Removal of Naturally Occurring Radioactive Material From Flowback/Produced Water From the Hydraulic Fracturing Process

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ABSTRACT

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Removal of Naturally Occurring Radioactive Material From Flowback/Produced Water From the Hydraulic Fracturing Process

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Naturally occurring radioactive material (NORM) is present in many of the deep Marcellus shale deposits in the Appalachian Basin. During the hydraulic fracturing process these radioactive particles are brought to the surface with the Flowback/Produced (F/P) water. Currently, the primary way to dispose of this contaminated water is through the use of deep injection wells. However, this process can be extremely expensive due to the limited number of injection wells near the production source. For this reason, treatment options are being investigated.

Two key ways to remove radium from a water supply exist; ion exchange and barium sulfate coprecipitation. Under ideal conditions these processes have been shown to effectively remove 97-99% of radium from water. However these treatments are sensitive to the physical and chemical composition of the water source. In this study these different treatment options will be evaluated. First a set of batch experiments will evaluate the effectiveness of the treatment options, as well as radium selectivity when other ions are present in solution. Second a bench scale column experiment will show the sorbent breakthrough profile. The results of this testing will be used to design on-site treatment as an alternative to the costly transportation and disposal costs of F/P water through deep injection wells.

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CHAPTER 1: INTRODUCTION

Background

In the past several decades, natural gas has become an increasingly important resource. In 2012 natural gas accounted for approximately 27% of all energy consumption in the United States, and this number is projected to increase through 2040 (US EIA, 2014). While the United States ranks outside the top ten in crude oil reserves, they rank number 4 for the largest proven natural gas reserves and number 1 for production of natural gas (US EIA, 2013). This production has grown significantly since 1999, primarily as the result of shale gas development for the retrieval of natural gas. In 2012 the natural gas produced from shale formations accounted for nearly 40% of the total gas produced in the US (US EIA, 2011/12). This increase in production not only provides job opportunities for thousands of Americans, but also may lead the US to become more energy dependent.

The principal driving force behind the increasing production of natural gas from shale formations is the advancement in horizontal drilling coupled with hydraulic fracturing. By combining these two technologies the contact area for production is thousands of times greater than a typical vertical well (Barbot, 2013). In this process approximately 3-5 million gallons of water are pumped into the subsurface over a 2-5 day period. Once this fracturing process is complete and pressure is released fluid begins to flow back up the well (Boschee, 2014). In the first several days of the process the largest quantity of water is recovered from the well. This is called flowback water. Once the well begins producing gas in the recovered fluid it transitions to the produced water phase (Beckman, 2013). Flowback/produced (F/P) water recovery from these wells can range from 9-35% of the fracturing fluid used in Marcellus shale formations (Boschee, 2014).

This F/P water can often pose a significant health risk upon human exposure, so great care must be taken to properly dispose of it. These contaminants include very high salinity, organics, dissolved gasses, heavy metals, and naturally occurring radioactive materials (NORMs) (Basu, 2013). Currently the most common way to dispose of these fluids is through underground injection wells. However in the Appalachian Basin these injection wells are not often located near the production wells so transportation costs run high (Hammar, 2012). For this reason on-site treatment options are being investigated for water reuse or surface disposal. This paper will be address the removal of NORM from F/P water so that the water can be safely reused or disposed of.

Integrated Precipitative Supercritical Process

The research presented in this paper is part of a larger process being developed at Ohio University. The process is known as the Integrated Precipitative Supercritical (IPSC) Process. The goal of this process is to take in the contaminated F/P water and convert it into a product that can either be reused or disposed of (Carow, 2012). Figure 1-1 shows a schematic of the overall process.

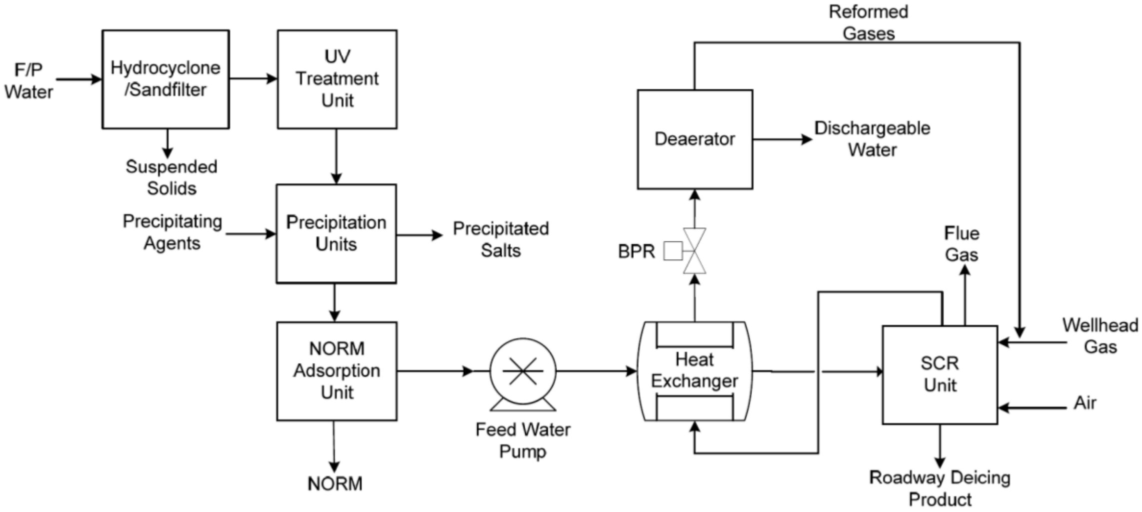

Figure 1-1: Schematic of the IPSC Process being developed at Ohio University

The first stage of the process is a sand filter to remove the initial suspended solids which contribute to the turbidity (El-Taweel, 2000). Next, the ultraviolet treatment unit is utilized in order to destroy the microorganisms in the water stream, particularly sulfate reducing bacteria. By using UV treatment no waste stream is generated (Al-Bastaski, 2004). The third stage is the preliminary precipitative unit. In this stage a precipitative agent acts as a catalyst in order to precipitate out solids from an aqueous solution. The following unit, the NORM adsorption unit, is the focus of this paper and research. This will remove the radioactive material from the wastewater stream. Lastly is the supercritical stage of the process. At a supercritical state, water will precipitate nearly all inorganic material from solution (Reverchon, 1999). These salts can then be processed and used for other commercial applications.

Experimental Objectives

Objective 1: Capacity

The first objective is to evaluate the capacity of different sorbents to remove radium from solution. The sorbents that we will be testing are barium sulfate ($BaSO_4$), clinoptilolite, and Dowex exchange resin. The capacity of these sorbents will first be tested in batch experiments, then in bench scale column test. From the results of these experiments the mass of sorbent needed to remove a certain activity of radium measured in nCi/L will be determined.

Objective 2: Selectivity

The second objective is to observe the effects of the solution parameters on the sorption. It will be evaluated whether altering the solution with the radium sample in it will negatively impact the removal of the radium. Dissolved salts may compete for exchange sites with the radium, which can decrease the amount removed and therefore increase the amount of sorbent needed. Tests will be conducted in order to determine how selective the sorbents are for removing radium in the presence of other ions. Salt solutions of varying ionic composition will be used in order to observe the effect the salts in solution have on the radium removal capacity. Also altering the pH of a solution may positively or negatively impact this removal. This will be evaluated as well.

Objective 3: Kinetics

The third objective for this experiment is to observe the kinetics of the sorbents in a flow through experiment. For this objective a column experiment will be used as a bench scale test for a possible commercial application. Solution will be flowed through a packed bed of a sorbent and samples will be collected periodically from the effluent. These samples will be plotted in order to develop breakthrough curves for the different sorbents, as well as the different ionic strength solutions. Results from these tests will also be used to determine the contact time necessary to remove a known activity of radium.

CHAPTER 2: LITERATURE REVIEW

F/P Water Characteristics

The flowback/produced water that is brought to the surface during the hydraulic fracturing process contains many constituents that are harmful to humans (Basu, 2011). Among the many, NORM and high salinity are of particular interest to this project. Recent studies have found that F/P water can contain Radium-226 levels over 267 times the safe disposal limit, and thousands of times higher than the safe drinking water limit of 5 pCi/L (Hopey, 2011 and US EPA, 2013). Salt levels from F/P waters in Marcellus shale operations are also extremely high. Levels of total dissolved solids (TDS) can vary from 5,000-360,000 mg/L, with an average of approximately 190,000 mg/L (Shaffer, 2013). These salts, which include but are not limited to; barium, calcium, sodium, potassium, magnesium, and strontium chlorides, carbonates, and sulfates, can compete with radium for exchange sites in the sorbents (Basu, 2011 and Baeza, 2008). These salts also greatly exceed the limit for surface water disposal of 2,000 mg/L of TDS (US EPA, 2013).

Because of costs associated with disposal of these fluids, recycling the F/P water may be a more economic solutions. One of the more attractive options is to reuse the produced water in the fracturing process. In this option the F/P water is often treated to reduce TDS, then blended with fresh water (Boschee, 2014). Another option in some states is a surface application of the produced brine. This solution is applied to roads or highways for dust or ice control (Nicholson, 2013). A third solution is to treat the produced water then dispose of it into a nearby water body.

However the last two of these options have been become much more strictly regulated in the past few years (Easton). This places an increased importance on recycling and reuse through the development of treatment technology.

Radium-226 Characteristics

Radium is a naturally occurring mineral that is a member of the alkali-earth metals family. It was first discovered by Marie and Pierre Curie in 1898 when they were experimenting with uranium ore (Hammond, 2011). It is rarely found in its pure form as it is a highly reactive ion that always exhibits an oxidation state of +2. It will typically forms inorganic salts which are mostly insoluble in water (Kirby, 1964). Radium is a highly toxic element, and if ingested will accumulate in the bones and remain there for the rest of one's life. Ingestion or elongated exposure can cause a wide variety of cancers, as well as aplastic anemia (US EPA, 2012). Because of its highly toxic nature and difficultly to remove from, radium is a highly problematic constituent to a wastewater stream.

Radium-226 is one of the many isotopes of radium. It is the most stable of them all, with a half-life of approximately 1600 years (Kirby, 1964). It is produced in the Uranium-238 decay chain through the decay of Thorium-230 (Argonne National Laboratory, 2005). Because of its long half-life this makes it the most common of the isotopes and can be found in seawater and in the Earth's crust. The radium in seawater is at harmless levels, but the levels in the crust can be found at much higher and more dangerous concentrations (Lide, 2005). Ra-226 is primarily an alpha particle emitter (Kirby, 1964). Because alpha particles have a very low penetration of matter, this makes them less dangerous when handling, but much more toxic if ingested. This in turn makes the treatment to take radium out of water of high importance, so that it does not come in to contact with the nearby populations.

Radium Treatment/Removal

There are many treatment options being investigated for radium removal. These includes: Selective membrane mineral extraction (SMME), reverse osmosis (RO), barium sulfate coprecipitation, ion exchange, acrylic fibers, lime-soda softening, aeration, and filtration (Kosarek, 1979). The more traditional water treatment methods such as lime-soda softening, aeration, and filtration have been found to be mostly ineffective in the removal of radium contamination. In lime-soda softening, the principle goal is to remove water hardness and not radium removal so the removal efficiencies are very low. This process also increases the amount of salts in the solution and produces a large amount of radioactive sludge. The costs of proper disposal would become very high at a commercial scale process (Cothern, 1991). Aeration processes are very limited in their radium removal. Averaging only an 18% removal efficiency, they are unsuitable for the high amount of radionuclides found in F/P water (Kosarek, 1979). Filtration methods are limited because they only remove the suspended fraction of the radium. It often needs to be used in conjunction with another, more aggressive removal technology (Chen, 2011). In highly turbid waters only 20% of the radium will be suspended, with 80% being dissolved an unable to be removed by simple filtration methods (Kosarek, 1979).

Unlike the previous three methods described, reverse osmosis processes have excellent removal efficiency of radium. The removal efficiencies with the use of high pressure RO filtration have been observed exceeding 99% (Clifford, 1988). The main drawback of this process are the costs involved. RO filtration is a highly expensive approach for radium removal because of the massive energy demand that is required. Also because of the extremely high concentrations of dissolved salts membrane fouling happens much more rapidly than in other applications. Another major disadvantage of this process is that it creates a large waste stream. Only approximately 50% of the water input to the system is recovered as a usable product (Sauvet-Goichon, 2006). When scaling to a commercial process, that still leaves a massive amount of water that would need to be disposed of through a deep injection well. Another effective technology that has been investigated is the use of acrylic fibers. Manganese impregnated fibers have been shown to remove up to 95% of the radium from seawater or groundwater (Moore, 1973 and Patel, 1992). One drawback, however, is that removal efficiency can be decreased from 95% to 70% in water with high hardness (Patel, 1992).

Ion exchange, in both synthetic resins and natural minerals, have proven to be a reliable treatment option for removing radium from a contaminated water supply. Barium sulfate coprecipitation has also been shown to display high removal efficiencies of radium from water. These are the removal technologies that will be investigated in depth for this project, and the focus of the rest of the paper.

Clinoptilolite Properties

Clinoptilolite is a naturally occurring zeolite material, which is an aluminosilicate material with a crystalline micropore structure. Specifically, clinoptilolite has a Si/Al ratio of greater than 4.0 (Zhao, 1998). What makes these zeolites unique is their micropore structure. They have an array of channels and cages that hold cations, which can be exchanged with other cations in a liquid when the liquid flows through it. This equilibrium reaction is the basis for cation removal from water, but is also important because in most cases the reaction can be reversible (Colella, 1996). This allows the zeolite to be reused as a sorbent as long as it retains its crystalline structure.

Clinoptilolite is used for the removal of many different problematic constituents, including radium. In ideal conditions it has been shown that removal efficiencies for radium using clinoptilolite can reach 98-99% (Kosarek, 1979 and Dutu, 1996). One of the main factors influencing this removal is the chemical composition of waste water. The composition will often have a detrimental effect on the removal efficiency of radium (Dutu, 1996).

One factor that must be considered is the effect of the pH of the solution. The removal efficiency drops significantly to below 15% in acidic waters (Kosarek, 1979). It has been shown that the removal efficiency for uranium in clinoptilolite is maximized around a pH of 6.0, and it is expected that this is similar for radium as well (Camacho, 2010). Another major factor that influences the removal efficiency of radium in clinoptilolite is the competition for exchange sites with other cations. Although clinoptilolite has a very high affinity for radium the presence of other cations, especially barium, can lead to decreased removal efficiencies (Dutu, 1996 and Jurado-Vargas, 1996). Because radium and barium share many similarities they both can fit into the same pores, and therefore compete for these spaces (Jurado-Vargas, 1996). Table 2-1 shows a summary for removal efficiencies for radium and barium in a solution.

Table 2-1: Percentage sorption of radium and barium in zeolites (from Jurado-Vargas et al. 1996)

a: 0.0016 meq of barium/cm^3, b: 0.0144 meq of barium/cm^3

Ion	Condition	Zeolite		
		3A	5A	Y
Ra^{2+}	Carrier Free	98±1	99±1	97±2
	a	100±1	63±2	97±1
	b	60±4	27±2	51±3
Ba^{2+}	a	100±1	52±4	100±1
	b	55±4	23±2	90±6

From Table 2-1 it can be seen that the presence of barium in solution can greatly impact the removal efficiency for radium in zeolites. On top of this sodium, potassium, calcium, and others will also compete for the exchange sites, but to a lower degree than barium (Jurado-Vargas, 1996). However, prefiltration and running column tests in series have been shown to counteract these inhibitory effects (Kosarek, 1979 and Dutu, 1996). In the proposed research for these experiments two different grain sizes of clinoptilolite will be used. A fine powered grain size, as well as a course granulated mesh. These mesh sizes were determined using a sieve pass test.

Ion Exchange Resin Properties

An ion exchange resin works very similarly to a natural zeolite, however these resins can be specifically engineered to remove a wide variety of problematic constituents from water. These reactions occur on the surface of the resins so surface area is very important to removal efficiencies. Nontoxic ions are loaded onto the surface of the resins, and these ions are substituted with the target ions from the solution that need to be removed (De Dardel, 2008). The two main types of resins are cation exchange resins and anion exchange resins. The cation resins are typically preloaded with Na^+ and the anion resin are loaded with Cl^-. In the case of this radium removal experiment a strong acid cation exchange resins is used to target the Ra^{2+} ions in the solution. This strong acid resin uses H^+ ions instead of Na^+. This reaction can be shown by the following equation (Clifford):

$$2\,RH + Ra^{2+} \leftrightarrow R_2Ra + 2\,H^+$$

In this equation it can be seen that because of the charge on the ions, two H^+ exchange sites are needed to remove one Ra^{2+} ions from the solution. Also this process is an equilibrium reaction that can be readily reversible. The resin can be regenerated by backwashing the resin. This process is typically done by flowing a high strength acid solution through the resin (DeSilva). When regenerating the resins, the Ra^{2+} ions that were initially removed are put back into solution. However when doing this the target ions are concentrated in a smaller volume of solution than before treatment (Marcus, 1995). This is more economical than disposing of the untreated water because there is a much lower volume of water that needs to be properly disposed of, albeit this water is much more toxic.

Using ion exchange resins it has been shown that removal rates of radium can reach over 99% under ideal conditions (Kosarek, 1979). However in high saline waters there is a large degree of competition for exchange sites on the resin. This occurs because the radium is often at such a low concentration compared to the other ions in the solution. One advantage of the use of ion exchange resin however is the ability to be regenerated many times and still have a high degree of removal. After regenerating the resin the level of radium that can be measured is near that of the level of the unused resin (Cole).

Table 2-2: Total Radium in Ion Exchange Resin (from Cole et al.)

