

# STUDENT SUMMER INTERNSHIP TECHNICAL REPORT

## ***In Situ* Precipitation of Silver Chloride for Treatment of $^{129}\text{I}$ -Contaminated Groundwater**

### DOE-FIU SCIENCE & TECHNOLOGY WORKFORCE DEVELOPMENT PROGRAM

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**Applied Research Center**

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## ABSTRACT

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Iodine-129 ( $^{129}\text{I}$ ) contamination in groundwater is a problem at both Hanford and Savannah River Sites. Hanford plumes are large, but dilute compared to the SRS plumes in which  $^{129}\text{I}$  concentrations have been as high as 1000 pCi/L, almost 1000 times over the drinking water limits. Currently,  $^{129}\text{I}$  is addressed in the SRS plume by injecting silver chloride particles to sequester the  $^{129}\text{I}$  as silver iodide. This method could be enhanced if silver chloride could be precipitated in situ and experiments were done to test this possibility. Sediment-filled columns were used in this research to examine the in-situ precipitation of AgCl in sediments and to determine if mineral surfaces affect particle size and morphology, as well as to assess the mobility of particles and their aptitude in immobilizing  $^{129}\text{I}$ . Results from these column tests will aid in determining whether enhancements to the AgCl technology are viable and how to best design a treatment system. Preliminary results show a decrease in the concentration of silver in the effluent, which is indicative of silver retention. Initial readings show no significant increase in the iodide concentration over time, suggesting removal of iodide from the aqueous phase.

## TABLE OF CONTENTS

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ABSTRACT.....	iii
TABLE OF CONTENTS.....	iv
LIST OF FIGURES .....	v
LIST OF TABLES .....	v
1. INTRODUCTION .....	1
2. EXECUTIVE SUMMARY .....	3
3. RESEARCH DESCRIPTION.....	4
4. RESULTS AND ANALYSIS.....	6
5. CONCLUSION.....	11
6. REFERENCES .....	12

## LIST OF FIGURES

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Figure 1. Iodine-129 contaminant plume at SRS F-Area. ....	1
Figure 2. AgCl particles precipitated from $\text{AgNO}_3$ addition to a NaCl solution. ....	2
Figure 3. Schematic of microcosm apparatus (Shehadeh et al. 2015). ....	5
Figure 4. Experimental apparatus constructed in a fume hood. Light sensitive chemicals are contained in foil-covered containers and lines. Pressure sensors monitor for plugging of column and a fraction collector is used to collect samples during final stage of the experiment. ....	5
Figure 5. Specific conductance (mS) observed in the control over the total volume injected (mL). ....	6
Figure 6. Inlet and outlet pressure readings over cumulative volume injected into the control column. ....	7
Figure 7. Breakthrough curve of iodide in the control column. ....	7
Figure 8. Specific conductance (mS) readings over the total volume injected (mL) in the target column. ....	8
Figure 9. Inlet pressure (PSI) readings over cumulative volume (mL) injected in the control column. ....	8
Figure 10. Silver concentration (ppm) as a function of volume (mL) collected in the target column. ....	9

