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THE USE OF BENCH- AND FIELD-SCALE DATA FOR DESIGN OF AN IN SITU CARBON TETRACHLORIDE BIOREMEDIATION SYSTEM

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DESIGN OF AN IN SITU CARBON TETRACHLORIDE BIOREMEDIATION SYSTEM

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ABSTRACT

A suite of simulation models were developed as a design tool in support of an in situ bioremediation demonstration at the Hanford site in Washington state. The design tool, calibrated with field- and bench-scale data, was used to answer four field-scale system design questions: (1) What are the important reaction processes and kinetics? (2) How will biomass distribute in the aquifer in response to injected substrate? (3) What well configuration best ensures proper nutrient transport and process control? (4) What operating and monitoring strategy should be used to confirm effective remediation? This paper does not describe the design tool itself, but describes how the design tool was used to optimize field site design parameters such as well spacing, hydraulic control, contaminant destruction, and nutrient injection strategies.

INTRODUCTION

In situ bioremediation of the chlorinated solvent, carbon tetrachloride (CCl_4), and nitrate is being performed at the U.S. Department of Energy's (DOE's) Hanford Site as part of the DOE Office of Technology Development's VOC Arid Integrated Demonstration. The CCl_4 is in groundwater in highly stratified sediments 76 m (250 ft) deep. In addition to its relative inaccessibility, CCl_4 is degraded by a cometabolic process that requires careful system control. The characteristics of both the contaminant and the site posed challenges in the design of the in situ process. The design tool was developed to help overcome these challenges. Of main concern were the four basic design questions, given in the abstract, which guided research and bench-scale test efforts.

The design tool was calibrated with field- and bench-scale data. Bench-scale batch tests with a native denitrifying consortium were used to determine reaction kinetics, including electron donor and acceptor consumption rates, CCl_4 degradation rate, inhibition constants, and by-product formation kinetics. Bacterial transport was investigated and nutrient injection strategies were tested in continuous-flow soil columns instrumented to continuously measure pH, pressure, and tracer concentrations. Field data included geological, hydrological, and microbiological characterization. In addition, the simulation design tool was developed to account for the interrelated effects of each process in various scenarios and to identify means to overcome rate-limiting steps in CCl_4 degradation. The design tool will also be an integral part of data evaluation during the field demonstration.

CCl_4 REACTION PROCESSES AND KINETICS

The demonstration at the Hanford Site will implement in situ bioremediation of CCl_4 and nitrate by supplying nutrients to indigenous microorganisms to stimulate metabolic activity and CCl_4 degradation. Biodegradation of CCl_4 using acetate as the carbon and energy source and nitrate as the terminal electron acceptor has been observed by Criddle et al. (1990); Lewis and Crawford (1993); Bae and Rittmann (1990); and Bouwer and Wright (1988). The denitrifying bacteria transform CCl_4 to carbon dioxide and chloride ions, while denitrification yields biomass, water, carbon dioxide, and nitrogen gas. Under some conditions, chloroform ($CHCl_3$) was produced as an undesirable byproduct. Research is currently under way to determine its production and degradation kinetics.

Biodegradation of CCl_4 under denitrifying conditions is of particular interest at Hanford because both CCl_4 and nitrate are present in the unconfined aquifer. This, coupled with preliminary results showing CCl_4 destruction by subsurface microbes obtained from the Hanford Site (Brouns et al. 1990; Koegler et al. 1989), shows promise for successful in situ CCl_4 bioremediation.

A series of fed-batch experiments with a Hanford denitrifying consortium preceded the design of

the in situ demonstration to formulate CCl_4 stoichiometry and validate kinetic expressions for CCl_4 degradation (Petersen et al. 1994, Hooker et al. 1994). The CCl_4 destruction expressions are first order in CCl_4 concentration and biomass and the rate is inhibited by the presence of more than 20 mg/L nitrate. Figure 1 shows the experimental data and model predictions of biomass, acetate, nitrate, and CCl_4 concentrations for a typical fed-batch treatability test. The resulting CCl_4 degradation kinetic expressions were used in the design tool.

