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REMEDIATION OF GROUNDWATER CONTAMINATED WITH BENZENE (LNAPL) USING IN-SITU AIR SPARGING

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Abstract

This paper presents the results of laboratory investigation performed to study the role of different air sparging system parameters on the removal of benzene from saturated soils and groundwater. A series of one-dimensional experiments was conducted with predetermined contaminant concentrations and predetermined injected airflow rates and pressures to investigate the effect of soil type and the use of pulsed air injection on air sparging removal efficiency. On the basis of these studies, two-dimensional air sparging remediation systems were investigated to determine the effect of soil heterogeneity on the removal of benzene from three different homogeneous and heterogeneous soil profiles. This study demonstrated that the grain size of the soils affects the air sparging removal efficiency. Additionally, it was observed that pulsed air injection did not offer any appreciable enhancement to contaminant removal for the coarse sand; however, substantial reduction in system operating time was observed for fine sand. The 2-D experiments showed that air injected in coarse sand profiles traveled in channels within a parabolic zone. In well-graded sand the zone of influence was found to be wider due to high permeability and increased tortuosity of this soil type. The influence zone of heterogeneous soil (well-graded sand between coarse sand) showed the hybrid airflow patterns of the individual soil test. Overall, the mechanism of contaminant removal using air sparging from different soil conditions have been determined and discussed.

1. INTRODUCTION

Air sparging is a technique that has proven to be efficient for the remediation of saturated soils and groundwater that have been contaminated with volatile organic compounds (Ardito and Billings 1990; Reddy and Adams 1998). During air sparging, a gas, usually air, is injected into the subsurface below the lowest known point of contamination. Due to effects of buoyancy, the injected air will begin to rise through the saturated zone toward the surface. Through a variety of mass transfer processes, the contaminant is either transferred into the migrating air or oxygen is transferred into the subsurface, effectively stripping or assisting in the degradation of the contaminant. As the contaminant-laden air continues to rise, it encounters the vadose zone, where it is captured using a soil vapor extraction system (Reddy et al. 1995). Air sparging owes its effectiveness to a variety of mass transfer mechanisms, including volatilization, dissolution, adsorption/desorption, and biodegradation, as well as transport processes, including advection, dispersion, and diffusion that have been described in detail by Semer and Reddy (1997).

When volatile organic contaminants are released into the saturated subsurface, they commonly exist in dissolved phase as well as free or non-aqueous-phase liquids (NAPL). Volatile organic compounds that commonly contribute to subsurface contamination (such as BTEX, chlorinated solvents and petroleum compounds) often have low water solubilities; therefore, the contaminant often exists in the NAPL phase. Contamination that has dissolved into the groundwater will migrate with groundwater flow. When contaminant exists in NAPL phase, groundwater flow may still induce migration through different mass transport mechanisms, including advection. Additionally, if the contaminant is lighter than water, commonly referred to as light NAPLs (LNAPLs), the contaminant may float on the water table, forming a NAPL-phase pool. When water table levels fluctuate, the pool may be smeared, contributing to contaminant entrapment within the soil pores.

Many studies have been performed to assess air sparging, involving either the evaluation of field studies, physical models or mathematical models, assuming that contaminant exists as dissolved phase. The effectiveness of such air sparging experiments depends primarily on two factors:

(1) Vapor/dissolved phase partitioning of the constituents determines the equilibrium distribution of a constituent between the dissolved phase and the vapor phase. Vapor/dissolved phase partitioning is, therefore, a significant factor in determining the rate at which dissolved constituents can be transferred to the vapor phase.

(2) Permeability of the soil determines the rate at which air can be injected into the saturated zone. It is the other significant factor in determining the mass transfer rate of the constituents from the dissolved phase to the vapor phase.

In general, air sparging is more effective for constituents with greater volatility and lower solubility and for soils with higher permeability. The rate at which the constituent mass will be removed decreases as air sparging operations proceed and concentrations of dissolved constituents are reduced. Soil characteristics will also determine the preferred zones of vapor flow in the vadose zone, thereby indicating the ease with which vapors can be controlled and extracted using SVE (if used). Stratified or highly variable heterogeneous soils typically create the greatest barriers to air sparging. Both the injected air and the stripped vapors will travel along the paths of least resistance (coarse-grained zones) and could travel a great lateral distance from the injection point. This phenomenon could result in the contaminant-laden sparge vapors migrating outside the vapor extraction control area. Currently, the design of air sparging systems for field implementation is based on an empirical approach that relies heavily on limited past experience and past tests that have been performed on-site (Brown et al. 1991; Marley et al. 1992; Schima et al. 1996). Unfortunately, the findings of these few site-specific previous investigations may lead to either overdesign or underdesign of the actual air sparging systems at other sites.

To develop a rational design basis for air sparging systems, a comprehensive research program has been under way at the University of Illinois at Chicago (UIC) since 1993. This paper provides an overview of the 1-D as well as 2-D air sparging laboratory experiments that were performed at UIC to investigate the effects of system variables-particularly the soil type, the mode of air injection, and subsurface heterogeneities on air sparging removal efficiency.

2. EXPERIMENTAL METHODOLOGY

2.1 One-Dimensional Test Setup and Testing Program

A one-dimensional apparatus consisting of a Plexiglas column 93 cm in height and 9 cm in diameter was used for the testing. A schematic of this apparatus is shown in Figure 1 and has been described in detail by Reddy and Adams (1998).