Sample Description	Lab Code	Concentration (pCi/G wet) Total Radium
Non-Regenerated (never used)	SPW-2552	0.006 ± 0.004
Exhausted Resin	2553	5.440 ± 0.0090
Regenerated Resin	2554	0.020 ± 0.006

The error given is the probable counting error at 95% confidence level.

In this experiment the resin that will be used is the DOWEX G-26 (H) exchange resin. This resin is a strong acid cation exchange resin made of a styrene-divinylbenzene (gel) matrix with a density of 1.22 g/mL. It uses sulfonic acid as a functional group for the exchange sites. Regeneration of the resin is done by flowing 3-6 bed volumes (BV) of a regenerant solution composed of 1-10% H_2SO_4 or 4-8% HCl through the resin at a flow rate of 0.4-4.0 gpm/ft^2 (DOW Water & Process Solutions). No research has previously been done using this specific resin on radium removal so this data may be of high importance if it can be shown to significantly reduce the levels of radium from a water supply. Especially in highly saline waters.

Barium Sulfate Properties

Barium sulfate ($BaSO_4$) is a mostly insoluble inorganic salt ($BaSO_4$ MSDS). Barium is a member of the alkali earth metals group along with radium, so both share many physical and chemical similarities. Both radium and barium form salts with the same crystalline form (Curie, 1926). Because of this property they can easily substitute with each other in an equilibrium reaction. The distribution law for the formation of $(Ba,Ra)SO_4$ solid solutions follows the equation:

$$\frac{\{Ra\}_{surface}}{\{Ba\}_{surface}} = \lambda \frac{[Ra]_{solution}}{[Ba]_{solution}}$$

Where λ is a proportionally constant, $\{Ra, Ba\}_{surface}$ are the fractions on the solid surface, and $[Ra, Ba]_{solution}$ are the concentrations in solution (Grandia, 2008). As shown by this equation the amount of radium removed is directly related to the amount of barium sulfate added to the solution. The removal efficiency seems to follow a logarithmic relationship based upon the amount of barium sulfate added to the solution (Germann, 1921). The removal is maximized at approximately 97%, but the removal efficiency varies greatly on the solutions physical and chemical composition (Kosarek, 1979).

One of the main factors that influence this removal is the pH of the solution. Radium and barium precipitates are unstable at a pH under 3 or over 11, and dissolution of the salts will often occur at these levels (Grandia, 2008). Another factor is the amount of sulfate in the solution for the radium/barium to react with. Often sulfuric acid (H_2SO_4) will be added to the solution to aid the co-precipitation (Doerner, 1925). When doing this, the pH must be monitored so it does not drop below 3. The co-precipitation is also dependent on the amount of other salts in the solution. An excess of calcium in the solution can have a negative impact on the amount of radium that will precipitate (Kudryavskii, 206). The final factor that can influence this treatment is the effect of temperature. Generally at higher temperatures the amount of precipitate formed will be slightly higher (Gordon, 1957).

CHAPTER 3: EQUIPMENT AND DATA COLLECTION

RadEye HEC Alpha/Beta Scintillation Counter

For these experiments all radiological data will be collected using a RadEye HEC sample counting system. The RadEye can measure both alpha and beta radiation simultaneously, with alpha being of particular importance to this research project. For this project the detection unit will be in counts per minute (CPM), where the device is able to measure values in 0.6 CPM increments. Calibration is done by introducing samples with a known activity to the RadEye. The samples will have an activity measured in nanocuries per liter (nCi/L). Using a conversion of 1 nCi = 2220 DPM (disintegrations per minute) and a known volume, an activity value in DPM can be determined. The efficiency can then be determined by for following equation:

$$\frac{Measured\ CPM}{Calculated\ DPM} * 100 = \%\ Efficiency.$$

This piece of equipment has a sliding tray where a 2” diameter metal dish with the sample on it is inserted into the machine. Before the liquid sample is run through the RadEye it is dried in an oven at approximately 100 °C. This is done because alpha particles have an incredibly low penetration of matter; so even the thin film of water containing the radium sample will block the radiation from registering on the detector of the RadEye. By drying the sample the efficiency of the detection is increased significantly.

Review of Objectives and SOP

The overall goal of this project is to determine a practical and cost effective way to remove NORM from a polluted water supply, namely in the form of F/P water from the hydraulic fracturing process. In order to accomplish this overall goal there are three individual objectives that need to be met. The first is to determine the effectiveness of our four sorbents; Barium sulfate, powdered clinoptilolite, granulated clinoptilolite, and the DOWEX exchange resin. The second is to evaluate the effect of the solutions ionic strength on the effectiveness of the sorbents. There will be a total of 6 different solutions in varying ionic strengths to see how the ionic strength will influence the percent removal of the radium. The third and final objective is to determine the breakthrough capacity for the sorbents. This will be accomplished by running column tests where the irradiated samples are pumped through a packed bed of sorbent.

In order to achieve these objectives a Standard Operating Procedure (SOP) has been developed detailing how to set up, run, and analyze the batch and column experiments. The first step for all of the experiments, as well as the RadEye calibration, is solution preparation. There are 6 total stock solutions that will be used, varying in ionic strength from 0.0 M (Deionized [DI] Water) to 4.0 M. Table 3-1 shows the ionic concentrations of these solutions, while Table 3-2 details the solutions preparation guidelines.

Table 3-1: Solution Compositions for NORM Sorption Testing

Solution #	Solution Name:	Ionic Strength (M)	Na^+ (mg/L)	Ca^{2+} (mg/L)	Ba^{2+} (mg/L)	Mg^{2+} (mg/L)	Sr^{2+} (mg/L)
6	High IC(4)	4	70,000	27,500	5,000	2,000	2,500
5	High IC(2)	2	35,000	14,000	2,500	1,000	1,250
4	Med IC(1)	1	16,000	6,500	1,500	650	1,000
3	Low IC(0.5)	0.5	8,300	3,300	750	350	500
2	Low IC(ppt)		26,000	1,775	600	400	300
1	Zero IC(0)	0	0	0	0	0	0

Table 3-2: Mass Amount Needed to Prepare Stock Solutions for 1-L Solutions

	Mass of Salts Required for Each Solution (g)				
Salts	Sol. 6	Sol. 5	Sol. 4	Sol. 3	Sol. 2
NaCl	177.94	88.97	40.67	21.1	66.09
$CaCl_2$	76.15	38.77	18	9.14	4.92
$BaCl_2$	8.89	4.45	2.67	1.33	1.07
$MgCl_2$	7.83	3.92	2.55	1.37	1.57
$SrCl_2$	7.61	3.8	3.04	1.52	0.91

Another major section of the SOP that holds true for any experiment that may be run is safety. Because of the use of radioactive isotopes extra precaution must be used in order to minimize the exposure to them. All work must be done while wearing the proper Personal Protective Equipment (PPE). Also any spills or leaks must immediately be cleaned in order to prevent accidental exposure. Work will be conducted over absorbent pads in order to prevent spreading if a spill or leak does occur. There are also specific guidelines for how to clean up the area in the event of a spill, or to cleanse the system after a column experiment. In order to ensure that the work area is clean and free of radiation a survey was recorded daily using a handheld survey meter, and wipes were conducted once a month and analyzed using a liquid scintillation counter.

Finally, the SOP includes a detailed procedure for how to operate the batch and column experiments. This includes a step by step approach for preparing the experiments, creating solutions, taking samples, and analyzing the results. These procedures will be described in detail in Chapter 4 of this document.

Objective 1: Effectiveness of Various Sorbents

Batch Experiments

The first sets of experiments that were run were the batch tests. In these experiments a known activity of Ra-226 was added to a mass of each sorbent. The samples were allowed to have adequate contact time with the sorbents so that the concentrations could reach equilibrium and the maximum removal efficiency can be observed. By measuring the activity of the samples before and after treatment the effectiveness of the sorbents were evaluated. Comparisons will be made from this removal efficiency to the available surface area of each sorbent. This surface area determination will be conducted using a Micrometrics ASAP 2020. On top of this, qualitative observations were made about the different sorbents and if their physical structure was altered after contact with the high ionic strength solutions. This process helped to determine the appropriate mass of each sorbent that is needed in order to remove the radium to an undetectable level. Using that data the column tests can move forward with already having an idea of how much sorbent is needed in the packed bed.

Column Experiments

The second set of experiments that were run were on a bench scale column test. For this objective the approach was very similar to that of the batch experiments. Tests were be run in order to determine the mass of each sorbent that was needed in order to remove the radium in the samples to an undetectable level. The difference in these tests being that the contact time between the solution and the sorbent were much lower in the flow through experiment. The sorbents needed to not only be able to completely remove the radiation, but continue doing so over a period of time. This data was quantified in terms of Bed Volumes (BV) of water treated.

Objective 2: Evaluation of Solution Variation

The second objective that was evaluated was the effect of various ionic strength solutions on the removal efficiency of the different sorbents. The different solutions that were tested are described in Table 3.1. Knowing that these ions in solution compete with the radium for sorption sites it can be hypothesized that these ions will negatively impact the removal efficiency of radium. This test will either verify or disprove that hypothesis. Also part of this objective was to determine what mass of sorbent will be needed to completely remove the radium from each solution and if it is different than in the previous objective. Table 3-3 shows the test matrix that has been created in order to quantify and compare the results from the different solutions.

Table 3-3: Test Matrix for Varying Ionic Concentration Solutions

Solution	Replicate	BaSO$_4$ Mass(g)											
		1			2.5			5			7.5		
		α	nCi/L	% Removal	α	nCi/L	% Removal	α	nCi/L	% Removal	α	nCi/L	% Removal
6 High IC (4)	1												
	2												
	3												
5 High IC (2)	1												
	2												
	3												
4 Med IC (1)	1												
	2												
	3												
3 Low IC (.5)	1												
	2												
	3												
2 Low IC (ppt)	1												
	2												
	3												
1 Zero IC (0)	1												
	2												
	3												

Table 3-3 is for the barium sulfate results, but a similar table has been designed for the other three sorbents as well. Each specific solution/mass of sorbent trial was run in triplicate in order to ensure the results. The columns labeled 'α' were the direct readings from the RadEye. The column labeled 'nCi/L' was the calculated activity above background of the samples. This conversion will be calculated based on the results of calibration data for each of the different ionic strength solutions. The calibrations for the specific tests being run will use the same counting time and conditions used in the experiment being conducted. The column labeled '% Removal' was the calculated removal efficiency based on the activity calculated previously. This % removal was limited by the results of the calibration data and the LOD.

Objective 3: Sorbent Breakthrough

The third and final objective that was completed was to determine the breakthrough capacity of the various sorbents. This objective was carried out during the column tests. By taking samples periodically over the course of a column experiment and plotting them vs. time, the time to breakthrough was determined. The breakthrough point happens when the eluent sample concentration begins to climb from its initial value. Also determined for this objective was the time to exhaustion. The exhaustion point is when the eluent concentration is the same as influent. This point is the ultimate failure point of the sorbent, and when it no longer is taking contaminants out of solution. An example breakthrough plot can be seen below in Figure 3-1.

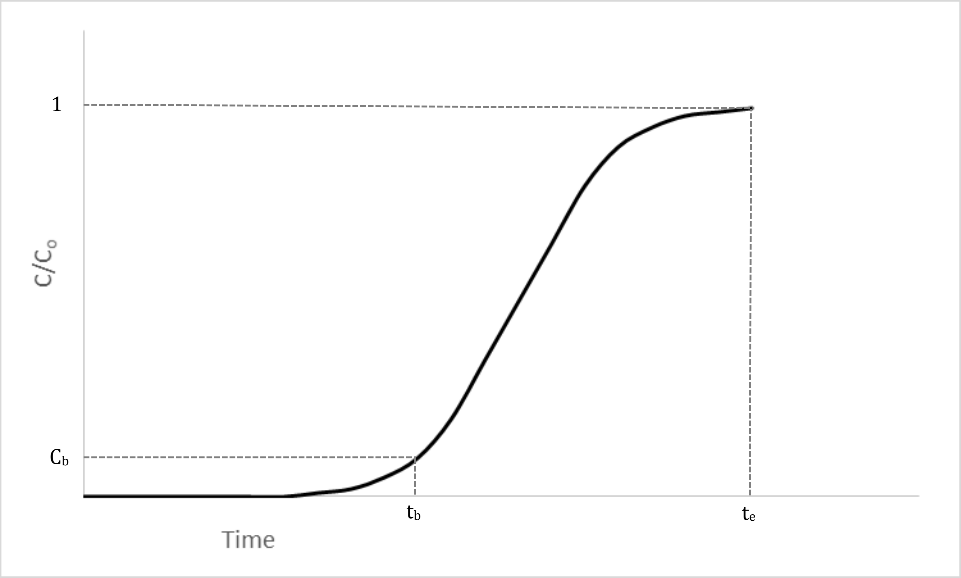

Figure 3-1: Example Breakthrough Plot

In addition to evaluating the sorbents ability to remove radium from solution, their preference for removing certain ions will also be tested. The ions that will be measured are Na, Ca, Mg, Ba, and Sr. This analysis will be conducted using a Fisher icap 6000 ICP –AES. By comparing the breakthrough plots for both radium and these ions the preferential selectivity of each sorbent can be evaluated.

CHAPTER 4: EXPERIMENTAL METHODS

Batch Experiments

The batch experiments were the first set of tests that were run to determine the effectiveness of the 4 different sorbents. The data gathered in this stage of the project helped to accomplish Objectives 1 and 2 by observing the ability of the sorbents to remove radium from solution with and without additional ions in solution. These batch tests also helped to determine the operating conditions used in the column tests.

Firstly, the appropriate solutions for a given experiment were created following **Error! Reference source not found.**. Once the solutions were prepared a sufficient number of plastic flat-top centrifuge tubes were gathered and labeled. Each tube was filled with the appropriate sorbent and mass of sorbent as dictated by the test matrix. Each mass of sorbent for a given solution was made in triplicate as shown in the example test matrix in Table 3.3. Once all tubes were prepared, the solution(s) that were used were dosed with the Ra-226 standard to a 10 nCi/L activity of the radium. Next, 10 mL of the diluted radium solution was added to each centrifuge tube. These tubes were then placed in a shaker plate. The shaker plate was set to 250 rpm, and run for 12-hours. After this shaking period the samples were allowed to sit for an additional 12-hours in order to settle.

After this 24-hour contact period the samples were ready for analysis. From each centrifuge tube 4 mL of liquid was pipetted out and onto a clean metal sample tray. These trays were placed in a drying oven set at 100 ^{o}C until the sample dish was dry. Once dry, the sample dish was introduced to the RadEye scintillation counter for a 10-minute or 35-minute counting time, depending on the trial. This data was then be entered into the test matrix, and repeated until all samples had been analyzed.

Once the test matrix was completed the mass of sorbent needed for complete removal was known. Also it was seen whether or not the additional ions in solution negatively affected this removal. If so it should have been seen that a larger mass of sorbent was needed to remove the radium to an undetectable level.

Column Experiments

The column experiments were the second set of tests that were run for this project. The results from these experiments helped to accomplish Objective 1 and 2, but was primarily used to complete Objective 3. By measuring the activity in the solution across a period of time it was seen how long it takes for the column to reach breakthrough and failure. The breakthrough point is when the eluent concentration beings to climb from its initial value, while the failure point is when the media is saturated and the eluent concentration is the same as the influent. However it may be prudent to lower the value of the effluent activity to determine breakthrough in order to better mimic actual operating conditions for a large scale operation. For this experiment a bench scale column apparatus has been developed. A Piping and Instrumentation Diagram (P&ID) of the column system that will be used has been developed. It can be seen below along with a description table in Figures 4-1 and 4-2 and Table 4-1.

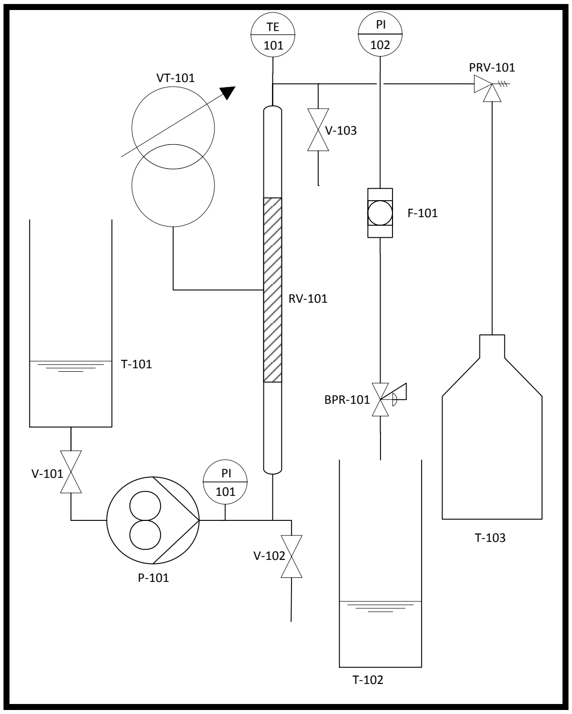

Figure 4-1: P&ID of the NORM Sorption Reactor

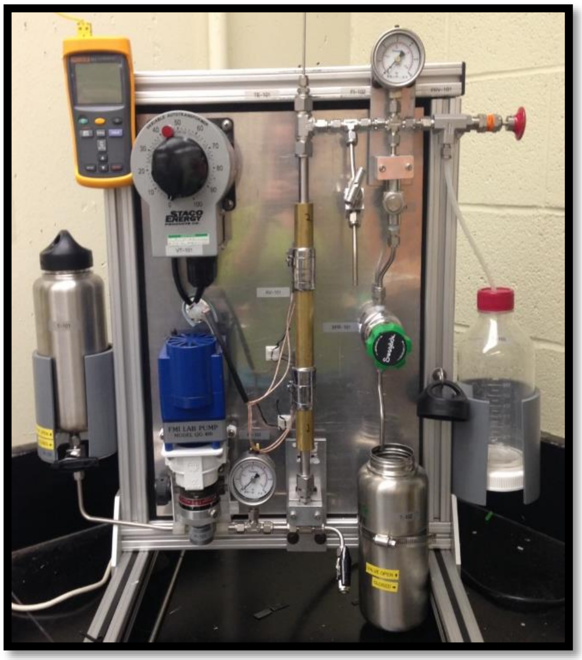

Figure 4-2: Picture of the NORM Sorption Reactor

Table 4-1: List of Labels & Definitions for P&ID

LABEL	OBJECT	PURPOSE
T-101	Tank 1	Inlet Tank
T-102	Tank 2	Effluent Tank
T-103	Tank 3	Pressure Relief Effluent Tank
V-101	Valve 1	Inlet Valve
V-102	Valve 2	Pre-Reaction Draining Valve
V-103	Valve 3	Post-Reaction Sample Valve
P-101	Pump	Displacing Water in the Rig
RV-101	Reaction Vessel	Location of Sorbent Reactions
PI-101	Pressure Indicator 1	Reads Pressure After P-101
PI-102	Pressure Indicator 2	Reads Pressure After V-101
VT-101	Variable Transformer	Controlling the Temperature
TE-101	K Type Thermocouple Probe	Measuring the Temperature
PRV-101	Pressure Relief Valve w/ Manual Override Handle	Prevention of Excess Pressure Buildup
BPR-101	Back Pressure Regulator	Controls Pressure Within the System
F-101	Filter	Protects BPR-101 from Solids Buildup

The first step in this experiment was to set the temperature, pressure, and flow rate of the column. This procedure is described in full in the SOP, but will not be detailed here. Once these parameters were set, RV-101 was disassembled by disengaging the nuts above and below the column. An appropriate mass of sorbent was weighed out according to the test being conducted. First a layer of glass wool was packed into the column to act as a bedding. The packing tool that will be used was marked so that the bedding was packed to the appropriate depth in the column. This depth was determined in order to make sure that the thermocouple did not disturb the packed material once it was placed back in the column. Next the measured mass of sorbent was added, followed by another layer of glass wool. After packing these down to the appropriate depth the sorbents were sandwiched between the wool so that it was held in place and the bed did not become fluidized.

