

STUDENT SUMMER INTERNSHIP TECHNICAL REPORT

**Optimizing Remediation of I-129 using AgCl
Colloidal-Sized Particles in SRS F-Area
Sediments**

**DOE-FIU SCIENCE & TECHNOLOGY
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ABSTRACT

Silver chloride (AgCl) is currently being used at the Savannah River Site F-Area for the *in-situ* remediation of the radioactive Iodine-129 (I-129) plume, which has progressed from a series of unlined seepage basins. The AgCl particles are injected underground to react with the soluble I-129 to form low solubility AgI solids; thus hindering the growth of the I-129 plume. The objective of the experiments performed during the 10 week internship were to characterize the morphological differences between AgCl particles made under various conditions and to better understand the reactivity between AgCl and iodine and to test the concept of precipitating AgCl particles in situ. The use of scanning electron microscope (SEM) and energy dispersive spectroscopy (EDS) technologies help to answer questions that arose during the experiments. The information gathered may prove to be a useful tool for current and future applications of AgCl as a means to attenuate I-129.

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1. INTRODUCTION

The Savannah River Site (SRS) was once home to five fully functioning nuclear reactors which produced base materials for nuclear weapons on the 310 square mile site. Since the end of the Cold War all but one of these reactors has been decommissioned and the site is currently involved in an extensive clean-up/remediation initiative. A series of unlined seepage basins located in the SRS F-Area received approximately 1.8 billion gallons of acidic waste solutions containing radionuclides and dissolved metals. Large contaminant plumes now stem from these basins and are spreading with the flow of groundwater.

One of these contaminants is the soluble and radioactive Iodine-129 (I-129) whose plume and concentration levels can be seen in Figure 1. Iodine-129 contaminant plume at SRS F-Area. Large portions of the plume contain iodine concentrations well over the drinking water standard of 1 pCi/L. Iodine-129 emits both beta and gamma radiation and has a half-life of over 15 million years. With health effects that include the reduction of thyroid function and hormone production and potentially thyroid cancer, it is imperative that the I-129 contamination is addressed before it can spread into local groundwater sources.

Current *in-situ* remediation efforts for I-129 include the use of silver-chloride (AgCl) particles, which are injected directly into the F-Area sediments at different height intervals. The AgCl reacts with the iodine to precipitate AgI and thus retards the spreading of the plume. The experiments conducted this summer were used to understand the morphology of AgCl particles created under different conditions and to determine the reactivity of the AgCl particles with iodine.

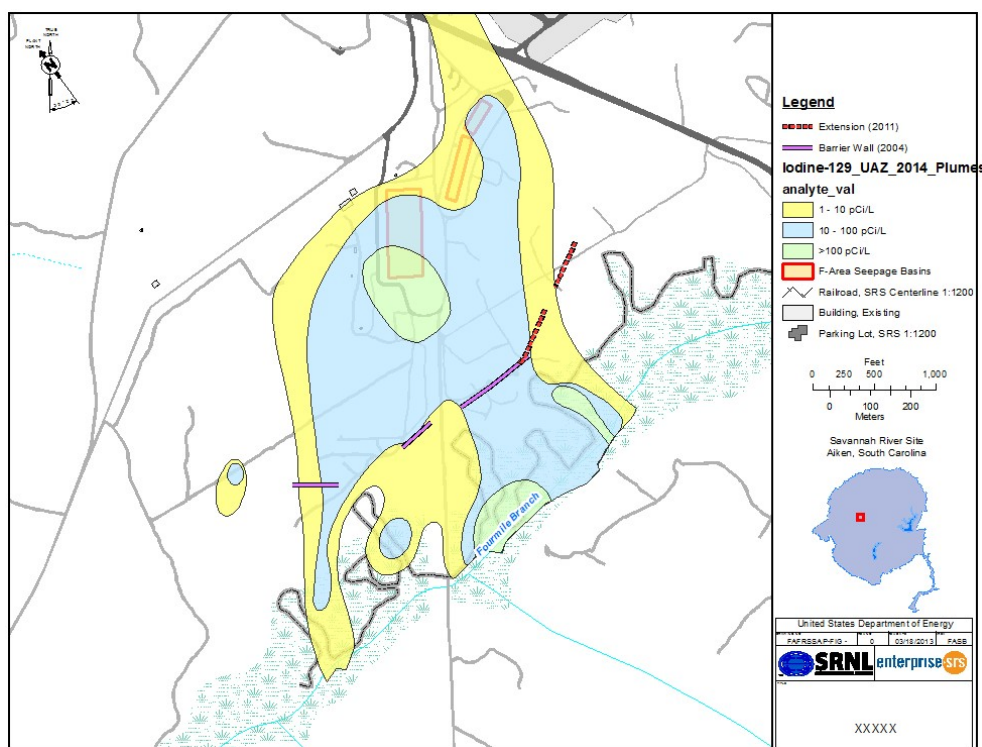


Figure 1. Iodine-129 contaminant plume at SRS F-Area.

2. EXECUTIVE SUMMARY

This research work has been supported by the DOE-FIU Science & Technology Workforce Initiative, an innovative program developed by the US Department of Energy's Office of Environmental Management (DOE-EM) and Florida International University's Applied Research Center (FIU-ARC). During the summer of 2015, DOE Fellow intern, Aref Shehadeh, spent 10 weeks doing a summer internship at the Savannah River Site (SRS) in Aiken, SC with the Savannah River National Laboratory (SRNL) under the supervision and guidance of Dr. Miles Denham. The intern's project was initiated on June 1, 2014, and continued through August 8, 2014 with the objective of optimizing remediation of I-129 using AgCl colloidal-sized particles in SRS F-Area sediments.

3. RESEARCH DESCRIPTION

Creation of Silver Chloride Particles

The first step of the experiment was to create the AgCl particles in the lab under different conditions to determine how these conditions affect particle morphology. There were a total of 6 different types of AgCl particle samples. All six of the samples began with a 400 mg/L silver nitrate (AgNO_3) solution for the silver source; from there the particles utilized either a 34 mg/L sodium chloride (NaCl) solution, an artificial groundwater solution with a low iodide concentration (AGW-Low I^-), or an artificial groundwater solution with a high iodide concentration as the chloride source (AGW-High I^-). Once these particles were created, they were subdivided into two groups; the particles washed in DI water and the particles washed in 0.01 N nitric acid (Figure 2).

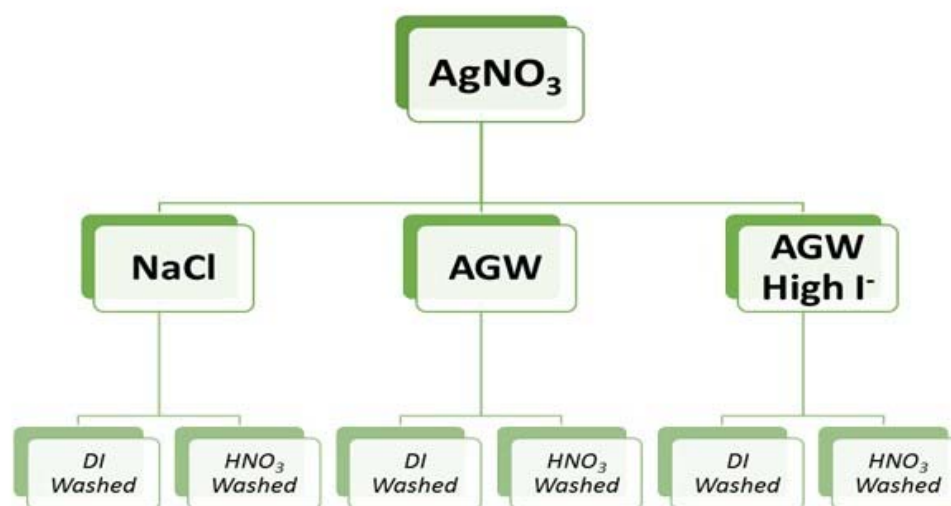


Figure 2. Flowchart for steps in creating AgCl particles.

The AgNO_3 solution was created by measuring approximately 40 mg of AgNO_3 powder and adding it to a 100 mL volumetric flask for a final concentration of 400 mg/L. The NaCl solution was prepared by dissolving approximately 34 mg of NaCl powder into a 1 L volumetric flask for a final concentration of about 34 mg/L. The AGW-Low I^- was made in a 1 L container using 382 mg of sodium nitrate (NaNO_3), 33 mg of NaCl , 47 mg of sodium sulfate decahydrate ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$), and 0.02 mg sodium iodide (NaI). To create the AGW-High I^- solution, 200 mL of the AGW-Low I^- was combined in a container with 34 μL of 1000 mg/L iodine standard.

The pH of the AgNO_3 solution and the three chloride source solutions (NaCl , AGW-Low I^- , and AGW-High I^-) were adjusted to pH 3.5 using 0.01 N HNO_3 acid to mimic the pH conditions at the F-Area. For simplicity and safety reasons the iodine used in these experiments was stable I-127 and not the radioactive I-129 found in F-Area sediments. The reactions between I-127 and the AgCl are comparable to the reactions that would occur if I-129 had been used.

Due to the photosensitivity of AgCl, all the beakers and centrifuge tubes used to make the particles were wrapped in aluminum foil and kept away from direct light as much as possible. To create a set of particles, two 100 mL beakers were filled with 40 mL each of one of the chloride-source solutions. Next the beakers were placed onto separate stir plates and a magnetic stir bar was added. The stir plates were set to create a vortex in each beaker approximately $\frac{1}{4}$ - inch deep from the surface. The AgNO_3 was then pipetted into the beakers in the amount of 10 mL per beaker to precipitate the AgCl particles. To allow the reaction to occur, the beakers were capped with aluminum foil and allowed to stir for half an hour (Figure 3). At the end of half an hour, the magnetic stir bars were removed from the beakers using a magnetic retriever rod.



Figure 3. Creating AgCl particles on stir plate.

The AgCl particles were now visible on the surface of the solutions in the beakers and would next need to be centrifuged. The contents of each beaker were poured into two 50 mL centrifuge tubes per 100 mL beaker for a total of four tubes. A few mLs of DI water were used to loosen any particles stuck to the side walls of the beakers. All four tubes were then centrifuged using a Marathon 8K centrifuge at 4000 rpm for 10 minutes to allow the particles to pack together.

After the sample was centrifuged the particles clumped together at the bottom of each of the tubes. Excess liquid was poured off into a liquid waste container with caution to not lose any of the particles. The next step was to wash the particles left in the tubes. All four tubes now received 10 mL each of the same washing solution (DI water or 0.01 N nitric acid dependent on the set that was being created) and the tubes were placed on a vortex mixer for approximately 3 seconds. The excess liquid was poured off after the particles were given sufficient time to settle and the washing process was repeated two more times for all the tubes. The tubes were then placed into a dim corner of the lab fume hood and left uncapped for 2 to 3 days to allow any liquid still in the tube to evaporate. The same steps were used for each of the six samples. The

variations between samples occurred in the type of chloride source used and the type of wash used for the particles. All sample compositions and sample IDs can be found in Table 1.

Table 1. Sample Identification for Lab-Produced AgCl Particles

Sample ID	Sample Composition
A	NaCl solution and AgNO ₃ washed with DI water
B	NaCl solution and AgNO ₃ washed with HNO ₃
C	Artificial groundwater solution (low iodide) and AgNO ₃ washed with DI water
D	Artificial groundwater solution (low iodide) and AgNO ₃ washed with HNO ₃
E	Artificial groundwater solution (high iodide) and AgNO ₃ washed with DI water
F	Artificial groundwater solution (high iodide) and AgNO ₃ washed with HNO ₃

Once the particles were completely dried they were removed from the tube with a fine-pointed spatula and placed in a small petri dish. Care was taken to not scrape the inside of the tube which would result in small plastic particles in the sample. When the petri dishes were not in use they were wrapped in foil to prevent light exposure. The next step was to analyze the particles using a scanning electron microscope (SEM) equipped with energy dispersive spectroscopic (EDS) capabilities. To prepare the SEM stubs, the adhesive covering was removed from the stub and the adhesive side was pressed into the petri dish to attach the particles to the stub. The stubs were stored away from light sources until they were ready to be analyzed. SEM and EDS analyses were then used to determine the particle size, crystal structure and composition of the particles. The SEM information can be found in the results section of this report.

Titration with AgCl and Iodine

For the second part of the experiment, titrations were conducted to determine the reactivity of the AgCl particles with I⁻ and to find out if the AgCl particles reacted on just the surface of the particle or with the entire particle. In addition, the titrations were used to determine the rate limiting step of the reaction. The titrations were conducted using both commercially produced AgCl particles and the lab-made AgCl particles from the first part of the experiment. The amount of iodine needed to fully react with the particles was calculated based on the amount of AgCl particles used in the titration. If the particles were to react fully then all of the iodine would be used up in the titration, however, if they did not react fully this may have indicated that the reaction was occurring on the particle's surface instead.

Iodine standards were created using a 1000 mg/L iodine stock solution. The standards were prepared at 0.05, 0.1, 0.5, 1, 10, and 50 mg/L concentrations and the probe was calibrated before each titration event. The probe used in the experiment was the Nico 2000 Ion-Selective Electrode (ELIT 8281- crystal membrane) which had an ideal slope for the calibration curve between -52 to -59. The beakers used in the titrations were all wrapped in aluminum foil to prevent any particles from breaking down due to exposure to direct light. The beaker was placed on a stir plate and a small magnetic stir bar was added to ensure proper mixing during the titration.

Titration 1 was done using the commercially produced AgCl particles. The 100 mL beaker used in the titration held 5.1 mg of AgCl particles, 1 mL of 5 M NaNO₃ Ionic Strength Adjuster (ISA), and 50 mL of DI water. The titrant was a 100 mg/L iodine solution and was pipetted into

the beaker in 50 μL increments or spikes. The probe was left in the beaker between spikes until the concentration stabilized. The titration continued until the iodine probe indicated that there was an increasing iodine concentration in the beaker which would suggest that all of the AgCl particles in the beaker had already reacted. It was found that when the beaker was left alone and given time to react that the iodine concentration would drop significantly. As a result, the titration of these particles lasted a period of two days with two separate titration events for the same beaker and same solution. It is believed that this was caused by the rate limiting step associated with the dissolution of AgCl which is discussed in further detail in the “Results” section.

Titration 2 was done using the Sample A particles produced in the lab, which were made using the AgNO_3 and NaCl solutions and washed with DI water. The 100 mL beaker used in the titration held 1.1 mg of Sample A AgCl particles, 1 mL of 5 M NaNO_3 ionic strength adjuster (ISA), and 50 mL of DI water. The titrant originally used in this titration was 10 mg/L iodine solution added to the beaker in 50 μL increments or spikes. It was later noted that the 10 mg/L solution was added in error and the titrant was switched to a 100 mg/L iodine solution to be added in 10 μL spikes. As seen in the first titration, the solution in the beaker was affected by the rate limiting step and therefore needed time to react. Titration events occurred three separate times using the same beaker and same solution over a period of 4 days.

When it was decided that the titrations had produced sufficient data, the titration was stopped for both the commercially produced AgCl and lab-made AgCl particles. The solution in the beaker was then poured into a liquid waste container with care to not pour out any particles which had formed. The particles in the beaker and any remaining liquid were then left in the fume hood to dry. Once dry, the particles were collected into a petri dish and the SEM stub was prepared in the same way as noted in the first part of the experiment. Results of the SEM and EDS analyses conducted on these particles are shown in the “Results” section.

4. RESULTS AND ANALYSIS

Synthesis of AgCl particles

The precipitation of the AgCl particles yielded roughly 4 mg of AgCl particles per sample. The particles were white-grey in color and formed into small aggregates at the bottom of each centrifuge tube. No significant differences could be made between particles from the different samples by simple visual observation. SEM and EDS analyses were required in order to observe the particles more closely.

SEM/EDS Data for the Creation of AgCl particles

SEM and EDS analyses were conducted on Samples A-F to determine the particle size, morphology and overall composition. The photosensitivity of the AgCl particles would play a factor in the use of SEM. When the particles were observed closely, the reaction to the electron beam was almost immediate and the particles began to decompose. Samples A and B, since these were the first samples to be analyzed, underwent a high magnification during the EDS analysis. As a result, photodecomposition was observed and recorded mostly in samples A and B. The EDS analysis for samples C, D, E, and F were all conducted at lower magnifications to preserve the clarity of the unreacted AgCl particles. The reaction of the AgCl particles with the electron beam from the SEM/EDS over the period of a few seconds can be seen in Figure 4.

