Abstract No.: Vair0385

Speciation of chromium and intracellular sulfur in the transformation of chromate by bacteria

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Beamline: X19A

Introduction and Approach: Many industries release chromium during their operations (e.g, the metal-finishing industry, petroleum refining, leather tanning, and iron- and steel-production). In its hexavalent form chromium (Cr(VI)) is highly toxic, and recognized as a major metal contaminant in the environment. An important pathway for Cr(VI) transformation in the environment involves its reduction to the trivalent form (Cr(III)) by bacteria. Under aerobic conditions, the bacterial reduction is likely to occur in the cytoplasm after an active uptake of the chromate ion by the bacteria. In general, biochemical reductions occur through mediation with reductase enzymes which are mainly distributed in the cytoplasm. Several reductases have active sulfhydryl sites which directly take part in the redox process. However, neither the chromate redox mechanism nor the nature of chromate reductases are well understood. To gain more insights about this pathway, we investigated the reduction of Cr(VI) by a highly resistant *Bacillus* sp. We used XANES spectroscopy performed at the X-19A beamline to understand the changes in chromium and sulfur speciation associated with bacterial transformation.

Results: Our results show that hexavalent chromium is reduced to trivalent form by the bacteria. While a large fraction of the reduced chromium is associated with the bacterial mass, it is not clear whether it is present internally in the cytoplasm or externally on the outer surface of the bacteria. We did not detect any intermediate oxidation state species of chromium between 6 and 3, suggesting either they are transient or not generated in the reduction. The bacteria grown in media without chromium showed mainly the presence of reduced sulfur corresponding to a combination of sulfidic and sulfhydryl sulfur. However, a significant fraction of sulfur was present in highly oxidized forms corresponding to sulfonate sulfur in bacteria grown in the presence of chromate. These results show that intracellular sulfur plays a direct role in the bacterial transformation of chromate in the environment.

Acknowledgment: This research was supported by the NABIR Program, Office of Biological and Environmental Research, U.S. Department of Energy of Energy under Contract DE-AC02-98CH10886.