BIOMASS DISTRIBUTION

In situ bioremediation relies on developing and maintaining microbial activity in contaminated regions. The main limitation to achieving this goal is the inability to evenly disperse rapidly reacting nutrients by recirculation wells. Radial groundwater flow patterns, in which fluid velocity diminishes rapidly with distance, cause injected nutrients to react near the well bore, thus limiting microbial activity at remote points in the flow field. This phenomenon occurs both in the laboratory (Cunningham and Wanner 1993) and in the field (Semprini et al. 1991). To extend the biologically active region, based on the work of others (Semprini et al. 1991; Shouche et al. 1993; Roberts et al. 1989), we focused on developing nutrient feeding strategies that minimize near-well growth in order to optimize substrate transport.

The design tool predicts and soil column data indicate that the use of time-skewed acetate and nitrate pulses can reduce near-well biofouling. The design tool incorporates biofilm processes such as growth, attachment, and detachment. A sensitivity analysis determined that the detachment rate coefficient was a dominant parameter in predicting biomass distribution profiles (Peyton et al. 1994). To determine attachment and detachment rates, laboratory soil columns were fed acetate and nitrate continuously or in pulses. The 10.1 cm (4-in) diameter soil columns were packed with coarse sand, or in later tests, actual site sediments. The sediments were inoculated with approximately $1x10^7$ colony forming

units of an indigenous Hanford denitrifying consortium per gram of soil. Comparisons of experimental results and design tool predictions indicate good agreement between effluent acetate and nitrate profiles. Biomass profiles, measured as protein, correlate well with predicted results (Figure 2). The primary independent variable that was manipulated to give agreement between the actual results and design tool predictions was the first order biomass detachment rate coefficient, 0.003 min^{-1} , which was within 25% of that observed by Peyton et al. (1994).

WELL CONFIGURATION, NUTRIENT TRANSPORT, AND PROCESS CONTROL

A well configuration was selected which incorporated into the design three preexisting characterization wells. The configurations assessed with the design tool included 2-well, 3-well, 4-well, and 5-well recirculation systems. Selection of the field design was based on design tool predictions of CCl_4 destruction which was a function of reaction kinetics and of hydraulic control. The amount of hydraulic control determines the amount of nitrate and CCl_4 that enters the reaction zone through the injection well. The desired process operation requires dispersion-induced mixing of acetate and nitrate pulses at a distance from the well bore to (1) keep nitrate concentration below 20 mg/L during acetate pulses and (2) limit biomass production, and thus biofouling, adjacent to the well bore. At 100% hydraulic control, no additional CCl_4 will enter the reaction zone, and therefore the reaction can be completely controlled by injection of the desired amounts of acetate and nitrate. At low hydraulic control, the amount of CCl_4 and nitrate entering the system from outside the reaction zone increases. The increased CCl_4 makes measuring CCl_4 destruction rates much more difficult and the increased nitrate permits biomass to grow adjacent to the well after an acetate pulse.

The design tool showed that steady-state CCl_4 destruction was essentially constant from about 70% to 95% hydraulic control. Destruction of CCl_4 was greatly enhanced with a hydraulic control near 100% and rapidly declined below 65%. Because 100% hydraulic control is not possible in the field, the

design for the demonstration was selected to achieve a "simulated" hydraulic control of about 85%. Tracer tests indicate that the hydraulic control of the installed field system is approximately 90%

Predictions from the design tool were combined with other characteristics of each well configuration to select the best design for the demonstration. Two primary issues were key to the selection: the ability to obtain measurable responses in monitoring parameters and the versatility of the design in testing strategies relevant to full-scale applications. These and other site-related criteria led to the selection of a 2-well recirculation configuration. This pattern provides adequate hydraulic control, so that reaction kinetics and biomass distribution can be controlled, and permits multiple well spacings between pumped wells with an acceptable number of monitoring points.