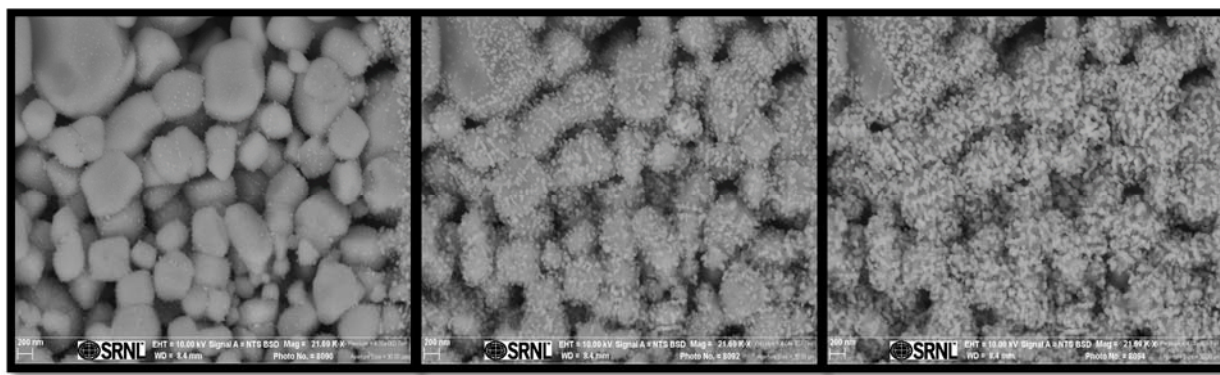


Figure 4. Decomposition of a AgCl sample under SEM beam exposure.

Sample A

Sample A particles were created from the NaCl solution, AgNO₃ solution and washed with DI water. SEM data showed that the small amorphous particles were mostly about 0.5 μm in diameter with some much larger particles scattered in the sample (Figure 5). In the EDS analysis the shape of the particles was distorted due to their reaction to light (Figure 6); nonetheless, the composition is clearly AgCl. It is seen that EDS recorded similar peaks for Cl⁻ and Ag⁺ in the

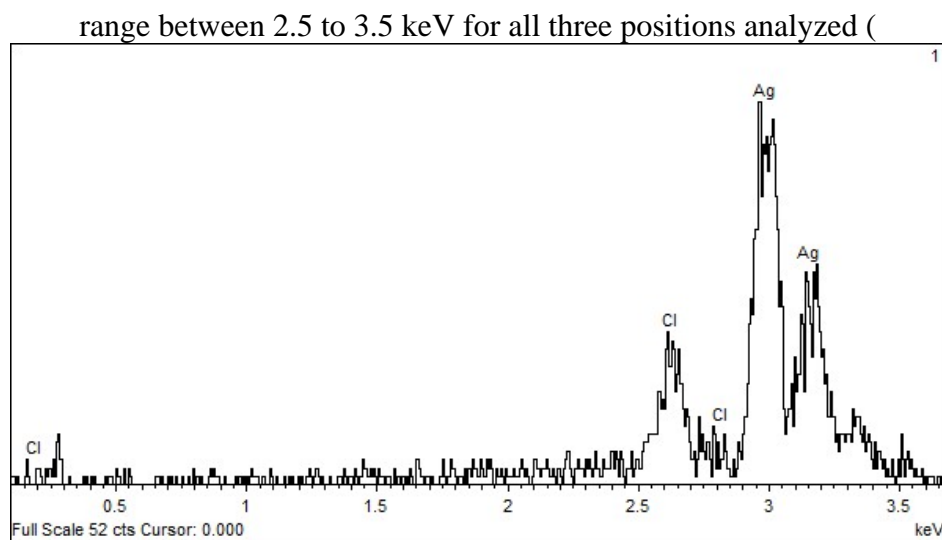


Figure 7. EDS Sample A – Position 1 analysis.

, Figure 8, and Figure 9).

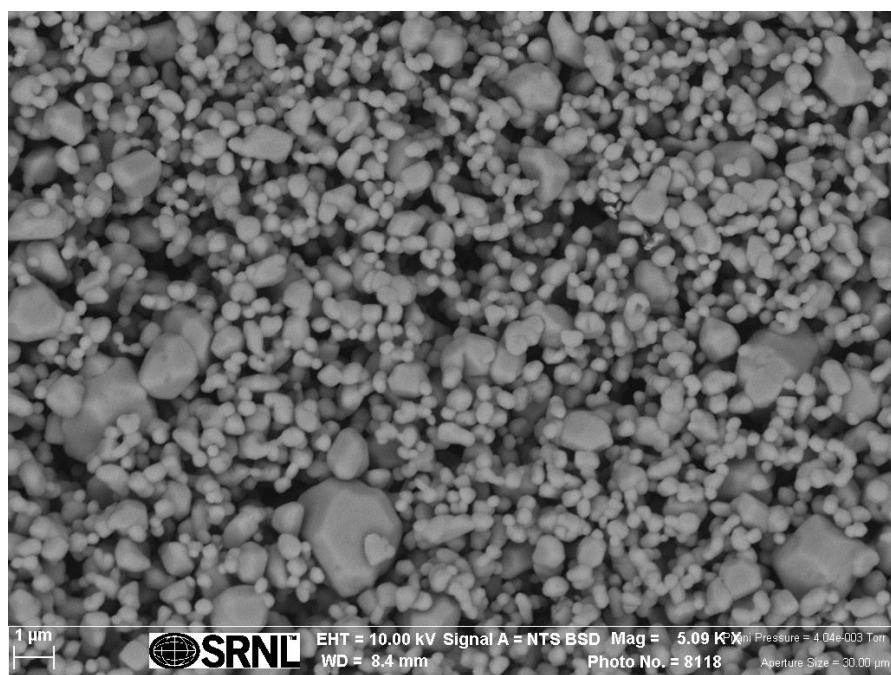


Figure 5. Sample A SEM analysis (NaCl solution and AgNO₃ washed with DI water).

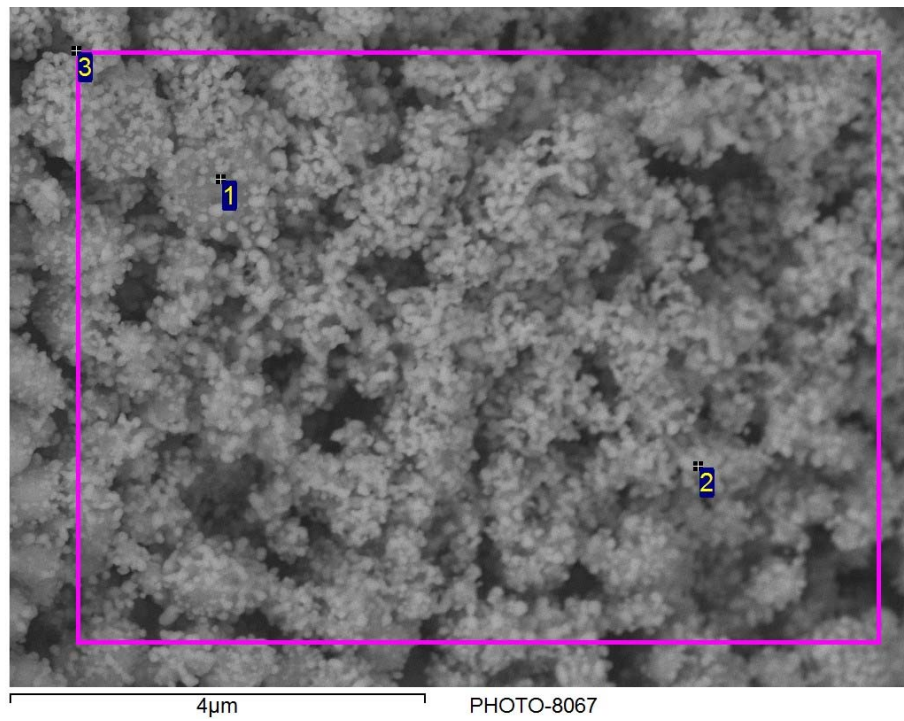


Figure 6. Sample A EDS analysis.

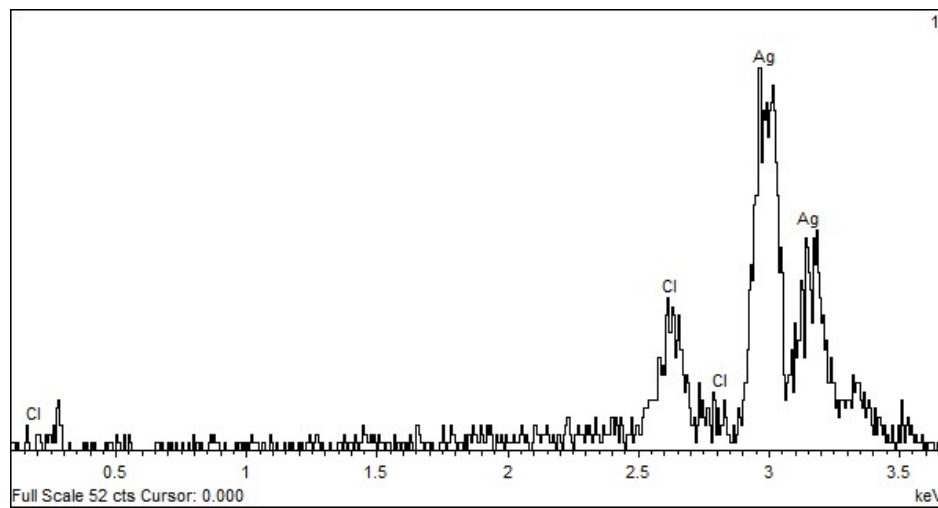


Figure 7. EDS Sample A – Position 1 analysis.

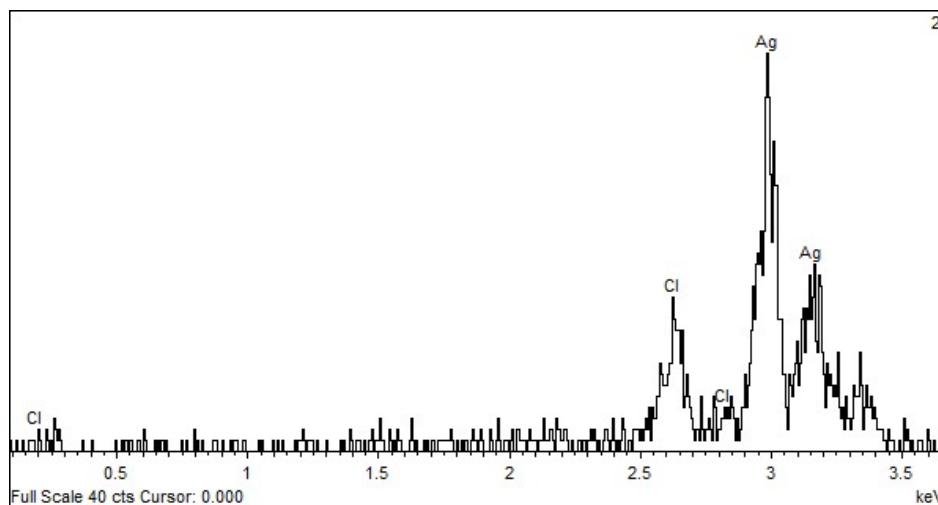


Figure 8. EDS Sample A – Position 2 analysis.

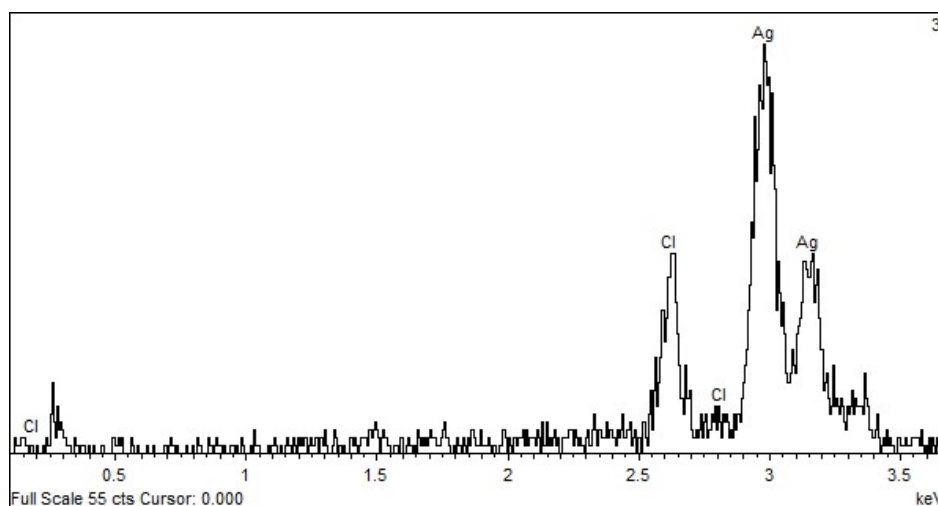


Figure 9. EDS Sample A – Position 3 analysis.

Sample B

Sample B particles were created from the NaCl solution, AgNO₃ solution and washed with HNO₃ acid. SEM images revealed small amorphous particles that were on average about 0.5 μm in diameter and had a fairly uniform size distribution (Figure 10). As seen in the EDS analysis of Sample A, the EDS analysis of Sample B distorted the shape of the particles due to their reaction to light at high magnification (**Error! Reference source not found.**). In Figure 12, Figure 13, and Figure 14 the composition of the particles was observed to be AgCl due to the recorded peaks for Cl⁻ and Ag⁺ in the range between 2.5 to 3.5 keV for all three positions analyzed. A second round of EDS analyses were conducted on Sample B with a lower magnification to improve the image of the particles (Figure 15). The EDS data in Figure 16 shows that the particles had the same peaks for Cl⁻ and Ag⁺ as in the first EDS analysis but with a higher peak for Cl⁻ at 2.65 keV. It is not known if the lower Cl⁻ peaks in the first EDS analyses were caused by photodecomposition.

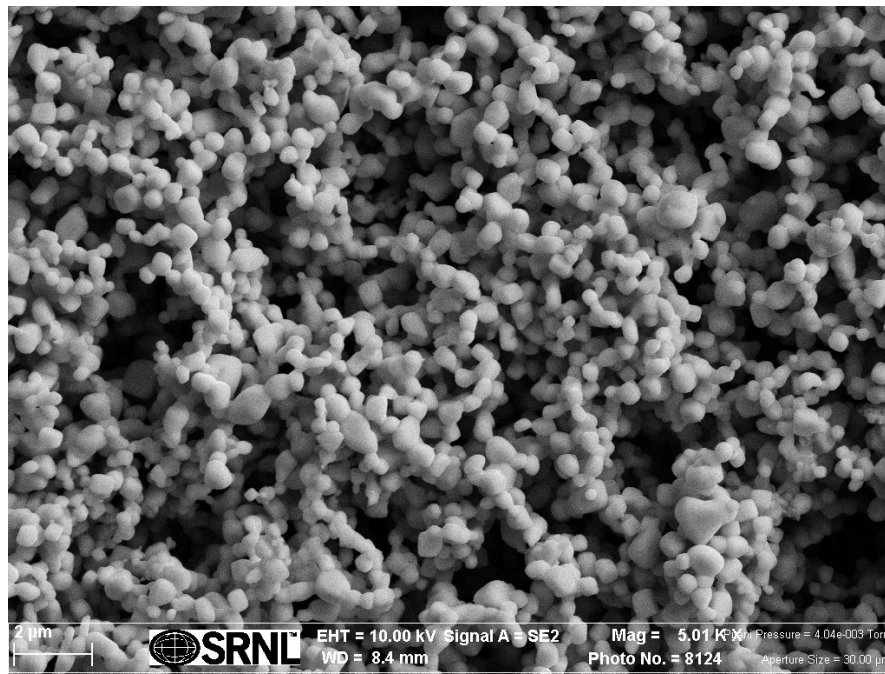


Figure 10. Sample B SEM analysis (NaCl solution and AgNO₃ washed with HNO₃).

