Paper 3D-22, in: A.R. Gavaskar and A.S.C. Chen (Eds.), *Remediation of Chlorinated and Recalcitrant Compounds—2004.* Proceedings of the Fourth International Conference on Remediation of Chlorinated and Recalcitrant Compounds (Monterey, CA; May 2004). ISBN 1-57477-145-0, published by Battelle Press, Columbus, OH, www.battelle.org/bookstore.

ASSESSMENT OF CHITIN DISTRIBUTION AND FRACTURE PROPAGATION DURING BIO-FRACING™

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ABSTRACT: "Bio-fracing™" is a term used to describe the hydraulic fracturing of a soil with the simultaneous delivery of a bio-amendment incorporated into the fracture slurry. The Bio-Frac™ process has been successfully employed to introduce a sand prop-pant with a solid-phase, slow release electron donor, "chitin", into variably saturated, low permeability soils contaminated by chlorinated aliphatic hydrocarbons. Chitin is a natural polymeric organic material consisting of shrimp and crab shells. The Bio-Frac™ process simultaneously enhances bulk soil permeability while introducing the solid phase bio-amendment (chitin) into contaminated media in low permeability sediments for enhanced in situ bioremediation. This paper describes the incorporation, delivery, and mapping of chitin with frac sand during injection into fine-grained, low permeability sediments at a superfund site in Kentucky, USA.

INTRODUCTION

The growing use of in situ bioremediation for contaminated sediments and ground-water has led to the realization that its effectiveness in low permeability soil (i.e. <100 millidarcys or 10^{-6} m/s hydraulic conductivity equivalent) is severely limited. These limitations are primarily due to geologic constraints in fine grained soils that inhibit bio-availability and microbial access to essential substrates and nutrients. Biodegradation rates for hydrocarbon compounds show an increasing trend with hydraulic conductivity (Lu and Zheng, 2003). For in situ bioremediation to be effective in low permeability soils, it requires that essential substrates and nutrients are distributed throughout the contaminated zone and sufficient permeability exists to assure long-term sustainability of the bioremediation process.

Knowing the final configuration of subsurface fracture and bioamendment emplacement is extremely useful for assessing the subsequent performance of enhanced in situ bioremediation at sites contaminated by chlorinated solvents. This is especially true for determining relative chitin distribution in contaminated soil and groundwater media for subsequent remedial performance monitoring and modeling purposes. There-fore, a robust and accurate geophysical method of mapping the distribution and geometry of fractures containing injected bioamendment is required. Tiltmeter fracture mapping was identified as a reliable, repeatable, and accurate method of geophysics and has been used successfully on many soil fracturing projects. It has been recently employed to map the distribution of injected bioamendments, including chitin, and correlated with the results of soil coring.

BACKGROUND

Individual subsurface fractures containing chitin were mapped at a former Brickyard site located southwest of Louisville, KY that was contaminated by chlorinated aliphatic hydrocarbons, primarily Trichloroethylene (TCE) and cis-1,2 Dichloroethene (DCE). That work was conducted in 2001 under the direction of North Wind, Inc. who were under contract to the U.S. National Science Foundation to investigate the viability of bioremediation using "chitin" as a bioamendment. The 2001 field pilot consisted of fracturing silty sand and silty clay soils and emplacing 325 lbs of chitin and 1550 lbs of frac sand into three fractures initiated from a testhole within the former contaminant source area. The results of the field pilot after 9 months of performance monitoring demonstrated that chitin, where emplaced in fractures, was able to increase hydraulic conductivity by an order of magnitude, affect redox conditions (i.e. create more reducing conditions) and support enhanced anaerobic reductive dechlorination (Martin et al., 2002). Based on the positive results of the field pilot, a full-scale field program for soil fracturing and co-injection of chitin bioamendment was commenced at the site on April 28, 2003. Ongoing soil coring and groundwater sampling are being conducted to assess chitin longevity and monitor geochemical changes to the subsurface environment resulting from anaerobic reductive dechlorination.

