Environmental Science & Technology

Article

pubs.acs.org/est

Effect of Variations of Washing Solution Chemistry on Nanomaterial Physicochemical Changes in the Laundry Cycle

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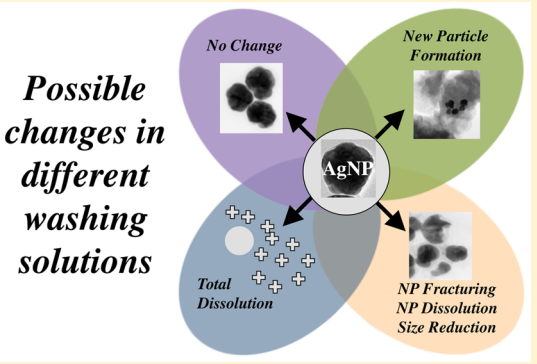
Supporting Information

ABSTRACT: Engineered nanoparticle (ENP) life cycles are strongly dependent on the life-cycle of the nanoenhanced products in which they are incorporated. An important phase for ENP associated with textiles is washing. Using a set of liquid and powdered commercially available detergents that span a wide range of different chemistries, washing studies were performed with one "standard" nanoparticle suspended in wash solution to systematically investigate (changes to) particle size distribution, dissolution, reprecipitation (i.e., "new" particle formation), and complexation to particulate matter. Au ENPs were used as a "tracer" through the system. TEM and EDX analysis were performed to observe morphological and chemical changes to the particles, and single-particle ICP-MS was used to build a size distribution of particles in solution. Varying the washing solution chemistry was found to dictate the extent and rate of dissolution, particle destruction, surface chemistry change(s), and new particle formation. Detergent chemistry, dominated by oxidizing agents, was a major factor. The detergent form (i.e., powder vs liquid) was the other decisive factor, with powder forms providing available surfaces for precipitation and sorption reactions. Control experiments with $AgNO_3$ indicated metallic Ag particles formed during the washing process from dissolved Ag, implying not all Ag-NPs observed in a textile washing study are indicative of released Ag-ENPs but can also be the result of sequential dissolution/reduction reactions.



1. INTRODUCTION

To date, the predominant focus of environmental health and safety of engineered nanoparticles (ENPs) has lain in assessing the fate, transport, and toxic properties of pristine (i.e., as-manufactured) materials.[1,2] Because environmental systems are dynamic and the surfaces of ENPs are highly reactive, physiochemical changes to engineered or incidental coatings and subsequent reactions will greatly complicate how the particle(s) behave.[3] This is also true for ENPs that are released from products, where the same particle may have different transformation byproducts depending on its use or purpose.[4,5] Exemplifying this is the case of Ag ENPs used in textiles, whereby, depending on material design and external impacts to the textile, ENPs may be released as single particles, agglomerates, embedded in the matrix, or as dissolved ions with total Ag release rates ranging from nondetectable to 30%.[6−10] In a comparison of home and laboratory washing of one textile sample, Lombi et al. showed differences in speciation of Ag remaining on the textile, with additional differences noted between laundering the fabric with phosphate-containing or phosphate-free detergents.[11] This highlights the importance of understanding the chemistry between the nanomaterials and the wash water more intimately: both in terms of the water used and the chemical makeup of the washing detergent.

Detergents can consist of a large number of individual components whose structures can vary greatly; modifications to the formula are made to comply with ecological and/or economic issues that arise over time. Modern key ingredients added for optimized washing include, among others, ion exchangers (zeolites), fluorescent whitening agents, and bleach activators/catalysts, the latter of which are highly oxidizing.[12,13] Furthermore, a metal catalyst in cooperation with H_2O_2 can lead to a better bleaching efficiency, where the transition metal complex forms a metal−oxo intermediate with the active oxygen species (H_2O_2).[13]

Surfaces treated with ENPs will be subjected to oxidants during disinfection and cleaning, and nanomaterials embedded in textiles will transform after exposure to detergents during washing.[14−16] The release and transformation process is complex[17] with the extent and rate of dissolution being

Received: May 6, 2015
Revised: July 15, 2015
Accepted: July 22, 2015

DOI: 10.1021/acs.est.5b02262
Environ. Sci. Technol. XXXX, XXX, XXX−XXX

dependent on a multitude of factors ranging from solution chemistry[18] to redox environment to particle specific characteristics such as capping agents and incorporation method into the fabric. For fabrics incorporating metallic silver, oxidation from Ag(O) to Ag(I) is a prerequisite for appearance of Ag^+ in solution.[19] The sensitivity of nano-Ag to oxygen is well-known,[20] and the chemisorbed Ag^+ formed during exposure to air or water can be released when the textile is laundered. Whereas dissolution plays an important role in the Ag ENP and textile story, the particles may not dissolve completely but rather also undergo surface and morphology changes. A hypothesis that will be investigated further in this current work is if changes to the particle (size, surface chemistry, speciation) can be linked directly to the chemistry of the washing solutions.

Multiple transformations of silver particles have been observed, where the release of Ag ENPs from clothing was simulated by sequential contact with artificial sweat (human contact), model laundry detergent solutions (washing cycle), and synthetic freshwater.[21−23] And still then, the chain of possible transformations after release is not complete; Ag ENPs may alter in the tap water, in the wash water, or in the wastewater treatment plant transforming to Ag^+, AgCl,[24] or Ag_2S,[25] respectively. The released Ag can undergo reduction reactions in washing liquid with new formation of Ag-ENP.[6,7]

The approach of placing individual transformations into a broader context allows researchers to better understand changes to particles in a more holistic way rather than a simple snapshot with a narrow scope of parameters in one portion of the release scheme. The body of work presented here suggests that even under one aging paradigm, the washing cycle, multiple end products of one aged Ag nanomaterial may result based on variations in product (textile) use. This systematic approach to understand one compartment highlights the complexity of further possible transformations at the next stage(s) of the product life cycle and as ENPs move onward in the chain of events for either the nanoenhanced product or the released ENPs.

