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## Enhancing Aquifer Cleanup with Reinjection

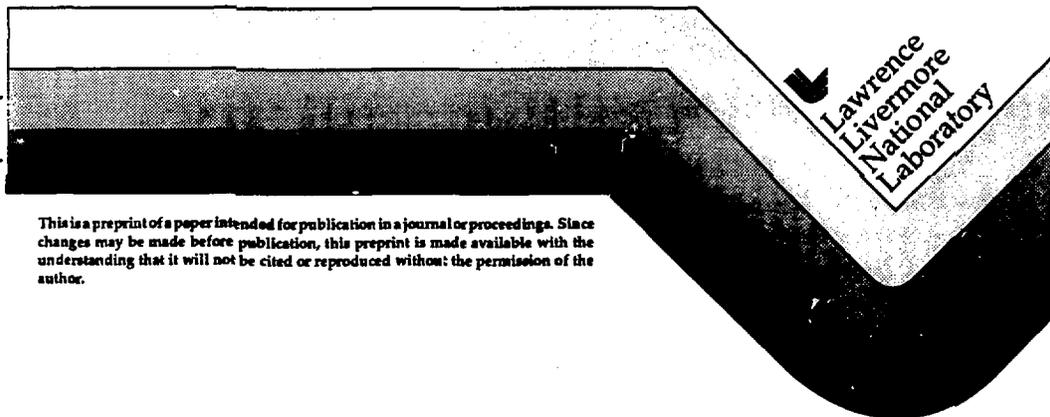
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## **Enhancing Aquifer Cleanup with Reinjection<sup>1</sup>**

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Pump and treat remains the industry standard for ground water remediation. In most cases, contaminants have had decades to advect, diffuse, and sorb into aquifer materials. Consequently, we cannot realistically expect that simply pumping ground water out of the affected regions will remove the contaminants any faster than they were emplaced. Until more advanced *in-situ* methods can be developed, we recommend leveraging the pump-and-treat process by initiating reinjection of treated water in a way that will enhance the natural subsurface processes that accelerate cleanup.

Computer modeling demonstrates that reinjection of surface-treated ground water has several major advantages in aquifer restoration. First, the injectate can be used to control hydrologic flow by controlling head gradients. In some situations, decreasing or reversing gradients can be used to contain contaminants by preventing migration beyond the bounds of current contamination. In other situations, enhancing gradients increases the flow rate, thus flushing the high-concentration subsurface regions.

The second major advantage of reinjection is to allow the introduction of energy or substances that will enhance the natural processes that accelerate cleanup. Heating of the injected water, even by a few degrees, has significant advantages by (1) accelerating degradation by both chemical and biochemical processes; (2) reducing the sediment/water partitioning coefficient, thereby reducing the mass of contaminants sorbed to the aquifer solids; (3) increasing the air/water partitioning coefficient, promoting loss of volatile compounds from the top of the water table, allowing some fraction to escape eventually to the atmosphere; and (4) increasing the rate of molecular diffusion out of low-permeability materials.

Besides heat, reactants (e.g., hydrogen peroxide, as an oxidant), surfactants (to enhance desorption), and biological nutrients or chemical degrading microbes can be introduced during the reinjection. Because of the time necessary for such materials to migrate throughout an aquifer system, it is important to begin their injection early in the pump-and-treat process.

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## I. Introduction

Injection of water or steam, with or without chemical surfactants, is a common petroleum industry technique to enhance product recovery. In the geothermal industry, reinjection (re-injection is used to mean the injection of ground water that was previously injected) of heat-depleted subsurface fluids is commonly used to maintain reservoir pressure, thus prolonging field productivity. The use of reinjection in ground-water remediation projects allows for the application of both traditional production field management and a variety of additional enhancements to the cleanup process. Development of the ideas in this paper was stimulated by an initial suggestion by Dr. Jacob Bear (personal discussions, 1990-1991) that re-injected water might be heated to aid the desorption process.

There are three major classes of benefits for ground-water remediation reinjection. First is the ability to extract more fluids without excessive drawdown, i.e., pressure support. Secondly, the injectate may be modified to enhance contaminant degradation and desorption by either adding *other materials or changing its physical properties*. For example, this could include temperature, chemistry, or biology. Thirdly, reinjection allows the optimization of the contaminant mass removal by hydraulically controlling the direction of the flow towards the extraction wells.

