The number of commercial applications of nanotechnology is burgeoning. Products containing nanoparticles are entering the marketplace, and the environment, at a rapidly increasing rate, and well before their safety has been definitively determined. Among the products on store shelves today are socks that contain silver (Ag) nanoparticles with antibacterial and fungicidal properties. Laboratory experiments using zebrafish, the laboratory rat of the aquatic environment, have demonstrated serious developmental defects and mortality of fish exposed to ionic Ag nanoparticles in purified water. But the fate and toxicity of Ag nanoparticles in aquatic systems outside the lab remains uncertain, so gaining a better understanding of the chemical transformations that nanoparticles experience under a variety of real-world conditions is vital in assessing any potential health risks from this new technology. A research team from the U.S. Environmental Protection Agency (EPA) utilized the APS to explore the ways in which sock fabric impregnated with Ag nanoparticles reacts to simulations of an ordinary laundry process, using bleach, detergent, and tap water, and uncovered some enlightening transformations.

X-ray absorption near edge structure (XANES) spectroscopy was carried out at the MR-CAT beamline 10-ID to compare unwashed sock material with fabric that went through the washing process. The team also gathered XANES spectra from an Ag chloride reference material and elemental nanopowder in a chloride solution (NaCl). The researchers exposed samples of fabric to a mixture using products in common use around the house: bleach and detergent. The solution was agitated for two minutes and left to soak for 10 minutes, and this cycle was repeated once. Using tap water from Argonne, they then rinsed the fabric, wrung it out three times, and mounted the 10-cm² samples for XANES analysis.

The researchers found that ionic Ag nanoparticles react with chloride present in the hypochlorite bleach/detergent mixture, resulting in an inert and more stable compound, Ag chloride (AgCl). In the one wash and rinse operation, about 50% of the nanoparticles were converted to the chloride form. The EPA scientists suggest that repeated laundering of the sock material may convert additional Ag nanoparticles to AgCl, thus reducing or eliminating the odor-eating and antibacterial properties of the relatively expensive apparel.

The elemental Ag nanopowder immersed in an ionic saline (NaCl) solution, however, remained in its elemental, and potentially more toxic, state. It appears that the hypochlorite bleach/detergent solution used to wash the sock fabric provides an oxidation step necessary to transform ionic nanosilver into a stable, non-reactive compound. This is indicated by a distinct shift in the edge energy that is similar for the washed fabric and the reference material AgCl (Fig. 1). The scientists caution that

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the solution used in this experiment may not be typical of an ordinary laundry process. Further studies with laundry detergent in ordinary washing machines may further clarify whether Ag nanoparticles are consistently converted to an inert form. Furthermore, the team proposes that as Ag nanoparticles enter public sewer systems and finally wastewater treatment plants, very little if any ionic Ag will remain because chloride is so common. Should Ag impregnated socks wind up in landfills, it is also likely that repeated washing in a chloride solution will have converted most of the Ag to the less reactive form.

Silver has been used since ancient times as a disinfectant. But only in the modern era have there been calls for its use to be regulated, whether by the U.S. Food and Drug Administration or the EPA. Some groups have petitioned the EPA to regulate ionic Ag nanoparticles as a pesticide. It is only by examining the properties of Ag species in real world conditions that regulators can ascertain whether Ag nanoparticles pose any real threat to aquatic resources or human health.

— Elise LeQuire