FRACTURED BEDROCK PUMP-AND-TREAT CONVERSION TO IN SITU BIOREMEDIATION

William Smith, P.G./Jason Early, Hydrogeologist/Kevin Morris, Bioremediation Specialist/Christopher Underwood, P.E. (cunderwood@envalliance.com)
(Environmental Alliance, Inc., Wilmington, DE, U.S.A.)

ABSTRACT: A groundwater pump-and-treat system was installed at an industrial facility in the early 1990s to address chlorinated volatile organic compound (VOC) contamination in a deep aquifer. Following the detection of perchlorate in the deep aquifer in September 2001, the pump-and-treat system was shut down. Perchlorate is a highly soluble inorganic ion that is not amenable to remediation via air stripping or carbon adsorption. After examination of the existing pump-and-treat system, it was determined that with modifications the existing system could be converted to a bioremediation system capable of promoting the in situ anaerobic reduction of VOCs and perchlorate, while maintaining hydraulic control of the dissolved contaminant plumes. A pilot test was conducted to evaluate the potential effectiveness of the proposed bioremediation system. The pilot test was conducted from October 2002 to May 2003, with approximately 3,000,000 gallons of water being extracted, treated for VOCs, amended with an electron donor substrate, and subsequently reinjected. After eight months of operation, the perchlorate level at the extraction well was reduced by approximately 71%.

INTRODUCTION
A groundwater pump-and-treat system was installed at an industrial facility in the early 1990s to address chlorinated volatile organic compound (VOC) contamination in an aquifer over 250 feet below ground surface (bgs). The treatment process consisted of an air stripping tower, a coarse filtration system, and a carbon adsorption system that were capable of achieving a combined removal efficiency for VOCs of approximately 99.99%. Following the detection of perchlorate in the deep aquifer in September 2001, the pump-and-treat system was shut down. Perchlorate is a highly soluble inorganic ion that is not amenable to remediation via air stripping or carbon adsorption. After examination of the existing pump-and-treat system, it was determined that the existing system could be converted to a bioremediation system capable of promoting the in situ anaerobic reduction of VOCs and perchlorate, while maintaining hydraulic control of the contaminant plumes.

The bedrock identified beneath the site in the groundwater treatment area consists of two major types: a Jurassic igneous diabase and a Triassic metamorphosed siltstone/sandstone (metasediments). The diabase is located throughout most of the facility, with the metasediments located primarily in the north central portion of the facility. Based on site testing activities, including aquifer pump tests and downhole geophysical testing of selected wells, the diabase was found to have minimal to no primary or secondary fracturing and to lack any significant quantities of groundwater. Further evaluation of the collected data indicated the diabase to be relatively
impermeable and to act as an aquitard. The physical evaluation of the metasediments indicated the formation to be more permeable and exhibit substantial fracturing in comparison to the diabase. Significant quantities of groundwater from the metasediments (historically sufficient to meet the facility process water requirements) have been documented at the facility. The results of a deep aquifer test within the metasediments indicated aquifer responses consistent with confined or leaky (semi-confined) conditions that are fracture-controlled and have a radial flow component. From these deep aquifer test results, the metasediment aquifer is generally shown to be anisotropic and heterogeneous with two primary fracture zones connecting the wells located in the deep groundwater treatment area.

Chemical characterization of the deep groundwater aquifer has been accomplished via multiple investigations and periodic groundwater sampling events. Both historical and recent sampling data have shown perchlorate and VOC plumes centered in the north-central and central portions of the facility (i.e., the treatment zone). The most recent facility-wide sampling event (May 2003) indicated perchlorate concentrations in the treatment zone ranging from 11.7 $\mu$g/L to 8,293 $\mu$g/L. The deep groundwater perchlorate plume extends approximately 2,250 feet in a direction parallel to the natural deep hydraulic gradient and to a maximum width of approximately 1,750 feet in the cross-gradient direction. Recent total VOC concentrations in the area historically treated for VOCs ranged from 1.0 $\mu$g/L to 327.9 $\mu$g/L (November 2001). The smaller deep groundwater VOC plume lies within the horizontal extents of the perchlorate plume. Dissolved oxygen (DO) concentrations in the deep groundwater were also measured during recent sampling events, and ranged from 0.22 mg/L (May 2003) to 1.19 mg/L (November 2002). These relatively low DO concentrations are indicative of an environment that is anoxic to anaerobic. Such low DO concentrations are typical of deep semi-confined to confined aquifers, and are a positive indication that the aquifer is naturally pre-conditioned for anaerobic bioremediation.