Pump and treat remains the most commonly applied technique for ground-water remediation. In most pump-and-treat applications, ground water is pumped to the surface from extraction wells, the contaminants are removed from the ground water, and the treated water is usually allowed to percolate into the ground water outside the contaminated region. In many cases, contaminants have had decades to advect, diffuse, and sorb into the aquifer materials. It is not realistic to expect that pumping ground water out of the affected regions will remove all contaminants significantly faster than they were implaced. Because more advanced *in-situ* methods will take time to develop, pump and treat is likely to frustrate impatient operators, unless methods can be found to accelerate the process.

Reinjection of surface-treated ground water (injectate) can accelerate pump-and-treat remediation. The first major advantage to pump-and-treat remediation is to allow increased pumping rates. The injectate mass permits higher extraction pumping rates by providing localized pressure support.

The second major advantage of reinjection is to allow the introduction of energy or materials that will enhance the natural processes that facilitate cleanup. Heating of the injected water, even by a few degrees, has significant advantages by (1) potentially accelerating degradation by both chemical, biological, and biochemical processes; (2) reducing the contaminants' sorption constants, thereby reducing the mass of contaminants bound to the rock particles; and (3) increasing the loss of volatile compounds from the top of the water table, allowing some fraction to escape eventually to the atmosphere. In addition to heat, reactants (e.g., hydrogen peroxide, as an oxidant and source of oxygen), surfactants (to enhance desorption), and biological nutrients or microbes themselves can be introduced during the reinjection.

The third major advantage is optimization of contaminant mass extraction through plume control. Hydrologic flow can be managed by controlling head gradients. In some situations,

decreasing or reversing gradients can be used to contain contaminants by preventing ground water flow beyond the bounds of current contamination. In other situations, steepening gradients accelerates flushing of contaminated regions by increasing subsurface flow rates.

## II. Benefits of Injection

In the process of pumping for remediation, there are a number of reasons for reinjection of the extracted ground water. If, for example, extraction of ground water dewater a contaminated zone, contaminants may be left behind, sorbed to formation particles or remaining as part of the residual liquid left in the pores. When ground-water levels return to pre-pumping levels, the contaminants will again enter the ground water, and it may appear that the pump-and-treat scheme did not work. Also, reinjection can maintain ground-water levels over much of the region being remediated and can limit dewatering to the immediate vicinity of extraction wells.

Hydrologic barriers to the migration of ground-water plumes can be created by injection in front of a plume. Injection outside a plume in the cross-gradient direction can also be part of the containment strategy, while increasing the flushing of contaminated ground water towards pumping wells. Hence, a "herding" of the contaminants by gradient control is part of many extraction plans.

This use of head-gradient control for flushing the formation increases the potential extraction of ground water and allows the desorption and diffusion of trapped contaminants by increasing the concentration gradients as clean water replaces contaminated water.

Through comprehensive optimization modeling, one can determine pumping and injection locations that maximize contaminant mass extraction under other constraints. Application of the resultant field management strategies is particularly effective when the locations of both extraction and injection are managed with time. At Lawrence Livermore National Laboratory (LLNL), for example, the projected cleanup time for an aquifer with dissolved volatile organic compounds (VOCs) over an area of 3 square km was reduced from about 100 years to less than 50 years. This was accomplished by simply reinjecting the extracted and treated water and changing extraction and injection locations to follow the cleanup process, thereby eliminating stagnation regions.

Disposal of treated ground water is sometimes a concern. Treated ground water generally is not considered acceptable for domestic purposes, regardless of any quality standards that may apply. The options for using extracted water for process water may be limited by local need and the mineral content of the ground water. Reinjection addresses the disposal problem and is generally accepted by regulatory agencies, as long as treatment discharge standards meet their criteria.

In optimized scenarios, treated ground water is reinjected throughout the overall region requiring remediation and interacts with the contaminants not carried in the aqueous phase on the first "flush" of the aquifer. Once one considers conditioning of the reinjected water, many possibilities unfold.

A sensitivity analysis of the factors affecting cleanup times using pump and treat for the LLNL site demonstrated that the contaminant degradation rate is by far the most influential factor. Thus, accelerating the natural degradation processes may have a tremendous impact on the time required for remediation. This is true because of the long timeframe over which the VOC plumes would

migrate before impacting offsite wells and the commensurate long time involved for pump and treat remediation. Simple biodegradation options are not practical because of the large scale of the plumes involved, the contaminants involved, and the specifics of the local (aerobic) subsurface environment. But changing the reinjected water to enhance the natural biological or chemical processes could pay substantial dividends.

### III. Leveraging Injection

Reinjection can affect the fate and transport of contaminants by altering the processes of degradation, desorption, and diffusion through modifying the temperature, biology, and chemistry of the injectate.

#### Abiotic Reactions

In chemical reactions, rates are controlled by the rate and duration of encounters of the reacting species, as well as their energy and orientation. Kinetics can be zero-, first-, second-, or higher-order.