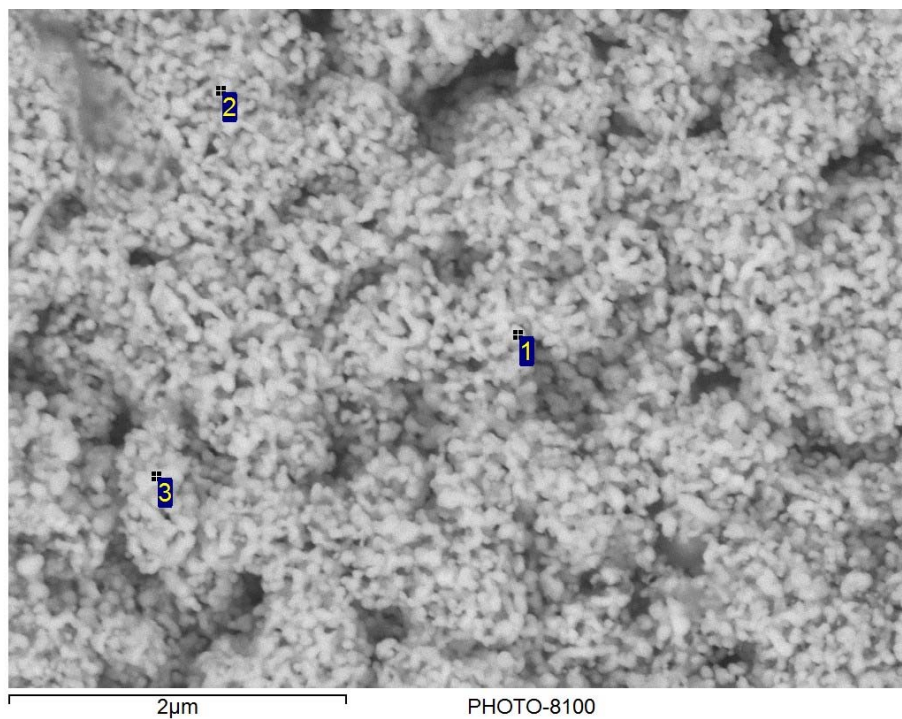


Figure 11. Sample B EDS analysis #1.

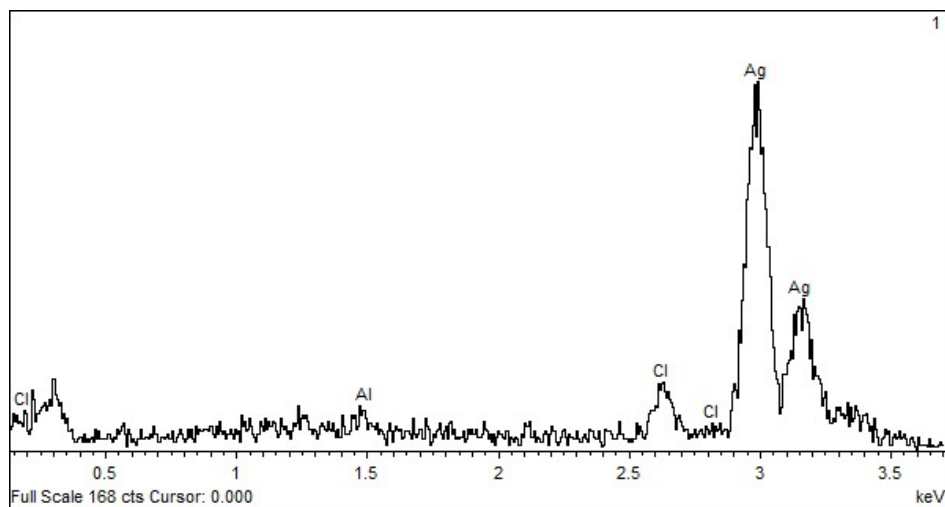


Figure 12. EDS #1 Sample B – Position 1 analysis.

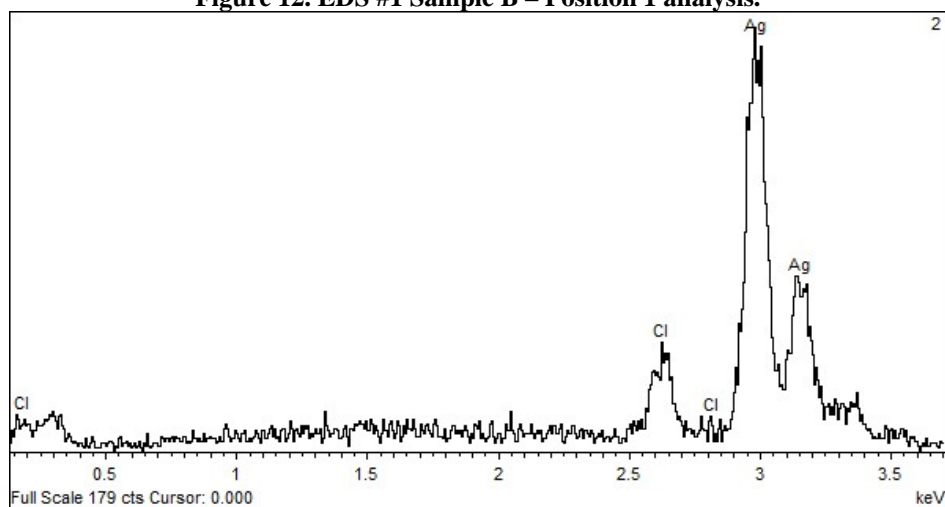


Figure 13. EDS #1 Sample B – Position 2 analysis.

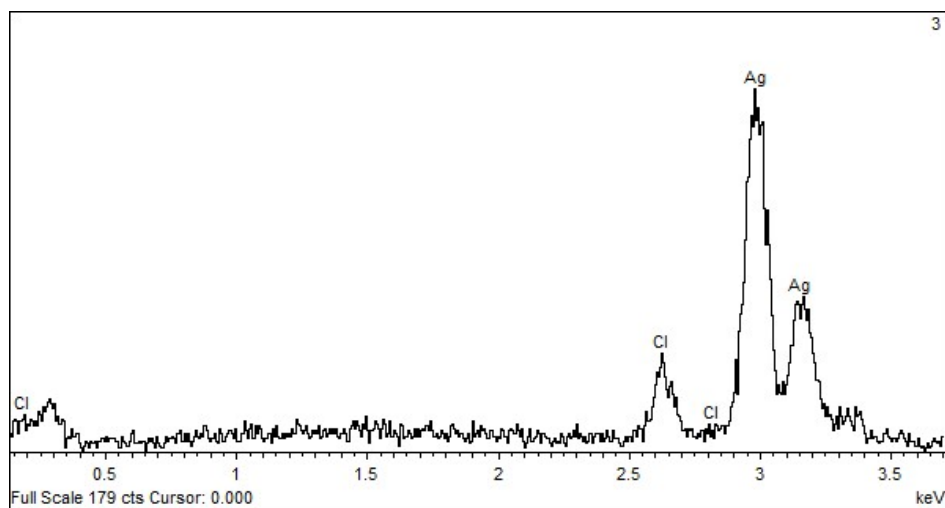


Figure 14. EDS #1 Sample B – Position 3 analysis.

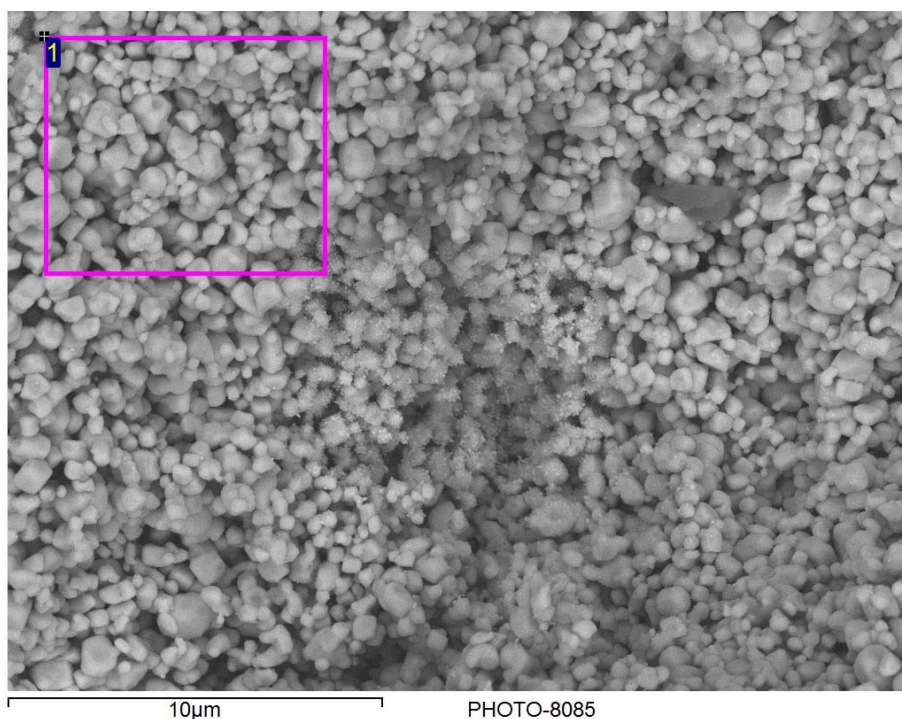


Figure 15. Sample B EDS analysis #2.

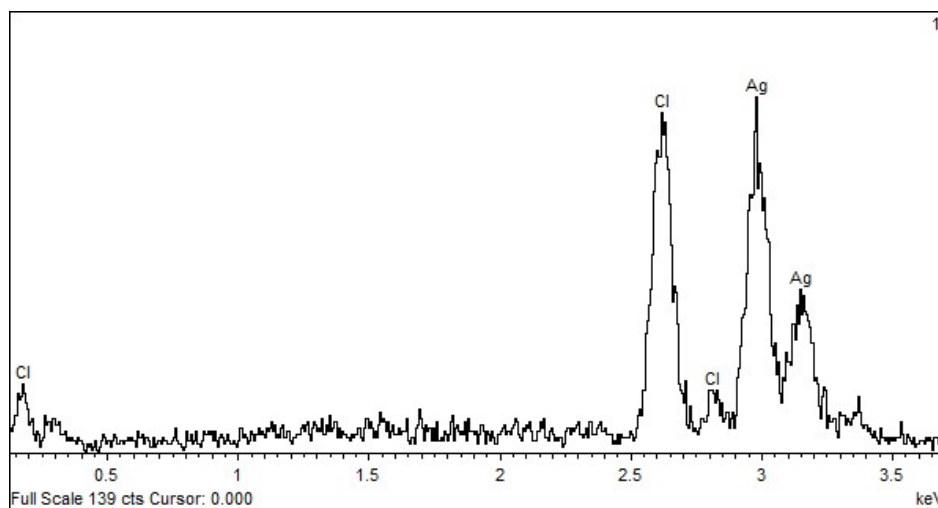


Figure 16. EDS #2 Sample B – Position 1 analysis.

Sample C

Sample C particles were synthesized from the artificial groundwater solution (low iodide), AgNO_3 solution, and washed with DI water. SEM images revealed that Sample C particles were mostly amorphous; however, the sample also contained many large crystalline particles (Figure 17). The amorphous and crystalline particles ranged in diameter from about 0.5 μm to 2 μm , respectively. EDS analysis of the Sample C particles was done at low magnification and therefore did not cause the particles to undergo photodecomposition (Figure 18). The EDS analysis also displayed peaks for Cl^- and Ag^+ in the range between 2.5 to 3.5 keV (Figure 19, Figure 20, and Figure 21).

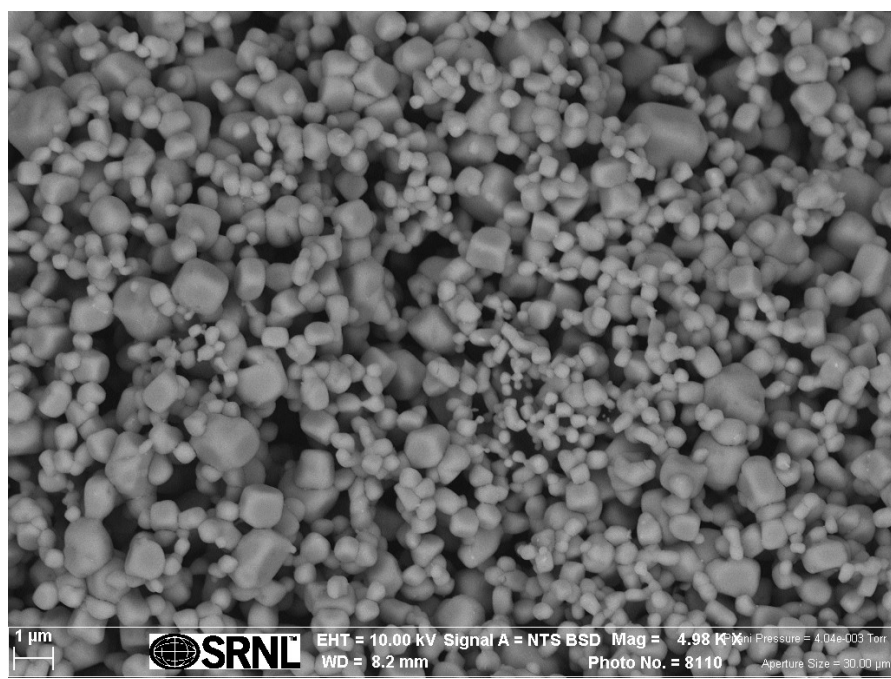


Figure 17. Sample C SEM analysis (Artificial groundwater solution (low iodide) and AgNO_3 washed with DI water).

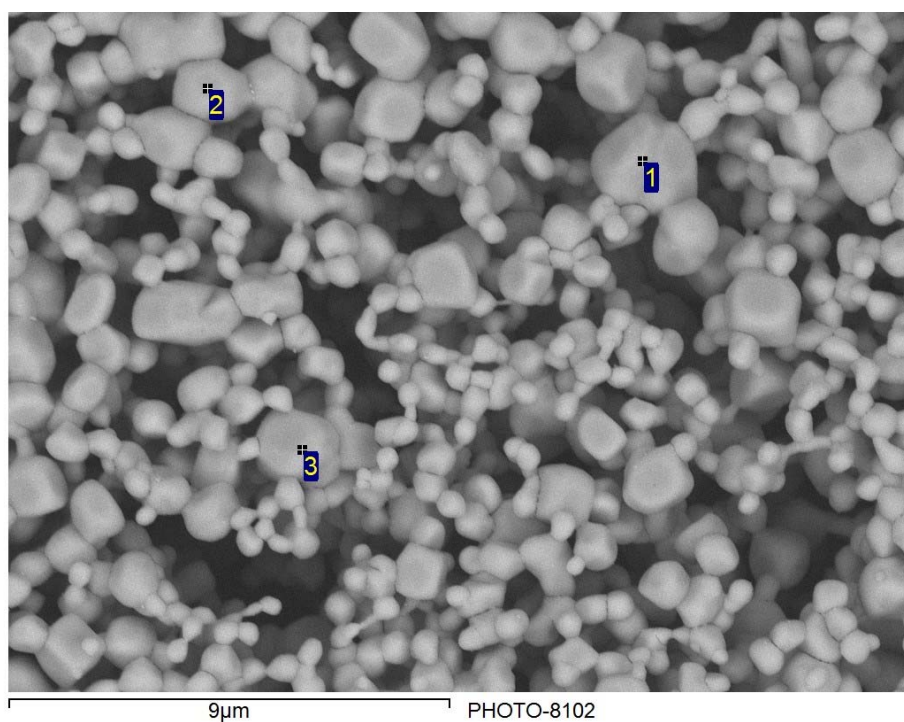


Figure 18. Sample C EDS analysis.

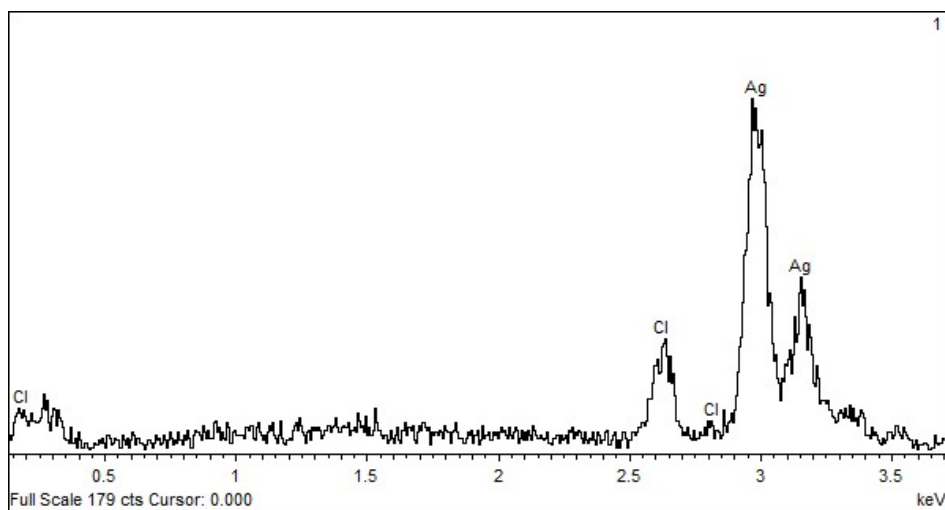


Figure 19. EDS Sample C – Position 1 analysis.