Once RV-101 was completely packed it was then reattached to the test rig in its original position making sure that all nuts were tightened sufficiently so that no leaks occurred. A sufficient amount of flat-top centrifuge tubes were prepared and labeled for collecting samples. The appropriate ionic strength solution for the given test was created following the guidelines in Table 3.2. A test solution was then created by diluting the Ra-226 standard with the appropriate stock solution so that the concentration of the radium was 10 nCi/L. This solution was then poured into T-101. Once all of the valves were set to their appropriate positions P-101 was turned on and the solution was pumped through the system. The fluid exited the system and flowed into T-102. As soon as the first drop were seen exiting the system a stopwatch is started and that point was deemed the initial time. Also at this initial time the first sample was taken. Samples were taken at V-103. A labeled centrifuge tube was held under the pipe, then the valve was opened and fluid was allowed to flow into the tube. Once a sufficient amount of solution was collected the valve was then closed. A sample was collected in time intervals based on the test being conducted until all of the fluid had passed through the rig.

After the sampling period was complete all excess fluid was drained from the system and P-101 was turned off. RV-101 was then taken off of the rig and the spent sorbent and glass wool was disposed of. RV-101 was reattached and then care was taken to decontaminate the rig for safety as well as to not skew later experiments.

Once the rig had been properly decontaminated the samples were ready to be analyzed. One of the centrifuge tubes was taken and 4 mL of the solution was pipetted onto a clean metal sample dish. The dish as placed in a drying oven set at 100 ^{o}C and allowed to dry for approximately 1-hour. Once the dish was completely dry it was introduced to the RadEye for a 35-minute counting time. This analysis was repeated for all samples. Once all samples had been analyzed the data was tabulated, and a breakthrough curve is plotted.

CHAPTER 5: RESULTS AND DISCUSSION

Efficiency Calibration and Limit of Detection Calculations

In order to ensure that the results of this experiment are accurate and meaningful, care had to be taken in the data analysis planning stages. In preparation for running these experiments the Limit of Detection (LOD) was determined using a program called RadCalcLE™ from the Ludlum Measurements Inc. website. Using a background value of 0.6 CPM and a background counting time of 2.5-hours a value for the LOD was determined. This background value was determined by running a large number of empty metal trays in the RadEye and averaging the data. The full data set for this can be seen in the Appendix in Table A-1. For the batch experiments a sample counting time of 10-minutes was used. Using that counting time it was determined that the LOD is 1.132 CPM over background, so a value of 1.2 CPM above background was used because of the 0.6 CPM increment capabilities of the RadEye. For the column experiments the sample counting time was increased to 35-minutes in order to decrease the LOD to 0.5641 CPM above background. This allowed a reading of 0.6 CPM above background to be used.

The next step was to determine the detection efficiency of the RadEye for each of the six solutions that would be tested. In order to accomplish this, a test matrix was created for each solution. Each was run at six different dilutions, and each dilution was prepared in triplicate. This data was also used in order to calculate the Minimum Detectable Activity (MDA) for each solution. The MDA is the lowest activity that can be detected by the RadEye in order to give a signal above the background level. Once known, the MDA can be used to calculate the maximum detectable removal efficiency.

Firstly this process was run at a 10-minute counting time in order to prepare for the batch experiments. All data was gathered for each of the six solutions, and the detection efficiency was calculated for each sample. This data can be seen in Tables A-2 through A-7. It was then determined that because the efficiency was so low, Solutions 2, 5, and 6 were to be dropped from the test matrix. This is due to the fact that because the detection is so close to the background levels it could not be seen that the treatment is effective or not. It was also determined that the 0.25 nCi/L samples would not be used in the MDA calculations for Solution 1. This decision was made because the efficiency for these samples is much different than the lower dilutions. This variation is due to the fact that the samples are so near the detection capabilities of the RadEye. This same reasoning is used in Solutions 3 and 4 for dropping both the 1.0 and 0.25 nCi/L samples. Once these determinations were made, the data was plotted by Measured Disintegrations (CPM) vs. Activity (nCi/L) as shown in Figures 5-1, 2, and 3.

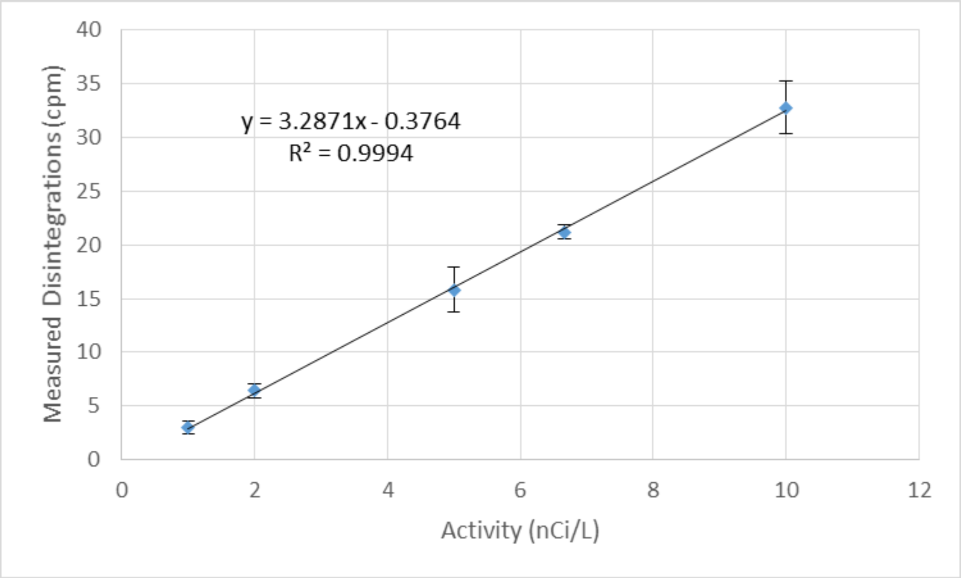

Figure 5-1: Calibration Plot for Solution 1 at a 10-Minute Counting Time

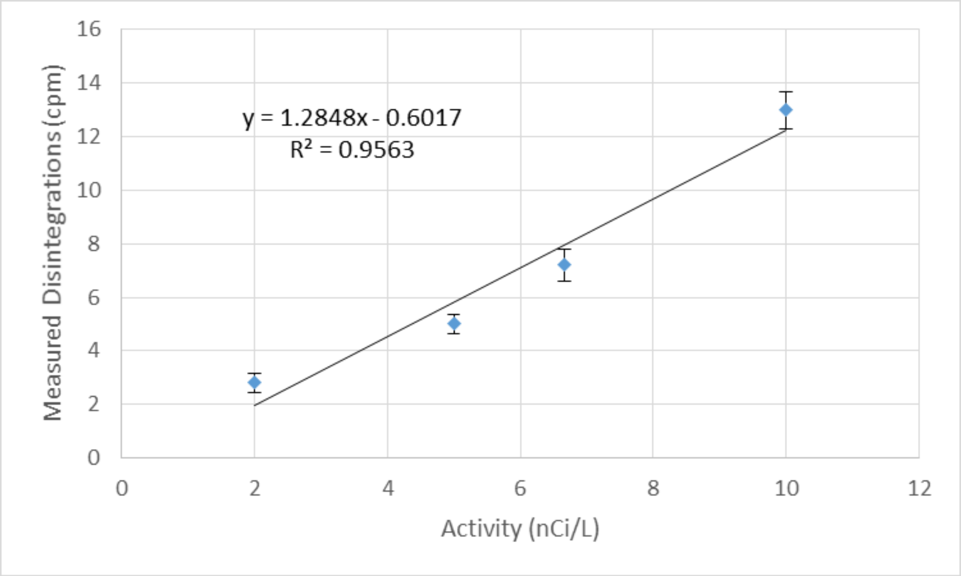

Figure 5-2: Calibration Plot for Solution-3 at a 10-Minute Counting Time

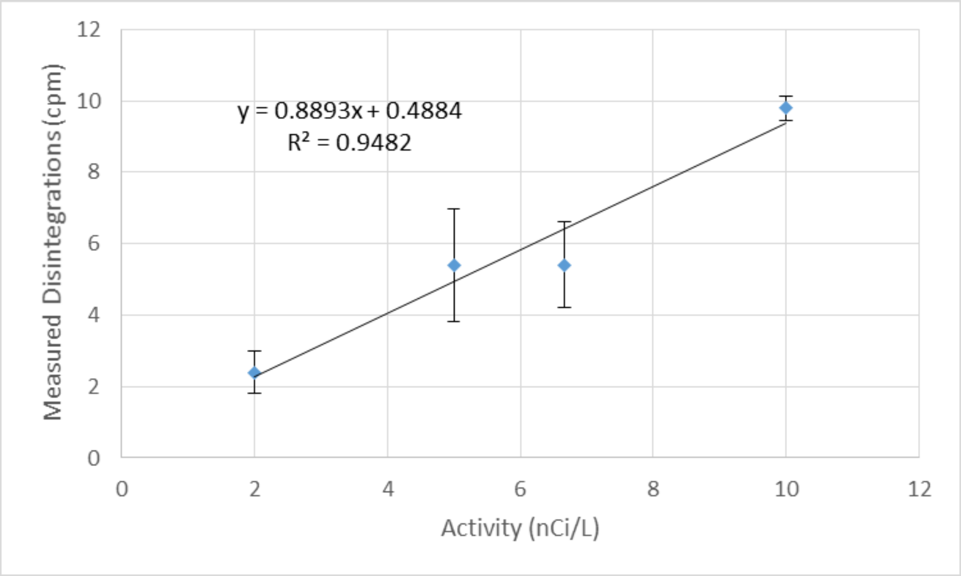

Figure 5-3: Calibration Plot for Solution 4 at a 10-Minute Counting Time

This same process was repeated at a 35-minute counting time for the column experiments. For the column experiments it was decided that only Solutions 1 and 3 would be run. Only these solutions were chosen because of the large amount of time that the column tests take to complete. By only using these two solutions a larger number of tests could be completed at higher resolution. The results using these two solutions would be sufficient in order to compare the radium removal with and without additional ions in solution, and the higher resolution would lead to higher quality results that could be more repeatable. The data for these tests can be seen in Tables A-8 and A-9, and Figures 5-4 and 5-5.

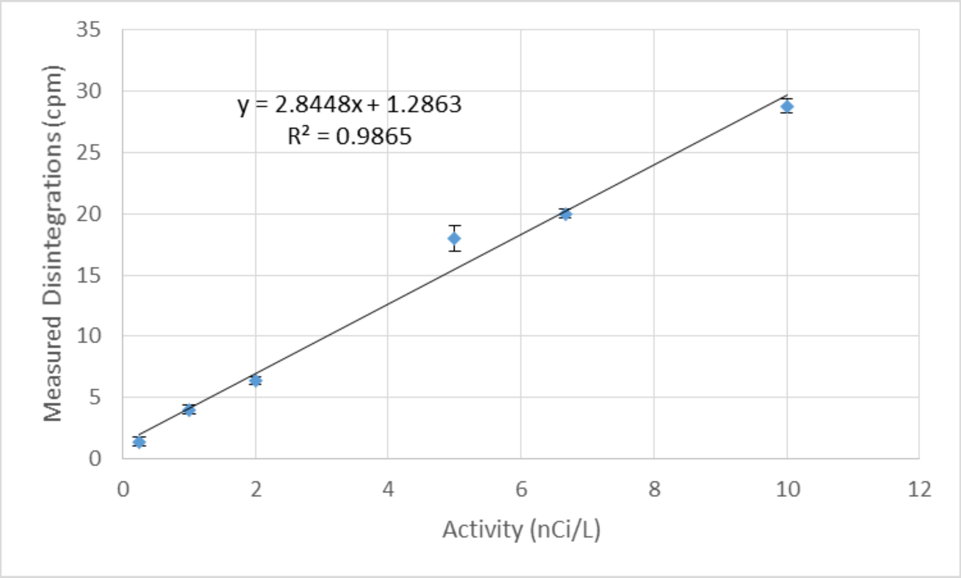

Figure 5-4: Calibration Plot for Solution 1 at a 35-Minute Counting Time

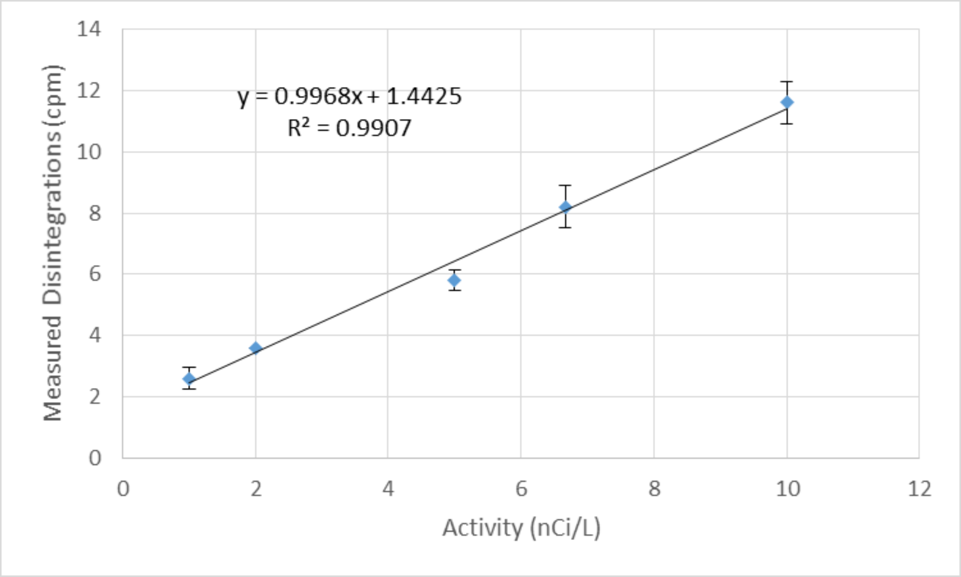

Figure 5-5: Calibration Plot for Solution 3 at a 35-Minute Counting Time

A linear regression was created for each plot. The equation of this line was then used to calculate the MDA of each solution. This was done by using the LOD as the ‘y’ value and solving for the activity. Next, by knowing the minimum activity that can be confidently detected the maximum removal efficiency was calculated. With a known initial concentration of 10 nCi/L that will be used this efficiency was calculated by:

$$Maximum\ Removal\ Efficiency\ (\%) = \frac{10 - (MDA)}{10} * 100$$

A table detailing the results of these calibrations can be seen below in Table 5-1. The LOD that was used for each calculation was the value determined using the RadCalcLE™ plus the background value of 0.6 CPM. These values will be used when presenting the results of the batch and column tests in order to convert the raw data into more appropriate units.

Table 5-1: Descriptive Table of MDA and Maximum Removal from Calibration Data

Counting Time (min)	Solution #	LOD used (CPM)	MDA (nCi/L)	Maximum Removal (%)
10	1	1.8	0.662	93.4%
10	3	1.8	1.869	81.3%
10	4	1.8	2.573	74.3%
35	1	1.2	-0.030	100.3%
35	3	1.2	-0.243	102.4%

Batch Experiment Results

Clinoptilolite

The first of the sorbents that was tested was the natural zeolite clinoptilolite. The experiments were set up according to the test matrix in **Error! Reference source not found.**, except samples were not conducted using Solutions 2, 5, or 6. The first of the two clinoptilolite samples tested was the granulated mesh size. Firstly it should be noted that after the samples were allowed to settle a fair amount of sludge was produced. An example of the sludge buildup can be seen in Figure 5-7. Because of this sludge, the samples were extracted with a syringe and filtered using a .45-µm syringe tip filter. This was done to ensure that none of the sorbent would be pipetted onto the dish which could negatively impact the results. The data gathered from these experiments can be seen in Table A-10 and Figure 5-6.

