FINAL REPORT

IN SITU BIORESTORATION OF NITRATE CONTAMINATED WATER WELLS

Volume 1

EXPERIMENTAL STUDIES

Project Investigators:

M. Yavuz Corapcioglu and W. Michael Stallard

Department of Civil Engineering
Texas A&M University
College Station, TX 77843-3136

Phone (409) 845-9782
e-mail yavuz@acs.tamu.edu

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ABSTRACT

The investigation of a technique for protecting a downstream drinking water well from nitrate contamination of groundwater is presented. A recirculating nitrate treatment well system is proposed in which groundwater is drawn into the well, denitrified in the treatment chamber, and returned to the top of the aquifer. Well hydraulics were experimentally examined in a two-dimensional aquifer model, and ambient groundwater velocities of 1 to 3 m/day were simulated in combination with well recirculation rates of 25 to 200 ml/min. An on-line feed control system was developed for testing the treatment barrier associated with well recirculation and biological denitrification. The impacts of carbon feed, groundwater flow, nitrate loading, and well recirculation on the performance of system operation were also investigated.

Hydraulic problems identified with experimental apparatus included blow-through of contaminant at the well intake by high ambient groundwater velocities and submergence by the well hydraulics of depth-distributed contaminant plumes without interception. The problems associated with biological denitrification were found to be possible permeability loss by screen fouling and blinding of soil pores by overfeed of carbon. These identified problems were corrected by maintaining a greater well recirculation rate and adjusting carbon feed at stoichiometric ratio of nitrate load to the well.

This study has demonstrated that the recirculating nitrate treatment well system may be a feasible process for protecting drinking water wells from groundwater contamination in a sandy unconfined aquifer. Experimental results provide guidance in identifying affecting parameters that could possibly affect the performance of the treatment system. On the basis of experimental results, the procedures of system design were also developed for evaluating the feasibility of the proposed methodology.

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CHAPTER I

INTRODUCTION

BACKGROUND

Groundwater stored pore water beneath the ground surface is considered a rechargeable resource from precipitation. Groundwater serves a primary water supply of potable water and agricultural irrigation in the United States. It has been estimated that almost 100 million people, or about half of the nation's population, is served by ground water as its source of drinking water (Bittion and Gerba, 1984). An aquifer, defined as a geologic formation transmitting significant quantities of groundwater under ordinary field conditions, can be contaminated by a variety of sources. Often groundwater pollution is not detected until the pollutant appears at a well some distance from the source of pollution, making the problems associated with groundwater contamination more difficult and complicated. Such problems, however, have made the public aware of the growing importance of maintaining groundwater quality.

Groundwater quality trends vary widely, depending on the local geology, cultivation activities, and the release from industrial and municipal sources. In agricultural regions, groundwater pollution might be caused by high pesticide and fertilizer residues. According to a EPA national pesticide survey, almost 57% of rural domestic water wells were detected with nitrate contamination, and 4.2 % of the nitrate contaminated wells were above USEPA maximum contaminant level of 10 mg/L as nitrogen (USEPA, 1990). Nitrate is identified as one of the most common groundwater contaminants in the United States, and it may originate from a number of non-point sources. Accumulation of nitrate in groundwater has been attributed to the excessive use of fertilizers. Nitrate contamination of groundwater can result from many other causes, including natural deposits of nitrate origins, effluent from septic tanks, seepage from livestock urine and manure, and percolation of urban stormwater runoff.

The extent of nitrate contamination of groundwater varies greatly from region to region, but major areas of nitrate pollution often occur where irrigation and nitrogen fertilizers are applied. It has been estimated that almost 100 kg nitrogen per hectare is lost into the

environment under irrigation because the utilization efficiency of nitrogen in cropping system is seldom more than 50% (Power and Schepers, 1989). U.S. Geological Survey and Texas Water Development Board have conducted groundwater monitoring over a period of 30 years to gain insight on the extent of nitrate contamination of groundwater The nationwide survey showed that 6.4 % of the well samples in the United States had nitrate concentrations over 10 mg/L as nitrogen. Nitrate contamination of groundwater is a particular problem for the heavily populated states in the north-east and for the Great Plains and western states with relatively large areas under irrigation (Madison and Brunett, 1985).

Frequently, high nitrate concentrations are distributed in the upper zone of an aquifer and decrease as the depth increases. Thus, depth of groundwater is an important factor in determining frequency of nitrate contamination (Power and Schepers, 1989). In an Iowa rural well water survey, 35% of private wells less than 15 m deep exceed the health advisory level of 10 mg/L nitrate as nitrogen, and only 4% of the private wells statewide were more than this value (Kross et al., 1993). Highly nitrate-contaminated wells are those that do not extend far into the aquifer, so depth of well penetration could be the best predicator of the contamination level of drinking water wells. Shallow wells may contain greater concentrations, or even unsafe levels, of nitrate. Even though efforts have been made by agriculturists to improve nitrate utilization efficiency, nitrate contamination is still an unsolved problem in the shallow unconfined aquifer.

Some epidemiological studies showed that high doses of nitrate intake can cause adverse health effects in humans and domestic animals. There is insufficient information currently available to determine the relationship between nitrate intake and human cancer, but some evidence demonstrates that high levels of nitrate in drinking water is linked to birth defects (Dorsch et al., 1984; Arbuckle et al., 1988) and gastric cancer (Fraster et al., 1980; Forman et al., 1985). Nitrate itself is not a direct toxicant. However, nitrate becomes a health hazard when it is converted to nitrite in the gastrointestinal tract. Nitrite will react with hemoglobin to form methemoglobin and thus reduce the oxygen-carrying capability of blood. The disease known as methemoglobinemia or the blue baby syndrome sometimes can result in a high risk for infants. In addition, nitrite in the gastrointestinal tract might react with secondary amines and amides to form nitrosamines which are responsible for the occurrence of stomach cancer. Hartman (1983) reported that nitrate ingestion is correlated to gastric cancer mortality, implying that nitrate is a procarcinogen.

Nitrate could be sequentially transformed to nitrogen gas by the denitrification processes. Natural denitrification does occur in many aquifers, but the removal of large

amounts of nitrate in many aquifer systems requires more than natural processes. Natural denitrification of groundwater is not extensive and is limited by the availability of organic carbon. Citing an example from a site near Tampa, Florida, Bradley et al. (1992) pointed out that denitrification rates were carbon limited in a shallow anaerobic groundwater system. According to Thurman's survey (1985), the median dissolved organic carbon content of groundwater was 0.7 mg/L for sandstone, limestone, and sand and gravel aquifers in the United States. Thus, artificial approaches for the removal of nitrate from groundwater would be required to maintain the high quality of drinking water.

There are several alternatives available for nitrate removal from groundwater. These nitrate removal alternatives include ion exchange, biological denitrification, chemical reduction, reverse osmosis, and electrodialysis; however, only ion exchange and biological denitrification are considered feasible and practical for the large-scale treatment of drinking water (van der Hoek and Klapwijk, 1987). A problem with ion exchange technology is the disposal of brine with high concentrations of nitrate, sulfate, and chloride. Biological denitrification may cause a potential risk of bacteriological contamination of groundwater. After comparing several nitrate removal technologies, Hiscock et al. (1991) pointed out that the stimulation of artificial denitrification as water treatment processes may offer a simple and inexpensive method of nitrate removal.

Conventional pump-and-treat techniques for groundwater cleanup are not economical since the costs of above ground facility establishment and long-term operation and maintenance are tremendous. A vertical groundwater circulation system currently being used for stripping volatile organic compounds implied that local groundwater interception could be achieved. Thus, the attempt of protecting a drinking water well could be hydraulically accomplished by the application of this specially designed groundwater circulation well. Due to the need for maintaining drinking water quality, the hydraulic technique of local groundwater interception associated with a reliable method of decontamination against nitrate contamination has been devised as a scheme for removing nitrate contamination from individual drinking water wells and protecting uncontaminated wells.

PROPOSED SCHEME

The proposed treatment system that consists of one or more large diameter recirculating nitrate treatment wells containing a population of denitrifying bacteria will be installed upstream of the drinking water well. There are two functions of the recirculating nitrate

treatment well: a hydraulic function to perform vertical groundwater recirculation and a biological function to achieve decontamination. A recirculating nitrate treatment well consists of an injection casing on the top and a withdrawal casing at the bottom; each casing having the same size openings allows an equal flow entering or exiting the recirculating well. As the recirculating well operates, groundwater is vertically recirculated in such a way that water particles are driven into the withdrawal casing, drawn into the recharge casing, and returned to the aquifer (FIG 1). In the recirculating nitrate treatment well, the carbon source is amended to support its biological function of denitrification. As groundwater contaminants migrate near the recirculating nitrate treatment well, upgradient contaminated water will be forced into the well, treated within the well, and released to the aquifer. Nitrate will be intercepted upstream by the treatment barrier around the well; only denitrified water can reach the drinking water well.

OBJECTIVES

The overall objective of this research is to demonstrate the feasibility of protecting a drinking water well from migrating nitrate contamination by the application of a recirculating nitrate treatment well system in a simulated unconfined aquifer. This goal will be achieved by completing the following tasks:

1. Develop an experiment method to observe the hydraulic behaviors of a recirculating nitrate treatment well.
2. Determine the factors that could possibly affect the design and placement of the recirculating nitrate treatment well.
3. Determine kinetic parameters and model equations that quantify the denitrification processes.
4. Evaluate the overall performance of the recirculating nitrate treatment well system.

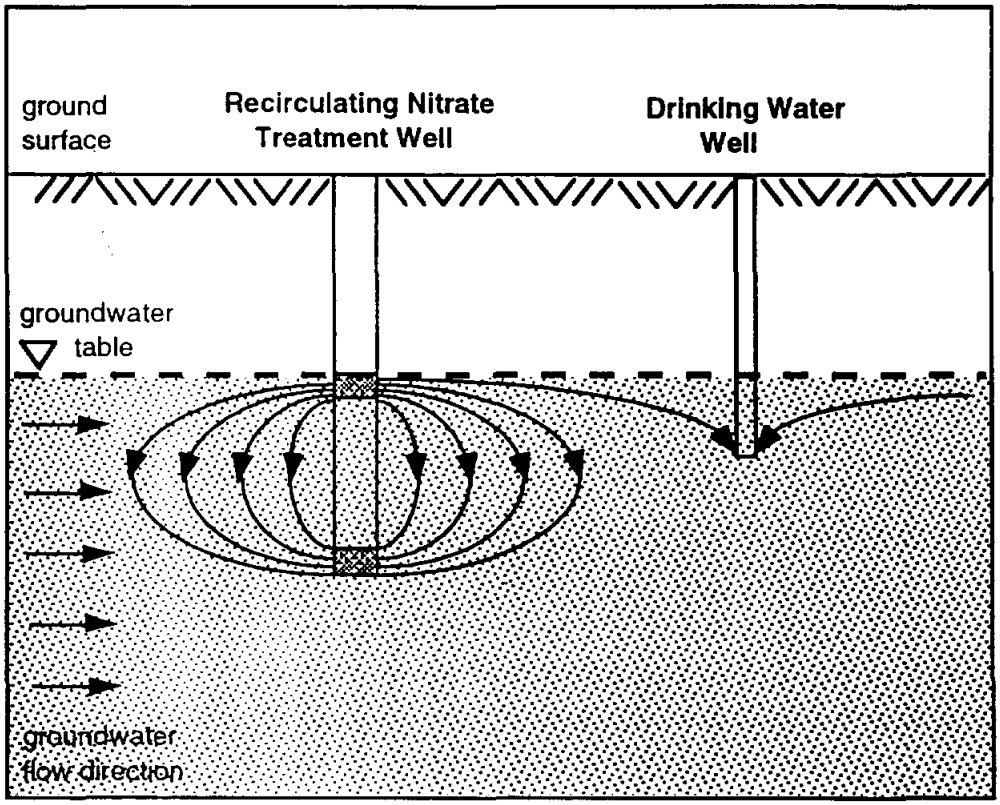


FIG 1. The Proposed Scheme of Protecting an Individual Drinking Water Well by the Recirculating Nitrate Treatment Well System

CHAPTER II

LITERATURE REVIEW

Assuming the groundwater supply has been seriously contaminated, the option is either to provide treatment technology to remediate groundwater contamination or to abandon the source of water supply. The available treatment methodologies for dealing with groundwater contamination fall within four categories: (1) containing the contaminants in place, (2) removing contaminants from ground altogether, (3) treating the contaminants in situ, and (4) attenuating the possible hazard by institutional controls (OTA,1984). Generally, several treatment techniques are combined in order to achieve the desired results. In some situations, it might be reasonable to attempt to degrade or immobilize a contaminant or to contain it within a specified or general area (Pettyjohn, 1987). The Environmental Engineering Research Council of ASCE (1990) also pointed out that in situ treatment techniques typically require the simultaneous use of containment technologies to isolate the treatment zone. The proposed remediation scheme for nitrate contamination of groundwater is essentially to apply containment technology incorporated with in-situ treatment.

Groundwater cleanup or aquifer restoration technologies have been typically viewed as time-consuming, costly, and sometimes unreliable undertakings. Thus, a good understanding of groundwater hydraulics, treatment methodology, microbiology, and geochemistry is essential for carrying out a successful groundwater remediation. Conventional on-site treatment methods and laboratory studies on the removal of nitrate nitrogen were reviewed to aid the treatment system design.

GROUNDWATER HYDRAULICS

Conventional pump-and-treat technology has been employed as the primary method to remediate groundwater contamination for the past 10 years. Groundwater is pumped from the contaminated aquifers and decontaminated at the surface by any of various treatment technologies, including air stripping, carbon adsorption, catalytic oxidation, and thermal or biological treatment. Pump-and-treat technology can be effective in reducing contaminant mass or keeping contamination from spreading, but it does a poor job of cleaning aquifers to drinking water standards (Hasbach, 1993). EPA's Kerr Lab (1987) also made a similar comment on pump-and-treat remediation, noting that the goal of reaching stringent health-

based cleanup standards is very remote and the ultimate cost of cleanup very high. Even though the effectiveness of pump-and-treat technology is hampered by a long period of cleanup time, it is still known as an effective process for remediating inorganic contamination of groundwater.

Controlling the movement of contaminated groundwater by means of recharge and discharge wells has been practiced for several years. In this method, recharge wells are used to develop a hydraulic barrier to force the contaminant plume to move in a preferred direction (Pettyjohn, 1987). The concept of inducing a horizontal hydraulic circulation from recharge wells toward discharge wells is applied as a technique for protecting downgradient groundwater. The originally contaminated aquifer water will be replaced with cleaned water, extracted above ground or treated in situ, and restored to the aquifer. Through repeated contaminant extraction and hydraulic restoration, the aquifer will slowly become restored, and downgradient groundwater will be simultaneously protected. The practical use of the horizontal hydraulic circulation system can run transverse to or against the direction of groundwater movement, and one or a series of treatment zone will be transversely developed under the regime of horizontally circulating flow fields (McCarty et al., 1989).

More recently, vertically circulating flow fields have been applied as the means of extracting groundwater contaminants. The technique entails completing a well in two compartments and inducing extraction from one compartment and injection to the other compartment, thereby inducing a circulating flow field near the well (Philip and Walter, 1992). Inducement of a vertical hydraulic circulation from a single well was first introduced as a technique for measuring vertical permeability in petroleum reservoirs (Burns, 1969). The application of vertical circulation flows for remediating strippable volatile contaminants has been currently operated at several locations in Germany (Herrling and Buermann, 1990). At numerous locations in Germany and recently in the United States, the vertical circulation flows are utilized for physical and/or, recently, for biological in situ groundwater remediation (Herrling and Stamm, 1992). However, the capture zones of vertical circulation wells will be significantly smaller than those associated with traditional capture wells of equivalent discharge (Philip and Walter, 1992). Further advantages of the application of vertical circulation wells as reported by Herrling et al. (1991) are as follows:

- Space requirement is small,
- Investment and operating cost will be considerably lower,

- Soil vapor extraction can be possibly operated at the same time,
- Remediation operation is continuous even at low well capacity, and
- Remediation of the groundwater can take place down to the bottom of the aquifer.

Thus, the application of vertically circulating flow fields may form a hydraulic barrier to retard the transport of groundwater contaminants. The containment methodology can confine groundwater contaminant in a specified zone, but groundwater contaminants won't be automatically disappeared. For the cleanup of groundwater contamination, another remedial strategy should be incorporated for the removal of the contaminated content in groundwater.

TREATMENT METHODOLOGY

In-situ treatment technologies are basically categorized as biological degradation and chemical degradation. Biological degradation of contaminants is aimed at enhancing the growth of existing population of bacteria through the addition of a carbon source, growth nutrients, or electron acceptors. Chemical degradation is an attempt to treat contaminants by precipitation through the addition of an appropriate chemical agent. Overall, the methodology of chemical degradation is much less developed than are the biological approaches with few commercial applications (OTA, 1984). In situ bioremediation of contaminated soils and groundwater aquifers is a renovated technology, and current knowledge is at a relatively early stage of development with most existing applications. Some successful applications of in-situ bioremediation have been implemented, but most cases have been focused on the degradation of organic contaminants.

Selection of Treatment Method

Ideally, a remediation project for contaminated sand and gravel aquifers would be designed based on a solid understanding of the mass and types of pollutants released, the current location of all the mass remaining in the subsurface, and the processes controlling the removal of the mass from subsurface (McCay and Cherry, 1989). Nitrate contamination of groundwater is a potential cumulative effect of a number of non-point sources. Several quantitative models can predict nitrate formation from agricultural practices (Honeycutt et al., 1991) and on-site sewage disposal practices (Hantzsche and Finnemore, 1992), but the level of nitrate contamination still relies on the samplings from the monitoring wells. It was found that the level of nitrate contamination significantly decreased with increased well depth (Hallberg, 1989), but the factors affecting the vertical

distribution of nitrate in aquifers are complex and poorly understood. Spalding and Exner (1993) attributed the distribution of the nitrate contamination to source availability, thickness and composition of the vadose zone, precipitation and irrigation, vertical flow, aquifer heterogeneity, dissolved oxygen concentrations, and electron donor availability. The removal of nitrate from groundwater can be approached by the biological process or the physical-chemical process (FIG 2). The physical-chemical processes include ion exchange, membrane separation, and chemical reduction. Membrane processes such as reverse osmosis and electrodialysis have very little economy of scale; also, chemical reduction is not feasible and practical for full-scale treatment of drinking water. Only ion exchange and biological denitrification would be considered applicable for the removal of nitrate from larger groundwater sources and surface water sites.

Ion exchange is a process that nitrate is exchanged for chloride or bicarbonate across an anion exchange resin. The removal of nitrate from drinking water by the operation of the full-scale ion exchange systems has been successfully demonstrated at several locations in Europe. Ion exchange systems are particularly suitable for treating groundwater supplies, but purified water contains a much higher concentration of chloride ions than normal. Unless the water is diluted with normal supplies, it could corrode pipes, although it is safe to drink. Another drawback with ion exchange is that saline waste from the regeneration process must be treated before disposal.

As an alternative, some combinations of the existing removal processes have been proposed to come up with novel processes for nitrate removal. *Process Engineering* (1988) reported that Dow Chemical proposed a combined membrane and sorption process for selective nitrate removal. In such cases, the resulting solution is highly suited for use as a fertilizer and eliminates any problems of disposal of the used regenerating solution. As revealed in *Process Engineering* (1989), a combined ion exchange and electrolysis process produce much less waste than conventional ion exchange (FIG 3). Depending on the conditions in the electrolytic cell, ammonia may be generated instead of nitrogen. By careful control of the electrolysis conditions, it should be possible to produce salable nitrogen-based fertilizer products, thus offsetting the cost of the nitrate cleanup. The combined ion exchange and biological denitrification processes have been applied in the Netherlands (van der Hoek and Klapwijk, 1987). Nitrate is removed from the groundwater by ion exchange and a denitrification reactor is used for the regeneration of an exhausted resin (FIG 4). Very high salt concentrations can have an inhibiting effect on the

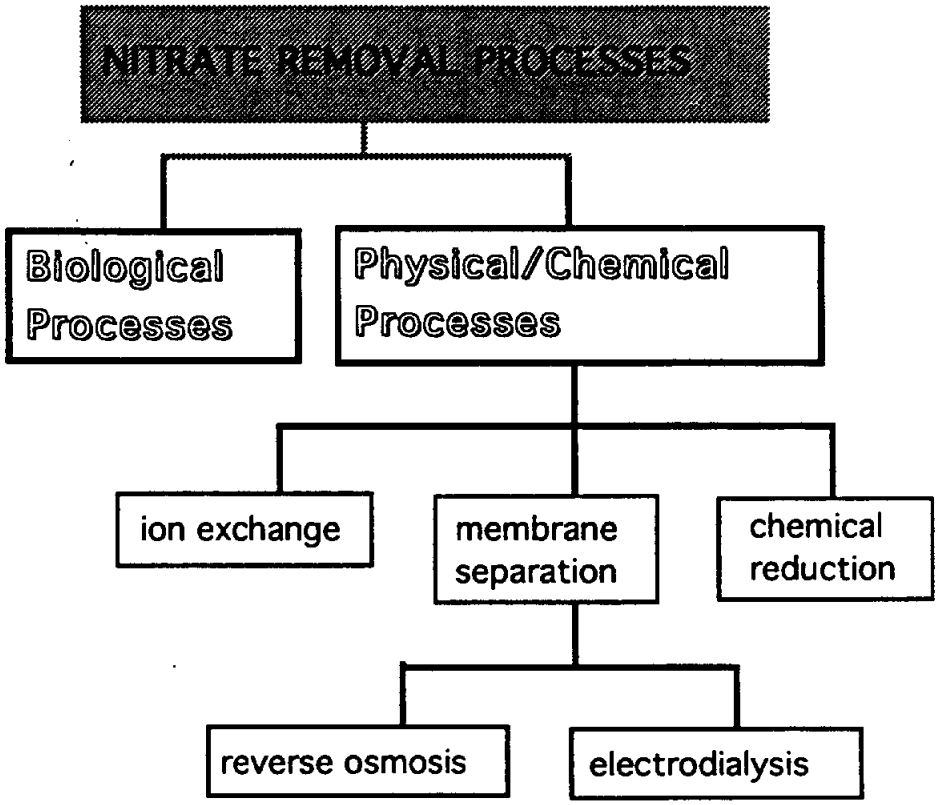


FIG 2. A Summary of the Available Nitrate Removal Techniques

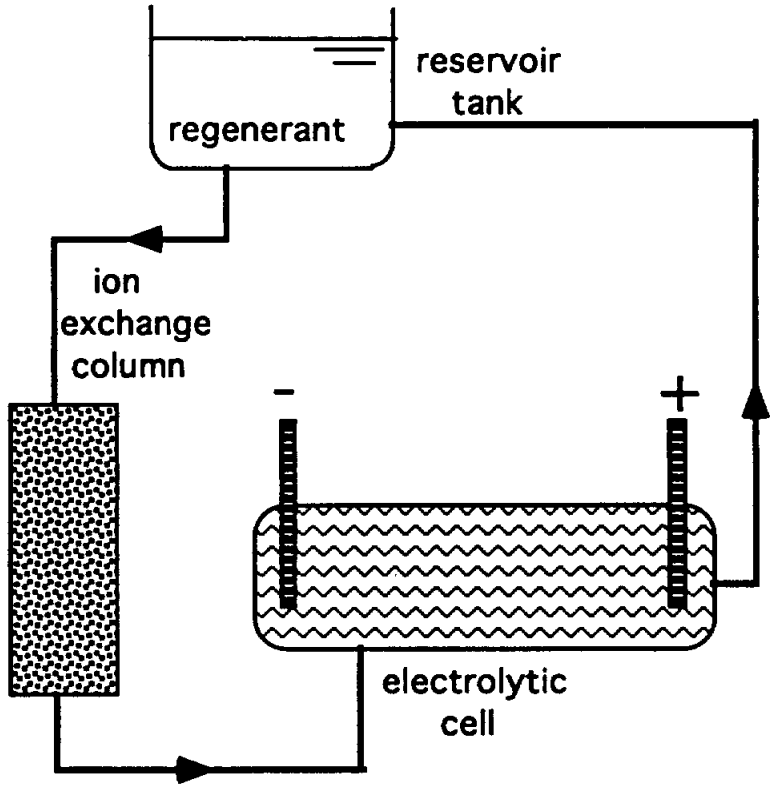


FIG 3. Nitrate Removal System by the Combination of Ion Exchange and Electrodialysis (From Process Engineering, 1989)

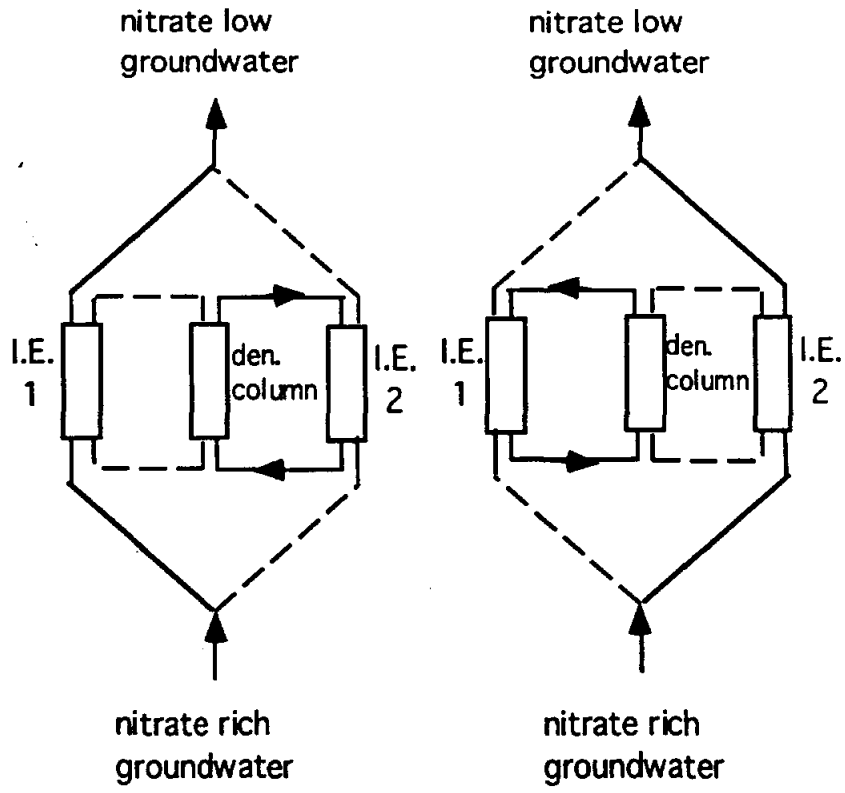


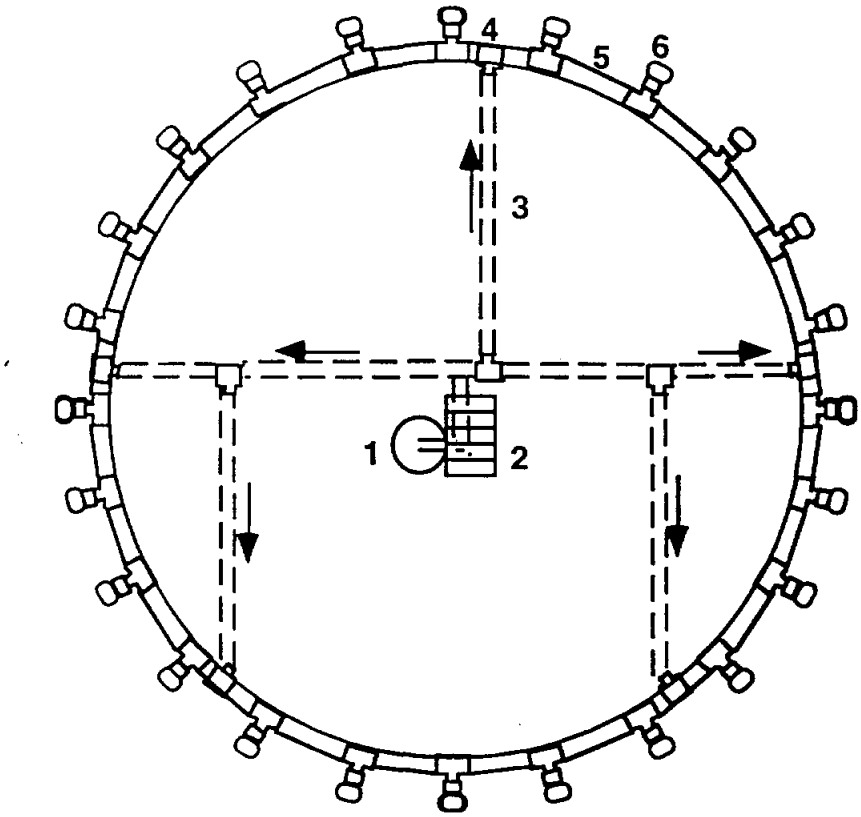
FIG 4. Nitrate Removal System by the Combination of Ion Exchange and Biological Denitrification (From van der Hoek and Klapwijk, 1987)

biological denitrification, but the salt concentration must be high enough to produce sufficient regeneration of the resin within a reasonable time.

Biological denitrification is a process by which nitrate is reduced to nitrogen gas by the dissimilation of denitrifying bacteria. Biological denitrification appears to be the most economical process of nitrate removal because it doesn't create the need for disposal and/or treatment of waste (Soares et al., 1988). Anoxic denitrification has been used as a water treatment process for over a century; heterotrophic microorganisms are usually involved in biological treatment units to remove nitrogen in wastewater through the provision of a suitable carbon source. In situ biological denitrification techniques have also been developed, relying on bacterial growth within the aquifer, and initiated by injecting of a carbon source into the water at strategic points around an abstraction well (Hall, 1992). The application of an in situ denitrification reactor is demonstrated in FIG 5.

Denitrification can also be catalyzed by autotrophic bacteria that obtain their carbon from bicarbonate and their energy from the oxidation of inorganic compounds, particularly hydrogen (Gahrs et al., 1989) and sulfur (Schippers et al., 1987). Less commonly reported is the full-scale application of autotrophic denitrification. Denitrification catalyzed by autotrophic bacteria has been successfully performed at the sulfur/limestone denitrification plant in the Netherlands (van der Hoek et al., 1992). As shown in FIG 6, the sulfur/limestone filtration process for nitrate removal from groundwater is based on autotrophic denitrification by Thiobacillus denitrificans.

The two types of process currently most favored for nitrate removal, ion exchange and biological denitrification, are compared for the guideline of process selection and design. Hall et al. (1986) have compared the advantages and disadvantages of both biological nitrate removal and ion exchange treatment , the results of which are summarized in TABLE 1. On the basis of cost-effectiveness, biological denitrification is an attractive remedial scheme for a large scale application. The successful application of biological denitrification has been demonstrated in a sand and gravel aquifer located on Cape Cod, Mass. The results of this case study suggested that denitrification can occur in groundwater systems and, thereby, serve as a mechanism for nitrate removal from groundwater (Smith and Duff, 1988). If denitrification processes were installed for routine production of potable water, then their operation would have to be monitored most carefully because improper operation can bring a hazard far greater than that which is being removed (Solt, 1987). The potential risks caused by biological denitrification include residual carbon, nitrite production, and bacteriological contamination; therefore, these



Notation:
(1) water abstraction well
(2) substrate storehouse
(3) underground mains
(4) flow rate gate
(5) circular main
(6) injection well

FIG 5. The Diagram of In Situ Denitrification Reactor (From Hamon and Fustec, 1991)

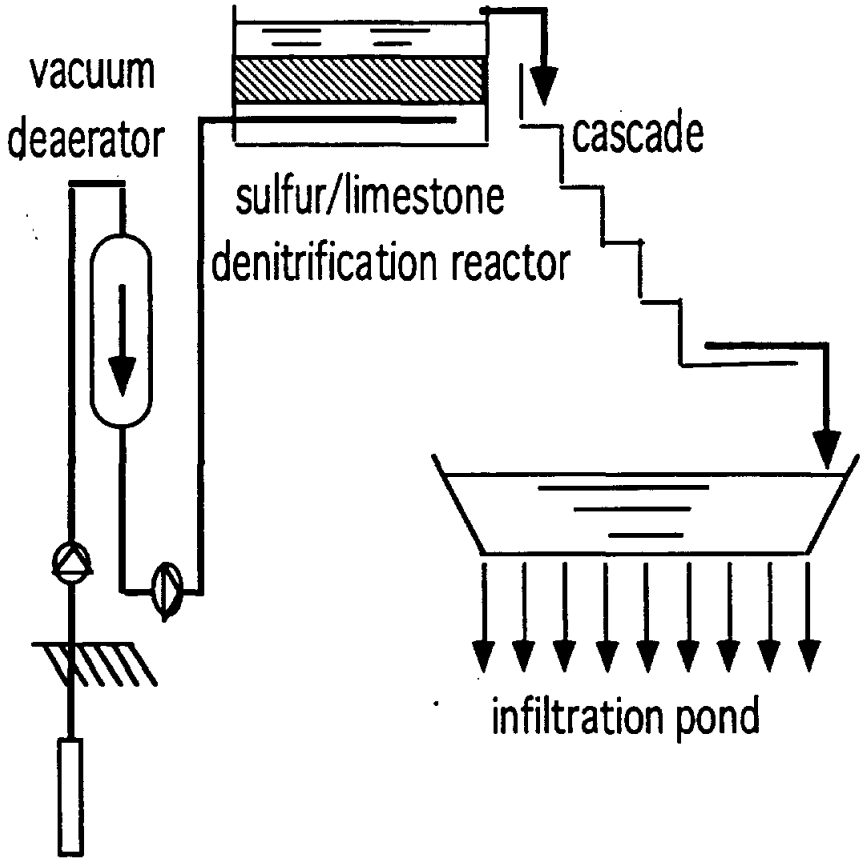


FIG 6. An Example of Autotrophic Denitrification: The Sulfur/ Limestone Denitrification Plant (From van der Hoek et al., 1992)

TABLE 1. Comparison of Above-Ground Biological Denitrification and Ion Exchange Treatment Plant (From Hall et al., 1986)

Characteristic	Ion Exchange Treatment	Biological Denitrification[a]
Raw Water Composition	High chloride and sulfate concentrations undesirable Suspended solids not a problem with groundwater	Little effect Temperature not a problem with groundwater[b]
Start-up[c]	Immediate	Slow, up to 1 month
Plant Complexity	Fixed resin bed process simple and readily amenable to automation Continuous-loop process more complex	Mechanically more complex and more difficult to automate
Process Control	Monitoring of nitrate	Monitoring of carbon source, nitrate, and nitrite
Treated Water Quality	Increased chloride concentration can cause corrosion problems in distribution Ionic quality variable from fixed resin bed process, but more constant from continuous-loop process	Low dissolved oxygen and increased suspended solids Residual nitrite and carbon source in denitrified water possible
Further Treatment	pH correction may be required	Re-aeration and filtration to remove biomass carry-over
Waste Disposal	Large volumes of spent regenerant and rinse water high in chloride, nitrate and sulfate	Nitrate transformed into nitrogen gas Small volumes of waste biomass sludge

[a] assuming a continuous fluidized sand bed reactor.
[b] groundwater temperature remains constant at about 10 °C.
[c] time taken for optimum denitrification to be achieved.

potential drawbacks should be carefully examined to provide information on system design.

Lab Studies on Denitrification

Nitrate in wastewater can be effectively removed by the use of floating aquatic plants and natural and man-made wetlands. McIntyre and Riha (1991) reported that aquatic macrophyte-based artificial wetland systems can effectively reduce nitrogen in water. Although the wetland systems offer a potential alternative to conventional wastewater treatment, more information on the release of pathogens is needed (Jensen, 1988).

Biological processes for nitrogen removal from wastewater have been extensively studied; sequencing batch reactor systems are especially popular in lab studies and field operation. Palis and Irvine (1985) found that denitrification was substantially encouraged by the presence of exogenous electron donors in a sequencing batch reactor. For heterotrophic denitrification, organic carbon is used as an exogenous electron donor. Due to economical and operational reasons, most denitrifying systems use methanol as an exogenous electron donor. Dahab and Lee (1988) used static upflow reactors to examine the potential use of biological denitrification for nitrate removal from potential groundwater supplied. The results indicated that the reactors resulted in near total removal of nitrate at a C/N ratio of 1.5 when using methanol as carbon source. A wide variety of organic compounds can serve as electron donors during biological denitrification process, but different types of organic compounds may affect biomass yield differently. Grabinska-Loniewska et al. (1985) reported that the most favorable C/N ratio is 1.0 with glycerol as a carbon source. The efficiency of denitrification was found to be dependent on nitrate load as well as on cell residence time. Hamon and Fustec (1991) determined the C/N ratios of the two carbon sources authorized in France for use in drinking water denitrification: ethanol and acetic acid. Ethanol, as a carbon source for denitrification, gave better results than acetic acid; the optimal C/N ratio was found to be 1.25 for ethanol in soil column studies.

The removal of nitrate from groundwater can be achieved by in situ denitrification treatment. Provided that a suitable carbon source is available, the success of an in situ biological denitrification operation depends mainly upon the prevention of well or aquifer clogging. Soares et al. (1991) found that gas production resulting from the biological denitrification led to decreases in hydraulic conductivity and porosity of the column, higher water velocities through the column, higher dispersion and anomalies in the head difference

to flow rate ratios. The results suggest that pulse application of the carbon source is preferable to a continuous supply regime in an in situ aquifer denitrification plant. Hamon and Fustec (1991) agreed that discontinuous injection and pumping conditions enabled clogging risks of in-situ reactors to be limited.

In aerobic groundwater systems, the repression of nitrogen oxide reductase's activity by molecular oxygen readily contributes to the limitation of denitrification. In anaerobic aquifers, the conditions limiting denitrification are less obvious. Bradley et al. (1992) evaluated potential denitrification rates in a shallow anaerobic groundwater system as a function of nitrate concentrations, carbon availability, and pH. He determined that:

- Nitrate availability limited denitrification activity only where the in situ concentration was less than 0.7 μM,
- A significant relation was observed between denitrifying activity and sediment organic carbon content; showing that carbon limitation can be a significant factor contributing to nitrate accumulation in anaerobic aquifers, and
- Indigenous denitrifiers are adapted to in-situ pH conditions. Under a range in pH from 4.0 to 8.0, there was no significant correlation between the rate of denitrification and the pH of the groundwater.

Microcosms are useful tools to examine biological transformations of chemical contaminants in unconsolidated aquifer material. Obenhuber and Lowrance (1991) found that carbon addition of 0.4 mg/L as carbon had no effect on the microbial or chemical properties of the microcosms. However, the remediation of nitrate contaminated aquifers by organic infusion is possible and appears to be a function of microbial denitrification.

MICROBIOLOGY

In general, biological wastewater and solid waste treatment processes take advantage of the microorganisms' normal function of metabolizing organic materials to obtain energy for synthesis and maintenance (McCarty, 1988). Several absolute requirements need to be satisfied for microbial activity to occur: availability of a carbon source, energy source, electron acceptor, essential nutrients, growth factors, and sufficient moisture; absence of compounds toxic to microorganisms; and a reasonably favorable range of various environmental factors, such as temperature, pH, oxidation-reduction potential, osmotic pressure, salinity, and others (Grbic-Galic, 1990).

The advantages of bioremediation are more rapid removal of contaminants and destruction of that portion removed biologically (McCarty et al., 1989). The complete

mineralization of a compound may require the sequential metabolism of two or more organisms because no single species within the culture contains the complete genetic complement of the whole culture (Grady, 1985). It is best to use the indigenous consortium because these organisms are already acclimated to the site's environment (McCarty et al., 1989). Thus, a mixed culture of in-situ denitrifying bacteria must be present to transform nitrate in groundwater if bioremediation has been applied as the remedial strategy.

Biological Denitrification

There are three microbiological reactions of nitrate: (a) a complete reduction to ammonium, frequently with the transitory appearance of nitrite, (b) an incomplete reduction and an accumulation of nitrite in the medium, and (c) a reduction to nitrite followed by the evolution of gaseous compounds (Alexander, 1977). Biological denitrification carrying out reaction (c) is the major mechanism of nitrogen loss from the soils. The general requirements for denitrification include terminal electron acceptors, suitable electron donors, the presence of denitrifying bacteria, and anoxic conditions. All bacteria need an electron donor as an energy source, and an electron acceptor is also required to complete the oxidation-reduction reaction (Korom, 1992). Thermodynamically, organic carbon serving as electron donor tends to be oxidized preferentially by the electron acceptor that yields the most energy to the bacteria (Stumm and Morgan, 1981). In the saturated aquifer, aerobic bacteria utilize oxygen to oxidize organic carbon until oxygen supplies become limited. Thereafter, facultative anaerobes switch to using nitrate and oxygen as electron acceptors, and obligate anaerobes begin to use nonoxygenous electron acceptors when oxygen level continually decrease. The pathway of biological denitrification that starts electron transfer from nitrate is shown in FIG 7.

There are four reductases involved in the pathway of biological denitrification. During biological denitrification, the reduction of nitrate to nitrite is catalyzed by dissimilatory nitrate reductase. Nitrate reductase may be located in the outer region of the membrane (Sawada and Satoh, 1980) or be membrane bound in most denitrifiers (Haddock and Jones, 1977). The presence of Fe or Mo chelating or binding agents strongly inhibits the activity of nitrate reductase (Stouthamer, 1976). The reduction of nitrite to yield gaseous products is catalyzed by nitrite reductase that appears to be of two general types: a Cu-containing protein and a cytochrome cd. Several microbiological studies agreed that nitrite reductase does not occupy a trans-membrane location but disagreed on the exact location of

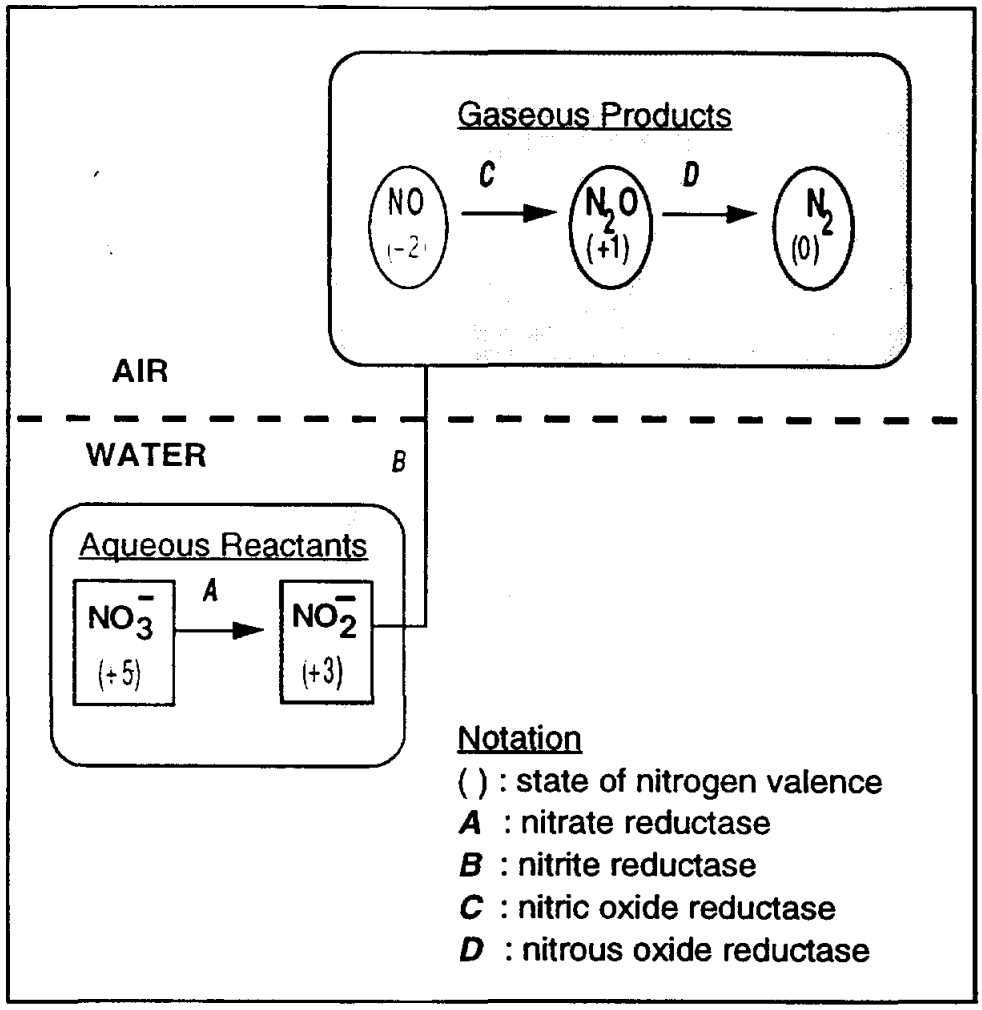


FIG 7. The Pathway of Biological Denitrification

nitrite reductase in the cell (Firestone, 1982). The products of nitrite reduction by nitrite reductases were found to be nitric oxide and nitrous oxide in several organisms (Zumft and Vega, 1979), but nitric oxide has most commonly been produced by nitrite reductase (LeGall et al., 1979; Zumft et al., 1979). Nitrite reductase often releases nitric oxide as a major product whereas whole cells do not. Nitric oxide reductase is responsible for catalyzing the reduction of nitric oxide to nitrous oxide, but some reports suggested that nitric oxide may be an intermediate in the denitrification process. Therefore, the role of nitric oxide and the existence of nitric oxide reductase remain debatable (Knowles, 1982). The reduction of nitrous oxide to dinitrogen is catalyzed by nitrous oxide reductase that is inhibited by acetylene and sulfide. Acetylene does not interfere with nitrous oxide binding by the enzyme, and the degree of inhibition is independent of the concentration of nitrous oxide (Kristjansson and Hollocher, 1980). The presence of sulfide allows the development of anaerobic microorganisms that require a low redox potential and are not readily inhibited by acetylene (Tam and Knowles, 1979).

Denitrifying Bacteria

Typically, soils and sediments contain an average of 10^8 to 10^{10} total bacteria per gram of dry solids, as determined by direct microscopy, or a range from 10^5 up to 10^8, as determined by plate counts (Alexander, 1977). The numbers in aquifers are usually in the range of 10^6 to 10^7 bacteria per gram of dry aquifer material (Ghiorse and Balkwill, 1983). Biological activity can be obtained by measuring ATP extracted from subsurface samples, and it was found that usually between 1 and 10 % of the cells were metabolically active . (Webster et al., 1985). Davidson et al. (1985) reported that enzyme activity assays and most probable number enumerations were weakly correlated. The enzyme assay indexes denitrification potential of soils under the environmental conditions at the time of sampling; the most probable number enumeration indexes the denitrifying capability of the populations inhabiting soils.

The genera of soil bacteria capable of denitrification include *Alcaligenes*, *Agrobacterium*, *Azospirillum*, *Bacillus*, *Flavobacterium*, *Halobacterium*, *Hypomicrobium*, *Paracoccus*, *Propionibacterium*, *Pseudomonas*, *Rhizobium*, *Rhodopseudomonas*, *Thiobacillus* (Firestone, 1982). The genus *Pseudomonas* includes the most commonly isolated denitrifying bacteria from both soils and aquatic sediments and may represent the most active denitrifiers in natural environments (Knowles, 1982). Almost all denitrifiers are aerobic bacteria capable of anaerobic growth to undertake denitrification, so the growth

of denitrifiers is not dependent on the reduction of nitrates. The abundance of substrate-non-specific microorganisms should never be taken as a sign that any single one of their biochemical activities is prominent in the habitat from which the organisms were isolated (Alexander, 1977). It means that the presence of many denitrifying cells does point to a large denitrifying potential, not the occurrence of denitrification. On the other hand, the occurrence of denitrification should indicate that numerous denitrifiers do exist under favorable conditions.

