Early-stage phase transformation and growth of iron oxyhydroxides during neutralization of simulated acid mine drainage

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Metal and coal mines produce iron-rich sulfuric acid solutions that contain a broad range of toxic elements [1]. These solutions, referred to as acid mine drainage (AMD), adversely affect environmental quality. When AMD mixes with neutral water bodies, such as in rivers or during wetland treatment, interacts with rock surfaces, or reacts with lime during remediation, neutralization occurs. As a result, ferric iron (Fe3+) hydrolyzes and precipitates as Fe oxyhydroxide nanoparticles, such as ferrihydrite and schwertmannite. However, the formation pathways of these nanoparticles are relatively unknown largely due to their rapid formation rates and low abundances of initially-formed species. In this study, we used in situ time-resolved synchrotron radiation X-ray diffraction (XRD), quick-scanning extended X-ray absorption fine structure (QEXAFS) and UV-Vis spectroscopic techniques to study the products formed initially (2 < t < 60 minutes) when ferric iron sulfate solutions ([Fe3+] = 0.2 M) are partially neutralized ([HCO3-]/[Fe3+] < 3) by addition of NaHCO3.

When [HCO3-]/[Fe3+] = 0.6 (initial pH ~ 2.2), the only particles formed were ferrihydrite-like clusters that were stable throughout the duration of the experiment. When [HCO3-]/[Fe3+] = 1 (initial pH ~ 2.5), the ferrihydrite-like molecular clusters formed initially but mostly disappeared and were replaced by schwertmannite. Schwertmannite and larger ferrihydrite particles formed immediately when [HCO3-]/[Fe3+] = 2 (initial pH ~ 2.7), but the ferrihydrite particles completely disappeared and were replaced by schwertmannite. The schwertmannite particle size increased with reaction time, and extensive particle aggregation occurred.

The ferrihydrite-like cluster is very intriguing and its structure deserves further characterization. The data are consistent with Fe13+ having Baker-Figgis δ-keggin structure, i.e., the motif in the ferrihydrite structure proposed by Michel et al. [2]. The existence of the cluster may result from sulfate binding on its surface, preventing the cluster from growing into larger ferrihydrite particles.

In conclusion, the results suggest that particular molecular clusters and small nanoparticles may be important, early-formed components of natural acidic solutions.


XPS study of bioleached arsenopyrite by Acidithiobacillus ferrooxidans

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Arsenopyrite (FeAsS) is a commonly discarded sulfide mineral in mining wastes. The arsenic release from it due to oxidation can cause serious environment contamination in mines. It has been well proved previously that microorganisms can remarkably accelerate the oxidation of arsenopyrite. However, the detailed oxidation mechanism is still unclear. This study on surface chemistry of bioleached arsenopyrite may cast insights into it.

In our experiments, the arsenopyrite obtained from a W-Sn deposit and a strain of Acidithiobacillus ferrooxidans isolated from the acid mine drainage in Tongling, eastern China, were used. The sterilized 9K culture with an adjusted Fe2+ concentration of 16 mM was poured into 6 flasks and then divided into two groups. Three flasks were inoculated with Acidithiobacillus ferrooxidans and the other three were only abiotic. Arsenopyrite particles were dropped into flasks simultaneously, and then extracted after 4 days, 7 days and 10 days, respectively. The reacted samples were freeze-dried in vacuum and ready for SEM observation and XPS analysis.

Several types of secondary mineral, such as elemental sulfur and scorodite, can be observed on the surface of 4 days-biooxidized arsenopyrite. However, native sulfur diminished gradually as bio-oxidation continuing and finally disappeared on the 10 days-biooxidized surface. The XPS depth profiles show that the altered layer of biooxidized arsenopyrite is much thicker than that of abiotic case. In addition, the contents of Fe(III), As(V) and sulfate in surface layer of biooxidized arsenopyrite are all higher than those of abiotically oxidized sample. The oxidation progress varies with the elements in both experimental systems. In the biotic system, the oxidized sequence is in the order of As, S, and then Fe, whereas in the abiotic system Fe is preferentially oxidized than As and S. In the depth profile of altered layer of each systems, a transition depth can be identified, where the contents of As, S and Fe change sharply. This depth of bio-oxidized arsenopyrite is about 450 nm, and that of abiotically oxidized one is around 30 nm. The change of Fe speciation in depth profile reveals that A. ferrooxidans initially breaks Fe(II)-AsS to form Fe(III)-AsS and a small quantity of Fe(III)-OH, and at a very late stage a trace fraction transform into Fe(III)-SO4.

Acknowledgement: We appreciate the support from the National Science Foundation of China (40930742 and 10979018).