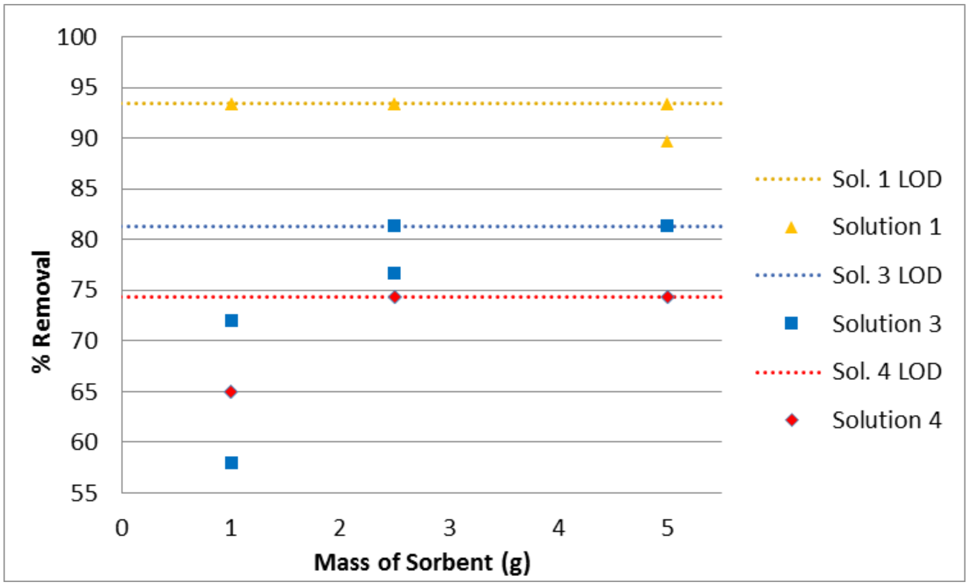

Figure 5-6: Granulated Clinoptilolite Batch Experiment Data and Limits of Detection

All of the samples using Solution 1 with no salts had the radium removed completely to a detectable level using the smallest mass of sorbent. However the low and medium ionic strength solutions needed the 2.5 g of sorbent in order to completely remove the radium to detection. This shows that the ions present in solution do compete with the radium for selection sites in this sorbent.

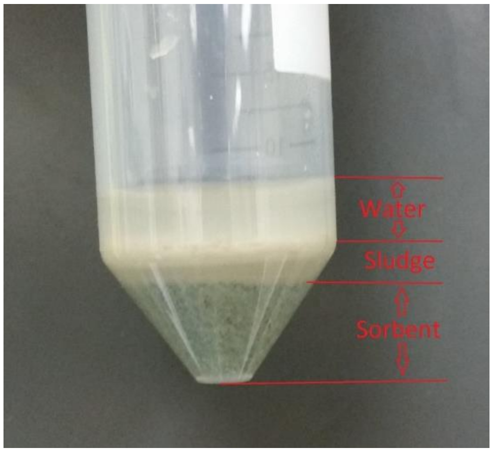

Figure 5-7: Sludge Buildup Using Clinoptilolite in Batch Experiments

The next sorbent that was tested was the powdered mesh size of the clinoptilolite. It was observed that when using this smaller grain size more of the sludge was produced in the sample vials. This became a problem when dealing with the 5g and 7.5g masses of sorbent because 4 mL of clean fluid could not be gathered from the sample vial. For the 5g samples only 3 mL could be filtered out, and for the 7.5g samples only 1.5 mL of fluid could be dried and tested. Because of this the 7.5g samples were excluded from Figure 5-6 as well.

This was not a large problem moving forward however because it was determined that the powdered clinoptilolite was highly effective at removing the radium to a detectable level using only the 1g samples. The results from this set of trials can be seen in Table A-11 and Figure 5-8. All nine samples tested at this mass completely removed the radium to the respective Limit of Detection. Because a high level of removal was observed, even for the higher ionic content solutions, it was decided that moving forward that the 7.5g mass of sorbent trials would not be carried out for the other two sorbents that would be tested.

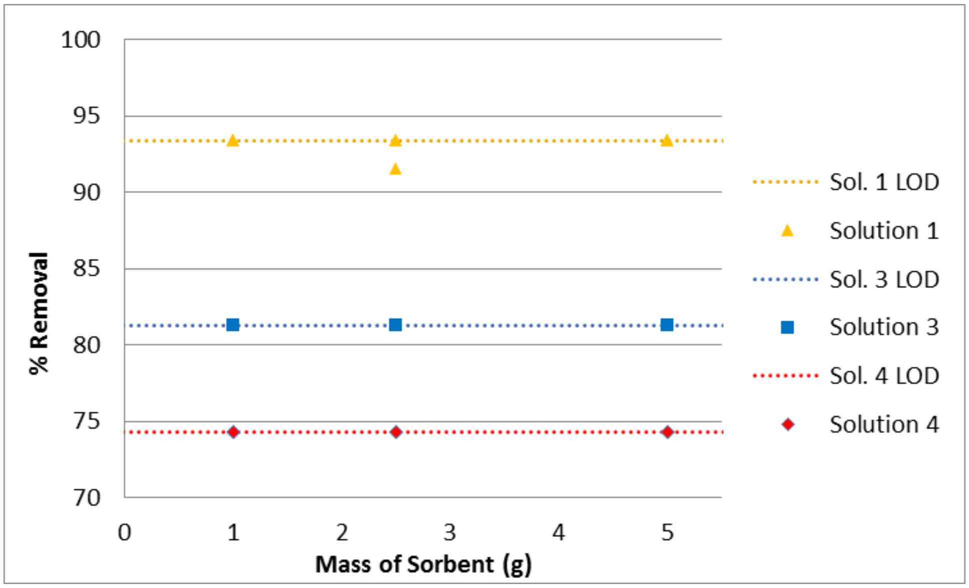

Figure 5-8: Powdered Clinoptilolite Batch Experiment Data and Limits of Detection

DOWEX

The second of the sorbents that was tested was the DOWEX ion exchange resin. For this sorbent the modified test matrix described in Section 5.2.1 was used. From the original test matrix shown in **Error! Reference source not found.** only Solutions 1, 3, and 4 were used and for only the 1g, 2.5g, and 5g masses of sorbent. When running the trials it was observed that the DOWEX resin settled almost immediately after being set upright. Even though this was the case the samples were still allowed to settle for 12-hours after being on the shaker plate to provide consistency between the experiments. Also because the resin did not produce any sludge there was no need to use the syringe tip filter on the samples. The sample could be pipetted directly out of the test vial onto the sample plate. The results of these tests can be seen in Table A-12 and Figure 5-9.

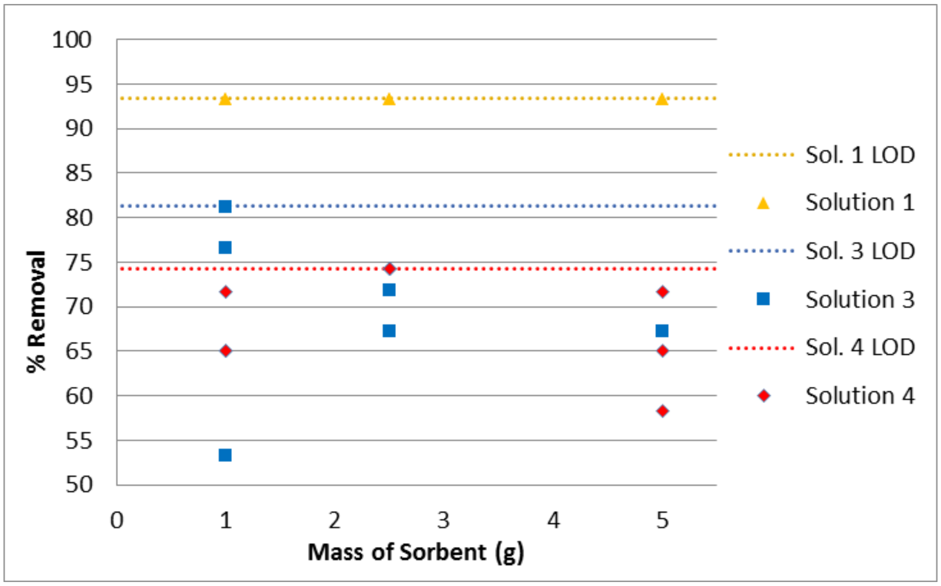

Figure 5-9: DOWEX Batch Experiment Data and Limits of Detection

The data shows that the DOWEX is very good at removing the radium from solution when there are no other ions present. All samples using Solution 1 had the radium removed from solution to the detection limit. Conversely, when using Solutions 3 and 4 the radium was not efficiently removed. The salts in the solution used up many of the sorption sites which can be seen because there was only 3 samples out of 18 where the measured activity was below the MDA. However, there was not a steady correlation between the mass of sorbent used and the amount of radium detected after treatment. The only sample using Solution 3 where the radium was removed to the detection limit was using the 1g mass of sorbent, while higher detected activities were observed using the larger masses. Also for Solution 4 it was seen that the lowest detected activity were measured from the samples that used the medium 2.5g mass of sorbent.

Barium Sulfate

The final material tested in the batch stage was the barium sulfate. The experiments followed the same test matrix used for the DOWEX resin. This material behaved much more like the clinoptilolite than the DOWEX, in that a very large amount of sludge was produced. However, after the 12-hour settling period there was no clear supernatant above the sludge. Instead there was a milky white liquid. These samples were filtered using the syringe tip filters before being pipetted onto the sample plates. The results of this set of tests can be seen in Table A-13 and Figure 5-10.

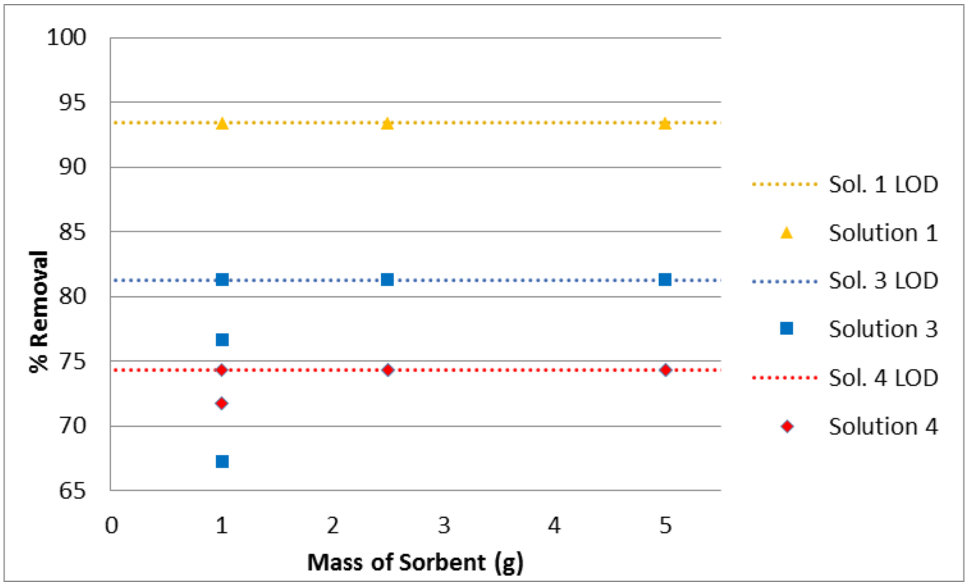

Figure 5-10: Barium Sulfate Batch Experiment Data and Limits of Detection

Similar to the rest of the treatments, all of the radium was removed to a detectable level using Solution 1 at the lowest mass. When using Solutions 3 and 4 however the 1g mass was not able to remove everything. However when using the 2.5g and 5g masses of $BaSO_4$ the radium was removed from solution to below the MDA for every sample tested.

Sorbent Comparison

When comparing removal efficiencies for the different sorbents using the three different ionic strength solutions, several important distinctions can be made: In Figure 5-11 it can be seen that all four of the tested sorbents are good at removing the radium from solution when no other ions are present. Only two data points tested had activities above the MDA out of the 36 total. However, all of the 1g masses showed the highest detectable removal.

On the other hand in Figures 5-12 and 5-13 it can be seen that the removal efficiencies are significantly lower when using the higher ionic strength solutions. For both types of clinoptilolite as well as the barium sulfate the 2.5g or 5g masses of sorbent was needed to see the treated samples fall below the MDA. The DOWEX performed even worse with the salts in solution, and rarely would reach the LOD. This shows that increasing the ionic strength of the solution negatively impacts the radium removal. Also it shows that the clinoptilolite and the barium sulfate are more highly selective for removing radium than the DOWEX is.

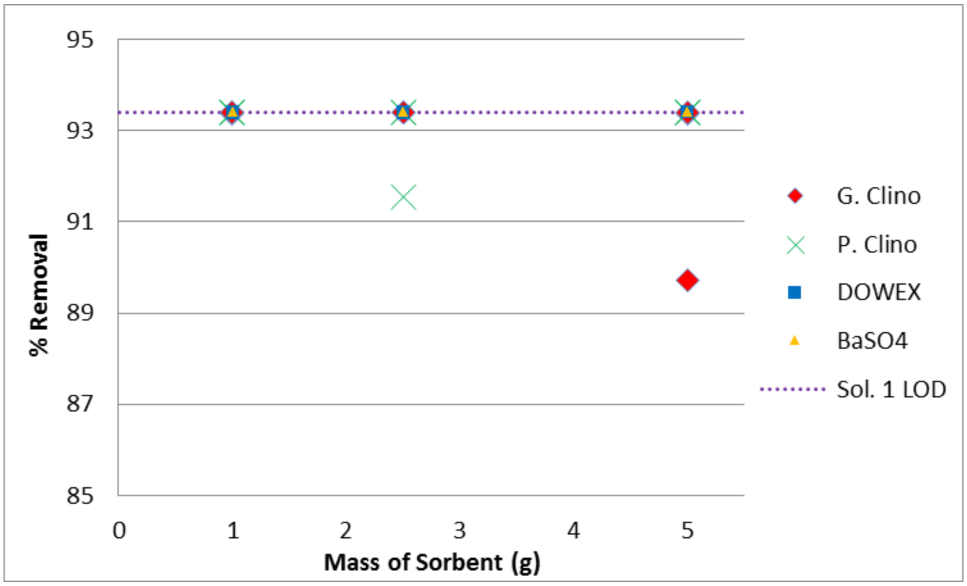

Figure 5-11: Batch Experiment Data for All Sorbents Using Solution 1

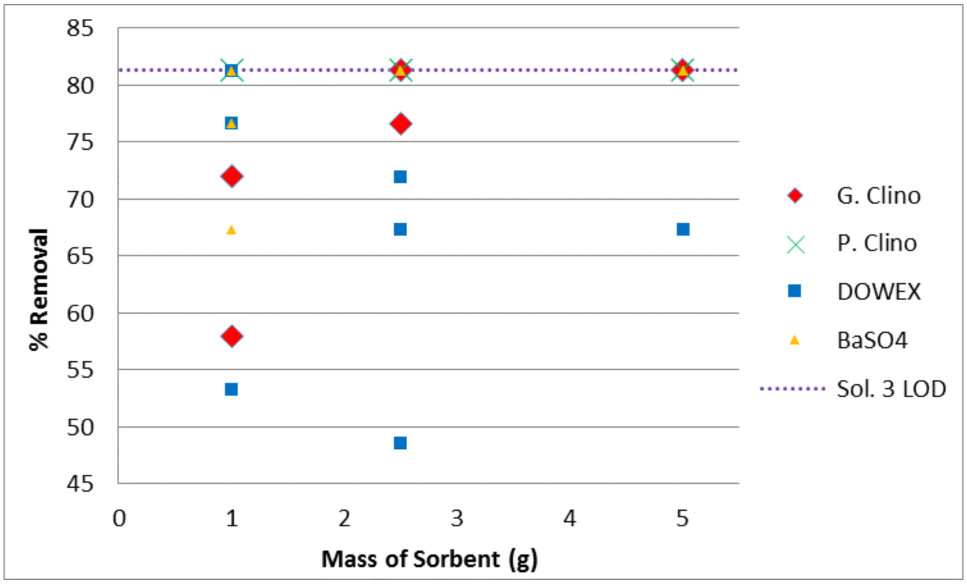

Figure 5-12: Batch Experiment Data for All Sorbents Using Solution 3

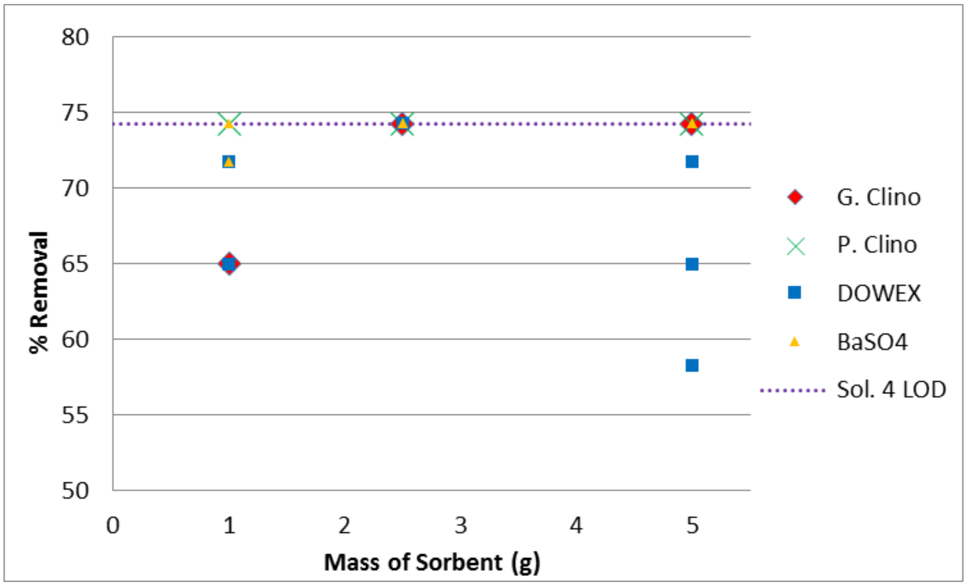

Figure 5-13: Batch Experiment Data for All Sorbents Using Solution 4

When looking at the BET surface area data it can be seen that these removals shown above have no correlation to the surface area of the sorbent being used. The data from the Micrometrics ASAP 2020 can be seen below in Table 5-2. The clinoptilolite samples have the largest surface area by a large degree, but the barium sulfate performed equally as well across all four solutions. This shows that the mechanism of removal is not surface area driven.

