The Relationship Between Pyrite Stability and Arsenic Mobility During Aquifer Storage and Recovery in Southwest Central Florida

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Abstract

A common problem with ASR systems that store surface water is the occurrence of elevated concentrations of arsenic in recovered water. Analyses of recovered water from more than 15 cycle tests from three ASR facilities in the study area indicated arsenic levels that frequently exceeded 10 ug/l and were sometimes much higher. The elevated arsenic concentrations are cause for concern in light of the fact that the Environmental Protection Agency recently reduced the drinking water standard for arsenic from 50 ug/l to 10 ug/l. Although arsenic can be removed relatively easily from the recovered water during the final treatment phase, the mobilization of arsenic in the aquifer at levels that exceed the drinking water standard is problematic under current Florida Department of Environmental Protection (FDEP) rules. Mineralogical investigations of cores from 19 wells open to the Suwannee Limestone, the preferred storage zone for ASR systems, have shown that the highest concentrations of arsenic are associated with framboidal pyrite. In this investigation, geochemical modeling was used to examine the stability of pyrite in limestone during simulated injections of oxygenated surface water. The goal was to determine whether redox conditions would be altered to the degree that pyrite would become unstable, thereby releasing arsenic into the formation water. The modeling simulation injected surface water into the same wells the Suwannee Limestone cores were obtained from. Injection water was titrated into the formation water in a series of steps with the ratio of injection water to formation water increasing at each step. At the end of each step, the program provided a listing of the concentration of aqueous species, the mixing ratio, and the pH. Reaction paths were constructed from these data and plotted on pyrite stability diagrams. The unmixed formation water in the wells plotted within the pyrite stability field indicating that redox conditions were sufficiently reducing to allow for pyrite stability. Since arsenic is immobilized in the pyrite, it follows that arsenic concentrations in formation water would be low. Analysis of arsenic in water samples from the wells indicated concentrations of < 0.1 ug/l. As the ratio of injection water to formation water increased, redox conditions became less reducing, pyrite became unstable and dissolved. At this point, arsenic would be released into the formation water. The simulation also showed that the ratio of injection water to formation water necessary to cause pyrite to become unstable was highly variable depending on the chemistry of the formation water.

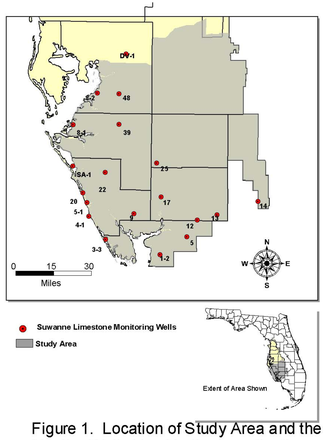

Figure 1. Location of Study Area and the Monitor Wells Used in the Investigation.

Methods

Water quality data used in this investigation for geochemical characterization and modeling were obtained from samples collected from 19 existing monitor wells in the study areas open entirely to the Suwannee Limestone. Water quality data from the 19 wells were plotted on a Piper Diagram (Figure 2) and three wells that represented the end members of the major water types in the study area were selected for modeling.

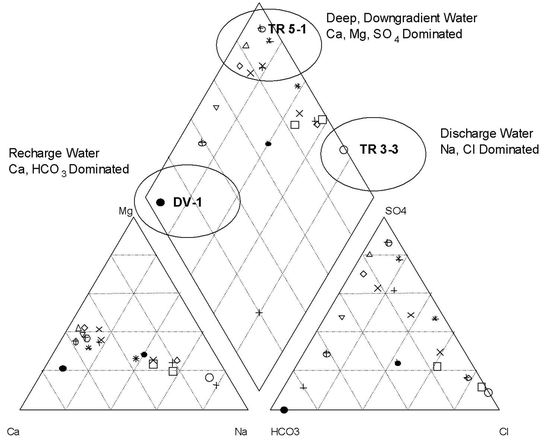

Figure 2. Piper Diagram Showing the Chemistry of the Formation Water in the Monitor Wells Used in the Investigation. The Three Wells Chosen for the Simulation Represent the End Members of the Water Types in the Study Area. The End Member Wells were Chosen for the Simulation so that the Effect of Mixing Different Formation Water Quality Types with Injection Water on Pyrite Stability Could Be Determined.

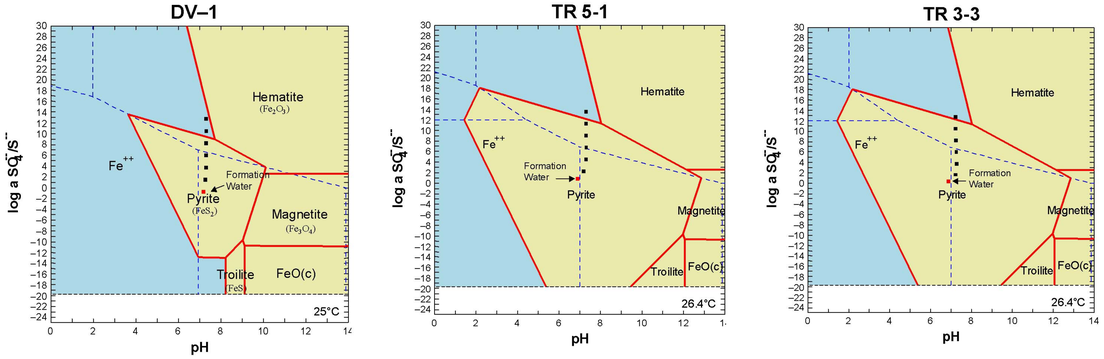

Figure 3. Reaction Paths Representing the Chemical Evolution of Formation Water Quality, in Three Wells in the Study Area, as it is Mixed with Increasingly Larger Volumes of Injection Water. The Reaction Paths are Plotted on a Stability Diagram of the Iron-Sulfur System to Highlight Pyrite Stability. At the Point Where the Reaction Path Exits the Pyrite Stability Field, Pyrite Dissolves and it is Assumed that Arsenic is Released into the Formation Water.

Results and Conclusions

The red square on the plots in Figure 3 represents the unmixed formation water. The formation water plots within the pyrite stability field for all wells, which indicates that redox conditions in the Suwannee Limestone allow for pyrite stability. Since arsenic is immobilized in the pyrite, the arsenic concentration in formation water should be very low. This was verified by the analysis of arsenic in water samples from the wells, which indicated total arsenic concentrations of < 0.1 ug/l. At injection water to formation water ratios of approximately $1X10^{7}$ to 1, $1X10^{12}$ to 1, and $1X10^{12}$ to 1, in DV-1, TR 5-1, and TR 3-3 respectively, pyrite becomes unstable and dissolves and it is assumed that arsenic is released into the formation water. The ratio at which pyrite becomes unstable in DV-1 is 100,000 times less than the ratio for TR 5-1 and TR 3-3. The reason for the difference is the chemistry of the formation water. DV-1 is located in a recharge area where sulfate concentrations are very low compared to those of the downgradient wells, TR 5-1 and TR 3-3. The sulfate concentration in DV-1 is 0.14 mg/l whereas sulfate concentrations in TR 5-1 and 3-3 are 1,520 mg/l and 1,195 mg/l respectively. Repeated runs of the model that varied the sulfate concentration in formation water showed that size of the pyrite stability field is directly proportional to the sulfate concentration. It follows then that when oxygenated surface water is injected into DV-1, redox conditions favoring pyrite stability are overcome at a much lower ratio of injection water to formation water than for the two down-gradient wells.

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