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**Removal of Iodide from Groundwater Using Silver Chloride -White  
Paper**

**A report of preliminary results prepared by**

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Releases from the F and H Area Seepage Basins on the Savannah River Site (SRS) have caused groundwater plumes that contain a variety of contaminants. These plumes are releasing contaminants into Fourmile Branch, which is a small tributary of the Savannah River. The metallic contaminant releases to the branch are being controlled by base injection. The base injection targets cationic contaminants and was not intended to reduce the concentration of I-129 in groundwater. SRS and the regulatory agencies believe it is appropriate to investigate remedial alternatives that could reduce the I-129.

The Savannah River Site Area Closures Projects (ACP) and the Savannah River National Laboratory (SRNL) are developing an innovative in situ treatment for I-129 using silver chloride (AgCl). The proposed AgCl amendment has a very small particle size and is designed to be injected into the contaminated aquifer to capture I-129. The solubility of AgI is several orders of magnitude lower than the solubility of AgCl. Thus, when I-129 comes in contact with AgCl it forms silver iodide (AgI), which is very stable and essentially insoluble in water.

SRNL has been performing bench-scale column tests on the effectiveness of silver chloride to capture iodine in an aqueous solution. These initial tests evaluate silver chloride in four different particle sizes; 4-5 millimeters (standard reagent silver chloride), approximately 1 millimeters (sieved reagent silver chloride), approximately 2 micrometers (ultra fine grind without a grinding agent), and <1 micrometer (ultra fine grind with a grinding agent). The first two experiments with macro-sized particles were proof of principle tests. In these the AgCl was mechanically mixed into a portion of the soil filling the columns. The last two were to test the effectiveness of injecting particles suspended in an aqueous solution – the ability to inject the particles, their retention in the column and their effectiveness at removing dissolved iodide from solution. The amendments for these two columns were obtained from a private company specializing in ultra-fine grinding of materials. They were ground in propylene glycol because when ground in water silver metal electroplated onto the steel grinding equipment. Table 1 shows the list of columns and the amendment characteristics.

Column	Amendment Characteristics
0	Control, no AgCl amendment
1	AgCl, 1 millimeter sieved, exposed to light, mechanically mixed in soil
2	AgCl, 4-5 millimeters, mechanically mixed in soil
3	AgCl, ~2 micrometers, injected into soil
4	AgCl, <1 micrometer, Al <sub>2</sub> O <sub>3</sub> used as grinding agent, injected into soil

### **Column 1**

Column 1 was a control column in which the influent was a nitrate and iodide solution. The results (Figure 1) show that iodide is only very slightly retarded relative to highly mobile nitrate in F-Area plume sediments. Thus, any retardation observed with the silver

amendments added is due to reaction with the amendments and not adsorption to the sediments themselves.

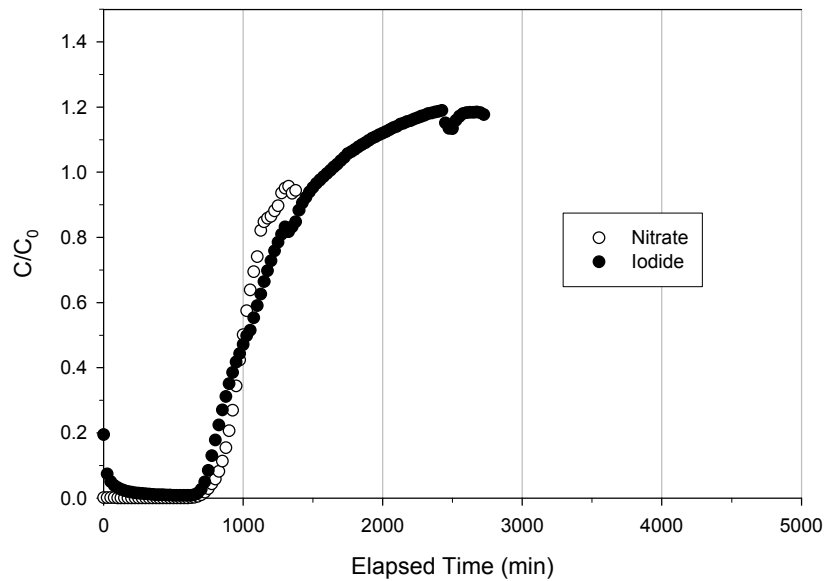


Figure 1: Control column.

### **Columns 1 and 2**

Initial silver chloride (AgCl) amended columns used reagent grade AgCl from Fisher Scientific. The 1 millimeter AgCl was achieved by sieving the finer particles from the bulk reagent AgCl. During the sieving process it the AgCl was exposed to light and darkened in color. For the second column, un-sieved AgCl was used to minimize light exposure and contact with metallic surfaces prior to being placed in the column. Both columns were 6-inches long with a 3-inch diameter. Both had an overall concentration of AgCl of 0.05 wt.%. The inlet solution passed through both columns was 10 mg/L iodide and 150 mg/liter nitrate at a rate of about 0.3 ml/min. At this flow rate 1 day equals about 1.6 pore volumes.

The results of the first column are shown in Figure 2. For the first 50 days nearly all iodide was removed during passage through the column. Over the next 50 days the effluent iodide concentration rose to 5 mg/L or 50% iodide removed. The iodide concentration appeared to stabilize there, just prior to termination of flow through the column.

