Nanoparticles in the Environment: A Study of Surface Reactivity of Pyrite and Arsenopyrite

Anthony S. Breitbach
Chemistry, Clarke College

NNIN REU Site: Michigan Nanofabrication Facility, University of Michigan
NNIN REU Principal Investigator: Professor Udo Becker, Department of Geological Sciences, University of Michigan
NNIN REU Mentor: Devon Renock, Department of Geological Sciences, University of Michigan
Contact: tbreits@yahoo.com, ubecker@umich.edu, drenock@umich.edu

Abstract:

The surface reactivities of pyrite (FeS$_2$) and arsenopyrite (FeAsS) were compared by analyzing how surface characteristics influence the deposition of gold. FeAsS and FeS$_2$ samples were immersed in 100 ppm Au(III) solution for 24 hours. Scanning electron microscopy (SEM) coupled with energy dispersive spectroscopy (EDS) showed that FeAsS had a higher surface coverage of gold after equal exposure time. Surface analysis using x-ray photoelectron spectroscopy (XPS) indicated that gold was reductively adsorbed as Au(0), and that arsenic was oxidized during the reaction in the case of FeAsS. Atomic force microscopy (AFM) was used to image the growth of gold nanoparticles on the FeS$_2$ and FeAsS surfaces as a function of time. The AFM results show preferential growth on surface defects and a higher rate of growth on the FeAsS within the first hour of deposition. In conclusion, the surface of FeAsS was found to better facilitate the reductive adsorption of gold.

Introduction:

Mineral surface reactivity is ultimately dependent on three surface properties: chemical composition, atomic structure (which determines which atoms are exposed to the surface), and microtopography. The purpose of this project was to compare the surface reactivity of FeS$_2$ and FeAsS by analyzing how surface characteristics, such as surface chemistry and topography, influence the deposition of gold.

Gold ore deposits may form in low temperature aqueous environments by reductive adsorption on FeS$_2$ and FeAsS. FeAsS deposits usually contain more gold than FeS$_2$ deposits, and the gold content of arsenian pyrites generally increases with arsenic content. Much of this gold is present as “invisible” gold (particles less than 0.1 µm) [1]. A proposed mechanism for sulfide adsorption involves a redox reaction where gold reduction on As-rich areas is coupled with oxidation at nearby S-rich areas [2].

Understanding the role of Fe, As, S, and Au in these experiments has implications for the recovery of gold from ore deposits, the control of acid mine drainage, and understanding the release of As into the environment.

Gold Adsorption Experiment:

Cleaved FeS$_2$ and FeAsS samples were placed in 100 ppm KAuCl$_4$/1M NaCl for 24 hrs. The FeAsS surface became darker and its solution less yellow, while there was no observable change with the FeS$_2$ sample.

SEM/EDS Analysis:

The exposed samples were analyzed using SEM/EDS. The SEM images in Figure 1 show that FeAsS had a higher surface coverage after 24 hour exposure time compared to FeS$_2$. EDS showed that the adsorbed material contained gold, and the lack of a chlorine peak in the spectra suggested that gold was deposited in a reduced form.

XPS Analysis:

Flat polished samples with a surface roughness of <0.1 µm were prepared for XPS analysis. XPS is a technique that is able to determine the surface composition and oxidation states of surface components. Here XPS was used to determine how Au(III) is adsorbed on FeS$_2$ and FeAsS by comparing to Au(0) and Au(III) standards. In Figure 2, the FeS$_2$ and FeAsS Au4f peaks are located near the same binding energy as the Au(0) standard, thus Au(III) was reduced on the surface during adsorption.
In addition, the FeS$_2$ peaks exhibit shoulders that extend into the region of the Au(III) standard. This suggests that there may have been adsorption of Au(III) or partially reduced Au(I) on the FeS$_2$ surface. No shoulders on the FeAsS peaks indicate that FeAsS facilitates reductive adsorption to a greater extent compared to FeS$_2$.

In Figure 3, the As3d peaks of the FeAsS standard and the FeAsS sample are compared to determine if As was oxidized and thus facilitating the reduction of gold. The difference in the peak intensities between the standard and the exposed sample indicates a greater proportion of As at a higher oxidation state after exposure. Future studies will determine whether or not the oxidation of As is coupled to the reduction of Au on the FeAsS surface.

AFM Analysis:

Tapping mode AFM was used to image the gold growth on the polished FeS$_2$ and FeAsS surfaces as a function of time. At the beginning of the experiment, both the FeS$_2$ and the FeAsS surfaces appeared relatively smooth. After 10 minutes, adsorbed material was evident on the surface of both samples, but to a greater extent on FeAsS. By 60 minutes, the FeAsS surface appeared completely covered while the FeS$_2$ surface appeared more sparsely covered.

AFM was also used to see if there was any preferential adsorption due to surface topology. Shown in Figure 4 are the AFM height images of the FeS$_2$ and FeAsS surfaces after exposure to the Au(III) solution for 10 minutes. Both samples displayed preferential adsorption on surface defects as indicated, but to a greater extent on the FeAsS sample.

Conclusions:

It was determined that Au(III) adsorbs to a greater extent on the surface of FeAsS compared to FeS$_2$. Au(III) is reduced to Au(0) on the surface of FeAsS, while the FeS$_2$ surface exhibited signs of Au(III), Au(0), and partially reduced Au(I). The oxidation of As during Au(III) adsorption on FeAsS is one possible explanation for the greater extent of reduction. It was also found that surface defects help assist Au(III) adsorption. In conclusion, the surface of FeAsS was found to better facilitate the reductive adsorption of gold.

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References: