APPLICATION OF OXYGEN MICROBUBBLES FOR GROUNDWATER OXYGENATION TO ENHANCE BIODEGRADATION OF HYDROCARBONS IN SOIL SYSTEMS.

by

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(ABSTRACT)

Aerobic decomposition of hydrocarbon contaminants in anaerobic groundwater would be enhanced by oxygenating the water. This was done by injecting oxygen microbubbles in the soil matrix packed in a 7 ft by 7 ft by 5 inch in width Vertical Slice Test Cell, VSTC, and in a 30 inch column, also packed with sand. Transfer of oxygen to water was monitored after injecting oxygen microbubbles.

Compared to sparged air and hydrogen peroxide injections documented in the literature to have transferred less than 2 percent oxygen to water, oxygen microbubbles transferred over 40 percent oxygen to the flowing groundwater. Also, after injection of microbubbles gas retentions over 70 percent were achieved. Oxygen Transfer Coefficients, KLa(s), were higher in layered soil in VSTC compared to non-layered soil when the same amounts of microbubbles were injected in the cell. The effect of cell layering, quality, stability, and the amount of

microbubbles injections on transfer efficiency and gas holdup were studied.

It was concluded that high initial gas holdups, KLa values oxygen transfer per time and percent oxygen transferred were important parameters in maintaining a sustained oxygen transfer zone. These experiments demonstrated that only one of these parameters can be at a maximum, say, a high percent oxygen transfer or a high percent initial retention or a high KLa value. However, a maximum value for one parameter is usually at the expense of the other two being low. The optimum values for these parameters would be dictated by the biochemical, sediment and chemical oxygen demands placed on the oxygen transfer system.

TO MY LOVE, NASRIN

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CHAPTER I

INTRODUCTION

Contamination of groundwater by hydrocarbons is not a new phenomenon and has been a part of modern life for decades. However, public awareness concerning the environment in general and our groundwater supply in particular, have been gathering momentum since a few decades ago.

As an example, in the United States, concerns over groundwater contamination is well justified since 96% of all freshwater in this country is originated from groundwater and approximately 50% of the population uses groundwater as its source of drinking water. In recent studies, concentrations of contaminants far above previous levels were reported in the groundwater (Tangley, 1984). United States Environmental Protection Agency estimated that TCE alone, a commonly used industrial solvent, had contaminated approximately 4% of the nation's groundwater supply (Anon., 1984).

Soil and groundwater remediation have been attempted both above ground and in-situ with varied degrees of success, reflecting process limitations and the site characteristics. Above-ground remediation methods such as pump and treat approach are currently being used in which the groundwater is first pumped above ground and then passed through activated carbon beds or air stripping towers where organic contaminants are separated from water. Treated water is then pumped back into the ground.

In-ground remediation methods such as combining extraction wells (which normally are at the center of a cone of depression) and injection wells. The hydrocarbons riding on top of the water table are first pulled into the cone of depression of the extraction well and are skimmed off the top of the water. The cleaned water is then injected through the injection wells. The in-situ remediation methods can be physico-chemical or biological. Biodegradation option has the advantage of ultimately destroying the contaminants and not merely transferring them from one medium to the next.

In aquifers with a high concentration of hydrocarbon contaminants, oxygen would have to be supplied to the liquid phase in order to maintain a high concentration of biomass and a high degradation rate of contaminants. However, the options for supplying oxygen to the liquid phase are limited to a few which include air sparging, oxygen sparging, hydrogen peroxide injection, oxygenated water injection and oxygen microbubble injection.

Air sparging and injections of hydrogen peroxide into the soil have been tried and have had some successes on site specific cases. The low transfer rate of oxygen from air to the water phase and rapid depletion of oxygen by the microbes makes air sparging less attractive. Hydrogen peroxide, commonly used to supply oxygen for in-situ biodegradation of organics, increases the biological activity by several orders of magnitude. However, the rate of hydrogen peroxide decomposition also increases accordingly, usually by an enzymatic decomposition (Britton, 1985). The latter alternative source for supplying oxygen in-situ in the list of the options, above, is injection of oxygen microbubbles in the saturated zone was used by Lotfi and Michelsen (1990a).

The overall goal of this study was to optimize the delivery of oxygen to flowing groundwater, while minimizing the losses of oxygen vented upon injection and committed to surfactant biodegradation under sustained testing conditions. Several objectives were evaluated to approach this goal. These objectives include the following:

- To evaluate the effect of injecting oxygen microbubbles, compared to air microbubbles, in the Vertical Slice Test Cell (VSTC).
- To derive and compare oxygen transfer coefficients and percent oxygen transferred after microbubble injection.

- To evaluate the effect of stratification, (layering the cell with alternative sand and clay strata) on gas hold up and oxygen transfer after oxygen microbubble injection.
- To evaluate the effect of microbubble quality (% dispersion of gas in water) and stability as well as the amount injected, on gas hold up, oxygen transferred and oxygen transfer coefficient.
- To synthesize the results of short term and long term tests as a repository of information about microbubble injections for groundwater oxygenation.
- To justify field demonstration.

These objectives were achieved by three groups of tests:

In the first group of tests, VSTC was capped by a clay layer. Tests reported in this group include Test #13 in which VSTC was overloaded with microbubbles, Test #15 in which the amount of microbubbles were reduced to half of Test #13, and higher gas hold up was achieved, Test #16, in which air was spared in the VSTC and Tests #18 and 19 in which microbubbles were injected and high gas holdups were achieved. These tests were short term tests and oxygen transfer results were not conclusive. A vertical barrier with two windows aligned with microbubble injections were placed in the cell for Tests #15-19.

In the second group of tests, a Vertical Column Test Cell was used. The objective of these tests was to study the efficiency of utilizing CGA, sparged air and oxygenated water to deliver oxygen to the water phase under more controlled conditions. Earlier experiments by Smith, 1988, had proven the potential for use of air CGA but due to experimental limitations only 5% oxygen was transferred to the water phase. Experiments with the vertical packed column were designed to determine transfer efficiency irrespective of physical test set up inherent with the Vertical Slice Test Cell (VSTC) such as packing configuration, injection methods, and lack of layering. This test cell was equipped with a gas collection system and the effect of oxygen microbubble, air sparging and oxygenated water injection on oxygen transfer was evaluated. The effect of the amount, quality and stability of microbubbles were more closely evaluated in this group of tests. However, these tests were not extensive.

In the third group of tests, VSTC was alternatively layered with sand and clay layers in order to direct groundwater flow to pass closer to the microbubble injectors and to help increase gas holdup in the cell. These tests were long term over a period of a week or more as opposed to a day or less. In Tests #27-29 oxygen microbubbles were injected in the upper and lower sand layers. The amount of microbubble injection was varied and its effect on oxygen transfer coefficients, gas holdup and oxygen transfer was evaluated. In Tests #30 and #31, oxygen microbubbles were injected only in the lower layer and the effect on gas holdup, oxygen transfer and oxygen transfer coefficients was evaluated.

CHAPTER II

BACKGROUND AND FUNDAMENTALS

In this section an overview of the fundamentals of oxygen transfer in porous media is reviewed and mathematical models describing oxygen transfer phenomenon are presented. A general description of microbubbles, also known as colloidal gas aphrons (CGA), and the method of their generation are given. A conceptual design in which CGA is utilized to enhance biodegradation is presented. Unless otherwise specified, terms microbubbles and CGA are used interchangeably. Also term oxygen CGA is interchangeably used with CGA unless indicated otherwise.

2.1 Colloidal Gas Aphrons or Microbubbles

Colloidal gas aphrons (CGA) are defined as "a collection of spherical, micron-sized gas bubbles dispersed in an aqueous surfactant solution with a volumetric gas fraction (quality) of at most 0.74 and 95% of its bubbles not exceeding 100 microns in diameters" (Longe, 1989). This description places CGA in the wet category of the foams. Higher than 74% gas dispersed foams are known as dry foams which will not be discussed here.

The bubble diameters of the wet foam are widely distributed and depend on the generation technique, type and concentration of the surfactant used and the characteristics of the water.

Foams with bubble diameters less than 250 microns are more stable than larger diameter foams. However, colloidal properties, such as the ability to remain dispersed in the liquid without significant coalescence for several minutes, become transparent as bubble size is reduced to below 50 microns with few greater than 100 microns (Longe, 1989). Sebba and Barnet (1981) named these foams as colloidal gas aphrons to reflect their colloidal nature. Sebba (1986) gave a size range of 25 to 50 microns, however Longe (1989) showed a size range of 15 to 120 microns with an average of 50.7 ± 22.7 microns. The technical aspects of CGA were further discussed by Sebba (1987).

Microbubbles are characterized by two relatively accurate parameters, quality and stability. These parameters as defined by Michelsen (1990) are as follows:

- Quality is defined as the percent of gas in a gas plus water dispersion.

- Stability (H') is defined as the volume (ml) of clear liquid interface in one minute after pouring the dispersion into a standard 250 cc glass graduate.
- Stability (H) is defined as the percent of the total liquid volume coalesced in one minute. These parameters are determined by filling a 250 cc glass graduate cylinder with a sample of a CGA, weighing it and measuring the clear liquid (ml) in the bottom after one minute.

Quality is found as:

$$Q = \left(1 - \frac{W_D}{250}\right)100 \tag{2.1}$$

where W_D is the weight of dispersions filled in a 250 cc graduate cylinder. The typical H' values of 8 to 30 ml clear water in one minute for a 66% quality translates into H values of 9.4 to 35.3%. Hence, the lower the volume of the clear phase the more stable the dispersion would be. Bubble size distribution can be determined by microscopic techniques (Suggs, 1987).

Several advantages of in-situ injection of oxygen microbubbles for groundwater oxygenation can be summarized.

- The encapsulated microbubbles maintain their integrity for extended periods of times (Michelsen, et al., 1984).
- As the groundwater passes by the microbubbles, oxygen is transferred gradually to the water phase, as shown by the results of this study.
- Microbubbles can be manufactured with nutrients mixed in their aqueous phase and injected in-situ.
- Oxygen microbubbles are more efficient in transferring oxygen to the water phase, as demonstrated by the results of this study.

Disadvantages of microbubble injection include:

- The cost of their generation, which is more than air sparging but less than hydrogen peroxide injection (Michelsen, et al., 1990).
- Injection of surfactant solution in the ground, which is usually less than 150 ppm and is diluted by the flowing groundwater upon injection.
- Parts of biologic activity is diverted to degrade the surfactant, which uses some of the injected oxygen, about 12% of injected oxygen.

Microbubbles are generated by adding surfactants to water and making a 100-200 ppm solution, lowering its surface tension and then shearing the solution between a spinning head and stationary baffles of a microbubble generator, the details of the microbubble generation process can be found elsewhere (Sebba, 1985).

Transfer of oxygen to the water phase is limited by the relatively low solubility of oxygen in water and by the tendency of oxygen gas to escape from the saturated zone, causing low retentions, hence increasing the cost of oxygenation of ground water. Oxygen microbubble injection is an attempt to increase the retention of oxygen gas in the saturated zone and to increase the transfer efficiency of oxygen to the ground water (Michelsen, et al., 1984).

This report presents the results of a recent study in which oxygen microbubbles were injected in the saturated soil matrix and transfer to water phase (over 40% for some tests) was realized and the results are promising.

Generation of microbubbles is discussed in detail by Longe (1989), Smith (1988) and Sebba (1985). Several devices have been tested for microbubble generation, including a venturi device drawing a fine stream of air into the vortex for bubble formation, close tolerance rotary pumps, packed beds of glass spheres or other solid particles, air sparged hydrocyclones and tube reactors using sintered bayonet fingers.

The high volume continuous generation of CGA was accomplished by Michelsen, et al., (1988). Yoon (1987) through an earlier association with Sebba developed a large scale microbubble generator and has been able to contribute to cleaning coal by microbubble flotation. Regardless of the applications of CGA, their development and earlier study of their properties is attributed to Felix Sebba.

The shearing of gas bubbles in both the batch spinning disk and continuous generators is provided by stationary baffles and rotating heads. However, the details of these designs are not released to satisfy patent law requirements (Michelsen, et al., 1990)

2.2 Transfer of Oxygen in Aeration Systems

The mass transfer of oxygen from the gas to the water phase has been well documented in wastewater treatment literature, in which biological degradation occurs in activated sludge systems, oxidation ditches and aerobic digestors. Most often, in all cases Ficks Law of Diffusion has been applied to describe the first order transfer rate of oxygen to water as follows:

$$\frac{dc}{dt} = KLa\ (C_s - C_L) \tag{2.2}$$

where C_s = saturation concentration of oxygen (mg/l) at the interface

C_L = concentration of oxygen in liquid phase at time t

dc/dt = rate of change in dissolved oxygen concentration mg/L-time

KLa = the overall oxygen transfer coefficient

The above expression has been widely used to evaluate the oxygen transfer characteristics of an aeration device. However, when biodegradation is occurring and oxygen is being depleted, the deficiency has to be replenished by the aeration system. The rate of change of dissolved oxygen can be calculated by

$$\frac{dc}{dt} = KLa\ (C_s - C_L) - R_r \tag{2.3}$$

where R_r equals the rate of oxygen utilization (Benefield and Randall, 1980). There are different methods of determining KLa when the microbial oxygen demand is being applied. Under steady state where dc/dt = 0,

$$KLa = \frac{R_r}{(C_s - C_L)} \tag{2.4}$$

The above expressions describe oxygen transfer coefficients in water and wastewater in an aeration device but these principles must be applied to oxygen transfer within the pores and openings of the soil or other porous media. Although the material balance for oxygen mass transfer is similar, expression of KLa must be defined in somewhat different terms.

2.3 Oxygen Transfer Model in Soil Systems

Microbubbles can be generated and injected into a permeable matrix (coarse sand) set-up as a treatment zone for biodegrading flowing contaminated groundwater. The microbubbles upon injection either adhere or are physically held by the soil matrix. Depending on conditions, 50 to 85% of the microbubbles can be physically bound (or adhered) to the soil matrix with the remainder vented to the surface (Michelsen, et al., 1984). Furthermore, the bubbles which initially adhered to the soil matrix tend to remain stationary for months, providing oxygen for biodegradation of contaminants in the flowing groundwater. Physically, in the Vertical Slice Cell modeled as a vertical trench, the microbubbles are injected and form an annular cylinder around the injectors. Thus, a 5 in. x 30 in. cross sectional (rectangular) treatment zone extending 6 inches (Z) down gradient to provide contact of the flowing water with the stationary microbubbles was assumed (see Figure 2.1).

Treybal (1980) has addressed mass transfer in a packed bed as follows:

$$L\,(X_2 - X_1) = KLa\ z\ (X_A - X_{A,L})$$
$$\frac{g\ mol\ H_2O}{cm^2\ hr}\ (g\ mol\ O_2/g\ mol\ H_2O) = \left[\frac{g\ mol}{cm^2 hr\left(\frac{g\ mol}{cm^3}\right)}\right]\left[\frac{cm^2}{cm^3}\right]\ cm\left[\frac{g\ mol\ O_2}{cm^3}\right] \tag{2.5}$$

Measurement of the groundwater flow, L, and cross sectional area was straight forward (12.7 Cm x 71.12 cm). Concentrations of the dissolved oxygen (D.O.) were measured by pumping a 50 ml sample from the Vertical Slice through a 30 ml agitated cell within which a D.O. probe was mounted horizontally. Numerous samples were obtained upstream and downstream in order to profile D.O. as a function of location in the Vertical Cell at some fixed time. These data provided a reasonable estimate of dissolved oxygen transferred to the flowing groundwater (left side of the equation). On the right side the mass transfer coefficient, KL, as a

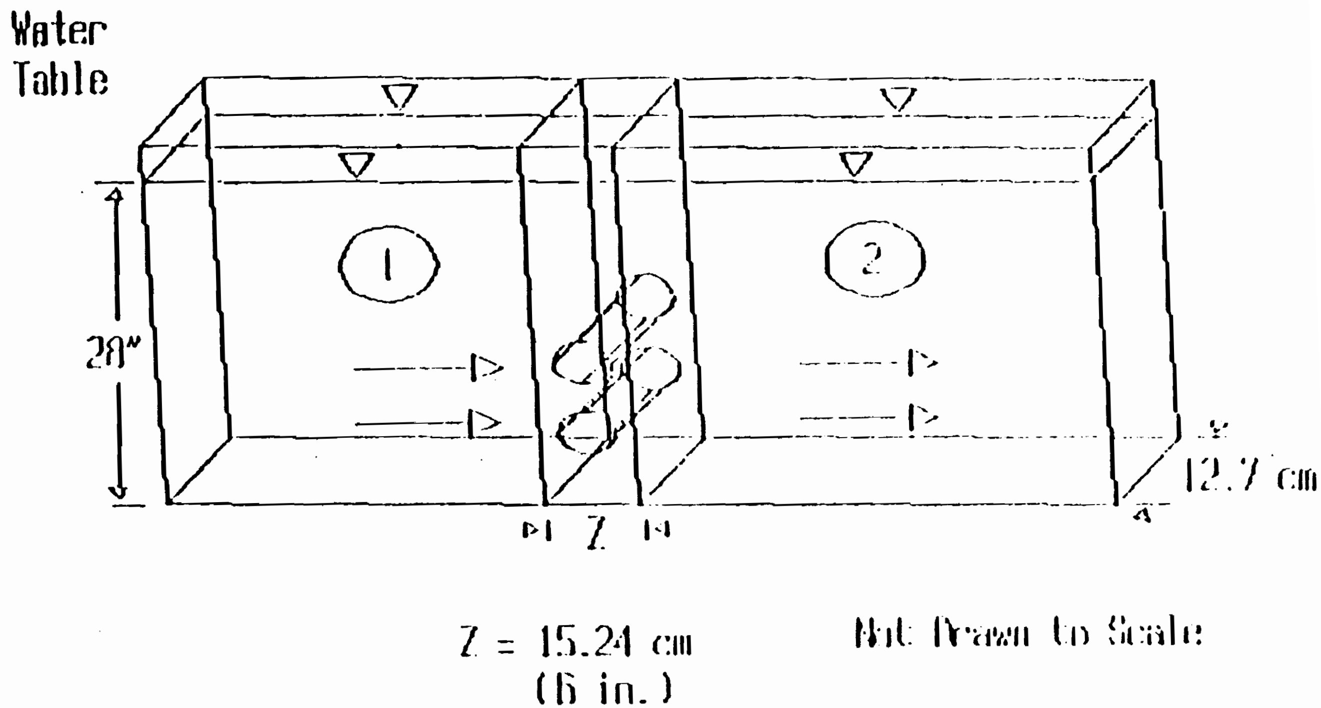

Figure 2.1 Mass Transfer Model: Vertical Column Test Cell.

function of the reactor volume, 1 cm^3, was back calculated. This calculation assumed knowledge of Z--the distance the groundwater was exposed to the bubble dispersion. The liquid phase driving force was quite definitive and was the difference between the O_2 concentration of saturation (pure O_2 CGA bubbles) minus the concentration of the O_2 (D.O.) in the flowing groundwater measured up and down gradient.

At the interface between O_2 gas and water where oxygen was first dissolved, the maximum dissolved level of oxygen was present, say 40 mg/l at 25°C and 1 atm pressure. Hence, this was the saturation concentration of dissolved oxygen, C_s. The driving force (for mass transfer) at the bubble/water interface was concentration potential or the difference between saturation concentration, C_s, and concentration of dissolved oxygen, C_L, at time t.

For the packed column used in this study, Z, the distance in which oxygen had a chance to transfer into the water phase was measured from the point of O_2 injection to the first D.O. port (about 6 inches). The "Z" distance was marked on Figure 4.6 in Chapter 4 and is similar to the model in Figure 2.1.

$$\Delta_1 \text{ D.O.} = C_s - C_{LI} \qquad (2.6)$$

where D.O. = dissolved oxygen

C_s = saturation concentration of O_2

C_{LI} = groundwater concentration of O_2 at time t at point of injection

At some distance from injection point, Z, along the flow path at time, t, the D.O. concentration would be C_{L2}. Hence,

$$\Delta_2 \text{ D.O.} = C_s - C_{L2} \tag{2.7}$$

The average D.O. along the length Z would be

$$\frac{\Delta_1 D.O. + \Delta_2 D.O.}{2} = D.O.\ average \tag{2.8}$$

The log mean method expresses the mean D.O. more accurately

$$D.O._{log\ mean} = \frac{\Delta_1 - \Delta_2}{\ln \frac{\Delta_1}{\Delta_2}} \tag{2.9}$$

where

$$\Delta_1 = C_s - C_{LI} = \Delta_1 D.O. \tag{2.10}$$
$$\Delta_2 = C_s - C_{L2} = \Delta_2 D.O. \tag{2.11}$$

If Cs = 40 mg/l and D.O.(s) at points 1 and 2 are 1 and 5 mg/l, respectively, then Δ_1 = 39, Δ_2 = 35 and D.O.$_{log\ mean}$ would be 36.96 mg/l.

The product of Z cm and D.O. mg/l gives a concentration per unit area (Z x Δ D.O.).

Where $\Delta D.O.$ is the increase in D.O. from its original value right before injection of CGA, C_{L1}, at the distance Z from the point of injection at time t. Hence, $\Delta D.O. = C_{L2} - C_{L1}$. Also,

$$\frac{\text{oxygen transferred per}}{\text{unit time - per unit area}} = \frac{Q \times \Delta D.O.}{A} \tag{2.12}$$

$$\text{where } Q = \text{flowrate } ml/\min \times \frac{60 \min}{hr} \tag{2.13}$$

Oxygen transferred per unit time per unit area is proportional to the concentration per unit area

$$\frac{Q \times \Delta D.O. \text{ water}}{A} \propto z \times \Delta D.O._{\log mean} \tag{2.14}$$

and KLa, the oxygen transfer coefficient, is the proportionality constant. Hence

$$\frac{Q \cdot \Delta D.O. \text{ water}}{A} = KLa\,(\,Z\,)\,(\Delta D.O._{\log mean}) \tag{2.15}$$

where dimensions for KLa are found to be time $^{-1}$ (i.e. hr^{-1}). Therefore,

$$KLa = \frac{(Q \cdot \Delta D.O.\ water)/A}{z \cdot \Delta D.O._{\log\ mean}} (60)\ hr^{-1} \qquad (2.16)$$

where Q ml/min

D.O. mg/l

Z cm

A cm^2

2.4 Conceptual Design of a Treatment Zone and VSTC Model

The concept of a biological treatment zone through which hydrocarbon contaminated water passes and the contaminants are mineralized by microbial action is of interest in regions with optimal hydrogeological conditions. These are regions with relatively high hydraulic conductivities i.e. sandy strata. Fundamentally, microbubbles can be injected into saturated zones along with nutrients to sustain bacterial growth and degradation of organics. However, injection of microbubbles and nutrients in an area through which groundwater is funnelled can be managed better by placing localized control mechanisms i.e., D.O. ports, flow meters, and conductivity meters in the treatment zone. The Vertical Slice Test Cell represents the model of a section or slice along the width of one such trench. Further details can be found elsewhere (Michelsen and Lotfi, 1990 submitted for publication).

2.5 Conceptual Design of a Treatment Zone and VCTC Model

The experiments with VCTC were designed to determine the effect of forcing the flow through the "CGA cloud", which is the cluster of microbubbles packed in the immediate vicinity of the injector heads. The theoretical basis, of the design, was that if the low D.O. water was forced through the CGA cloud in the packed column, it would pick up oxygen from the oxygen saturated cloud. The transfer force would remain high in the vicinity of the cloud as long as there remained oxygen CGA to be transferred to the water phase. It was further hypothesized that the column would represent a single layer in a treatment trench for biodegradation of hydrocarbon contaminants when considering an actual in-situ treatment zone. Based on the promising results of oxygen transfer of over 30% to water phase in these experiments it was decided that Vertical Slice Test Cell, was to be packed in a layered fashion in order to maximize the oxygen transfer to the water phase.

CHAPTER III

REVIEW OF LITERATURE

A cursory review of groundwater decontamination methods shows three categories of treatment; in-ground containment methods; hydrodynamic control measures and in-situ treatment. Since findings of this report would be applicable to biological in-situ treatment of groundwater, a more detailed presentation of relevant biodegradation literature is given here. However, a brief review of the above methods is also provided for the sake of completeness.

3.1 Groundwater Remediation Methods

In-ground barriers are used to contain the contaminated groundwater and to prevent its further migration through the aquifer. These barriers are placed down gradient of a contaminated site to reduce contaminant migration, or placed up gradient of a contaminated site to reduce groundwater flow through the plume. Barriers can be placed by forcing low permeability material to replace soil(displacement walls). Example of displacement walls are steel shell piling, vibrating beam slurry wall, jet grouting, and membrane walls.

Hydrodynamic control or hydraulic measures includes extraction/injection wells. In this category the groundwater table is hydrodynamically lowered or elevated in order to remove contaminants. Different injection and extraction sequences are designed to collect the hydrocarbons. For example, by lowering the water table floating hydrocarbons can be partitioned. Recovery wells are used to create a cone of depression and to collect contaminants for above ground treatment (Freeze and Cherry, 1979, Canter, et al., 1988).

In situ treatment methods can be either physicochemical or biological. The in-ground methods are generally novel techniques with great potentials for commercialization. Treatment zones or trenches can be placed in the path of the contaminated groundwater. In these zones the contaminants are decomposed or neutralized by bacterial or chemical methods respectively. A lime treated zone, for instance, can be used to treat acidic waters.

In a biological treatment zone contaminants in the groundwater are degraded by microbial action. The indigenous bacteria are stimulated by adding soil nutrients and an electron acceptor; i.e., oxygen for aerobic reactions. The process has been demonstrated for degrading petroleum hydrocarbons, chlorinated solvents, polynuclear aromatics and a variety of other contaminants. Dibble and Barthu (1979), Wilson, et al. (1988), Kinsella (1989), Novak, et al. (1984).

3.2 In situ Biorestoration of Groundwater

Microorganisms decompose hydrocarbons through enzymatically mediated reactions in groundwater. In situ biorestoration was first spot lighted when Richard Raymond, Virginia Jameson and coworkers pioneered the field by enhancing biorestoration in situ (Raymond, 1974, Wilson, et al., 1986). In their process Raymond and others enhanced the indigenous hydrocarbon degrading microflora. The process first pretreated contaminated water by physical extraction methods to recover as much of the hydrocarbons as possible. Also, treatability studies, investigations of the hydrogeology of the site and the study of the extent of contamination were concurrently performed while continuing to pretreat the groundwater. Upon establishing optimal conditions for growth of indigenous microflora, in the Raymond method, the injection systems for mixing nutrients, oxygen and the circulating water in the formation were designed. Degradation rates were controlled by the groundwater circulation process. This method is reported to have been relatively successful in recovering and degrading gasoline spills (Wilson, et al., 1986).

Despite early contentions, recent findings, using epifluorescence microscopy has shown that the deeper subsurface contains significant microorganism populations.

(Wilson, et al., 1986). The rates of biodegradation varies two to three orders of magnitude between different aquifers. However, these rates are fast enough to restore these aquifers in many regions (Wilson, et al., 1986). Degradation rates are dependent on environmental factors such as temperature, pH, dissolved oxygen, Oxidation-reduction potential, availability of mineral nutrients, salinity, soil moisture (if unsaturated), the concentration of pollutants and the nutritional quality of dissolved organic carbon in the ground water (i.e. BOD).

Wilson, et al. (1986) reviewed decomposition of several organic species. Aerobic degradation of benzene, toluene, the xylenes, and other alkylbenzenes which leaked into the groundwater has been reported (Wilson, B., et al., 1986, Lee and Ward, 1984). Also degradation of napthalene, the methylnaphthalenes, fluorene, acenaphthene, dibenzofuran and different polynuclear aromatic hydrocarbons released from spilled diesel oil or heating oil were reported (Wilson and Rees, 1985). Degradation of acetone, isopropanol, methanol, tertiary butyl alcohol, from solvents and gasoline, were reported by Novak, et al. (1984), Lokke (1984), Jhaveri and Mazzacca (1983). Degradation of other synthetic organics such as dichlorobezenes (Kuhn, et al., 1985), the mono-,di-, and tri-chlorophenols (Suflita and Miller, 1985) and methylene chloride (Jhaveri and Mazzacca, 1983) were also reported.

Biodegradation of these compounds is greatly affected by the availability of oxygen. Approximately 1 part of the above organic compound required 2 parts of oxygen to be metabolized, (i.e. 4 ppm O_2 can degrade 2 ppm benzene). Due to the limited solubility of oxygen in water, less than 40 ppm,ground water with a high concentration of organic compounds are not suitable for biodegradation. When oxygen is depleted anaerobes take over and degradation would continue anaerobically.

In general, aerobic conversions of long chain hydrocarbons to small chains and eventually to CO_2 is faster than anaerobic degradation (Borden and Bedient, 1986), by orders of magnitude. Aerobic degradation has been explained by several models, but the most favored is the Monod model. In these models, the rate limiting factors would often dictate the kinetics of the reaction. In subsurface environments, when ground water is generally anaerobic, oxygen can become the rate limiting factor. Oxygenation of ground water would eliminate this limitation and enhance the reaction (Borden and Bedient, 1986).

The changes in hydrocarbon concentration is a function of total microbial concentration and availability of oxygen, and the change in oxygen concentration is proportion to the change in hydrocarbon concentration. The rate of creation of biomass is then a function of hydrocarbon concentration and oxygen concentration. Hence, the component with smaller concentration (stoichiometrically) may become the rate limiting component.

In aquifers with a high concentration of hydrocarbon contaminants, oxygen would have to be supplied to the liquid phase in order to avoid its becoming rate limiting and to maintain a high concentration of biomass, and subsequently to sustain a high degradation rate. However, the options for supplying oxygen to the liquid phase are limited. A review of these options will shed more light on the problem.