The aim of this present investigation was to use one standard Ag nanomaterial (and Au ENPs as a control) and change the simulated washing conditions with particles in suspension using commercially available detergents with varied oxidant concentration, ionic composition, and physical form (liquid or powder). Alongside observing the initial changes to the particles after washing, continued degradation profiles of some particles were also investigated to better understand how various detergents may alter the rate and extent of particle dissolution and form after the wash cycle. Characterization of particle transformations and new particle formation was accomplished by (1) measuring free Ag^+ concentrations by ultra centrifugation and ICP-MS analysis, (2) performing single-particle ICP-MS measurements to observe particle size distribution change before and after washing and across detergent types, and (3) TEM/EDX analysis to visualize changes to the particle shape and changes to speciation.

2. MATERIALS AND METHODS

2.1. Ionic and Nanoparticulate Standards. $AgNO_3$ and Au solutions (1000 mg/L in 0.5 M HNO_3 or HCl, Merck) were diluted accordingly as experimental positive controls (Ag only) and as instrument calibration solutions ranging from 0 to 5 μg/L. Citrate-stabilized metallic Ag ENPs (100-nm; Sigma-Aldrich) were used for the majority of the work presented here. Au ENPs (60- or 100-nm; NanoComposix) were used as inert "tracers" to ensure the various solution chemistries of the washing liquids/powders did not change the transport efficiency, ICP-MS sensitivity, or other metrics that may have influenced particle analysis by spICP-MS. In select experiments (Section 3.5 Influence of Water Chemistry on Washing Profiles), an Au/Ag core/shell particle was used (NanoComposix; 48-nm core, 15-nm shell, total diameter 83 nm as measured by TEM). When analyzed by spICP-MS, the total mass of Ag equated to approximately a 70-nm metallic Ag particle, where a decrease in calculated "diameter" can be used as a proxy for dissolution of Ag from the shell of the particles. The sizes of all particles used were verified by sp-ICP-MS measurements in DI H_2O and/or by TEM.

2.2. Laundry Detergent Solutions. Seven washing solutions were investigated. Five were "grocery store brand" detergents from a Swiss store, are commercially available, and intended for use in private homes. Two liquid detergents ("color" and "all purpose") and three powder detergents ("color", "all purpose", and "oxi") were chosen. Additionally, two detergents (one liquid, one powder) was acquired from a company producing detergents for industrial-scale laundering, e.g. for hospitals, nursing homes, restaurants, etc. (labeled industrial detergent hereafter). Detergent compositions are given in Supporting Information (SI) Table S1. The detergents are distinguished by the presence/absence of oxidizer, the presence/absence of particulate matter, and pH. The industrial detergents are purposefully stronger to increase brightening potential and kill microbial growth. In particular, the liquid detergent can be diluted as a mixture with other detergents or used alone as an intense cleansing step after a normal washing cycle, as done here.

All detergents were used at 4 g/L and diluted in DI water, or in a few cases tap water. pH was measured using a Metrohm 827 pH meter. All detergents had pH values between 8.9 and 11.5, except for the commercial liquid detergent measuring 3.1 (Table S2). Chloride is an important ion that leads to precipitation of AgCl and so was measured in the raw (settled) solution by a Metrohm 733 ion chromatograph equipped with a MetroSep A Supp 5 column. Concentrations ranged from 0.5 to 5 mg/L, except for the industrial powder detergent measuring nearly 12 mg/L (Table S2). In the single experiment conducted at the Colorado School of Mines in Golden, CO, USA, tap water was collected from the laboratory, which contains 1 mg/L residual free chlorine, to make the wash solutions.

2.3. Simulated Washing Procedures. In an abbreviated version of washing procedures from previously published literature,[6,19] simulated washing experiments were conducted where each detergent was made up in 18 m-ohm DI water (except where noted) at 4 g/L and the washing medium was kept at a constant temperature of 40 ± 2 °C, controlled by a thermostat. Each replicate (three total for each experimental variation) was made in 15-mL polypropylene tubes (sample volume of 10 mL) with regular end-over-end agitation throughout the 45-min wash cycle. Initial particle concentration in the wash solutions was 80 μg/L for ENPs (Ag and Au) and 250 μg/L for Ag^+ (added as $AgNO_3$), which was further diluted to 100 ng/L for spICP-MS analysis. The concentration of ENPs in solution represents a realistic concentration of Ag that is released from washing a silver-enhanced textile in one wash.[6,19] Slightly higher Ag^+ concentrations made for a better probability

