

**Site Characterization for the *in Situ* Bioremediation of the Vadose Zone**

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**ABSTRACT**

Studies were conducted to determine whether bioremediation can be used to treat a diesel fuel spill in the deep vadose zone (>30 m). After laboratory studies confirmed the ability of the natural population of organisms to degrade the diesel fuel, the technological issue of transporting the required mass of nutrients to the contaminated soils was addressed.

Laboratory studies demonstrated that nutrient and oxygen transport can be enhanced by the addition of divalent cations to injected waters. This addition of minerals caused the observed hydraulic conductivity to be maintained at elevated levels that allowed the macronutrient nitrogen, provided as ammonium ion, to be more uniformly distributed to target soil domains.

**INTRODUCTION**

The motivation for this study was to develop a mechanism to clean up hydrocarbon contamination in the vadose zone. In particular, this effort was directed toward the design and implementation of a remediation technology to restore a hydrocarbon-contaminated site in northern California.

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**MASTER**

In February 1975, a 225.2-m<sup>3</sup> spill of No. 2 diesel fuel resulted from the puncture of an underground transfer line buried about 1.2 m below the land surface. Evaluation at the site indicated that 162 m<sup>3</sup> of diesel fuel, or about 72% of the initial volume spilled, remains in the unsaturated zone to a depth of approximately 33 m.

At the location of the diesel fuel spill, most of the underlying material consists of Quaternary alluvial deposits. These deposits are composed of unconsolidated clay, silt, sand, and gravel. The irregular deposition causes individual beds or layers to be generally discontinuous. Geochemical analysis of the spill site indicated that the contamination is concentrated along four major interfaces between the sand and gravel layers, with higher permeability, and the silt and clay layers, with lower permeability. These units have variable thicknesses and depths of 8-12 m, with the deepest at approximately 30 m.

Extensive engineering analysis has determined (1) that *in situ* biotreatment is the only economically viable remediation alternative (DOE, 1989) and (2) that the great variability in hydraulic conductivity makes the success of the *in situ* remediation program dependent on effective and predictable transport of nutrients and an exogenous electron acceptor. To gain both greater understanding and better control of the site hydrodynamics, a study was conducted to determine the natural transport characteristics of the soil and the potential to modify the soil's native geochemical and physical properties.

## METHODOLOGY

### Hydraulic Conductivity Modification

Hydraulic conductivity measurements of the soils were obtained by using a modified falling-head permeameter test on core samples. Undisturbed soil plugs were obtained from the interior of 18.5-cm-diameter cores. These soil plugs were 10 cm long and by 4.5 cm in diameter. Before hydraulic conductivity measurements were obtained, the sample plugs were allowed to imbibe the test water until the free water surface was above the level of the soil. The sample was then placed within the permeameter, and the hydraulic conductivity was measured.

After baseline hydraulic conductivity measurements were made, the hydraulic conductivity was measured by using University of Notre Dame tap water amended with magnesium and calcium. Two general types of soil were tested. Type I soils were representative of the deeper soils and came from the core segments at 25.3, 26.8, and 28.9 m. The two Type II soils were from depths of 8.6 and 17.0 m and generally represented the shallower soils. These soils and the calculated exchangeable sodium percent (ESP) and cation exchange complex (CEC) values are summarized in Table 1.

Tap water amended with magnesium (500 mg/L) and calcium (1,000 mg/L) was passed through each of the soil subsamples for 24 hr. The hydraulic conductivity was then measured and recorded in ft/day. This procedure was repeated with tap water amended with higher levels of magnesium (1,000 mg/L) and calcium (2,000 mg/L), then a third time with tap water amended with still higher levels of magnesium (1,500 mg/L) and calcium (3,000 mg/L). The hydraulic conductivity values measured after each of these three tests are summarized in Table 2 for both soil types tested.

## Nutrient Transport and Adsorption Studies

Nutrients, especially nitrogen, must be added if the microbial populations present in the soil are expected to consume the total petroleum hydrocarbon (TPH) contaminants at a reasonable rate. Because ammonia exchanges with soil cations, amounts beyond those needed solely for organism growth must be added to distribute nitrogen to zones of contamination distant from injection wells. Thus, adsorption isotherms were obtained for both ammonia and urea (a possible alternative nitrogen source) for the soils present in the cores from 8.6, 18.5, and 28.9 m, for a better understanding of this exchange potential. Adsorption isotherms obtained for the core from 8.6 m, which are typical, are shown in Fig. 1.