Abiotic contaminant transformation rate is affected by the chemistry of the ground water and the injectate. Eh conditions can be changed to alter the valence state of metals, surfactants can be used to solubilize contaminants, and thermochemical reactions can be used to affect transformations.

Contaminant transformation rate is affected by temperature. The reaction rate  $k$  of a thermochemical reaction is  $k = A e^{-E/RT}$ , where  $A$  is the reaction-specific constant,  $E$  is the enthalpy of the reaction,  $R$  is the universal reaction constant, and  $T$  is the absolute temperature. The reaction rate is seen to have an exponential dependence on the temperature. As a result of this functional dependence, raising the aquifer temperature by several degrees could increase reaction rates significantly.

#### Biodegradation

Some organic compounds can serve as primary energy substrates either aerobically or anaerobically. These compounds may be degraded by indigenous bacteria if the contaminant level is not inhibitory and sufficient inorganic nutrients are present. If the environmental conditions are made suitable, the microbial community may become enriched with microorganisms possessing enzymes capable of utilizing the contaminant.

Cometabolism is another biotransformation process in which degradation of a compound occurs only in the presence of other organic material that serves as the primary energy source. In mixed bacterial communities, the organic products of contaminant utilization may in themselves be resistant to further biological transformation. Otherwise, they may be transformed further by cometabolism or can be used by the same or other organisms for energy.

A number of factors affect biotransformation rates. Primary factors in determining if a contaminant can be degraded are its structure, concentration in the environment, and toxicity to the

indigenous microbial population. The physical state of the compound (aggregated, spreading, or adsorbed) can cause the contaminant to be more difficult to degrade.

Temperature influences both chemical evaporation and microbial and chemical degradation rates. The availability of electron donors and acceptors is a major influence on biotransformations. For aerobic metabolism, the availability of oxygen and nitrate is required. In anaerobic metabolism, sulfate and carbon dioxide often are used.

Additional factors that effect biotransformation are the availability of mineral nutrients such as nitrogen, phosphorous, and iron. The sediment pH can limit the reaction; for example, a pH of less than 5 will stop some microbial degradation. The presence of microorganisms, with the enzymes and coenzymes capable of degrading the target contaminant, is of major importance.

There are methods to enhance bioremediation through reinjection. Adding abiotic factors that are necessary for microbial growth may enhance biotransformation. Adding electron donors and acceptors will alter the redox conditions to favor enzymatic reactions. Many microorganisms are dependent on the presence of molecular oxygen or nitrate for biotransformation. The redox potential of the environment alters heterotrophic activity. For example, low Eh due to depletion of available oxygen influences the catabolically active group in the microbial community.

The abundance of organisms will be determined by the nutrient present in the lowest concentration. Amendments may be organic compounds that favor the growth of particular populations with specific catabolic activity. Most subsurface microorganisms live in low-nutrient habitats. Addition of inorganic compounds, such as the essential nutrient gases (oxygen, carbon dioxide, nitrogen, or ammonia), may enhance biotransformations. The addition of limited anions, such as phosphate, carbonate, bicarbonate, sulfide, sulfate, nitrite, nitrate, and chloride, can increase catabolic activity. In the case of cometabolism, the addition of primary substrates will enable the bacteria to cometabolize the contaminant.

Pure or mixed cultures, with enzymes capable of degrading the contaminant, may be grown in large fermentors and injected into the contaminated environment. Larger populations of microorganisms that biotransform the contaminant will increase the rate of remediation.

Temperature greatly influences the contaminants' chemistry and the microorganism community and number. Growth and activity of bacteria may double for each 10°C increase in temperature, up to the species' tolerance limit.

## **Desorption**

Partitioning of contaminants between the dissolved, sorbed, and gas phases may be affected by temperature, biological activity, and chemical conditions.

Before chemical enhancements to reinjection are attempted, detailed understanding of the relative contributions of chemical and physical processes limiting pump and treat are needed. Chemical enhancements will not contribute significant gains when the constraints on contaminant removal are caused by the physical attributes of the hydrogeologic system. For example, if there is little chemical interaction between the contaminant and the sediment porous media, contrasts in hydraulic conductivity in heterogeneous porous media may be the primary contributors to lengthy "tailing" of contaminant concentrations, because advective transport through lower permeability

media is small. As aqueous contaminants are transported through high-permeability regions, they diffuse into lower permeability regions. During aquifer cleanup, contaminants in the high-permeability regions are removed relatively quickly, and the lower permeability regions act as diffusive sources, bleeding contaminants back into the high-permeability regions for long periods of time.

