

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

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**Objectives:** The overall goal of this project is 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 are synthesized iron sulfide (FeS) and pyrite (FeS<sub>2</sub>). These compounds have the ability to remove arsenic, selenium and mercury from solution as well as to react with them to produce solid phases that are stable when disposed in landfills. Therefore, removal of these compounds from wastewaters will be less likely to result in contamination of soils and groundwaters.

**Accomplishments:** Methods for synthesizing pyrite and iron sulfide were developed and analysis 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.

Experiments have been conducted to describe removal of arsenic (As(III) and As(V)), selenium (Se(IV) and Se(VI)) and mercury (Hg) by iron sulfide (FeS) and pyrite (FeS<sub>2</sub>). Initial kinetic experiments were conducted to determine appropriate times for conducting removal experiments. Batch removal experiments were conducted to evaluate the effects of concentration of target compound, pH and concentration of sulfate on removals. These experiments were conducted in a way that is similar to that for systems in which adsorption equilibrium is believed to occur. The concentrations of target compound removed to the surface of the solid were calculated and expressed as the amount removed per mass of solid. The relationship of the solid-phase concentration and the concentration of the target compound in the liquid phase was evaluated. In some cases, equations were used to model this relationship and equation parameters were determined by least squares regressions. The models that were used to correlate data were models that are often used to correlate data obtained in equilibrium adsorption experiments (Langmuir, Freundlich, BET). However, it is not believed that the experiments conducted were at equilibrium, nor is it believed that adsorption was the only important process affecting the behavior of the target compounds. Results of these experiments indicate that the target compounds are initially removed by a mechanism that can be considered to be adsorption, but then they react with the surfaces of the solids. The surface reactions may not be at equilibrium when the experiment is completed.

Behavior of the target compounds varied depending on which adsorbent-reactant was used.

Mercury was the target compound that was removed most strongly. The amounts of mercury removed were sometimes greater than the amount of adsorbent-reactant. Release of iron was small, so simple replacement of mercury for iron would not explain observed results. Surface reactions are probably forming mixed solid phases containing mercury, iron, sulfur and an anion (hydroxide, chloride, sulfate) removed from solution to balance the charge of mercury. The anion may be removed from solution along with mercury in the form of a mercury-anion complex. Sulfate was observed to have small effects on removal of mercury by both adsorbent-reactants. Removal of both oxidation states of arsenic by pyrite was observed to be affected by sulfate to small degree. An optimum pH for removal of As(V) was observed in the range between pH 8 to pH 9, while removal of As(III) continued to increase as pH increased. Removal of arsenic by iron sulfide showed more evidence of surface reactions. Removal of As(V) was improved at lower pH, while pH had little effect on removal of As(III). Sulfate showed only small effects on removal of arsenic by iron sulfide. Removal of selenium in both oxidation states showed some evidence of surface reaction on pyrite and iron sulfide. Sulfate showed moderate to small effects on removal of both forms of selenium.

The batch removal experiments indicate that arsenic, selenium and mercury can be removed by pyrite and iron sulfide. Generally low levels of inhibition by sulfate indicate that the process could be applied to waters high in sulfate, such as found in ash and scrubber ponds. In many cases, the target compounds appear to be removed by pyrite or iron sulfide and then react on the surface. This is shown by slow removal kinetics and increased removal at higher concentrations. These reactions are expected to produce lower solubility solid phases that will result in residuals that can be disposed with less likelihood of release.

**Future Work:** Experiments will be conducted to further evaluate surface reactions of selenium, mercury and arsenic on pyrite and iron sulfide by investigating the leachability of the target compounds.

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