Proceedings of the Annual International Conference on Soils, Sediments, Water and Energy

Volume 16 Article 8

2011

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Recommended Citation

Falatko, David M.; Fam, Sami A.; and Pon, George (2011) "Applications and Benefits of Groundwater Recirculation for Electron Donor Delivery and pH-Adjustment During Enhanced Anaerobic Dechlorination," *Proceedings of the Annual International Conference on Soils, Sediments, Water and Energy*: Vol. 16 , Article 8.
Available at: https://scholarworks.umass.edu/soilsproceedings/vol16/iss1/8

Chapter 7

APPLICATIONS AND BENEFITS OF GROUNDWATER RECIRCULATION FOR ELECTRON DONOR DELIVERY AND PH-ADJUSTMENT DURING ENHANCED ANAEROBIC DECHLORINATION

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ABSTRACT

The enhanced anaerobic dechlorination (EAD) process is used for in-situ degradation of various chlorinated organic compounds. Electron donors must be delivered to the targeted treatment area and anaerobic subsurface conditions must be maintained for a period of time to degrade both the soluble and adsorbed contaminants. The most common EAD approaches use batch addition of either small volumes of high strength electron donors such as emulsified oil or solid phase hydrogen release compounds, or large volumes of diluted dissolved donors such as molasses or other carbohydrates. Both approaches typically rely on groundwater transport to carry the additives across the entire EAD targeted area. However, groundwater flow is generally laminar, predominantly horizontal, and soluble electron donors added in batch mode can only be adequately distributed in the subsurface with either high-density point installation or large volume addition, or some balanced combination of both. In addition, both batch approaches often require relatively high groundwater flow velocity to distribute the additives down gradient in reasonable time frames and before the electron donor is fully degraded. These difficult requirements for proper batch donor addition often cause dechlorination to stall midway through the process or have a limited treatment area due to a lack of donor distribution. Proper maintenance of neutral pH is a second important requirement for EAD, and is often not controlled adequately during batch addition approaches. Dehalococcoides, the organisms responsible for breakdown of cis-dichloroethene to vinyl chloride and ethene, are not active at a pH below 6.0-6.3. Batch addition methods provide little recourse to

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adjust pH without excessively raising pH in the area immediately surrounding the injection location. Continuous groundwater extraction and recirculation approaches to electron donor and pH buffer addition, however, address these issues and can provide faster and more thorough remediation than the batch processes. Groundwater recirculation provides greater donor distribution through increased injection volumes and hydraulic gradients. Alkalinity can be added as needed to counter decreases in pH and conducted in the form of a large scale titration. Bioaugmentation cultures, when needed, can also be added and quickly dispersed throughout the area. Groundwater recirculation systems for EAD typically divide the treatment area into sections and recirculate and amend groundwater as needed within each section depending on the size of the target area and the aquifer conditions. The proper design and implementation of groundwater recirculation for EAD will be presented and concepts reviewed.

Keywords: anaerobic dechlorination, groundwater remediation

1. INTRODUCTION

There has been an increasing awareness and application of enhanced anaerobic dechlorination (EAD) process for in-situ biodegradation of chlorinated aliphatic hydrocarbons (CAH) in groundwater such as tetrachloroethene (PCE), trichloroethene (TCE), and trichloroethane (TCA) (USEPA, 2000). Anaerobic dechlorination occurs when bacteria utilize CAHs for respiration as alternate electron acceptors under anaerobic conditions in place of oxygen, a process called halorespiration. This dechlorination process occurs naturally if anaerobic conditions are present in the subsurface, or it can be enhanced in the subsurface with the introduction of biologically degradable substrates such as molasses, corn syrup, lactate, whey, oil, or ethanol. These substrates act as electron donors, and biological degradation of these substrates requires electron acceptors. Electron acceptors are typically utilized sequentially based on the energy they yield to the microbe as follows: oxygen, nitrate, manganese, iron, sulfate, and carbon dioxide (CO_2) until methanogenic conditions are established. Dechlorination typically occurs under sulfate reducing and methanogenic conditions, when other electron acceptors are scarce and the energy yielded by halorespiration of CAHs is more favorable.