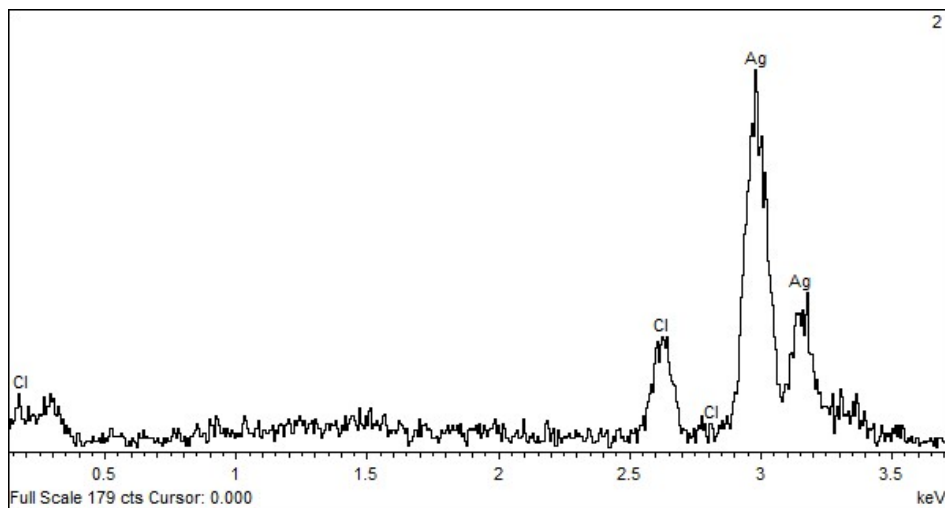


Figure 20. EDS Sample C – Position 2 analysis.

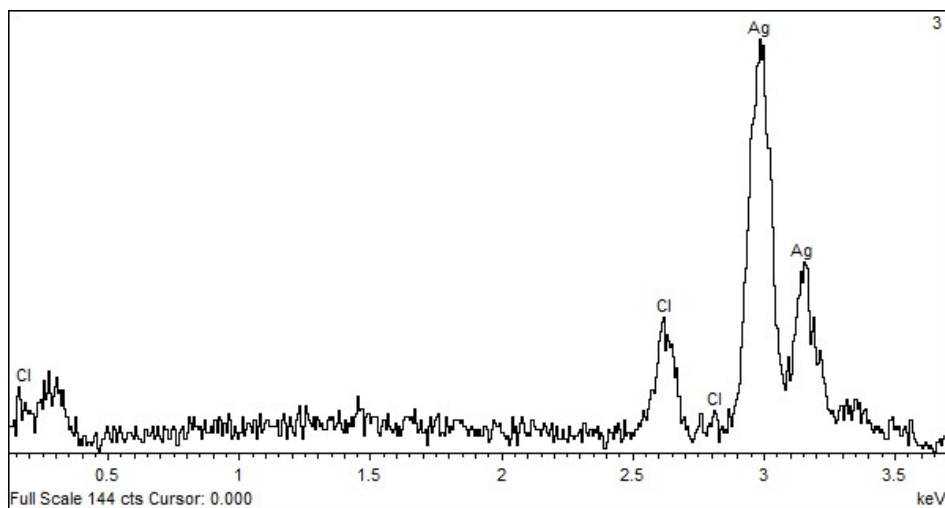


Figure 21. EDS Sample C – Position 3 analysis.

Sample D

Sample D Particles were created from the artificial groundwater solution (low iodide), AgNO_3 solution, and washed with HNO_3 acid. SEM images showed that Sample D particles were mostly large crystalline particles whose diameter averaged at about $2\ \mu\text{m}$ (Figure 22). EDS analysis of the Sample D particles was done at low magnification and therefore did not cause the particles to undergo photodecomposition (Figure 23). The EDS analysis also displayed peaks for Cl^- and Ag^+ in the range between 2.5 to 3.5 keV (Figure 24, Figure 25, and Figure 26).

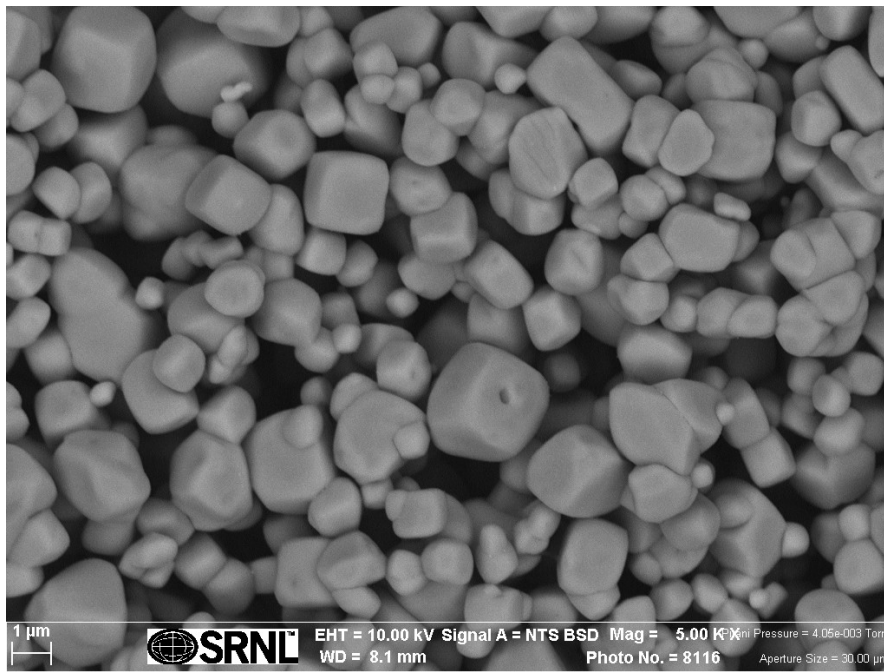


Figure 22. Sample D SEM analysis (Artificial groundwater solution (low iodide) and AgNO_3 washed with HNO_3).

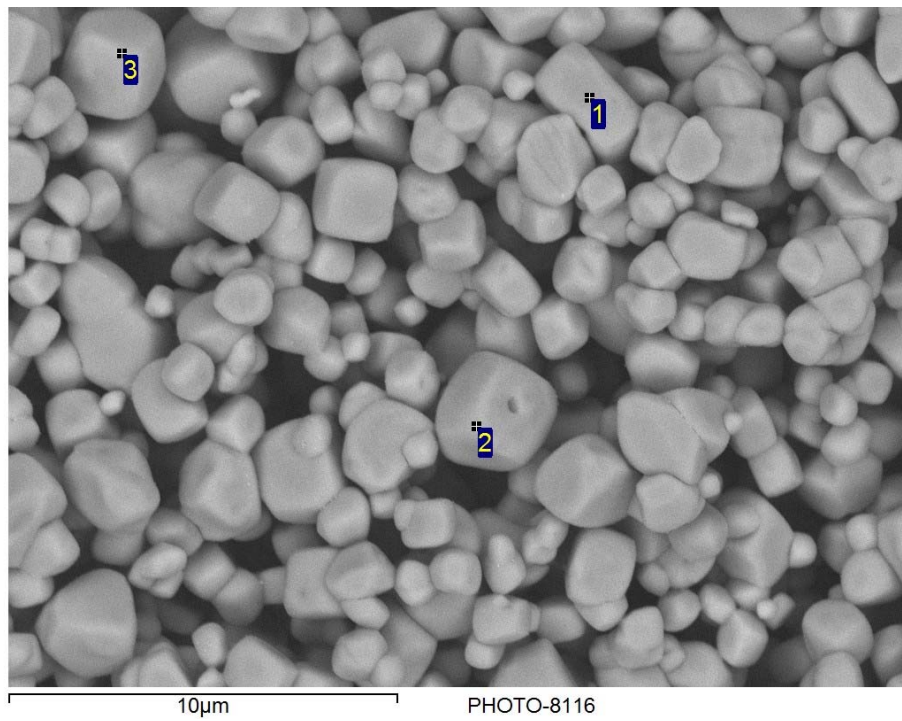


Figure 23. Sample D EDS analysis.

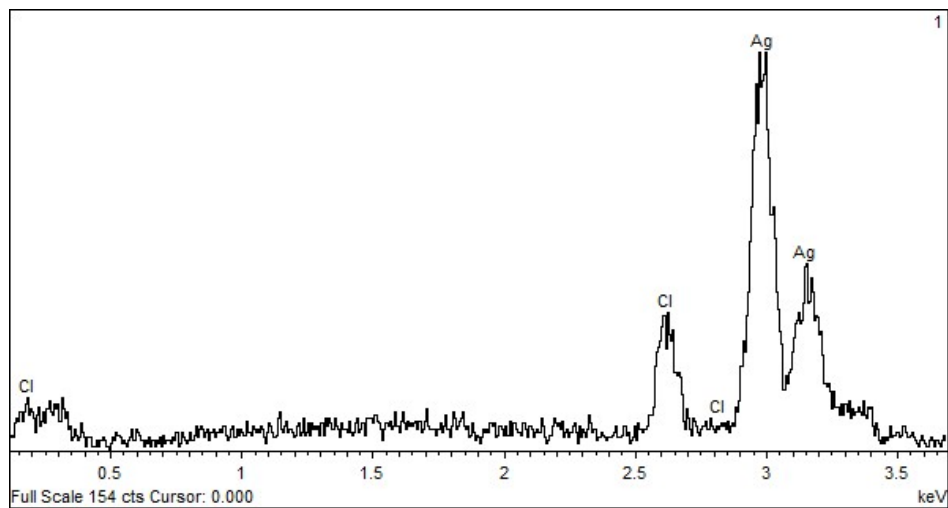


Figure 24. EDS Sample D – Position 1 analysis.

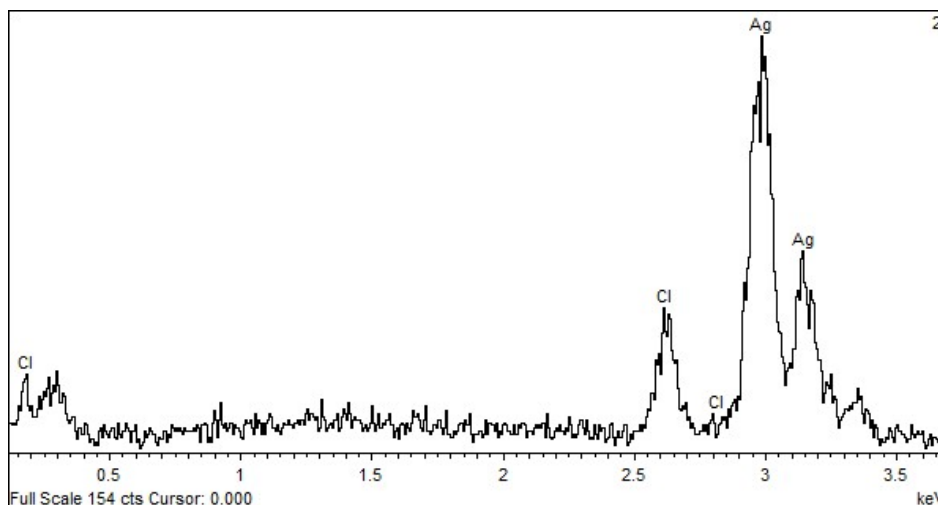


Figure 25. EDS Sample D – Position 2 analysis.

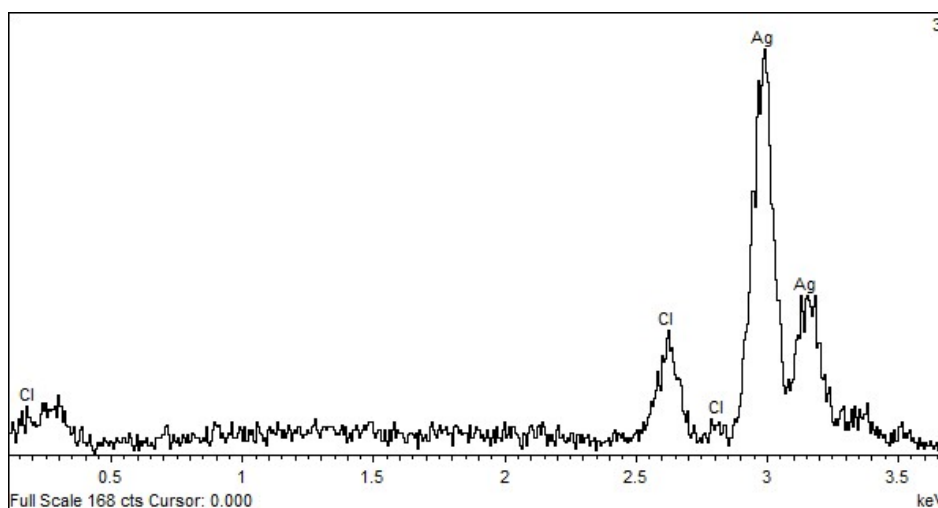


Figure 26. EDS Sample D – Position 3 analysis.

Sample E.

Sample E particles were created from the artificial groundwater solution (high iodide), AgNO_3 solution, and washed with DI water. SEM images revealed that Sample E particles were mostly small and amorphous, though the sample also contained a considerable portion of large crystalline particles (Figure 27). The amorphous and crystalline particles ranged in diameter from about 0.5 μm to 1.5 μm , respectively. It is noted that the particles are very densely clustered together in Sample E. EDS analysis of the Sample E particles was done at low magnification and therefore did not cause the particles to undergo photodecomposition. In the same figure it was also observed that the distribution of the small amorphous and larger crystalline particles can be seen (Figure 28). The EDS analysis displayed large peaks for Cl^- and Ag^+ in the range between 2.5 to 3.5 keV for all the positions analyzed (Figure 29, Figure 30, and Figure 31).

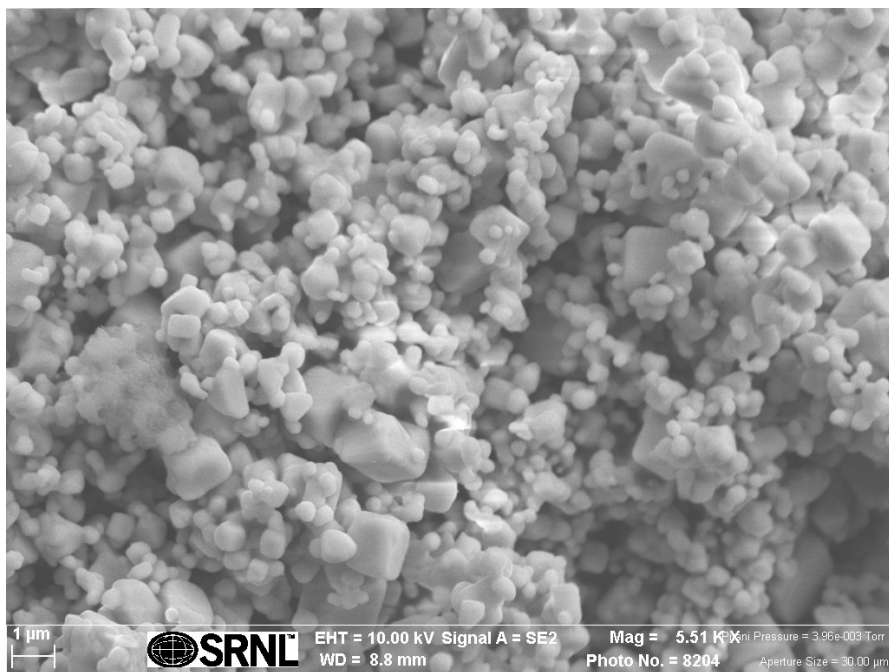


Figure 27. Sample E SEM analysis (Artificial groundwater solution (high iodide) and AgNO_3 washed with DI water).