The results of the second AgCl amended column using 4-5 millimeter are shown in Figure 3. The amendment in this column had a smaller “outer” surface area than the amendment in the first column because of the larger particle size. All iodide was removed for only a few days before the effluent iodide concentration began to climb. After 35 days the effluent iodide concentration reached about 5 mg/L or 50% removed and stabilized there for the next 35 days.

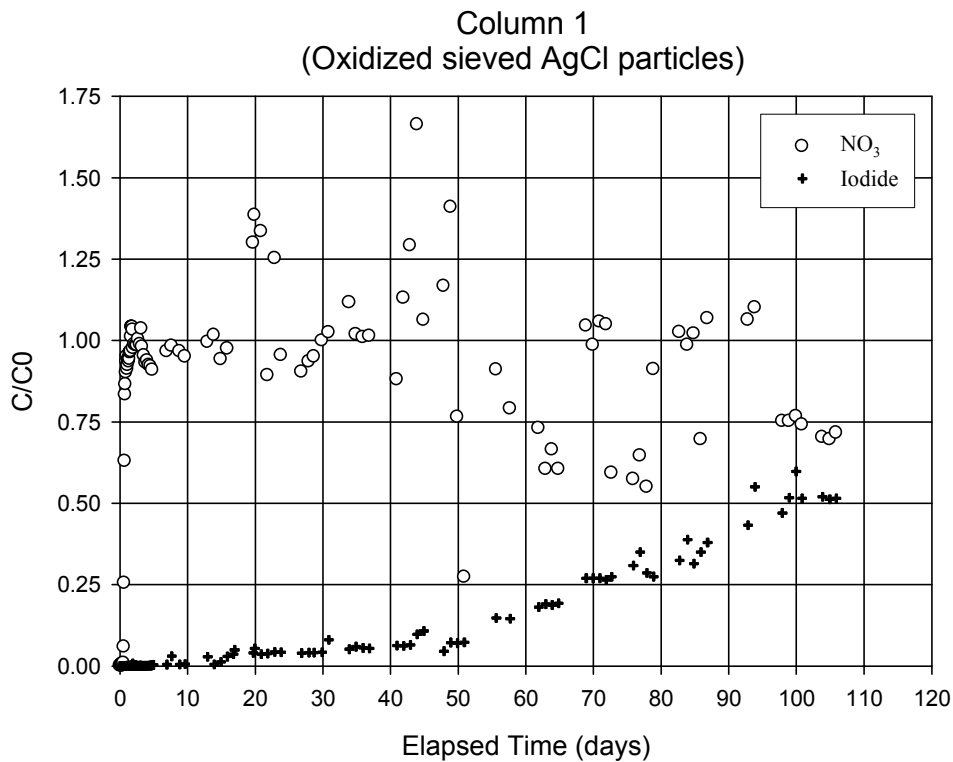


Figure 2: Results of the first amended column using 1 millimeter sieved AgCl .

A possible explanation for the initial complete iodide removal followed by stabilization of removal at about 50% is the existence of microporosity in the amendment particles. Figure 4 shows a scanning electron microscopy image of a particle (A) from the second column. It shows that the macroparticles are actually agglomerations of small spherical particles of about 5 micrometers in diameter (B). In the first column, the smaller diameter macroparticle size meant that more of the microparticles at the “outer” surface were directly exposed to passing fluid in the column. Thus, there was a larger surface area of AgCl directly exposed to the pore fluids. This resulted in the near complete removal of iodide for 50 days compared to only a few days for the second column. The stabilization of the removal efficiency at 50% in both columns may be because access to the inner microspheres of any macroparticle is controlled primarily by diffusion. It may be that the diffusion rate of iodide into the macroparticles relative to the advection rate for fluid through the column resulted in stabilization at a 50% removal efficiency regardless of the macroparticle size.

