The optimum soil moisture content in the vadose zone is between 50% to 75% of the soil moisture holding capacity.in clean soils. Soil moisture is often the major limiting growth factor in the vadose zone. Water content in the soil will affect degradation of contaminants in a variety of ways. An over supply of moisture can reduce gas exchanging and limit oxygen which is depleted by microbial metabolisms. Thus an aerobic environment is created. An increase in soil water may allow more concentration to be present in the aqueous phase or dilute the chemical concentration, both of which would tend increase degradation rates. Reduction of water content in soil may increase sorption of contaminants onto soil particles and reduce their accessibility to microorganisms.

Available oxygen in the soil matrix is often a major limiting factor for in situ bioremediation. Oxygen is needed as the terminal electron acceptor for some microorganisms[15]. The availability of oxygen in soil will determine whether aerobic or anaerobic processes are dominate. Aerobic processes are typically favored because an aerobic system will produce a great deal more energy than an anaerobic system.[12] This will tend to accelerate the reaction rates of the degradation process, which is the objective of the in situ bioremediation. For this reason, control of available oxygen is crucial to the success of a bioremediation system.

Nutrients, such as nitrogen, phosphorus, and iron, play a important role in biodegradation process. Nutrient requirements for in situ bioremediation projects are site specific, and in some cases nutrient addition may not be necessary. Although most microorganisms can efficiently extract inorganic nutrients from their environment, their activity may be limited by the availability of nutrients. This is specially true if available carbon is excessive relative to the amount of nitrogen or phosphorous the microorganisms need to degrade it. If the ratio of organic C:N:P is wider than about 300:15:1 and available inorganic forms of N and P do not narrow the ratio to within these limits, supplemental nitrogen or phosphorous should be added[15]. 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.

Soil pH for the optimum growth rate of microorganisms should be close to neutral. There are some instances where a certain species will prefer acidic or alkaline conditions. In such situations it may be desirable to radically change the pH of the soil[15]. 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.

Soil temperature is one of the most important factors controlling microbiological activity and the rate decomposition of organic matter[15]. Based on optimum growth rate temperatures, microorganisms are divided into three groups. Psychophiles exhibit maximum growth rates at temperatures of less than 20°C, and can grow under freezing conditions. Mesophiles grow best in the temperature range of 25°C to 40°C, while thermophiles grow best at temperatures above 45°C[16]. Most microorganisms involved with in-situ biremediation would be classified as mesophiles. It is noted that temperature of subsoil typically ranges from 8°C to 12° C, and it may be the limiting factor for biodegradation.

Another important factor that must be considered for in situ bioremediation is the *availability of the chemical* to the microorganism. The organic chemical contaminant is utilized by the microorganisms as carbon and energy source for their growth. The chemical must be accessible, both on the macroscopic and 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 performing bioremediation[15]. This can be remedied by moving microorganisms to the more sparsely populated locations. At the microscopic level, situations often occur in which the chemical are sorbed onto the soil particles. Although there are cases in which the degradation rates of sorbed compounds are high, this phenomenon usually results in repression of chemical degradation[15].

CHAPTER 3

EXPERIMENTAL APPROACH AND ANTICIPATED BENEFITS

The objective of integrating surfactants and time release nutrients with Pneumatic Fracturing process is to make two novel improvements to the present systems, and to extend its present applications. The first improvement involves use of surfactants solution during pneumatic injection. It is believed that surfactants will act as a lubricating agents and enhance the fracture network under certain geologic conditions, thereby accelerating in situ treatment. They may also help to desorb contaminants which are bound to the geologic media. The second proposed improvement is subsurface injection of "time-release" nutrient pellets for enhancement of in situ bioremediation.

3.1 Surfactant Foams and Liquids

3.1.1 Experimental Approach

The concept of enhancing pneumatic fracturing with surfactants, i.e., "foam fracturing", is new, although surfactants have been used for decades in the water well and oil well industries to supplement drilling fluids and muds[17]. Also, surfactants are sometimes used for enhancement of the hydraulic fracturing process in the oil recovery industry[31]. A variety of surfactants will be considered for integration with the pneumatic fracturing system. The most important properties will be high wetting abilities on soil and rock materials, rapid biodegradation, and low cost. In combination with pneumatic fracturing it is planning to use inexpensive biodegradative surfactant which are presently commercial available and applied in the practice of soil treatment.

Modifications have been made to the existing pneumatic fracturing equipment to inject the surfactant foam. Combined mixer and pressurized injector was fabricated to introduce the surfactant solution into injected air stream above the ground surface. This provides sufficient time for receiving a stream of foam which travels below grade, and decreases friction losses in the piping, hoses, and HQ injector.

During the experimental approach of the integration of surfactants with the pneumatic fracturing process, a surfactant foam was used during the initial pneumatic injection to create a fracture network. Thereby, this process can be called "foam fracturing". In order to retain the viscosity advantages of pneumatic injection over hydraulic injection methods, a low density foam consisting of 2-5% (volume) surfactant solution in air was used. The concentration of surfactant in solution was 0.5% (volume).

Evaluation of the foam fracturing was conducted in the laboratory at a bench scale using 14.5 in. × 14.5 in. × 40 in. high Plexiglas test cells filled uniformly with soil. The soil behavior containing surrogate contaminant after regular pneumatic fracturing and foam fracturing was compared. Evaluation was based on :

(1) Measurement of the mass of contaminant removal from soil during a 16 days period
(2) air flow measurements through the soil under an applied vacuum
(3) pressure requirements to initiate fracturing
(4) direct visual observations of fracture patterns through the test cells

3.1.2 Surfactant Selection

A variety of surfactants was considered for integration with the pneumatic fracturing system. The most desirable properties were high wetting abilities on soil and rock minerals, rapid biodegradation, record of successful application in soil treatment technology, and low cost.

Anionic surfactants have less affinity to mineral surfaces because they are charged negatively at common pH values, and their integration with the pneumatic fracturing seems more promising. Cationic surfactants are strongly adsorbed by soil mineral surfaces, although they are usually more costly and may posses bactericidal properties.

The selected surfactant for these tests is commercially available under the product name "Drilfoam" produced by Barold drilling fluids, Inc. of Houston, Texas[25]. It contains the mixture of anionic surfactants (84%), isopropyl alcohol (12%) and ethanol (4%). In appearance, it is clear to yellow transparent liquid with density and viscosity of 8.5 lb/gal and 195 (70°F) respectively. It has no objectionable color, odor, or flavor as it breaks down. It is usually used in practice as 0.5-2.0% (by volume) aqueous solution. The price of "drilfoam" is $ 14/gal and it is also commercially available. It is biodegradable and very effective in air-drilling operations and is extensively used in water well and mineral exploration[17]. Treatment concentration and injection rates vary with the field conditions and should be adjusted to obtain foaming efficiency. In summary, the major reasons for selecting surfactants were: environmentally acceptability, economy, acceptable product history, and versatility (it has other uses).

3.1.3 Anticipated Benefits Of Surfactant

Surfactants have the beneficial property of lowering water surface tension, and reducing capillary pressure. This results in reduced energy requirements to move water through the equipment and the formation. This superior wetting ability is the main reason for integrating surfactants into the pneumatic fracturing process. It is anticipated that surfactants will increase the penetration ability of the injected air, resulting in a fracture network which is both finer and more extensive. They may also provide the additional benefit of loosening contaminants bound to the soil particles, and make them more accessible. Air flow and infiltration is also expected to improve. The end result will be more efficient removal and treatment by integrated technologies such as bioremediation and vapor extraction.

3.2 Time Release Nutrients

3.2.1 Experimental Approach

In standard in situ bioremediation applications, oxygen is usually the limiting factor for successful microbial growth and contaminant degradation. By integrating pneumatic fracturing with bioremediation, the permeability of the formation can increase to the point where oxygen supply is no longer critical. Under these conditions, the rate of degradation is likely to become nutrient limited. This has been the motivation for modifying the pneumatic fracturing system to inject nutrients and other biological supplements (e.g. acclimated microorganisms, buffer solutions) over the past two years. When liquid nutrient solutions such as nitrate salts are used, there is a risk of microorganism toxicity and ground water entry. Also periodic reinjections may be necessary to replenish the nutrient supply. The use of a time-release dry nutrient can overcome these difficulties, since nutrients are introduced gradually over a period of several months.

The incorporation of time-released dry nutrients with the pneumatic fracturing process is expected to provide better conditions for in situ bioremediation. A key question regarding the feasibility of pneumatically injecting dry nutrient is whether the particles will mechanically degrade during the injection process. Time release nutrients are produced in the shell of linseed oil which retards the speed of nutrient release in the soil. If this linseed oil coating on the particles is damaged , the time release rate will be skewed. For this reason, initial bench scale experiments were performed to assess the mechanical effects of injection. First, samples were sieved to establish a baseline particle size distribution. The samples were then forced through the pneumatic injection system at standard operating pressures and collected in a funnel hood. The samples were sieved again, and the results compared with baseline curves to assess the degree of mechanical degradation. The sieve analysis was supplemented by examination of individual particles under a microscope.

Nutrient release of the injected pellets was evaluated by weight loss in solution and electroconductivity tests. Results of the two tests for the injected pellets were compared with the control pellets before injection.

The use of water solution during injection was also studied to reduce the mechanical damage of pellets. The abrasive wear on the pneumatic fracturing equipment was also evaluated.

3.2.2 Selection of Time Release Nutrients

The only time release nutrient available on the market at the commencement of the project was "Max Bac" developed and manufactured by Grace Sierra of Milipitas, California[22]. The first wide application of the product was on the Exxon Valdez oil spill. To date, the product has only been used for surface remediation, subsurface pneumatic injection would expand the utility of the product.

Max Bac is comprised of one to three millimeter diameter spheres of nutrients, coated with a polymerized natural oil forming a controlled release membrane. Once Max Bac is applied to a moist environment, water vapor is drawn through the controlled release membrane towards the soluble nutrients. As a result, the spheres swell developing micro fissures in the controlled release membrane. Nutrients are released into the surrounding environment through the micro fissures in a regulated manner. Figure 3.1, in the following page, shows the working principle of these time release nutrients (Max Bac).

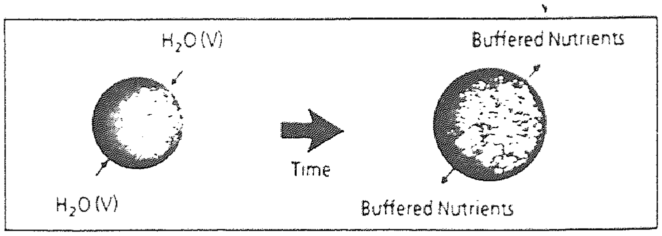


Figure 3.1 Max Bac's working principle

Max Bac delivers nitrate and ammonium nitrogen, soluble phosphate, and a small amount of vitamins to soil. The nutrients are available continuously, unaltered by undesirable soil reactions, and uninfluenced by the soil moisture content (as long as there is moisture present). Since the nutrient delivery is controlled, there is less chance of creating an environment where nutrient concentrations are limiting or excessive. The major factor controlling the nutrient release is temperature. The higher the temperature, the more actives the microbes become, and the faster the nutrients are released. As temperature drops, the nutrient release slows, and as does the microbial metabolism. For this reason, less Max Bac nutrients are needed to achieve faster bioremediations when compared with traditional practice.

The cost of the Max Bac time release nutrients is relatively modest at $ 1.20 per pound, which treats about 0.5 to 2.0 cubic yards of soil, depending on contaminant concentration and soil texture.

3.2.3 Anticipated Benefits Of Time Release Nutrients

Max Bac time release nutrient is environmentally safe and more efficient than traditional liquid nutrients. Nutrient waste is minimized, since less is leached due to its time release property. This makes it possible to apply less Max Bac than traditional nutrients, creating a more efficient and faster bioremediation. Time release nutrients also reduce the risk of nitrate and phosphate leaching into ground and surface waters. It also prevents toxic overloading of microbes as it delivers nutrient to the microbes in a controlled manner. The application of time release nutrients is not as frequent as liquid nutrient. By using the time release nutrients site testing, labor, maintenance, management and operational cost can be decreased. An additional benefit of dry nutrients may be temporary propping of the fractures.

CHAPTER 4

DESIGN OF EXPERIMENTAL STUDY

Two separate laboratory tests were designed for the experimental study: 1) Soil fracturing with and without surfactants; and 2) Dry injection of time release nutrient pellets through the pneumatic fracturing system. Each of these designs will now be described.

4.1 Pneumatic Fracturing With Surfactant

A series of bench-scale laboratory experiments were carried out to investigate integration of surfactants with present pneumatic fracturing process, and to determine the feasibility of using surfactants during pneumatic injection. Experiments were conducted in two identical 15 inch square by 40 inch high plexiglass tanks uniformly filled with silty sand. Tap water was used as a surrogate contaminant. Tanks were equipped with identical vapor extraction system. After fracturing with and without surfactants, contaminant (water) removal rate was measured.

4.1.1 Apparatus for Soil Fracturing

The apparatus used for each series of experiments is shown schematically in Figure 4.1 and major components for this test are described below.

1) Two identical tanks (1) 40 inches high by 15 inches square base, were fabricated using 1/2 thick Plexiglas. The tanks were open on the top and uniformly filled with soil.
2) A steel pipe (2) with 1 in. (I.D) was installed into the soil. The lower end of that pipe was equipped with a special nozzle (3) to spread the air flow in

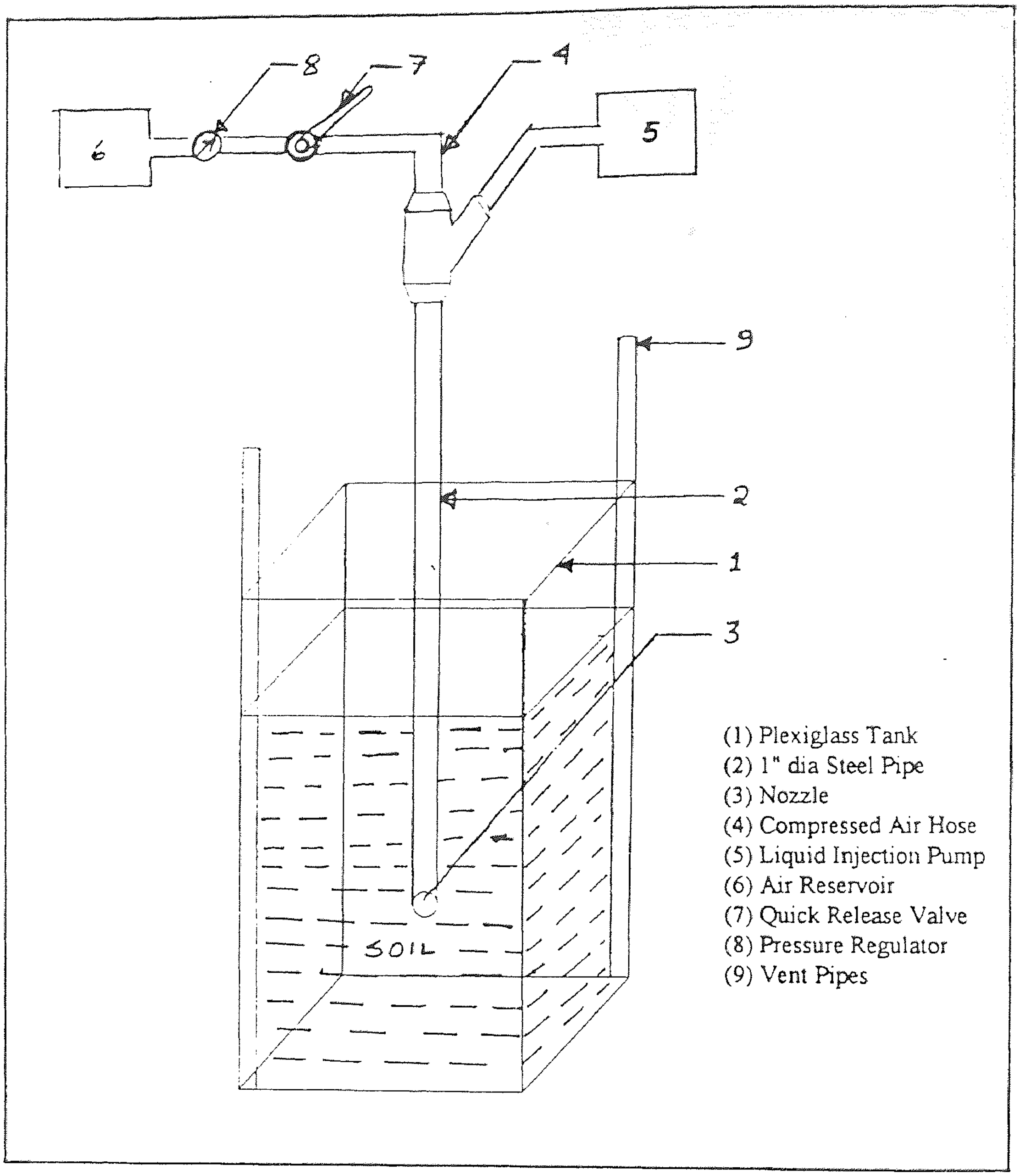


Figure 4.1: Schematic of Tank Test

the tank horizontally. The top end of that pipe was connected to the bottom of a Y pipe section. One top of the Y was connected to an air tight tank (4) through a 1/2 in rubber hose, and the other was connected to the liquid injection pump (5) through a 1/4 in. (I.D.) rubber hose.

