Aquifer Recharge Through Direct Injection: Geochemical Considerations

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Managed aquifer recharge has become a major component in numerous water supply initiatives. According to the American Ground Water Trust (2009), direct aquifer recharge is being used at 95 sites with more than 500 wells in the United States, in addition to the numerous projects that use surface spreading to increase aquifer infiltration. Recharge projects have the potential to address many water management issues, including declining groundwater levels, saltwater intrusion, declining or seasonally variable surface water supplies, environmental opposition to surface reservoirs, storage and treatment of stormwater and reclaimed water, and increasing concerns regarding global climate change and the need for large-scale water storage and more fully integrated water resource management. Historically, the emphasis on developing aquifer recharge projects has been on characterizing the factors that control the inflow, outflow, and movement of water in the aquifer system. As a result, geologic and hydraulic factors that affect feasibility of aquifer recharge programs are becoming better understood, even in complex settings.

Because artificial recharge processes add large volumes of water to a receiving aquifer at rates much faster than would occur with natural infiltration, the recharge water may not have adequate time to reach geochemical equilibrium in aquifer systems. This condition can result in a number of potential adverse effects that should be considered. Typically, the primary impacts that could occur include increased biological growth of iron bacteria, dissolution and subsequent re-precipitation of the aquifer matrix, and dissolution and mobilization of trace elements that, in many cases, could negatively affect the underground source of drinking water. In addition to these geochemically related impacts, changes in dissolved oxygen and assimilable organic carbon can also influence the potential for biological growth. Secondary impacts could include aquifer clogging due to precipitation of oversaturated minerals or microbial growth, as well as degraded water quality and increased treatment requirements of water during the recovery stage. The focus here is on identifying the source of these impacts with respect to the geochemical phenomenon of direct aquifer recharge; biological reactions will not be included.

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Geochemical Considerations and Challenges

Groundwaters are complex aqueous solutions, having different dissolved solid and gas phases present. There are a number of factors that control the chemical state of these phases, including temperature, pH, redox potential, and biogenic activity. The interaction of these factors must be understood to design, permit, and develop aquifer recharge systems that minimize the potential for adverse geochemical reactions. There are critical parameters for evaluating geochemistry of aquifer recharge systems that allow the compatibility of recharge water and native groundwater to be determined. Additionally, there are simple, geochemical methods for evaluating the potential impacts of mixing recharge water in an aquifer.

Chemical Precipitation and Clogging

When designing water treatment and distribution systems, engineers are acutely aware of issues that may arise in conjunction with mineral scaling, or with corrosion when dealing with aggressive water. However, many of the tools that engineers have traditionally used to characterize these issues are based on carbonate chemistry. Commonly used indicator indices include the Langlier Saturation Index, the Ryznar Index, and others based on carbonate chemistry. The drawback to using these indices is that they do not consider the potential impacts of noncarbonate mineral chemistry. In addition to the common carbonate minerals that are typically planned for, there are common iron minerals, such as ferric hydroxides and oxyhydroxides, which are often the source of chemical precipitation. These minerals are often causes of decreases in effective pipe diameters for systems transporting groundwater; an example of this phenomenon

Figure 1. Iron mineral precipitation in a water distribution system.

is shown in Figure 1. This phenomenon also occurs within aquifer matrices, which could ultimately result in decreased injectivity rates during recharge, as well as decreased recovery rates during recovery.

To develop a better understanding of the geochemical conditions that could occur in an aquifer system, saturation indices for the most prevalent minerals that could occur should be evaluated. The mineral saturation index (SI) is a measure that is relevant to the evaluation of mineral precipitation and should be estimated during an evaluation of any aquifer recharge project. The mineral SI is a parameter that is indicative of the tendency of a water solution to dissolve or precipitate a particular mineral. Its value is negative when the mineral may be dissolved, positive when it may be precipitated, and zero when the solution and mineral are at chemical equilibrium. The SI is calculated by comparing the chemical activities of the dissolved ions of the mineral with their solubility product. While these values can be calculated by hand, there are a wide range of geochemical tools available through open access over the Internet. A brief discussion of two of these tools is provided in the geochemical modeling section.