DOI: 10.1021/acs.est.5b02262
Environ. Sci. Technol. XXXX, XXX, XXX−XXX

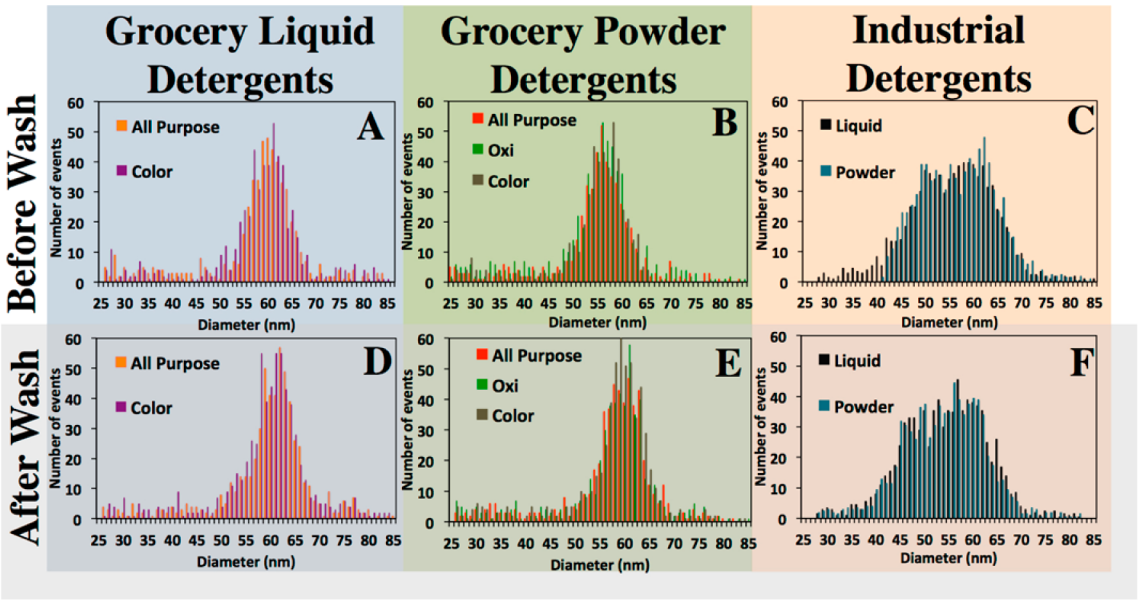


Figure 1. Au 60-nm particle size distribution analyzed by spICP-MS in various washing solution chemistries, before and after simulated washing (average of triplicate samples). (A) grocery liquid detergents before wash; (B) grocery powder detergents before wash; (C) industrial detergents before wash; (D) grocery liquid detergents after wash; (E) grocery powder detergents after wash; and (F) industrial detergents after wash.

of detecting the formation of particulate matter and/or Ag^+ which could adhere to the solids in the washing solutions.

In each washing solution, total Ag measurements in addition to ultrafiltration (VIASPIN centrifugal filters, 10-kDa cutoff) Ag analysis were made by ICP-MS, with samples acidified to 2% HNO_3. Additionally, aliquots were taken for spICP-MS analysis before and after the wash cycle. In studies designed to represent extended aging of the particles after the washing cycle, the same particle suspension was analyzed on day 1, day 2, and day 5, with samples stored in the dark in the interim.

2.4. Filtration Studies. In an effort to vet the spICP-MS technique over another standard practice of serial filtration with subsequent total metals analysis to determine ENPs in various size fractions, we used 60-nm Au ENPs at the same concentration and volume as in the simulated washing tests (80 μg/L; 10 mL), filtered the samples and diluted appropriately for spICP-MS. We used Au ENPs opposed to Ag to ensure only physical mechanisms were tested opposed to additional possible chemical changes of Ag ENPs (e.g., dissolution, surface changes, etc.). Tests in a variety of solutions (DI water, liquid and powder detergents) investigated if solution chemistry or form played a significant role in filtration efficiency. Finally, we tested if larger sample volumes would increase the proportion of particles passing the filter, which related to our previous washing studies, where 70 mL of solution was passed through one filter. The Au ENP profile was determined in triplicate samples by spICP-MS for the unfiltered, 0.45-, and 0.1-μm filtrates (cellulose nitrate filters, Sartorius Stedim) at 50 ng/L.

2.5. Single-Particle (sp)ICP-MS Measurements. Particle concentrations and size before and after laundering were measured using single-particle (sp)ICP-MS as described according to published methods.[18,26−28] In this current study, the Ag and Au content and spICP-MS measurements of the majority of experiments were performed with an Agilent ICP-MS. Here, 5-ms dwell times were used to capture ion plume events as pulses with a reduced settling time of 100 ms seconds. When the PerkinElmer NexION 300Q ICP-MS, equipped with a Type-C Miramist nebulizer and baffled cyclonic spray chamber, was used, dwell time of 3 ms with settling time of 100 ms were used. In both cases, data were collected for 120 s. Instrument calibration utilized a blank and four dissolved Ag solutions made in 2% HNO_3 (0−1 μg/L), collected in spICP-MS mode. Au ENPs of 100 nm (and associated dissolved Au calibration curve) were used for determination of transport efficiency on a daily basis. To monitor instrumental drift over time, a single 100 ng/L Ag dissolved calibration check standard was analyzed in spICP-MS mode after approximately every ten ENP samples. If drift in the standard signal was detected, the particle sizing equation was adjusted accordingly for the change in sensitivity.

2.6. Scanning Transmission Electron Microscopy and EDX Analysis. Pristine nanomaterials were drop-deposited onto carbon-coated Cu TEM grids. Washing solution(s) that contained nanomaterials were centrifuged under gentle conditions (500 rpm for 4 min) to settle large solids from the washing powder. The supernatant was transferred to new vials where particles were deposited directly onto TEM grids by centrifugation using a swinging bucket rotor, with rotation speed of 4500 rpm for 2 h. Under the applied conditions, deposition of metallic Ag particles (density 10.1 g/cm^3) > 10 nm would be completely deposited on the grid. All samples used for microscopic analysis were processed within 24 h of preparation.

Particle images were obtained via scanning transmission electron microscopy (STEM) combined with EDX for element detection using a JEOL 2200FS TEM/STEM operated at 200 kV. The nominal spot size of the STEM probe was 0.7 nm using a beam convergence angle of 10.8 mrad. High-angle annular dark-field STEM micrographs were recorded using an inner detector angle of 100 mrad, while the bright-field STEM images were recorded with a detector angle of approximately 15 mrad. EDX spectra of individual particles were recorded either by positioning the electron probe on a selected particle or by scanning the electron probe on a small frame centered on the particle.