REMOTE FRACTURE MAPPING

Fractures placed in the subsurface can be mapped remotely using surface mounted tiltmeters. Tiltmeters are highly sensitive instruments (to microradian resolution) used in the hydraulic fracturing industry to measure the minute ground surface deformations created during the fracturing process. The direction and magnitude of ground surface deformation or "tilt" measured by tiltmeters is used to determine the shape, thickness, extent and orientation of fractures in the subsurface. This information is useful in confirming the extent and areal coverage of fractures placed in the subsurface, as few fractures ever propagate in a perfectly radial or horizontal manner. Knowing the configuration and geometry of individual fractures initiated and propagated in subsoils is extremely useful for assessing the subsequent performance of remediation technologies at fracture-enhanced sites. This is especially true in cases where the soil fracturing process includes delivering chemical or biological amendments for expediting in situ remediation.

Typically, an array of surface-mounted tiltmeters is set up in a grid or radial configuration around each fracture borehole location. The tiltmeter spacing and configuration is determined by the number of fractures placed per borehole and the depth of fracture placement. During fracturing, ground surface "tilt" is measured at each tiltmeter station and the information is stored in on-site dataloggers. The tilt data allows an assessment of the nature of fracture propagation and orientation (i.e. predominantly horizontal vs. vertical) and is used in the geophysical analysis and interpretation of fracture geometry. The results of geophysical fracture analysis are presented in tabular two-dimensional forms which are subsequently transformed to 3-dimensional images using advanced computer graphics software.

MATERIALS AND METHODS

The objective of the full-scale soil fracturing work was to assess whether various grades of chitin could be uniformly distributed into contaminated sediments to effect long term and sustained anaerobic reductive dechlorination. A secondary objective was to assess whether the results of fracture mapping using tiltmeter geophysics could be correlated to chitin-fractures identified during subsequent soil coring activities.

Fracture Slurry Formulation and Pumping. "Blender stall" laboratory testing carried out in the phase 1 pilot work in 2001 and full-scale program in 2003 indicated that chitin was compatible for incorporation into a water-based fracture slurry. Batch formulation and mixing of fracture slurry was identified as the optimal method of slurry preparation in the field. The volume of each batch was matched to the total volume of fracture slurry to be injected for each fractured borehole to minimize the frequency of mixing. The fracture sand or "proppant" used to prop open the induced fractures was US American Petroleum Institute (US API) 20-40 mesh sized sand for enhancing soil permeability and ensuring fracture longevity.

The base gel comprised a mixture of water and hydroxypropyl guar to form a gel polymer. Chitin, and in turn sand proppant, were added to the base gel and mixed until uniformly distributed in the resulting fracture slurry. A small amount of liquid borate cross-linker was subsequently added to viscosify the slurry and ensure sand/chitin suspension during fracture slurry injection. Just prior to pumping the slurry downhole, an amount of liquid enzyme breaker sufficient to time the breakdown of the slurry viscosity within two to three hours of fracture placement, was added. The average slurry volume pumped per fracture was 265 gallons containing 550 lbs of frac sand and 150 lbs of chitin.

Fracture Initiation and Propagation. A total of thirty-three fractures were initiated at ten fracture borehole locations on the site between April 28 and May 2, 2003. The initial fracture borehole, FR01, was fractured with a slurry containing 20-40 mesh chitin, fractured boreholes FR02 and FR03 were fractured with slurry containing coarser SC40 chitin, and fractures at FR04 to FR10 were initiated with slurry containing SC20, the coarsest chitin. Fractures were initiated in silty clays and silty sands from depths of 24 ft. to 45 ft. below the ground surface. Fracture slurry volumes and vertical spacing intervals were derived so as to provide the optimal fracture coverage and chitin distribution in the contaminated zone (Table 1).