Environmental Influences

Laboratory denitrification rates from aquifer samples have been reported at a range of 0.004 and 1.16 mg N/kg dry sediment per day; field denitrification rates in aquifers were estimated from 0.014 to 0.73 mg N/L per day (Korom, 1992). Since most denitrifying bacteria seem to be attached to an aquifer's porous matrix, denitrification rates in water samples are expected to be lower than rates with core samples. However, the rates of denitrification in aquifers are markedly affected by the in-situ environment. Among the environmental influences, the major impacts on biological denitrification are attributed to carbon supply, oxygen control, nitrate supply, temperature, and pH.

The effectiveness of organic nutrients in promoting denitrification in waterlogged soils is proportional to the availability of carbon supply (Alexander, 1977). Nitrate reduction in carbon-limited aquifer favors denitrification over dissimilatory nitrate reduction to ammonium (Tiedje et al., 1982), but denitrification was predominantly responsible for the nitrate reduction in the same aquifer (Smith et al., 1991). To some degree, the changes in denitrifying activity that occurs with increasing depth in soil reflect the distribution of organic matter in the soil profile. An exponential decrease in denitrification rates with depths was found to parallel microbial activity but not total organic matter content (Cho et al., 1979). Conclusively, the regulatory role of carbon supply in soil denitrification is tightly intertwined with oxygen regulation of the process (Firestone, 1982).

Because of the preferential use of oxygen as the electron acceptor, denitrification proceeds only when oxygen supply is insufficient to satisfy the microbiological demand. As stated previously, the activity of nitrate reductase could be repressed under aerobic conditions. Gillham and Cherry (1978) reported that the upper dissolved oxygen limit for denitrification to proceed is 2.0 mg/L. The oxygen supply to metabolically active microsites is strongly affected by the amount of water through which oxygen must diffuse, since the rate of diffusion of oxygen through water is about 10^4 times less than through air

(Firestone, 1982). The effect of moisture is attributed to its role in governing the diffusion of oxygen to sites of microbiological activity. There is usually no detectable loss of nitrate at moisture levels below 60 percent of the water-holding capacity (Alexander, 1977).

The kinetics of denitrification at nitrate concentrations greater than 1 mg/l as nitrogen are zero order, that is, independent of nitrate concentration (Smith and Duff, 1988). At higher nitrate concentrations, an inverse linear relationship is reported between the denitrification rate and nitrate concentration (Trudell et al., 1986). At very low nitrate concentrations, nitrate controls the rate of the denitrification reaction with first-order kinetics (Blackmer and Bremner, 1979). Also, the release of nitrous oxide as the end product of denitrification is conditioned by the nitrate condition. The proportion of nitrous oxide and dinitrogen produced during denitrification increases with the enhancement of the nitrate supply (Firestone, 1982).

Denitrification is markedly affected by temperature, and the effect of temperature on the kinetic rate of biological activity is traditionally described by the Arrhenius equation:

$$\ln v = (-\Delta H^* / RT) + C \quad \text{..... (1)}$$

where v is the reaction rate, ΔH^* is the activation energy, R is the gas constant, T is the absolute temperature, and C is a constant. Usually, the minimum temperature for biological activity is several degrees above the freezing point of water, and the maximum temperature is established by thermal denaturation of proteins (Stanier et al., 1976). The optimum temperature for denitrification is 25 ^{o}C (Alexander et al., 1977). The cooler temperatures reduced microbial activity and led to slower denitrification rates (Lind, 1983). Decreasing temperature would increase oxygen solubility and decrease oxygen consumption, so the interaction of temperature with oxygen control is quite complex (Craswell, 1978). The inhibitory effect of oxygen resulting from temperature change could negatively affect make the exponential relationship. Surprisingly, the relationship between denitrification intensity and temperature was found to be linear between 2.7 and 20 ^{o}C (Cho et al., 1979).

In general, the pH range and optima for denitrifying organisms appear to be similar to those for heterotrophic organisms. The denitrification rate is positively related to pH, with an optimum in the range of 7.0 to 8.0 (Knowles, 1982). Some studies showed that denitrifying activity was highly correlated with soil pH but not with organic carbon content (Mueller et al., 1980). Denitrification activity is inhibited with pH ranging from 3.5 to 6.5 (Klemedtsson et al., 1978). Besides, acidity governs not only the rate of denitrification but also the relative abundance of the various gases. At neutral or slightly acid conditions,

nitrogen tends to be the dominant product. Nitrous oxide reductase is progressively inhibited at low pH, and the effect of acidity on nitrous oxide production appears to be immediate (Tiedje et al., 1981). Nitrous oxide frequently makes up more than half of the nitrogenous gases evolved from acid habitats, and nitric oxide only appears in significant quantities when the pH is low (Alexander, 1977).

GEOCHEMISTRY AND GEOLOGY

For the protection and remediation of groundwater resources, it is necessary to: (1) predict the time of arrival and concentration of contaminants at a water-supply well; (2) design safe, cost-effective waste facilities; (3) install effective monitoring systems; and (4) develop efficient and effective strategies for remediation of contaminated aquifers (Palmer and Johnson, 1989). However, all groundwater remediation technologies will be severely hampered by geological complexities and the difficulty of locating the subsurface contaminant sources (Mackay and Cherry, 1989). Accurate interpretation of site geology is crucial for the design of a treatment system and the operation of the successful remediation.

The most representative hydrogeological parameters for generalizing the properties of an aquifer are groundwater velocity and direction of flow, hydraulic conductivity, and porosity. The ideal conditions of a homogeneous aquifer and uniform groundwater flow were usually assumed to reduce the difficulties of lab studies. In some cases, groundwater velocity and velocity variation become of greater importance than aquifer-averaged parameters, such as transmissivity. Geologic heterogeneity is always a critical factor in determining the performance of remediation. Because of its significant influences on treatment effectiveness and the required remediation time, geologic heterogeneity should not be excluded from the design of a remediation scheme. For example, high dispersion of solute transport would yield a wide-spread plume that requires a longer remediation time.

Of all the processes that influence solute transport, the dissolution and precipitation of solids are two of the most important in terms of their control on groundwater chemistry (Domenico and Schwartz, 1990). Because of the high solubility of nitrate ions, the precipitation process has very little impact on retarding the transport of nitrate. In other words, the dissolution process might be important if natural deposits of nitrate origins are present in the aquifer. Among nitrogenous oxides, nitrate is the most susceptible to biological and chemical transformation and to movement out of the system with soil water (Baker et al., 1982). Nitrate is considered a non-reactive contaminant with regard to physical transport mechanisms, but a loss of nitrate might result from the chemical and

biological reaction. The rates of chemical and biological reactions depend on environmental conditions, such as temperature, pH, Eh, DO, solution and solid phase composition, and bacterial population (Gillham et al., 1990).

Anoxic microenvironments are generally characterized by low oxidation-reduction potentials, complex microbial communities, and a variety of electron acceptors that substitute for oxygen and are unused by microorganisms in the aerobic world (Grbic-Galic, 1990). Biotransformation in anaerobic environments is initially reductive. From the view of geochemistry, biological denitrification is basically a reduction-oxidation reaction that is sensitive to the environmental condition in the subsurface. Environmental influences on biological denitrification have been discussed in the previous section. Geochemical conditions will have a tremendous impact upon biological reactions, even though geochemical characterization of the aquifer is frequently neglected in the design of remediation schemes.

SUMMARY

Nitrate contamination of groundwater limits its continuing use as a potable water supply, so there is an urgent need to develop a reliable and economical method for the protection of drinking water wells. The design of a timely and cost-effective scheme should be based upon the knowledge of groundwater hydraulics, microbiology, geology, and geochemistry. Reviewing conventional treatment methodology on nitrate removal, ion exchange and biological denitrification are frequently applied as the remedial method. In Europe, ion exchange over biological denitrification is commonly involved in the treatment system of water supplies; however, biological denitrification is favored for in-situ treatment. On the basis of economical consideration, a renovated system that introduces biological denitrification in a recirculating well is designed. Previous literature suggests that monitoring of nitrate, nitrite and carbon is required when anaerobic denitrification system is operated. Thus, the amendment of carbon source to stimulate biological denitrification should be carefully controlled to minimize nitrite production and the residual carbon level.

Denitrifying bacteria have shown great promise in removing nitrate from groundwater under laboratory conditions. Through the operation of a recirculating nitrate treatment well, the contaminated plume would be treated before entering the downstream. The retention time in the treatment system should be maintained long enough for the undertaking of biological denitrification. According to previous literature, the kinetic rate of biological

denitrification seems to be a function of the geochemical condition of the surroundings. This suggests that maintenance of the optimum geochemical conditions is viewed as a critical step of process control.

From the point view of groundwater hydraulics, the flow field of vertical recirculation must be identified during the operation of the recirculating well. A pilot-scale aquifer model will provide new insights for realizing the potential of the renovate recirculating nitrate treatment well system. Under experimental conditions, illustrating the dependence of system performance on the operational conditions is required for the engineering design of a full-scale application.

Chapter III

EXPERIMENTAL APPROACHES ON WELL HYDRAULICS

The design idea of the recirculating nitrate treatment well system is to remove excess nitrate nitrogen content by in-well biological denitrification and to improve treatment efficiency by vertically recirculating treated/untreated groundwater simultaneously. In this way, the hydraulic recirculation incorporates with the biological treatment to form a treatment barrier around the proposed treatment system. This treatment barrier will intercept groundwater nitrate nitrogen content coming from upstream, so the downstream drinking water well can be protected from nitrate contamination within the protection zone of the proposed treatment system.

Lab studies on evaluating the feasibility of the proposed methodology can be approached from two aspects: well hydraulics and biological treatment. The purpose for investigating well hydraulics is to evaluate the extent of vertical hydraulic circulation around the proposed recirculating well and further to experimentally confirm the interception of upgradient groundwater contaminants by a formed treatment barrier. The examination of biological treatment is to determine the kinetics of microbial growth and to evaluate the overall treatment efficiency of biological denitrification under the operation of the proposed treatment scheme. The experimental approaches in biological treatment will be detailed in Chapter IV. To aid the experimental design, the investigation of well hydraulics begins with the understanding of groundwater hydraulics.

THEORY OF HYDRAULICS

The French engineer Henry Darcy (1856) first formulated one-dimensional fluid flow through porous media as the function of the cross-sectional area, the head loss and the length along the flow path. The mathematical expression of Darcy's law is shown below:

$$Q = KA \Delta h/L \quad \ldots\ldots (2)$$

where Q is the flow rate through the porous media; K is a constant dependent on fluid and media characteristics; A is a cross sectional area along the flow path; Δ h is the head loss; and L is the length along the flow path. The specific discharge is directly proportional to the derivative of the head in the direction of flow (de Vries, 1975). A general form of Darcy's law can be expressed as the terms of Darcy velocity.

$$q = - K dh/dx \quad \ldots\ldots (3)$$

where q is often referred to as Darcy velocity; and -dh/dx is the hydraulic gradient by definition. Because the ratio of Darcy velocity and actual flow velocity is defined as the porosity of the medium, the actual flow velocity through the groundwater medium depends on the porosity and size distribution of the medium.

The flow through a single withdrawal well is a complex three-dimensional field. In an infinite homogeneous porous medium, the flow to a point sink representing the withdrawal well may be simplified by spherical approximation (Strack, 1989).

$$Q = - 4\pi r^2 q_r \quad \text{..... (4)}$$

where Q is the sink rate of the withdrawal well; r is the radial distance from the withdrawal well; and q_r is the specific discharge in inward normal radial direction. Applying Darcy velocity to substitute for q_r,

$$\partial h = \frac{Q}{4\pi K} \cdot \frac{\partial r}{r^2} \quad \text{..... (5)}$$

Integrating with respect to r, the solution for the hydraulic head change caused by a point sink in an infinite porous medium of homogeneous conductivity K is:

$$h = \frac{-Q}{4\pi K} \cdot \frac{1}{r} \quad \text{..... (6)}$$

For a positive sink rate, the change in the head in the porous medium will be negative. Transforming to cylindrical coordinates, the solution is (Philip and Walter, 1992):

$$h = \frac{-Q}{4\pi K} \cdot \frac{1}{\sqrt{r^2 + (z - z_0)^2}} \quad \text{..... (7)}$$

where the point sink is centered at r=0, $z=z_0$.

If we assume that the drawdown at the wells is small compared with the saturated thickness of the aquifer, the principle of linear superposition may be applied. The three-dimensional flow field around the recirculating well can be obtained by the superposition of a horizontal uniform groundwater flow and of radial symmetric flow fields for the recirculating well. Using cylindrical coordinates, the radial symmetric flow around the recirculating well can be formulated as (Herrling and Buermann, 1990):

$$\frac{\partial}{\partial r}\left(2\pi r K_r \frac{\partial h}{\partial r}\right) + \frac{\partial}{\partial z}\left(2\pi r K_z \frac{\partial h}{\partial z}\right) = 0 \quad \text{..... (8)}$$

where h is the piezometric head; K_r and K_Z represent the anisotrophic hydraulic conductivity coefficient in horizontal and vertical directions.

The boundary conditions and the numerical techniques to solve the three-dimensional flow field will not be discussed here. To those interested in the numerical method, the three-dimensional flow field has been solved by a numerical model using a Galerkin finite

element method (Herrling and Buermann, 1990; Herrling and Stamm, 1992). The attempt to introduce the theory of well hydraulics is used as a tool to identify some control conditions in experimental design. Due to experimental difficulty, the three-dimensional flow field is simulated in a two-dimensional aquifer model.

EXPERIMENTAL SETUP

The experimental apparatus for the hydraulic studies mainly consists of an aquifer model tank, a scaled recirculation well, and a contaminant monitoring device. The simulation model of the groundwater aquifer was constructed to simulate groundwater flow under the operation of well pumping. A pilot-scale aquifer model tank was made of a stainless steel U-channel frame, reinforced with structural steel, with Arcylic sides. The dimensions of the aquifer model tank are 245 cm long, 15 cm wide, and 120 cm high. With a series of twelve manometers mounted along the length of the aquifer model tank, the fluctuations of the piezometric head can be observed at different locations within the tank during operation. A self-made manometer is composed of two pieces of 6 mm O.D. glass tubings, interconnected with a piece of 5 mm O.D. clear Naphthalene tubing, with a cotton-stuffed end. In addition, 1.25 cm diameter sampling ports are located at 10 cm intervals on both sides and the bottom of the U-channel frame. A 3 cm by 3 cm # 200 mesh screen was attached at each port to prevent the access of aquifer materials. Through each of these ports, pore water can be restored or withdrawn, groundwater samples can be collected, and the piezometric head can be monitored.

The selected aquifer materials were uniform sand particles ranging in size between 0.45 and 0.55 mm purchased from Vulcan Materials Company of Fort Worth, TX. The aquifer model tank was fully loaded with the selected aquifer materials which weighed about 1,600 lb. Two 4 cm diameter pipes extending vertically through the full tank depth were placed against both ends of the pilot-scale model tank. Each pipe has a screened slit along its full length for the access of water but not aquifer materials. An ambient groundwater flow can be simulated in the tank by introducing water into the pipe at one end of the tank and withdrawing water from the pipe at the opposite end.

A vertical hydraulic recirculating well was placed at the center of the pilot-scale model tank. The vertical hydraulic recirculating well consists of a withdrawal compartment and a recharge compartment. Two scaled vertical hydraulic recirculating wells were built for the investigation of well hydraulics; the geometries of both wells are illustrated in FIG 8. The

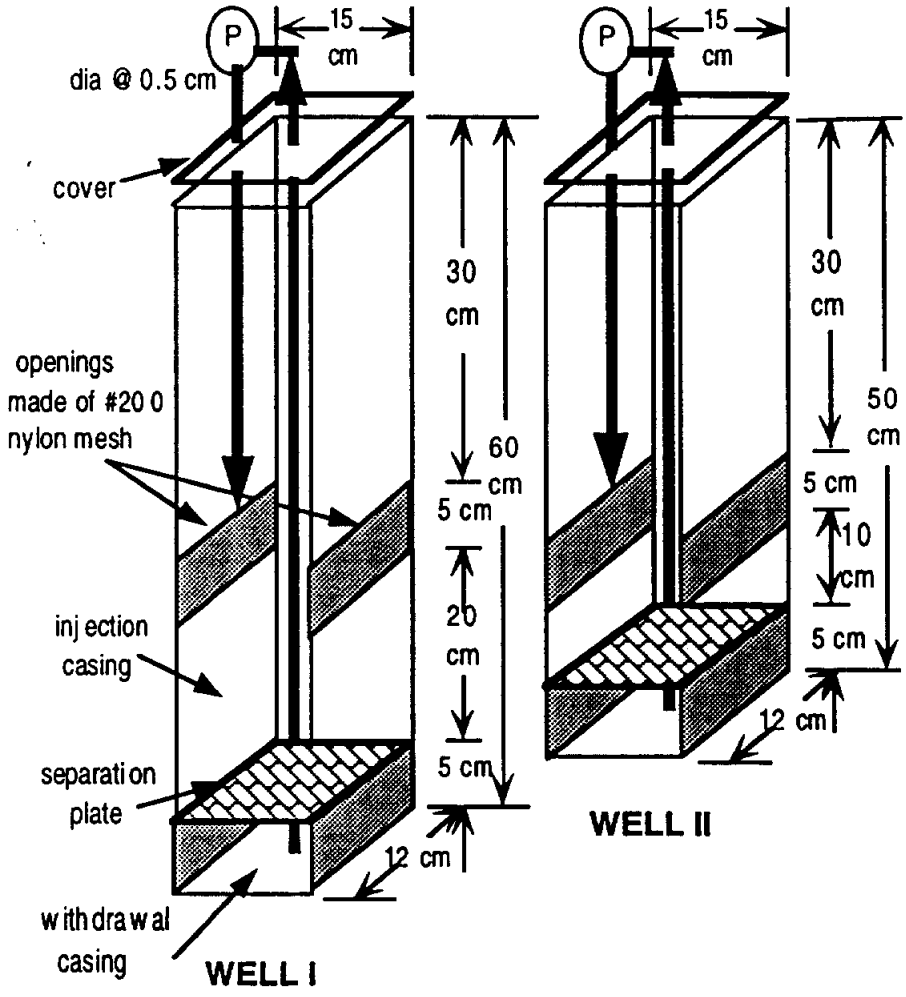


FIG 8. Geometric View of Two Scaled Vertical Hydraulic Recirculating Wells

total height of the first well was 60 cm and that of the second well was 50 cm. Each well was made of an acrylic rectangular casing 15 cm long by 12 cm wide, and the casing of each well was capped by an acrylic plate at the well bottom. A separation plate, located 5 cm above the well bottom, divided the vertical hydraulic recirculating well into withdrawal and recharge compartments. There were two screened openings 12 cm wide by 5 cm high for each compartment at the direction normal to the ambient groundwater flow. The screened sections in the recharge compartment were located 20 cm above the separation plate of the first well, and 10 cm above the separation plate of the second well. The screen material used to prevent sand from entering groundwater remediation well was nylon cloth #200 from Gilson Company, Inc. of Worthington, OH. Also the recirculating well was 12 cm wide 20% less than the width the aquifer model tank, so the block effect of the recirculating well was greatly reduced because of the allowable passing flow. The overall experimental setup for the investigation of well hydraulics is schematically demonstrated in FIG 9.

The well separation plate is pierced by a 5 mm diameter nalgene tubing through which water is withdrawn by the driving of a peristaltic pump. The pump then discharges into a reservoir in which the concentration of groundwater contaminant can be monitored. The monitoring reservoir is maintained at a constant hydraulic head, so the water will be returned to the recharge compartment of the recirculating well after being retended at the reservoir. Of course, chemicals can be added to the monitoring reservoir and monitored to control a desirable contaminant level. A similar setup can be applied to ambient groundwater flow to monitor the contaminant level downstream or control the contaminant level upstream.

The aquifer model tank is simulated as a two-dimensional flow system. The aquifer condition is simplified by the use of uniform aquifer materials. Thus, an ambient groundwater flow controlled by a variable-speed peristaltic pump is considered as a one-dimensional uniform flow condition. The recirculating flow that moves vertically and horizontally around the well is modeled as a two-dimensional flow condition.

EXPERIMENTAL METHOD

Measurement of Soil Properties

Before the recirculating well is operated, the soil property characteristics must first be identified to define an environment where the treatment process will be applied. The

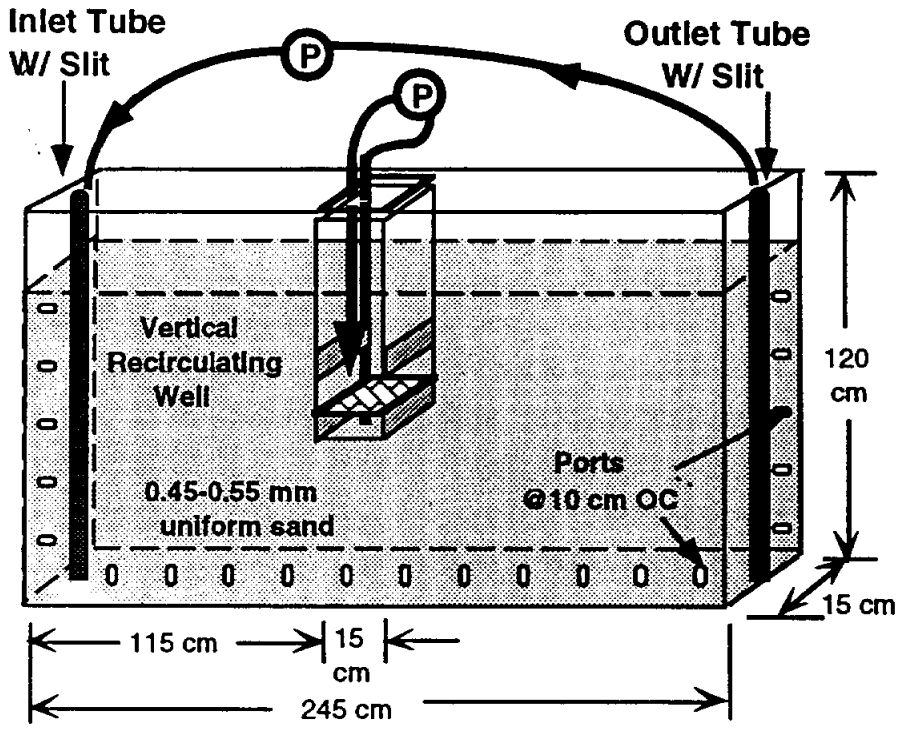


FIG 9. The Sketch of the Dimensioned Aquifer Model Tank

measurements of soil properties include hydraulic conductivity, porosity, and specific gravity of solids. If the soil testing is directly measured from the aquifer model tank, the measurement should be more representative of the system-dependent soil properties. However, the sampling technique is normally used for soil testing because of experimental difficulty and impracticality. Several 2.5 cm diameter 10 cm open-ended glass tubes were used as sampling core, and four core samples were taken from the aquifer model tank vertically as well as horizontally. The vertical core samples were taken by a conventional method: a sampling core was vertically punched into the artificial aquifer at a desirable depth and then unearthed. For the sampling of horizontal samples, a sampling core was horizontally punched into the soil from a pre-created ditch at a desirable depth. The core samples were ready for soil testing after being trimmed at both ends.

Hydraulic conductivities of aquifer samples were measured by the experimental setup of a constant head permeability test referred to as the ASTM Standard Method (FIG 10). Since the vertical permeability should be a little less than the horizontal permeability because of soil compaction by its own weight, the hydraulic conductivity of aquifer materials inside the model tank is assumed uniform but anisotropic. The constant head across the specimen is determined by the total head differences between two water reservoirs, and each reservoir is equipped with an overflow hose to maintain its hydraulic head corresponding to the top or bottom of the specimen. The flow passing through the specimen is directly measured from the overflow hose of the lower reservoir; therefore, hydraulic conductivity can be calculated according to Darcy's Law. For statistical reliability, at least three different constant heads were used for the measurement of hydraulic conductivity.

The measurement of porosity is correlated to the specific gravity of solids. The specific gravity of solids can be directly measured by the water displacement technique. Applying Archimedes' principle, the volume of 15 grams of oven-dried sand was determined after removing entrapped air by boiling for 10 minutes in the 50 mL pycnometer. Then, the specific gravity was calculated from the mass to volume ratio of the measured solids. The same core samples were used for the porosity test after finishing the permeability test. The core samples were dried for 24 hours at 105 ^{o}C to remove water residual content, and then the total mass of dry solid samples was directly measured by an analytical balance. Porosity is defined as the ratio of the void volume to the total volume, and the volume of the voids is the difference between the total volume and the volume of solids. Thus,

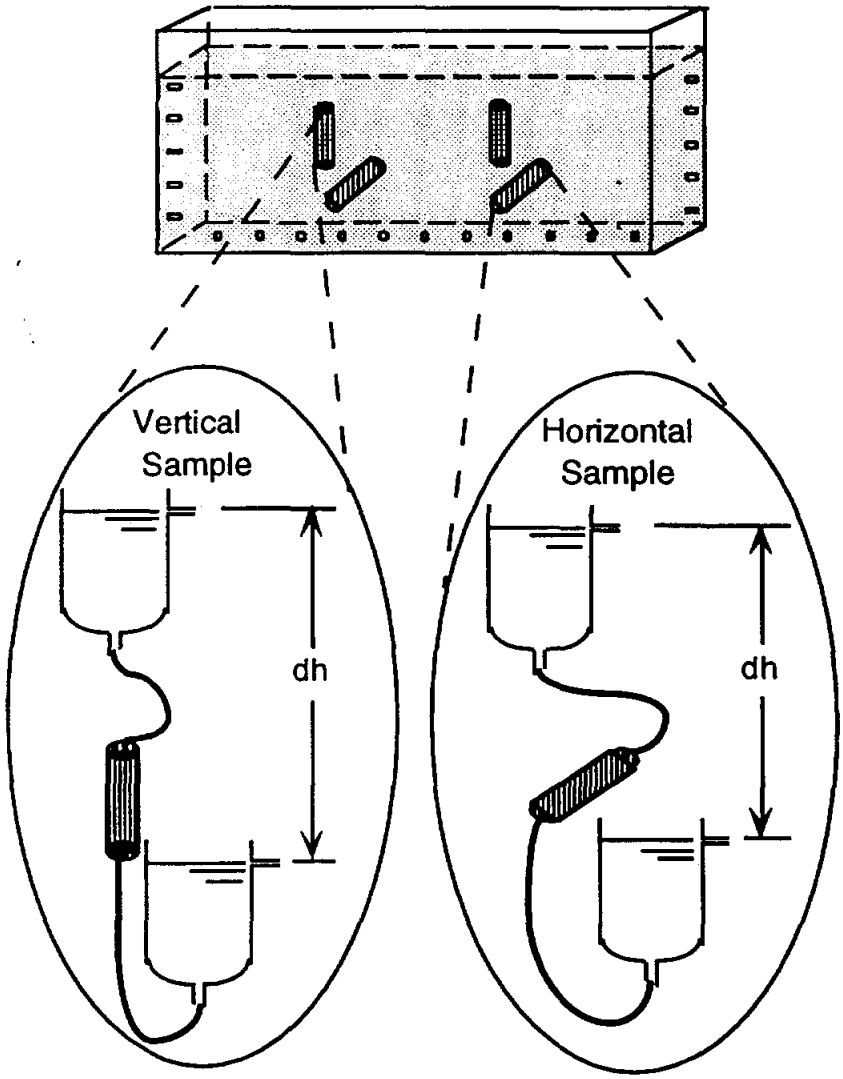


FIG 10. Constant Head Measurements of Horizontal and Vertical Hydraulic Conductivity

porosity can be calculated from a known volume of solids that can be derived from the mass of solid soil particles.

Tracer Selection

The investigation of well hydraulics is expected to demonstrate that groundwater contaminants can be intercepted by a treatment barrier in an aquifer model tank. An experimental observation of the recirculating flow around the well is achievable by the aid of the tracer tests. The streamlines of groundwater flows are basically invisible, but a visible transport plume would be created as a tracer being carried by groundwater flows. The transport of the plume is theoretically attributed to the mechanisms of advection, dispersion, and diffusion, so the observed plume should not represent the streamlines of groundwater flows. Advection, the dominant mechanism of the tracer transport, forces the tracer to stay on the streamlines of groundwater flows, while dispersion and diffusion drive the tracer away from the streamlines simultaneously. Much experimental observation is focused upon the transport of a groundwater contaminant not the groundwater flow. In a real case, groundwater contaminants migrate in a similar way as the tracer transport; thus, the observation of a simulated plume can be applied to define the presence of groundwater contaminants at an interested location.

Based on the experimental requirements, the preselected tracer should be tested in a small soil sample. The first criterion for the tracer selection is that the tracer should not react with soil matrix to change its own property. The materials of dye, such as methylene blue and methylene orange, cannot be selected as the preferred tracer because much extra work would be required for the cleanup of the dyed sand after conducting each experiment. Another consideration is related to the color of a tracer present in the aquifer materials. Generally, the tracer with a sharp color is much easier for experimental observation. Besides, the impact of a treatment process on an aquifer system can also be investigated if the color of a tracer is changeable. Therefore, the sensitivity of the color change becomes an important criterion for the tracer selection because the change of tracer color should be noticeable while being used as a control factor of experimental observation.

On the basis of the above criteria, sodium hydroxide with a phenolphthalein indicator solution can make a good tracer. Hydroxide ion is normally colorless, but it becomes visible in solutions with the addition of pH indicators. With the presence of phenolphthalein, hydroxide solutions remain colorless at pH less than 8.3 and turn red at a pH higher than this value.

Tracer Tests

After a desirable tracer has been selected, the investigation of well hydraulics can be approached by the means of the tracer tests. The investigation of well hydraulics should include characterizing the recirculation zone around the recirculating well, evaluating the feasibility of the proposed system, and identifying the critical factors affecting well design and replacement. To satisfy the requirements of the experimental objectives, the use of the tracer tests can be developed into four different cases.

Case 1. the recirculating flow only

The influence zone is one of the crucial characteristics for the operation of a single well. The recirculation well is much different from the conventional well, so the influence zone cannot be determined by the zero drawdown from the pumping test. However, it is still a great concern in the regions that could be covered by the operation of the recirculating well. One possibility of determining the extent of vertical hydraulic recirculation is to graphically record the development of the plume by using the proposed tracer test.

The recirculating flow is the only flow in the simulated aquifer system in FIG 11, and the recirculating flow is controlled by the pumping rate of the recirculating well. Under the operation of the recirculating well, contaminant capture around the well can be determined by the developed tracer simulation method. The first step of the tracer test is to restore phenolphthalein into the pilot-scale aquifer model tank so that the whole model tank becomes highly pH sensitive. Before conducting the tracer tests, the pH of the simulated groundwater was maintained near pH 8.0 to show colorless in the aquifer model tank. The water was withdrawn from the aquifer and retended in a reservoir where the pH was monitored and adjusted to pH 12. The monitoring reservoir was maintained at a constant hydraulic head by the overflow hose to the injection compartment of the well. The constant pH in the monitoring reservoir was maintained by the addition of 10 N concentrated sodium hydroxide solution; thus, the required amendment of a strong base to the recirculating well was minimized to approximate the constant volume of the well. Under a different time scale, the plume development was graphically traced on a sheet of vinyl clear that was attached on the side of the aquifer model tank.

Case 2. the recirculating flow with an ambient groundwater flow

The flow condition in FIG 12 involved the recirculating well being operated under the background of an ambient groundwater flow. The same experimental setup for Case 1 was used in Case 2, and the experiments for both cases were conducted using a similar

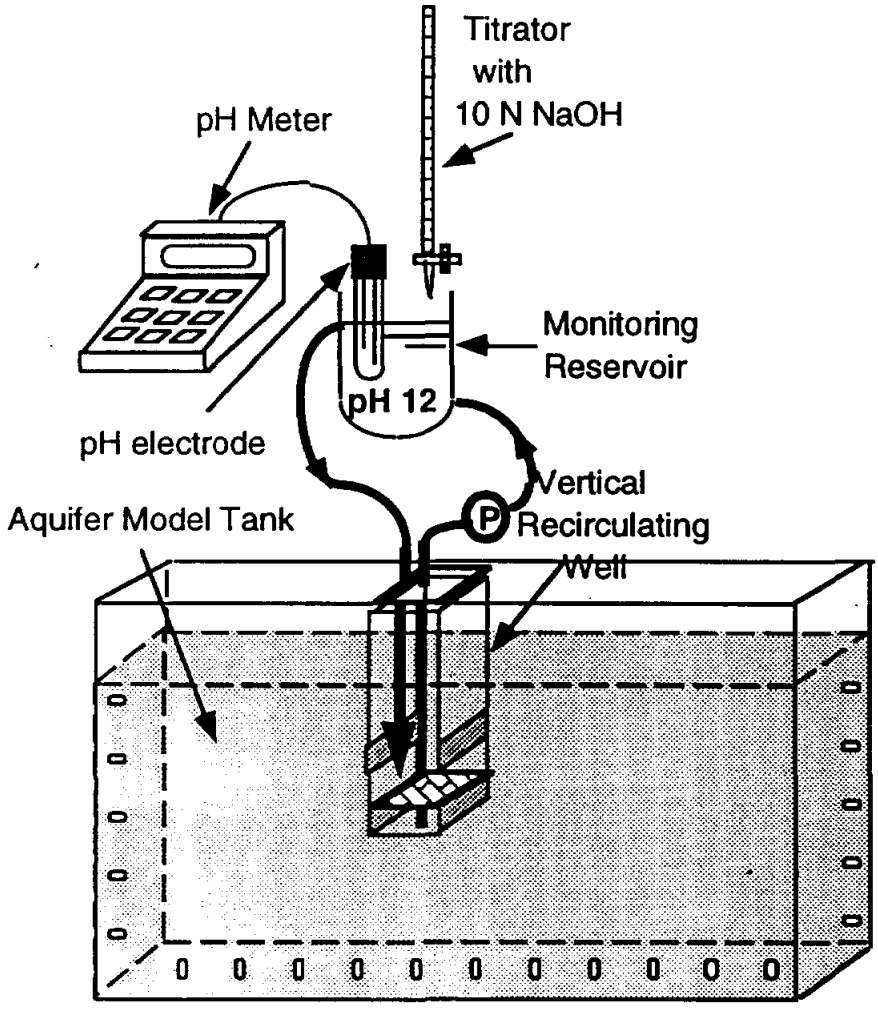


FIG 11. The Setup of Experimental Apparatus for Case 1 in Tracer Simulation Tests

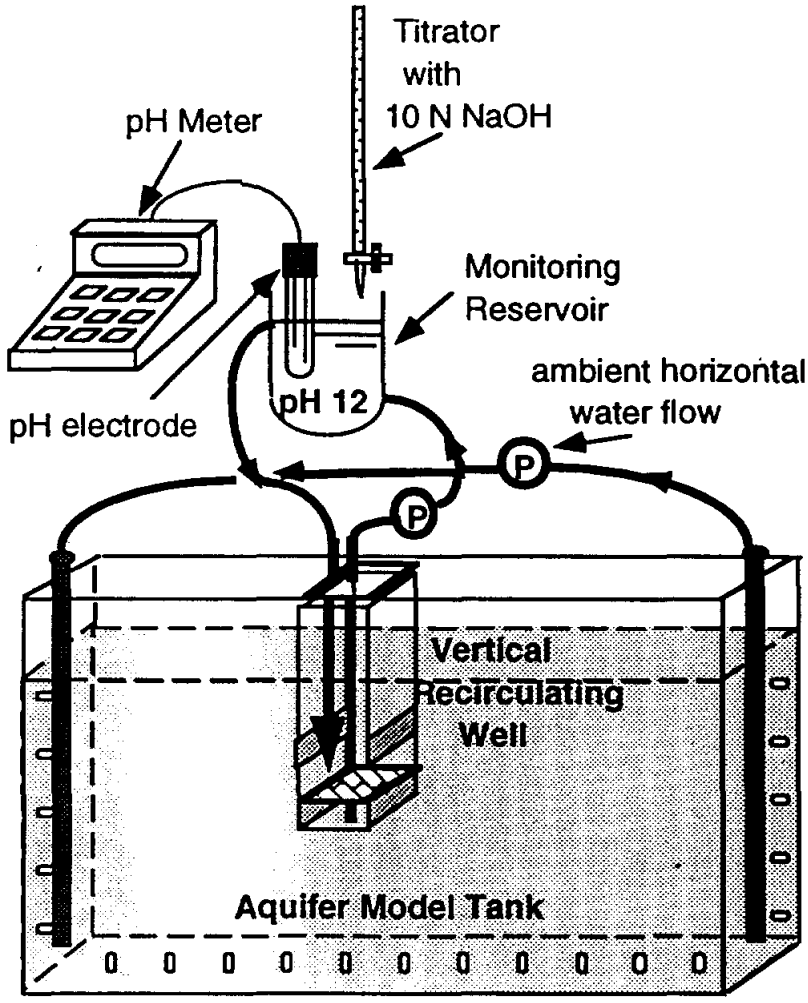


FIG 12. The Setup of Experimental Apparatus for Case 2 in Tracer Simulation Tests

experimental setup. Two peristaltic pumps were involved in flow control. One pump was used to control a desirable flow rate of an ambient groundwater flow, and the other was the driver of the recirculating well. Similarly, a phenolphthalein solution was first restored in the aquifer model tank. Before the operation of the recirculating well, an ambient groundwater flow was turned on for at least 6 hours to reach the steady state condition. After the recirculating well was operating for more than one hour, the transport of the tracer was started from the recirculating well. The pH of the water entering the recirculation well was monitored and adjusted to approximately pH 12 in the recharge compartment of the well. The development of a transport plume was graphically recorded from time to time, and the tracer test wasn't stopped until the downstream plume reached the boundary of the aquifer model tank.

Case 3. depth-distributed contaminant source

The recirculating well system is conceptually utilized as an underground wastewater treatment plant to remove groundwater contaminants. Not only the efficiency of treatment processes is a major concern, but also the size of the protection zone by the operation of the recirculating well determines the performance of the proposed treatment system. There is a need to develop a tool to assess the effectiveness of contaminant interception by the recirculating well.

Because of the selected tracer's dependence on pH, the value of pH can be employed as a control factor to simulate the contaminant level in the model tank. Thus, a red plume with a high concentration of hydroxide ions is simulated as the presence of contaminant, a colorless region with a low concentration of hydroxide ions is considered as an uncontaminated zone, and a neutralization process is correspondent to the applied treatment processes. In this manner, the tracer simulation method can be developed as a scheme to examine the feasibility of the proposed system to protect the downstream areas on the basis of hydraulic operation.

The simulated situation in Case 3 is that the recirculating well attempts to intercept the uniformly contaminated groundwater from the upstreams. In FIG 13, two peristaltic pumps were utilized for the control of an ambient groundwater flow and for the operation of the recirculating well. Two monitoring reservoirs were established for controlling a constant concentration of groundwater contaminants and adjusting the consistency of the treatment processes respectively.

The restoration of phenolphthalein solutions into the pilot-scale aquifer model tank is the essential procedure for the simulated tracer method. An ambient groundwater flow was

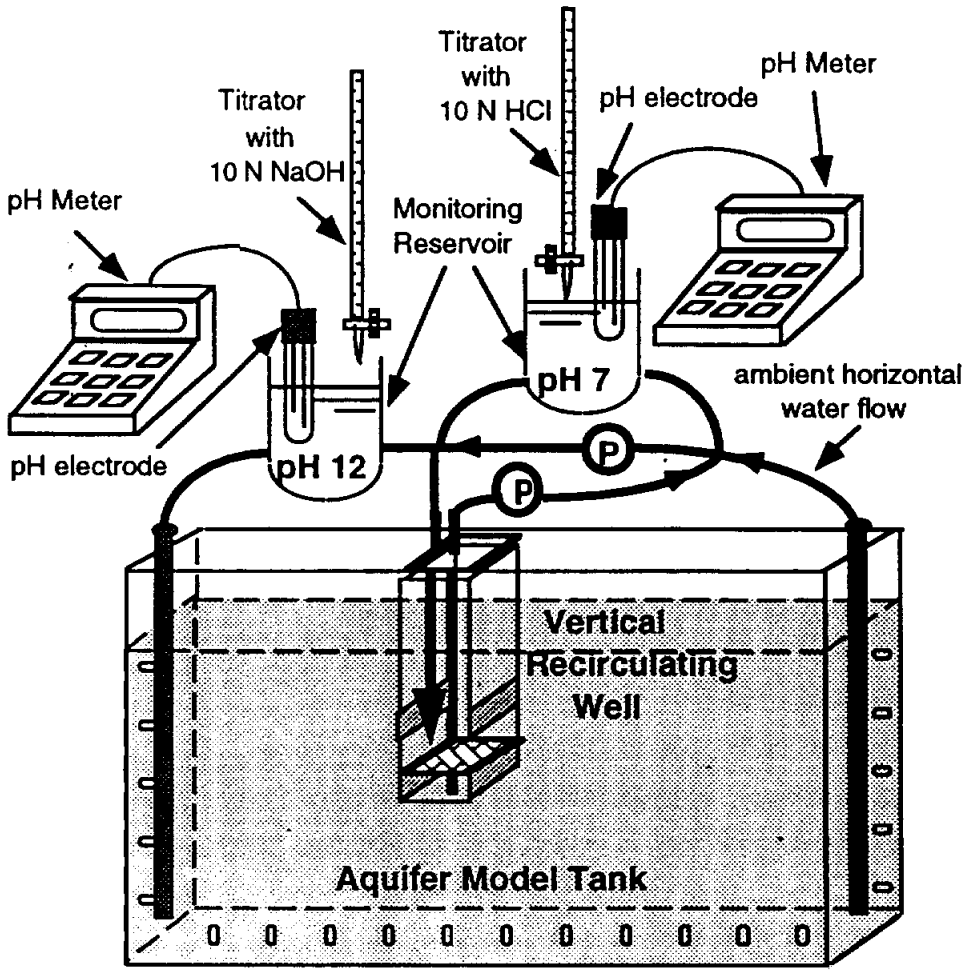


FIG 13. The Setup of Experimental Apparatus for Case 3 in Tracer Simulation Tests

withdrawn from one end of the tank, retended in the contaminant monitoring reservoir, and returned to the aquifer model tank from the other end. The pH of the water was monitored and adjusted to pH 12 before being returned to the aquifer. Thus, the transport of an ambient groundwater flow was represented as a red plume. The recirculating flow was withdrawn from the aquifer model, retended in the treatment monitoring reservoir, and then returned to the injection compartment of the recirculating well. Neutralization took place in the treatment reservoir where the pH was monitored and adjusted to pH 7 by the addition of concentrated hydrochloric acid solutions. Due to the effect of hydraulic mixing, the untreated water remaining red was replaced by the treated water becoming colorless within the influence zone of the recirculating well. Therefore, the feasibility of the recirculating well application is judged by the interception of the colored plume.

Case 4. surface contaminant leakage

In Case 4, a condition of a surface contaminant leakage was simulated. Three peristaltic pumps were equipped to control an ambient groundwater flow, a constant contaminant leakage, and the recirculating flow around the well (FIG 14). Two similar monitoring reservoirs were installed to control a constant concentration of a contaminant leakage source and to adjust the consistency of the treatment processes respectively. The restoration of phenolphthalein initiated the similar experimental procedures. The leakage flow could not exceed ten percent of the ambient groundwater flow to avoid distorting the uniform groundwater flow, and it was not be turned on until the ambient groundwater flow and the recirculating flow were both stabilized. The contaminant monitoring reservoir was connected to the pump that drives a constant leakage into the aquifer model tank, and the pH of the water retended in the contaminant monitoring reservoir was consistently controlled at pH 12. The pH of the water entering the treatment monitoring reservoir was adjusted around pH 7 before returning to the aquifer.

The same judgment was used to evaluate the feasibility of the proposed system. The extent of contaminant interception was determined by graphical observation of the transport plume under different operational conditions. The desired result was to see the transport plume being totally blocked around the well.

EXPERIMENTAL PLAN

The experimental design for the investigation of well hydraulics was basically the arrangement of an ambient groundwater flow and the recirculating flow around the well.

The groundwater flow in a natural aquifer is very slow, and the groundwater velocity in most natural aquifers is usually in the range of 0 to 1 m/day. The general case of the flow conditions was simulated in the aquifer model tank; thus, an ambient groundwater flow was controlled at 1.0 m/day for the most of hydraulic experiments. Due to the size limitation of the aquifer model tank, the recirculating well could not be operated at a high pumping rate that would cause the recirculating flow to reach the boundary of the tank. Effects of the recirculating flow around the well were tested by increasing the well pumping rate from 25 to 200 mL/min, corresponding to the in-well vertical velocity of 2.0 to 16.0 m/day.

The experimental result of the same flow conditions from different cases were graphically compared to discover the significance of the interaction between the water flows. In order to evaluate the critical factors affecting the system design, the flow conditions, including the recirculating flow and the ambient flow, were controlled and tested for different cases. Also, well configuration directly affects the performance of the proposed system, and two recirculating wells were constructed for the significance test. For the statistical reliability, one set of the tracer tests for three different cases was duplicated under the same flow conditions.

Chapter IV

EXPERIMENTAL APPROACHES ON BIOLOGICAL TREATMENT

Nitrate removal processes play the most important role in determining the performance of the whole treatment system. Since the nitrate removal process has been successfully demonstrated in many biological systems, biological denitrification could be employed as a nitrate removal scheme in a recirculating nitrate treatment well system. Therefore, the nitrate treatment well itself has to be designed as a bioreactor.

For the purpose of carrying out biological denitrification, a population of denitrifying bacteria should be maintained within one or more large diameter nitrate treatment wells. Denitrifying bacteria are classified as autotrophic and heterotrophic denitrifiers, and both groups of denitrifiers are ubiquitous. Because the application of autotrophic denitrifiers in potable water treatment has not been well established, a mixed culture of heterotrophic denitrifiers will be employed as the means of denitrification. For accomplishing a successful application, the growth and maintenance of a large population of healthy denitrifying bacteria is inevitable.

Besides the presence of denitrifying bacteria, the occurrence of denitrification is generally controlled by the environmental conditions, including carbon source, electron acceptor, and growth nutrients. As an operating biological treatment, it is essential to control the surrounding environment to create a favorable condition for the applied microorganisms. In the case of biological denitrification, an anoxic condition has to be maintained to eliminate the competition of oxygen because nitrate serves as an electron acceptor. The appropriate amendment of the carbon source is also required to stimulate the occurrence of denitrification. Methanol is commonly used in wastewater treatment, but ethanol could be chosen as the carbon source in potable water treatment based on human health considerations.

Since biological retention time should be maintained long enough for the in-well culture to carry out efficient denitrification, well operation cannot attain a high rate for acquiring a sufficient hydraulic retention time. The other alternative is to construct an extremely large diameter treatment well; thus, hydraulic retention time can be greatly reduced at the same well operation rate. The required size of the nitrate treatment well will depend upon system-specific factors, such as the concentration of the applied microorganisms, the

efficiency of biological denitrification, groundwater contaminant level, well recirculation rate, the properties of aquifer materials, etc.

The work on biological treatment is expected to develop an automated system for the ease of denitrification process control. The experimental approach will start from the understanding of the theory of microbial kinetics. Sequentially, a series of batch reactors will be used to study microbial kinetics. An automated system will be developed to support the control of carbon amendment to stimulate biological denitrification, and the critical factors of process control will be examined in the tests of system operation.

THEORY OF MICROBIAL KINETICS

Almost all biological reactions are catalyzed by specific enzymes, and the relationship between microbial growth and substrate utilization is shown in FIG 15. A proportional relationship between the reaction rate and the total amount of present enzyme was assumed. The rate of reaction is first order at a relatively low concentration of substrate, and the order of reaction rate diminishes continuously from one to zero as substrate continually increases. The kinetic model of microbial growth has been developed by Monod for single strains of microorganisms using a single soluble energy source. A critical assumption of Monod model is that microbial growth is limited by the availability of one substrate. The specific microbial growth rate is defined as:

$$\mu = \frac{1}{X}\frac{dX}{dt} \qquad \text{..... (9)}$$

where, μ is defined as the specific growth rate of microorganisms, time^{-1}; and X is microbial mass concentration, mass/volume. For a suspended growth condition, the rate of microbial growth can be expressed as below:

$$\mu = \frac{\mu_m S}{K_s + S} \qquad \text{..... (10)}$$

where, μ_m is maximum specific growth rate, time^{-1}; K_S is substrate concentration when the reaction rate reaches half of the maximum specific growth rate, mass/volume; and S is substrate concentration surrounding the microorganisms, mass/volume.

The yield coefficient is defined to describe the relationship of the microbial growth rate and the substrate utilization rate.

$$\frac{dS}{dt} = \frac{1}{Y}\frac{dX}{dt} \qquad \text{..... (11)}$$

where, Y is growth yield coefficient, mass/mass. The rate of substrate utilization for

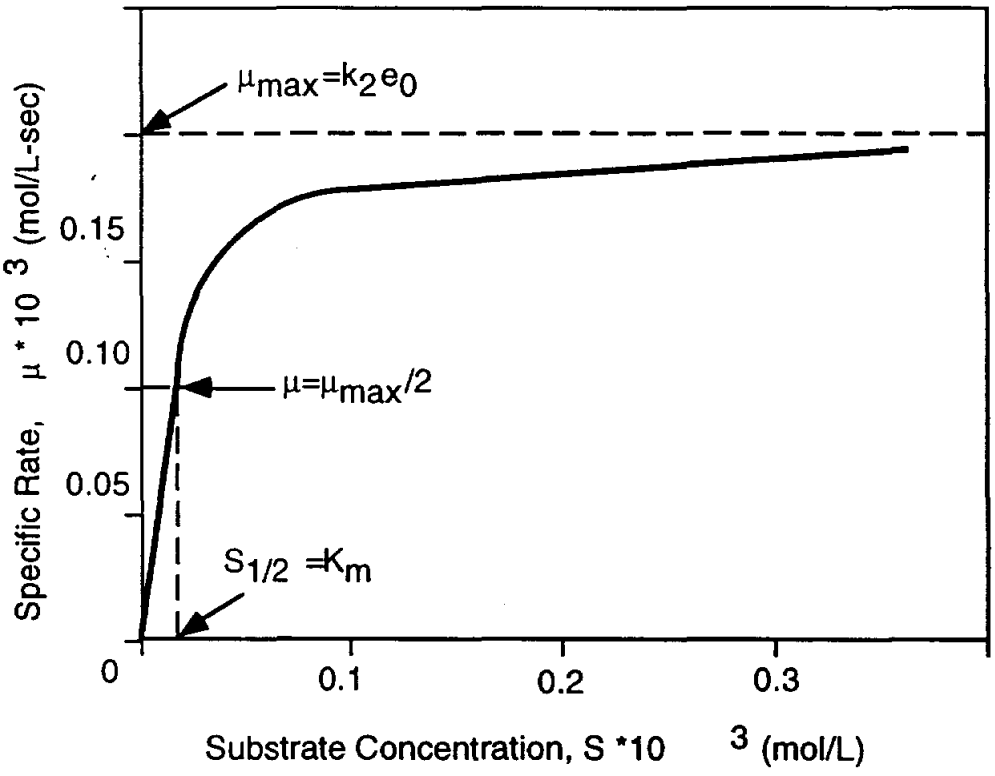


FIG 15. The Relationship of the Specific Microbial Growth Rate and the Substrate Concentration (From Baily and Ollis, 1986)

microbial growth is related to the concentration of microorganisms and the concentration of substrate surrounding the microorganisms. By substituting Eq(9) and (10) into Eq(11), the rate of substrate utilization could be formulated as the following equation:

$$\frac{dS}{dt} = \frac{\mu_m}{Y}\frac{SX}{K_s + S} \quad \text{..... (12)}$$

where, $\frac{\mu_m}{Y}$ represents maximum substrate utilization rate, time^{-1}.

In addition to microbial growth following substrate utilization, a decrease in biomass concentration may occur spontaneously due to the death or inactivation of microbial cells. If the decay of biomass has been considered in the kinetic model, the relationship of microbial growth rate and substrate utilization rate can be reformulated as:

$$\frac{dX}{dt} = Y\frac{dS}{dt} - K_d X \quad \text{..... (13)}$$

where, K_d represents decay rate of microorganisms, time^{-1}. The parameters of microbial growth kinetics including μ_m, K_s, Y, K_d can be determined from direct measurements of substrate concentration and biomass concentration in a series of batch reactors.

The recirculating well is a continuous flow reactor that can be characterized by the type of plug flow, completely mixed flow, or arbitrary flow. The mass balance for any reactor can be formulated as:

Accumulation Rate = Input Rate - Output Rate - Reaction Rate ..... (14)

Conventional anaerobic treatment systems are usually simulated by completely mixed reactors without recycle flow. The rate of inflow and outflow through the reactor is equal for maintaining a constant reactor volume. The concentrations of biomass and substrate in the effluent are assumed to be the same as those in the reactor. The conceptual model of a completely mixed reactor is shown in FIG 16. The mass balance equation for the net rate of change of microbial mass in the reactor that represents the difference between net growth rate in the reactor and net washout rate can be written as:

$$V\frac{dX}{dt} = Q(X_0 - X) + (Y\frac{dS}{dt} - K_d X)V \quad \text{..... (15)}$$

where, Q is the flow rate through the reactor, volume/time; V is reactor volume, volume; and X_0 is biomass concentration in the inflow, mass/volume.

If a steady state condition is reached, then microbial mass in the reactor will eventually keep a constant value, i.e., dX/dt = 0. Thus, Eq(15) can be rewritten as:

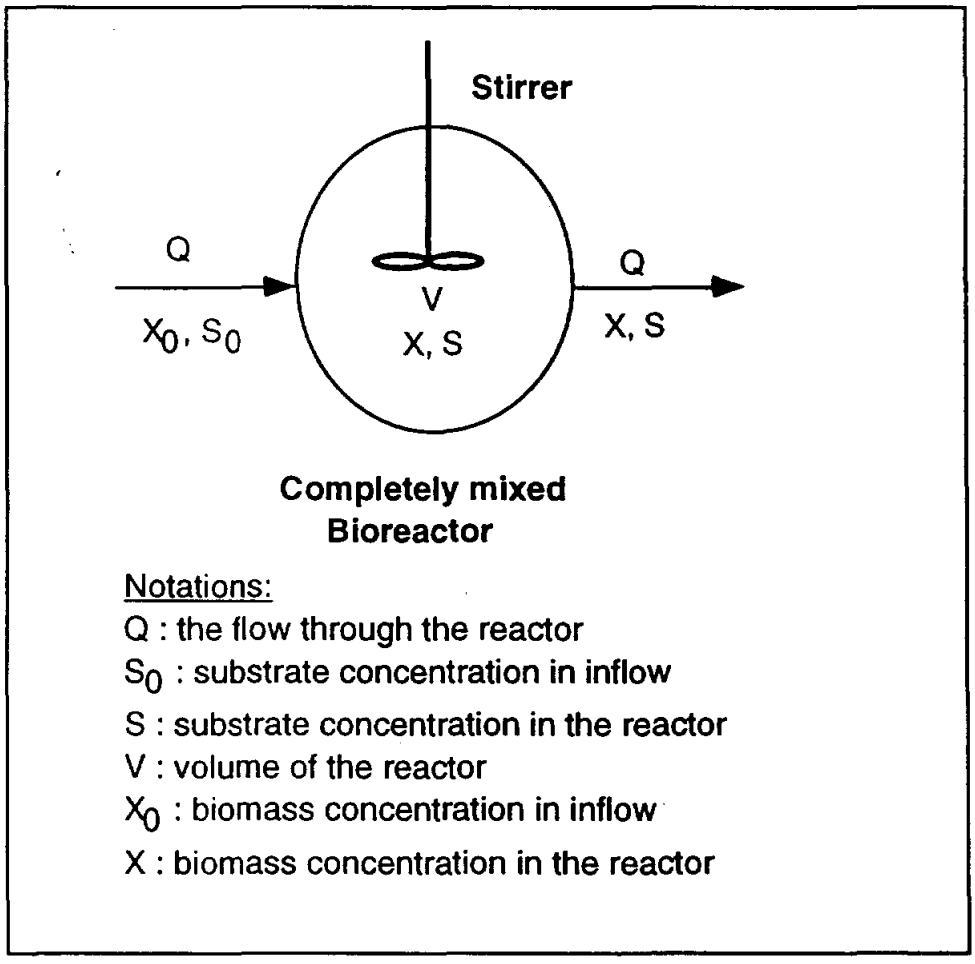


FIG 16. Conceptual Model of a Completely Mixed Bioreactor

$$\frac{1}{\theta} = \frac{Y\frac{dS}{dt} - K_d X}{X - X_0} \quad \text{..... (16)}$$

where, θ represents the hydraulic retention time(V/Q), time. Substituting Eq(12) into (16), effluent substrate concentration can be express as a function of retention time and biomass concentration.

$$S = \frac{K_s\left(1 + K_d\frac{X\theta}{X - X_0}\right)}{\frac{X\theta}{X - X_0}(\mu_m - K_d) - 1} \quad \text{..... (17)}$$

The assumption that there is no biomass in the inflow through the reactor is usually applied to simplify the relationship between retention time and effluent substrate concentration. Thus, the effluent substrate concentration can be simplified as a function of hydraulic retention time, and Eq(18) is similar to the treatment model developed by Lawrence and McCarty (1970).

$$S = \frac{K_s(1 + K_d\theta)}{\theta(\mu_m - K_d) - 1} \quad \text{..... (18)}$$

Another approach to derive the effluent substrate concentration is developed. The mass balance equation for the net change of substrate concentration can be formulated as:

$$V\frac{dS}{dt} = Q(S_0 - S) - (\frac{\mu_m}{Y}\frac{SX}{K_s + S})V \quad \text{..... (19)}$$

where, S_0 is influent substrate concentration, mass/volume. If the steady state condition of substrate concentration in the reactor is reached, Eq(19) can be rewritten as:

$$\frac{1}{\theta} = \frac{1}{(S_0 - S)}\frac{\mu_m}{Y}\frac{SX}{K_s + S} \quad \text{..... (20)}$$

Rearranging Eq(20),

$$\frac{X\theta}{S_0 - S} = \frac{YK_s}{\mu_m}\frac{1}{S} + \frac{Y}{\mu_m} \quad \text{..... (21)}$$

Thus, effluent substrate concentration decreases when retention time is elongated and biomass increased. The relationship of retention time and effluent substrate concentration can be solidified if the parameters of microbial growth kinetics were determined.

BATCH EXPERIMENTS

As stated previously, a heterotrophic group of indigenous soil denitrifying bacteria would be employed as the means of the denitrification process. The origin of indigenous soil denitrifying bacteria was extracted from a soil sample after being incubating in a batch reactor for about one week. The soil sample was collected from the top 15 cm surface soil outside the Civil Engineering Laboratory Building, Texas A&M University, College Station, TX. Ten grams of soil sample were initially amended in a one liter batch reactor, and the initial nitrate concentration in the batch reactor was maintained at 140 mg/l as nitrogen. For enhancing microbial growth, an excessive amount of ethanol was dispensed into the bioreactor to reach an extremely high carbon concentration of 2400 mg/l TOC. Salt solutions that consist of 1 mg/l $MgCl_2 \cdot 6H_2O$, 1 mg/l $FeCl_3 \cdot 6H_2O$, 1 mg/l $MnSO_4 \cdot H_2O$, 1 mg/l $CaCl_2 \cdot 2H_2O$, and 17.5 mg/l KH_2PO_4 were also fed to the acclimation bioreactor at 20 ml per day. After three days of acclimation, several tiny gas bubbles were noticeable near the water table.

Once the biological denitrification process was undertaken in the acclimation bioreactor, indigenous soil denitrifying bacteria could be acquired from the acclimation reactor by the separation technique. The common separation technique used for biomass extraction is the membrane filtration technique. The selected membrane for biomass extraction was a 47 mm glass fiber grade 30 filter paper from Schleicher & Schuell Inc., Keene, NH. Soil residual in the acclimation bioreactor would be totally removed by membrane filtration. A mixed culture of soil denitrifying bacteria extracted from the acclimation reactor was transferred to another one liter batch reactor as the bacteria source.

After acquiring the bacteria source of indigenous soil denitrifying bacteria, biological denitrification experiments could be initiated in a series of batch reactors. Microbial growth kinetics used to characterize the applied microbial culture will be examined by the conduction of batch experiments. Carbon availability is considered as the controlling factor in the occurrence of biological denitrification, so each batch reactor is maintained at a different level of carbon concentration. A set of batch reactors is consistently maintained under anaerobic conditions to eliminate the competition of oxygen serving as the terminal electron acceptor. The anaerobic batch reactor is a 250 mL amber glass bottle with a 125 mil Teflon-Silicone septum on an open-top closure made by I-Chem Research. A 1 cm diameter, 2.5 cm long magnetic stir bar is installed in each batch reactor to enhance homogeneity of batch cultures. A series of batch reactors is set on a multiposition

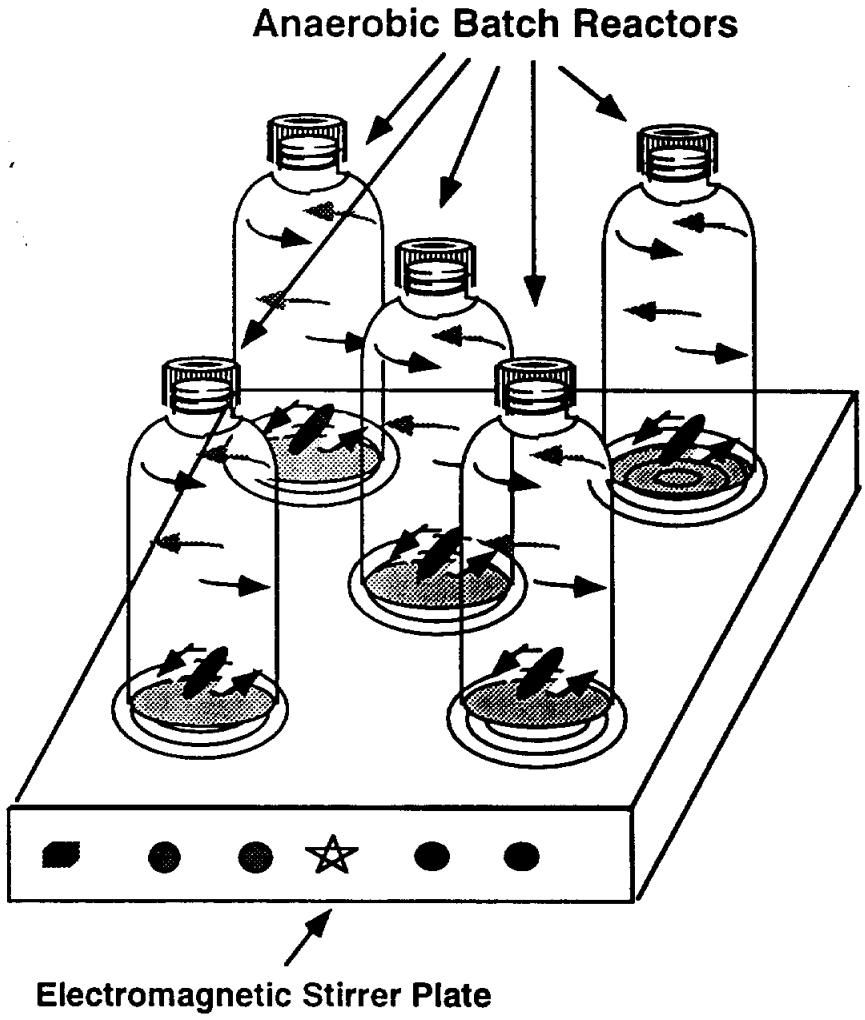


FIG 17. Experimental Setup of Anaerobic Batch Reactors

electromagnetic stirrer plate, and the typical setup of the batch experiments is schematically demonstrated in FIG 17.

Before conducting batch experiments, indigenous soil denitrifying bacteria were transferred to each batch reactor. In order to precisely control the content of the bioreactor solution, an extraction technique was required for transferring biomass only. Thirty ml of solution sample from the bacteria source bioreactor were centrifuged at 4 ^{o}C, 5,000 rpm for 15 minute in an IEC B-20A high-speed refrigerated centrifuge from International Equipment Company. In order to prevent the microbial cell from breaking, biomass extracted from each centrifuge tube was then mixed in a 10 mL buffer solution by a vortex mixer. The initial nitrate contamination level for each batch reactor was maintained at 100 mg/L as nitrogen, ten times as high as USEPA's regulation standard. In order to evaluate the impact of carbon availability, each batch reactor was maintained at a different carbon-to-nitrogen ratio(C/N) ranging from 0.5 to 2.5. Biological denitrification processes were examined at different microbial growth conditions, so the reaction rate could be determined from batch experiments.

Sampling and Analysis

The main concern of denitrification is the rate of nitrate consumption and nitrite production since gas products including nitric oxide, nitrous oxide, and nitrogen gas will escape into the air. Analysis of nitrate and nitrite would be directly measured by ion chromatography. Substrate concentration could be determined from COD measurement. Biomass would be estimated from the amount of total suspended solid.

A 10 mL syringe was used for sample collecting and nutrient feeding to maintain an anaerobic environment within the batch reactors at all times (FIG 18). The analysis of nitrate and nitrite content within the bioreactor was conducted in Dionex ion chromatography laboratory system featuring a conductivity analyzer. Quantitative analysis was based on the comparison of the response of the detector of an analyte in the sample to the detector response for the same analyte in a standard solution of known concentration. The detector response was measured as peak area, since peak areas are less affected by minor changes in temperature, flow rate, or analyte retention time. By using the external standard method, nitrate and nitrite were linearly calibrated within the concentration range of 0 to 10 mg/L as nitrogen and 0 to 6 mg/L as nitrogen separately. During the sample preparation, an aqueous solution sample collected from each batch reactor was filtered through a 0.45 μm membrane filter paper to remove biomass content. The filtered samples

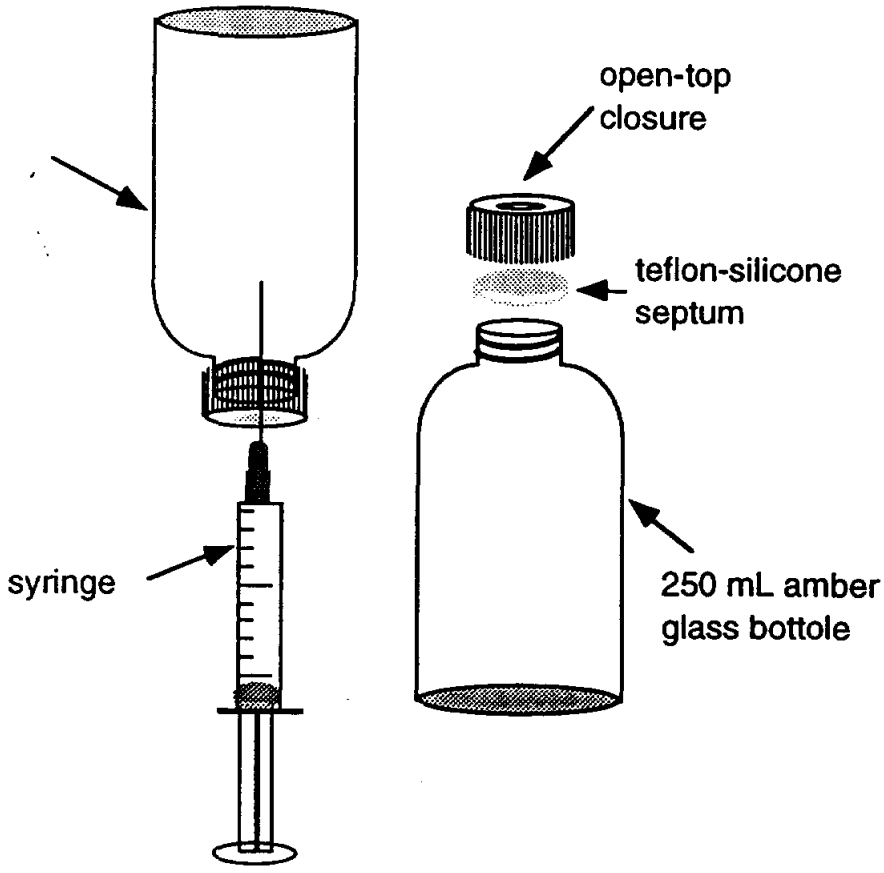


FIG 18. The Diagram of Sample Collecting from an Anaerobic Batch Reactor

were sequentially diluted at a 1 to 10 ratio to bring the analyte concentration within the analytical range of the chromatographythat is the concentration range of linear calibration. Only 1 mL of the prepared sample was injected into the Ion Chromatography, and peak area output responded at a different retention time for quantitative analysis of each detected analyte. According to typical chromatogram output, analyte retention time was 2.04 min for nitrite and 3.57 min for nitrate. The operation procedure is detailed in the manufactures' manual.

The chemical oxygen demand(COD) test is used to determine the relative oxygen requirement for the organic matter content of a sample that is susceptibly oxidized by a strong chemical oxidant. The determination of COD can be related empirically to the total organic carbon(TOC) content of the sample; the theoretical COD/TOC ratio is 4.0 for ethanol. The closed reflux colorimetric method was used for COD determination as described in the Standard Methods. All the required COD reagents with the detection limit of 1500 mg/L were purchased from Hach Company, Loveland, Colorado. A 2 mL sample was pipetted to 3 mL prepared COD reagents during the measurement. After being shaken to provide a better mixture, the samples were heated at 150 ^{o}C for 2-hour digestion in a Hach model 45600 COD reactor. The reacted sample was directly measured from a Hach DR/2000 spectrophotometer that features the preprogrammed COD calibration curve. The Hach water analysis handbook will provide experimental procedures step by step.

Biomass quantitation is essential for microbial kinetic studies, since the amount of biomass directly affects microbial activity. In laboratory studies, microbial density can be estimated from total suspended solids. The measurement of total suspended solid was determined by the photometric method as well as the gravimetric method. The gravimetric procedure for solid determinations was the EPA specified method using the membrane filter technique. Only 5 mL of the bioreactor sample was available for measurement each time because of the small volume of batch reactors. The collected samples were filtered through a 47 mm-diameter 0.45 μm-pore membrane filter paper, and the filter discs were then dried in an oven at 103 ^{o}C for one hour. The nonfilterable residuals were calculated from the weighing difference of the filter discs by an analytical balance. The second approach of total solid determinations is the photometric method, and the direct measurement from the colorimeter is reliable within the range of 0 to 750 mg/L of suspended solids. Since a spectrophotometer was used as the major instrument for quantitative analysis, the wavelength had to be set at 810 nm based on an analysis of the absorption spectrum. Twenty-five ml of bioreactor sample was measured each time, and it was returned to each

batch reactor to prevent a dilution effect after measurement. Before each measurement, the colorimeter had to be zeroed by the blank measurement. Calibration for this test was prestored in the Hach DR/2000 spectrophotometer, so the measurement could be directly read from the colorimeter.

TREATMENT SYSTEM EXPERIMENT

Carbon source is the usual growth-limiting substance of heterotrophic microorganisms, while all other growth requirements are present in excessive amounts. The proposed recirculating nitrate treatment well itself serves as a bioreactor, so carbon amendment into the well is used as a means of process control. According to the results of batch experiments, the derived microbial growth kinetic parameters would be used for the control of automated carbon feeding system.

System Setup

An automated carbon feeding system was developed to control the stimulation of the biological denitrification process. The proposed automated system consists of a nitrate nitrogen monitoring device and a carbon substrate feeding device. Basically, in-well nitrate nitrogen concentration would be monitored by an ion meter equipped with a nitrate probe. The nitrate probe used was a Cole-Parmer 27502 nitrate electrode with a detection range of 0.5 to 62,000 ppm as nitrate ion, and a Fisher Accumet Model 925 pH/mv meter was utilized as the required ion meter. The milivolt mode of the pH/mv meter was used for the measurement of electrode potential with a detection range of 0 to 1,999.9 mV. The recorder output of the ion meter was then connected to a Strawberry Tree T-31 terminal panel for data transmission. A Strawberry Tree ACjr-12 interface card that features a T-31 terminal panel was also installed in an IBM personal computer as a data acquisition device. Thus, the analog signals could be transmitted from the ion meter to the interconnected computer via a data acquisition board, and the electric signals were translated to the values of ion concentration by a system calibration. According to electrode theory, measured electrode potentials are a log function of ion concentrations in solution. A standard curve was generally calibrated from at least five known ion standards, and the calibrated Nernst equation was stored in the computer to interpret measured electrode potential.

The carbon substrate feeding device mainly depends upon the use of Metrohm 665 Dosimat. Metrohm 665 Dosimat is equipped with a 1 liter reservoir and an 5 mL exchange unit that can expel liquid at a desirable constant rate and refill from the reservoir after

running out of liquid. An extensive remote control of the feeding device can be normally accomplished by a proper interconnection between an IBM personal computer. Data transmission occurs serially via an interface according to RS 232 C in a half duplex procedure. A control software needs to be developed for the proceeding of remote control, and all commands involved in the control software refer to the user's manual of the Metrohm 665 Dosimat.

After a proper hardware installation, the designed control system was automated by using a well-developed control software. According to the electrical signal of a nitrate monitoring device, in-well nitrate concentration was interpreted and automatically logged into a disk once every two minutes. The requirement of carbon amendment was calculated based on the control criteria of the treatment model, and the appropriate carbon amendment was undertaken under the control of the feeding device at a correspondent feeding rate. Thus, the automated system was operated in this way so that carbon feeding could be controlled based on nitrate monitoring. The setup of the automated control system is schematically demonstrated in FIG 19, while the flowchart of the system-control software is shown as FIG 20.

System Operation

The installed hydraulic well was too small to maintain a reasonable retention time, and it had to be replaced by a large denitrification well that was 35 cm long, 12 cm wide, and 60 cm high. The denitrification well that modified the previous design of hydraulic wells consisted of withdrawal, treatment, and sedimentation compartments. Groundwater was withdrawn through the withdrawal chamber and treated in the treatment chamber, and particulate materials migrating with groundwater precipitated in the sedimentation compartment. The geometric view of the scaled recirculating nitrate treatment well is shown in FIG 21.

After accomplishing the studies of microbial growth kinetics, a population of the same species of denitrifying bacteria was transferred and acclimated within the recirculating nitrate treatment well. Two liters of batch reactor mixtures rich in indigenous soil denitrifying bacteria were restored in the recharging compartment of the treatment well. Denitrification processes were expected to mainly occur within the well, so the recirculating nitrate treatment well had to be enclosed to maintain an anoxic condition. A 12 cm by 25 cm acrylic plate was capped on the top of the treatment well, and aquaseal materials from Essex Fire & Safety were used to seal the gaps between the capping plate and the treatment

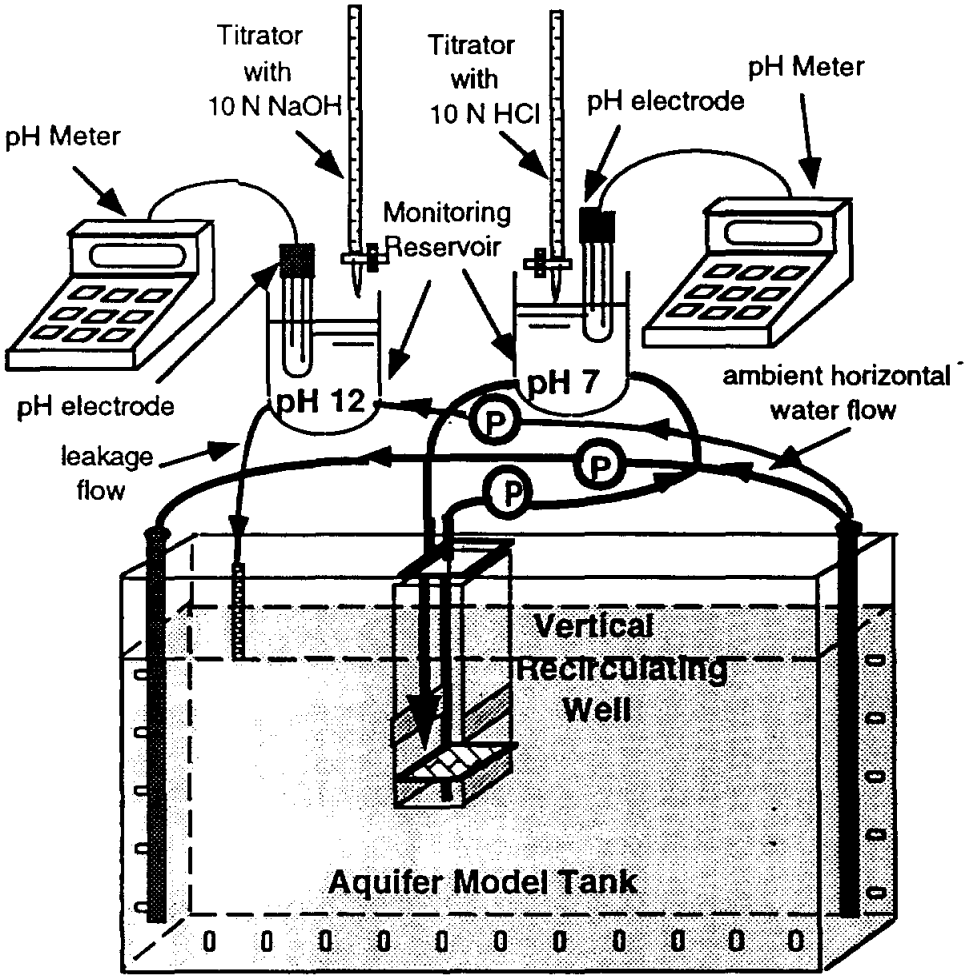


FIG 14. The Setup of Experimental Apparatus for Case 4 in Tracer Simulation Tests

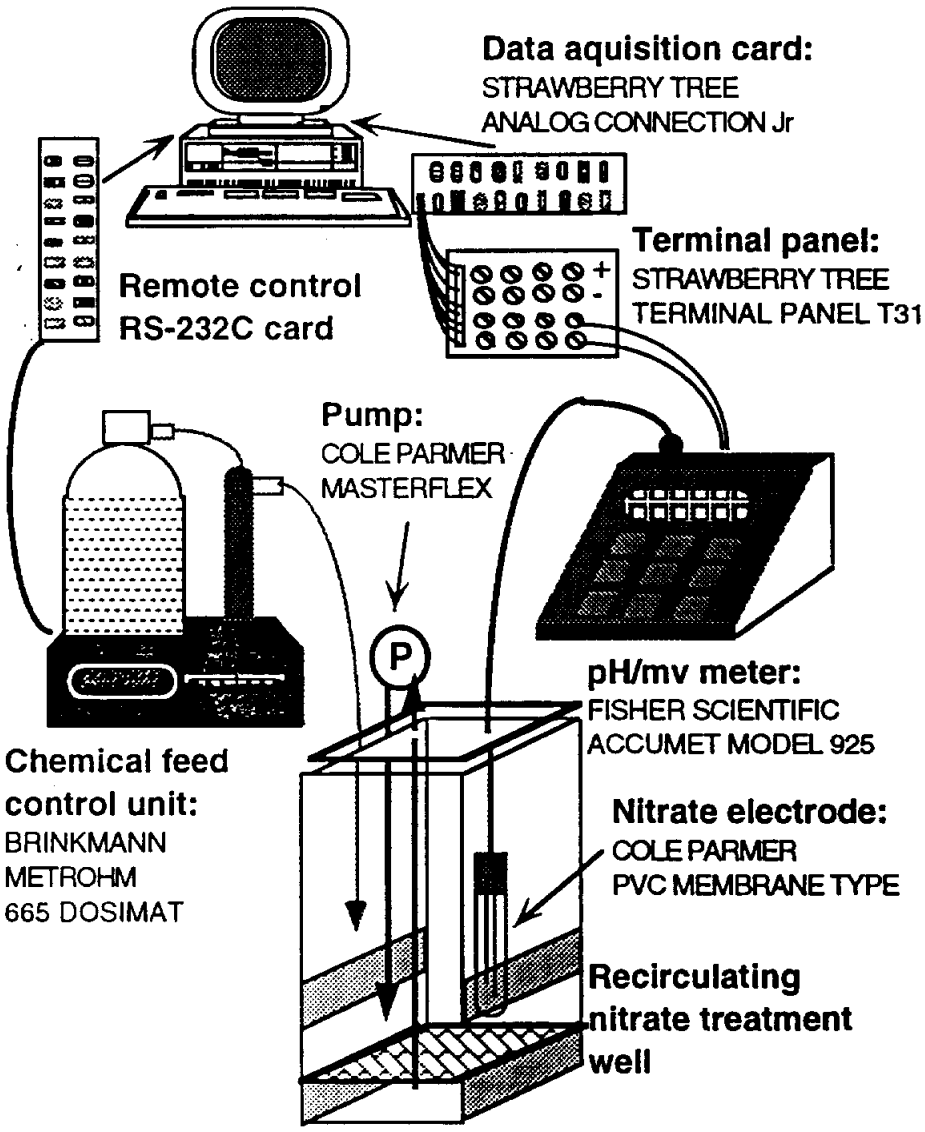


FIG 19. Schematic Setup of the Automated Control System of Carbon Amendment

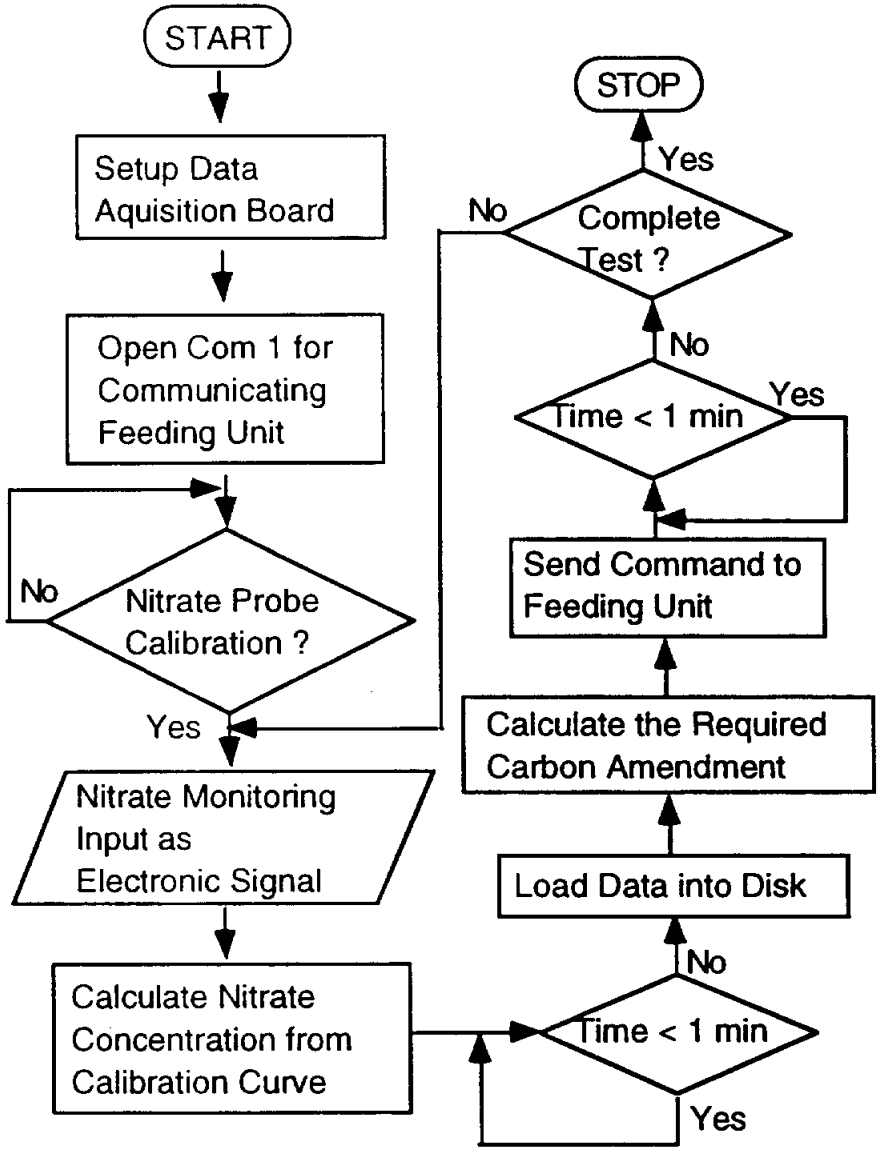


FIG 20. Flowchart of the System-control Software

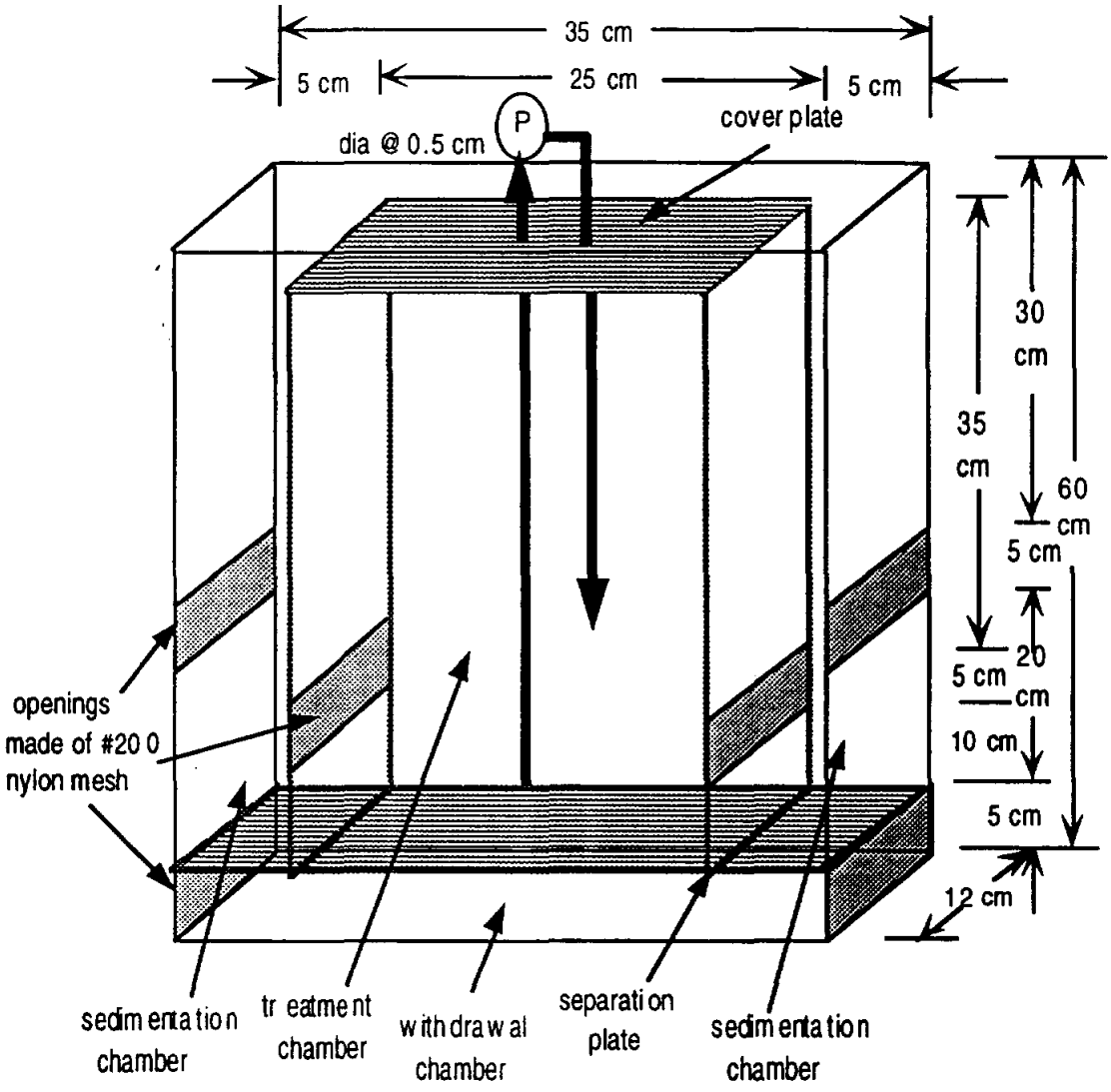


FIG 21. Geometric View of the Scaled Recirculating Nitrate Treatment Well

well. The automated system was connected to the treatment well through the capping plate, and carbon feeding line and nitrate probe were installed in the treatment well. The gas confined in the well was circulated at the rate of 3,600 cm^3/min through an air pump into the aqueous phase to create a homogeneous condition. Two bubble curtains were installed below the screen sections to improve mixing and to reduce screen fouling.

The system was operated under a similar condition as case 4 simulation in the tracer tests. A surface contaminant source containing nitrate concentration of 1,000 mg/L as nitrogen was leaking to the aquifer model tank at a rate of 2.5 mL/min. With a background ambient horizontal water flow of 1 m/day, the treatment well was tested at different well recirculation rates. Because a well recirculation rate corresponds to a specific hydraulic retention time, the well recirculating rate is considered as one of control factors in the evaluation of system performance. As another factor affecting system performance, the carbon feeding rate was adjusted to optimize system performance during experiments. The effects of well recirculation on system performance can be only tested at the rate lower than 50 ml/min because of size limitation of the physical model. Besides, the impact of ambient groundwater flow on system performance was also examined at the velocity range of 1 to 4 m/day.

The evaluation of system performance is based on the monitoring of nitrate level downstream of the treatment well. The nitrate level was determined from ion chromatography measurement of the aqueous samples. In order to identify the contaminant plume, the sampling positions were distributed on two sampling lines at different depth. One sampling line was located at the same depth of recharge screen sections, and another was at the same depth of the withdrawal compartment. The sampling positions are schematically shown in FIG 22. According to the evaluated performance, nitrate leakage rate and well operation rate could be readjusted to optimize system performance. The main objective of this research will be accomplished by lab demonstrations.

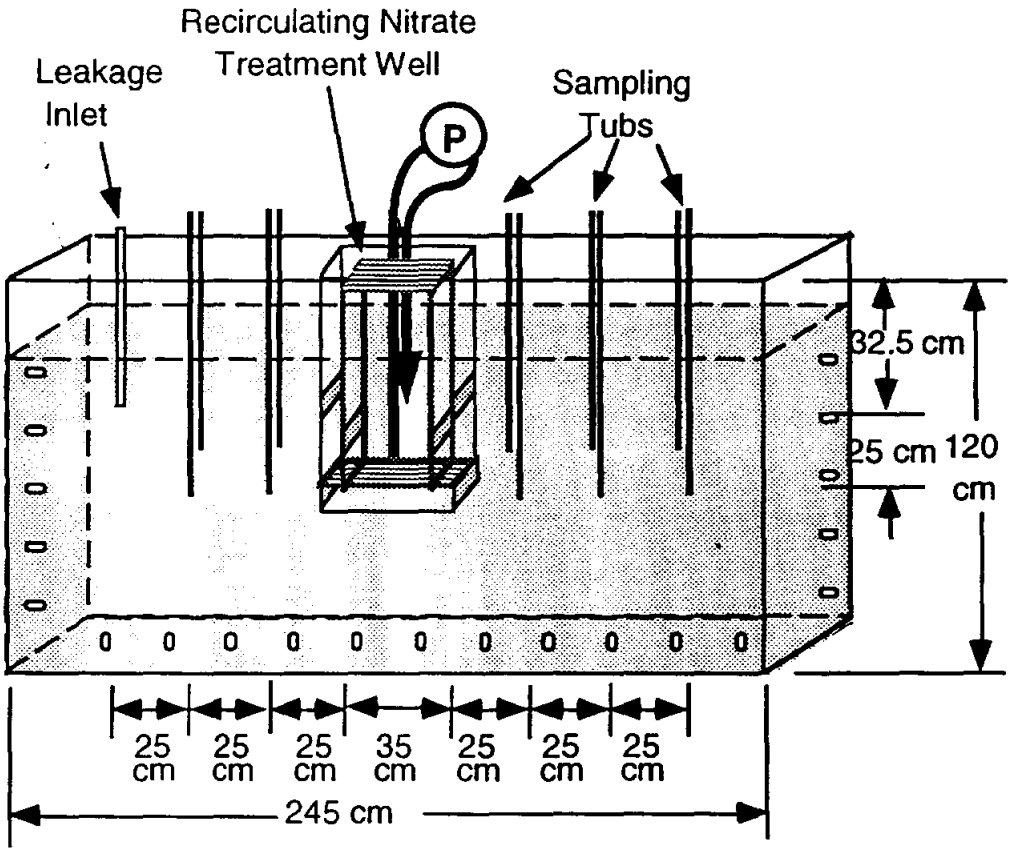


FIG 22. Sketch of the Aquifer Model Showing Sampling Positions

Chapter V

RESULTS AND DISCUSSIONS ON HYDRAULIC STUDIES

The vertical circulation flows around the recirculating well are partial three-dimensional flow systems as described in Chapter III. It is impractical to employ a three-dimensional physical modeling for experimental observation because of technical difficulties and enormous cost. However, it is applicable to project two-dimensional physical modeling onto three-dimensional flow situations by using some suitable simplifications and assumptions. The simplifications and assumptions of experimental observation consist of simplifying aquifer conditions and neglecting experimental randomness.

1. Simplifying aquifer conditions:
   - The aquifer type is an unconfined aquifer.
   - The aquifer material is fine uniform sand.
   - The aquifer thickness is constant.
   - The groundwater flow is a consistent uniform flow.
   - The groundwater table is at constant head.
2. Neglecting experimental randomness:
   - The packing is homogeneous and but anisotropic in the modeling tank i.e., same vertical and horizontal permeability values at every point.
   - The fluctuations of the water table due to evaporation, pumping, and the additions of contaminant source are negligible.
   - The pH indicator is uniformly distributed in the modeling tank to obtain equal pH sensitivity at any points.
   - The cleanup level of the contaminant is simulated by the color change of pH indicator.
   - Tracer transport due to gravity effect is negligible.
   - The inflow and outflow of the recirculating well due to pumping is assumed to be symmetrical and uniform.
   - The headloss resulting from screen sections is neglected.
   - The operational errors of mapping plume are neglected.

When two-dimensional modeling is applied to three-dimensional flow system, the sphere of three-dimensional flow system is assumed to be split into three two-dimensional flow situations. The flow on the plane(y-z) normal to groundwater flow direction wouldn't be affected by groundwater flow, so the flow situation can be simulated in a no

groundwater flow condition. The flow on the plane(x-z) parallel to groundwater flow direction would be directly influenced by groundwater flow; therefore, the flow condition can be modeled with the introduction of groundwater flow. Because the plume on the top view plane(x-y) could not be observed from this designed modeling tank, the flow situation should be interpolated from the flow conditions on the other two views.

The influence of the capture zone and the sphere of the protection zone by the operation of the recirculating well are major concerns in hydraulic studies. The properties of aquifer materials and the characteristics of the groundwater remediation well play important roles in determining the scope of the capture zone and the protection zone, so to define these two factors became the first task. The properties of aquifer material are measured before defining the scope of the capture zone and the protection zone.