3) A 3 cubic foot capacity cylindrical metal tank was used as an air reservoir.
4) A quick release air valve (6) was used to provide the instantaneous high-pressure required to fracture the soil.
5) A pressure regulator (7) was connected to the quick release valve to preset the desired air pressure for soil fracturing.
6) Two pressure gauges were used to determine the pressure existing inside the air reservoir and to indicate the pressure of the air that was going into the soil tanks.
7) Two 3/8 in. (I.D.) by 32 in. long polyvinyl chloride (P.V.C) perforated tubes (8) were installed at two corners of the Plexiglas tanks to serve as vent wells.
8) A vacuum system was used to extract vapor through the fracturing well.
9) A stop watch was used to record injection time.
10) An electronic scale with a total capacity of 1000 lbs and accuracy of ±0.05% of reading was used for weighing the tanks. The load cells were connected to an SB-10 Switch and Balance Unit and reading was taken using a P-3500 Digital Strain Indicator, both manufactured by Measurements Group (see Appendix A). This system gave accurate readings of any weight loss from the system.
11) The main piece of equipment selected for surfactant solution injection into the air stream was a Graco, President series 10:1 air powered pump (5) which can generate liquid pressures of well over 1000 psi. A schematic diagram of this pump is shown in Figure 4.2.

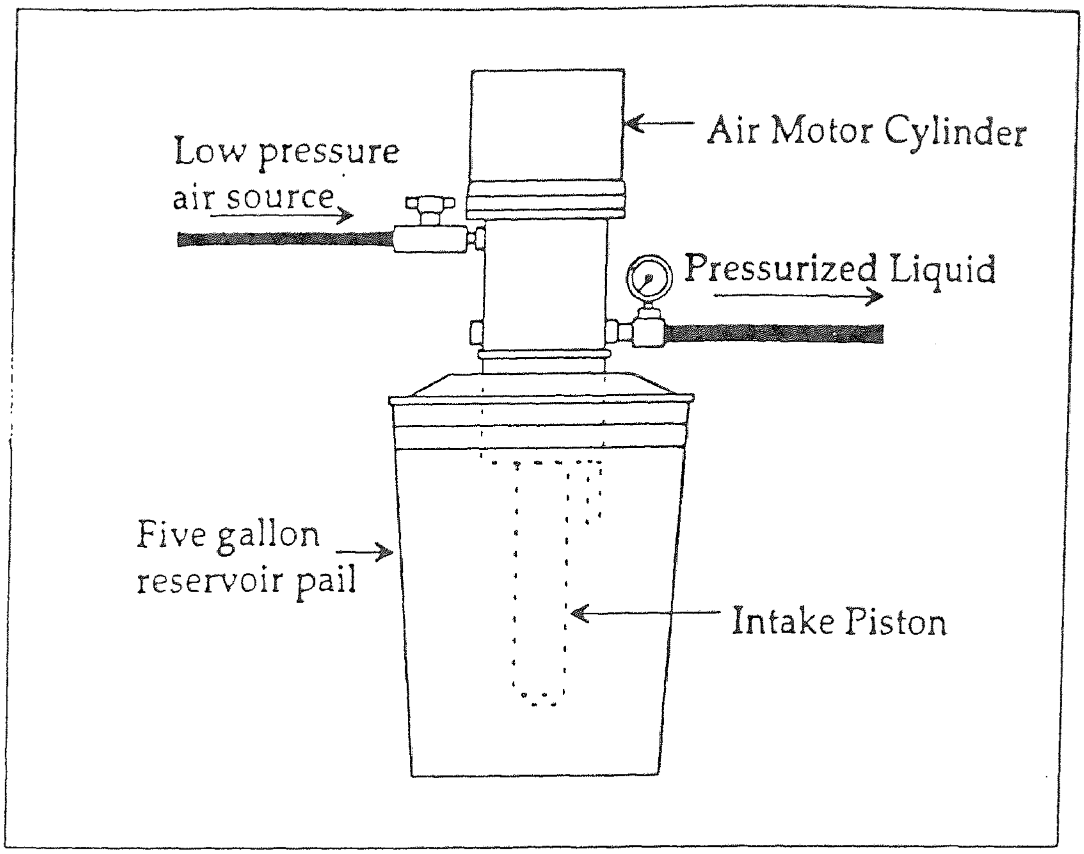


Figure 4.2 Conceptual diagram of Pneumatic liquid injection pump

Surfactant solution was placed in the reservoir pail befrore injection and then the pump was pressurized in order to inject surfactant at high pressure. The flow of the surfactant solution could be altered by changing the position of the valve (valve angle degree) while air flow rate was maintained constant. Preliminary experiments were run to define them relatively, and the results are summarized in Table 4.1.

Table 4.1: Characteristic of Surfactant Solution Injection

Surfactant Injection pressure	Valve angle	Time	Volume of surfactant solution	Surfactant flowrate	Air flowrate	Ratio of air flow & surfactant flow	% of Surfactant Solution in Air Steam
psi	degree	seconds	ml	cft/min	cft/min		
40	25	5	300	1.29	40	31 : 1	3.2
40	30	5	400	1.72	38	22: 1	4.5
40	35	5	550	2.4	36	15: 1	6.7
40	40	5	800	3.36	37	11: 1	9.1
40	45	5	1380	0.58	37	64:1	1.6
40	55	5	1400	0.59	38	64:1	1.6
40	90	5	1500	6.5	39	6: 1	16.7

12) To determine prefracture and postfracture airflow through the tanks a flow manifold system was used.

4.1.2 Experimental Procedure

The standard procedure that was followed for contaminant removal and soil fracture initiation is described below.

1) The soil used to fill the tank was silty sand (USGS Lab soil 1)[31]. Initial moisture content of the test soil was measured using ASTM D 2216-90 standard methods[30], and tap water was added to that soil to reach target moisture content of 15 percent.

2) The soil was equally compacted into two identical Plexiglas tanks using a tamper. The target dry density for the soil was 100 lbs per cubic foot.

3) Exact measurements of the soil lifts in the tanks were made to control soil volume and density.

4) During Test-1, soil in the first tank was pneumatically fractured at 8 psi. Fracture initiate time for this test was 3 seconds. Soil in the second tank was fractured using surfactant under the same condtions.

   The fracture nozzle for both tests was placed 9 inches height from bottom of the tank.

   For Test-2, two tanks were fractured at 10 psi for 3 seconds.

   Nozzle height was maintained at 9 inches from the bottom for both tests.

7) Surface elevation of the soil of the both fractured tanks were measured, and photos were taken to evaluate the effect of pneumatic fracturing on the soil volume and density.

8) The initial weight of the two tanks was recorded using the electronic weighing system at the beginning of the test and measurements were made periodically throughout the experiment. Load cells were calibrated just before the start of each experiment. Calibration was done by loading and unloading weights on the weighing platform. A constant factor of 16.6 was derived for each of the three GSE load cells to convert the P-3500 read out into FPS system (Appendix A) . The settings for the P-3500 were:

   a) AMP - 0 b) Gage Factor - 1

   c) Balance - 0 d) Run at full bridge circuit

9) Vacuum extraction was applied to both tanks after soil fracturing. During first test, vacuum pressure in two tanks was somewhat different (See Table B-2 of Appendix B). To provide a better methods of comparison, the

vacuum pressure was maintained constant at 30 inches of water in the second test.

10) Postfracture air flow through the two tanks was measured using the air flow manifold.
12) The tank weights were recorded over a period of 16 days to determine the rate of contaminant removal.
13) Photographs were made at different stages of the experiment to record the soil color change and the fracturing patterns.

4.2 Injection of Time Release Nutrients

The objective of these tests was to investigate the extent of damage of nutrients and the rate of nutrients release applying pneumatic fracturing equipment under different conditions. An induced flow injection system was used to introduce the dry nutrient into the pneumatic air stream. Although it is envisioned to eventually use this technique to distribute product radially into a fracture network. All experiments in this study were above ground injections. Experimental data for nutrients of different particle size utilizing various nozzle design and injection pressures were obtained. Two different size of pellets fine and coarse (fine pellets size<2.0 mm; coarse pellet size>2.0 mm and <4.75 mm) were selected initially for this test. Preliminary dry injection tests were performed for both fine and coarse pellets. Afterwards, nutrient loss in solution test, for both type of original pellet, was performed at 5 and 21°C temperature (Table B-3 of Appendix B). Preliminary test results showed fine pellets are more resistant to mechanical damage, less degradation in water solution, and higher flowrate through pneumatic injection system than the coarse ones. As a result, further study of pellet injection and degradation tests were performed using only fine pellets.

4.2.1 Equipment Description for Dry Injection

The equipment selected for dry injection of time release nutrients is a portable sandblaster of Model 200EA, manufactured by Lindsay Sandblasting Co. A schematic diagram of this equipment is shown in Fig 4.3.

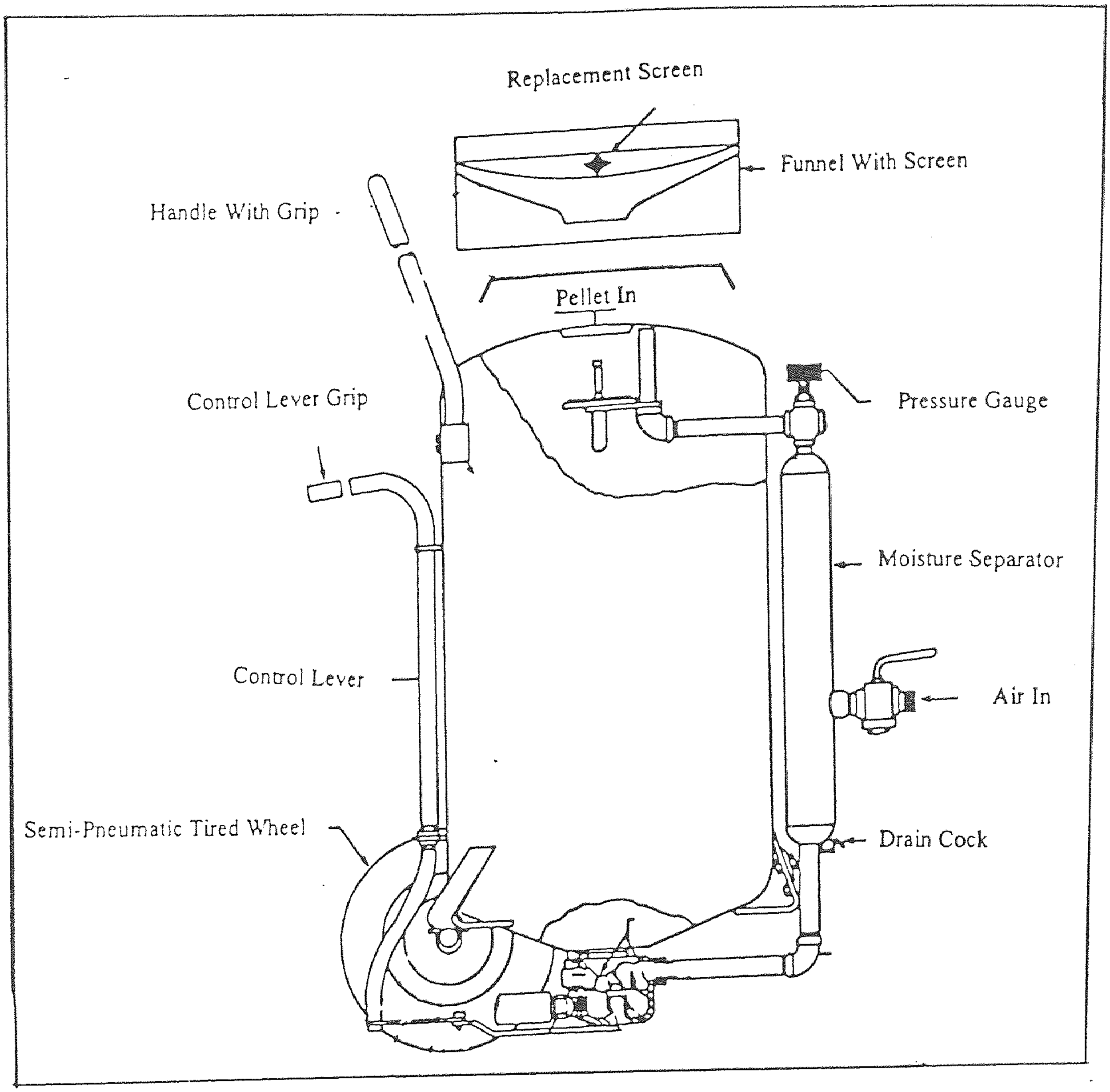


Figure 4.3 Conceptual diagram of Portable sandblaster

The maximum operating pressure is 125 psi, and it has capacity of holding 100 lbs of pellets. There is a valve on one side to control the flow, and a pressure gauge on top to measure pressure in the sandblaster during injection. A funnel with screen on top of the sandblaster in odrer to control proper size of injected pellets (pellets size < 2.0 mm). Pellets with size larger than 2.0 mm will not pass through the sandblaster and will clog its flow pathway. The sandblaster is pressurized with air pressure line in order to inject pellets. Pellets flow rate can be controlled both by a valve and by changing air pressure into system. Preliminary injection of fine size pellets were performed using the sandblaster at different pressure. The result of pellets injection flowrate were summarized in Table 4.2.

Table 4.2: Pellets Flowrate through Sandblaster for Various Injection Pressure

Experiment	Pressure	Time of Injection	Fine Pellet Injected	Flow rate
	psi	seconds	grams	gm/sec
1	20	5	325	65
2	40	5	400	80
3	50	5	475	95
4	60	5	575	115
5	75	5	675	135

4.2.2 Experimental Procedure of Lab Dry Injection Test

The ability of dry particles to penetrate a fractured soil matrix was studied using the previously described Plexiglas test cell. For this test, geotextile pieces were placed on the side of the tank for air flow. The tank was filled with soil and was fractured first. Afterwards the dry sand was injected into the fractured soil using the sandblaster. The same test was performed for several times to make sure that injected sand fill the fractured space at certain time. The same procedure can be applied in case of injection of nutrient pellets into subsurface. Photographs were taken at different stages to figure out the distribution of the injected pellet into the soil. The result of successful injection of sand into soil indicates the feasibility of the dry injection of pellet into subsurface. Figure G-1 in Appendix G, shows the typical distribution of sand into soil after pneumatic fracturing.

4.2.3 Pilot Test Of Pellet Injection

Bench scale injection of pellets were performed to investigate the mechanical damage of the injected pellets at high pressure (50-100 psi). To run this test, a system was developed integrating subsurface pellet injection with the present pneumatic fracturing process.