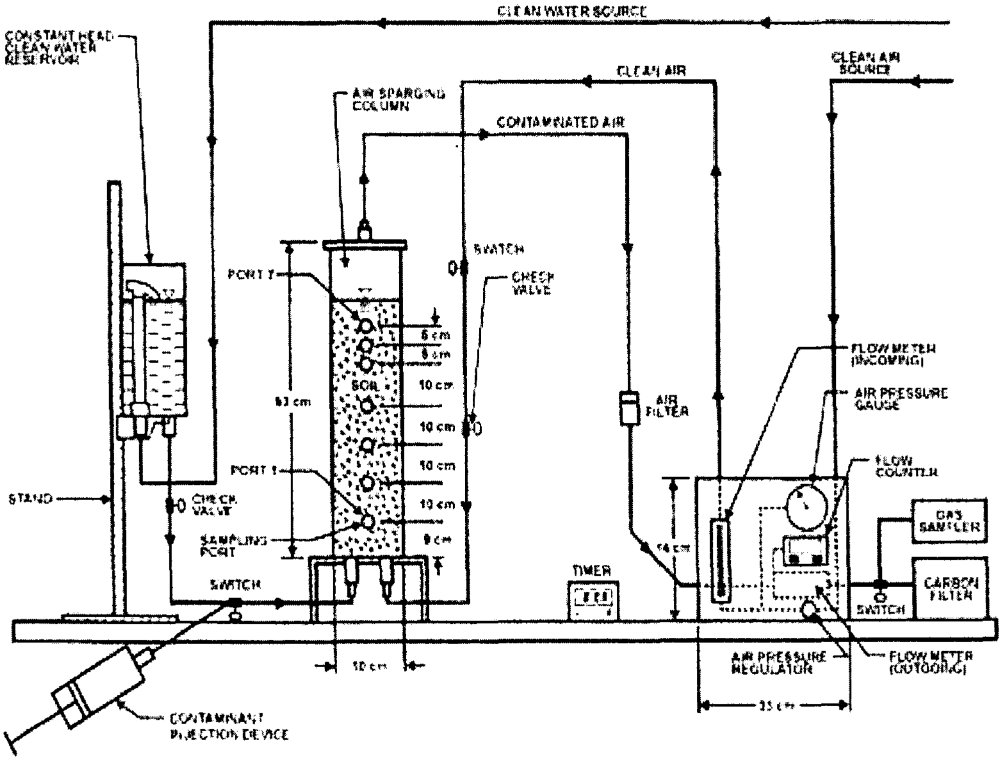


Fig. 1. Schematic of Air Sparging Column Test Setup

A special contaminant injection device was used to prevent volatilization losses before injection into the soil. The device was designed to prevent any head space during injection. The test column itself featured seven sampling ports spaced 5-10 cm apart. A gas-tight syringe was used to extract pore water from various ports along the column. Once the soil had been loaded into the column and saturated with the contaminant, the initial dissolved contaminant profile within the soil column was determined by sampling the contaminated pore water from the sampling ports. These samples were then analyzed using gas chromatography (GC). After the determination of the initial dissolved concentration profile, the air injection procedure began. Pore water was sampled at different time intervals to monitor the concentration profiles and the removal times. In addition the effluent gas was sampled at different time intervals and analyzed using GC. The reproducibility of the testing was verified by performing selected duplicate tests with identical conditions.

Benzene (300 mg/L) was chosen as the VOC contaminant for all the tests. Five different clean soils namely fine gravel, well graded sand, and three differently (or poorly) graded sands denoted here as coarse sand, medium sand, and fine sand, were chosen to determine the effect of soil grain size and distribution on the efficiency of air sparging system. All the tests were conducted with an air injection rate of 2225 mL/min under a pressure of 6.9 kPa. Effect of pulsed air injection was also studied to improve the efficiency of the system.

2.2 Two-Dimensional Test Setup and Testing Program

A 2-D aquifer simulation test apparatus, shown in Figure 2, has been developed to study spatially dependent variables that may affect the air sparging. The large dimensions of the test apparatus allow for the simulation of a soil profile. The simulator also offers flexibility by allowing better control of contaminant placement and groundwater flow. The apparatus is made of Plexiglas and measures 111cm length, 72 cm height, and 10 cm in width. This assembly and testing program have been described by Adams and Reddy (2001).

Two homogeneous soils (a coarse uniform sand profile and well-graded sand profile) were used to investigate the effect of grain size and grain size distribution on the air flow patterns and contaminant removal. To simulate soil heterogeneity, tests were performed using soil profiles consisting of different soils arranged in layers and lenses. Four heterogeneous soil profiles were used: (1) well-graded sand between coarse uniform sand; (2) fine uniform gravel under coarse uniform sand; (3) fine uniform gravel between coarse uniform sand; and (4) fine uniform sand lenses embedded within coarse uniform sand. All tests were performed with an air injection rate of 2,500 mL/min under a pressure of 4.5 kPa.

