Paper A-32, in: B.C. Alleman and M.E. Kelley (Conference Chairs), *In Situ and On-Site Bioremediation—2005*. Proceedings of the Eighth International In Situ and On-Site Bioremediation Symposium (Baltimore, Maryland; June 6–9, 2005). ISBN 1-57477-152-3, published by Battelle Press, Columbus, OH, www.battelle.org/bookstore.

Phased Pilot Testing for In Situ Bioremediation of Chlorinated Solvent/Perchlorate-Impacted Groundwater in Fractured Bedrock

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ABSTRACT: Phased recirculating anaerobic bioremediation (RAB) pilot studies were initiated in October 2002 and July 2004 at an industrial facility overlying a perchlorate and VOC-impacted fractured bedrock aquifer. The first phase pilot test consisted of retrofitting existing pump and treat (P&T) system equipment to extract, treat, and amend groundwater before reinjection to the aquifer. Results of the first phase were incorporated into the design of the second pilot test. The pilot tests indicated that the converted system was capable of hydraulically capturing most of the perchlorate and VOCs plumes and also indicated significant concentration reductions ranging from 33 to 99% at the extraction well and surrounding monitoring wells. In addition, a soluble organic electron donor (methanol) was found to be a better alternative than an inorganic substrate such as calcium magnesium acetate due to mineral fouling issues. Increasing backpressure in excess of 90 psi at the injection well indicated the need for multiple active injection wells to distribute treated and amended water and reduce injection backpressure. Overall, the RAB pilot studies suggest that the retrofitting of historical remediation systems, including P&T, for use as in situ bioremediation systems may be a cost-effective method to address newly discovered contaminants and/or to accelerate the remediation of impacted sites. This phased technology approach to site remediation is gaining acceptance and can lead to reduced project costs and timelines while maintaining protection of human health and the environment.

INTRODUCTION

A groundwater pump and treat (P&T) system was installed at an industrial facility in the late 1980s to extract and treat groundwater from a deep fractured bedrock aquifer impacted by chlorinated volatile organic compounds (VOCs). The P&T system consisted of two extraction wells, a forty-foot air stripper tower, and two 8,000-pound granular activated carbon vessels. The stripper tower and GAC vessels removed approximately 99.9% of the VOCs from the system influent. In 2001, ongoing environmental investigations at the facility detected the presence of perchlorate in the bedrock aquifer. Consequently, the P&T system was deactivated, as it was not originally designed to treat perchlorate.

Perchlorate is an inorganic ion of ammonium perchlorate (AP; NH_4ClO_4), the primary rocket propellant oxidizer used in military and space rocket systems. AP is relatively soluble in water, and when released into the environment dissociates into the ammonium cation (NH_4^+) and the perchlorate (ClO_4^-) anion. In solution, perchlorate is readily transported via infiltration through the vadose zone into groundwater aquifers. AP is a vigorous

oxidizer at elevated temperatures; however, it is a weak oxidizer under ambient environmental conditions. As a result, perchlorate does not degrade rapidly and may persist in the environment despite the presence of natural electron donors. Naturally occurring bacteria can facilitate the biodegradation of perchlorate (Coates et al. 1999, Kastner et al. 2001) under anaerobic conditions to chloride, water, and carbon dioxide (Cox et al. 2000). Likewise, a great deal of research (e.g., Major et al. 1995, Acree et al. 1997, Graves et al. 1997) has shown that naturally occurring bacteria can degrade chlorinated VOCs under anaerobic conditions. The process of introducing suitable electron door substrates such as acetate, vegetable oil, and methanol to stimulate the naturally occurring bacteria is termed in situ anaerobic bioremediation.

The fractured bedrock aquifer has been characterized via multiple facility investigations and periodic groundwater sampling events. Historical and recent sampling data have shown perchlorate and VOCs plumes centered in the north-central and central areas of the facility (i.e., the treatment zone). A facility-wide sampling event conducted in May 2003 indicated perchlorate concentrations in the treatment zone ranging from 11.7 µg/L to 8.3 mg/L. The perchlorate plume extends approximately 2,250 in a direction parallel to the natural hydraulic gradient and to a maximum width of approximately 1,750 feet in the cross-gradient direction. During a sampling event conducted in November 2001, total VOCs concentrations in the area historically treated for VOCs ranged from 1.0 µg/L to 327.9 µg/L. The smaller VOCs plume lies within the horizontal extents of the perchlorate plume.