EXPERIMENTAL RESULTS

Soil Properties

The measurements of soil properties include hydraulic conductivity, porosity, and bulk density; the results of soil property measurement are shown in Fig 23. Hydraulic conductivity is assumed to be homogeneous and anisotropic in aquifer model tank. As the results show, hydraulic conductivity is 19% lower in the vertical direction than in the horizontal direction. This implies that the layering problem is not significant in the aquifer model tank, and a larger vertical hydraulic conductivity can be expected from soil compaction by its own weight. The density of selected aquifer materials is 2.59 g/cm^3, and the porosity of selected aquifer material in the model tank averaged 0.44.

Tracer Tests

The graphical mappings for the tracer tests are shown in FIG 24 through FIG 27. The flow condition of case 1 is the recirculating flow only. A red plume with high pH gradually developed around the recirculating well when hydroxide ion was carried out of the well. The symmetric shape of the developed plume is a sign of the homogeneity of aquifer materials in the model tank. For a partially penetrated well, the plume is distorted downwards because the recirculating flow was suppressed by the groundwater table. As other information reveals in FIG 24, the transport of aqueous contaminants is not limited in the saturated zone. Furthermore, the transport rate in the unsaturated zone seems to be slower than that in the saturated zone because a low water content will result in a low hydraulic conductivity in the unsaturated zone. The transport of aqueous contaminants may

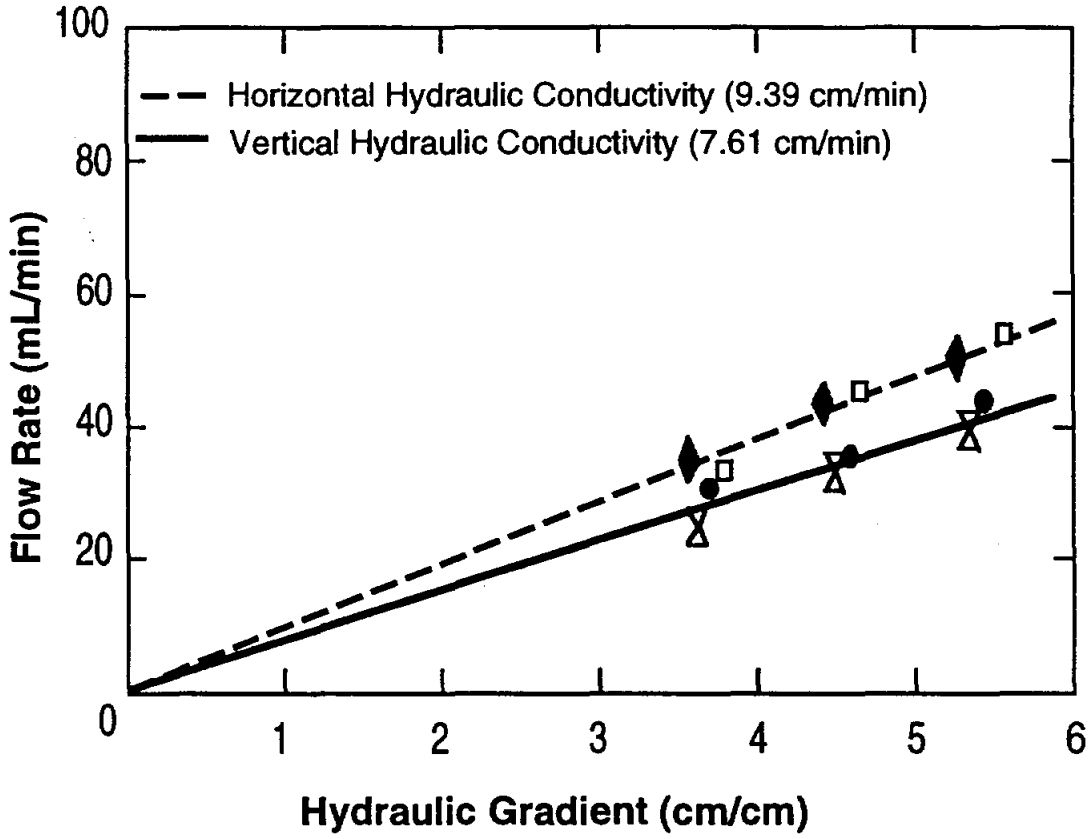


FIG 23. The Results of Hydraulic Conductivity Measurements from the Constant Head Tests

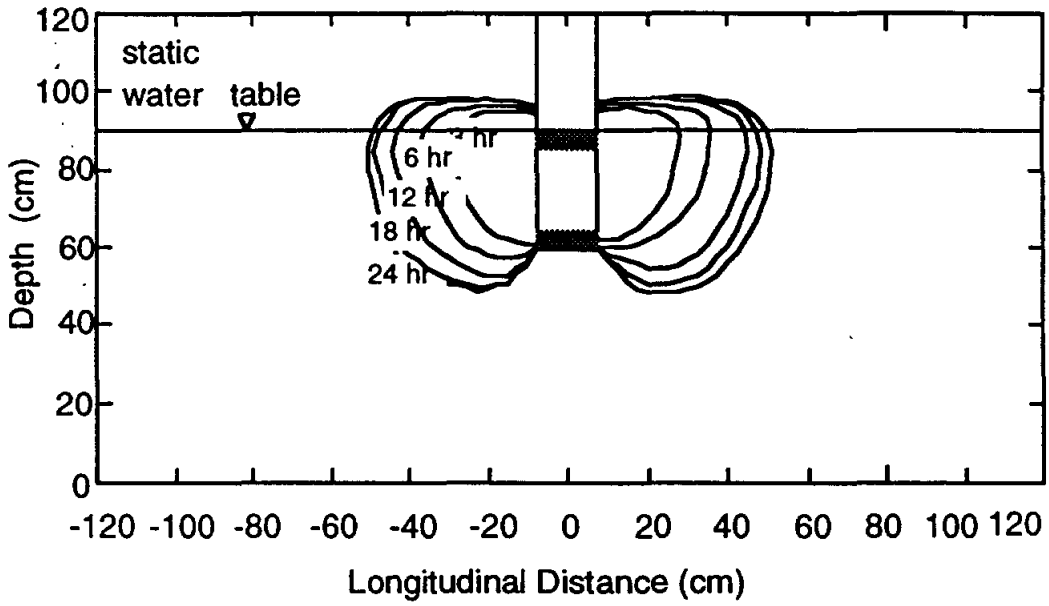


FIG 24. Case 1 Simulation of the Tracer Tests: Zero Ambient Flow Velocity and 50 mL/min Well Recirculation Rate for Hydraulic Well 1

migrate into the unsaturated zone and return to the saturated zone; thus, the transport may be retarded during the migration in the unsaturated zone. The rate of plume development is slower when the plume moves away from the recirculating well; theoretically, the development of the contaminated plume will reach the steady-state condition.

For case 2, the flow field is subjected to an ambient horizontal water flow in addition to the recirculating flow in the well. Ambient horizontal flows tended to distort the plumes around the recirculating well, with the upstream side of the plume compressed and the downstream side of the plume elongated. As illustrated in FIG 25, the nonsymmetry of the plume is not obvious at the beginning of plume development. This implies that the recirculating flow near the well circulates faster than it does away from the well. The transport of aqueous contaminants is controlled by the recirculating flow as well as an ambient horizontal water flow. By increasing the distance from the well, the ambient horizontal groundwater flow became more dominant because of the gradual decrease in the recirculating flow velocity. Comparing FIG 25 with FIG 24, the ambient flow also reduced the extent of the plume below the bottom of the recirculation well. The plume development upstream will stagnate for a period of transport time, while the plume development downstream never relinquishes because of the delivery of an ambient horizontal water flow.

For case 3, the flow field is the combination of the recirculating flow and an ambient horizontal flow. In addition, a uniformly distributed source of groundwater pollutants is delivered by an ambient horizontal flow. Before entering the influence zone of the recirculating well, the plume is horizontally transported. The treatment barrier does intercept the upper portions of the plume, and a similar shape of clear region with the plume created in case 2 covered the top half of the aquifer. Consequently, the plume would submerge and intrude downstream of the recirculating well. As FIG 26 illustrates, there is a depth limitation of the treatment barrier zone created by the partially penetrated well. The maximum depth that the treatment barrier can reach is about double the depth of the well penetration, but the maximum reachable depth also depends upon the well pumping rate.

For case 4, the flow field is the combination of the recirculating flow, an ambient horizontal flow, and a tiny leakage flow. The distribution of a pollutant would be typical of a solute that had been applied to the groundwater from the surface, such as agricultural source nitrate. The effect of the leakage flow on the flow field is usually neglected because of its small flow rate, but the concentration of the leakage will affect the transport of the

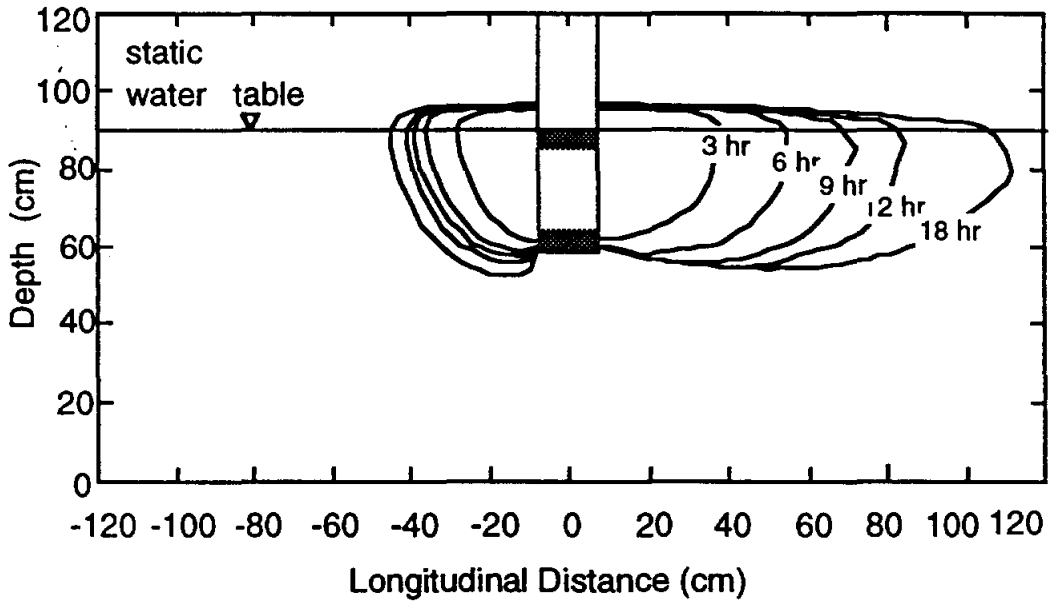


FIG 25. Case 2 Simulation of the Tracer Tests: 1 m/day Ambient Flow Velocity and 50 mL/min Well Recirculation Rate for Hydraulic Well 1

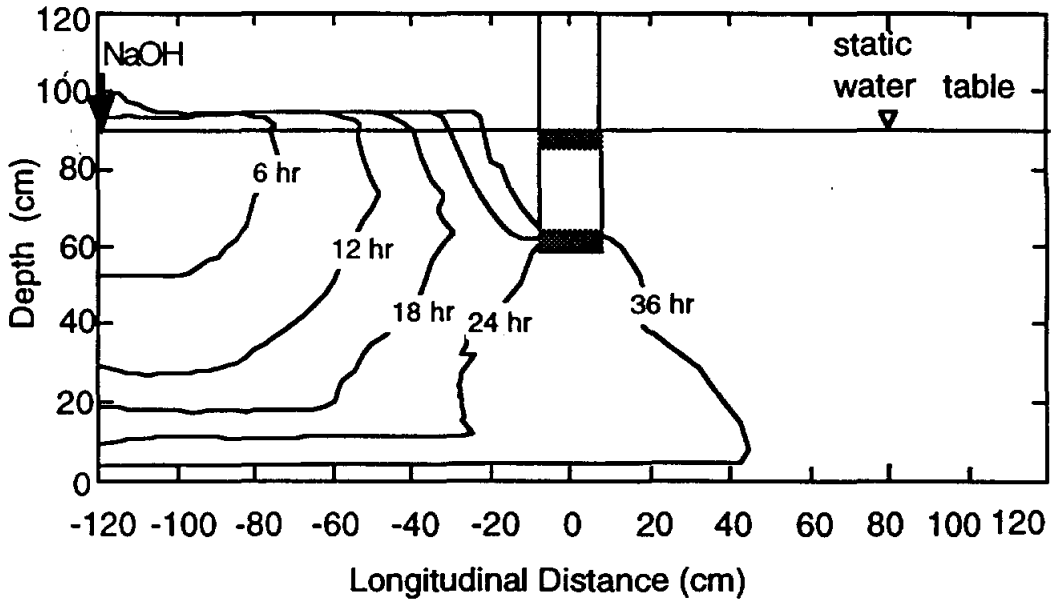


FIG 26. Case 3 Simulation of the Tracer Tests: 1 m/day Ambient Flow Velocity, 50 mL/min Well Recirculation Rate, and with a Depth Distributed Source of NaOH for Hydraulic Well 1

contaminated plume. As FIG 27 illustrates, the plume was successfully drawn into the well and treated before returning to the aquifer. The plume was pulled downward when it entered the influence zone of the treatment barrier, and the plume was sequentially forced to the withdrawal compartment from both upstream and downstream sides. Thus, the graph mappings illustrated that the surface pollutant can be effectively intercepted by the created treatment barrier.

Reproducibility

The reliability of experimental results was examined from the duplication of tracer tests under the same operating conditions. The experimental results of the duplicated tracer tests with well 2 have been compared in case 1, 2 and 4 simulations. The comparison of duplicated tracer tests would give inevitable differences in the operations due to coarseness of pump controls, the change of hydraulic conductivity, and other random errors.

The comparison in case 1 simulation illustrated that the difference in the plume diameter was less than 7 percent, and the divergence in the plume depth was about 12 percent at 24 hours of plume development. Without an ambient horizontal flow, the nonsymmetry of the plume is a sign of the heterogeneity of hydraulic conductivity. FIG 28 shows that the variations of plume size are noticeable at the bottom of the upstream plume and the side of the downstream plume. It implies that the expected reduction of permeability at the upstream side of the withdrawal sides is the best explanation for the divergence of plume size. The decrease in permeability is a major cause of the plume shrinkage upstream. Also, the water was withdrawn more from downstream than from upstream due to the permeability loss upstream, so a stronger recirculating flow will lead to a greater size of the downstream plume. The loss of permeability upstream corresponds to the loss of energy cost, and the shrinkage of the capture zone should be considered to avoid the blow-through of plume between two recirculating wells. Therefore, the rate of well recirculation should be increased after a long period of well operation, or the treatment system should be more conservatively designed for the operating condition.

The effect of the ambient horizontal water flow is demonstrated in FIG 29. The divergence of the downstream plume is a sign of the shift of the permeability and the rough control of the ambient horizontal flow. The upstream plume is insensitive to the alternations of the permeability and the ambient horizontal flow because the strength of the recirculating flow is larger closer to the well. The shifts of the permeability and the ambient

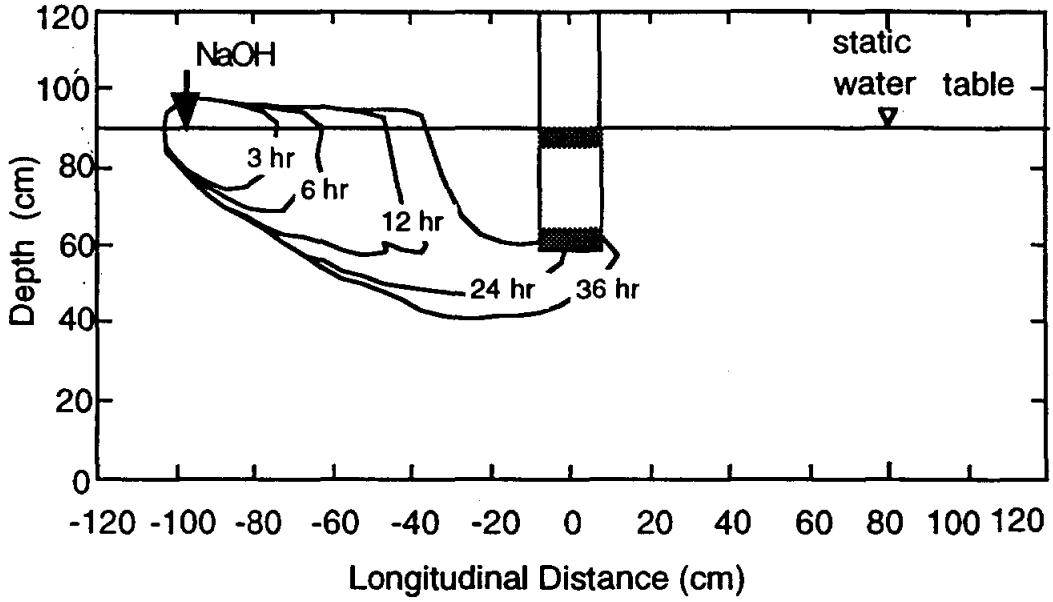


FIG 27. Case 4 Simulation of the Tracer Tests: 1 m/day Ambient Flow Velocity, 50 mL/min Well Recirculation Rate, and with a Surface Source of NaOH for Hydraulic Well 1

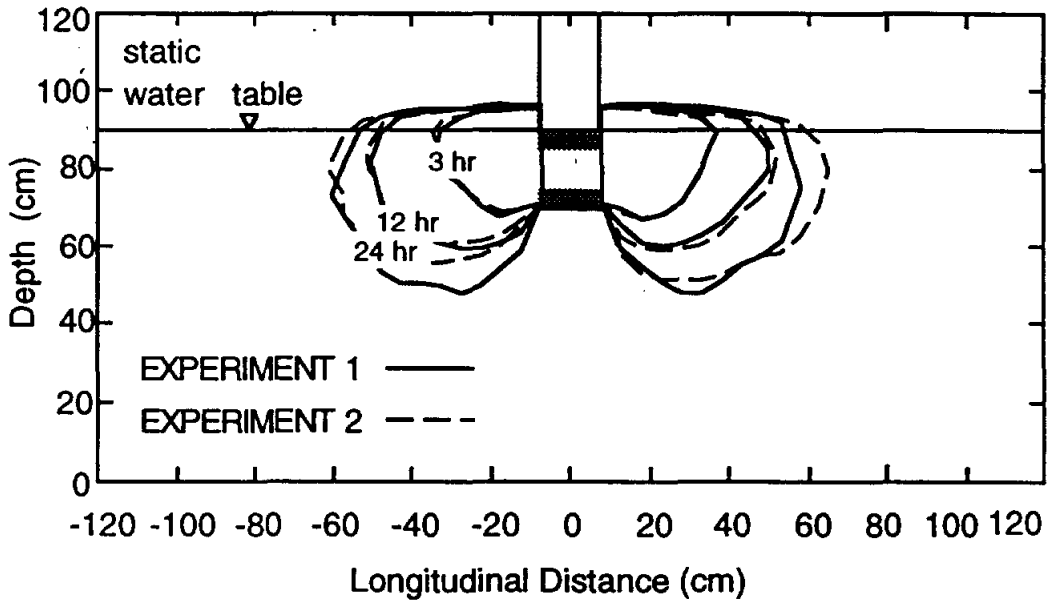


FIG 28. Reproducibility in Case 1 Simulation: Zero Ambient Flow Velocity and 100 mL/min Well Recirculation Rate for Hydraulic Well 2

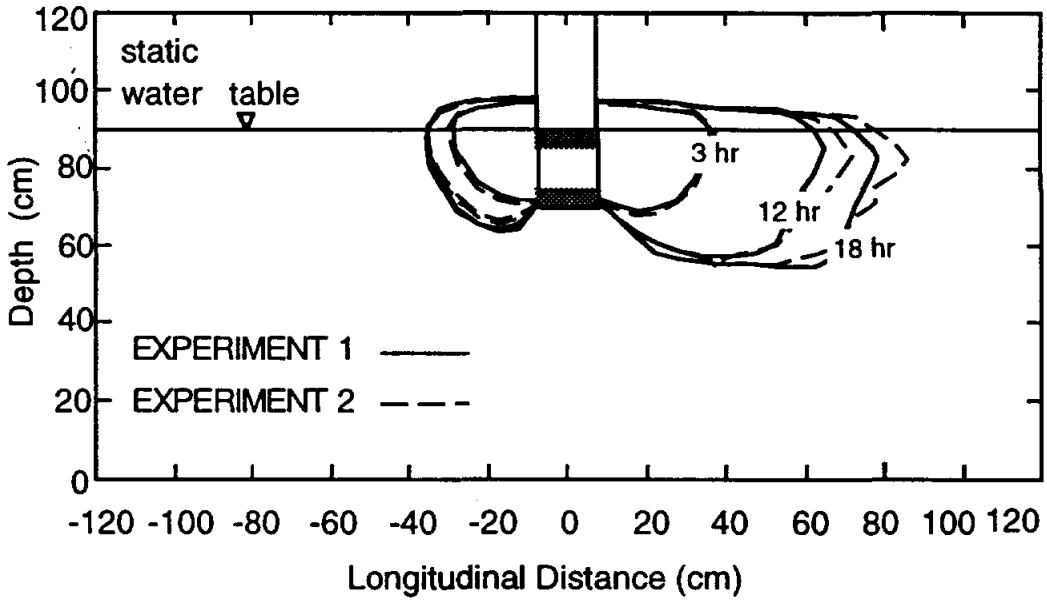


FIG 29. Reproducibility in Case 2 Simulation: 1 m/day Ambient Flow Velocity and 100 mL/min Well Recirculation Rate for Hydraulic Well 2

horizontal flow were also supported by the sign in FIG 30. It was found that the change in vertical permeability is greater than that in horizontal permeability. The surface plume seems to follow the same path to the well, and the only difference is the rate of contaminant transport. This result strongly recommends that the interception of a surface plume can be consistently and reliably judged by the tracer simulation. Overall, experimental results from tracer simulation are reliable because of their own high reproducibility.

DISCUSSIONS

Capture Zone

In order to apply the proposed system for the aquifer cleanup, the proper design of such an operation is very important, both economically and environmentally. The determination of the optimum number of recirculating wells and their rates of hydraulic recirculation and locations is based on the concept of a capture zone. For a withdrawal well, the capture zone is traditionally defined as the region with a zero flow velocity boundary. The capture zone of a withdrawal well is usually a cylinder sphere that can be characterized by the influence radius. The influence radius is defined as the distance between the withdrawal well and the boundary of its capture zone. The region within the influence radius is a radial flow field, and the region beyond the influence radius is a horizontal flow field dominated by groundwater flow. In contrast to a normal withdrawal well, where the capture zone is delimited by a simple separating streamline, the capture zone of a vertical recirculating well must be outlined by a curved surface. Thus, it is difficult to characterize the capture zone sphere of a vertical recirculating well.

Under the experimental simulation, the capture zone can be viewed from cross sections at the direction parallel to and perpendicular to the ambient horizontal water flow. The width of the capture zone is an important design parameter for dimensioning the distance between well arrangement. The width of the capture zone could possibly be determined by experimental observation of plume development from the case 1 simulation. It is assumed that groundwater flow has no effect on contaminant transport at the cross section perpendicular to the groundwater flow. The basic criterion for the experiment method is to operationally define the width of the capture zone under the operation of the vertical recirculating well. The cross section of the capture zone at the direction perpendicular to groundwater flow is operationally defined as the domain of the observable hydroxide plume that was circulated around the vertical recirculating well.

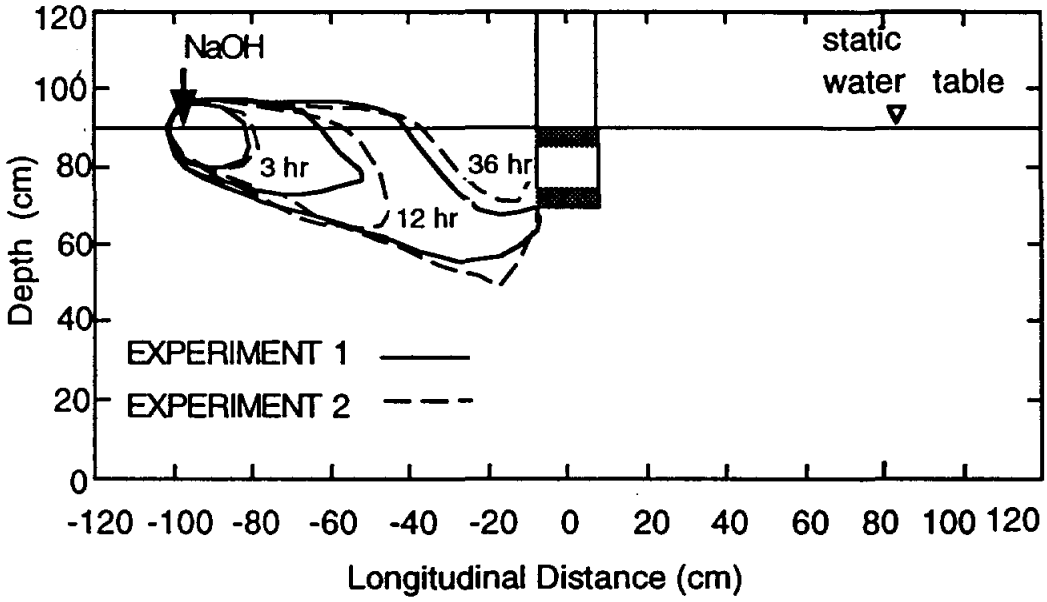


FIG 30. Reproducibility in Case 4 Simulation: 1 m/day Ambient Flow Velocity and 100 mL/min Well Recirculation Rate for Hydraulic Well 2

During the development of the contaminated plume, the plume was gradually transported away from the recirculating well and finally stagnated during a period of plume development. From experimental observation, it is difficult, if not impossible, to attain a steady-state condition of the stagnated plume. It takes a long time to reach the steady-state condition because the flow boundary of the streamlines is infinite under case 1 simulation. Experimental observation of the stagnated plume is affected by the boundary effect of the aquifer model tank even though the reflecting flow from the boundary may be insignificant. FIG 31 illustrates that the dispersion effect will show its significant influence on plume transport after a long period of transport time. The rate of plume development is usually less than 0.5 cm/hr after 24 hours; thus, the plume size at 24 hours of transport can be used to approximate the pseudo steady-state stagnated plume. On the basis of this operational definition, the effective width of the capture zone is considered as the distance between the recirculating well and the boundary of the 24-hour plume on the groundwater table.

Of greatest concern is the effective width of the capture zone, for it corresponds to the maximum distance between well arrangement to form an incorporated protection zone. The numerical results show that the width of the capture zone is dependent on the recirculation rate of the well, on the horizontal and vertical hydraulic conductivities, on the length of screen openings, and on the separation distance between injection and withdrawal intervals (Herrling et al., 1991). The width of the capture zone is strongly dependent on anisotropy, and a greater ratio of horizontal to vertical permeability will yield a greater width of the capture zone. The length of the screen sections has only a small influence even though longer screen sections lead to broader capture zones (Philip and Walter, 1992). Under experimental simulation, the influences of the well recirculation rate and the well penetration depth were examined to determine the optimum operation conditions.

The capture zone is pumpkin-shaped at the cross section normal to groundwater flow. Some numerical results agree that the width of the capture is greatest in depth in the vicinity of the extraction interval of the vertical circulation well and smallest in the vicinity of the injection interval (Philip and Walter, 1992). Under the same geological conditions, a higher well recirculation rate would lead to a greater capture zone as shown in FIG 32, but there is not a proportional relationship between the well recirculating rate and the effective width of the capture zone. Herrling et al. (1991) suggested that the width of the capture zone is independent of the discharge through the well, but dependent on the ratio of the

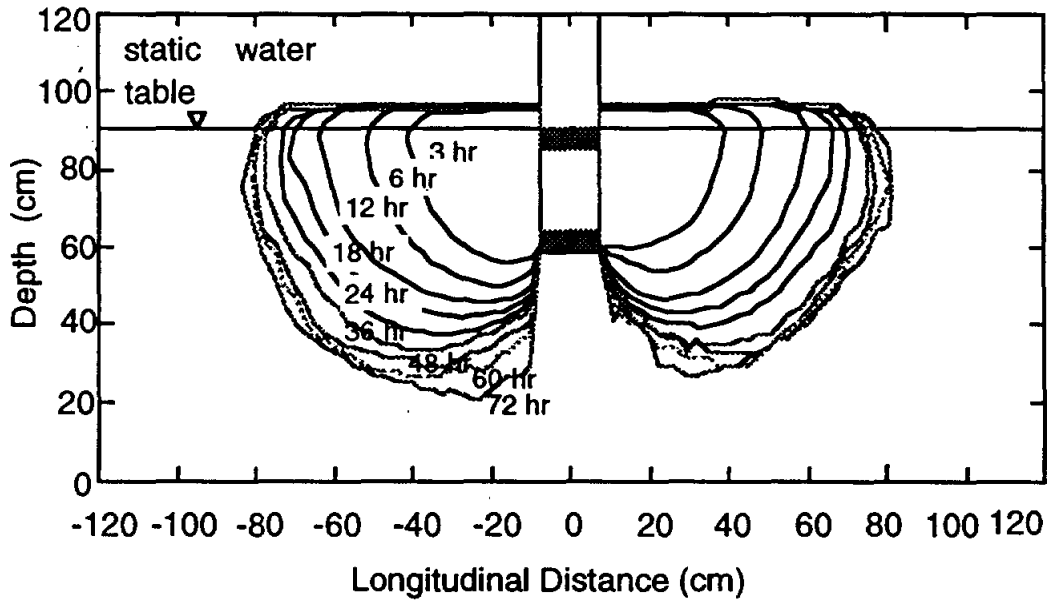


FIG 31. Case 1 Simulation of the Tracer Tests: Zero Ambient Flow Velocity and 100 mL/min Well Recirculation Rate for Hydraulic Well 1

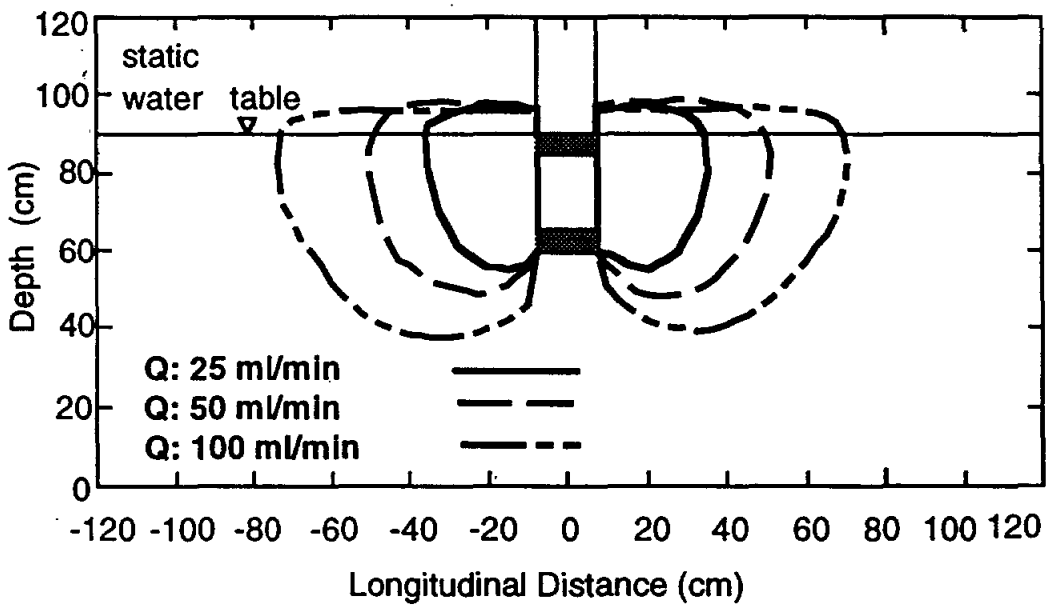


FIG 32. Comparing the Effect of Well Recirculation Rate on 24-hr Plume Size for Hydraulic Well 1

considerable recirculating flow to the discharge through the well. The disagreement on the determination of the capture width may result from the assumption of a pseudo steady-state condition because of limitations of the tank size and the time required to approach equilibrium. The width of the capture zone is mathematically infinite, so the ratio of the considerable recirculating flow to the discharge through the well, defined as the recirculation efficiency, is used to describe the strength of a circulation flow at the considered boundary of the capture zone. At the same recirculation efficiency, a larger well recirculation rate will lead to a stronger recirculating flow at the same boundary of the capture zone. Under the numerical definition, the considerable recirculating flow at the boundary of the capture zone is not the same magnitude at a different well recirculation rate. However, the considerable recirculating flow at the boundary of the capture zone should be taken as a constant large enough to conquer the dispersion effect under the operational definition.

Groundwater flow might affect the sphere of the capture zone, so the width of the capture zone is not the same in all radial directions. Usually, the influence of groundwater flow on the capture zone can be ignored at a large well recirculation rate. If the recirculating well was operating at a small recirculating rate, groundwater flow would depress the capture zone upstream of the well and enhance the capture zone downstream of the well. The view of the capture zone at the cross section parallel to groundwater flow can be simulated by plume development in the case 2 simulation. FIG 33 illustrates that the ambient horizontal flow tends to push the plume upward and to blow the plume downstream. The captured plume is quite stable upstream of the recirculating well, but the plume downstream seems not to be captured because of the continuous delivery by the ambient horizontal flow. If groundwater flow is significant compared with the recirculating flow, there might be a blow-through problem and a failure to capture groundwater pollutants by the recirculating well. FIG 34 demonstrates a special case where the upstream plume was blown through the withdrawal compartments downstream under a significant ambient horizontal water flow. Therefore, there should be a minimum well recirculation rate to prevent the contaminant plume from blowing-through before groundwater pollutants can be treated.

Two vertical recirculating wells have been constructed to examine the effect of the separation distance between the recharge and withdrawal compartments. The dimensions of the two recirculating wells are shown in FIG 9, and the width of the capture zone

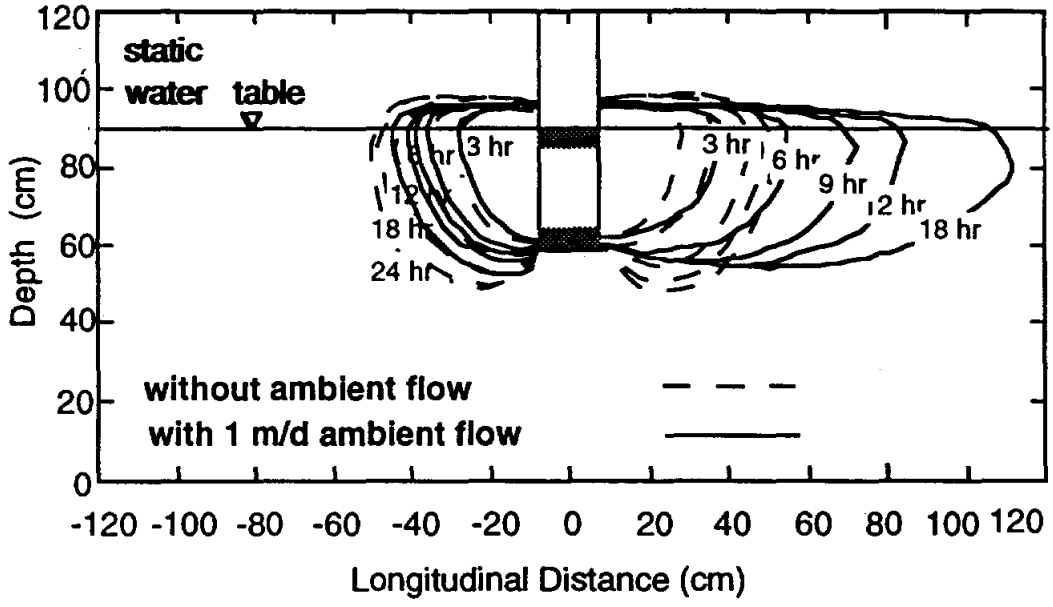


FIG 33. Comparing the Effect of Ambient Groundwater Flow on Plume Development at 50 mL/min Well Recirculation Rate for Hydraulic Well 1

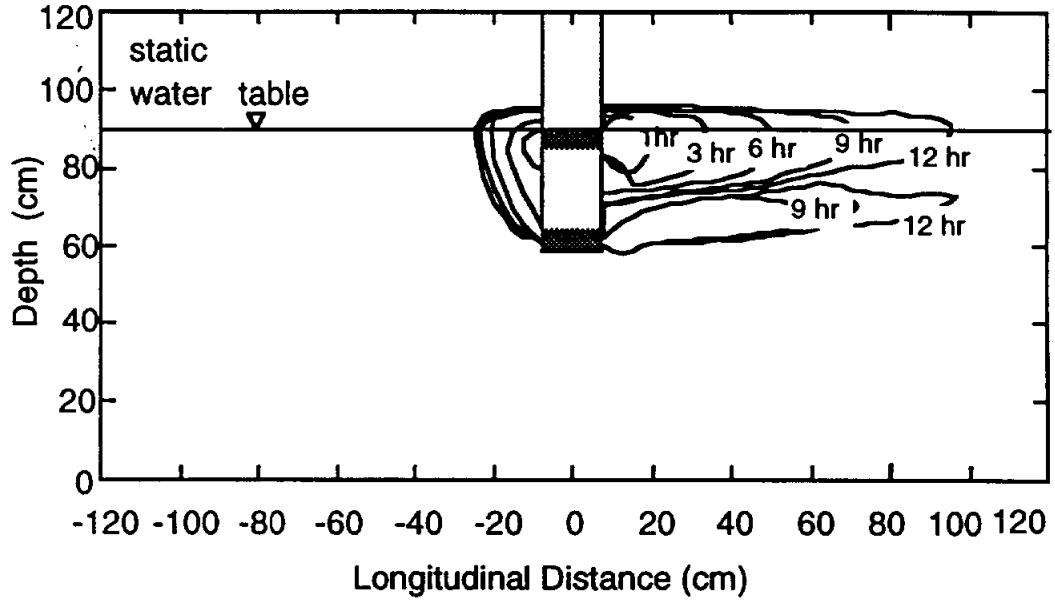


FIG 34. Blow-through of Plume Development in Case 2 Simulation: 2 m/day Ambient Flow Velocity and 25 mL/min Well Recirculation Rate for Hydraulic Well 1

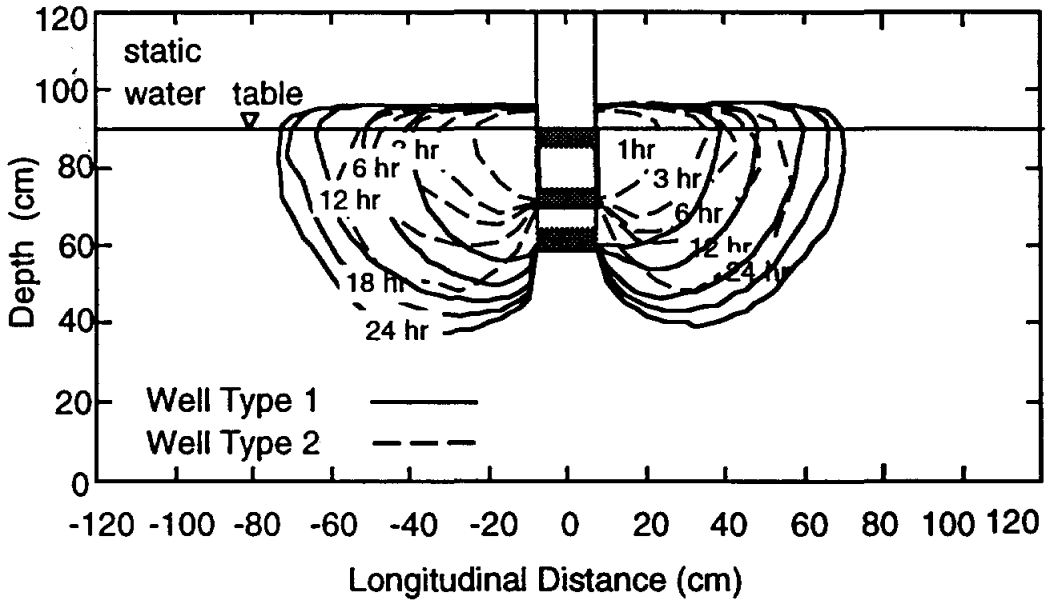


FIG 35. Comparing the Effect of Well Penetration Depth on Plume Development at 100 mL/min Well Recirculation Rate for Hydraulic Well 1 and 2

resulting from the two recirculating wells has been compared in FIG 35. Philip and Walter (1992) agreed that decreasing the separation distance between the recharge and withdrawal compartments decreases the effective width of the capture zone. Reducing the separation between the recharge and withdrawal compartments may increase the short circuiting of flow between the withdrawal and recharge zones.

Protection Zone

Protection zone is usually defined as the regions that upstream contaminants cannot transgress when a treatment barrier is formed around an incorporated recirculating well system. It is obvious that the recirculating well can intercept the contaminant plume from experimental results, but great interest should be focused on the extent of groundwater pollutant interception by the treatment barrier around the recirculating well. Generally, the protection zone is referred to an incorporated multi-well system, and the capture zone refers to a single vertical recirculating well. The determination of the protection zone from a single recirculating well is based on the experimental results of case 3 and 4 simulations.

Hydroxide ion as a contaminant source is continuously installed upstream of the simulated groundwater flow, and then a red plume would develop from one side to the other side of the aquifer model tank. The red plume with high pH would be neutralized upon entering the recirculating well. The red plume becoming colorless is recharged back to the aquifer after neutralization; therefore, a colorless zone would be created at groundwater downgradient. In this simulation case, a red plume is recognized as contaminated water, colorless water as clean, and neutralization as a decontamination process. The experimental observation of plume movement could show evidence of achieving the scope of groundwater interception by the recirculating well to provide a protection zone for an individual drinking water well.

According to experimental observation, a clean zone is always formed downstream of the recirculating well. The sphere of the protection zone is determined by the type of contaminant source, the strength of groundwater flow, and the well recirculation rate. For a depth distributed source of groundwater pollutants, the sphere of a formed protection zone is similar to that of the capture zone of the recirculating well. Because only the captured water can be treated to form a protection zone, the domain of the protection zone would be covered by the capture zone. As demonstrated in the case 2 simulation, the capture zone also covers some regions below the recirculating well. The depth of the formed protection zone definitely depends on the depth of well penetration and the

recirculation rate of the well. FIG 36 shows that a larger well recirculation rate will lead to a deeper protection zone, but its influence is not significant.

For a surface source of groundwater pollutants, the plume seems to be totally intercepted upstream of the recirculating well. The recirculating flow tends to push the plume downward when the plume is entering the upstream capture zone, and the plume seems to move along the mixing edge of the capture zone. A stronger treated flow could exit the recirculating well to distort the plume downward at a larger well recirculation rate, so there might be a chance that the plume moves deeper to bypass the recirculating well. None of the submerged bypass plume has been found based on the experimental results; therefore, it appears that the protection zone can cover the whole downstream region. The size of capture zone is much smaller for a less penetrated well, and a small capture zone causes the plume to enter the withdrawal compartment from the upstream side. A large well recirculating rate causes the plume to enter the withdrawal compartment from the upstream and downstream sides. The depth of well penetration and the recirculation rate of the well can change the shape of the plume as shown in FIG 37 and 38, but it does not change the downstream protection zone. The strength of the ambient horizontal water flow would have the potential to change the downstream protection zone. As stated previously, the recirculating flow should be maintained at a rate greater than the minimum requirement to conquer the ambient horizontal flow, otherwise there would be a blow-through plume to spoil the downstream protection zone as illustrated in FIG 39.

Feasibility

The feasibility studies will be judged on the formation of the protection zone downstream of the recirculating well. Under the tracer simulation, tracer was released from upstream to simulate the transport of groundwater contaminant. The red plume was carried downstream by the ambient horizontal water flow, then migrated into the recirculating well by the radial flow around the well. After being neutralized, the red plume turned colorless and consecutively migrated downstream. Thus, the presence of the clear zone downstream confirms that groundwater contaminant could be intercepted by a treatment barrier around the recirculating well.

