In-situ Bioremediation Application Strategies for Soil and Groundwater Impacted by PAHs

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Biotreatability studies conducted in our laboratory used soils from two former wood treatment facilities to evaluate the use of *in-situ* bioventing and biosparging applications for their potential ability to remediate soil and groundwater containing creosote. The combination of chemical and microbiological analytical data from these studies suggested that biodegradation of creosote polycyclic aromatic hydrocarbons (PAHs) could be stimulated by adding oxygen and nitrogen to the indigenous microflora (Mueller *et al.* 1989; Mueller *et al.* 1995). Over the relatively short time frame of these studies, however, biodegradation of potentially carcinogenic PAHs (pc PAHs) was limited, which is in accordance with much of the existing scientific literature. Nevertheless, on a site-specific basis, appropriately designed *in-situ* bioremediation systems may represent effective strategies for degrading PAHs and affecting *in-situ* chemical containment (Mueller *et al.* 1993).

Critical to the future success of bioventing/biosparging applications for PAH-impacted environments is the continued development and refinement of effective implementation tools. These must offer better means of delivering essential co-reagents, such as oxygen and nitrogen, and must possess the potential to integrate biotechnological advances. One such system attempting to increase the efficiency of site remediation is the 'Multifunctional Well' technology, which is described below in more detail.

To maximize remediation progress, different technologies are combined to operate in one multi-process remediation well (see Figure 1). Here, various remediation processes are integrated to remove certain types and/or suites of contaminants. For example, vapor extraction/air stripping removes volatile organics (e.g. naphthalene), while bioremediation of more persistent organics (e.g. fluoranthene) is enhanced by circular air and water flow (see below). Remediation success can be maximized by applying these complementary processes. Depending on the extent and degree of contamination, individual treatment steps can be omitted or operated simultaneously. All four treatments can be carried out in one remediation well *in-situ* which offers significant advantages over other systems.

Four of the remediation technologies that can be implemented in the multifunctional well are summarized below:

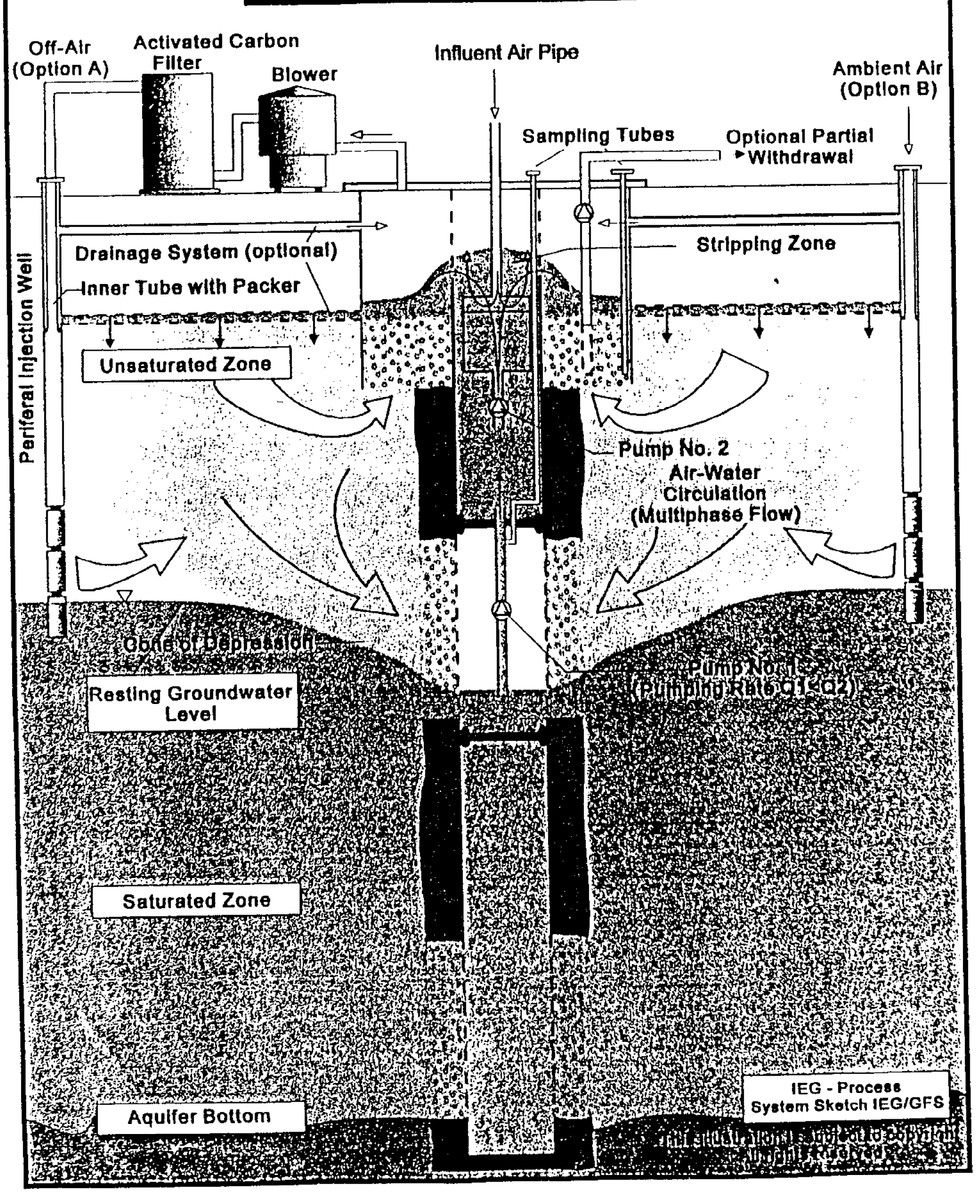
I. **Free Product Recovery.** Free product floating on the groundwater moves in the direction of the negative pressure gradient (50–80 mbar) towards the treatment well in which it accumulates. A vacuum pump produces a vacuum inside a receiver tank and the attached piping, which is connected to a double cased screen containing hydrophobic material (Bernhardt 1989; Alesi and Rehner 1988). The free product is thus transported to the surface as a single phase, leaving the groundwater in the subsurface.