Recirculating anaerobic bioremediation (RAB) technology uses an extraction well or wells to hydraulically control plume migration and to provide source water for mixing with the selected electron donor substrate. After mixing, the amended water is reinjected to the aquifer through one or more injection points, creating a closed-loop system without the need for surface discharge and associated permitting. In addition, the RAB technology may speed up groundwater flow rates by increasing hydraulic gradients, thereby enhancing substrate coverage in the treatment zone. Phased pilot-testing was performed beginning in October 2002 and consisted of two studies to evaluate the effectiveness of the RAB technology at the facility. The phased pilot study approach was undertaken to evaluate the most cost-effective RAB system design by incorporating results from each pilot study into the subsequent phase, thereby expanding the system to enhance positive results and utilizing existing P&T system components as much as possible.

PHASE 1 PILOT STUDY

The first phase of pilot testing was conducted from October 2002 to May 2003 with approximately six weeks of downtime for system repairs and upgrades. Initially, the RAB system consisted of an existing extraction well, air stripping tower, and sediment filtration. A substrate amendment system was added, and an existing extraction well was converted to an injection well. An inflatable packer was later installed in the injection well to facilitate pressurized injections (Figure 1). During Phase 1, extracted groundwater entered the air stripping tower, passed through the sediment filters, and was subsequently amended with electron donor substrate before reinjection into the bedrock aquifer via the injection well located upgradient of the extraction well. A 25% (by weight) calcium magnesium acetate (CMA) solution was used during this phase as the electron donor.

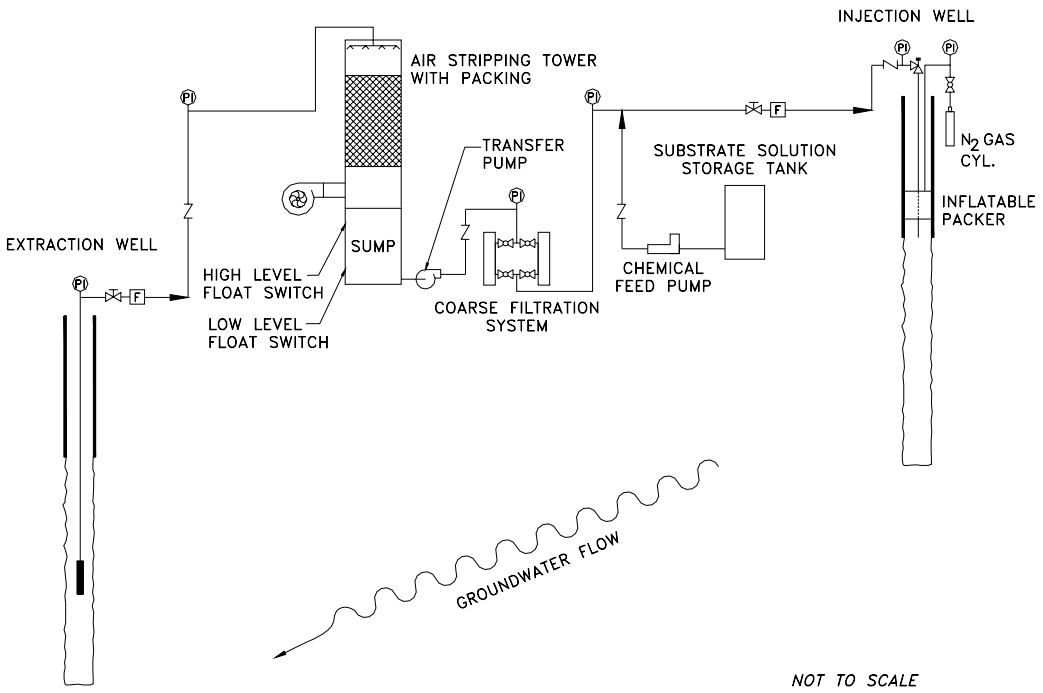

FIGURE 1. Simplified system design for Phase 1 pilot test.