DOI: 10.1021/acs.est.5b02262
Environ. Sci. Technol. XXXX, XXX, XXX−XXX

3. RESULTS

3.1. Suitability of Filtration to Separate Size Fractions. Because Au particles are stable and smaller than the nominal pore sizes in all cases it would be expected to have a steady particle number in all solutions. Evidence of filtration "artificially" reducing the particle number detected in solution when smaller volumes of washing solutions were filtered was observed. As seen in Figure S1, 60-nm Au particles adhered to the 0.1-μm filters to varying extents regardless of solution chemistry (DI water, liquid detergent, powder detergents) despite particles being smaller than the nominal pore size. The 0.45-μm filter allowed a representative distribution with generally high recoveries for most solutions; notably, when a larger volume of the samples (Panel E), a larger percent recovery of ENPs is realized. We see a change in the breakthrough curve of particles passing through the filter, where approximately 90% of the 60-nm Au particles were recovered after filtration through the 0.1-μm filter (Table S3). The liquid detergent allowed more particles to pass through the filter than DI water or powder detergents; possibly because of increased surfactants and (other) particulate not blocking filter pores, respectively.

3.2. Analysis of Au Particles in Various Washing Solutions. Au nanoparticles of 60 nm were suspended in each detergent and analyzed before and after the simulated washing procedure (Figure 1). This was done to ensure the matrices of the various solutions themselves or the washing process did not affect the analysis either in terms of recovered particle number or altering the pulse intensity for each nanoparticle event. Because Au particles are stable, we expected to size the particles similarly in each iteration of the experiment with similar particle number and size distributions regardless of the matrix. Apparent changes to particle size would indicate signal suppression due to the matrix (which was not expected because of the high dilution factor necessary for spICP-MS) while changes to particle number after the washing procedure would indicate a physical loss of the particles during the process (e.g., adhering to the side of the experiment container, aggregation and settling, and/or complexing to washing detergent components and settling).

No changes were observed either to particle size or number; indicating that the Au particles are suitable to be used as a conservative tracer in the experiments and that the various washing solution chemistries themselves did not affect spICP-MS analysis. This is true regardless of the washing detergent form (i.e., liquid or powder) or chemistry (i.e., variety of oxidizing agents, pH, etc.). Therefore, we expect spICP-MS analysis to be representative of the particle size and number distribution in each experiment with no analysis complications due to the nature of the matrix.

3.3. Analysis of Dissolved Silver. Soluble silver species, as measured by ultracentrifugation, detected after washing 100-nm Ag particles in each of the detergents was a minimal fraction of the total silver added to solution, less than 2% of the total Ag in most cases (Table S4). The exception to this was the industrial detergents, where the powder form dissolved 6% of the total Ag added as ENPs and the liquid form completely dissolved all Ag. This indicates that, aside from the industrial liquid detergent, outright dissolution of particles to remain as Ag^+ is not a prominent fate in the detergent solutions. Upon $AgNO_3$ addition to grocery powder detergents, a minimal fraction (less than 5%) remained in the dissolved form after the simulated washing procedure.

3.4. Behavior of $AgNO_3$ and Ag ENP in Various Washing Solutions. Both Ag ENPs and $AgNO_3$ were added into the washing solutions and analyzed for particle number and particle size by sp-ICP-MS. Average histograms of triplicate experiments for each of these experiments can be found in Figure 2, with average particle number recorded in Table S5. Two representative example TEM images of Ag ENP suspended in each solution after the washing procedure and in solutions where $AgNO_3$ produced pulses by spICP-MS are

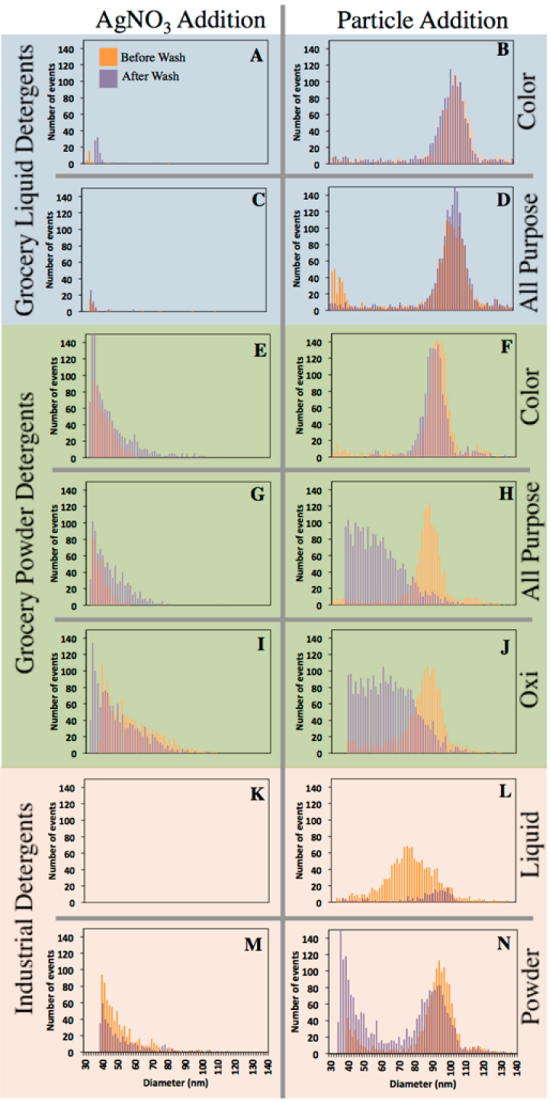


Figure 2. Averaged histograms of triplicate sample analysis of the addition of $AgNO_3$ or 100-nm citrate-coated Ag nanomaterials to a variety of washing solutions, analyzed by spICP-MS before and after a simulated washing procedure. Two household liquid detergents are shaded in blue (color detergent panels A and B; all-purpose detergent panels C and D) with measured Ag particles found before and after wash indicated by orange and purple histograms, respectively. Powder variations of household detergents are shaded in green (color detergent panels E and F; all-purpose detergent panels G and H; oxi detergent panels I and J). Finally, two industrial strength detergents, highlighted in peach, were investigated both in liquid (panels K and L) and powder (panels M and N) forms.