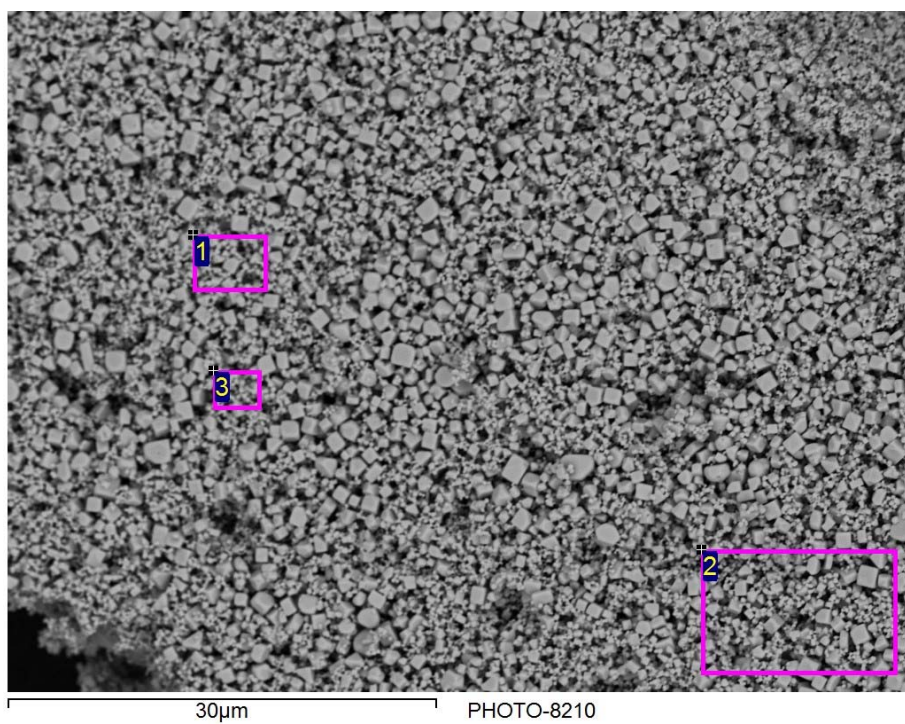
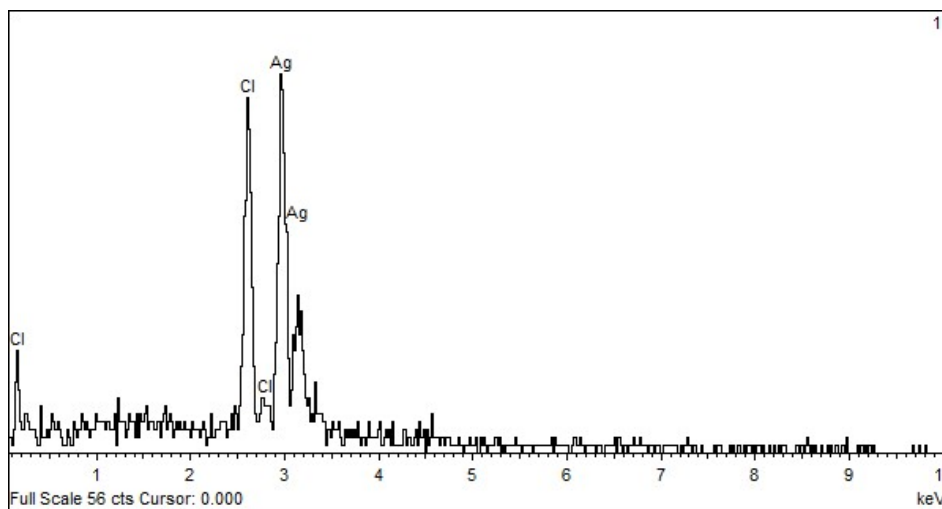
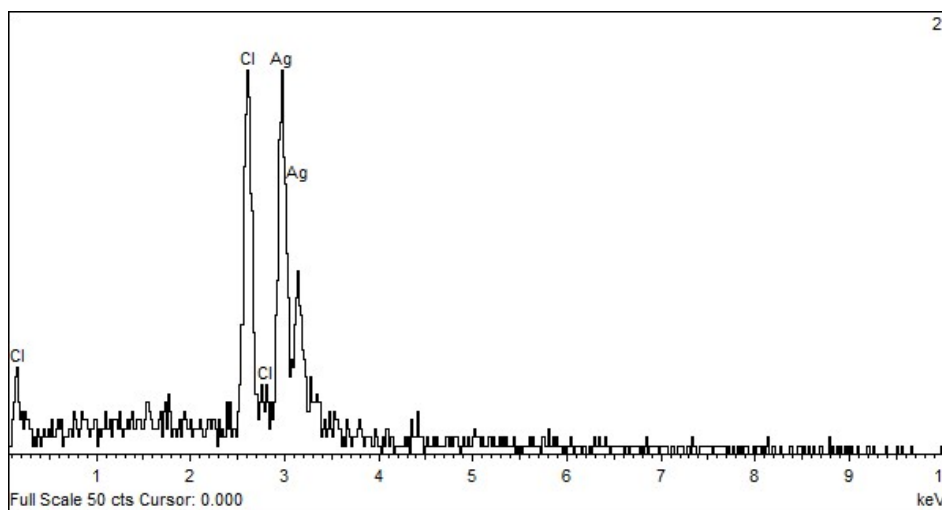
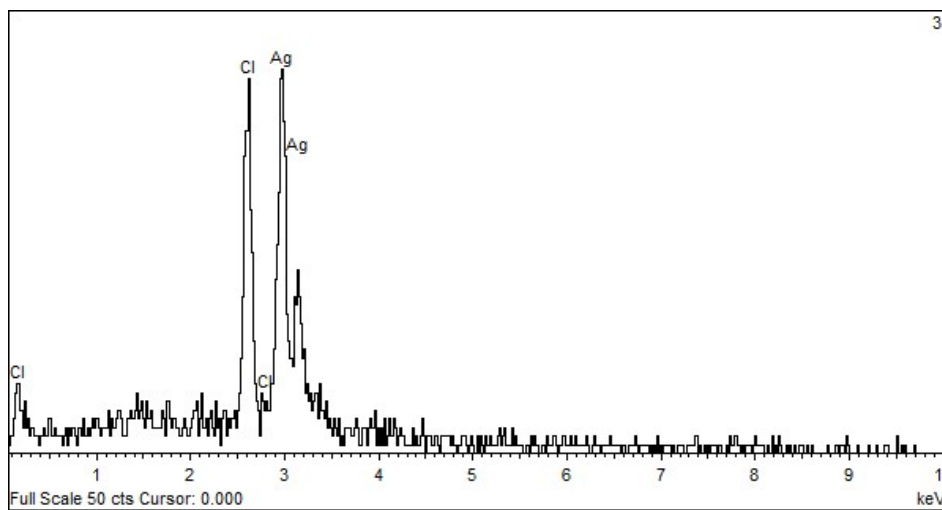


Figure 28. Sample E EDS analysis.

**Figure 29. EDS Sample E – Position 1 analysis.****Figure 30. EDS Sample E – Position 2 analysis.****Figure 31. EDS Sample E – Position 3 analysis.**

Sample F

The Sample F particles were created from the artificial groundwater solution (high iodide) and AgNO_3 washed with HNO_3 acid. The SEM images revealed particles that were mostly small and amorphous with some slightly larger crystalline particles scattered throughout (Figure 32). The amorphous and crystalline particles ranged in diameter from about $0.5\ \mu\text{m}$ to $1\ \mu\text{m}$, respectively. EDS analysis of the Sample F particles was done at low magnification and therefore did not cause the particles to undergo photodecomposition. In the same figure, it was also observed that the particles were loosely packed and contained large spaces between particle clusters (Figure 33). The EDS analysis displayed large peaks for Cl^- and Ag^+ in the range between 2.5 to 3.5 keV for all the positions analyzed. The three EDS graphs for Sample F also recorded peaks for Cl^- and Ag^+ in between 0 to 0.4 keV (Figure 34, Figure 35, and Figure 36). This range contained only small Cl^- peaks for Samples A through E.

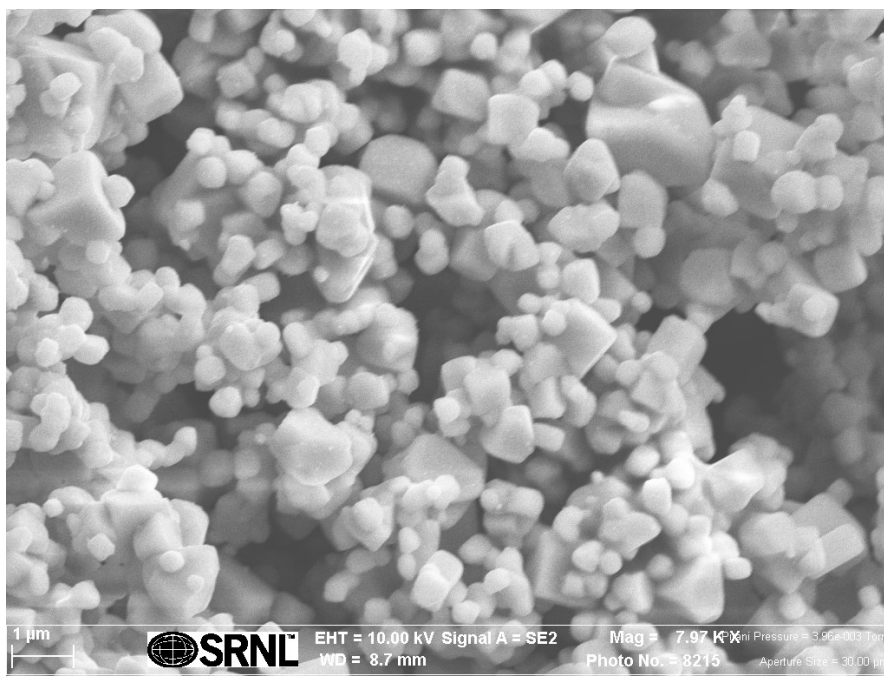


Figure 32. Sample F SEM analysis (Artificial groundwater solution (high iodide) and AgNO_3 washed with HNO_3).

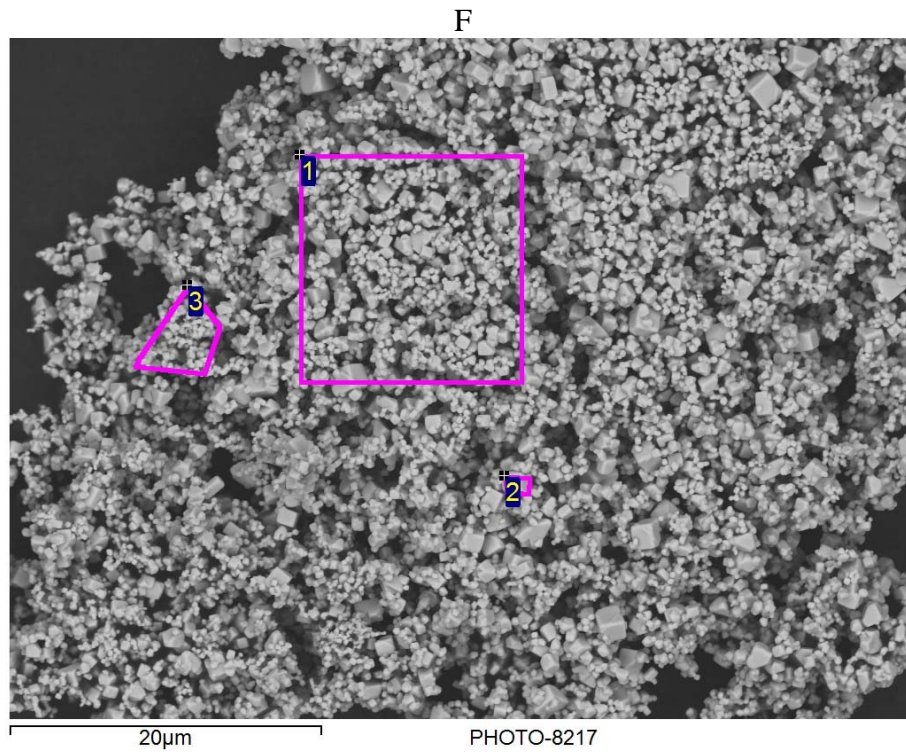


Figure 33. Sample F EDS analysis.

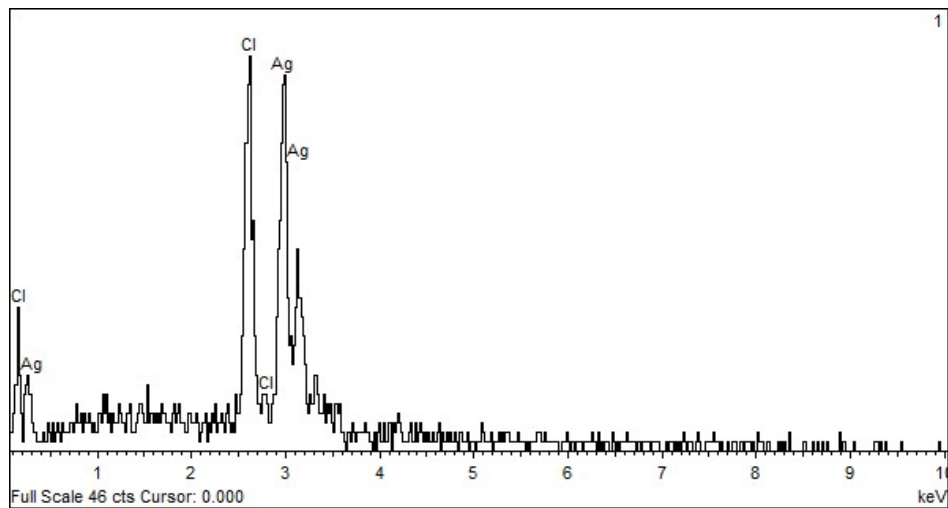


Figure 34. EDS Sample F – Position 1 analysis.

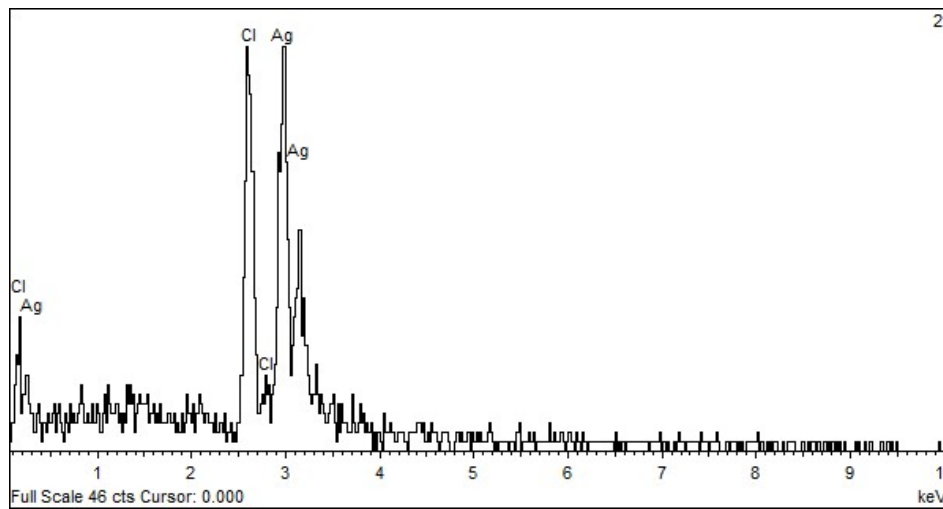


Figure 35. EDS Sample F – Position 2 analysis.

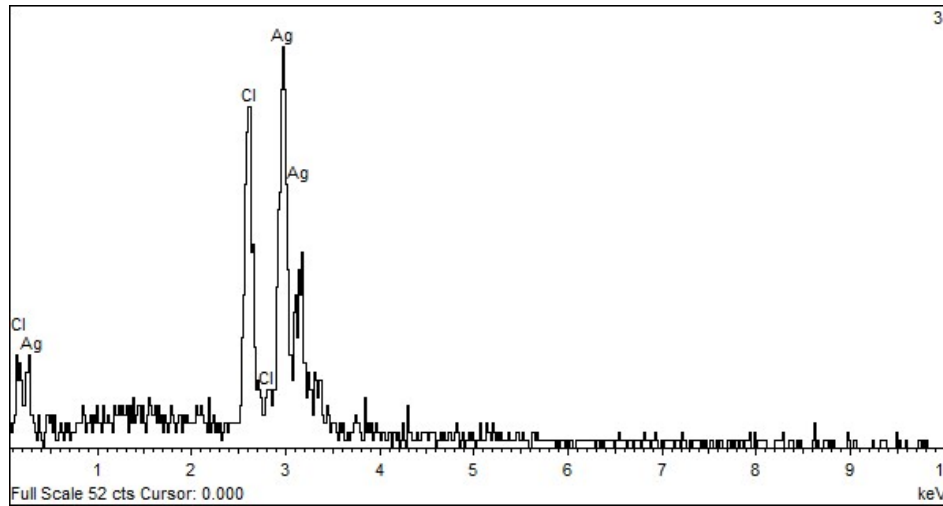


Figure 36. EDS Sample F – Position 3 analysis.