A steel hopper of 4 ft. diameter was used to collect the injected pellets. The internal surface of the hopper was coated with self-stick polyurethane foam sheeting of 1/8" thickness in order to reduce pellet damage after exiting the nozzle.

A sandblaster and nozzle were used to inject the pellets and distribute them into hopper. Injections were performed at 50, 75 psi for various nozzle/injection configurations. Figure 4.4 depicts the typical setup of pellet injection.

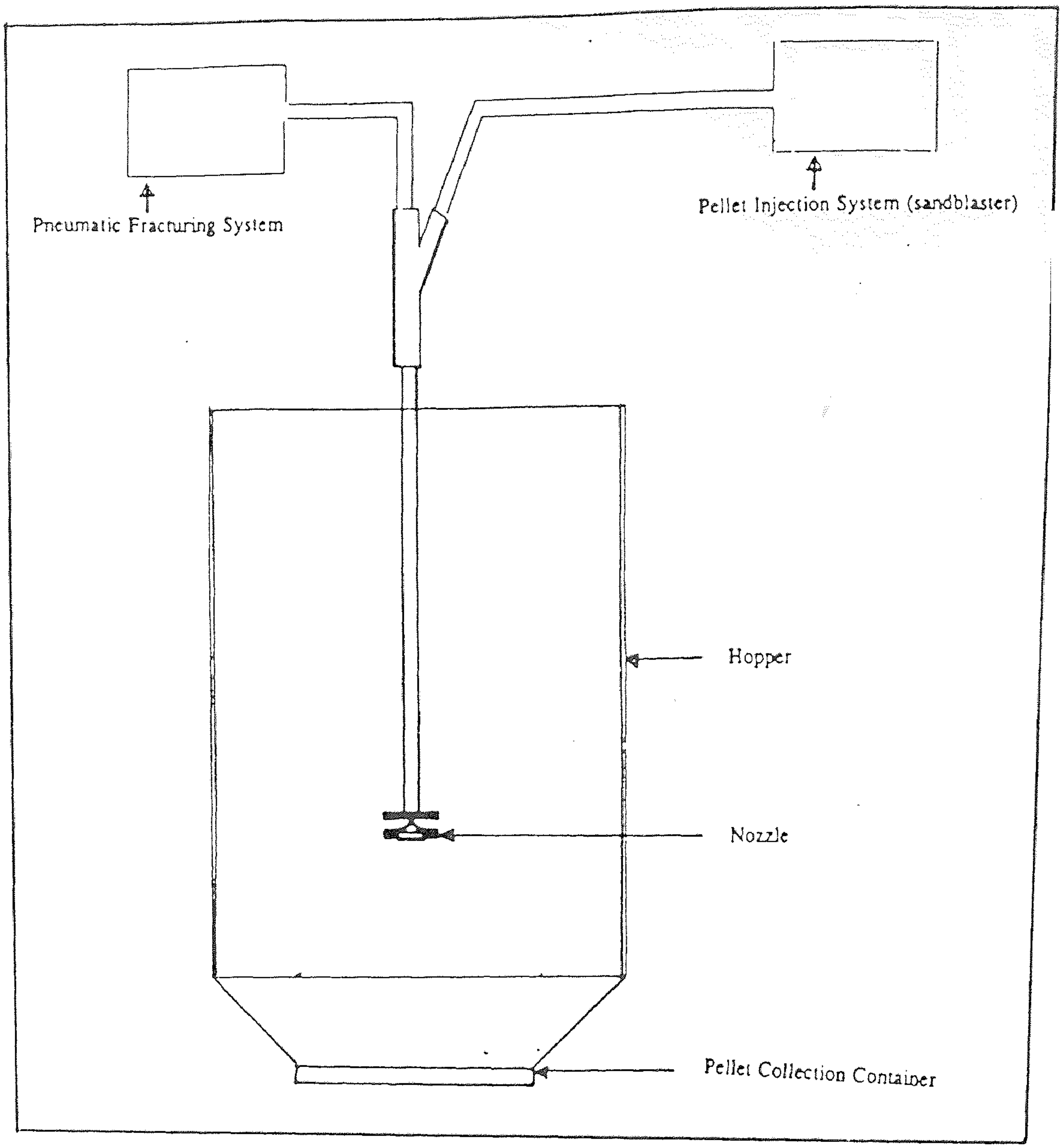


Figure 4.4: Typical Setup of Pellet Injection for Pilot Study

The injected pellets were collected in a bowl and taken in the laboratory for sieve analysis. Particle size distribution before and after injection was determined using ASTM D 422 standard method (Appendix E). The results of all test samples were plotted and compared to the original gradation to evaluate the extent of mechanical degradation.

Two series of pellet injection tests were performed during the study. Experimental setup for two series of dry injection test were described in Table 4.3 and Table 4.4 respectively.

Table 4.3: Experimental Setup For Dry Injection Of Fine Pellets Test 1

Case	Nozzle Status	Injected Pressure	
		System Pressure	Sandblaster Pressure
		psi	psi
1	Regular Nozzle	0	50
			75
		50	50
2	Rubber Coated	0	50
	Nozzle		75
		50	50
3	Rubber Base	0	50
	Nozzle		75
		50	50
4	No Nozzle	0	50
			75
		50	50

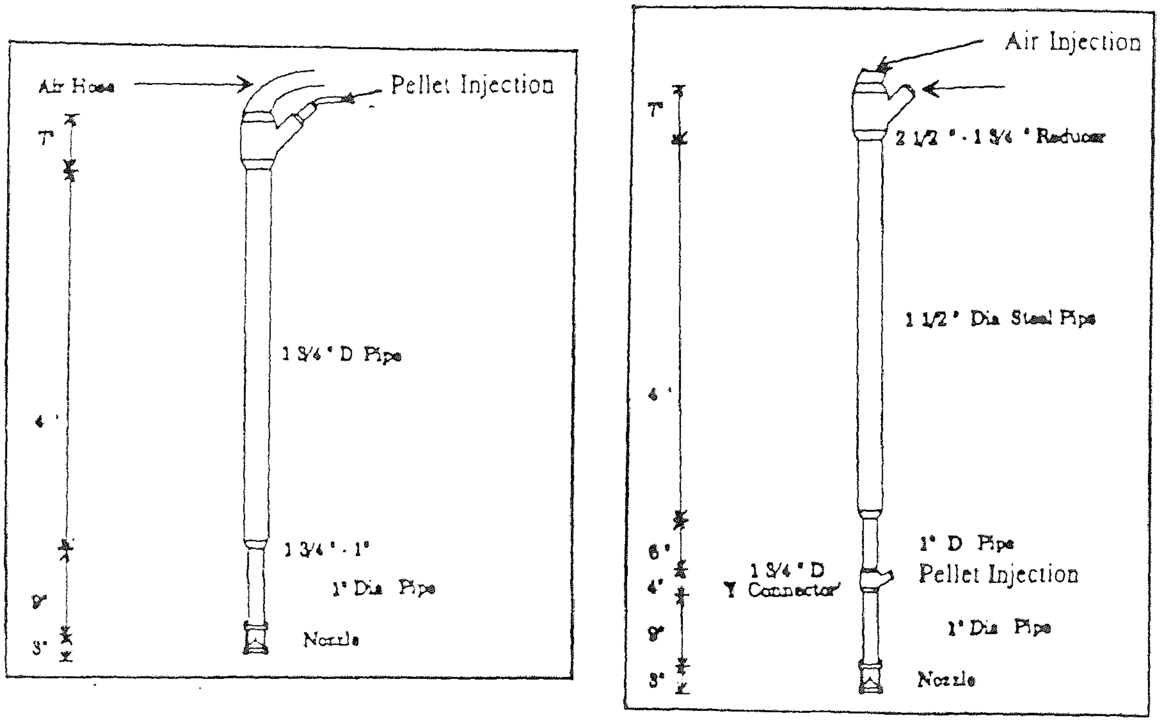
Table 4.4: Experimental Setup For Dry Injection Of Fine Pellets Test 2

Case	Pellets Injection Type	Pellets Injection pressure	
		System	Sandblaster
		psi	psi
1	Dry	0	50
		0	75
		50	50
2	Dry	0	50
		0	75
		50	50
3	Dry	0	50
		0	75
		50	50
	Dry	0	50
4		0	75
		50	50
	Liquid	0	50
5		0	75
		60	60

Note: Liquid was injected at pressure 30 psi
Regular type nozzle was used for all tests

The first series included four dry injection tests with different types of nozzle. In the first test, regular nozzle for pneumatic fracturing process was used. In the second test, the regular nozzle cone was coated with soft rubber to a thickness of 1/8 inch. In the third test, a semicircular rubber ball of 2 inch diameter was substituted as the nozzle cone. For the fourth test, no nozzle was used during dry injection of pellets. The objective of these tests was to investigate whether the nozzle was a significant cause of damage to the pellets.

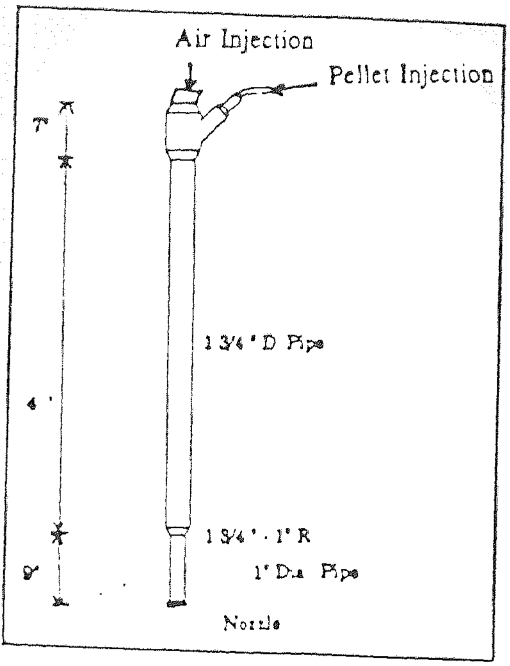
For the second series of pellet injection tests, several modification of the present system were accomplished including modification of the pathflow of pellet injection and liquid injection. Injection of pellets were performed using different combination of injection system to find out which set up gave best result. Various combinations of nozzle/injector setup was performed during the second series of pellet injection. The schematic of these setup was shown is Figure 4.6.



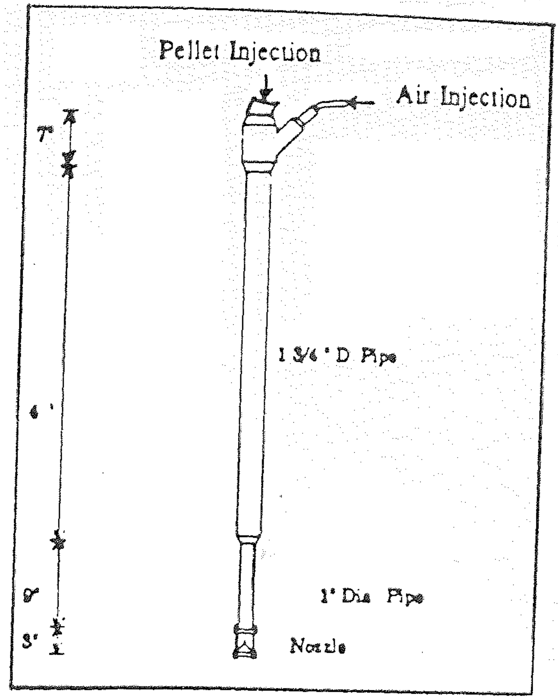
Case 1

Case 2

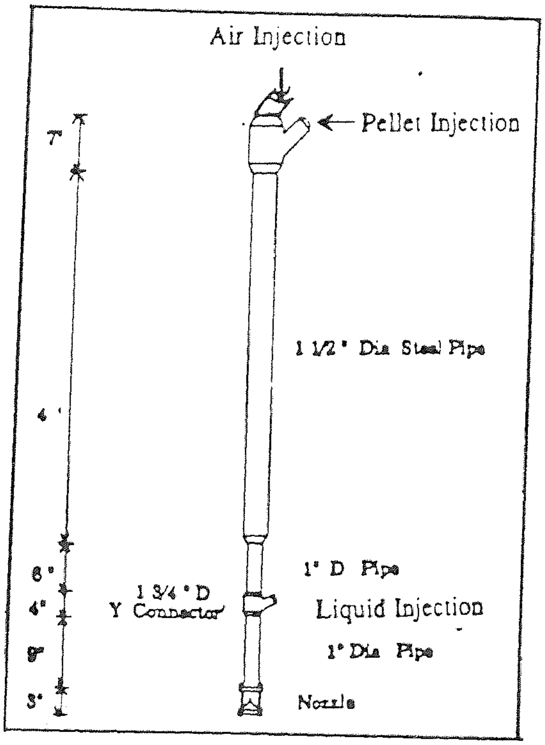
Figure 4.5: Schematic of Pellet Injection Setup for Test Series 2



Case 3



Case 4



Case5

Figure 4.5: Schematic of Pellet Injection Setup for Test Series 2 (continued)

4.3 Determination of Pellet Degradation

To evaluate the mechanical damage of injected pellets, several different laboratory analysis were performed. The first two tests were mechanical, and involved both microscopic examination and particle size analysis. In addition, degradation was evaluated by weight loss in solution and electroconductivity tests. All four tests are described below.

4.3.1 Microscopic Examination of Pellets

About 100 grams of pellets were randomly selected before and after injection. Small lots of pellets were placed on a thin glass under a microscope at 30 x magnification. Partially or totally damaged pellets were separated and total number of undamaged pellets and damaged pellets were counted . In the similar way, two random samples were taken from the injected pellets and the same procedure was followed to count damaged and undamaged pellets. From the average of these three results, percent of damaged pellets was calculated for all the tested samples.

4.3.2 Particle Size Analysis of Injected Pellets

Particle size analysis of pellets was performed according to ASTM D-422 method. For this test, 200 grams of nutrient pellets before and after injection were put on sieves of # 10, 20, 40, 60, 100 and 200. The whole assembly of sieves were kept on mechanical vibrator for 2 minutes. Pellets retained in each sieved were weighed and a grain size distribution curve was plotted. The curve shows the relative distriubution of different sizes of the total pellets. The deviation of the sample curve from the original plot showed the mechanical damage caused by injection. From these particle size distribution plots, the best dry injection setup was determined.

4.3.3 Evaluation of Nutrient Release by Weight Loss in Solution

The extent of pellets destruction was evaluated by immerging the pellets in distilled water and monitoring the resulting weight loss. Experiments were performed at water temperatures of 5° and 21°C. 10 gram of pellets were mixed in a jar with 50 ml of distilled water. After one week, the pellet/water mixture was filtered and pellets were dried for 15 minutes at 100°C, cooled and weighed. The lost weight was proportional to their degradation at given test conditions.

4.3.4 Evaluation Of Nutrients Release By Electroconductivity Determination

Since nutrients released from pellets are mostly nitrates salts, electroconductivity determination of their aqueous suspension verses time allowed yet another means to evaluate the rate of degradation. These tests were performed at 4° and 20□C with the fine pellets of nutrients.

First, 1 gram of pellets was mixed in 100 ml of de-ionized water. The temperature of the solution was recorded. Next the electrode of the conductivity meter (Model No YSI #3140) was immersed in the solution to measure the water conductivity. Three different sample solutions were prepared using three different pellets samples. Initial conductivity readings were recorded for three samples and measurements were carried out for 1 hour interval. When the nitrate salts were totally dissolved in water, the conductivity of solutions became practically constant. The conductivity of solutions was proportional to the extent of pellets degradation and indicated nutrients release. The experimental procedure of conductivity test is atttached in Appendix A.