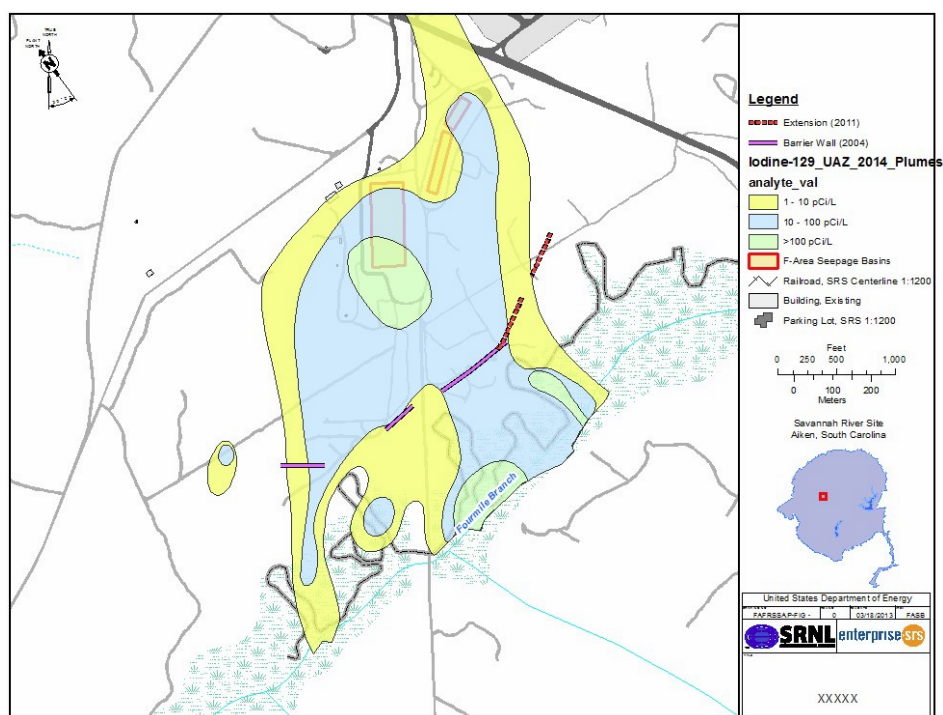
## LIST OF TABLES

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Table 1. Simulant Groundwater Preparation .....	4
Table 2. Iodide Concentration in Samples Collected from the Target Column. ....	10

# 1. INTRODUCTION

At the peak of the cold war, the U.S. nuclear weapons complex stretched across the continent with 18 nuclear weapons producing facilities. Savannah River Site (SRS) and Hanford Site were the two major plutonium producing sites for over 50 years. An estimated 36 metric tons of plutonium were produced from 1953 to 1988. Due to the chemical separation processes approximately 3.4 billion gallons of hazardous waste solution were produced and received in the SRS F and H areas. Low-level radioactive waste solutions were disposed in unlined ponds known as seepage basins. Although it was originally assumed that the hazardous material would bind to the subsurface soil, this was only true for contaminants that adsorb strongly to soil such as plutonium. Other radionuclides like iodine-129 are highly mobile in a variety of environmental conditions.



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

Iodine-129 ( $^{129}\text{I}$ ) contamination in groundwater is a problem at both Hanford and Savannah River Sites. While Hanford plumes are large, they are dilute compared to the SRS plumes in which  $^{129}\text{I}$  concentrations have been as high as 1000 pCi/L, almost 1000 times over the drinking water limits. Radioactive iodine ( $^{129}\text{I}$ ) is both a beta and gamma emitter with a half-life of 15 million years. Exposure to  $^{129}\text{I}$  can lead to reduction of thyroid function and hormone production, and potentially thyroid cancer (Shehadeh *et al.* 2015). In 2010, preliminary research was initiated in an attempt to find a suitable treatment for iodide-129 contamination. Savannah River National Laboratory (SRNL) collaborated with Environmental Compliance and Area Completion Projects (EC&ACP) to develop a treatment for  $^{129}\text{I}$  contamination in groundwater that involves injecting silver chloride ( $\text{AgCl}$ ) particles into the aquifer. Silver chloride was used because of its difference in solubility with silver iodide ( $\text{AgI}$ ).  $\text{AgCl}$  is fairly insoluble with a solubility product

constant ( $K_{sp}$ ) of approximately  $10^{-10}$ , but  $\text{AgI}$  ( $K_{sp}$  of  $10^{-16}$ ) is almost 6 orders of magnitude less soluble than  $\text{AgCl}$ . Hence,  $\text{AgCl}$  particles will react with iodide in the groundwater to produce  $\text{AgI}$ .

In 2008, bench-scale column tests served as proof of principal, as well as proof of the effectiveness of the technology in removing  $^{129}\text{I}$  from the aqueous phase (Denham *et al.* 2008; Denham *et al.* 2010a). Although highly effective in the removal of  $^{129}\text{I}$ , silver chloride particles are limited in their mobility through the soil column. Field demonstrations conducted by EC&ACP in 2010 and 2011 validated preliminary research. The concentration of  $^{129}\text{I}$  never recovered to its original concentration at the injection site, but the  $\text{AgCl}$  nanoparticles did not distribute through the entire soil column limiting the efficiency of the technology. This limitation in distribution was addressed in 2015, when batch experiments were used to prove *in-situ* precipitation of silver chloride in the presence of natural groundwater chloride concentration and silver nitrate (Shehadeh *et al.* 2015). Figure 2 shows  $\text{AgCl}$  particles precipitated from silver nitrate ( $\text{AgNO}_3$ ) addition to a sodium chloride ( $\text{NaCl}$ ) solution (Denham *et al.*, 2015a). The batch experiments were conducted in solution (no solids) (Denham *et al.* 2015a). In this investigation, sediment-filled columns were used to examine the *in-situ* precipitation of  $\text{AgCl}$  in sediments and to determine if mineral surfaces affect particle size and morphology, as well as assess the mobility of particles and their aptitude in immobilizing  $^{129}\text{I}$ . Results from these column tests will aid in determining whether enhancements to the  $\text{AgCl}$  technology are viable and how to best design a treatment system.

