

ELECTROCHEMICAL INVESTIGATION OF ARSENIC REDOX PROCESSES ON PYRITE

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The specific Eh-pH conditions and mechanism(s) for reduction of arsenite, As(III), by pyrite is incompletely understood. A fundamental question is what role the pyrite surface plays in the reduction process. We used electrochemical methods to evaluate the reduction of As(III) under controlled redox conditions. As(III) reduction to elemental As(0) occurs on the pyrite surface under suboxic-reducing conditions and is promoted at low pH. Remarkably, As(III) reduction on pyrite occurs at similar potentials to those for reduction on platinum metal suggesting a similar mechanism/kinetics for these surfaces. The onset for As(III) reduction at $\text{pH} \leq 3.5$ coincides with the potential for hydrogen electroadsorption on pyrite, $E \sim +0.1$ V (vs. RHE). Batch reactions show that As(III) is reduced on pyrite at the Eh-pH predicted by the electrochemical study. X-ray photoelectron spectroscopy reveals that, at $\text{pH} \leq 3.5$, a significant fraction of the surface arsenic (30-60%) has an oxidation state consistent with As(0). Here, we propose a mechanism whereby atomic hydrogen that forms on ferric (hydr)oxide surface layers promotes As(III) reduction at low Eh and pH. Insights provided by this study will have implications for understanding the controls on dissolved As(III) concentrations in suboxic-anoxic environments.