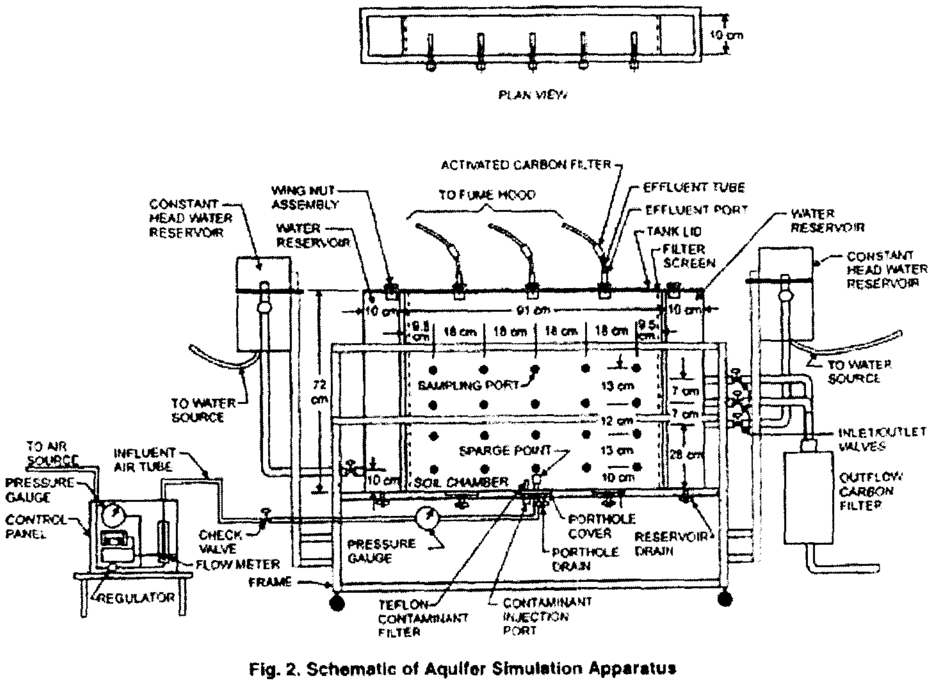


Fig. 2. Schematic of Aquifer Simulation Apparatus

3. RESULTS AND ANALYSIS

3.1 One-Dimensional Air Sparging Tests

The results of the experiments were used to evaluate (1) the effect of particle size and distribution and (2) the effect of pulsed air injection.

3.1.1 Effect of Particle Size and Distribution

The grain size distribution of all the tested soils are shown in Figure 3. Figure 4 shows the total benzene remaining in the soil versus elapsed time for each of the five soils. At one extreme, the benzene in the fine gravel was completely removed within 65 minutes. At the other extreme, almost 20% of the benzene within the fine sand still remained even after 600 minutes of treatment time. This variance was due to the differences in the mode of injected air travel observed within these soils.

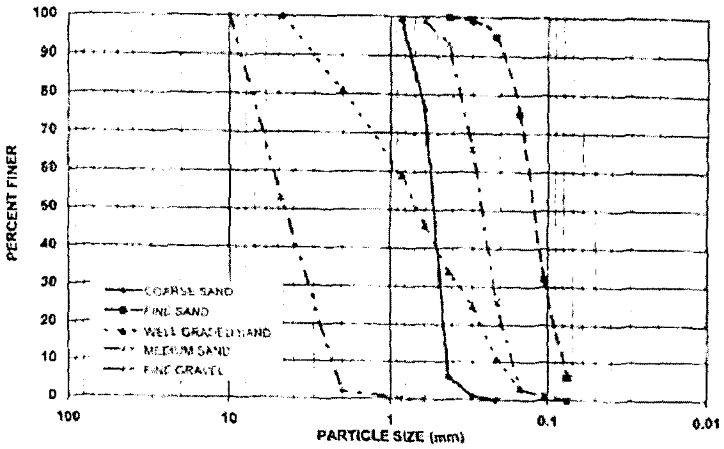


Fig. 3. Grain Size Distribution of Different Soils Tested

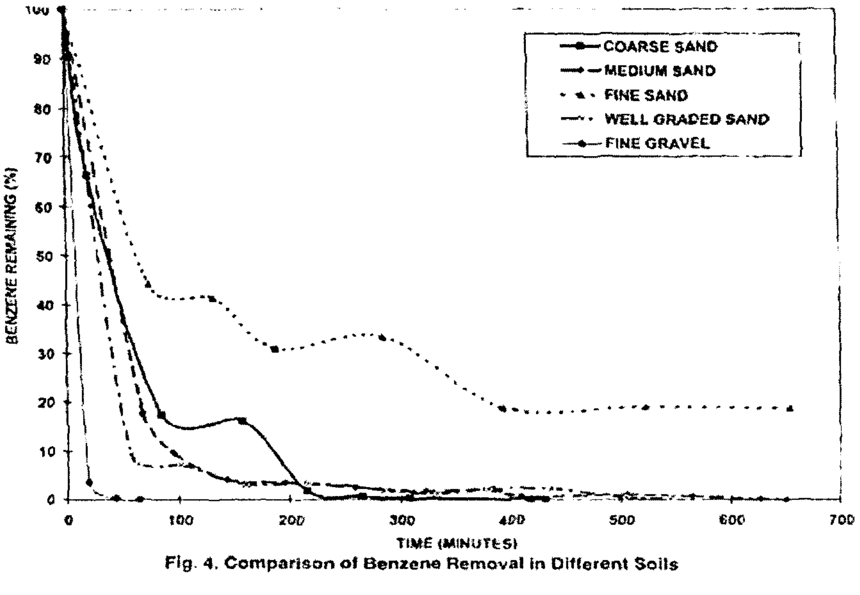


Fig. 4. Comparison of Benzene Removal in Different Soils

Within the fine gravel, the air traveled in bubble form and was distributed uniformly throughout the soil. Since the migration occurred uniformly throughout the soil, the injected air easily reached all the locations throughout the profile, which greatly accelerated volatilization of the benzene. Conversely, the fine sand required higher air entry pressure, and once this pressure was reached, it was observed that a very small number of channels were formed that maintained their integrity during the entire testing period. This small number of channels meant that the majority of the benzene had no direct contact with the injected air and had to migrate to the air channels via diffusion, a process that requires much more time than volatilization. These results also showed that the well-graded sand behaved similarly to the medium sand, which implies that the grain size may be a more critical factor than the grain size distribution when considering contaminant removal efficiencies.