OPERATING AND MONITORING STRATEGY

Phase 1, abiotic recirculation, was performed from February 6, 1995 to March 29, 1995 and consisted of control operationswith no addition of nutrients; the groundwater was continuously mixed and then sampled weekly. A hydraulic control of 90% was demonstrated with a bromide tracer. Data from this phase will be used to detect any abiotic removal of contaminant due to groundwater mixing and to calibrate the transport portion of the process model. Nutrient injection will be initiated in Phase 2, active bioremediation. An operation strategy based on design tool predictions and data from Phase 1 will be implemented and maintained for at least three months to collect sufficient information to assess the strategy. The strategy will be changed only if major problems occur, such as production of non-inert persistent by-products (chloroform and nitrite); undesirable changes in the hydraulic mixing pattern; insufficient or excessive biomass accumulation; or insufficient contaminant destruction. Phase 3 will implement a revised strategy to optimize performance.

The number of samples needed to demonstrate a statistical difference in CCl_4 concentration between the injection well and a monitoring well was calculated from the anticipated CCl_4 destruction rate

of 15 g/day. Statistical analysis assumed a standard deviation of 25% of the mean for the field samples and an initial CCl_4 concentration of 2 mg/L. Phase I results to date indicate standard deviation for CCl_4 field samples is ~15%. At steady-state, the design goal results in a monitoring- well concentration of about 1.3 mg/L. Demonstration with 95% confidence that the steady state concentration is lower than the initial concentration requires 20 samples; however, to back calculate the actual CCl_4 destruction rate will require statistical proof that the steady-state concentration is lower by a specific amount. For an observed difference of 0.4 mg/L, 100 samples are needed to show that the difference is 0.3 mg/L with 90% confidence.

SUMMARY

A design tool, calibrated with field- and bench-scale data, was used to answer field-scale system design questions. Bench-scale batch tests with the native denitrifying consortium were used to determine reaction rate kinetics. Bacterial transport parameters were determined, and nutrient injection strategies were tested in continuous-flow soil columns. Key to determining the best design were the ability to obtain measurable responses in necessary monitoring parameters and the versatility of the design. The simulation design tool combined bench and field data to account for the interrelated effects of each process in various scenarios. A 2-well recirculation configuration was selected. Phase 1 of the operation strategy collected baseline data without nutrient injection; Phase 2 is the initial remediation phase; results from Phase 2 will be used to develop an optimized Phase 3 remediation strategy.

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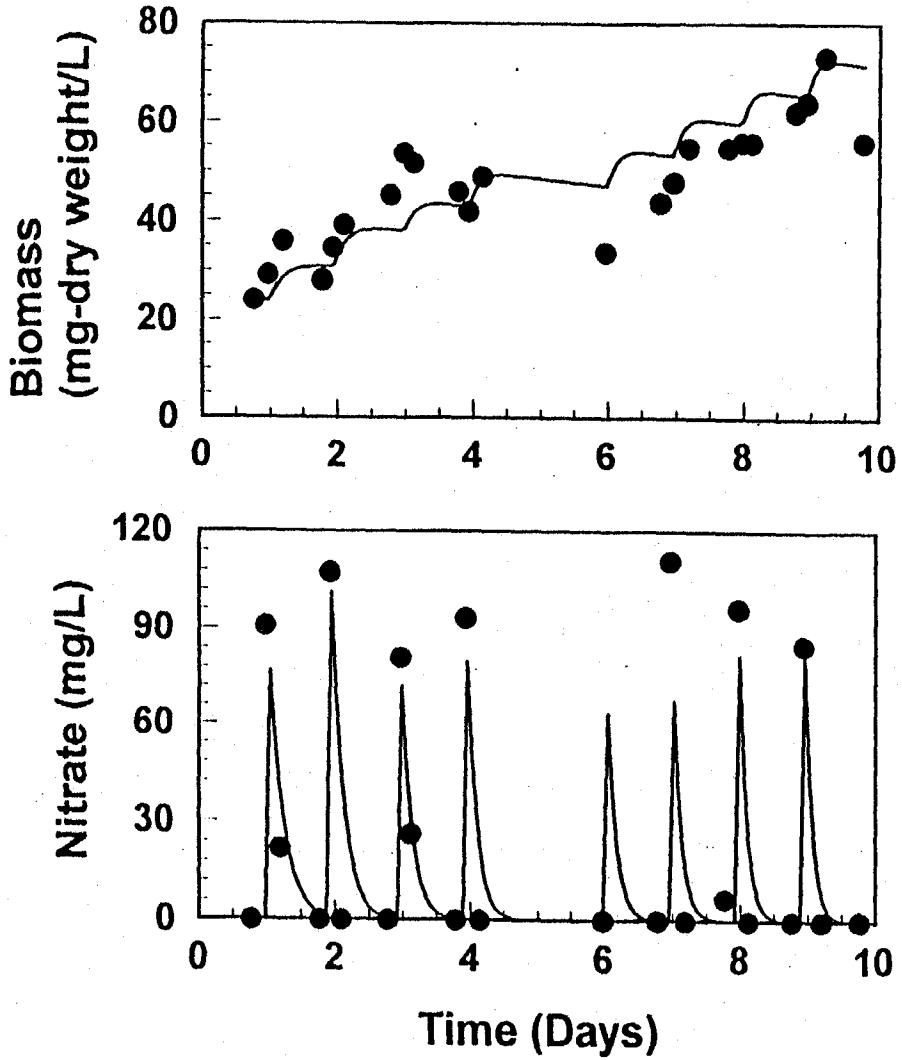
Figure Captions