In these reactions, hydrogen (H_2) is produced from the fermentation of the organic substrate by a mixed microbial community and then hydrogen serves as the direct electron donor for the reduction of the chlorinated compound. The degradation of the substrate and the production of hydrogen occur with a mixed microbial culture that take the primary substrates and produce a variety of secondary substrates such as ethanol, lactate, propionate, and butyrate, which in turn are degraded and produce acetate, CO_2 and H_2. The hydrogen utilization rate for dechlorination is very small, however, due to often significant hydrogen demands from other electron acceptors, including methanogens. Therefore, enough organic substrate must be added to produce hydrogen in quantities sufficient to satisfy all electron acceptor demand and then be able to maintain hydrogen concentrations for the time required to complete dechlorination of the CAHs present.

Dechlorination occurs first for the most heavily chlorinated CAHs, with PCE being degraded with the substitution of one chloride ion with one hydrogen ion to form TCE. Dechlorination proceeds sequentially in the same manner through TCE to cis-1,2-dichloroethene (DCE), to vinyl chloride (VC), and then to ethene. Each step in the dechlorination process requires one mole of hydrogen per mole of CAH and yields one mole of hydrochloric acid (HCl), such that one mole of PCE yields four moles of HCl with complete dechlorination. Dechlorination of high concentrations of CAH can cause significant alkalinity demand or a sharp drop in pH if sufficient buffering capacity is not present.

Dechlorination can often be accomplished with mixed microbial cultures, with a wide variety of microbes capable of dechlorinating PCE and TCE to DCE; many of these are also sulfate reducers. Less common are microbes that are able to dechlorinate DCE completely to ethene; *Dehalococoides Ethanogenes*, (DE) is the only species that has shown the ability to completely degrade PCE to ethene. EAD performance will be optimized if the proper conditions for viability of DE are maintained. Viability of DE and related mixed cultures is very pH-dependent, and complete dechlorination has been shown to slow significantly at a pH below 6.0-6.3.

The conditions required for complete dechlorination to occur in the subsurface with the EAD process are:

- strongly anaerobic conditions (sulfate reducing to methanogenic);
- presence of a microbial community (DE) capable of complete dechlorination; and,
- buffering capacity sufficient to maintain a near-neutral pH.

The proper design of an EAD system provides processes to achieve and maintain these conditions.

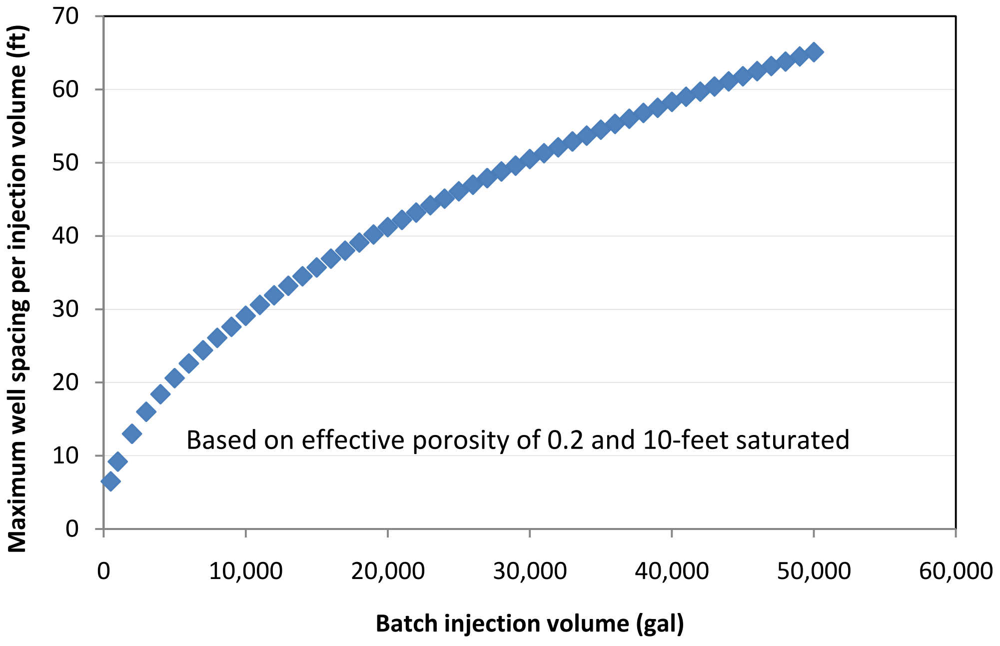
2. SUBSTRATE AND ADDITIVE DELIVERY APPROACHES