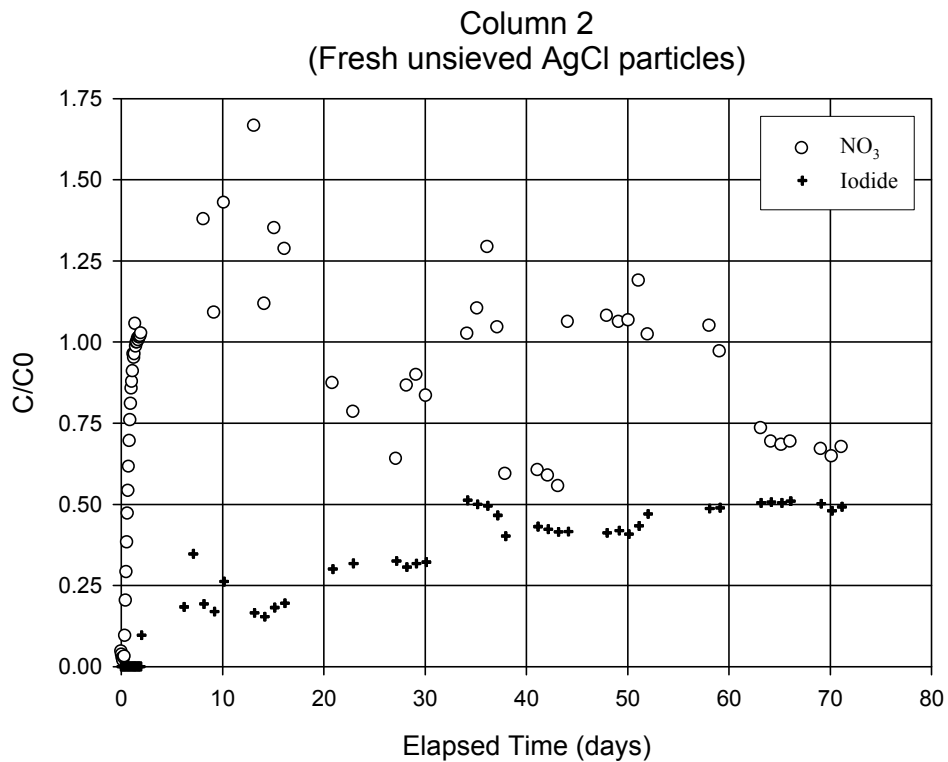
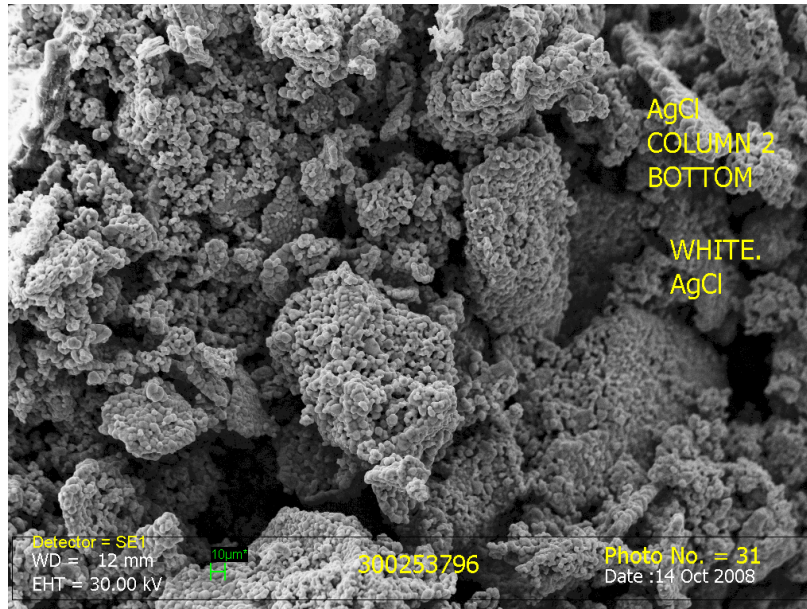


Figure 3: Results of the second AgCl amended column using 4-5 millimeter unsieved AgCl.

The nitrate concentration in the column effluent appears to decrease with time in both columns. The nitrate was measured with a ion selective probe and it is possible that the accuracy of the probe decreased with time. Two samples that were composites of some of the apparent low nitrate samples were analyzed for nitrate by ion chromatography and found to be 138 and 140 mg/L nitrate compared to the influent concentration of 150 mg/L. This suggests that the nitrate probe was behaving erratically. This was further confirmed by subsequent analysis of archived samples by colorimetric methods.

Upon close examination of amendment particles removed from column 2 after the experiment, many of the particles were coated with a yellowish precipitate. Figure 5 shows a scanning electron photomicrograph of one of these yellowish areas. Hexagonal crystals typical of silver iodide are precipitated on the AgCl amendment particles. The identity of the hexagonal particles was confirmed with energy dispersive x-ray spectroscopy as silver iodide, proving that dissolved iodide was removed by precipitation of silver iodide.

A)



B)

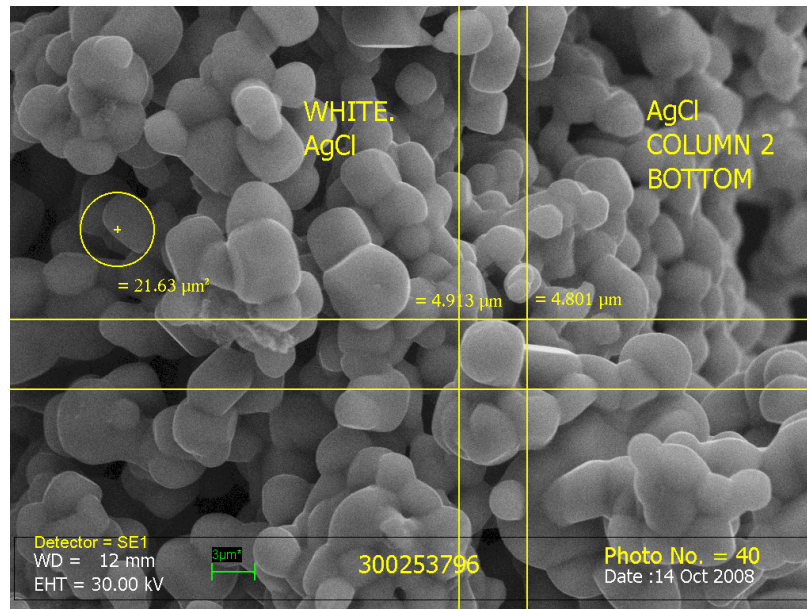


Figure 4: Scanning electron photomicrographs of the AgCl amendment used in the second amended column.