In all the five soils, a large portion of the benzene was removed very quickly; for example even in the fine sand almost 60% of the benzene was removed within 100 minutes. A plot of the effective grain size (D_{10}) of the five soils versus the time necessary for benzene removal is shown in Figure 5. In the fine sand, total removal was not achieved and the time required 80% benzene removal was plotted. In this plot, it appears that when D_{10} of a soil is greater than 0.2 mm, the benzene may be removed efficiently; however, when the D_{10} is less then 0.2 mm, the necessary time for complete benzene removal increases drastically.

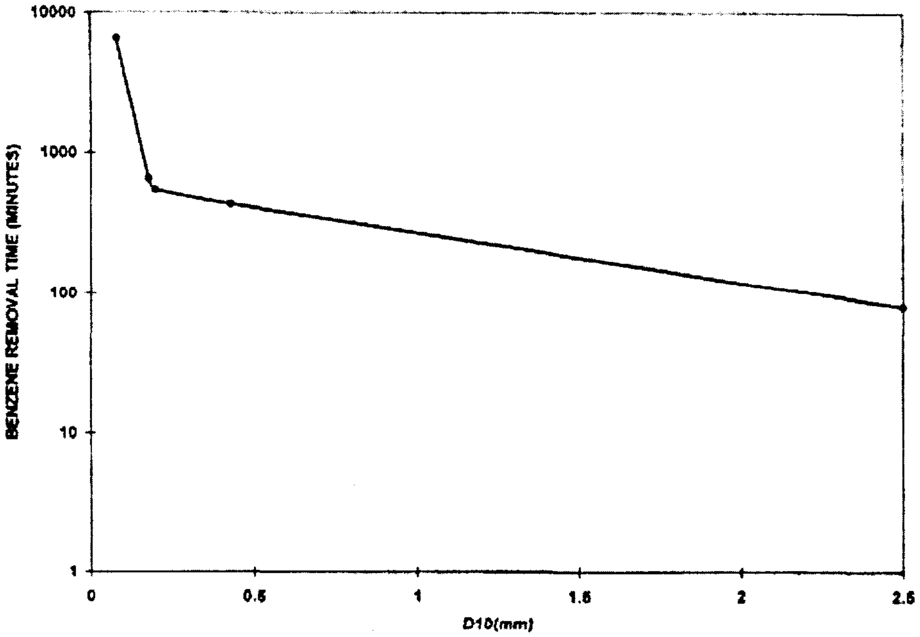


Fig. 5 Effect of Soil Type on Benzene Removal Time

3.1.2 Effect of Pulsed Air Injection

Figures 6(a) and 6(b) show the benzene remaining versus operating time (the actual time during which air is injected) for the three injection regimes for coarse sand and fine sand, respectively. Figure 6(a) shows that pulsing may not offer any appreciable benefit in the coarse sand when compared to continuous injection. This may be due to the relatively higher permeability of the coarse sand, which allows the development of an extensive channel network that permits easier migration of the injected air. The channel network shortens the possible paths of benzene diffusion. On the other hand, Figure 6(b) shows that all the three of the curves are close to each other until about 200 minutes into the test. After 200 minutes, the continuous injection curves levels out, leaving high amount of residual benzene (20%), but the two pulsed regimes continues to remove benzene. This indicates that well established channel network, including short diffusion paths and mixing are not achieved in the fine sand. As a result, the resting of the soil profile during shut down allows diffusion to occur. In addition when air is reinjected into the fine sand, a very small number of channels are again formed but are located in different regions throughout the soil profile. Thus benzene that may not have been previously removed because of long diffusion paths may be suddenly be in the vicinity of a channel allowing faster removal. By allowing better coverage and increased mixing and diffusion, the use of pulsed air injection may offer greater efficiency than continuous air injection when dealing with residual contamination in fine sands.