Table 5-2: BET Surface Area Data for All Sorbents

	BET Surface Area (m^2/g)
Powdered Clinoptilolite	25.5
Granulated Clinoptilolite	70.2
$BaSO_4$	1.25
DOWEX	0.0410

Additional Tests

After the test matrix was completed for all four sorbents, additional tests were conducted on the powdered clinoptilolite and the DOWEX. These are the only two sorbents that were used for these tests because only they were used in the column experiments. The reasoning for not using the granulated clinoptilolite and the barium sulfate is explained in the following section. The goal of these two additional experiments would be to evaluate the lower limit of radium removal by using lower masses, and also to evaluate the effect that changing the pH has on the removal efficiency.

In order to evaluate the lower masses more accurately, the samples were run at a 35-minute counting time so that a MDA of 0.6 CPM could be used. This was done for only the 0.1g and 0.5g samples that had a neutral pH. This is the reasoning that higher removal efficiencies can be observed for those samples than for the 1.0g samples or the different pH tests. However by using the lower LOD it means that the removal efficiencies cannot not be plotted together, and instead all figures use the post-treatment α activity in CPM. The first sorbent to be tested was the powdered clinoptilolite. The results of these experiments for Solution 1 and 3 can be seen in Figures 5-14 and 5-15, respectively, as well as Table A-14. For reference, the average pretreatment activity at a 10-minute counting time is 32.8 CPM for Solution 1 and 13.0 CPM for Solution 3, while at a 35-minute counting time the activities are 28.8 CPM for Solution 1 and 11.6 CPM for Solution 3.

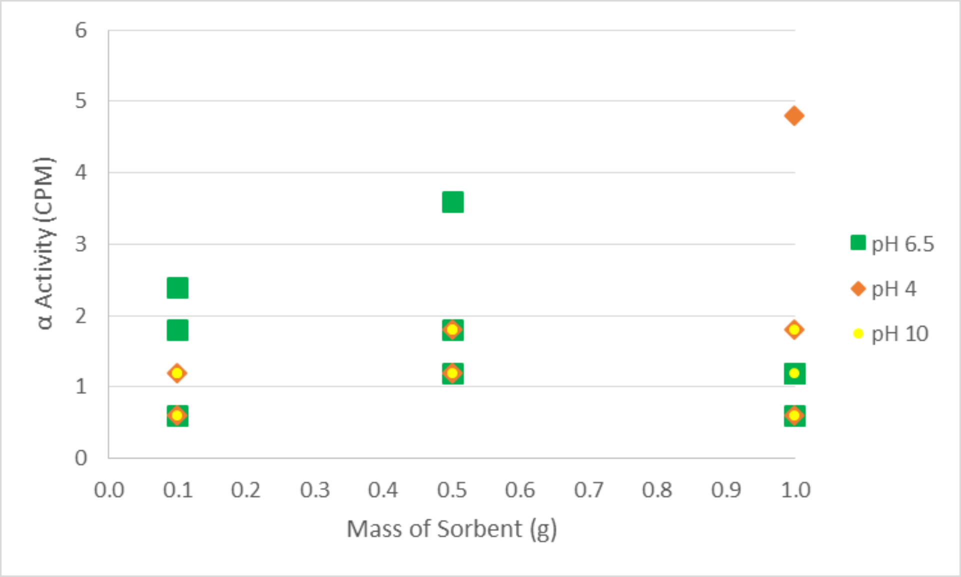

Figure 5-14: Solution 1 Batch Tests to Evaluate pH Variation Using Powdered Clinoptilolite

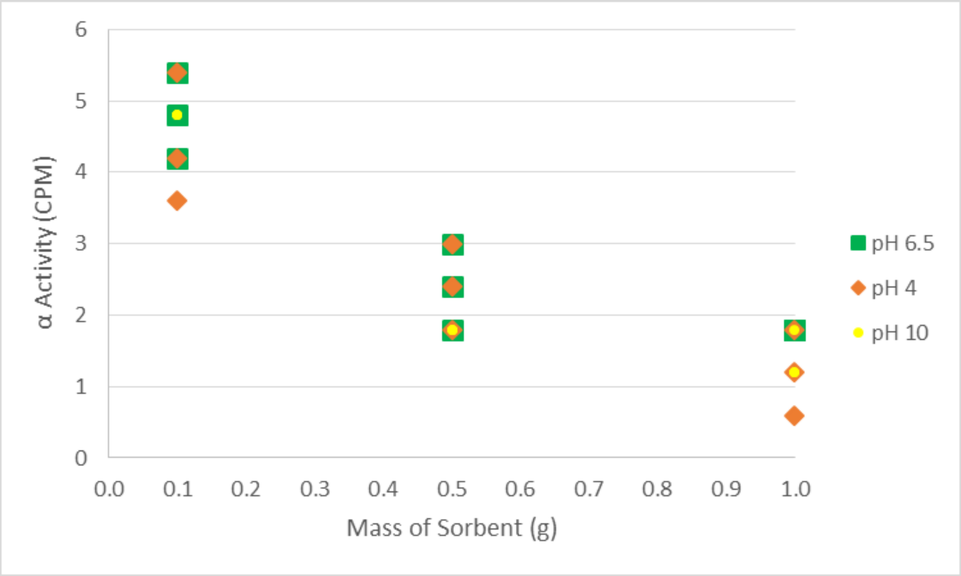

Figure 5-15: Additional Solution 3 Batch Tests to Evaluate pH Variation Using Powdered Clinoptilolite

In these experiments it can be seen that a very high rate of removal is observed for Solution 1, even using a 0.1g mass of sorbent. With Solution 3 however, there is a drop off in the removal efficiency in the lower masses. These trends are the same regardless of the working pH of the solutions. In all samples using the acidic or basic solutions the radium was removed to below the MDA. The trend is very similar regardless of the pH of the solution, so it does not seem to affect the removal. The second sorbent tested was the DOWEX resin. These results are shown in Figures 5-16 and 5-17, and in Table A-14.

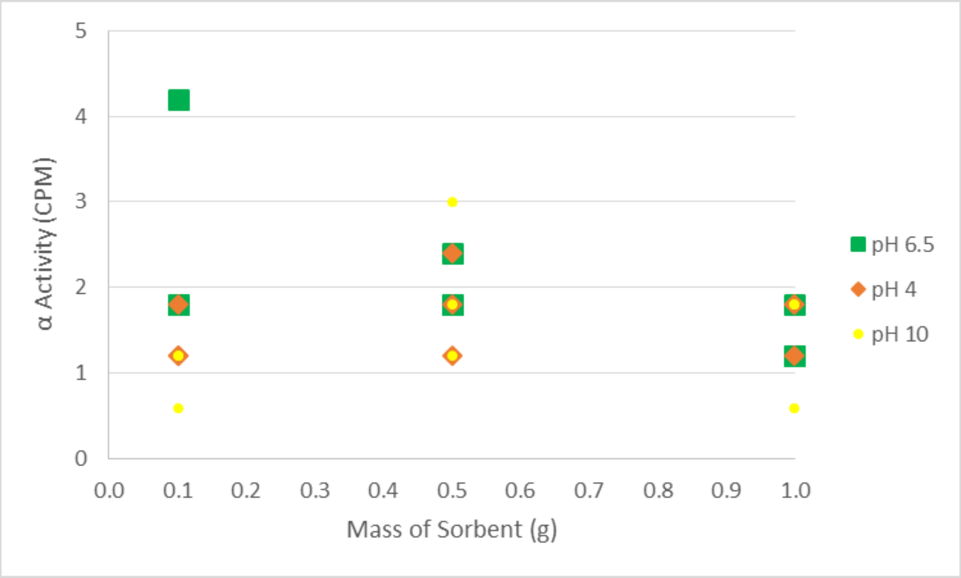

Figure 5-16: Additional Solution 1 Batch Tests to Evaluate pH Variation Using DOWEX

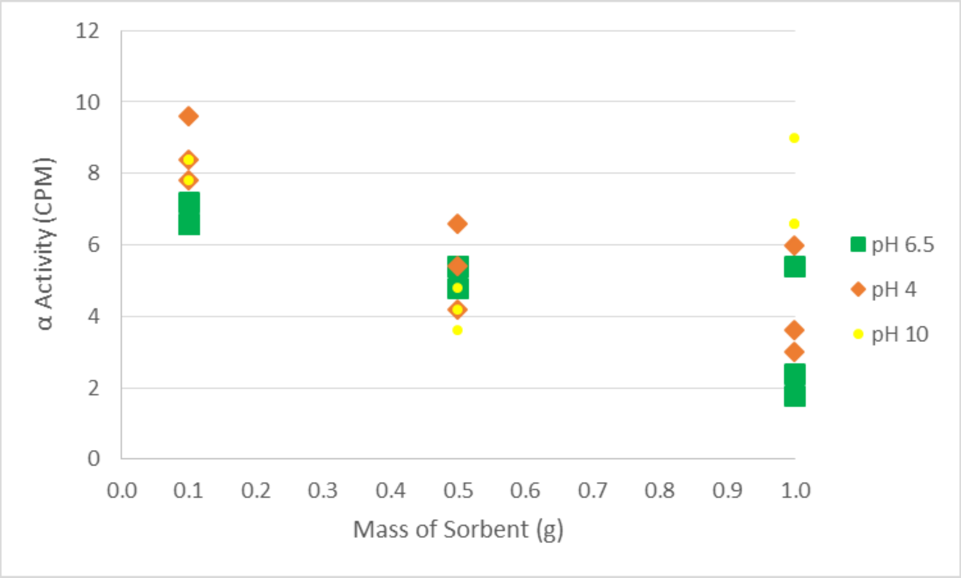

Figure 5-17: Additional Solution 3 Batch Tests to Evaluate pH Variation Using DOWEX

Except for one data point, the DOWEX again showed that it is excellent at removing radium from solution when no other ions are present, even at the 0.1g mass. However when using Solution 3 the removal became much less efficient. At the 1.0g mass of sorbent, there is a high degree of variation in the results. However the data seems to follow an upward trend when decreasing the amount of sorbent that was used. The pH does not seem to strongly affect this removal, especially for the 0.1g and 0.5g samples.

Column Experiment Results

Scoping Tests

In the first stage of the column experiments several shakedown tests were conducted in order to first see how the packed beds would perform. The goal of these tests would be to evaluate how the sorbents would physically hold up during a flow through experiment. Trials were run using deionized water with no radium in order to scope how the sorbents would perform during these column tests. During these first tests, 5.0g of each sorbent was used, along with 0.5g of glass wool on each side of the sorbent bed in order to keep the bed fixed. The reaction vessel that was used had an outer diameter of 0.5”, and a fluid flow rate of 25 mL/min.

The first material tested was the DOWEX resin. This was chosen because it produced no sludge, and is easily the most simplistic sorbent to work with. When conducting these trials it was observed that no excess pressure buildup was generated in the rig, and the flow rate was not affected by the packed bed being introduced to the system. The second sorbent tested was the granulated clinoptilolite. Even though sludge was observed during the batch tests, none was seen in the effluent stream of the column tests. Also a very minimal pressure increase was observed, but it was well within the safe operating conditions of the test rig.

With the third sorbent tested, the barium sulfate, many problems arose. Firstly, a major pressure increase was observed. The pressure in the system exceeded the safe operating pressure within the first minute of operation. This pressure buildup triggered the PRV to open in order to maintain the integrity of the rig so that no damages would occur. The second problem was that a large amount of sludge was observed in the effluent stream. The glass wool bedding was not enough to keep the barium sulfate within the packed bed. When this was observed, the pump was shut off, and the sorbent was removed. Because radium would be introduced in later experiments, this became a major safety issue. This combined with the massive amount of cleaning time that was required to remove the barium sulfate sludge from the test rig, led to the decision that the barium sulfate would be excluded from the column experiments.

Preliminary Radium Tests

After the scoping tests were completed, a set of tests were conducted in order to plan forward for the experiments that would need to be conducted to complete the research objectives. All of these tests were conducted using a reaction vessel with an outer diameter of 0.5”, and a fluid flow rate of 25 mL/min. The DOWEX resin was chosen for these preliminary experiments because it is the easiest of the sorbents to work with. For all tests 0.5g of glass wool was used on both top and bottom of the sorbent in order to keep the bed fixed within the reaction vessel.

The first experiment that was conducted used 5.0g of DOWEX and the operating conditions listed above. The data for this test can be seen in Figure 5-18 and in Table A-16. Several important observations can be made from this data. The first is that the initial effluent samples have activity values right at background levels. This shows that under these operating conditions there is adequate contact time to remove radium from solution to the LOD. The second observation, however, is that no breakthrough was observed. The effluent samples stayed at fairly consistent levels throughout the duration of the experiment. Using this mass of sorbent there is too much exchange capacity to see a breakthrough with the amount of radium that was used.

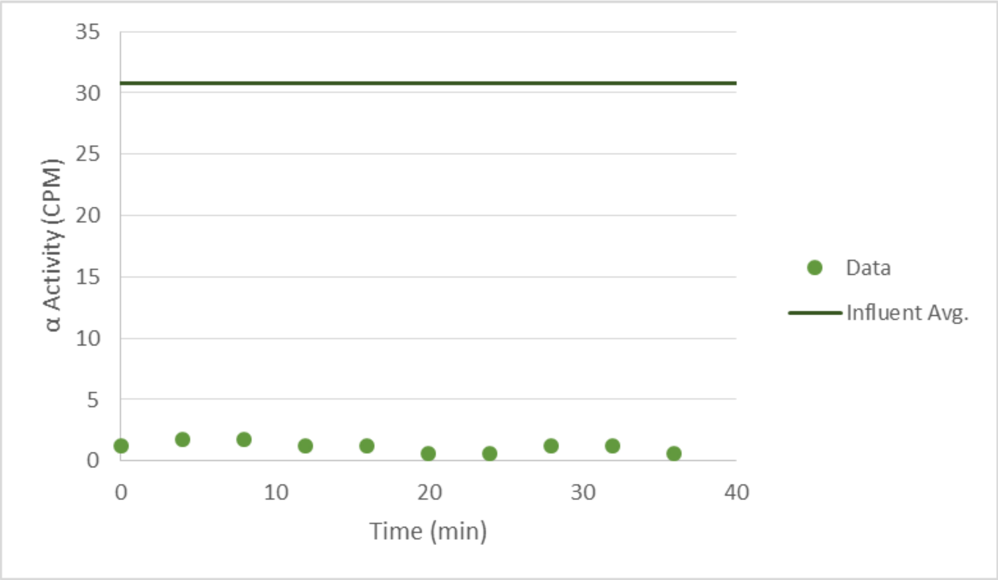

Figure 5-18: Column Experiment Data Using 5.0g DOWEX Resin in a 0.5" Reaction Vessel, Solution 1 at 25 mL/min (1)

In the second experiment that was conducted the mass of sorbent used was halved compared to the first. The results of this experiment can be seen in Figure 5-19 and in Table A-17. The idea behind lowering the mass was to try to observe the breakthrough that was not seen using the 5.0g test. This still was not the case. The effluent samples stayed at a fairly consistent value throughout the duration of the experiment. There was one major difference though, and that was the initial effluent samples were higher than in the previous test. The means that the 2.5g mass of sorbent did not provide an adequate contact time to remove the radium to detection, even though no exhaustion of the resin was observed.

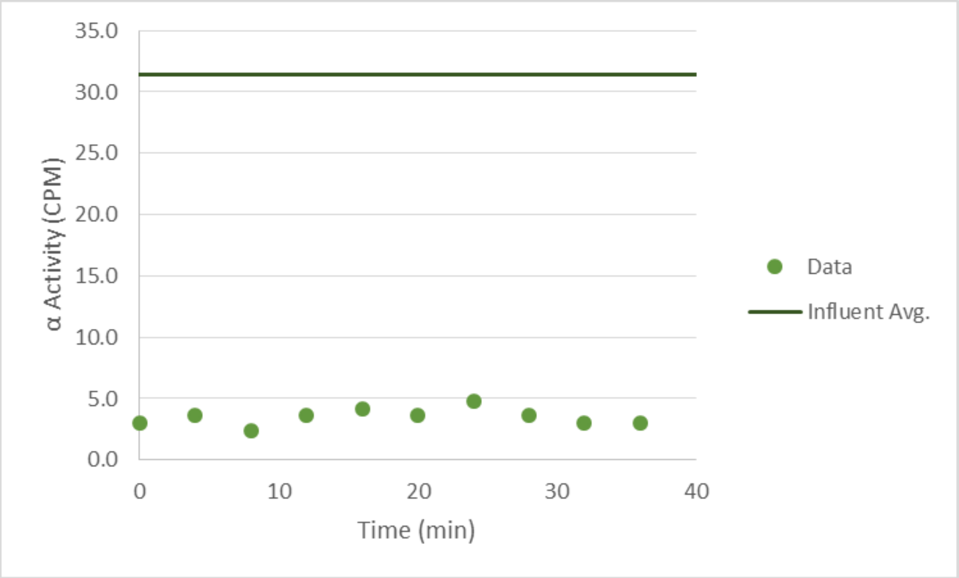

Figure 5-19: Column Experiment Data Using 2.5g DOWEX Resin in a 0.5" Reaction Vessel, Solution 1 at 25 mL/min

The next experiment that was conducted was again using 5.0g of DOWEX in order to maintain the complete removal of radium to the LOD, but four times as much radium solution in order to observe some breakthrough of the bed. These results can be seen in Figure 5-20 and in Table A-18. Similar to the first test, it was again seen that the initial activity of the effluent stream was near background levels. However, even with the increased volume pumped through the bed no breakthrough of the resin was observed.