CHAPTER 5

RESULTS OF EXPERIMENTAL STUDY

5.1 Soil Fracturing with Surfactant

The experimental results for the two tests of pneumatic fracturing with surfactants are presented in Tables 5.1 and 5.2, and in Figures 5.1 and 5.2. Tap water was used as surrogate contaminant in both tests. For the first test, initial moisture contents in the normal fractured tank and surfactant fractured tank were set at 14.5% and 14.0%, respectively. Injection pressure and injection time was also consistent for both tests. In the second test, initial moisture contents for normal fractured tank and surfactant fractured tank were 15.6% and 15.5%, respectively. Injection pressure and injection time were again consistent for both tanks. Prefracture and post fracture air flow were also recorded for both tests, and are summarized in Tables B-1 and B-2 of Appendix B, respectively.

For both tests, photographs of fracture patterns were taken and are presented in Appendix C as Exhibits C-1 and C-2. These photographs also document soil color change during the experiments for various time intervals.

5.1.1 Observed Trends

One of the first observations during the test was the effect of surfactants on the fracture pattern. Fracture patterns achieved with surfactant solution injection were more extensive and more branched (see photographs in Appendix C).

A second observation made during the tests was the extracted air flow for the surfactant tank was consistently higher than the control tank. For first test, air flow was averaged 2% higher in the surfactant tank, even though vacuum pressure was lower. For the second test set, both tanks were maintained at the

Table 5.1: Water Loss Data for Pneumatic Fracturing with and without Surfactant: Test 1

Day	Weight of Tank		Weight Loss		% Weight Loss	
	lbs	lbs	lbs	lbs		
	Normal Fracture	Surfactant Fracture	N. Fracture	S. Fracture	N. F.	S.F.
	Tank 1	Tank 2	Tank 1	Tank 2	Tank 1	Tank 2
0	525.939	520.363	0	0	0	0
1	523.072	517.349	2.867	3.014	0.548	0.583
2	520.674	514.816	5.265	5.547	1.006	1.072
3	518.168	512.38	7.771	7.983	1.486	1.543
4	515.816	509.678	10.123	10.685	1.935	2.065
5	513.585	507.216	12.354	13.147	2.362	2.541
6	511.505	504.799	14.434	15.564	2.759	3.008
7	509.524	502.542	16.415	17.821	3.138	3.445
8	507.552	500.195	18.387	20.168	3.515	3.898
9	505.3	498.414	20.036	21.949	3.83	4.242
10	504.275	496.675	21.664	23.688	4.141	4.579
11	502.785	495.4	23.154	24.963	4.426	4.825
12	501.56	494.326	24.379	26.037	4.66	5.033
13	500.546	493.349	25.393	27.014	4.854	5.221
14	499.654	492.375	26.285	27.988	5.025	5.409
15	498.922	491.396	27.017	28.967	5.165	5.599
16	498.203	490.509	27.736	29.854	5.302	5.77

Experimental Conditions:

Normal Fracturing

Air Injection Press System Air Pressure = 8 psi
Injection Time = 3 seconds
Moisture Content = 14.5%

Surfactant Fracturing

Air Injection Pressure = 8 psi
Surfactant Injection Pressure = 40 psi
Injection Time = 3 seconds
Moisture Content = 14.0%
Volume of Injected Surfactant Solution
(0.5% Drillfoam in Water) = 300 ml
Ratio of surfactant solution /Air = 1:22 (volume)

Table 5.2: Water Loss Data for Pneumatic Fracturing with and without Surfactant: Test 2

Day	Weight of Tank		Weight Loss		% Weight Loss	
	lbs	lbs	lbs	lbs		
	Normal Fracture	Surfactant Fracture	Normal Fracture	Surfactant Fracture	N. Fracture	S. Fracture
0	598.44	607.41	0	0	0	0
1	594.66	603.34	3.78	4.07	0.635	0.675
2	591.39	599.85	7.05	7.56	1.185	1.253
3	588.46	596.64	9.98	10.77	1.678	1.785
4	585.76	593.62	12.68	13.79	2.132	2.285
5	583.19	591.09	15.25	16.62	2.564	2.755
6	580.69	588.13	17.75	19.28	2.985	3.195
7	578.19	585.38	20.25	22.03	3.405	3.651
8	575.99	582.74	22.45	24.67	3.775	4.088
9	573.66	580.36	24.78	27.05	4.167	4.483
10	571.68	578.09	26.76	29.32	4.5	4.859
11	569.84	575.87	28.6	31.54	4.809	5.227
12	568.09	573.74	30.35	33.67	5.103	5.58
13	566.4	571.76	32.04	35.65	5.387	5.908
14	564.68	570.14	33.76	37.26	5.677	6.175
15	563.17	568.52	35.27	38.89	5.931	6.445
16	561.56	566.95	36.88	40.46	6.202	6.706

Experimental Conditions:

Normal Fracturing

Air Injection Pressure = 10 psi
Injection Time = 3 seconds
Moisture Content = 15.6 %

Surfactant Fracturing

Air Injection Pressure = 10 psi
Surfactant Injection Pressure = 40 psi
Injection Time = 3 seconds
Moisture Content = 15.5%
Volume of Injected Surfactant Solution
(0.5% Drillfoam in Water) = 275 ml
Ratio of Surfactant Solution/Air = 1:22 (volume)

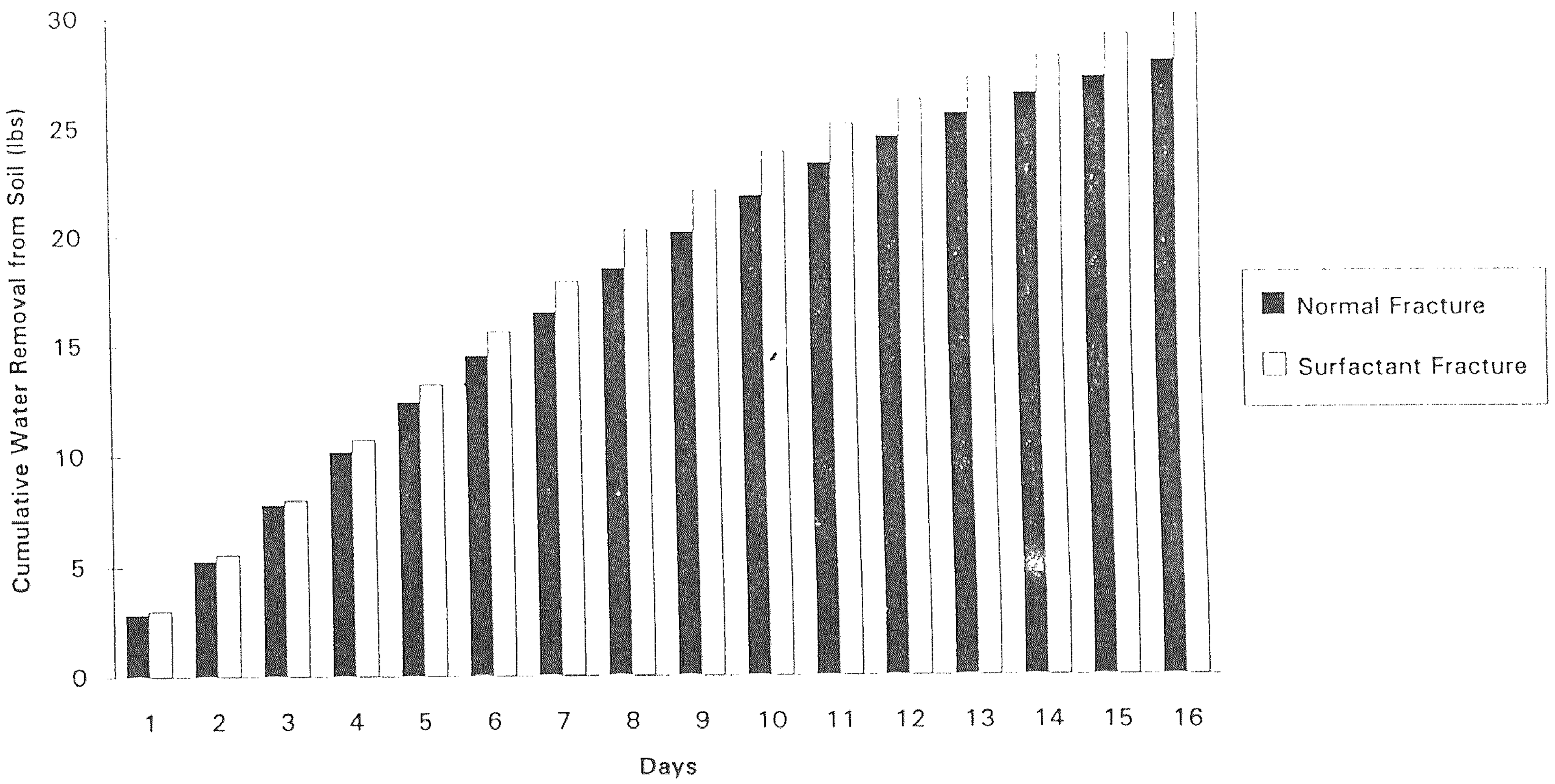


Figure 5.1: Kinetics of Water Removal for Test-1

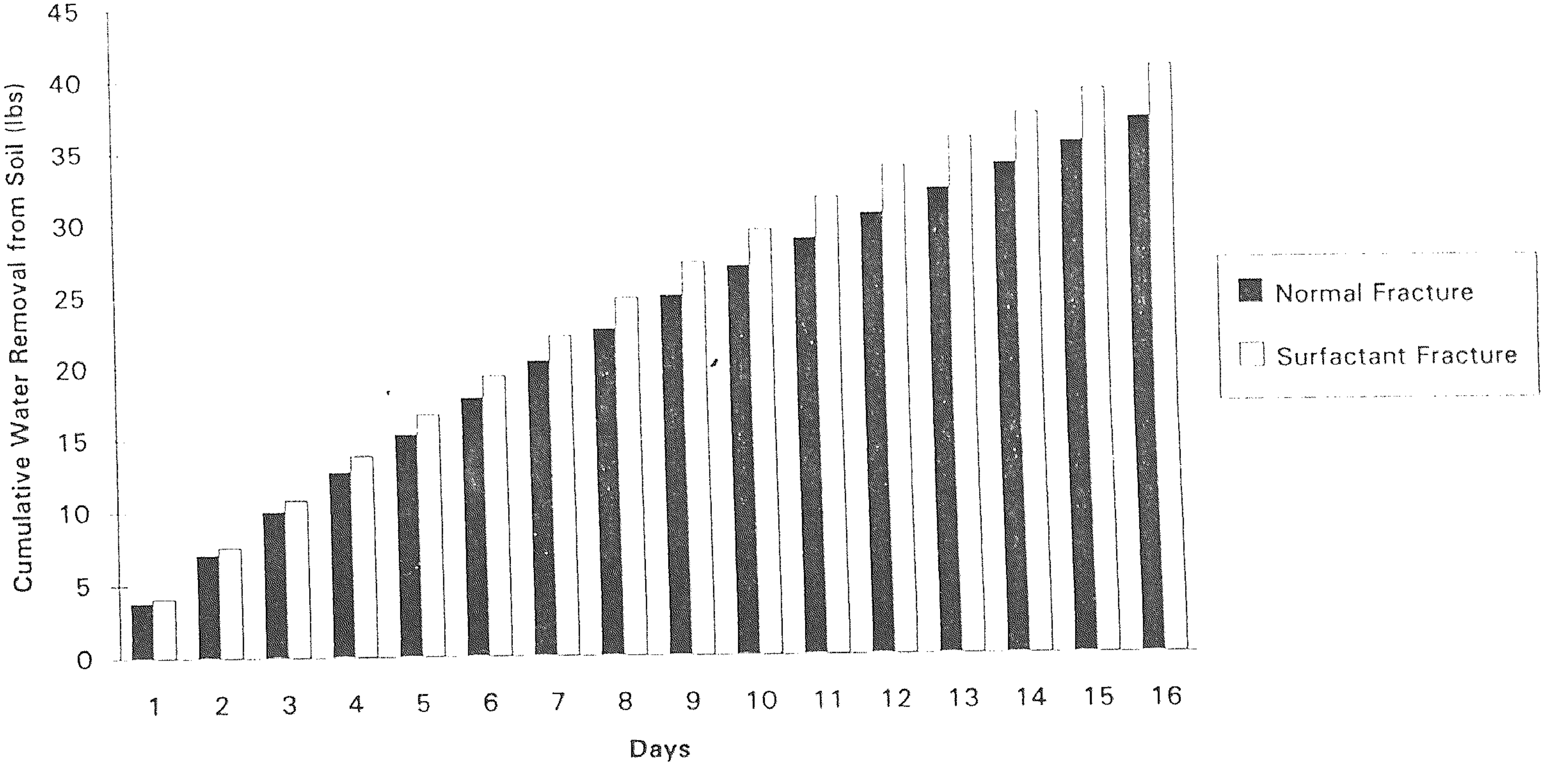


Figure 5.2: Kinetics of Water Removal for Test-2

same vacuum pressure. Under these conditions, airflow for the surfactant tank was 8% higher than the control (see Appendix B).

The removal rate of contaminant (water) for both tests was faster in the case of foam fracturing. The total amount of water removed in first test for 16 days was 27.7 lbs for the normal fractured tank and 29.8 lbs for the surfactant fractured tank. This corresponds to 8% increase in removal rate for the tank fractured with surfactant solution.

The second soil fracturing test was performed using a directional nozzle. The fracture network using this nozzle was more extensive, and ultimately demonstrated higher rate of contaminant removal. The total amount of water removed from the tanks during the 16 days run was 40.4 and 36.8 lbs, respectively, for fracturing with and without surfactant. This corresponds to a 10% increase in water removal rate for foam fracturing.

Observations of soil color change provided qualitative data on water removal rates. During the first test, initial soil color change was observed around the two perforated vent wells at the tank corners and around top layer of soil on the first day of the experiment. By the second day the soil color change had extended downwards from the top. The rate of color change increased at an average rate of 1.5 inches/day for the normal fracture tank. The color change in the surfactant fractured tank was more rapid, averaging 1.65 inches/day. At the conclusion of the test, soil in the surfactant fractured tank dried 2 inches deeper than in the regular pneumatic fractured tank (see Figure C-1 of Appendix C).

For the second test, the rate of soil color change was 1.7 inches/day for normal fractured tank and 1.9 inches/day for surfactant fractured tank. At the end of the test, the surfactant fractured tank soil dried 3 inches deeper than the regular fractured tank. (see Figure C-2 of Appendix C).

5.1.2 Discussion

Comparing the results of the two tank experiments it can be concluded that foam fracturing enhances to some extent both the fracture network and contaminant removal rate. Air flow in the surfactant fractured tank also increased under the same vacuum pressure. Fracturing done using the directional nozzle was more effective, and resulted more extensive fracture networks at lower pressures.

It is expected that surfactants will enhance pneumatic fracturing process in field conditions to a greater extent than in laboratory experiments for the following reasons. First, surfactants cause partial desorption of volatile organic contaminants from soil pores. Second, the enhanced desorption from soil particles will make contaminants more accessible to soil microorganisms[19]. This is especially important for nonvolatile organic like polyaromatic hydrocarbons. Third, the fracturing process in the field is not limited by tank walls (as in laboratory experiments), and it is expected that foam fracturing will be more effective in developing of longer and more branched soil cracks to intensify contaminants remediation.

In the laboratory, a 0.5% aqueous solutions of surfactant was used. In field application of soil washing, soil flushing and drilling, 1-3% solutions are typically applied. For field application of pneumatic fracturing, then, a higher surfactant concentration might be advantageous.

Under field conditions, other variants of surfactant applications can be performed during pneumatic fracturing process. One possible variant involves injection of a surfactant solution into the well prior to pneumatically fracturing the formation. After the solution has wetted the intended fracture zone, the excess solution can be pumped out. Afterwards, the usual pneumatic fracturing with compressed air should be applied to the formation. It is expected that the reduced capillary pressure in the pores of the formation will result in more effective fracturing.

In the other variant, the usual pneumatic fracturing process can be performed, followed by surfactant solution injection into the newly fracture network. A repeat injection should then be made for further extending and/or branching the fracture network.