The methods utilized for delivery of degradable organic substrates and other additives can be grouped into three primary approaches: stationary or solid phase substrate addition, batch liquid phase substrate addition, and continuous recirculation with liquid substrate. The different approaches all have to be able to distribute the substrate evenly across the width of the targeted treatment area, and provide substrate concentrations sufficient to distribute substrate throughout the entire targeted area.

Stationary or solid phase addition generally uses substrates such as high viscosity lactate, vegetable oil (either straight or emulsified), or materials such as chitin or mulch. Liquid phase batch substrate addition typically uses soluble substrates such or molasses, corn syrup, whey, alcohol, or emulsified oil, diluted slightly or significantly prior to injection. In both of these approaches, the substrate is placed in the ground and is dissolved and degraded as groundwater flows across and through it under existing site gradients. The major limitation of these two approaches is that they rely on groundwater velocity and dispersion to distribute substrate. Groundwater velocity can be easily calculated from site data, but often plumes have been established over long periods of time, so it is difficult to place enough substrate in batches to cover the entire area over reasonable time frames. Dispersion effects have been shown to be limited also, with standard estimates of longitudinal dispersion at a maximum of approximately ten percent of plume length (EPA 1992). Transverse dispersivity has also been shown to be very low and is essentially negligible for design purposes (Grathwohl and Klenk, 2000).

Large volume batch substrate addition can address these limitations somewhat if the target treatment area is completely covered with transects of injection wells and the wells are closely spaced such that the outer limits of injection volumes meet midway between adjacent injection wells. Spacing of the injection wells is a balance between number of wells and the time/effort required to inject enough liquid substrate volume to reach the midpoint between the next adjacent injection well. For example, with an aquifer with a saturated thickness of ten-feet, effective porosity of 0.2, and well spacing of 30-feet, it takes approximately 10,000 gallons of liquid substrate injected into each well in the transect to push substrate midway to the next adjacent well and provide complete coverage. Figure 1 illustrates this issue and shows the substrate injection volumes required for coverage under various well spacing distances. Large volumes of injected batch substrate can also displace the dissolved phase contamination since the groundwater is not immediately biologically active, and as such, plume spreading is likely with tap water batch addition approaches unless site groundwater is utilized as make-up water to dilute the substrate. In a practical field application of this batch approach, injection of these large volumes into the aquifer simultaneously can become very difficult when applied to several wells and transects across a plume.

Figure 1. Maximum spacing allowed between injection wells for complete coverage per batch injection volume.



Even with sufficient coverage between batch injection wells, distribution of substrate down gradient is still dependent on groundwater velocity to carry substrate across the targeted area at least to the next down gradient transect of batch injection wells. Multiple transects of batch injection wells are therefore typically used to provide sufficient coverage over large plumes which developed over many years. Design of spacing between transects is a balance of the substrate concentration in the diluted batch volume, the half-life of the substrate in groundwater, and the groundwater velocity between transects. Groundwater substrate concentrations need to be sufficient to sustain biological growth and maintain anaerobic conditions for an extended time period. Empirical data from industry practice has indicated that at least 50 mg/l of total organic carbon (TOC) needs to be maintained for a minimum of 100 days time from the point of substrate addition (AFCEE et al, 2004). Initial batch substrate concentrations in the injected volume need to be sufficiently high such that residual TOC concentrations remain within these guidance values after groundwater has traveled through the batch injection area. Selecting the right substrate with a long half-life and at a sufficiently high initial concentration to last between injection transects is therefore required. Experience has shown that initially starting at a high concentration of TOC at the injection wells can cause a drop in pH due to excessive production of organics acids and generated carbon dioxide gas, therefore the TOC concentration of an injected substrate solution should be less than 3,000 mg/l. Figure 2 shows the residual TOC concentrations for various substrates with time after subsurface injection based on their estimated half-lives.