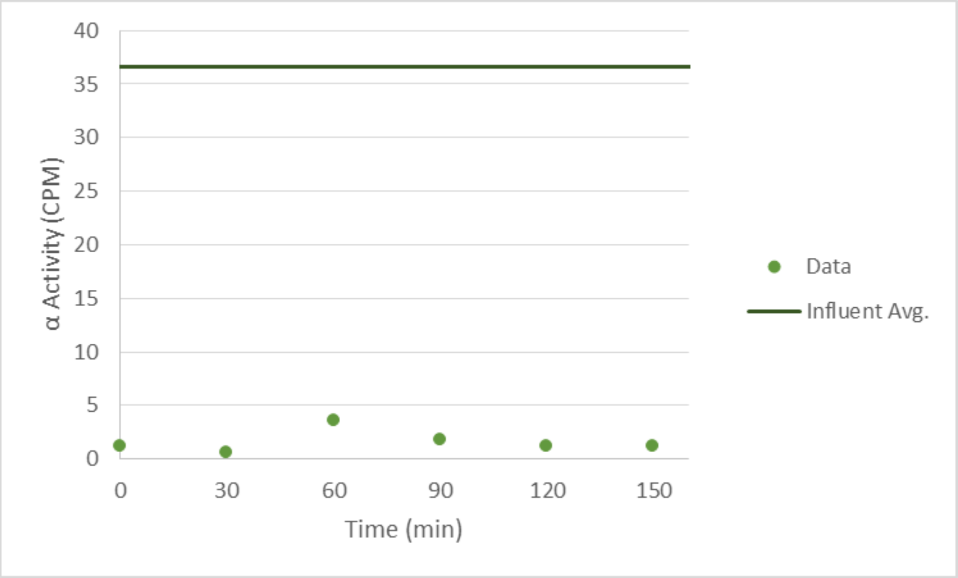

Figure 5-20: Column Experiment Data Using 5.0g DOWEX Resin in a 0.5" Reaction Vessel, Solution 1 at 25 mL/min (2)

The last of these style of experiments that was conducted was see how the bed would perform using a salt solution. Solution 3 was used along with 2.5g of the DOWEX resin. These results can be found in Figure 5-21 and Table A-19. Similar to the other experiment using 2.5g of sorbent, the initial effluent activity was slightly above the LOD. After this initial point, however, there is a huge difference between the two data sets. The resin began to breakthrough almost immediately, and was exhausted before the 20-minute mark. However contrary to the hypothesis, several of the effluent samples actually had an activity higher than the influent average. There was a high degree of variation in the effluent activity, as can be seen in Table A-17, however the effluent values are higher than even the highest influent sample that was recorded. The values after exhaustion were fairly consistent excluding the one point at $t = 40\ min$ when there is a large increase.

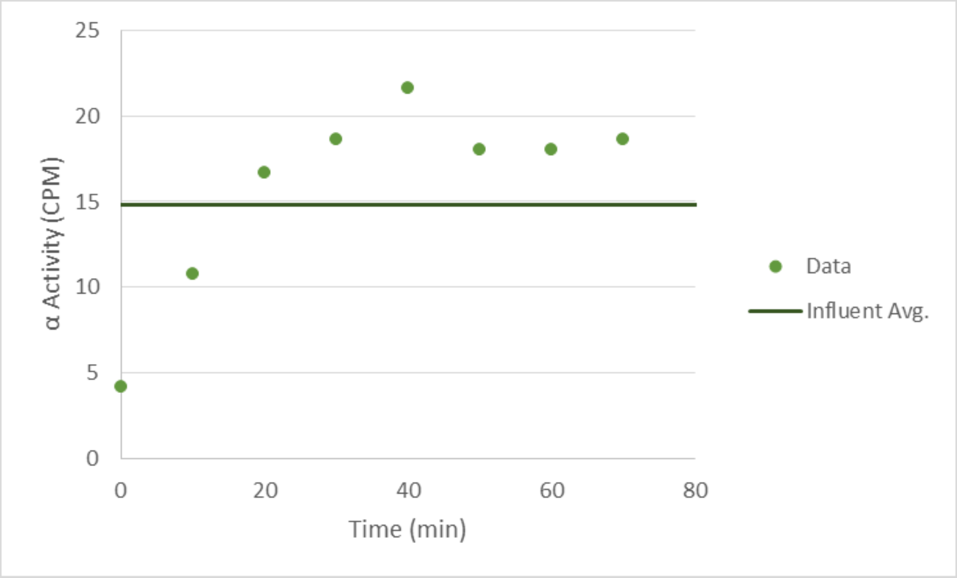

Figure 5-21: Column Experiment Data Using 2.5g DOWEX Resin in a 0.5" Reaction Vessel, Solution 3 at 25 mL/min

The final experiment that was run as part of these preliminary tests was to evaluate the sorption of that glass wool itself. This was done to ensure that any radium adsorbed by the glass wool was negligible and did not influence the results of further column tests. The data for this experiment can be seen in Figure 5-22 and Table A-20. It can be seen that initially a small amount of radium is adsorbed by the glass wool, but the wool is exhausted the next sample. By taking the area between the two curves it was found that approximately: $A = \frac{1}{2}[(35.7 - 15.6)cpm][2min] = 17.1\ counts$ were absorbed by the glass wool. Then by taking the area between the curves of Figure 5-20 approximately: $A = [(36.6 - 1.6)cpm][150min] = 5250\ counts$ were absorbed while still not observing any exhaustion of the resin. This shows that at a maximum the glass wool only absorbs $\frac{17.1}{5250} = 0.33\%$ of the activity that the DOWEX does. Because of this, it is safe to say that the amount of radium adsorbed by the glass wool is negligible and can be ignored in any ensuing experiments.

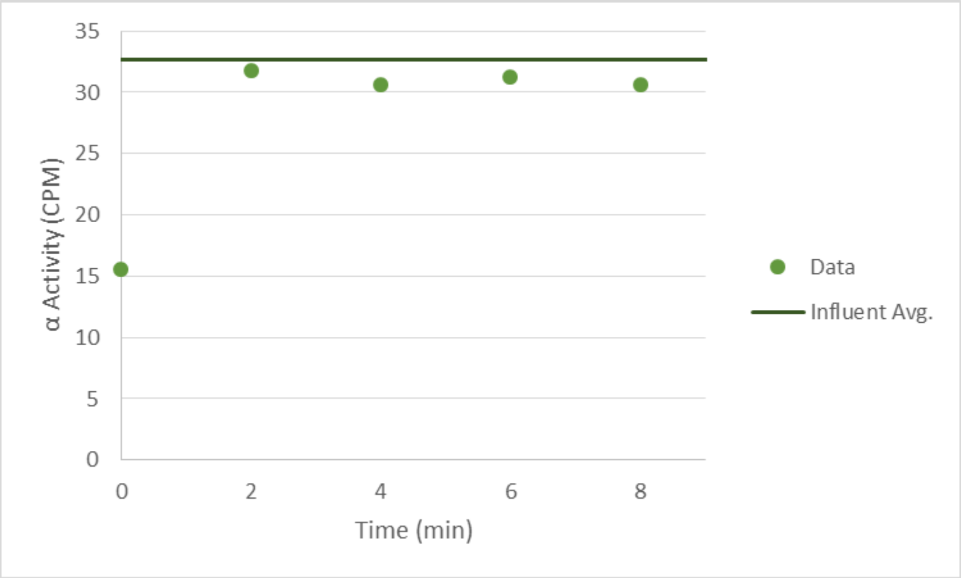

Figure 5-22: Column Experiment Data Using 1.0g Glass Wool in a 0.5" Reaction Vessel, Solution 1 at 25 mL/min

Sorbent Breakthrough and Comparison

After the preliminary tests were completed, a more detailed test plan was put in place in order to complete the research objectives. In the ensuing experiments, comparisons will be made to the removal efficiencies of DOWEX vs. clinoptilolite.

These will be done using both Solution 1 and Solution 3. One major change that will be made however is that for the remainder of the experiments a smaller reaction vessel and flow rate will be used. By downsizing the RV to 0.25” from 0.5”, a smaller mass of sorbent can be used while still having a high enough bed height to provide adequate contact time between the fluid and the sorbent. Also because there was a smaller column diameter, less glass wool was needed to properly act as a secure bedding for the sorbents. Only 0.1g of glass wool was used on top and on bottom of the sorbent bed. In order to further increase the contact time, the flowrate was also dropped from 25 mL/min to 10 mL/min. All of the experiments in this section used this new set of operating conditions. The goal of changing these parameters was to observe some breakthrough unlike the previous radium column tests that were conducted.

The first experiment that was conducted for this section was using 1g of powdered clinoptilolite and Solution 1. The powdered mesh size was chosen for these tests because when using the smaller reaction vessel the granulated particles were too large to provide adequate contact area across the column. The results from this test can be seen in Figure 5-23 and in Table 5-21. The effluent samples that were collected did indeed show an upward trend, and followed a fairly linear pattern. This showed that under these operating conditions and using powdered clinoptilolite a breakthrough could be observed. Because of the length time required to run this test data was not taken all the way to the exhaustion of the sorbent. However the data that was collected shows a good trend that can be used to make comparisons and conclusions.

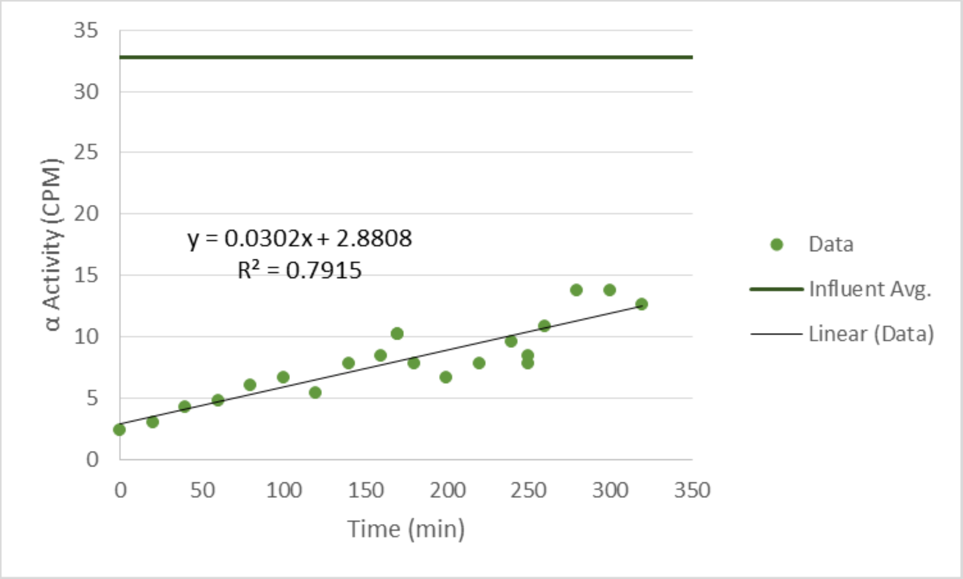

Figure 5-23: Column Experiment Data Using 1.0g Powdered Clinoptilolite in a 0.25" Reaction Vessel, Solution 1 at 10 mL/min

In the next experiment 1g of the DOWEX resin was used with the same operating conditions. The results are shown in Figure 5-24 and Table A-22. Unlike the first experiment, the effluent samples that were collected and analyzed showed no upwards trend whatsoever. There was a lot of variation in the samples, but the linear fit showed almost zero slope. Even with the smaller mass of DOWEX, there was still no breakthrough observed.

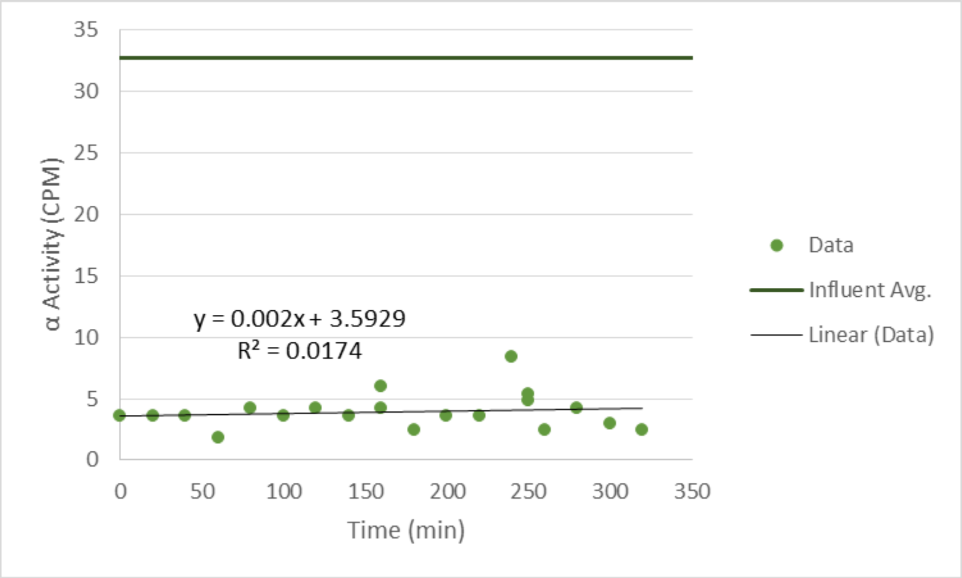

Figure 5-24: Column Experiment Data Using 1.0g DOWEX Resin in a 0.25" Reaction Vessel, Solution 1 at 10 mL/min

The next tests that were conducted was running these same operating conditions using Solution 3. The first sorbent tested was again the powdered clinoptilolite. The results can be seen in Figure 5-25 and Table A-23. There are two main differences between this data and that in Figure 5-23. The first is that the breakthrough is observed almost immediately, and the sorbent is exhausted in approximately 75 minutes when using Solution 3. This differs greatly from the Solution 1 experiment where after over 300 minutes the sorbent was still not exhausted. The second major difference is that the initial effluent activity at $t = 0$ is much higher when using Solution 3. This is the opposite of what was seen in comparing Figures 5-15 and 5-17. In those tests the same mass of sorbent was used, yet the initial activity was very similar when using Solution1 or Solution 3. This shows that at a lower mass of sorbent, more contact time is needed when additional ions are in solution to remove the radium from solution.

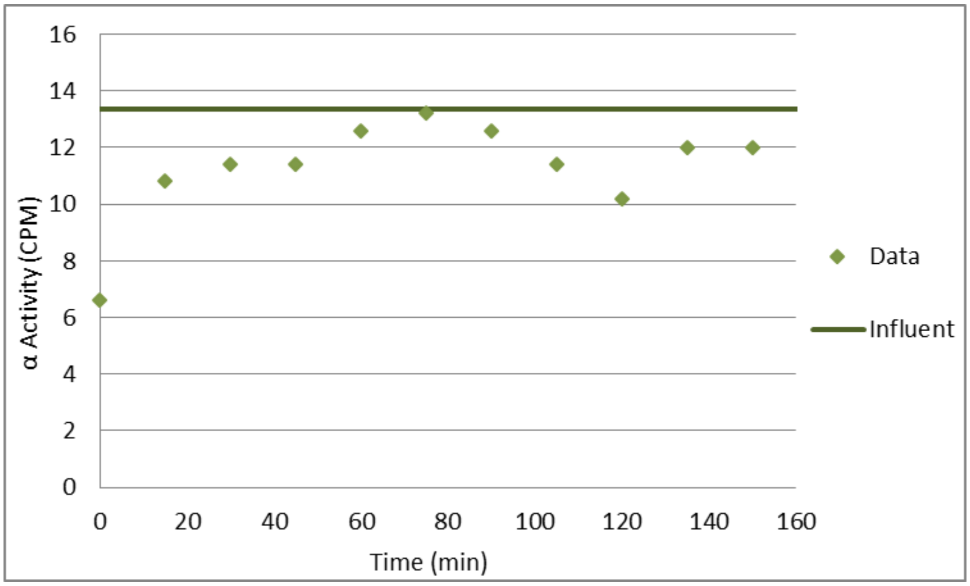

Figure 5-25: Column Experiment Data Using 1.0g Powdered Clinoptilolite in a 0.25" Reaction Vessel, Solution 3 at 10 mL/min

The second sorbent tested using Solution 3 was the DOWEX resin. This data can be found in Figure 5-26 and Table A-23. These results show that this resin behaved very similarly to the powdered clinoptilolite in the previous experiment. Unlike the results using Solution 1, a breakthrough and exhaustion was observed using the DOWEX with Solution 3. The exhaustion came at approximately the 75 minute mark, same as the clinoptilolite. Also like the previous experiment, the initial effluent sample had a recorded activity much higher than the same point using

Solution 1. One additional thing to note for both sorbents using Solution 3 is that after exhaustion was reached the ensuing samples did not follow any sort of a trend.