TABLE 1. Chitin-fracture placement summary.

Fracture Well No.	Fracture Initiation Depth (ft bgs)	Number of Fractures Initiated at each Depth	Total Number of Fractures Initiated in Well	Chitin Type
FR01	31	1	1	20-40
FR02	27,30,33,38	1,1,1,1	4	SC40
FR03	31,34,37,38.5	1,1,1,1	4	SC40
FR04	32.5,37.5,45	1,1,1	3	SC20
FR05	34,39,44	1,1,1	3	SC20
FR06	32,37	1,2	3	SC20
FR07	30,35	2,2	4	SC20
FR08	35,38,43.5	2,1,1	4	SC20
FR09	39,40	1,2	3	SC20
FR10	24,44	1,3	4	SC20

The theoretical fracture design radius (i.e. perpendicular to the fracture borehole) for the volumes injected was 15 ft. A new batch of fracture fluid was formulated after the first fracture in each borehole was pumped to completion. While the new batch of frac slurry was being prepared, the fracture tool assembly was advanced to the next fracture initiation depth where the above-described procedure was repeated.

During the soil fracturing events, fracture pressure vs. time and flow rate vs. time was monitored and recorded using a computer data acquisition system in the data recording van. These fracture monitoring data are presented in Figure 1.

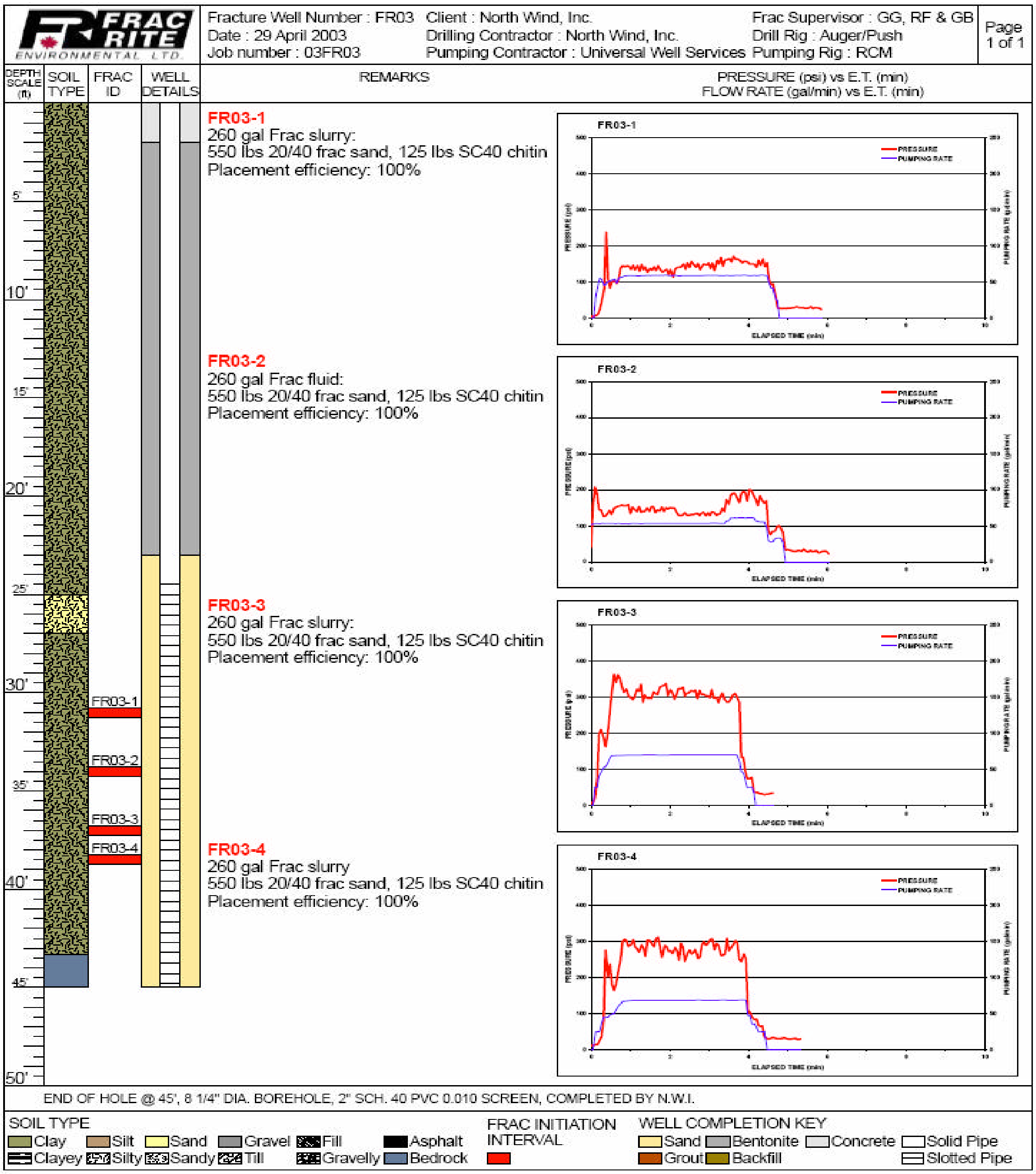

FIGURE 1. Soil fracture log.

Fracture Mapping and Computer Imaging. Chitin-fractures emplaced into subsoils were mapped using tiltmeter geophysics and limited soil coring. A total of 8 tiltmeter stations were set up in a radial pattern around each fractured well in order to monitor baseline ground movements and ground movement induced during individual fracturing events. Fracture mapping was conducted by Eco-Scan Inc. using surface-mounted ES Model 700 biaxial tiltmeters. This method of fracture mapping was chosen due to its quick set-up in the field, past success on previous fracturing projects, high signal sensitivity, and rapid data acquisition capability. Prior to fracturing, tiltmeters were aligned along a north-south axis and electronically leveled. Tiltmeter input parameters (soil rheological constants, depth, spacing, etc.) were entered into a laptop computer and tiltmeters connected via cables to data loggers. A total