

QUANTIFYING THE NEAR-BOREHOLE GEOCHEMICAL RESPONSE DURING
AQUIFER STORAGE AND RECOVERY: APPLICATION OF “*PUSH-PULL*”
ANALYTICAL TECHNIQUES TO ASR CYCLE TESTING

By

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To my loving wife. Thank you for allowing me to pursue my academic interests. Your commitment to this research and self sacrifice cannot be overstated.

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LIST OF SYMBOLS AND ABBREVIATIONS

AFMW-1	Arcadia Monitoring Well No. 1
As	arsenic
ASR	Aquifer Storage and Recovery
ASR-1	Aquifer Storage and Recovery Well No. 1
AsS ₂ -	arsenic sulfide
bls	below land surface
C _r	concentration of reactant
C _{tr}	concentration of tracer
DO	dissolved oxygen
FAC	Florida Administrative Code
FDEP	Florida Department of Environmental Protection
HFOs	ferric hydrox/oxyhydroxides
HMOs	metal hydrox/oxyhydroxides
HPD	hierarchical patch dynamics
HSPS	High Service Pump Station
H ₂ S	hydrogen sulfide
IGW	Interactive Groundwater Model
k	reaction rate coefficient
MG	million gallons
mg/kg	milligram per kilogram
mg/L	milligram per liter
msl	mean sea level
NELAC	National Environmental Laboratory Accreditation Conference
ORP	oxidation reduction potential

PDWS	Primary Drinking Water Standards
PPT	Push-Pull Test
PVC	polyvinyl chloride
SDWS	Secondary Drinking Water Standards
SOPs	standard operating procedures
SZMW-1	Storage Zone Monitoring Well No. 1
TDS	total dissolved solids
TMR	telescopic mesh refinement
TSV	target storage volume
UFA	Upper Floridan Aquifer
$\mu\text{g/L}$	microgram per liter
UIC	Underground Injection Control
USDW	Underground Source of Drinking Water
V_{ext}	extracted volume
V_{inj}	injected volume
WTMW-1	Water Table Monitoring Well No. 1
WTP	water treatment plant
YSI	Yellow Springs Instrument Company
ΔH_r	molar enthalpy of reaction

Abstract of Thesis Presented to the Graduate School
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Arsenic mobilization has become the primary regulatory issue for Aquifer Storage and Recovery (ASR), posing a significant problem to the long-term viability of this alternative water supply technology. We compared the current conceptual model for arsenic mobilization in ASR with results from field tests (i.e., Cycle Tests) completed at an ASR facility in southwest Florida that uses the Suwannee Limestone for aquifer storage. We developed a framework for conducting field-scale tests, based on single-well Push-Pull Test analytical methods, to determine first-order reaction rates for dissolved oxygen (DO), the primary oxidant, in ASR. The measured DO decay rates from four test cycles ranged from 0.41/day to 0.72/day and were shown to be temperature dependent. The methods presented herein potentially extend the application of the Push-Pull Test to quantify the near-borehole geochemical response during ASR. To confirm the appropriateness of the historical ASR operational approach (i.e., Target Storage Volume) for managing ASR recovery efficiency and attenuating arsenic, field results from ASR cycle tests and results from the 3-D Interactive Groundwater (IGW) Model calibrated to the case site were evaluated. The findings of this research indicate that the TSV approach can be used to increase ASR recovery efficiency but is not a viable means of attenuating arsenic.

CHAPTER 1 INTRODUCTION

With an annual average rainfall of 54-inches (1), Florida's climate produces much of the water needed to support its growing population. However, most of the rainfall occurs during the rainy (wet) season, typically May through September. In south Florida, over 70 percent of the annual rainfall occurs during the wet season (2). Much of the excess wet season flow is lost to evaporation or to streams where it is discharged to the ocean. Because the capacity of above-ground storage reservoirs is limited, little of the excess flow is placed in storage.

In contrast to the summer months, Florida's springtime is usually dry, with rainfall of a tenth of an inch or more falling fewer than six days in April (2). Springtime in Florida is also the height of the growing season, when many residents increase residential lawn irrigation to combat the lack of precipitation. Because the dry season occurs when the demand for water is greatest and when surface reservoirs are experiencing low water levels, significant stresses are placed on groundwater resources. The temporal disproportion of water supply to demand not only creates seasonal supply shortfalls, but also contributes to groundwater quality declines in one of the most prolific aquifers in the world, the Floridan aquifer.

Florida's Water Management Districts are the primary regulatory agencies responsible for managing the water resources of the State. Because of the historical overproduction of groundwater resources across peninsular Florida, the Water Management Districts have been enacting strict measures that limit groundwater withdrawals (3). In fact, the Southwest Florida Water Management District, the South Florida Water Management District, and the St. Johns River Water Management District have recently established the Central-Florida Coordination Area covering central and east-central Florida including parts of Brevard and Lake Counties and all of Polk, Osceola, Orange, and Seminole Counties. This interagency agreement established

that no additional withdrawals from the Upper Floridan Aquifer (UFA) may occur beyond those permitted through 2013, despite an anticipated increase in potable water demands in the area (3). To continue to meet the demands of a growing population in the face of this new restriction, alternative water supply technologies such as Aquifer Storage and Recovery (ASR) must be developed (4).

Artificial recharge techniques such as ASR have the potential to alleviate seasonal water supply shortfalls for many communities. In Florida, ASR is typically employed to meet seasonal supply shortfalls by storing excess water in non-potable (brackish) aquifers during the wet season, when demand is low, and recovering the stored water during the dry season, when demand is high. ASR facilities in Florida typically use a single well for both injection and recovery of the stored water.

As with other water supply technologies, such as surface water reservoirs or reverse osmosis, ASR has technical challenges that must be addressed. Each ASR facility is held to a stringent set of water quality regulations set forth in the Florida Administrative Code (FAC), as administered by the Florida Department of Environmental Protection (FDEP) Underground Injection Control (UIC) program (5). These regulations require that, for injection into an Underground Source of Drinking Water (USDW), defined in FAC Ch. 62-520.410 as an aquifer with a background total dissolved solids (TDS) concentration of less than 10,000 mg/L (6), the injectate must meet the Primary and Secondary Drinking Water Standards (PDWS & SDWS) within FAC Ch. 62-550 (7). FDEP applies this rule to both the recharge water (injectate) and the water recovered in ASR. This implies that the injectate can neither introduce a contaminant into the aquifer nor produce a response that releases a contaminant from the aquifer matrix. However, the injectate may be allowed to exceed some of the SDWS (e.g., color, odor, TDS)

providing that the concentration of the SDWS in the injectate is lower than that of the background concentration of the aquifer.

To demonstrate compliance with the regulations, FDEP requires that full-scale operational tests (Cycle Tests) be conducted at each facility before the facility is placed into operation. Cycle Tests are designed and permitted on a site-specific basis, generally reflecting the intended operational approach of the ASR facility. To simulate ASR operational practices, Cycle Tests typically include a large-volume recharge (injection) phase, a short or long-term storage phase, and a recovery (pumping) phase. Cycle Tests, while conducted on a much larger scale in terms of recharge and recovery volumes, are similar in design to Istok's Push-Pull Test method (8). Therefore, the approach presented here uses existing Push-Pull Test (PPT) analytical methods for ASR Cycle Test data analysis. PPT analytical methods are discussed in greater detail in the Methods section of this thesis.

ASR facilities in southwest Florida have recently reported arsenic concentrations in recovered water at levels greater than 112 $\mu\text{g/L}$ (9). The elevated arsenic concentrations are likely due to a geochemical response that mobilizes native arsenic and other trace metals during aquifer recharge (9, 10). Since the PDWS for arsenic was lowered from 50 $\mu\text{g/L}$ to 10 $\mu\text{g/L}$ (Ch. 62-550 F.A.C., Table 1) in January 2006 (7), arsenic mobilization above the PDWS has become the primary regulatory concern for ASR facilities.

In the past, the FDEP has allowed continued operation of ASR facilities as long as the PDWS for arsenic was not exceeded at the property boundary closest to the ASR well. Therefore, the historical operational approach for Floridian ASR facilities was focused on meeting the arsenic standard at the closest property boundary and maintaining a high recovery efficiency for the facility. Typically this was accomplished by recharging the aquifer with large

volumes of water during the initial ASR cycles, while only recovering a small percentage of the stored water. This approach, termed the “Target Storage Volume (TSV),” leaves large volumes of injected water in the formation, allowing for a ‘buffer zone’ or ‘transition zone’ between the native (brackish) groundwater and the recharge water. By allowing for the loss of recharge water during the initial ASR cycles, the recovery efficiency of subsequent cycles may approach the designed capacity of the facility (11). It has been proposed that, by allowing for a ‘transition zone’ between redox zones of native groundwater and recharge water, the TSV approach may also ‘attenuate’ arsenic within the formation (11). With this approach, the recharge and recovery volumes of the facility are limited so that arsenic will not exceed the PDWS at the nearest property boundary during aquifer recharge or at the ASR well during recovery.

Recently the FDEP has adopted a strict position on arsenic in ASR by prohibiting any exceedance of arsenic above the 10 µg/L standard, either at the ASR borehole or onto adjacent properties (12). According to FDEP, compliance with the arsenic standard must be met “at all times” and “at all points” within the aquifer. Therefore, arsenic concentrations may not exceed the standard in onsite monitoring wells, nor can the standard be exceeded in water recovered from the ASR well (12). ASR facilities will now be required to demonstrate compliance with the arsenic standard by recovering the full volume of the injected water during operational testing (i.e., Cycle Testing).

Due to the changing regulatory position on arsenic, changes in the operational approach for Florida ASR facilities must be considered. To address these issues, this thesis will 1) compare the current conceptual model for arsenic mobilization in ASR with results from Cycle Tests conducted at the Bradenton ASR facility, 2) present a framework for conducting field-scale tests based on Push-Pull Test analytical methods to quantify the near-borehole geochemical response

that occurs during ASR, 3) compare Bradenton ASR Cycle Test results with numerical modeling results using the 3-D Interactive Groundwater (IGW) Model calibrated to the Bradenton ASR Site, and 4) evaluate the appropriateness of the TSV approach for managing ASR recovery efficiency and attenuating arsenic.

CHAPTER 2 BACKGROUND

Mobilization of Metals During ASR

The first occurrence of arsenic in Florida ASR sites was reported by the Florida Geological Survey (FGS) while conducting research funded by FDEP (9, 10, 13). This research included a detailed mineralogical and geochemical review of ASR facilities in southwest Florida including the NW Hillsborough County Reclaimed ASR facility, the Rome Avenue ASR facility (Hillsborough County), the Punta Gorda ASR facility (Charlotte County), the Peace River ASR facility (DeSoto County) and others, all of which use the Suwannee Limestone as the storage zone for ASR. Elevated concentrations of uranium, arsenic, manganese, nickel, vanadium, molybdenum, and other metals were detected in water recovered from these sites. Because the concentrations of these metals were low in both the injected water and native groundwater, and after ruling out anthropogenic sources, FGS concluded that the source of the metals is likely from dissolution of minerals (e.g., pyrite) within the aquifer matrix (9, 10).

The injection of source water with high levels of oxidizers, such as DO, into a reduced aquifer releases (mobilizes) metals by mineral (e.g., pyrite) oxidation (9). Variables effecting the mobilization of metals during ASR include 1) the chemistry of the native and recharge waters, 2) the mineralogy of the aquifer matrix, 3) the amount of time the recharge water is in contact with

the aquifer matrix along with the number of operational or test cycles conducted, and 4) site-specific hydrogeology and geochemistry (9, 10).

Occurrence of Arsenic-Bearing Minerals in the Suwannee Limestone

To identify the source of arsenic in ASR, Price and Pichler (14) completed a mineralogical and geochemical analysis of more than 300 core samples collected from the Suwannee Limestone formation in southwest Florida. The results of this analysis indicate that arsenic was present within “clean” limestone (relatively pure limestone without minor mineral phases) samples of the Suwannee Limestone at concentrations of around 1.7 mg/kg. Arsenic was reported at higher concentrations of 9.5 mg/kg in “targeted” samples (samples containing visible trace minerals, minor constituents, or organic material). The “targeted” samples were selected because of the suspected association of arsenic with trace mineral phases, such as pyrite, and organic material. Therefore, the resulting average arsenic concentration of 3.5 mg/kg reported by Price (14) for the bulk Suwannee Limestone may be skewed slightly as the calculated value included the concentrations from the “targeted” samples. However, the average arsenic concentration of 3.5 mg/kg is near the 2.6 mg/kg global average concentration for limestone reported by Smedley and Kinniburgh (15). The results of this study indicate that 1) the high arsenic concentrations present within the Suwannee Limestone are associated with pyrite minerals and 2) the bulk aquifer matrix contains relatively low levels of arsenic (14).

Price and Pichler (14) concluded that mineral grains of pyrite are generally associated with high-porosity zones. Samples of pyrite were selected from the cores and were analyzed for arsenic concentration. The results show that pyrite is generally rich in arsenic with an average arsenic concentration of 2300 mg/kg. This is within the arsenic concentration range for pyrite of 100 to 77000 mg/kg provided by Smedley and Kinniburgh (15). Additionally, organic material

and other trace minerals identified within core samples were analyzed and were not found to be a significant source of arsenic (14).

Principles of Arsenic Mobility

The speciation of arsenic is predominately controlled by the Redox potential (Eh) and by the pH of the system (15). However, it is unlikely that differences in system pH play a dominant role in the dissolution of arsenic at ASR sites in Florida. SDWS require pH levels of 6.5 to 8.5 for recharge in ASR. Most municipal water suppliers maintain slightly alkaline conditions (pH approximately 7.2 or greater) to prevent corrosion of distribution pipes. This is near the average background pH value of 7.3 ± 0.4 measured in monitoring wells open to the Suwannee Limestone in southwest Florida (16). If we also neglect other geochemical, physical and biological (i.e., microbial) processes, we can simplify the arsenic issue to focus on phase shifts, from the solid arsenic phase to the dissolved phase, that result from changes in the redox (Eh) state of the system.