Aqueous contaminants tend to flow on the top of the aquifer, but might be dispersed down for a long period of transport time. If the recirculating well was installed deeper than the contaminant plume, the whole aquifer would be protected downstream of the

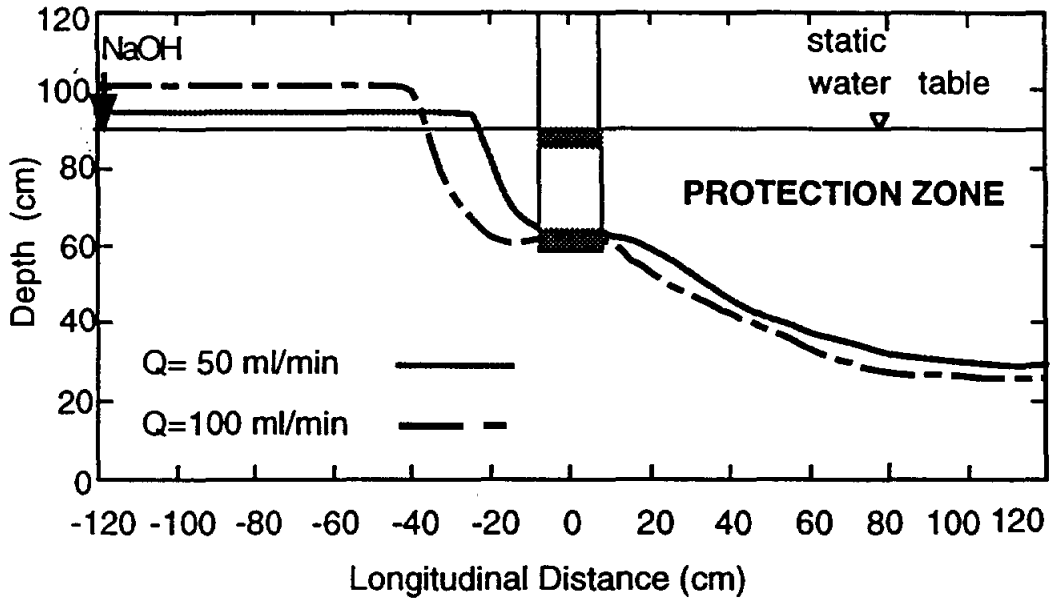


FIG 36. Comparing the Effect of Well Recirculation Rate on Plume Interception at 1 m/day Ambient Flow Velocity for Hydraulic Well 1

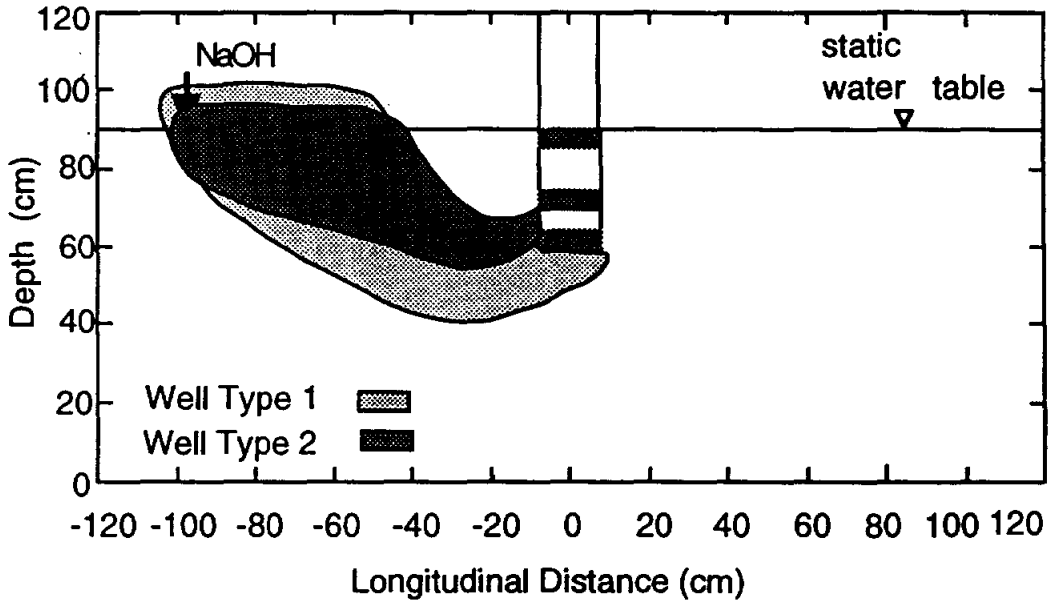


FIG 37. Comparing the Effect of Well Penetration Depth on Plume Size at 1 m/day Ambient Flow Velocity for Hydraulic Well 1 and 2

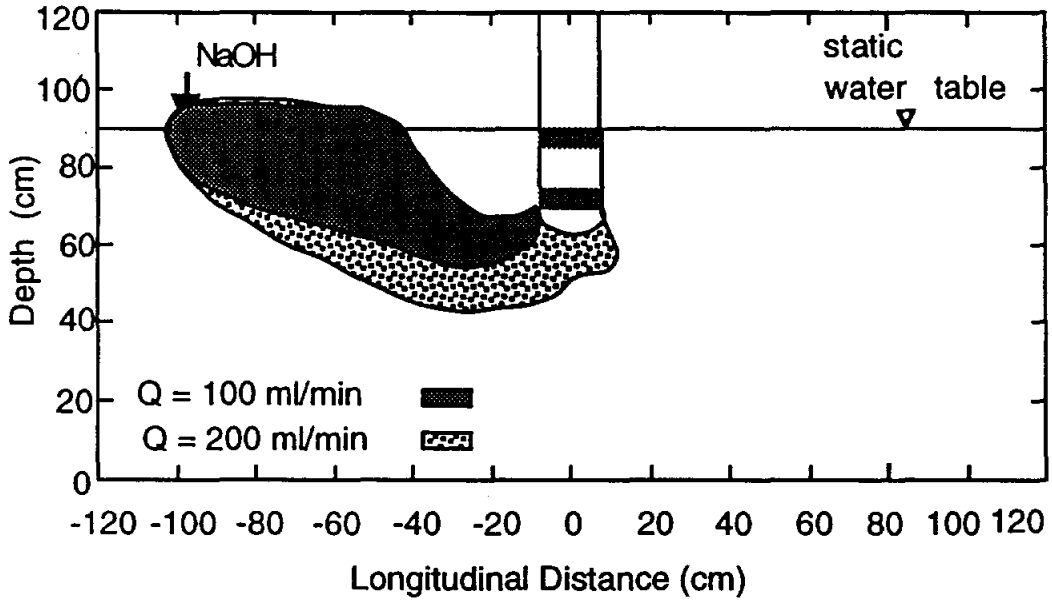


FIG 38. Comparing the Effect of Well Recirculation Rate on Plume Size at 1 m/day Ambient Flow Velocity for Hydraulic Well 2

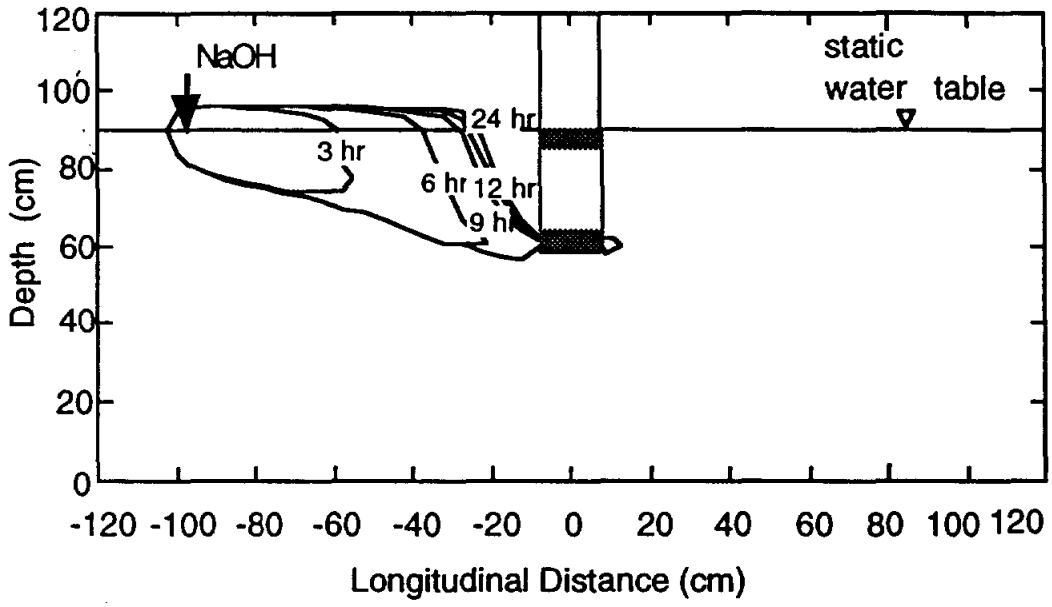


FIG 39. Blow-through of Plume Development in Case 4 Simulation: 3 m/day Ambient Flow Velocity and 50 mL/min Well Recirculation Rate for Hydraulic Well 1

Chapter VI

RESULTS AND DISCUSSIONS ON BIOLOGICAL TREATMENT

BATCH REACTOR RESULTS

Microbial kinetic parameters for biological denitrification were obtained from batch experiments. On the basis of the daily monitoring, a set of batch reactors was approximately adjusted to a different fixed substrate level to reduce the same initial level of nitrate. The static approach operates in such a way that the substrate level was controlled at a fixed level during the analysis of microbial kinetic parameters. As described in Chapter IV, the dynamic approach of kinetic analysis is to trace the substrate level from an initial high level to the final residual level during biological denitrification processes. Therefore, the kinetic rate at a different substrate level can be acquired from the progressive curve.

From the static approach, microbial kinetics can be determined by the initial rate experiments. During the initial rate experiments, reaction time for each batch reactor would last only long enough to measure a difference in biomass concentration. A general pattern of data obtained from the substrate-controlled batch reactors is shown in FIG 40. The disappearance of nitrate was enhanced as reaction time elongated, but there is a significant level of nitrite built up under a low substrate level of 200 mg/L COD simultaneously. It is implied that an insufficient substrate supply could be a major cause of incomplete denitrification. If only one substrate is considered as the limiting factor of microbial growth, then the kinetics of microbial growth can be described by the Monod model. Applying the kinetic equation in the Monod model, the relationship of cell growth rate (μ) and substrate level (S) can be reformulated as:

$$\frac{1}{\mu}=\frac{1}{\mu_{max}}+\frac{K_S}{\mu_{max}}\frac{1}{S} \quad \text{..... (22)}$$

Maximum specific growth rate (μ_{max}) and half-velocity constant (K_S) can be determined from the intercept and slope of the Lineweaver-Burk plot (FIG 41). The Lineweaver-Burk plot showed a high affinity between specific growth rate and substrate level, and the correlation coefficient was 0.972 from linear regression of initial rate data. On the basis of the regression results, the derived parameters of microbial kinetic are maximum growth rate (μ_{max}) of 1.178 day^{-1} and half-velocity constant (K_S) of 474 mg/L as TOC.

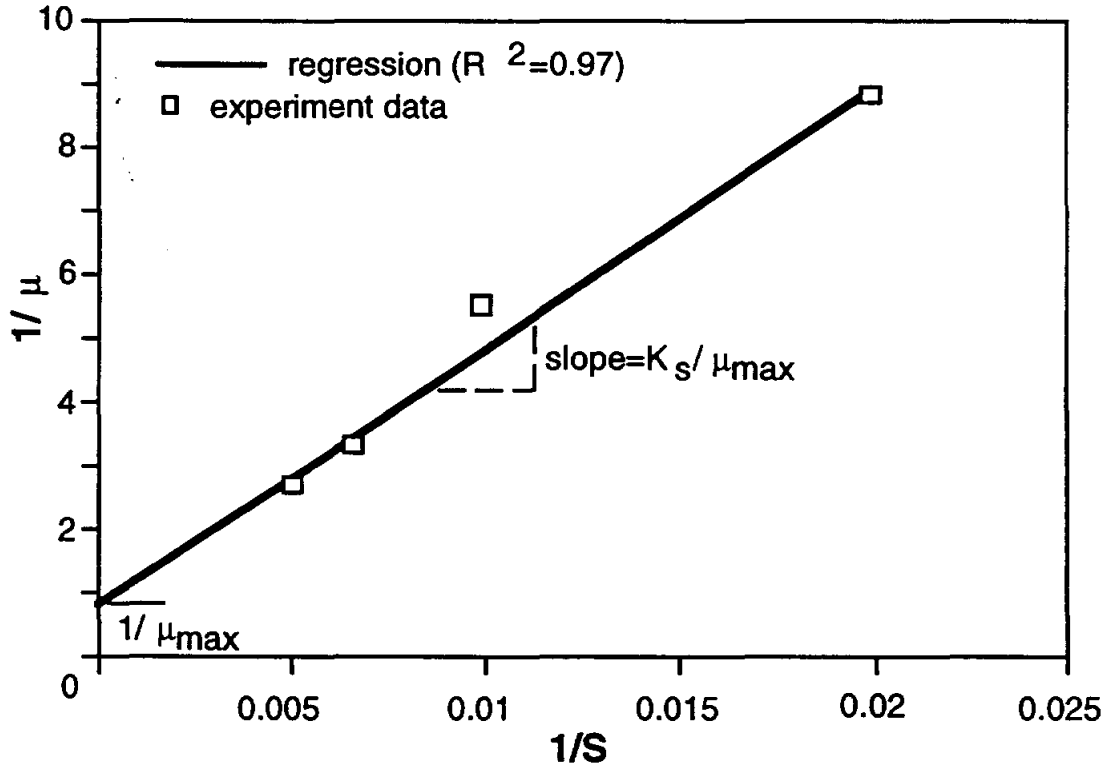


FIG 41 Lineweaver-Burk Plot of Initial-Rate Data from a Set of Batch Reactors with a Substrate Range of 200 and 800 mg/L COD

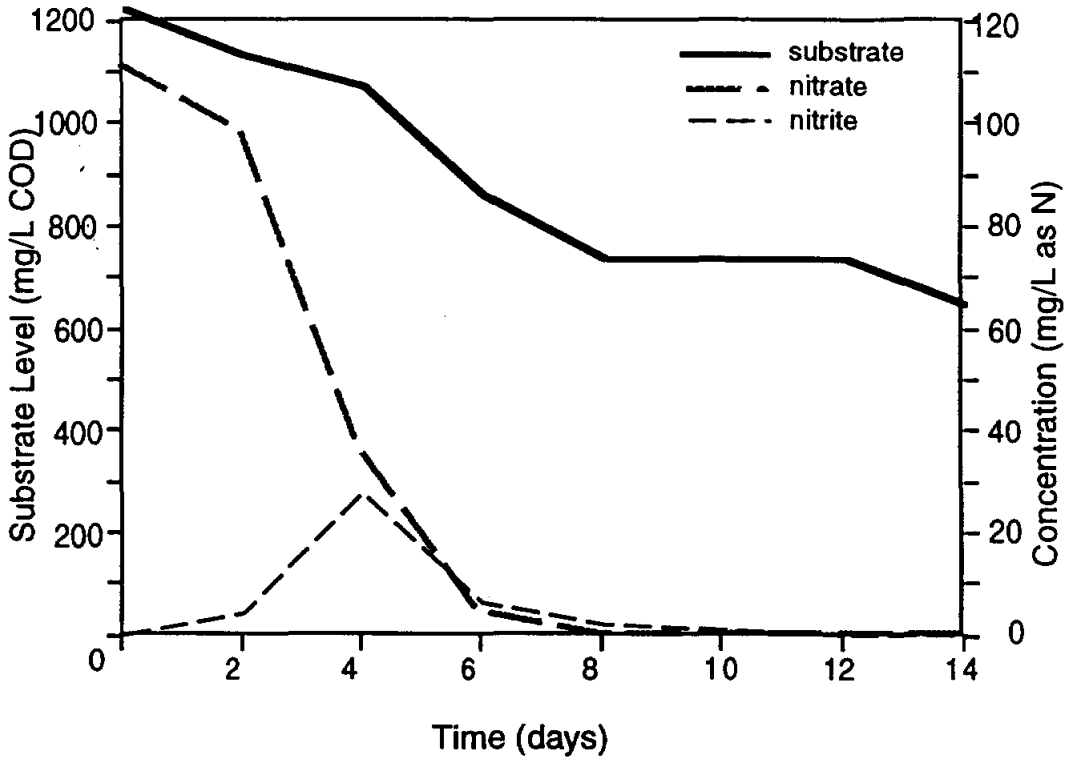


FIG 42. Progressive Curves of Substrate Uptake, Nitrate Reduction, and Nitrite Formation in the Batch Reactor with an Initial Level of 1,200 mg/L COD and 110 mg/L NO_3^- as N

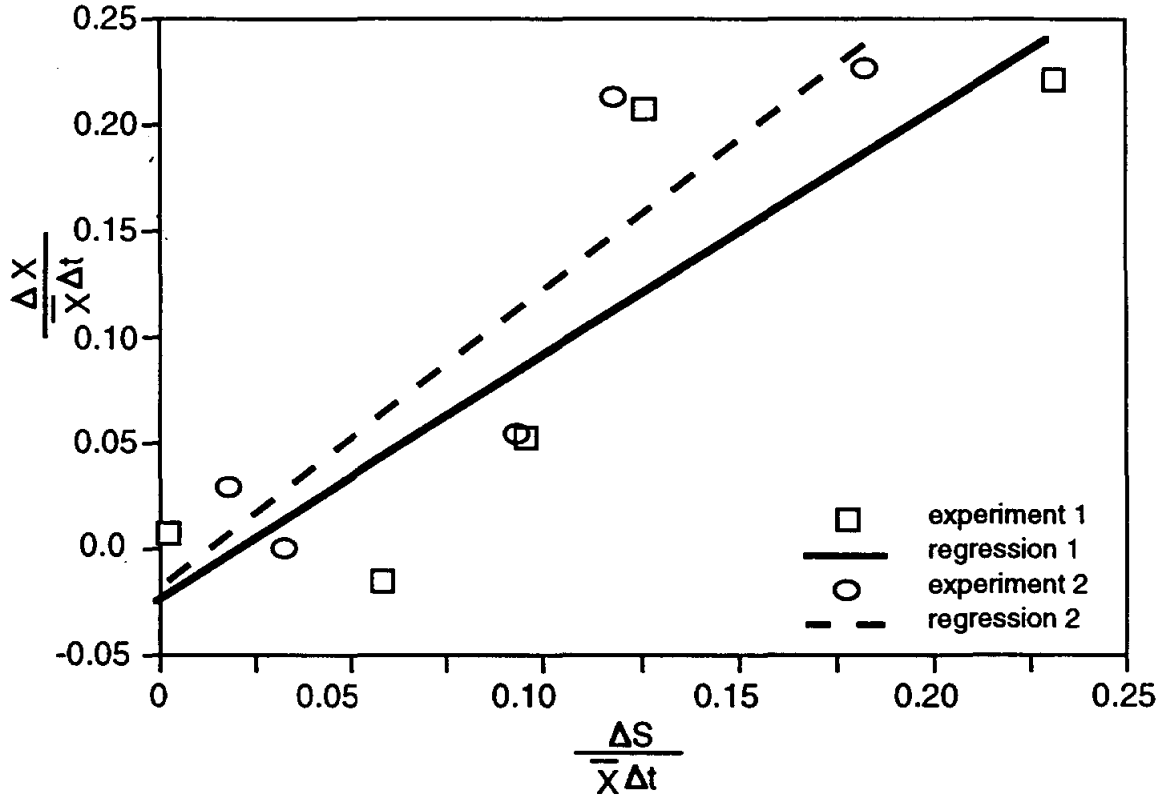


FIG 44. The Determination of Yield Coefficient and Decay Rate

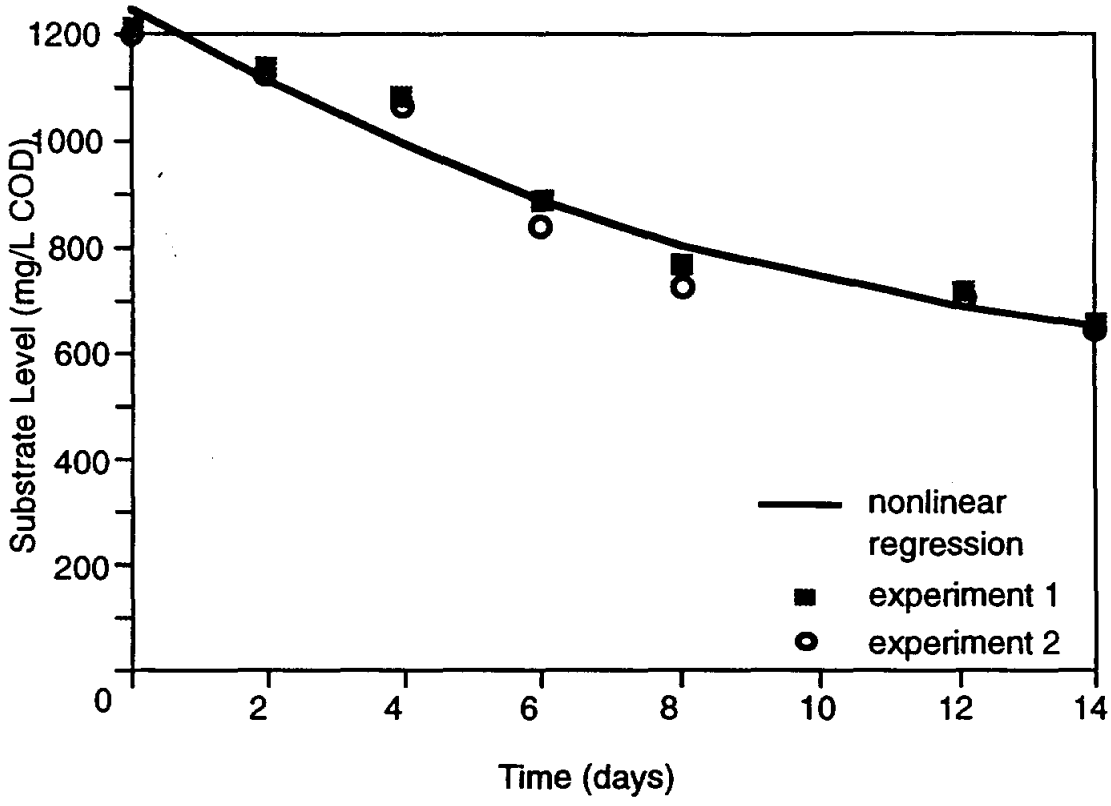


FIG 45. Nonlinear Regression of Substrate Uptake in the Batch Reactor with an Initial Level of 1,200 mg/L COD and 110 mg/L NO_3^- as N

The theoretical carbon to nitrogen ratios for complete denitrification are 0.88 and 0.71 for the reaction of assimilation and dissimilation respectively. According to a carbon conversion efficiency of 56%, the carbon to nitrogen ratio was calculated to be at least 0.81 for complete denitrification. This result suggested that the C/N ratio must be maintained at 0.81 or above to prevent the accumulation of nitrite nitrogen in the bioreactor.

The utilization of carbon versus nitrate in the closed batch reactors was 0.97 and 0.92, which is a little higher than the stoichiometric ratio of 0.81, and the excessive uptake of the carbon source may be caused by the reduction of dissolved oxygen. In addition to carbon requirements, the rate of denitrification reaction is the greatest concern. In FIG 42, the rate of nitrate reduction seems to be slowed down as carbon levels decrease, but the effect of carbon level on the reaction rate of denitrification is not significant at such a high substrate level. The relationship between the rate of nitrate reduction and substrate level can be obtained from the initial rate experiments, and it was found that the specific reaction rate of nitrate reduction seems to be a half-order kinetic of the substrate level (FIG 47). The results of regression showed that the correlation coefficient is 0.82 and the specific rate constant is 0.069 $(mg/L)^{-1/2}day^{-1}$. Thus, the specific rate of denitrification reaction can be formulated as:

$$\frac{\Delta N}{\overline{X}\Delta t} = K_N S^{1/2} \qquad \text{..... (30)}$$

where ΔN is the uptake of nitrate, mg/L as N; $\overline{X}$ is mean biomass concentration, mg/L; Δt is time duration, day; K_N is specific rate constant, $(mg/L)^{-1/2}day^{-1}$; and S is substrate concentration, mg/L as TOC.

The kinetic parameters derived from batch experiments are summarized in TABLE 2. Compared with previous works by others, the obtained microbial growth rate is smaller than the value from the literature review. The differences between batch experiments and the literature review may be caused by the measurement error of microbial mass. Microbial mass was determined by the turbidity test during batch experiments, and the obtained values from the literature review were measured as suspended solid or volatile suspended solid from continuous flow reactor tests and batch experiments. Therefore, it is difficult to compare kinetic parameters with others because operation conditions, microbial species, and reactor types may be quite different. The kinetic parameters from the literature review are listed altogether to recognize the possible range of those kinetic parameters.

KEY FOR AUTOMATED CONTROL

An automated control system was set up for on-line nitrate monitoring and carbon

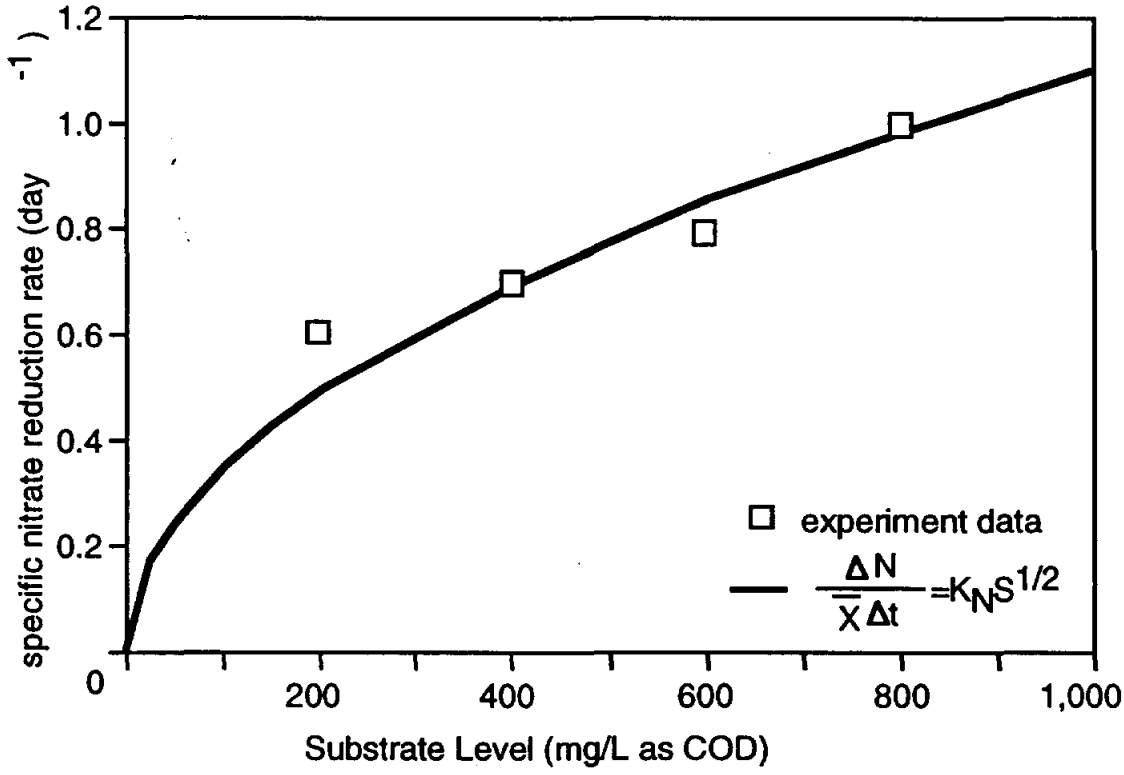


FIG 47. The Relationship between the Substrate Level and the Specific Nitrate Reduction Rate

TABLE 2. The Summary of the Microbial Kinetic Results from Batch Experiments

	Batch Experiments	Literature Review
Maximum specific growth rate (μ_{max})	1.178 day^{-1}	13.3-25 day^{-1}[a] 1.8-2.0 day^{-1}[b]
Half-velocity constant (K_s)	1,896 mg/L COD	60-72.5 mg/L COD[a] 16.2-116.7 mg/L COD[b]
Yield coefficient (Y)	1.14-1.46 mg cell / mg carbon	0.73-0.78 mg suspended solid / mg carbon[a]
Decay coefficient (K_d)	0.021-0.026 day^{-1}	0.02-0.04 day^{-1}[a]
Carbon conversion efficiency	56-77 %	
Reaction Kinetics	half-order	

a. Stensel et al, 1973.
b. Lee and Dahab, 1988.

amendment as described in Chapter IV. The concept of the treatment system design is that the recirculating nitrate treatment well serves as a black-box model of denitrification. The amendment of the carbon source might be expected to stimulate the denitrification process, and optimum carbon amendment should be the key to a successful application of the proposed system.

The steady-state condition for biomass is widely used for the control of substrate supply in most biological systems. Based on the completely mixed treatment model, the steady state condition for biomass concentration doesn't exist under a hydraulic retention time shorter than 0.868 days. Microbial growth rate is so small that biomass may be washed out of the treatment well before microorganisms can grow. Based on the assumption of a completely mixed condition, there might be no calculated microorganisms within the treatment well under a short retention time. This bizarre calculation result implied that the partial plug-flow condition does exist within the treatment well. Besides, a specific microbial growth rate is a system-dependent parameter that, derived from the batch reactors, should not be necessary to reflect the same value in the continuous-flow bioreactors. Therefore, the steady-state condition for biomass is not applicable for the control of the recirculating nitrate treatment well system.

The control criteria for system operation are to minimize nitrate and nitrite content in the downstream and to minimize carbon content outside the treatment well. According to the biological pathway of denitrification, biological denitrification defined as the reduction of nitrate or nitrite to nitric oxide and nitrogen gas must occur step by step. Gas products such as nitric oxide and nitrogen gas produced from biological denitrification might be entrapped in soil pores to reduce permeability around the well if denitrification occurred outside the well. As discussed previously, the designed well has to serve as a bioreactor as well as a recirculating well. Thus, the limited amendment of the carbon source is crucial for reducing the occurrence of denitrification outside the well. According to the results of batch experiments, carbon limitation may slow down the rate of denitrification processes. The art of control is how to balance the slow reaction rate and the permeability loss. Under the condition of carbon limitation, the minimum carbon requirement can be controlled at the stoichiometric C/N ratio of 0.81.

The C/N ratio is maintained in the treatment well by the control of an automated carbon feeding system. The concentration of nitrate content is monitored from the on-line measurement of a nitrate electrode, and carbon amendment is controlled at the stoichiometric C/N ratio of on-line nitrate measurement. Thus, the precise control of the

carbon supply is dependent upon on-line measurement of nitrate. According to electrode theory, the level of nitrate ion corresponds to the measured electrode potential across the membrane. The membrane fouling problem could affect on-line measurement, so it is necessary to clean the membrane and to calibrate the nitrate probe regularly to maintain the accuracy of the on-line control of the carbon supply.

The electrode potential is measured against a constant reference potential that is system-dependent. By using a calibrated nitrate electrode, the measured electrode potential in the treatment well is found to be quite different from the measurements under an aerobic environment. The difference between the measured electrode potentials is suspected to result from the different levels of the constant reference potential under contrary environments. Under an anaerobic system, the constant reference potential showed a negative value to undertake the reduction reactions. Thus, the nitrate electrode should be calibrated in the treatment well to acquire a consistent result.

OPERATION OF TREATMENT SYSTEM

The treatment system was tested under a similar condition as case 4 in the hydraulic studies as described in Chapter III. If the problem of groundwater contamination was formed from an upstream leakage, then the effect of the downstream's protection by a treatment barrier would be tested by the distribution of the nitrate level within the aquifer model. Nitrate distribution within the aquifer model is affected by transport phenomena and biological denitrification. The effects of transport phenomena were clarified in the hydraulic studies, and the effect of biological denitrification would be evaluated under different operation conditions. Nitrate level in the treatment well would be used as the sign of the performance evaluation of the treatment system because biological denitrification took place in the treatment well.

Effects of Groundwater Velocity

Because hydraulic studies in Chapter V indicated that a blow-through plume might occur under a large ambient groundwater flow, the impact of a large ambient groundwater flow on the treatment system was examined as well. Under the same conditions of well recirculation rate and contaminant loading rate, an ambient groundwater flow was operated at 1 to 4 m/day. The well recirculation rate was controlled at 50 mL/min to maintain a retention time of 2.5 hours, and an upstream nitrate loading to the aquifer model was about 2.5 mg/min as N. According to the stoichiometric ratio of the overall nitrate loading, the

required carbon feeding was calculated to be 2.0 mg/min as TOC for complete denitrification in the aquifer model tank.

After three to seven days of system operation for each case, nitrate distribution along the aquifer model tank was approximated to a steady-state condition. As expected, a high level of nitrate at the upstream was immediately diminished through the treatment barrier, and nitrate residual downstream was reduced to a constant level below drinking water standard. The detected nitrate levels along the sampling ports are plotted in FIG 48 through 50. On the basis of the results from hydraulic studies, a treatment barrier can extend about 35 cm upgradient from the well exit under a well recirculation rate of 50 mL/min and an ambient groundwater flow of 1 m/day. Under the same hydraulic conditions, FIG 48 illustrates the agreement that the level of nitrate contamination still remains high where a treatment barrier cannot reach. Compared with FIG 48, FIG 49 reveals that the regime of a treatment barrier is decreased as a result of an increased ambient groundwater flow velocity. As noticed in hydraulic studies, a blow-through problem will occur under the operation of a 50 mL/min well recirculation and a 3 m/day ambient groundwater flow. Nitrate distribution in the blow-through case is demonstrated in FIG 50. The blow-through plume cannot be identified from the nitrate distribution plot, but the level of nitrate residual was greatly enhanced downstream.

It was believed that groundwater flow would have a significant impact on the size of a treatment barrier at the upstream side. The effects of groundwater flow on the treatment system were examined, comparing nitrate level, biomass concentration, and residual carbon level (TABLE 3). A higher level of nitrate was detected in the influent to the treatment chamber as groundwater flow velocity increased. The most logical explanation for the withdrawal flow with high concentrated nitrate is less dispersion of the leakage plume and less mixture of the recirculating flow under the condition with a high groundwater flow velocity. The recirculating flow was significantly suppressed at the upstream side at a higher groundwater flow velocity, so an upstream plume would be less diluted before entering the treatment well. The initial level of nitrate within the influent should be responsible for the increased level of nitrate residual in the treatment chamber as groundwater flow velocity is enhanced. A relinquishing in biomass concentration within the treatment chamber implied that microorganisms tend to be washed out of the treatment chamber in the blow-through case. Similarly, carbon feed to the treatment chamber might also be washed out to some extent in the blow-through case.

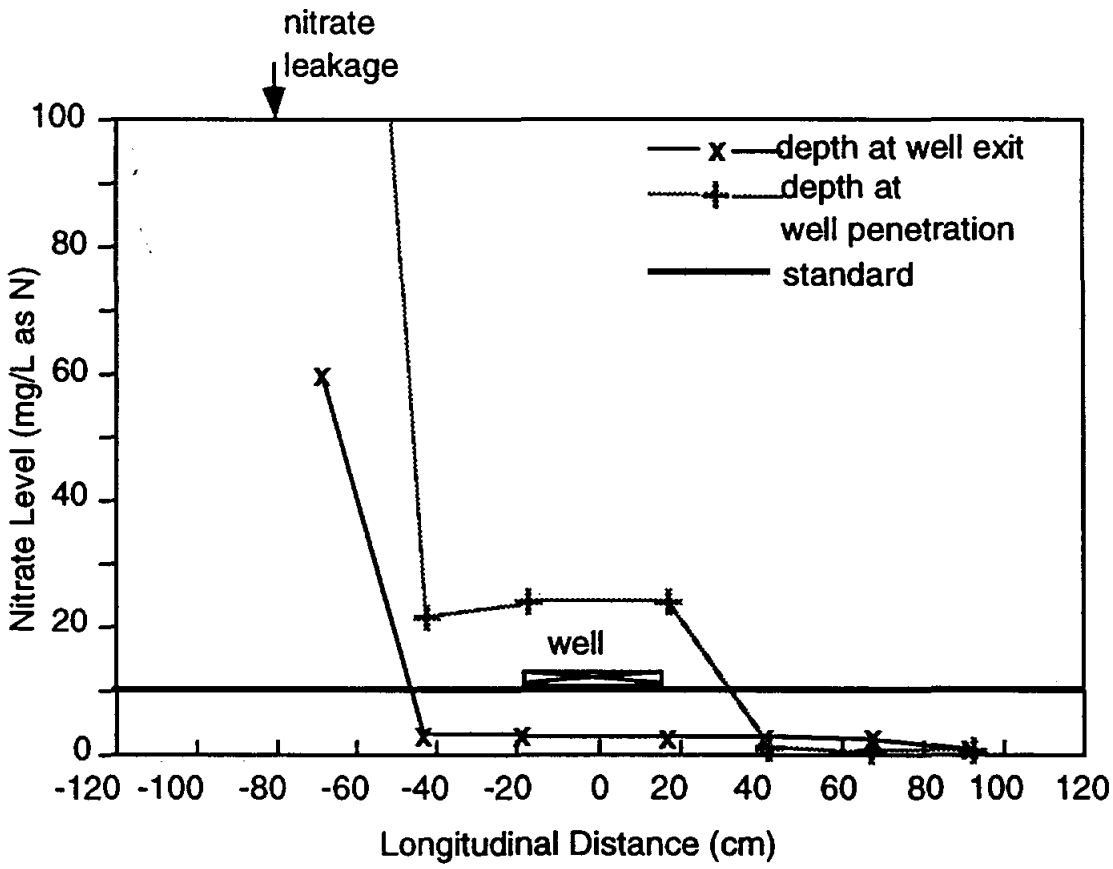


FIG 48. Nitrate Distribution Plot: 50 mL/min Well Recirculation Rate, 1 m/day Ambient Flow Velocity, 2.5 mg/min as N Nitrate Loading, and 2.0 mg/min as TOC Carbon Feed

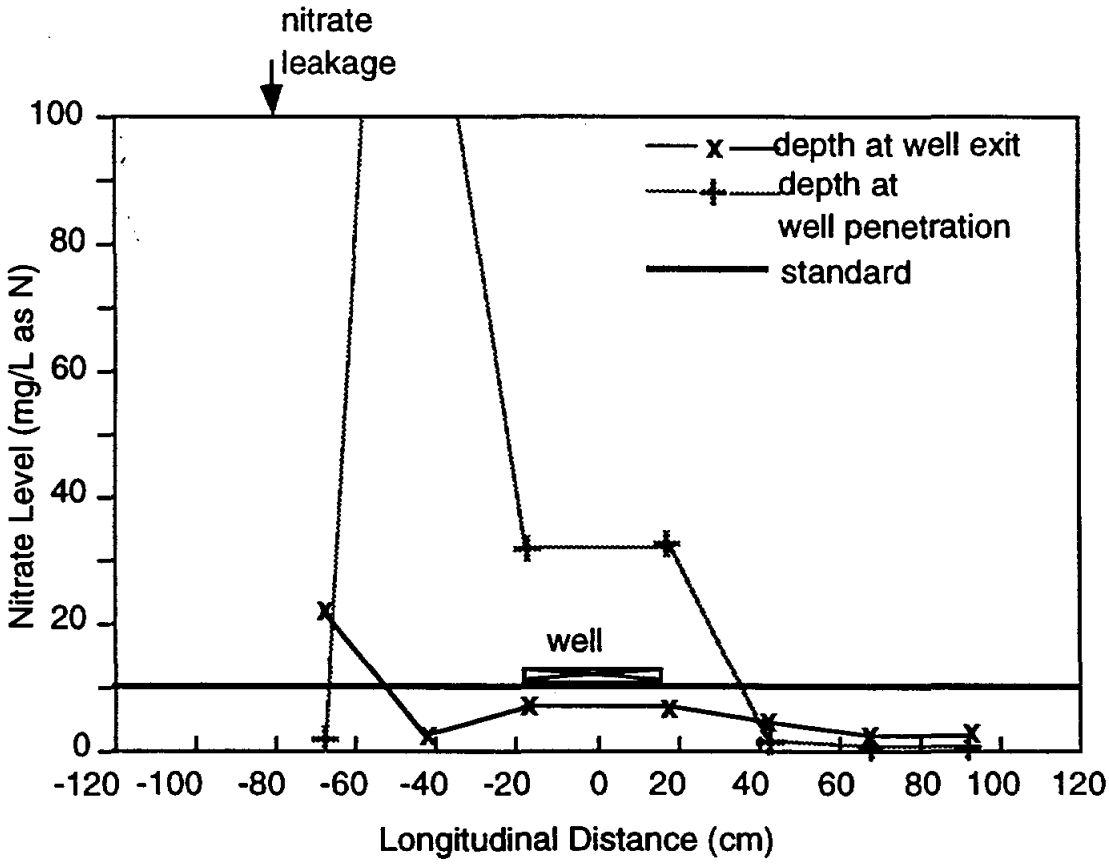


FIG 49. Nitrate Distribution Plot: 50 mL/min Well Recirculation Rate, 2 m/day Ambient Flow Velocity, 2.5 mg/min as N Nitrate Loading, and 2.0 mg/min as TOC Carbon Feed

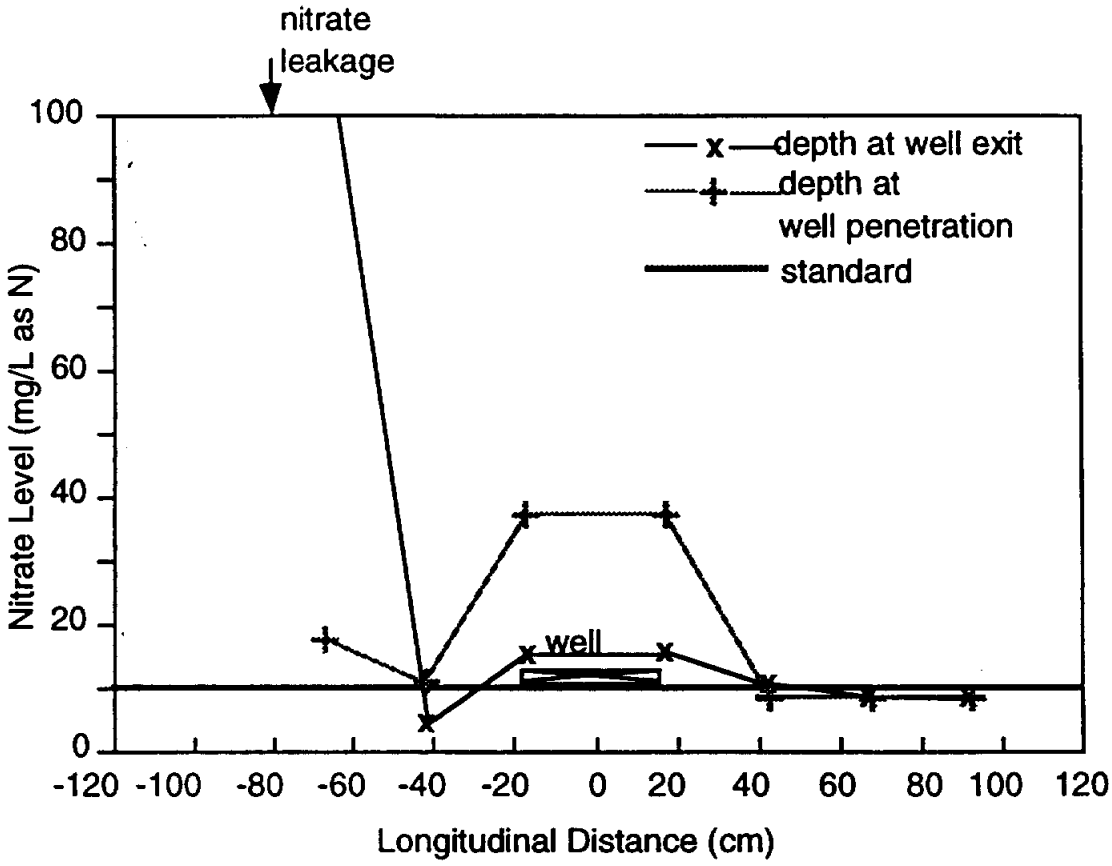


FIG 50. Nitrate Distribution Plot: 50 mL/min Well Recirculation Rate, 4 m/day Ambient Flow Velocity, 2.5 mg/min as N Nitrate Loading, and 2.0 mg/min as TOC Carbon Feed

TABLE 3. Comparisons of the Effects of Groundwater Flow on the Treatment System under the Operation of a 50 mL/min Well Recirculation Rate, a 2.5 mg/min as N Nitrate Loading Rate, and a 2.0 mg/min TOC Carbon Feed Rate

Ambient Groundwater Flow	V=1 m/d	V=2 m/d	V=4 m/d
Nitrate level in withdrawal chamber (mg/L as N)	22.28	34.05	37.11
Nitrate level in treatment chamber (mg/L as N)	1.66	8.89	13.88
Biomass in treatment chamber (mg/L)	493-590	634-758	425
Residual carbon in treatment chamber (mg/L as COD)	135-243	7-86	19
Nitrate conversion ratio in the treatment chamber	82-93 %	69-85 %	59-63 %
Average residual nitrate in the downstream (mg/L as N)	0.51	4.82	8.29

Nitrate conversion ratio is defined as the percentage of nitrate being conversed to other species; it can be expressed as:

$$R_{nc} = 1 - \frac{N_t}{N_w} \quad \text{..... (31)}$$

where R_{nc} is the nitrate conversion ratio, %; N_t is the nitrate concentration in the treatment chamber, mg/l as N; and N_w is the nitrate concentration in the withdrawal chamber, mg/l as N. The comparisons in TABLE 3 point out that the nitrate conversion ratio in the treatment chamber declined as groundwater flow velocity increased. There are two possibilities for the decrease of the nitrate conversion ratio in the treatment chamber: either the amendment of carbon was partially washed out before being utilized as a food source in the treatment chamber, or the retention time was not great enough to break down a higher nitrate level within the influent to the treatment chamber.

It was observed that biological denitrification was continuing in the downstream aquifer during the groundwater velocity test. The evidence that nitrate level downstream was lower than the level in the treatment chamber is a sign of the occurrence of in-situ biological denitrification. Biological denitrification couldn't be extinguished outside the treatment well because residual carbon within the recharge flow from the treatment chamber serves as a continual carbon supply to stimulate microbial activity. A serious problem associated with excessive carbon supply is hydraulic permeability loss due to screen fouling and soil matrix clogging.

The loss of hydraulic permeability would result in the increase of the water table in the treatment chamber and the stagnation of recharge flow to the aquifer. After about one week of operation during a groundwater flow velocity test of 1 m/day, the headloss through the exit screen section increased from the initial 0.8 cm to 1.6 cm. This implicates that the clogging problem does occur in the soil matrix around the treatment well even though it is not serious after the first run. Following three days of operation during the groundwater flow velocity test of 2 m/day, the headloss through the exit screen section greatly enhanced from the initial 1.6 cm to 5 cm. According to observations during the tests, the clogging problem in the soil matrix was primarily attributed to gas bubble formation during in-situ biological denitrification. A similar result reported from the column studies showed that the permeability of a sand column was reduced from 9 to 1 m/day over 4 days of operation due to the build-up gas of biological denitrification (Soares et al., 1988).

The restoration of the loss of hydraulic permeability would rely on the cleanup of the clogged gas bubbles. The entrapped bubbles in the soil matrix can possibly be stripped by

a vertical upflow of groundwater or partially squeezed out by shaking the soil matrix; however, both methods of entrapped gas removal are unrealistic. Prevention is the best solution of the problems. With the clogging problem in mind, carbon amendment should be underfed to the treatment well to prevent the loss of hydraulic permeability.

Effects of Well Recirculation

The rate of well recirculation will apparently affect the size of a treatment barrier, and it also determines the retention time of a treatment chamber. Although the retention time of a treatment chamber is also dependent upon the capacity of the treatment chamber, well recirculation rate would have a significant impact on the operation of the treatment system. Two cases have been compared, and the rates of well recirculation were set at 25 and 50 mL/min for each case. In order to prevent clogging problems at the well exit, the amendment of carbon to the treatment chamber was dynamically controlled at the stoichiometric ratio of the detected nitrate loading rate to the treatment chamber.

A successful case under the operation of a 25 mL/min well recirculation rate is demonstrated in FIG 51. The range of carbon residual in the treatment chamber is between 4 and 13 mg/L as COD, and the biomass concentration differentiates from 209 to 289 mg/L in the treatment chamber. The nitrate loading rate from upstream is 2.5 mg/min as N, and the nitrate level within the inflow of the treatment chamber remained at the range of 10.27 and 13.15 mg/L as N. At the starving control of the biological denitrification processes, nitrate conversion ratio in the treatment chamber was maintained at 18-26 %. The residual nitrate level in the treatment chamber was dropped to 8.5 and 9.5 mg/L as N, and the detected nitrate levels downstream were below the drinking water standard of 10 mg/L as N.