Trace Inorganic Mineral Mobilization and the Arsenic Issue

Previous investigations of artificial recharge of aquifers has shown that mobilization of arsenic, cobalt, nickel, and zinc to the groundwater can be a concern (Stuyfzand, 1998; de Ruiter and Stuyfzand, 1998; Brun et al., 1998; Arthur et al., 2001; Arthur et al., 2003; Mirecki, 2005; Arthur et al., 2009), as can other trace minerals, including uranium, chromium, and molybdenum. Most trace inorganic contaminant issues found in groundwater supply systems are related to natural processes, while some inorganic contamination is known to be related to human activities. There are numerous reports of the presence of trace element contamination in shallow groundwaters that are anthropogenic in nature; urban and agricultural activities are potential sources of trace element contamination, particularly arsenic, copper, and lead (De Carlo and Anthony, 2002).

Urban activities, such as turfgrass maintenance in golf courses, have increased concentrations of arsenic in some groundwater through the use of the herbicide, monosodium methane arsenate (Swancar, 1996). Other potential sources of trace element contamination in groundwater include arsenic used in cattle dipping for disease control (Blasland, Bouck, and Lee Inc., 1992), as well as arsenic and copper used as fungicide on citrus and as a wood preservative (Sherwood et al., 1973). While many of these trace metals have very low drinking water maximum contaminant limits (MCLs), the difficulty lies primarily with arsenic, which remains relatively mobile. Trace metals, such as nickel and cobalt, are less mobile and likely to co-precipitate or adsorb onto iron hydroxides further away from the injection well (Stuyfzand, 1998).

Arsenic is present in a variety of solid phases in the hydrogeologic environment, and the source of arsenic mobilized to groundwater in aquifer storage and recovery (ASR) projects is most often attributed to the release from sulfide minerals, such as pyrite (FeS_2). Arsenic has also been found in iron and manganese hydroxide coatings on saturated sediments with concentrations reported up to 30 parts per million (ppm) arsenic (Thomas and Saunders, 1998), and these coatings can desorb or dissolve, releasing arsenic to the groundwater (Schlottmann and Breit, 1992; Welch, 1999). However, the primary source of mobilized arsenic is most often attributed to pyritic minerals in which arsenic occurs as a trace element or as an impurity in the solid phase, which can occur at concentrations up to 11,200 ppm arsenic (Price and Pichler, 2006).

The presence of arsenic, within the range of pH values that occur naturally in aquifers, is highly dependent on the oxidation-reduction potential and the concentration of dissolved oxygen of the groundwater. Pyrite exists when the oxidation reduction potential (ORP) is low (negative) and dissolved oxygen (DO) is low, such as in confined aquifers. Pyrite can also occur deep in unconfined aquifers where the ORP and DO concentrations are sufficiently low for pyrite to exist. The presence of pyrite has been well-documented in confined drinking water aquifers throughout Florida (e.g., the Floridan Aquifer system). However, there are some systems in Florida that are less understood with respect to geochemistry, despite having excellent characterization with respect to hydrogeology. As such, it is critical to investigate the geochemical properties of the receiving aquifer for any direct recharge project. The investigation should include a well-defined plan to characterize both the geology and geochemistry of the aquifer materials and compatibility of the recharged water with the receiving aquifer. A description of the methods that may be used to develop this information follows.