The relationship between the oxidation state of the system and the speciation of arsenic is shown in the Eh – pH (Pourbaix) diagram (Figure 2-1). At a near neutral pH, the solid arsenic species (As) is present at low Eh (reduced) conditions of approximately -0.35 to -0.60 millivolts (mv). As the Eh increases from highly reduced conditions to more oxidized conditions (Eh values above -0.35 mv), arsenic (As) is dissolved to the arsenic-sulfide (AsS_2^-) species (17).

Geochemical Models

Mirecki (18) used the geochemical model code PHREEQC-2 to simulate water quality changes during ASR test cycles at the Olga, North Reservoir, and Eastern Hillsboro potable water ASR systems. The study was conducted in support of the Comprehensive Everglades Restoration Plan (CERP). PHREEQC-2 is a computer program written in the C programming

language and developed by USGS. The program is designed to perform a wide variety of low-temperature aqueous geochemical calculations and is available for free download (19).

The geochemical models employed by Mirecki (18) were used to simulate mixing during ASR recharge, geochemical reactions during storage and recovery, and the fate and transport of arsenic during ASR cycle testing as well as to investigate uncertainties in the model to identify additional data needed to support future modeling efforts. Mirecki (18) suggests that oxidizers in recharge water, primarily DO, dissolve native pyrite minerals releasing arsenic, iron, and other trace metals into solution. The iron re-precipitates locally as iron-oxyhydroxides (HFOs) during recharge, providing surface sites for the adsorption of arsenic. During recovery, the sorbed arsenic is re-released when native (i.e., sulfate reducing) conditions return near the well, destroying the arsenic adsorption sites (18). This suggests that HFOs act as an arsenic ‘sink’ during recharge and as an arsenic ‘source’ during recovery.

Mirecki (18) concluded that 1) recharge mixing curves differ between the sites due primarily to hydraulic factors; 2) pyrite oxidation, HFOs precipitation, and sulfate reduction and hydrogen sulfide (H₂S) production occur in sequence during ASR cycle testing; 3) while iron-oxyhydroxides (HFOs) can reduce the mobility of arsenic during ASR, the small masses of HFOs predicted in the models may not be sufficient to account for the high arsenic concentrations measured during recovery. A conceptual model of arsenic mobilization during ASR was also presented by Mirecki (18) and is expanded upon below.

To demonstrate pyrite instability during ASR, Jones and Pichler (16) simulated injection of treated surface water at three ASR sites in southwest Florida. Mixing of native water and ASR source water was modeled by the construction of Fe-S mineral stability diagrams. Stability fields were plotted for Fe-S minerals in contact with various mixing ratios of injection water to

storage-zone water. Results indicate that pyrite was stable under native groundwater (i.e., sulfate reducing) conditions and becomes less stable as the ratio of oxygenated water increased during injection. Variation in the pyrite stability fields for the three sites was attributed to differences in native (i.e., background) groundwater sulfate concentrations (16).

Unlike the results of geochemical modeling presented by Mirecki (18), the stability diagrams constructed by Jones and Pichler (16) suggest that HFOs are not stable under conditions found during ASR and, therefore, cannot be a source for adsorption of dissolved arsenic. However, the models developed by Jones and Pichler (16) did not consider water-rock interactions or the effects of other potential arsenic adsorbing metal-oxides/hydroxides (HMOs) of aluminum, manganese, magnesium, molybdenum, or other trace metals. Given their abundance in aquifer materials, and because of their chemistry, oxides of aluminum, iron, and manganese are potentially the most important source and sink for arsenic in aquifer sediments (17).

Conceptual Model

The potential mechanisms by which arsenic is mobilized during ASR have been identified. However, uncertainty remains regarding the mechanisms that control the fate and transport of mobile arsenic. Based on the conclusions of the research completed to date (9, 10, 13-18), we can hypothesize a conceptual model for arsenic in ASR:

The injection of water containing high levels of oxidizers (e.g., DO) into a strongly reducing (i.e., sulfate reducing) environment produces a geochemical response that solubilizes native minerals (i.e., pyrite) releasing arsenic, iron, and other trace metals into solution (Figure 2-2).

The dissolved metals re-precipitate locally as metal-hydroxides (HMOs). Arsenic adsorbs onto the freshly precipitated HMOs surface sites some distance farther away from the injection (i.e., ASR) well (Figure 2-2).

During recovery of the stored water, native groundwater (i.e., sulfate reducing) conditions advance toward the ASR well. The reprecipitated metals are solubilized under the reduced conditions, which destroys the HMOs adsorption sites and re-releases arsenic into solution (Figure 2-3).

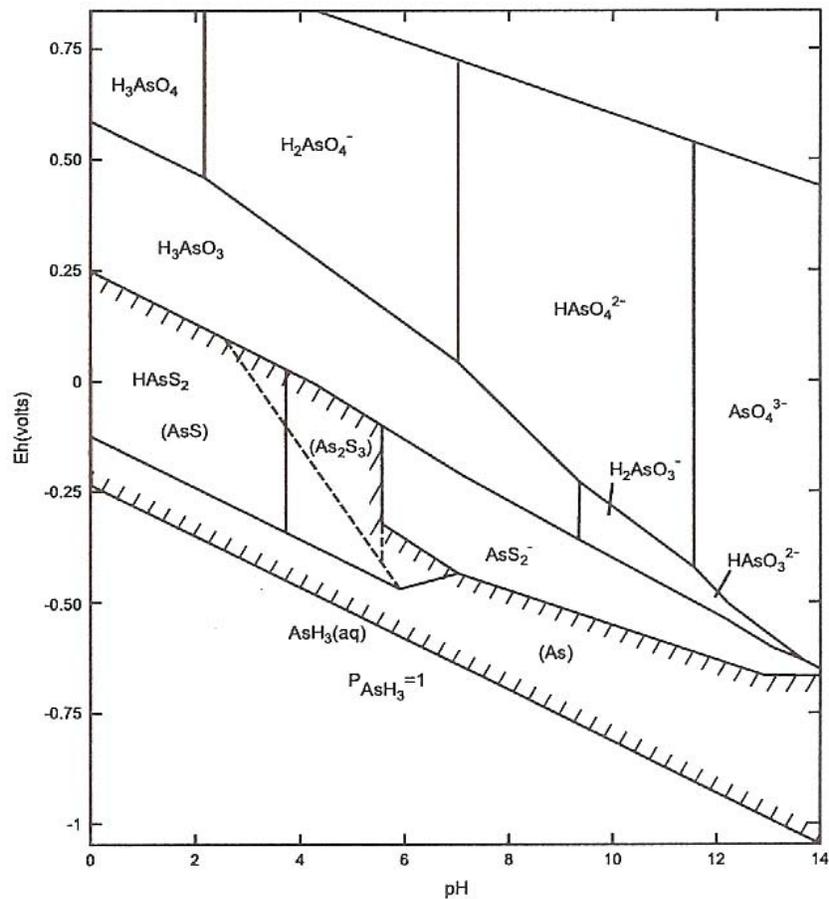


Figure 2-1. The Eh-pH diagram for arsenic at standard conditions with total sulfur 10^{-3} mol/L and total arsenic 10^{-5} mol/L. Solid species are enclosed in parentheses in the cross-hatched area (Welch et al. (17)).

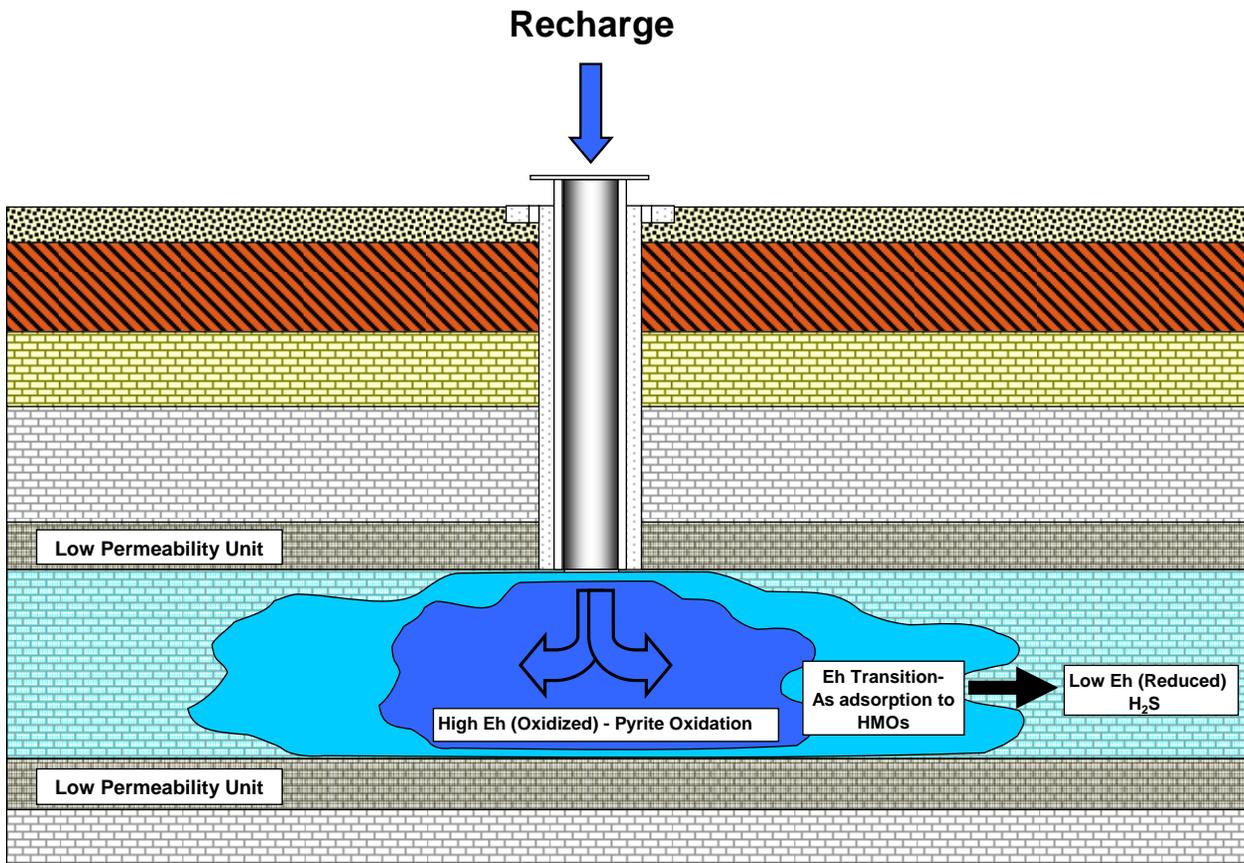


Figure 2-2. Pyrite oxidation, leading to arsenic mobilization and formation of arsenic adsorption sites, during aquifer recharge

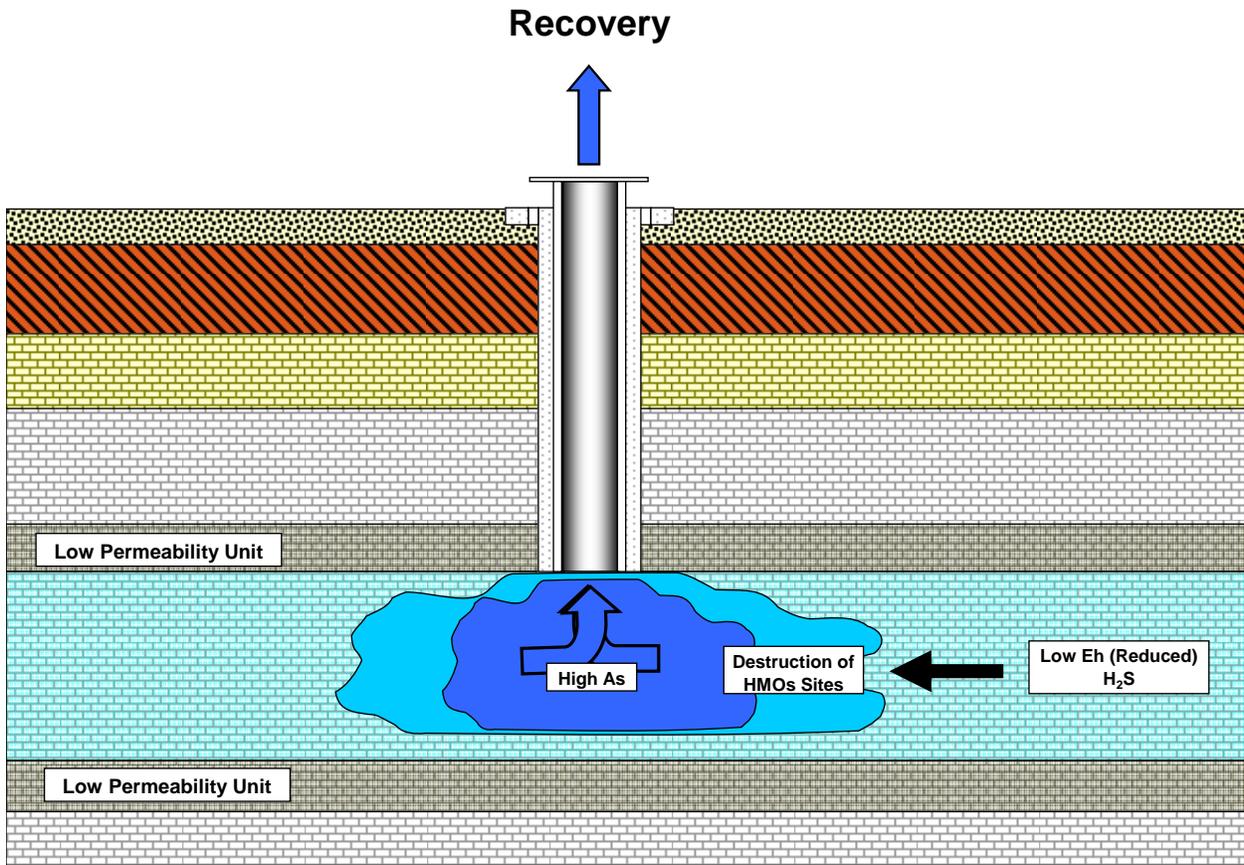


Figure 2-3. Reductive dissolution of arsenic (metal-hydroxide instability) during recovery

CHAPTER 3 METHODS

Site Selection

The City of Bradenton High Service Pump Station (HSPS) Potable Water ASR Facility (ASR-1) was used as the case study for this research project. The site is located near downtown Bradenton in western Manatee County, Florida (Figure 3-1). Site selection was based on both the availability and comprehensiveness of data sets collected during seven test cycles conducted at the project site. Information presented in this study was obtained from the October 2006, City of Bradenton, Potable ASR Cycle Test Summary Report (20) and the February 2004, City of Bradenton, ASR Program, Phase II Well Construction Report (21).