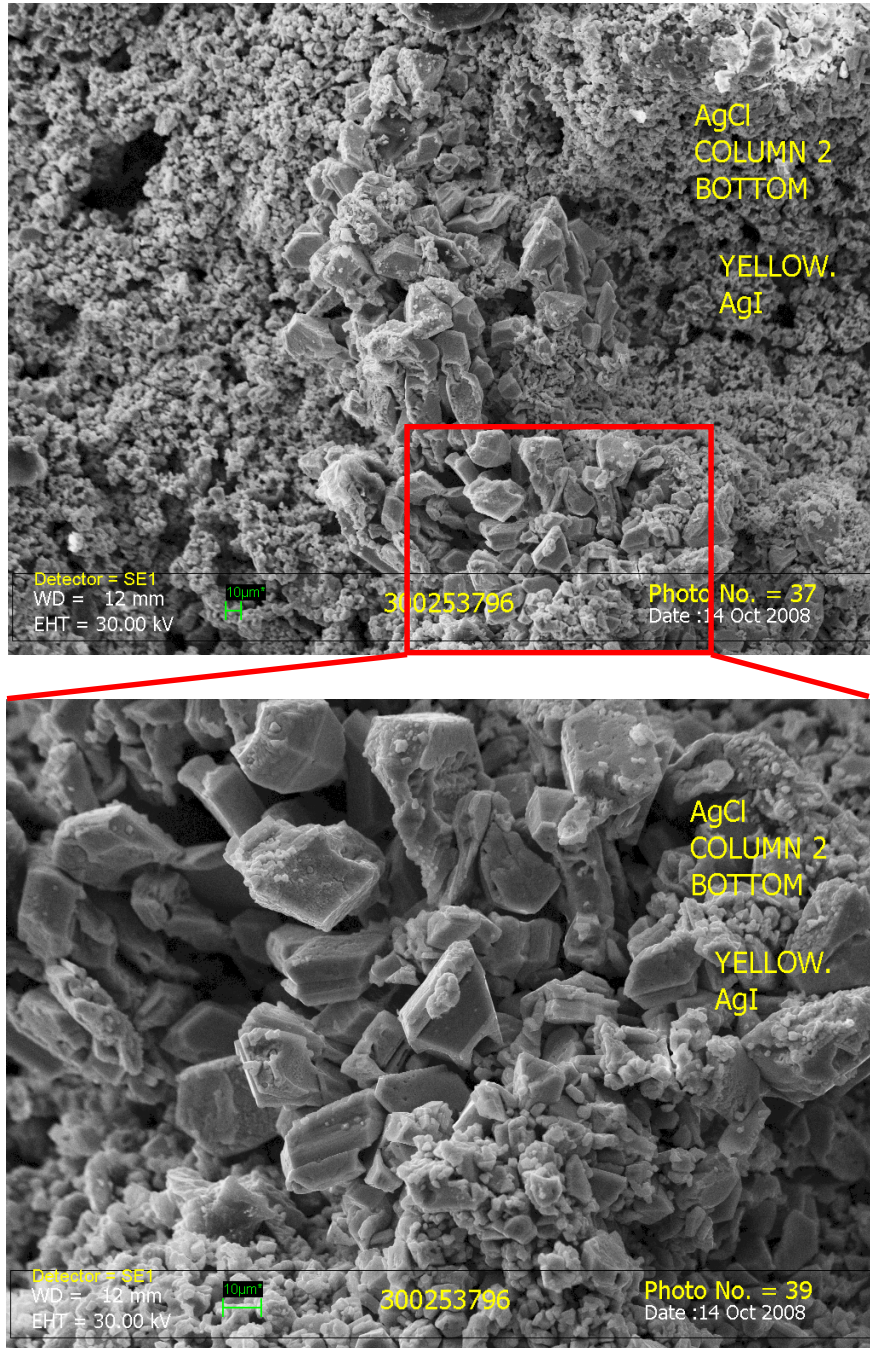


Figure 5: Scanning electron photomicrograph of silver iodide crystals precipitated on AgCl amendment from the second amended column.



### Column 3

The first ultra-ground amendment to be tested was ground without the aid of a grinding agent and had a minimum particle size of about 1-2 micrometers. This was tested in a column study and the results are shown below (Figure 6). The calculated surface area for this product is about  $0.5 \text{ m}^2/\text{g}$  assuming spherical particles. Figure 7 illustrates the calculated surface area of spherical particles versus particle diameter.

The test of this 1-2 micrometer amendment was conducted using a 7.5cm inside diameter column 30.5 cm long packed with 2128.8 gm dry sand (dry bulk density  $1.52 \text{ gm/cc}$ ). Saturated hydraulic conductivity prior to AgCl injection was  $8.9\text{E-}3 \text{ cm/s}$  or 9.3 darcy. A solution containing 133 mg/L AgCl from the amendment was injected into the top of the column at a rate of 5.5 mL/min. If all of the amendment was retained in the column, there would have been a AgCl concentration of 0.05 wt.%. Following AgCl injection the saturated hydraulic conductivity was found to be  $7.2\text{E-}3 \text{ cm/s}$  or 7.5 darcy.

A solution containing 150 mg/L  $\text{NO}_3$ , 10 mg/L I, and a pH of 8.3 from  $\text{NaHCO}_3$  was injected into the column at 0.3 mL/min.  $\text{NO}_3$  broke through the column ( $C/C_0 = 0.5$ ) at 1.2 days after initiating injection. While iodide did not break through at  $C/C_0 = 0.5$  during the test it was initially detected after 5 days of injection and reached a  $C/C_0$  of 0.33 after 19 days of injection.