Overall, the laboratory test results show that foam fracturing is feasible and possesses some additional advantages compared with routine pneumatic fracturing. Field demonstrations of pneumatic fracturing with and without surfactants at the same contaminated sites are necessary to ultimately establish the utility of the process.

5.2 Results of Time Release Nutrients Injection Tests

Two separate series of pellet injection tests were performed. The fine time release nutrients were used for both test series. For the first series, dry injection of pellets was performed for four different nozzle configurations at various injection pressures. In the second series, pellet injection was investigated for five different nozzle/injector configurations. Above ground wet and dry injections of fine pellets with pneumatic fracturing process were also performed during the second series test. Injected pellet samples for both test series were recovered and examined under microscope to estimate the extent of the pellet damage. The results of these microscopic observations are presented in Tables 5.3 and 5.4, respectively.

Grain size analysis of injected pellet was also performed for both test series to further evaluate the extent of mechanical damage of injected pellets. The results of these tests are presented in Figures 5.3 and 5.4, respectively. Additional data of this test are furnished in Appendix D.

Table 5.3: Microscopic Observation of Fine Pellets after Injection Test-1

Case	Nozzle Status	Injected Media	Injected Pressure		Duration of Injection	Flow		Microscopic Observation
			System Pressure	Sandblaster Pressure		System	Sandblaster	Of Collected Pellet
			psi	psi	seconds	cfm	cfm	
1	Regular Nozzle	Fine Pellet	0	50	5	0	195	Damage < 15%
		Fine Pellet	0	75	5	0	215	Damage (50% - 40%)
		Fine Pellet	50	50	5	1250	225	Damage (90% - 80%)
2	Rubber Coated Nozzle	Fine Pellet	0	50	5	0	214	Damage < 10%
		Fine Pellet	0	75	6	0	220	Damage (35% - 25%)
		Fine Pellet	50	50	5.5	1175	228	Damage (80% - 70%)
3	Rubber Base Nozzle	Fine Pellet	0	50	6	0	186	Damage < 13%
		Fine Pellet	0	75	5	0	210	Damage (45% - 35%)
		Fine Pellet	50	50	5	1224	230	Damage (85% - 75%)
4	No Nozzle	Fine Pellet	0	50	5	0	205	Damage < 5%
		Fine Pellet	0	75	5	0	215	Damage (25% - 15%)
		Fine Pellet	50	50	4.5	1150	230	Damage (65% - 50%)

Table 5.4: Microscopic Observation of Fine Pellets after Injection Test-2

Experiment	Duration of	Pressure		Air Flow		Mass Flow	Experiment	Microscopic
No	Injection	System	Sandblaster	System	Sandblaster	of Pellet	Condition	Observation of
	secs	psi	psi	cfm	cfm	gm/sec		Collected Pellet
1	5	0	50	0	205	54	Case 1	Damage < 15%
2	5	0	75	0	257	78	Case 1	Damage (50% - 35%)
3	5	50	50	1371	214	45	Case 1	Damage (85% - 70%)
4	4.5	0	50	0	197	80	Case 2	Damage <8%
5	5	0	75	0	240	115	Case 2	Damage (35% - 20%)
6	5	50	50	1333	205	50	Case 2	Damage (70% - 50%)
7	5	0	50	0	197	87	Case 3	Damage < 5%
8	5	0	75	0	222	130	Case 3	Damage (30% - 15%)
9	5	50	50	1285	205	77	Case 3	Damage (60% - 40%)
0	6	0	50	0	180	62	Case 4	Damage < 8%
11	6.5	0	75	0	214	91	Case 4	Damage (35% - 20%)
12	5	50	50	1251	188	50	Case 4	Damage (70% - 45%)
13	6	60	60	1200	235	80	Case 5	Damage (85% - 75%)
14	5	60	60	1143	228	75	Case 6	Damage (50% - 40%)

Case 1: Regular Injection
Case 2: Sand blaster Hose Connected at 1' top of Nozzle
Case 3: Regular Injection Without Nozzle
Case 4: Sandblaster Hose Connected Vertically and Air Hose Inclined
Case 5: Sandblaster Hose 1' Top of Nozzle and Air Hose Inclined
Case 6: Sandblaster Hose 1' Top of Nozzle, Air Hose Inclined and Water Hose Vertical

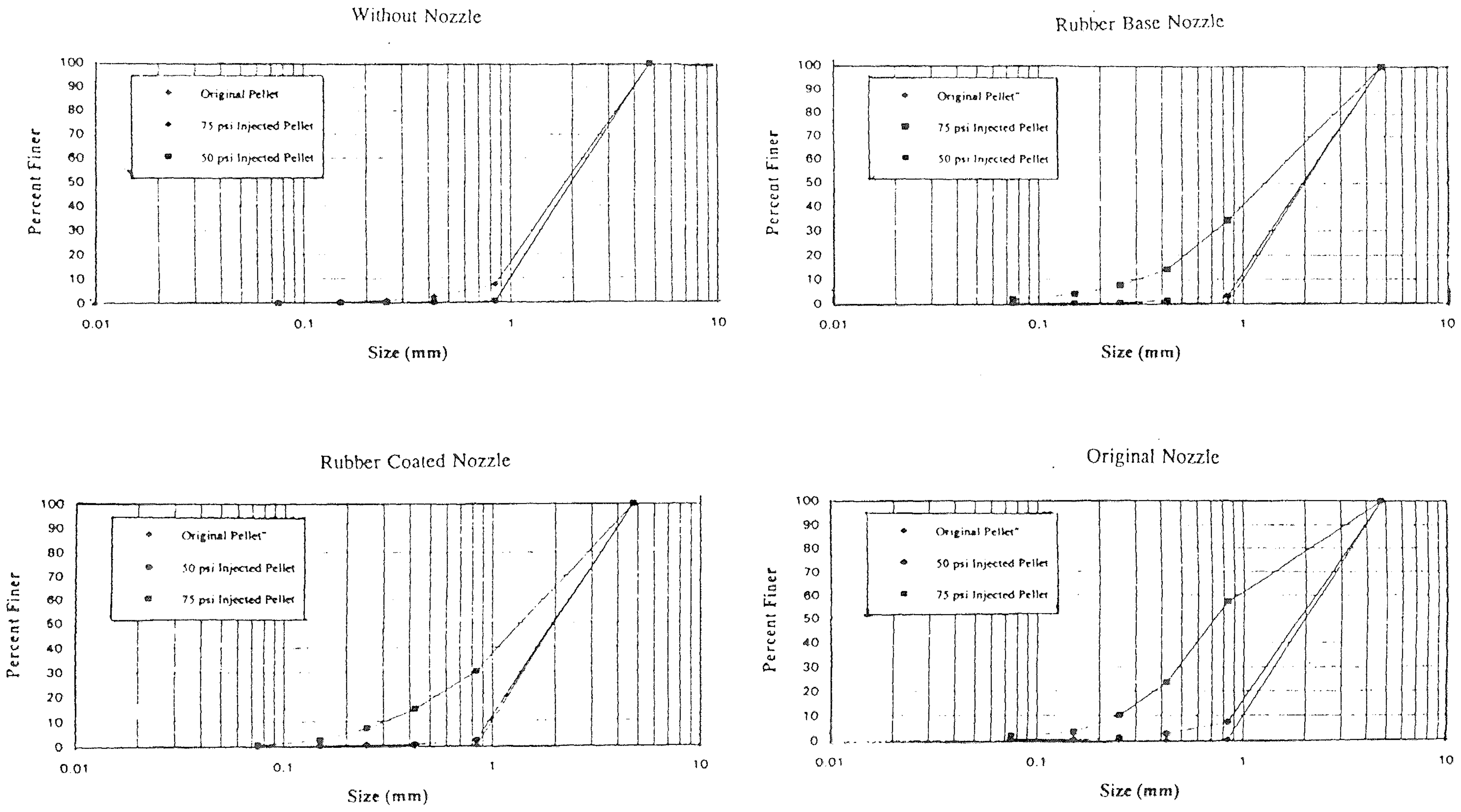


Figure 5.3: Mechanical Analysis of Injected for Test Series 1

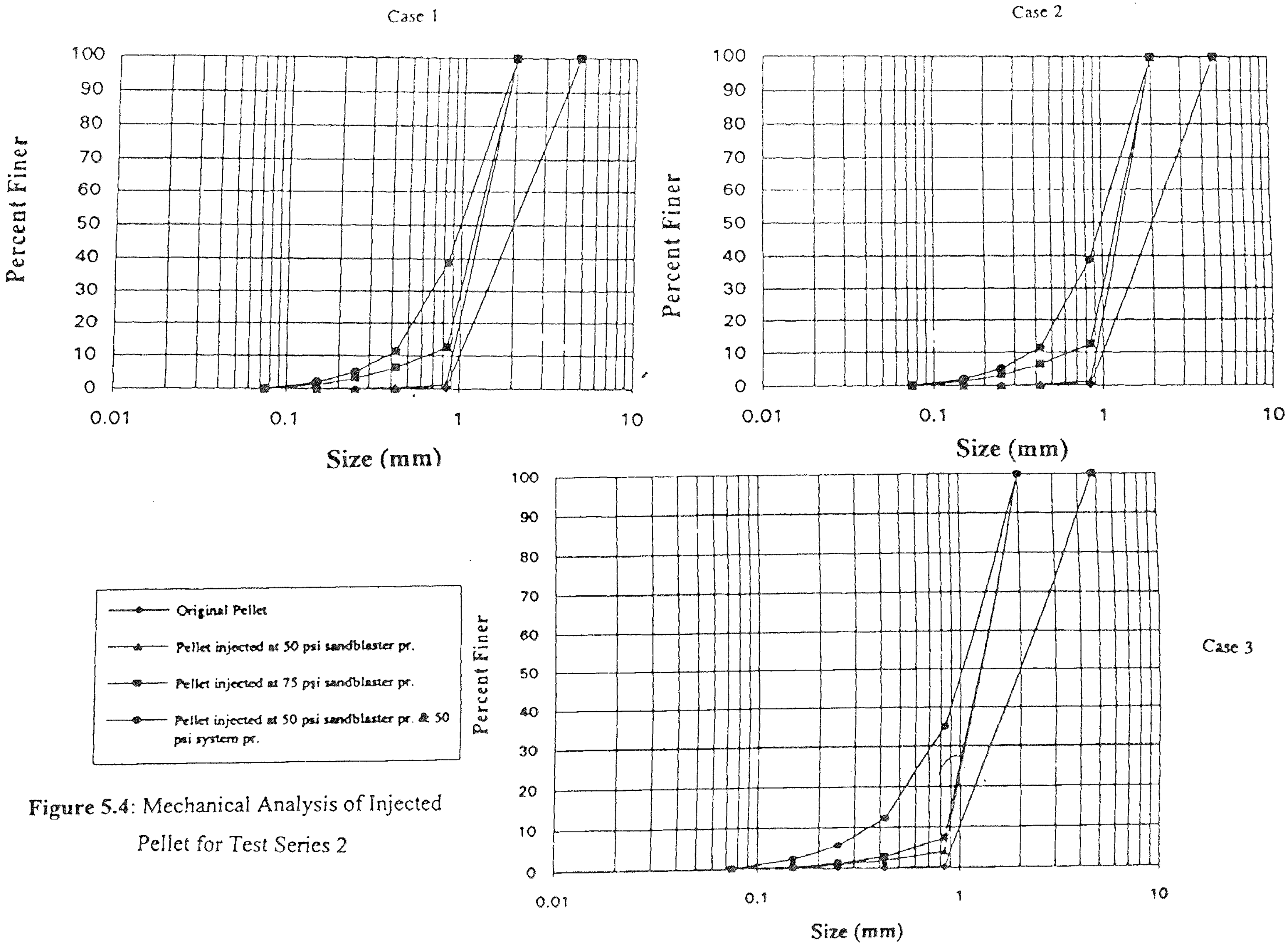
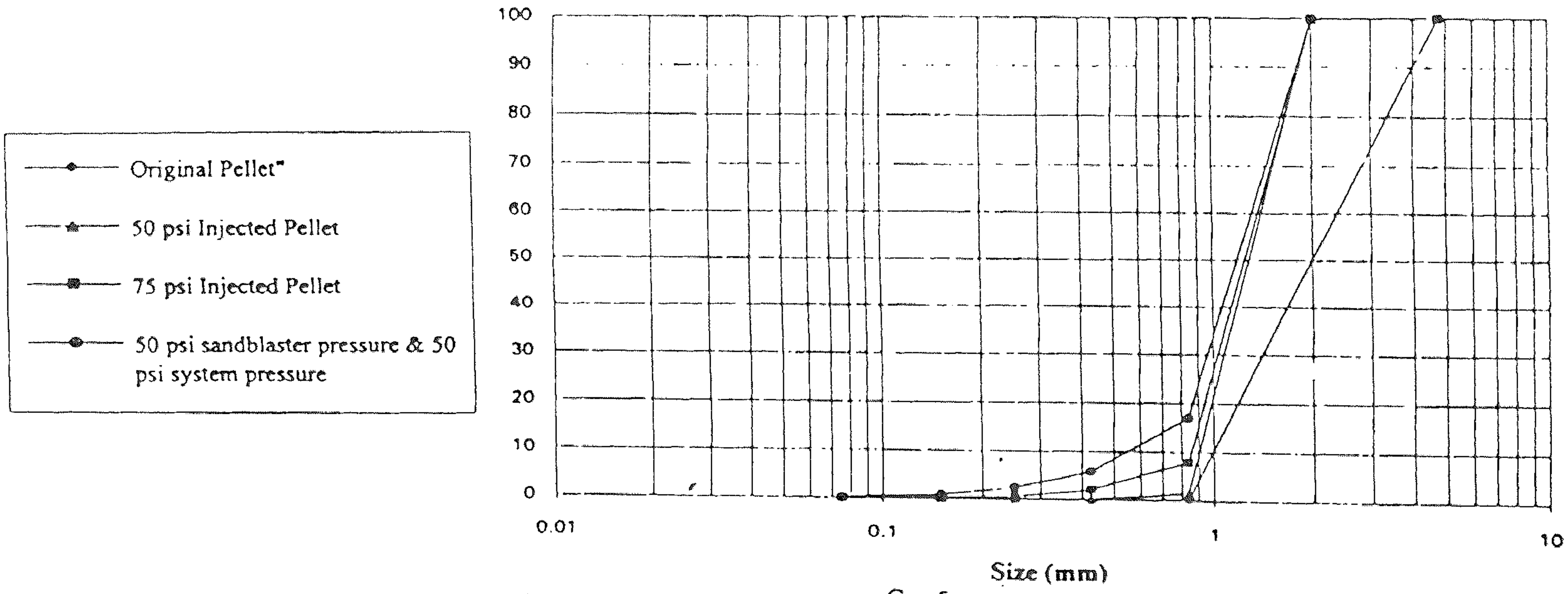
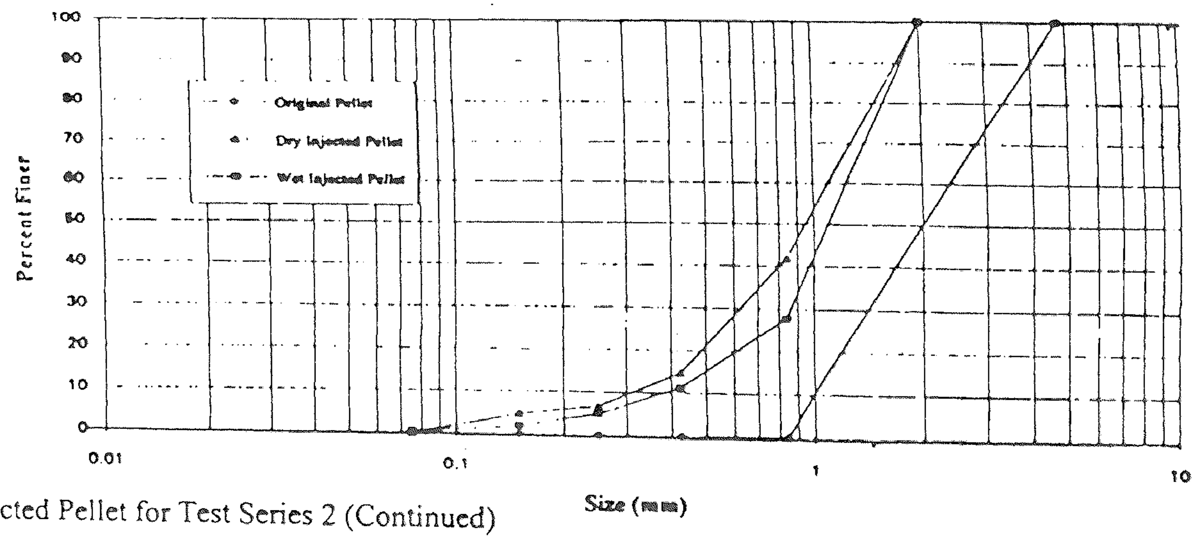


Figure 5.4: Mechanical Analysis of Injected Pellet for Test Series 2

Case 4



Case5



Case1: Regular Injection System
Case 2: Pellet injection 1 ' Top of Nozzle
Case 3: Regular Injection Without Nozzle
Case 4: Pellet Injected Vertically
Case 5: Wet Injection of Pellet

Figure 5.4: Mechanical Analysis of Injected Pellet for Test Series 2 (Continued)

Evaluation of the rate of nutrient release was carried out by two different methods including measurement of weight loss in solution and electroconductivity. For the first series of injected pellets, nutrient release was determined from the weight loss in solution only. These results are summarized in Table 5.5.