3.3 Modes of Oxygen Transfer

Aerobic activity depends on availability of molecular oxygen, generally in the liquid phase. The options for supplying oxygen to water for enhancing biodegradation of hydrocarbon contaminants are limited. Air sparging, pure oxygen sparging and injection of hydrogen peroxide into the soil has had limited success due to their inherent limitations (Lotfi and Michelsen, 1990a, Hinchee, 1990). Air sparging, due to low O_2 transfer rate from air to water phase, rapid depletion of oxygen by the microbes and stripping of volatiles into the atmosphere, is not an attractive option. Hydrogen peroxide, commonly used to supply oxygen for in-situ biodegradation of organics, increases biological activity by several orders of magnitude. However, the rate of hydrogen peroxide decomposition also increases accordingly, since it is an enzymatic decomposition (Britton, et al., 1985; Spain, et al., 1989). In fact the use of H_2O_2 at an Air Force Base site was determined not to be economical (Hinchee, 1988). An alternative source for supplying oxygen in-situ is to inject and retain oxygen microbubbles in the saturated zone (Michelsen, et al., 1984, Lotfi and Michelsen, 1990 b and c).

Microbubbles, also referred to as colloidal gas aphrons (CGA), are a dispersion of 50 ± 40 microbubbles in water. The bubbles are encapsulated by a soap solution which prevents coalescence (Sebba, 1982). A more detailed discussion is given in Chapter II, Background.

Kaster, et al. (1989) compared the effect of using CGA vs. sparged air and found oxygen transfer coefficients of 100 to 580 hr^{-1} for CGA and 55 to 132 hr^{-1} for sparged air in a stirred tank bioreactor.

CHAPTER IV

EXPERIMENTAL DESIGN AND TEST APPARATUS

4.1 Experimental Design Objectives and Implementation

The objective of the experimental design was to develop a series of controlled tests which evaluated the efficiency of oxygen transfer in the saturated zone of a soil matrix upon injecting microbubbles (with pure oxygen in their cores), sparging with air, or injecting oxygenated water. Four parameters were evaluated:

- oxygen retention results
- changes in dissolved oxygen level and oxygen transferred to the flowing ground water
- oxygen transfer coefficient, KLa.
- oxygen transfer per time

The experimental design was intended to evaluate oxygen transfer in a conceptual treatment zone or trench which intercepted a plume of a hydrocarbon spill or a stream of leachate from a landfill. An "actual size" slice of such a trench was constructed (VSTC) and used in the study as shown in Figure 4.1. A Vertical Column Test Cell (VCTC) which allowed conditions for a more complete oxygen material balance was used to evaluate the efficiency of transfer to the

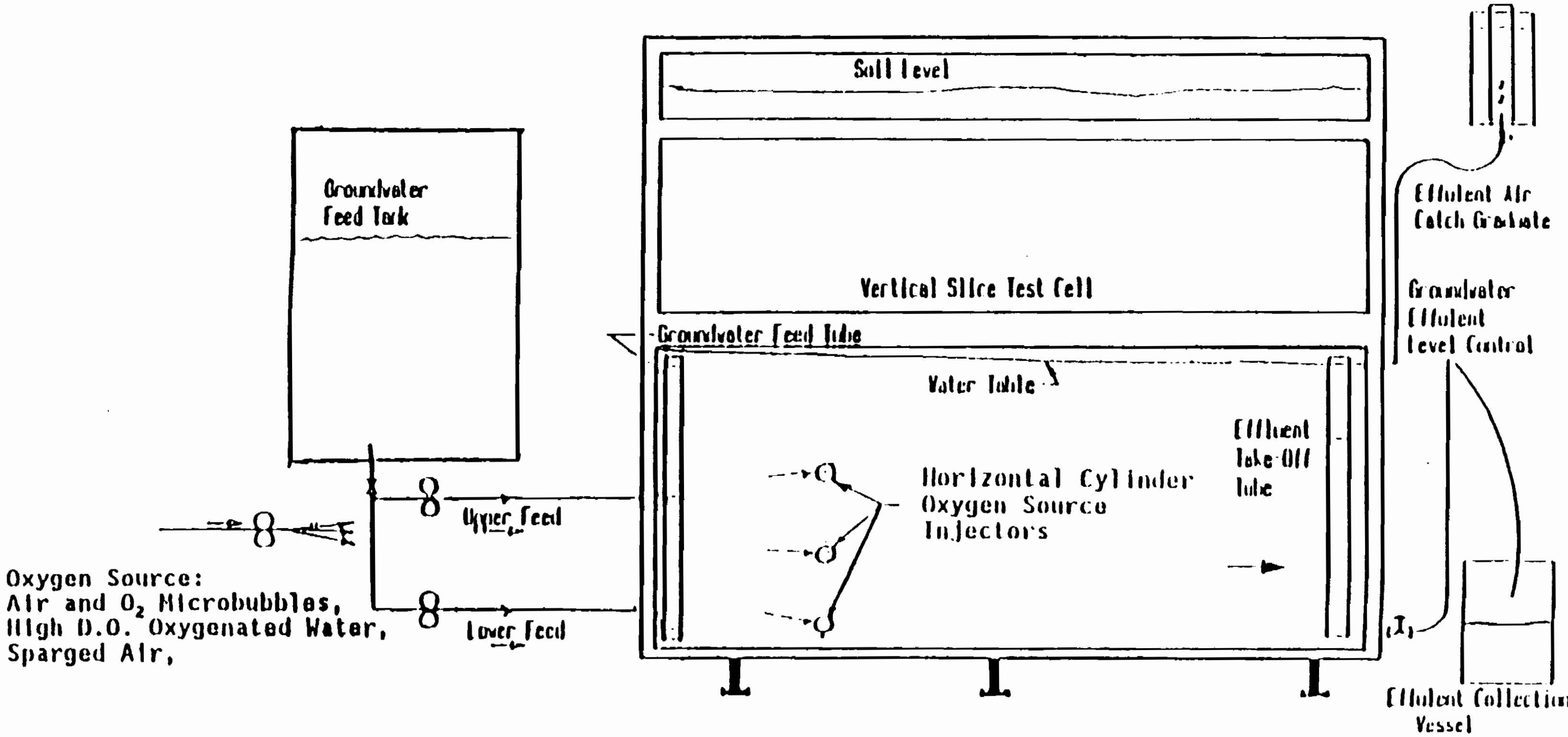

Figure 4.1 Vertical Slice Test Cell schematic, showing influent and effluent piping and movements of water.

groundwater flow directed through the injection zone as shown in Figure 4.7.

Three groups of tests were designed to evaluate the efficiency of oxygen transfer system. The first group included short term Vertical Slice Cell tests in which dissolved oxygen levels, after injections of oxygen, were monitored for about a 24 hour period. The VSTC was packed with concrete sand and capped by a layer of impermeable clay as shown in Figure 4.2. With the exception of test # 13, the plexiglass barrier was emplaced for other tests in this group. Seven tests, numbers 13 through 19, were performed in which two tests, 14 and 16, were sparged air tests. Therefore, the thrust of these experiments were on evaluating the effect of CGA injections on oxygen transfer. The three parameters listed above, namely, gas retention, D.O. level and % oxygen transferred, and KLa(s) were evaluated by injecting CGA in the cell and by monitoring the following variables:

- CGA flow rate (ml/minute)
- CGA injection duration (minutes)
- CGA injection amount (a product of flow rate and duration) (ml)
- One single clay layer capped the sand matrix in all tests

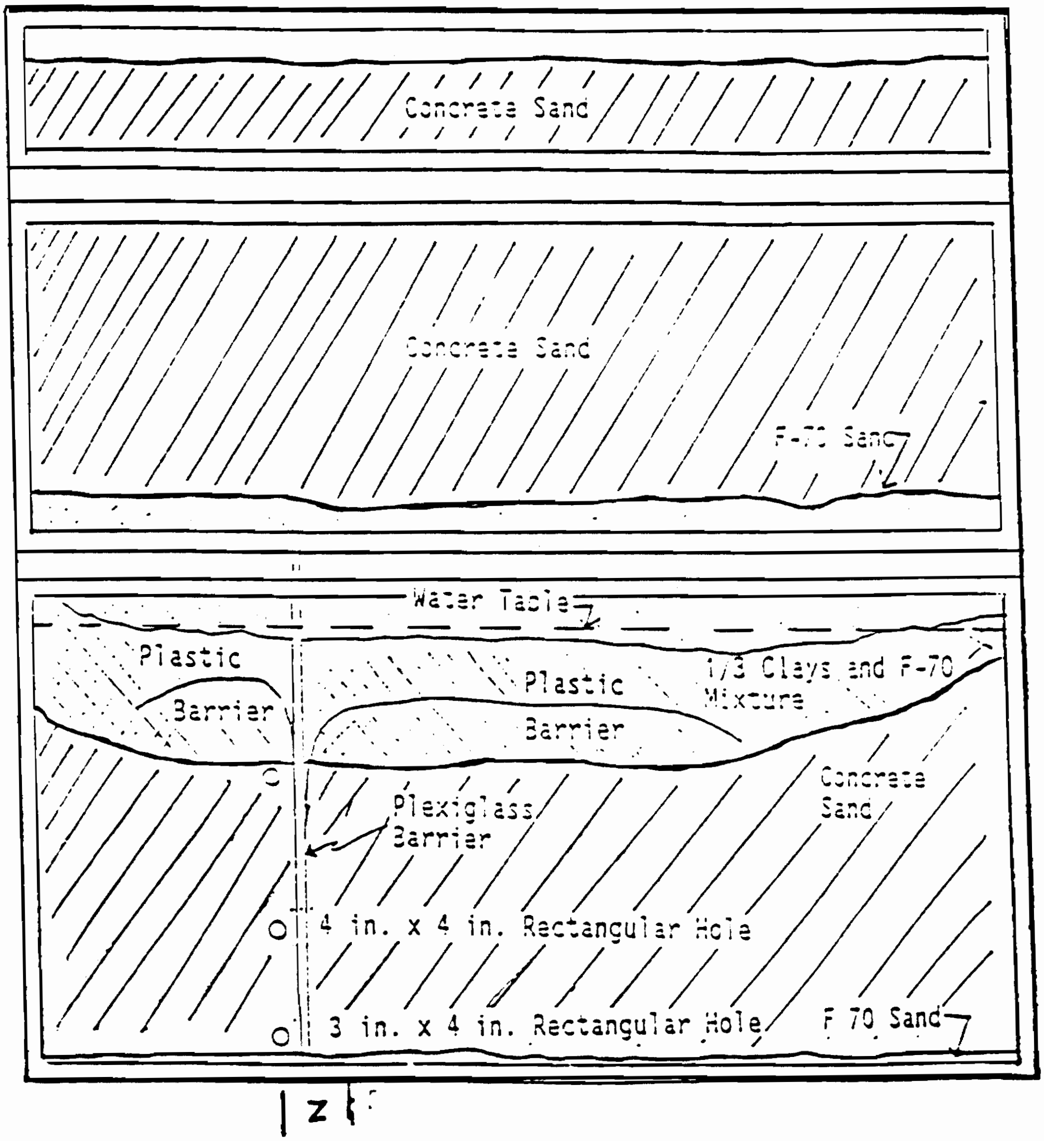

Figure 4.2 Vertical Slice Test Cell, sediment loading for oxygen microbubble injections, Test #15 to 19.
Note: Same set up without plexiglass barrier and plastic barrier was used for Test #13.

- For Tests 15 through 19, cell packing was not changed. Hence, continued injections for each test was a variable in itself (as injections continued less gas was held up in the cell).
- Air sparging in Test #16 seemed to have affected gas retentions in Tests 17-19. Hence, air sparging prior to Test 18 and 19 was considered as a variable in these tests (the results of Test #17 were not considered).

In Test #13, the VSTC was filled as described in section 4.2.5. The cell was flushed/treated with a 0.2 g/l solution of sodium azide to prohibit microbial growth, then flushed for 4 days with low D.O. water. This procedure was typical of all the tests. 200 ppm NaDBS surfactant solution was used in a spinning disk CGA generator modified to generate oxygen CGA. This procedure was also used for the rest of the tests presented here. Eight 2-liter injections of CGA were done into the VSTC.

In Test #14, the VSTC was further flushed with low D.O. water after test #13 injection while the cell packing remained unchanged.

Air was sparged at the rate of 100 ml/min. for 1400 minutes and 140 liters of air or 29 liters of oxygen was passed through the cell via the two injector heads.

The VSTC was repacked as in Test #13, however, the vertical barrier with the two windows was also placed in front of the injectors as described before. Figure 4.2 shows the configuration of the cell packing, vertical barrier and the position of a plastic extension from the plexiglass barrier to prevent gas escape along the length of the barrier. As in Test #13, about 2 liters of CGA per injection was delivered through both injector heads. Compared to Test #13, the amount of injected oxygen CGA in Test #15 was reduced in half.

During the course of this study trial and error were used to establish research trends and objectives. Test #16 served in raising some questions and establishing several points as follows: Air sparging in a porous medium created channeling. Could air bubbles block the channels, so that subsequent injections of CGA were held longer in the sand matrix? If so, did that mean that oxygen transfer would also increase? An attempt will be made to answer these questions.

Air was introduced into the cell through the two injectors at 50 ml/min. for 50 minutes. A total of 25.5

liters of air or 5.35 liters of oxygen was introduced in the cell. Data for Test #16 will not be introduced here due to problems that arose in their acquisition. However, it is possible that the subsequent tests were affected by air sparging when the same cell packing was continued to be used.

In this test CGA were injected in the same soil matrix as was used for Test #15, with the clay horizontal layer and the vertical plexiglass barrier still emplaced.

Test #19 was to duplicate the first 4 injections of Test #18 and the effect of continued injections of CGA on oxygen holdup and transfer were evaluated.

The second group of tests included three modes of oxygenation, namely, CGA injections, sparged air and oxygenated water injections in the Vertical Column Test Cell, with the exception of Tests 6 and 7, which were oxygenated water injections and sparged air tests, respectively, the rest of the tests, 1 through 8, were CGA injection tests. The mode of oxygenation was a variable between these tests.

The CGA injection tests included the following variables:

- CGA flow rate (ml/min)
- CGA injection duration (minutes)

- CGA injection amount (ml)
- CGA stability and quality

The third group of tests included long term Vertical Slice Cell Tests in which D.O. levels, after injection of oxygen CGA were monitored for over a week. The VSTC was packed with alternating layers of concrete sand and clay. The cell packing was not changed throughout Tests #27 to 31. Hence, sustained testing was also a variable between these tests since gas hold up or retention normally was diminished as injections continue and breakthrough paths develop in the cell packing. The sand layered between clay layers directed groundwater to pass through the CGA cloud, defined earlier. Injections were made in upper and lower layers of the two sand layers in Tests 27 through 29. However, as injections continued, gas retention was reduced. Hence, in Tests 30 and 31, injections were only made in the lower sand layer. The variables in these tests included:

- CGA flow rate (ml/min)
- CGA injection duration (min)
- CGA amount (ml)
- Effect of sustained injection (as explained above)
- Multi-layering of VSTC
- Injections in both sand layers vs. lower sand layer

In these tests VSTC was filled with 2 inches of Federal Fine sand, then the cell was sectioned into 3 parts. The start and the end sections were filled with Federal Fine sand and the middle section was layered from bottom to top, with 10 inches of concrete sand layer, 7 inches of clay layer, 12 inches of concrete sand layer, 8 inches of clay layer, and finally topped with 36 inches of concrete sand to provide an overburden weight. Water table was kept at the level in the middle of the second clay layer. Figure 4.4 shows the cell and its packing configuration. It also shows the position of the CGA injectors used in the concrete sand layers, as well as the optional injectors not used in these experiments.

The cell was flushed/treated with sodium azide as before. 150 ppm surfactant solution, a 3:1 weight ratio of Tergitol 15S12 (Union Carbide, Ethylene Oxide Derivatives Division, Danbury, CT), and PolyStep A-7 (Control No. 823-27018, Stepan Company, Northfield, Illinois) was used to generate the CGA as before. The CGA were injected in both sand layers.

In Test #28, duration of injection of CGA was increased, to 2.30 minutes compared to Test #27. Also, the flow rate of CGA was increased and ranged from 700 to 718 ml/min.

In Tests #30 and 31, the same cell packing configuration as in Test #29 was used, but CGA injection was made only in the lower concrete sand layer. At the end of Test #29, percent retention had reduced to 50%. Due to the weight of the upper sand layers (high loads) exerted on the lower layers, it was more probable for the upper concrete sand layer to have lost its hold-up capacity than the lower sand layer. Based on this fact, it was decided to make injections through two injector heads already emplaced in the lower concrete sand layer.

4.2 Test Apparatus and Material

Two test cells were used to evaluate oxygen transfer to groundwater. A test cell, 7 feet by 7 feet and 5 inches in thickness was constructed to simulate a slice of a treatment trench inside the saturated zone of a soil matrix in which hydrocarbon contaminants were to be biologically degraded. This physical model, referred to as a Vertical Slice Test Cell, VSTC, was constructed to evaluate oxygen pick up by the flowing anaerobic groundwater after the injection of oxygenated microbubbles or sparged air into the soil matrix, see Figures 4.1 and 4.3. The oxygen would subsequently be used by the aerobic microbes as the primary electron acceptor. A vertical column was constructed and used to further represent a segment of the slice along the direction of the

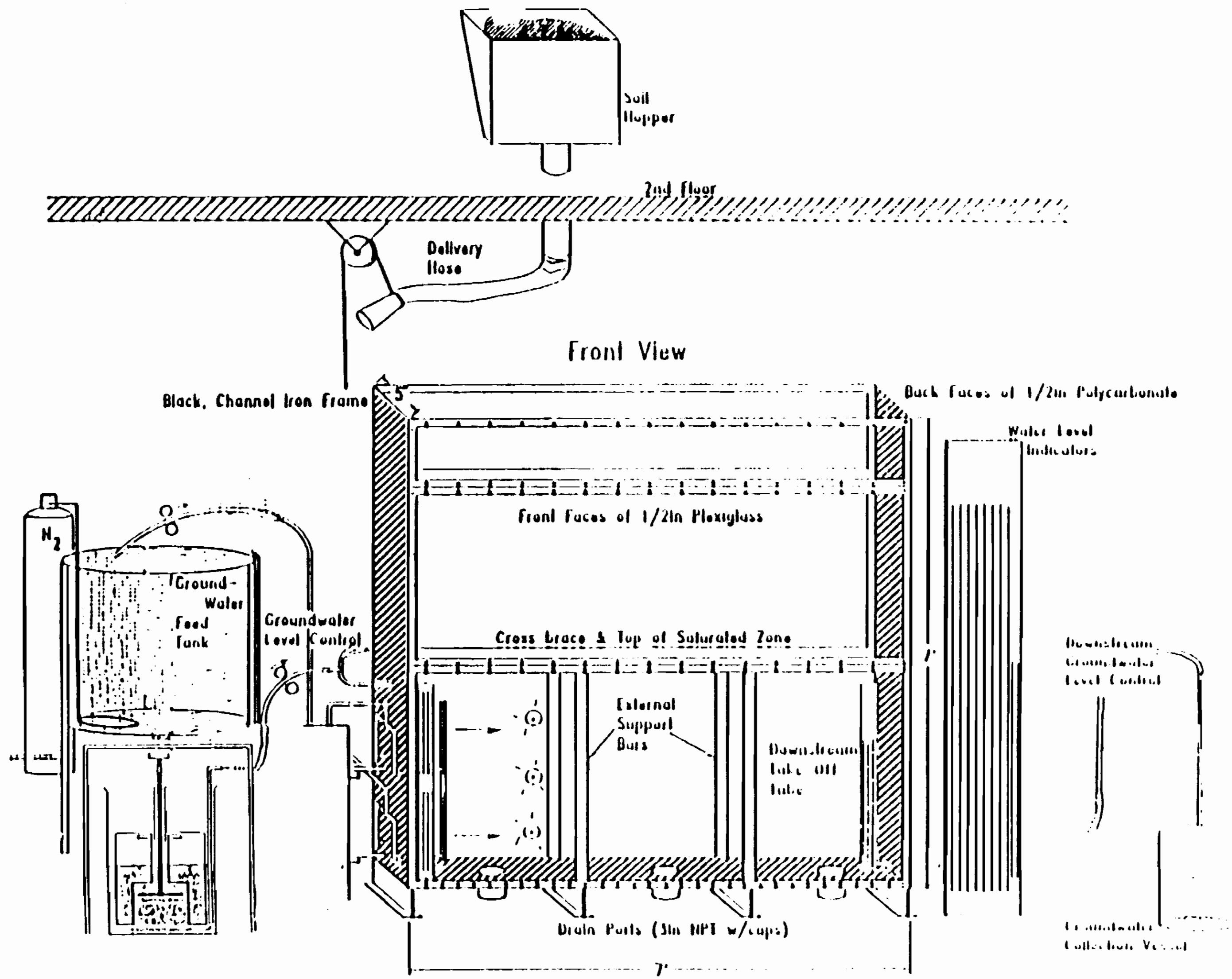

Figure 4.3 Vertical Slice Test System - Major component Layout

flow through the microbubble injection zone. The fundamentals of oxygen transfer to the water phase in the soil matrix were studied by utilizing the Vertical Column and further correlating the results with the Vertical Slice Test Cell, see Figure 4.7.

4.2.1 Vertical Slice Test Cell

The efficiency of transfer of oxygen gas to the water phase, after the injection of oxygen microbubbles and sparged air, was evaluated in the Vertical Slice Test Cell shown in Figure 4.1. This apparatus was a modified version of an existing system first designed by Fugate (1984) and later modified by Smith (1988). Michelsen, et al., 1990 used this system to further investigate the efficiency of air microbubbles in transferring oxygen into the water phase. Hence, two fundamental modifications were addressed in this system:

1. The mode of injection (changed from air-CGA to oxygen-CGA and sparged air.
2. Physical changes (location of injection ports, presence of barriers and inclusion of an impervious layering system,as shown in Figures 4.2 and 4.5.

The system simulated a two dimensional change in the levels of dissolved oxygen in the x, y plane assuming the changes in the width of the VSTC (5") to be negligible. The skeleton of the cell was made of welded iron bars covered by 3/4 inch polycarbonate sheets. The cell was loaded via a soil hopper located directly above the cell. Figure 4.3 presents this system in more detail. The 7 feet long test cell with about 4 feet of saturation height (water and sand) and 3 feet of unsaturated zone height (sand, some water and air) was supported by a 9 inch wide, 3/8 inch thick steel plate 9 feet in length. The frame of the cell was made of 1/4 inch flat iron welded to the base. Four crossbolts connect the cross beams of the front and back panels as shown in Figure 4.3. The frame was then mounted on four 7 inch "I" beams.

Inlet and outlet holes 1/2 inch in diameter are drilled on the left and right sides of the frame. Air collection release ports are also located on the left and right sides of the frame as shown only on right side of Figure 4.1. At the base, three equally spaced outlet holes, 3 inches in diameter, are used to empty the cell of sand and water. Hence, the system is top loaded but bottom dumped. The front and the back of the cell is covered by 1/2 inch thick plexiglass and polycarbonate sheets respectively. Through the back face 1/2 inch diameter holes are drilled to accommodate dissolved oxygen and conductivity meter probes. These ports are located at regular intervals as shown in Figure 4.4. For convenience,

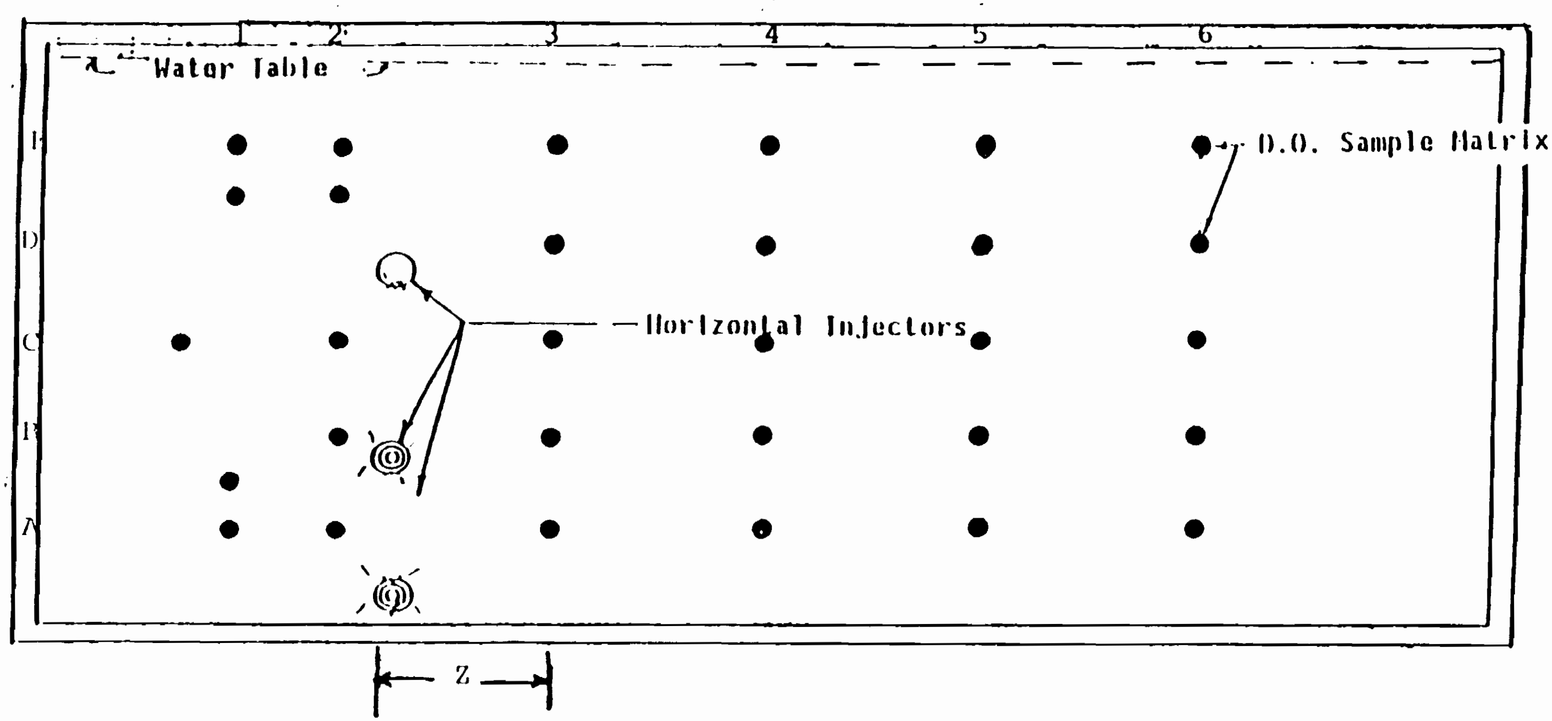

Figure 4.4 Vertical Slice Test Cell: Sampling ports, and injector locations in the back face of the cell. Black dots represent D.O. sampling ports and concentric circles represent CGA injection locations used for Tests 13-19.

these ports are numbered along the length (1-6) and lettered along the height of the saturated zone (A-E). Only two of the three horizontal injectors as shown in Figure 4.4 delivered CGA to the cell in Tests 13-19 (indicated in the test description of this report). Also, an injector matrix as shown in Figure 4.4 was used to inject CGA in Tests 27-31 (as indicated in test descriptions of this report). The changes in hydraulic conductivity were monitored by a set of water level indicators (piezometers) connected to the piezometer ports in the back of the cell but the data from these measurements will earlier data showed reduced hydraulic conductivity as injections continued. Ground water was fed from two tanks into the cell by a peristaltic pump after nitrogen gas was sparged in the tanks and D.O. was reduced to less than one. Tap water was used as ground water.

4.2.2 Microbubble and Sparged Air Delivery Systems

A detailed description of the delivery system has been given by Smith (1988). However, an overview of the system with modifications for this experiment will be presented here. This system was also used to deliver microbubble and sparged air to the vertical column used for oxygen transfer in this report.

The surfactant solution was prepared in a 17 liter graduated vessel. A peristaltic pump transported the surfactant solution to the microbubble generator via 1/4 inch tygon tubing. Oxygen was supplied from an oxygen capsule and a blanket of oxygen was maintained over the solution (a brief description of the microbubble generator will follow). The air was also sparged, bypassing the microbubble generator, by an air calibrated peristaltic pump into the soil matrix via distributors.

Distributor injection tubes were PVC tubes 4 inches long, 3/4 inch in diameter with 1/8 inch holes equidistant from each other about the circumference of the PVC tubes. A 150 mesh stainless steel screen was held in place around the PVC tubing by plastic utility straps. The lower two PVC-screened injectors as shown in Figure 4.1 were used for Tests 13-19 in the Vertical Slice Test Cell. In Tests 27-31, out of a matrix of nine injectors, two injectors were used. These injectors were four inch long aquarium air stones 1/4 inch in diameters. See Figure 4.5 for locations of these injectors. A similar distributor was used in the Vertical Column Test Cell (as in the PVC-screened distributors) except the tube was hard plastic 1/4 inch in diameter, 3 1/2 inches in length with 1/32 inch holes peripherally drilled and wrapped with 150 mesh screen as in PVC-screened distributors.