We are currently analyzing the distribution of the amendment in the column. Initial observations showed a darkened area at the top of the column, suggesting that much of the amendment was trapped there. Yet, visual observation suggests that some of the amendment moved deeper into the column and preliminary x-ray fluorescence data indicates the presence of silver at least 18 centimeters into the column. A backscatter image of a sample from 14 centimeters into the column is shown in Figure 8. The bright spots are particles containing higher atomic number elements than the gray background material. The x-ray energy dispersive spectra shown in Figures 9, 10, 11, and 12 confirm that these are predominantly AgCl (Figure 10), AgI (Figure 12), and some Ag metal (Figure 11) particles on kaolinite (Figure 9) from the soil used in the columns. The Ag particles may be left over from the initial grinding trials in which Ag plated out on the grinding equipment. The AgCl particles are unreacted amendment and the AgI particles are amendment that sequestered iodide from passing pore fluid.

The results of the Column 3 experiments suggest that a substantial amount of the AgCl amendment was transported at least 18 centimeters into the column and was effective at removing dissolved iodide as precipitated AgI. It can be assumed that higher flow rates would carry particles further in the subsurface, but the fact that a substantial amount of the amendment was captured in a 1-foot column suggests that the particles are not highly mobile and would not travel long distances.

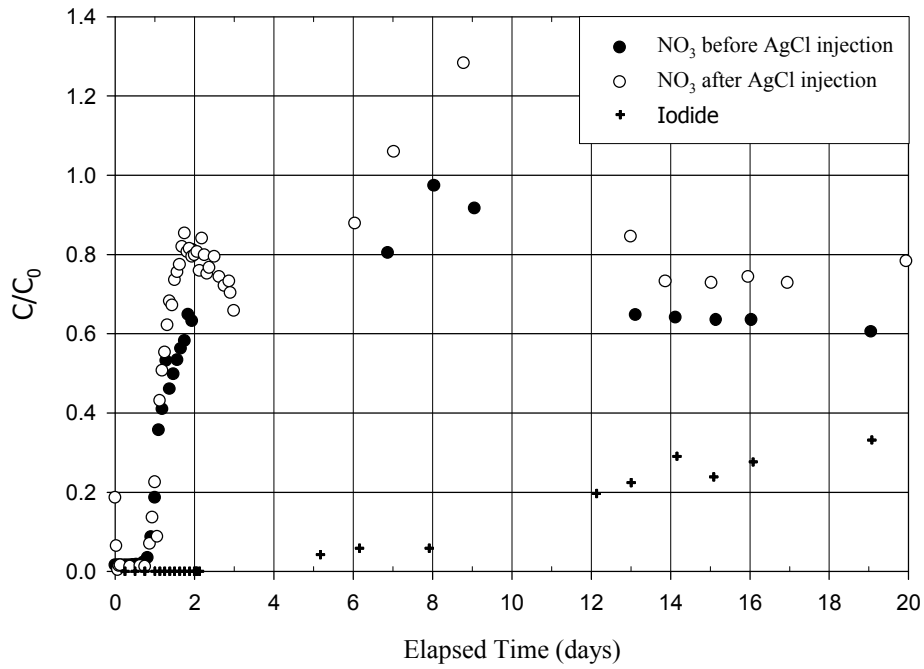


Figure 6: Results of 3<sup>rd</sup> amended column – ultra-ground AgCl amendment with estimated mean particle diameter of 2 micrometers.

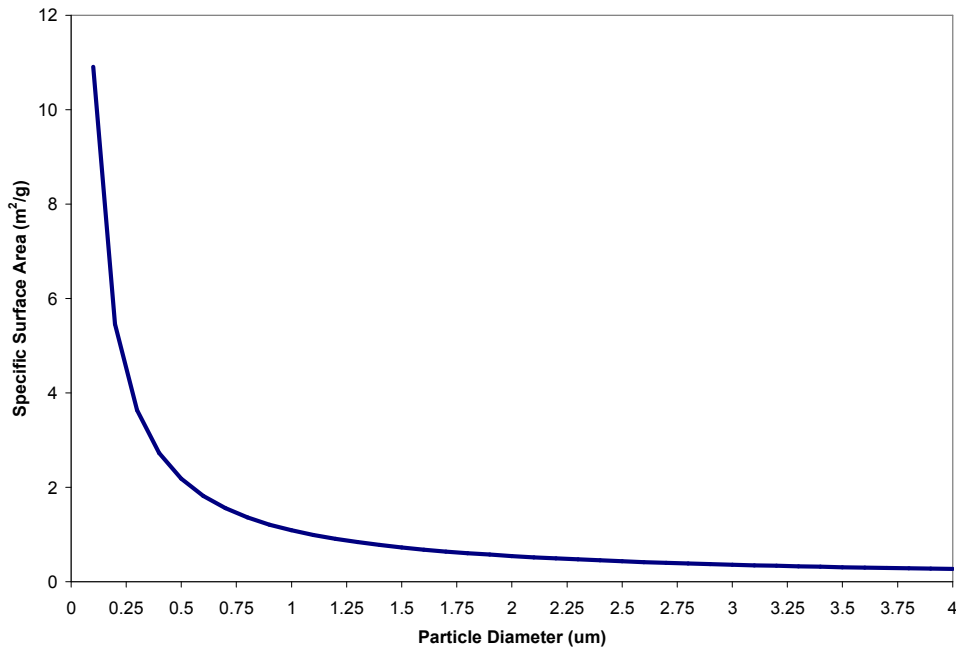


Figure 7: Calculated specific surface area of spherical particles of AgCl versus particle diameter.

