

Analysis of the controls on arsenic distribution in the upper Floridan aquifer during ASR

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ABSTRACT

Authigenic pyrite has been determined to occur in the Upper Floridan aquifer (UFA) and, during aquifer storage recovery (ASR) operations, arsenic released from pyrite occurs at low concentrations in the storage zone during cycle tests. However, arsenic has been detected in recovery wells at significantly greater concentrations than observed in monitoring wells in the storage zone, located approximately 200 to 350 ft from the ASR well. Several ASR studies have concluded that varying geochemical conditions during injection, storage, and recovery create conditions that result in the dissolution of pyrite and arsenopyrite and the increase of arsenic in solution. Bacteria-mediated reactions at or near the well have also been identified as a cause.

This research will investigate the theory that fracture networks are a potentially significant control on the migration and distribution of arsenic during ASR operations by evaluating fluid flow, chemical reactions, and transport characteristics of authigenic arsenic in the Upper Floridan aquifer (UFA) during ASR operations. Fractures potentially present across the site were identified through the use of geophysical well logs that were run in monitoring and ASR wells during their construction. Numerical three-dimensional models were then constructed that included the representation of these fractures. The geochemical reaction (PHREEQC) and transport (MT3DMS) models coupled to the numerical flow model (MODFLOW 2000), PHT3D- 2003, was utilized to test various scenarios. The scenarios consisted of representations of the flow field with equivalent continuum and discontinuum fracture network models, and variations of the geochemical conditions. These results indicate that fracture flow significantly controls the distribution of all solutes affected by the flow system associated with this ASR system. Due to the relatively low TDS concentrations observed in a vertical section of the aquifer, density stratification and buoyancy effects do not appear to affect solute migration at the site. The occurrence and general distribution of arsenic generally agrees with observed data.

INTRODUCTION

Authigenic pyrite has been determined to occur in the Upper Floridan aquifer (UFA) and, during aquifer storage recovery (ASR) operations, arsenic released from pyrite occurs at low concentrations in the storage zone and during cycle tests. Several ASR studies have concluded that varying geochemical conditions during injection, storage, and recovery create conditions that result in the dissolution of pyrite and the increase of arsenic in solution. Investigations of this problem have generally relied on the interpretation of observed data and the theoretical analysis of the geochemical environments through the use of various geochemical models.

The Peace River ASR facility located in Desoto County, Florida was selected for this investigation. An extensive record of hydraulic, geochemical, and operating conditions was available for this site that has been in operation since approximately 1985. The effects of the varying geochemical conditions were investigated with the numerical model PHT3D.

Background

Arsenic has been reported to occur in the UFA at concentrations ranging from 0.01 to 54.1 milligrams per kilogram (mg/Kg), with an average concentration of 3.5 mg/kg and exceeding 1000 mg/kg in framboidal pyrite that occurs in the UFA (Price and Pichler; 2005). The occurrence of arsenic, as detected in injection/recovery wells and monitoring wells in the UFA during ASR operations, has been reported to vary with low concentrations, i.e., less than 3 micrograms per liter ($\mu\text{g/l}$) detected in the storage zone during cycle tests and high concentrations in the recovered groundwater (greater than 10 $\mu\text{g/l}$). Arsenic-free water is injected into the aquifer, which initially exhibits reducing conditions resulting in pyrite stability and the immobility of arsenic. With the injection of recharge water that is typically oxic, with dissolved oxygen concentrations greater than 2 mg/l, pyrite becomes unstable and arsenic is mobilized and detected in the monitor wells at low concentrations. However, upon recovery the extracted groundwater often contains moderate to high levels (10 to 130 $\mu\text{g/l}$) of arsenic (Jones and Pichler, 2007) that exceed the Federal and State MCL of 10 $\mu\text{g/L}$. With increasing number of cycles, the arsenic concentrations detected in the ASR wells significantly decrease. Arsenic also occurs in ASR systems operating in the Netherlands and Australia. The scenario described above consisting of varying oxygen concentrations and reduction-oxidation (redox) conditions is documented in several ASR systems that are in operation in the UFA. The Peace River facility primarily operates an ASR system in the Suwannee Limestone aquifer that occurs between approximately 580 and 920 feet below land surface (ft bls). Well logs from a previous study indicate that the major flow zone contributing between 60% and 80% of the groundwater from the production zone appears to occur below 820 ft bls. Another significant flow zone occurs near the top of the interval between 580 and 770 ft bls.