Geochemical Modeling

Geochemical models can be used to quantify reactions, reaction rates, and mineral phase transfer between water and aquifer material in diverse hydrogeological settings. In the context of aquifer recharge, storage, and recovery, geochemical models have been developed to quantify reactions that affect water quality and the rates at which they occur (Castro 1995; Mirecki et al., 1998; Herczeg et al., 2004; Prommer and Stuyfzand 2005). However, most of these models were developed at sites that had a significant research component marked by an intensive data collection effort. There have been geochemical models developed based on existing water-quality data obtained during cycle testing at ASR systems in Florida (Mirecki 2004 and 2006); however, this necessitates the construction and operation of the ASR system to obtain the appropriate data.

During the planning phase of an aquifer recharge project, there are simple methods that can be applied to evaluate the impacts of mixing recharge water with the native aquifer water and aquifer matrix. These methods are based on groundwater quality data and aquifer matrix characteristics that can be obtained during an exploratory well study. This type of feasibility study can allow for the development of preliminary engineering design criteria for the recharge project to determine planning-level costs of a project, and if the geochemical conditions induced in the injection zone are of concern. Often, if there are concerns regarding either chemical precipitation or arsenic release, then there are pretreatment methods that can be designed to produce injection water of the quality necessary to prevent undesired geochemical effects. However, the key to developing this information lies in developing good chemical characterization data for the native aquifer matrix, native groundwater, and the recharge water.

Characterizing Aquifer Matrices

Aquifer matrix samples should be collected in the vicinity of the proposed project site by a licensed drilling subcontractor using a continuous coring technique, such that aquifer matrix samples can be obtained at representative locations and depths. Continuous cores should be preserved under nitrogen to prevent oxidation of materials in the matrix once they have been brought to the surface. The core samples can be shipped to a qualified laboratory that can provide analyses for whole rock geochemical analysis. Suggested analysis methods for samples from various depths throughout the proposed injection or storage zone include whole rock digestion and inductively coupled plasma mass spectrometry (ICP-MS) and/or laser ablation (LA) ICP-MS for multi-elemental analysis. In addition to the ICP analyses, powder X-ray diffraction (XRD) and scanning electron microscope (SEM) electron dispersive spectrometry (EDS) analyses can be conducted to identify the mineral composition of samples at various core depths. In some instances, electron microscope and probe microanalyses of polished thin sections from the core collected adjacent to the core material for which geochemical analysis is completed may also be recommended. These include where the previous analyses indicate that there are minerals and/or trace elements that could cause concern. A scanning electron micrograph showing the presence of pyrite minerals embedded in a sample is provided in Figure 2.

Table 1. Recommended field parameters for developing a geochemical model.

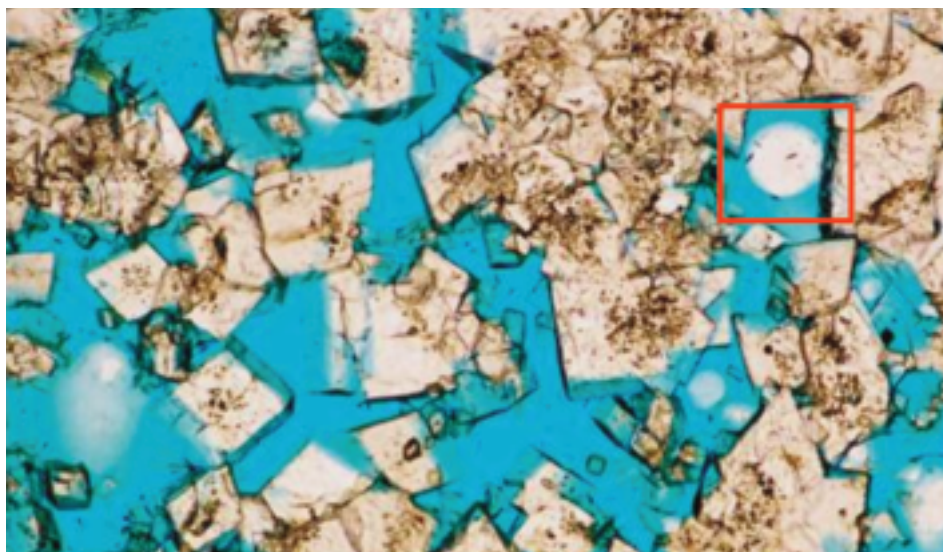| Analyte	Units
Ferrous Iron	mg/L
Total Iron (Ferric Iron is calculated by subtraction)	mg/L
Field pH	std. units
Field Temperature	degrees C
Oxidation-Reduction Potential	milliVolts
Oxygen, Dissolved	mg/L
Specific Conductance	micromhos
Turbidity	Nephelometric Turbidity Units (NTU)