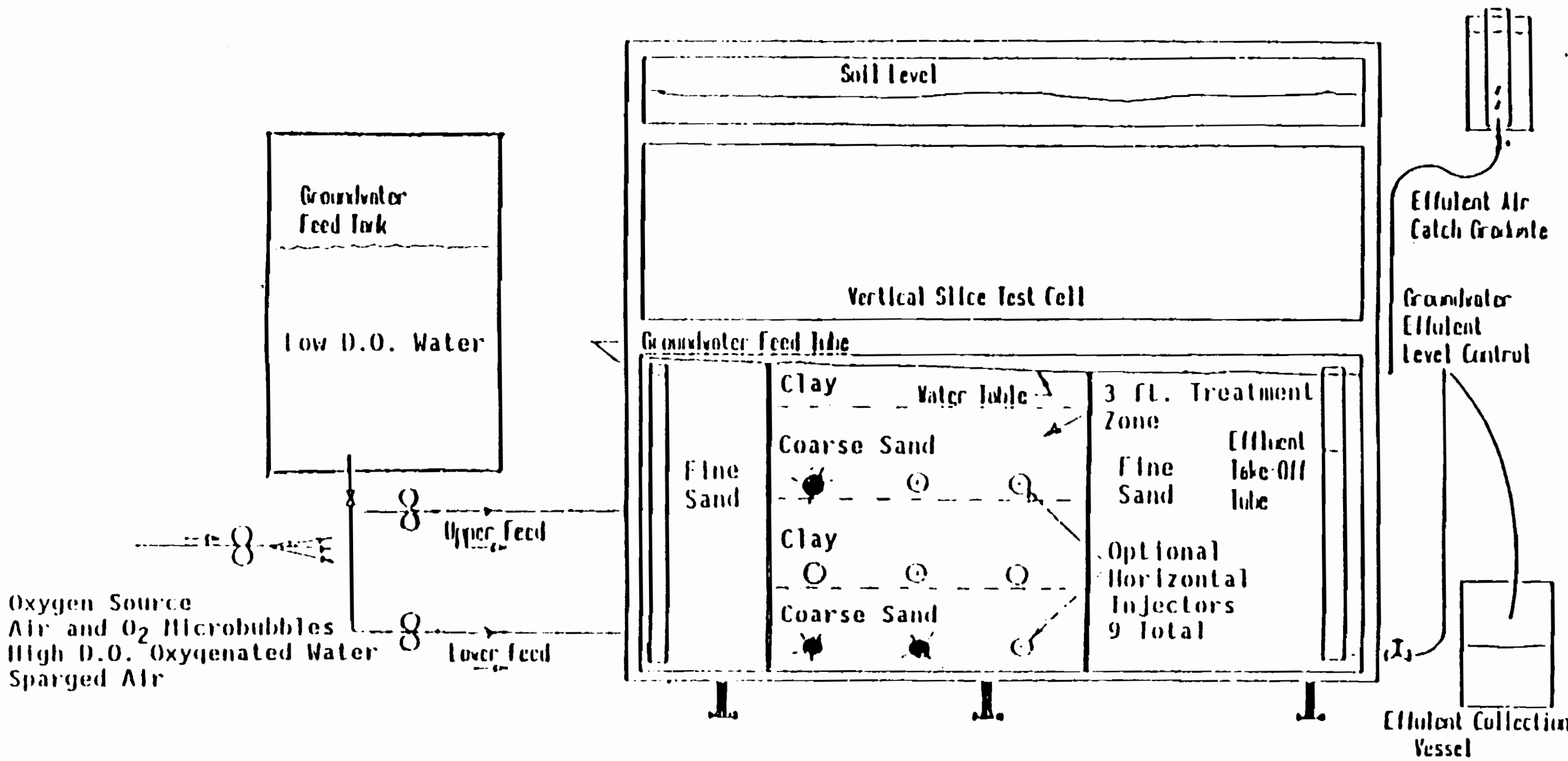

Figure 4.5 Vertical Slice Test Cell Schematic: Treatment Zone Modification for O_2 Microbbuble Injection. The filled circles represent injectors used in Tests 27-31. Empty circles are optional injectors not used in these experiments.

4.2.3 Microbubble Generator

The spinning disc microbubble generator originally developed by Sebba (1987) was used in this experiment. A detailed description of the generator can be found in numerous publications, Sebba (1987), Smith (1988), and Michelsen, et al. (1988). The shearing action between the spinning disk and emplaced baffles imparted the gas into the surfactant solution lamella. Figure 4.6 presents a diagram of CGA generator used in the study. In these experiments oxygen was imparted into the water lamella. This was done by maintaining a blanket of oxygen over the surfactant solution. The top of the generator vessel was covered and a fan was used to keep the bearings cool in order to minimize the risk of fire and explosion in the presence of the pure oxygen.

4.2.4 Vertical Column Test Cell (VCTC)

A tighter balance on oxygen utilization and material balance was maintained in the VCTC. Figure 4.7 illustrates the VCTC. This test apparatus consisted of a 3 3/4 inch diameter plexiglass tube 1/4 inch in thickness and 30 inches in length which was flanged and covered at both ends. The bottom 6 inches of the column was packed with Federal fine sand and plugged with a perforated plate mounted 6 inches above the bottom. The injector, as described in the previous section was 3 inches in length and horizontally placed 3

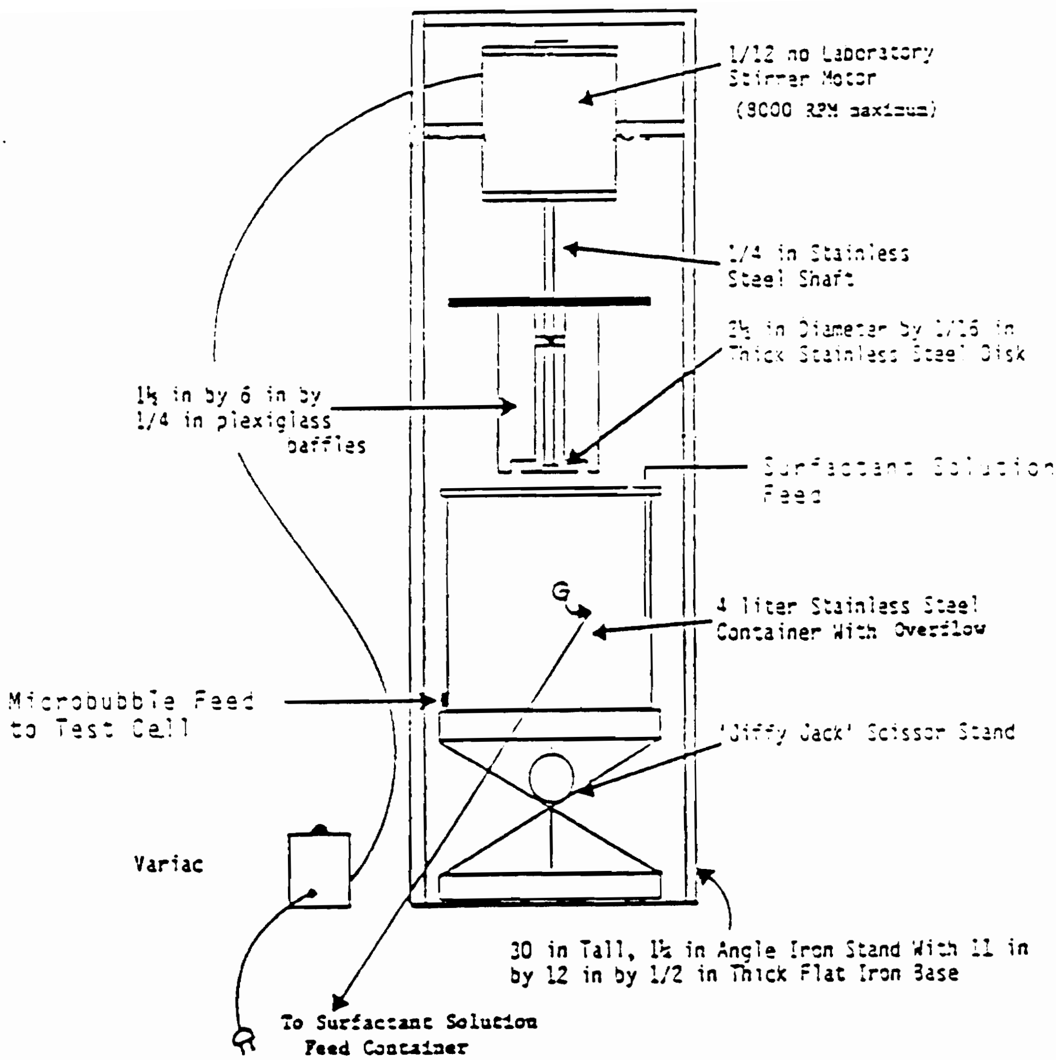

Figure 4.6 Spinning Disk Generator

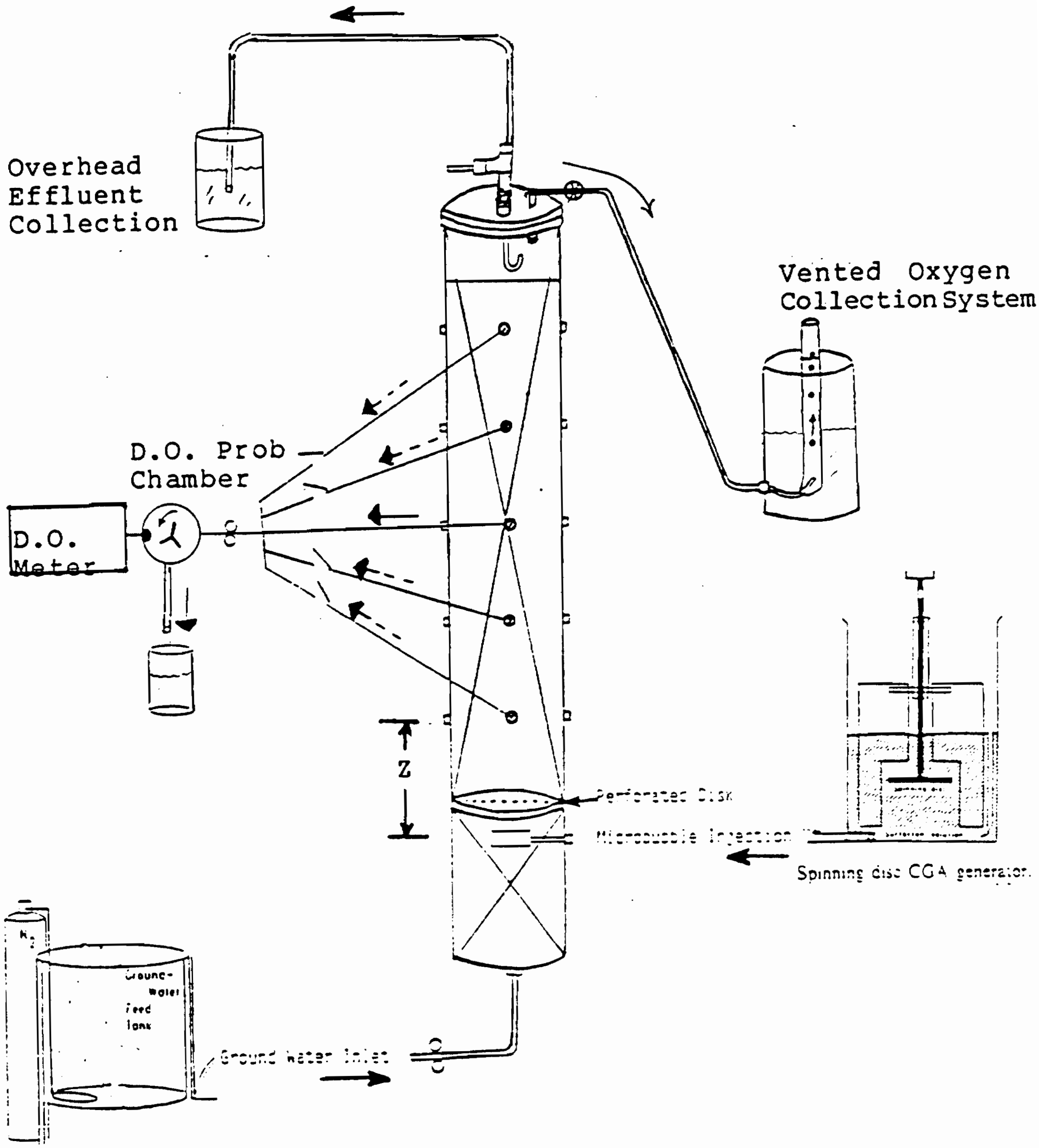

Figure 4.7 Vertical Column Test System - Major Compoent Layout

inches above the bottom through the side of cylinder which covered the length of the diameter of the column. Microbubbles, sparged air and oxygenated water were injected through this injector into the column. Dissolved oxygen ports were drilled 4 inches apart on the same line along the length of the column and 1/4 stainless pipe threads were mounted in the holes. Stainless steel 1/8 inch tubes were mounted in these holes by Swagelok Fittings. Inside the column the stainless steel tubes were covered with a 150 mesh stainless steel screen to prevent the flow of sand into the tubes and on the outside the stainless tubes were connected via Swagelok Fittings into quick connect male nipples. A female nipple was mounted at the inlet of a peristaltic pump which pumped water from the column, via D.O. ports into a D.O. probe chamber and out of the system. The female nipple was connected to each of the male nipple connections as needed for sampling dissolved oxygen from various regions of the column.

Vented gas, the portion of oxygen not transferred to water, was collected at the top of the column and was eventually vented out of the system via an outlet through a 1/8 inch tygon tubing and through a gas valve into an inverted graduate cylinder filled with water. The effluent, was accumulated in a partially filled overhead tank. The water column pressurized the gas and forced it to exit the column when the gas valve was opened. This hydrostatic pressure drained the gas and maintained an accurate measure of the vented gas. As the system was drained of the vented gas, it collected under the inverted cylinder and the volume of gas was read in the cylinder. The gas was vented periodically in this fashion by opening the gas valve.

4.2.5 Packing Material

The packing material, often referred to as soil in this report, was generally a type of sand known as concrete sand with a tannish brown color. This sand was characterized by size and porosity (40%) as shown in Figure 4.8. The sand was from the South River region and was ordered through West Sand Company of Grottos, Virginia. In addition, other packing materials were used either to line the bottom of the cell units or as packing material in the cell for some of the tests. This was the Federal fine, F-70, sand with a size distribution shown in Figure 4.8 from Ottawa Sand Corporation, Ottawa, Illinois.

The clay layer capping the concrete sand cell packing improved the retention. This 10 inch layer, made of 25% bentonite clay, 75% Federal find sand, and water was first mixed into a dough like consistency. The layer was then laid on top of the concrete sand cell-packing by hand. Then an

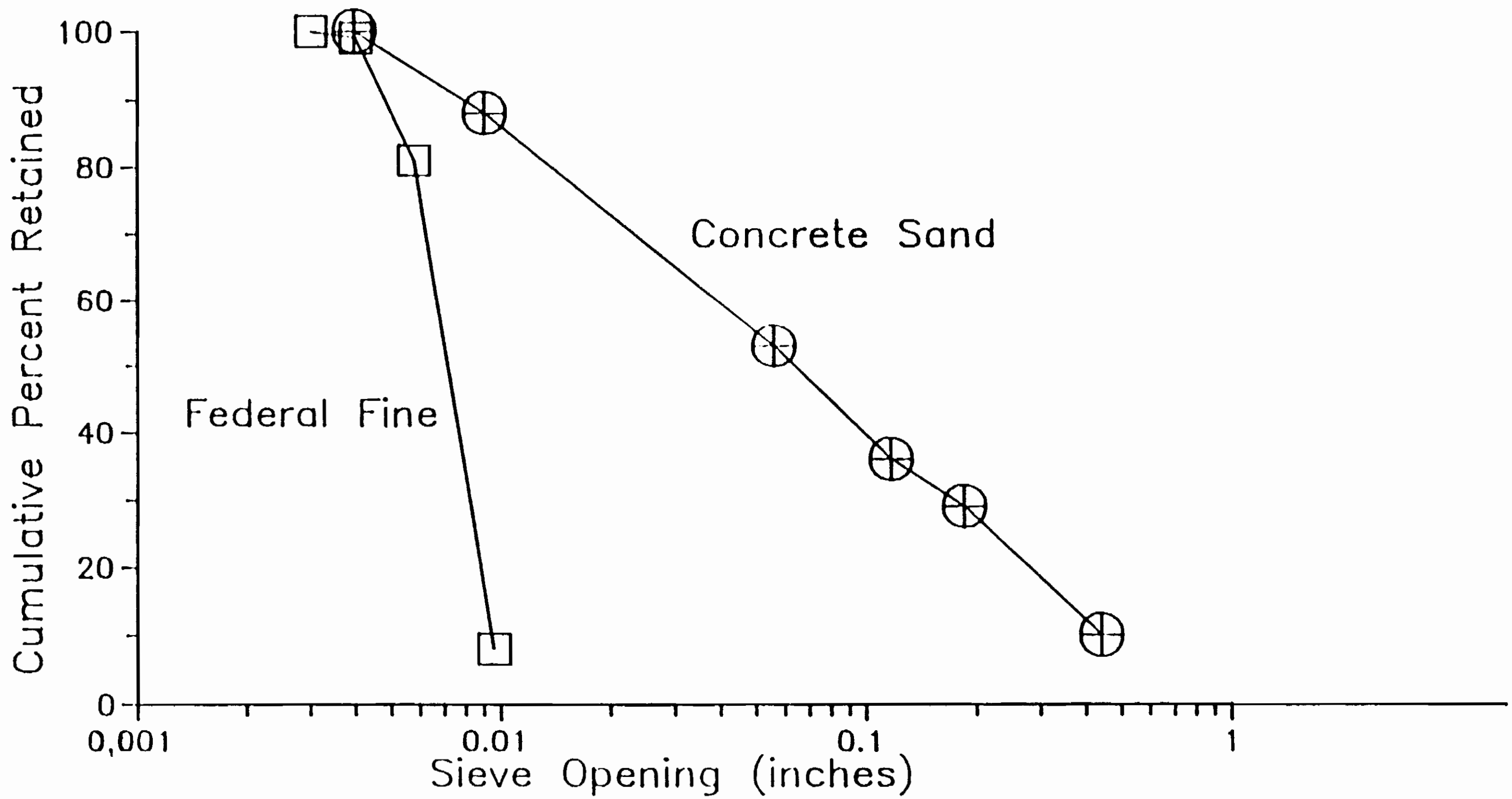

Figure 4.8 Particle Size Distribution of Concrete Sand and Federal Fine Sand

eight inch layer of Federal fine sand was laid on top of the clay layer. Finally three feet of concrete sand was placed on the Federal fine sand layer. Also a plexiglass vertical barrier was placed up flow ahead of the two CGA injector heads with its two windows aligned with the injectors (Test #13 did not have this) as shown in figure 4.2. This barrier was to direct the groundwater flow to pass into the CGA clouds around the injector heads, through the two windows.

4.2.6 Test Procedure

<u>Vertical Slice Test Cell Experiments</u>

For each test run, the test cell had to be 'prepared' in order to meet anaerobic specifications (by lowering D.O. of the water). Before Testing:

1. Prepared test cell by flushing VSTC with low D.O. water.
2. Low D.O. water was prepared by sparging nitrogen into the ground water feed tank.

<u>Day of Test</u>:

1. Record manometer levels at normal flow rate (60-80 ml/min).
2. Increase ground water feed flow rate to about 150~ ml/min to 200.
3. Allow cell to stabilize at high flow rate. Take D.O. of all feed tanks during this time.
4. Record manometer levels at high flow rate.

5. Reduce flow rate (to normal flow rate).
6. Record all D.O.(s)
7. Run CGA injections (See note at the end of the procedure.)
8. Allow cell to stabilize (~10-15 minutes).
9. Record manometer settings.
10. Take D.O.s

Note: After completion of each injection, water in the cell continued to overflow into the effluent tank while there was no ground water flow. When overflow was stopped, the next injection was started until all injections were completed.

All pumps were calibrated by running them at different speeds and measuring the collected water, CGA or air in a graduated cylinder (inverted under water when calibrating air flow).

CHAPTER V

RESULTS

The results of oxygen injection in Vertical Slice Test Cell and Vertical Column Test Cell are presented. As oxygen was injected in these cells by oxygen CGA, sparged air or oxygenated water, the flow rate, amount of oxygen and cell configuration where varied. The changes in dissolved oxygen, the amount of oxygen held up in the cell, the percent oxygen transferred and the rate at which oxygen was transferred were calculated. For the sake of continuity of verbal presentation of discussions, most of the tabulated results and methods of their derivations are appended to this report while graphs and summary tables of results, of more immediate interest, are provided in this section. This study was a part of an on-going investigation of in situ oxygen injections. Some of the injection experiments with their original test numbers are presented in this report.

Three groups of oxygen injection tests were performed, as described in detail previously, group I were the short term tests in VSTC. Group II were the injection tests in VCTC and group III were long term tests in VCTC, multilayered with sand and clay.

5.1 Experimental results of oxygen injection and transfer to water in Vertical Slice Test Cell (VSTC) groups one and three.

5.1.1 Over View of Tests

In Tests #13 and 14, the saturated zone of VSTC was capped by a clay layer in order to improve oxygen retentions in the cell as shown in figure 4.2. In Test #15, the cell packing was replicated as in test #13 with the addition of a vertical barrier with two windows aligned at the CGA injectors positions. In Test #16, air was sparged in the cell. In Test #17, CGA was injected in the cell but the results were inconclusive (as will be explained later).

In Tests #18 and 19 oxygen CGA were injected after the cell was sparged with air in Test #16. Earlier aquarium studies by Foss, et al. (1989) had shown that gas retention was improved when in a series of aquarium injection tests CGA injection was combined with air sparging. In these tests the cell packing was unchanged since the start of Test #15.

The oxygen CGA were injected into the cell at different intervals, durations and flow rates, details of which are given for individual tests.

Tests 27 - 31 were long term tests for determining the effect of intermittent layering of porous sand with impervious clay layer, on retention and oxygen transfer, see Figure 4.5. In these tests, CGA injection intervals, durations, and flow rates were varied. The oxygen transfer to the water phase was above 25% and increased to a maximum of 59%. Test condition details will follow later in this report. Data for tests 13 - 31 are tabulated in Tables 5.3 to 5.11. In these tables the following terms were used:

Duration is the number of minutes for each injection.

Quality is the percent of oxygen dispersion in water.

Stability is the one minute rise (ml) of clear phase at bottom of 250 ml graduate filled with CGA.

Overflow is the weight of water displaced from the cell after each CGA injection (in pounds).

Water out is the overflow converted to gram which is numerically equal to ml.

Water in is the amount of water in the CGA and is found by multiplying percent water by CGA injected in each period of injection.

Oxygen in is found by multiplying quality by the amount of CGA injected in each period of injection, divided by one hundred.

Oxygen holdup is water in minus water out.

Percent retention is oxygen holdup divided by oxygen in times one hundred.

Test parameters and major objectives for each test are also given in each table. Oxygen transfer coefficient, KLa, was also determined for test 13-31. However, due to variations in the quality of data and the availability of desired D.O. readings at a distance 'Z', (6 inches down flow from oxygen injection point) these values should be used for comparative purposes. For this reason KLa(s) will be compared by orders of magnitude rather than exact values. Where D.O. data were not available at the 6 inch distance down flow from oxygen injection points, influent and effluent D.O.(s) were used to determine ΔD.O.(s) and the distance between injections and effluent point was used as Z. For Test #27 and 28 complete sets of data were available at Z = 6 inches and Z = 52 inches and both KLa(s) were computed. It was found that at Z = 6 inches KLa(s) were larger than KLa(s) at Z = 52 inches by one order of magnitude.

5.1.2 Overview of Results

The results of oxygen transfer for Groups I and III of VSTC are summarized in Tables 5.1 and 5.2. A more detailed description of these results can be found in Section 5.1.3. The detailed tabulated results are given in Appendix A. The oxygen transfer coefficients for Tests #27 and 28 are given in Figures 5.1 and 5.2, respectively. A more detailed

Table 5.1. Oxygen Transfer in VSTC Short Term Tests (First Group of Tests)

Test #	Initial %, O_2 hold-up	Total O_2 Injected (mg)	Total O_2 Transferred (mg)	% O_2 (Mass Balance)		
				Initial Loss	Transferred To Water	Unaccounted For
13	42	14614	869.4	58	5.9	36.1
15	62	7107.8	821.6	38	11.5	50.5
18	93	6038	464.7	7	7.6	85.4
19	73	3182	173	27	5.4	67.6

Test #	Cumulated Time (hr)	Total O_2 Transferred/ Total Time (mg/hr)	KLa (hr^{-1}) Avg.
13	28.8	30.2	0.09
15	45.3	18.1	0.08
18	57.0	8.2	0.04
19	71.5	2.4	0.05

Table 5.2. Oxygen Transfer in VSTC Long Term Tests in Multilayered Cell Packing (Third Group of Tests)

Test #	Initial %, O_2 hold-up	Total O_2 Injected (mg)	Total O_2 Transferred (mg)	% O_2 (Mass Balance)		
				Initial Loss	Transferred To Water	Unaccounted For
27	89	2738	794.7	11	29	60
28	46	6000	1830.5	54	30	16
29	47	2978	1005.7	53	34	13
30	42	3005	1786.2	58*	59	0
31	62	3063	1339.7	39	44	18

*Abnormally high due to a low reading of retention

Test #	% O_2 Available to Degrade Hydrocarbons	Cumulated Time (hr)	Total O_2 Transferred/ Total Time (mg/hr)	KLa (hr^{-1}) Avg.**
27	17	133.3	5.94	0.01
28	18	225.0	8.10	0.02
29	22	132.0	7.60	0.02
30	47	250.7	7.20	0.04
31	32	176.7	7.6	0.04

**Equivalent KLa values for Z = 6" was found by multiplying Avg. KLa values at 52" by 10, from Appendix B description of KLa(s) for Tests #13-31 are given in Section 5.1.3 and tabulated results are given in Appendix B.

The short term tests in Group I, included Tests #13-18. In comparing Test #13 with Test #15, it was noted that % O_2 transferred was increased by a factor of 2 (as shown in table 5.1), in Test #15, in which the injected amount of CGA was reduced in half. Since the cell holdup capacity was exceeded in Test #13, its initial holdup was lower, as shown in Table 5.1. Tests 18 and 19, which followed air sparging practice in Test #16, showed increased initial holdups which averaged 93% and 73%, respectively. Tests 13-19 showed that high initial retentions did not correspond to high oxygen transfers to flowing groundwater. As shown in Table 5.1, Oxygen transferred in Tests 18 and 19 were 7.6% and 5.4%, respectively while their retention were higher than Tests 13 and 15. Likewise, in Tests #27-31, as Shown in Table 5.2, high initial holdups did not translate into high oxygen transfers. In fact, these results showed the opposite.

Oxygen mass balance for Tests #13 to 31 is also summarized in Tables 5.1 and 5.2. The initial % O_2 loss is the difference between 100% (total) oxygen injected and the % initial retentions. When % O_2 transferred and % initial O_2 loss are subtracted from the total injection (100%), the percent O_2 unaccounted for is found. The % unaccounted for can be the oxygen which is in the gas form and is still available to be transferred to the water phase or it can be the oxygen which has escaped from the cell starting a few days after the injection and throughout the time period D.O.'s were being read. Despite sodium azide treatment some biological activity might still use up some of the unaccounted for oxygen.

The initial oxygen loss for Test #13 was highest, 58%, as shown in Table 5.1 and as the injection amount was reduced in half in Test #15, the initial loss was reduced to 38%. Tests #18 and #19, which were injected after the sparging VSTC with air in Test #16 had low initial losses but oxygen transfer did not significantly improve.

For Test #27, initial loss was the lowest, but % unaccounted for was the highest. For Test #30, the initial % O_2 lost seems to be abnormally high due to low initial retentions reported. Test #31 in which CGA were injected in the lower sand layer (same as Test #30) showed a lower initial loss and a relatively lower % unaccounted oxygen. Hence, when oxygen was injected deeper in the sand matrix, as in Tests #30 and #31, the percent initial loss as well as percent unaccounted for were lower.

The surfactant in CGA, if biodegradable, exerts BOD on the system. Roughly 12% of total O_2 injected would be used by aerobes to degrade a 150 ppm surfactant solution. Therefore, % O_2 available to degrade hydrocarbons would be 12% minus % O_2 transferred. As shown in Table 5.2, % oxygen available to aerobes follows the same trend as % O_2 transferred. Also, when total mg O_2 transferred is divided by cumulated time (in hour), mass transfer per time (mg/min) is found. The mass transfer per unit time did not follow the same trend as % O_2 transfer which followed a more erratic trend.

Comparing Tests #13 and #15, the mass transfer per time was highest in Test #13, 30.2 mg/hr, in which almost two times as much CGA was injected, as shown in Table 5.1. The average KLa values did not follow this trend.

When comparing Tests #27 and 29 which had the same amount of CGA injections and similar test conditions, it was noted that Test #29 had a higher value for mass transfer per time. Tests with the highest % O_2 transferred did not have the highest mass transfer per unit time. In fact, the highest mass transfer per unit time was noted for Test #28 which had almost the lowest % O_2 transfer.

The average KLa values for Tests #13-19 seemed to be higher than Tests #27-31 as shown in Tables 5.1 and 5.2. However, the tests with nearly equal injection amounts of CGA in both groups had nearly equal average KLa(s) (with some exceptions).

Figures 5.1 and 5.2 show the variations in KLa values for Tests #27 and #28, respectively. The KLa values were one order of magnitude higher in the lower sand layers than in upper sand layers in both tests. Also, KLa values in test #28, in which CGA injections were doubled, were higher, by about one order of magnitude, than Test #27, while oxygen transfer period was also doubled in Test #28. Test #27 showed a more sustained level for KLa values over a period of 100 hours with only one injection episode. Figure 5.2 shows that the level of KLa values in Test #28 were not as sustained as in Test #27 but it took about 200 hours of continuous groundwater flow to reduce KLa values by one order of magnitude. These results, although not conclusive, suggest that oxygen microbubbles transfer oxygen in a time-released manner to the flowing groundwater. This is in contrast to sparging with air or pure oxygen or even injecting hydrogen peroxide in the soil matrix in which there seems to be no control in holding up oxygen gas in the saturated zone. Due to breakthroughs (gas escape routes) in the upper layer of

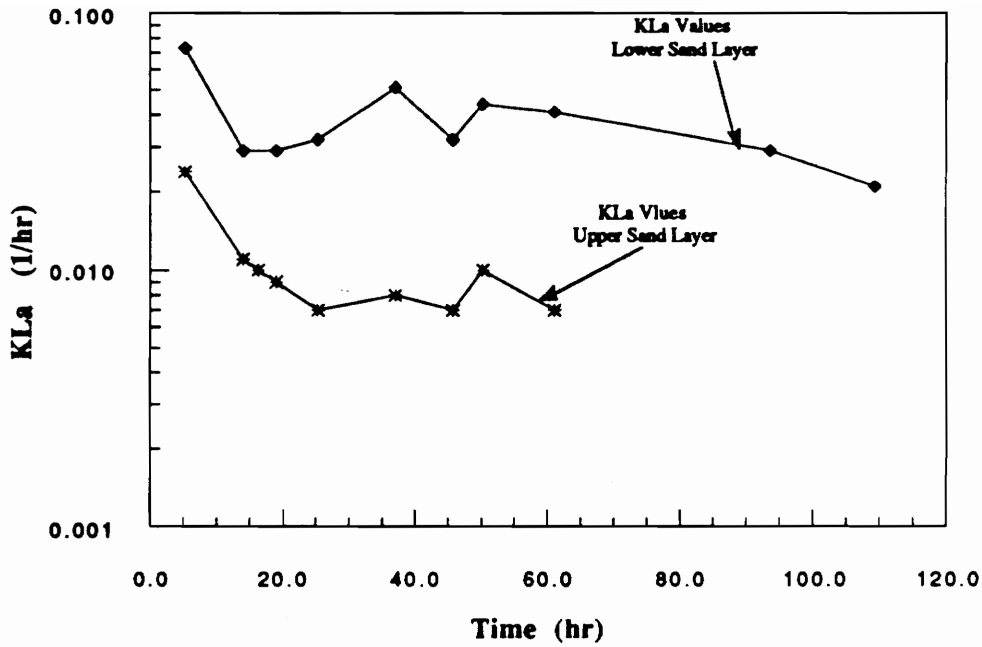

Figure 5.1 Test #27 variation of oxygen transfer coefficient (KLa) with respect to cumulative time after injection of oxygen CGA.