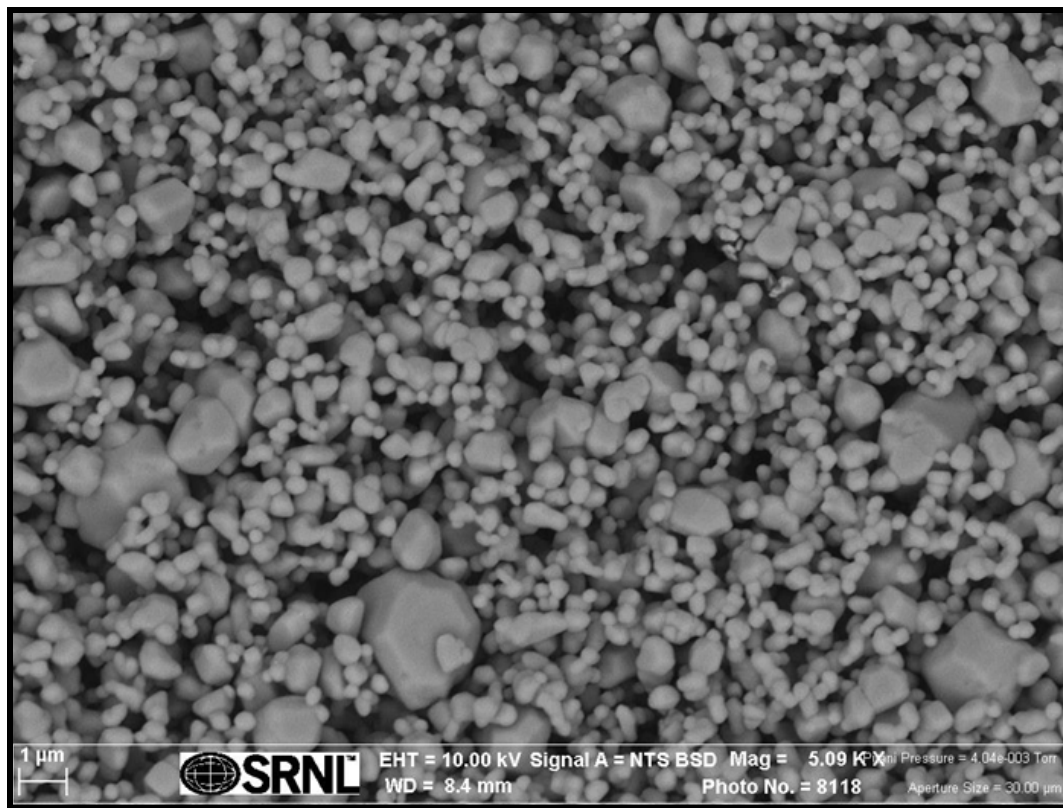


Figure 2.  $\text{AgCl}$  particles precipitated from  $\text{AgNO}_3$  addition to a  $\text{NaCl}$  solution.

## 2. EXECUTIVE SUMMARY

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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 Environmental Management (DOE-EM) and Florida International University's Applied Research Center (FIU-ARC). During the summer of 2016, a DOE Fellow intern, Alejandro Hernandez, spent 10 weeks doing a summer internship at Savannah River National Laboratory under the supervision and guidance of Mr. Ralph Nichols, and Dr. Miles Denham. The intern's project was initiated on June 6, 2016, and continued through August 13, 2016 with the objective of examining the *in-situ* precipitation of AgCl in sediments and determining if mineral surfaces affect particle size and morphology, as well as assessing the mobility of particles and their aptitude in immobilizing  $^{129}\text{I}$ .



### 3. RESEARCH DESCRIPTION

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Column experiments were conducted to test the viability of *in situ* precipitation of AgCl as a potential technology for the immobilization of  $^{129}\text{I}$  from contaminated groundwater. Two 1-foot columns were filled with SRS sediments (oven dried) in lifts (i.e., stages) and packed between each lift. After packing the columns, they were saturated with de-aired water from the bottom up (vertically) by capillary action. The water reservoir was raised over the water level in the column to minimize the formation of air bubbles. After saturation, pressure sensors (in the inlet and outlet) and conductivity sensors (in the outlet) were placed to monitor the flow of solutions through the columns and as detection tools for potential clogging of the columns.