Figure 2. Scanning electron microscope electrograph with pyrite.

Characterizing Recharge Water and Native Groundwater Quality

It is necessary to characterize the water quality of the native groundwater in the receiving aquifer, as well as the water to be used for recharge. With respect to the native groundwater, in addition to reviewing historical literature for baseline data, groundwater samples should be collected in the vicinity of the project site. During the sampling, field parameters should be collected on-site, due to their short hold time; a summary of field parameters is provided in Table 1. Samples for a range of analytes that will allow an evaluation of the saturation indices of major minerals should also be collected (Table 2).

In addition to the parameters listed in Table 2, it is beneficial to analyze samples for bacteria using a heterotrophic plate count or similar method; with organic carbon, this can be a good indicator of the potential for increasing the biological activity in the aquifer during recharge.

Geochemical Modeling Tools

When evaluating geochemical conditions that are estimated to be at or very near chemical equilibrium, the U.S. Environmental Protection Agency (EPA) model, MINTEQ, or mineral temperature equilibrium (Allison et al., 1991), can be used to define the saturation indices of minerals in solution. With respect to understanding the redox conditions of native groundwater (that is, baseline conditions prior to recharge), the pE (the negative log of the electron activity in solution) and Eh (oxidation potential) values can estimated using Visual MINTEQ. The concentrations of major ions can be entered into the graphical interface along with known minerals in the aquifer matrix that are infinite solid phases. If the pH has been measured in the field, that value can be held constant and an initial estimate guess for Eh can be provided, based on field-measured ORP. Once the model has been run, the user should first check the resultant ion balance (the sum of the concentrations of cations should equal to the sum of the concentration of anions) of the solution. If the ion balance is within 10 percent, the major anions and cations can be assumed to be accounted for in the analytical results. The most up-to-date version of the MINTEQ model can be downloaded at http://www2.lwr.kth.se/English/Our Software/vminteq/.

The equilibrium pE and Eh values can then be used as input for modeling the mixing of recharge water with native groundwater. The geochemical model PHREEQC, or pH redox equilibrium calculations (Parkhurst and Appelo, 1999), developed by the U.S. Geological Survey, is a thermodynamic equilibrium program designed to model chemical speciation in aqueous solutions to determine the saturation states of solutions with minerals and gases, and to predict the results of various reactions such as dissolution of minerals and oxidation. There is an interactive version of the PHREEQC model that has a graphical user interface that simplifies the evaluation of mixing of recharge water and native groundwater in the presence of the native aquifer materials. This method allows the initial geochemical conditions to be used to calibrate the model, and can predict the conditions induced in the aquifer when various ratios of recharge water are mixed with native groundwater in the aquifer matrix. The most up-to-date version of the PHREEQC model can be downloaded at http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/index.html.

Engineering Solutions

If geochemical modeling indicates that there are potential issues with respect to chemical precipitation or trace mineral release, there are options for pretreatment of the recharge water that can change the chemistry of the injection water such that it more closely resembles

Table 2. List of recommended water quality parameters, methods, and detection limits for developing a geochemical model.