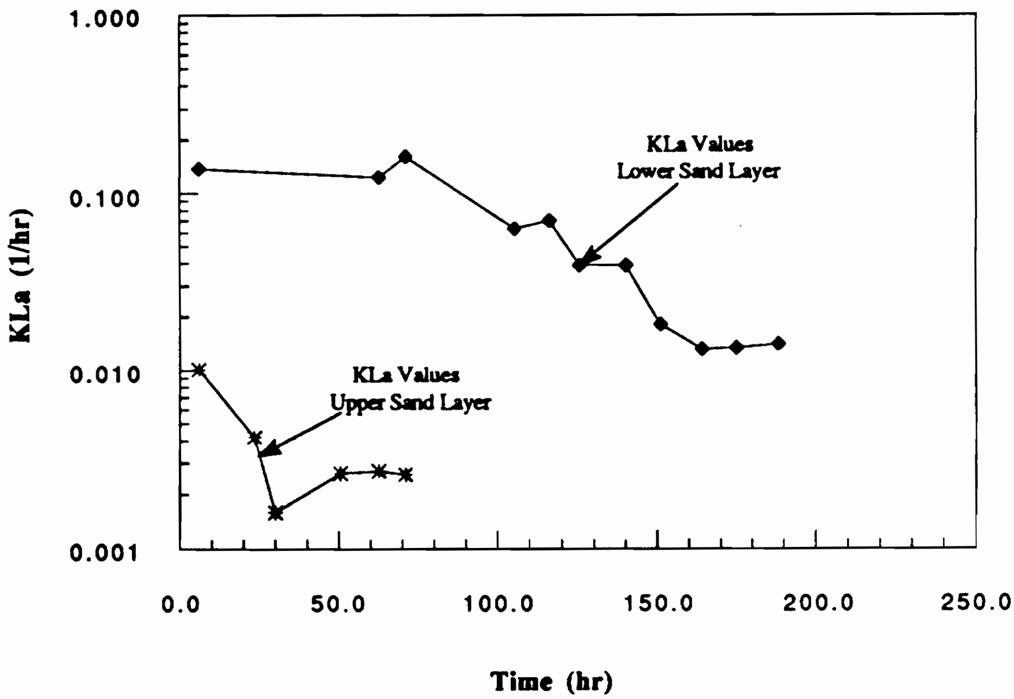

Figure 5.2 Test #28 variation of oxygen transfer coefficient (KLa) with respect to cumulative time after injection of oxygen CGA.

sand, however, the KLa(s) in the upper layer were lower than the lower layer in both tests.

5.1.3 Detailed Description of Tests 13-31

Test #13, Determination of VSTC holdup capacity and the effect of the clay layer on gas retention and oxygen transfer to the water phrase:

Table 5.3 presents the data for test #13. In the first 3 injections, percent retentions were relatively high, in the 70(s). Retention started to decline after the third injection and was low between the fifth and the eighth injections. Hence, cell capacity was reached when the fourth injection was completed. Relative to the results given by Smith (1988) who did not use a barrier, the clay barrier was effective. Figure 5.3 contrasts experimental oxygen retention with theoretical lines for 100% and 50% retention.

Oxygen transferred to the water phase, in milligrams, was determined by multiplying groundwater flow (liter/min.) by time interval for that flow (min.) and by the changes in dissolved oxygen, D.O., (mg/liter) during the interval. ΔD.O. was the difference in D.O. of effluent and influent groundwater. Table 5.1 and in more detail Table A.1 in

Table 5.3 Test # 13 , retention of oxygen after injection of oxygen CGA into VSTC soil matrix: The cell was overload with CGA.

Injection#	1	2	3	4	5	6	7	8
Time	10:15	10:24	10:34	10:45	10:55	11:06	11:17	11:27
Duration (min)	2.75	2.75	2.75	2.75	2.75	2.75	2.75	2.75
Quality%	70	70	70	70	70	70	68	68
Overflow (lbs)	3.75	3.75	3.6	2.7	1.9	2.0	1.5	1.9
Water Out (ml)	1703	1703	1637	1226	863	908	681	863
Water In (ml)	600	600	600	600	600	600	640	640
Oxygen In	1400	1400	1400	1400	1400	1400	1360	1360
Oxygen Holdup	1103	1103	1034	626	263	308	41	223
%Retention	79	79	74	45	19	22	3	16

Test Parameters:
- Spinning Disk generator was modified for oxygen CGA generation.
- 200 ppm Na DBS surfactant solution.
- Low D.O. water in cell prior to injection.
- G.W. flow stopped during injection.
- 10" clay cap, topped by 6" F-70 sand below the water table.
- Cell was flushed/treated with 0.2 g/l sodium azide to prohibit microbial growth.
- CGA flow rate 727 ml/min.
- Cells did not contained a vertical physical barrier near the injectors.

Objectives:
- To determine the effectiveness of a clay barrier to increase retention.
- To test the effect of oxygen CGA in increasing D.O. in cell (oxygen CGA was first used in this test).

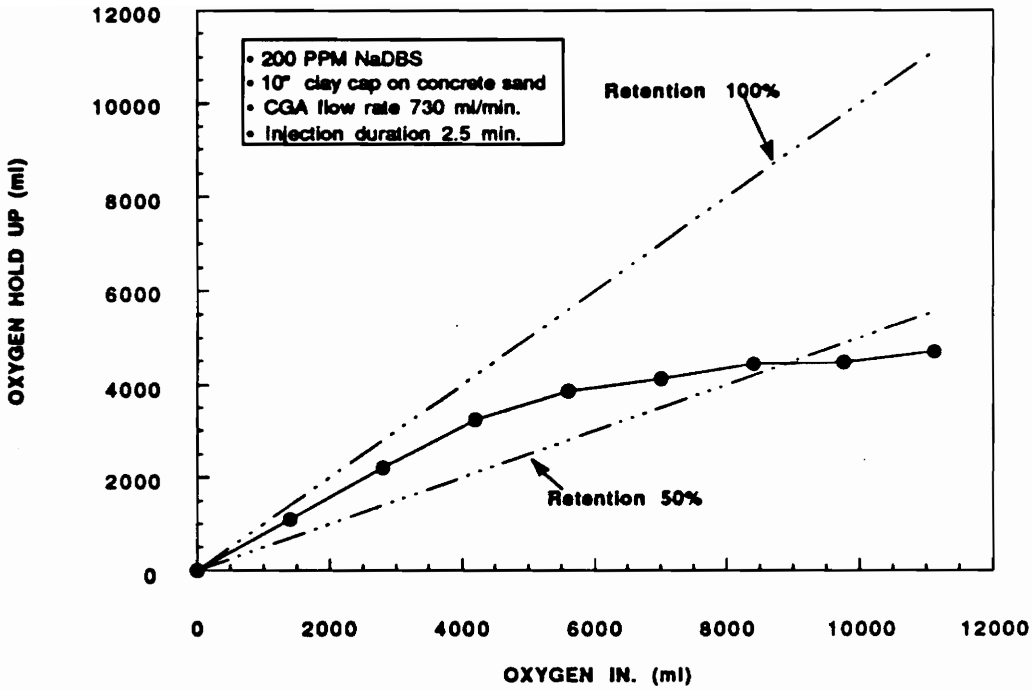

Figure 5.3 Test # 13 retention of oxygen in the VSTC after injection of oxygen CGA in the concrete sand matrix: Cell capacity for gas holdup was exceeded, eight injections were made.

Appendix A present oxygen transfer values for Test #13. In this test 14614 mg O_2 was injected in the form of CGA and 870 mg O_2 was transferred to the water phase. Only 5.9% of the oxygen was transferred.

The oxygen transfer coefficients, KLa(s), are given in Appendix B. Table B1 gives initial KLa values ranging from 0.10 to 0.17 hr^{-1} and eventually falling to 0.04. These are among the highest KLa values in this report, by two orders of magnitude, which reflect the highest volumes of CGA, 16 liters, injected in the cell.

Test #14, Determination of oxygen transferred by sparging air in the VSTC:

A total of 4429 mg of oxygen was sparged in the cell and only 54 mg O_2 was transferred to the water phase. Hence only 0.13% oxygen was transferred. The KLa values ranged from 0.05 to 0.11 hr^{-1} (see Table B.2, Appendix B). The VSTC was emptied after the D.O. readings were collected.

Test #15, Determination of VSTC oxygen holdup capacity and oxygen transfer with horizontal clay layer and vertical barrier emplaced:

Oxygen injection was reduced in half compared with test #13 but oxygen transfer was doubled. Also noticed was a reduction in percent retention in injections #3 and #4 from 74 and 48 in Test #13, to 58 and 38 in Test #15. Table 5.4 shows percent retentions and the test parameters. CGA flow rates were lower in Test #15 than Test #13, at 700 ml/min. but duration of injection was slightly higher in Test #15. It was previously determined that cell holdup capacity for gas was reached after four 2-liter injections, hence only 4 injections were made during Test #15. Figure 5.4 compares experimental oxygen retention with theoretical oxygen retention of 50 and 100% for Test #15.

Table 5.1 and in more detail Table A2 of Appendix A presents oxygen transfer values for Test #15. A total of 17078 mg O_2 was injected in the cell and 822 mg O_2 was transferred. Hence oxygen transfer was 11.5%. The KLa values are given in Appendix B, Table B3. The values range from 0.016 to 0.06 hr^{-1} for a Z (oxygen transfer distance), of 6 inches. These values are reduced by one order of magnitude compared to Test #13. As noted before, the volume of CGA injected was reduced in half (7924) in Test #15 while percent retention was similar to Test #13. Test #18, Determination of VSTC gas holdup capacity and oxygen transfer pretreated with air sparging:

Table 5.4 Test # 15 retention of oxygen after injection of oxygen CGA into VSTC soil matrix: CGA volume was reduced.

Injection#	1	2	3	4
Time	9:38	10:05	10:20	10:42
Duration (min)	2.83	2.83	2.83	2.83
Quality%	70	69	68	69
Overflow (Ibs)	3.5	3.75	3.125	2.5
Water Out (ml)	1589	1703	1418	1135
Water In (ml)	595	615	635	615
Oxygen In	1388	1368	1348	1368
Oxygen Holdup	994	1088	784	520
%Retention	72	80	58	38

Test Parameters:

- Spinning Disk generator was modified for oxygen CGA generation.
- 200 ppm Na DBS surfactant solution.
- Low D.O. water in cell prior to injection.
- G.W. flow stopped during injection.
- 10" clay cap, topped by 6" F-70 sand below the water table.
- Cell was flushed/treated with 0.2 g/l sodium azide to prohibit microbial growth.
- CGA flow rate 700 ml/min.
- Cell contained a vertical physical barrier near the injectors with two windows aligned with CGA injectors to for the G.W. flow through the CGA clouds and the windows.

Objectives:
- To evaluate the effect of a forced flow of water through oxygen CGA cloud.
- To evaluate the effect of reduced volume of oxygen CGA injection.

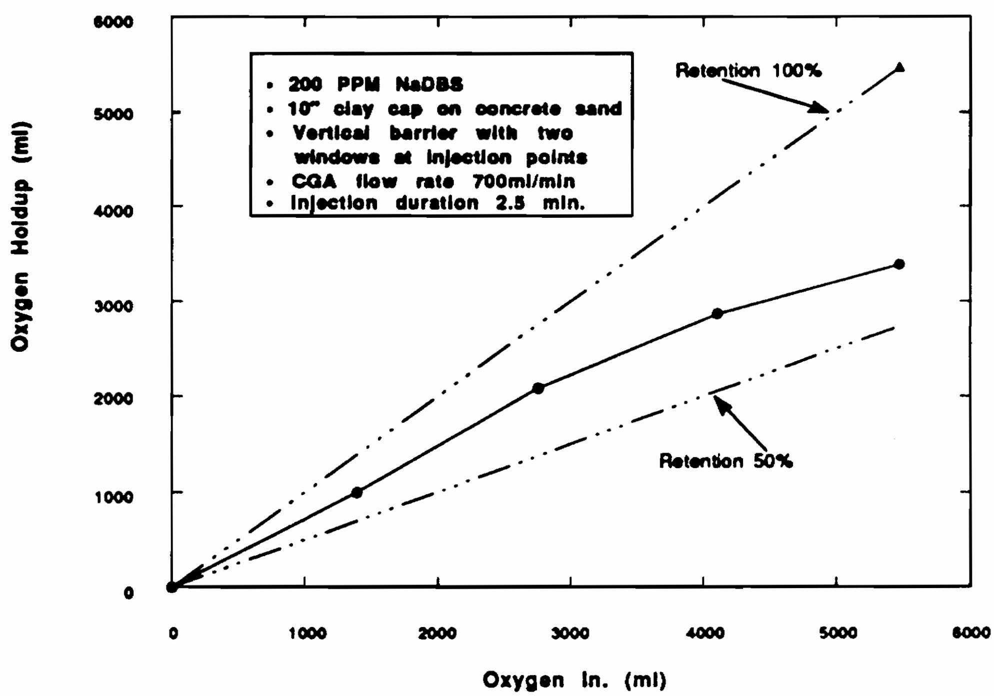

Figure 5.4 Test # 15 retention of oxygen in the VSTC after injection of oxygen CGA in the concrete sand matrix: Effect of slightly reduced CGA injection rate and four injection of CGA in contrast with Test # 13.

Previously, air sparging had developed breakthroughs in the clay layer evidenced by visual inspection. Hence the concern over oxygen retention capability of the cell was seemingly justified. However, it was noted that quite the opposite of the expectations had happened and oxygen holdup was actually increased. This was in agreement with results by Foss, et al. (1989) which showed increases in air retention in his aquarium tests after supplementing CGA injections with air injections in the same injector head (sparging).

The explanation, even though subjective, offered here is that the air bubbles had actually sealed the breakthrough paths temporarily and to the point that CGA injected in subsequent tests, could not escape via the breakthrough paths. Table 5.5 and Figure 5.5 show almost 100 percent retentions, even in injections 48 hours apart during two injection episodes in test #18. In this test injection duration was 1.5 minutes and CGA flow rate was 600 ml/min, giving a CGA injected volume almost half as much as in Test #13. One would expect that with such a high degree of retention oxygen transfer would also be high. Table 5.1 and Table A.3 of Appendix A showed that 7.6% oxygen was transferred to the water phase. Compared to Test #15 transfer was somewhat lower.

Table 5.5 Test # 18 retention of oxygen after injection of oxygen CGA into VSTC soil matrix with prior air sparging in the cell: Air sparging could be responsible for high gas retentions.

Injection#	1	2	3	4	1	2	3	4
Time	9:25	9:37	9:50	10:00	11:00	11:15	11:25	11:40
Duration (min)	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Quality%	64	65	63	55	67	67	67	67
Overflow (lbs)	1.75	1.875	1.875	2.125	2.0	1.75	1.875	1.875
Water Out (ml)	795	851	851	965	908	795	851	851
Water In (ml)	324	315	333	405	297	297	297	297
Oxygen In	576	583	567	495	603	603	603	603
Oxygen Holdup	471	536	516	560	611	498	554	554
%Retention	82	92	91	113	100	83	92	92

Test Parameters:

- Spinning Disk generator was modified for oxygen CGA generation.
- 200 ppm Na DBS surfactant solution.
- Low D.O. water in cell prior to injection.
- G.W. flow stopped during injection.
- 10" clay cap, topped by 6" F-70 sand below the water table.
- Cell was flushed/treated with 0.2 g/l sodium azide to prohibit microbial growth.
- CGA flow rate 600 ml/min.
- Cell contained a vertical physical barrier near the injectors with two windows aligned with CGA injectors to force the G.W. flow through the CGA clouds and the windows.

Objectives:

- To evaluate the effect of two CGA injection episodes 48 hours apart, on the oxygen retention, the high retentions could be due to prior air sparging.

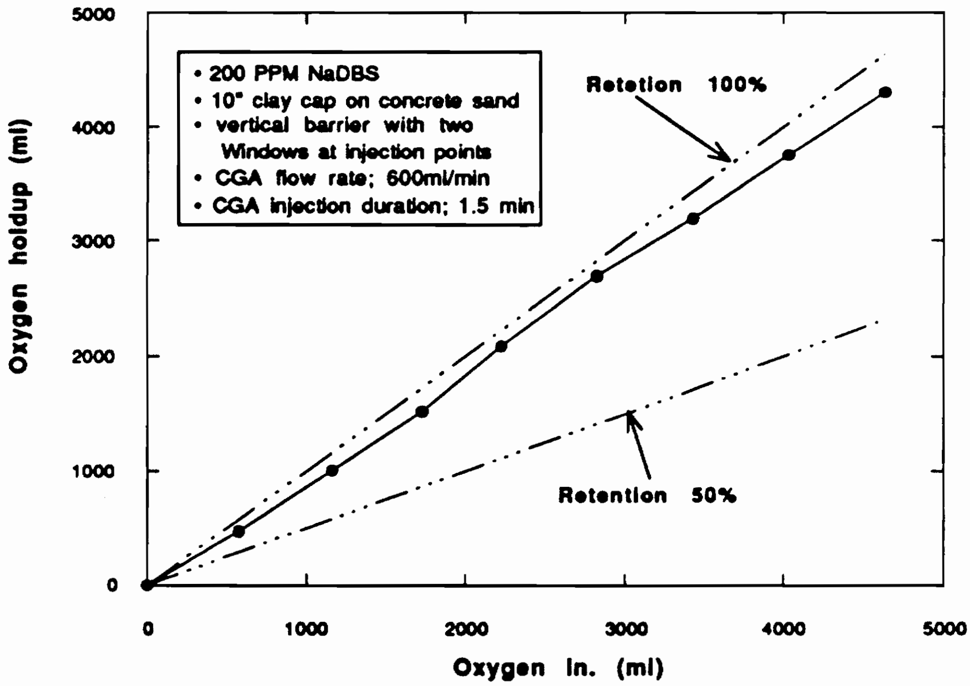

Figure 5.5 Test # 18 retention of oxygen in the VSTC after injection of oxygen CGA in the concrete sand matrix: Effect of air sparging/CGA injection on gas holdup in the cell. Two episods of injection 48 hours apart at 4 injection per episod.

The results of CGA injection in Test #17 which immediately followed the air sparging, (which will not be given because the results were inconclusive due to overall retention measurements of 175%) further supports the explanation that air sparging improved oxygen retention. The retention measurements were based on displacement of water from the cell. The volume of displaced water was 1.75 times greater than the volume of CGA injected. Therefore, it was concluded that due to previous air sparging the effluent pipe was clogged by the air bubbles forcing the water table to rise above the pip outlet. The effluent pipe finally had unclogged during the injections of Test #17 and drained the excess water above the level of effluent pipe. This resulted in erroneously high retention results. The usefulness of these results is in the fact that even the water flow in the effluent pipe was clogged by air bubbles, supporting the earlier explanations for high retention as a result of air clogging. The KLa Values for Test #18 are given in Tables 5.1 and B4 of Appendix B. The range is from 0.016 to 0.063 hr^{-1} and the magnitudes are similar to Test #15.

Test #19, Determination of VSTC gas holdup capacity and oxygen transfer: Effect of sustained injections on oxygen transfer:

Table 5.6 and Figure 5.6 again show a high percent retention of oxygen in Test #19, 83%, however, oxygen transfer was lower than Test #18, 5.4%, as shown in Tables 5.1 and A4, Appendix A.

The KLa values were in the same range as in Test #18 at 0.038 - 0.054 hr^{-1}, as shown in Table B5 the Z value for Tests 13-19 was 6 inches.

Test #27, #28, and #29, Determination of VSTC oxygen holdup and oxygen transfer using horizontal multi-layering of clay with concrete sand upon injection of CGA in each concrete sand layer:

Table 5.7 and Figure 5.7 show percent retention of oxygen when CGA were injected in the layered concrete sand matrix in Test #27. The layering, by constricting the flow, directed the groundwater through the CGA 'cloud' formed around the CGA injector heads. Also, the configuration of layers of concrete sand alternated with the impervious clay layers which capped the concrete sand layers reduced gas escaping from the layers. The percent retention in test #27, ranged from 110 to 72, at a CGA flow rate of 600 ml/min. For the four injections, the injection duration ranged from 1.12 to 1.30 minutes. Oxygen transfer over 29% was realized in this test, see Table 5.2 and

Table 5.6 Test # 19 retention of oxygen after injection of oxygen CGA into VSTC soil Matrix with prior air sparging: Effect of sustained testing.

Injection#	1	2	3	4
Time	10:50	11:05	11:10	11:15
Duration (min)	1.5	1.5	1.5	1.5
Quality%	68	70	67	66
Overflow (lbs)	1.25	1.75	1.75	1.75
Water Out (ml)	567	794	794	794
Water In (ml)	288	270	297	306
Oxygen In	612	630	603	594
Oxygen Holdup	279	524	497	488
%Retention	46	83	82	82

Test Parameters :

- Spinning disk generator was modified for oxygen CGA generator.
- 200 ppm NaDBS surfactant solution.
- Low D.O. water in cell prior to injection.
- G.W. flow stopped during injection.
- 10" clay cap, topped by 6" F-70 sand below the water table.
- Cell was flushed / Treated with 0.2 g/l sodium azide to prohibit microbial growth.
- CGA flow rate 600 ml/min.
- Cell contained a vertical physical barrier near the injectors with two windows aligned with CGA injectors to force the G.W. flow through the CGA clouds and the windows.

Objectives:

- To duplicate the results of test # 18 (1st episode).
- To evaluate the effect of reduced CGA flow rate and duration with the vertical physical barrier in place.
- To further evaluate the effect of sustained flow with periodic injection of CGA (this was done at the end of the one month period).

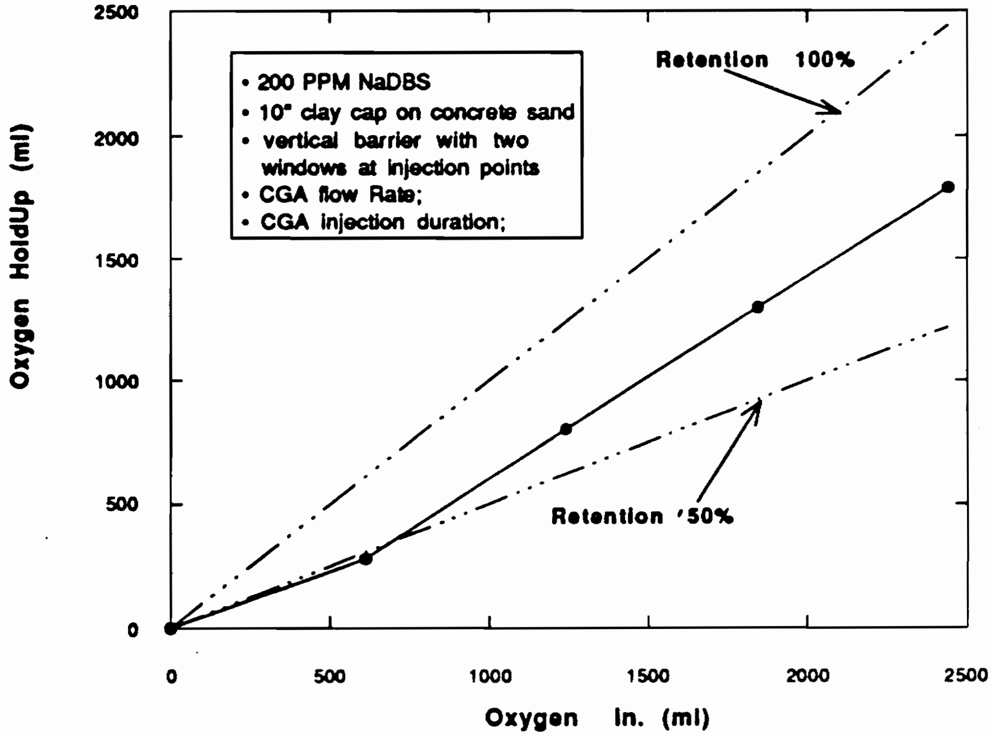

Figure 5.6 Test # 19 retention of oxygen in the VSTC after injection of oxygen CGA in the concrete sand matrix: Effect of sustained CGA injection on gas holdup. One episod of four injections were made.

Table 5.7 Test # 27, retention of oxygen after injection of oxygen CGA into VSTC layered with concrete sand and clay: Injections were made in both sand layers.

Injection#	1	2	3	4
Time	12:05	1:15	2:15	3:15
Duration (min:sec)	1:30	1:30	1:120	1:120
Quality%/ stab	64/10	68/6	65/10	62/11
Overflow (lbs)	1.12	3.14	1.18	6.77
Water Out (ml)	794.5	964.7	737.7	721
Water In (ml)	324	288	315	274
Oxygen In	576	612	585	447
Oxygen Holdup	470.5	676.7	422.7	379
Flow (ml/min)	600	600	600	643
%Retention	82	110	72	85

Test Parameters:
- Spinning Disk generator was modified for oxygen CGA generation.
- 150 ppm surfactant solution (3:1 Tergital (Nonionic)/(Anionic)).
- Low D.O. water in cell prior to injection.
- G.W. flow stopped during injection.
- Cell was flushed/treated with 0.2 g/l sodium azide to prohibit microbial growth.
- Intermittent layering of concrete sand with clay

Objectives:
- To evaluate oxygen transfer in the multilayered sand and clay systems.
- To improve gas retention.
- To force the water flow to pass through the CGA cloud.

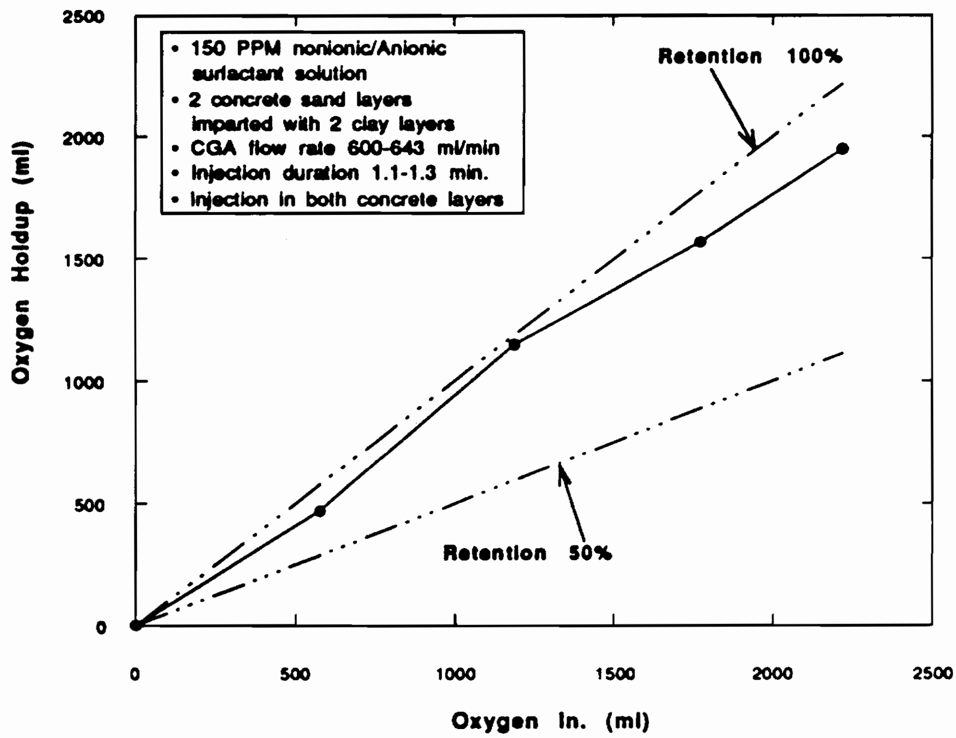

Figure 5.7 Test # 27 retention of oxygen in the multilayered cell packing in the VSTC after injection of oxygen CGA in both concrete sand layers.

for further detail see Tables 5.1 and A5, Appendix A. The KLa values ranged from 0.021 to 0.082 hr^{-1} as shown in Table B6, Appendix B, for Z = 6 inches and were reduced by one order of magnitude for Z = 52 inches when influent, effluent D.O.(s) were used to calculate KLa(s).

Table 5.8 and Figure 5.8 show the percent retentions of oxygen in test #28. A comparison of Tests #27 and #28 showed that when volume of injected CGA was doubled the percent retention was halved. The doubling of the CGA injection volume resulted in KLa(s), as shown in Table 5.2 and in more detail in Table B7 of Appendix B, one order of magnitude higher than Test #27 in the lower sand layer and at least one order of magnitude lower in the upper sand layer.

When the amount of injected CGA was doubled it was evidenced from the results of the retention that over half of the injection had broken through the cell, possibly through the newly formed breakthrough paths in the upper layers of sand and clay. Oxygen transfer of 30% was achieved in Test #28 as shown in Tables 5.2 and A6, Appendix A.

Test #29 was a repeat of Test #27, with the same amount of CGA injected. The cell holdup capacity was reduced in Test #29 see Table 5.1. Table 5.9 and Figure 5.9 show that

Table 5.8 Test # 28, retention of oxygen after doubling the injection of oxygen CGA into VSTC layered with concrete sand and clay compared with test #27. : Injections were made in both sand layers.