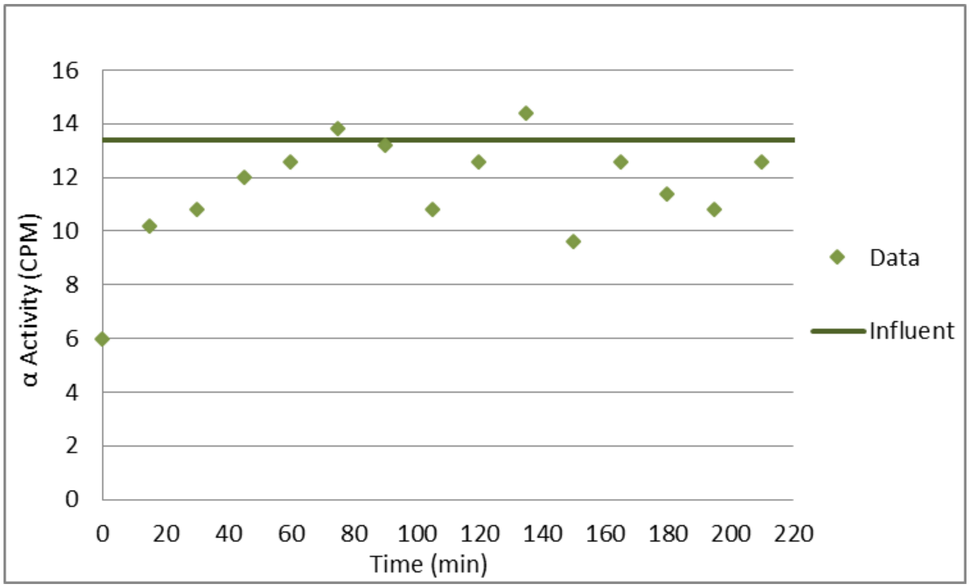

Figure 5-26: Column Experiment Data Using 1.0g DOWEX Resin in a 0.25" Reaction Vessel, Solution 3 at 10 mL/min

Before the exhaustion, however, the two sorbents performed almost identically. This can be better illustrated when the two tests are plotted on the same graph. As can be seen in Figure 5-27, the two sorbents followed a very similar trend at the beginning of the tests. For every time interval a sample was taken, there was no more than a 0.6 CPM difference between the two sorbents. The initial point and the time to exhaustion are also nearly the same. This shows that in a dynamic test, both sorbents are equally as effective from removing radium from solution in the presence of other ions.

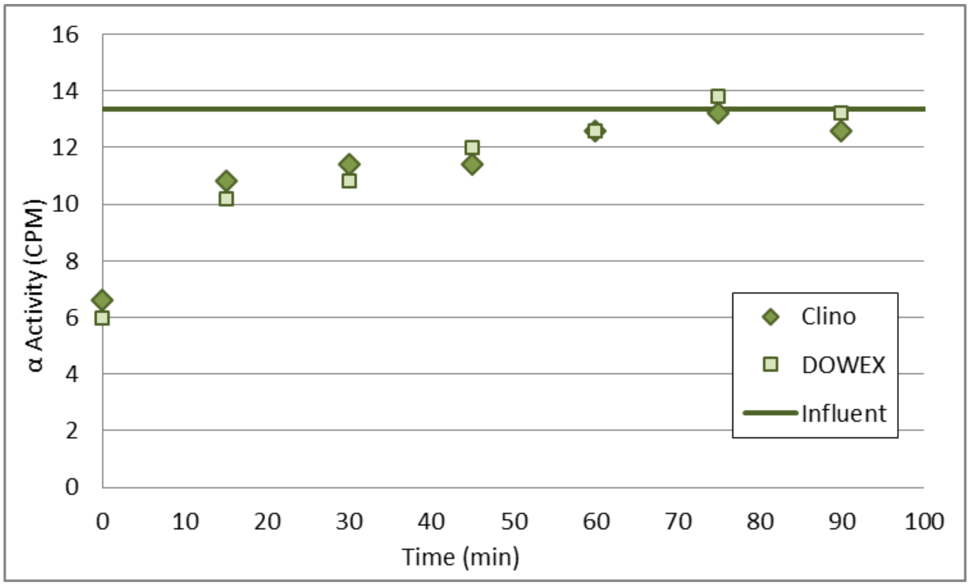

Figure 5-27: Column Experiment Data Using 1.0g DOWEX Resin or 1.0g Powdered Clinoptilolite in a 0.25" Reaction Vessel, Solution 3 at 10 mL/min

The final tests that were conducted as part of the column experiments was to evaluate the removal of the ions from Solution 3 using the DOWEX and powdered clinoptilolite. This was done without the presence of radium because the ICP that the analysis was completed on could not be exposed to any radioactive material. However other than not having radioactive material added the experiments were conducted in exactly the same fashion as the previous experiments using Solution 3. The results of these tests can be seen in Figures 5-28 and 5-29, as well as Table A-24 and A-25. Unlike the removal of radium for Solution 3, there were some differences in the removal of ions between the two sorbents. Using the clinoptilolite the samples reached their influent values almost immediately. This sorbent also displayed more variation in the data. There are several samples where the values were well above the influent, however this increase above influent was consistent between ions at the same time points. The DOWEX on the other hand displayed more uniformity once the data reached the exhaustion. Also more importantly the effluent samples did not immediately reach exhaustion at influent levels, but instead tailed off until reaching the influent concentration. This is most apparent in the barium and strontium data sets where it took up to 30-minutes to reach influent levels. The reason for this is likely that the DOWEX has an affinity for larger ionic radii cations, which is beneficial for the removal of radium.

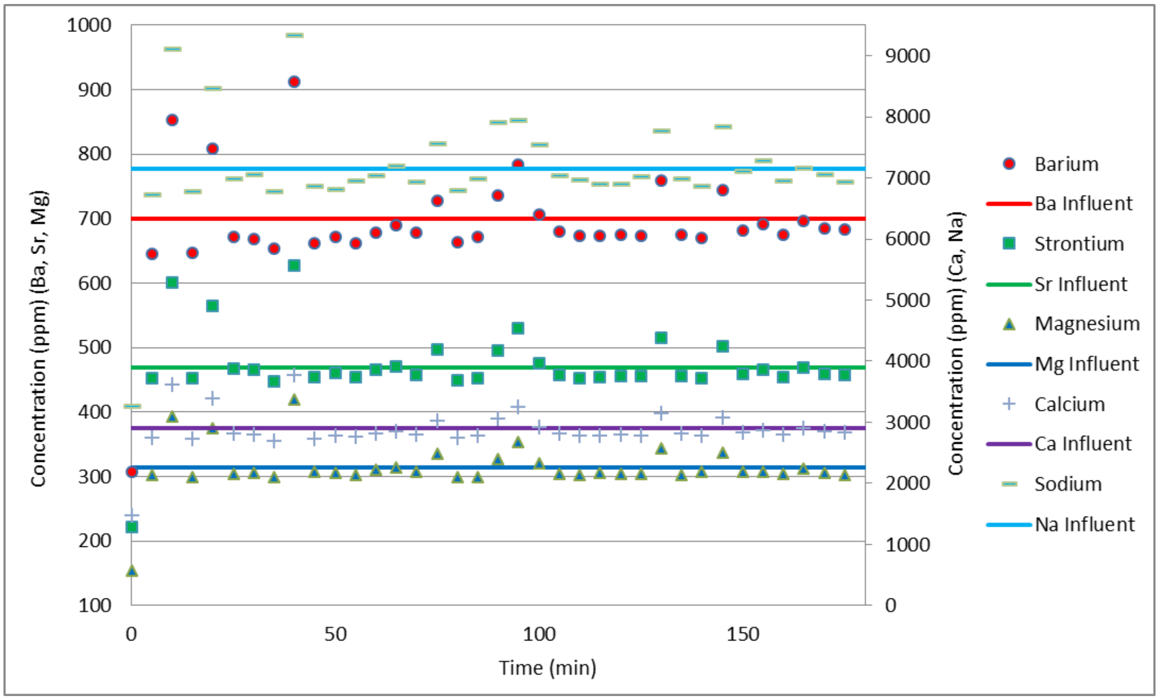

Figure 5-28: Ion Breakthrough Data Using 1.0g Powdered Clinoptilolite in a 0.25" Reaction Vessel, Solution 3 at 10 mL/min

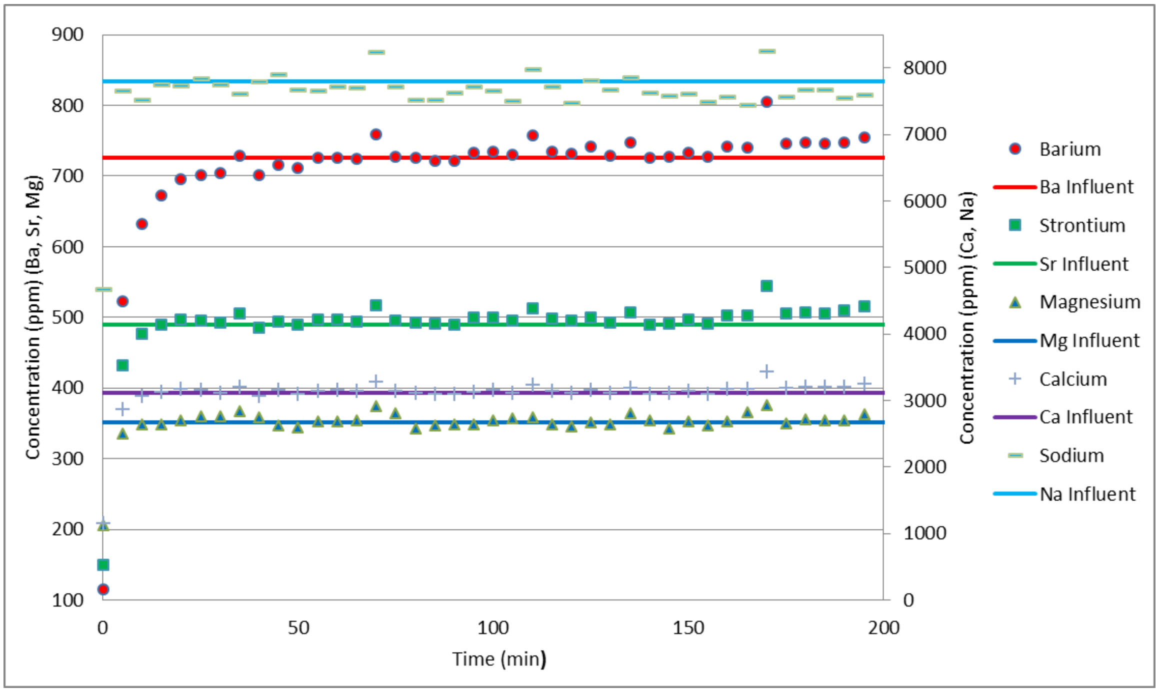

Figure 5-29: Ion Breakthrough Data Using 1.0g DOWEX Resin in a 0.25" Reaction Vessel, Solution 3 at 10 mL/min

CHAPTER 6: CONCLUSIONS

Introduction

In this research project four different sorbents were evaluated for their effectiveness in removal radium from a contaminated water source. Initially all four were considered a viable option when running the batch stage of the research. However when running scoping tests for the column experiments it was found that the barium sulfate was not able to be fixed within a bedding of glass wool. Also, a smaller reaction vessel was needed in order to see a breakthrough than was initially thought. Because of this the granulated particle size of the clinoptilolite could not be used in the column studies. Subsequently only two sorbents remained to be evaluated; the powdered clinoptilolite and the DOWEX ion exchange resin.

Exchange Capacity and Selectivity

In the batch stage of this process the sorbents were evaluated for their ability to remove radium from a contaminated water source given maximum contact time. It was found that both the powdered clinoptilolite and the DOWEX resin were both highly effective at removing radium when no other ions were present in solution. They both exhibited removal efficiencies over 98% at the lowest mass of sorbent that was tested. Additionally it was found during the column tests that the DOWEX had a higher capacity to remove ions from solution. This information is significant in fulfilling Objective 1 of the research objectives. The removal became less efficient however when other ions were introduced to the solution. This effect was more pronounced in the DOWEX than for the clinoptilolite. At the lowest mass tested the removal fell off from 98% to an average of 66% for the powdered clinoptilolite, and to 46% for the DOWEX. This shows that in the presence of other ions the clinoptilolite is more selective for removing radium than the DOWEX, which accomplishes Objective 2.

This finding was further confirmed in the column stage of testing. When comparing Figures 5-23 and 5-24, as well as 5-28 and 5-29, it can be seen that the DOWEX has a longer operational time before the sorbent reaches saturation. This shows that the DOWEX has a higher overall capacity to remove ions from solution. That being said, in Figure 5-27 it can be seen that the radium breakthrough profiles using Solution 3 are nearly identical. Because clinoptilolite demonstrated similar radium uptake with a lower cation capacity, it again proves the clinoptilolite is more selective for radium than the DOWEX. These column experiments are sufficient for meeting the goals of Objective 3.

These results indicate that the clinoptilolite is a better sorbent choice for Flowback/Produced water remediation. It is naturally occurring, has lower costs, and has higher radium selectivity. Because of this selectivity more radium is concentrated on a smaller mass of sorbent. If sorbent regeneration was required clinoptilolite would result in a more concentrated and smaller volume radium contaminated product. This would also yield lower costs.

Future Work

The main limitations encountered during this project was the analytical capabilities of the detection equipment, and the time that was allotted for the experiments. The equipment that was used had a high degree of variation in the readings when lower activity samples were analyzed. The 0.6 CPM increments of the RadEye made it difficult to read these low activity samples. These variations are a product of the time limitations as well. By increasing the counting times for background and samples the MDA could be reduced and maximum removal efficiency increased. A higher degree of accuracy could be accomplished using a high resolution liquid scintillation counter with a 28-day counting period.

If additional research was to be conducted, it is recommended that two additional goals be accomplished. The first is to better evaluate the lower limit for complete removal. If more precision could be maintained in the results the actual cation capacity of the different sorbents could be calculated and compared. The second recommendation would be to improve the radium breakthrough profiles. With Solution 1 this would mean extending the length of the tests in order to see powdered clinoptilolite reach exhaustion, and also to see how long before the DOWEX reaches breakthrough. Also this could include a higher resolution for the Solution 3 profile. If a better detector was used smoother curves could be developed, and also more samples could be taken in order to fill in some of the gaps in the data.

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APPENDIX: SUPPLEMENTAL TABLES

Table A-1: Background Data from RadEye HEC Using a Clean Plate

2.5 Hour Background											
Run #	β CPM	α CPM	Run #	β CPM	α CPM	Run #	β CPM	α CPM	Run #	β CPM	α CPM
1	45.0	1.2	11	46.2	0.6	21	46.2	0.6	31	50.4	0.6
2	45.0	0.6	12	44.4	0.0	22	46.8	0.6	32	48.6	1.2
3	45.0	1.2	13	45.6	0.6	23	47.4	0.6	33	49.8	1.2
4	47.4	0.6	14	46.2	0.6	24	48.0	0.0	34	50.4	1.2
5	46.2	0.6	15	42.0	0.0	25	47.4	0.6	35	49.2	0.0
6	46.8	0.6	16	48.0	0.6	26	47.4	1.2	36	48.6	0.6
7	47.4	0.6	17	48.6	0.6	27	47.4	0.6	37	47.4	0.6
8	46.2	0.6	18	46.2	0.6	28	47.4	0.6	38	48.0	0.6
9	45.0	0.6	19	46.2	0.6	29	47.4	0.6	39	49.8	0.6
10	46.8	0.6	20	47.4	0.6	30	48.0	0.6	40	47.4	0.6
									Average =	47.12	0.63
									STDEV =	1.69	0.30

Table A-2: Calibration Data for Solution 1 at a 10-Minute Counting Time

Solution 1 (Distilled Water)										
Date	Dilution	Concentration (nCi/L)	Amount Solution (mL)	Calculated DPM	Background α CPM	Measured α CPM	Measured - BG α CPM	Efficiency (CPM / DPM)	Average Efficiency	Standard Deviation
5-Sep	10	10.0	4.0	88.8	0.6	34.2	33.6	37.8%	36.26%	2.73%
5-Sep	10	10.0	4.0	88.8	0.6	30.0	29.4	33.1%		
5-Sep	10	10.0	4.0	88.8	0.6	34.2	33.6	37.8%		
5-Sep	15	6.7	4.0	59.2	0.6	21.6	21.0	35.5%	34.80%	1.17%
5-Sep	15	6.7	4.0	59.2	0.6	21.6	21.0	35.5%		
5-Sep	15	6.7	4.0	59.2	0.6	20.4	19.8	33.4%		
5-Sep	20	5.0	4.0	44.4	0.6	18.0	17.4	39.2%	34.23%	4.75%
5-Sep	20	5.0	4.0	44.4	0.6	15.6	15.0	33.8%		
5-Sep	20	5.0	4.0	44.4	0.6	13.8	13.2	29.7%		
5-Sep	50	2.0	4.0	17.8	0.6	6.0	5.4	30.4%	32.66%	3.90%
5-Sep	50	2.0	4.0	17.8	0.6	6.0	5.4	30.4%		
5-Sep	50	2.0	4.0	17.8	0.6	7.2	6.6	37.2%		
5-Sep	100	1.0	4.0	8.88	0.6	3.6	3.0	33.8%	27.03%	6.76%
5-Sep	100	1.0	4.0	8.88	0.6	3.0	2.4	27.0%		
5-Sep	100	1.0	4.0	8.88	0.6	2.4	1.8	20.3%		
5-Sep	400	0.25	4.0	2.22	0.6	3.0	2.4	108.1%	90.09%	15.60%
5-Sep	400	0.25	4.0	2.22	0.6	2.4	1.8	81.1%		
5-Sep	400	0.25	4.0	2.22	0.6	2.4	1.8	81.1%		
							Average =	33.00%	(Excluding 1:400)	
							STDEV =	4.91%		