The initial extraction rate was set at 20 gpm during October 2002, and was increased to 30 gpm during January 2003. To maintain system water balance, extraction and injection rates were adjusted so that the injection rate was approximately twice the extraction rate. Prior to shutdown, the extraction rate was approximately 25 gpm. Extraction rates quickly decreased to less than 5 gpm during the first two weeks of May 2003, and as a result, the pilot system was deactivated in mid-May 2003. At the conclusion of the test, the system had processed approximately 3,132,000 gallons of water.

Backpressure at the injection well ranged from 30 to 68 psi during injection cycles and dissipated to background (0 psi) levels within two minutes following cessation of an injection cycle. The substrate amendment system was operated for approximately three weeks, but was discontinued due to both mineral and bio-fouling in the injection well. In addition, during the modification of the existing P&T system, significant mineral scaling that had accumulated during P&T system operation was observed inside the air stripping tower and other system components. The scaling was removed to the extent possible using mechanical methods before starting the system.

Baseline hydraulic monitoring was initiated just before system activation in October 2002. System monitoring during startup periods occurred on an hourly to daily basis for one to three days. Subsequent routine monitoring occurred on a weekly schedule. Hydraulic monitoring of the system included: 1) recording extraction and injection flow rates, 2) recording backpressure at the injection well during injection cycles, and 3) water level gauging at deep wells in and around the groundwater treatment zone. Air stripping tower influent and effluent were sampled periodically during system operation to monitor changes in groundwater quality. Samples were analyzed for perchlorate, chlorate, acetate, and VOCs.

Results. Geochemical sampling and modeling of the RAB system indicated that natural deep groundwater at the facility, prior to air stripping, exhibits low potential for mineral scaling. However, oxidation via the air stripping tower followed by CMA amendment supersaturates the reinjection water with respect to numerous calcium-magnesium-carbonate and calcium/ferric-oxide minerals and could lead to an estimated 10 pounds per day of mineral buildup. This result indicated the need for an alternative substrate to minimize the scaling problem.

Hydraulic head measurements indicated significant drawdown in the core of the treatment zone surrounding the extraction well. The pilot RAB system induced a capture zone encompassing the majority of the perchlorate and VOCs plumes at only 30 gpm extraction. Compared to the historic 60 to 80 gpm extraction rates for the P&T system, the RAB was able to provide hydraulic control while pumping 50 to 63% less groundwater. Furthermore, the RAB facilitated reinjection of all extracted groundwater back into the aquifer for no net storage loss.

Water samples collected during the first pilot study also showed positive results. Influent samples exhibited perchlorate concentrations ranging from 6.2 mg/L in October 2002 to 1.8 mg/L in May 2003. This represents approximately 71% reduction in perchlorate at the extraction well after only eight months of system operation. Acetate was detected in the influent sample from November 2002 at 1.0 mg/L, indicating that acetate had traveled from the injection well to the extraction well. This result confirmed the hydraulic connection between these two wells, and therefore that the substrate was being distributed within the targeted treatment zone.

PHASE 2 PILOT STUDY

The second phase of pilot testing was conducted from July through December 2004 with approximately seven weeks of downtime for repairs and maintenance. Based on the results of Phase 1, the following modifications were made to the Phase 2 pilot system:

- A new submersible pump was installed in the extraction well.
- A programmed logic/interlock system was installed to automate system operation and deactivate the system in the event of high fluid level or high pressure alarms.
- A 33% (by volume) methanol in water solution was added to the injection water to replace the CMA used in the Phase 1. Methanol was selected for its high solubility in water and because it is an organic compound and would therefore not contribute to mineral buildup.
- Treated and amended water was re-piped to flow into the existing 5,000-gallon process holding tank outside the treatment building. The holding tank was used to store the processed water before reinjection.
- A progressive cavity pump was installed to replace the centrifugal transfer pump used during Phase 1 to pump processed water into the injection well. The progressive cavity pump is designed for use under higher backpressures than the centrifugal pump.
- The existing GAC vessels were used instead of the air stripping tower for treatment of VOCs. Use of the GAC reduced the oxidation effects of the stripper and therefore reduced the likelihood of mineral precipitation.

