

## Transformation products from inorganic ligand promoted oxidation/dissolution of silver nanoparticles

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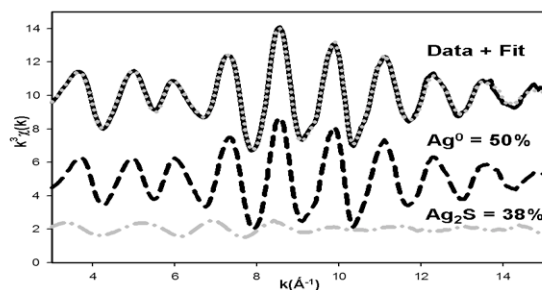
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Silver nanomaterials are being used in a range of commercial products, thus increasing their potential for introduction into the environment. The lifetime and persistence of silver metal nanoparticles will be determined in part from their oxidation and dissolution rates and in part from the types of phase transformations that may occur in the presence of organic and inorganic ligands. In this study manufactured silver nanoparticles, both coated and uncoated, were exposed to several environmentally relevant aqueous inorganic ligands ( $S^{2-}$ ,  $CN^-$ ,  $Br^-$ ,  $Cl^-$ , and  $I^-$ ) and dissolved oxygen to determine their effects on the rate of silver oxidation/dissolution. Synchrotron-based X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (XAFS) spectroscopy and TEM were used to elucidate the amount of zero-valent silver that remained as the particles were oxidized by the inorganic ligands and to determine the speciation of the products formed. These results have implications for the persistence, transport, bioavailability, and fate of silver nanoparticles in the environment.



**Figure 1:** EXAFS linear combination fit of Ag(0) nanoparticles aged in 5mM  $Na_2S$  solution for 24 hours with the species and percent contribution of individual model compound spectra listed. The original particle contained ~90% Ag(0) and 10%  $Ag_2O$ . The resulting material does not contain significant amounts of  $Ag_2O$ .

## The immobilisation of toxic heavy metals by biofilms in mine drainage groundwater outflow regions

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The biooxidation of metal sulfides in mine wastes, e.g. tailings, leads to the generation of acidic solutions possessing toxic heavy metals [1]. Bioremediation of heavy metal contamination is an active area of research because it represents a green technology with the potential for high efficiency at a low cost. There is a wide range of active and passive biogeochemical processes that bacteria can employ to immobilise toxic heavy metals from solution, all of which can occur within biofilms. Biofilms, containing aerobic heterotrophic and dissimilatory sulfate reducing bacteria, from 14 locations in an active uranium mine site were examined for their capacity to immobilise metals from solution. Most (eight) of the samples had pH values ranging from 5 to 8. However, five of them were below pH 5 and one has pH value of 12.35, which did not support sulfate reducing bacteria.

Using ICP-AES, the concentration of metals in groundwater samples, and in 2% nitric acid extracts from biofilms collected at the groundwater outflow sites revealed that the biofilms possessed higher concentrations of metals than the groundwater 'feeding' them. For example, one of the biofilms was found to contain 33 times higher concentration of Pb as well as 19 times higher Ni, 135 times higher As, 588 times higher Cd and 436 times higher Hg, respectively. Examination of the biofilms using transmission and scanning electron microscopy has demonstrated the presence of secondary minerals entrapped within exopolymer materials.

A laboratory-based column treatment system, employing dissimilatory sulfate reducing bacteria is being evaluated to determine the maximum bioremediation efficiency versus this field system and the ability of sulfate reducing bacteria to form mixed metal sulfides.

[1] Nordstrom, D.K., and G. Southam. (1997) *Rev. Mineral* **35**, 361-390