The City of Bradenton operates a conventional surface water treatment plant (WTP) located at the Bill Ever's Reservoir on Ward Lake (Figure 3-1). The lake was created in 1936 when the City constructed an 838-foot broad-crested weir impounding the Braden River. As the sole source of water for the City, the reservoir was expanded in 1985 to meet the growing demands of the City's population (22). Water treated at the WTP is piped approximately 6 miles to the City's High Service Pump Station (HSPS) site for storage and distribution to downtown Bradenton (Figure 3-1).

In 2003 the City constructed an ASR facility (ASR-1) at the HSPS site as a way to store large volumes of water near the City's population center to meet seasonal and emergency water supply shortfalls. Potable water is injected into ASR-1 either via high-service pumps or by gravity flow from onsite above-ground storage tanks. Water stored in ASR-1 is recovered via a single-vertical turbine pump. During testing, recovered water is piped to waste in the City's storm water collection system. Once the system is operational, the recovered water will be

disinfected and piped either directly to the City's water distribution system or to storage in existing above-ground storage tanks.

As shown in Figure 3-2, ASR facilities at the HSPS Site include an ASR well (ASR-1) with a single storage zone monitoring well (SZMW-1) located 224 ft North of ASR-1. An intermediate aquifer monitoring well (AFMW-1) and a water table monitoring well (WTMW-1) are located 20.4 and 11.2 ft east of ASR-1, respectively. Well construction details, including screen or open-hole intervals, and casing size and elevations are provided in Table 3-1.

Site Hydrogeology

Peek (23) described the geologic formations of Manatee County to include surficial soil, sands, and limestone of recent to Pliocene age of approximately 0 to 60 feet thickness. The surficial soils are underlain by Miocene-age sediments that make up the Hawthorn Group. The Hawthorn Group is an interlayered sequence of sediments that includes phosphatic clays, marl, sands, silts and limestones with an approximate thickness of 150 to 360 feet (23). The Miocene age Tampa Member, of the Arcadia Formation, forms the base of the Hawthorn Group and is described by Peek (23) as a white, gray, and/or tan, generally dense, hard, sandy, and partly phosphatic limestone with an approximate thickness of 125 to 235 feet.

The Oligocene age Suwannee Limestone is separated from the Hawthorn Group by sandy-clay to clayey-sand confining unit (24). The Suwannee Limestone is described as a creamy white and tan, soft to hard, granular, porous, crystalline, and partly dolomitic limestone with a thickness of approximately 150 to 300 feet (23). The Suwannee Limestone is underlain by a thick (approximately 1700 to 2000 feet) sequence of carbonate rocks that includes the Eocene age Ocala Limestone, Avon Park Formation, Lake City Limestone, and Oldsmar Limestone (23).

The sedimentary deposits described by Peek (23) form the multi-layered aquifer system present in the study area. Three aquifers - the surficial aquifer, intermediate aquifer system, and

Floridan aquifer – are present (24). All deposits overlying the Hawthorn Group make up the surficial aquifer. The surficial aquifer is separated from the Hawthorn Group by a confining unit consisting of sandy-clay, clay, and marl. The Hawthorn Group sediments form the intermediate aquifer system that contains up to three water-producing zones within the study area. The producing zones are separated by confining units and are composed primarily of carbonate rocks (24). The Suwannee Limestone and Avon Park Formation are the two major water-producing zones within the Upper Floridan aquifer and are separated by the less-permeable Ocala Limestone (24).

A review of boring logs, geophysical logs, and a video survey log completed during well construction indicates that the surficial aquifer is approximately 35 feet thick at the Bradenton HSPS site (21). The surficial aquifer consists of silty sand, of medium to coarse grains, with some shell present in the lower portion. Limestones, clays, and siltstones of the Hawthorn Group are present at the site from approximately 35 to 295 feet bls. Gray to yellow, hard, fossiliferous limestone, likely the Tampa Member, is present from approximately 295 to 400 feet bls. Carbonates of the Upper Floridan aquifer underlay the Tampa Member with the Suwannee Limestone contact at approximately 400 feet bls. The Suwannee Limestone was described as a brownish-gray to yellowish-gray, partly micritic or crystalline, hard, limestone. Borings completed at ASR-1 and SZMW-1 were terminated at approximately 550 feet bls (21). Therefore, the thickness of the Suwannee Limestone and depth to the Ocala Limestone contact were not determined. A generalized geologic profile is included below (Figure 3-3).

Both ASR-1 and SZMW-1 were initially drilled to approximately 550 feet bls. However, ASR-1 was grouted back to 505 feet bls due to the presence of a horizontal cavity of approximately ½-foot thick at 499.5 to 500 feet bls, as noted in the ASR-1 video survey log. The

geophysical logs and video survey completed at ASR-1 indicate that the primary productive interval of ASR-1 is between 460 and 485 feet bls with a few thin, approximately 2-inch-thick, porous intervals or solution features present. No other significant high porosity zones were identified (21).

Bradenton Cycle Test Program

As with most ASR facilities in Florida, the testing program for the Bradenton ASR facility was designed to demonstrate compliance with FDEP regulations. To date, seven Cycle Tests (Cycles 1–6a) have been completed at the Bradenton ASR-1 site, in accordance with FDEP Permit Number 133098-027-UC. Testing began in November 2003 and was completed in June 2006 (20).

The first series of tests (Cycles 1-4) were conducted to measure the near-borehole geochemical response that occurs during ASR. Therefore, Cycles 1-3 were limited to 10-MG recharge events with approximately one week of storage and nearly complete recovery of the stored water. Test volumes for Cycle 4 were similar to the first three tests but the storage duration was extended to 29-days to allow the injected water to further equilibrate with the aquifer.

Cycles 5 and 6 were designed to test water quality changes as recharge water moves past SZMW-1 during build-out of the planned TSV of 160-MG. Cycle 5 included a 50-MG recharge event, with only 10-MG recovered, and was followed by Cycle 6 which included a 120-MG recharge event, with an additional 10-MG recovered. This design allowed for monitoring of the ‘leading edge’ (i.e., the advective front) of recharge water as it moved past SZMW-1.

Cycle 6a was initially designed to test the recovery efficiency of the ASR system at a limited recovery volume of 25-MG. However, given the pending change in regulatory positions on arsenic, the recovery volume was increased to a total of 120 MG in order to determine the

possible magnitude of arsenic concentrations at the nearest property boundary from ASR-1 (r = 75 ft). Additional details of the Cycle Test program are provided in Table 3-2.

Bradenton Sampling Program

Water quality data from Bradenton ASR facility were collected in accordance with the FDEP construction permit. While a more extensive dataset was collected to support permitting, the parameters discussed in this thesis include analytical laboratory results for TDS, arsenic, magnesium, sulfate, and calcium and field data for temperature, DO, and oxidation reduction potential (ORP).

As required by the construction permit, all groundwater samples were collected in accordance with FDEP Standard Operating Procedures (SOP) 001/01 (20). Samples were collected by City staff and the City's consulting Engineer in laboratory-supplied containers. Upon collection, the samples were immediately chilled (iced) to 4°C and were shipped to an offsite laboratory for analysis. All laboratory analyses, with the exception of the City's in-house analysis for arsenic during Cycles 1-4, were performed by National Environmental Laboratory Accreditation Conference (NELAC) certified labs using FDEP-approved analytical methods. Field parameters were measured using a Yellow Springs Instrument (YSI), Inc. 556 MPS instrument or YSI 6600-EDS datalogging sonde (20). All field instruments were calibrated and deployed in accordance with FDEP SOPs. Performance specifications for the field instruments can be found at www.yisi.com.

Push-Pull Tests

Istok (8) and others (25-31) have used the single-well Push-Pull Test (PPT) as an analytical tool for investigating contaminated sites and for remediation design and optimization. The PPT technique includes the injection (Push) of a tracer and/or reactant into an aquifer through a single well and, subsequently, the recovery (Pull) of the injectate from the same well.

During the recovery phase, solute concentrations are measured to obtain breakthrough curves, to determine the amount of reactant(s) consumed and product(s) formed, and to calculate reaction rates (8).

The PPT method has been adapted to a variety of applications and sites. McGuire et al. (25) used this analytical method to evaluate the behavior of oxygen, nitrate and sulfate during aquifer recharge at a chlorinated solvent site. Kim et al. (26) evaluated the in-situ aerobic cometabolism of ethylene, propylene, and c-DCE at a contaminated site using the PPT method. Leap and Kaplan (27) and Hall et al. (28) proposed a single-well pump and drift test method similar to the PPT. These tests included a drift phase between recharge and recovery events that allowed for estimating local groundwater velocity and effective porosity. Scroth et al. (29) proposed methods for in situ evaluation of solute sorption onto aquifer sediments using single-well PPT methods.

The approach detailed in this thesis was modeled after the simplified method for estimating first-order reaction rate coefficients k (T^{-1}) from Push-Pull Test data presented by Haggerty et al. (31). As described, ‘simplified’ implies that the reaction rate estimates are solely based on measured concentrations of tracer and reactant. Estimates of the physical properties of the aquifer, such as hydraulic conductivity, dispersivity, or porosity, which are subject to uncertainty, are not required.

The method proposed by Haggerty et al. (31) is based on the First-order decay equation

$$\frac{dC_r}{dt} = -kC_r \quad (3.1)$$

where C_r is the concentration of the reactant and t is time. Thus the decrease in the concentration of the reactant during time t is proportional to the decay rate and the concentration of the reactant.

For a well-mixed reactor (assuming complete and instantaneous mixing of the injected solution within the aquifer) the relative concentration (i.e., the measured concentration C divided by $C_{\text{injection}}$, respectively) of the reactant at any time t can be computed by

$$C_r^*(t) = C_{tr}^*(t)e^{-kt} \quad (3.2)$$

where C_r^* is the relative concentration of reactant at time t , C_{tr}^* is the relative concentration of tracer at time t , and $k[t^{-1}]$ is the rate coefficient (32). Assuming consumption of the reactant begins immediately upon injection (i.e., some of the reactant is being consumed during the finite length injection phase) the extraction phase breakthrough curve for a reactant is given by

$$C_r(t^*) = \frac{C_{tr}(t^*)}{kt_{inj}} \left[e^{-kt} - e^{-k(t_{inj}-t^*)} \right] \quad (3.3)$$

where t^* is the elapsed time since the end of the injection and t_{inj} is the duration of the injection phase. Equation 3.3 can be re-written as

$$\ln \left(\frac{C_r(t^*)}{C_{tr}(t^*)} \right) = \ln \left(\frac{1 - e^{-kt_{inj}}}{kt_{inj}} \right) - kt^* \quad (3.4)$$

Using a standard least squares routine, a plot of $\ln(C_r(t^*)/C_{tr}(t^*))$ versus t^* generates a straight line with slope equal to $-k$. and an intercept = $\ln((1 - e^{-kt_{inj}})/(kt_{inj}))$. For more details on the method development the reader is referred to Haggerty et al. (31).

This method was applied to the Bradenton Site to obtain First-order decay rates to investigate dissolved oxygen consumption during ASR. A non-linear least squares regression was used to fit breakthrough data to equation 3.4. For our case $C_{tr}(t^*)$ is the relative Total Dissolved Solids (TDS) concentration and $C_r(t^*)$ is relative DO concentration. At Bradenton, background concentrations of the reactant (i.e., DO) were negligible. However, the background concentration of the tracer (i.e., TDS) was detectable at levels above 1100 mg/L, while

concentrations of the injectate were generally less than 400 mg/L. Therefore, C_{tr} was calculated as a proportion between the injected TDS concentration and the background concentration as

$$C_{tr} = \left(\frac{TDS_b - TDS_m(t^*)}{TDS_b - TDS_m(t^o)} \right) \quad (3.5)$$

where TDS_b is the measured background TDS concentration, $TDS_m(t^*)$ is the measured TDS concentration at time t (i.e., time elapsed since end of the injection), and $TDS_m(t^o)$ is the measured TDS concentration at time $t = 0$ (i.e., end of the injection). This is similar to the approach presented by Maguire et al. (25).

The major assumptions presented by Haggerty et al. (31) requires that 1) both tracer and reactants exhibit identical retardation during transport in the aquifer and 2) there be complete and instantaneous mixing of the injected test solution in the portion of the aquifer investigated by the test (i.e., the system behaves like a well mixed reactor). To evaluate the second major assumption, Schroth and Istok (30) presented two alternative models to estimate First-order decay (k) rates that were based on different mixing assumptions including plug-flow and variably mixed reactor models. Using a semi-analytical solution to govern the solute transport equation, the authors performed sensitivity analysis on the three mixing models (i.e., well-mixed reactor, plug flow, and variably mixed reactor models) to compare the accuracy of the obtained rate coefficients. Computations were performed for a homogenous, confined aquifer, with variable aquifer parameters and a heterogeneous, unconfined aquifer. For the well-mixed reactor model, Schroth and Istok (30) reported less than 9% error for the confined homogenous aquifer case. The authors reported the largest errors for cases were the porosity (n) was low (estimated error = 5.1%), dispersivity (α_L) was low (estimated error = 8.9%), and the injection time (t_{inj}) was high (estimated error = 8.5%). For more details on the model sensitivity analysis, the reader is referred to Schroth and Istok (30).