A variable speed peristaltic pump was also connected to the columns and used for the remainder of the experiment. A conceptual diagram of the set-up can be seen in Figure 3. Deionized (DI) water was used to condition the columns for 24 hrs at 3 mL/min. Following conditioning with DI water, simulant groundwater (sGW) was pumped through the columns for 4 days at 0.9 mL/min. The sGW composition is shown in Table 1. Subsequently, a series of pulse injections (5 injections, 1.5 hr in duration at 12 mL/min) were administered to the columns. Both columns were treated the same except one column was designated as a control and was injected with sodium nitrate ( $\text{NaNO}_3$ ). The other column was selected as the target column and was injected with 300 ppb of  $\text{AgNO}_3$ . The pH of all the solutions was adjusted to 3.5 prior to entering the columns.

**Table 1. Simulant Groundwater Preparation**

Simulant Groundwater Solution			
Compound	$\text{NaNO}_3$	$\text{NaCl}$	$\text{NaSO}_4$
Amount (g)	19.1	1.65	3.35

After completing the injections, the columns were switched from sGW to sGW spiked with 1 ppm iodide (sGWI) for the remainder of the experiment (37 days) pumped at a rate of 0.1 mL/min. Samples were collected between injections and an auto sampler was used to collect all effluent fractions after the columns were switched to sGWI. Collected samples were analyzed using ion selective electrodes (ISE) to determine the iodide and silver concentrations in both the control and the target columns. Figure 4 demonstrates the final experimental setup.

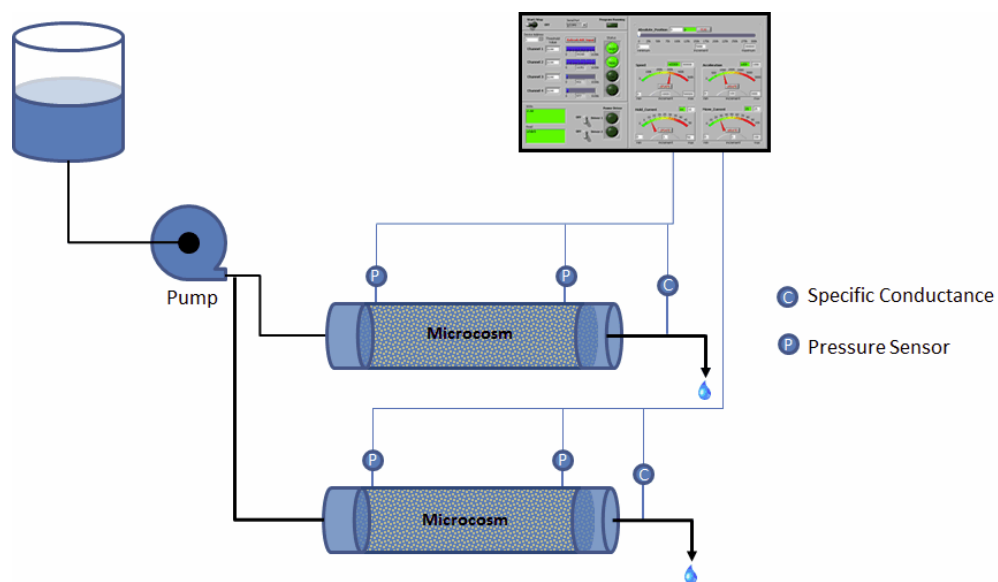


Figure 3. Schematic of microcosm apparatus.



Figure 4. Experimental apparatus constructed in a fume hood. Light sensitive chemicals are contained in foil-covered containers and lines. Pressure sensors monitor for plugging of column and a fraction collector is used to collect samples during final stage of the experiment.

## 4. RESULTS AND ANALYSIS

Currently the investigation is still in its initial experimental phase, and all data presented in this report are preliminary results that are somewhat inconclusive.

### Control Column

Specific conductance readings taken from the outlet port of the control column are shown in Figure 5. A visual analysis of Figure 5 illustrates a repetitive pattern in the data and a drop in specific conductivity. This outline is attributed to the injection of  $\text{NaNO}_3$ , each drop representing an injection. As noted in the previous section, there were 5  $\text{NaNO}_3$  injections in the control column.