A pilot test was conducted during October 2002 to May 2003 to evaluate the potential effectiveness of the proposed bioremediation system. The initial configuration for the bioremediation system consisted of the existing deep groundwater extraction well, air stripping tower, and coarse filtration system, along with a substrate amendment system and an existing deep groundwater extraction well converted to an injection well. An inflatable packer system was later installed in this injection well to facilitate pressurized injections (Figure 1). The existing carbon adsorption system was not used because of historical mineral fouling issues in the pump-and-treat system that resulted in the concretion of the granular activated carbon. During the pilot test, extracted deep groundwater entered the air stripping tower, passed through the coarse filtration system, and was subsequently amended with substrate prior to reinjection into the deep aquifer via the injection well located upgradient of the extraction well.

MATERIALS AND METHODS

The pilot-scale deep groundwater system consists of one extraction well and one injection well. These wells were selected based on location (within the core area of impacted deep groundwater) and historically proven hydraulic connection (to maintain hydraulic control of the perchlorate and VOC plumes). An existing submersible pump installed in the extraction well was initially used to continuously pump groundwater
(from approximately 300 feet bgs) through the treatment system. Extracted groundwater entered the existing air stripping tower to remove VOCs prior to reinjection at the injection well. A collection sump associated with the air stripping tower is equipped with low-level and high-level float switches that controlled the cyclic operation of a 10-horsepower centrifugal transfer pump. After a specified amount of extracted groundwater had accumulated in the sump, the transfer pump was activated and pumped the treated groundwater water from the sump through the coarse filtration system to remove any particles larger than 50 microns in effective diameter.

Following filtration, the extracted groundwater was amended with substrate. A polyethylene tube fed from a chemical metering pump was connected to the transfer pump discharge piping. The metering pump was supplied by a 1,100-gallon plastic tank containing 25% (by weight) calcium magnesium acetate (CMA) solution. Sodium iodide was added to the CMA solution in sufficient quantity to result in an iodide (tracer) concentration of 100 mg/L. After substrate addition, the extracted groundwater was reinjected into the deep aquifer via the existing piping system and the converted injection well. The inflatable packer system installed in the injection well enabled the reinjection of groundwater at elevated pressures. A downhole submersible video camera was used to determine the most effective location for packer placement. The steel well casing was observed to end at a depth of 50 feet bgs, and the packer was placed just above the casing edge at 45 feet bgs to achieve a proper seal and minimize/prevent short-circuiting of the injected water through the casing. A standard pressure relief valve rated for 125 pounds per square inch (psi) is installed at the injection wellhead to ensure that potentially harmful backpressures are not maintained during injection cycles.
The extraction rate was initially set at 20 gallons per minute (gpm) during October 2002, and was increased to 30 gpm during January 2003. To maintain the system water balance, the extraction and injection rates were adjusted such that the injection rate was approximately twice the extraction rate (i.e., 60 gpm). Existing flow meters were used to monitor the flow rates of extracted and reinjected groundwater. After the extraction rate was increased during January 2003, the performance of the existing submersible pump was observed to steadily decline, likely due to the age of the pump. Pumping rates from the extraction well quickly decreased to less than five gpm during the first two weeks of May 2003, and the pump was subsequently deactivated. Prior to shutdown in May 2003, the extraction rate was approximately 25 gpm. Backpressures at the injection well were observed to range from 30 to 68 psi during injection cycles, and to dissipate to background levels within two minutes after an injection cycle ceased.

Hydraulic monitoring of the deep groundwater pilot system was initiated just prior to the beginning of the pilot test in October 2002. Monitoring of the pilot system during start-up periods (e.g., beginning of the pilot test, following system repairs and/or upgrades) occurred on a frequent (hourly to daily basis for a period of one to three days) basis. Subsequent routine monitoring occurred on a less frequent (weekly) schedule. Routine hydraulic monitoring of the deep groundwater pilot system included: 1) recording of flow rates (gpm) for the extraction and injection wells using existing flow meters; 2) recording of backpressure (psi) readings at the injection well during injection cycles using existing pressure gauges; and 3) water level gauging at deep wells in and around the groundwater treatment zone using an electronic water level meter. In addition to the active water level monitoring, a pressure transducer was installed in a deep well located downgradient of the extraction well during November 2002. This transducer was programmed to record water levels every 15 minutes.