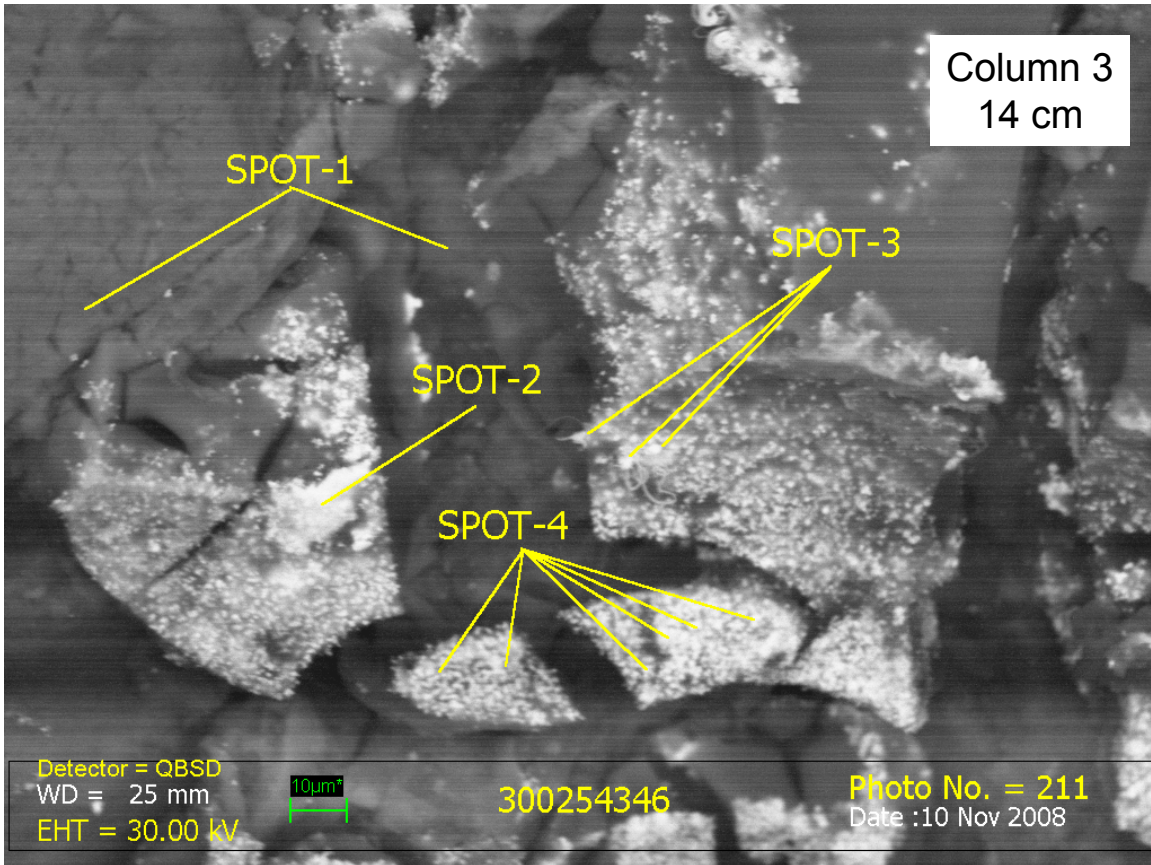


Figure 8: Scanning electron microscope backscatter image of material removed from 14 centimeters deep within column 3; bright spots contain higher molecular number materials (e.g, silver).

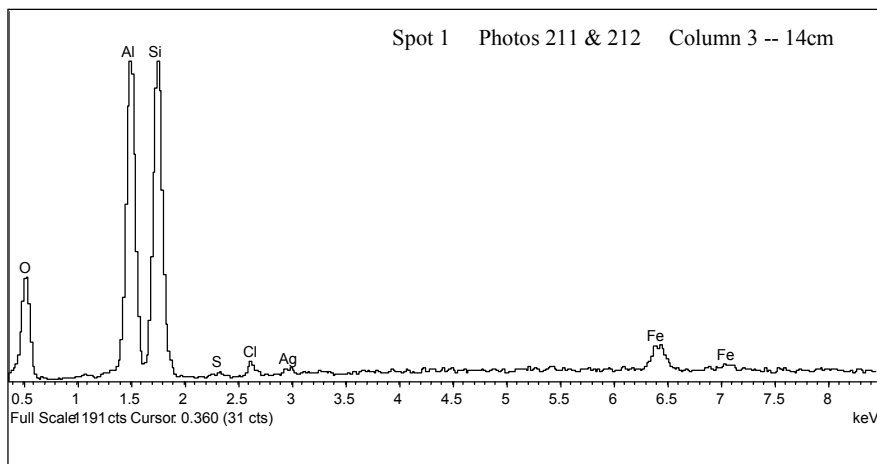


Figure 9: Energy dispersive x-ray spectra of spots corresponding to Spots 1 in Figure 8.