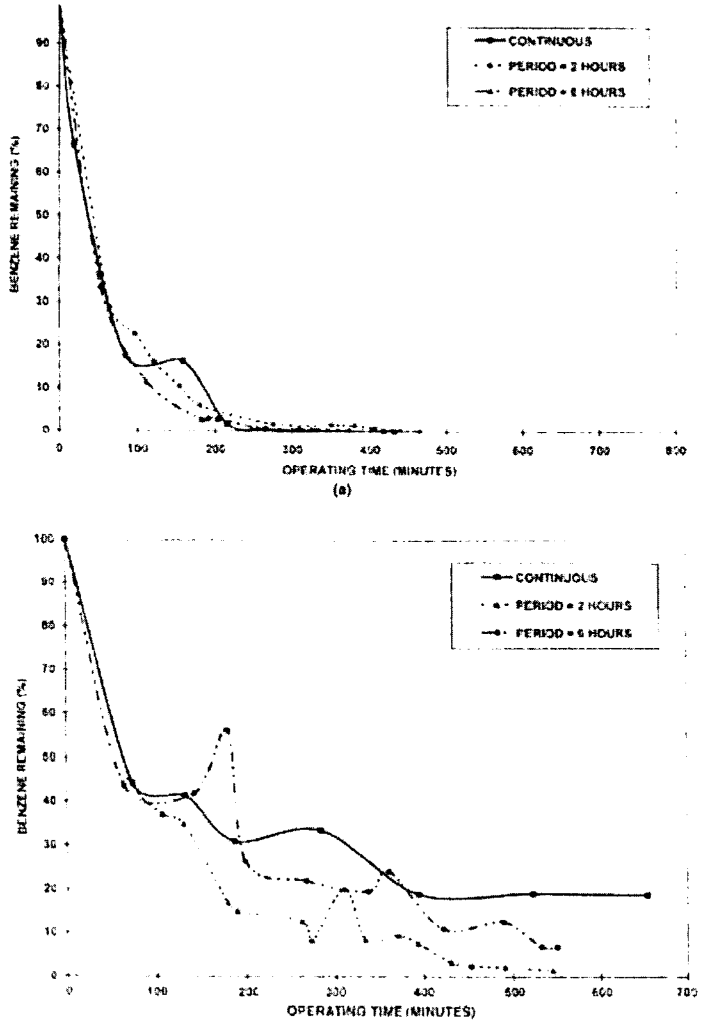


Fig. 6 Remaining Benzene versus Operating Time for (a) Coarse Sand (b) Fine Sand

3.2 Two-Dimensional Air Sparging Tests

3.2.1 Coarse Uniform Sand (Homogeneous Soil Profile)

Figure 7 shows the homogeneous coarse uniform sand profile, including the soil profile height and width as well as the depth of the saturated zone. The figure also shows the arrangement of the sampling ports within the soil profile. Upon air injection into the saturated homogeneous coarse sand profile, air formed a parabolic zone of influence emanating from the point of injection. As a result, the injected air did not traverse the lower left and lower right regions of the initial contaminated zone. As the injected air migrated vertically towards the surface, lateral migration also occurred, resulting in an increased radius of influence with increased height. The initial contaminant distribution, as shown in Figure 8(a) was relatively uniform throughout the initial contaminant zone but lower contaminant level was detected in the upper left region of this zone. Figures 8(b) to 8(d) show the benzene distribution within the soil after 135, 500, and 2875min, respectively. Because airflow was highest directly above the point of injection, this region experienced the greatest contaminant reduction during the initial stages of testing. Benzene removal occurred in a bottom to top pattern; the region immediately above the injection source experienced significant removal first with regions above experiencing in a consecutive manner. As the injected air migrated upward, substantial contaminant partitioned into the vapor phase. During migration, the benzene concentration within the air may have approached saturation, reducing the driving force for further volatilization and in turn resulting in less efficient removal at greater soil elevations (Hayden et al. 1994). Additionally, the contaminant-laden air may have caused repartitioning into the aqueous phase at greater elevations (Johnston et al. 1998). Figures 8(b) and 8(c) show that as the middle regions became contaminant-free, the regions to the left and right also experienced significant benzene reduction, but at a slower rate than the middle regions. As stated earlier, these regions were subjected to substantial airflow but less than within the middle regions.

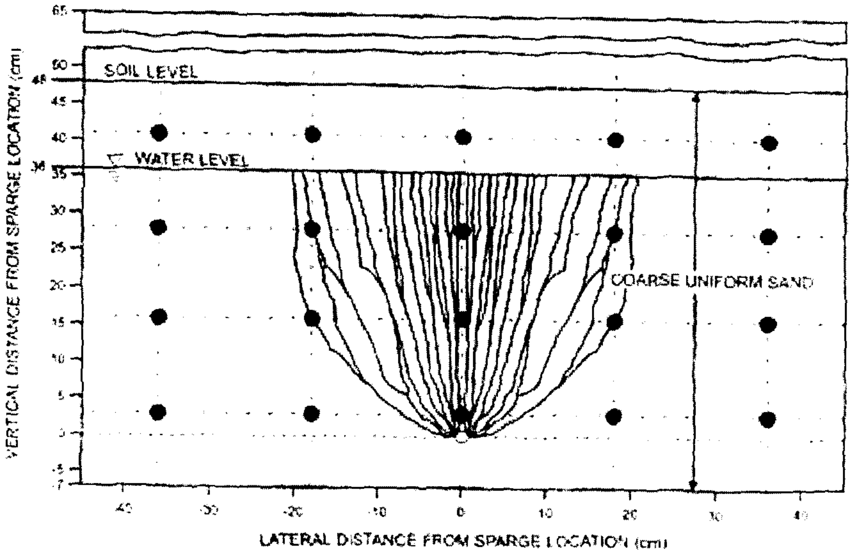
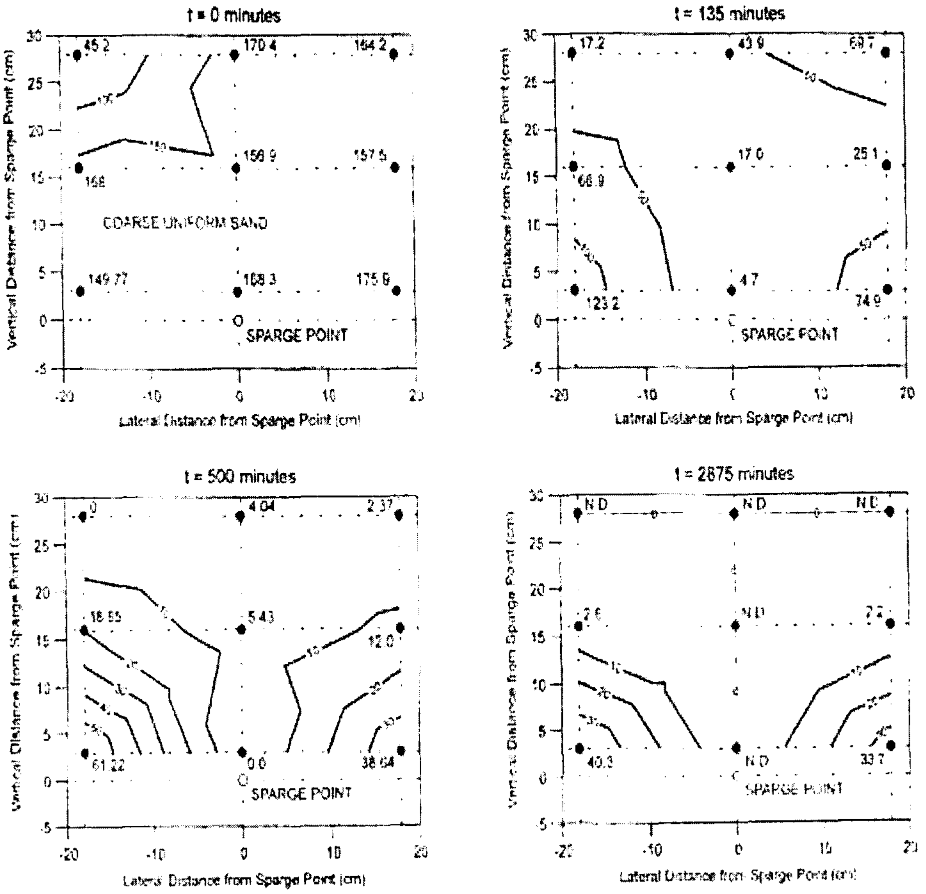