The successful application of the treatment system didn't hold under the operation of a 50 ml/min well recirculation rate. The nitrate level within the inflow of the treatment chamber rose to 26.19 mg/L as N even though the overall nitrate loading rate of 2.0 mg/min as N is lower than that in the successful case. The residual nitrate level in the treatment chamber remained at 22.97 mg/L as N which is beyond the regulation's allowance. The greatest possibility was that the retention time of 2.5 hr for this case was not quite enough to carry out a successful application. The unsuccessful case may partially result from the high nitrate level within the treatment chamber influent, and a low well

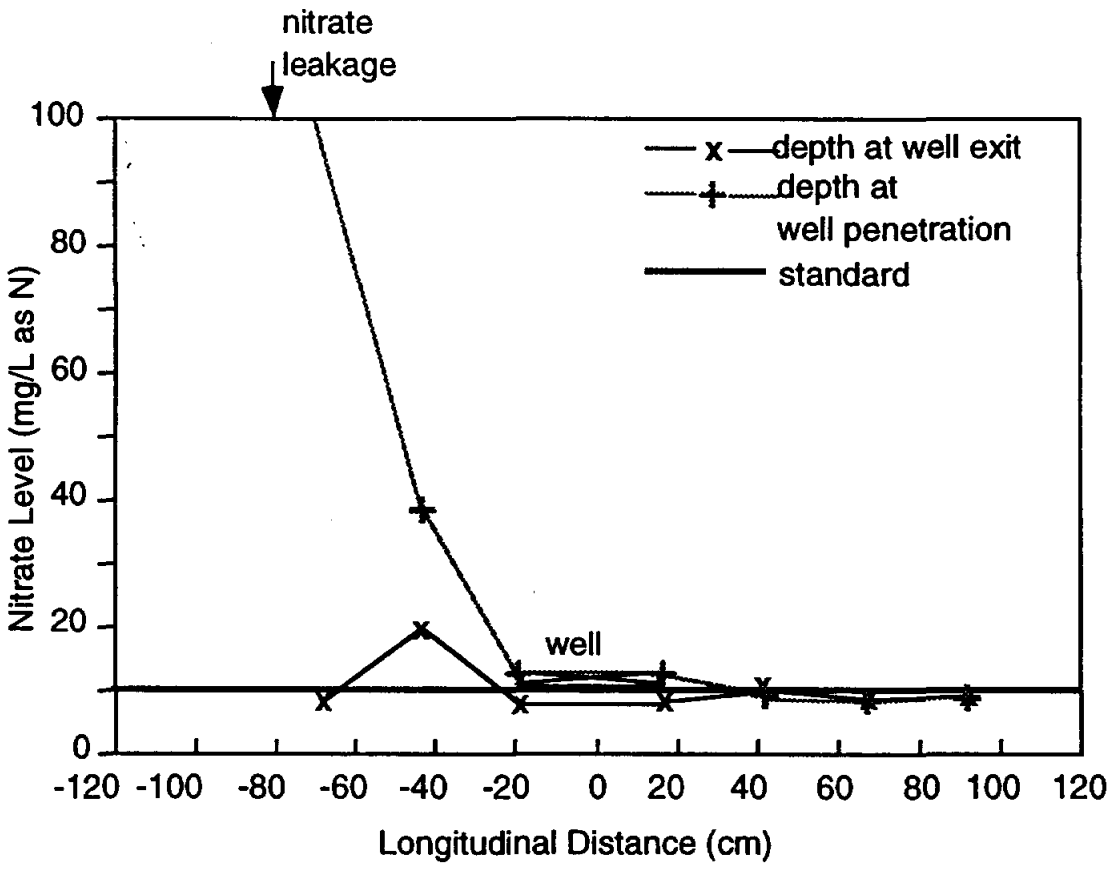


FIG 51. Nitrate Distribution Plot: 25 mL/min Well Recirculation Rate, 1 m/day Ambient Flow Velocity, 2.5 mg/min as N Nitrate Loading, and Stoichiometric Carbon Feed

recirculation rate is correlated to a high nitrate level of the influent to the treatment well. Thus, a long retention time would be required because the denitrification rate is extremely slow under the condition of carbon underfeed.

The major concern of system operation is the retention time required to reduce the nitrate level within the influent of the treatment chamber to achieve the drinking water standard. Applying the denitrification rate equation derived from batch experiments, the retention time can be formulated as a function of nitrate concentration, carbon concentration, and biomass concentration:

$$\theta = \frac{N_w - N_t}{K_N S^{1/2} \overline{X}} \quad \text{..... (32)}$$

substituting (31) into (32),

$$R_{nc} = \frac{K_N S^{1/2} \overline{X} \theta}{N_w} \quad \text{..... (33)}$$

Under the condition of carbon underfeed, the level of residual carbon should be close to zero in the treatment chamber. If it was assumed that residual carbon in the treatment chamber was maintained at the same level in both cases, then the nitrate conversion ratio should be a function of influent nitrate level, retention time, and microbial mass. Compared with the successful case, the influent nitrate level is doubled and the biomass concentration is almost quadrupled in the case with a retention time of 2.5 hours. It should yield the same nitrate conversion ratio based on the formulation, and the results seemed to show a good consistency because the average nitrate conversion ratio is about 15% for both compared cases.

Using the data from the successful case, the required retention time was calculated to be 3 hours to reduce the nitrate level to the drinking water standard and 4 hours to reduce it to the average nitrate residual of 9 mg/L as N in the treatment chamber. The calculated results seem to be underestimated because of the measurement error of microbial mass and substrate residual. The treatment chamber should be maintained at an anaerobic condition at all times, so the samples from the treatment chamber may lose their representatives without being completely mixed during the sampling procedures. Also, activated microbial mass may be over counted under a high biomass condition because the precipitated aggregate of microbial mass won't be able to efficiently denitrify.

Effects of Nitrate Loading

It is obvious that a higher nitrate loading upstream would cause a more serious problem of groundwater contamination. Because biological denitrification is applied as the treatment

methodology, the performance of a treatment system is dependent upon hydraulic retention time and nitrate loading of the treatment chamber. The main concern with nitrate loading is the corresponding retention time needed to carry out a successful application at a specific nitrate loading rate.

Under a 50 mL/min well recirculation rate and a 0.5 m/day ambient groundwater flow, two different nitrate loading rates of 1.0 and 2.0 mg/min as N have been tested. The amendment of carbon to the treatment chamber was controlled at a stoichiometric ratio of the detected nitrate level within the treatment chamber influent. The plots of nitrate distribution within the aquifer model are shown in FIG 52 for a nitrate loading rate of 2.0 mg/min as N and FIG 53 for a nitrate loading rate of 1.0 mg/min as N.

The comparisons between two experiments with different nitrate loading rates are tabulated in TABLE 4. A higher level of the overall nitrate distribution was expected in the case with a high nitrate loading rate, and the detected nitrate level within the aquifer model was 2.2 to 2.4 times larger than that in the case with a low nitrate loading rate. The ratio of the detected nitrate level showed a little larger than the nitrate loading ratio, and this may be the result of the randomness of the experiment measurement. Based on a stoichiometric ratio of carbon amendment, nitrate conversion ratios in the treatment chamber were found to be similar for both cases with different nitrate loading rates. However, the nitrate conversion ratio was supposed to be 1.4 times smaller in the case with doubled nitrate loading according to the formulation.

Under the condition of limited carbon supply, the rate of biological denitrification would be extremely slow. A long retention time in the treatment chamber would be required for a small reaction rate of denitrification to carry out a successful application because of the reciprocal relationship between retention time and reaction rate. Based on the stoichiometric feed of carbon, the detected nitrate level downstream won't be attenuated unless the retention time of the treatment chamber is elongated or the nitrate loading from upstream is lessened. If the nitrate conversion ratio in the treatment chamber is controlled at about 15 % for a retention time of 2.5 hours, then upstream nitrate loading should not be larger than the loading rate of 1.0 mg/min as N to assure a successful application. In other words, the retention time of the treatment chamber should not be shorter than 2.5 hours for a nitrate loading rate larger than 1.0 mg/min as N based on a stoichiometric ratio of the carbon supply.

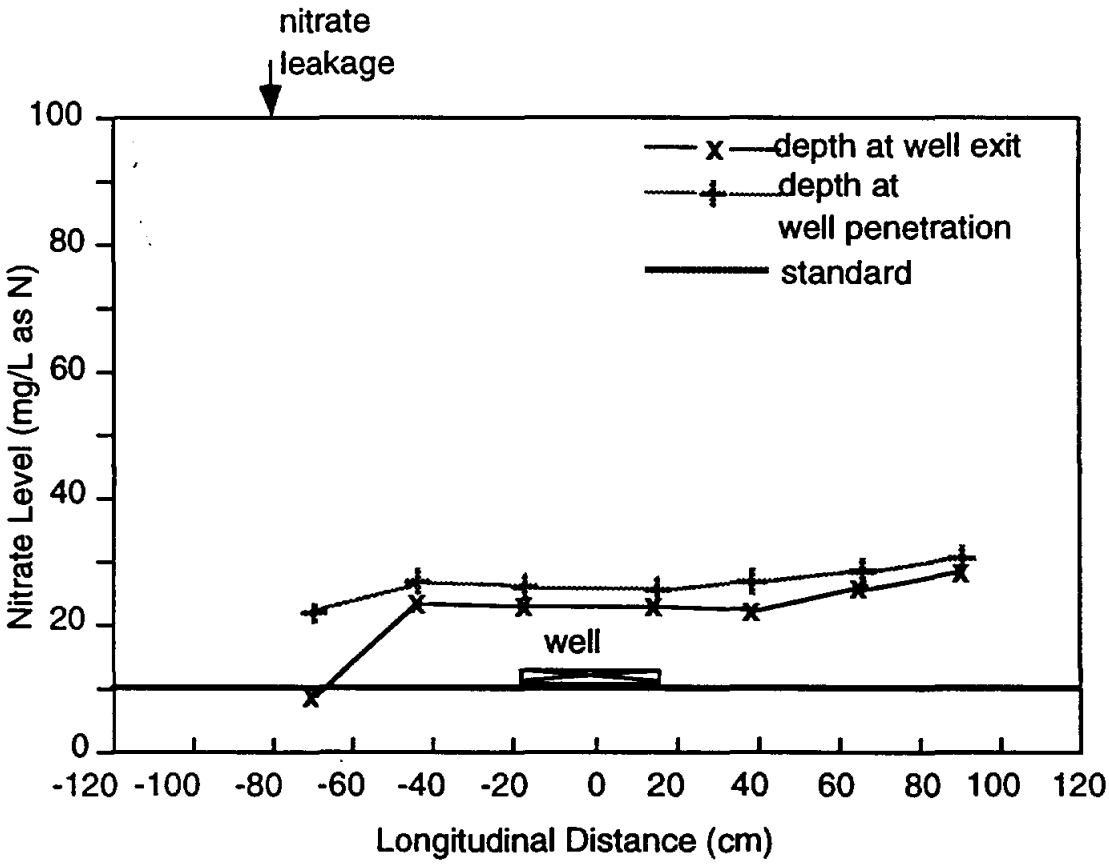


FIG 52. Nitrate Distribution Plot: 50 mL/min Well Recirculation Rate, 0.5 m/day Ambient Flow Velocity, 2.0 mg/min as N Nitrate Loading, and Stoichiometric Carbon Feed

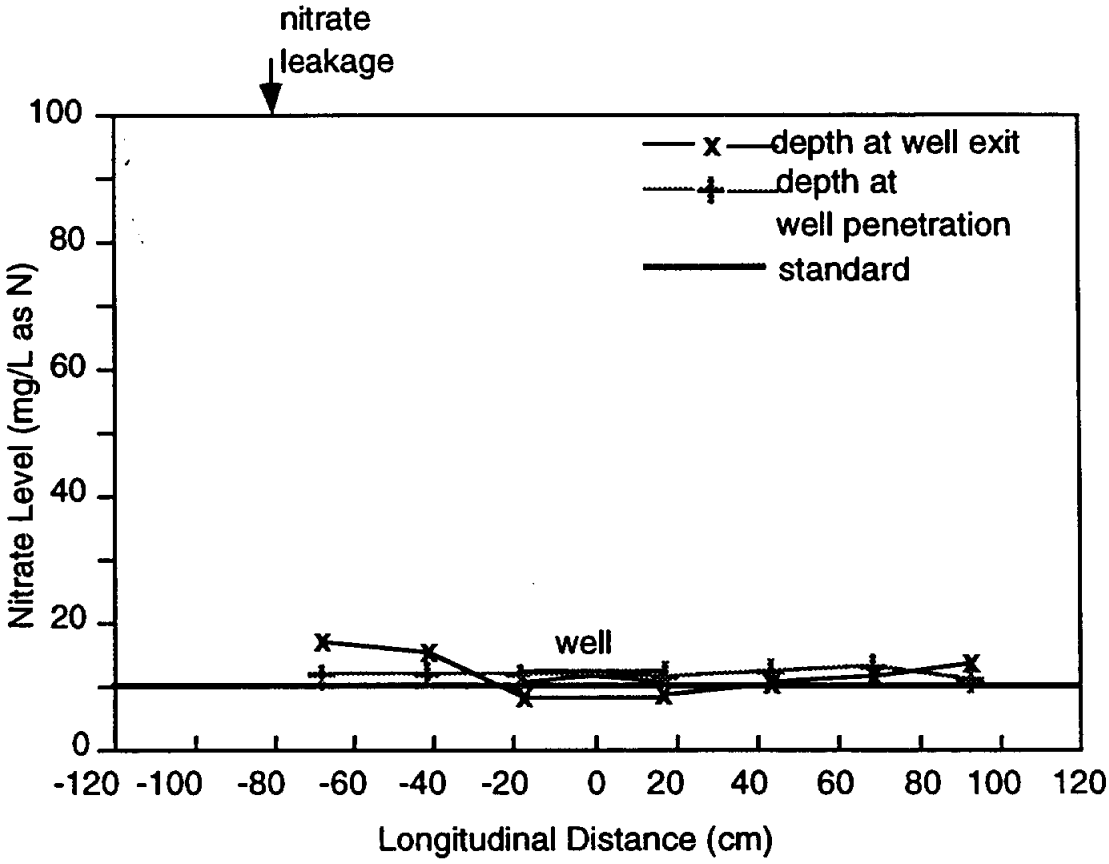


FIG 53. Nitrate Distribution Plot: 50 mL/min Well Recirculation Rate, 0.5 m/day Ambient Flow Velocity, 1.0 mg/min as N Nitrate Loading, and Stoichiometric Carbon Feed

TABLE 4. Comparisons of the Effects of Nitrate Loading on the Treatment System under the Operation of a 50 mL/min Well Recirculation Rate, a 0.5 m/day Groundwater Flow Velocity, and a Stoichiometric Feed of Carbon

Nitrate loading rate	L=1.0 mg/min as N	L=2.0 mg/min as N
Nitrate level in withdrawal chamber (mg/L as N)	11.90	26.19
Nitrate level in treatment chamber (mg/L as N)	9.50	22.97
Biomass in treatment chamber (mg/L)	825	835-1030
Residual carbon in treatment chamber (mg/L as COD)	33	0
Nitrate conversion ratio in the treatment chamber	12-20 %	12-18 %
Average residual nitrate in the downstream (mg/L as N)	11.88	28.46

Effects of Well Type

Without well recirculation, the transport of upstream contaminants should be determined by the ambient groundwater flow only, and the effect of biological denitrification should not be included in contaminant transport. Two cases with different well configurations were tested under the identical conditions of ambient groundwater flow, nitrate loading, and carbon supply. The plots of nitrate distribution within the aquifer model are shown in FIG 54 for the hydraulic well type II and FIG 55 for the denitrification well.

Under two-dimensional flow conditions, the placement of the treatment well may have created undesirable flow nets in the aquifer (FIG 56). The block effects of the well were noticeable in both cases because the downstream nitrate level at the groundwater table was much lower than that at the depth of well penetration. A low detected nitrate level at the downstream water table may be partially caused by the washout flow from the treatment well. As is shown in Table 5, there is more contaminated flow passing through the withdrawal chamber in the test of hydraulic well II than in the test of the denitrification well. It is possible that the permeability around the entrance of the withdrawal chamber was different during the two tests; however, the block effect of the well was more significant when well penetration goes deeper.

Without well recirculation, the retention time of the treatment chamber seems to be very large. It was assumed that the detected nitrate level in the withdrawal chamber should be able to represent the initial nitrate level in the treatment chamber; therefore, the nitrate conversion ratio in the treatment chamber can be considered as the maximum treatment efficiency for the specific well. Compared with hydraulic well II, the denitrification well seemed to have a higher treatment efficiency because of its large capacity. This suggests that well configuration as well as the retention time of the well could affect the treatment efficiency of the system.

EXPERIMENTAL LIMITATIONS

The results obtained from the aquifer model and batch reactors have utilized the knowledge from previous laboratory studies to reduce mistakes, but experimental limitations and flaws must be recognized. Of course, the variations of the flow condition in the aquifer model caused some data variability. The recharge flow with residual carbon tended to be blocked by the formed gas bubble around the exit of the treatment well. The

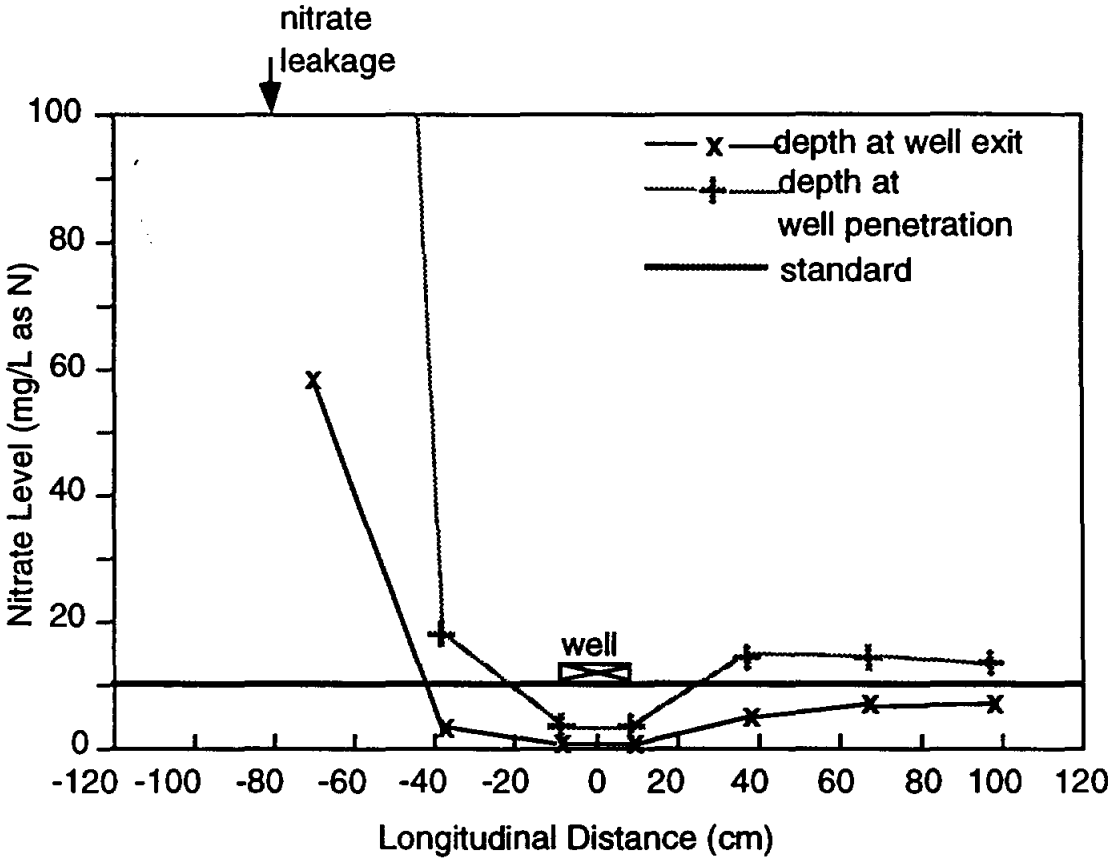


FIG 54. Nitrate Distribution Plot with Hydraulic Well 2: Zero Well Recirculation Rate, 1 m/day Ambient Flow Velocity, and 2.5 mg/min as N Nitrate Loading

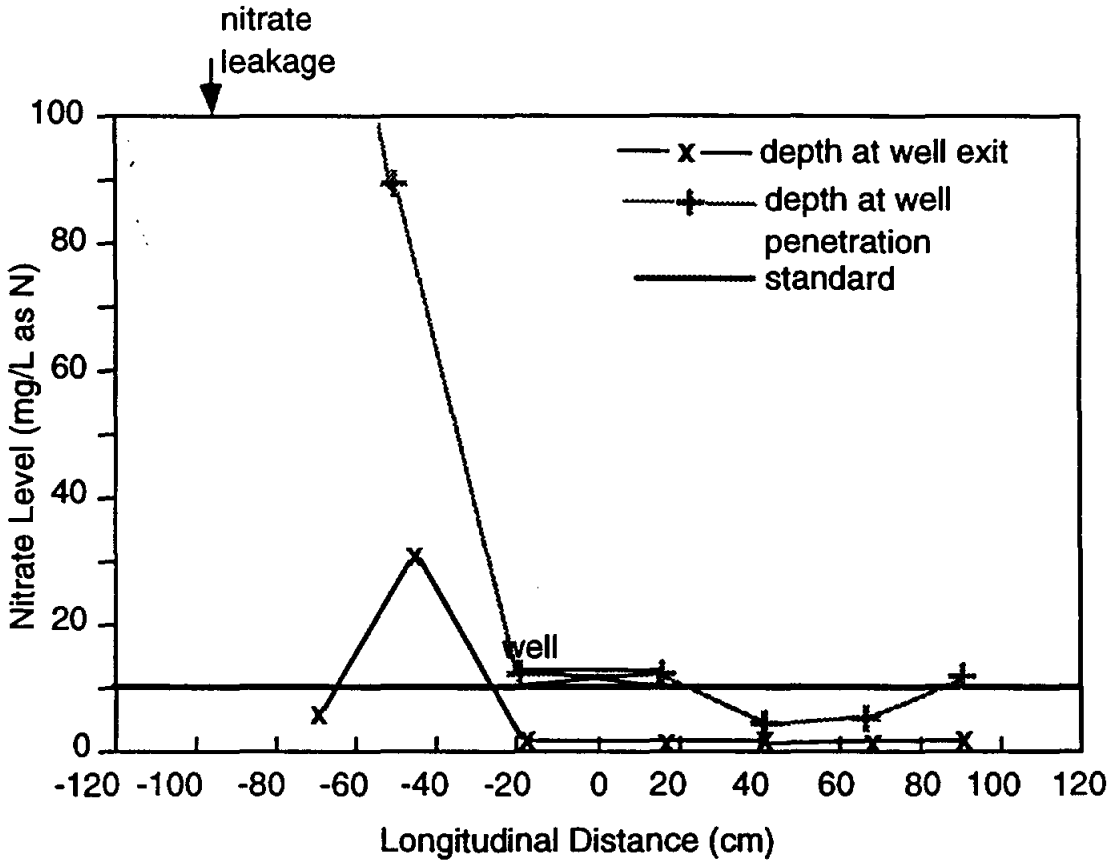


FIG 55. Nitrate Distribution Plot with Denitrification Well : Zero Well Recirculation Rate, 1 m/day Ambient Flow Velocity, and 2.5 mg/min as N Nitrate Loading

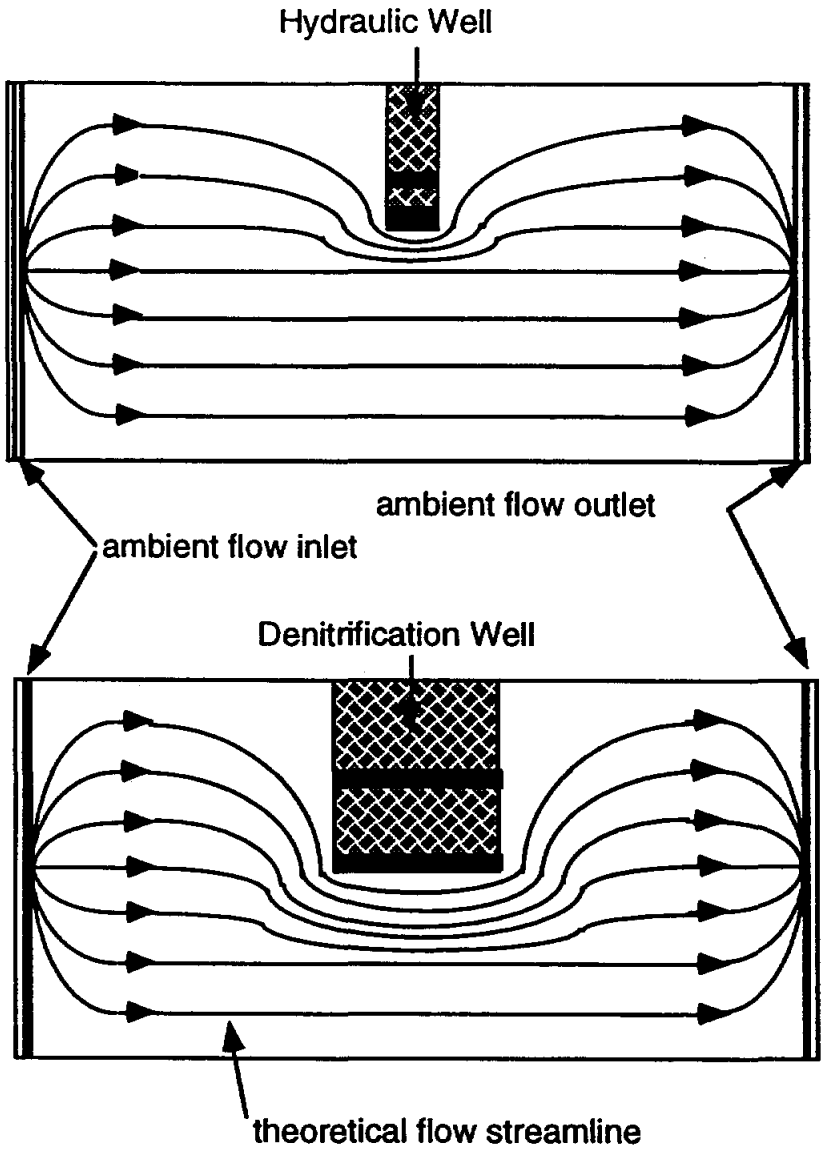


FIG 56. Conceptual Flow Streamlines without the Operation of the Treatment Well

TABLE 5. Comparisons of the Block Effects of Well Type on the Treatment System without Well Recirculation and with a 1.0 m/day Groundwater Flow Velocity and a 2.5 mg/min as N Nitrate Loading Rate

Well Type	Hydraulic Well II	Denitrification Well
Nitrate level in withdrawal chamber (mg/L as N)	2.34	9.21
Nitrate level in treatment chamber (mg/L as N)	0.44	1.03
Biomass in treatment chamber (mg/L)	249-530	333-465
Residual carbon in treatment chamber (mg/L as COD)	220-492	140-583
Nitrate conversion ratio in the treatment chamber	64-87%	87-92%
Average downstream nitrate residual at groundwater table (mg/L as N)	6.95	1.20
Average downstream nitrate residual at the depth of well penetration (mg/L as N)	14.01	6.17

fluctuations of flow control may be due in part to the use of peristaltic pumps. In addition, the permeability of the aquifer model was subject to variation when sand particles were repacked by the ambient groundwater flow and the recirculating flow.

The manual errors during the sampling procedures were prone to experimental variations. Much of the experimental variation was a direct result of analytical inaccuracies, particularly ethanol and biomass analysis. The volatility of ethanol caused inaccuracies in determining actual concentration, even though the variations were minimized. For the most part, experimental analysis of biomass was a constant source of variation and error. The inaccuracy of biomass measurement would be reflected in the denitrification rate calculations. On the contrary, the errors associated with nitrate measurement were minimized because both standards and experimental samples were handled in the same fashion.

As described in the hydraulic studies, the flow system around the recirculating well is a three-dimensional field. A two-dimensional physical model won't be able to simulate a three-dimensional problem, so it might bring some system variations, with the exception of measurement errors. Transport phenomena may be disturbed by the block effect of the well and the flush effect of the passage gate behind the well. In addition, the boundary effect of the physical model would be a constant source of system errors.

Chapter VII

CONCLUSIONS

CONCLUSIONS

Based on the results of hydraulic studies, the recirculating system has demonstrated an effective interception of migrating pollutants. The imperfectly penetrated wells were tested from 22% to 33 % penetration of the aquifer depth, and it was found that the interception of surface migrating pollutants seems to be independent of the depth of well penetration. It is important that the wells are shown to work for imperfect penetrating conditions, because the vast number of applications will involve imperfectly penetrating wells. However, imperfectly penetrating wells don't work well for the interception of the depth distributed pollutant sources since the submergence of depth distributed plume was observed from tracer simulation tests. With the problems of the submerged plume in mind, the installation of wells should penetrate deeper than the identified contaminant plumes to ensure an effective interception of migrating pollutants.

Another hydraulic problem identified with the experimental apparatus is blow-through of contaminant at the well intake by high ambient groundwater velocities. The migration of groundwater pollutants would result from the associated effect of the well recirculation rate and ambient groundwater flow velocity. With the operation of well recirculation, a withdrawal velocity will be created at the well intake as well as a recharge velocity at the well exit. If an ambient groundwater flow velocity was superimposed, then the overall withdrawal velocity would be inflated at the upstream side and diminished at the downstream side. Most of the recirculating flow would be withdrawn from the upstream side because of the influence of a high ambient flow velocity, and there won't be any withdrawal downstream until the ambient groundwater flow velocity is equal to or greater than the withdrawal velocity. Therefore, there is a minimum requirement of the well recirculation rate to carry out a successful application.

The blow-through problem was observed in the two-dimensional aquifer model, but the determination of a minimum well recirculation rate must be expanded to a three-dimensional case. If the withdrawal velocity is greater than the component of groundwater flow velocity in the direction normal to the well intake, then the resultant of the withdrawal velocity and groundwater flow velocity is considered to flow into the withdrawal casing.

The relationship between the withdrawal velocity and the groundwater flow velocity can be formulated as:

$V_W > V_G \cos\beta$ ..... (34)

where V_W is the withdrawal velocity; V_G is groundwater flow velocity; and β is the angle between the direction of groundwater flow velocity and the direction normal to the withdrawal casing. In order to prevent the blow-through problem, a minimum well recirculation rate should be maintained to create a withdrawal velocity greater than the ambient groundwater flow velocity. The withdrawal velocity is a function of the well recirculation rate, screen openings of the well intake, porosity of the aquifer, and permeability around the well intake. Applying Darcy's Law, the withdrawal velocity at the screen openings can be roughly estimated. It was assumed that groundwater is uniformly withdrawn through screen openings, and the headloss of screen openings won't be considered. A simplified formulation of the minimum well recirculation rate can be expressed as:

$Q_{min} > \pi D w K n V_G$ ..... (35)

where Q_{min} is the minimum well recirculation rate; D is the diameter of the withdrawal chamber; w is the width of the screen openings; K is hydraulic conductivity; and n is porosity.

It should be mentioned that the vertically recirculating treatment system does not aim at remediating the whole aquifer. Compared with a horizontally recirculating treatment system, the recirculation zone is much smaller for the vertically recirculating treatment system. The great interest in applying the vertically recirculating system is to create a protection zone by local decontamination, so the installation of several wells is unavoidable to form a large incorporated protection zone (FIG 57). It is important to determine the distance between well placements in the design of the system operation. The distance between well placements is related to the size of the capture zone which was found dependent upon well recirculation rate. If the size of the capture zone is enlarged because of the increase of well recirculation rate, then fewer wells should be installed to cover a desirable region under a higher rate of well recirculation. Unfortunately, the relationship between the size of the capture zone and the well recirculation rate cannot be finalized because of a narrow range of experiment data.

Hydraulic studies have demonstrated the feasibility of protecting a drinking water well from migrating nitrate contamination with the treatment well system. Since the treatment efficiency applied in tracer simulation tests was almost 100 % of pollutant removal, the

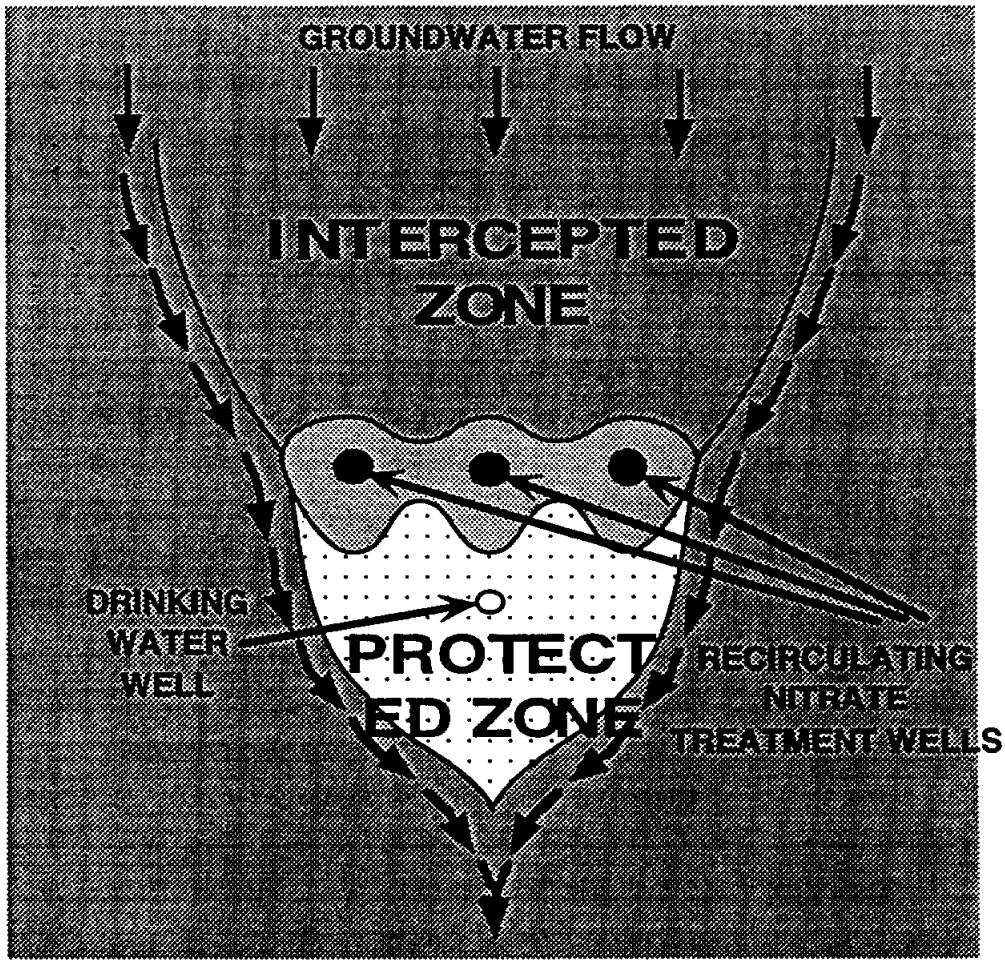


FIG 57. Conceptual Plane View of the Protection of an Individual Drinking Water Well by an Incorporated Recirculating Nitrate Treatment Well System

results of hydraulic studies could have represented the performance of system operation under ideal conditions. The operational characteristics and treatment efficiency ranges should be directly determined from the biological nitrate removal system.

Based on the performance of the treatment system, the identified operational and design parameters include the well recirculation rate, the hydraulic retention time, the carbon feed rate, and the nitrate loading rate. Most microbial activity is limited by the supply of the carbon source, so the rate of biological denitrification in the treatment chamber of the well will depend on the carbon feed rate. The rate of biological denitrification was found to be a half order reaction of the carbon level from batch experiments. Under the operations of the treatment system in the aquifer model, the carbon feed rate was suggested to be controlled at a 0.8 to 1.0 ratio of the nitrate loading rate to the treatment chamber for preventing the blinding problems from produced gases in the soil matrix.

The limitation of the carbon supply in the treatment chamber will lower the reaction rate of the treatment processes. Therefore, a high value of treatment efficiency won't be expected from a slow reaction rate of the treatment system even though a large retention time could correct this problem. The treatment efficiency may be up to 85 % in a condition of carbon overfeed or an extremely long retention time, while the treatment efficiency drops to 15 % in a condition of stoichiometric carbon feed. If the stoichiometric ratio of carbon feed is applied in the treatment chamber of the well, the required retention time should be dependent upon the nitrate level in the influent of the treatment chamber to ensure that the outflow nitrate level is lower than the drinking water standard. The required retention time was found to be at least 5 hours to provide downstream protection under a nitrate loading of 2.5 mg/min as N. If system nitrate loading was reduced to 1.0 mg/min as N, then the retention time should not be shorter than 2.5 hours to carry out a successful application.

Nitrate content in the treatment chamber of the well originates from nitrate loading of the system, but the influent nitrate level of the treatment chamber is determined by transport phenomena. It is implied that the well recirculation rate indirectly affects the required retention time according to its relationship with the influent nitrate level of the treatment chamber. Therefore, the well recirculation rate could be the most important operational parameter because it is also linked to the determination of well placements. The higher rate of well recirculation is preferred to cover a larger protection zone, but the increase in the well recirculation rate will result in a shorter retention time in the treatment chamber of the well. The shortened retention time in the treatment chamber could possibly reduce the

degree of pollutant removal; therefore, large well diameters would be designed to maintain the required retention time.

The performance of the treatment well can be judged from the outflow nitrate level of the treatment chamber. The influences of the operational and design parameters on treatment well performance can be formulated as:

$$N_t = N_w - K_N S^{1/2} \overline{X} \theta \qquad \text{..... (36)}$$

There are two possibilities to maintain the outflow nitrate level below the drinking water standard: either the influent nitrate level of the treatment chamber is low, or the removal of nitrate is significant due to the combination of abundant carbon supply, crowded microbial mass, and large retention time. The influence of microbial mass on the treatment well performance won't be discussed because constant microbial mass is expected at the steady-state condition. The operational parameters that determine the removal of nitrate in the treatment chamber are carbon supply and hydraulic retention time. Carbon supply is controlled at the stoichiometric ratio of nitrate loading, so the only controllable parameter is retention time for determining nitrate removal from the treatment chamber.

The operations of the recirculating nitrate treatment system have been successfully demonstrated in the aquifer model. The results showed that the retention time is the main affecting factor of the treatment well performance. Since the well recirculation rate must be maintained above the minimum requirement to prevent the blow-through problem, the required capacity of the treatment chamber should be a multiple of the required retention time and minimum well recirculation rate. Thus, the capacity of the treatment chamber might be very large with large groundwater flow velocity or high nitrate contamination, and the practicality of applying the proposed treatment system under such a specific condition is questionable. Conclusively, the application of the recirculating nitrate treatment system may be a feasible process for protecting drinking water wells from groundwater contamination in a sandy unconfined aquifer.

DESIGN PROCEDURES

The operational and design parameters that could possibly affect the performance of the treatment system include the depth of well penetration, the rate of well recirculation, groundwater flow velocity, hydrogeological characteristics of the aquifer, the extent of nitrate contamination, the feed rate of carbon amendment, the types and quantities of applied microorganisms, the retention time, and the screen openings of the well. The aquifer-specific parameters that should be used as the design criteria are hydrogeological

characteristics of the aquifer, groundwater flow velocity, and the extent of nitrate contamination; the operational parameters that must be adjusted to optimize the treatment system include the rate of well recirculation, the concentration of applied microorganisms, and the feed rate of carbon amendment. The design procedures of the treatment system are developed step by step.

1. The extent of nitrate contamination has to be identified first, including the concentration and the distributed depth of the nitrate plume.
2. The depth of well penetration must be deeper than the distributed depth of the identified plume to prevent the submergence problem.
3. In order to prevent the blow-through problem, the minimum rate of well recirculation is calculated from Eq(35) based on the characteristics of the aquifer.
4. The reaction rate constant (K_N) must be determined from the results of batch experiments that should apply indigenous culture at the stoichiometric C/N condition.
5. The required retention time of the treatment chamber can be estimated from Eq(32) based on the identified level of nitrate contamination.
6. The minimum diameter of the treatment chamber is calculated from the required capacity of the treatment chamber which is the multiple of the minimum well recirculation rate and the required retention time.
7. The applicability of these treatment systems should be judged by the minimum diameter of the treatment chamber. If not applicable, the depth of well penetration must be designed deeper to reduce the minimum diameter of the treatment chamber.
8. The maximum allowable well recirculation rate is recalculated based on the designed diameter of the treatment chamber which should not be greater than 20 m.
9. Applying the numerical model, the maximum distance between well placements is calculated from the maximum allowable well recirculation rate.
10. The required number of well installations can be determined to cover the aimed protection zone.
11. Next, design work should be focused on the ease of the control and maintenance of the treatment system, such as the cleanup of the fouled screen, the removal of sludge, the stripping of entrapped gas outside the well exit, etc.

FUTURE WORKS

The migration of contaminant plumes is controlled by transport phenomena. The operational condition must be optimized to prevent the blow-through and submergence problems identified in the hydraulic studies. The purpose of applying the proposed system is to protect a downstream drinking water well, but the operation of a drinking water well could have an impact on the flow system of the aquifer. The potential of contaminant blow-through between two treatment wells has to be evaluated when a downstream drinking water well is operating. The submergence problem also needs to be reconfirmed in the well-pair system, especially in the case of partially penetrated wells. In addition, the main concern of the maximum distance from the treatment well to exempt all hydraulic problems with the operation of drinking water wells needs to be answered.

The automated feed system is designed to boost biological denitrification, so any problems of nitrate monitoring would reflect the inaccuracy of system control. The problem with membrane clogging of the nitrate electrode was noticed in lab, and it may become more serious when the nitrate electrode is applied in the field. The problem of membrane clogging could cause extra maintenance work on the nitrate electrode, but the filtration of microorganisms and particulate precipitates could correct this problem. Thus, there is a need to develop a reliable nitrate monitoring system for reducing maintenance work. Once the development of a nitrate monitoring system is completed, biological denitrification should be able to be automated.

In order to prevent the blinding problem of soil pores from the produced gases, the treatment process was forced to limit carbon supply that will result in a low treatment efficiency. Low treatment efficiencies certainly narrow the applicable range of the vertically recirculating treatment application. The treatment efficiency of biological processes must be improved before the proposed system could be widely applied. If the treatment chamber is operated as a plug flow reactor instead of a completely mixed reactor, then the level of the carbon supply should be able to increase to improve the treatment efficiency of the biological processes. Another alternative to improve the treatment efficiency is to increased the population of the applied microorganisms by the use of the attached growth instead of the suspended growth condition. However, the possible improvement of treatment efficiency by employing the plug flow reactors or the attached growth condition has not yet been proved.

The proposed technology may offer an economical alternative for improving local groundwater quality that could be beneficial for small rural townships. The greatest interest

of applying the proposed treatment system is the possibility that the application could remediate groundwater contamination other than nitrate. Besides, the linkage between the vertically recirculating system and the treatment processes other than biological processes is another concern.

NOTATION

A	Cross-sectional area along flow path [L^2]
C	Constant.in Arrhenius equation
D	Diameter of the withdrawal chamber of the well [L]
h	Piezometric head [L]
Δh	Head loss [L]
ΔH^*	Activation energy
K	Hydraulic conductivity of the media [L/T]
K_d	Decay rate of microbial growth [T^{-1}]
K_N	Rate constant of nitrate reduction [$M^{1/2}L^{1/2}T^{-1}$]
Kr,Kz	Anisotrophic hydraulic conductivity in horizontal and vertical directions [L/T]
Ks	Substrate concentration when reaction rate reaches the half of maximum specific growth rate [M/L^3]
L	Length along flow path [L]
n	Porosity of media
N_t	Nitrate concentration in treatment chamber [M/L^3]
N_w	Nitrate concentration in withdrawal chamber [M/L^3]
ΔN	Uptake of reduced nitrate [M/L^3]
q	Darcy velocity [L/T]
qr	Specific discharge in inward normal radial direction [L/T]
Q	Water flow rate [L^3/T]
Q_{min}	Minimum rate of well recirculation to prevent blow-through of the plume [L^3/T]
r	Radial distance from the withdrawal well [L]
R	Gas constant
R_{nc}	Nitrate conversion ratio, %
S	Substrate concentration surrounding the microorganisms [M/L^3]
S_0	Substrate concentration in the inflow of the reactor, [M/L^3]
ΔS	Uptake of substrate in reactor [M/L^3]
t	Time [T]
T	Absolute temperature, ^oK
v	Reaction rate in Arrhenius equation
V	Volume of the reactor [L^3]

V_G Ambient groundwater flow velocity [L/T]

V_W Withdrawal velocity created by well recirculation [L/T]

w Width of screen openings [L]

X Microbial mass concentration [M/L^3]

$\overline{X}$ Mean biomass concentration during time duration of measurements [M/L^3]

X_0 Biomass concentration in the inflow of the reactor [M/L^3]

ΔX Increase of biomass concentration [M/L^3]

Y Growth yield coefficient [M/M]

μ Specific growth rate of microorganisms [T^{-1}]

μ_m Maximum specific microbial growth rate [T^{-1}]

θ Hydraulic retention time of the reactor [T]

β Angle between the direction of groundwater flow velocity and the direction normal to the withdrawal casing

REFERENCES

Abdelmagid, H. M., and Tabatabai, M. A. (1987). "Nitrate reductase activity of soils." *Soil Biol. Biochem.*, 19(4), 421-427.

Alexander, M. (1977). *Introduction to soil microbiology.* 2nd ed., John Wiley & Sons, Inc. New York.

American Public Health Association, American Water Works Association, and Water Pollution Control Federation (1985). *Standard methods for the examination of water and wastewater.* 16th ed., American Public Health Association, Washington, DC.

Arbuckle, T. E., Sherman, G. J., Corey, P. N., Walters, D., and Lo, B. (1988). "Water nitrate and CNS birth defects: A population-based case-control study." *Arch. Environ. Health.*, 43, 162-167.

Baily, J. E., and Ollis, D. F. (1986). *Biochemical engineering fundamentals.* 2nd ed., McGraw-Hill, Inc. New York.

Baker, J. L., Johnson, H. P., Fenton, T., O'Toole, J., and Grauer, T. (1982). *Nitrate movement and denitrification defined relative to bromide tracer in tile-drained land.* Iowa State Water Resources Research Institute, Ames, IO.

Bengtsson, G., and Annadotter, H. (1989). "Nitrate reduction in a groundwater microcosm determined by ^{15}N gas chromatography-mass spectrometry." *Appl. Environ. Microbiol.*, 55(11), 2861-2870.

Bitton, G., and Gerba, C. P. (1984). "Groundwater pollution microbiology: the emerging issue." In: *Groundwater pollution microbiology*, G. Bitton and C.P. Gerba, eds., John Wiley and Sons, Inc. New York.

Blackmer, A. M., and Bremner, J. M. (1979). "Stimulatory effect of nitrate on reduction of N_2O to N_2 by soil microorganisms." *Soil Biol. Biochem.*, 11, 313-315.

Bouchard, D. C., Williams, M. K., and Surampalli, R.Y. (1992). "Nitrate contamination of groundwater: Sources and potential health effects." *AWWA J.*, 84(9), 85-90.

Bradley, P. M., Fernandez, M., and CHapelle, F. H. (1992). "Carbon limitation of denitrification rates in an anaerobic groundwater system." *Environ. Sci. Technol.* 26(12), 2377-2381.

Burns, W. A., Jr. (1969). "New single-well test for determining vertical permeability." *J. Pet. Tech.*, 21, 743-752.

Button, D. K. (1985). "Kinetics of nutrient-limited transport and microbial growth." *Microbil. Rev.*, 49, 270-297.

Cho, C. M., Sakdinan, L., and Chang C. (1979). "Denitrification intensity and capacity of three irrigated alberta soils. " *Soil Sci. Soc. Am.* J., 43, 949-950.

Craswell, E. T. (1978). "Some factors influencing denitrification and nitrogen immobilization in a clay soil." *Soil. Biol. Biochem.*, 6, 241-245.

Dahab, M. F., and Lee, Y. M. (1988). "Nitrate removal from water supplies using biological denitrification." *J. Water Pollut. Control Fed.*, 60(9), 1670-1674.

Darcy, H. (1856). *Les fontaines publiques de la ville de Dijon.* Dalmont, Paris.

Davidson, E. A., Strand, M. K., and Galloway, L. F. (1985). "Evaluation of the most probable number method for enumerating denitrifying bacteria." *Soil Sci. Soc. Am. J.*, 49, 642-645.

de Vries, J. J. (1975). *Groundwater hydraulics.* Editions Rodopi. Amsterdam.

Doherty, R. E. (1992). "Operation and maintenance issues are crucial to the overall site remediation process." *Pollut. Engrg.*, 24(3), 61-64.

Domenico, P. A., and Schwartz, F. W. (1990). *Physical and chemical hydrogeology.* 2nd ed., John Wiley & Sons, Inc. New York.

Dore, M., Simon, P., Deguin, A., and Victot, J. (1986). "Removal of nitrate in drinking water by ion exchange: Impact on the chemical quality of treated water." *Wat. Res.*, 20(2), 221-232.

Dorsch, M. M., Scragg, R. K., McMichael, A. J., Baghurst, P. A., and Dyer, K. F. (1984). "Congenital malfunctions and maternal drinking water supply in rural South Australia: A case control study." *Am. J. Epidemiol.*, 119, 473-486.

Dowd, R. M. (1986). "Groundwater protection programs." *Environ. Sci. Technol.*, 20(9), 862.