Interactive Groundwater Model

To investigate solute transport during ASR, a 3-D model of the Bradenton site was developed using the Interactive Groundwater Model (IGW) version 4.7 (33). IGW is currently available for free download in 2-D and 3-D versions. IGW presents a new approach to groundwater modeling where the user can view the graphic output of the model while the model is running, stop the computational process, edit the model input parameters, and re-run the simulation. Because post-processing of the model output isn't necessary, IGW allows the user to calibrate the model to site conditions as the model is being developed (i.e., refined) (33-35).

To reduce computational time and provide real time visualization of the model out-put, IGW relies on hierarchical patch dynamics (HPD) (33). HPD allows modeling of complex systems across multiple-scales by coupling a sub-model(s) to a parent model. This approach is a generalization of the telescopic mesh refinement (TMR) technique as the model uses a coarse grid (i.e., large grid size) over a large parent-model domain and a fine grid (i.e., small grid size) over a small sub-model(s) to increase the resolution of the model within the sub-model area(s) (33).

A stable version of the 2-D model (Version 3.5.6 released on January 30, 2004) is available and includes a manual and tutorial with downloadable videos. However, the 3-D model is only currently available in a beta-version (Version 4.7 released on July 18, 2006) and therefore may not be completely stable on the user's computer. A user's manual for the 3-D was not available for download at the time of this study. For more information on IGW, the reader is directed to the IGW host website (34).

The 3-D IGW model (Version 4.7) developed for the Bradenton ASR site was based on a six-layer system. Layer one represents the surficial aquifer. Layers two and three represent a confining layer and producing zone of the intermediate aquifer, respectively. Layer four

represents the ASR storage zone. Layer five represents the sub-ASR storage zone and layer six represents the base of the model domain. The horizontal boundary of each layer was assigned a constant head that corresponded to the initial head given for each layer (Figure 3-4). Each layer was also assigned an initial concentration reflecting background TDS concentrations of 1200 mg/L. A constant source boundary was also applied to the horizontal boundaries of layers three (i.e., intermediate producing zone), four (i.e., storage zone), and five (i.e., sub-ASR layer) to represent background TDS conditions (1200 mg/L) during large-volume recovery events. Layer six was assigned a constant head, equal to the initial head, and a constant source to represent background TDS conditions.

The parent-model domain was set at 9600 by 9600 feet with a coarse grid spacing of 282.4 feet (35 x-grids and 35 y-grids). A sub-model, with a fine grid spacing of 43.2 by 44.2 feet (40 x-grids and 40 y-grids), was used to increase the resolution (i.e., discretization) of the parent-model in the vicinity of the ASR well. The injection/pumping well (ASR-1) well was located in the center of the model domain (i.e., x-direction = 4800 feet, y-direction = 4800 feet). To monitor horizontal flux during ASR a storage zone monitoring representing SZMW-1 was located 224 feet north (i.e., plus 224 feet in y-direction) of ASR-1. To monitor vertical flux during ASR, an intermediate aquifer monitoring well representing AFWM-1 was located 20.4 feet east (i.e., plus 24 feet in x-direction) of ASR-1 and a water table monitoring well representing WTMW-1 was located 11.2 feet east of ASR-1. Additional details of the model layers and attributes are provided in Figure 3-4.

The default model solver settings were used to calibrate the model and run simulations. The default settings include the Algebraic Multigrid flow solver and the Successive Over Relaxation (SOR) transport solver. The model was calibrated against both TDS breakthrough

curves and heads measured at ASR-1, SZMW-1, and AFMW-1, and heads measured at WTMW-1, during Cycle Tests 5, 6, and 6a. Numerous simulations were run with additional model refinement during model calibration. Calibration of the model was achieved with the model attributes listed in Figure 3-4.

Once calibrated, the model was run to simulate successive operational cycles at the Bradenton ASR Site over a four-year period. These cycles were based on the initial design of the Bradenton facility with 150 MG recharged during the wet season and 120 MG recovered during the following dry season. However, the model does not consider loss due to drift under natural aquifer gradients as storage intervals were not simulated.

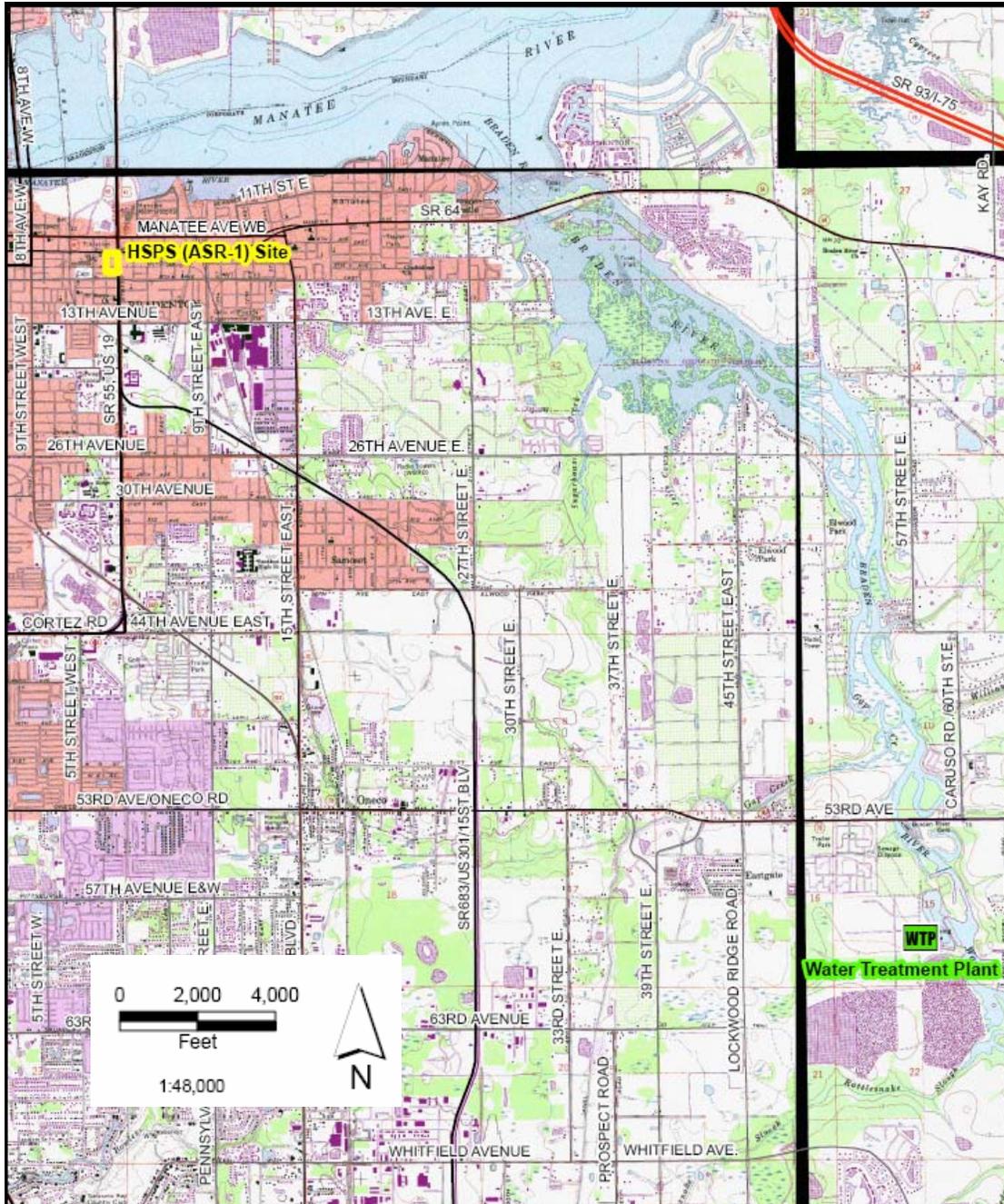


Figure 3-1. Site location map (modified from Jones Edmunds (20))

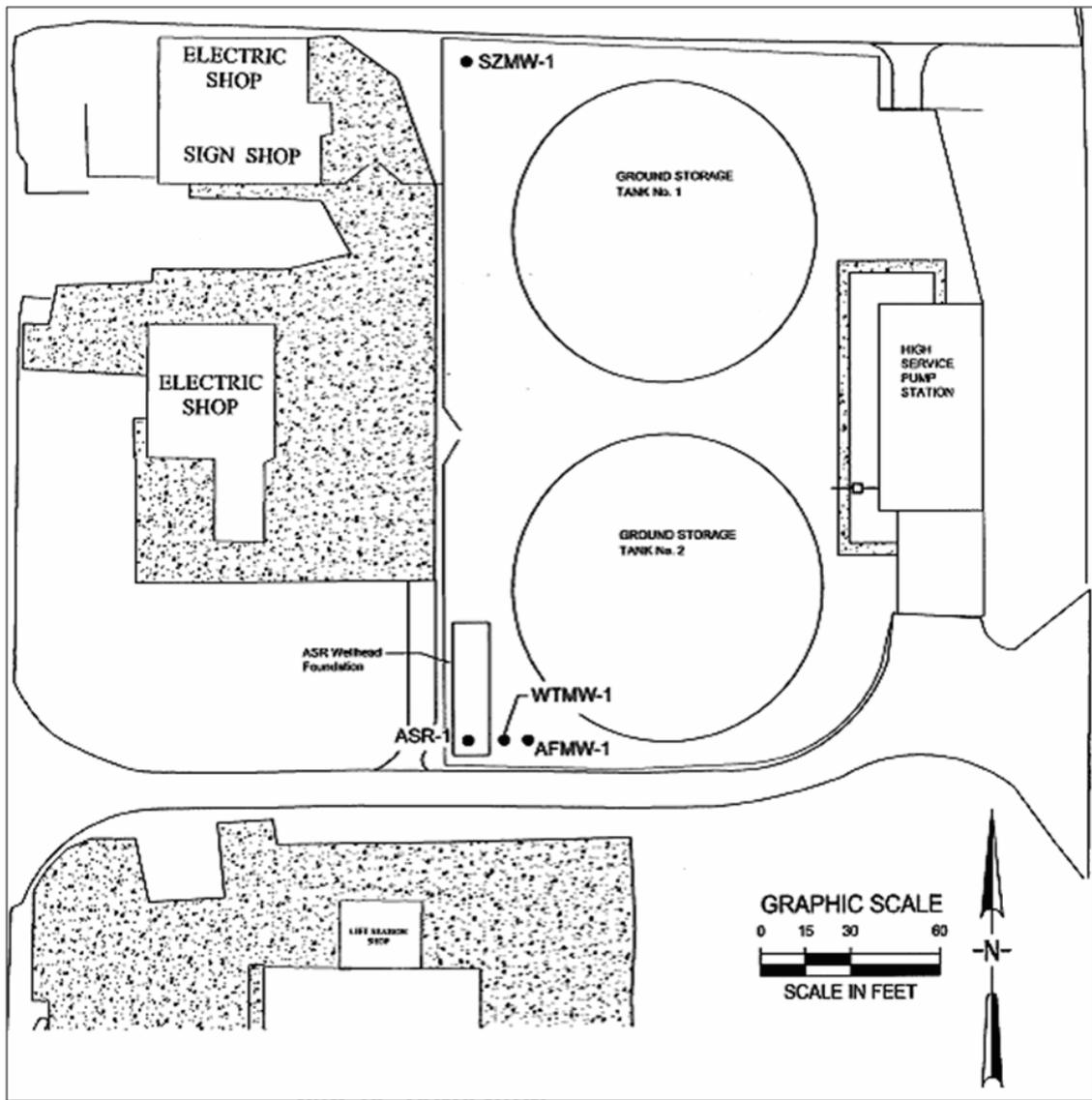


Figure 3-2. Site plan (modified from Jones Edmunds (20))

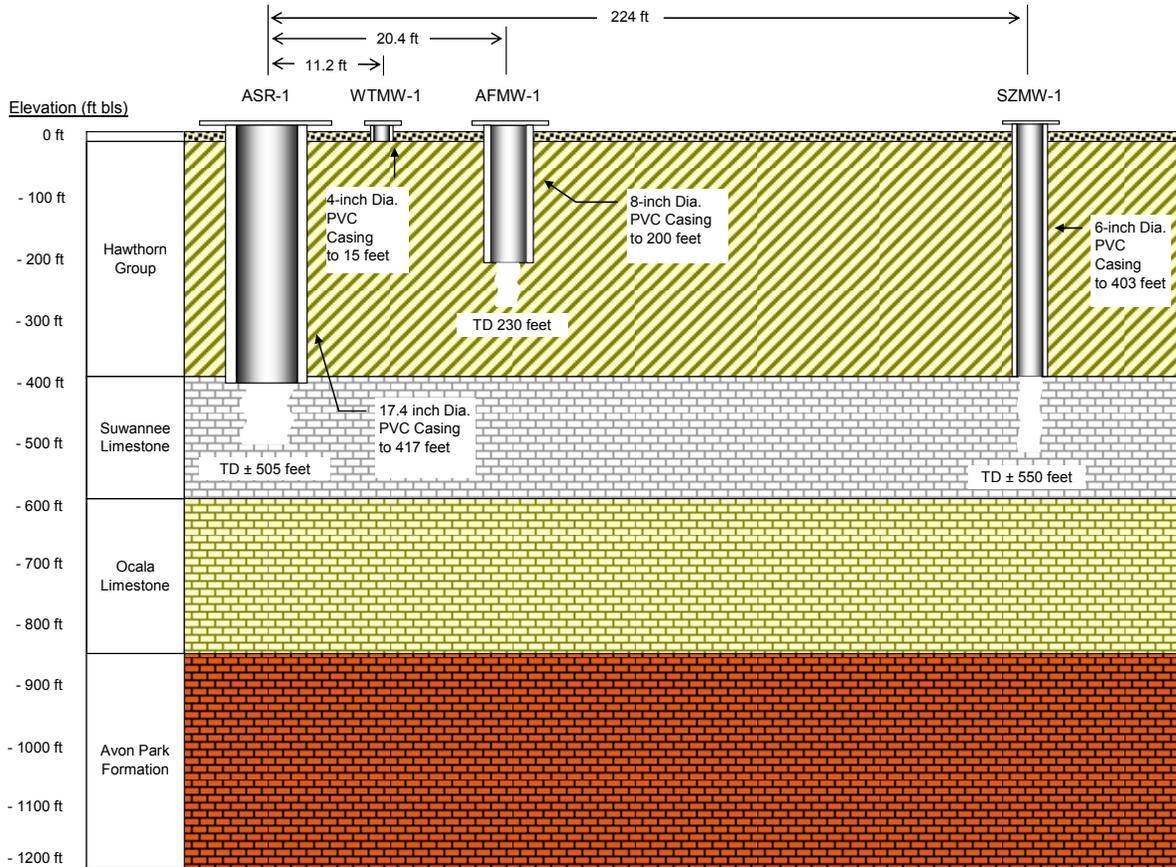


Figure 3-3. Generalized geologic profile and well construction details (modified from Jones Edmunds (20)). Vertical scale greatly exaggerated