In many cases, a major portion of the contaminant mass will not be dissolved in the ground water but will be sorbed to sediments or remain as precipitates. This undissolved contamination must be transferred into the aqueous phase before it can be removed during pump and treat. This transfer can be enhanced through the addition of chemicals to the reinjected ground water. Critical chemical parameters that must be characterized before selection of a chemical enhancement include: spatial distribution of contaminants relative to lithology; organic contaminant partitioning coefficients; ionic adsorption parameters, e.g., cation exchange capacity; pH; redox conditions; and oxidative or reductive capacity of the aquifer. Depending on the process controlling the "tailing" in the contaminant concentration versus time curve for extraction wells, different reactive agents may be chosen (Palmer and Fish, 1992).

Partitioning involves the transfer of "sorbate" (contaminant) at the interface of two or more phases. After a sufficient time, the concentrations within the phases will reach a characteristic equilibrium. The sorptive capacity of a "sorber" phase is determined by the sorber chemical properties; sorber physical properties, such as specific area and pore size distribution; and size of the sorbate molecule. The partitioning properties of the sorbate are related to its chemical properties; most importantly, its solubility (hydrophobicity), vapor pressure, and enthalpy of phase transfer. Sorption processes are governed by the thermodynamic and physical characteristics of the system and may be "sorber-limited" or "solvent-limited," as in, for example, ion-exchange or the partitioning of hydrophobic compounds, respectively. At equilibrium, the relative concentrations of pore-gas ( $C_g$ ), pore-water ( $C_w$ ) and solid-sorbed ( $C_s$ ) phases are related by Henry's constant ( $H$ ) and the solid-sorbed partition coefficient ( $K_D$ ) as follows:

$$\begin{aligned}C_g &= H C_w \\C_w &= C_s / K_D \\C_g &= (H / K_D) C_s\end{aligned}$$

Partitioning may be affected by temperature, biological activity, and chemical conditions. An increase in temperature will shift the equilibrium by transferring contaminants from the more-dense to the less-dense phase. The extent of the shift is determined by the enthalpy of phase transfer and by the reaction equilibrium constant. The phase transfer that involves the greatest change in enthalpy is favored. For volatile organic compounds (VOCs), the gas/solid-sorbed phase involves the greatest change in enthalpy ( $\Delta H_{sg}$ ) and, therefore, is the most sensitive to temperature changes. Accordingly, an increase in temperature would result in an increase in the pore-gas concentration and in a decrease in the pore-water and solid-sorbed phase concentration. However, if a gas phase is not present, a temperature increase results only in the transfer of mass from the solid-sorbed phase to the aqueous phase. Raising the aquifer temperature by several degrees will increase the equilibrium water concentration. Raising the temperature is seen to increase the concentration in the aqueous phase, while decreasing the concentration in the solid-sorbed phase.

## **Diffusion**

In porous materials of low permeability, the most significant mass-transport process may be molecular diffusion. Diffusion into or out of low-permeability materials within the aquifer may significantly limit the rate of cleanup of a contaminated aquifer. The rate of diffusive flux into or out of the low-permeability materials is proportional to the concentration gradient and the effective aqueous diffusion coefficient.

Reinjection of treated water can increase the concentration gradient at the interface between low-concentration, high-permeability material and the higher-concentration, low-permeability material. Such increases in concentration gradient would help increase the rate of diffusive flux of contaminants from the low-permeability into the higher-permeability materials.

The molecular diffusion coefficient  $D$  is affected by the temperature of the water. However, the relation is not well known. The diffusion coefficient for gas is related to temperature according to the relation  $D = D_0(T/298)^{3/2}$  where  $D_0$  is the diffusion coefficient at 298°C. In this case, raising the aquifer temperature by 20°C would increase the rate of molecular diffusion by about 10%, which would enhance the rate of transport of contaminants out of low-permeability materials.

## **IV. Summary**

Reinjection of treated ground water should be evaluated for all large-scale pump-and-treat operations. Reinjection can be part of a containment approach, used to increase extraction rates and to "herd" the contaminants toward extraction wells. Conditioning the injectate has the further potential in leveraging the natural degradation process and enhancing desorption. The benefits of accelerating natural processes may persist long after active pumping has ceased.

Simply heating treated water before reinjection has numerous potential benefits, but has not been field demonstrated on a large scale. Injectate conditioning may be relatively inexpensive to implement; however, it requires considerable up-front characterization of the subsurface system to ensure a beneficial outcome.

## **Reference**

Palmer, C. D., and W. Fish (1992), "Chemical Enhancement to Pump-and-Treat Remediation," U.S. EPA (EPA/540/S-92/001).