Environmental Engineering Research Council of ASCE. (1990). "Ground-water protection and reclamation." *J. Envir. Engrg., ASCE,* 116(4), 654-662.

Fernandes, L., and McKyes, E. (1991). "Theorical and experimental study of a sequential batch reactor treatment of liquid swine manure." *ASAE,* 34(2), 597-602.

Firestone, M. K. (1982). " Biological denitrification." In: *Nitrogen in agriculture soils*, F. J. Stevenson, ed., American Society of Agronomy, Madison, Wis., 289-326.

Forman, D., Al-Dabbagh, S., and Doll, R. (1985). "Nitrates, nitrites and gastric cancer in Great Britain." *Nature.*, 313, 620-625.

Fraster, P., Chilvers, C., Beral, V., and Hill, N. J. (1980). "Nitrate and human cancer: A review of the evidence." *Int. J. Epidemiol.*, 9, 3-9.

Gahrs, J. H., Rutten, P., and Schnoor, G. (1989). "Drinking water treatment using hydrogen." *Water and Sewage International* , 1(1), 35-39.

Ghiorse, W. C., and Balkwill, W. C. (1983). "Enumeration and morphological characterization of bacteria indigenous to subsurface environments." *Dev. Ind. Microbiol.*, 24, 213-224.

Gillham, R. W., and Cherry, J. A. (1978). " Field evidence of denitrification in shallow groundwater flow systems." *Water Pollut. Res. Can.*, 13(1), 53-71.

Gillham, R. W., Starr, R. C., and Miller, D. J. (1990). "A device for in situ determination of geochemical transport parameters 2 biochemical reactions." *Ground Water*, 28(6), 858-862.

Goretski, J., and Hollocher, T. C. (1989). "The kinetic and isotopic competence of nitric oxide as an intermediate in denitrification." *J. Biol. Chem.*, 265(2), 889-895.

Grabinska-Loniewska , A., Slomczynski, T., and Kanska, Z. (1985). "Denitrification studies with glycerol as a carbon source." *Wat. Res.*, 19(12), 1471-1477.

Grady, C. P. Leslie Jr. (1985). " Biodegradation: Its measurement and microbiological basis." *Biotechnology and bioengineering* , 27, 660-674.

Grbic-Galic, D. (1990). " Anaerobic microbial transformation of nonoxygenated aromatic and alicyclic compounds in soil, subsurface, and freshwater sediments." In: *Soil biochemistry* 6, J.M. Bollag and G. Stotzky, eds., Marcel Dekker, New York.

Haddock, B. A., and Jones, C. W. (1977). "Bacterial respiration." *Bacteriol. Rev.*, 41, 47-99.

Hall, T. (1992). "Biological dentrification for potable water treatment." *J. Chem. Tech. Biotechnol.*, 54, 185-186.

Hall, T., Walker, R. A., and Zabel, T. F. (1986). " Nitrate removal from drinking water-preliminary guide to process selection and design." *Proceedings of the congress "Nitrates in Water"*, Water Res. Centre, Medmenham, 422-425.

Hallberg, G. R. (1989). "Nitrate in ground water in the United States." In: *Nitrogen management and ground water protection, developments in agricultural and managed-forest ecology 21*, R. F. Follett, ed., Elsevier, New York, 35-74.

Hamon, M., and Fustec, E. (1991). "Laboratory and field study of an in situ groundwater denitrification reactor." *J. Water Pollut. Control Fed.*, 63(7), 942-949.

Hantzsche, N. N., and Finnemore, E. J. (1992). " Predicting ground-water nitrate-nitrogen impacts. " *Ground Water* , 30(4), 490-499.

Harrington, J. R., Mihelcic, J. R., Planinsek, T. L., and Lewis, R. A. (1993). "FATE estimates pollutant treatability." *Wat. Environ. Technol.*, 5, 49-53.

Hartman, P. E. (1983). "Review: Putative mutagens and carcinogens in foods." *Environmental Mutagenesis*, 5, 111-121.

Harvey, R. W., and Geroge, L. H. (1989). "Transport of microspheres and indigenous bacteria through a sandy aquifer: Results of natural- and forced-gradient tracer experiments." *Environ. Sci. Technol.*, 23, 51-56.

Hasbach, A. (1992). "Sequencing batch reactor treats wastewater." *Pollut. Engrg.*, 24(7), 73.

Hasbach, A. (1993). "Moving beyond pump-and treat." *Pollut. Engrg.*, 25, 36-39.

Henze, M. (1987). "Theories for estimation of the fraction of denitrifiers in combined nitrifying-denitrifying treatment plants." *Wat. Res.*, 21(12), 1521-1524.

Herrling, B., and Buermann, W. (1990). "A new method for in-situ remediation of volatile contaminants in groundwater: Numerical simulation of the flow regime." In: *Computational methods in subsurface hydrology*, G. Gambolati, A. Rinaldo, C.A. Brebbia, W.G. Gray, and G.F. Pinder, eds., Springer. Berlin.

Herrling, B., and Stamm, J. (1992). "Numerical results of calculated 3D vertical circulation flows around wells with two screen sections for in situ or on-site aquifer remediation." In Proc. IX Int. Conf. on *Computational Methods in Water Resources*, Denver, CO.

Herrling, B., and Stamm, J. (1992). "Groundwater circulation wells (GZB) for in situ and on-site aquifer remediation." *In nuclear & hazardous waste management international tropical meeting*, Boise, ID.

Herrling, B., Stamm, J., Alesi, E. J., Brinnel, P., Hirschberger, F., and Sick, M. R. (1991). "In situ groundwater remediation of strippable contaminants by vacuum vaporizer wells (UVB): Operation of the well and report about cleaned industrial sites." On *innovative hazardous waste treatment technologies: Domestic and international*, Dallas, TX.

Herrling, B., Stamm, J., and Buermann, W. (1991). "Hydraulic circulation system for in situ bioreclamation and/or in situ remediation of strippable contamination." *In situ and on-site bioreclamation*, R. Hinchee.,ed., Proc. Int. Symp., San Diego, CA.

Hiscock, K. M., Lloyd, J.W., and Lerner, D. N. (1991). "Review of natural and artificial denitrification of groundwater." *Wat. Res.*, 25(9), 1099-1111.

Honeycutt, C. W., Potaro, L. J., and Halteman, W. A. (1991). " Predicting nitrate formation from soil, fertilizer, corp residue, and sludge with thermal units." *J. Environ. Qual.*, 20, 850-856.

Irvine, R. L., Murthy, D. V. S., Arora, M. L., Copeman, J. L., and Heidman, J. A. (1987). "Analysis of full-scale SBR operation at Grundy Center, Iowa." *J. Water Pollut. Control Fed.*, 59(3), 132-138.

Javandel, I., and Tsang, C. F. (1986). "Capture-Zone Type Curves: A Tool for Aquifer Cleanup." *Ground Water*, 24(5), 616-625.

Jensen, R. (1988). "Natural wastewater treatment systems." *Texas Water Resources,* 14(2), Texas Water Resources Institute, College Station, TX.

Jones, W. L., Schroeder, E. D., and Wilderer, P. A. (1990). "Denitrification in a batch wastewater treatment system using sequestered organic substances." *J. Water Pollut. Control Fed.*, 62(3), 259-267.

Jones, W. L., Wilderer, P. A., and Schroeder, E. D. (1990). " Operation of a three-stage SBR system for nitrogen removal from wastewater." *J. Water Pollut. Control Fed.*, 62(3), 268-274.

Kinzelbach, W., Schafer, W., and Herzer, J. (1991). "Numerical modeling of natural and enhanced denitrification processes in aquifers." *Water Resour. Res.*, 27(6), 1123-1135.

Klemedtsson, L., Svensson, B.H., Lindberg, T. and Rosswall, T. (1978). "The use of acetylene inhibition of nitrous oxide reductiase in quantifying denitrification in soils." *Swed. J. Agric. Res.*, 7, 179-185.

Knowles, R. (1982). "Denitrification." *Microbiological Reviews*, 46(1), 43-70.

Kohl, D. H., Vithayathil, F., Whitlow, P., Shearer, G., and Chien, S. H. (1976). "Denitrification kinetics in soil systems: The significance of good fits of data to mathematical forms." *Soil Sci. Soc. Am. J.*, 40, 249-253.

Korom, S. F. (1992). "Natural denitrification in the saturated zone: A review." *Wat. Res. Res.*, 28(6), 1657-1668.

Kristjansson, J. K., and Hollocher, T.C. (1980). "First practical assay for soluble nitrous oxide reductase of denitrifying bacteria and a partial kinetic characterization." *J. Biol. Chem.*, 255, 704-707.

Kross, B. C., Hallberg, G. R., Bruner, D. R., Cherryholmes, K., and Johnson, J. K. (1993). "The nitrate contamination of private well water in Iowa." *Am. J. Public Health.*, 83(2), 270-272.

Lawrence, A.W., and McCarty, P. L. (1970). "Unified basis for niological treatment design and operation." *J. San. Eng. Div., Proc. Amer. Soc. Civil Engr.*, 96(3), 757-778.

Lee, Y. M., and Dahab, M. F. (1988). "Kinetics of low solids bio-denitrification of water supplies." *J. Water Pollut. Control Fed.*, 60(10), 1857-1861.

LeGall, J., Payne, W. J., Morgan, T.V., and DerVartanian, D. (1979). "On the purification of nitrite reductase from *Thiobacillus denitrificans* and its reaction with nitrite under reducing conditions. *Biochem. Biophys. Res. Commun.*, 87, 335-362.

LeGrand, H. E., and Rosen, L. (1992). "Common sense in ground-water protection and management in the United States." *Ground Water,* 30(6), 867-872.

Lewandowski, Z. (1986). "Biological reactor resistance to inhibition." *Wat. Res.*, 20(7), 847-850.

Lind, A.M. (1983). "Nitrate reduction in the subsoil." In:*Denitrification in the Nitrogen Cycle*, H.L. Golterman, ed., Plenum Press, New York.

MacDonald, T. R., and Kitanidis, P.K. (1993). "Modeling the free surface of an unconfined Aaquifer near a recirculation well." *Ground Water,* 31(5), 774-780.

Mackay, D. M., and Cherry, J. A. (1989). " Groundwater contamination: Pump-and-treat remediation." *Env. Sci. Tech.*, 23(6), 630-636.

Madison, R. J. and Brunett, J. O. (1985). "Overview of the occurances of nitrates in groundwater of the United States. " *US Geological Survey Water Supply Paper* , 2275, 93-105.

McCarty, P. L. (1988). "Bioengineering issues related to in situ remediation of contaminated soils and ground water." In: *Environmental Biotechnology*, G. S. Ommen ,ed., PlenumPress, New York.

McCarty, P. L., Semprini, L., and Roberts, P. V. (1989). "Methodologies for evaluating the feasibility of in-situ biodegradation of halogenated aliphatic groundwater contaminants by metanotrophs." In: *Proceeding of the 1989 symposium on hazardous waste treatment: biosystems for pollution control.*, Air and Waste Management Association, Pitsburgh, PA, 69-82.

McIntyre, B. D., and Riha, S. J. (1991). "Hydraulic conductivity and nitrogen removal in an artificial wetland system." *J. Environ. Qual.*, 20, 259-263.

Muller, M. M., Sundman, V., and Skujins, J. (1980). " Denitrification in low pH spodosols and peats determined with the acetylene inhibition method." *Appl. Environ. Microbiol.*, 40, 235-239.

Murray, R. E., Parsons, L. L., and Smith, M. S. (1989). "Kinetics of nitrate utilization by mixed populations of denitrifying bacteria." *Appl. Environ. Microbiol.*, 55(3), 717-721.

Obenhuber, D. C., and Lowrance, R. (1991). "Reduction of nitrate in aquifer microcosms by carbon additions." *J. Environ. Qual.*, 20, 255-258.

Office of Technology Assessment. (1984). *Protecting the nation's groundwater from contamination.* Office of Technology Assessment, Washington, DC, 244.

Olsen, R. L., and Kavanaugh, M. C. (1993). "Can groundwater restoration be achieved?" *Wat. Environ. Technol.*, 5, 43-47.

Oren, A., and Blackburn, T. H. (1979). "Estimation of sediment denitification rates at in situ nitrate concentrations." *Appl. Environ. Microbiol.*, 37(1), 174-176.

Palis, J. C., and Irvine, R. L. (1985). "Nitrogen removal in a low-loaded single tank sequencing batch reactor." *J. Water Pollut. Control Fed.*, 57, 82-86.

Parkin, T. B., and Tiedje, J. M. (1984). "Application of a soil core method to investigate the effect of oxygen concentration on denitrification." *Soil. Biol. Biochem.*, 16(4), 331-334.

Pettyjohn, W. A. (1987). *Protection of public water supplies from ground water contamination.* Noyes Data Corporation, Park Ridge, NJ.

Philip, R. D., and Walter, G. R. (1992). "Prediction of flow and hydraulic head fields for vertical circulation wells." *Ground Water,* 30(5), 765-773.

Power, J. F., and Schepers J. S. (1989). "Nitrate contamination of groundwater in North America." *Agriculture, ecosystems and environment.*, 26, 165-187. Elsevier Science Publishers B.V., Amsterdam, Netherlands.

Process Engineering. (1988). "Seletively removes nitrates from ground water supplies." *Process Engineering*, November 1988, 23.

Process Engineering. (1989). " Removes nitrates from ground water supplies." *Process Engineering*, February 1989, 21.

Rajagopal, R., and Tobin, G. (1989). "Expert opinion and ground water quality protection: The case of nitrate in drinking water." *Ground Water*, 27(6), 835-847.

Reynolds, T. D. (1982). *Unit operations and processes in environmental engineering.* Wadsworth, Inc. Belmont, CA.

Robert S. Kerr Environmental Research Laboratory. (1987). *Practical limits to pump and treat technology for aquifer remediation.*. U.S. Environmental Protection Agency, Ada, OK.

Sawada, E., and Satoh, T. (1980). " Periplasmic location of dissimilatory nitrite reductases in a denitrifying photorophic bacterium, *Rhodopseudomonas sphaeroides* forma sp. *denitrificans.*" *Plant Cell Physiol.*, 21, 205-210.

Schippers, J. C., Kruithof, J. C., Mulder, F. G., and van Lieshout, J. W. (1987). "Removal of nitrate by slow sulphur/ limestone filtration." *Aqua.*, 5, 274-280.

Slater, J. M., and Capone, D. G. (1987). "Denitrification in aquifer soil and nearshore marine sediments influenced by groundwater nitrate." *Appl. Environ. Microbiol.*, 53(6), 1292-1297.

Smith, R. L., and Duff, J. H. (1988). "Denitrification in a sand and gravel aquifer." *Appl. .Environ. Microbiol.*, 54(5), 1071-1078.

Smith, R. L., Howes, B. L., and Duff, J. H. (1991). "Denitrification in nitrate-contaminated groundwater: Occurrence in steep vertical geochemical gradients." *Geochim. Cosmochim. Acta* , 55(76), 1815-1825.

Soares, M. I. M., Belkin, S., and Abeliovich, A. (1988). "Biological groundwater denitrification: laboratory studies." *Wat. Sci. Tech.*, 20, 189-195.

Soares, M. I. M., Braester, C., Belkin, S., and Abeliovich, A. (1991). "Denitrification in laboratory sand columns: Carbon regime, gas accumulation and hydraulic properties." *Wat. Res.*, 25(3), 325-332.

Solt, G. (1987). "Removing nitrate from potable water." *Chemical Engineer,* May 1987, 33-36.

Spalding, R. F., and Exner, M. E. (1993). " Occurrence of nitrate in groundwater- A review. " *J. Environ. Qual.*, 22, 392-402.

Stanier, R. Y., Adelberg, E. A., and Ingraham, J. (1976). *The microbial world.* 4th ed., Prentice-Hall, Inc. Englewood Cliffs, N.J.

Stensel, H. D., Loehr, R. C., and Lawrence, A.W. (1973). "Biological kinetics of suspended-growth denitrification." *J. Water Pollut. Control Fed.*, 45(2), 249-261.

Stephenson, T. (1992). "Extended summaries: Environmental biotechnology group meeting biotechnology in the clean water industries." *J. Chem. Tech. Biotechnol.*, 54, 183-184.

Stouthamer, A. H. (1976). "Biochemistry and genetics of nitrate reductase in bacteria." *Adv. Microb. Physiol.*, 14, 315-375.

Strack, O.D. L. (1989). *Groundwater mechanics.* Prentice-Hall, Englewood Cliffs, N.J.

Strand, S. E., and McDonnell, A. J. (1985). " Mathematical analysis of oxygen and nitrate consumption in deep microbial films." *Water Res.*, 19(3), 345-352.

Strand, S. E., McDonnell, A. J., and Unz, R. F. (1985). "Concurrent denitrification and oxygen uptake in microbial films." *Water Res.*, 19(3), 335-344.

Stumm, W., and Morgan, J. J. (1981). *Aquatic chemistry.* 2nd ed., John Wiley and Sons, Inc. New York.

Tam, T. Y., and Knowles, R. (1979). "Effects of sulfide and acetylene on nitrous oxide reduction by soil and by *Pseudomonas aeruginosa.*" *Can. J. Microbiol.*, 25, 1133-1138.

Thurman, E. M. (1985). *Organic geochemistry of natural waters.* Martinus Nijhoff Netherlands, Dordrecht, Netherlands.

Tiedje, J. M. (1981). "Use of nitrogen-13 and nitrogen-15 in studies on the dissimilatory fate of nitrate." In: *Genetic engineering of symbiotic nitrogen fixation and conservation of fixed nitrogen,* Lyons, J. M. et al., eds., Plenum Press, New York,481-497.

Tiedje, J. M., Sexstone, A. J., Myrold, D., and Robinson, J. A. (1982). "Dentrification: ecological niches, competition, and survival." *Antonie van Leeuwenhoek J. Microbiol. Serol.*, 48, 569-583.

Trudell, M. R., Gillham, R.W., and Cherry, J. A. (1986). "An in-situ study of the occurrence and rate of denitrification in a shallow unconfined sand aquifer." *J. Hydrol.*, 83(3/4), 251-268.

United States Environmental Protection Agency (1990). "National pesticide survey: a project summary." United States Environmental Protection Agency, Washington, DC.

van der Hoek, J. P., and Klapwijk, A. (1987). "Nitrate removal from ground water." *Wat. Res.*, 21(8), 989-997.

van der Hoek, J. P., Kappelhof, J.W.N.M., and Hijnen, W.A.M. (1992). "Biological nitrate removal from ground water by sulphur/limestone denitrification." *J. Chem. Tech. Biotechnol.*, 54, 197-200.

van Hecke, K., van Cleemput, O., and Baert, L. (1990). "Chemo-denitrification of nitrate-polluted water." *Environ. Pollut.*, 63(3), 261-273.

Webster, J. J., Hampton, G. J., Wilson, J. T., Ghiorse, W. C., and Leach, F. R. (1985). "Determination of microbial cell numbers in subsurface samples." *Ground Water*, 23(1), 17-25.

Young, A. N., Jr. (1993). "Batch treatment avoids nitrate contamination." *Wat. Environ. Technol.*, 5, 20.

Zumft, W. G., Sherr, B. F., and Payne, W. J. (1979). "A reappraisal of the nitric-oxide-binding protein of denitrifying *Pseudomonas*." *Biochem. Biophys. Res. Commun.*, 88, 1230-1236.

Zumft, W. G., and Vega, J. M. (1979). "Reduction of nitrite to nitrous oxide by a cytoplasmic membrane fraction from the marine denitrifier *Pseudomonas perfectomarinus*." *Biochim. Biophys. Acta*, 548, 484-499.

APPENDIX 1

SUPPLEMENTAL DATA ON HYDRAULIC STUDIES

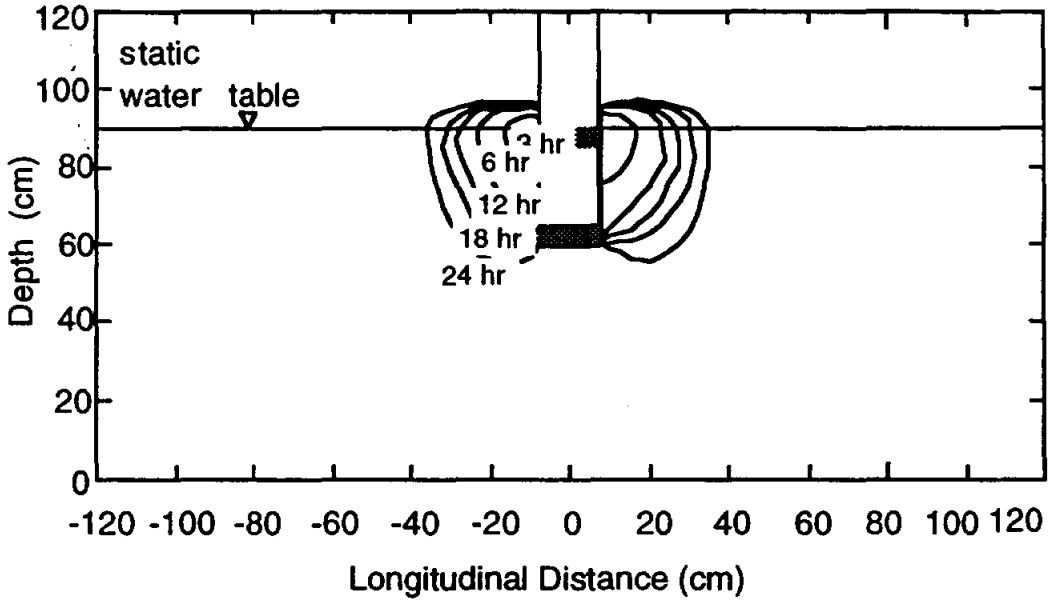


FIG 58. Case 1 Simulation of the Tracer Tests: Zero Ambient Flow Velocity and 25 mL/min Well Recirculation Rate for Hydraulic Well 1

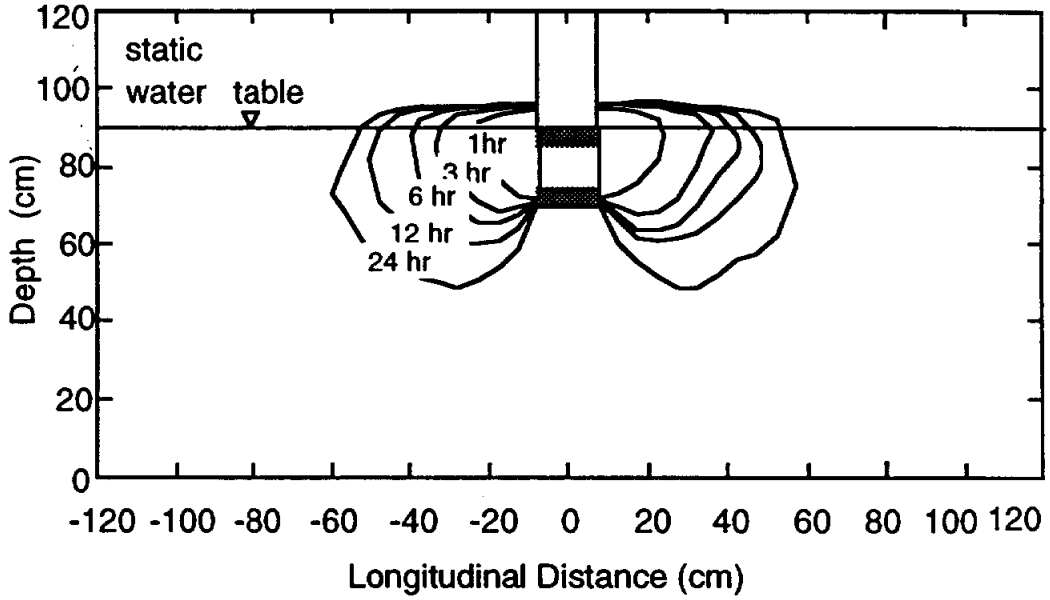


FIG 59. Case 1 Simulation of the Tracer Tests: Zero Ambient Flow Velocity and 100 mL/min Well Recirculation Rate for Hydraulic Well 2 (Run 1)

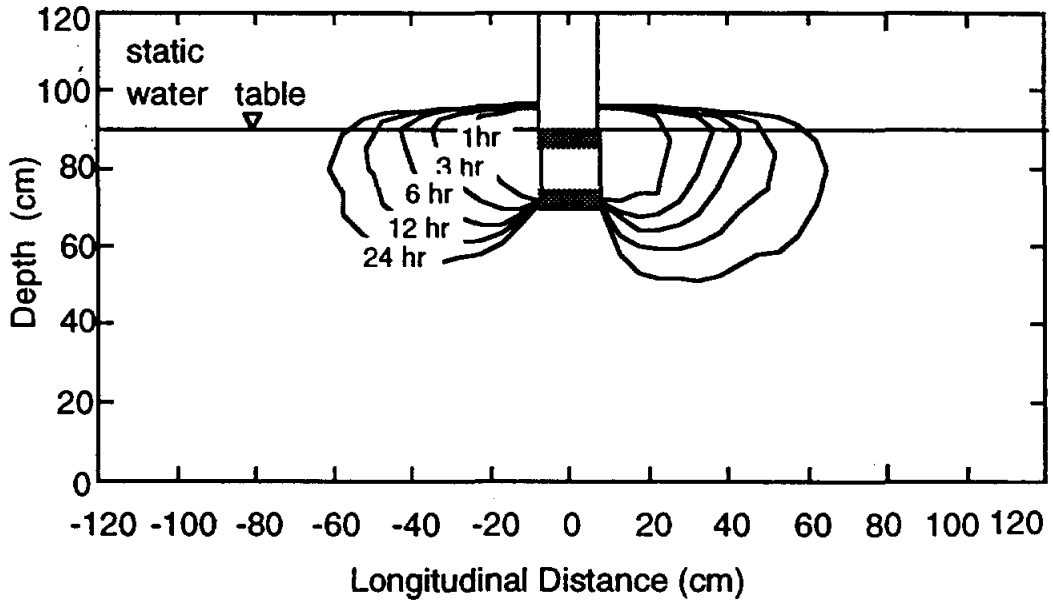


FIG 60. Case 1 Simulation of the Tracer Tests: Zero Ambient Flow Velocity and 100 mL/min Well Recirculation Rate for Hydraulic Well 2 (Run 2)

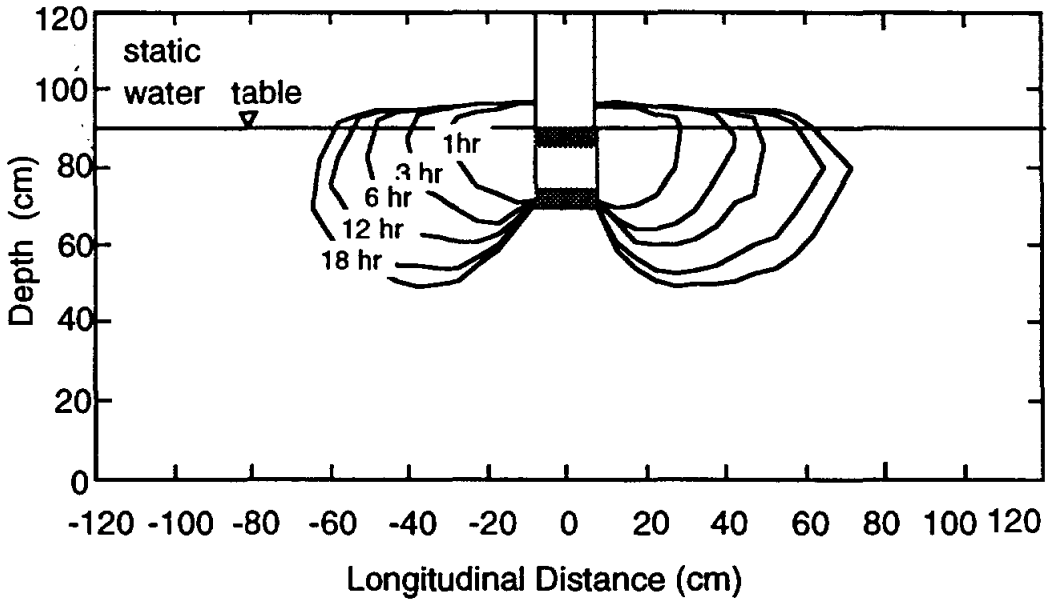


FIG 61. Case 1 Simulation of the Tracer Tests: Zero Ambient Flow Velocity and 200 mL/min Well Recirculation Rate for Hydraulic Well 2

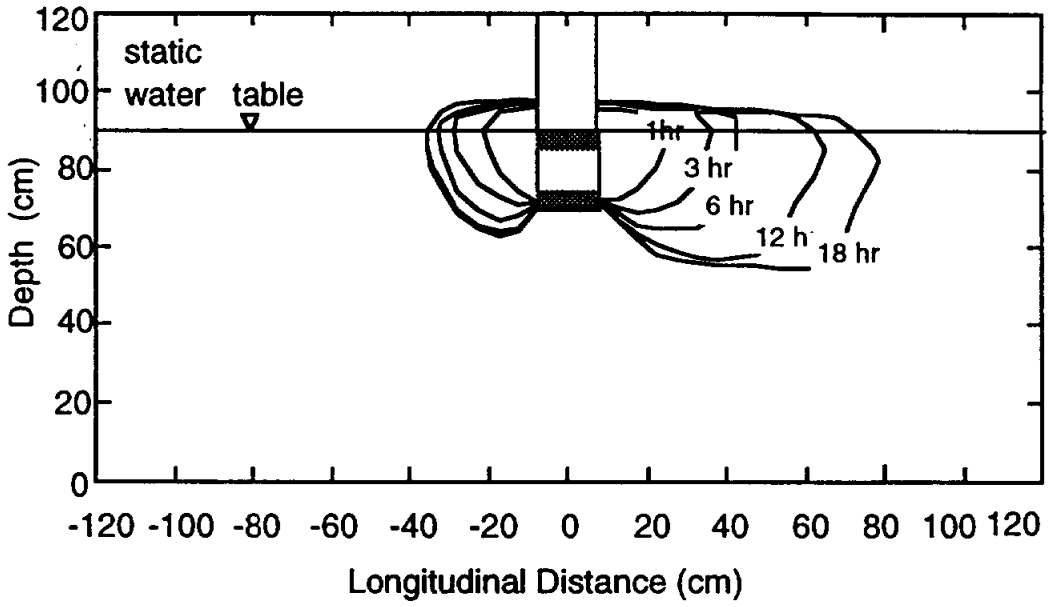


FIG 62. Case 2 Simulation of the Tracer Tests: 1 m/day Ambient Flow Velocity and 100 mL/min Well Recirculation Rate for Hydraulic Well 2 (Run 1)

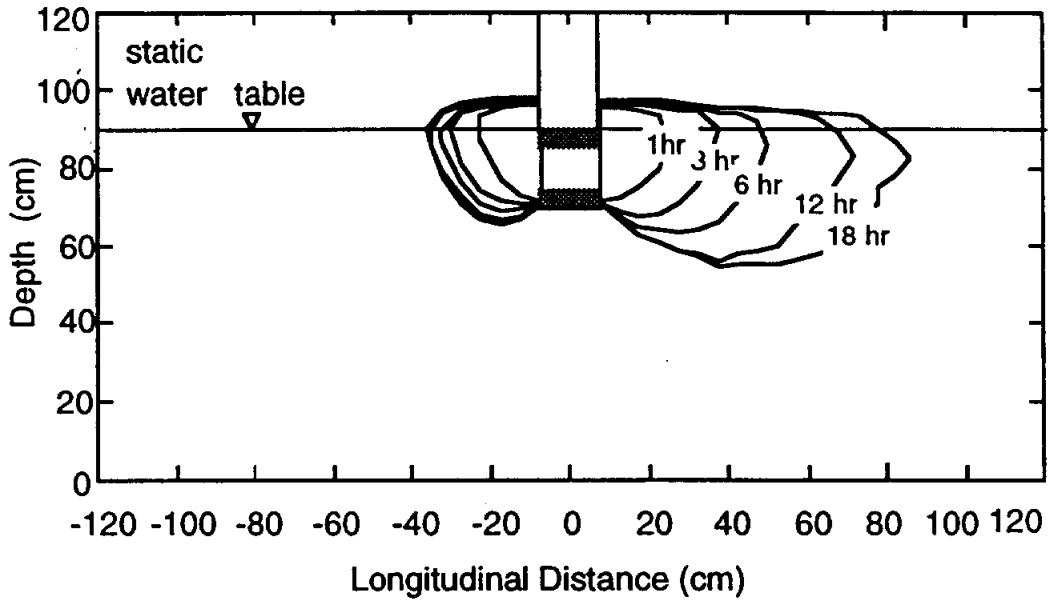


FIG 63. Case 2 Simulation of the Tracer Tests: 1 m/day Ambient Flow Velocity and 100 mL/min Well Recirculation Rate for Hydraulic Well 2 (Run 2)

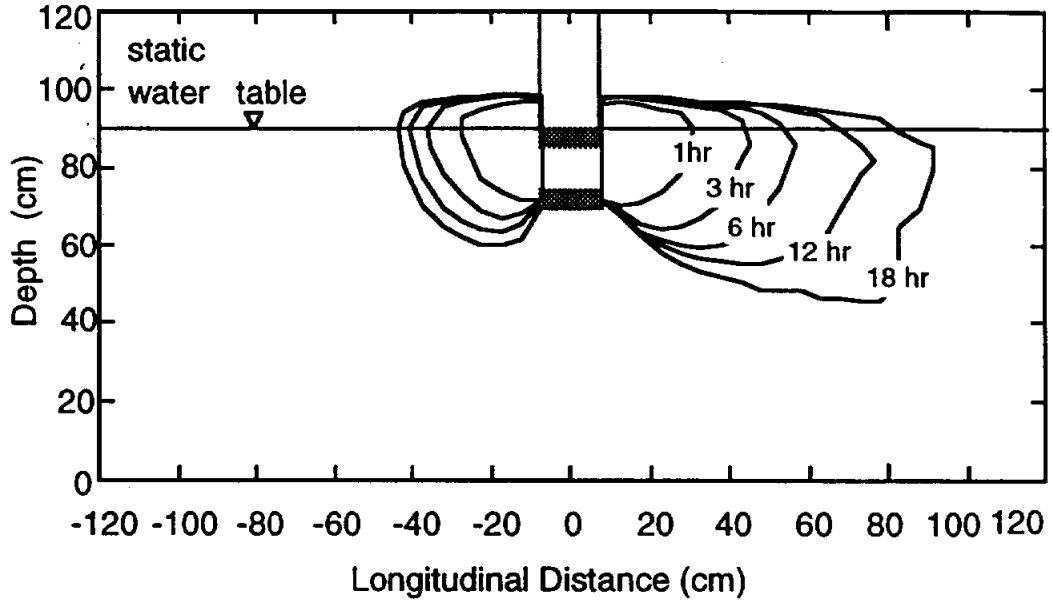


FIG 64. Case 2 Simulation of the Tracer Tests: 1 m/day Ambient Flow Velocity and 200 mL/min Well Recirculation Rate for Hydraulic Well 2

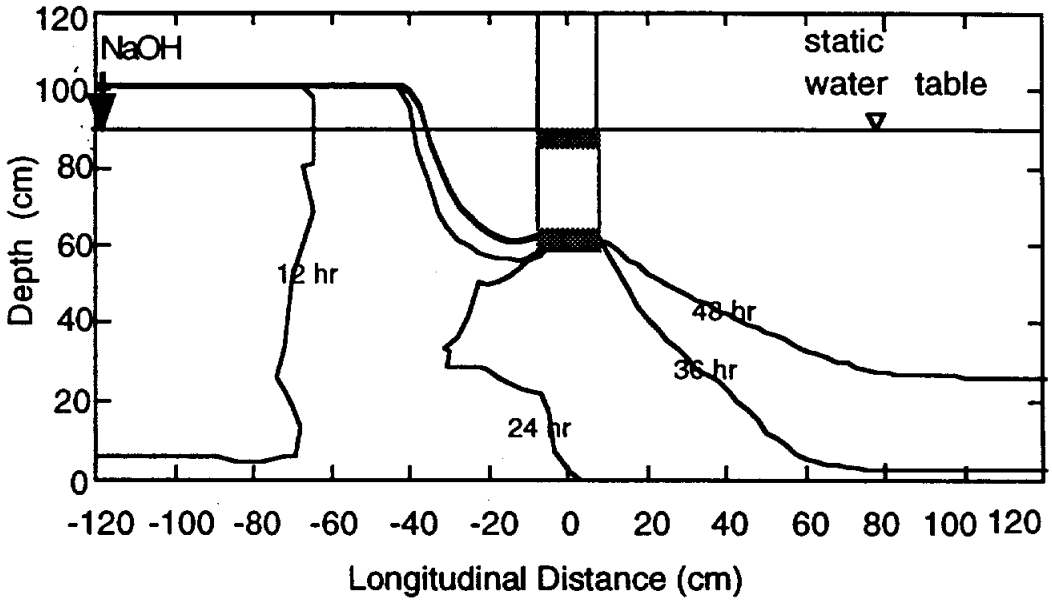


FIG 65. Case 3 Simulation of the Tracer Tests: 1 m/day Ambient Flow Velocity, 100 mL/min Well Recirculation Rate, and with a Depth Distributed Source of NaOH for Hydraulic Well 1

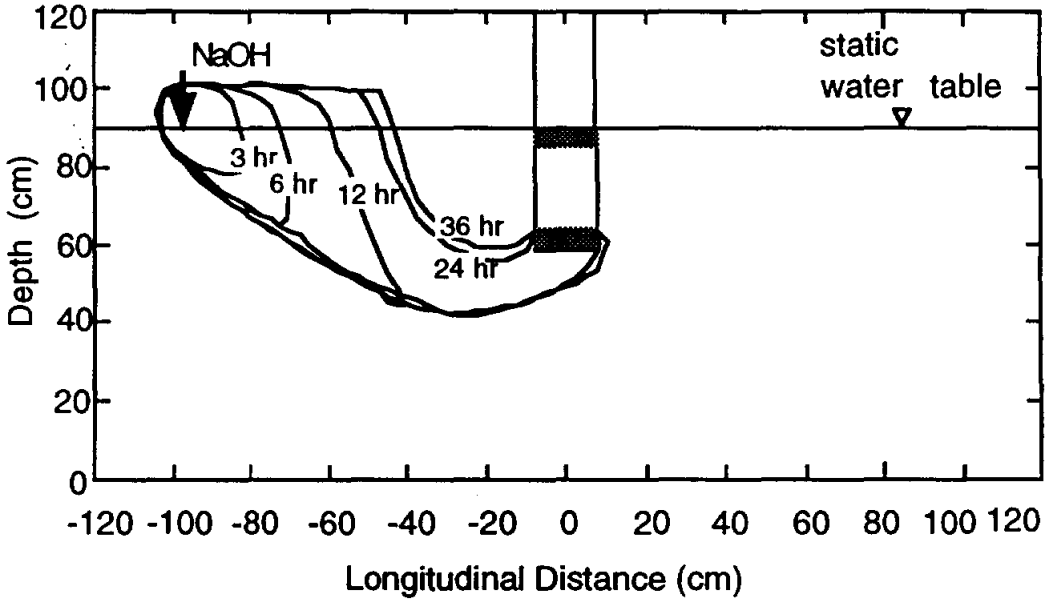


FIG 66. Case 4 Simulation of the Tracer Tests: 1 m/day Ambient Flow Velocity, 100 mL/min Well Recirculation Rate, and with a Surface Source of NaOH for Hydraulic Well 1

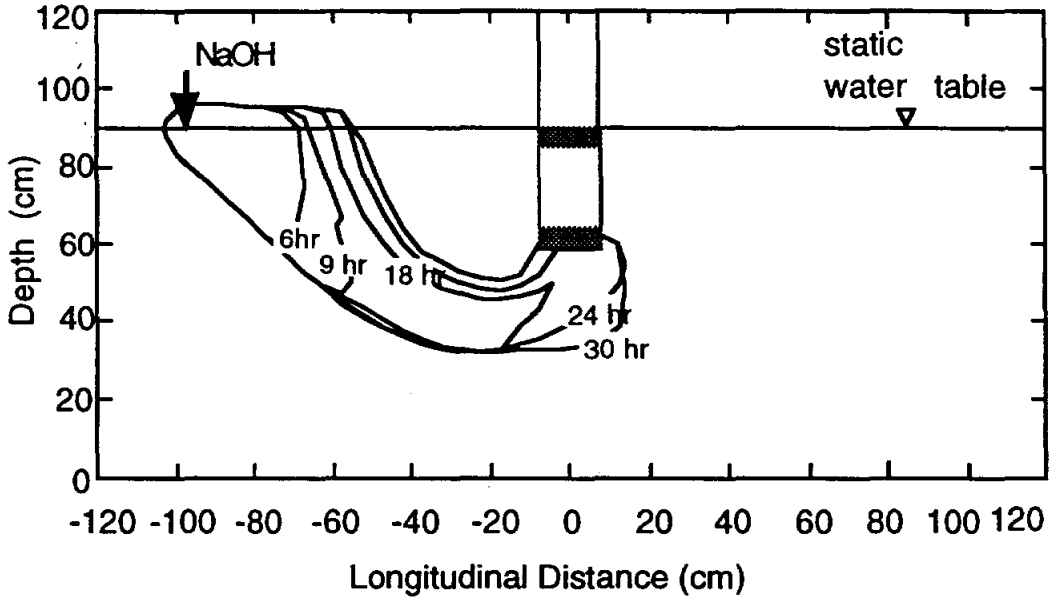


FIG 67. Case 4 Simulation of the Tracer Tests: 1 m/day Ambient Flow Velocity, 150 mL/min Well Recirculation Rate, and with a Surface Source of NaOH for Hydraulic Well 1

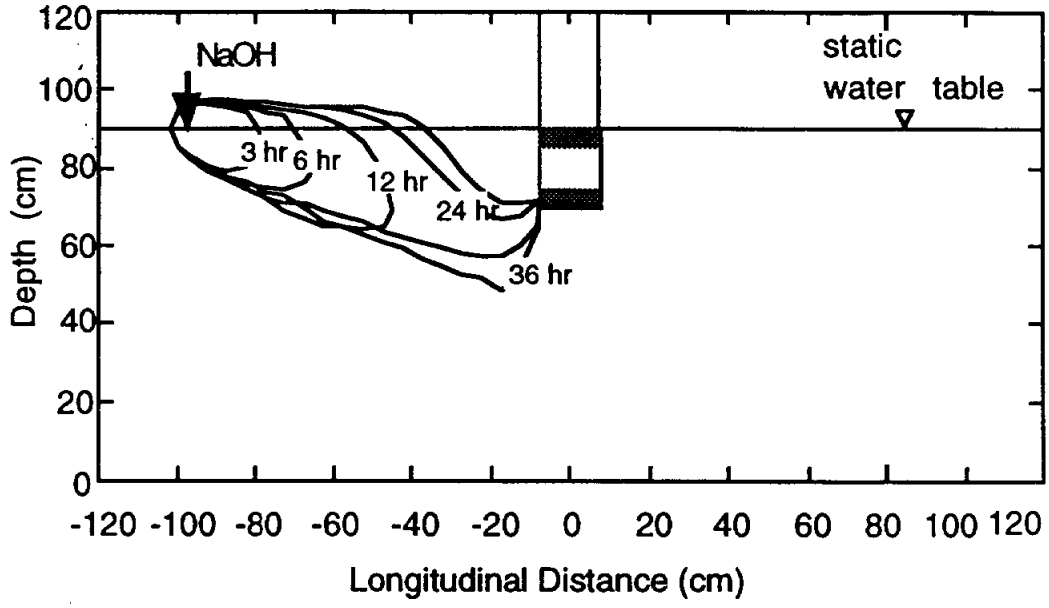


FIG 68. Case 4 Simulation of the Tracer Tests: 1 m/day Ambient Flow Velocity, 100 mL/min Well Recirculation Rate, and with a Surface Source of NaOH for Hydraulic Well 2 (Run 1)

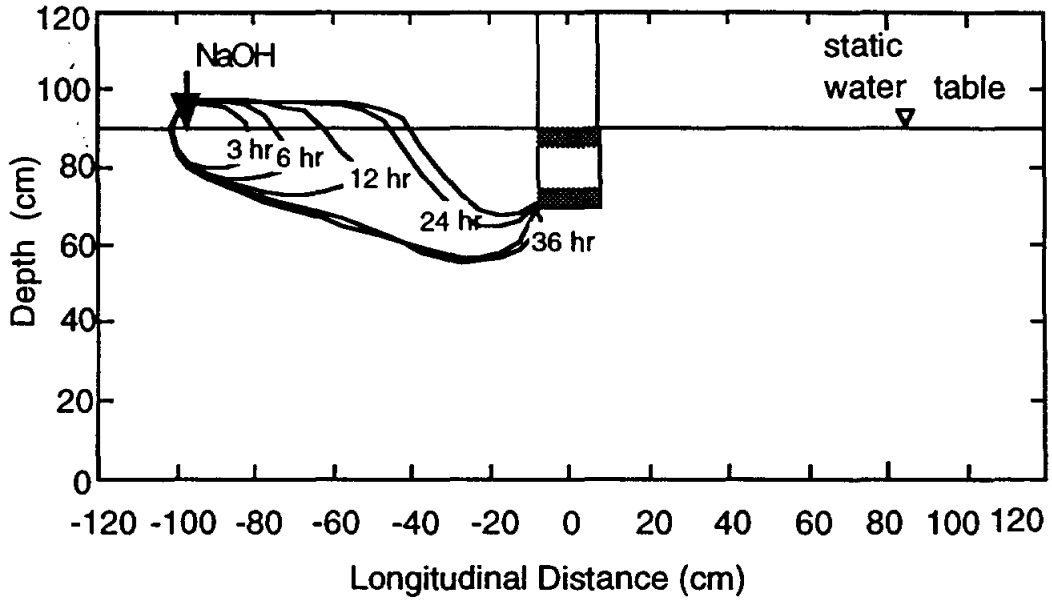


FIG 69. Case 4 Simulation of the Tracer Tests: 1 m/day Ambient Flow Velocity, 100 mL/min Well Recirculation Rate, and with a Surface Source of NaOH for Hydraulic Well 2 (Run 2)

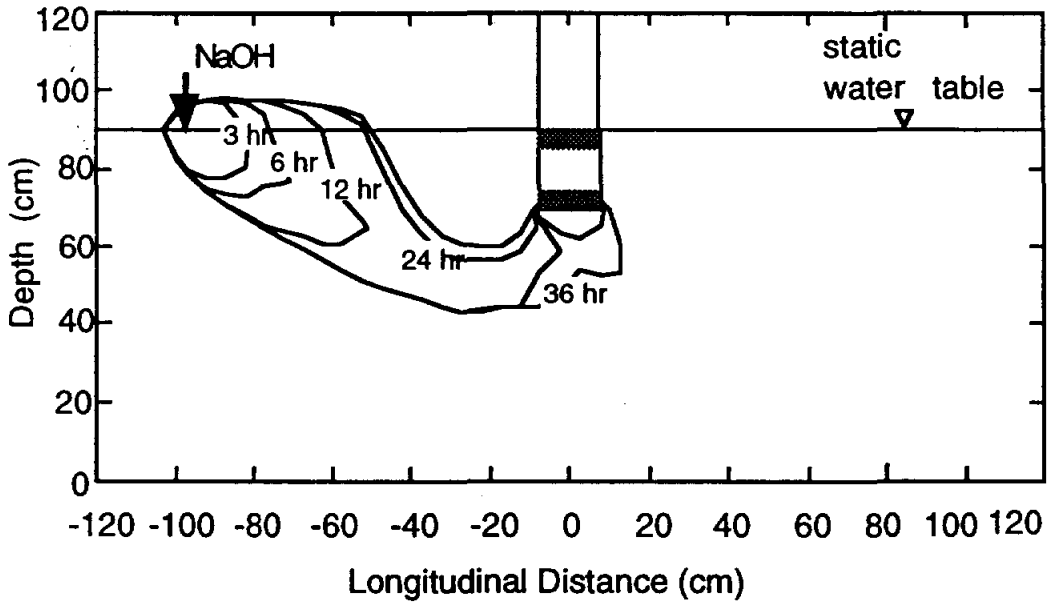


FIG 70. Case 4 Simulation of the Tracer Tests: 1 m/day Ambient Flow Velocity, 200 mL/min Well Recirculation Rate, and with a Surface Source of NaOH for Hydraulic Well 2