Injection#	1	2	3	4
Time	2:31	3:31	4:31	5:31
Duration (min)	2:5	2:5	2:5	2:5
Quality%/ stab	63/10	67/8	65/10	64/10
Overflow (Ibs)	2:14	5:8	8:00	10:2
Water Out (ml)	1305	1192	1135	965
Water In (ml)	656.7	585.7	628.2	630
Oxygen In	1118	1189	1166	1120
Oxygen Holdup	648	606	507	335
Flow (ml/min)	710	710	718	700
%Retention	57	51	43	30

Test Parameters:
- Spinning Disk generator was modified for oxygen CGA generation.
- 150 ppm surfactant solution (3:1 Tergital (Nonionic)/Polystep/A-7 (Anionic)).
- Low D.O. water in cell prior to injection.
- G.W. flow stopped during injection.
- 10" clay cap, topped water table.
- Cell was flushed/treated with 0.2 g/l sodium azide to prohibit microbial growth.
- Intermittent layering of concrete sand with clay.

Objectives:
- To evaluate oxygen transfer in the multilayeredsand and clay systems.
- To improve gas retention.
- To force the water flow to pass through the CGA clouds.

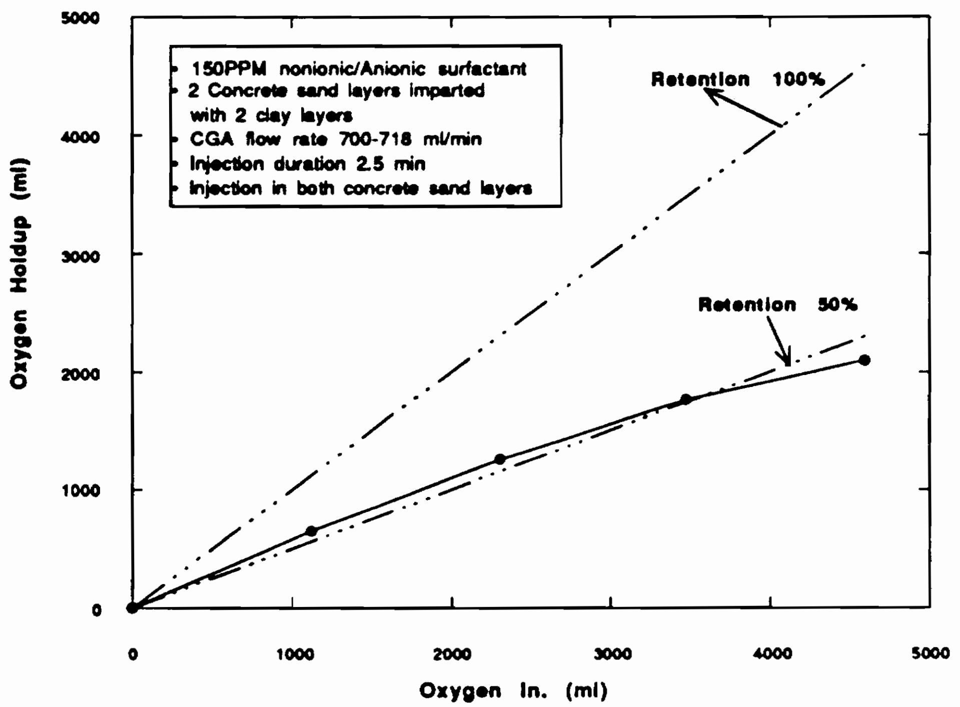

Figure 5.8 Test # 28 retention of oxygen in the multilayered cell packing in the VSTC after doubling the injection of oxygen CGA in both concrete sand layers, compared to Test # 27.

Table 5.9 Test # 29, retention of oxygen after injection of oxygen CGA into VSTC layered with concrete sand and clay, same injection as in test 27: Injections were made in both sand layers.

Injection#	1	2	3	4
Time	11:10	12:25	1:20	2:10
Duration (min)	1.5	1.5	1.5	1.5
Quality%/ stab	62/14	63/12	63/12	64/13
Overflow (lbs)	1.125	1.5	1.37	1.38
Water Out (ml)	511	681	624	626
Water In (ml)	342	352	327	324
Oxygen In	558	600	557	576
Oxygen Holdup	148	329	297	302
Flow (ml/min)	610	635	590	600
%Retention	30	54	53	52

Test Parameters:
- Spinning Disk generator was modified for oxygen CGA generation.
- 150 ppm surfactant solution (3:1 Tergital Nonionic/PolystepA.7(Anionic)).
- Low D.O. water in cell prior to injection.
- G.W. flow stopped during injection.
- Cell was flushed/treated with 0.2 g/l sodium azide to prohibit microbial growth.
- Intermittent layering of concrete sand with clay

Objectives:
- To evaluate oxygen transfer in the multilayered sand and clay system.
- To improve gas retention.
- To evaluate the effect of sustained CGA injection and compared with test # 27.

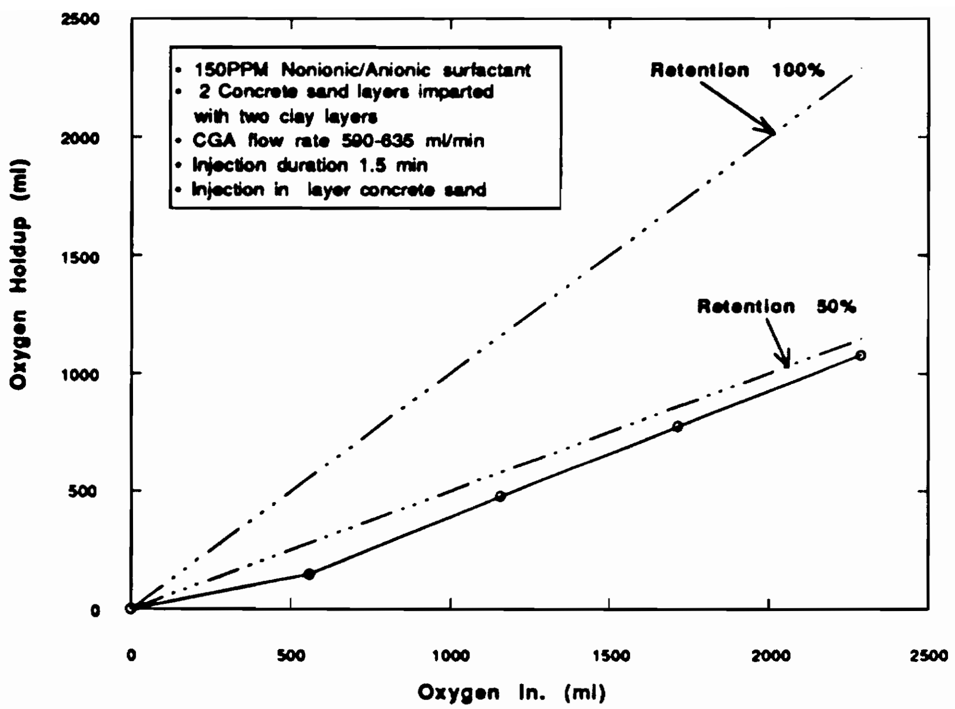

Figure 5.9 Test # 29 retention of oxygen in the multilayered cell packing in the VSTC after injection equivalent amount of oxygen CGA, as in Test # 27 in the two concrete sand layers.

percent retention, ranged from 30 to 52, compared to 72 to 110 for Test #27. As long as breakthroughs were kept to a minimum by controlled yet sufficient CGA injection, the retention remained high. Table B8 of Appendix B shows the KLa values for Test #29. Since dissolved oxygen data for Z = 6 inches were not available for this test, the dissolved oxygen data for Z = 52 inches were used to calculate KLa(s) and compared with those in test #27 at Z = 52. Similar magnitudes are found in both tests. The oxygen transfer for Test #29 was 34% as shown in Tables 5.2 and A7, Appendix A.

Test #30 and 31, Determination of VSTC oxygen holdup and oxygen transfer by injecting CGA only in the lower layer of concrete sand in the multilayered system:

Table 5.10 and Figure 5.10 present percent retention of oxygen injection of CGA in Test #30. Injection duration was from 1.5 to 2 minutes and flow-rate varied from 630 to 975 ml/min. The high flow rate of 975 ml/min might have been responsible for the low retention (16%) in the last injection in Test #30. Also the 16% seems to be abnormally low since 59% of the injected oxygen was transferred to the water phase as shown in Tables 5.2 and A8, Appendix A, never the less retention range from 67 to 16 percent. The oxygen transfer coefficient, KLa, was only available for Z = 52 inches and it ranged, for most

Table 5.10 Test # 30, retention of oxygen after injection of oxygen CGA into the lower VSTC concrete sand layer.: Continued injections in the original cell packing as in test # 27.

Injection#	1	2	3
Time	1:45	3:45	4:45
Duration (min)	1.5	1.5	2.0
Quality%/ stability	64/14	63/12	62/17
Overflow (Ibs)	1.56	3.10	4.70
Water Out (ml)	709	699	607
Water In (ml)	324	374	479
Oxygen In	576	638	781
Oxygen Holdup	385.4	324	128
Flow (ml/min)	635	975	630
%Retention	67	51	16

Test Parameters:
- Spinning Disk generator was modified for oxygen CGA generation.
- 150 ppm surfactant solution (3:1 Tergital (Nonionic)/PolystepA.7 (Anionic)).
- Low D.O. water in cell prior to injection.
- G.W. flow stopped during injection.
- Cell was flushed/treated with 0.2 g/l sodium azide to prohibit microbial growth.
- Intermittent layering of concrete sand with clay
- Injection of CGA only in lower concrete sand layer through two injectors.

Objectives:
- To evaluate oxygen transfer in the multilayered sand and clay system.
- To improve gas retention by injecting in the lower sand layer only.
- To evaluate the effect of sustained CGA injection.
- To force the water to pass through the CGA cloud.

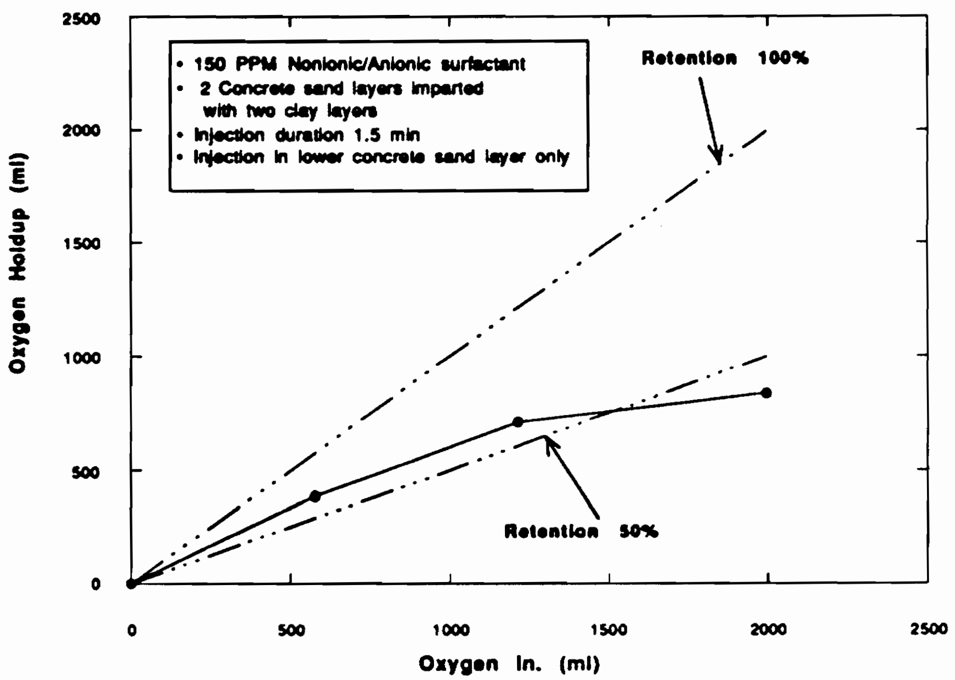

Figure 5.10 Test # 30 retention of oxygen in the multilayered cell packing in the VSTC after injection equivalent amount of oxygen CGA, as in Test # 27 in the lower concrete sand layer via two horizontal injectors.

values, between 10^{-4} - 10^{-3} hr $^{-1}$. These KLa values are very encouraging when compared with those of Test #27 and seem to have yielded slightly higher KLa(s). Also, it was noted that the KLa values in Test #27, for Z = 6" and Z = 52" were different by 1 to 2 orders of magnitude. Assuming that the same difference in orders of magnitude existed for Z = 6 inches and Z = 52 inches in Test #30, then KLa values in Test #30 for Z = 6" can be estimated to range from 0.013 to 0.064, when only one order of magnitude of adjustment was used for Test #30. Table B.9 of Appendix 13 presents these results.

Test #31 is a repeat of Test #30, injecting CGA only in the lower concrete sand layer, however in this test a more regular injection schedule was followed. Gas retention ranged from 78 to 49 percent, which showed a definite increase compared to Test #30 (See Table 5.11 and Figure 5.11). The oxygen transferred to the water phase was 40%, as shown in Tables 5.2 and A9, Appendix A. The KLa(s) ranged for most values between .0017 to .0055 hr^{-1} for Z = 52 inches and if adjusted for Z = 6 inches the range would be 0.017 to 0.055 hr^{-1} which is also in agreement with other tests (see Table B10, Appendix B).

Table 5.11 Test # 31, retention of oxygen after injection of oxygen CGA into the lower VSTC concrete sand layer.: Continued injection in the original cell packing as in test # 27.

Injection#	1	2	3	4
Time	10:45	11:45	12:45	2:45
Duration (min:sec)	1.5	1.5	1.5	1.5
Quality%/ stab	61/8	63/10	62/11	57/11
Overflow (Ibs)	1.875	1.625	1.375	1.75
Water Out (ml)	851.25	732.75	624.25	794.5
Water In (ml)	380	338.5	346.6	468.9
Oxygen In	604.5	576.4	561.8	621.6
Oxygen Holdup	471	399.2	277.7	325.6
Flow (ml/min)	650	612	603	727
%Retention	78	69	49	52

Test Parameters:

- Spinning Disk generator was modified for oxygen CGA generation.
- 150 ppm surfactant solution (3:1 Tergital Nonionic/PolystepA.7 Anionic.
- Low D.O. water in cell prior to injection.
- G.W. flow stopped during injection.
- Cell was flushed/treated with 0.2 g/l sodium azide to prohibit microbial growth.
- Intermittent layering of concrete sand with clay.
- Injection of CGA in both concrete sadnd layers.
- Injection of CGA only in lower concrete sand layer through 2 injectors.

Objectives:

- To evaluate oxygen transfer in the multilayered sand and clay system.
- To improve gas retention by injecting in the lower sand layer only.
- To evaluate the effect of sustained CGA injection.
- To compare withj test # 30.

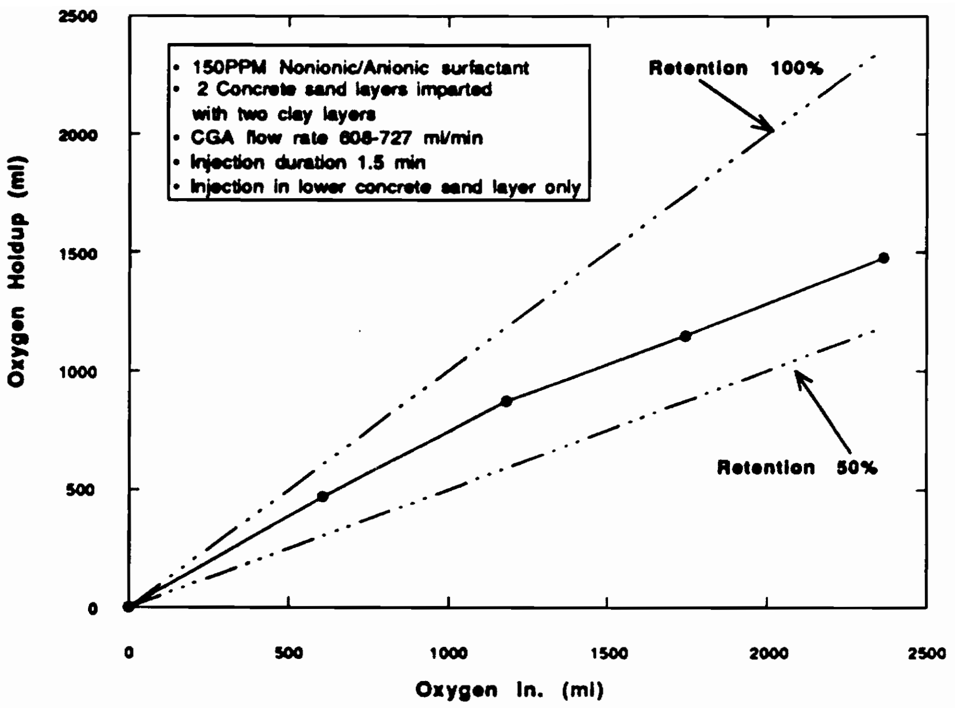

Figure 5.11 Test #31 retention of oxygen in the multilayered cell packing in the VSTC after injecting equivalent amount of oxygen CGA as in the Test #27 in the lower concrete sand layer via two horizontal injectors.

5.2 EXPERIMENTAL RESULTS OF OXYGEN INJECTION AND TRANSFER TO WATER IN VERTICAL COLUMN TEST CELL (VCTC)

5.2.1 Overview of Results

Oxygen CGA, sparged air and oxygenated water were injected in the VCTC packed with concrete sand, as described before. These experiments were evaluated by calculating oxygen transfer rates and percentages of oxygen transfer to the water phase, after injecting CGA, sparged air and oxygenated water into the sand matrix. Oxygen transfer efficiencies between these modes of oxygen deliveries were compared.

Procedure for calculating oxygen transfer and tabulated results found in Appendix E are the same as in Appendix A. Also the tabulated results of KLa values and dissolved oxygen profiles for Vertical Column Test Cell are given in Appendix C. The procedure for finding KLa values for VCTC are the same as in Appendix B. All KLa values are determined based on a Z value of 6 inches as indicated on Figure 4.7. The computer program in Appendix D was used to calculate these values.

A major weakness in the experimental design was the frequent sampling which resulted in over draining of the cell. Also, the high sampling frequency resulted in removal of the dissolved oxygen from the system. Hence, the material balance on these tests are not as tight as they were hoped to have been. However, these results are only presented for comparative purposes and show interesting trends.

The vertical column experiments were designed to evaluate the effect of forcing the groundwater flow through the oxygen source, i.e. the CGA 'cloud'. These tests were performed to establish the feasibility of designing a multi-layering sand/clay system in the Vertical Slice Test Cell. This feasibility was established when oxygen transfers in excess of 37% were realized in the Vertical Column Test Cell and KLa values one order of magnitude greater than KLas in VSTC were realized. Tests #27 through 31 using alternating layers of sand and clay were consequently designed based on the findings in VCTC experiments, and the results were already presented in this report.

Table 5.12 presents the mass transfer results of Tests 1-8. The total oxygen injected was relatively constant in these test, with the exception of Test #2, and ranged between 80 to 109 mg. The total O_2 transferred is the mg O_2 actually transferred to the water phase. The total O_2 transferred and vented column in Table 5.12 is the amounts of oxygen transferred to water phase and collected in gas form. The percent unaccounted for, is the portion of the oxygen which

Table 5.12 Oxygen Transfer in VCTC (second group of tests)

Test #	Total O_2 Injected (mg)	Total O_2 Transferred (mg)	Total O_2 Transferred and Vented (mg)	% O_2 (Mass Balance)		
				Transferred to Water	Transferred and Vented	Unaccounted For
1	-	-	-	-	-	-
2	198	37	103	18.6	52.0	47.0
3	93	30	30	32.0	32.0	68.0
4	80	7	-	8.0	-	-
5	109	45	66	41.0	60.0	40.0
6	-	-	-	-	-	-
7	-	-	-	-	-	-
8	96	32	35.8	33	37	63

Table 5.12 (continued)

Test #	% O_2 Available to Degrade Hydrocarbons	Cumulated Time (hr)	Total O_2 Transfer/Total Time (mg/hr)	Avg. Kla (hr^{-1})
1	-	3.3	-	0.22
2	6.6	2.5	14.8	0.40
3	20.0	2.7	11.1	0.26
4	0	2.2	3.2	0.05
5	29.0	8.2	5.5	0.18
6	-	2.5	-	0.07
7	-	3.3	-	0.14
8	21	4.2	7.6	0.17

Remarks:

- Test #1, 220 ml CGA injected
- Test #2, 220 ml CGA injected
- Test #3, 110 ml CGA injected
- Test #4, 110 ml CGA injected
- Test #5, 110 ml CGA injected (maximum quality and stability)
- Test #6, Oxygen and water injection
- Test #7, Air sparged, 588 ml
- Test #8, 110 ml CGA injected less frequent D.O. sampling

was not transferred and was not collected under the graduate cylinder.

Comparing Tests #2 and 3, Table 5.12 shows that injected oxygen was almost reduced in half from 198, in Test #2, to 93 mg in Test #3 and oxygen transfer was doubled in Test #3. The average KLa value was reduced from 0.4 hr^{-1}, in Test #2, to 0.26 hr^{-1} in Test #3. Oxygen transferred per unit time was higher (14.8 mg/hr) in Test #2.

The quality and stability were high in Test #5 and lower in Test #4. Since the same amount of CGA were injected in the cell, Test #4 with the lower quality yielded less oxygen injected (80 mg). Oxygen transferred was 8% in Test #4 while it was 41% in Test #5. Test #5 had 29% of injected oxygen available (12% of O_2 Transferred was to degrade the surfactant) for the aerobes while Test #4 had no oxygen available for the aerobes. Oxygen transferred per unit time was higher (5.5 mg/hr) in Test #5 than in Test #4 (3.2 mg/hr). The average Kla value was higher by one order of magnitude in Test #5 (0.18 hr^{-1}) than in Test #4 (0.05 hr^{-1}) as shown in Table 5.12. In these tests the D.O. readings were Terminated when Δ D.O. approached zero.

5.2.2 Detailed Description of Results

In Test's #1 and 2, 220 ml CGA were injected into the concrete sand matrix (see Tables C1 and C2, Appendix C). Both tests showed high vent losses, an indication that cell was becoming overloaded by CGA. In the subsequent test #3 when CGA volume was reduced, vent losses became negligible as shown in Table 5.12 and Tables E1 and E2, Appendix E. Test #1 showed sudden vent losses of over 50 percent and D.O. profile between ports 1 and 5 increased only in the first two hours. Test #2 showed gradual vent losses, and the D.O. profile beyond 2 hours varied from 6 to 13.6 to 3.4 mg/l. The KLa(s) ranged from 0.646 to 0.187 hr^{-1}, as shown in Tables C1 and C2, Appendix C. The oxygen transferred to water phase in Test #2 was 18.6% and oxygen plus vent losses were 52% as shown in Figure 5.12 Table E.1, and Appendix E. Figure 5.12 also shows cumulative millimoles of O_2 transferred and vented with respect to time. Oxygen transfer results for Test #1 were inconclusive because D.O. reading were incomplete. The unaccounted portion of total O_2 injected was 48% as shown in Figure 5.12.

In Test #3 the volume of CGA injected into the cell was reduced to 110 ml (from 220 ml in test #2). No vent losses were observed as shown in Figure 5.13 and Table 5.12 (also see Table C.3, Appendix C). The D.O. profiles increased with

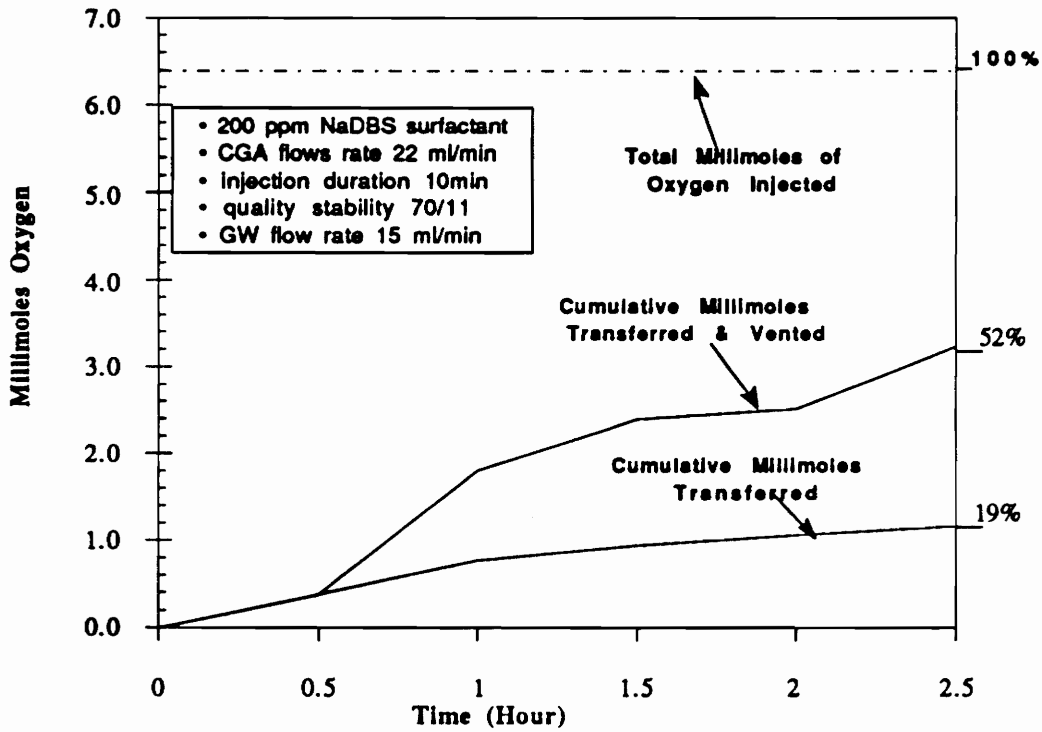

Figure 5.12 Test #2 Oxygen transfer and material balance in the packed Vertical Column Test Cell after injection of 220 ml oxygen CGA in the sand matrix: Effect of over loading the sand matrix with CGA; considerablevolume of CGA was vented out of the sand due to over loading.

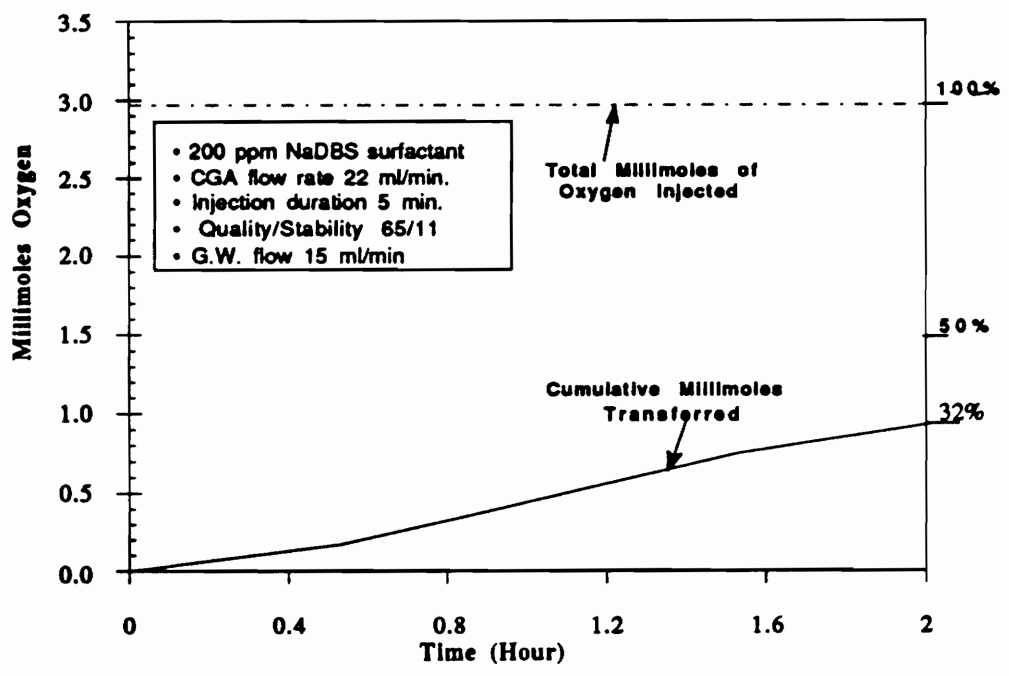

Figure 5.13 Test #3 Oxygen transfer and material balance in the packed Vertical Column Test Cell after injection of 110 ml oxygen CGA in the sand matrix: Effect of reduced volume of CGA injection compared with test # 2; volume of CGA injected was reduced in half, consequently no vent losses were realized.

time. For example at 70 minutes only port No. 1 showed an elevated D.O. and at 100 minutes ports No 1 and 2 showed elevated D.O.(s), and so on. This orderly increase in D.O. from port to port was indicative of plug flow reaction due to movement of high D.O. water and not due to upward movement of O_2 gas ahead of water front (rather than oxygen bubbles running upward through the cell). This meant that microbubbles were localized. The oxygen transfer, as shown in Tables 5.12 and E.2, Appendix E, was 32%. Figure 5.13 shows cumulative values of O_2 with respect to time. The percent unaccounted for is 68%. The KLa(s) ranged from 0.311 to 0.187 hr^{-1}, slightly lower than Test #2 (Table C.3).

Test #4 is a duplicate of Test #3, except the quality and stability were reduced from 65% and 11 to 57% and 19 respectively (high number for stability indicates a less stable dispersion) the oxygen transfer for test #4 is given in Figure 5.14. D.O. profiles, as shown in Table C.4, were reduced and showed no significant transfer. The KLa(s) were also lower than Test #3, by almost one order of magnitude as shown in Tables 5.12 and C.4. The oxygen transfer, as shown in Tables 5.12 and E.3, was 8.2%. Figure 5.14 shows cumulative oxygen transfer with respect to time.