II. **Soil Vapor Extraction and Bioventing.** Soil vapor is extracted from two different levels of the well. Using an adjustable inner tube, the length of the well casing can be altered depending on the vertical contaminant distribution in the vadose zone. Additional air injection wells arranged at some distance away from the remediation well provide a continuous supply of oxygen-enriched air flowing through the contaminated vadose zone in the direction of the negative pressure gradient towards this central well. A majority of the volatile constituents (e.g. naphthalene) are removed from the vadose zone and, simultaneously, biodegradation of semi- and nonvolatile constituents by naturally occurring microorganisms is stimulated and enhanced.

III. **Soil Circular Flushing Well (SZB).** The remaining semi-volatile material is reduced and/or treated using the SZB step. An air/water flow is induced around the remediation well (Bernhardt 1995). The circulating water flow supplies oxygen for biodegradation and also carries the contaminants to the well, where a treatment unit designed for treatment of the constituents of interest is placed. If needed, nutrients (e.g. nitrate or phosphate) can be added to the air/water flow to enhance biological activity. Air injection wells described in step two can provide oxygen-enriched air to the outer boundary of the circulation cell.

IV. **Vacuum Vaporizer Well (UVB Technology).** A vertical circulation flow is induced in the aquifer (Herrling and Buermann 1990; Philip and Walter 1992). Contaminants dissolved in the groundwater are continuously transported to the well where they are stripped under negative pressure. Treated, oxygen-enriched ground-

Figure 1:
Multifunctional Well with
Integrated UVB and SZB Technologies



water leaves the well and enhances biodegradation in the surrounding aquifer (Borchert and Sick 1992). The direction of circulation can be reversed depending on the vertical distribution of the contaminants in the saturated zone.

IMPLEMENTATION OF THE MULTIFUNCTIONAL WELL

Results of Phase I

This multifunctional well was implemented at a BTEX site in May 1994 at a Department of Defense (DOD) site in Karlsruhe, Germany. Less free product was recovered during the first phase of operation than was anticipated from the site characterization. Therefore, the remediation well was quickly adjusted to begin with the second phase. Results of this and of the third mode of operation (SZB) are described below. In addition, an attempt was made to differentiate the quantities of petroleum hydrocarbons physically removed as opposed to those biodegraded. Ultimately, the applicability of the multifunctional well at MGP sites with high concentrations of PAHs is discussed.

Results of Phases II and III

The soil vapor extraction and bioventing phase (II) went into operation on July 12, 1994. Physical removal of petroleum based fossil fuels as measured in the system's off-air during the first five months amounts to 1236 kg. As was expected, the rate of contaminant removal decreased considerably over time. During initial operation the rate was as high as 33 813 g/day, however, during the first quarter of 1995 the rate dropped to below 800 g/day of volatile to semivolatile constituents. The remediation well was reconfigured once again to begin the third phase of operation (SZB) on April 3, 1995.

Both BTEX and PAHs were analyzed in the groundwater before and during operation of the SZB. After an initial mobilization/increase in the concentration of the contaminants, a steady decrease was discernable. For example, naphthalene concentrations of 0.69 µg/l were analyzed in the groundwater collected before Phase III (SZB) began operating ($t<0$). Approximately 2 hours after the remediation system was turned on, this concentration rose to 155 µg/l. In the subsequent samples during the first week of operation, the naphthalene values dropped to 130 followed by 128 µg/l.

In order to achieve the air/water flow around the remediation well, a negative pressure of 35 mbar was applied to the well chamber and the central pump (P1) was adjusted to a flow rate of 0.45 m^3/h. The volume of air drawn into the stripping reactor as a result of the negative pressure was approximately 200 m^3/h and soil air extracted continuously from the unsaturated to semi-saturated zone amounted to approximately 400 m^3/h. Combined, the total off-air was in the range of 600 m^3/h. With a high air to water ratio (at least 200 to 0.45), a stripping efficiency of over 99% was attained and the concentration of dissolved oxygen (DO) in the groundwater circulating around the remediation well increased to saturation. This oxygen enhances *in-situ* biodegradation in the subsurface.