Figure 2. Residual TOC concentrations for various substrates with time

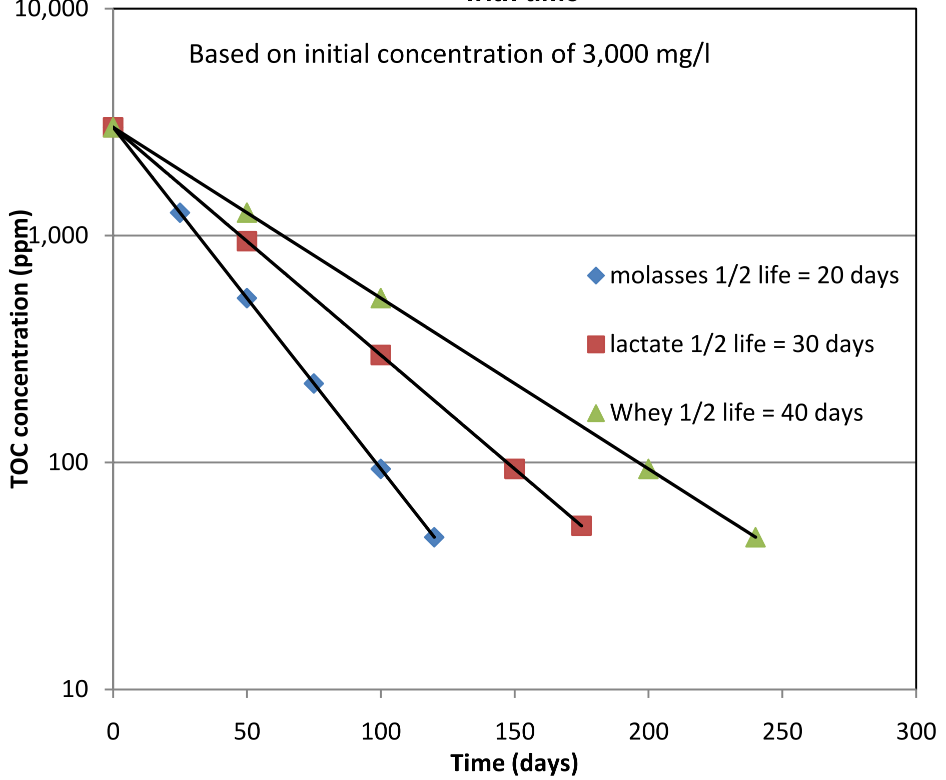


Figure 2 can be used to estimate treatment distance down gradient from the injection transect. As an example, at a groundwater velocity of 1 foot/day, a substrate solution with a half-life of 20 days (such as molasses) added at an initial concentration of 3,000 mg/l TOC would provide effective treatment 120-feet down gradient from the point of addition. More complex substrates (such as whey) with longer half-lives (40+ days) would provide coverage further down gradient (250 feet). Increasing the initial substrate concentration also can provide coverage further down gradient up to a point, but risks causing a pH drop and stalling the EAD process. The upper limit of acceptable substrate concentration combined with the substrate degradation half-life constants indicate that the maximum period of time in which substrate added to groundwater can exist above 50 mg/l TOC varies from approximately 120 days for molasses up 250 days for whey. Spacing of batch injection well transects therefore have to be designed such that the travel time between transects is short enough that there will still be effective concentrations of substrate present by the time the injected water reaches the next down gradient transect; i.e., 120 to 250 days travel time, depending on the substrate used. Ideally, large batch volumes of dilute substrate should be injected frequently, but often in practice, small volumes of highly concentrated substrates are injected infrequently due to the cost and difficulty in handling and injecting large volumes. The result is that the performances of many EAD batch injection systems suffer because of inadequate substrate distribution and low pH issues. A proper EAD design needs to consider a combination of groundwater velocity, substrate half-life, and initial and residual TOC concentrations to determine injection well transect spacing.