METHODS

This research focused on the use of the three-dimensional numerical model, PHT3D (Prommer, 2005), which is a MODFLOW-based three-dimensional program that couples PHREEQC-2 and MT3DMS, and is capable of simulating pyrite-arsenic reactions (under a variety of conditions) and transport in the UFA to determine the factors and processes that control flow, transport, and distribution of arsenic in the UFA during ASR operations. The models constructed for this study included a scaled-down preliminary model (510 x 250 x 10 m) used to determine an adequate domain for large-scale models and to test several geochemical factors that control the solubility and distribution of arsenic. In addition, continuum and discontinuum models (1000 x 500 x 100 m) representative of the entire aquifer were subsequently constructed. All of the models were constructed to represent half of the horizontal flow system in order to reduce simulation times and modeling requirements. Although the ASR facility consists of numerous recharge-recovery wells, only one well was generally used for these simulations. The models were bound by general head and constant concentration boundaries on three sides. The general head boundaries were used to allow the boundaries to adjust to the model stresses and constrain the dimensions of the models, without affecting the flow system. The constant concentration boundaries represented all geochemical parameters that were activated for the

models, with the exception of pyrite and arsenopyrite. The continuum models were uniformly discretized throughout with 10 x 10 m cells in order to reduce numerical dispersion associated with the dynamic flow field. An average hydraulic conductivity (27 m/day) was assigned to the single layer continuum model that was determined from the results of previous aquifer pumping tests that were conducted. The discontinuum or heterogeneous model was divided into 23 layers whose contacts were determined from geophysical logs. The presence and continuity of the fractures and fracture zones among the boreholes were most evident from the caliper and sonic porosity logs. The fractures are assumed to exist throughout the model domain and their distributions throughout the model were determined by extrapolation with the contouring program Surfer. The hydraulic conductivity distribution used for the heterogeneous model was determined by assigning an average hydraulic conductivity to the matrix of the UFA, determined from a detailed study conducted from a continuous core from a Regional Observation Monitoring Program (ROMP) well in the general vicinity of the site. The average hydraulic conductivity of the matrix determined from this study was approximately 0.5 m/day. With this value, the thickness of the aquifer not occupied by fractures, and the aquifer transmissivity, the hydraulic conductivity of the fractures and fracture zones was estimated to be approximately 61 m/day.

The 1500-day pumping schedule was discretized into 50 monthly stress periods that represented four periods or cycles of recharge, storage, and recovery. The background and injectate parameter concentrations used in the model were generally averaged over a multi-year period. Monthly temperature variations of the injected water were included in the models, as temperature has been shown to affect the solubility of pyrite. Pyrite and arsenopyrite concentrations were included as initial immobile phase constituents at concentrations ranging from 0.0075 to 0.2 moles per liter (bulk). The dissolution of arsenopyrite was linked to pyrite dissolution by setting the dissolution parameter PARM 1 to 0.001 and 0.01, which results in the dissolution of 1 and 10 micromoles of arsenopyrite per each millimole of pyrite, respectively. The concentrations of pyrite and arsenopyrite estimated to occur in the aquifer were determined by using these minerals as calibration parameters.