of 4 tiltmeters were accommodated per datalogger. Data loggers were set to continuously record tiltmeter signals about 30 minutes prior to each fracture event to obtain a baseline signature and during each fracture event to characterize the orientation and geometry of every discreet fracture induced in the subsoils.

Tiltmeter signal data was modeled using geophysics based on analyses of soil stress, strain, and displacement induced by sand-filled fracture intrusions into soils (method of Yang and Davis, 1986). The interpreted geophysical results were subsequently input into “solidworks,” a computer graphics program, to provide three-dimensional computer images of all fractures placed in subsoils at the site. The geophysical results were subsequently compared to the results of North Wind’s initial round of soil coring work in an attempt to correlate fractures mapped visually in soil cores to geophysical fracture mapping. A total of six continuous soil core holes were drilled by North Wind in the vicinity of fracture borehole locations immediately after the conclusion of the soil fracturing field work. Soil core samples were visually examined by North Wind and Frac Rite personnel to identify and record the presence and nature of any chitin/sand fractures encountered in the cores.

RESULTS AND DISCUSSION

Fracture Emplacement of Chitin. A total of thirty-three fractures containing chitin and sand were successfully placed at ten fracture borehole locations. Fractures were placed in the upper and lower silty clays units and in the intermediate silty sand (where present). The greatest fracture distance achieved from the fracture borehole was 25 ft. at FR05. Fracture boreholes FR02, FR03, and FR08 also contained one or more fractures that extended at least 20 ft. from the borehole. The estimated lateral coverage of chitin/sand fractures within the 100 ft. diameter source area based on fracture mapping was good (at least 75%). The vertical coverage of chitin/sand fractures was excellent, and extends from the bedrock surface into the partially saturated upper clay.