Control of pH within the EAD treatment zone also needs to be monitored and controlled to stay near neutral (greater than 6.0-6.3) order for the DE microbe to complete dechlorination. The dechlorination process produces hydrochloric acid in a molar ratio of four moles of HCL per mole of PCE, with lesser chlorinated compounds producing correspondingly less acid. For each mg/l of PCE, 1.2 mg/l of alkalinity is required to neutralize the acid formed, and this affect is more pronounced when high concentrations of PCE are encountered (McCarty et al, 2007). Significant alkalinity is also needed to neutralize the carbon dioxide and acetic acid and other organic acids produced from the fermentation of the different substrates used as electron donors. Glucose generally requires the most alkalinity to maintain neutral pH levels, and formate and lactate require the least. Batch substrate addition systems often need at least some inherent pH buffering capacity added with the substrate in order to counter the acid generating effects of dechlorination, organic acid production, and production of carbon dioxide in the aquifer. In practice, it is very difficult to provide sufficient buffer in a batch process such that the pH starts and remains near neutral during biological degradation of the substrate and chlorinated solvents. For this reason, many EAD systems suffer from low pH conditions and dechlorination stalls at DCE and VC since the DE microbe is inhibited at low pH. Adjusting pH in groundwater after a batch addition is also very difficult, and there can be a significant time delay since delivery of alkalinity is also dependent on groundwater velocity.

Recirculation systems can overcome many of the limitations of batch injection systems since they can manipulate groundwater flow velocity and travel times, move and inject large volumes of substrate-amended groundwater, and can be operated to provide pH buffering by adding small amounts of alkalinity continuously to the recirculated groundwater. Recirculation EAD systems use similar substrates as liquid phase batch systems, but with the addition of extraction and injection wells to increase gradients and move substrate faster than under existing conditions. Substrate addition can occur either continuously with the liquid substrate added to the extracted groundwater and re-injected, or batch added to the subsurface and the groundwater recirculated through the area of substrate addition. The design approach of EAD systems with groundwater recirculation is presented in the following sections.

3. DESIGN OF EAD RECIRCULATION SYSTEMS

The design of an EAD recirculation system evaluates and considers the following variables:

- Evaluate existing biogeochemical conditions and assess need for bioaugmentation;
- Identify targeted treatment area/volume, aquifer parameters, and existing groundwater velocity;
- Estimate substrate demand from electron acceptors;
- Assess alkalinity demands and need for additional buffering capacity; and,
- Design of extraction and injection system pumps, piping, and controls.

3.1 Evaluate Existing Biogeochemical Conditions

The existing site biogeochemical conditions should be evaluated to assess the extent to which the EAD process is occurring naturally, and the degree to which it may need to be enhanced for it to completely degrade the target contaminants. Electron donors which can biologically degrade and create anaerobic conditions should be measured and may include non-chlorinated VOCs, petroleum hydrocarbons, and other forms of degradable organic carbon collectively measured as TOC. Electron acceptors such as oxygen, nitrate, iron and manganese (as oxides in the aquifer matrix), and sulfate should be measured or estimated, and provide an indication of competing electron donor demands that must be met before anaerobic conditions are fully established. The presence/absence of electron acceptors and the presence/absence of reduced end products such as ferrous iron, sulfide, and methane can indicate the degree to which anaerobic conditions have been established. Water quality parameters such as pH and alkalinity should be measured and assessed for the potential buffering capacity of the groundwater and aquifer matrix materials.

Evidence of anaerobic conditions leading to anaerobic dechlorination would include a lack of oxygen, nitrate, and sulfate, and the presence of reduced iron and manganese, sulfide, carbon dioxide, methane, and suitable electron donors (summarized as TOC). Evidence of on-going dechlorination with anaerobic conditions would include the presence of degradation by-products such as DCE, VC, and ethene. Conversely, the presence of oxygen, nitrate, and sulfate, and a lack of electron donors and reduced end products or dechlorination by-products indicate that anaerobic conditions are not present and dechlorination is not proceeding. The degree to which the site is more aerobic or anaerobic may vary between these two extremes and will influence the ease of establishing the EAD process.