The second pilot system utilized the same existing extraction well, inflatable packer, and injection well as in Phase 1. Extraction was originally set at 20 gpm at startup in July 2004 and was gradually increased to 30 gpm by early August 2004. Due to elevated injection backpressure, however, the extraction rate was reduced back to 25 gpm by late October 2004. As of mid-December 2004, the pilot system processed approximately 3,240,000 gallons of water.

Backpressure at the injection well ranged from 48 to 93 psi during injection cycles (Figure 2) and dissipated to background within two minutes following cessation of an injection cycle. The substrate amendment system was operated the entire time while the recirculation system was active. In mid-October, the packer was removed briefly to inspect for obstructions or evidence of borehole clogging. This inspection revealed no evidence of obstructions or mineral fouling. However, a green microbial film was observed along the inside of the packer, indicating that bio-fouling was at least partly responsible for the elevated backpressure.

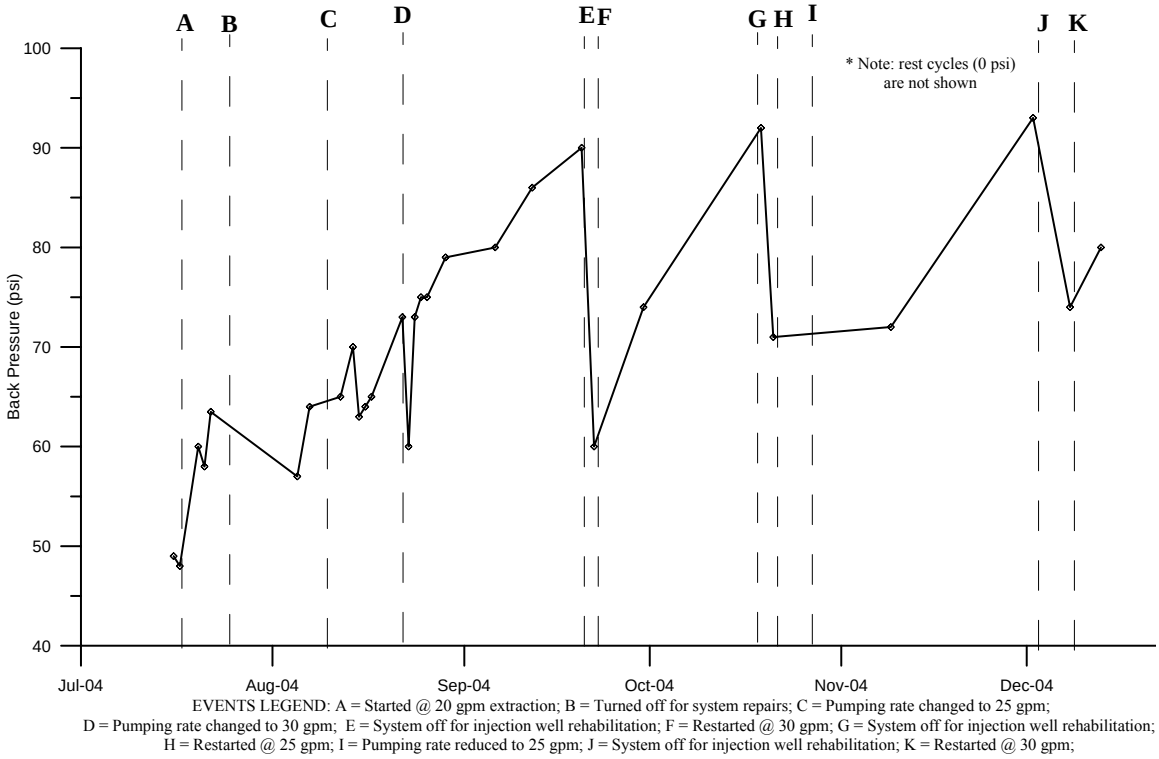

FIGURE 2. Backpressure at the injection well.