Fig. 7 Airflow Pattern in Coarse Uniform Sand Profile



Note: All Concentrations at the Ports are Expressed in mg/L

Fig. 8 Benzene Distribution in Coarse Uniform Sand Profile: (a) t = 0 min; (b) t = 135 min; (c) t = 500 min; (d) t=2,875 min

Volatilization resulting from the extensive airflow within these regions accounted for the efficient removal of benzene. The flowing air also created mechanical dispersion within the groundwater in these locations, aiding in further benzene movement toward the channels. Migration of contaminant as a result of mechanical dispersion is more effective than diffusion for removal (Johnson et al. 1998). However, benzene migration resulting from aqueous phase advection was detected. This effect may have contributed to the higher benzene concentrations within the upper initial contaminant region compared to middle regions as shown in Figure 8(b). While the benzene in regions of substantial airflow removed efficiently, benzene outside such regions remained for at relatively higher concentrations for a longer time as shown in Figure 8(d). Because these regions are free of airflow, dissolved phase benzene did not partition into the vapor phase through volatilization. Instead contaminant removal was controlled by the aqueous diffusion through the porous media to the air channels as a result of induced concentration gradients.

The rate of transport of aqueous phase benzene was slow enough to require a substantial amount of time for diffusion to occur, regardless of the short transport path lengths. Eventually, benzene is removed; however, complete benzene removal required nearly 4000 min of air injection. Regions experiencing high airflow, however, were contaminant-free after approximately 500 min of air injection. This demonstrates that diffusion becomes the rate limiting factor for contaminant removal. It should be noted that no spreading of contaminant (migration into previously clean areas) occurred, either as a result of diffusion or airflow-induced advection.

3.2.2 Well-Graded Sand (Homogeneous Soil Profile)

Figure 9 shows the homogeneous well graded sand soil profile as well as depth of saturated zone. Once the air injection into the saturated well-graded sand profile began, the injected air traveled in pore scale mode, but the extent of the zone of influence observed was much wider than in the previous test with coarse sand as depicted in Fig. 9. While the permeability of the well-graded sand (hydraulic conductivity = 1.30 x 10^{-2} cm/s) was slightly lower than that of the homogeneous coarse sand (hydraulic conductivity = 4.640 x 10^{-2} cm/s), the porosity of the well-graded sand (porosity = .35) was also lower than in the coarse sand (porosity = .45). The lower value of porosity led to increased tortuosity within the well-graded sand. The greater the tortuosity leads to greater lateral air migration and a wider zone of influence.