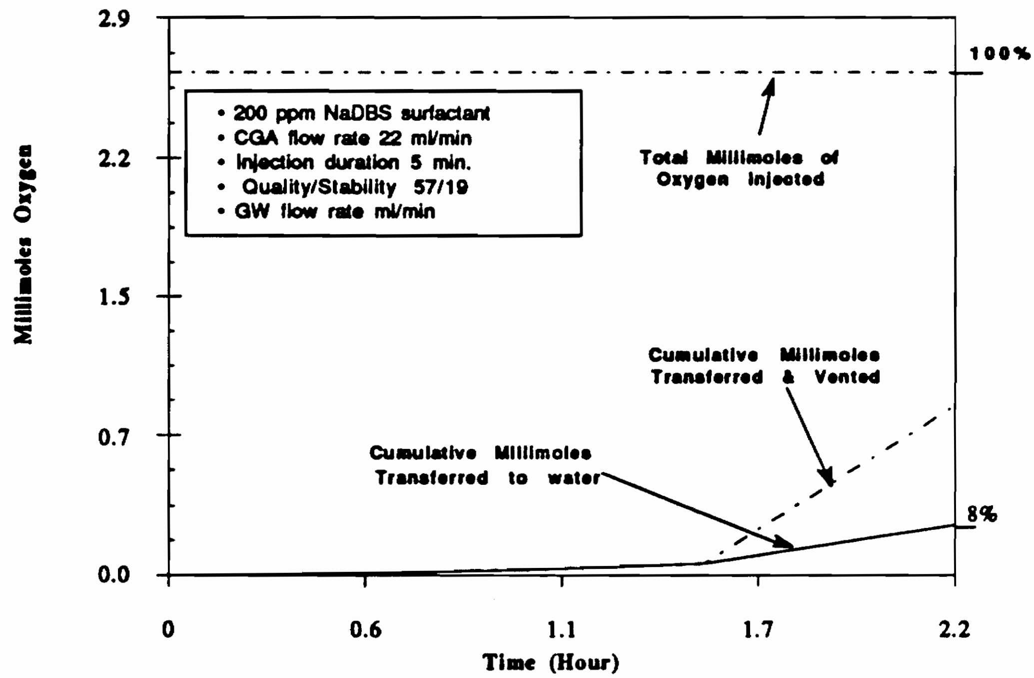

Figure 5.14 Test #4 Oxygen transfer and material balance in the packed Vertical Column Test Cell after injection of 110 ml oxygen CGA in the sand matrix: Effect of reduced quality and stability; compared to test # 3 quality and stability of CGA was reduced, consequently vent losses are increased and oxygen transfer to water decreased.

Test #5 is a duplicate of Test #4, except the injected CGA have a higher quality and stability, increased from 57% and 19 in Test #4 to 76% and 6, respectively. These two tests represented the opposite end of the spectrum for quality and stability. Table C.5 of Appendix C shows that after 495 minutes, oxygen was still being transferred to the water phase and D.O. profiles were high, even at 285 minutes after the injection of the 110 ml CGA. The high quality and stability of CGA in this test also yielded a sustained and elevated KLa, increased by one order of magnitude compared to Test #4; the KLa(s) ranged from 0.217 to 0.119 hr^{-1} after 285 minutes. The oxygen transfer was also increased to 41%, see Table 5.12 and Table E.4 in Appendix E. Figure 5.15 shows cumulative oxygen transfer and oxygen transferred plus vented, with respect to time.

Injections of oxygenated water into the cell were evaluated in Test #6. The results of Test #6 showed D.O. profiles which ranged from 3.9 to 0.7 at 88 minutes and KLa(s) at least one order of magnitude less than Test #5, with CGA injection, see Table C.6. After 1.1 hour still 100% O_2 was in the cell, but 3.1 hours later less than 2% of injection was in the cell. (See Table E.5).

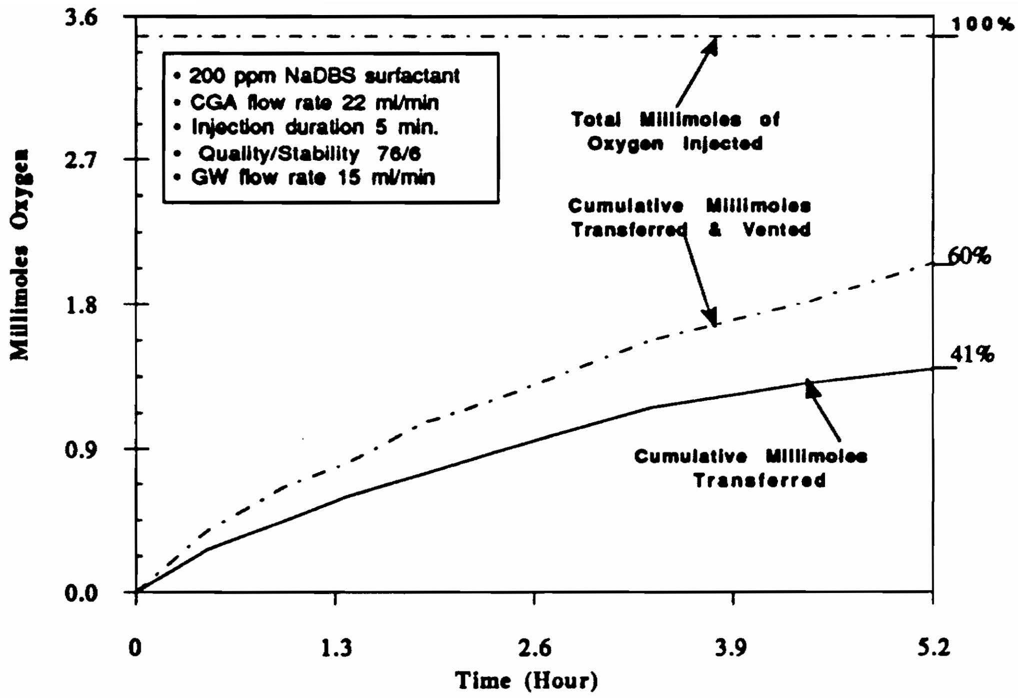

Figure 5.15 Test # 5 Oxygen transfer and material balance in the packed Vertical Column Test Cell after injection of 110 ml oxygen CGA in the sand matrix: Effect of increased quality and stability compared with test # 4 quality and stability of CGA was increased, consequently oxygen transfer to water increased by a factor of 2.6.

Test #7 was air sparging test in which 588 ml air was sparged, equivalent of 160 mg oxygen, in contrast with 100 mg oxygen in 110 ml CGA (70% quality). Table C.7 of Appendix C shows D.O. profile after 90 minutes to vary from 1.77 to 2.23 to 1.80 and KLa(s) ranging from 0.038 to 0.011 hr^{-1} one order of magnitude less than CGA injection.

Test #8 is a repeat of Test #3 with only 3 samples taken per reading instead of 5, as in Test #3. Table C.8, Appendix C, shows that at 255 minutes oxygen transfer to the water was still continued. The KLa(s) were also sustained and ranged from 0.30 to 0.150 hr^{-1} for most readings. The frequency of sampling definitely interfered with an objective material balance. Oxygen transfer of 33% resulted as shown in Tables and E.6.

CHAPTER VI

DISCUSSION OF RESULTS

6.1 General Discussions

In situ oxygenation of anaerobic groundwater (for aerobic degradation of hydrocarbon contaminants) was attempted. Stoichiometrically remediation of groundwater with high concentrations of hydrocarbons, i.e. B.T.X., would be limited by the saturation concentration of oxygen (C_s) in water. Since C_s for oxygen is relatively low in water, percent degradation of high concentrations of hydrocarbons in groundwater would not be significant and for such cases pump and treat methods would work more effectively. Also, in some cases high concentrations of hydrocarbons can be toxic to the microorganisms. On the other hand low concentrations of hydrocarbons in water, say 10 ppm, can be degraded biologically. For this purpose a long treatment zone or trench, perpendicular to groundwater flow, can be supplied with oxygen and nutrients to enhance bacterial growth and biodegradation of hydrocarbons was proposed in Chapter II. The Vertical Slice Test Cell was to represent a slice of one such trench. Previous studies by Smith (1988) showed less than 10 percent transfer of oxygen and less than 25 percent gas retention in the saturated soil matrix of the VSTC which was not stratified by clay layers and was injected with air CGA.

In this report three major changes to Smith's procedure were made. First, oxygen CGA were utilized in place of air CGA to increase the transfer force and oxygen partial pressure. Second, the sand was layered with impervious clay layers to increase gas hold up. Third, the duration, frequency and CGA flow rate of injection were reduced so that cell hold up capacity was not exceeded. These changes resulted in gas holdups as high as 89 percent, for some tests and oxygen transfer to water phase of about 40 percent and in one case transfer over 59 percent was achieved.

The three layering configuration were used in the VSTC, namely, the clay cap on top of concrete sand, the clay cap plus the vertical plexiglass with two windows aligned with the CGA injectors and multi-layering of sand and clay. In these tests gas hold up in the cell and consequently the increase in oxygen transfer to the water phase were evaluated.

Clay layering of the cell increased gas hold up (also referred to as percent retention) in all the tests in this report by 2-3 times compared with previous studies (Michelsen, et al., 1990). In Test #13 retention was over 70 percent.

This number however represented only one injection episode (eight injections pre episode) and generally retention decreased with the increase in the number of injection episodes or sustained injections.

6.2 VSTC, Short Term Tests

Oxygen transfer, was about 6 percent in Test #13. Hence, the high initial retention did not correlate with the low oxygen transfer see Table 5.1. Premature termination in D.O. readings could have been responsible for the low percentage of oxygen transfer. The KLa(s) however were relatively high which also reflected the high volume of CGA injected in this test.

In test #15, the amount of oxygen CGA was reduced in half compared to Test #13 which seemed to have been overloaded with CGA. The percent oxygen transfer increased to almost 12 percent.

This value, however, is based on a more conservative calculations based on a ΔD.O. between influent and effluent D.O. level. If oxygen transfer was based on ΔD.O. between influent and D.O. at the end of Z, the transfer zone of 6 inches, the oxygen transfer would be higher.

The percent retention slightly reduced compared to Test #13, possibly due to gas escape along the vertical plexiglass barrier. The KLa(s) were reduced by one order of magnitude in Test #15. In these tests increased oxygen injection was directly proportional to increase in KLa. This is to be expected since usually high injection volumes results in high D.O. values at Z distance from the injection points.

The cell was sparged with air after Test #15 in order to evaluate oxygen transfer using air. This effort, termed Test #16, resulted in disruption of water flow-paths and development of visible breakthroughs were noted. Also, very low and insignificant changes in D.O.(s) were resulted which were not recorded. However, this test turned into a treatment of the cell for the subsequent injections of CGA. Several days after air sparging the retention results of Test #17 which was a CGA injection similar to Test #15 were inconclusive and readings were to be scrapped.

The results of Test #18 and 19 which showed retention as high as 100 and 83 percent, respectively, were unexpected. These high retention, as explained before, could have been the result of the earlier air sparging in Test #16. Plugging of effluent pipe, similar to Test #17, was unlikely since at the time of test #18 injection, water had been flowing through for 5 days after test #17. Oxygen transfers remained low and KLa(s) were the same as Test #15.

There seemed to have been a trade off between KLa(s), oxygen injected and transferred, and oxygen holdup. As oxygen injection increased less of it was held in the cell but KLa(s) increased because Δ D.O.(s) were higher. The efficiency of the oxygen transfer in the VSTC seemed to have been kept at a low level due to cell limitation at the completion of Test #19. However, it was concluded that this soil packing configuration with the clay cap on top was effective in holding up gas in the cell.

Oxygen transfers were not taking place as expected probably due to premature stoppage of D.O. readings. It should be pointed out that criteria for concluding the D.O. readings for these tests, (13-19), were to stop D.O. readings when Δ D.O. at the start and the end of the oxygen transfer zone, Z=6", was equal to one or less. This criteria was changed to stopping the D.O. reading when Δ D.O. between influent and effluent D.O. of the cell was equal to one or less for Tests 27-31.

6.3 VCTC Tests

Upon injection of oxygen CGA, water was replaced by microbubbles radially from the injector head. This area of high gas concentration was referred to as CGA cloud, which offered resistance to the water flow and caused it to by pass the cloud. A hypothesis offered here for oxygen transfer is that oxygen bubbles either gradually move upward and/or the cloud is dissolved peripherally similar to dissolution of a large halite crystal in the path of flowing water. This 'shaving-off' effect by the flowing water gradually releases the oxygen into the anaerobic groundwater and maintains high D.O.(s) for days. The question can be asked; what if water is directed or forced to pass through the CGA cloud? What would happen to the KLa values? Can layering of sand assist in increasing holdup(s) and KLa values? The hypothesis was first tested by using the Vertical Column Test Cell in which water flow was forced to pass through or close to the oxygen source. Since the Vertical Column Test Cell was much smaller than the VSTC it was more efficient in transferring oxygen to the water phase.

When the Vertical Column Test Cell was overloaded with CGA, vent losses increased accordingly as in Test #1 and 2 with 220 ml of CGA injected. The size of the CGA cloud was large enough to block the cell cross sectional area, which exposed the bubbles to the flow of water. This resulted in the bubbles becoming dislodged from the cloud, loosing their surfactant jacket and moving in the direction of the flow. In these tests the KLa(s) were high accordingly and reflected the high level of oxygen injected.

When the cell was injected with 110 ml CGA in Test #3, vent losses became negligible and the size of the cloud was reduced gradually as in Test #3 Table 5.12. A sustained plug flow of elevated D.O. level was observed. Consequently, the oxygen transfer was increased from 18.6 percent in Test #2 to 32 percent. The KLa(s) were the same magnitude as in Test #2 (slightly lower) even though CGA volume was reduced in half.

The effect of reduced quality and stability on oxygen holdup and transfer was contrasted in Tests #4 and #5. Low quality and stability resulted in low oxygen retention and transfer as shown in Table 5.12. When quality/stability increased from 57/19 in Test #4 to 76/6 in Test #5 the oxygen transfer increased from 8.2 to 41 percent respectively. The KLa(s) were also increased by one order of magnitude in Test #5. This finding is quite significant and stresses the importance of stable dispersions. In Test #6 the cell oxygen level was elevated by injecting highly oxygenated water. The results are discouraging. After two hours from injection only 2 percent of the oxygen remained in the cell.

The less frequent sampling in Test #8 resulted in similar oxygen transfers and KLa(s) as in Test #3. In general, oxygen transfer improved through the VCTC, the narrow sand filled tube which represented a permeable sand layer sandwiched between two impermeable clay layers. The results of these tests were encouraging and lead to multi-layering the Vertical Slice Test Cell alternatively with sand and clay layers.

6.4 VSTC Long Term Tests

Upon changing the cell configuration to multi-layering of sand and clay in the VSTC, and monitoring the change in D.O. between the influent and effluent D.O., periods of D.O. reading over 10 days for the tests were maintained until ΔD.O. was less than one mg/l between the influent and effluent ports.

In Tests #27 and #28 the effect of CGA injection and doubling of injection were evaluated in a multilayered sand and clay packing configuration. As the volume of CGA injection doubled in Test #28, the percent retention was halved compared to Test #27. So, it is critical not to surpass the cell capacity to accept CGA. Oxygen transfer to water phase of 30% was achieved in Test #28, Table 5.2, that means more oxygen mass (in milligram) was transferred to water than in Test #27.

In calculating KLa values, an oxygen transfer zone or distance, Z, was assumed based on the extent to which CGA 'cloud' was to have been extended. A value of 6 inches was thought to have been a reasonable distance along which oxygen was transferred to the water phase. Hence, at the start and end of this distance D.O.(s) were read. Tests #27 and 28 were the only tests for which D.O. data were available at the 6 inch 'Z' distance. Therefore a more detailed discussion of KLa values for these two tests is given.

Comparing Test #29 and #27, which are similar with respect to the controlled conditions such as CGA amount, and packing, it becomes evident that as the result of sustained CGA injections in the cell, gas retention decreased from a range of 72 to 110 percent in Test #27 to 30 and 52 percent in Test #29 as shown in Table 5.2. Oxygen transfers did not change significantly in these tests, which again meant that high initial retention does not always translate into high oxygen transfer to the water phase. The similar magnitudes of KLa(s) between the two tests further supported the inconsistency, of the initial gas holdup values to oxygen transfer values. Comparison of these two tests shows the diminishing gas holdup capacity of the cell as CGA injections are continued.

In Tests #30 and #31 the same soil packing (unchanged since Test #27) was continued to be used, but due to reduced gas retention in Test #29, believed to be due to gas escapes via the breakthrough paths in the upper sand layer, the injections were made through two injectors in the lower sand layer. With exception of the abnormally low retention of 16% in the last injection of Test #30, generally retention increased to 67% for Test #30 and 70% for Test #31. The KLa(s) were also similar in magnitude to other tests in this group. However, oxygen transfers were at 59% for Test #30 and 38% for Test #31, the highest in these series of tests. Oxygen transfer per time , for Tests 30 and 31 as shown in Table 5.2 was 7.2 and 7.6 mg/hr, respectively.

The four values evaluated, namely, initial oxygen holdup, percent oxygen transferred and oxygen transfer coefficient, and oxygen transfer per time should be evaluated jointly and any one parameter cannot be the measure of the optimality of these tests. There seems to be a trade off point between these four parameters. This trade off point was not established in these tests. Only through long and sustained testing it might become transparent, that for example, at what amount of CGA injection overloading would occur which results in reduced percent retention and increased KLa(s) and oxygen transfer per time which are necessary for the biological oxygen demand placed on the system.

CHAPTER VII

CONCLUSIONS AND RECOMMENDATIONS

In aerobic treatment of hydrocarbon contaminated groundwater where rapid decomposition of contaminants in the flowing groundwater is desired, concentration of dissolved oxygen in the water phase would often be the rate limiting factor. Often, oxygen in water is depleted rapidly, either chemically and/or biologically, leaving the aerobes starved for oxygen. This research explored the means of supplying oxygen in the saturated soil matrix in order to enhance aerobic degradation of the hydrocarbons. The experiments were designed to show the capability of oxygen microbubbles and other modes of oxygen injection for transferring oxygen to the water phase.

The purpose of these experiments were to improve gas holdup and increase the efficiency of oxygen transfer to the water phase. In these experiments the initial gas holdup, the percent oxygen transferred to water and oxygen transfer rate were measured.

The oxygen transfer coefficient, KLa, was highest when cell was over loaded with CGA compared to the subsequent tests in which cell holdup capacity was not exceeded. When cell holdup capacity did not exceed the retention improved but KLa(s) were lowered. It was noted that percent oxygen transferred also improved. When the cell was sparged with air followed by CGA injections it was noted that gas holdup was dramatically improved to above 80 percent.

Injection of microbubbles resulted high sustained KLa(s) compared with sparged air and oxygenated water injection. In the VCTC the highest oxygen transfer was noted when oxygen CGA were injected. When the high quality/stability injected CGA in VCTC were compared with the low quality/stability tests, it was noted that much higher KLa(s) and percent transfer of oxygen to water phase were realized when the former was injected. When the amount of the CGA injected in the cell was doubled the percent retention was reduced to almost half. Oxygen transfers over 37% were realized in these tests.

In the layered cell configuration, Group III, the oxygen transfer improved and showed similarity with the Vertical Column Test Cell. KLa(s) increased by one order of magnitude, in the lower layer of sand where gas retention was high, when CGA injection was doubled. The gas holdup of the cell was reduced as the result of sustained CGA injections. In the last two tests, Tests #30 and #31, CGA were injected only in the lower layer of sand. This seemed to have improved initial gas retention and oxygen transfer, 59% for Test #30 and 40% for Test #31.

In order to conclude this report several points must be highlighted:

- Oxygen microbubbles were effective in transferring oxygen in VSTC with 29%-59%, efficiency, to the water phase.
- Compared to air sparging and oxygenated water injection, the microbubbles were more efficient in transferring oxygen to the flowing groundwater.
- The oxygen transfer coefficients were somewhat higher in air sparging than with CGA, but KLa values were decreased with time and therefore were not sustained at a high level with air sparging. On the other hand, CGA injections resulted in relatively high KLa(s) at sustained values over period of days with only one injection episode.
- Layering, and specially multi-layering of the VSTC improved retention and transfer of oxygen.
- Excessive CGA injected into the sand matrix exceeded cell capacity and a proportional volume of oxygen escaped and was collected.
- The highest KLa values were realized when cell capacity was exceeded and the cell was overloaded with CGA.

- High quality and stability increased gas retention, oxygen transfer and KLa values while low quality and stability adversely affected these parameters.
- Sparging a cell with already reduced holdup capacity may improve holdup two to three times.

It is recommended that this work be continued in the future with the following points in mind:

- Continued effort must address improved gas retention, especially when long range injections of CGA is planned. At present long range testing seems to reduce retention.
- Retentions may be improved by air sparging and clay injection should also be tried in a more systematically to determine its effect on gas holdup.
- KLa values can be improved by overloading the cell with CGA while recovering/recycling the oxygen. This can also be combined with intermittent injection of oxygen gas in the soil matrix via CGA injectors.
- Other modes such as hydrogen peroxide, not addressed in this report, can be combined with CGA.
- The tests must continue, with a biologically active cell, especially tests in which bacterium places oxygen demand on the oxygen transfer system and degrades the hydrocarbons.

- Since the oxygen microbubbles have shown that oxygen can be held emplaced and transfer to flowing groundwater more efficiently than other modes of oxygenation, their capability of sustaining an acceptable level of D.O. for aerobes must be tested as a natural step in the development of this technology.
- In order to justify field demonstration technical feasibility of this method in a biologically active system should be evaluated. Well characterized soils from contaminated sites should also be used in the study. Also the effects of biomass and precipitated salts such as ferric hydroxide, on the hydraulic conductivity of the soil must be tested in the pilot scale VSTC.

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APPENDIX A

Oxygen Transfer And Material Balance In Vertical Slice Test Cell

CALCULATIONS OF OXYGEN TRANSFER

The amount of Oxygen Transfer was found as follows:

$$O_2 \text{ Transferred} = \Delta \text{ time (min)} \times \text{D.O. (mg/liter)} \times \text{flow rate of water (liter/min)}$$

Where; Δ time is time increments between each reading

Δ D.O. is the difference between effluent and influent D.O.

$$\text{Total } O_2 \text{ Transferred} = \sum_1^n \Delta O_2 \text{ transferred}_{(i)},\ i = 1 \ldots n$$

Where; O_2 transferred is the incremental oxygen transfer

i is the increment for each Δ D.O.

The amount of oxygen injected (O_2 in.) was found as follows:

$$O_2 \text{ in.} = Q \times T_{TCGA} \text{ (Liter)} \times \frac{32000 \text{ mg } O_2}{22.4 \text{ liter } O_2} (300/273)$$

where T_{TCGA} = Total Volume of CGA injected

Q = quality

Percent Total Oxygen Transferred was found as follows:

$$\% \ O_2 \text{ Transferred}_{(Tot.)} = \frac{\text{Total } O_2 \text{ Transferred}}{O_2 \text{ in.}} \times 100$$

Overall or average percent oxygen holdup (V/V) was found as follows:

$$O_2 \text{ holdup}_{avg.} = \frac{\text{Total } O_2 \text{ Holdup (ml)}}{\text{Total } O_2 \text{ Injected (ml)}} \times 100$$

Table A.1 Test #13 Oxygen transferred in VSTC after oxygen CGA injection through the two injectors in concrete sand: the cell was overloaded with CGA.

Δ D.O. (mg/l)	Time ΔT (min)	Time Cum. (min)	Flow (l/min)	O_2 Transferred Increm. (mg)	O_2 Transferred Cum. (mg)
3.4	200	200	$90x10^{-3}$	61.0	61.0
5.31	110	310	$90X10^{-3}$	52.6	113.6
6.5	110	420	$90X10^{-3}$	64.3	177.9
7.87	180	600	$74X10^{-3}$	104.8	282.7
8.76	230	830	$75X10^{-3}$	151.0	433.7
6.78	600	1430	$77X10^{-3}$	313.2	746.9
5.85	110	1540	$77X10^{-3}$	49.5	796.4
4.93	185	1725	$80X10^{-3}$	73.0	869.4

Remarks:

- CGA injection rate;730 ml/min.
- CGA injection duration; 2.75 min per injection.
- No of CGA injection; 8.
- Ave. quality; 70%.
- Stability < 10.
- mg O_2 in; 14614.
- % transferred; 5.9.
- Temperature; 27°C.
- Avg. Oxygen holdup upon CGA injection:
  First four injections; 69%.
  Second four injections; 14%.
  Overall holdup ; 42%.

Table A.2 Test #15 Oxygen transferred in VSTC after oxygen CGA injections through the two injectors in concrete sand: CGA injection was reduced to 4 , also flow rate reduced compared to test #13.

Δ D.O. (mg/l)	Time ΔT (min)	Time Cum. (min)	Flow (l/min)	O_2 Transferred Increm. (mg)	O_2 Transferred Cum. (mg)
1.67	60	60	$60X10^{-3}$	6.0	6.0
0.2	175	235	$60X10^{-3}$	2.1	8.1
0.3	65	300	$60X10^{-3}$	1.2	9.3
5.7	270	570	$60X10^{-3}$	92.3	101.6
5.9	705	1275	$105X10^{-3}$	436.7	538.3
6.93	280	1555	$65X10^{-3}$	126.1	664.4
6.07	170	1725	$65X10^{-3}$	67.0	731.5
1.4	990	2715	$65X10^{-3}$	90.1	821.6

Remarks:

- CGA injection rate; 700 ml/min.
- CGA injection duration; 2.83 min per injection.
- No of CGA injection; 4.
- Ave. quality; 69%.
- Stability < 10.
- mg O_2 in; 7107.8 mg.
- % transferred; 11.5.
- Temperature; 27°C.
- Avg. oxygen holdup upon CGA injection; 62%.

Table A.3 Test #18 Oxygen transferred in VSTC after eight oxygen CGA injections through the two injectors in concrete sand: the cell had first been sparged with air in a previous test after which high holdups of oxygen CGA were observed.

Δ D.O. (mg/l)	Time ΔT (min)	Time Cum. (min)	Flow (l/min)	O_2 Transferred Increm. (mg)	O_2 Transferred Cum. (mg)
----	40	40	----	----	----
1.6	190	230	$62X10^{-3}$	18.85	18.85
1.7	340	570	$62X10^{-3}$	35.84	54.69
3.23	120	690	$62X10^{-3}$	24.03	78.72
0.8	660	1350	$60X10^{-3}$	33.12	111.84
5.6	405	1755	$60X10^{-3}$	136.08	247.92
1.48	990	2745	$60X10^{-3}$	82.91	330.83
2.2	345	3090	$60X10^{-3}$	45.54	376.37
4.4	128	3218	$60X10^{-3}$	33.79	440.16
4.5	202	3420	$60X10^{-3}$	54.53	464.69

Remarks:

- Two episods of injections 48 hrs apart.
- CGA injection rate; 600 ml/min.
- CGA injection duration; 1.5 min per injection.
- No of CGA injections; 4.
- Ave. quality ; injection episod1; .62%, injection episod2; .67%.
- Stability < 12.
- mg O_2 in; episode1; 2902, episod2; 3136, total; 6038mg.
- % transferred; 7.6.
- Temperature ; 27°C.
- Ave. oxygen holdup upon CGA injection; 93%.

Table A.4 Test #19 Oxygen transferred in VSTC after four oxygen CGA injections through the two injectors in concrete sand: this test was to be contrasted with the first four injection of test #18.

Δ D.O. (mg/l)	Time ΔT (min)	Time Cum. (min)	Flow (l/min)	O_2 Transferred Increm. (mg)	O_2 Transferred Cum. (mg)
0.13	80	80	$88X10^{-3}$	0.94	0.94
3.34	180	260	$88X10^{-3}$	52.9	53.84
2.66	190	450	$88X10^{-3}$	44.48	98.3
0.23	3840	4290	$85X10^{-3}$	75.1	173.0

Remarks:

- CGA injection rate; 600 ml/min.
- CGA injection duration; 1.5 min per injection.
- No of CGA injections; 4
- Ave. quality; 68%.
- Stability < 10.
- mg O_2 in; 3182 mg.
- % transferred; 5.4.
- Temperature; 27°C.
- Ave. oxygen holdup upon CGA injection; 73%.

Table A.5 Test #27 Oxygen transferred in VSTC, packed with intermittent layers of concrete sand and clay , after four oxygen CGA injections through the air diffuser in each concrete sand layer.

Δ D.O. (mg/l)	Time ΔT (min)	Time Cum. (min)	Flow (l/min)	O_2 Transferred Increm. (mg)	O_2 Transferred Cum. (mg)
0.2	315	315	$40X10^{-3}$	2.52	2.52
1.71	525	840	$40X10^{-3}$	35.90	38.42
1.13	140	980	$40X10^{-3}$	6.33	44.75
1.37	160	1140	$40X10^{-3}$	8.77	53.52
1.73	375	1515	$40X10^{-3}$	25.95	79.47
2.20	705	2220	$40X10^{-3}$	62.04	141.51
2.68	523	2743	$55X10^{-3}$	77.01	218.52
2.80	270	3013	$42X10^{-3}$	31.75	250.27
2.86	645	3658	$52X10^{-3}$	95.92	346.19
2.58	1950	5608	$60X10^{-3}$	301.86	648.05
1.69	950	6558	$60X10^{-3}$	96.33	744.38
1.20	745	7303	$40X10^{-3}$	35.76	780.14
0.84	695	7998	$25X10^{-3}$	14.59	794.73

Remarks:

- 2 concrete sand layers alternated with 2 clay layers.
- One injector in each layer of sand.
- Location of injectors; at start of each sand layer.
- CGA injection rate; 300 ml/min per injection.
- CGA injection duration; 5.4 min.
- Total No of CGA injections; 4.
- Ave. quality; 65%
- Stability < 10
- mg O_2 in; 2738 mg.
- % transferred; 29.
- Temperature; 27°C.
- Avg. oxygen holdup upon CGA injector; 89%.

Table A.6 Test # 28 oxygen transfer in VSTC, packed with intermittent layer of concrete sand and clay , after four oxygen CGA injections through the air diffusers in each sand layer: the amount of CGA was doubled compared to test # 27.