Titration with AgCl and Iodine

Two separate titrations were conducted using commercially produced AgCl for Titration 1 and AgCl produced in the lab for Titration 2. The main objective of the titrations was to determine how the AgCl particles reacted with I^- and to determine the rate limiting step of the reaction. The titrations revealed that the commercially produced and lab-produced particles may react differently with I^- due to the variation in particle size. The titrations also showed that the rate limiting step of the reaction was dependent on the dissolution of AgCl.

Titration 1 – Commercially Produced AgCl

Calibration of Iodine Probe

The iodine probe required a five point calibration to achieve a slope between -52 to -59. The standards were prepared at 0.05, 0.1, 0.5, 1, 10, and 50 mg/L from a 1000 mg/L iodine solution and readings in mV were recorded in **Error! Reference source not found.** in Appendix A and in Figure 37.

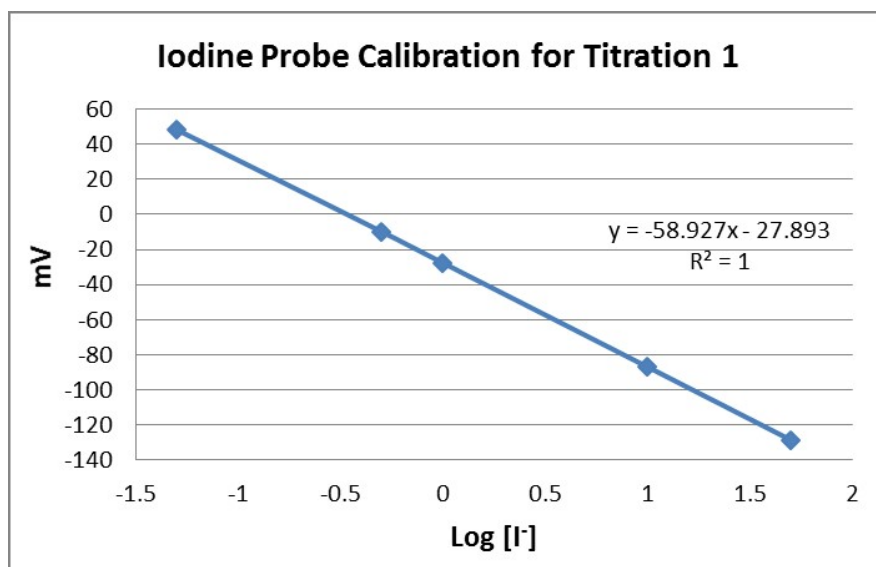


Figure 37. Titration 1 iodine probe calibration curve.

Titration 1 Results

Results from Titration 1 using the commercially produced AgCl indicated that there was indeed a rate limiting step in the reaction that would need to be determined. The titrant used was a 100 mg/L iodine solution and was pipetted into the beaker in 50 μ L spikes. As the NaI was added to the beaker the concentration I^- remained fairly constant at nearly 0 mg/L until spike 4 at which the concentration began to steadily increase. This indicated that the AgCl particles were no longer reacting with I^- . Two more spikes were added to confirm the increasing I^- concentration before the titration was stopped at an I^- concentration of 0.221 mg/L. After leaving the beaker overnight, the I^- concentration dropped to 4.96×10^{-6} mg/L indicating that the reaction was limited by an unknown factor. The titration was continued and at spike 17 the reaction was

stopped with a concentration of I^- at 0.279 mg/L. As seen on the previous day the concentration of I^- again dropped and was measured the next day at 9.89×10^{-6} mg/L. The results of Titration 1 can be found in **Error! Reference source not found.** in Appendix A and in Figure 38 Below. After the reading at spike 18 it was decided that the particles formed in the beaker would be taken for SEM/EDS analysis to determine their composition.

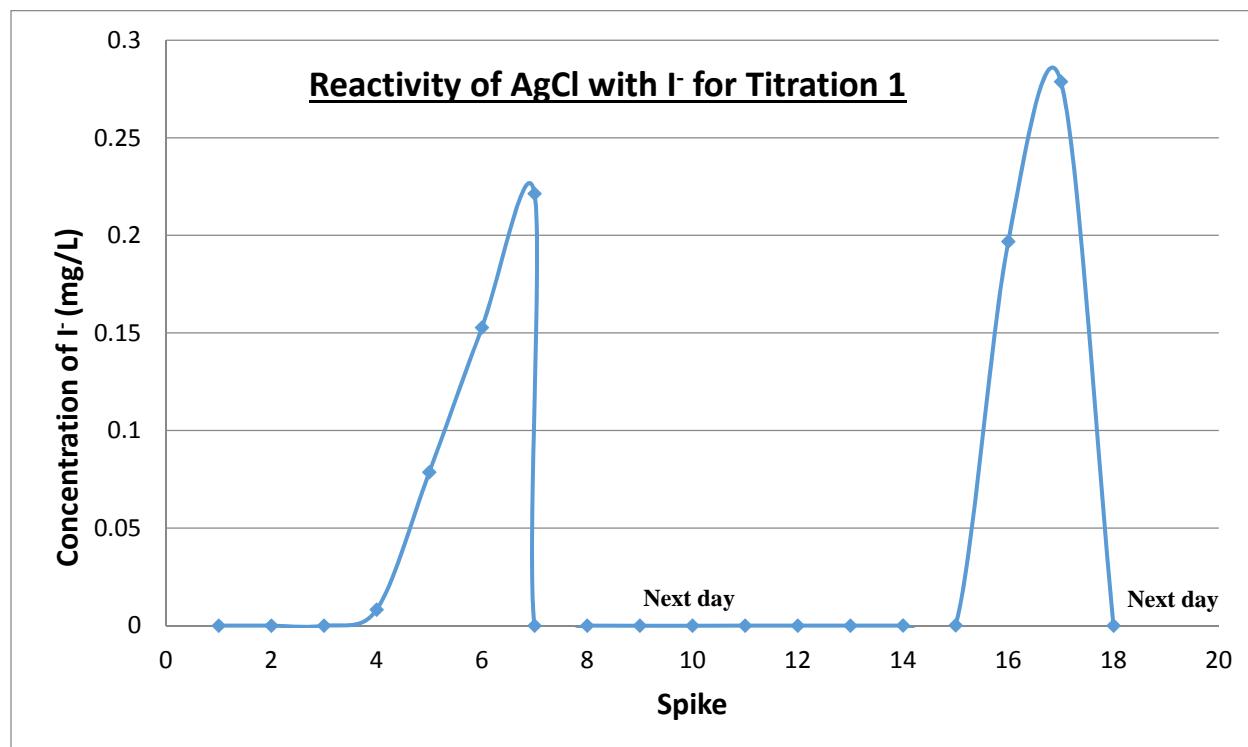


Figure 38. Titration 1 results.

Titration 2 – Lab Produced AgCl

Calibration of Iodine Probe

The iodine probe required a five point calibration to achieve a slope between -52 to -59. The standards were prepared at 0.05, 0.1, 0.5, 1, 10, and 50 mg/L from a 1000 mg/L iodine solution and readings in mV were recorded in **Error! Reference source not found.** in Appendix A and in Figure 39.

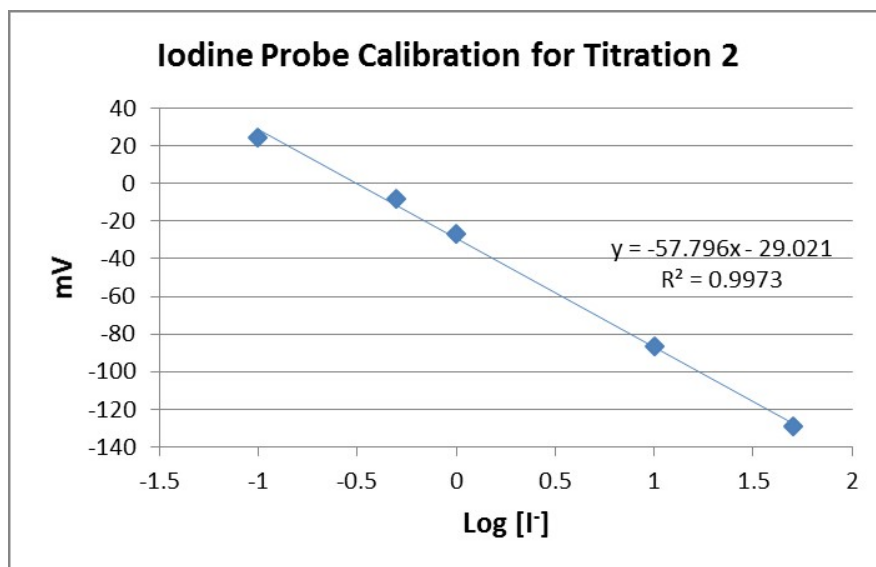


Figure 39. Titration 2 iodine probe calibration curve.

Titration 2 Results

Results from Titration 2 using the lab produced AgCl also indicated that there is a rate limiting step in the reaction. The lab-produced particles were smaller in size than those used in Titration 1 as shown in the SEM/EDS section on Page 35. The titration began using a 10 mg/L iodine solution added to the beaker in 50 μ L spikes and was stopped at spike 35 with an I⁻ concentration of 0.007 mg/L. A few hours later the concentration was read at 2.53×10^{-8} mg/L and the titration began again, but now using a 100 mg/L iodine solution in 10 μ L spikes. At spike 58 the titration was stopped at an I⁻ concentration of 0.133 mg/L and was found the next day to be 1.46×10^{-5} mg/L. At spike 77 the concentration was found to be 0.0367 mg/L and was measured two days later at 8.51×10^{-6} mg/L. The results of Titration 2 can be found in **Error! Reference source not found.** in Appendix A and in Figure 40.

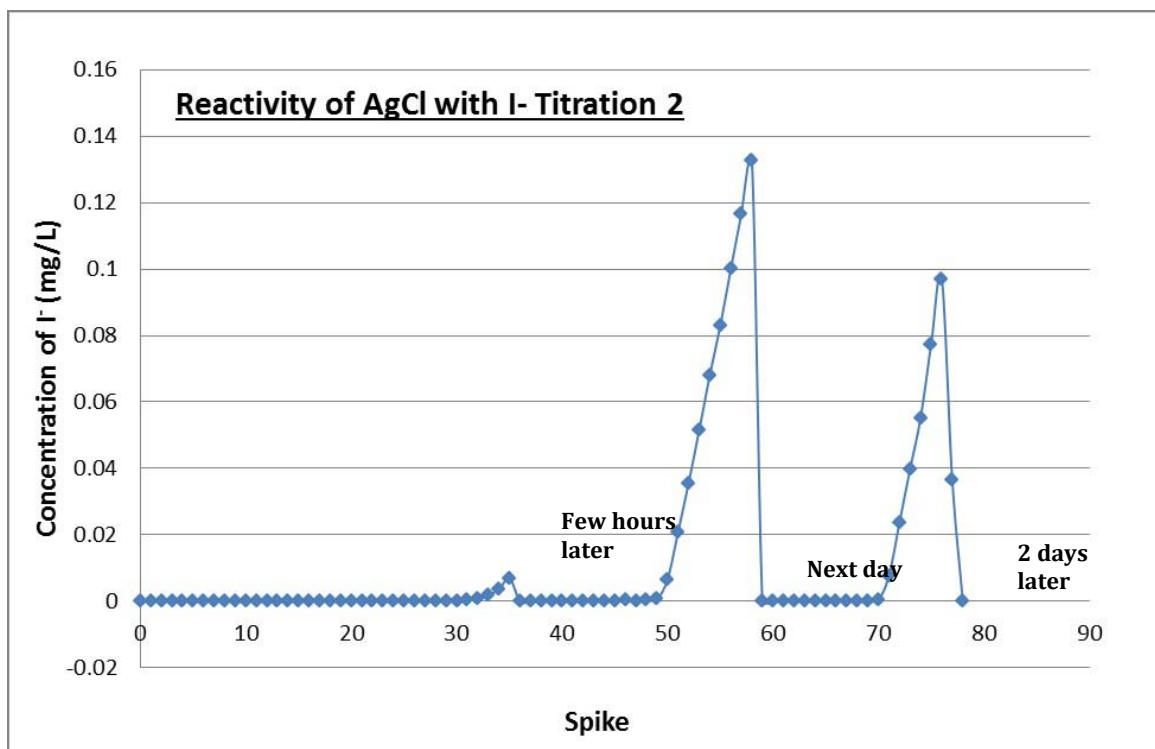


Figure 40. Titration 2 results.

The amount of iodine needed to react with the entire AgCl particle sample was determined based on the following calculations and a one-to-one stoichiometric ratio:

- MW of AgCl = 143.32 g/mol
- MW of I⁻ = 127 g/mol
- $1.1 \text{ mg AgCl} \div 1000 \text{ mg/g} \div 143.32 \text{ g/mol} = 7.67 \times 10^{-6} \text{ moles of AgCl}$
- Mass of I⁻ needed to react stoichiometrically = $7.67 \times 10^{-6} \text{ moles of AgCl} \times 127 \text{ g/mol} = 0.975 \text{ mg I}^-$

It is believed that the surface area of the particles had likely already finished reacting at spike 24 when the graph just begins to break as seen in Figure 41, which compares the differences in iodine concentrations vs spike number. By spike 77 the amount of iodine added to the AgCl sample was 0.214 mg (**Error! Reference source not found.**) which accounts for about 22% of the 0.975 mg of I⁻ needed to react the entire particle. It was decided that the surface area of the particles would not be able to account for all of the iodine reacted and that the reaction was not reacting solely on the surface of the particles.

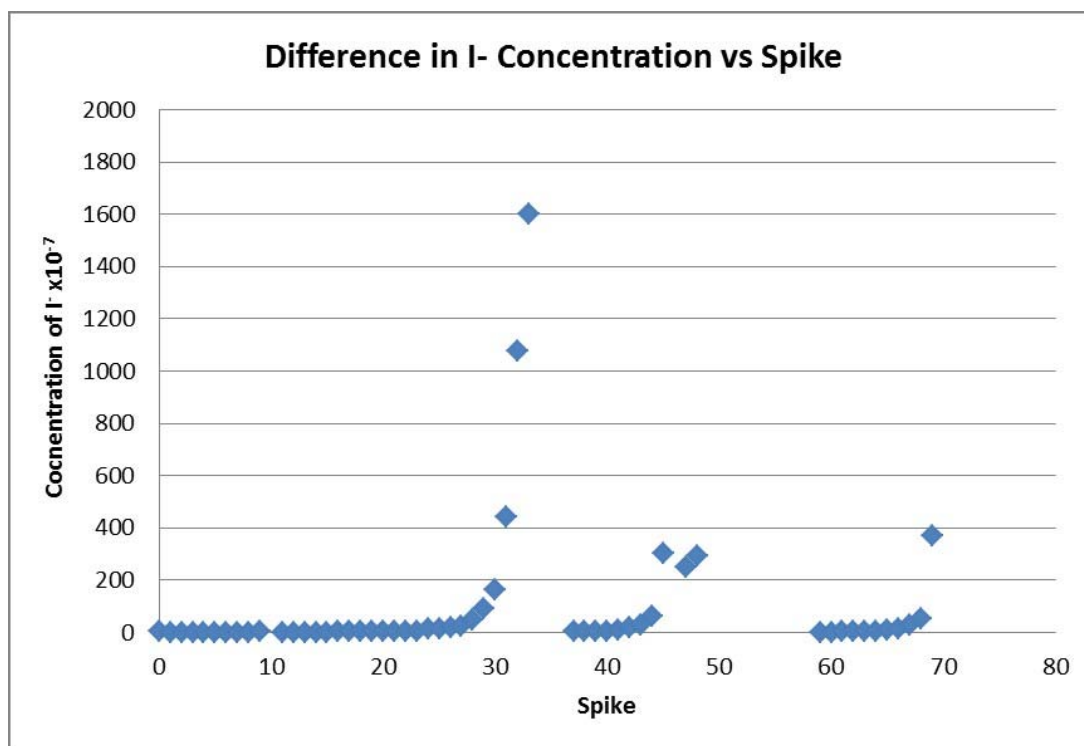


Figure 41. Titration 2- Differences in I⁻ concentration per spike.