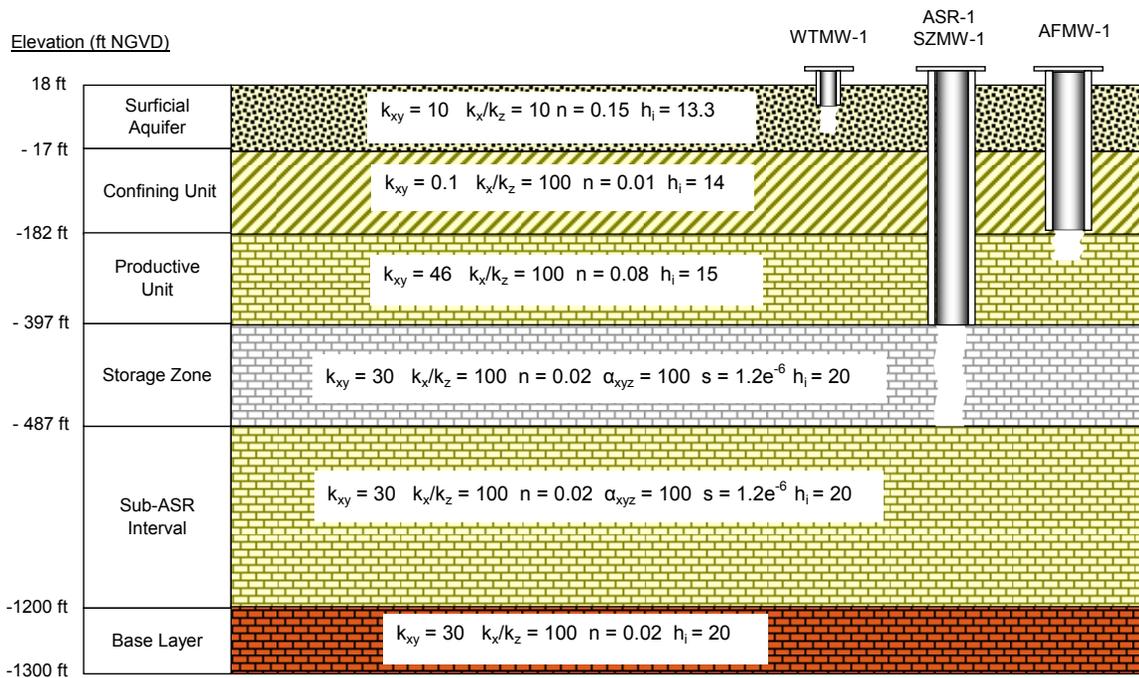


Figure 3-4. Model details and input parameters

Table 3-1. Well construction details for the Bradenton HSPS ASR facility

Well Name	Casing Depth (feet bls ^a)	Nominal Casing Outside Diameter (inches)	Casing Material	Open Hole Interval (feet bls ^a)	Top of Well Casing Elevation ^b (msl ^c)
ASR-1	415	17.4	PVC	415-550 (plugged back with cement to 505)	20.54
SZMW-1	400	6.625	PVC	400-548	20.16
AFMW-1	200	8.625	PVC	200-230	19.58
WTMW	15	4	PVC	screened from 5-15	20.26

^a = feet below land surface (bls); ^b = as surveyed on October 8, 2003; ^c = feet above mean sea level (msl) (Jones Edmunds (20))

Table 3-2. Bradenton ASR cycle test program summary

Cycle Test	Start Date	End Date	Storage Duration (Days)	Average Recharge / Recovery Rates (MGD)	Recharge Volume (MG)	Recovery Volume (MG)	Net Volume (MG)
1	9/9/2004	12/1/2004	9	1.69 / -1.87	10.25	10.39	0
2	12/1/2004	12/20/2004	6	1.67 / -1.87	10.02	10.63	0
3	12/24/2004	1/19/2005	13	1.67 / -1.87	9.97	10.03	0.06
4	1/20/2005	3/1/2005	28	1.65 / -1.78	9.36	9.37	0
5	8/9/2005	9/22/2005	0	1.38 / -1.43	50.18	8.89	41.29
Inter-Cycle Storage Period			18				
6	10/11/2005	1/20/2006	0.9	1.30 / -1.53	120.1	10.15	151.24
Inter-Cycle Storage Period			56				
6a ^a	3/21/2006	4/7/2006	-	-1.53	-	24.96	126.28
Inter-Cycle Storage Period			10				
6a ^a	4/18/2006	6/23/2006	-	-1.51	-	94.93	31.35

^a = Cycle Test 6a was interrupted due to FDEP permitting issues

CHAPTER 4 RESULTS

Water Chemistry

Background water quality samples were collected at SZMW-1 during the startup of Cycle Test 1 (Table 4-1). With the exception of chloride concentrations, native groundwater at the Bradenton Site is consistent with ambient water quality in the coastal UFA of southwest Florida (16). Native groundwater at the Site contains high levels of dissolved species as indicated by measured TDS and sulfate concentrations and is highly reduced (strongly negative field ORP values). The quality of the recharge water (injectate) is consistent with potable water supplied by a conventional surface water treatment process. In contrast to native groundwater, the recharge water is well oxygenated, with consistently high DO and ORP values, and contains relatively low concentrations of dissolved constituents such as sulfate, calcium, magnesium, and arsenic (Table 4-1).

Chloride in UFA groundwater of coastal southwest Florida often exceeds 750 mg/L (16), while recharge water for potable ASR systems is generally less than the SDWS of 250 mg/L. However, this was not the case for Bradenton as the background concentration of chloride in the UFA is close to that of the recharge water (Table 4-1). Therefore, TDS was used as a tracer for this investigation. While TDS is not an ideal tracer, due to the reaction of DO with sulfur minerals in the UFA, the effect on the TDS concentration due to the dissolution of sulfur minerals is assumed to be negligible. Also, there is a clear contrast in the background TDS concentration in ASR-1 (approximately 1200 mg/L) and that of the recharge water (approximately 323 +/- 23 mg/L; see Table 4-1).

Cycle Test Results

Elevated arsenic concentrations, along with rapid DO consumption and ORP equilibration, indicate that a near-borehole geochemical response was measured at ASR-1 during Cycles 1-4 (Figures 4-1 and 4-2). Arsenic increased above the background concentration ($<3 \mu\text{g/L}$) during each of the recovery events, with the highest value of $23 \mu\text{g/L}$ reported during Cycle 3. DO concentrations decreased rapidly at ASR-1 during storage from recharge water levels that were near or above saturated conditions (7.83 to $9.95 \mu\text{g/L}$) to less than $2.09 \mu\text{g/L}$ at the end of each storage event. There were no significant changes in the water quality trends for arsenic, DO, or ORP measured at ASR-1 during the extended storage period (29 day) of Cycle 4. Arsenic, DO, and ORP remained near background levels at SZMW-1 ($r = 224$ feet) during these small-volume tests.

The TDS increased to near background conditions (1200 mg/L) at ASR-1 during Cycle 1 recovery. However, TDS values did not recover to background conditions during subsequent tests (Figure 4-2). This may be attributed to mixing (loss due to dispersion) between the 'brackish' native groundwater and lower salinity or 'fresh' potable water during ASR or loss due to the natural gradient during storage. The noticeable decline in TDS concentrations at SZMW-1 during recharge events is likely the result of preferential flow paths (Figure 4-2). This correlates with the high-permeability layer between 460 and 485 feet below land surface reported in the 2004 Construction Report (21).

There was no storage period between the Cycle 5 and 6 recharge and recovery events. This allowed for measurement of the rapid equilibration of ORP values and consumption of DO during ASR at the Bradenton Site (Figure 4-3). ORP values decreased from recharge water levels of 400 mv to approximately 100 mv in the recovered water during Cycle Test 5 and 6 recovery events. DO values ranged from 6.05 to 10.99 mg/L during Cycle Test 5 and 6 recharge

events and decreased to background (0.02 mg/L) levels during both 10 MG recovery events. This is further evidence of the near-borehole geochemical response that results from the rapid shift in water quality conditions during ASR. As expected, ORP increased from highly reduced conditions (-100 to -200 mv) to more oxidized conditions (approximately 100 mv) at SZMW-1 during the Cycle 5 and 6 recharge events. DO values remained near the resolution of the probe (<0.02 mg/L) during Cycle 5 and 6 at SZMW-1 (Figure 4-3).

The advective front was detected at SZMW-1 during the 50-MG recharge event of Cycle 5 as TDS decreased sharply to near recharge water concentrations between approximately 30 to 40 MG recharged and increased sharply during the 10-MG recovery event (Figure 4-4). This indicates that, while loss due to mechanical dispersion may be occurring, the transport of this parameter is not significantly influenced or is not retarded by the limestone matrix.

While results from Cycle Test 1 through 6 indicate a near-borehole geochemical response that releases arsenic during ASR, arsenic remained near background levels at SZMW-1 during the Cycle 5 and 6 recharge events (Figure 4-5). This suggests that arsenic is retarded (absorbed) by the limestone matrix during aquifer recharge. Arsenic concentrations increased above background levels at SZMW-1 during Cycle 5 recovery and storage, which may indicate reductive dissolution of arsenic is occurring. Other than a slight increase in arsenic concentrations, there was no significant change in water quality, from recharge water levels, at ASR-1 during the 10-MG Cycle Test 5 and 6 recovery events (Figure 4-4).

TDS increased steadily at ASR-1 during Cycle 6a and approached background levels near the end of the recovery event (Figure 4-5). The broad, shallow slope TDS trend indicates a high degree of mixing (loss) during ASR at the Bradenton Site. Arsenic was detected at or slightly greater than background concentrations at ASR-1 during the beginning of both Cycle 6a

recovery events, which is similar to the trend shown during the Cycle Test 5 and 6 recovery events. Arsenic concentrations spiked up to 75 µg/L during recovery at ASR-1 indicating dissolution of pyrite during ASR.

Data Collected at SZMW-1 during Cycle 6a shows TDS increasing at a rate similar to the concentrations measured at ASR-1 (Figure 4-5). However, TDS reached stability at 990 to 1000 mg/L at SZMW-1 near the end of the recovery event. Arsenic concentrations increased above the MCL at SZMW-1 during Cycle 6a with the highest concentration of 20 µg/L detected at approximately 105 MG recovered. Arsenic concentrations were not detected at these levels At SZMW-1 during the Cycle Test 5 and 6 recharge events (Figure 4-5). This suggests reductive dissolution of arsenic occurs during ASR. Arsenic levels remained elevated after the end of Cycle 6a recovery (Figure 4-5). Based on this, it appears that arsenic released during the ASR recovery phase does not rapidly reabsorb to the matrix and, therefore, remains in a dissolved (mobile) state after ASR recovery.

PPT Results

To demonstrate the application of the method proposed by Haggerty (31) to ASR Cycle Tests, we apply this method to estimate DO decay rates in ASR. Using measured concentrations for C^*r (field DO values) and C^*tr (TDS lab data) collected during cycle tests conducted at the Bradenton ASR Site, we estimated DO decay rates as follows (see Figure 4-6):

- Cycle 1 decay rate (k) = 0.43/day
- Cycle 2 decay rate (k) = 0.43/day
- Cycle 5 decay rate (k) = 0.72/day
- Cycle 6 decay rate (k) = 0.41/day

The decay rates estimated for Cycles 1, 2 and 6 fall within a narrow range of 0.41/day to 0.43/day. However, the decay rate estimated for Cycle 5 was much higher at 0.72/day. This increase may be attributed to an increase in recharge water temperature during Cycle 5.

Prommer and Stuyfzand (36) measured the temperature dependency of reactions with dissolved oxygen during deep well injection at the Dizon Site in the Netherlands.