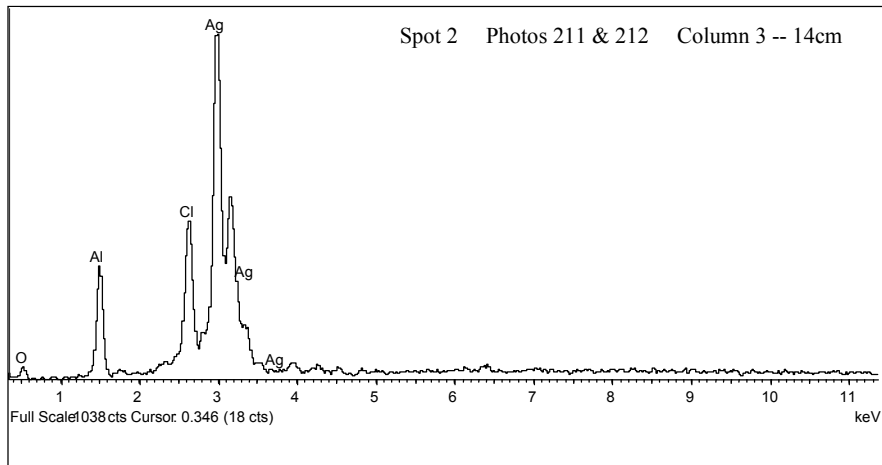


Figure 10: Energy dispersive x-ray spectra of spots corresponding to Spots 2 in Figure 8.

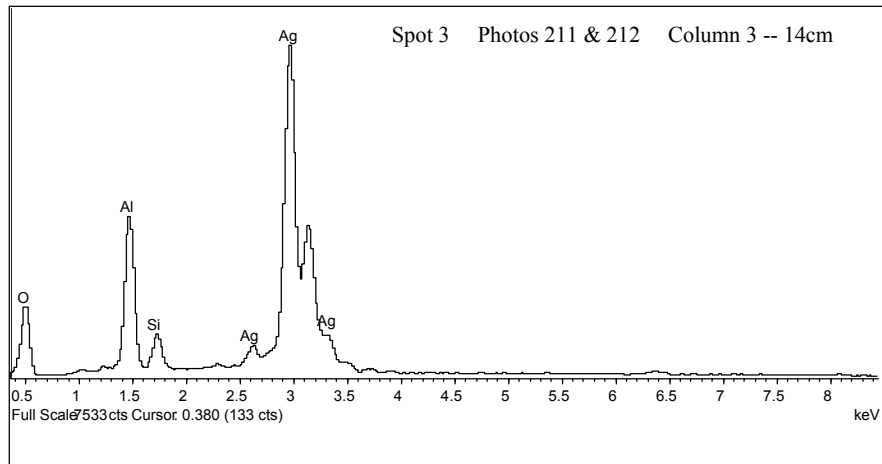


Figure 11: Energy dispersive x-ray spectra of spots corresponding to Spots 3 in Figure 8.

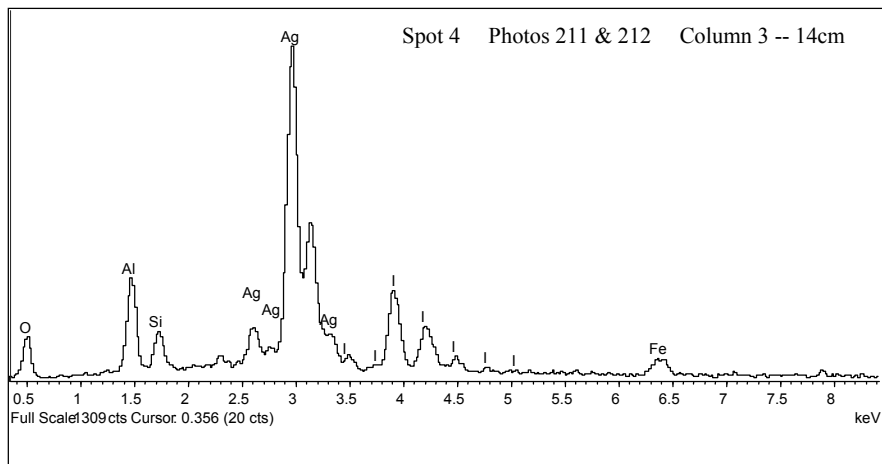


Figure 12: Energy dispersive x-ray spectra of spots corresponding to Spots 4 in Figure 8.

**Column 4**

A test of the <1 micrometer AgCl was conducted using a 7.5cm inside diameter column 30.5 cm long packed with 2169 gm dry sand (dry bulk density 1.61 gm/cc). Saturated hydraulic conductivity prior to AgCl injection was 4.6E-3 cm/s or 4.8 darcy. A conditioning fluid of 150 mg/L NO<sub>3</sub> and a pH of 8.3 from NaHCO<sub>3</sub> was injected into the column at 0.3 mL/min for 17 days until the effluent had a pH of 8.3.

The colloidal AgCl suspension was injected following column conditioning. Seven and a half liters of a diluted solution of this amendment containing 133.3 mg/L AgCl, 533 gm/L Al<sub>2</sub>O<sub>3</sub> (grinding agent), and 1600 mg/L TOC from propylene glycol and was injected into the top of the column at a rate of 5.2 mL/min.

Following AgCl injection, injection (0.3 mL/min) of conditioning fluid was resumed and continued for approximately 4 days. Effluent samples were collected when conditioning was resumed at 45 minute intervals using an autosampler. Nitrate ion concentration was measured using an ion selective electrode and TOC to track propylene glycol was measured using an OI Analytical 1020A Total Organic Carbon (TOC).

Figure 13 below shows the results of the effluent sampling during post AgCl injection conditioning. Nitrate broke through the column ( $C/C_0 = 0.5$ ) at 2000 minutes after initiating injection. The pore volume of column 4 is estimated to be 530 mL which equals a porosity of 39%. This results in an equivalent groundwater pore velocity of 280 ft/year. Figure 13 also shows propylene glycol (measured as TOC) being flushed from the column during post injection conditioning.