Table 5.5: Weight Loss of Fine Pellets at Different Injection Pressure

Pellet Type	Container Wt Gram	Wt of Pellet + Container (After Drying) Gram	Pellet Wt. Initial Gram	Pellet Wt (After Drying) Gram	Water Temperature Centigrade	% Wt. Loss of Pellet
S1	11.4256	18.0836	10	6.658	21	33.42
S2	10.7037	14.9243	10	4.221	21	57.79
S3	11.2276	14.2317	10	3.004	21	69.96
S4	10.8071	13.0872	10	2.28	21	77.2

S1 = Fine Original Pellet
S2 = Fine 50 psi Injected Pellet
S3 = Fine 75 psi Injected Pellet
S4 = Fine 100 psi Injected Pellet

Test Condition:

Pellet : Water = 10 gm : 50 ml
Duration of Test = 7 Days
Water Temperature = 21 C

For the second test series, electroconductivity testing was exclusively used to evaluate the rate of pellet degradation. Results of the electroconductivity tests are summarized in Table 5.6. From the electroconductivity data of Table 5.6, kinetics of pellet damage is calculated, and are presented in figure 5.5 as a function of time. In addition, the results of percent damage of the injected pellets, and their conductivity at elevated temperature are furnished in Tables E-1 and E-2 of Appendix E.

Table 5.6: Kinetics of Pellets Degradation
(According to Electroconductivity Data)

Time	Regular Pellet	Case 1			Case 2			Case 3			Case 4			Case 5	
Hour	No Pressure	50psi Sb.Pr.	75 psi Sb.Pr.	50 psi Sb.Pr.	50 psi Sb.Pr.	75 psi Sb.Pr.	50 psi Sb.Pr.	50 psi Sb.Pr.	75 psi Sb.Pr.	50psi Sb.Pr.	50 psi Sb.Pr.	75 psi Sb.Pr.	50 psi Sb.Pr.	60 psi Sb. Pr. 60 psi Sys. Pr. 30 psi Water Inj. Pr.	
				50 psi Sys. Pr.			50 psi Sys. Pr.			50 psi Sys. Pr.			50 psi Sys. Pr.	Dry Inj.	Liquid Inj.
	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11	S12	S13	S14	S15
0	49	1802	4915	5691	432	1802	4505	338	636	5149	360	569	4541	4915	2703
2	77	2703	6360	8317	1368	2637	7208	601'	2457	5406	2703	2162	7208	7457	3862
4	95	3862	7208	9011	1663	3277	7457	2703	3089	6007	2846	2772	8318	7723	4541
6	168	4915	7274	9164	2458	5149	7723	3089	5691	6360	3003	4005	8447	8581	6360
8	300	5029	8317	9321	2845	5406	8009	3277	6007	7208	3604	4505	8660	8791	7208
24	831	5406	9010	9485	3604	6788	8317	4158	7208	3604	4505	7208	8791	9241	7723
36	1744	6007	9086	9569	4325	7206	8447	4827	7325	9163	5876	7562	8863	9581	8009
48	2002	7723	9321	9655	6360	7723	9321	5691	7561	9241	6178	7724	9321	9743	8321
72	2575	8009	9569	9741	7723	8317	9402	6533	8650	9581	8009	9010	9830	9902	8564
96	3089	8564	9654	9830	8001	8581	9743	8009	9163	9741	8530	9163	10012	10012	8791
120	3488	9321	9741	9902	8581	9163	9902	8581	9902	9902	9165	9743	10347	10397	9010

Case 1: Regular System
Case 2: Sandblaster Hose 1' Top of Nozzle
Case 3: Regular System With No Nozzle
Case 4: Sandblaster Hose Vertical, Air Hose Inclined
Case 5: Water Hose Vertical, Air Hose Inclined, Sandblaster Hose 1' Top of Nozzle

Test Condition:

Pellet : Water = 1 gram : 100 ml
Water Temperature = 21 C

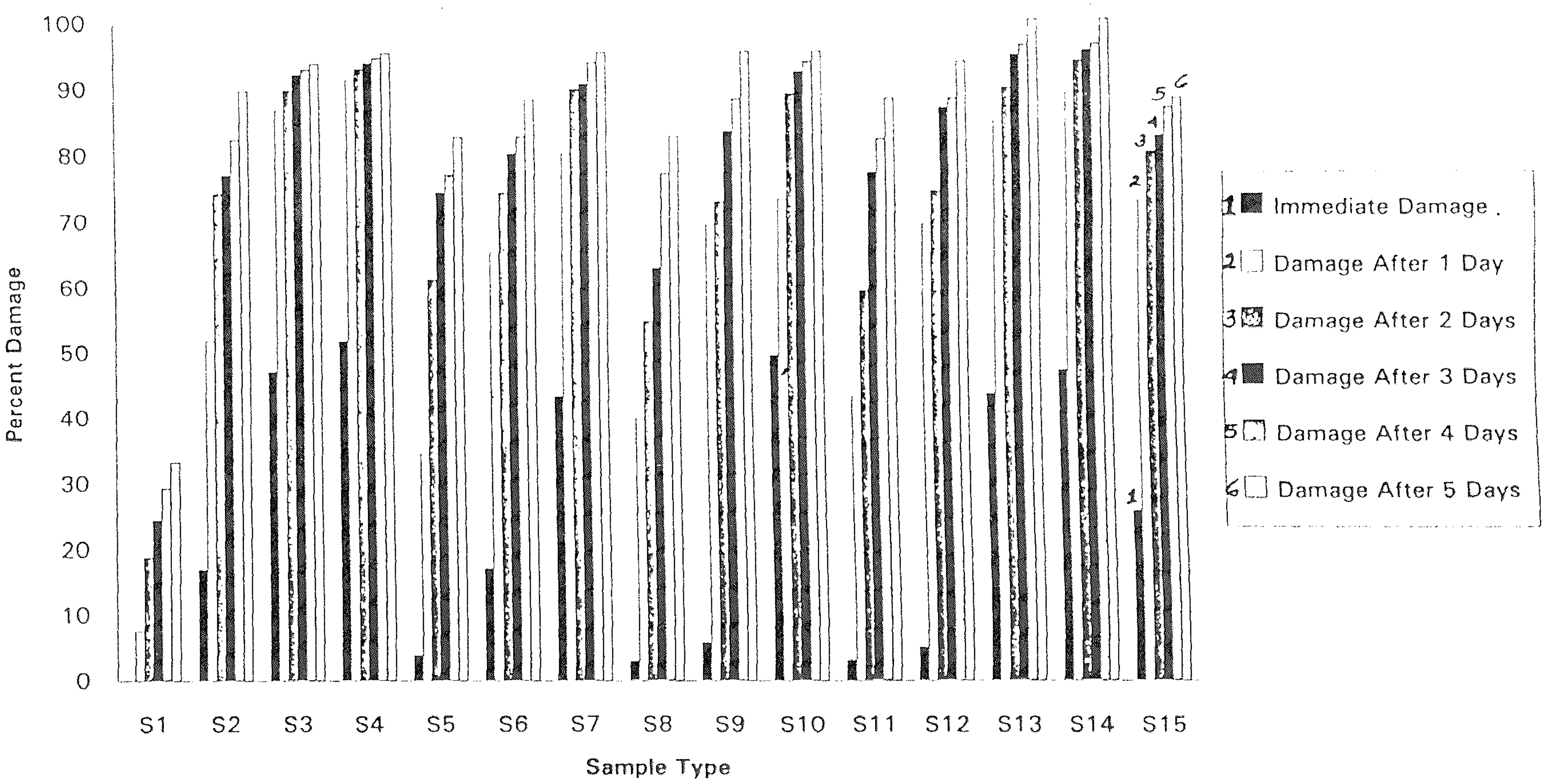


Figure 5.5: Percent of Pellet Damage for Test Series 2
(According to Electrocunductivity Test)

5.2.1 Experimental Trends

One of the first experimental trends observed during the pellet injection tests was that damage is directly proportional to the pressure. The pellets had good resistance at a pressure level of 50 psi in the sandblaster, since pellet damage was minimal (within range of 5 - 15%). Breakage of pellets increased as pressures were elevated. At 75 psi sandblaster injection pressure, moderate damage (25 - 50 %) was observed. When the full injection system was used along with sandblaster, damage of pellets was severe (60 - 85%) at 50 psi. This additional damage was attributed to the impact of pellets within the internal pipe and nozzle surfaces. During preliminary experiments, the finer pellets were found more resistant to damage and were therefore used for all further experiments.

The second observation was that the degree of damage was not significantly affected by the four different nozzle configurations. Dry injection without a nozzle was slightly better thab the other nozzles, followeed by the rubber base nozzle (see Figure F-1 of Appendix F).

During second test series, it was found that Case 3 (regular system without nozzle) produced the least damage. Also, when a rubber sandblaster hose was connected 1 ft. from top of nozzle (case 2), damage was also reduced. This strongly suggests that reduction of rigid pipe reducers and minimization of the flow pathway through injection system is advantageous.

From electroconductivity and sieve analysis results, it was found that pellets injected with plain water experienced less damage than dry injected pellets. This is apparently due to the lubricating efforts of the liquid supplement.

5.2.2 Discussion

From Test Series 1 of pellet injection, it was concluded that pellet damage was not related to nozzle design since different nozzle modifications resulted in similar degradation rates.

Based on this result, Test series 2 focused on changing the upstream portion of the system. The results of these tests showed that pellet damage could be minimized by eliminating pipe reducers and flow path length. This series of pellet injection tests also demonstrated the advantage of adding small amount of plain water to the pellets for lubrication.

Bench scale test results of pellet injection showed that some modifications are necessary before applying this technology in the field. Mechanically stronger pellets are desirable to tolerate pressure of 100-200 psi for pneumatic fracturing. A new type of rubber based nozzle with a softer surface may also reduce pellet damage Also, fine pellets are more resistant than coarse ones and also have better flow characteristics through the sandblaster. Wet injection of pellets seems to be promising, especially if liquids like hydrogen peroxide solution or surfactants are simultaneously injected into the fracture zone to enhance contaminant desorption or biodegradation.

5.3 Recommendations For Field Design

Eventually, it is planned to demonstrate surfactant fracturing and dry injection of nutrients in the field. The following guidelines have been developed based on the results of the bench scale studies.

5.3.1 Field Design For Foam Fracturing

The results of the laboratory tests of foam fracturing can be used as a guide to apply the technology in the field. It is anticipated that field tests may overcome some of the drawbacks faced during laboratory test of foam fracturing. First, foam fracturing in the field is not limited by the tank walls, so the fracture network will be more extensive and continuous. Also there will no problem of wall interface friction in field test. Surfactant desorption of contaminants may also occur in the field test, therefore enhancing the rate of contaminant removal by vacuum extraction as well as by biodegradation

Field test of foam fracturing could utilize one of the following approaches:

1. Surfactant solution is injected into the subsurface as part of high pressure air stream (foam fracturing). This is the same approach used in the present laboratory study.
2. The area is presoaked by surfactant solution before fracturing.
   Afterwards, the soil is fractured using the regular pneumatic fracture
   process.
3. The soil is pneumatically fractured first, and then fractured again using surfactant.

After field tests, advantages and drawbacks of these approaches will be evaluated. Additional considerations which should be taken into account include:

1. *Screen selection*: The screen may create problem during foam fracturing if the aperture of screen slot is less than 1/16 inch. During laboratory foam fracturing tests, it was difficult to initiate fractures for apertures less than that size. Although surfactant apparently lubricates the screen, the liquid also tends to restrict airflow through the screen slot. In the laboratory study, this resulted higher injection pressures, and caused the screen to pop upwards in one test.

2. *Nozzle selection*: Either a regular or directional nozzle can be used to disperse surfactant uniformly into soil formation during foam fracturing. To obtain better fracture pattern in contaminated zone, the directional nozzle may be preferable.

3. *Surfactant injection pressure*: Surfactant flowrate can be controlled by changing the parameters like injection pressure and valve angle of liquid injection pump. By increasing valve angle and injection pressure, surfactant flowrate can be increased.

4. *Surfactant concentration and type*: For field demonstrations of foam fracturing, a concentration range of 0.5% - 2.0% of anionic surfactant such as "Drilfoam" with some addition of alcohol can be used. The advantages of this product is commercial availability, record of application in soil drilling, high rate of biodegradation, and relatively low price. Alternatively, other anionic surfactants applied in environmental engineering, like sodium dodecyl sulfate that are applied for soil washing and flushing, might be used.

5. *Surfactant solution/Air ratio:* For field design, the ratio of surfactant solution and air is very important. Laboratory tests of foam fracturing were performed using 1:22 volume ratio or 4.5% (volume) of surfactant solution and air. During field testing, this ratio is recommended as a starting point..

6. *Vacuum extraction of well*: For a field demonstration, two wells on the same site should be fractured: one by regular pnematic fracturing process and the other by foam fracturing. Afterwards, the same vacuum pressure should be maintained in these two wells. Results will be compared and analyzed.

6. *Tiltmeter*: As an indication of fracture propagation, tiltmeters should be used to measure surface heave during the field demonstration.

5.3.2 Field Design For Dry Injection of Pellets

From the bench scale experiments of dry injection of pellets, it can be concluded that integration of pneumatic fracturing with dry media injection is feasible in the field. The following recommendations are offered for field applications:

1. *Use more abrasion resistant pellets*: The pellets used for bench scale dry injection were satisfactory up to 50 psi injection pressures. Above this pressure, the

damage was proportionate to increasing pressure. In regular pneumatic fracturing applications, injection pressures typically exceed 100 psi. The producer of the tested pellet has indicated their intention to make a stronger pellet in the near future.

2. *Nozzle design*: Bench scale tests were performed using different nozzle designs. The results suggest that a rubber based nozzle is preferred for dry injection of pellets.

3. *Sandblaster*: During bench scale studies, a small capacity sandblaster was used. For field tests a larger commercial-type sandblaster with higher flowrates and capacity will be required.

4. *Best dry injection system*: Since wet injection of pellets gave better results than dry injection with the same experimental conditions, wet injection is recommended for field injection of pellets. Water can be used as the liquid media, or possibly other supplemental liquids such as hydrogen peroxide or surfactants. System setup for the field test should be like Case 2 of the pellet injection Test Series 2 (Figure 4.6) which yielded the best result of pellet injection.

5. *Controlling Key Parameters*: The major factor which controls the nutrient release rate is temperature. It is also desirable to maintain a pH level of 6.5 to 7.5, and a soil moisture level of 40 to 60% of the holding capacity, and it is obviously desirable to maintain an environment in which oxygen is not limiting.