Bradenton Cycle Tests 1, 2, and 6 were completed during the winter months, while Cycle Test 5 was completed during late summer. The following average recharge water temperatures were measured during these tests:

- Cycle 1 = 24.34°C ± 0.59
- Cycle 2 = 22.18°C ± 0.57
- Cycle 5 = 30.12°C ± 0.48
- Cycle 6 = 22.60°C ± 3.50

The dependence of the rate coefficient (k) on temperature can be evaluated by applying the van't Hoff equation (37)

$$\ln \frac{k_{T_2}}{k_{T_1}} = \frac{\Delta H_r}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad (4.1)$$

where k_{T_2} and k_{T_1} are empirically derived rate coefficients, ΔH_r is the molar enthalpy of reaction, R is the universal gas constant, and T is temperature. Solving equation (4.1)

$$\Delta H_r = \frac{\ln \left(\frac{k_{T_2}}{k_{T_1}} \right) R}{\left(\frac{1}{T_1} - \frac{1}{T_2} \right)} \quad (4.2)$$

given Cycle 5 $k_{T_1} = 0.72/\text{day}$ at $T_1 = 30.12^\circ\text{C}$ (303.12 K) and Cycle 6 $k_{T_2} = 0.41/\text{day}$ at $T_2 = 22.18^\circ\text{C}$ (295.18 K) we calculate ΔH_r for this system to be 52.75 kJ/mol.

Assuming ΔH_r is constant (independent of temperature), given $k_{T_1} = 0.72/\text{day}$ at $T_1 = 30.1^\circ\text{C}$ (303.1 K) for Cycle 5, we now solve equation (4.2) for k_{T_2} for 25°C (298 K). As calculated, the decay rate for DO in this system at 25°C (298 K) is estimated to be 0.50/day.

The temperature dependence of the reaction rate can also be evaluated by plotting $\ln k$ versus $1/T$ (37). When plotted, the Bradenton Cycle Test data fit the linear equation $\ln k = -6279.6 K/T + 20.365$, with slope equal to $-\Delta H_r / R$ (see Figure 4-7). Therefore, ΔH_r for this system equals 52.21 kJ/mol. Plugging a value of $T = 25^\circ\text{C}$ (298K) into the equation of the line ($\ln k = -6279.6 K/T + 20.365$) given by the van't Hoff plot, we estimate k at 25°C to be 0.49/day, which is close to the value calculated above.

Breakthrough (recovery) curves can also be useful for characterizing ASR systems. Breakthrough curves for species of interest at the Bradenton ASR Site are shown in Figure 4-8. Sulfate, magnesium, calcium, and TDS are present in high concentrations in the native groundwater of the Bradenton Site as compared to the concentrations of these parameters in the injected water (Table 3-1). Therefore, the increase in the concentration of these parameters during recovery is driven by mixing between the native water and injected water. The broad slope of these curves indicates that the Bradenton ASR-1 system behaves as a well-mixed reactor. The curves for these parameters also show an early breakthrough, with an initial increase around 22% recovered ($V_{\text{ext}}/V_{\text{inj}} = 0.22$). This indicates that, while mixing or loss in this system is primarily governed by dispersion, the transport of these parameters is primarily driven by advection with little retardation in the matrix.

Arsenic is not present at high concentrations in the native water or injected water at the Bradenton Site. Therefore, the high concentration of arsenic in the recovered water is due to mobilization of arsenic from the aquifer matrix. In contrast to sulfate, magnesium, calcium and TDS, arsenic has a fairly steep breakthrough with an initial increase around 40% recovered ($V_{\text{ext}}/V_{\text{inj}} = 0.40$). This indicates that mobilized arsenic is retarded within the matrix, with respect to TDS.

An explanation of the spiky pattern of the breakthrough curve with multiple peaks shown in the recovery curves for arsenic and sulfide is that the aquifer consists of two zones having different hydraulic properties. Based on this, the two peaks of the curve represent two different rates of groundwater velocities. Alternatively, the multiple peaks may be an artifact of cycle testing where the build-out of the storage volume occurred in two successive but separate events. First, during Cycle 5, 50 MG was recharged with 10 MG recovered. After an 18-day storage period, Cycle 6 recharge was initiated, which included 120 MG recharged with 10 MG recovered. That is, the interim recovery of 10 MG increased mixing or loss due to dispersion separating the Cycle 5 front from the Cycle 6 front.

IGW Model Results

The 3-D IGW model was successfully calibrated to the TDS values measured at the storage zone monitoring well SZMW-1 during Cycle Test 5, 6, and 6a given the input parameters (i.e., aquifer properties) presented in Figure 3.7. The measured and simulated TDS curves at SZMW-1 for the Cycle Test 5 recharge event are very similar (Figure 3.9). However, there is a slight separation (lag) from the measured and simulated TDS values at SZMW-1 during the Cycle Test 5 and Cycle Test 6 recovery events. This is possibly due to an increase in dispersion (α) as, during recharge, the water moves past the monitoring well (SZMW-1) out to the lateral extent of the stored water.

The model derived TDS breakthrough curves for ASR-1 are similar to the simulated curves for SZMW-1 (Figure 4-10). However, the TDS values measured at ASR-1 during the Cycle Test 6a recovery event showed that breakthrough is delayed at ASR-1 with a slope steeper than that measured at SZMW-1 (Figures 4-9 and 4-10). This may be a result of the vertical gradients measured at ASR-1 during recharge and recovery that may be related to the well efficiency (i.e.,

loss) previously discussed. Dispersion also likely plays a significant, if not dominant, role in the shape and height of the breakthrough curves.

Vertical flux was simulated by calibrating the IGW model to the TDS values measured at monitoring well AFMW-1 during Cycle Tests 5-6a (Figure 4-11). While the simulated TDS values are slightly lower than the measured values, the model successfully accounts for the vertical movement (loss) of solute during recharge events by the ‘freshening’ of the intermediate aquifer.

The 3-D IGW model calibrated closely to the heads measured at SZMW-1 and AFMW-1 during Cycle 5 (Figure 4-12). However, there is a separation from the heads measured at ASR-1 and the simulated results. This is possibly due to well loss (i.e., bore-hole loss) at ASR-1 as the model does not account for well efficiency. Jones Edmunds (21) reported a well-loss coefficient of $2.6E-5$ ft/gpm², while pumping ASR-1 at 1274 gpm during the initial well tests. Jones Edmunds (21) calculated that during the initial tests 45 feet of the measured 127 feet of drawdown in this well was due to well loss.

Once calibrated, the 3-D IGW model was used to evaluate the TSV approach for managing recovery efficiency at the Bradenton ASR facility. Simulated results for four full-scale operational cycles (i.e., Cycle 5-6a, Cycle 7, Cycle 8, and Cycle 9) at the Bradenton ASR facility are presented in Figure 4-13. The peak TDS values predicated by the model, which represent the end of the recovery events, decreases from 980 mg/L during Cycle 5-6a to 841 mg/L during Cycle 9 (Figure 4-13). These results indicate that the TSV operational approach (i.e., recharging 150 MG and recovering 130 MG annually) can increase the recovery efficiency of the Bradenton ASR site.