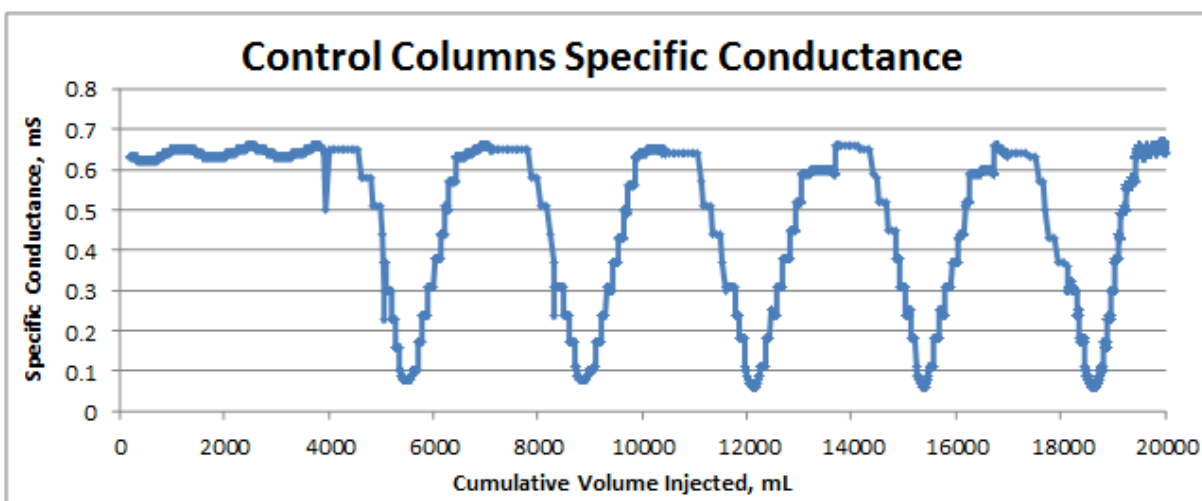


Figure 5. Specific conductance (mS) observed in the control over the total volume injected (mL).

The drop in specific conductance occurs when  $\text{NaNO}_3$ , which has a lower conductivity, is injected into the column that is saturated with sGW which has a higher conductivity. Specific conductance can be used as a monitoring tool if there is a significant difference between the conductivity of two solutions. In this investigation it was used to monitor the flow from sGW to the injected solution and back to sGW (in both the control and target columns).

Pressure measurements were also recorded throughout the duration of the investigation. Readings are taken from both the inlet and outlet ports of the column as can be seen in Figure 6. This analysis also revealed a unique pattern, as did the conductivity analysis. Like the specific conductance results shown above, this pattern can also be credited to the sequence of injections. The 5 injections were carried out at a much higher flow rate (12 mL/min) than the normal (0.75 mL/min). This explains the abrupt increase and decrease in pressure, as well as its short duration. Pressure was used as means of detection for potential clogs in the columns since the target column was injected with  $\text{AgNO}_3$ , which was expected to react with chloride and create nanoparticles that could theoretically clog the system.

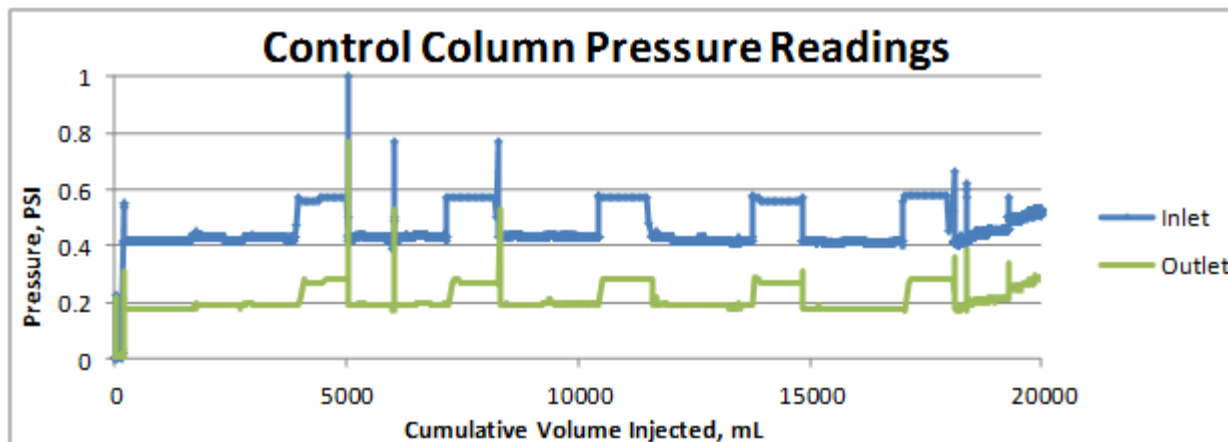


Figure 6. Inlet and outlet pressure readings over cumulative volume injected into the control column.