Δ D.O. (mg/l)	Time ΔT (min)	Time Cum. (min)	Flow (l/min)	O_2 Transferred Increm. (mg)	O_2 Transferred Cum. (mg)
1.00	120	$1.2X10^2$	$45X10^{-3}$	5.4	5.4
0.69	120	$2.4X10^2$	$80X10^{-3}$	6.6	12
4.50	140	$3.8X10^2$	$62X10^{-3}$	39	51
1.46	520	$9.0X10^2$	$42X10^{-3}$	32	83
0.15	240	$1.14X10^3$	$76X10^{-3}$	2.7	85.7
1.70	270	$1.41X10^3$	$63X10^{-3}$	29	114.7
1.60	210	$1.62X10^3$	$64X10^{-3}$	21	135.7
2.00	180	$1.80X10^3$	$42X10^{-3}$	15	150.7
3.49	525	$2.33X10^3$	$49X10^{-3}$	90	240.7
3.98	235	$2.56X10^3$	$51X10^{-3}$	47.7	288.4
4.33	245	$2.8X10^3$	$60X10^{-3}$	63.7	352.1
4.00	225	$3.03X10^3$	$36X10^{-3}$	32.5	384.6
4.44	180	$3.21X10^3$	$30X10^{-3}$	24.0	408.6
3.95	540	$3.75X10^3$	$38X10^{-3}$	81.0	489.6
4.30	288	$4.04X10^3$	$56X10^{-3}$	69.3	558.9
4.80	210	$4.25X10^3$	$60X10^{-3}$	60.5	619.4
4.56	480	$4.73X10^3$	$55X10^{-3}$	120	739.4
4.10	270	$5.00X10^3$	$46X10^{-3}$	51	790.4
5.80	240	$5.24X10^3$	$42X10^{-3}$	58.5	848.9
5.51	240	$5.48X10^3$	$56X10^{-3}$	74	922.9
4.30	600	$6.08X10^3$	$54X10^{-3}$	139.3	1062.2
4.42	240	$6.32X10^3$	$60X10^{-3}$	63.6	1125.8
4.85	660	$6.98X10^3$	$50X10^{-3}$	160.0	1285.8
3.1	560	$7.54X10^3$	$58X10^{-3}$	100.6	1386.4
2.59	220	$7.76X10^3$	$38X10^{-3}$	21.6	1408.0
3.23	240	$8.0X10^3$	$40X10^{-3}$	31.0	1439.0
2.96	240	$8.24X10^3$	$40X10^{-3}$	28.4	1467.4
2.70	180	$8.42X10^3$	$40X10^{-3}$	19.5	1486.9
2.80	660	$9.08X10^3$	$63X10^{-3}$	116.4	1603.3
1.60	780	$9.86X10^3$	$61X10^{-3}$	76.0	1679.3
0.90	630	$1.05X10^4$	$52X10^{-3}$	29.5	1708.8
1.40	780	$1.13X10^4$	$73X10^{-3}$	79.7	1788.5
0.40	1350	$1.26X10^4$	$78X10^{-3}$	42.0	1830.5
0.00	840	$1.35X10^4$	$108X10^{-3}$	0.0	1830.5

Table A.6 (Continued)

Remarks:

- 2 concrete sand layers alternated with 2 clay layers.
- One injector in each layer of sand.
- Location of injectors; at start of each sand layer.
- CGA injection rate; 710 ml/min.
- CGA injection duration; 2.5 min. per injection.
- No of CGA injections; 4.
- Ave. quality; 65%.
- Stability < 12.
- mg O_2 in; 6000 mg.
- % transferred; 30.
- Temperature; 27°C.
- Avg. oxygen holdup upon CGA injector; 46%.

Table A.7 Test #29 Oxygen transfer in VSTC, packed with intermittent layers of concrete sand and clay, after four oxygen CGA injections through the air diffusers in each sand layer: This test was to be contrasted with test # 27 to evaluate the prolonged effect of CGA injection on O_2 holdup and transfer to water.

Δ D.O. (mg/l)	Time ΔT (min)	Time Cum. (min)	Flow (l/min)	O_2 Transferred Increm. (mg)	O_2 Transferred Cum. (mg)
0.2	545	545	$55X10^{-3}$	6.0	6.0
1.53	440	985	$46X10^{-3}$	31.0	37.0
1.29	280	1265	$43X10^{-3}$	15.5	52.5
1.59	165	1430	$43X10^{-3}$	11.3	63.8
3.33	540	1970	$44X10^{-3}$	79.1	142.9
3.54	490	2460	$46X10^{-3}$	40.7	183.6
4.20	480	2940	$46X10^{-3}$	92.7	276.3
4.85	180	3120	$49X10^{-3}$	42.8	319.1
4.90	495	3615	$48X10^{-3}$	116.4	435.5
4.70	225	3840	$50X10^{-3}$	52.9	488.4
3.89	495	4335	$40X10^{-3}$	77.0	565.4
3.20	225	4560	$85X10^{-3}$	61.2	626.6
3.32	555	4115	$52X10^{-3}$	95.8	722.4
2.25	205	5320	$48X10^{-3}$	22.1	744.5
2.68	260	5580	$50X10^{-3}$	34.8	779.3
2.00	240	5720	$48X10^{-3}$	23.0	802.3
2.00	180	6000	$50X10^{-3}$	18.0	820.3
4.10	560	6560	$48X10^{-3}$	106.3	926.6
1.70	250	6810	$49X10^{-3}$	21.0	947.6
1.60	210	7020	$46X10^{-3}$	15.4	963.0
1.42	240	7260	$44X10^{-3}$	15.0	978.0
1.36	180	7440	$44X10^{-3}$	11.0	989.0
0.30	555	7990	$46X10^{-3}$	7.6	996.6
1.17	165	8160	$47X10^{-3}$	9.1	1005.7

Table A.7 (Continued)

Remarks:

- 2 concrete sand layers alternated with 2 clay layers.
- One injector in each layer of sand.
- Location of injectors; at start of each sand layer.
- CGA injection rate;609 ml/min. (Avg.)
- CGA injection duration; 1.5 min.
- No of CGA injections; 4
- Ave. quality; 63%.
- Stability < 10
- mg O_2 in; 2978 mg
- % transferred; 34%
- Temperature; 27°C.
- Avg. oxygen holdup upon CGA injection; 47%
- Notice the similar conditions with test # 27 and the effect of prolonged CGA injection on oxygen holdup and transfer in this test.

Table A.8 Test #30 Oxygen transfer in VSTC, packed with intermittent layers of concrete sand and clay, after four oxygen CGA injections through two air diffusers in the lower concrete sand layer: No injections were made in the upper sand layer.

Δ D.O. (mg/l)	Time ΔT (min)	Time Cum. (min)	Flow (l/min)	O_2 Transferred Increm. (mg)	O_2 Transferred Cum. (mg)
0.2	210	210	$54X10^{-3}$	2.3	2.3
---	540	750	-----	---	2.3
0.52	240	990	$41X10^{-3}$	5.1	7.4
1.24	490	1480	$37X10^{-3}$	22.5	29.9
1.10	180	1660	$34X10^{-3}$	6.7	36.6
1.34	577	2237	$30X10^{-3}$	23.2	59.8
2.05	563	2800	$35X10^{-3}$	40.4	100.2
3.60	240	3040	$43X10^{-3}$	37.2	137.4
2.68	540	3580	$42X10^{-3}$	60.8	198.2
4.50	240	3820	$42X10^{-3}$	45.4	243.6
4.40	270	4090	$39X10^{-3}$	46.3	289.9
4.70	190	4280	$35X10^{-3}$	31.3	321.2
4.50	200	4480	$38X10^{-3}$	34.2	355.4
4.50	1020	5500	$34X10^{-3}$	156.1	511.5
3.50	250	5750	$34X10^{-3}$	29.8	541.3
1.90	720	6470	$28X10^{-3}$	38.3	579.6
1.96	330	6800	$28X10^{-3}$	18.1	597.7
2.60	390	7190	$38X10^{-3}$	38.5	636.2
4.30	240	7430	$48X10^{-3}$	49.5	685.7
2.20	600	8030	$40X10^{-3}$	52.8	738.5
3.70	270	8300	$40X10^{-3}$	40.0	778.5
4.30	1080	9380	$42X10^{-3}$	195.4	973.9
1.28	240	9620	$42X10^{-3}$	12.9	986.8
1.15	510	10130	$42X10^{-3}$	26.6	1013.4
0.88	555	10685	$35X10^{-3}$	17.1	1030.5
1.27	555	11240	$24X10^{-3}$	16.9	1047.4
3.20	1000	12240	$56X10^{-3}$	174.5	1221.9
3.40	280	12520	$56X10^{-3}$	53.4	1275.3
4.07	360	12880	$58X10^{-3}$	85.0	1360.3
4.20	1200	14080	$40X10^{-3}$	202.0	1562.3
4.40	960	15040	$53X10^{-3}$	223.9	1786.2

Table A.8 (Continued)

Remarks:

- 2 concrete sand layers alternated with 2 clay layers.
- Both injections in the lower sand matrix.
- Location of the two injectors; at start and 1 1/2 ft from the start of the lower sand layer.
- Avg. oxygen holdup upon CGA injection; 42%
- Temperature 27°C.
- Eratic injections.
- CGA injection rates; 635, 975 and 630 ml/min.
- CGA injection duration; 1.5, 1.5 and 2 min(s).
- No of CGA injections; 3.
- Avg. quality; 63% .
- Avg. Stability; 14.
- mg O_2 in; 3005.
- % transferred; 59%.
- Due to reduction in O2 holdup capacity of cell in test #29 injections were made in the lower sand layer.

Table A.9 Test #31 Oxygen transfer in VSTC, packed with intermittent layers of concrete sand and clay, after four oxygen CGA injections through two air diffusers in the lower concrete sand layer, No injections were made in the upper sand layer: A repeat of test #30.

Δ D.O. (mg/l)	Time ΔT (min)	Time Cum. (min)	Flow (l/min)	O_2 Transferred Increm. (mg)	O_2 Transferred Cum. (mg)
0.2	75	75	$40X10^{-3}$	0.62	0.62
4.3	720	795	$43X10^{-3}$	133.13	133.75
3.1	420	1215	$43X10^{-3}$	56.0	189.75
4.1	360	1575	$43X10^{-3}$	64.0	253.75
1.2	690	2265	$43X10^{-3}$	35.6	289.35
1.3	15	2280	$40X10^{-3}$	0.78	325.73
4.3	600	2880	$40X10^{-3}$	103.2	428.93
4.6	720	3600	$40X10^{-3}$	132.48	561.41
4.5	180	3780	$40X10^{-3}$	32.40	593.81
4.8	540	4320	$40X10^{-3}$	103.68	697.49
3.9	260	4580	$41X10^{-3}$	41.6	739.09
3.6	220	4800	$37X10^{-3}$	29.3	768.39
3.9	240	5040	$42X10^{-3}$	39.3	807.69
3.8	180	5220	$35X10^{-3}$	23.9	831.59
3.6	570	5790	$44X10^{-3}$	90.3	921.89
3.3	240	6030	$62X10^{-3}$	49.1	970.99
3.2	210	6240	$48X10^{-3}$	32.3	1003.29
3.2	255	6495	$33X10^{-3}$	27.0	1030.29
3.1	150	6645	$35X10^{-3}$	16.3	1046.59
4.4	600	7245	$40X10^{-3}$	105.6	1152.19
2.37	270	7515	$42X10^{-3}$	26.9	1179.09
1.0	160	7675	$42X10^{-3}$	6.7	1185.81
2.1	980	8655	$40X10^{-3}$	82.3	1268.13
1.8	210	8865	$40X10^{-3}$	15.1	1283.25
0.8	255	9120	$38X10^{-3}$	7.8	1291.05
0.7	180	9300	$39X10^{-3}$	4.9	1295.95
1.04	225	9525	$38X10^{-3}$	8.9	1304.80
1.0	600	10125	$38X10^{-3}$	22.8	1327.65
0.6	240	10365	$39X10^{-3}$	5.6	1333.25
0.6	120	10485	$44X10^{-3}$	3.2	1336.45
0.7	120	10605	$39X10^{-3}$	3.3	1339.75

Remarks:

- CGA injection rate 700ml/min.
- CGA injection duration 2.83 min.
- No of CGA injections , 4
- Ave. quality 69%
- Stability < 10
- mg O_2 in; 3063 mg
- % transferred; 44.0
- Avg. oxygen holdup upon CGA injection; 62%
- Due to reduction in O_2 holdup capacity of cell injections were made in the lower sand layer

APPENDIX B

Determination of KLa(s)

In Vertical Slice Test Cell

APPENDIX B

OXYGEN TRANSFER COEFFICIENTS, KLa's

In order to calculate the oxygen transfer coefficient for a specified time period the following parameters must be known:

Port D.O.:		Port D.O. is the concentration of dissolved oxygen at the desired distance, Z, from the point of injection. The first (lowest) reading at this port is the base D.O. (CL1), and the subsequent readings are CL2, where CL2 - CL1 is Δ D.O.
CL1	:	Designated in Tables by (**)
GW D.O.	:	Ground Water D.O. is the concentration of dissolved oxygen coming into the point of injection. (CLI)
Flow	:	Flow represents the groundwater flow rate in ml/min.
Z	:	The distance from the point of injection to the desired port D.O., where KLa's are computed.
A	:	Is the cross-sectional area of the concrete sand layer through which groundwater passes.

C_s : C_s is the saturation concentration of dissolved oxygen at a given temperature.

Example Calculation of KLa:

Let's take the second reading of Test #31 (*)

Port D.O. (Base) CL1 = 1.62

Port D.O. (Second Reading) CL2 = 8.6

CI, GW D.O. = 0.6 (Second Reading)

T, Temperature = 21.9°C

Q, flow rate = 21 ml/min (flow for the lower layer of cell)

KLa will be an overall KLa for Z = 52 inches for the bottom layer:

Z = 52" or 132.1 cm

A = 50 in^2 or 322.6 cm^2

First Saturation concentration of oxygen, C_s, at T 21.9°C and elevation of 1975 ft must be computed:

$$C_s = \frac{\text{Atmospheric pressure above sea level } (\text{mg } O_2/\text{liter } H_2O)}{\text{Henry's Constant (Adjusted)}}$$

Find Henry's Constant (H) at 21.9°C or 294.9 K

$$\log H = \frac{-\Delta H}{RT} + K$$

Where H = Henry's Constant
R = Universal Gas Constant, 1.987 Kcal/kmole
K = Empirical Constant, 7.11 for oxygen
Δ H = Heat absorbed in the evaporation of 1 mole of compound, 1.45 x 10^3 Kcal/Kmole
T = Temperature in Kelvin

$$\text{Log H} = \frac{-1.45 \times 10^{3} \text{ Kcal/Kmole}}{1.987 \text{ Kcal/Kmole - K } (294.9 \text{ K})} + 7.11$$

$H = 4.3197 \times 10^{4}$

Presure at 1975 ft above sea level is 0.93 Atm

$$C_s = \frac{0.93 \text{ (Atm)}}{4/3108\text{x}10^{4} \text{ (Atm)}} \times \frac{1000 \text{ gr } H_2O}{\text{liter}} \times \frac{1 \text{ mole}}{18\text{gr } H_2O} \times \frac{32000 \text{ mg } O_2}{\text{mole}}$$

$$C_s = \frac{1.65 \times 10^{6}}{4.32 \times 10^{4}} = 38.27 \text{ mg/liter}$$

$$\text{D.O.}_{\text{log mean}} = \frac{\Delta_1 - \Delta_2}{\ln \dfrac{\Delta_1}{\Delta_2}}$$

$\Delta_1 = C_s - \text{CLI} = 38.27 - 0.6 = 37.67$

$\Delta_2 = C_s - CL_2 = 38.27 - 8.6 = 29.67$

CL_1 = G.W. D.O.

CL_2 = effluent D.O.

$CL_2 - CL_1 =$ D.O.

$CL_2 = 1.62$

$$\text{D.O.}_{\text{Log mean}} = \frac{37.67 - 29.67}{\ln \dfrac{37.67}{29.67}} = 33.51$$

$$\text{KLa} = \frac{(Q) \ (\Delta \text{ D.O.})/A}{(Z) \ (\text{D.O.}_{\text{log mean}})} (60), \ hr^{-1}$$

$$\frac{(21) \ (6.98)/322.6}{(1\ 32.1) \ (33.51)} (60) = 0.0062 \ hr^{-1}$$

Table B.1 Test #13: Determination of oxygen transfer coefficients (KLas) in VSTC after injection of CGA in concrete sand matrix capped by a clay layer: values of KLa were adjusted for O_2 saturation concentration, Henry's constant, temperature, pressure, flow rate, groundwater D.O. and cross sectional area of the cell (A).

Port D.O. mg/l	**GW D.O. mg/l**	**Temp. °C**	**Flow (ml/min)**	**KLa (hr^{-1})**
0.13**	0.38	27.0	60	----
13.03	0.32	28.3	90	0.17
8.8	0.67	28.9	90	0.10
11.13	0.54	29.2	90	0.14
9.68	0.66	29.5	74	0.10
8.03	0.63	29.4	75	0.08
4.6	1.07	28.2	77	0.04
4.4	1.51	28.2	77	0.04
4.05	1.55	29.1	80	0.04

Remarks:

- CGA injection rate; 730 ml/min
- CGA injection duration; 2.75 min per injection.
- No. of CGA injection; 8
- Ave. quality; 70%
- Stability < 10.
- mg O_2 in; 14614.
- ** 15 C_{L1}
- % transferred; 5.9
- Temperature; 27°C
- Avg. Oxygen holdup upon CGA injection
  - First four injections; 69%
  - Second four injections; 14%
  - Overall holdup; 42%
- Z = 6"
- A = 32" x 5"

Table B.2 Test #14: Determination of oxygen transfer coefficients (KLas) in VSTC after air sparging in concrete sand matrix capped by a clay layer: values of KLa were adjusted for O_2 saturation concentration, Henry's constant, temperature, pressure, flow rate, groundwater D.O. and cross sectional area of the cell (A).

Port D.O. mg/l	**GW D.O. mg/l**	**Temp. °C**	**Flow ml/min**	**KLa hr^{-1}**
0.27**	0.61	27.7	66	----
1.57	0.96	27.6	60	0.05
2.78	1.52	27.3	60	0.11

Remarks:
- Air sparging rate; 100 ml/min
- Air sparging duration; 1395 minutes
- No. sparging; 1
- ** C_{L1}

Table B.3 Test #15: Determination of oxygen transfer coefficients (KLas) in VSTC after injection of CGA in concrete sand matrix capped by a clay layer and a vertical barrier with two windows aligned with the CGA injectors: values of KLa were adjusted for O_2 saturation concentration, Henry's constant, temperature, pressure, flow rate, groundwater D.O. and cross sectional area of the cell (A).

Port D.O. mg/1	**GW D.O. mg/1**	**Temp. °C**	**Flow (ml/min)**	**KLa (hr^{-1})**
0.6**	0.8	25.1	98	----
12.5	1.4	25.2	60	0.09
16.9	2.0	25.9	60	0.08
13.5	2.1	25.0	60	0.11
9.5	2.8	25.0	105	0.12
7.1	0.6	26.0	65	0.05
3.6	3.4	25.5	65	0.02

Remarks:

- CGA injection rate; 700 ml/min.
- CGA injection duration; 2.83 min/injection
- No. of CGA injection; 4.
- Ave. quality; 69%.
- Stability < 10.
- mg O_2 in; 71078 mg.
- ** C_{L1}
- % transferred; 11.5.
- Temperature; 27°C.
- Avg. oxygen holdup upon CGA injection; 62%
- Z = 6"
- A = 32" x 5"

Table B.4 Test #18: Determination of oxygen transfer coefficients (KLas) in VSTC after injection of CGA in concrete sand matrix capped by a clay layer and a vertical barrier with two windows aligned with the CGA injectors: values of KLa were adjusted for O_2 saturation concentration, Henry's constant, temperature, pressure, flow rate, groundwater D.O. and cross sectional area of the cell (A). Cell was previously pretreated with sparged air.

Port D.O. mg/l	GW D.O. mg/l	Temp. °C	Flow (ml/min)	KLa (hr^{-1})
1.6	0.4	26.7	135	---
0.8**	0.4	28.6	107	---
6.63	1.8	26.1	70	0.051
6.2	2.3	26.1	62	0.041
6.65	1.0	27.8	62	0.046
8.63	1.8	27.0	62	0.063
6.2	2.4	26.6	60	0.04
4.9	2.3	27.0	60	0.030
3.2	0.4	27.2	60	0.016
6.43	0.7	25.7	60	0.040
7.3	1.0	25.9	60	0.048
6.9	1.0	26.4	60	0.048

Remarks:

- Two episods of injections 48 hrs apart
- CGA injection rate; 600 ml/min.
- CGA injection duration; 1.5 min/injection.
- No. of CGA injection; 4.
- Ave. quality; injection episode 1; 62%, injection episode 2: 67%
- % transferred; 7.6.
- Temperature; 27°C.
- Avg. oxygen holdup upon CGA injection 93%.
- Z = 6"
- A = 32" x 5"
- Stability < 12.
- mg O_2 in; episode 1; 2902; episode 2; 3136; total; 6038 mg
- ** C_{L1}

Table B.5 Test #19: Determination of oxygen transfer coefficients (KLas) in VSTC after injection of CGA in concrete sand matrix capped by a clay layer and a vertical barrier with two windows aligned with the CGA injectors: values of KLa were adjusted for O_2 saturation concentration, Henry's constant, temperature, pressure, flow rate, groundwater D.O. and cross sectional area of the cell (A). Cell was previously pretreated with sparged air.

Port D.O. mg/l	**GW D.O. mg/l**	**Temp. °C**	**Flow (ml/min)**	**KLa (hr^{1-})**
1.5	1.6	25	90	----
1.35**	1.7	25	88	----
5.9	1.0	25	88	0.045
6.8	0.26	25	88	0.054
6.4	0.3	25	88	0.051
1.9	1.6	25	88	0.038

Remarks:

- CGA injection rate; 600 ml/min.
- CGA injection duration; 1.5 min/injection.
- No. of CGA injection; 4.
- Ave. quality; 68%.
- Stability < 10.
- mg O_2 in; 3182 mg.
- ** C_{L1}
- % transferred; 5.4.
- Temperature; 27°C.
- Avg. oxygen holdup upon CGA injection; 73%
- Z = 6"
- A = 32" x 5"

Table B.6 Test #27: Determination of oxygen transfer coefficients (KLa) in VSTC after injection of CGA in the two layers of concrete sand separated by a clay layer and capped by second clay layer.

PORT D.O. UPPER Z=6" mg/l	PORT D.O. LOWER Z=6" mg/l	GW D.O. mg/l	TEMP. °C	FLOW ml/min	KLa UPPER hr^{-1}	KLa LOWER hr^{-1}	PORT D.O. Z = 52" mg/l	KLa Z = 52" hr^{-1}
0.2**	0.1**	0.20	17.7	29(58)	----	----	1.00**	----
4.8	10.8	1.10	17.5	20(40)	0.024	0.073	1.30	0.0010
2.3	4.7	0.26	17.8	20(40)	0.011	0.029	1.97	0.0030
2.1	11.85	0.34	18.4	20(40)	0.010	0.082	1.47	0.0016
1.9	4.5	0.94	18.7	20(40)	0.009	0.029	2.31	0.0048
1.63	5.2	0.50	18.0	20(40)	0.007	0.032	2.23	0.0043
1.7	7.8	0.50	18.3	20(40)	0.008	0.051	2.70	0.0062
1.5	5.1	0.50	18.6	20(40)	0.007	0.032	3.20	0.0085
2.1	6.2	0.40	18.7	21(42)	0.010	0.044	3.20	0.0089
1.23	5.0	0.54	18.9	26(52)	0.007	0.041	3.40	0.0012
----	3.0	0.73	21.4	30(60)	----	0.029	2.31	0.0150
----	2.18	0.70	23.6	30(60)	----	0.021	3.39	0.0086

Remarks:

- 2 concrete sand layers alternated with 2 clay layers.
- One injector in each layer of sand.
- Location of injectors; at start of each sand layer.
- CGA injection rate; 300 ml/min per injection.
- CGA injection duration; 5.4 min.
- Total No. CGA injection; 4.
- Ave. quality; 65%
- Stability < 10
- mg O_2 in. 2738 mg.
- % transferred; 29.
- Temperature; 27°C.
- Avg. oxygen holdup upon CGA injector; 89%
- Z = 6" and 52" as noted.
- A upper = 12" x 5"
- A lower = 10" x 5"
- ** C_{L1}

Table B.7 Test #28: Determination of oxygen transfer coefficients (KLa) in VSTC after injection of CGA in the two layers of concrete sand separated by a clay layer and capped by a second clay layer. CGA injection was doubled compared to Test #27.

PORT D.O. UPPER Z=6" mg/l	**PORT D.O. LOWER Z=6" mg/l**	**GW D.O. mg/l**	**TEMP. °C**	**FLOW ml/min**	**KLa UPPER hr^{-1}**	**KLa LOWER hr^{-1}**	**PORT D.O. Z = 52" mg/l**	**KLa Z = 52" hr^{-1}**
0.9**	0.28**	0.8	18.8	80	----	----	1.1**	----
2.2	12.50	0.87	18.8	62	0.0101	0.138	5.6	0.0048
1.1	----	1.1	18.1	42	----	----	1.65	0.00029
----	----	2.1	17.9	76	----	----	2.15	0.001
1.43	----	1.5	17.9	63	0.0042	----	3.2	0.0018
----	----	1.8	17.5	64	----	----	3.4	0.0019
1.2	----	1.9	17.6	42	0.0016	----	3.7	0.0024
0.92	----	1.24	16.9	49	----	----	4.73	0.0027
----	----	1.11	16.9	51	----	----	5.1	0.0037
----	----	1.4	16.7	60	----	----	5.73	0.0018
1.8	----	1.03	16.8	36	0.00264	----	5.0	0.0016
----	----	0.8	16.6	30	----	----	5.24	0.0027
1.46	17.6	2.45	16.4	38	0.0027	0.123	6.4	0.0032
----	----	1.2	16.2	56	----	----	5.5	0.0041
1.25	15.4	1.5	15.8	60	0.0026	0.162	6.3	0.0039
----	----	1.8	15.6	46	----	----	6.4	0.0026
1.0	----	1.4	15.6	46	----	----	5.5	0.0030

Table B.7 Test #28 (continued)

PORT D.O. UPPER Z=6" mg/l	PORT D.O. LOWER Z=6" mg/l	GW D.O. mg/l	TEMP. °C	FLOW ml/min	KLa UPPER hr^{-1}	KLa LOWER hr^{-1}	PORT D.O. Z = 52" mg/l	KLa Z = 52" hr^{-1}
----	----	0.73	16.7	42	----	----	6.5	0.0035
0.8	----	0.89	16.8	56	0	----	6.4	0.0031
0.7	7.3	1.0	16.9	54	0	0.063	5.3	0.0030
0.7	7.4	0.98	17.8	60	0	0.070	5.4	0.0035
0.7	5.2	0.85	17.8	50	0	0.039	5.7	0.0031
----	----	1.47	18.2	58	----	----	4.6	0.0027
----	----	0.7	17.7	26	----	----	3.9	0.00098
----	----	0.88	17.0	26	----	----	3.8	0.00092
0.48	2.4	1.0	17.9	120	0	0.039	3.7	0.0041
0.65	2.1	1.2	18.7	63	0	0.018	4.0	0.0024
0.5	1.7	1.1	18.2	61	0	0.0131	2.7	0.0013
0.45	1.8	1.5	19.5	52	0	0.0134	2.4	0.00092
0.6	1.5	1.0	19.4	73	0	0.014	2.4	0.0013
0.55	1.1	1.0	19.4	78	0	0.001	1.4	0.00031
0.35	0.6	1.0	20.4	108	----	----	1.0	----

Table B.7 Test #28 (continued)

Remarks:

- 2 concrete sand layers alternated with 2 clay layers.
- One injector in each layer of sand.
- Location of injectors; at start of each sand layer.
- CGA injection rate; 710 ml/min.
- CGA injection duration; 2.5 min. per injection.
- No. of CGA injection; 4.
- Ave. quality; 65%.
- Stability < 12.
- mg O_2 in; 60001 mg.
- % transferred; 30.
- Temperature; 27°C.
- Avg. oxygen holdup upon CGA injector; 46%
- Z = 6" and 52" as noted
- A upper = 12" x 5"
- A lower = 10" x 5"
- ** C_{L1}

Table B.8 Test #29: Determination of oxygen transfer coefficients (KLa) in VSTC after injection of CGA in the two layers of concrete sand separated by a clay layer and capped by a second clay layer: effect of sustained CGA injection to be compared with Test #27.

PORT D.O. UPPER Z=6" mg/l	PORT D.O. LOWER Z=6" mg/l	GW D.O. mg/l	TEMP. °C	FLOW ml/min	KLa UPPER hr^{-1}	KLa LOWER hr^{-1}	PORT D.O. Z = 52" mg/l	KLa Z = 52" hr^{-1}
4.1	----	2.2	18.4	45	----	----	1.0**	----
1.75	----	0.8	17	55	----	----	1.0	----
----	----	0.6	17.7	46	----	----	2.13	0.0007
0.92	----	0.76	17.1	43	----	----	2.05	0.0006
----	----	0.84	16.8	43	----	----	2.43	0.0008
0.72	----	0.95	16.0	44	----	----	4.28	0.0021
0.47	----	1.03	16.7	46	----	----	4.28	0.0019
----	----	1.14	16.7	----	----	----	4.68	----
0.75	----	1.3	17.8	46	----	----	5.5	0.0028
----	----	1.1	17.4	49	----	----	5.9	0.0032
0.55	----	0.7	17.1	48	----	----	5.6	0.0029
----	----	1.0	18.5	50	----	----	5.7	0.0032
----	----	1.22	19.3	40	----	----	5.11	0.0023
0.55	----	1.3	19.2	85	----	----	4.5	0.0049
0.55	----	0.56	18.8	52	----	----	3.88	0.0020
----	----	0.71	19.9	48	----	----	3.26	0.0015
0.46	----	0.73	22	50	----	----	3.41	0.0017

Table B.8 Test #29 (continued)

PORT D.O. UPPER Z=6" mg/l	PORT D.O. LOWER Z=6" mg/l	GW D.O. mg/l	TEMP. °C	FLOW mg/min	KLa UPPER mg/l	KLa LOWER hr^{-1}	PORT D.O. Z = 52" mg/l	KLa Z = 52" hr^{-1}
----	----	0.7	22.2	48	----	----	2.7	0.0012
0.5	----	0.8	21.0	50	----	----	2.7	0.0012
0.5	----	0.8	20.7	48	----	----	6.9	0.0027
----	----	0.7	20.2	49	----	----	2.4	0.0010
----	----	0.61	20.8	46	----	----	2.21	0.0008
----	----	0.61	21.2	44	----	----	2.03	0.0008
----	----	0.60	20.9	44	----	----	1.96	0.0006
----	----	1.54	19.6	46	----	----	1.84	0.0006
----	----	0.57	20.4	47	----	----	1.74	0.0004
----	----	0.62	20.3	46	----	----	1.66	0.0005

Remarks:

- 2 concrete sand layers alternated with 2 clay layers
- One injector in each layer of sand
- Location of injectors; at start of each sand layer
- CGA injection rate; 609 ml/min (Avg.)
- CGA injection duration; 1.5 min
- No. of CGA injection; 4
- Ave. quality; 63%
- Notice the similar conditions with test #27 and the effect of prolonged CGA injection on oxygen holdup and transfer in this test.

