

Arsenic mineral kinetics: Arsenopyrite oxidation

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Data on the dissolution rates of arsenic minerals are needed to understand and model the contamination of natural waters by arsenic, and to predict the success of *in situ* remediation strategies based upon the forced precipitation of these minerals. A batch flow reactor experiment design and the initial rate method have been used to determine the effect of dissolved O₂, pH, dissolved Fe³⁺ and temperature on the kinetics of oxidation of natural arsenopyrite.

In the absence of initial dissolved Fe³⁺ arsenopyrite oxidizes non-stoichiometrically over the pH range 2.0 to 4.5, with As and S being released into solution less completely than Fe. The rate of release of dissolved Fe is thus used to define the rate of mineral decomposition, but this will overestimate the rate of release of dissolved arsenic. Oxidized arsenopyrite grains may therefore exhibit a build-up of undissolved As and S on their surfaces in low-pH, Fe-poor solutions.

In the presence of initial dissolved Fe³⁺, Fe and As are released stoichiometrically and either product can be used to define the rate of mineral decomposition. The rate of oxidation by dissolved O₂ is strongly dependent on the initial concentration of dissolved Fe³⁺, and the latter is a much more effective oxidant of the mineral at low pH.

The derived rate law for the oxidation of arsenopyrite by dissolved O₂ has the form:

$$R = -k [\text{O}_2]^{0.40} [\text{H}^+]^{0.24}$$

The activation energy is 14.5 kJ/mol. These parameters are much different than those of pyrite, indicating that pyrite oxidation rates should not be used as proxies for this and other As-bearing sulfides. Experiments are currently being conducted to determine the rates of arsenopyrite and arsenical pyrite oxidation by dissolved ferric iron and nitrate.

Vadose zone remediation by *in-situ* gaseous reduction

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Vadose zone remediation and development of *in situ* barriers is an important aspect of environmental management. Immobilization of selected contaminants by reduction with diluted hydrogen sulphide gas mixtures is a potentially useful approach and also can produce a permeable reactive barrier through reduction of native sediment iron oxide phases.

Recent work directed towards development of the *In Situ* Gaseous Reduction approach has focused on collection of laboratory data related to treatment and reoxidation processes. During gaseous treatment, most of the hydrogen sulfide component is consumed in soil and results in the generation of FeS. This constituent is the active agent that maintains reducing conditions in the barrier needed for contaminant immobilization. Experimental work has been completed that provides information related to scaling the treatment process to the field. Another aspect of current testing activities involves determining the reducing capacity of treated soil during reoxidation. This data is needed to assess the effectiveness and lifetime of a vadose zone barrier.

Initial testing activities have also been completed that indicate Cr(VI) and Tc(VII) can be immobilized in sediments that have been reduced by gaseous treatment. Testing is now being conducted to understand the potential for immobilization of U(VI) by the gaseous treatment approach. Evaluation of this application requires consideration of the role of carbonate complexation with uranium in the aqueous phase and the adsorption of uranium to solid media in addition to reduction and precipitation processes.