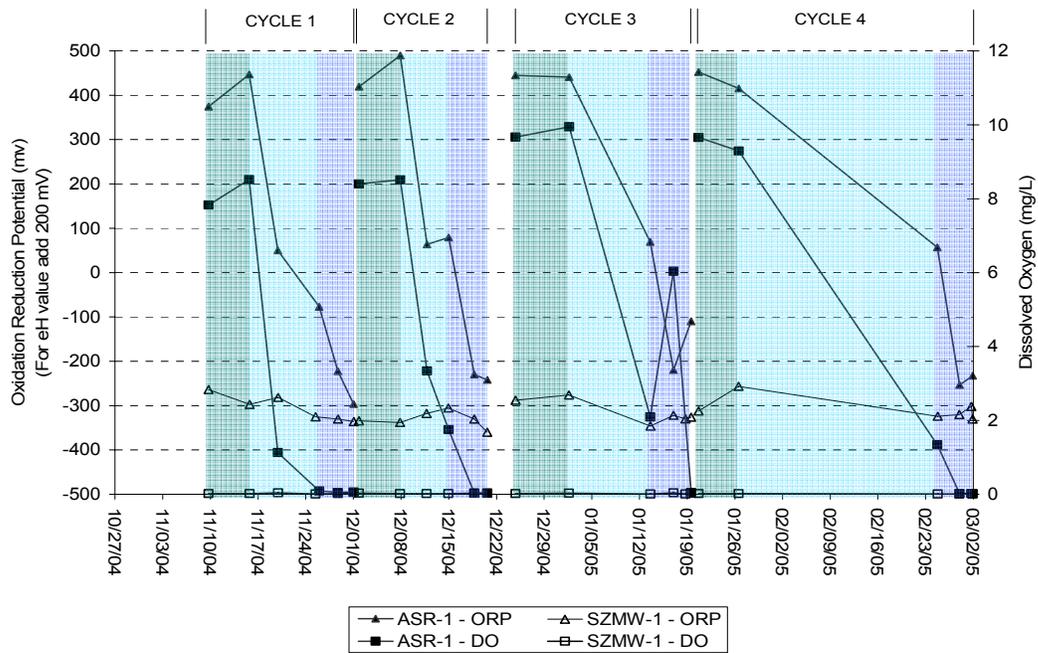


Figure 4-1. Field parameters measured during Cycle Tests 1-4

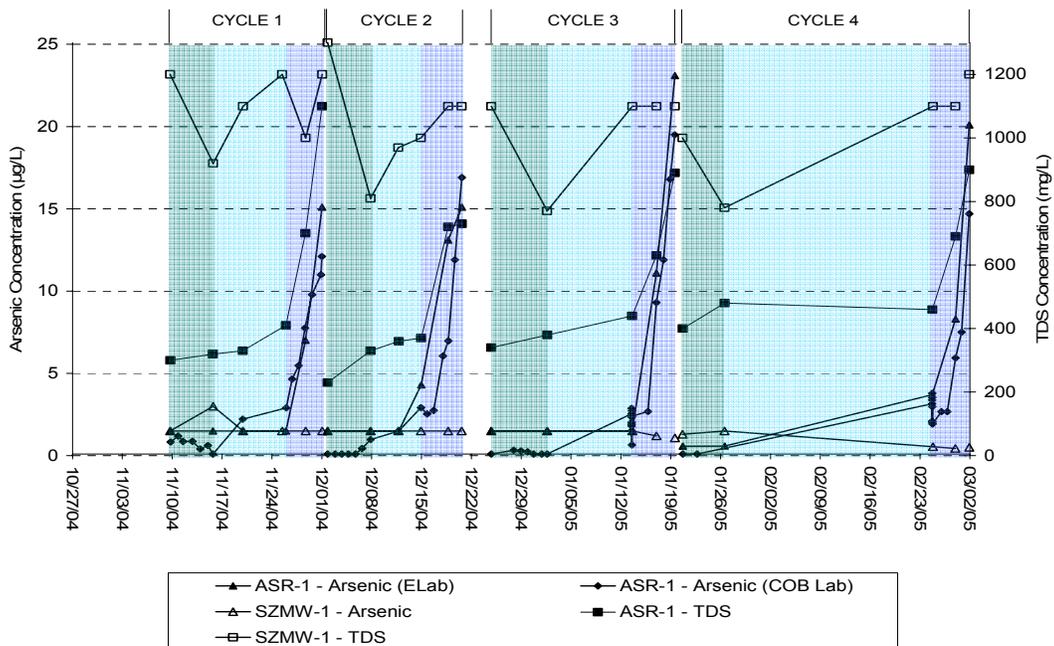


Figure 4-2. Analytical parameters reported for Cycle Tests 1-4

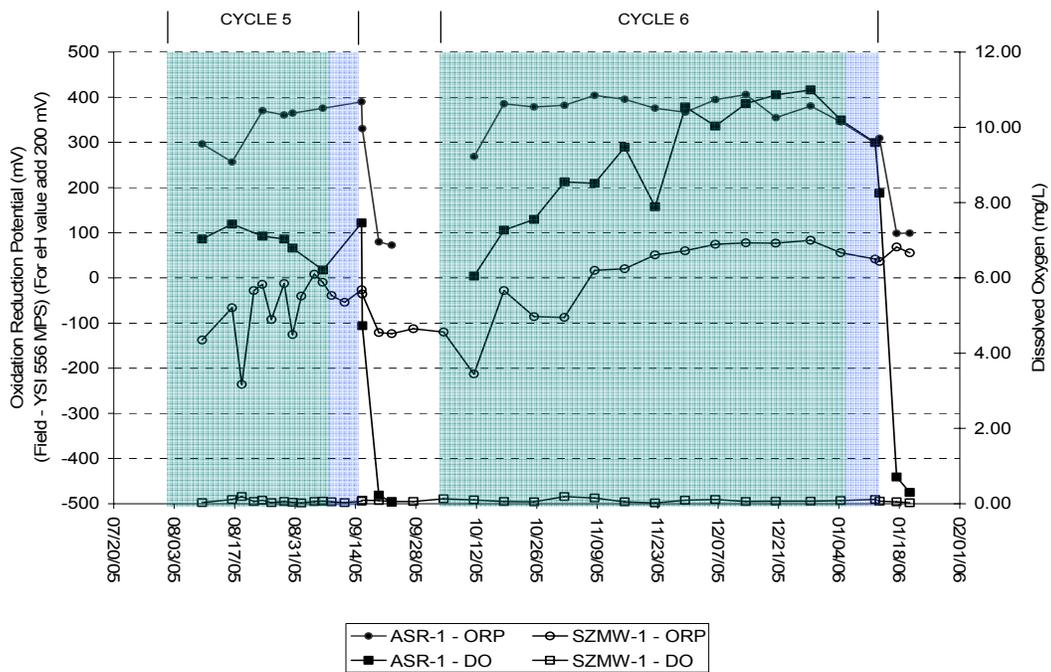


Figure 4-3. Field parameters measured during Cycle Tests 5 and 6

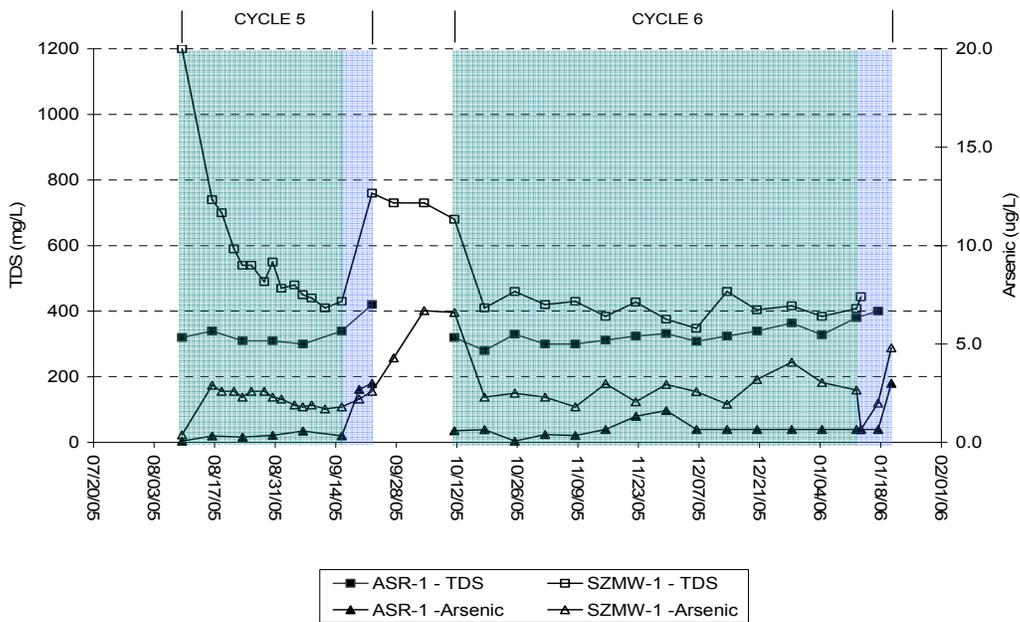


Figure 4-4. Analytical parameters reported for Cycle Tests 5 and 6

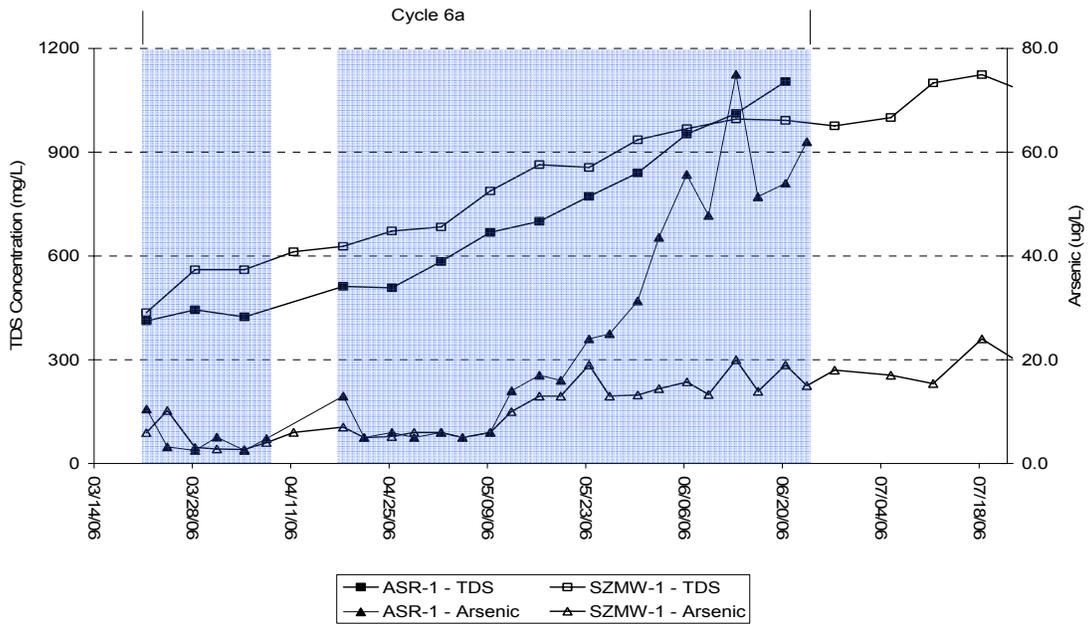


Figure 4-5. Analytical parameters reported for Cycle Test 6a

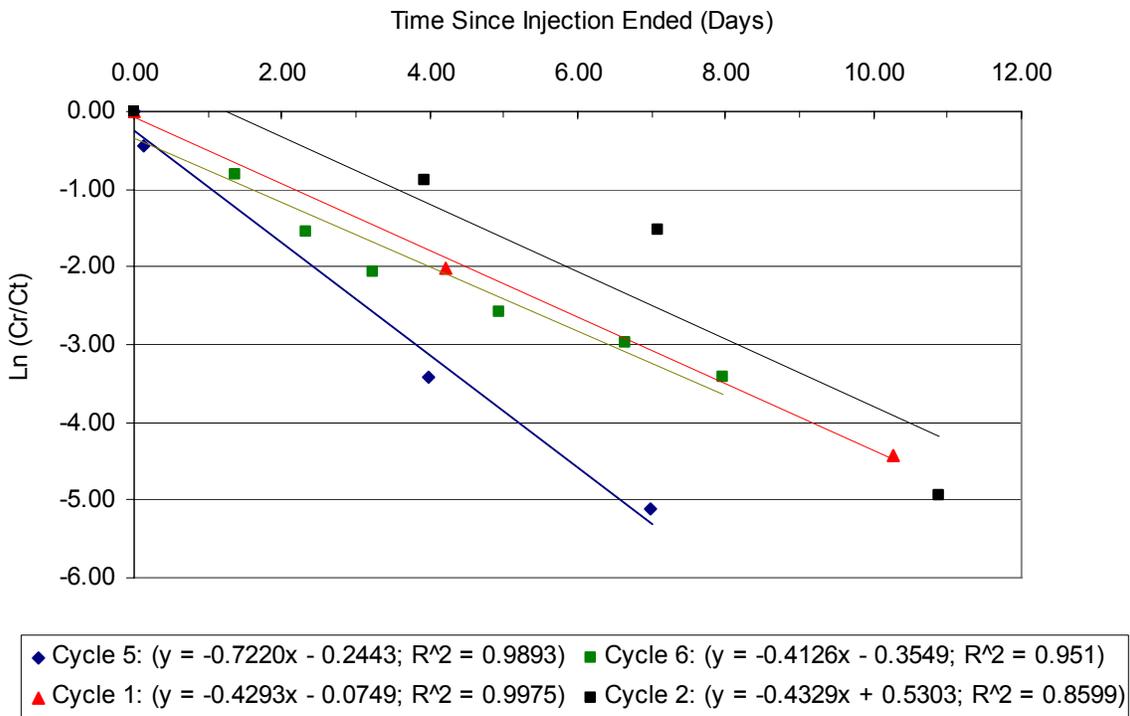


Figure 4-6. Plot of $\ln(C^*r(t)/C^*tr(t))$ versus t^* for Bradenton ASR Cycles Tests 1, 2, 5, and 6. Decay rates (k) are estimated as the negative of the slope of the line

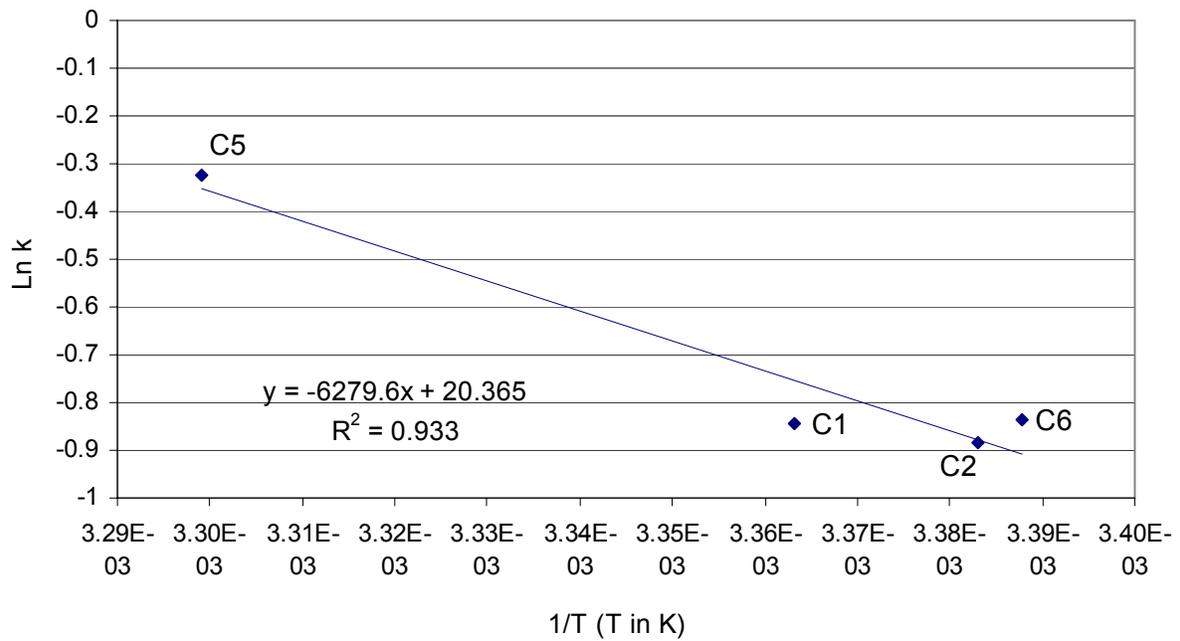


Figure 4-7. van't Hoff Plot of Bradenton ASR cycle test data

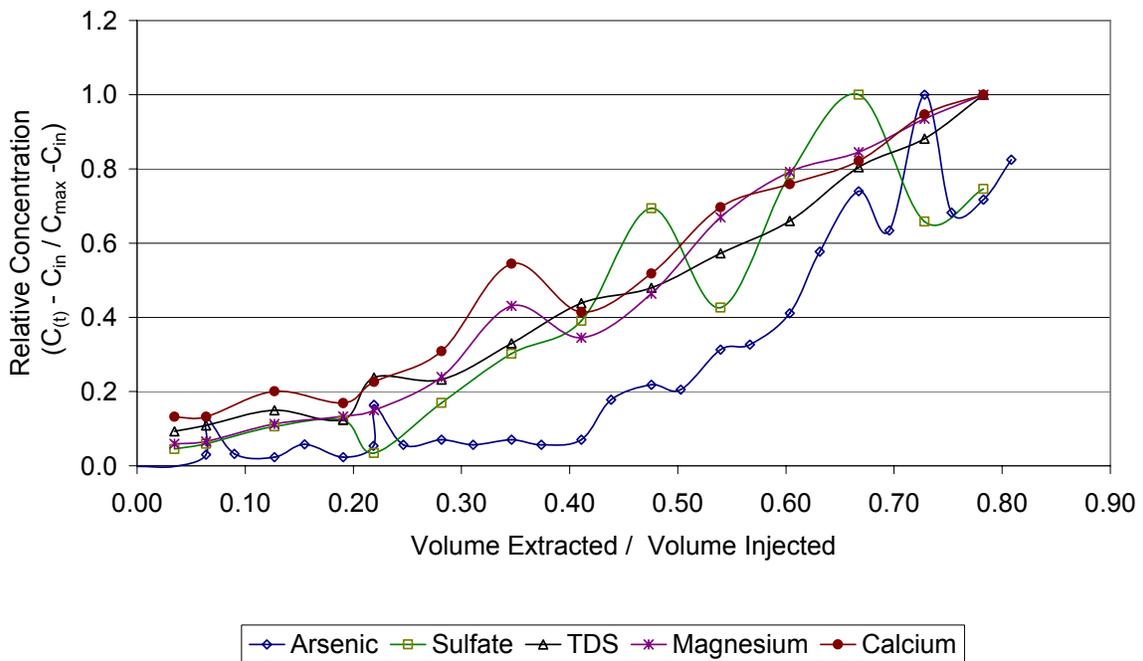


Figure 4-8. PPT breakthrough curve for Bradenton ASR. Parameter concentrations were measured during Cycle 6 and Cycle 6a recovery events

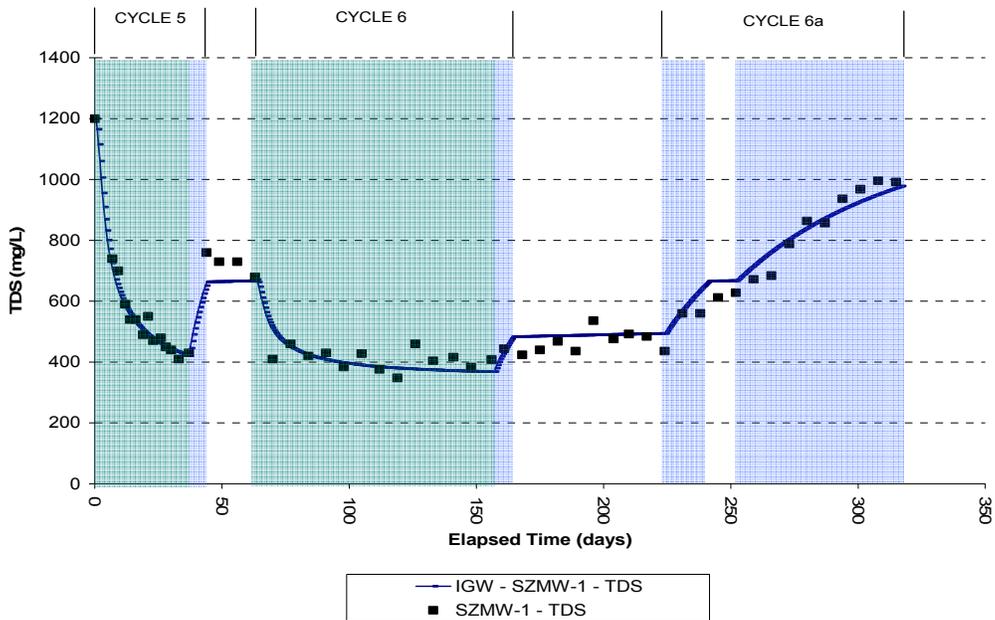


Figure 4-9. IGW model calibration results for TDS measured at SZMW-1 during Cycle Tests 5-6a