FIGURE 1. Experimental data and model predictions of biomass, acetate, nitrate, and CCl_4 concentrations for a typical batch treatability test.

FIGURE 2. Biomass profiles in the soil columns, measured as protein, correlate well with simulation results.

Keywords - models, in situ bioremediation, CCl_4, carbon tetrachloride, biomass distribution, porous media, design, chlorinated solvent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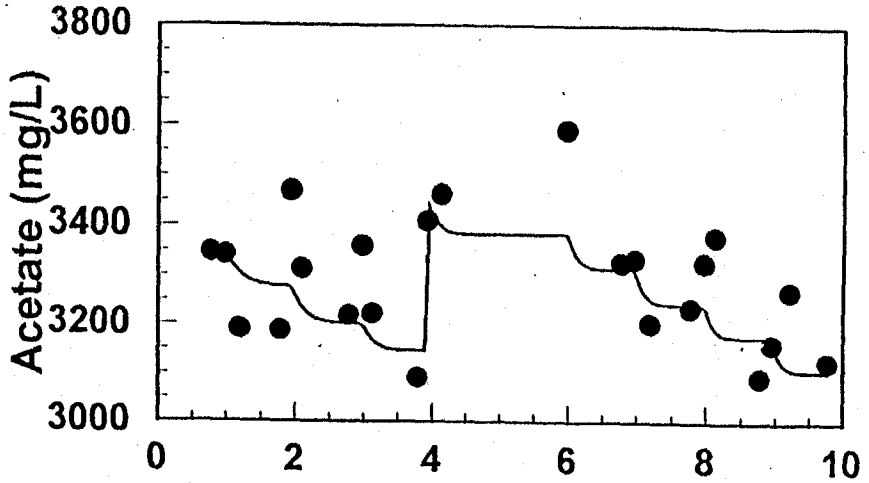
60
40
20
0
0
2
4
6
8
10


Acetate (mg/L)
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3600
3400
3200
3000
0
2
4
6
8
10