APPENDIX 2

SUPPLEMENTAL DATA ON BIOLOGICAL TREATMENT

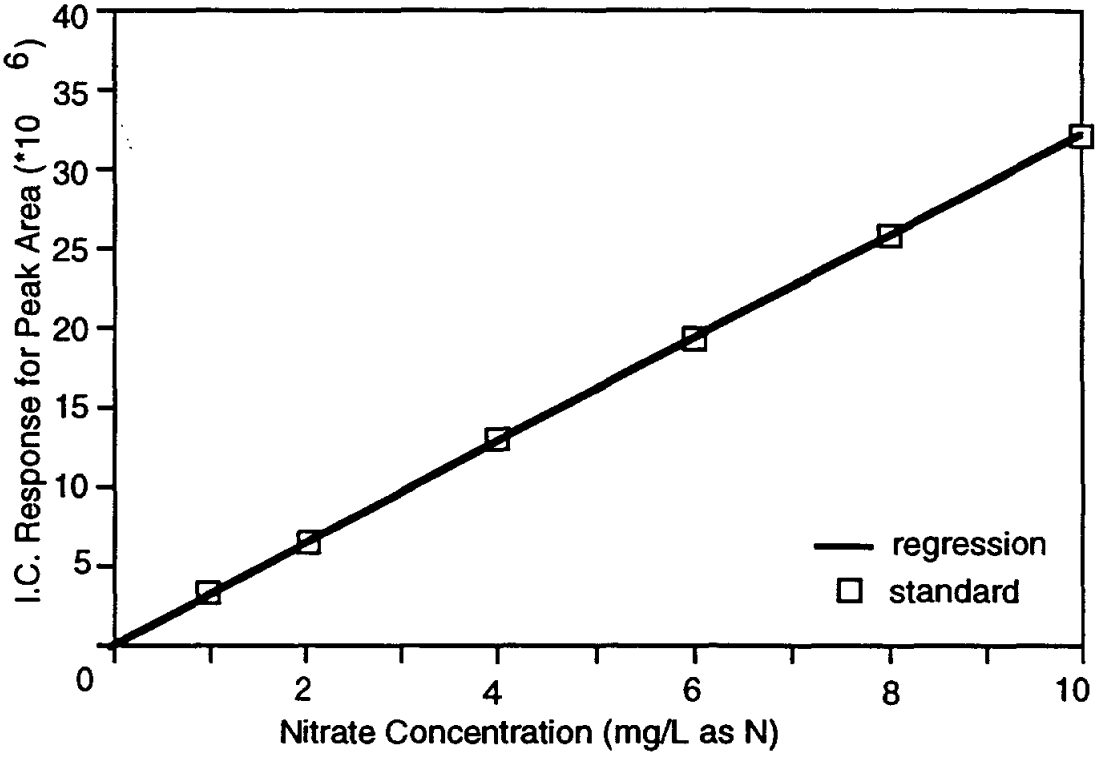


FIG 71. Calibration Curve of Nitrate Standards from the Ion Chromatography Outputs

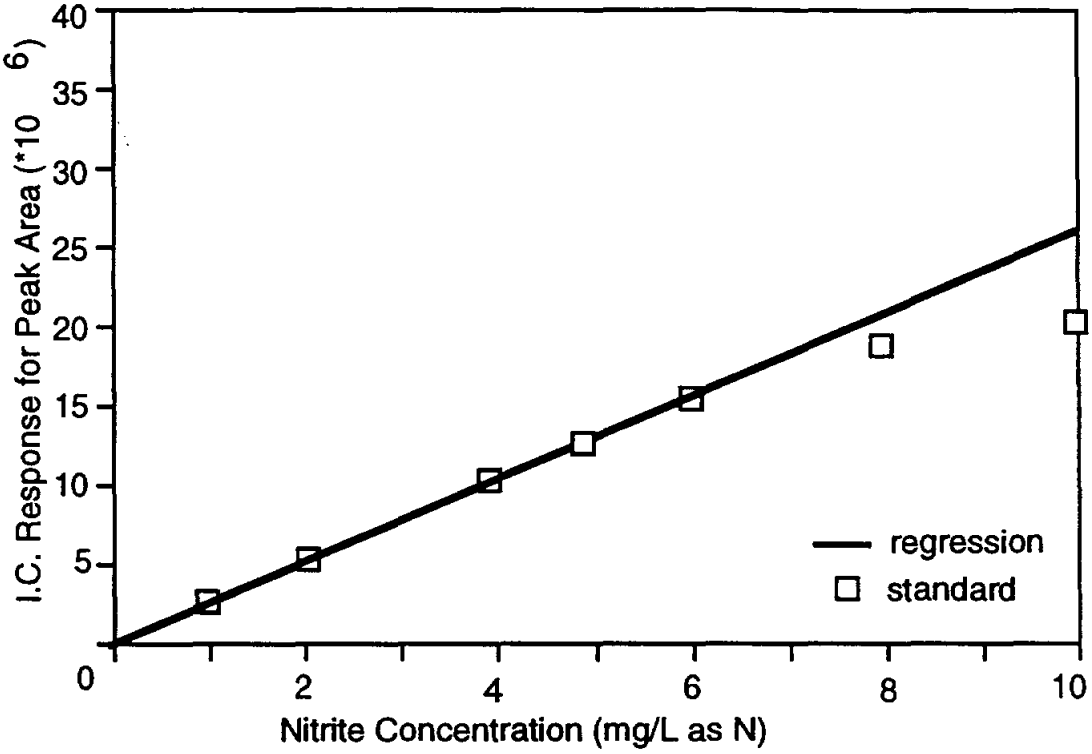


FIG 72. Calibration Curve of Nitrite Standards from the Ion Chromatography Outputs

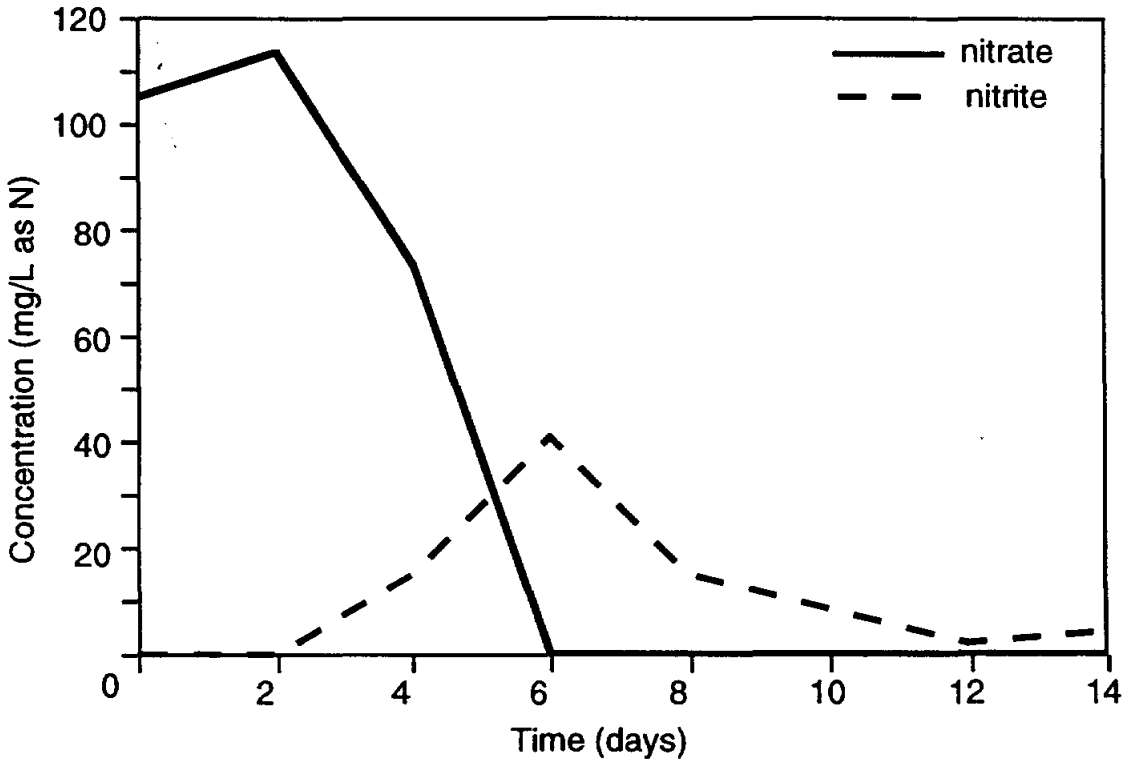


FIG 73. Progressive Curve of Biological Denitrification in the Batch Reactor with a Substrate Level of 400 mg/L COD

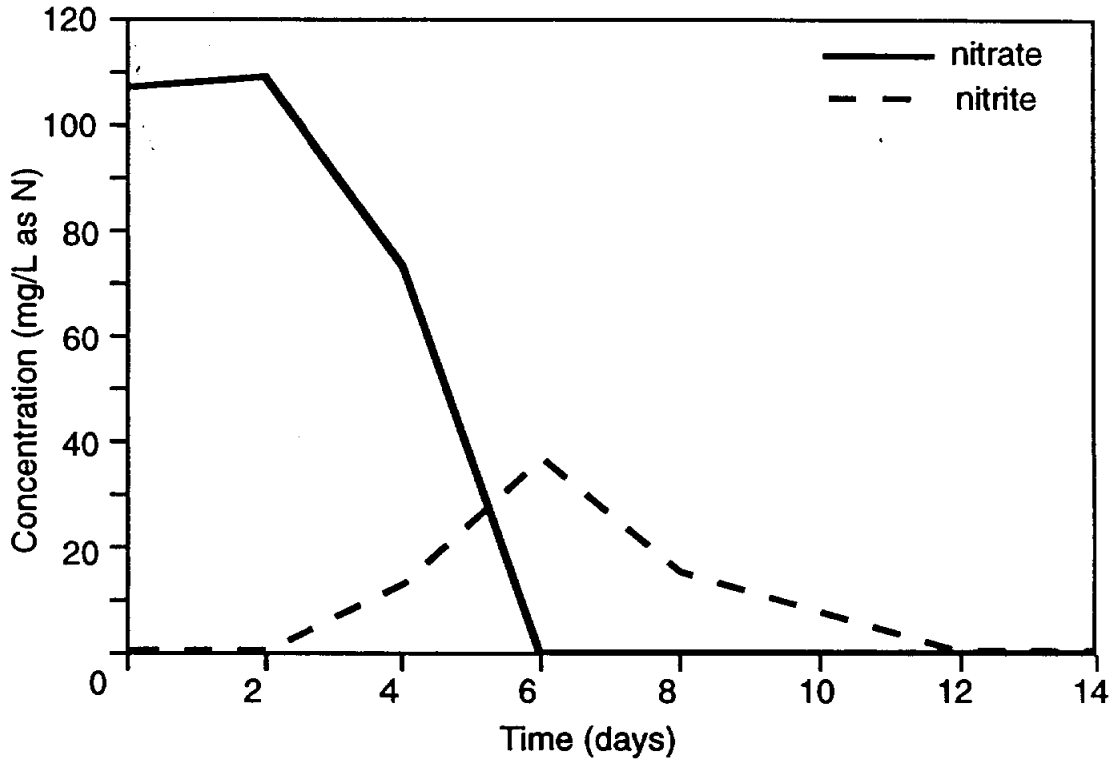


FIG 74. Progressive Curve of Biological Denitrification in the Batch Reactor with a Substrate Level of 600 mg/L COD

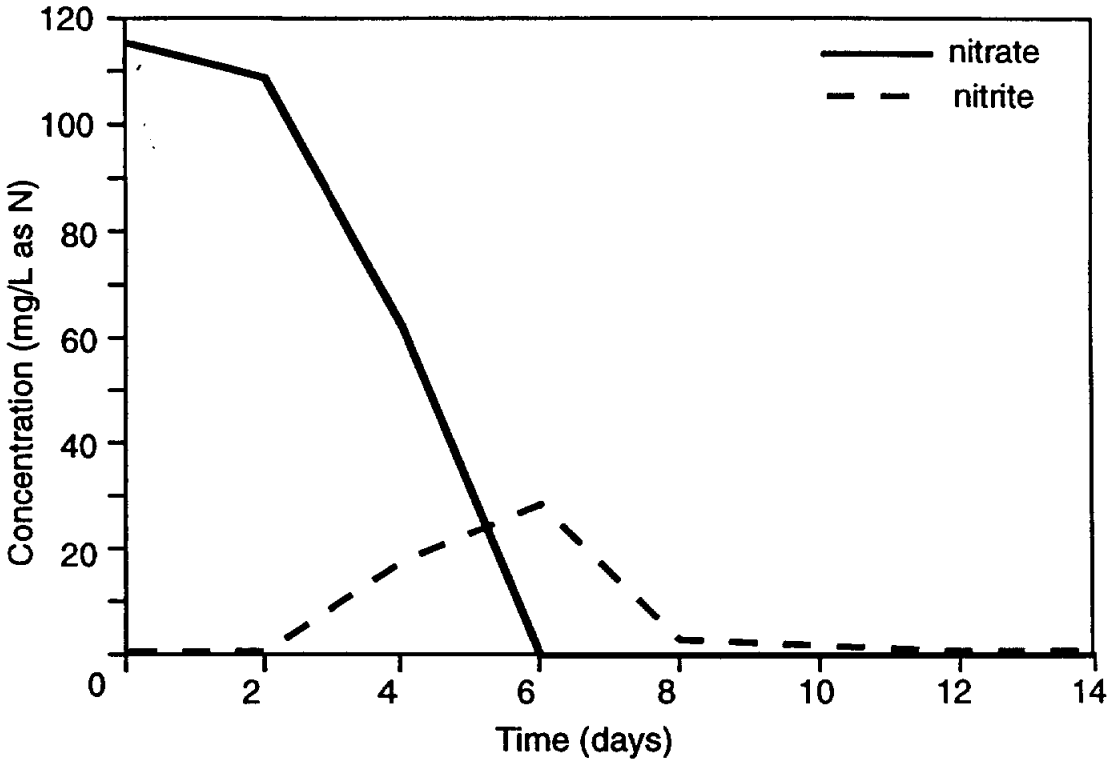


FIG 75. Progressive Curve of Biological Denitrification in the Batch Reactor with a Substrate Level of 800 mg/L COD

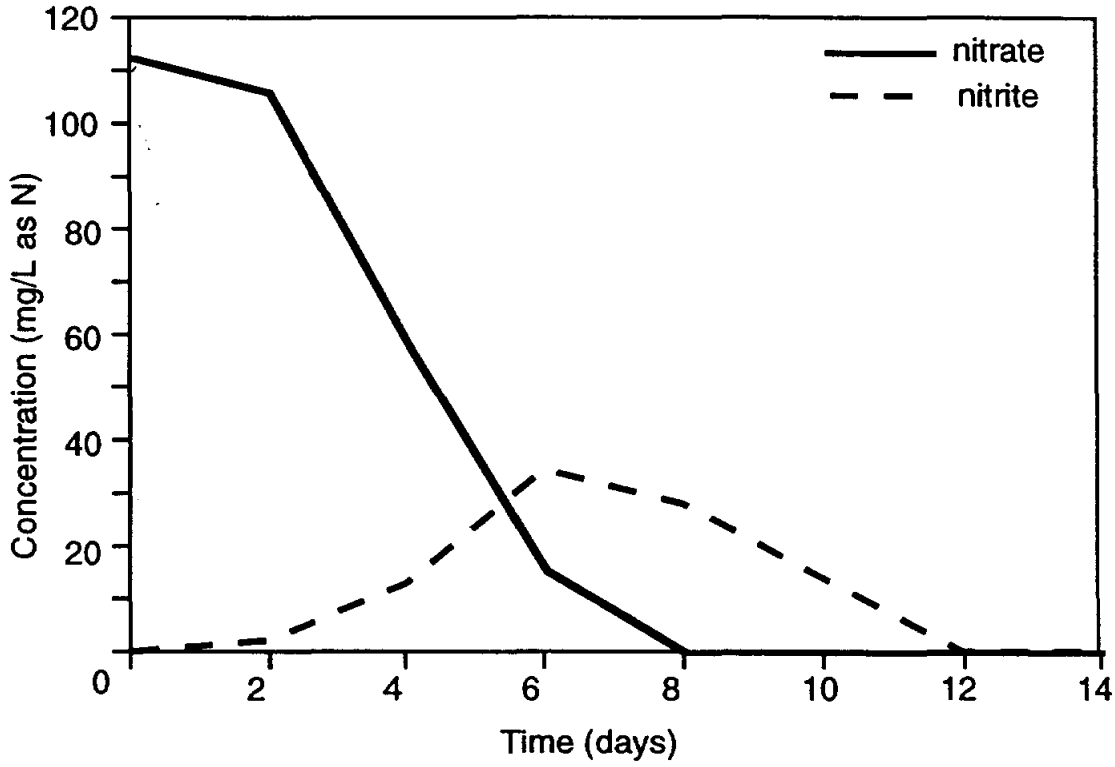


FIG 76. Progressive Curve of Biological Denitrification in the Batch Reactor with a Substrate Level of 1,000 mg/L COD

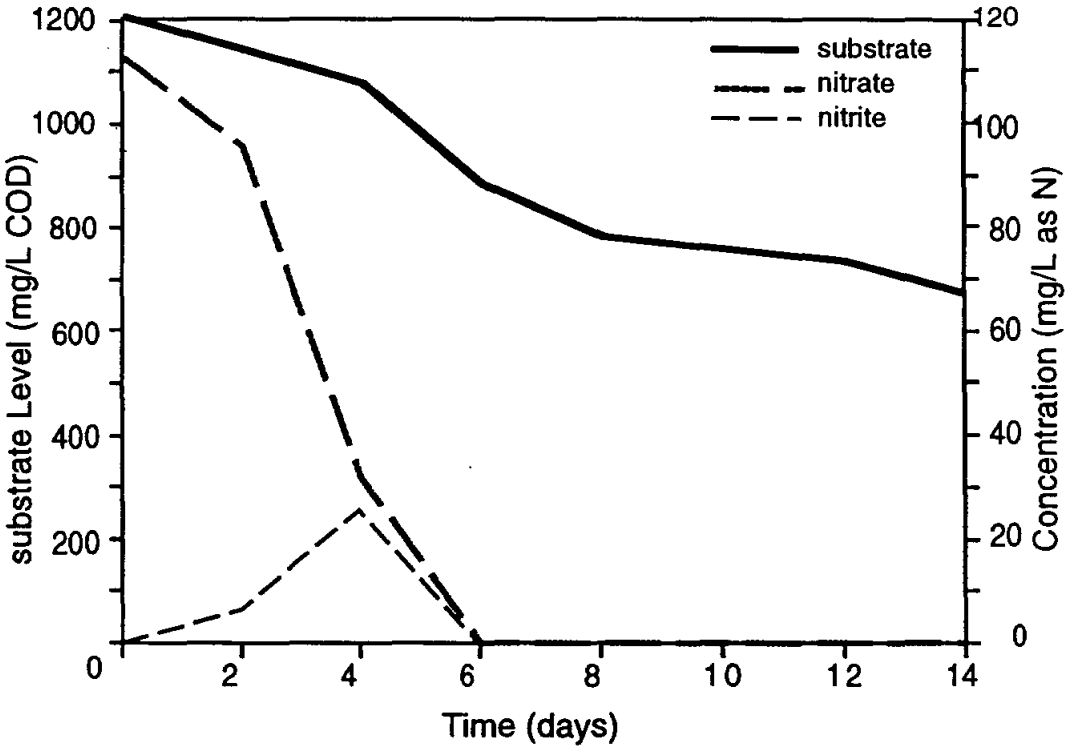


FIG 77. Progressive Curves of Substrate Uptake, Nitrate Reduction, and Nitrite Formation in the Batch Reactor with an Initial Level of 1,200 mg/L COD and 110 mg/L NO_3^- as N (Test 2)

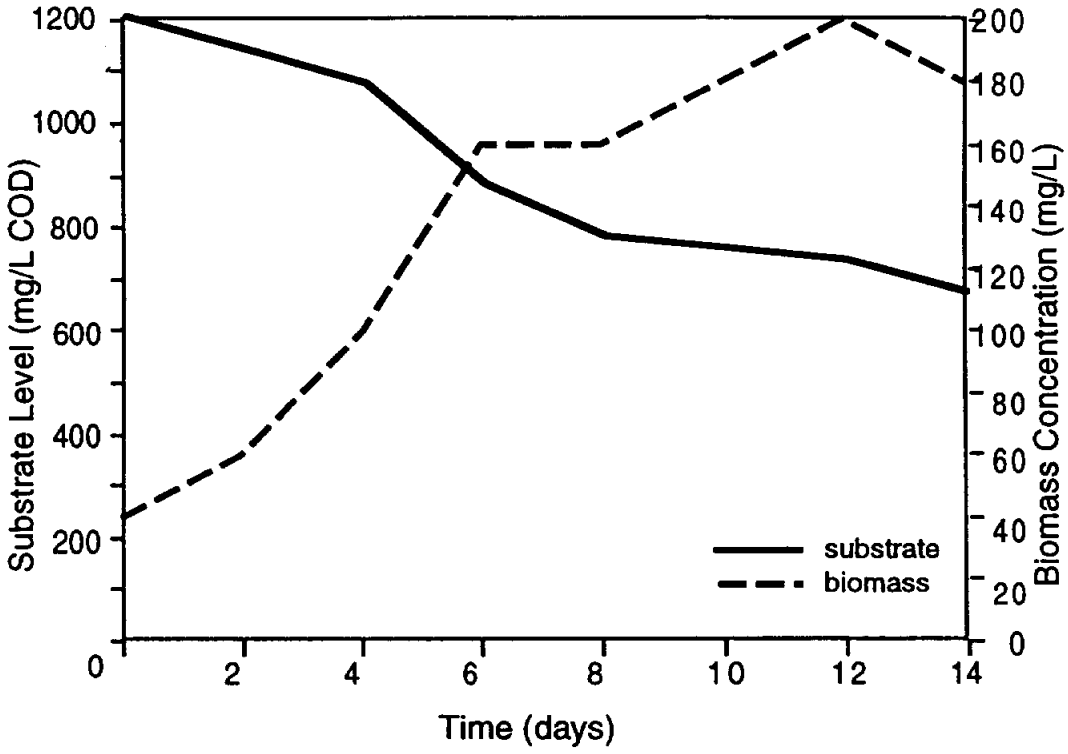


FIG 78. Progressive Curves of Substrate Uptake and Biomass Growth in the Batch Reactor with an Initial Level of 1,200 mg/L COD and 110 mg/L NO_3^- as N (Test 2)

APPENDIX 3

SOFTWARE OF AUTOMATED SYSTEM CONTROL

```
10 SCREEN 0
20 CLS
30 COLOR 3
40 PRINT " "
50 PRINT TAB(10); "*********************************************************"
60 PRINT TAB(10); "*                                                       *"
70 PRINT TAB(10); "*          Automated System Control of Carbon Feeding   *"
80 PRINT TAB(10); "*          for a Recirculating Nitrate Treatment Well System *"
90 PRINT TAB(10); "*                                                       *"
100 PRINT TAB(10); "*          DATA ACQUISITION: AC jr board                *"
110 PRINT TAB(10);"*          FEEDING CONTROL : 665 DOSIMAT                *"
120 PRINT TAB(10); "*                                                       *"
130 PRINT TAB(10); "*          Programmed by  K.C. WU                       *"
140 PRINT TAB(10); "*                         March, 1994                   *"
150 PRINT TAB(10); "*                         ASC Ver. 1.01                 *"
160 PRINT TAB(10); "*                                                       *"
170 PRINT TAB(10); "*********************************************************"
180 PRINT " "
190 PRINT " "
200 PRINT TAB(15);"PLEASE TURN ON THE ION/MV METER AND 665 DOSIMAT"
210 PRINT TAB(15);"IF READY THEN PRESS ANY KEY TO CONTINUE"
220 W$ = INKEY$: IF W$ = "" THEN 220
230 PRINT " "
400 'INSTANEOUS DATA READING AND SAVING TO EXTERNAL FILES
410 '
420 ' *** DIMENSIONING VARIOUS PARAMETERS (A%s AND Bs) ***
430 REM SN%=8:SM%=15                    'No. of analog and digital channels
440 REM DIM A%(15), B(15)               'ALLOW for 16 channels & I/O's
450 DIM X(2, 20), Y(2, 20), XP(2, 20), YP(2, 20)
460 DIM AV(20), MV(20)
470 '
500 ' ***** PROLOGUE *****
510 ' THIS CODE CHECKS FOR THE PRESENCE OF THE DRIVER BEFORE TRYING TO USE IT
520 ' ADAPTED FROM THE ACQ MANUAL P. 143. AND ASUBR.BAS FILE IN DEVELOPMENT
      SYSTEM DISK
530 '
540 DATA &H50, &HE8, &H18, &H00, &H3D, &HFF, &HFF, &H74, &H0C, &H58, &HFA, &HB8,
      &H59, &H47, &HCD, &H60, &H90, &H90, &HCA, &H06, &H00, &HB8, &HFF, &HFF,
      &H5D, &HCA, &H06, &H00, &H56, &H06, &HB8, &H00, &H00, &H8E, &HC0, &H26,
      &HA1, &H80, &H01, &H3D, &H00, &H00, &H74, &H1A, &H8B, &HF0, &H26
550 DATA &HA1, &H82, &H01, &H3D, &H00, &H00, &H74, &H0F, &H8E, &HC0, &H26, &H8A,
      &H04, &H3C, &H3D, &H75, &H06, &H07, &H5E, &HB8, &H00, &H00, &HC3, &HB8,
      &HFF, &HFF, &H07, &H5E, &HC3,0
560 DEF SEG
570 APROG$ = SPACE$(80): APROG1$ = SPACE$(80)
580 A% = VARPTR(APROG$): AM1 = PEEK(A% + 1) + PEEK(A% + 2) * 256
590 AX% = VARPTR(APROG1$): AM2 = PEEK(AX% + 1) + PEEK(AX% + 2) * 256
600 RESTORE 540
610 FOR I = 0 TO 76                     'INSTALL routine to call driver
620     READ A%
630     POKE I + AM1, A%
640     POKE I + AM2, A%
650 NEXT I
660 POKE AM2 + 19, 16
670 POKE AM2 + 26, 16
680 C$ = "Fn" + CHR$(0)
```

```
690 CALL AM1(A%(0), B(0), C$)
700 PRINT " "                                   ' Get no. of chans & I/O's installed
710 IF A%(0) = 0 AND A%(2) = 0 THEN PRINT "Driver, ADRIVE.COM, not installed, or analog card
        not installed.": END
720 IF A%(0) = 0 AND A%(2) <> 0 THEN PRINT "No analog card selected.  BRD SEL switch set to 0.":
        END
730 IF A%(0) <> 0 AND A%(6) = 0 THEN PRINT "CALIB.DAT file not correct or FIND.EXE was not
        run.": END
740 IF A%(0) > A%(6) THEN PRINT "Calibration numbers are not correct.": END
750 IF A%(0) > 16 OR A%(2) > 16 THEN PRINT "Too many channels installed.  Change DIM statement
        on line 240.": END
760 '
770 ' ***** END OF PROLOGUE *****
780 '
800 ' INITIAL SETUP OF I/O's, RANGE, AND RESOLUTION
810 DEF SEG
820 C$ = "a" + CHR$(0)
830 A%(0) = 12                                  'Set initial resolution to 12-bit
840 CALL AM1(A%(0), B(0), C$)
850 REM RANGE CODE IS ADAPTED FROM THE ACQ MANUAL P.185
860 REM RANGE -- 0=50 mV, 1=500 mV, 2=10 V, 3=+/-25 mV, 4=+/-250 mV, 5=+/- 5 V
870 REM RANGE -- 6=2 mA, 7=20 mA, 8=+/-1 mA, 9=+/-10 mA, 10=+/-50 mA
880 REM RANGE -- 16=autorange/UP V, 17=autorange/BP V, 18=autorange/UP C, 19=autorange/BP C
890 FOR A=0 TO SN% -1                           'Set initial range to auto
900       A%(0) = 16
910 NEXT A
920 C$ = "rc" + CHR$(0)
930 CALL AM1(A%(0), B(0), C$)
940 REM I/O CODE -- 0=input, 1=output
950 REM FOR A=0 TO SM%                          'Set I/O's to input or output
960   A%(0) = 0
970 REM NEXT A
980 C$ = "S" + CHR$(0)
990 CALL AM1(A%(0), B(0), C$)
1000 ' INITIAL SETUP OF OUTPUT FILES
1010 CLS
1020 R$="REGRESS.DAT"
1030 PRINT " "
1040 PRINT " "
1050 PRINT "HAVE YOU CALIBRATED THE ION PROBE ?" ;
1060 CA$=INKEY$: IF CA$="" THEN 1060
1070 IF CA$="Y" OR CA$="y" THEN GOTO 1100
1080 IF CA$="N" OR CA$="n" THEN GOTO 3000
1090 GOTO 1060
1100 PRINT CA$
1110 PRINT " "
1120 PRINT "Your calibration file is named as REGRESS.DAT (Y/N)?" ;
1130 CA$=INKEY$: IF CA$="" THEN 1130
1140 IF CA$="Y" OR CA$="y" THEN GOTO 1200
1150 IF CA$="N" OR CA$="n" THEN GOTO 1170
1160 GOTO 1130
1170 PRINT CA$
1180 PRINT " "
1190 INPUT "Enter the filename of your CALIBRATION FILE :", R$
1200 OPEN R$ FOR INPUT AS #2
1210 INPUT #2, SLOPE, INTER, RSQUA
```

```
1220 CLOSE 2
1300 ' SET COM1 AS RS232C REMOTE CONTROL
1310 KEY OFF
1320 OPEN "COM1:9600,E,7,1,LF" FOR RANDOM AS #1          '9600 baud,even parity
1330 OUT (&H3FC), 0
1340 EOT$ = CHR$(13) + CHR$(10) + CHR$(4)                'cr,lf,eot
1350 DIM s$(20), P(14)
1490 '
1500 ' ***** INPUT PROGRAM *****
1510 '
1520 ' Internal calibration of analog input
1530 C$ = "C" + CHR$(0)
1540 A%(0) = IC(0)
1550 CALL AM1(A%(0), B(0), C$)
1560 '
1600 CLS
1610 PRINT " "
1620 PRINT TAB(10); "******   THIS IS THE MAIN MENU   ******"
1630 PRINT " "
1640 PRINT "CHOOSE THE COMMAD AT YOUR WILL BY THE CORRESPONDENT NUMBER"
1650 PRINT " "
1660 PRINT "  RESOLUTION SETUP OF ANALOG INPUT CHANNELS          1"
1670 PRINT " "
1680 PRINT "  INPUT RANGE SETUP OF ANALOG INPUT CHANNELS         2"
1690 PRINT " "
1700 PRINT "  LINEAR CALIBRATION OF ANALOG INPUT CHANNELS        3"
1710 PRINT " "
1720 PRINT "  MANUAL CONTROL OF FEEDING DEVICE                  4"
1730 PRINT " "
1740 PRINT "  RUN ON-LINE DATA ACQUISITION & CONTROL            5"
1750 PRINT " "
1760 PRINT "  EXIT PROGRAM                                      6"
1770 PRINT " "
1780 INPUT "ENTER THE NUMBER OF DESIRED COMMAND : ", X
1790 PRINT " "
1800 PRINT " "
1810 IF X = 1 GOTO 2000
1820 IF X = 2 GOTO 2500
1830 IF X = 3 GOTO 3000
1840 IF X = 4 GOTO 8000
1850 IF X = 5 GOTO 5000
1860 IF X > 6 OR X < 1 GOTO 1780
1870 '
1900 '******   EXIT PROGRAM   ******
1910 REM FOR I=1 TO N-1
1920   CLOSE 3
1930 REM NEXT I
1940 PRINT "THE PROGRAM HAS BEEN TERMIATED."
1950 PRINT " "
1960 PRINT "TYPE 'RUN ASC.BAS ' TO REBOOT THE PROGRAM OR"
1970 PRINT "TYPE 'SYSTEM' TO ENTER DOS PROMPT"
1980 IF X = 7 THEN END
1990 '
2000 'RESOLUTION SETUP ROUTINE
2010 CLS
2020 PRINT " "
```

```
2030 PRINT " "
2040 PRINT "THIS TABLE LISTS THE CODE OF RESOLUTIONS FOR EACH INPUT CHANNEL : "
2050 PRINT " "
2060 PRINT " 9-bit for a 12-bit card    1   10-bit for a 12-bit card       2"
2070 PRINT " "
2080 PRINT " 11-bit for a 12-bit card   3   12-bit for a 12-bit/18-bit card  4"
2090 PRINT " "
2100 PRINT " 13-bit for a 18-bit card   5   14-bit for a 18-bit card       6"
2110 PRINT " "
2120 PRINT " 15-bit for a 18-bit card   7   16-bit for a 18-bit card       8"
2130 PRINT " "
2140 PRINT " 18-bit for a 12-bit/18-bit card (low noise mode)              10"
2150 PRINT " "
2160 REM FOR I= 0 TO N-1
2170   INPUT "DESIRED RESOLUTION FOR CHANNEL 1 :", B$
2180     IF B$ = "" GOTO 2170
2190     IF VAL(B$) = 9 OR VAL(B$) < 1 OR VAL(B$) > 10 GOTO 2170
2200     A%(0) = 8 + VAL(B$)
2210     PRINT B$: PRINT
2220 REM NEXT I
2230 C$ = "A" + CHR$(0)
2240 CALL AM1(A%(0), B(0), C$)
2250 GOTO 1600
2260 '
2500 'INPUT RANGE SETUP ROUTINE
2510 CLS
2520 PRINT " "
2530 PRINT " "
2540 PRINT "THIS TABLE LISTS THE INPUT RANGE OF ANALOG INPUT CHANNEL : "
2550 PRINT " "
2560 PRINT "   +/- 25 mV          1      +/-1 mA          2"
2570 PRINT " "
2580 PRINT "   +/- 250 mV         3      +/-10 mA         4"
2590 PRINT " "
2600 PRINT "   +/- 5 V            5      +/-50 mA         6"
2610 PRINT " "
2620 PRINT "   +Autorange/voltage  7"
2630 PRINT " "
2640 FOR I= 0 TO N-1
2650     PRINT "DESIRED INPUT RANGE FOR CHANNEL 1 :";
2660     B$ = INKEY$: IF B$ = "" GOTO 2660
2670     IF VAL(B$) < 1 OR VAL(B$) > 7 GOTO 2660
2680     IF B$ = "1" THEN A%(0) = 3
2690     IF B$ = "2" THEN A%(0) = 8
2700     IF B$ = "3" THEN A%(0) = 4
2710     IF B$ = "4" THEN A%(0) = 9
2720     IF B$ = "5" THEN A%(0) = 5
2730     IF B$ = "6" THEN A%(0) = 6
2740     IF B$ = "7" THEN A%(0) = 16
2750     PRINT B$: PRINT
2760 NEXT I
2770 C$ = "rc" + CHR$(0)
2780 CALL AM1(A%(0), B(0), C$)
2790 GOTO 1600
2800 '
3000 ' ***** LINEAR CALIBRATION *****
```

```
3010 REM MV -- measured value (mV), AV -- actual value (mg/l)
3020 REM typical nitrate electrode calibration curve MV = K - 56*LOG(AV)
3030 CLS
3040 AVTOT = 0: MVTOT = 0
3050 SXX = 0: SYY = 0: SXY = 0
3060 C$ = "h" + CHR$(0)
3070 PRINT " "
3080 PRINT " "
3090 PRINT "YOU HAVE ENTERED CALIBRATION MODE."
3100 PRINT " "
3110 PRINT "PLEASE PREPARE AT LEAST THREE NITRATE STANDARDS FOR
       CALIBRATION."
3120 PRINT " "
3130 PRINT "DO YOU WANT TO CONTINUE CALIBRATION ?"
3140 INPUT "IF NO PROGRAM GOES BACK TO MAIN MENU (Y/N) ", Z$
3150 PRINT " "
3160 PRINT " "
3170 IF Z$ = "Y" OR Z$ = "y" GOTO 3200
3180 IF Z$ = "N" OR Z$ = "n" GOTO 1600
3190 GOTO 3130
3200 CLS
3210 INPUT "No. of Calibration Points "; CP
3220 PRINT " "
3230 FOR I = 1 TO CP
3240    MVSUBTOT = 0:
3250    LOCATE 3 + I * 2, 1: INPUT "CONCENTRATION OF STANDARD SOLUTION "; AV(I)
3260    LOCATE 20, 5: COLOR 15
3270    PRINT "PLEASE PUT ION PROBE INTO STANDARD SOLUTION AND STIR IT"
3280    PRINT "NOTE !!!  ALLOW 1 MINUTE FOR STABILIZATION"
3290    PRINT "If Ready Then Press ANYKEY to Calibrate Point #"; I
3300    Z$ = INKEY$: IF Z$ = "" THEN 3300
3310    LOCATE 20, 5: COLOR 3
3320    PRINT "                                                "
3330    PRINT "                                                "
3340    PRINT "                                                "
3350    FOR J = 1 TO 100
3360            CALL AM1(A%(0), B(0), C$)
3370            MVSUBTOT = MVSUBTOT + B(0)
3380    NEXT J
3390    MV(I) = MVSUBTOT / 100
3400    AVTOT = AVTOT + LOG(AV(I))
3410    MVTOT = MVTOT + MV(I)
3420 NEXT I
3430 AVAVG = AVTOT / CP
3440 MVAVG = MVTOT / CP
3450 FOR I = 1 TO CP
3460    SXX = SXX + (LOG(AV(I)) - AVAVG) ^ 2
3470    SYY = SYY + (MV(I) - MVAVG) ^ 2
3480    SXY = SXY + (LOG(AV(I)) - AVAVG) * (MV(I) - MVAVG)
3490 NEXT I
3500 'LINEAR REGRESSION
3510 SLOPE = SXY / SXX
3520 INTER = MVAVG - SLOPE * AVAVG
3530 RSQUA = SXY ^ 2 / SXX / SYY
3540 CLS
3550 PRINT " "
```

```
3560 PRINT " "
3570 PRINT TAB(10); "REGRESSION OUTPUT"
3580 PRINT TAB(10); "----------------"
3590 PRINT TAB(10); "Slope    : "; SLOPE
3600 PRINT TAB(10); "Intercept: "; INTER
3610 PRINT TAB(10); "R-Square : "; RSQUA
3620 PRINT " "
3630 PRINT " "
3640 LOCATE 20, 5: COLOR 15
3650   PRINT "REGRESSION OUTPUT has been Saved as REGRESS.DAT automatically."
3660   PRINT "DO YOU WANT TO SAVE AS ANOTHER NAME (Y/N) ?"
3670   PRINT "IF NO THEN Return to MAIN MENU."
3680 A$ = INKEY$: IF A$ = "" THEN 3680
3690 LOCATE 20, 5: COLOR 3
3700   PRINT "                                                    "
3710   PRINT "                                                    "
3720   PRINT "                                                    "
3730 R$ = "REGRESS.DAT"
3740 IF A$ = "Y" OR "y" THEN GOTO 3770
3750 IF A$ = "N" OR "n" THEN GOTO 3780
3760 GOTO 3640
3770 INPUT "ENTER THE NAME OF FILE TO SAVE REGRESSION OUTPUT "; R$
3780 OPEN R$ FOR OUTPUT AS #2
3790 PRINT #2, SLOPE, INTER, RSQUA
3800 CLOSE 2
3810 GOTO 1600
3820 ' ***** END OF LINEAR CALIBRATION *****
3830 '
4000 ' * GET CLOCK SUBROUTINE *
4010 ' APPLY TIME FUNCTION(TIME$) AND DATE FUNCTION(DATE$)
4020 SC=61: MN=61
4030 T$=TIME$
4040 D$=DATE$
4050 MIN=VAL(MID$(T$,4,2))
4060 SEC=VAL(MID$(T$,7,2))
4070 LOCATE 22,2:COLOR 3
4080 IF SEC<>SC THEN PRINT; T$                'SHOW TIME ON SCREEN
4090 LOCATE 23,2:COLOR 3
4100 IF SEC<>SC THEN PRINT; D$
4105 LOCATE 3,55:PRINT "MV :";TOT/100
4110 SC=SEC
4120 IF MIN-MN=1 THEN GOTO 4150               'SET DELAY FOR 1 MIN
4130 MN=MIN
4140 GOTO 4030
4150 RETURN
4160 ' * END OF GET CLOCK SUBROUTINE *
4170 '
5000 ' ***** ON-LINE MEASUREMENT *****
5001 s$ = "REM ON" + EOT$
5002 GOSUB 11000
5003 s$ = "DOS" + EOT$                        ' SET MODE ON 665 DOSIMAT
5004 GOSUB 11000
5010 ' OUTPUT FILE NAMING
5020 CLS
5030 PRINT " "
5040 PRINT " "
```

```
5050 PRINT TAB(10);"YOU HAVE ENTERED ON-LINE MEASUREMENT MODE."
5060 PRINT " "
5070 PRINT "ON-LINE MEASUREMENT DATA will be logged in ONLINE.OUT automatically."
5080 PRINT "DO YOU WANT TO USE ANOTHER NAME FOR OUTPUT FILE (Y/N) ?"
5090 PRINT "IF NO THEN start ON-LINE MEASUREMENT."
5100 F$ = INKEY$: IF F$ = "" THEN 5100
5110 IF F$ = "Y" OR F$ = "y" THEN GOTO 5140
5120 IF F$ = "N" OR F$ = "n" THEN GOTO 5160
5130 GOTO 5100
5140 INPUT "ENTER THE OUTPUT FILENAME FOR LOGGING DATA "; O$
5150 GOTO 5170
5160 O$ = "ONLINE.OUT"
5170 OPEN O$ FOR OUTPUT AS #3
5180 '
5200 'DATA READING
5210 CLS
5220 SCREEN 9
5230 LINE (0,0)-(639,349),1,B
5240 YL=0
5250 'DATA READING
5260 LOCATE 1,30: PRINT"On-line Measurements"
5270 'LOCATE 2,30: PRINT"-----------------"
5280 LOCATE 3,20: PRINT"CONCENTRATION :"
5300 C$ = "h" + CHR$(0)                          'READ DATA FROM ANALOG INPUT
5310 A%(0)=1:TOT = 0
5320 FOR J = 1 TO 100
5330   CALL AM1(A%(0), B(0), C$)
5340   TOT = TOT + B(0)
5350 NEXT J
5360 OLM = EXP((TOT/100-INTER) / SLOPE)
5370 LOCATE 3, 35
5380   PRINT  OLM; " mg/l"
5390 '
5500 GOSUB 4000                                  ' SET DELAY FOR 1 min
5520 PRINT #3, MN, OLM                           ' DATA LOGGING ON DISK
5530 GOSUB 6000                                  ' PLOT DATA ON SCREEN
5540 GOSUB 9000                                  ' FEEDING CONTROL
5550 LOCATE 22, 15:COLOR 5
5560   PRINT "MEASUREMENT have been logged in "; O$;" once per minute."
5570 LOCATE 23, 15:COLOR 5
5580   PRINT "Press 'B' to stop ON-LINE MEASUREMENT."
5590 J$=INKEY$
5600   IF J$="" THEN GOTO 5300
5610   IF J$="B" OR J$="b" THEN CLOSE 3 : SCREEN 0 :COLOR 3: GOTO 1600
5620 GOTO 5300
5980 ' *****   END OF ON-LINE MEASUREMENT   *****
5990 '
6000 ' *** GRAPHING SUBROUTINE ***
6010 'DRAWING BOX & SCALE
6020 LINE (59, 19)-(599, 259), 3, B
6030 XAXIS = 540 / 60                            ' SET X-AXIS FOR 1 HOUR RANGE
6040 YAXIS = 240 / 120                           ' SET Y-AXIS FOR 120 mg/l RANGE
6050 FOR I = 0 TO 12                             ' PLOT X-AXIS and Y-AXIS SCALE
6060   LINE (54, 19 + (I) * 20)-(59, 19 + (I) * 20), 3
6070   LINE (59 + (I) * 45, 259)-(59 + (I) * 45, 264), 3
6080 NEXT I
```

```
6090 XU = 59 + (MN) * XAXIS
6100 YU = 259 - (OLM) * YAXIS
6110 IF YL=0 THEN GOTO 6130
6115 IF XU=59 THEN GOTO 6130
6120 LINE (XL, YL)-(XU, YU), 13
6130 XL=XU
6140 YL=YU
6150 LOCATE 2, 1                          'MARK Y-axis scale
6160   PRINT "120 mg/l"
6170 LOCATE 19, 1
6180   PRINT "0 mg                        'MARK X-axis scale
6200   PRINT "0 min"
6210 LOCATE 20, 74
6220   PRINT "60 min"
6230 IF XU = 590 THEN GOTO 6300
6240 RETURN
6300 CLS                                  ' RESET screen for new plot
6310 SCREEN 9
6320 LINE (0,0)-(639,349),1,B
6340 YL=0
6350 LOCATE 1,30: PRINT"On-line Measurements"
6360 LOCATE 3,20: PRINT"CONCENTRATION :"
6370 GOTO 5300
6380 ' *** END OF GRAPHING SUBROUTINE ***
6390 '
8000 ' *** REMOTE OFF ***
8050 s$ = "REM OFF" + EOT$
8060 GOSUB 11000
8070 CLS
8080 PRINT "THE REMOTE MODE IS OFF"
8090 KEY ON
8100 GOTO 1600
9000 '*** CALCULATION OF CARON REQUIREMENT ***
9010 REM THE CONTROL CRITERIA USES C:N RATIO= 0.81
9020 CFR=0.81*OLM
9030 Z$=STR$(2*CFR*50/5000)               'CFR*Q = C* Z$
9040 IF VAL(Z$)>1.0 THEN LET Z$=1.0
9050 LOCATE 4,20: PRINT"CARBON AMENDMENT :",Z$," ml/min"
10000 '*** FEEDING DEVICE CONTROL BY ADJUSTING RATE ***
10110 s$ = "VLI" + Z$ + EOT$              ' SET LIMITING VOLUME
10120 GOSUB 11000
10130 s$ = "G" + CHR$(4)                  ' START COMMAND
10140 GOSUB 11000
10150 GOSUB 4000                          ' SET DELAY FOR 1 MIN
10160 s$ = "F" + CHR$(4)                  ' FILL COMMAND
10170 GOSUB 11000
10180 RETURN
11000 C% = 1                              ' SEND ROUTINE
11010 OUT (&H3FC), 2
11020 D% = INP(&H3FE)
11030 s% = D% AND 16
11040 FOR s% = 1 TO 500: NEXT s%
11050 D% = ASC(MID$(s$, C%, 1))
11060 OUT (&H3FC), 0
11070 OUT (&H3F8), D%
11080 C% = C% + 1
```

```
11090 IF MID$(s$, C%, 1) = CHR$(4) THEN RETURN
11100 GOTO 11010
```