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

The following conclusions were drawn from this study:

1) Pneumatic fracturing can be successfully performed using injected air containing 2-5% (by volume) of surfactant solution (foam fracturing). Equipment for simultaneous injection of air and surfactant solution into subsoil was demonstrated and tested, and is recommended for future field application. A 0.5%-2% (by volume) aqueous solution of biodegradable commercial product is recommended for foam fracturing.

2) The results of the laboratory study have shown a 9% to 12% increase in the rate of surrogate contaminant (water) removal for the foam fracturing process in comparison with regular pneumatic fracturing under the same experimental conditions. Fracture patterns achieved with surfactant solution were more branched and extended. Air flowrate was also observed to increased in the case of foam fracturing.

3) Additional advantages of surfactant application under field conditions may include partial desorption of hydrophobic contaminants from soil particles, facilitating their vacuum extraction and biodegradation. This factor, combined with application to VOC's instead of water as in the lab test, should lead to even greater enhancement of removal rates. Other variants of surfactant application in combination with pneumatic fracturing process are suggested for field tests.

4) Pneumatic fracturing can be successfully integrated with injection of pelletized time release nutrients to enhance in situ bioremediation. Equipment for nutrient

pellet injection during pneumatic fracturing process was developed and tested, and is recommended for field application.

5) Mechanical damage of pelletized nutrients as a result of injection equipment and applied pressure was evaluated by different methods. The damage was reduced by the use of fine pellets, a rubber base nozzle, and modification of the nozzle/injector. However, the extent of degradation in all of the tests was significantly greater than the original intact pellets. The use of wet injection techniques also exhibited reduced damage compare with dry injection under the same conditions.

6) Above 100 psi, the pelletized time release nutrients sustained serious damage under the experimental conditions. Since most pneumatic fracturing applications exceed this pressure level, new pellets with higher mechanical strength characteristics should be developed and incorporated with the present pneumatic fracturing process.

6.2 Recommendations for future study

The following are recommendations for the future study.

1. Field demonstration of foam fracturing based on the results and recommendations of presented ressearch should be performed in the field and compared with regular pneumatic fracturing at the same conditions.

2. Other variants of surfactant injection with pneumatic fracturing process should be tested. In the first variant, the area surrounding the well is presoaked by injecting surfactant before fracturing. Afterwards, the soil is fractured using the regular pneumatic fracture process. In the second variant, the soil is pnematically fractured first, and then refractured using surfactant.

3. Other anionic surfactants like sodium dodecyl sulphate and nonionic like triton 100X which are used in soil washing should be tried in different concentrations.

Data about effect of surfactants on rates of desorption, leakage and biodegradation should be reviewed and analyzed.

4. In cooperation with a commercial supplier, new pelletized time release nutrients with better and stronger mechanical characteristics should be developed. If the pellets are capable of sustaining system pressure of 100 to 200 psi, the process should be scaled up to a field demonstration..

APPENDIX - A

Strain Indicator Switch & Balance box
and
Conductivity meter

SPECIFICATIONS

MODEL P-3500

RANGE:
±19 999µε at Gage Factor <6.000.

$\pm\frac{6.000}{G \cdot F} \times 19\ 999\mu\varepsilon$ at Gage Factor >6.000.

Above ranges increased by factor of 10 when using X10 multiplier switch. Example: ±199 990 at Gage Factor <6.000.

ACCURACY:
±0.05% of reading ±3µε for Gage Factor settings of 1.000 to 9.900.
±0.05% of reading ±10µε for Gage Factor settings of 1.000 to 9.900 when using X10 multiplier.

SENSITIVITY (RESOLUTION):
±1µε at all Gage Factor settings.
±10µε when using X10 multiplier.

GAGE FACTOR:
Range 0.500 to 9.900. Precisely settable by 10-turn potentiometer and four-position switch to a resolution of 0.001. Gage Factor accuracy ±0.02% at all settings. Displayed by LCD.

BALANCE:
Coarse: 5 switch positions: Off, ±2000µε, and ±4000µε (GF=2.000). Tolerance ±1% nominal.
Fine: 10-turn potentiometer with turns-counting dial. ±1050µε min. range (GF=2.000). Zero position of potentiometer calibrated for zero ±2µε.
All balance voltages are electronically injected at input of amplifier. No bridge loading by balance controls, and no compromise of measurement range.

BRIDGE EXCITATION:
2.0 Vdc ±0.1%. Temperature stability better than ±0.02% per °C. Readings are fully ratiometric, and not degraded by variation in excitation voltage.

BRIDGE CONFIGURATIONS:
Quarter-, half-, and full-bridge circuits. Internal dummy gages provided for 120 and 350Ω quarter bridges. 60 to 2000Ω half or full bridge.

AMPLIFIER:
Warm-up drift: Less than ±3 counts at GF=2.000, cold start to three min.
Random drift at constant ambient temperature: Less than ±1 count at GF=2.000.
Common-mode rejection: Greater than 90 dB, 50 to 60 Hz.
Temperature effect on zero: Less than 1 µV/°C referred to input.
Temperature effect on span: Less than 0.005% /°C.
Input impedance: Greater than 30 MΩ.

All specifications nominal or typical at +23°C unless noted.

CALIBRATION:
Shunt calibration across 120 and 350Ω dummy gages to simulate 5000µε (±0.05%).

ANALOG OUTPUT:
Linear ±2.50V max. Adjustable from 40 µV/µε to 440 µV/µε, nominal.
Output load 2 KΩ min. Bandwidth, DC to 4 kHz, −3 dB nominal.
Noise: Less than 400 µV rms at 40 µV/µε output level.

REMOTE-SENSE:
Provided at the transducer connector. Remote-sense error less than 0.001% /Ω of lead resistance.

POWER:
Internal battery pack using six "D" cells. Battery life 300 hours nominal.

CASE:
Aluminum.

SIZE & WEIGHT:
9 x 6 x 6 in *(228 x 152 x 152 mm)*. 6.3 lb *(2.9 kg)* including batteries.

ACCESSORIES:

Line voltage adapter for 115 V or 230 V, 50 or 60 Hz operation.
Transducer input connector.

MODEL SB-10

(when used with Model P-3500)

CIRCUITS:
10 channels plus OPEN position.

INPUTS:
Will accept quarter-, half- or full-bridge circuits in any combination, including three-wire quarter bridges.

BALANCE RANGE:
±5800µε for quarter-, half-, and 350Ω full-bridge inputs.
±2000µε for 120Ω full-bridge inputs.

SWITCHING REPEATABILITY:
Better than 1µε.

SIZE & WEIGHT:
9 x 6 x 6 in *(228 x 152 x 152 mm)*. 5.5 lb *(2.5 kg)*.

The Measurements Group is a leading supplier of strain gage instrumentation. Available instruments include portable indicators, signal conditioners/amplifiers, strain gage installation tester, instrument calibrator, and sophisticated computer-controlled systems for the acquisition, storage, and reduction of test data. Call or write for all of your strain gage instrumentation needs.

MEASUREMENTS GROUP

MEASUREMENTS GROUP, INC.
P.O. Box 27777
Raleigh, NC 27611, USA
(919) 365-3800
Telex 802-502 • TWX-510-920-0770

[illegible]
Printed in U.S.A.

be expressed in millisiemens/meter, which is equal to 10 µmhos/cm. Report results of water tests as conductivity in terms of micromhos/centimeter.

A conductance cell and a Wheatstone bridge may be used for measuring the electrical resistance of the sample or the conductance may be measured as the ratio of electrical current through the cell to the applied voltage.

Electrolytic conductivity (unlike metallic conductivity) increases with temperature at a rate of approximately 2%/degree C. Significant errors can result from inaccurate temperature measurement. Potassium chloride solutions have a temperature coefficient of conductivity that is lower than that of the typical potable water. Sodium chloride, on the other hand, has a temperature coefficient that closely approximates that found in most waters from wells and surface sources. Note that each ion has a different temperature coefficient; thus, for precise work, the conductivity must be determined at 25.00 C.

2. Apparatus

a. Self-contained conductance instruments: These are commercially available. Most of these instruments consist of a source of alternating current, a Wheatstone bridge, a null indicator, and a conductivity cell. Other instruments measure the ratio of alternating current through the cell to voltage across it and have the advantage of a linear reading of conductance. The instrument chosen should be capable of measuring conductivity with an error not exceeding 1% or 1 µmho/cm, whichever is the greater.

b. Thermometer, capable of being read to the nearest 0.1 C and covering the range 23 C to 27 C. An electrical thermometer having a small thermistor sensing element is convenient because of its rapid response.

c. Conductivity cell:

1) Platinum-electrode type: Conductivity cells containing platinized electrodes are available in either the pipet or the immersion form. Cell choice will depend on the expected range of conductivity and the resistance range of the instrument. Experimentally check the range for complete instrument assembly by comparing the instrumental results with the true conductances of the potassium chloride solutions listed in Table 205:I. Clean new cells with chromic-sulfuric acid cleaning mixture and platinize the electrodes before use. Subsequently, clean and replatinize them whenever the readings become erratic, when a sharp end point cannot be obtained, or when inspection shows that any of the platinum black has flaked off. To platinize, prepare a solution of 1 g chloroplatinic acid (platinum chloride) and 12 mg lead acetate in 100 ml water. A stronger solution will reduce the time required to platinize electrodes and may be used when time is a factor, e.g., when the cell constant is 1.0/cm or more. Immerse the electrodes in this solution and connect both to the negative terminal of a 1.5-V dry cell battery. Connect the positive side of the battery to a piece of platinum wire and dip the wire into the solution. The amount of current should be such that only a small quantity of gas is evolved. Continue the electrolysis until both cell electrodes are coated with platinum black. The platinizing solution may be saved for subsequent use. Rinse the electrodes thoroughly and when not in use keep them immersed in distilled water.

Table 205:I. Conductance of Potassium Chloride Solutions at 25 C*

Concentration *M*	Conductance *µmhos/cm*	
	Equivalent	Specific
0	149.85	
0.0001	149.43	14.94†
0.0005	147.81	73.90
0.001	146.95	147.0
0.005	143.55	717.8
0.01	141.27	1,413
0.02	138.34	2,767
0.05	133.37	6,668
0.1	128.96	12,900
0.2	124.08	24,820
0.5	117.27	58,640
1	111.87	111,900

*Data drawn from Robinson & Stokes[1]

†Computed from equation given in Lind et al[2]

2) Nonplatinum-electrode type: Conductivity cells containing electrodes constructed from durable common metals (stainless steel among others) are widely used for continuous monitoring and field studies. Calibrate such cells by comparing the conductivity of the water being tested with the results obtained with a laboratory instrument. Determination of the cell constant with KCl may introduce a significant error if the cell and instrument are not properly designed and mated.

3. Reagents

a. Conductivity water: Pass distilled water through a mixed-bed deionizer, discarding the first 1,000 ml. The conductivity of this water should be less than 1 µmmho/cm.

b. Standard potassium chloride, 0.0100*M*. Dissolve 745.6 mg anhydrous KCl in conductivity water and make up to 1,000 ml at 25 C. This is the standard reference solution, which at 25 C has a specific conductance of 1,413 µmhos/cm. It is satisfactory for most waters when using a cell with a constant between 1 and 2. For other cell constants, stronger or weaker potassium chloride solutions listed in Table 205:I will be needed. Store in glass-stoppered pyrex bottles.

4. Procedure

a. Determination of cell constant: Rinse the conductivity cell with at least three portions of 0.01 *M* KCl solution. Adjust the temperature of a fourth portion to 25.0±0.1 C. Measure the resistance of this portion and note the temperature. Compute the cell constant, *C*:

$$C = \frac{0.001413\, R_{KCl}}{1 + 0.0200(t-25)}$$

b. Conductivity measurement: Rinse the cell with one or more portions of the sample to be tested. Adjust the temperature of a final portion of the sample to 25.0±0.1 C. Measure the resistance of the sample and note the temperature.

5. Calculation

The following directions apply to the commonly used Wheatstone bridge instruments. Instruments may be calibrated to read conductivity (or conductance) directly; in that case follow the manufacturer's instructions.

a. The conductivity *G*, in µmhos/cm, is given by the equation:

$$G = \frac{1{,}000{,}000\, C}{R[1 + 0.0200(t-25)]}$$

APPENDIX - B

Airflow Data of Tank Test

Table B-1 Air flow data for test 1

Time	Vacuum Pr.	Air Flow	Vacuum Pr.	Air Flow	Time	Vacuum Pr.	Air Flow	Vacuum Pr.	Air Flow
hour	inch of water	scfm	inch of water	scfm	hour	inch of water	scfm	inch of water	scfm
		Normal		Surfactant			Normal		Surfactant
		Fracture		Fracture			Fracture		Fracture
0	50	3.18	48	3.28	158	48	2.75	46.5	2.75
2	50	3.15	48	3.22	162	47.5	2.75	47	2.8
4	50	3.2	48	3.25	166	48	2.78	47	2.8
6	49	3.12	47.5	3.2	170	47	2.65	46	2.75
16	49.5	3.15	48	3.15	180	47	2.65	46.5	2.7
20	49	3.08	48	3.1	184	47	2.75	46	2.7
24	48.5	3.06	48	3.05	188	47	2.75	46	2.75
28	49	3.08	47.5	3.1	192	47.5	2.75	46	2.75
32	48.5	2.95	47.5	2.95	202	47	2.7	46	2.75
42	49	3.1	47	3.05	206	47	2.7	46	2.8
46	49	3.15	46	3.05	210	47	2.7	46.5	2.8
50	48	2.98	46.5	2.95	214	47	2.8	47	2.85
60	48	2.95	46	2.9	224	48	2.85	47	2.9
64	49	3.05	46	2.95	228	48	2.8	46	2.85
68	48	2.85	46	2.9	232	48	2.8	46	2.85
72	48	2.85	46	2.9	236	47.5	2.75	46	2.8
82	48	2.8	47	2.9	246	47.5	2.8	46	2.85
86	47	2.85	47	2.85	250	47	2.75	45.5	2.8
90	47.5	2.8	47.5	2.85	254	47	2.75	45.5	2.8
94	47	2.75	47.5	2.85	258	47	2.75	46	2.8
104	48	2.8	46	2.8	268	48	2.85	46	2.85
108	48	2.75	46.5	2.8	272	48	2.8	46	2.8
112	47	2.75	47	2.8	276	48	2.8	46	2.85
116	47	2.7	47	2.8	280	47	2.75	46	2.8
126	47	2.75	47	2.85	284	47	2.8	46.5	2.8
130	47	2.85	46	2.9	288	47	2.75	46	2.8
134	47	2.8	46	2.75	292	48	2.85	46	2.85

Table B-2 Air flow data for test 2

Time	Vacuum Pr.	Air Flow	Vacuum Pr.	Air Flow	Time	Vacuum Pr.	Air Flow	Vacuum Pr.	Air Flow
hour	inch of water	scfm	inch of water	scfm	hour	inch of water	scfm	inch of water	scfm
		Normal		Surfactant			Normal		Surfactant
		Fracture		Fracture			Fracture		Fracture
0	30	2.75	30	2.95	148	30	2.8	30	2.75
2	30	2.8	30	2.9	162	30	2.75	30	2.75
4	30	2.8	30	2.9	166	30	2.75	30	2.8
6	30	2.8	30	2.85	170	30	2.65	30	2.7
16	30	2.8	30	2.85	180	30	2.7	30	2.75
20	30	2.75	30	2.8	184	30	2.75	30	2.75
24	30	2.8	30	2.85	188	30	2.75	30	2.75
28	30	2.85	30	2.85	192	30	2.75	30	2.75
32	30	2.8	30	2.85	202	30	2.7	30	2.7
42	30	2.8	30	2.85	206	30	2.7	30	2.8
46	30	2.8	30	2.9	210	30	2.7	30	2.8
50	30	2.8	30	2.9	214	30	2.65	30	2.75
60	30	2.85	30	2.9	224	30	2.6	30	2.75
64	30	2.85	30	2.9	228	30	2.55	30	2.7
68	30	2.8	30	2.9	232	30	2.5	30	2.7
72	30	2.75	30	2.85	236	30	2.5	30	2.65
82	30	2.8	30	2.85	246	30	2.5	30	2.65
86	30	2.75	30	2.8	250	30	2.45	30	2.6
90	30	2.75	30	2.8	254	30	2.4	30	2.6
94	30	2.75	30	2.8	258	30	2.35	30	2.7
104	30	2.8	30	2.85	268	30	2.3	30	2.65
108	30	2.8	30	2.85	272	30	2.4	30	2.65
112	30	2.8	30	2.85	276	30	2.3	30	2.6
116	30	2.75	30	2.8	280	30	2.35	30	2.65
126	30	2.8	30	2.8	284	30	2.25	30	2.7
130	30	2.75	30	2.8	288	30	2.2	30	2.65
134	30	2.75	30	2.8	292	30	2.1	30	2.6