RESULTS AND DISCUSSION

The deep groundwater pilot test was conducted from October 2002 to May 2003, with approximately six weeks of downtime for system repairs and upgrades. As of the conclusion of the pilot test in May 2003, approximately 3,132,000 gallons of water had been extracted, treated for VOCs, and reinjected. Hydrographs of injection and extraction area wells indicate these wells have experienced an overall gradual increase in hydraulic head during the pilot test. This long-term rise can be attributed to recharge from over 14 inches of precipitation during the monitoring period from October 2002 to April 2003. On a shorter timeframe, hydraulic heads are also clearly influenced by system operation, with small but noticeable drawdowns in the wells closest to the extraction well. A review of mean hydraulic head among injection and extraction area wells and precipitation data suggests that the wells are also subject to significant head fluctuations as a result of precipitation events, with hydraulic heads being subject to short-term fluctuations over periods of less than one day. Well hydrographs indicate that the deep groundwater treatment system is competing with daily fluctuations due to barometric pressure changes and significant recharge events. Such fluctuations are to be expected in a semi-confined fractured bedrock system where very minor changes in storage can produce significant head fluctuations. However, the noted drawdown effects are a positive indication of the hydraulic connection in the groundwater treatment zone.
and the effectiveness of the treatment system at a relatively low extraction rate (i.e., 20 to 30 gpm) despite recharge effects.

Figure 2 illustrates the potentiometric surface at the facility prior to pilot system startup during October 2002. The natural gradient is relatively shallow and the contours are parabolic in shape, indicating convergent flow to the south. Figure 3 illustrates the potentiometric surface after approximately four months of pilot system operation during February 2003. As is evident from this figure, the recirculation system significantly altered the potentiometric surface, creating an extensive cone of depression surrounding the extraction well and a cone of recharge surrounding the injection well. During the pilot test, the capture zone for the extraction well was sufficient to hydraulically control most of the VOC and perchlorate plumes. Additionally, the system was capturing the majority of the reinjected groundwater.

The air stripping tower influent and effluent were sampled periodically during pilot system operation to monitor any changes in groundwater quality and to evaluate iodide tracer movement. Samples were analyzed for perchlorate via EPA Method 314.0 and for chlorate, acetate, and iodide via EPA Method 300.0B. Influent samples exhibited perchlorate concentrations ranging from 1.84 mg/L (May 2003) to 6.24 mg/L (October 2002). The iodide tracer was not detected in the influent, possibly due to the low concentration of iodide (i.e., 100 mg/L) in the CMA solution and/or the brief duration of CMA/iodide tracer solution injection. However, acetate was detected in the influent sample collected during November 2002 at a concentration of 1.02 mg/L. This detection indicates that acetate has been transported from the injection well to the extraction well. Furthermore, the presence of acetate indicates that a substrate capable of stimulating the indigenous anaerobic microbial population has been distributed within the targeted deep groundwater treatment zone. Chlorate has not yet been detected in the influent, suggesting that insufficient time and possibly insufficient amounts of electron donor have been allotted to initiate the anaerobic reduction of perchlorate.

The substrate amendment system was operated for approximately two weeks in October 2002 and one week during November 2002, but was discontinued due to injection well fouling/backpressure issues. During the modification of the existing groundwater treatment system, a significant amount of mineral scale was observed to have accumulated inside the air stripping tower, transfer piping, and other system components since the early 1990s. This scale was removed to the extent possible using mechanical methods. A file search and discussions with facility personnel revealed that the water at the facility is naturally hard (i.e., contains significant concentrations of calcium and magnesium ions). Use of an electron donor such as CMA, which contains both calcium and magnesium, may only contribute to mineral scaling. As a result, geochemical sampling and analysis and geochemical modeling were used to evaluate the source(s) of the scaling problem and to evaluate the effects of proposed electron donor substrate amendments on the process water.

The results of the geochemical sampling and analysis and geochemical modeling of the deep groundwater recirculation system indicated that the natural groundwater extracted from the deep aquifer, prior to air stripping, exhibits low potential for mineral scaling. However, following vigorous aeration via the air stripping process, the groundwater becomes very susceptible to mineral scaling. In addition to the effects of the air stripping process, the amendment of the groundwater with even small quantities of
FIGURE 2. Potentiometric Surface Map Prior to Pilot System Operation.