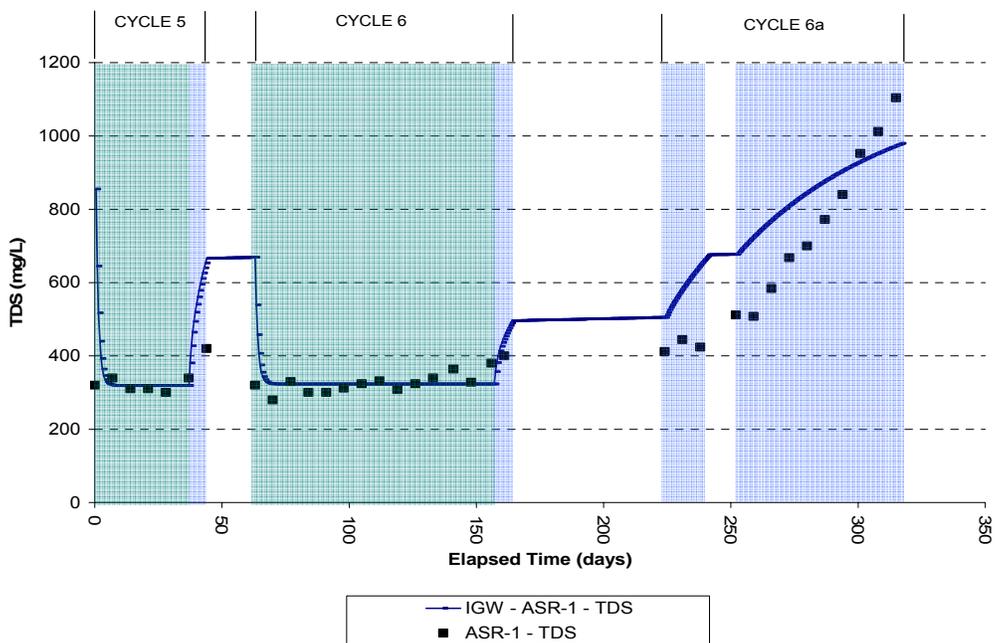


Figure 4-10. IGW model calibration results for TDS measured at ASR-1 during Cycle Tests 5-6a

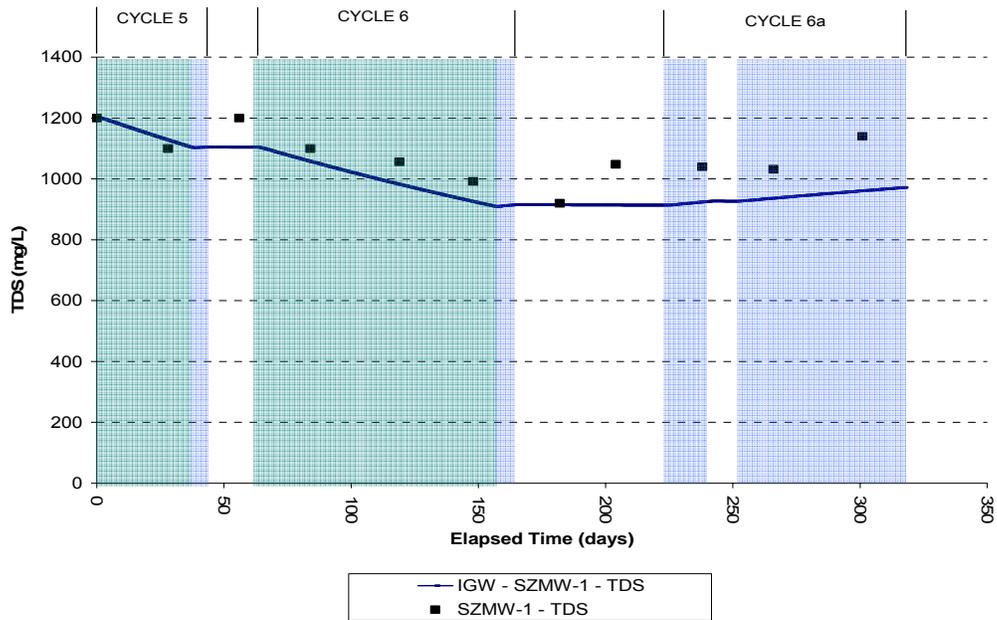


Figure 4-11. IGW model calibration results for TDS measured at AFMW-1 during Cycle Tests 5-6a

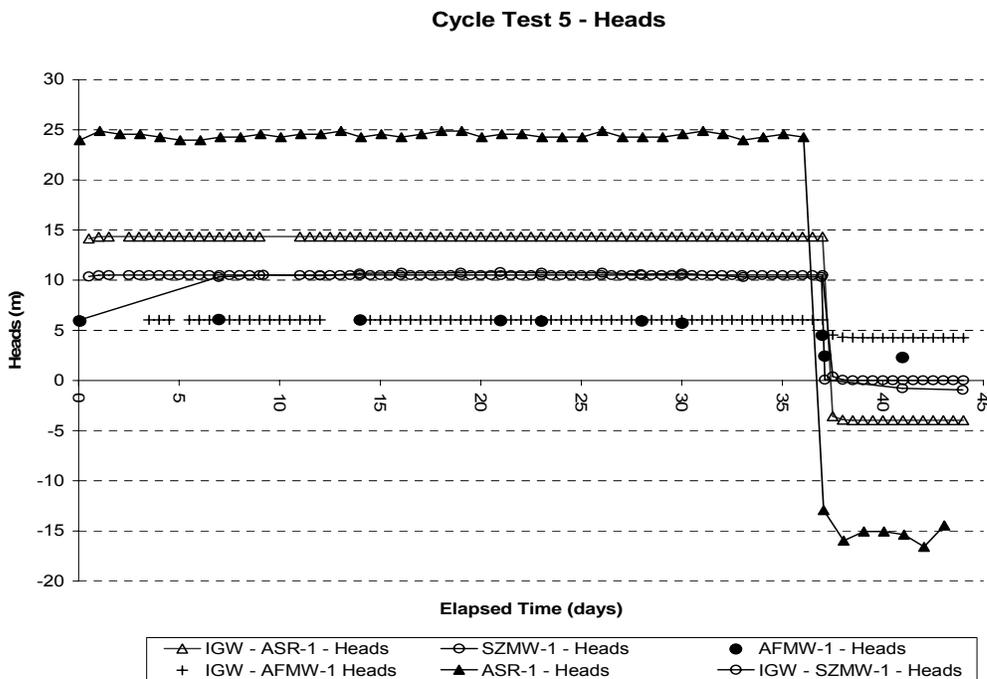


Figure 4-12. IGW model calibration results for water levels measured at SZMW-1, AFMW-1, and ASR-1 during Cycle Test 5

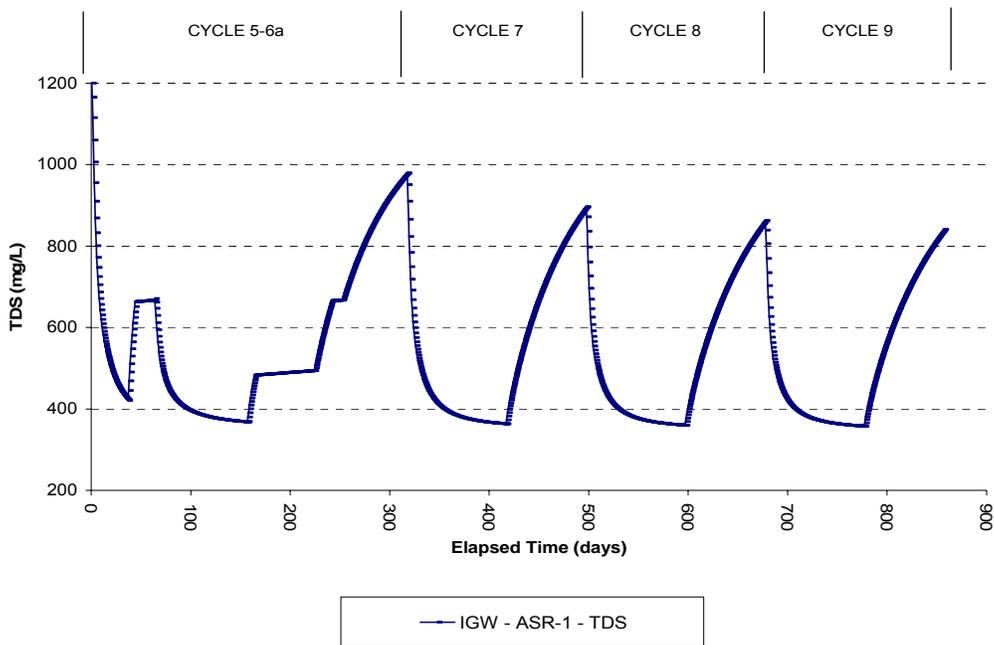


Figure 4-13. Simulated results for full-scale operations at the Bradenton ASR facility

Table 4-1. Bradenton ASR water quality summary

	Sample Location	SZMW-1 ^a	ASR-1 ^b
Field Parameters	ORP (mV)	-264	359 ± 32
	DO (mg/L)	0.02 [*]	8.44 ± 1.63
Laboratory Parameters	Chloride (mg/L)	38	30 ± 4
	Sulfate (mg/L)	640	154 ± 9
	Magnesium (mg/L)	N/A	8.8 ± 1.1
	TDS (mg/L)	1200	323 ± 23
	Arsenic (µg/L)	<2.8	<1.32

^aBackground (i.e., native) water quality results as measured on 11/9/2003

^bAverage recharge water quality concentrations measured during Cycle Test 5 and 6

^{*} measured value is at the resolution of the probe reported by the instrument manufacturer YSI.

CHAPTER 5 CONCLUSIONS

Results from the Bradenton ASR cycle tests and the PPT analytical techniques used in this research suggests a rapid near-borehole geochemical response occurs during ASR injection, with calculated First-order DO decay rates ranging from 0.41/day to 0.72/day. Other PPT analytical techniques, beyond those presented here, may also be applied to ASR. The ‘pump and drift’ PPT approach presented by Hall et al. (28) may be useful to quantify groundwater velocity(s) during ASR and calculate storage zone effective porosity, given adequate groundwater level monitoring for determining local hydraulic gradients. These methods may be adapted to help ASR operators demonstrate compliance with the current regulatory position on arsenic, help the practitioner optimize the ASR facility, and provide new methods for research scientists working to resolve these technical issues.

To quantify the near-borehole geochemical response that occurs during ASR, a series of small volume cycle tests, based on the PPT method, should be conducted before large-volume cycle testing. The scale of the tests should be based on site-specific conditions. However, a likely range for the volumes of the initial test should be 10 to 30 MG recharged with no storage. The initial test should be sized to fit the ASR system, including the number and location of monitoring wells, estimated porosity, storage interval thickness, and planned ASR operations (e.g., recharge and recovery rates). Recovery should be more than 100% of the injected volume to allow for complete breakthrough of reactants, products, and tracers. Subsequent cycles should be larger scale tests, in terms of recharge and recovery volumes, to focus on the geochemical response that occurs as water moves past storage zone monitoring well(s) and to estimate the recovery efficiency of the system.

While the results from Cycle Testing at the Bradenton Site correlate well with the conceptual model for arsenic mobilization during ASR presented here, uncertainty remains regarding the mechanisms controlling the fate and transport of arsenic. Additional research is needed to identify the potential mechanisms controlling arsenic transport during ASR.

Based on the results of the IGW Model, chemical gradient controls, such as the TSV approach, were found to be a reasonable means of managing the recovery efficiency of the Bradenton ASR facility. By allowing for an initial loss of recharge water, a relatively shallow chemical gradient can be established, increasing the recovery efficiency of subsequent cycles.

Arsenic was detected above the drinking water standard at the Bradenton ASR site in the ASR well (ASR-1) during Cycle Tests 1 through 4 and Cycle Test 6a and at the storage zone monitoring well (SZMW-1) during Cycle Test 6a. Therefore, the TSV approach does not adequately address the current regulatory position on arsenic in ASR, where compliance with the arsenic standard must be met at ‘all points’ and ‘all times’ in the aquifer. Given this, alternative methods must be considered. While beyond the scope of this research, such methods may be evaluated in future studies.

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BIOGRAPHICAL SKETCH

Stuart Bryan Norton was born on November 21, 1973 in Clinton, North Carolina. At the age of 16, Stuart and his family moved to Mandarin, a suburb of Jacksonville, Florida. While spending time with friends who owned a small environmental consulting firm, he developed a strong interest in environmental science and a deep respect for the environment. After graduating from Mandarin High School, he attended the University of Florida where he earned a Bachelor of Arts degree in geology in 1998.

In 1999 Stuart began his career with the consulting engineering firm Mactec, Inc. At Mactec, Stuart worked as a field geologist completing numerous rapid site assessments, implementing remedial actions, and performing post-closure assessments at industrial, petroleum, and dry-cleaner sites in Florida. In 2001 Stuart began working with the Florida-based consulting engineering firm Jones, Edmunds & Associates, Inc. During his tenure with Jones Edmunds & Associates, Inc., Stuart has been working towards his Masters of Science degree in environmental engineering sciences. His recent work experience includes both managing ASR and other water supply projects and working as the project technical lead.

Upon completion of his M.S. program, Stuart will begin working toward a Ph.D. in environmental engineering sciences at the University of Florida. His Ph.D. research focus will include geochemistry and groundwater hydrology with a specific emphasis on arsenic in ASR. The Ph.D. program will be an extension of the research presented in this thesis.

Stuart married Gladys Enid Santana in 2004, with whom Stuart spends much of his free time. The couple regularly pursues leisure interests including traveling, fishing, canoeing, tail-gating at University of Florida Gator football home games, and numerous other outdoor activities.