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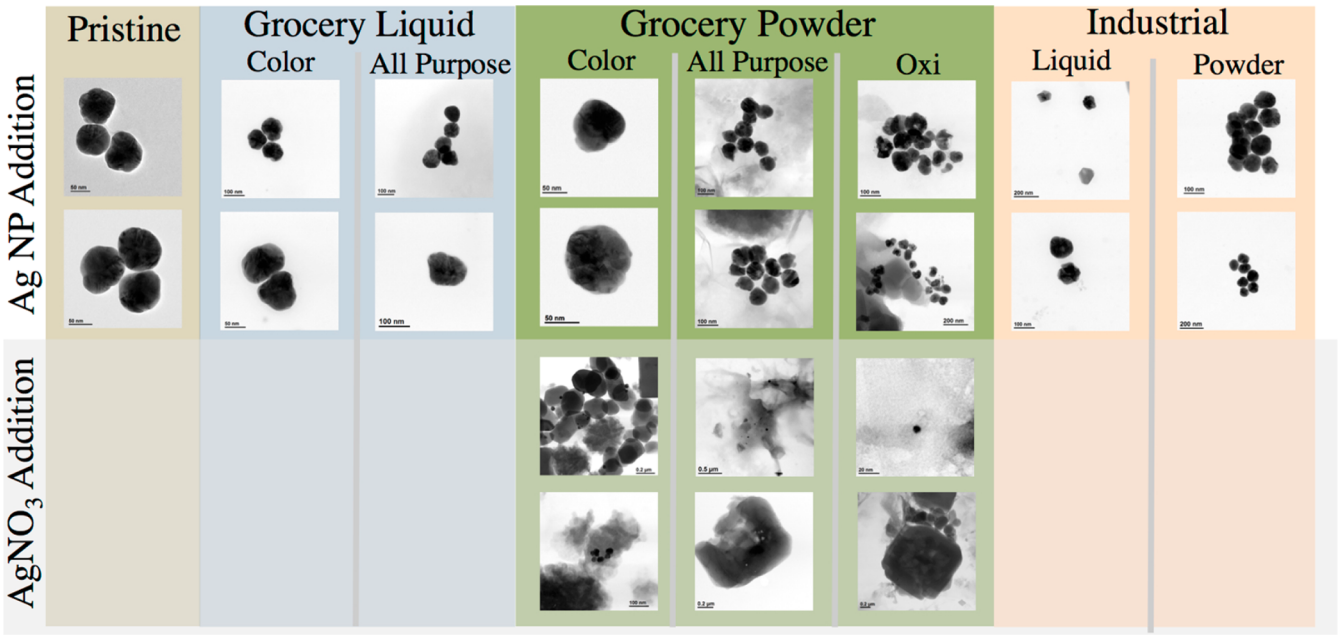

Figure 3. Two representative STEM images each of pristine Ag nanomaterials (beige shading), suspended in grocery liquid detergents (blue shading), grocery powder detergents (green shading), and industrial detergents (peach shading), all after the washing procedure. Additionally, particulate material formed through the addition of $AgNO_3$ to grocery powder detergents is depicted in the light green shaded box. The corresponding EDX spectra are shown in SI Figure S2.

depicted in Figure 3, with corresponding EDX analysis in Figure S2.

Grocery Liquid Detergents. No particle formation (with sizes over 30 nm, the approximate detection limit of the spICP-MS technique under these conditions) was detected with the addition of $AgNO_3$ in the liquid detergents and no dissolution was observed to the ENP added in the liquid samples (Figure 2, panels A–D). Along with the negligible size change in the TEM analysis (Figure 3, shaded blue boxes), there were few visible surface changes to the particles with no appreciable speciation change from the pristine metallic Ag ENPs (Figure S2). Moreover, the particle number found before and after washing (and between the color and all-purpose detergents) is the same; indicating the particles are stable and neither settle from solution nor adhere to the sample container during the wash cycle (Table S5).

Grocery Powder Detergents. Particle formation was visible with the addition of $AgNO_3$ in all powder detergents, both before and after the washing procedure. In Figure 3, TEM shows that very small metallic ENPs form (EDX analysis Figure S2), but are often grouped in or around larger silicate- or titanium-based materials originating from the washing solution.

ENP size in the grocery powder color detergent did not change appreciably during the washing process and the number of distinct particles detected remained constant before and after treatment. (Figure 2, panel F; Table S5) Conversely, a significant particle distribution shift to smaller sizes was noted in both the all-purpose and oxi detergents (Figure 2, panels H and J, respectively), likely due to the increased concentration of peroxide in these solutions. The distribution of particle size became broader and additionally 40% more distinct particles were observed in the all-purpose solution after washing. In the oxi detergent, the individual particles measured by spICP-MS nearly doubled (Table S4). Furthermore, the change in particle distribution is seemingly similar between both the all-purpose and oxi experimental sets, despite the all-purpose detergent having approximately only half the concentration of oxidizing agent contained in the formula; added as sodium carbonate peroxide at 6 and 13 wt %, respectively (Table S1).

For powder detergents containing an oxidizing agent, the morphology of added ENPs changed along with the overall mass associated with the particle (Figure 3, shaded dark green). Here, in 15–20% of the particles, the shape was no longer spherical but rather appeared fractured after the washing procedure as if the oxidant split the particles, possibly along (existing) fractures or facets in the particle (poly)crystallinity (Figure S3). Associated Ag fragments were also visible in the vicinity of the parent particle.

Industrial Detergents. There were no particles observed by spICP-MS upon $AgNO_3$ addition to the liquid variant of the industrial strength washing solution (Figure 2, panel K), and markedly less particle formation in the industrial powder formulation (Figure 2, panel M) versus the grocery powder detergents. The excessive concentration of oxidizing agents, in partnership with the very low pH in the liquid formulation, is likely responsible for keeping added $AgNO_3$ dissolved over time.