Fracturing “break” pressures (i.e. pressure at which soil parts or “breaks” and fracture propagation begins) typically ranged from 150 psi to 350 psi for the majority of fractures. The maximum break pressure recorded was 575 psi in fracture FR04-2 and the minimum break pressure recorded was 86 psi in fracture FR07-2. Break pressure is a function of the depth of fracture initiation, soil cohesion, slurry viscosity, sand/chitin loading, and sand to chitin ratio. Most of the break pressure monitored was attributable to overcoming friction losses due to sand loading and the high viscosity of the fracture slurry during pumping.

Placement efficiency of the chitin/sand slurry was 97% in the silty sands and 99% in the silty clays. Overall placement efficiency was 98%. The total amount of chitin and sand placed in soils within the contaminant source area at the site in 2003 was 4,820 lbs and 17,870 lbs, respectively. Minor losses of fracture slurry were attributable to borehole annular leakage and leakage through an improperly abandoned testhole from a previous subsurface investigation.

Fracture Mapping and Soil Coring. The results of fracture mapping did not indicate any preferred trend in fracture orientation, although there did appear to be a relationship between the degree of fracture inclination, or "dip", relative to the ground surface, and soil type. Approximately 50% of the 36 fractures placed at the site (including 2001 pilot well) were near-horizontal to gently dipping (i.e. had inclination or "dip angle" of 35° or less. Moderately dipping fractures (i.e. those with an inclination or dip angle from 36° to 60°) comprised 36% of the total, while steeply ascending fractures (dip angle greater than 60°) comprised the rest (Table 2).

TABLE 2. Summary of fracture inclination.

Fracture I.D..	Dip Angle (°)	Fracture Classification	Percentage of Total (%)
All at FR02, FR06, FR07, FR09; FR03-2,3; FR04-3; FR08-3,4; FR10-1,2	$\leq$ 35	Near-horizontal to gently dipping	50
FR03-1,3,4; FR04-1,2; FR08-1,3; FR10-3,4	36 to 60	Moderately dipping	36
All at FR05; FWB-1	> 60	Steeply dipping	14

The sand/chitin fractures found in the soil cores were primarily near-horizontal to gently dipping (i.e. =35 degrees). Chitin was observed to be proportionately well distributed with sand in most fractures. Two of the soil cores yielded near-vertical fractures at FR05 at shallower depths in the upper silty clay. These visual observations seem to confirm the results of tiltmeter data with regards to fracture inclination, that is, fractures present in the lower silty clay layer appear to be more horizontal than fractures in the upper silty clay layer. It was also observed in the soil cores that the lower silty clay layer had a well developed soil fabric (thinly bedded horizontal layers and laminae) whereas soil fabric was weakly developed or absent in the silty sand and upper silty clay layers.

The results suggest that although fractures did not seem to exhibit a preferred orientation, their relative inclination to the ground surface was affected by soil fabric and in situ stress conditions. Chitin fractures were found to be predominantly horizontal in laminated, silty clay soils (due to soil fabric – Figure 2) and moderately to steeply ascending in the silty, non-laminated sands and clays (due to soil stress regime – Figure 3). The typical radius of fracture propagation and chitin distribution ranged from 10 ft. to 15 ft. from the fracture borehole. The thickness of chitin and sand in fractures is estimated to range from 0.04 to 0.80 inch (i.e. 1 mm to 20 mm) based on soil core observations and tiltmeter geophysical modeling.

There was reasonably good correlation between the depth of fractures identified in soil cores at FR03 and FR05 and fracture depths interpreted using tiltmeter geophysics. The correlation was only fair at FR08. The tiltmeter results would not be expected to exactly coincide with actual fracture depths away from the borehole, because the model simplifies fractures to be planar features when in fact they have curved surfaces that are "dish shaped." A strong association appears to exist between fracture inclination to the ground surface and soil fabric present as horizontal, thinly bedded layers and laminae in the lower silty clay unit. This horizontal soil fabric appears to have an influence in the creation of near-horizontal to gently dipping chitin/ sand fractures as seen in soil cores and tiltmeter results. Soil fabric was absent to weakly developed in the silty sand and upper silty clay, and fractures placed in those soils were consequently moderately to steeply dipping. Strongly vertical fractures would be expected in normally consolidated, structureless soils.

