

## Sulfidation Kinetics of Silver Nanoparticles

Thursday, 19 September 2013 12:30 (2 hours)

Ag-NP released from consumer products to the environment may undergo transformations. Especially the sulfidation has been identified as one of the key transformation process, which strongly reduces the antimicrobial properties of Ag-NP. This is mainly due to the low solubility of Ag<sub>2</sub>S. Under aerobic conditions, bisulfide (HS<sup>-</sup>) is quickly oxidized and thus becomes unavailable for the sulfidation of Ag. Metal sulfides (MS), however, are relatively stable under aerobic conditions and may represent a reservoir of sulfide available for the sulfidation of Ag-NP even under aerobic conditions. ZnS and CuS are present in large quantities in wastewater. In aerobic surface waters, concentrations in the order of microgram / liter are reported, along with expected half-life times of the MS of approximately two weeks.

The goal of this study was to determine the sulfidation rates of Ag-NP in the presence of MS in comparison to HS<sup>-</sup>. We reacted citrate-capped Ag-NP with a diameter of 10 and 100 nm (0.16 mM Ag) suspended in TRIS buffered (10 mM, pH = 7.5) aqueous media with different MS (weakly-crystalline and well-crystalline CuS and ZnS; 0.34 mM) in order to assess the dependence of the Ag sulfidation kinetics on the type and crystallinity of the MS. In addition, 40 nm and 100 nm Ag-NP were reacted with dissolved HS<sup>-</sup>. To determine the degree of Ag-NP sulfidation as a function of time, the solids were analyzed by Ag K-edge (25.514 keV) at the Dutch Belgian Beamline (Dubble, BM01B) at the European Synchrotron Radiation Facility (ESRF, Grenoble, France) and at the SuperXAS beamline (X10DA) at the Swiss Light Source (SLS, Villigen, Switzerland). The sample spectra were analyzed by linear combination fitting (LCF) using crystalline Ag<sub>2</sub>S, poorly crystalline Ag-sulfide, and metallic Ag as references. The sulfidation rates of the Ag reacted with MS were additionally determined by measuring the increase of dissolved Cu or Zn after complexation with Zincon using UV-Vis analysis.

For Ag-NP reacted with MS, the results from LCF analysis were generally in very good agreement with the expected degree of Ag-NP sulfidation derived from UV-Vis measurements. Attempts to quantify the metallic Ag fraction via UV-vis measurements were not successful due to strong interferences with the Ag<sub>2</sub>S and the sulfidation rates of Ag-NP reacted with HS<sup>-</sup> were exclusively determined by XAS analysis. Larger Ag-NP showed a slower reaction kinetics, but not to the degree expected on the basis of their external surface derived from transmission electron microscopy images. The Ag-NP were more rapidly sulfidized when reacted with weakly-crystalline MS than with crystalline MS, and CuS lead to faster sulfidation than ZnS. The sulfidation of Ag-NP reacted with HS<sup>-</sup> seemed to be diffusion limited and thus also exhibited a strong size-dependence. Our findings highlight that the Ag-NP sulfidation rates result from a complex interplay of Ag-NP size, oxidation kinetics of the Ag-NP, and dissolution kinetics of MS. The sulfidation rates directly affect the half-life of Ag-NP in aquatic systems and consequently their potential (eco)toxicological effects on the aquatic environment.

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**Session Classification:** Poster session II and lunch