SEM/EDS Data for the titrations of AgCl and I⁻

The AgCl particles used in Titrations 1 and 2 (Table 2) were analyzed via SEM before the titrations to find any differences. It was found that the Sample H particles used in Titration 1 had a larger diameter than the Sample G particles used in Titration 2. Sample G particles had an average diameter of 3 μm while those used in Sample H had diameters of 1 μm and smaller (Figure 42). The difference in particle size could likely play a role in the reaction with I⁻. A larger fraction of surface area was also lost by fusion of particles to one another in the commercial AgCl. It was found through SEM that the rate limiting step of the reaction was most likely the dissolution of Ag⁺ from the AgCl particle. Rather than the AgCl particle being coated by AgI particles through ion exchange or precipitation of colloidal-sized AgI particles fused to the AgCl particle, it appears that what actually happens is that the the AgCl first dissolves into its constituent elements Ag⁺ and Cl⁻ at which point the I⁻ reacts with the Ag⁺ to form the AgI particle separately from the AgCl particle. In theory the smaller lab-produced AgCl particles (Sample H) should be able to dissolve Ag⁺ at a faster rate than the larger commercially produced particles due to their greater specific surface area. If this is true then the sample H particles should also be able to react with the I⁻ at a faster rate than those in Sample G.

Table 2. AgCl Particle Composition for Titrations

Sample ID	Sample Composition
G	Particles from Titration 1 with commercial AgCl
H	Particles from Titration 2 with lab-made AgCl

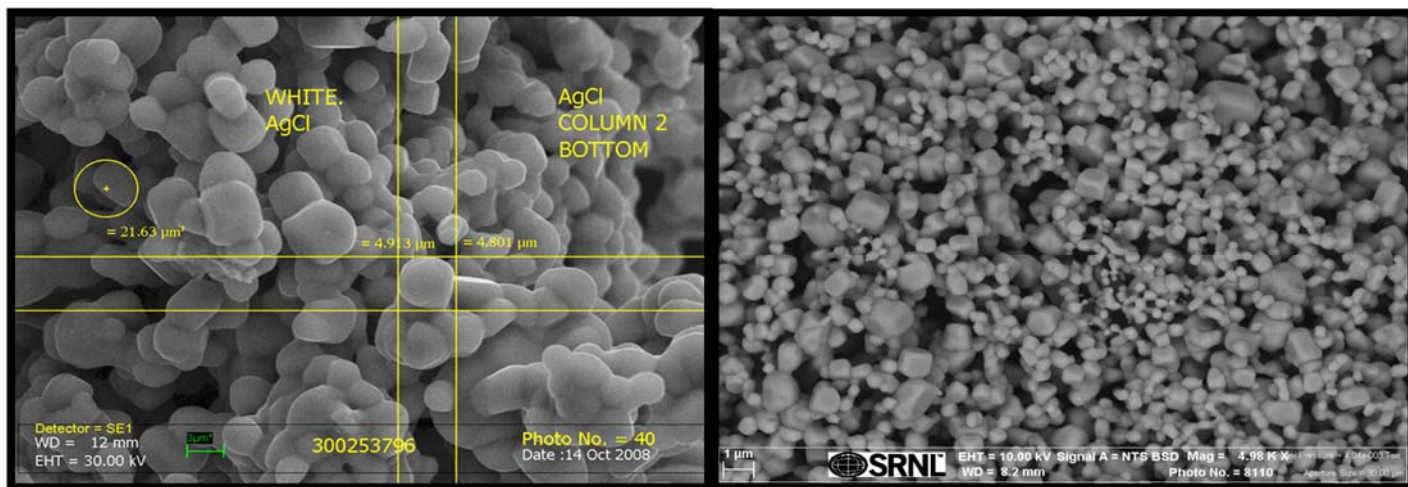


Figure 42. Sample G (left) and Sample H (right) SEM images.

Titration 1, Sample G

SEM/EDS analysis on the particles created in Titration 1 displayed fused masses of AgCl particles with AgI crystals growing on their surfaces (Figure 43). The first EDS analysis in Figure 44 displays this growth pattern. It is seen in that EDS of the first position (located on the large mass) was recorded as AgCl and had Ag⁺ and Cl⁻ peaks mostly in the range of 2.5 to 3.5 keV with no I- peaks detected (Figure 45). In position 2 which is located on the polyp-like growth forming on the surface of the mass there are readings for iodine in the range of 3.7 to 5 keV suggesting that these are AgI particles (Figure 46). In the second EDS in Figure 47, the polyp-like growths and euhedral crystals to the right are both analyzed and both display Ag⁺ peaks beginning around 3 keV and I peaks beginning around 3.8 keV. The euhedral crystals to the right are the form taken by the AgI after the polyp-like stage seen on the left (Figure 48 and Figure 49).

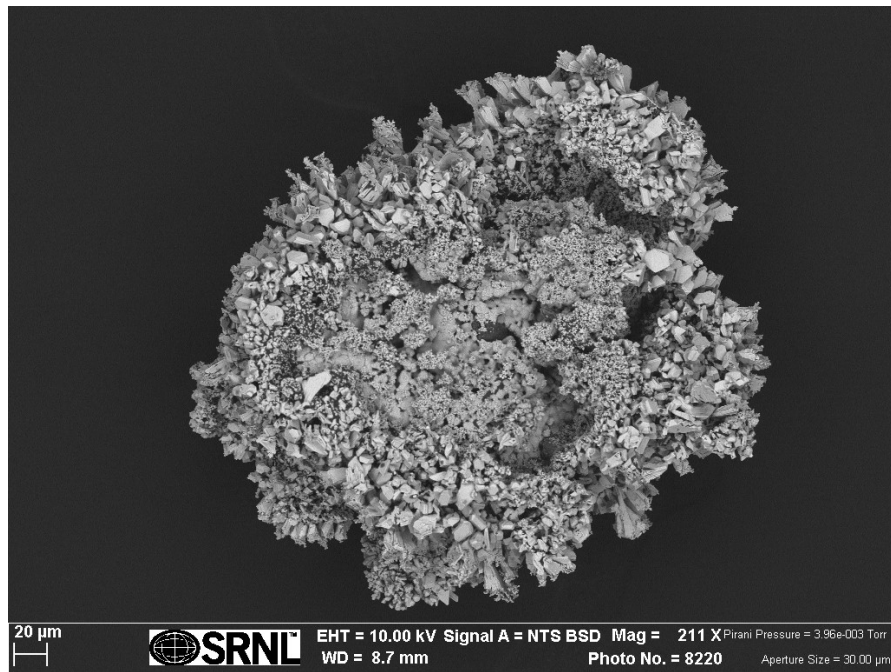


Figure 43. Sample G SEM analysis (commercially produced AgCl).

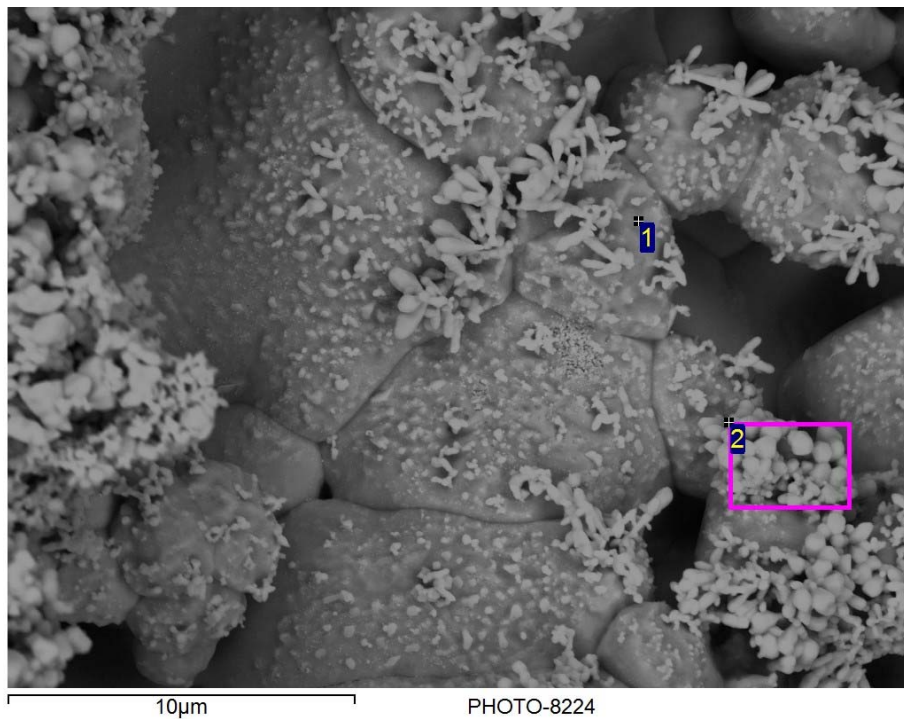


Figure 44. Sample G EDS analysis #1.

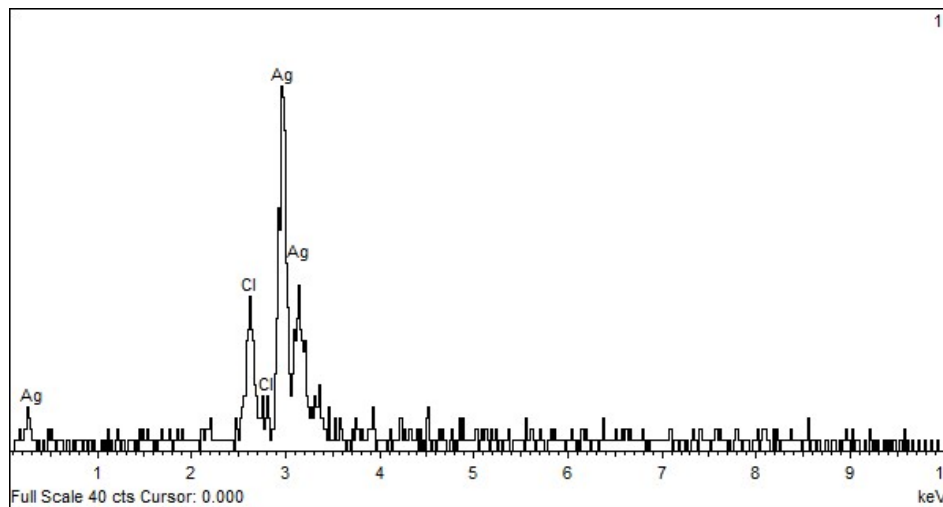


Figure 45. EDS #1 Sample G – Position 1 analysis.

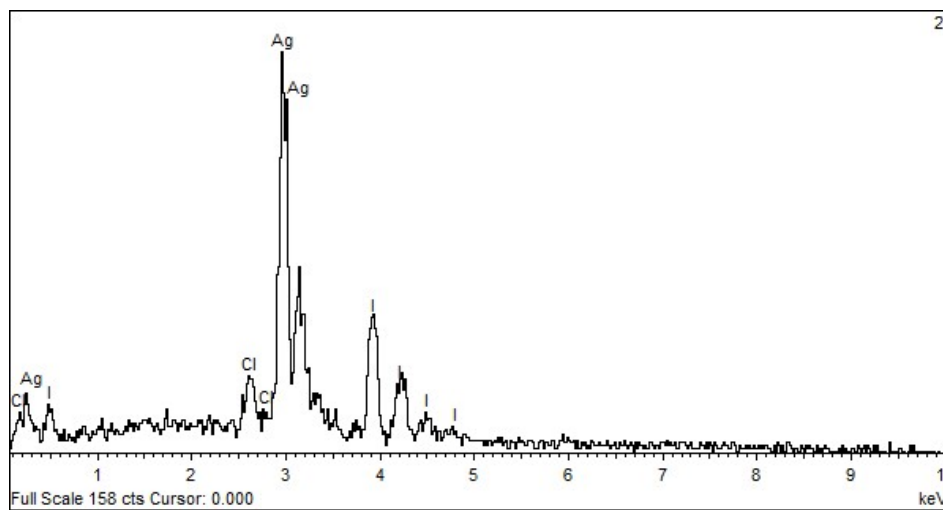


Figure 46. EDS #1 Sample G – Position 2 analysis.

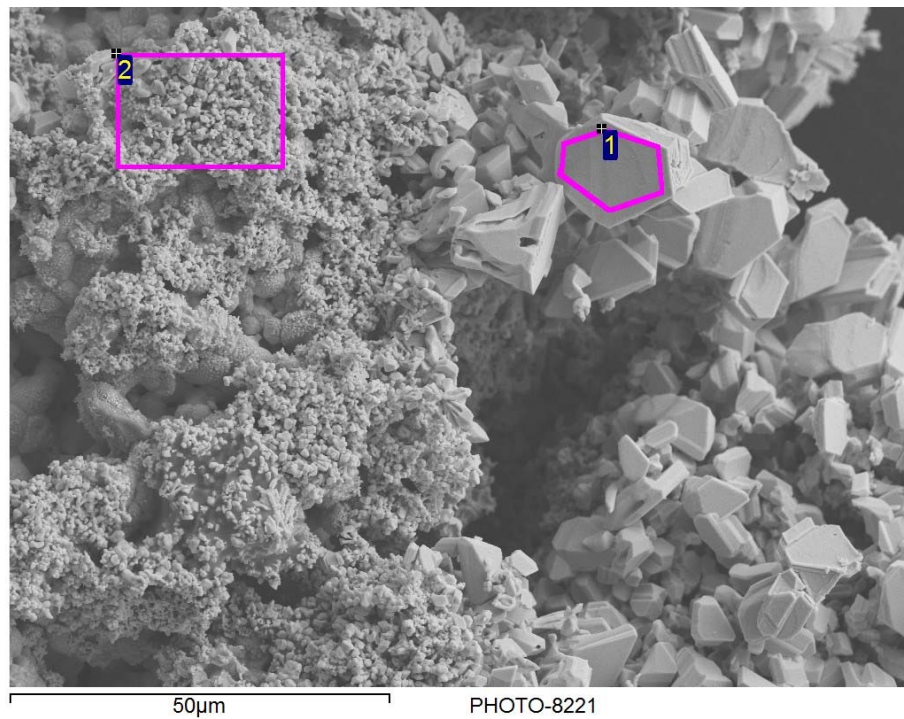


Figure 47. Sample G EDS analysis #2.

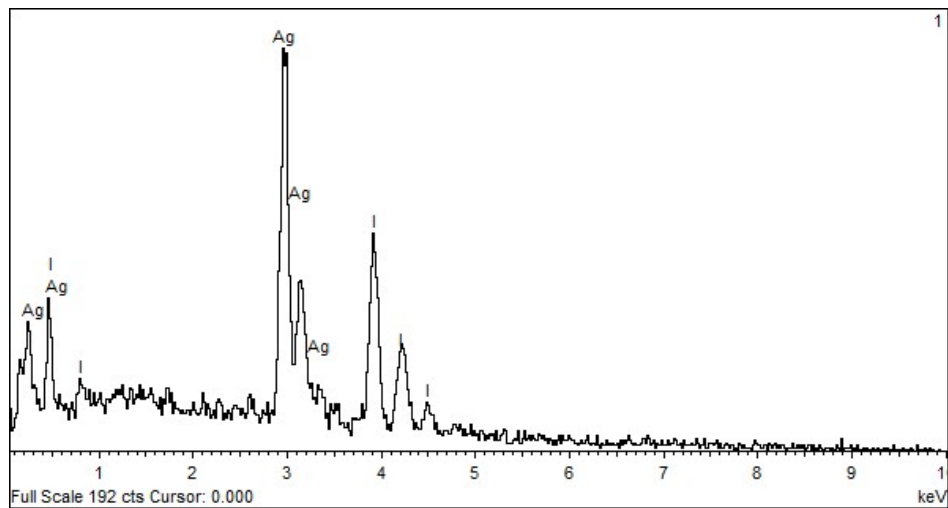


Figure 48. EDS #2 Sample G – Position 1 analysis.

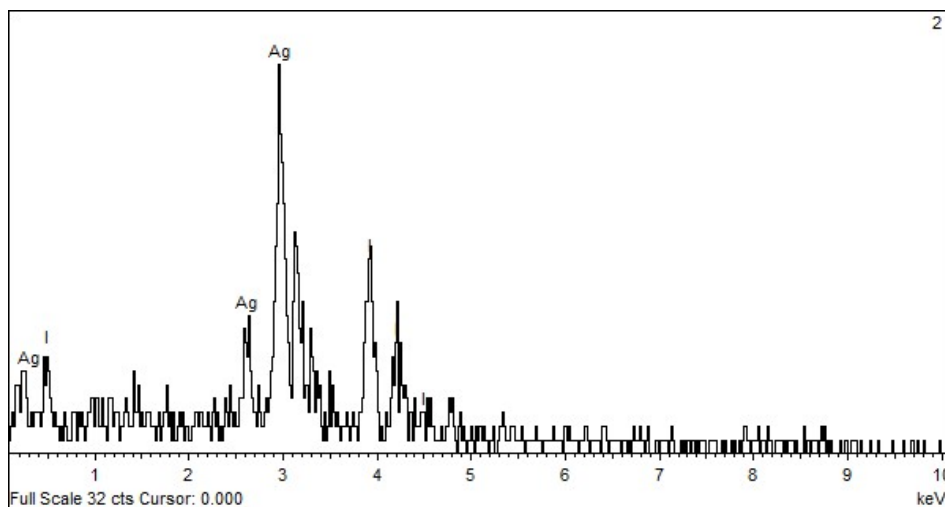


Figure 49. EDS #2 Sample G – Position 2 analysis.