Subsequent to termination of the injections with  $\text{NaNO}_3$ , the sGW was spiked with iodide and was allowed continuous flow through the columns for the duration of the investigation. Past this point all effluent fractions were collected and half of the samples were analyzed using iodide ISE. The results are shown in Figure 7. Continuous flow of iodine through the column creates a sigmoidal (breakthrough) curve as the concentration of iodine in the outlet is the same as in the inlet. This type of curve was expected in the control since iodide is highly mobile in the environment

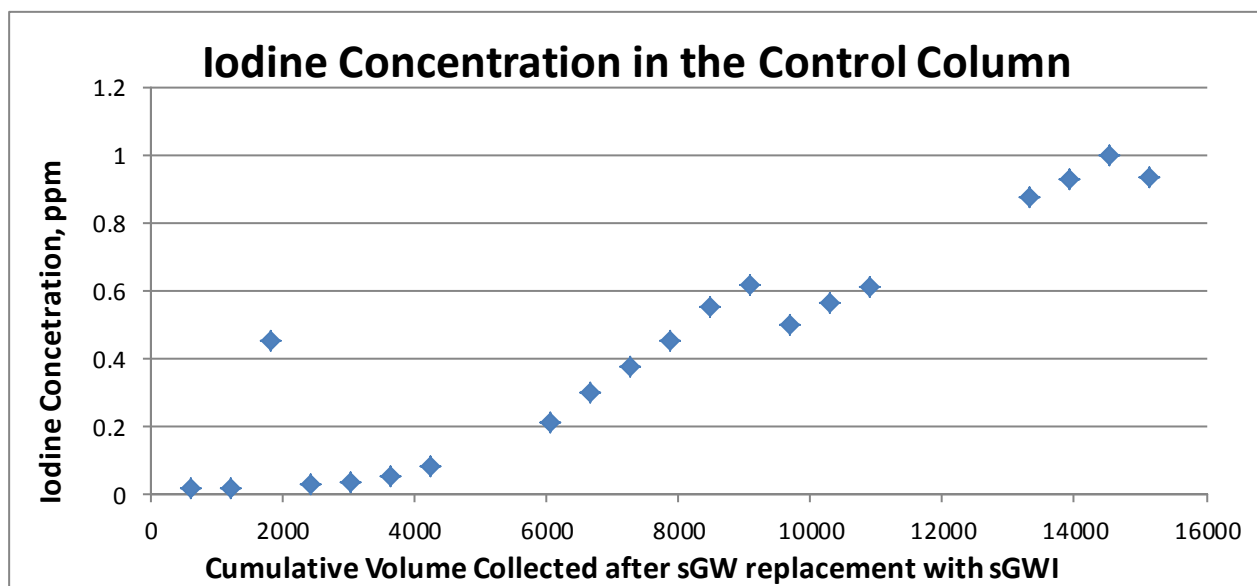


Figure 7. Breakthrough curve of iodide in the control column.

## Target Column

The column of interest (target column) was treated the same as the control column to assure comparability of the results, except for the injected solution, which was changed to  $\text{AgNO}_3$  instead of  $\text{NaNO}_3$  which was used in the control column. The control, therefore, was used as a standard reference to compare the results obtained from the target column. Figure 8 and Figure 9 display the specific conductance and pressure measurements, respectively.

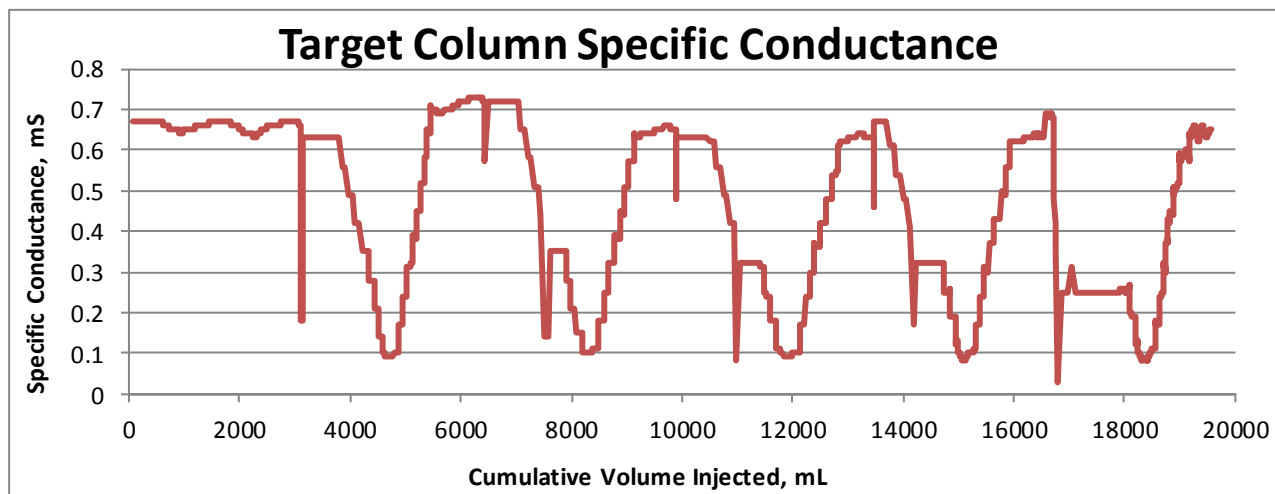


Figure 8. Specific conductance (mS) readings over the total volume injected (mL) in the target column.