The ENPs added to the industrial liquid detergent had a very rapid and significant size and distribution change (Figure 2, panel L). Even prior to washing, the particle size decreased in the short time frame between sample preparation and analysis (maximum 15 min), relaying the strength of this solution. After the washing procedure, few particles remained in solution (Table S5) and the majority of Ag measured by spICP-MS analysis and ultracentrifugation and ICP-MS analysis was in dissolved form. In this regard, the industrial liquid detergent promoted the highest dissolution extent of any detergent studied here. ENP addition to the industrial powder detergent resulted in markedly less change than the liquid variant, with only slight particle size change to the primary particle histogram (Figure 2, panel N). However, an increase in smaller Ag material was also observed after washing, as was seen previously

DOI: 10.1021/acs.est.5b02262
Environ. Sci. Technol. XXXX, XXX, XXX–XXX

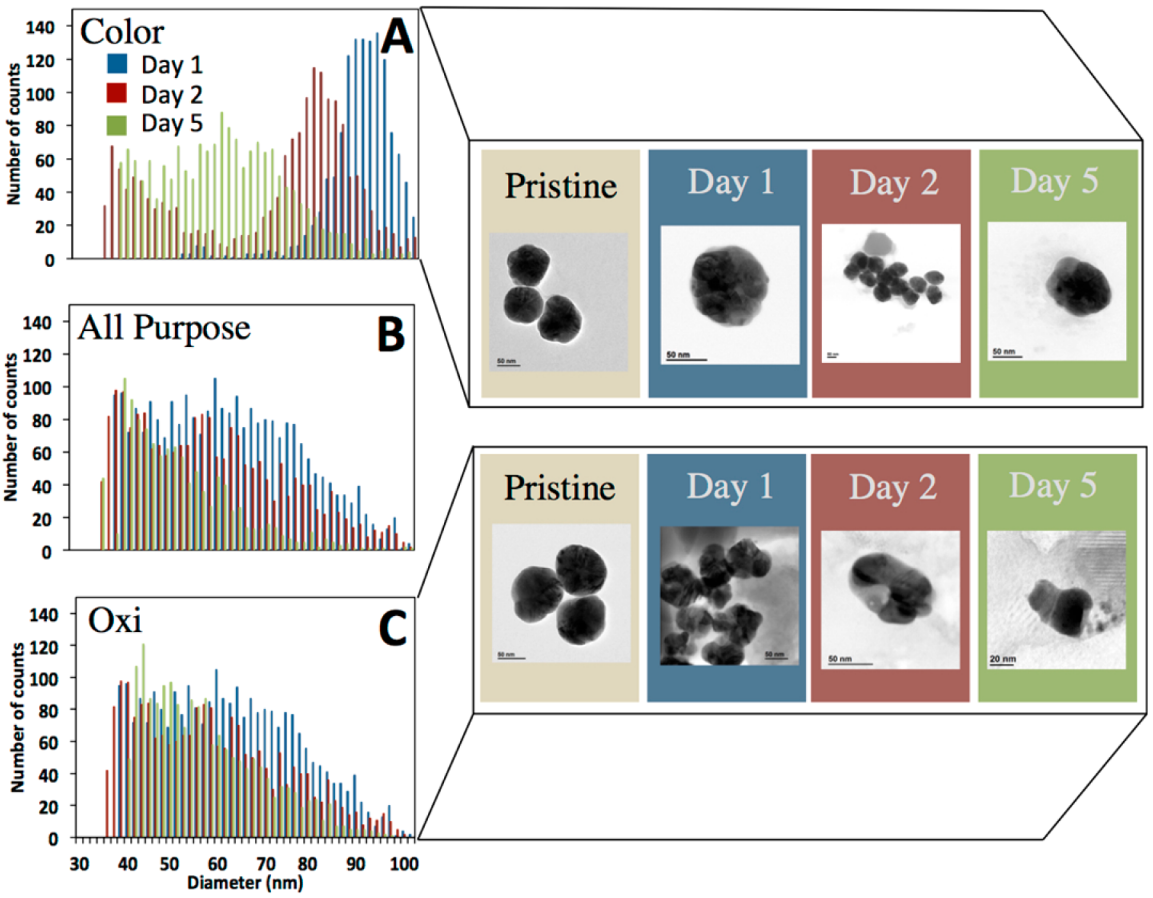

Figure 4. Averaged histogram of triplicate samples of 100-nm Ag particles that underwent a simulated wash cycle in various grocery powder detergents (panel A, color; panel B, all-purpose; panel C, oxi) over multiple time points (days 1, 2, and 5 with blue, red, and green histograms, respectively). Representative TEM image examples of nanoparticulate Ag found in color and oxi grocery powder detergent varieties over time intervals of 1 day (blue shading), 2 days (red shading), and 5 days (green shading). Reference of the pristine 100-nm particles shaded in beige. The corresponding EDX spectra are shown in SI Figure S5.

upon addition of $AgNO_3$ to powder detergents. TEM analysis of the particles in both the liquid and powder variants of the industrial detergents depict a smooth, regular surface structure (Figure 3, shaded peach) with EDX analysis confirming only metallic Ag (Figure S2).

3.5. Influence of Water Chemistry on Washing Profiles. Characteristic degradation profiles remained constant for grocery color detergents (Figure S4, panels A and C) and oxi detergents (Figure S4, panels B and D) regardless of whether the solutions were made in DI or tap water. Whereas previous studies suggested that the additional free residual chlorine in tap water promoted faster dissolution of particles than in DI water,[18] in this case the detergent chemistry appears to be the driving factor for either particle stability (e.g., in color detergent) or size changes (oxi-containing detergents).

3.6. Continued Degradation Profiles of Ag ENPs after Initial Wash Cycle. Initial, short contact/exposure time of Ag ENPs to an aging procedure (such as washing) can change the degradation profile over time, where particles may have different dissolution rates, surface chemistry reactions, agglomeration rates, etc. As described in Section 3.5, there was little change to both the Ag ENP size (distribution) and surface characteristics when washed in color detergent on the first day. However, spICP-MS analysis indicates that over time (2 and 5 days after washing) the particle size decreases and the size distribution becomes increasingly widespread (Figure 4, panel A), yet the particle number stays approximately constant over 5 days. The particle surface continued to evolve over time: with more pitting on the surface noted, and small Ag "droplets" forming around the primary/parent particles (Figure 4). Furthermore, by day 5, there is an increasingly complex speciation change noted, in some cases with Ag associated strongly with Si or O, suggesting binding with zeolites from the detergent or precipitation of new particle formations (Figure S5).