Titration 2, Sample H

SEM/EDS analysis on Sample H exhibited similar results to Sample G. The AgI particles in their euhedral crystalline form can be seen in Figure 50. It was also observed that there are fine-grained AgCl particles in between the crystals. The EDS analysis shows that in position 1, located on the fine-grained particles, the highest peaks are recorded in the range for Ag^+ and Cl^- between 2.5 to 3.5 keV (Figure 51 and Figure 52). In position 2 the larger euhedral crystal particle displays its highest peaks as Ag^+ and I^- beginning at 2.8 keV and ending at 5 keV (Figure 51 and Figure 53).



Figure 50. Sample H SEM analysis (lab produced AgCl).

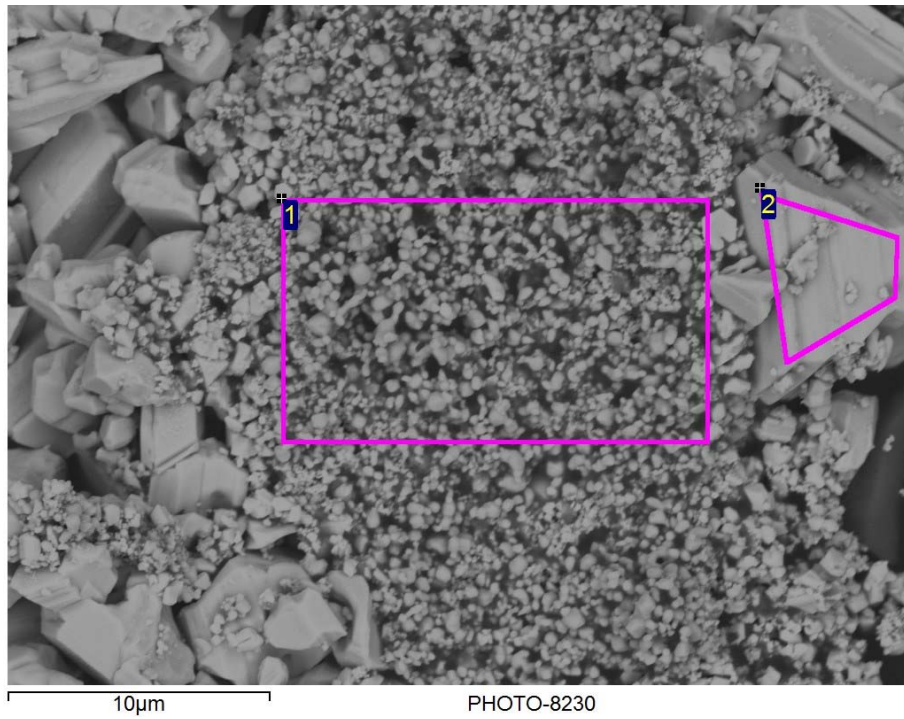


Figure 51. Sample H EDS analysis.

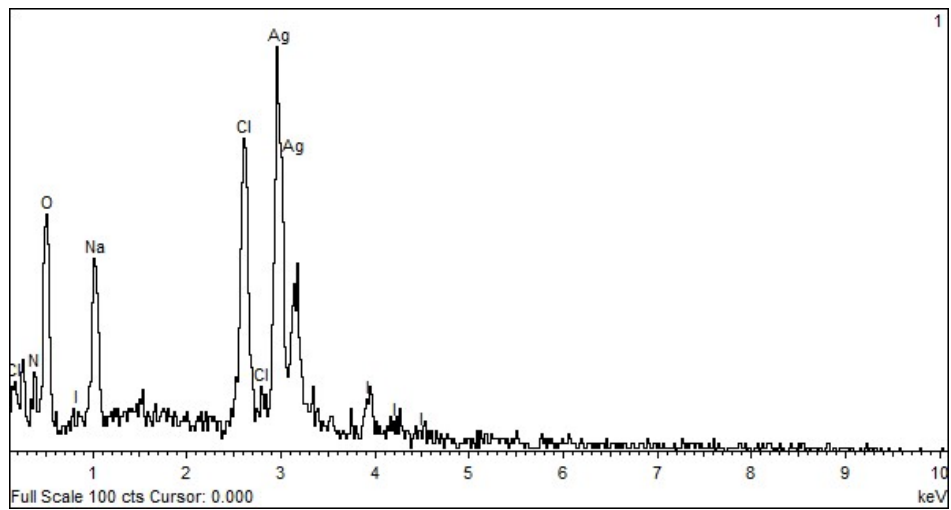


Figure 52. EDS Sample H – Position 1 analysis.

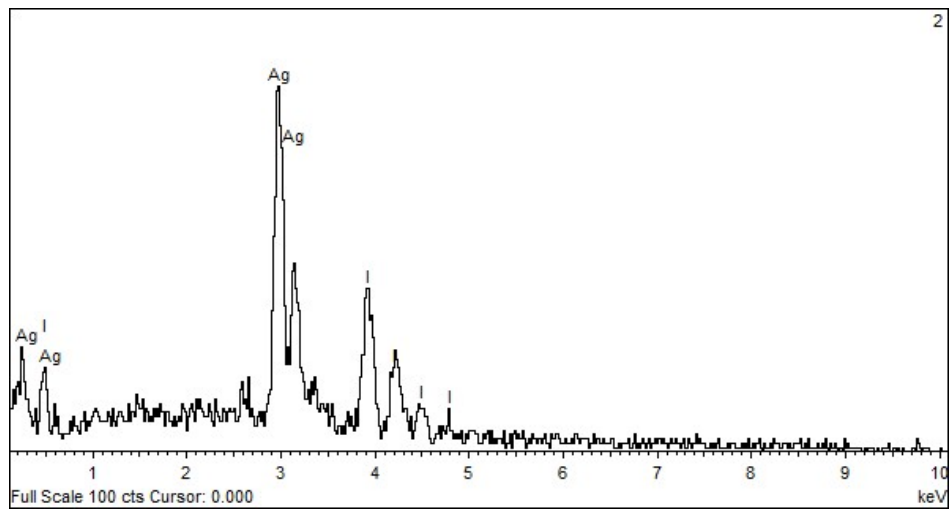


Figure 53. EDS Sample H – Position 2 analysis.

5. CONCLUSION

This summer research, “*Optimizing Remediation of I-129 using AgCl Colloidal-Sized Particles in SRS F-Area Sediments*” was conducted to determine the surface morphology and composition of AgCl particles created under different settings, and to evaluate the reactivity of AgCl particles towards I⁻. The experiment found that when using AgNO₃ as the silver source and varying both the chloride sources and the way the particles were washed, it was possible to produce AgCl particles with different characteristics. The particles differed most in size and in structure. Samples which used NaCl as the Cl⁻ source exhibited small amorphous particles in samples A and B. Samples using artificial groundwater as the chloride source produced a mix of small amorphous particles with larger cube-like crystal structures scattered throughout samples C through F. Titrations on the AgCl particles led to the conclusion that the AgCl particle’s reaction with I⁻ was not strictly a surface reaction. It was also found that the dissolution of AgCl is likely the limiting factor controlling the complexation reaction between AgCl particles and I⁻ to form AgI.

This project contributed to the “*Attenuation Based Remedies in the Subsurface Applied Field Research Initiative*” at SRS and the findings will be used to help better understand the reactions between AgCl and I-129. In addition, the findings may help guide future decisions for operational procedures for the *in-situ* remediation of I-129 at the F-area. Future work could include further titrations on particles from Samples B through F to find if there is any difference in the way they react with iodine. Other possibilities include the use of dispersants when creating the AgCl to allow for a better suspension of the particles. If this proves successful, it could be used to improve the attenuation of I-129.

6. REFERENCES

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APPENDIX A

Table 3. Titration 1 Iodine Probe Calibration

Conc. (mg/L)	log Conc.	mV
0.05	-1.30103	48.3
0.1	-1	17.8
0.5	-0.30103	-9.7
1	0	-27.6
10	1	-86.8
50	1.69897	-128.3

Table 4. Titration 1 Results

Spike	mV	Conc. (mg/L)	I added (mL)	Total I (mL)	I added (mg)	Total I (mg)
0	260	1.301E-05	0	0	0	0
1	260	1.301E-05	0.05	0.05	0.005	0.005
2	248	2.080E-05	0.05	0.1	0.005	0.01
3	242.2	2.609E-05	0.05	0.15	0.005	0.015
4	95	8.213E-03	0.05	0.2	0.005	0.02
5	37.2	7.859E-02	0.05	0.25	0.005	0.025
6	20.2	1.527E-01	0.05	0.3	0.005	0.03
7	10.7	2.213E-01	0.05	0.35	0.005	0.035
7 Next Day	284.7	4.957E-06	0.05	0.4	0.005	0.04
8	280	5.957E-06	0.05	0.45	0.005	0.045
9	274.5	7.385E-06	0.05	0.5	0.005	0.05
10	268	9.520E-06	0.05	0.55	0.005	0.055
11	259.7	1.317E-05	0.05	0.6	0.005	0.06
12	249.5	1.962E-05	0.05	0.65	0.005	0.065
13	235	3.457E-05	0.05	0.7	0.005	0.07
14	215.4	7.435E-05	0.05	0.75	0.005	0.075
15	189.7	2.030E-04	0.05	0.8	0.005	0.08
16	13.7	1.969E-01	0.05	0.85	0.005	0.085
17	4.8	2.787E-01	0.05	0.9	0.005	0.09
18 Next Day	267	9.89969E-06	0.05	0.95	0.005	0.095

Table 5. Titration 2 Iodine Probe Calibration

Conc. (mg/L)	log Conc.	mV
0.05	-1.30103	66.2
0.1	-1	24.5
0.5	-0.30103	-8
1	0	-26.5
10	1	-86.8
50	1.69897	-129.1

Table 6. Titration 2 Results

Spike	mV	Conc. (mg/L)	I- added (mL)	Total I- (mL)	mg I- added	Total mg I-	Total Volume
0	252	1.373E-05		0			50
1	250.7	1.872E-05	0.05	0.05	0.005	0.005	50.05
2	250.7	1.872E-05	0.05	0.1	0.005	0.01	50.1
3	250.4	1.894E-05	0.05	0.15	0.005	0.015	50.15
4	249.3	1.977E-05	0.05	0.2	0.005	0.02	50.2
5	248.2	2.064E-05	0.05	0.25	0.005	0.025	50.25
6	248	2.080E-05	0.05	0.3	0.005	0.03	50.3
7	246.8	2.180E-05	0.05	0.35	0.005	0.035	50.35
8	246	2.249E-05	0.05	0.4	0.005	0.04	50.4
9	245.2	2.320E-05	0.05	0.45	0.005	0.045	50.45
10	242.2	2.609E-05	0.05	0.5	0.005	0.05	50.5
11	243	2.529E-05	0.05	0.55	0.005	0.055	50.55
12	241.5	2.681E-05	0.05	0.6	0.005	0.06	50.6
13	240.2	2.821E-05	0.05	0.65	0.005	0.065	50.65
14	238.7	2.991E-05	0.05	0.7	0.005	0.07	50.7
15	237.2	3.172E-05	0.05	0.75	0.005	0.075	50.75
16	237.2	3.172E-05	0.05	0.8	0.005	0.08	50.8
17	234.7	3.498E-05	0.05	0.85	0.005	0.085	50.85
18	232.9	3.752E-05	0.05	0.9	0.005	0.09	50.9
19	230.7	4.089E-05	0.05	0.95	0.005	0.095	50.95
20	229	4.370E-05	0.05	1	0.005	0.1	51
21	226.4	4.837E-05	0.05	1.05	0.005	0.105	51.05
22	224.1	5.292E-05	0.05	1.1	0.005	0.11	51.1
23	221.2	5.927E-05	0.05	1.15	0.005	0.115	51.15
24	219.5	6.334E-05	0.05	1.2	0.005	0.12	51.2
25	215	7.552E-05	0.05	1.25	0.005	0.125	51.25
26	210.6	8.969E-05	0.05	1.3	0.005	0.13	51.3
27	205.3	1.103E-04	0.05	1.35	0.005	0.135	51.35
28	200	1.357E-04	0.05	1.4	0.005	0.14	51.4
29	192.5	1.819E-04	0.05	1.45	0.005	0.145	51.45
30	182	2.742E-04	0.05	1.5	0.005	0.15	51.5
31	170	4.383E-04	0.05	1.55	0.005	0.155	51.55

32	152.1	8.820E-04	0.05	1.6	0.005	0.16	51.6
33	131.7	1.957E-03	0.05	1.65	0.005	0.165	51.65
34	116.4	3.559E-03	0.05	1.7	0.005	0.17	51.7
35	99	7.024E-03	0.05	1.75	0.005	0.175	51.75
36 Three Hours Later	243	2.529E-05	0	1.75	0	0.175	51.75
37	253	1.711E-05	0	1.75	0	0.175	51.75
38	249.7	1.946E-05	0.01	1.76	0.001	0.176	51.76
39	245.6	2.284E-05	0.01	1.77	0.001	0.177	51.77
40	239.3	2.922E-05	0.01	1.78	0.001	0.178	51.78
41	234.6	3.511E-05	0.01	1.79	0.001	0.179	51.79
42	229.2	4.336E-05	0.01	1.8	0.001	0.18	51.8
43	220.6	6.068E-05	0.01	1.81	0.001	0.181	51.81
44	211.1	8.795E-05	0.01	1.82	0.001	0.182	51.82
45	197.1	1.520E-04	0.01	1.83	0.001	0.183	51.83
46	169.2	4.522E-04	0.01	1.84	0.001	0.184	51.84
47	193.8	1.729E-04	0.01	1.85	0.001	0.185	51.85
48	170.8	4.248E-04	0.01	1.86	0.001	0.186	51.86
49	157.3	7.199E-04	0.01	1.87	0.001	0.187	51.87
50	100.3	6.676E-03	0.01	1.88	0.001	0.188	51.88
51	71	2.098E-02	0.01	1.89	0.001	0.189	51.89
52	57.4	3.569E-02	0.01	1.9	0.001	0.19	51.9
53	48	5.153E-02	0.01	1.91	0.001	0.191	51.91
54	40.9	6.801E-02	0.01	1.92	0.001	0.192	51.92
55	35.8	8.301E-02	0.01	1.93	0.001	0.193	51.93
56	31	1.001E-01	0.01	1.94	0.001	0.194	51.94
57	27.1	1.166E-01	0.01	1.95	0.001	0.195	51.95
58	23.8	1.327E-01	0.01	1.96	0.001	0.196	51.96
59 Next Day	257	1.463E-05	0.01	1.97	0.001	0.197	51.97
60	255.3	1.564E-05	0.01	1.98	0.001	0.198	51.98
61	253.1	1.704E-05	0.01	1.99	0.001	0.199	51.99
62	249.8	1.939E-05	0.01	2	0.001	0.2	52
63	246.4	2.214E-05	0.01	2.01	0.001	0.201	52.01
64	242.7	2.559E-05	0.01	2.02	0.001	0.202	52.02
65	238.4	3.027E-05	0.01	2.03	0.001	0.203	52.03
66	230.7	4.089E-05	0.01	2.04	0.001	0.204	52.04
67	223	5.525E-05	0.01	2.05	0.001	0.205	52.05
68	213.1	8.134E-05	0.01	2.06	0.001	0.206	52.06
69	200.5	1.331E-04	0.01	2.07	0.001	0.207	52.07

70	166.5	5.025E-04	0.01	2.08	0.001	0.208	52.08
71	96.4	7.776E-03	0.01	2.09	0.001	0.209	52.09
72	67.8	2.377E-02	0.01	2.1	0.001	0.21	52.1
73	54.6	3.982E-02	0.01	2.11	0.001	0.211	52.11
74	46.2	5.529E-02	0.01	2.12	0.001	0.212	52.12
75	37.6	7.737E-02	0.01	2.13	0.001	0.213	52.13
76	31.8	9.705E-02	0.01	2.14	0.001	0.214	52.14
77	56.7	3.668E-02	-	2.14	-	0.214	52.14
78 2 days later	269.4	8.515E-06	-	2.14	-	0.214	52.14