Analyte	Recommended Detection Limit	Units	Specific EPA Method (unless otherwise noted)
Aluminum	10	ug/L	200.8
Antimony	0.05	ug/L	200.8
Arsenic	0.5	ug/L	200.8
Barium	0.5	ug/L	200.8
Beryllium	0.05	ug/L	200.8
Cadmium	0.05	ug/L	200.8
Calcium	50	ug/L	200.8
Cesium	0.1	ug/L	SW 6020A
Chromium	0.5	ug/L	200.8
Copper	0.1	ug/L	200.8
Iron	10	ug/L	200.8
Lead	0.1	ug/L	200.8
Magnesium	5	ug/L	200.8
Manganese	1	ug/L	200.8
Mercury	0.05	ug/L	245.1
Nickel	0.5	ug/L	200.8
Potassium	50	ug/L	200.8
Selenium	0.5	ug/L	200.8
Silver	0.05	ug/L	200.8
Sodium	50	ug/L	200.8
Strontium	0.1	ug/L	200.8
Thallium	0.5	ug/L	200.8
Zinc	5	ug/L	200.8
Bromide	0.01	mg/L	300.0
Chloride	0.1	mg/L	300.0
Fluoride	0.01	mg/L	300.0
Sulfate	0.1	mg/L	300.0
Sulfide	1	mg/L	SM 4500 S2 F
Ammonia (as N)	0.01	mg/L	350.1
Nitrogen, Kjeldahl	0.05	mg/L	351.2
Nitrate as N	0.1	mg/L	353.2
Nitrite as N	0.1	mg/L	353.2
Phosphorus	0.005	mg/L	365.1
Orthophosphate	0.005	mg/L	365.2
SiO_2, Silica	0.5	mg/L	200.7 Rev 4.4
Bicarbonate Alkalinity as $CaCO_3$	1.0	mg/L	SM 2320B
Carbonate Alkalinity as $CaCO_3$	1	mg/L	SM 2320B
Total Dissolved Solids	5	mg/L	SM 2540C
Total & Dissolved Organic Carbon	0.1	mg/L	SM 5310C

that of the native groundwater. To select engineering design criteria, it is necessary to establish the worst-case geochemical conditions that could arise in the proposed injection or storage zone of the site. This can be done through the geochemical modeling, as presented in the previous section. Once these conditions are defined, the model can then be used to evaluate the most appropriate and cost-effective methods to address the over- or under-saturated minerals, or establish redox, pH, temperature, and other geochemical conditions that prevent the dissolution or release of trace minerals.

Once the hydrogeochemical reactions of potential concern are identified, pretreatment options for recharge water to be compatible with native groundwater can be evaluated and pretreatment systems can be included as part of recharge project planning. In most cases, the issue is that recharge water either has a high dissolved oxygen concentration, and/or the ORP is high when compared to the native groundwater. Often, the solution is as simple as reversing the chemistry of the water treatment processes. This can be done by reducing the dissolved oxygen concentration of treated water by using alternatives to chlorine disinfection, providing reduction of dissolved oxygen through degasification systems, or reduction of ORP through chemical addition. In any case, the geochemical model can be used to evaluate these pretreatment measures with regard to the various impacts on saturation indices for key minerals, and of the redox conditions that could lead to oxidation of reduced minerals.

Summary and Recommendations

Ultimately, direct recharge projects have the potential to solve many challenging long-term water supply issues. However, these projects are not without risk, and there is significant value in reaching beyond the traditional tools that have been used in planning these projects. There are a number of excellent geochemical modeling tools available to project designers that should be used during the planning stage of a direct recharge project to identify project risks, and also as a means for evaluating engineering solutions that can be implemented to manage those risks.

In addition to evaluation and implementation of pretreatment options recommended for successful recharge projects, long-term monitoring should be included as part of any project. A plan of action should also be developed to address adverse geochemical effects if monitoring data indicates that these impacts are occurring (e.g., decreases in specific injectivity or increases in arsenic concentrations in groundwater). In-

cluding these practices as part of recharge projects allows better use of this water resource management tool and can provide a means for developing a strategy to help meet variable, and often stringent, regulatory frameworks.

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