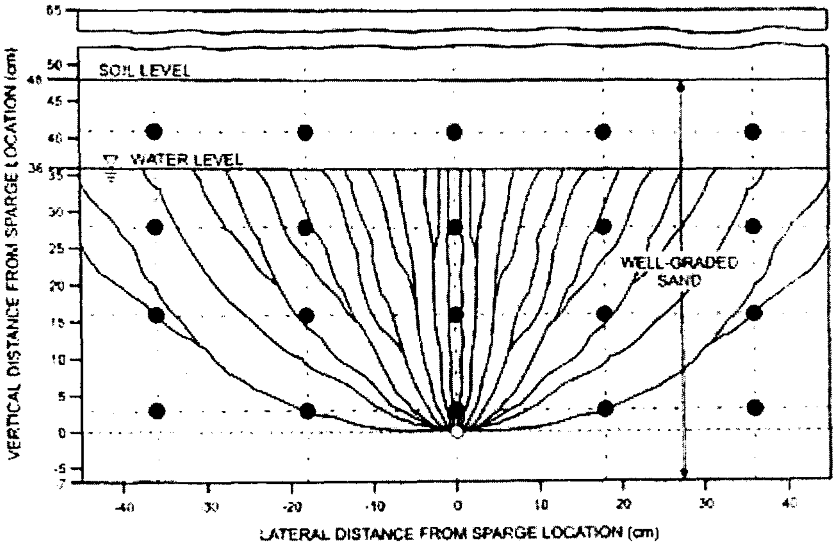
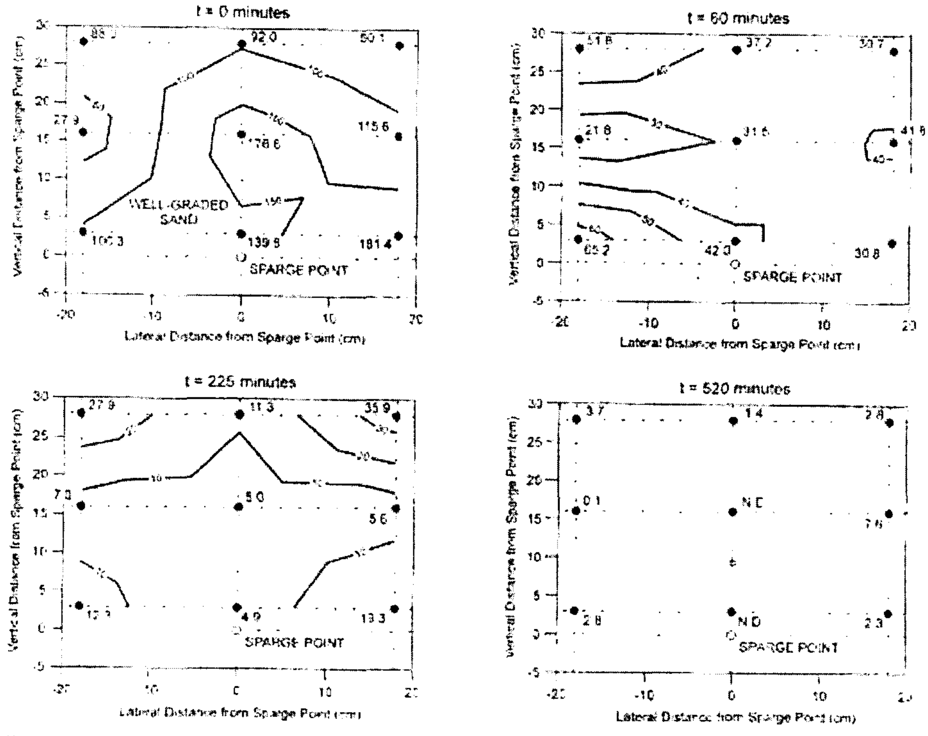


Fig. 9 Airflow Pattern In Well-Graded Sand Profile

Figure 10 (a) shows the initial contaminant concentration distribution of this test. As shown, the initial contaminant distribution is more uneven than in the homogeneous coarse sand test. Notably, the initial concentrations in the upper left and upper right regions of the initial contaminant zone are lower than other regions. Figures 10(b) to 10(d) show the contaminant distribution within the soil profile after an elapsed time of 60, 225, and 520 min, respectively. The middle region showed the first significant benzene concentration reductions due to the substantial airflow within these regions, resulting in efficient benzene removal through volatilization. Additionally, the bottom-up removal behavior seen in the uniform coarse sand test occurred; the region surrounding the injection point was remediated first, followed by the middle and upper regions, respectively. The center left and middle right regions also experienced substantial benzene concentration reductions early in the remedial program, but not as fast as within the middle regions. The lower airflow within these regions led to a smaller mass transfer area, slowing the rate of volatilization.



Note: All Concentrations at the Ports are Expressed in mg/L

Fig. 10 Benzene Distribution in Well-Graded Sand Profile: (a) t = 0 min; (b) t =60 min; (c) t = 225 min; (d) t=520 min

Unlike the coarse sand test, the lower left and lower right regions underwent substantial benzene reductions as illustrated in Figures 10(b) to 10(d). As stated before the zone of influence of injected air is wider than in the previous test with coarse sand. A substantial volume of air migrated through these lower regions, expediting benzene removal through volatilization. As a result, necessary diffusion paths were greatly reduced, eliminating the lingering contaminant effect seen within coarse sand layer. While benzene was removed faster within the lower layers, Figure 10(b) shows that benzene lingered in the upper left and upper right regions of the initial contaminant zone as a result of two phenomena. First, vertical benzene migration occurred as a result of advection due to the injected air. Second, since the zone of influence is wider than in the coarse sand but consists of the same volumetric airflow, the air channel density is reduced. This is especially true in the upper regions of the initial contaminant zone, where the flowing air has been subjected to substantial lateral expansion, greatly reducing air channel density within these regions.

Further, as shown in Figures 10(c) to 10(d), the benzene is removed from the entire soil profile in an expeditious manner; dissolved-phase benzene is almost completely removed from the soil profile after 520 min. Even though the zone of influence is not as dense as in the homogeneous sand layer, the zone was more extensive, which led to greater coverage of the contaminant zone. Additionally, the lower permeability may have led to greater air saturation within the zone of influence, enhancing the effect of volatilization (Chen et al. 1996). As a result, the reliance upon diffusion to assist in contaminant removal is reduced.