To determine the effect of waters amended with magnesium and calcium on ammonia adsorption, additional studies were performed on the four soils (from depths of 8.6, 9.0, 18.5, and 28.9 m) that had previously been tested for ammonia adsorption. The ammonia equilibrating solutions were modified by adding magnesium (1,000 mg/L) and calcium (2,000 mg/L). A comparison of adsorption data obtained with the amended and unamended ammonia solutions for the soil core from 8.6 m are shown in Fig. 2. These results are typical of the findings obtained for all four soils. At least three times as much ammonia was apparently adsorbed to the soil if the solution was not amended with magnesium and calcium. Ammonia adsorption results are presented in Fig. 3 for all four soils tested with amended ammonia solutions.

To assess the possible dynamic effects of amended injected waters on the transport of nutrients, two cores were flooded with water amended with calcium and magnesium. After 25 and 45 pore volumes had passed through Columns 1 and 2, respectively, the effluent cation concentrations and hydraulic conductivities were at relatively steady levels. Then  $\text{NH}_4\text{Cl}$  (50 mg/L, measured as nitrogen) was added to the

influent of both columns. The effluent  $\text{NH}_4\text{Cl}$  (measured as nitrogen) is shown in Fig. 4 as a function of the number of pore volumes subsequently passed.

## RESULTS AND DISCUSSION

In general, for the soils tested the use of waters amended with  $\text{Mg}^{2+}/\text{Ca}^{2+}$  greatly improved the native hydraulic conductivity of the soil and the transportability of nutrients.

In the first experiment, the greatest increase in hydraulic conductivity observed for the Type I soils occurred between the first and second days (i.e., after the  $\text{Mg}^{2+}/\text{Ca}^{2+}$  500/1,000 solution was replaced with the  $\text{Mg}^{2+}/\text{Ca}^{2+}$  1,000/2,000 solution). A very small increase was observed between the second and third days. On the other hand, the Type II soils showed the greatest increases from the second to the third day. To assess the possibility that physical deterioration of the soil was responsible for this improvement in hydraulic conductivity, the solution recycled through the Type II soil samples was switched from the  $\text{Mg}^{2+}/\text{Ca}^{2+}$  1,500/3,000 solution to unamended tap water. As Table 3 indicates, the hydraulic conductivity continued to increase during the next two days (Days 4 and 5) before it decreased on Day 6, the third day after the switch to unamended tap water.

During the core preparation for the dynamic equilibrium studies, the hydraulic conductivity was continually measured. The results shown in Fig. 5 clearly illustrate that for the life of a "normal" *in situ* remediation, the improved hydraulic conductivity will be maintained if the ionic composition of the passed fluid is maintained.

The data from the ammonia retardation studies clearly suggest that the amount of ammonia adsorbed, when the equilibrating solution is amended to contain sufficient magnesium and calcium, should not exceed that required for growth of the organisms. Figure 4 illustrates that the ammonia concentration in the effluent rapidly increased after

the passage of 18 additional pore volumes through the amended column, while the effluent from the unamended column had low concentrations of ammonia after more than 50 pore volumes had passed. These results indicate that in the unamended column the ammonia is bound to the soil and hence is unavailable for microbial growth. In contrast, the ammonia concentration in the effluent of the amended column indicates that ample bioavailable ammonia is present in that amended column.

In summary, both dynamic and equilibrium tests strongly suggested that ammonium ion transport will be positively affected by the addition of divalent cations. The total amount of ammonia added should be balanced to promote nitrogen availability for the growth of organisms but minimize the potential for nitrate contamination of the aquifer.

## CONCLUSION

The studies presented illustrate the importance of characterizing the ESP of soil when a site is evaluated for *in situ* bioremediation. Furthermore, these studies establish a methodology by which the subsurface environment can be modified to improve both the economic viability of bioremediation and the applicability to the technology.