The potential need for bioaugmentation can also be assessed at this time based on the site evidence for existing dechlorination, the results of treatability testing, or polymerase chain reaction testing (PCR). Current practice indicates that all three should be considered (Environmental Security Technology Certification Program, 2005), but bioaugmentation may not be warranted if there is existing evidence of complete dechlorination to final end-products. Bioaugmentation will likely be needed if there is no evidence of dechlorination, particularly if anaerobic conditions are not yet established.

3.2 Identify Targeted Treatment Area and Parameters

The area targeted for treatment with EAD should be determined from the lateral and vertical extent of impacts to determine total groundwater volume to be treated. In addition, the aquifer hydraulic conductivity and the hydraulic gradient need to be determined to assess groundwater velocity, associated travel times across the target area, and expected yield of extraction and injection wells. The targeted area volume and the aquifer parameters are then used to determine the recirculation system parameters based with the half-life of the substrate to be used. As noted previously, empirical evidence indicates that electron donor concentrations need to be maintained at levels above 50 mg/l as TOC in the aquifer to establish effective EAD conditions. Limitations in the maximum substrate concentration combined with the substrate degradation half-life constants indicate that substrate concentration can only effectively be maintained for between 120 and 250 days (depends on substrate), and this holds true for both batch injection and recirculation systems. A recirculation system should therefore be designed to turn over the targeted treated volume in a period of time that is less than the time it takes the substrate to degrade from its initial injected concentration to a residual concentration of 50 mg/l TOC.

The rate at which groundwater can be extracted, amended with substrate and re-injected, and the increased hydraulic gradients which can be established at a site will vary based on the site conditions. These recirculation parameters can be adjusted by the designer to allow controlled substrate addition and recirculation flow rates and predictable treatment times, which results in better distribution and therefore better treatment. This is in contrast to waiting for existing groundwater flow to distribute substrate throughout a plume than likely took many years to develop under static hydraulic gradients.

3.3 Estimate Substrate Demands

The total substrate demand in terms of hydrogen utilized should be estimated based on the potential electron acceptors, the levels of chlorinated compounds present in dissolved and adsorbed phases, and a safety factor to account for unknown demands and competing processes. Guidelines for completing this estimate are available (AFCEE et al, 2004), but require collection of the field data described previously in the biogeochemical evaluation. The greatest demand for electron acceptors does not typically come from the contaminants, but from the inorganic species that act as electron acceptors and must be reduced prior to establishing anaerobic conditions suitable for the EAD process. These inorganic species primarily include iron and sulfate, and to a lesser extent manganese, nitrate and oxygen. Sulfate does not have to be completely reduced to sulfide across the site, but sulfate reducing conditions have to at least be established. Competing reactions include the production of methane from carbon dioxide, which acts to increase the amount of substrate required to maintain the anaerobic conditions. A safety factor, often in the range of five to ten times the calculated demand is also incorporated at the end to account for unknowns and inefficiencies in the EAD process.

3.4 Assess Alkalinity Demands

The alkalinity demands of the aquifer in the EAD treatment area will be affected by the initial pH and alkalinity, the acidity generated by the mass of chlorinated compounds to be degraded, and the pH effects of the substrates used n the process. The initial pH can be easily measured and the amount of alkalinity needed to adjust the pH determined by traditional methods. The amount of alkalinity needed for neutralization of the acid generated during the dechlorination process can be determined from the total mass and type of chlorinated compounds present in the dissolved and adsorbed phases as discussed previously. The amount of alkalinity needed for these demands should be added at the beginning of substrate addition as a preventative measure. Lastly, the amount of alkalinity needed to control the acid generated from substrate degradation and maintain pH near neutral is hard to predict and should be tracked during the initial operational period. After a maximum operating period of three months, the extracted groundwater pH and alkalinity should be measured and the need for additional alkalinity considered if pH levels have decreased and are approaching 6.0-6.3. A recirculation system for EAD has a significant advantage over a batch injection system in terms of maintaining pH and adding alkalinity: alkalinity can be added in small quantities in the recirculated water on an as-needed basis to maintain pH levels. In a batch injection EAD system it is very difficult to adjust pH without having significant increases in pH at the point of substrate addition. The recirculation system can be used like a large scale titration to measure in small amounts of alkalinity as needed at any time during the process.