NOTES:
1) VALUES INTERPOLATED USING A KRIGING ALGORITHM
2) STATIC (NON-PUMPING) CONDITIONS
3) CONTOUR INTERVAL = 1 FOOT


NOTES:
1) VALUES INTERPOLATED USING A KRIGING ALGORITHM
2) EXTRACTION RATE SET AT 30 GPM
3) MAXIMUM CYCLED INJECTION RATE SET AT 60 GPM
4) CONTOUR INTERVAL = 1 FOOT
CMA increases the susceptibility of the groundwater to mineral scaling. Under typical operating conditions, the mineral precipitation could produce approximately 10 pounds of solids per day, leading to significant scaling in the process equipment and piping, as well as in the injection well borehole fractures. A possible solution to minor scaling problems is the periodic addition of an organic acid (e.g., citric acid), which may yield multiple positive effects, including acting as a solvent for mineral scale, as an oxygen scavenger to maintain low DO concentrations, and as an electron donor substrate to promote the anaerobic biodegradation process.

In addition to the pilot test, numerical groundwater flow and particle-tracking models were developed to gain a more thorough understanding of groundwater flow at the site, to evaluate the performance of current and proposed extraction and injection wells, and to assist in groundwater recirculation system design decisions. The groundwater flow model used MODFLOW (McDonald and Harbaugh, 1988) to represent the hydrogeological conditions at the facility. The particle-tracking model used MODPATH (Pollack, 1989) to define groundwater flow paths and travel times. Visual MODFLOW Pro (Waterloo Hydrogeologic, Inc.) was used for pre-processing data input files, the development of the model grid, and post-processing of output data files. To assist with the development of input data files (e.g., structure contour maps of the aquifer units, potentiometric surface contour maps, etc.), the contouring package SURFER (Golden Software, Inc.) was used.

CONCLUSIONS
Pilot Test. The results of the deep groundwater bioremediation system pilot test demonstrated the effectiveness of this type of system in the fractured bedrock aquifer setting at the test facility. Although perchlorate concentrations in the deep groundwater samples collected at the extraction well fluctuated during the pilot test, the most recent sampling event conducted during May 2003 indicated that after eight months of operation, the perchlorate level at the extraction well was reduced by approximately 71%. General conclusions derived from this study include: 1) The deep groundwater aquifer is subject to significant head fluctuations resulting from long-term events (seasonal changes in precipitation), intermediate-term events (individual precipitation events and system drawdown/mounding), and short-term events (daily barometric pressure fluctuations); 2) The specific capacity of the injection well (and possibly future proposed injection wells) was sufficiently small that pressurized reinjection using a downhole packer system was required to avoid overflow of reinjected groundwater; 3) The use of the air stripping tower and CMA should be avoided for the proposed bioremediation system to reduce the possibility of mineral scaling; and 4) Numerical groundwater modeling indicates that the current pilot test configuration would influence the perchlorate and VOC plumes, but a more efficient system design may consist of two extraction/injection well pairs.

Expanded Pilot Test Design. Based on the results of the pilot test, a modified bioremediation system design has been developed. This modified system will incorporate the extraction and injection wells used for the pilot test, and will allow for system expansion to include additional extraction and injection wells. The modified bioremediation system will consist of the existing extraction well, coarse filtration system, and carbon adsorption system, along with a substrate amendment system and the
existing injection well fitted with the inflatable packer system. The major differences between the proposed and pilot systems are the replacement of the air stripping tower with the carbon adsorption system for the treatment of VOCs and the use of a more suitable water-soluble substrate in lieu of CMA as an electron donor. Removing the air stripping process from the treatment system will minimize the amount of DO introduced to the extracted groundwater. This will maintain the anaerobic conditions necessary for the reduction of the constituents of concern and minimize the mineral scaling encountered during the pilot test. The change in electron donor from CMA to a more suitable water-soluble substrate is proposed to minimize any mineral scaling that may be associated with elevated concentrations of calcium and magnesium. Use of an appropriate alternative substrate may also minimize any biofouling that may occur in the injection well(s) during long-term operation of the bioremediation system.

**Application.** Overall, the results of this pilot test suggest that the retrofitting of existing remediation systems, including pump-and-treat, air sparge/soil vapor extraction, and dual phase extraction systems for use as bioremediation systems may be a cost-effective method to address newly discovered contaminants and/or accelerate the remediation of impacted sites. Phased technology approaches to site remediation have gained acceptance and can often lead to reduced projects costs and timelines. This pilot study also demonstrated that advanced computer modeling techniques can be useful tools in the design and optimization of groundwater recirculation systems.

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**REFERENCES**