APPENDIX - C

Photographs of Different Stages of Pneumatic Fracturing Tests

Regular Pneumatic Fracturing

Pneumatic Fracturing with Surfactant

Figure C-1 Photographs of tank test 1 (after 16 days)

Regular Pneumatic Fracturing

Pneumatic Fracturing with Surfactant

Figure C-2 Photographs of tank test 2 (after 16 days)

APPENDIX - D

Grain Size Analysis Data of Injected Pellets

Table D-1 Grain size analysis for pellet injection test series 2

Injection Pressure 50 psi

Case 1		Case 2		Case 3		Case 4	
Size	% Finer	Size	% Finer	Size	% Finer	size	% Finer
mm		mm		mm		mm	
4.75	99.899	4.75	99.806	4.75	99.86	4.75	99.854
0.84	15.151	0.84	1.266	0.84	4.006	0.84	1.554
0.425	5.783	0.425	0.342	0.425	1.758	0.425	0.243
0.25	2.706	0.25	0.148	0.25	0.915	0.25	0.146
0.15	0.981	0.15	0.1	0.15	0.353	0.15	0.098
0.075	0.102	0.075	0.052	0.075	0.125	0.075	0.02

Pellet Injection Pressure = 75 psi

Case 1		Case 2		Case 3		Case 4	
Size	% Finer	Size	% Finer	Size	% Finer	size	% Finer
mm		mm		mm		mm	
4.75	99.964	4.75	99.866	4.75	99.79	4.75	99.843
0.84	37.81	0.84	12.994	0.84	7.158	0.84	7.852
0.425	12.748	0.425	6.408	0.425	2.739	0.425	2.159
0.25	5.955	0.25	3.138	0.25	1.333	0.25	0.707
0.15	2.357	0.15	1.256	0.15	0.491	0.15	0.236
0.075	0.186	0.075	0.1	0.075	0.14	0.075	0

Fine Pellet Injection Pressure 50 psi
System Pressure = 50 psi

Case 1		Case 2		Case 3		Case 4	
Size	% Finer	Size	% Finer	Size	% Finer	size	% Finer
mm		mm		mm		mm	
4.75	99.84	4.75	99.916	4.75	99.916	4.75	99.92
0.84	37.86	0.84	38.744	0.84	34.987	0.84	17.07
0.425	10.672	0.425	11.38	0.425	12.237	0.425	5.817
0.25	4.709	0.25	5.104	0.25	5.593	0.25	2.483
0.15	1.974	0.15	2.009	0.15	2.313	0.15	0.892
0.075	0.283	0.075	0.084	0.075	0.089	0.075	0.176

Case 5:

Dry Injection		Wet Injection	
Size	% Finer	Size	% Finer
mm		mm	
4.75	99.84	4.75	99.92
0.84	37.86	0.84	38.74
0.425	10.672	0.425	11.38
0.25	4.709	0.25	5.104
0.15	1.974	0.15	2.009
0.075	0.283	0.075	0.084

APPENDIX - E

Electroconductivity Test Results

Table E-1 Damage ofInjected Pellets According to Electroconductivity Data

Sample No.	Percent Damage After Injection (Days)					
	0	1	2	3	4	5
S1	0	7.55	18.87	24.41	29.37	33.24
S2	16.9	51.76	74.15	76.92	82.28	89.6
S3	47.02	86.59	89.6	91.99	92.81	93.66
S4	51.62	91.18	92.82	93.66	94.52	95.21
S5	3.7	34.35	60.98	74.15	76.84	82.45
S6	16.94	65.12	74.15	79.89	82.45	88.07
S7	43.06	79.89	89.6	90.38	93.67	95.21
S8	2.79	39.7	54.52	62.65	76.92	82.45
S9	5.67	69.18	72.59	83.11	88.07	95.21
S10	49.28	73.01	88.82	92.11	93.66	95.21
S11	3.01	43.06	59.22	76.92	81.95	88.09
S12	5.02	69.18	74.16	86.59	88.07	93.67
S13	43.4	84.48	89.6	94.52	96.15	100
S14	47.02	88.82	93.67	95.21	96.27	100
S15	25.64	74.15	79.93	82.28	86.59	88.08

Percent Damage of Injected Pellet :

% Damage = (Current Conductivity - Initial conductivity) / (Final Conductivity - Initial Conductivity) * 100

Initial Conductivity of Undamaged Pellet = 49 mhos
Final Conductivity of Damaged Pellet = 10397 mhos

Table E 2 Electroconductivity of injected pellets at elevated temperature

Reading Time	Pellet Status	Temperature	Resistance	Conductivity
hour		Centigrade	ohms	mhos
1	Fine Original Pellet (A)	30	90 x 100	102.35
1	Coarse Original pellet (B)		5.5 x 100	1674.74
1	Fine 50 psi Injected Pellet (C)		2.2 x 100	4186.86
1	Fine 75 psi Injected Pellet (D)		130 x 100	70.85
2	Fine Original Pellet	72	5 x 100	1842.22
2	Coarse Original pellet		1.1 x 100	8373.73
2	Fine 50 psi Injected Pellet		.72 x 100	12793.2
2	Fine 75 psi Injected Pellet		11 x 100	837.37
3	Fine Original Pellet	72	3.05 x 100	3020
3	Coarse Original pellet		.65 x 100	14170.94
3	Fine 50 psi Injected Pellet		.6 x 100	1535.19
3	Fine 75 psi Injected Pellet		5.5 x 100	1674.74
4	Fine Original Pellet	72	2.2 x 100	4186.87
4	Coarse Original pellet		.6 x 100	15351.86
4	Fine 50 psi Injected Pellet		.55 x 100	16747.47
4	Fine 75 psi Injected Pellet		3.7 x 100	2489.48
5	Fine Original Pellet	72	1.9 x 100	4847.95
5	Coarse Original pellet		.57 x 100	16159.84
5	Fine 50 psi Injected Pellet		.52 x 100	17713.67
5	Fine 75 psi Injected Pellet		3.5 x 100	2631.75
6	Fine Original Pellet	72	1.5 x 100	6140.74
6	Coarse Original pellet		.55 x 100	16747.47
6	Fine 50 psi Injected Pellet		.5 x 100	18422.22
6	Fine 75 psi Injected Pellet		2.72 x 100	3386.43
7	Fine Original Pellet	72	1.14 x 100	8079.92
7	Coarse Original pellet		.49 x 100	18798.19
7	Fine 50 psi Injected Pellet		.45 x 100	20469.13
7	Fine 75 psi Injected Pellet		1.7 x 100	5418.3
8	Fine Original Pellet	72	.9 x 100	10234.56
8	Coarse Original pellet		.45 x 100	20469.14
8	Fine 50 psi Injected Pellet		.45 x 100	20469.14
8	Fine 75 psi Injected Pellet		1.1 x 100	8373.73

Pellet : Water = 1 gram : 100 ml

APPENDIX - F

Photographs of Injected Fine Pellet

Regular Nozzle

Without Nozzle

Rubber Base Nozzle

Figure F-1: Pellet Injection at 75 psi for Different Nozzle

Original Fine Pellet

Pellet Injected at 50 psi

Pellet Injected at 75 psi

Pellet Injected through Pneumatic Injection System (50 psi)

Figure F-2: Collected Fine Pellet after Injection

APPENDIX - G

Photographs of Sand Injection
and
Foam Fracturing

Figure G-1: Dry Injection of Sand

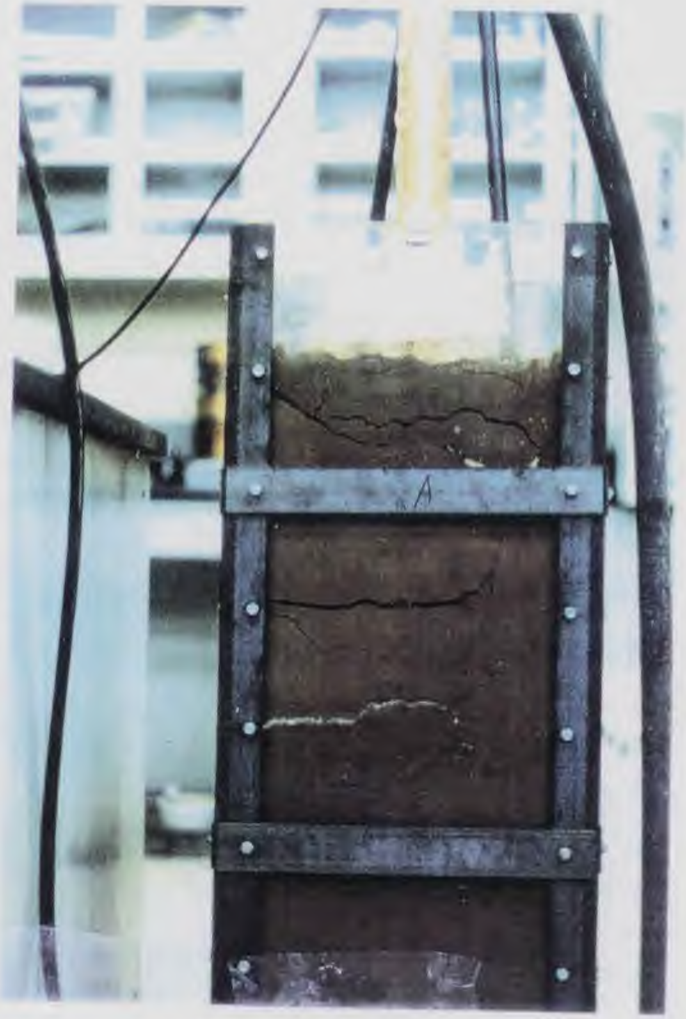


Figure G-2: Foam Fracturing

REFERENCES

1. Schuring, J. R. and P. C. Chan, "Removal of Contaminants from the Vadoze Zone by Pneumatic Fracturing", Hazardous Substance Management Research Center, Newark, NJ, 1992.

2. Shah, N. P. , *Study of Pneumatic Fracturing to Enhance Vapor Extraction of the Vadose Zone*, Masters Thesis, Department of Civil and Environmental Engineering, New Jersey Institute of Technology, Newark, NJ, 1991.

3. Fitzgerald, D. Conan, *Integration of Pneumatic Fracturing to Enhance In Situ Bioremediation*, Masters Thesis, Department of Civil and Environmental Engineering, New Jersey Institute of Technology, Newark, NJ, 1993.

4. Papanicolaou, P., *Laboratory Model Studies of Pneumatic Fracturing of Soils to Remove Volatile Organic Compounds*, Masters Thesis, Department of Civil and Environmental Engineering, New Jersey Institute of Technology, Newark, NJ, 1989.

5. Schuring, J. R. , Jurka, V. , and Chan, P. C., "Pneumatic Fracturing to Remove VOC's", Remediation Journal, Executive Enterprises Publications, New York, Vol 2, No. 1, Winter, 1991/92.

6. Myser, D., *Surfaces, Interfaces and Colloids*, VCH Publishers, Inc., 1991.

7. Rosen J. Milton, *Surfactants and Interfacial Phenomena*, John Wiley & Sons, Inc., New York, NY, 1978.

8. Raven Thomas; Gschwend M. Phillip, "An Evaluation of Surfactant Enhancement of Petroleum-product Contaminated Soils", Cambridge, MA, 1993.

9. Tadros F. Th., *Surfactants*, Academic Press, Inc., london, England, 1983.

10. Mercer, W. James; Cohen, M. Robert, *A Review of Immiscible Fluids in the subsurface*, Geo Trans, Inc., Herndon, VA, 1990.

11. United States Environmental Protection Agency, Risk reduction Laboratory, *Handbook on In Situ Treatment of Hazardous waste Contaminated Soils*, Cincinnati, OH, 1990.

12. Sims, J. L., Sims, R. C., and J. E. Mattews, "Bioremediation of Contaminated Surface Soils", Robert S. Kerr Environmental research Laboratory, US EPA , Ada, OK, 1989.

REFERENCES
(Continued)

13. Thompson, L. E, Bates, S. O., Hansen, J. E., "Technology Status Report: In Situ Vitrification Applied to Buried Wastes", Battelle Memorial Institute, Richland, Washington, 1992.

14. Angell, K. G., Bass, D. H., and Herman, C., "Air Sparging: An Innovative Technique For Site Remediation," Proceedings for the 18th Environmental Sysmposium and Exhibition, American Defense Preparedness Association, Alexandria, VA, February 24-27d, 1992.

15. Staps, S., "International evaluation Of In Situ Biorestoration of Contaminated Soil and Groundwater", Office of Emergency and Remedial response, US EPA, Washington DC, 1990.

16. Brock, Thomas D. and Michael T. Madigan, *Biology of Microorganisms*, 6th ed., Prentice Hall Inc., Englewood Cliff, NJ, 1991.

17. Driscoll, G. Fletcher, *Groundwater and Wells*, Second Edition, Johnson Filtration Systems Inc., St. Paul, Minnesota, 1986.

18. Harwell, J.H.; West, C.C., "Surfactants and Subsurface Remediation", Environmental Science and Technology, Vol. 26, No 12, 1992.

19. Abdul, A.S.; Gibson, T.L., "In Situ Surfactant Washing of Polychlorinated Biphenyls and Oils from a contaminated Site", Ground Water, Vol. 30, March-April 1992.

20. Nash, J. and R.P. Traver, "Field Evaluation of In situ Washing of Contaminated Soils With Water/Surfactants", Proceedings of the Twelfth Annual Research Symposium, 1986.

21. U.S. Environmental Protention Agency (USEPA), "Treatment of Contaminated Soils With Aqueous Surfactants", 1985.

22. Grace Sierra Technical Bulletins # B1-B5, Max Bac Controlled Release Nutrients, Milipitas, CA., December, 1991.

23. Wagner, S.; Schink, B. "Anaerobic Degradation of Nonionic and Anionic Surfactants in Enrichment Cultures and Fludized Bed Reactors", Water Research, 1987.

REFERENCES
(Continued)

24. McDermott, J. B.; "Two Strategies for PCB Soil Remediation: Biodegradation and Surfactant Extraction", AIChE Meeting, New Orleans, LA, Spring, 1988.

25. Handout of Drilfoam, Barold Drilling Fluids, Inc., Houston, Texas, 1990.

26. Robb, I.D., "Biosurfactants," in Industrial Applications of Surfactants, Vol. 2, editted by D.R. Karsa, Royal Society of Chemistry, Manchester, U.K., 1990.

27. Brown, M.I., Moses, V., et al, "Biosurfactants in Oil Recovery," CRC Crit. Rev. Biotechnology, Vol. 3, 1986.

28. Bikerman, J.J, *Foams*, Springer-Verlag, 1973.

29. United States Patent No. 5,032,042, "Method and Apparatus for eliminating Non-naturally Occuring Subsurface Liquid Toxic Contaminants from the Soil," July 16, 1991.

30. Bowels, J.E., *Engineering Properties of Soils and Their Measurement*, Fourth Edition, McGraw-Hill, Inc., 1992.

31. United States Environmental Protection Agency, Application Analysis Report, "Accutech Pneumatic Fracturing Extraction, and Hot Gas Injection, Phase-1, Cincinnati, Ohio, July 1993.