3.5 Design of Extraction, Amendment, and Injection System

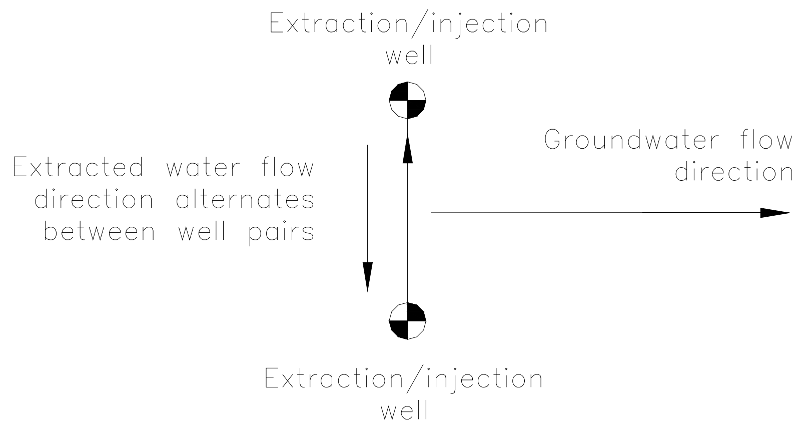
The design of the EAD recirculation system can be configured simply with three main components: the extraction wells and pumps, the amendment system, and the injection wells. The extraction wells are typically located down gradient of the injection wells, at a distance determined from the allowable travel time as discussed previously. The extraction wells can be operated with simple electrical or pneumatic recovery pumps. The amendment system should consist of a feed tank to hold several week's worth of amendment, and a feed system to add the substrate and alkalinity to the extracted and recirculated groundwater. The injection wells can be constructed in the same manner as the extraction wells but without the internals.

There are many patterns of extraction and injection well plans, but they are typically based on two approaches. In the first, most common approach, groundwater is recirculated between extraction and injection wells in a pattern that is parallel to the normal direction of groundwater flow, as shown in Figure 3. This is used to facilitate rapid delivery and distribution of substrate by increasing gradients between extraction and injection wells at a low to moderate groundwater velocity site.

Extraction wells are placed down gradient from the injection wells, at a distance based on the travel time between the extraction and injection wells and substrate half-life. The number of wells and lines of extraction and injection wells will vary based on site conditions. In the second approach, groundwater is extracted, amended with substrate, and then re-injection within a well pair orientated perpendicular to groundwater flow. This approach is used where the groundwater velocity is high to mix substrate within the groundwater as it flow through an area. In this case, groundwater velocity is sufficiently high to allow for distribution to down gradient locations and the recirculation system simply ensures it is well mixed within the groundwater. The extraction and injection directions within a well pair are alternated on a regular basis to ensure even substrate distribution within the aquifer; this approach is shown in Figure 4.

The locations of the extraction and injection wells typically focus on the source area, and groups of extraction/injection wells may be formed based on contaminant concentrations in groundwater. Recirculating substrate across source areas can add substrate and promote degradation where it is needed most, but can also dilute high concentrations to levels acceptable for biodegradation. Desorption and associated flushing of contaminants from source areas allows for a larger treatment zone and can significantly increase the overall remediation rate.

Figure 4. Typical recirculation well plan in high groundwater velocity conditions.



4. CONCLUSIONS

There are several benefits of groundwater recirculation for implementation of the EAD process including:

- Rapid and complete distribution of substrate and amendments to targeted areas;
- Distribution of amendments before they are consumed;
- Rapid distribution of bioaugmentation cultures when needed;
- Ability to add alkalinity as needed to maintain neutral pH;

- Promotes desorption and flushing of contaminants for subsequent degradation; and,
- Allows for manipulation of groundwater flow conditions to complete site remediation in reasonable time frames.

The benefits of recirculation systems for EAD far outweigh alternate approaches that use batch injection and should be considered for all EAD systems. The basic design approach outlined previously provides the methods to account for the aquifer characteristics and implement EAD remediation in reasonable timeframes. The increased capital costs and associated complexity of EAD recirculation systems is justified in that it provides faster and more complete remediation and an overall lower project cost by shortening the duration of remediation, monitoring, and associated project management.

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