While the wider zone of influence was able to efficiently treat a greater volume of soil than in the coarse uniform sand test, the wider zone of influence induced spreading of the contaminant into initially contaminant-free regions. The zone of influence of the airflow entered into regions that were previously free of contamination, resulting in lateral contaminant migration due advective-dispersive transport into these regions. Dissolved-phase benzene that infiltrated into these regions did not remain for an appreciable length of time; migrating air responsible for its efficient removal through volatilization.

3.2.3 Well-Graded Sand between Coarse Uniform Sand (Heterogeneous Soil Profile)

To study a heterogeneous setting in which two adjacent soil layers have different permeability and grain size distribution, a test was performed in which a layer of well-graded sand well-graded sand (hydraulic conductivity = 1.30 x 10^{-2} cm/s) was underlain by a layer of coarse uniform sand (hydraulic conductivity = 4.640 x 10^{-2} cm/s) as shown in Figure 11.

The airflow pattern resulting from air injection is depicted in Figure 11. This airflow pattern appeared to be a hybrid of two previous tests performed using a homogeneous coarse uniform sand layer and a homogeneous well-graded sand layer. The zone of influence maintained its characteristic parabolic shape as it migrated through the coarse uniform sand layer but expanded laterally when it encountered the well-graded sand layer similar to what was previously observed. This behavior significantly influences the contaminant distribution and removal (Adam and Reddy, 2001).

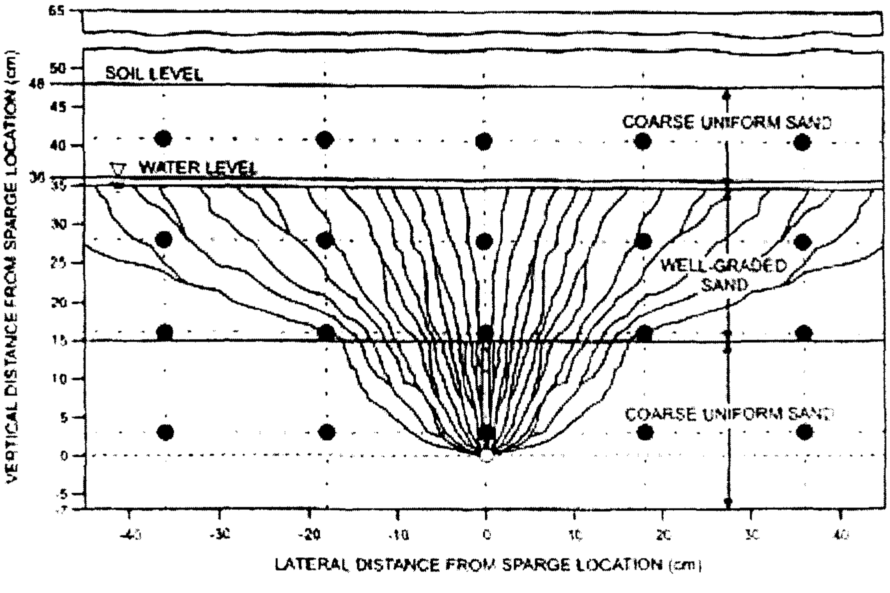


Fig. 11 Airflow Pattern in Well-Graded Sand between Coarse Uniform Sand Profile

4. SUMMARY

In-situ air sparging has been shown to be an effective means of remediating VOC-contaminated saturated soils and groundwater. One-dimensional column tests were performed to determine the effect of soil grain size and grain size distribution on the removal of benzene. The use of pulsed air injection was also investigated to enhance the efficiency of air sparging system. It is observed that fine gravel allowed the injected layer to travel in bubble form, while four different sands -well-graded sand, coarse sand, medium sand, and fine sand - allowed the injected air to travel in the form of discrete channels; the coarser the sand, the more extensive the channel network formed, which, in turn, led to faster removal times. Additionally, the grain size of the contaminated soils appears to be more critical than the grain size achieving high removal efficiency. No appreciable benefit was seen when pulsed air injection was used in the coarse sand. In the fine sand, however, pulsed air injection greatly increased the ability of air sparging to remove residual contamination, as well as aid in the removal of higher concentrations of contaminant. This occurred because when soil profile is allowed to rest, contaminant gradients were high enough to induce diffusion and mixing when using pulsed air injection. Also due to pulsed injection the location of air channels are found to be changed that accelerated removal.

The effects of soil heterogeneity on the efficiency of air sparging were investigated by conducting tests in a two-dimensional aquifer simulation apparatus. These tests showed that within coarse uniform sand soil profile, injected air led to the establishment of a parabolic zone of influence through which air flowed into channels with sizes on the scale of a few pore diameters. When a profile of well-graded sand was tested, the size of the zone of influence increased due to increased permeability and the increased effect of tortuosity resulting from the wider range of grain-size distribution. Within larger zone, however, the air saturation is not great as in smaller zone of influence for a given air injection flow rate. When the experiments were conducted with heterogeneous soil (well-graded sand in between of coarse sand), the airflow pattern appeared to be a hybrid of the test conducted using each homogeneous sand. Volatilization is found to be controlling removal mechanisms during the initial stages of air injection. Contaminant spreading due to advective-dispersive transport was observed in well-graded sand.

ACKNOWLEDGMENTS

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