In sharp contrast, there is little change to particle size (and distribution) for solutions washed in oxi detergent over time. This indicates that changes which occur to particles in these solutions, at least in terms of particle size distribution, occur during the initial wash treatment and remain constant and unchangeable over time. Indeed, the particle surface chemistry in the all-purpose and oxi detergents is changed significantly, with evidence of Ag/O and Ag/S formation (Figure S5), which can inhibit further particle dissolution of the primary particles. A number of Ag complexes did not resemble the original particle in size or shape at all, suggesting that the ionic Ag released from the particles during the first wash reprecipitated alongside the other washing solution components over the course of time but were stable thereafter.

DOI: 10.1021/acs.est.5b02262
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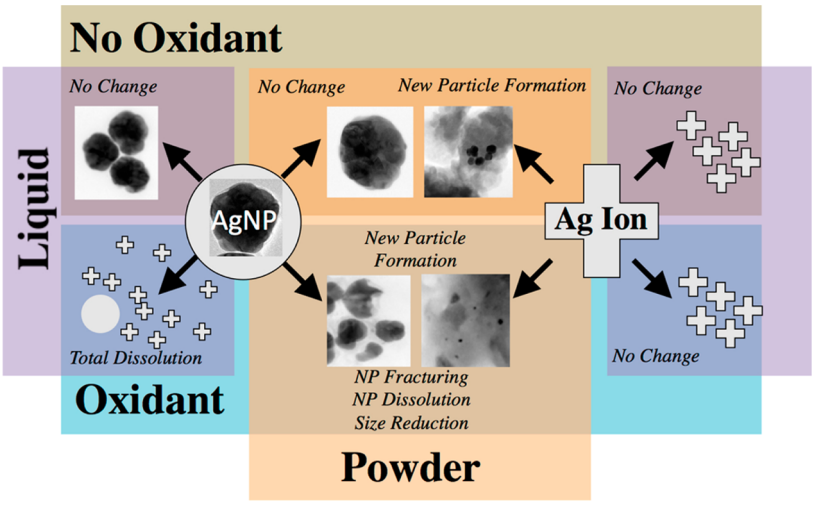

Figure 5. Venn diagram of the most likely transformations of Ag ENPs or Ag^+ added to various washing detergent solutions. TEM images depict examples of particles found in each condition. Note that a characterization defined as "no change" means no changes detected by our experimental techniques: e.g., screening by spICP-MS with further characterization of particulates measured by TEM. Furthermore, the figure does not explicitly depict the possibility of silver adhering to washing particulate matter or binding with washing solution additives, which could occur in any of the solutions.

4. DISCUSSION

The spICP-MS method employed in this work provides a more direct and accurate measurement of the particle size distribution as suspended in the native solution than total metal concentrations in size fractions from serial filtration. This is particularly true for small sample sizes or for dilute particle concentrations. The ability to measure inert Au tracer particles was possible regardless of solution chemistry or detergent physical makeup. In addition to providing detailed information on particle size and number in each of the experiments, another useful parameter garnered was (change in) particle number, where an increased particle number in powder detergents containing oxidants suggested toward primary particle dissolution/destruction and more, new, small particle formation. However, as evidenced by the addition of $AgNO_3$ that formed small aggregate particles registering as one pulse, spICP-MS cannot (always) be used as a stand-alone technique. A distinction must be made between metallic silver which formed discrete nanomaterials (i.e., metallic Ag; Ag/S, complexes Ag/Si complexes), or rather if the Ag had adhered to particulate matter in the washing solution and registered as a pulse event. TEM results support a combination of these factors: very small metallic ENPs are formed upon addition of dissolved silver to the powder detergents, but are often grouped in or around larger silicate- or titanium-based materials originating from the washing solution. Individually, the small size of these particles would normally not be sufficient to create the pulse intensities observed in the spICP-MS analysis, but when analyzed together here the cumulative mass of Ag is characterized as one particle. This is the first time particle aggregates have been definitively analyzed in this way via the spICP-MS technique and suggests caution must be given to sizing "particles" in complex media without complementary characterization techniques to ensure pulse incidences captured by spICP-MS are discrete particles. Although the formation of (new) particles is seemingly the dominant trend in these systems, there is the possibility that some incidental Ag+ may adhere to other washing material particulate, in particular TiO_2 or SiO_2, and thus not be adequately measured in this sampling and characterization scheme. However, the amount that would need to adhere to a single particle in order to produce a pulse via spICP-MS (the equivalent mass of a 30-nm particle) is unlikely to be adhered to a single detergent floc.

As a foil to previously published results where various Ag additives to fabrics washed in a standardized detergent resulted in more similar forms of Ag after the wash cycle, we found that the same Ag particles suspended and washed in different detergents showed much different aging profiles from one another. The detergent chemistry, dominated by oxidizing agents and secondarily by the physical presence/absence of nondissolvable solids, was a major factor in particle dissolution, surface chemistry change(s), and new particle precipitation/formation, as summarized in Figure 5 where we group transformations based on solution chemistry.

