

Final Report: Experimental and numerical modeling analysis of arsenic-sulfide precipitation in groundwater environments

Matthew F. Kirk, Laura J. Crossey
University of New Mexico Department of Earth and Planetary Sciences

Introduction

Stimulating microbial sulfate reduction in contaminated aquifers may offer a simple means of removing arsenic, a hazardous contaminant, from groundwater (Kirk et al., 2004). Sulfate reduction produces sulfide, which can react with arsenic and remove it from solution as an insoluble sulfide mineral. Several sulfide minerals can precipitate arsenic including iron sulfide minerals such as mackinawite (FeS) (Wolthers et al., 2005) and pyrite (FeS) (Lowers et al., 2007) as well as pure arsenic sulfide minerals such as orpiment (As₂S₃) (Newman et al., 1997) and realgar (AsS) (O'day et al., 2004).

However, there are several details about arsenic-sulfide precipitation that we do not understand. In particular, we do not clearly understand how effective any of these minerals can be at removing arsenic from groundwater. Answering this and related questions will tell us whether stimulating microbial sulfate reduction can be an effective strategy for arsenic remediation. Before this approach is field tested, therefore, these questions need to be resolved. We hypothesized that (1) arsenic removal by sulfide minerals is primarily controlled by the balance between the activities of iron and sulfate reducing microorganisms, (2) that iron sulfide minerals are more effective than pure arsenic sulfide minerals at removing arsenic, and (3) that mackinawite initiates arsenic removal by iron sulfides in groundwater environments.

We tested these hypotheses by performing four semi-continuous flow bioreactor experiments containing iron and sulfate-reducing microbial activity (Fe/SO₄²⁻), iron-reducing activity (Fe only), sulfate-reducing activity (SO₄²⁻ only), and no microbial activity (sterile) (Figure 1) using media containing solutes at environmentally relevant levels. These scenarios allow us to observe the behavior of arsenic in a range of conditions present in reducing groundwater, including those that could facilitate formation of iron sulfide and pure arsenic sulfide minerals. We can also observe the behavior of arsenic during reductive dissolution of iron minerals in these reactors and abiotic controls on arsenic.

Results and Discussion

We have not completed all of the analyses associated with our reactors nor numerical modeling. The results we summarize here are tentative. Final results will be forthcoming soon. Nonetheless, the actual experiment is complete. We ran the experiment from January 31, 2007 to November 20, 2007. We briefly summarize the results from each reactor as follows:

Fe/SO₄²⁻

Populations of arsenic, iron, and sulfate reducing microorganisms were active in the reactor throughout the experiment. Mackinawite formed in the reactor, which limited the accumulation of ferrous iron in the solution and prevented accumulation of sulfide. The mackinawite that formed, however, does not appear to have been very effective at

removing arsenic from solution. Arsenic accumulated to high levels as goethite, an important adsorption surface for arsenic in the reactor, was dissolved.

Although thermodynamically favorable, we would not expect to observe natural pyrite formation in this reactor because it is very slow under natural conditions (Benning et al., 2000). However, there are techniques to stimulate its formation (Benning et al., 2000; Wilkins et al., 1996). We successfully stimulated formation of pyrite in this reactor near the end of the experiment, though we have not yet assessed how effectively it removed arsenic from the reactor solution.

Fe only

Populations of arsenic, iron, and methanogenic microorganisms were active in the reactor throughout the experiment. Iron and methane accumulated to high levels. Arsenic also accumulated in solution as goethite dissolved.

SO₄ only

Populations of arsenic and sulfate reducing microorganisms were active in the reactor throughout the experiment. Sulfide concentrations were high in this reactor throughout the experiment. Arsenic content was also high throughout the experiment, approximately at the level of the inlet solution, because no goethite was present to keep its concentration initially low. We observed no or very limited formation of pure arsenic sulfide minerals in the reactor, likely due to formation of thioarsenic species which inhibit precipitation of these minerals (Bostick et al., 2005).

Sterile

No microbial populations were active in the experiment. No ferrous iron or sulfide concentrations were detected throughout the experiment. Arsenic concentrations were limited by adsorption onto goethite in the reactor throughout the experiment.

The composition of the solutions in each reactor evolved largely as expected based upon field relationships, previous experiments, and preliminary numerical models. The results of our numerical modeling, therefore, will be useful for interpreting the geochemistry of aquifers contaminated with arsenic. We were hopeful, however, that mackinawite would provide an effective sink for arsenic. Instead, our incomplete results suggest that pyrite or some other arsenic-sulfide solid phase is responsible for removing arsenic from groundwater where arsenic content is thought to be limited by sulfate reduction.

References

- Benning, L.G., Wilkin, R.T., and Barnes, H.L., 2000, Reaction pathways in the Fe-S system below 100 degrees C: *Chemical Geology*, v. 167, p. 25-51.
- Bostick, B.C., Fendorf, S., and Brown, G.E., 2005, In situ analysis of thioarsenite complexes in neutral to alkaline arsenic sulphide solutions: *Mineralogical Magazine*, v. 69, p. 781-795.
- Kirk, M.F., Holm, T.R., Park, J., Jin, Q.S., Sanford, R.A., Fouke, B.W., and Bethke, C.M., 2004, Bacterial sulfate reduction limits natural arsenic contamination in groundwater: *Geology*, v. 32, p. 953-956.
- Lowers, H., Breit, G.N., Foster, A.L., Whitney, J., Yount, J., Uddin, M.N., and Muneem, A.A., 2007, Arsenic incorporation into authigenic pyrite, Bengal Basin sediment, Bangladesh: *Geochimica et Cosmochimica Acta*, v. 71, p. 2699-2717.
- Newman, D.K., Beveridge, T.J., and Morel, F.M.M., 1997, Precipitation of arsenic trisulfide by *Desulfotomaculum auripigmentum*: *Applied and Environmental Microbiology*, v. 63, p. 2022-2028.
- O'day, P.A., Vlassopoulos, D., Root, R., and Rivera, N., 2004, The influence of sulfur and iron on dissolved arsenic concentrations in the shallow subsurface under changing redox conditions: *Proceedings of the National Academy of Sciences of the United States of America*, v. 101, p. 13703-13708.
- Wilkins, D.W., Schlottmann, J.L., and Ferree, D.M., 1996, *Chemical Analyses of Ground-Water Samples from the Rio Grande Valley in the vicinity of Albuquerque, New Mexico, October 1993 through January 1994*, Open-File Report 95-773: Albuquerque, U.S. Geological Survey, p. 27.
- Wolthers, M., Charlet, L., Van der Weijden, C.H., Van der Linde, P.R., and Rickard, D., 2005, Arsenic mobility in the ambient sulfidic environment: Sorption of arsenic(V) and arsenic(III) onto disordered mackinawite: *Geochimica Et Cosmochimica Acta*, v. 69, p. 3483-3492.

Figure

Figure 1.



As/Fe/SO₄²⁻ Fe only SO₄²⁻ only sterile