As can be appreciated in both figures, the patterns resemble that of Figure 5 and Figure 6 above as expected, since the flow rates and duration of the injections were the same for both columns. Unlike Figure 6, Figure 9 only shows readings from the inlet of the column. The outlet sensor data was not included as it malfunctioned during the investigation. Overall comparison of the specific conductance and pressure readings in the control and target columns reveals an increase in noise in the target column readings. This increase in noise is not surprising as the system becomes multiparameter by the addition of silver nitrate.

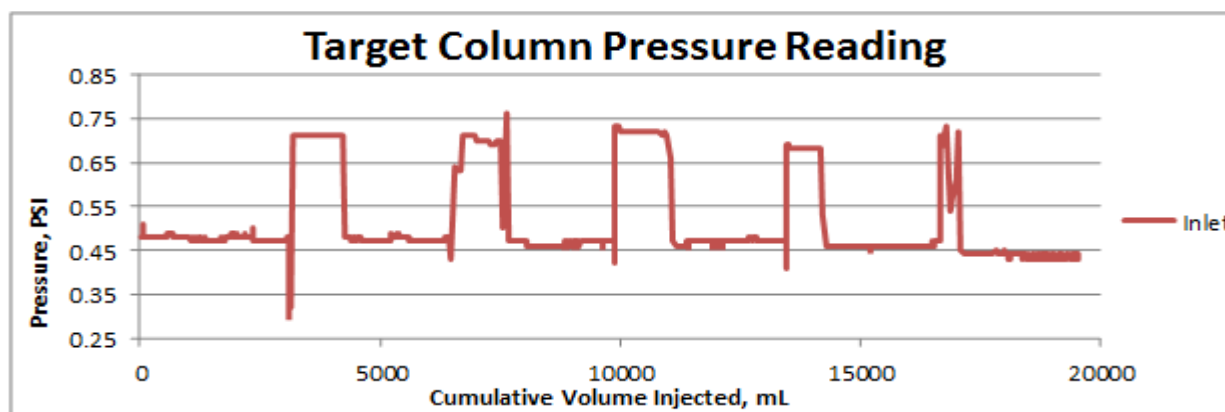


Figure 9. Inlet pressure (PSI) readings over cumulative volume (mL) injected in the control column.

After completing the  $\text{AgNO}_3$  injections, the sGW was spiked with iodide and was allowed continuous flow through the column for the remaining duration of the study. Preliminary analysis for silver was conducted on half of the samples collected. Initial silver concentration in the target column effluent was determined using silver ion selective electrodes (ISEs) and is shown in Figure 10. An observable preliminary decrease in the silver concentration as the volume collected increases, suggests that retention of silver in the column, was caused by the difference in solubility products of  $\text{AgCl}$  ( $K_{\text{sp}} 3.5 \times 10^{-10}$ ) and  $\text{AgI}$  ( $K_{\text{sp}} 2.6 \times 10^{-13}$ ). This suggests that silver concentration is initially correlated with  $\text{AgCl}$  as the  $\text{AgNO}_3$  moves through the columns and reacts with chloride. Subsequently as the iodide moves through the column, the silver concentration is controlled by the formation of silver iodide.