FIGURE 2. Near-horizontal fracture in horizontally interbedded silt and clay (FR03).

FIGURE 3. Near-vertical fracture in weakly structured silty sand (FR05).

CONCLUSIONS

A full-scale application of fracture-enhanced in situ bioremediation of chlorinated aliphatic hydrocarbons was conducted at a former brickyard site in April and May of 2003. Hydraulic soil fracturing was used to simultaneously improve the hydraulic conductivity of low permeability, impacted silty sands and clays, and to co-inject "chitin", a long-term solid-phase electron donor. This process is called "Bio-Fracing™".

An evaluation of the effectiveness of Bio-Fracing™ in incorporating, uniformly distributing, and mapping subsurface chitin fractures was conducted. The results demonstrated that:

- various grades of chitin were successfully incorporated into a water-based, fracture slurry containing frac sand;
- overall, 98% of chitin was successfully emplaced in low-permeability silty clays and silty sands within the contaminant source area;
- tiltmeter geophysics confirmed by soil coring was a practical and reliable means of mapping fractures and chitin distribution;
- lateral coverage of chitin within the source area was good (i.e. covering at least 75% of plume) and vertical coverage was excellent (i.e. extending from bedrock surface, through saturated sediments and into the unsaturated zone);
- soil fabric in the form of horizontal, thinly bedded soil layers and laminae present in the lower silty clay unit appeared to have a strong influence in the creation of near-horizontal to moderately inclined chitin/sand fractures;
- chitin was observed to be proportionately well distributed with frac sand in the fractures that were visually examined; and,
- visual correlation of chitin fractures in soil cores with fracture depths predicted by tiltmeter analysis was fair to good.

Bio-Fracing™ would appear to be a powerful tool for overcoming the challenges inherent in in situ bioremediation of contaminated sediments and groundwater in low permeability environments. Tiltmeter geophysics proved a reliable and useful mapping technique to determine the final configuration of soil fractures and bio-amendment emplaced in impacted subsoils. The ability to map the distribution of chitin treatment amendment facilitated the subsequent analysis of remedial performance data from wells within and proximate to the contaminant source plume.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the support received on this project by the U.S. National Science Foundation, U.S. Environmental Protection Agency, U.S. Department of Energy, Idaho National Engineering and Environmental Laboratory, U.S. Geological Survey, State of Kentucky, University of Illinois at Urbana-Champaign, Penn State University, Universal Well Services, and Eco-Scan, Inc.

REFERENCES

Lu, G., and C. Zheng. 2003. "Natural Attenuation of Fuel Hydrocarbon Contaminants: Hydraulic Conductivity Dependency of Biodegradation Rates in a Field Case Study". *International Groundwater Modeling Center, Colorado School of Mines,* Golden. Paper No: LBNL-53443, 5 pp, July 2003.

Martin, J.P., R.A. Brennan, K.S. Sorenson, L.N. Peterson, and G.H. Bures. 2002. "Enhanced CAH Dechlorination in a Low-Permeability, Variably Saturated Medium." In A.R. Gavaskar and A.S.C. Chen (Eds.), *Proceedings of the Third International Conference on Remediation of Chlorinated and Recalcitrant Compounds.* Battelle Press, Columbus, OH.

Yang, X.M., and P.M. Davis, 1986. "Deformation due to a Rectangular Tension Crack in Elastic Half-Space". *Bulletin of the Seismological Society of America.* Volume 76, No. 3, June. pp. 865 – 881.