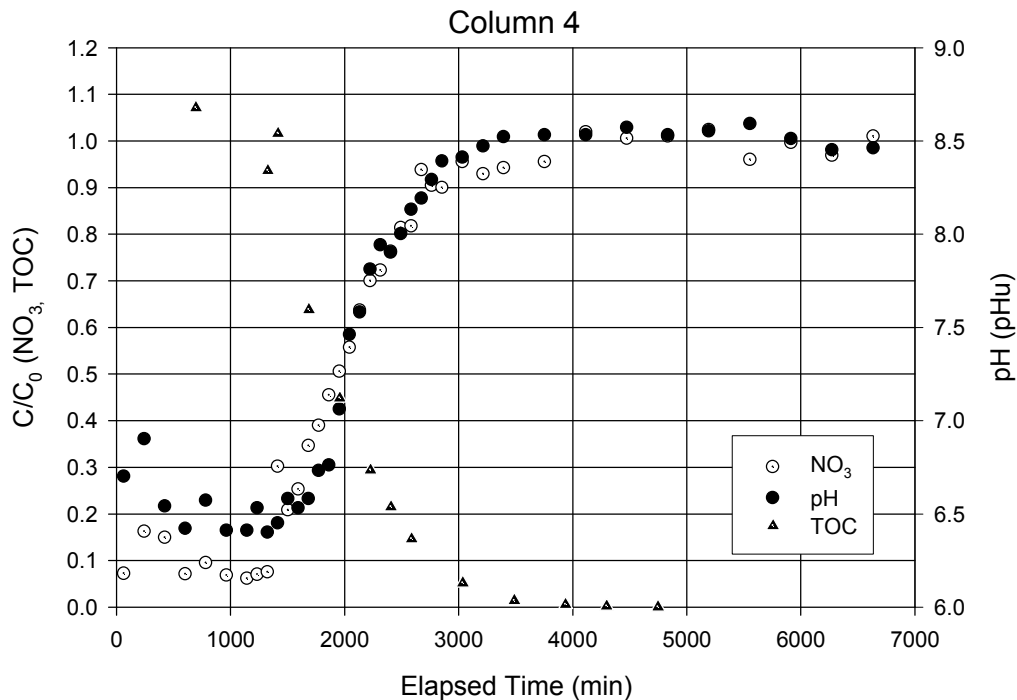


Figure 13: Breakthrough curves of nitrate and pH, with flushing curve for propylene glycol.

A solution containing 150 mg/L NO<sub>3</sub>, 8.5 mg/L I, and a pH of 8.5 from NaHCO<sub>3</sub> was injected into the column at 0.3 mL/min. Table 1 contains preliminary results from the first 2 weeks (10 pore volumes) of I<sup>-</sup> injection into Column 4. After nearly 11 pore volumes of iodide solution influx, there was little to no iodide in the column effluent.

Table 1. Results from Column 4 iodide injection.

Elap. Time (min)	pH (pHu)	I (mg/L)	C/CO	PVs
743.5		0.5	0.0	
2183.5	8.6	0.0	0.0	1.2
3830.5		0.0	0.0	2.1
5266.5	8.46	0.0	0.0	2.9
7222.5		0.0	0.0	3.9
8662.5	8.42	0.0	0.0	4.7
10102.5		0.0	0.0	5.5
11542.5	8.47	0.4	0.0	6.3
12982.5	8.53	0.6	0.1	7.0
14422.5	8.56	0.5	0.1	7.8
15862.5	8.65	0.4	0.0	8.6
17302.5	8.67	0.4	0.0	9.4
18742.5	8.42	0.0	0.0	10.1
20182.5	8.15	0.0	0.0	10.9

## Conclusions

The results of these column experiments demonstrate that solid silver chloride is highly effective at removing dissolved iodine from water and should be an effective amendment for removing I-129 from groundwater. Based on known groundwater chemistry and the reaction of AgCl with I<sup>-</sup> to produce AgI, the only interference will be natural dissolved stable iodine (I-127). Millings et al. (2002) reported a maximum I-127 concentration of 2.2 ug/L in groundwater from well P-27D, a background water table well near F-Area. The concentration of dissolved iodide used in these experiments is approximately 4500 times this natural concentration. Therefore, a AgCl amendment in the subsurface at the same concentration used in these experiments, might effectively remove I-129 for up to 4500 times the number of pore volumes of groundwater as observed here. This assumes homogenous distribution of the amendment and no occlusion by other minerals in the subsurface. The only reliable way to evaluate these effects is by trial in the field.

The column studies also suggest that the amendment is readily injectable into sediments, but will not be highly mobile. The fact that the effluent from Column 4 shows no iodide breakthrough after nearly 11 pore volumes indicates that some of the injected AgCl was trapped in the column. A mass balance on iodide reacted so far suggests that a minimum of 0.056 grams of silver chloride was trapped in the column to react with the iodide. This is 5.6% of the mass injected. Assume the 1-foot column represents the first foot of sediment in the subsurface into which the amendment is injected. If 5.6% of the AgCl particles are trapped in each subsequent foot of sediment through which the injectate moves, at 100 feet the concentration of particles will be 3% of the injection concentration. This is the maximum possible concentration indicated by these column studies, because far more AgCl may have been trapped in the column. Continued data collection will tell how much more.

Dissolved silver concentrations from the silver chloride amendment will be low. Effluent from Column 1 was analyzed for dissolved silver and the concentrations were below the detection limit of 0.2 mg/L.