- Stability < 10
- mg O_2 in; 2978 mg
- % transferred; 34%
- Temperature; 27°C
- Avg. oxygen holdup upon CGA injection; 47%
- A upper = 12" x 5"
- A lower = 10" x 5"
- Z = 6" and 52" as noted
- ** C_{L1}

Table B.9 Test #30 Determination of oxygen transfer coefficients (KLas) in multi-layered VSTC after injection of CGA in the lower concrete sand layer: Data were available only for Z = 52" but where available for Z = 6" KLa(s) were calculated.

PORT D.O. UPPER Z=6" mg/l	PORT D.O. LOWER Z=6" mg/l	GW D.O. mg/l	TEMP. °C	FLOW ml/min	KLa UPPER hr^{-1}	KLa LOWER hr^{-1}	PORT D.O. Z = 52" mg/l	KLa Z = 52" hr^{-1}
----	----	0.8	26.7	54(27)	----	----	1.26**	----
----	----	0.24	27.4	41(20)	----	----	1.3	0.0006
----	----	0.29	28.0	18	----	----	2.7	0.0007
----	----	0.8	27.7	17	----	----	3.4	0.0013
1.7	----	0.9	27.5	30(15)	0.0033	----	4.0	0.0015
----	----	0.5	26.5	30(15)	----	----	4.5	0.0017
----	----	0.5	28.3	42(21)	----	----	7.3	0.0049
----	----	0.3	24.9	42(21)	----	----	5.3	0.0029
----	----	0.6	25.4	42(21)	----	----	9.1	0.0062
----	----	0.7	25.1	38(19)	----	----	9.1	0.0056
----	----	0.66	25.7	34(17)	----	----	9.7	0.0054
----	----	0.7	24.8	38(19)	----	----	9.3	0.0057
----	----	1.6	25.0	34(17)	----	----	6.8	0.0034
----	----	0.68	25.2	34(17)	----	----	5.8	0.0027
----	----	0.9	25.1	34(17)	----	----	7.9	0.0041
----	----	0.99	24.5	28(14)	----	----	5.2	0.0019
----	----	0.28	26.4	30(15)	----	----	4.0	0.0015

Table B.9 Test #30 (continued)

PORT D.O. UPPER Z=6" mg/l	PORT D.O. LOWER Z=6" mg/l	GW D.O. mg/l	TEMP. °C	FLOW ml/min	KLa UPPER hr^{-1}	KLa LOWER hr^{-1}	PORT D.O. Z = 52" mg/l	KLa Z = 52" hr^{-1}
----	----	0.5	25.8	38(19)	----	----	5.5	0.0029
----	----	0.5	26.0	38(19)	----	----	8.6	0.0067
----	----	0.8	25.3	48(24)	----	----	5.4	0.0030
----	----	0.9	25.7	40(20)	----	----	8.2	0.0056
----	----	1.5	24.7	40(20)	----	----	10.4	0.0073
----	----	0.9	24.9	42(21)	----	----	3.9	0.0019
----	----	1.03	24.1	42(21)	----	----	3.9	0.0019
----	----	1.21	23.8	42(21)	----	----	3.8	0.0015
----	----	0.62	23.9	34(17)	----	----	3.2	0.0008
----	----	0.51	23.7	24(12)	----	----	6.6	0.005
----	----	0.5	23.8	54(27)	----	----	7.0	0.0056
----	2.8	0.53	23.8	56(28)	----	0.017	7.7	0.0061
----	2.0	1.0	22.3	58(29)	----	0.010	9.3	0.0057
----	----	1.0	20.7	40(20)	----	----	9.7	0.0075
----	----	1.05	20.8	52(26)	----	----	1.8	----
----	----	1.3	18.9	44(22)	----	----	1.8	------

Table B.9 Test #30 (continued)

Remarks:
- 2 concrete sand layers alternated with 2 clay layers.
- Both injections in the lower sand matrix.
- Location of the two injectors; at start and 1 1/2 ft from the start of the lower sand layer.
- Avg. oxygen holdup upon CGA injection; 42%
- Temperature; 27°C
- Eratic injections.
- CGA injection rates; 635, 975 and 630 ml/min
- CGA injection duration; 1.5, 1.5 and 2 min(s).
- No. of CGA injection; 3.
- Avg. quality; 63%.
- Avg. Stability; 14.
- mg O_2 in; 2593.
- % transferred; 69%.
- Due to reduction in O_2 holdup capacity of cell in Test #29 injections were made in the lower sand layer.
- ** C_{L1}

Table B.10 Test #31 Determination of oxygen transfer coefficients (KLas) in multilayered VSTC after injection of CGA in the lower concrete sand layer; a duplication of Test #30 with a more regular CGA injection schedule: where available, KLa(s) were also calculated for Z = 6".

PORT D.O. UPPER Z=6" mg/l	PORT D.O. LOWER Z=6" mg/l	GW D.O. mg/l	TEMP. °C	FLOW mg/min	KLa UPPER mg/l	KLa LOWER hr^{-1}	PORT D.O. Z = 52" mg/l	KLa Z = 52" hr^{-1}
----	----	0.7	21.2	40(20)	----	----	1.62**	0.0000
----	----	0.6	21.9	42(21)	----	----	8.6	0.0062*
----	----	0.8	21.9	40(20)	----	----	7.0	0.0044
----	----	0.7	20.7	42(21)	----	----	8.64	0.0060
----	----	1.5	20.3	42(21)	----	----	4.86	0.0026
----	----	0.6	21.7	40(20)	----	----	3.42	0.0015
----	----	0.8	22.5	40(20)	----	----	9.2	0.0065
----	----	0.4	23.6	40(20)	----	----	9.0	0.0065
----	----	0.5	23.5	40(20)	----	----	8.8	0.0063
----	----	0.5	23.3	40(20)	----	----	9.5	0.0069
----	----	0.13	24.6	36(18)	----	----	7.2	0.0048
----	----	0.28	24.6	34(17)	----	----	7.0	0.0042
----	----	0.3	27.1	42(21)	----	----	7.5	0.0046
----	----	0.4	26.2	34(17)	----	----	7.5	0.0056
----	----	0.4	25.0	44(22)	----	----	7.2	0.0042
----	----	0.7	25.9	62(31)	----	----	7.2	0.0055
----	----	0.58	25.9	88(44)	----	----	6.7	0.0070

Table B.10 Test #31 (continued)

PORT D.O. UPPER Z=6" mg/l	PORT D.O. LOWER Z=6" mg/l	GW D.O. mg/l	TEMP. °C	FLOW mg/min	KLa UPPER mg/l	KLa LOWER hr^{-1}	PORT D.O. Z = 52" mg/l	KLa Z = 52" hr^{-1}
----	----	0.32	26.5	32(16)	----	----	6.2	0.0089
----	----	0.52	26.6	34(17)	----	----	6.4	0.0034
----	----	0.53	24.9	40(20)	----	----	8.8	0.0055
----	----	0.99	25.4	42(21)	----	----	6.0	0.0038
----	----	2.14	26.5	42(21)	----	----	5.5	0.0037
----	----	0.5	26.4	40(20)	----	----	4.8	0.0029
----	----	1.1	26.0	40(20)	----	----	5.2	0.0031
----	----	1.2	26.8	38(19)	----	----	3.6	0.0017
----	----	1.34	26.7	38(19)	----	----	3.6	0.0017
----	----	0.86	27.3	38(19)	----	----	3.3	0.0014
----	----	0.82	26.9	38(19)	----	----	3.2	0.0013
----	----	0.9	26.8	38(19)	----	----	2.7	0.0009
----	----	0.9	26.7	44(22)	----	----	2.8	0.0010
----	----	0.93	27.0	38(19)	----	----	2.9	0.0010

Remarks:
- CGA injection rate; 700 ml/min
- CGA injection duration; 2.83 min
- No. of CGA injections; 4
- Ave. quality; 69%
- Stability < 10
- mg O_2 in; 3063 mg
- % transferred; 44
- Due to reduction in O_2 holdup capacity of cell injections were made in the lower sand layer
- ** C_{L1}

APPENDIX C

Tabulated D. O. Data Across The VCTC And The Corresponding KLa(s) After Injection of CGA, Sparged Air Or Oxygenated Water In The Vertical Column Test Cell

Table C1. Variations of oxygen transfer coefficient (KLa) in the packed vertical column after injection of 220 ml CGA: A case with high sudden vent losses of oxygen gas.

Test No.	Time (min)	D.O. Ports Sampled* (mg/l)						Vented Gas (ml)♦		KLa (h^{-1})
		1	2	3	4	5	GW	Over head	D.O. Ports	
1	0	0.5**	0.5	0.5	0.5	0.5	-	-	0	-
	120	10.30	-	-	-	5.30	-	70	0	0.391
	200	1.80	3.70	5.70	-	7.40	-	80	0	0.045
	1200	0.09	0.10	0.12	0.16	0.40	1.35	80	0	-
	2100	0.09	0.10	0.13	0.16	0.32	-	-	-	-

Test parameters

- CGA flow rate; 22 ml/min
- Duration of CGA injection; 10 min.
- Quality/Stability; 70/11
- Groundwater flowrate; 15 ml/min (cocurrent upflow)
- 200 ppm NaDBS surfactant solution
- Z = 6"

- **C_{L1}
- ♦ cumulative values
- *Port No. 1 is 6 inches above CGA injector

Table C2. Variations of dissolved oxygen profile and oxygen transfer coefficient (KLa) in the packed vertical column after injection of 220 ml CGA: A case with gradual and low vent losses.

Test No.	Time (min)	D.O. Ports Sampled* (mg/l)						Vented Gas (ml)♦		KLa (h^{-1})
		1	2	3	4	5	GW	Over head	D.O. Ports	
2	0	1.0**	1.9	2.19	1.4	0.68	-	-	-	-
	30	15.55	8.1	7.09	1.42	1.85	0.51	0	0	0.646
	60	13.88	14.10	12.12	4.85	1.76	0.50	25	0	0.551
	90	10.23	13.86	12.98	6.08	2.24	0.50	35	0	0.368
	120	7.66	13.4	12.97	6.96	3.29	0.48	35	0	0.254
	150	6.05	12.00	13.57	8.90	3.45	0.40	50	0	0.187

Test parameters:

- CGA flow rate; 22 ml/min
- Duration of CGA injection; 10 min.
- Quality/Stability; 70/11
- Groundwater flowrate; 15 ml/min (cocurrent upflow)
- 200 ppm NaDBS surfactant solution
- Z = 6"

- ** C_{L1}
- ♦ cumulative values
- *Port No. 1 is 6 inches above CGA injector

Table C3. Variations of oxygen transfer coefficient (KLa) in the packed vertical column after injection of 110 ml CGA: No overhead vent losses as the result of reduced volume of CGA injected.

Test No.	Time (min)	D.O. Ports Sampled* (mg/l)						Vented Gas (ml)♦		KLa (h^{-1})
		1	2	3	4	5	GW	Over head	D.O. Ports	
3	0	0.27**	0.48	0.55	0.69	0.89	0.2	0	0	-
	70	11.40	0.61	0.37	0.57	0.98	0.51	0	0	0.311
	100	13.26	8.05	1.06	0.49	0.74	0.22	0	0	0.187
	130	11.48	11.19	6.41	0.92	1.26	0.45	0	0	0.312
	160	8.61	9.97	10.44	4.35	0.75	0.48	0	0	0.221

Test parameters

- CGA flow rate; 22 ml/min
- Duration of CGA injection; 5 min.
- Quality/Stability; 65/11
- Groundwater flowrate; 15 ml/min (cocurrent upflow)
- 200 ppm NaDBS surfactant solution
- Z = 6"

- **C_{L1}
- ♦ cumulative values
- *Port No. 1 is 6 inches above CGA injector

Table C4. Variations of dissolved oxygen profile and oxygen transfer coefficient (KLa) in the packed vertical column after injection of 110 ml CGA: Effect of reduced surfactant concentration and reduced quality.

Test No.	Time (min)	D.O. Ports Sampled* (mg/l)						Vented Gas (ml)♦		KLa (h^{-1})
		1	2	3	4	5	GW	Over head	D.O. Ports	
4	0	0.1*	0.08	0.11	0.12	0.18	0.21	0	0	-
	30	0.22	0.11	0.14	0.16	0.33	0.20	0	0	0.003
	60	1.88	0.14	0.06	0.10	0.41	0.24	0	0	0.040
	90	-	0.15	0.11	0.25	1.53	0.30	0	15	-
	130	4.84	0.21	0.14	0.40	2.10	0.53	0	15	0.113

Test parameters:

- CGA flow rate; 22 ml/min
- Duration of CGA injection; 5 min.
- Quality/Stability; 57/19
- Groundwater flowrate; 15 ml/min (cocurrent upflow)
- 200 ppm NaDBS surfactant solution
- Z = 6"

- ** C_{L1}
- ♦ cumulative values
- *Port No. 1 is 6 inches above CGA injector

Table C5. Variations of dissolved oxygen profile and oxygen transfer coefficient (KLa) in the packed vertical column after injection of 110 ml CGA: Effect of increased quality and stability.

Test No.	Time (min)	D.O. Ports Sampled* (mg/l)						Vented Gas (ml)♦		KLa (h^{-1})
		1	2	3	4	5	GW	Over head	D.O. Ports	
5	0	0.24**	0.12	0.12	0.31	0.94	0.30	0	0	-
	30	8.47	6.61	4.31	1.87	0.62	0.46	0	3	0.217
	60	10.41	7.11	6.26	2.55	0.43	0.42	0	5	0.277
	85	10.11	7.59	6.55	4.24	0.81	0.36	0	5	0.267
	115	9.75	8.04	6.66	3.99	1.23	0.38	0	8	0.256
	145	9.38	7.90	7.23	4.84	1.38	0.46	0	8	0.245
	185	8.01	5.71	6.54	6.60	4.54	0.40	0	10	0.203
	235	6.06	5.11	6.04	6.80	5.43	0.47	0	12	0.147
	285	5.04	4.45	5.54	6.62	5.91	0.50	0	16	0.119
	345	1.65	2.89	4.02	5.21	6.62	0.47	0	16	0.033
	495	0.57	0.77	1.26	2.40	4.72	0.91	0	16	0.008

Test parameters:

- CGA Flow rate; 22 ml/min
- Duration of CGA Injection; 5 min.
- Quality/Stability; 76/6
- Groundwater flowrate; 15 ml/min (cocurrent upflow)
- Z = 6"
- 200 ppm NaDBS surfactant solution

- ** C_{L1}
- ♦ cumulative values
- *Port No. 1 is 6 inches above CGA injector

Table C6. Variations of dissolved oxygen profile and oxygen transfer coefficient (KLa) in the packed vertical column after injection of oxygenated water.

Test No.	Time (min)	D.O. Ports Sampled* (mg/l)						Vented Gas (ml)♦		KLa (h^{-1})
		1	2	3	4	5	GW	Over head	D.O. Ports	
6	0	0.80**	0.38	0.20	0.23	0.50	0.17	0	-	-
	30	6.04	1.82	1.13	0.62	0.56	0.87	0	2	0.125
	88	3.96	3.12	2.44	1.27	0.74	0.40	0	5	0.073
	148	1.21	2.52	2.80	2.01	1.20	0.65	0	5	0.009
	208	0.33	1.12	1.77	2.24	1.89	0.62	0	5	-

Test parameters:

- Oxygenated water injected in the cell
- D.O. of oxygenated water; 24.0 mg/l
- Oxygenated water flow rate; 22 ml/min
- Duration of injection of oxygenated water; 15.35 min
- Groundwater flow rate; 25.7 ml/min (upflow)
- Z = 6"

- ** C_{L1}
- ♦ cumulative values
- *Port No. 1 is 6 inches above oxygenated water injector

NOTE: For sake of consistency, (KLa(s) were derived same as for CGA or sparged air

Table C7. Variations of dissolved oxygen profile and oxygen transfer coefficient (KLa) in the packed vertical column after air sparging.

Test No.	Time (min)	D.O. Ports Sampled* (mg/l)						Vented Gas (ml)♦		KLa (h^{-1})
		1	2	3	4	5	GW	Over head	D.O. Ports	
7	0	0.12**	0.16	0.19	0.18	0.38	0.38	-	2	-
	30	1.80	2.52	2.24	1.97	1.69	0.56	560	3	0.220
	90	1.77	2.10	2.23	1.96	1.83	0.67	560	4	0.220
	150	0.72	1.78	1.92	2.04	1.90	0.47	560	6	0.070
	195	0.61	1.57	1.83	2.03	2.00	0.85	560	6	0.060

Test parameters:

- Air was sparged in the column
- Air flow rate; 34.1 ml/min
- Duration of air sparging; 17.23 min.
- Groundwater flow rate; 15 ml/min. (cocurrent upflow)
- Z = 6"

- ** C_{L1}
- ♦ cumulative values
- *Port No. 1 is 6 inches above air sparger (injector)

Table C8. Variations of dissolved oxygen profile and oxygen transfer coefficient (KLa) in the packed vertical column after injection of 110 ml CGA: A case in which less D.O. sampler were taken and oxygen transfer was extended to 255 minutes.

Test No.	Time (min)	D.O. Ports Sampled* (mg/l)						Vented Gas (ml)♦		KLa (h^{-1})
		1	2	3	4	5	GW	Over head	D.O. Ports	
8	0	0.14**	-	0.18	-	0.59	0.30	-	-	-
	60	1.76	-	3.65	-	0.37	0.60	2	0	0.038
	120	11.20	-	9.30	-	0.45	0.62	2	0	0.30
	175	7.70	-	10.33	-	0.96	0.69	2	0	0.193
	255	6.17	-	9.60	-	3.61	0.74	3	0	0.150

Test parameters:

- CGA flow rate; 22 ml/min
- Duration of CGA injection; 5 minutes
- Quality/Stability; 67/11
- Groundwater flowrate; 15 ml/min (cocurrent upflow)
- 200 ppm NaDBS surfactant solution
- A repeat of Test #3
- Z = 6"
- Less samples taken out

- ** C_{L1}
- ♦ cumulative values
- *Port No. 1 is 6 inches above CGA injector

APPENDIX D

Computer Program (In Basic) Used

To Compute The KLa Values

```
1 COLOR 2
10 PRINT "  Cs = SATURATION CONCENTRATION OF D.O. (mg/L)"
20 PRINT "  Ci = INITIAL CONCENTRATION OF GROUND WATER D.O. AT"
30 PRINT "       THE INJECTION PORT"
40 PRINT "  CL1 = INITIAL CONCENTRATION OF D.O. AT THE FIRST SAMPLE"
50 PRINT "        PORT (START OF PERIOD)"
60 PRINT "  CL2 = FINAL CONCENTRATION OF D.O. AT THE FIRST SAMPLE"
80 PRINT "  Q = FLOW RATE (ml/min)"
90 PRINT "  A = CROSS SECTIONAL AREA OF FLOW (SQ. cm.)"
100 PRINT "  Z = DISTANCE BETWEEN INJECTION PORT AND FIRST SAMPLE (D.O.)"
110 PRINT "      PORT"
120 PRINT "  KLa = OXYGEN TRANSFER COEFFICIENT (1/hr)"
130 PRINT "  LOGMEAN D.O. (LMDO) = THE AVERAGE OF D.O. DRIVING FORCE"
140 PRINT "                        BETWEEN INJECTION AND FIRST SAMPLE"
150 PRINT "                        PORTS"
160 REM
170 REM THIS PROGRAM IS DESIGNED TO CALCULATE THE KLa VALUES FOR THE
180 REM LARGE VERTICLE TEST CELL AND THE TEST CYLINDERS USED BY THE
190 REM HAZARDOUS WASTE TREATMENT GROUP.
200 REM
210 REM
211 INPUT "ENTER THE VALUE FOR TEMPERATURE IN CELSIUS",T
212 HHH=10^((-14501/(1.987*(T+273)))+7.11)
213 CS=1654656!/HHH
214 PRINT "IS THIS A REASONABLE VALUE FOR CS ? [Y/N]"CS
215 X$=INPUT$(1)
216 IF X$="Y" THEN GOTO 219 ELSE 211
219 CLS
220 INPUT "ENTER YOUR VALUE FOR CI  ",CI
221 PRINT "YOUR ENTERED VALUE FOR CI IS" CI
223 PRINT "IS THIS CORRECT ? [Y/N]"
224 X$=INPUT$(1)
225 IF X$="Y" THEN 230 ELSE 219
230 CLS
231 INPUT "ENTER YOUR VALUE FOR CL1  ",CL1
232 PRINT "YOUR CL1 VALUE IS" CL1
233 PRINT "IS THIS CORRECT? [Y/N]"
234 X$=INPUT$(1)
235 IF X$="Y" THEN 240 ELSE 230
240 CLS
241 INPUT "ENTER YOUR VALUE FOR CL2  ",CL2
242 PRINT "YOUR CL2 VALUE IS" CL2
243 PRINT "IS THIS CORRECT? [Y/N]"
244 X$=INPUT$(1)
245 IF X$="Y" THEN 250 ELSE 240
250 CLS
251 INPUT "ENTER YOUR VALUE FOR Q  ",Q
252 PRINT "YOUR FLOW [Q] VALUE IS" Q
```

```
253 PRINT "IS THIS CORRECT? [Y/N]"
254 X$=INPUT$(1)
255 IF X$="Y" THEN 259 ELSE 250
259 CLS
260 INPUT "ENTER YOUR VALUE FOR A  ",A
261 PRINT "YOUR AREA [A] VALUE IS" A
262 PRINT "IS THIS CORRECT? [Y/N]"
263 X$=INPUT$(1)
264 IF X$="Y" THEN 270 ELSE 259
270 CLS
271 INPUT "ENTER YOUR VALUE FOR Z  ",Z
272 PRINT "YOUR Z VALUE IS" Z
273 PRINT "IS THIS CORRECT? [Y/N]"
274 X$=INPUT$(1)
275 IF X$="Y" THEN 280 ELSE 270
280 REM
290 D1 = CS - CI
300 D2 = CS - CL2
310 LMDO = (D1-D2)/LOG(D1/D2)
320 KLA = (Q*(CL2-CL1)/A*60)/(Z*LMDO)
321 CLS
330 PRINT "CS =" CS
340 PRINT "CI =" CI
350 PRINT "CL1 =" CL1
360 PRINT "CL2 =" CL2
370 PRINT "FLOW (Q) =" Q
380 PRINT "AREA (A) =" A
390 PRINT "Z =" Z
391 PRINT "LMDO = " LMDO
400 PRINT "KLa =" KLA
401 PRINT "LMDO = " LMDO
410 PRINT "DO ANOTHER CALCULATION?"
420 X$=INPUT$(1)
430 IF X$="Y" THEN 10 ELSE 901 CLS
901 CLS
902 PRINT "PROGRAM TERMINATED"
903 END
```

APPENDIX E

Oxygen Transfer And Material Balance In Vertical Column Test Cell

Table E.1 Test #2: Oxygen transfer and material balance in the packed vertical column test cell after injection of 220 ml oxygen CGA in the sand matrix. Effect of overloading the sand matrix with CGA; considerable volume of CGA was vented out of the sand due to overloading.

TIME (HR)	DO (MG/L)	MOLES (O_2/HR)	MOLES (O_2)	CUM. MILLIMOLES	CUM. MILLIMOLES TRANS. & VENTED
0.5	26.84	.000755	.000377	.377	0.377
1.0	27.82	.000782	.000391	.768	1.805
1.5	12.06	.000339	.000170	.938	2.390
2.0	6.87	.000193	.000121	1.0591	2.510
2.5	6.87	.000193	.000097	1.156	3.230

Remarks:

- Concrete sand packing
- CGA injection rate, 22 ml/min
- CGA injection duration, 10 min
- No. of CGA injections, 1
- Ave. quality, 70%
- Ave. stability, 8
- Millimoles O_2 in, 6.2
- Oxygen transfer, 18.6%

Table E.2 Test #3: Oxygen transfer and material balance in the packed vertical column test cell after injections of 110 ml oxygen CGA in the sand matrix: effect of reduced volume of oxygen CGA injection compared with Test #2; volume of CGA injected was reduced in half, consequently no vent losses were realized.

TIME (HR)	DO (MG/L)	MOLES (O_2/HR)	MILLIMOLES (O_2)	CUM. MILLIMOLES
0.533	11.00	.000309	0.165	0.165
1.033	20.61	.000580	0.290	0.455
1.533	20.70	.000582	0.291	0.746
2.033	13.89	.000391	0.195	0.941

Remarks:
- Concrete sand packing
- CGA injection rate, 22 ml/min
- CGA injection duration, 5 min
- No. of CGA injections, 1
- Further reading not taken due to operator error

- Ave. quality, 65
- Ave. stability, 11
- Millimoles O_2 in, 2.9
- Oxygen transfer, 32%

Table E.3 Test #4: Oxygen transfer and material balance in the packed vertical column test cell after injection of 110 ml oxygen CGA in the sand matrix: Effect of reduced quality and stability; compared with Test #5 quality and stability of CGA was decreased, consequently oxygen transferred to water decreased.

TIME CUM. (HR)	D.O. (mg/l)	MOLES (O_2/hr)	MOLES O_2	CUM. MILLIMOLES
0.5	0.37	1.04×10^{-5}	5.21×10^{-6}	5.21×10^{-3}
1.0	1.65	4.64×10^{-5}	2.32×10^{-5}	2.84×10^{-2}
1.5	1.33	3.74×10^{-5}	3.74×10^{-5}	6.28×10^{-2}
2.2	5.35	2.00×10^{-4}	1.4×10^{-4}	2.06×10^{-1}

Remarks:
- Concrete sand packing
- CGA injection rate, 22 ml/min
- CGA injection duration, 5 min
- No. of CGA injections, 1
- Ave. quality, 57
- Ave. stability, 19
- Millimole O_2 in, 2.5
- Oxygen transferred, 8.2%

Table E.4 Test #5: Oxygen transfer and material balance in the packed vertical column test cell after injections of 110 ml oxygen CGA in the sand matrix: effect of increased quality and stability; compared with Test #4 quality and stability of CGA was increased, consequently oxygen transferred to water increased.

TIME (HR) CUM.	DO (MG/L)	MOLES (O_2/HR)	MOLES (O_2)	CUM. MILLIMOLES	CUM. MILLIMOLES TRANS. & VENTED
.4667	20.47	.000576	.000269	0.269	0.390
.9667	13.08	.000358	.000179	0.448	0.660
1.3834	12.53	.000352	.000147	0.595	0.810
1.8834	10.12	.000285	.000143	0.738	1.880
2.3834	10.43	.000293	.000147	0.885	1.220
3.3834	9.59	.000270	.000270	1.155	1.580
4.3834	5.65	.000159	.000159	1.314	1.810
5.2167	3.71	.000104	.000087	1.401	2.060

Remarks:

- Concrete sand packing
- CGA injection rate, 22 ml/min
- CGA injection duration, 5 min
- No. of CGA injections, 1
- Ave. quality, 76%
- Ave. stability, 6
- Millimole O_2 in, 3.4
- Oxygen transferred, 41%

Table E.5 Test #6: Oxygen transfer and material balance in the packed vertical column test cell after injection of oxygenated water in the sand matrix.

TIME (HR)	DO (MG/L)	MOLES (O_2/HR)	MOLES (O_2)	MOLES LEFT THE SYSTEM	% MOLES IN THE SYSTEM
1.10	8.06	.000227	.000250	0.00000	100
2.067	6.59	.000185	.000179	0.000071	72
3.067	1.76	.000050	.000050	0.00020	2

Remarks:
- Concrete sand packing
- Oxygenated water injection rate; 22 ml/min
- Oxygenated water injection duration; 15.33 min
- D.O. of water injected; 23.9 mg/l
- No. of injections; 1

Table E.6 Test 8: Oxygen transfer and material balance in the packed vertical column test cell after injection of 110 ml oxygen CGA. A repeat of Test #3 with less sampling frequency.

TIME (HR)	FLOW RATE L/MIN	DO (MG/L)	MOLES (O_2/HR)	MOLES (O_2)	CUM. MILLIMOLES	CUM. MILLIMOLESTRANS. & VENTED
0.5	17.5	15.87	0.000521	0.00026	0.26	0.340
1.5	12.08	16.33	0.00037	0.00037	0.63	0.710
2.417	7.27	8.62	0.000175	0.00011	0.74	0.820
3.75	11.25	7.4	0.000150	0.00021	0.95	1.030
6.65	7.20	1.35	0.0001825	0.000053	1.0	1.120

Remarks:

- Concrete sand packing
- CGA injection rate, 22 ml/min
- CGA injection duration, 5 min.
- No. of CGA injections, 1
- Ave. quality, 67
- Ave. stability, 11
- Millimoles O_2 in, 2.99
- Oxygen transfer, 33%

VITA

Mehran Lotfi was born on May 9, 1951, finished high school in June 1969 and received his B.S. in Geology from the University of Texas in December 1974. He started his graduate work at Virginia Tech in Mining and Minerals Engineering and received his M.S. in June 1978. He started his doctoral graduate work at West Virginia University in September 1979. In July 1982, he was invited to join Coal Technology Corporation as Director of Research and Development. During his stay with the company, Mr. Lotfi developed a new technology in manufacturing industrial bricks and consolidation of industrial and domestic waste. In 1984, he returned to West Virginia University to complete his Doctorate and received his Ph.D. in Mining Engineering in May 1985. Dr. Lotfi then started work with Unitech International Corporation as Coordinator, Research and Development and continued to work with waste stabilization, soil treatment and development of recycling and reclamation methods. In 1987, he entered in private consulting and in 1989 he started to work as Research Associate with the Hazardous Waste Group in the Department of Chemical Engineering at Virginia Tech. He ceased the opportunity to further his knowledge of Environmental Engineering by enrolling on a part-time basis in the Environmental Engineering program at Virginia Tech where he is currently a candidate for a Master of Science Degree in Environmental Engineering.

Dr. Lotfi and his wife, Nasrin, have a son, Puyan, and are expecting a second child in December 1990.