Nitrate (mg/L)
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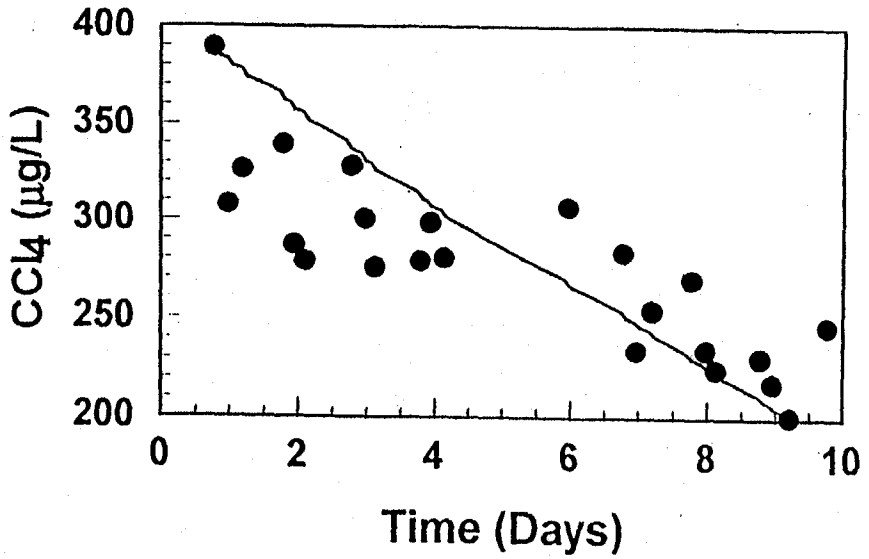
90
60
30
0
0
2
4
6
8
10
Time (Days)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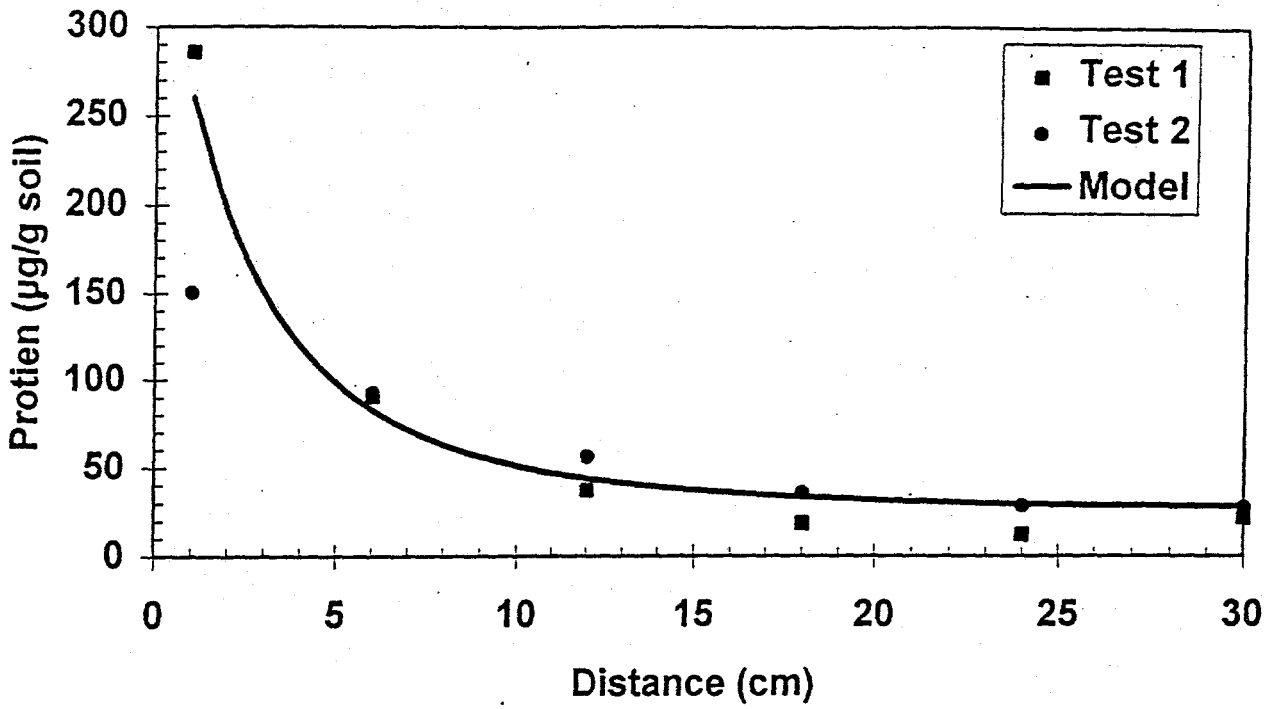
350
300
250
200
0
2
4
6
8
10
Time (Days)


300
250
200
150
100
50
0
Protien (µg/g soil)
0
5
10
15
20
25
30
Distance (cm)
Test 1
Test 2
Model