The presence of oxidizing agents appears to affect aging and transformations of Ag ENPs in three distinct ways: (1) a sharp decrease in particle size after washing, (2) sustained particle size over time (opposed to a slower, steady size decrease in solutions containing no oxidant), and (3) physical "fracturing" of particles along clear lines. A clear decrease in particle size is noted in nearly all experimental sets that contained oxidizing agents, the only exception being the industrial powder detergent. However, particles suspended in detergents containing these bleach alternatives changed less over time than those suspended in liquid detergents or the grocery powder color detergent. Expedited oxidative dissolution, therefore, is a significant transformation pathway that must be considered in only some of the experimental washing sets. Aside from absolute changes to the size (mass) of particles in the detergents containing oxidizing ingredients, there are distinct visual characteristics arising from washing. Instead of a gradual, even size reduction as might be expected from the release of surface Ag through dissolution, the particles washed in the oxidant-containing detergents appeared broken with clearly defined sharp edges, possibly along (existing) fractures or facets in the particle (poly)crystallinity. Alternatively, the particle surface may be unevenly decorated with the capping agent,

DOI: 10.1021/acs.est.5b02262
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where uncoated sections/regions are more susceptible to degradation in the presence of oxidant.

Initial changes to the particle surface in the oxidizing conditions could form Ag−O complexes or other weakly bonded surface compounds (e.g., silver carbonate), as was detected by Hedberg et. al.[29] In that study, the authors noted a shift in the Ag−O peak of the Raman spectra, which can not be attributed to the formation of bulk like Ag_2O at the particle surface,[30] but rather may originate from another form of silver oxide that is readily able to form at higher pH values. Meanwhile, the particles that did not form such a resistant "shell" in the color detergent tracked more typical dissolution profiles. This size change can be explained by simple dissolution of particles being suspended in solution for extended periods and not necessarily a function of change(s) caused directly by the grocery powder color detergent. For example, the dissolution rate of Ag was investigated by both Mitrano et al. and Liu et al.,[18,20] and depending on particle size and water chemistry, the calculated surface area-normalized mass loss of $Ag^+_{(aq)}$ from the particles presented as a log dissolution rate was cited as −13.9 to −11.5 mol cm^{-2} s^{-1}. When reducing the number of variables considered, calculated rates of 100 nm of a week-long dissolution were approximately −12.6 mol cm^{-2} s^{-1} in DI water or −13.07 mol cm^{-2} s^{-1} in creek water.[18] Compared to the dissolution rates of silver nanoparticles presented in those papers, we find the surface normalized dissolution of 100-nm Ag ENPs in the color liquid washing detergent to be −12.07 mol cm^{-2} s^{-1}, i.e. a faster dissolution rate.

Previously, we noted the formation/release of stand-alone Ag particles when washing conventional (non-nano) textiles,[6] an experiment which was conducted with a powdered form of a standard detergent. In addition to primary particles simply decreasing in diameter, we noted in our experiments an increase of particle number over the course of the washing procedure, which is also an indication of particle dissolution and reprecipitation (i.e., new particle formation through the washing process). The reduction of dissolved Ag into particulate forms of Ag seems reasonable in this instance, given the additional particulate matter observed when $AgNO_3$ was added to these solutions as noted above.

In the case of liquid detergents, a trend appears in which they do not promote ENP aggregation or dissolution and have no feasibility to spur new particle formation, as least within the detection limit of spICP-MS. The exception to this rule is the industrial liquid detergent, where the strong chemistry of the formulation simply entirely dissolves the ENPs added, also helped by the low pH of this formulation. Conversely, in the case of powder detergents, the undissolvable solid fraction appears to promote nucleation of small (new) nanoparticles; irrespective of whether the Ag is initially derived from $AgNO_3$ addition or from dissolved/fragmented primary ENP added to solution. Increased particle events are noted in solutions that contain higher concentrations of oxidants in the detergent, as these solutions promote more (primary) ENP particle dissolution and thus more subsequent formation of (new) particles through the wash cycle.

The dominating factor for particle change lies in the type of detergent that is used rather than the chemistry of the water used for washing, which did not have any discernible influence. The higher buffering capacity of the detergent solution likely compensates for the residual chlorine found in the tap water solution, where in unbuffered systems dissolution had previously been shown to be an important particle transformation in this matrix.[18] This suggests that differences in water treatment facilities in different locations or natural variations in the water chemistry used for washing may be inconsequential to particle (in)stability when compared to the detergent selected for laundering clothing.

This work highlights the fact that because Ag ENPs will be readily aged/transformed during a product's life cycle, it is prudent to consider how these byproducts differ from pristine ENPs before assessing their behavior. This is especially true when attributing toxicity or safety assessments to materials, which may be best done to the (relevantly) transformed particles rather than to the pristine version. During the initial washing phase, the detergent chemistry appears to play a significant role in intermediate-term stability of Ag ENPs that remain suspended in solution. Initial changes to particle speciation and morphology due to the detergent chemistry has significant impacts and can have ramifications on future environmental fate and transport of the nanomaterials themselves as well as associated release of ionic Ag over time. Although some washing procedures appear to keep the original ENP properties (size, surface chemistry) essentially intact and may release Ag slowly (e.g., liquid detergent chemistry), others force the particles to experience a more dramatic, persistent change after exposure to the washing solutions (e.g., oxidant-containing powder detergents). Apart from the dissolution potential change, surface properties, both in terms of morphology and speciation, will change and can dictate the reactivity and persistence of the now-transformed nanomaterial. This variance in behavior will have consequences for toxicity, environmental fate, and transport and should be considered when modeling the persistence of nanomaterials in different systems.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.5b02262.

Five figures (Au filtration study, EDX spectra of presented TEM analysis, additional TEMs of Ag ENP in oxi containing detergents, and results from experiments in DI vs tap water); five tables giving information on the laundry detergent chemistry, particle number measured by spICP-MS in various experiments, and Ag ultrafiltration results; further notes on analytical measurements of Ag in washing solutions. (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was funded by the European Commission within the Seventh Framework Program (FP7; NanoMILE project Grant Agreement NMP4-IA-2013-310451). We also thank Jim Ranville, Colorado School of Mines, for the use of his laboratory for portions of the study and Angie Barber for her laboratory support and collaboration while there.

DOI: 10.1021/acs.est.5b02262
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DOI: 10.1021/acs.est.5b02262
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