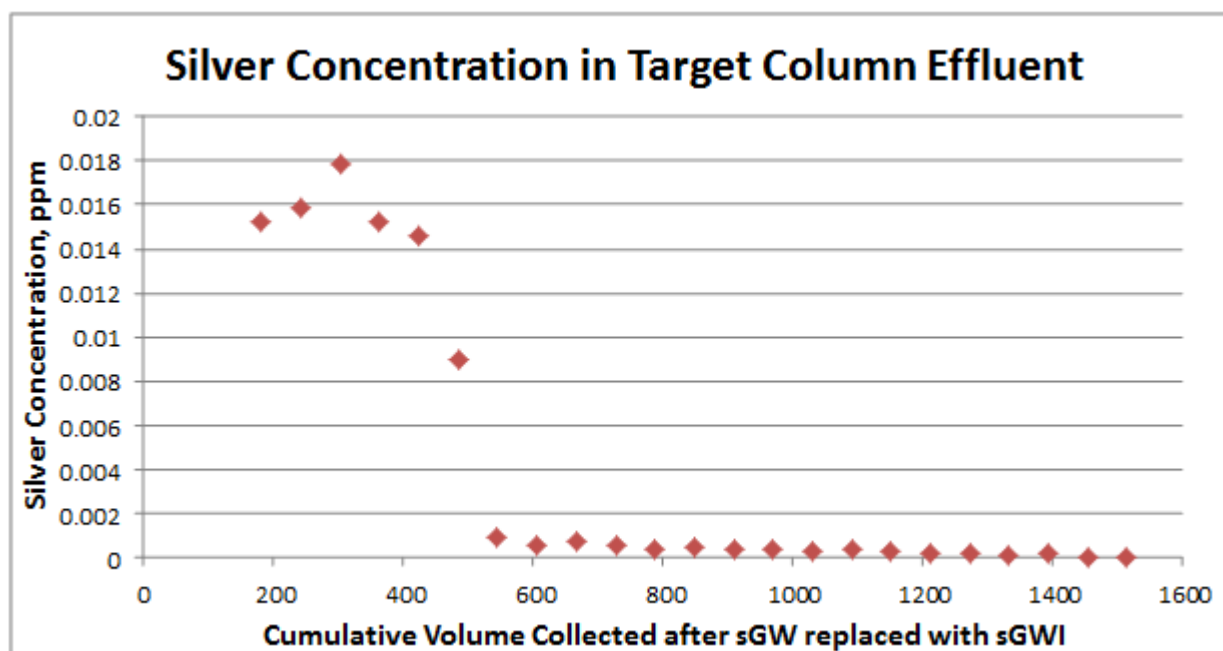


Figure 10. Silver concentration (ppm) as a function of volume (mL) collected in the target column.

The same samples that were analyzed for silver were also analyzed for iodide using iodide ISE, and the preliminary results are shown in Table 2. Preliminary readings show no significant increase in the iodide concentration over the time the samples were collected. This suggests that iodide mobility in the column has been reduced, possibly due to its reaction with the silver chloride nanoparticles derived from the silver injections.

The column experiments are ongoing and data is still being collected and analyzed. Future work will include a complete analysis of both silver and iodide in the samples obtained from the target column. Sediment samples from the columns will be collected for particle size, x-ray diffraction (XRD), x-ray fluorescence (XRF), and cation exchange capacity (CEC) analyses. The unanalyzed half of the samples will be sent for Coupled Plasma-Mass Spectrometry (ICP-MS) analysis, analysis of anions by Ion Chromatography (IC), and total inorganic iodide analysis, to achieve greater accuracy in ion concentration. Computerized tomography scanning (CT scan) may also be used to investigate  $\text{AgCl}$  precipitation and iodine removal after dismantling the columns.

**Table 2. Iodide Concentration in Samples Collected from the Target Column**

Samples	Time (hr)	Cumulative Volume Collected after sGW Replaced with sGWI (mL)	Iodine Concentration ppm
77	5	545.4	0.005317
79	15	606	0.003428
81	25	666.6	0.002469
83	35	727.2	0.002309
85	45	787.8	0.001963
87	55	848.4	0.001895
89	65	909	0.00175
91	75	969.6	0.001555
93	85	1030.2	0.081053
95	95	1090.8	0.001555
97	105	1151.4	0.001494
99	115	1212	0.001477
101	125	1272.6	0.001425
103	135	1333.2	0.001343
105	145	1393.8	0.003244
107	155	1454.4	0.036757
109	165	1515	0.093451

\*Time equals zero, for sample 66 recovered at 8/4/16 5:30 AM

## 5. CONCLUSION

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Sediment-filled columns were used in this investigation to examine the *in-situ* precipitation of AgCl in sediments and determine if mineral surfaces affect particle size and morphology, as well as to assess the mobility of particles and their capacity to immobilize  $^{129}\text{I}$ . Preliminary results from these column tests will aid in determining whether enhancements to the AgCl technology are viable and how to best design a treatment system. Overall analysis of the control column data will be used as a standard reference for future results still being gathered as the concentration of iodide in the outlet equals the concentration of iodide in the inlet. The breakthrough curve is evidence of the mobility of iodide in the environment (i.e., the columns).

As the investigation is still in its infancy, a lot remains unknown about the behavior of silver in the column. Nevertheless, preliminary results show a decrease in the concentration of silver in the effluent which is indicative of silver retention in the columns by mechanisms still being explored. Iodide analysis in the target column is still in its pilot stage, and a wider range of data points is necessary to get a better image of the trends. However, the results presented in Table 2 are as expected, since there is greater retention of silver in the column.



## 6. REFERENCES

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