RESULTS

The model simulation hydraulic head results from the continuum and discontinuum models were brought into reasonable agreement with observed data by adjusting the storage coefficient. This value was increased compared to the theoretical value used in a previous model to obtain an operating permit for the facility. The results from the reaction-transport model were also in general agreement with the observed distribution of arsenic after adjusting the concentrations of pyrite in the aquifer and sulfate in the injected water. In general, the simulated oxygen concentrations were highest during recharge periods (Figure 1) and, in contrast, arsenic concentrations in the vicinity of the injection well during recharge periods were significantly less than during the recovery periods (Figure 2). The arsenate specie was the dominant form of arsenic observed in the aquifer during the recovery periods. The average sulfate concentration of 0.00201 moles per liter (193 mg/L) was reduced to 0.00175 moles per liter, in order to reduce the concentration of oxygen in the immediate vicinity of the injection well to that of the injected water. The dissolved arsenic concentrations generally ranged from 1×10^{-7} to 1×10^{-6} moles per liter in the simulations. The models with maximum arsenic concentration of approximately 1×10^{-7} moles per liter were generally unaffected by pyrite concentrations greater than 0.01 moles per liter, when the rate of arsenopyrite to pyrite dissolution was set at 0.001. When the pyrite to arsenopyrite dissolution rate was set to 0.1,

the simulated arsenic concentrations in the aquifer were brought into general agreement with the observed concentrations.

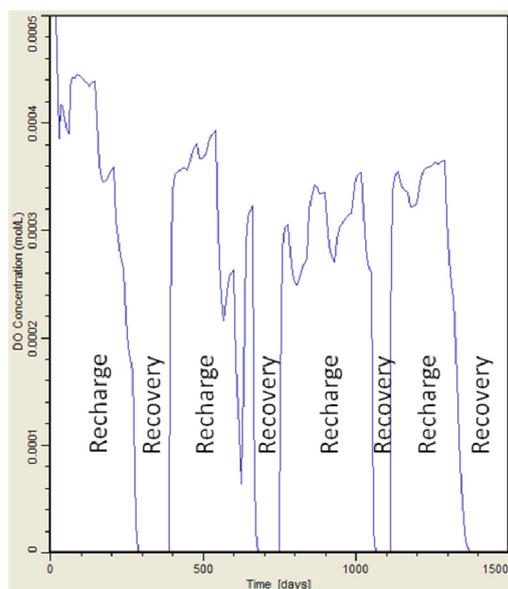


Figure 1. Simulated dissolved oxygen at ASR well S-19 during four ASR cycles.

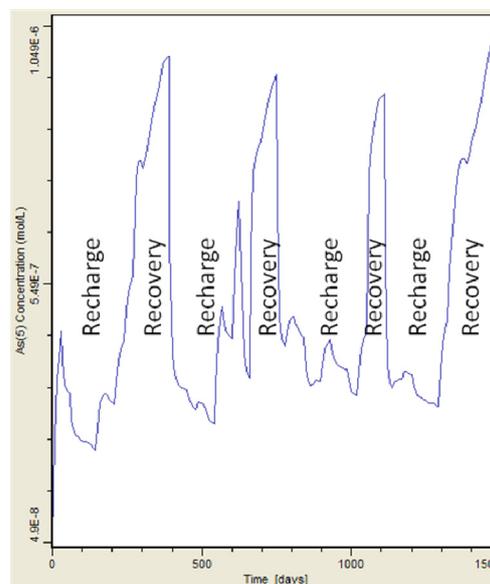


Figure 2. Simulated dissolved arsenic As(5) at ASR well S-19 during four cycles.

DISCUSSION AND CONCLUSIONS

The discontinuum model exhibited similar trends to the continuum model with respect to the geochemical parameters; however, all dissolved species penetrated further into the aquifer in the fractures and fracture zones. Fracture orientations also appear to affect solute distributions. The fractures and fracture zones that transport the greatest mass of dissolved arsenic tend to exhibit the greatest control on the water quality of the intersecting monitor wells. These modeling results indicate that the dissolution of pyrite and arsenopyrite in the UFA by the introduction of oxygenated water through recharge wells and the occurrence of elevated arsenic concentrations can be expected to occur in ASR systems operating under similar aquifer conditions. This study is part of an ongoing research project.

REFERENCES

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