To reduce injection well backpressure, injection well rehabilitation events were performed in September, October, and December 2004. Rehabilitation was performed by deactivating the system for at least two days and then adding 50 kg of citric acid mixed with 700 gallons of water for the September and October events or by adding 25 kg of citric acid directly to the injection well for the December event. The citric acid solution was allowed to sit inside the borehole for at least one day before system reactivation. Upon restart, the injection well was flushed with at least 500 gallons of treated but unamended water to force the citric acid solution into the surrounding formation.

As part of the second pilot test, batch injections of methanol substrate were injected into five passive injection wells to the south of the extraction well in October, November and December 2004. The purpose of the batch injections was to introduce the substrate into this VOCs and perchlorate-impacted area and allow the substrate to flow through the treatment zone via pumping at the extraction well. For each injection, a 4% solution of methanol in water was injected to each passive injection well using a pneumatic double-bladder pump. Each injection batch consisted of 700 to 1,400 gallons of methanol/water solution followed by 700 gallons of unamended water flush.

Baseline hydraulic monitoring was initiated just before system activation in July 2004. System and hydraulic monitoring were performed as in Phase 1. GAC influent and effluent were sampled periodically during system operation to monitor changes in groundwater quality. Samples were analyzed for perchlorate, chlorate, and VOCs.

Results. Hydraulic head measurements during the July through December 2004 pilot testing were generally in those from Phase 1. At 25 to 30 gpm, the pilot RAB system created a capture zone encompassing most of the VOCs and perchlorate-impacted areas. Despite the change to GAC and methanol substrate from the air-stripping and CMA used in the first phase, backpressure at the injection well continued to increase during the pilot study. The observation of a green microbial film in the injection piping in October 2004 suggested that bio-fouling is contributing to the backpressure problem. Backpressure was reduced by the rehabilitation events by as much as 30 psi (Figure 2); however, the reduction in pressure declined in both magnitude and duration over time.

Water samples collected during the second pilot study showed continued improvement in groundwater quality from the first phase. Prior to system startup, May 2004 perchlorate and VOCs concentrations at the injection well were 1.7 mg/L and 621 µg/L, respectively. Immediately following startup in July 2004, significantly higher perchlorate (10.7 mg/L) and VOCs (1,094 µg/L) concentrations were observed, attributed to continuing source effects and to increased mass fluxes from source areas upgradient from the extraction well. At the end of Phase 2, however, the perchlorate and VOCs concentrations at the extraction well had been reduced to 7.1 mg/L (33% reduction) and 940 µg/L (14% reduction), respectively. Furthermore, reductions in perchlorate and VOCs concentrations at wells in the treatment zone core ranging from 33 to 99% were observed over the duration of the pilot study.

Both phases of pilot testing indicated the need for multiple active injection points to distribute reinjection water, thereby reducing backpressure at the single injection well. In addition, reductions in perchlorate and VOCs in wells to the south of the extraction well indicated that batch injections to passive injection wells are a viable enhancement for the RAB system. These modifications are to be incorporated into the next phase of pilot testing planned for 2005.

CONCLUSIONS

The results of the pilot testing demonstrated the effectiveness of converting a former P&T system into an in situ RAB system in the fractured bedrock setting at this facility. This research suggests that retrofitting of historical remediation systems, including P&T, in a phased approach may be a cost-effective method to address newly discovered contaminants and/or to accelerate remediation of impacted sites. The phased technology

approach to site remediation reduces costly up-front capital expenditures for system construction and reduces the likelihood of long-term design difficulties resulting from hydrogeologic uncertainties. This approach is gaining regulatory acceptance and can lead to reduced project costs and cleanup timeframes while still being protective of human health and the environment.

ACKNOWLEDGMENTS

The authors would like to thank all the Environmental Alliance, Inc. project and administrative staff who have worked on this project.

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