

Novel Adsorbent-Reactants for Treatment of Ash and Scrubber Pond Effluents

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Objectives: The overall goal of this project will be to evaluate the ability of novel adsorbent/reactants to remove arsenic, selenium and mercury from ash and scrubber pond effluents while producing stable residuals for ultimate disposal. The adsorbent/reactants to be evaluated include micro- and nano-sized iron sulfides (FeS) and disulfides (FeS₂). These compounds have the ability to remove arsenic, selenium and mercury from solution as well as react with them to produce solid phases that are stable when disposed in landfills, so that removal of these compounds from wastewaters will not result in contamination of soils and groundwaters. Methods for reliably and economically producing these materials will be developed.

Accomplishments: Experiments have been conducted to describe removal of arsenic (As(III) and As(V)) and mercury (Hg) by pyrite. Initial kinetic experiments were conducted to determine appropriate times for conducting removal experiments. Removal experiments investigated the effects of initial concentration of target compound, pH, and sulfate concentration on the extent of removal and loading onto the pyrite (amount target compound removed/amount pyrite). These experiments were conducted in a way that is similar to those used to characterize adsorption equilibrium. However, it is recognized that surface reactions between target contaminants and the pyrite surface are probably continuing at the end of the removal experiments. Therefore, true chemical equilibrium is not being achieved.

Experiments on arsenic removal by pyrite showed that removal of As(V) from solution was faster than removal of As(III). This indicates that As(III) and As(V) are interacting differently with the pyrite surface. Mass transport limitations to removal kinetics should be similar for both As(III) and As(V), so any difference in removal kinetics must be attributed to differences in rates of reaction with the surface. The extent of removal of both As(III) and As(V) were more accurately described by the Langmuir adsorption model than the Freundlich adsorption model. This supports the hypothesis that all surface sites on pyrite have similar affinities for arsenic species and that there is a maximum removal capacity. Removal of As(III) was observed to increase as pH increased across the range investigated (pH 7 – pH 10). However, an optimum pH in the range between pH 8 and pH 9 was observed for removal of As(V). Sulfate had little effect on removal of As(III) or As(V) at the concentrations investigated (0, 1, 10 mM). There were small decreases in the amount of arsenic removed at the highest

concentration of sulfate and the effect was more apparent with As(V) than with As(III). This indicates that removal of arsenic by pyrite in ash pond waters should not be substantially affected by sulfate concentrations found there.

Kinetics of removal of mercury were very rapid at lower ratios of mercury/pyrite. Concentrations of mercury in solution were below detection limits within 10 minutes. The mercury/pyrite ratio needed to be increased by a factor of 25 to obtain measurable concentrations over a wide time period. This behavior supports the hypothesis that external transport limitations to removal kinetics are minimal and that removal kinetics are controlled by surface reactions that become important at higher loadings of mercury on the pyrite surface. Pyrite was observed to remove much more mercury than arsenic. Maximum loadings of arsenic were in the range of 100 – 300 $\mu\text{mol/g}$, while loadings of mercury typically exceeded 6000 $\mu\text{mol/g}$ and in some cases exceeded 20,000 $\mu\text{mol/g}$. These loading mean that the mass of mercury removed exceeded the mass of pyrite. The pH of the solution did not appear to have a major effect on the extent of removal. However, there was a substantial amount of variability within the results of removal experiments at different pH. Exceptionally high removals of mercury could be the result of surface reactions that are initiated in some systems more rapidly than in others. The more rapid initiation of surface reactions could be caused by differences in surface characteristics of some pyrite particles. If experiments were conducted over longer time periods that would allow for initiation of surface reactions in all system, then these differences would tend to decrease. Sulfate was observed to have little effect on removal of mercury by pyrite over the concentration range that was investigated (0 – 10 mM). The rapid removal kinetics, the high loadings and the lack of inhibitory effects of sulfate support application of pyrite to removal of mercury from ash and scrubber pond waters.

Analysis of pyrite and iron sulfide by TEM showed that they have particle sizes of 100 – 1000 nm and < 100 nm, respectively. Results of XRD analysis confirmed that pyrite crystals were being produced by the synthesis method employed and that the form of iron sulfide being produced was Mackinawite.

Future Work: Experiments will continue to evaluate removal of selenium, mercury and arsenic by pyrite and iron sulfide (FeS), with the focus on iron sulfide. Then the focus will shift to evaluating longer term reactions of these compounds on the surface of the adsorbent-reactants.

Publications: No publications have yet resulted from this work. Two graduate students have been supported by this project – Mr. Dong Suk Han and Ms Eun-Jung Kim.