BIODEGRADATION

The amount of contaminants mineralized (i.e. conversion of organic compounds to their terminal endproducts of CO_2 and CH_4) *in-situ* was estimated using concentrations of CO_2 and CH_4 measured in the system's off-air. Between initial operation of Phase II (Soil Vapor Extraction and Bioventing), which began on July 12, 1994 and December 19, 1994 the CO_2 concentration in the extracted air increased from 0.34 Vol.% to 0.6 Vol.%, while CH_4 concentrations in the off-air varied between 33 and 248 ppm. With off-air flow rates between 360 and 540 m^3/h, the total amount of CO_2 and CH_4 removed from the subsurface during the five months of operation was 4524 kg and 79.4 kg, respectively.

Recognizing that mineralization represents the most stringent evaluation of a biological system, it is possible to estimate biodegradation rates of hydrocarbons from the effective carbon dioxide production rates. Here, the following stoichiometric relationship for the oxidation of ethylbenzene (EB) was used as a model:

$$C_8H_{10} + 10.5\ O_2 = 8\ CO_2 + 5\ H_2O.$$

The equation indicates that one mole of EB is consumed for every eight moles of carbon dioxide produced. Knowing that the molecular weight of EB is 106 and that of carbon dioxide is 44, the mass ratio of EB to carbon dioxide required for mineralization can be calculated:

$$R\ CO_2 = 106/(8 \times 44) = 0.301\ g\ EB/g\ CO_2.$$

Alternatively, the following stoichiometric relationship for the oxidation of EB that accounts for microbial assimilation can be used where:

$$C_8H_{10} + 4.5\ O_2 + 0.5\ N_2O = C_5H_7O_2N + 3\ CO_2 + 1.5\ H_2O.$$

Again, knowing that the molecular weight of EB is 106 and that of carbon dioxide is 44, the mass ratio of EB to carbon dioxide required for mineralization can be calculated:

$$R\ CO_2 = 106/(3 \times 44) = 0.803\ g\ EB/g\ CO_2.$$

For purposes of the following calculations, R CO_2 was assumed equal to 0.55 g EB/g CO_2, the average of the above two calculated values. Hence, in a simple equation that does not consider other CO_2 sources and sinks, 4524 kg of CO_2 removed from the subsurface during the five month period of operation relates to the removal of 2488 kg of EB.

On the basis of the enhanced effective carbon dioxide production rate determined through field testing, approximately 0.5% per day, the biodegradation rate in terms of mg of EB equivalent per kg of soil per day can be estimated using the following equation:

$$KB\ CO_2 = (K\ CO_2)\ (A)\ (D\ CO_2)\ (RCO_2/100)$$

where:

KB CO_2 = Biodegradation rate based upon CO_2 production
K CO_2 = Effective CO_2 production rate
A = Volume of air/kg of soil
D CO_2 = Density of CO_2 gas
R CO_2 = Mass ratio of EB to CO_2 required for mineralization.

Assuming a porosity of 0.3 and a soil bulk density of 1600 kg/m^3, then A=0.000188 m^3 air/kg soil. Hence the resulting equation becomes:

$$\begin{aligned} KB\ CO_2 &= (K\ CO_2\ \%/day)(0.000188\ m^3\ air/kg)(1.98\ g\ CO_2/L)(0.55g/g)(1000\ L/m^3)/100 \\ &= 0.0020\ K\ CO_2\ (g\ EB/kg\ soil\text{-}day) \\ &= 2.0\ KCO_2\ (mg/kg\text{-}day). \end{aligned}$$

Substituting the experimentally determined effective carbon dioxide production rate, K CO_2 of 0.5%/day into the above equation results in a calculated hydrocarbon biodegradation rate of 1mg/kg-day.

With the system operating July 12 through December 19, 1994 (160 days) and the volume of soil being treated estimated at 1600 m^3, the weight of the soil is 2 560 000 kg. Therefore, a hydrocarbon degradation of 410 kg was to be expected, assuming 100% mineralization efficiency. Assuming a more typical mineralization efficiency of 30% of total evolved CO_2 (as determined by other laboratory studies), a minimum of 1370 kg EB were mineralized during the 160 day period. This value correlates well with other calculations conducted by a German consulting firm, which estimated the biodegradation of 4602 kg contaminants over this same period.

The flexibility of adapting the multifunctional well to changing constituents of interest during any given remediation make this an excellent tool to implement at bioremediation sites. The system design can accommodate *in-situ* bioreactors inside the remediation well.

Remediation processes using the multifunctional well are patented by IEG mbH, Reutlingen, Germany, while biotechnology to enhance biodegradation of specific constituents of interest are patented by the U.S. EPA under exclusive license to SBP Technologies, Inc.

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