Modifying the ESP of the soil can have two important benefits. First, nutrients that are required for microbial growth and activity can be transported long distances from the point of injection. In many soils, particularly in the vadose zone, the nutrients are immediately adsorbed by the soil. Modification of the cationic exchange potential allows the nutrients to be transported by a carrier fluid to the contaminated regions. Second, modification of the ESP increases the hydraulic conductivity of the soil, facilitating more rapid transport of both nutrients and exogenous electron acceptor/donors. Consequently, the time required for the remediation, the cost of capital equipment, and lifetime operating costs can be reduced significantly.

In summary, modification of the subsurface geochemical/physical environment is a potentially cost-effective methodology to improve the performance, expand the applicability, and reduce the cost of *in situ* bioremediation.

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## FIGURE CAPTIONS

- Figure 1** Adsorption Isotherms for Ammonia and Urea in the Soil from the 8.6-m Depth
- Figure 2** Comparison of Adsorption Isotherms with and without Amendment for Soil from the 8.6-m Depth
- Figure 3** Adsorption Isotherms for Soils Tested with Amended Solutions
- Figure 4** Effluent Ammonia Concentration versus Cumulative Pore Volumes Passed
- Figure 5** Hydraulic Conductivity Versus Cumulative Pore Volumes Passed (feet/day x 0.3 = meters/day)

TABLE 1 Ionic Properties of Native Soil at Selected Depths

Sample	Displaceable Cation Concentration (mg/L)				ESP <sup>a</sup> (%)	CEC <sup>b</sup> (meq/100 g)
	Na <sup>+</sup>	K <sup>+</sup>	Mg <sup>2+</sup>	Ca <sup>2+</sup>		
Notre Dame tap water	30	2	31	98	25.8	NA <sup>c</sup>
Tap water amended <sup>d</sup>	30	2	1031	2098	0.7	NA
Borehole site water	86	8	34	75	53.2	NA
Borehole site water, amended <sup>d</sup>	86	8	1034	2075	1.9	NA
Core from 8.6 m <sup>e</sup>	41	0	324	806	5.1	9.3
Core from 17.0 m <sup>e</sup>	102	100	866	1213	3.1	18.9
Core from 18.5 m <sup>e</sup>	19	75	442	588	1.2	9.3
Core from 25.3 m <sup>e</sup>	53	92	574	1263	2.0	15.6
Core from 26.8 m <sup>e</sup>	106	92	639	1296	3.7	16.8
Core from 28.9 m <sup>e</sup>	30	84	563	1296	1.1	15.8

<sup>a</sup>Exchangeable sodium percent = meq of Na<sup>+</sup>/total meq of all cations.

<sup>b</sup>Cation exchange complex is calculated from cations displaced from soil for the ESP test.

<sup>c</sup>NA = not applicable.

<sup>d</sup>Calculated after addition of magnesium (1,000 mg/L) and calcium (2,000 mg/L).

<sup>e</sup>Core segment from the indicated depth below the ground surface.

TABLE 2 Hydraulic Conductivity versus Time

Soil Type	Soil Depth (m)	Hydraulic Conductivity (ft/day) <sup>a</sup>		
		500/1,000 <sup>a</sup> (Day 1)	1,000/2,000 <sup>b</sup> (Day 2)	1,500/3,000 <sup>b</sup> (Day 3)
I	25.3	0.62	1.09	1.13
	26.9	0.87	1.44	1.54
	28.9	0.26	0.47	0.49
II	8.6	1.30	1.34	2.35
	17.0	1.21	1.41	1.99

<sup>a</sup> Feet/day x 0.3 = meters/day.

<sup>b</sup> Mg<sup>2+</sup> concentration in mg/L over Ca<sup>2+</sup> concentration in mg/L, applied on the day indicated.

**TABLE 3 Effect of Tap Water Solution on Improved Hydraulic Conductivity**

Soil Type	Soil Depth (m)	Hydraulic Conductivity in Unamended Tap Water (ft./day) on Day of Solution Supply <sup>a</sup>		
		Day 4	Day 5	Day 6
II	8.6	3.80	4.21	2.05
	17.0	2.61	3.02	1.59

<sup>a</sup> Feet/day x 0.3 = meters/day.