Table A-3: Calibration Data for Solution 2 at a 10-Minute Counting Time

Solution 2					Target Concentrations					
			Na^+ (mg/L) 26,000	C^{2+} (mg/L) 1,775	Ba^{2+} (mg/L) 600	Mg^{2+} (mg/L) 400	Sr^{2+} (mg/L) 300			
Date	Dilution	Concentration (nCi/L)	Amount Solution (mL)	Calculated DPM	Background α CPM	Measured α CPM	Measured - BG α CPM	Efficiency (CPM / DPM)	Average Efficiency	Standard Deviation
16-Sep	10	10.0	4.0	88.8	0.6	2.4	1.8	2.0%	4.28%	2.06%
16-Sep	10	10.0	4.0	88.8	0.6	6.0	5.4	6.1%		
16-Sep	10	10.0	4.0	88.8	0.6	4.8	4.2	4.7%		
16-Sep	15	6.7	4.0	59.2	0.6	3.6	3.0	5.1%	4.39%	1.17%
16-Sep	15	6.7	4.0	59.2	0.6	2.4	1.8	3.0%		
16-Sep	15	6.7	4.0	59.2	0.6	3.6	3.0	5.1%		
16-Sep	20	5.0	4.0	44.4	0.6	1.8	1.2	2.7%	3.60%	0.78%
16-Sep	20	5.0	4.0	44.4	0.6	2.4	1.8	4.1%		
16-Sep	20	5.0	4.0	44.4	0.6	2.4	1.8	4.1%		
16-Sep	50	2.0	4.0	17.8	0.6	0.6	0.0	0.0%	2.25%	3.90%
16-Sep	50	2.0	4.0	17.8	0.6	1.8	1.2	6.8%		
16-Sep	50	2.0	4.0	17.8	0.6	0.6	0.0	0.0%		
16-Sep	100	1.0	4.0	8.88	0.6	0.6	0.0	0.0%	0.00%	0.00%
16-Sep	100	1.0	4.0	8.88	0.6	0.6	0.0	0.0%		
16-Sep	100	1.0	4.0	8.88	0.6	0.6	0.0	0.0%		
16-Sep	400	0.25	4.0	2.22	0.6	0.6	0.0	0.0%	-9.01%	15.60%
16-Sep	400	0.25	4.0	2.22	0.6	0.6	0.0	0.0%		
16-Sep	400	0.25	4.0	2.22	0.6	0.0	-0.6	-27.0%		
							Average =	0.92%		
							STDEV =	7.38%		

Table A-4: Calibration Data for Solution 3 at a 10-Minute Counting Time

Solution 3			Target Concentrations Na^{+} (mg/L) 8,300	C^{2+} (mg/L) 3,300	Ba^{2+} (mg/L) 750	Mg^{2+} (mg/L) 350	Sr^{2+} (mg/L) 500			
Date	Dilution	Concentration (nCi/L)	Amount Solution (mL)	Calculated DPM	Background α CPM	Measured α CPM	Measured - BG α CPM	Efficiency (CPM / DPM)	Average Efficiency	Standard Deviation
17-Sep	10	10.0	4.0	88.8	0.6	12.6	12.0	13.5%	13.96%	0.78%
17-Sep	10	10.0	4.0	88.8	0.6	12.6	12.0	13.5%		
17-Sep	10	10.0	4.0	88.8	0.6	13.8	13.2	14.9%		
17-Sep	15	6.7	4.0	59.2	0.6	7.8	7.2	12.2%	11.15%	1.01%
17-Sep	15	6.7	4.0	59.2	0.6	6.6	6.0	10.1%		
17-Sep	15	6.7	4.0	59.2	0.6	7.2	6.6	11.1%		
17-Sep	20	5.0	4.0	44.4	0.6	4.8	4.2	9.5%	9.91%	0.78%
17-Sep	20	5.0	4.0	44.4	0.6	4.8	4.2	9.5%		
17-Sep	20	5.0	4.0	44.4	0.6	5.4	4.8	10.8%		
17-Sep	50	2.0	4.0	17.8	0.6	2.4	1.8	10.1%	12.39%	1.95%
17-Sep	50	2.0	4.0	17.8	0.6	3.0	2.4	13.5%		
17-Sep	50	2.0	4.0	17.8	0.6	3.0	2.4	13.5%		
17-Sep	100	1.0	4.0	8.88	0.6	1.2	0.6	6.8%	6.76%	6.76%
17-Sep	100	1.0	4.0	8.88	0.6	0.6	0.0	0.0%		
17-Sep	100	1.0	4.0	8.88	0.6	1.8	1.2	13.5%		
17-Sep	400	0.25	4.0	2.22	0.6	1.2	0.6	27.0%	18.02%	15.60%
17-Sep	400	0.25	4.0	2.22	0.6	1.2	0.6	27.0%		
17-Sep	400	0.25	4.0	2.22	0.6	0.6	0.0	0.0%		
							Average =	11.85%	(Excluding 1:100,400)	
							STDEV =	1.89%		

Table A-5: Calibration Data for Solution 4 at a 10-Minute Counting Time

Solution 4					Target Concentrations					
			Na^+ (mg/L)	C^{2+} (mg/L)	Ba^{2+} (mg/L)	Mg^{2+} (mg/L)	Sr^{2+} (mg/L)			
			16,000	6,500	1,500	650	1,000			
Date	Dilution	Concentration (nCi/L)	Amount Solution (mL)	Calculated DPM	Background α CPM	Measured α CPM	Measured - BG α CPM	Efficiency (CPM / DPM)	Average Efficiency	Standard Deviation
19-Sep	10	10.0	4.0	88.8	0.6	10.2	9.6	10.8%	10.36%	0.39%
19-Sep	10	10.0	4.0	88.8	0.6	9.6	9.0	10.1%		
19-Sep	10	10.0	4.0	88.8	0.6	9.6	9.0	10.1%		
19-Sep	15	6.7	4.0	59.2	0.6	5.4	4.8	8.1%	8.11%	2.03%
19-Sep	15	6.7	4.0	59.2	0.6	4.2	3.6	6.1%		
19-Sep	15	6.7	4.0	59.2	0.6	6.6	6.0	10.1%		
19-Sep	20	5.0	4.0	44.4	0.6	6.0	5.4	12.2%	10.81%	3.58%
19-Sep	20	5.0	4.0	44.4	0.6	6.6	6.0	13.5%		
19-Sep	20	5.0	4.0	44.4	0.6	3.6	3.0	6.8%		
19-Sep	50	2.0	4.0	17.8	0.6	1.8	1.2	6.8%	10.14%	3.38%
19-Sep	50	2.0	4.0	17.8	0.6	3.0	2.4	13.5%		
19-Sep	50	2.0	4.0	17.8	0.6	2.4	1.8	10.1%		
19-Sep	100	1.0	4.0	8.88	0.6	0.6	0.0	0.0%	0.00%	0.00%
19-Sep	100	1.0	4.0	8.88	0.6	0.6	0.0	0.0%		
19-Sep	100	1.0	4.0	8.88	0.6	0.6	0.0	0.0%		
19-Sep	400	0.25	4.0	2.22	0.6	0.6	0.0	0.0%	-9.01%	15.60%
19-Sep	400	0.25	4.0	2.22	0.6	0.6	0.0	0.0%		
19-Sep	400	0.25	4.0	2.22	0.6	0.0	-0.6	-27.0%		
							Average =	9.85%	(Excluding 1:100,400)	
							STDEV =	2.52%		

Table A-6: Calibration Data for Solution 5 at a 10-Minute Counting Time

Solution 5			Target Concentrations							
			Na^+ (mg/L) 35,000	C^{2+} (mg/L) 14,000	Ba^{2+} (mg/L) 2,500	Mg^{2+} (mg/L) 1,000	Sr^{2+} (mg/L) 1,250			
Date	Dilution	Concentration (nCi/L)	Amount Solution (mL)	Calculated DPM	Background α CPM	Measured α CPM	Measured - BG α CPM	Efficiency (CPM / DPM)	Average Efficiency	Standard Deviation
26-Sep	10	10.0	4.0	88.8	0.6	4.2	3.6	4.1%	5.63%	1.70%
26-Sep	10	10.0	4.0	88.8	0.6	5.4	4.8	5.4%		
26-Sep	10	10.0	4.0	88.8	0.6	7.2	6.6	7.4%		
26-Sep	15	6.7	4.0	59.2	0.6	4.8	4.2	7.1%	6.76%	0.59%
26-Sep	15	6.7	4.0	59.2	0.6	4.2	3.6	6.1%		
26-Sep	15	6.7	4.0	59.2	0.6	4.8	4.2	7.1%		
26-Sep	20	5.0	4.0	44.4	0.6	2.4	1.8	4.1%	3.60%	0.78%
26-Sep	20	5.0	4.0	44.4	0.6	2.4	1.8	4.1%		
26-Sep	20	5.0	4.0	44.4	0.6	1.8	1.2	2.7%		
26-Sep	50	2.0	4.0	17.8	0.6	1.2	0.6	3.4%	4.50%	1.95%
26-Sep	50	2.0	4.0	17.8	0.6	1.8	1.2	6.8%		
26-Sep	50	2.0	4.0	17.8	0.6	1.2	0.6	3.4%		
26-Sep	100	1.0	4.0	8.88	0.6	1.8	1.2	13.5%	9.01%	3.90%
26-Sep	100	1.0	4.0	8.88	0.6	1.2	0.6	6.8%		
26-Sep	100	1.0	4.0	8.88	0.6	1.2	0.6	6.8%		
26-Sep	400	0.25	4.0	2.22	0.6	0.6	0.0	0.0%	9.01%	15.60%
26-Sep	400	0.25	4.0	2.22	0.6	0.6	0.0	0.0%		
26-Sep	400	0.25	4.0	2.22	0.6	1.2	0.6	27.0%		
							Average =	6.42%		
							STDEV =	5.99%		

Table A-7: Calibration Data for Solution 6 at a 10-Minute Counting Time

Solution 6					Target Concentrations					
			Na^+ (mg/L) 70,000	C^{2+} (mg/L) 27,500	Ba^{2+} (mg/L) 5,000	Mg^{2+} (mg/L) 2,000	Sr^{2+} (mg/L) 2,500			
Date	Dilution	Concentration (nCi/L)	Amount Solution (mL)	Calculated DPM	Background α CPM	Measured α CPM	Measured - BG α CPM	Efficiency (CPM / DPM)	Average Efficiency	Standard Deviation
29-Sep	10	10.0	4.0	88.8	0.6	1.8	1.2	1.4%	0.90%	0.39%
29-Sep	10	10.0	4.0	88.8	0.6	1.2	0.6	0.7%		
29-Sep	10	10.0	4.0	88.8	0.6	1.2	0.6	0.7%		
29-Sep	15	6.7	4.0	59.2	0.6	1.2	0.6	1.0%	1.01%	0.00%
29-Sep	15	6.7	4.0	59.2	0.6	1.2	0.6	1.0%		
29-Sep	15	6.7	4.0	59.2	0.6	1.2	0.6	1.0%		
29-Sep	20	5.0	4.0	44.4	0.6	1.2	0.6	1.4%	1.35%	0.00%
29-Sep	20	5.0	4.0	44.4	0.6	1.2	0.6	1.4%		
29-Sep	20	5.0	4.0	44.4	0.6	1.2	0.6	1.4%		
29-Sep	50	2.0	4.0	17.8	0.6	0.6	0.0	0.0%	-1.13%	1.95%
29-Sep	50	2.0	4.0	17.8	0.6	0.0	-0.6	-3.4%		
29-Sep	50	2.0	4.0	17.8	0.6	0.6	0.0	0.0%		
29-Sep	100	1.0	4.0	8.88	0.6	3.6	3.0	33.8%	207.2%	218.6%
29-Sep	100	1.0	4.0	8.88	0.6	40.8	40.2	452.7%		
29-Sep	100	1.0	4.0	8.88	0.6	12.6	12.0	135.1%		
29-Sep	400	0.25	4.0	2.22	0.6	12.0	11.4	513.5%	423.4%	281.3%
29-Sep	400	0.25	4.0	2.22	0.6	3.0	2.4	108.1%		
29-Sep	400	0.25	4.0	2.22	0.6	15.0	14.4	648.6%		
							Average =	105.46%		
							STDEV =	205.84%		

Table A-8: Calibration Data for Solution 1 at a 35-Minute Counting Time

Solution 1 (Distilled Water)

Date	Dilution	Concentration (nCi/L)	Amount Solution (mL)	Calculated DPM	Background α CPM	Measured α CPM	Measured - BG α CPM	Efficiency (CPM / DPM)	Average Efficiency	Standard Deviation
5-Sep	10	10.0	4.0	88.8	0.6	28.8	28.2	31.8%	31.76%	0.68%
5-Sep	10	10.0	4.0	88.8	0.6	28.2	27.6	31.1%		
5-Sep	10	10.0	4.0	88.8	0.6	29.4	28.8	32.4%		
5-Sep	15	6.7	4.0	59.2	0.6	20.4	19.8	33.4%	32.77%	0.59%
5-Sep	15	6.7	4.0	59.2	0.6	19.8	19.2	32.4%		
5-Sep	15	6.7	4.0	59.2	0.6	19.8	19.2	32.4%		
5-Sep	20	5.0	4.0	44.4	0.6	16.8	16.2	36.5%	39.19%	2.34%
5-Sep	20	5.0	4.0	44.4	0.6	18.6	18.0	40.5%		
5-Sep	20	5.0	4.0	44.4	0.6	18.6	18.0	40.5%		
5-Sep	50	2.0	4.0	17.8	0.6	6.6	6.0	33.8%	32.66%	1.95%
5-Sep	50	2.0	4.0	17.8	0.6	6.0	5.4	30.4%		
5-Sep	50	2.0	4.0	17.8	0.6	6.6	6.0	33.8%		
5-Sep	100	1.0	4.0	8.88	0.6	3.6	3.0	33.8%	38.29%	3.90%
5-Sep	100	1.0	4.0	8.88	0.6	4.2	3.6	40.5%		
5-Sep	100	1.0	4.0	8.88	0.6	4.2	3.6	40.5%		
5-Sep	400	0.25	4.0	2.22	0.6	1.8	1.2	54.1%	36.04%	15.60%
5-Sep	400	0.25	4.0	2.22	0.6	1.2	0.6	27.0%		
5-Sep	400	0.25	4.0	2.22	0.6	1.2	0.6	27.0%		
							Average =	35.12%		
							STDEV =	6.36%		

Table A-9: Calibration Data for Solution 3 at a 35-Minute Counting Time

Solution 3					Target Concentrations					
			Na^+ (mg/L) 8,300	C^{2+} (mg/L) 3,300	Ba^{2+} (mg/L) 750	Mg^{2+} (mg/L) 350	Sr^{2+} (mg/L) 500			
Date	Dilution	Concentration (nCi/L)	Amount Solution (mL)	Calculated DPM	Background α CPM	Measured α CPM	Measured - BG α CPM	Efficiency (CPM / DPM)	Average Efficiency	Standard Deviation
17-Sep	10	10.0	4.0	88.8	0.6	12.0	11.4	12.8%	12.39%	0.78%
17-Sep	10	10.0	4.0	88.8	0.6	12.0	11.4	12.8%		
17-Sep	10	10.0	4.0	88.8	0.6	10.8	10.2	11.5%		
17-Sep	15	6.7	4.0	59.2	0.6	7.8	7.2	12.2%	12.84%	1.17%
17-Sep	15	6.7	4.0	59.2	0.6	9.0	8.4	14.2%		
17-Sep	15	6.7	4.0	59.2	0.6	7.8	7.2	12.2%		
17-Sep	20	5.0	4.0	44.4	0.6	6.0	5.4	12.2%	11.71%	0.78%
17-Sep	20	5.0	4.0	44.4	0.6	6.0	5.4	12.2%		
17-Sep	20	5.0	4.0	44.4	0.6	5.4	4.8	10.8%		
17-Sep	50	2.0	4.0	17.8	0.6	3.6	3.0	16.9%	16.89%	0.00%
17-Sep	50	2.0	4.0	17.8	0.6	3.6	3.0	16.9%		
17-Sep	50	2.0	4.0	17.8	0.6	3.6	3.0	16.9%		
17-Sep	100	1.0	4.0	8.88	0.6	3.0	2.4	27.0%	22.52%	3.90%
17-Sep	100	1.0	4.0	8.88	0.6	2.4	1.8	20.3%		
17-Sep	100	1.0	4.0	8.88	0.6	2.4	1.8	20.3%		
17-Sep	400	0.25	4.0	2.22	0.6	0.6	0.0	0.0%	9.01%	15.60%
17-Sep	400	0.25	4.0	2.22	0.6	0.6	0.0	0.0%		
17-Sep	400	0.25	4.0	2.22	0.6	1.2	0.6	27.0%		
							Average =	15.27%	(Excluding 1:400)	
							STDEV =	4.49%		

Table A-10: Test Matrix for Granulated Clinoptilolite Batch Experiment

Solution	Replicate	Granulated Mass(g)											
		1			2.5			5			7.5		
		α	nCi/L	% Removal	α	nCi/L	% Removal	α	nCi/L	% Removal	α	nCi/L	% Removal
4 Med IC (1)	1	3.6	3.499	65.0	1.8	1.475	**74.3**	0.6	0.125	**74.3**	0.0	-0.549	**74.3**
	2	3.6	3.499	65.0	1.8	1.475	**74.3**	1.2	0.800	**74.3**	0.0	-0.549	**74.3**
	3	3.6	3.499	65.0	1.2	0.800	**74.3**	0.6	0.125	**74.3**	0.6	0.125	**74.3**
3 Low IC (.5)	1	4.8	4.204	58.0	2.4	2.336	76.6	1.2	1.402	**81.3**	0.6	0.935	**81.3**
	2	3.0	2.803	72.0	1.8	1.869	**81.3**	1.2	1.402	**81.3**	0.6	0.935	**81.3**
	3	3.0	2.803	72.0	1.8	1.869	**81.3**	0.6	0.935	**81.3**	1.8	1.869	**81.3**
1 Zero IC (0)	1	1.8	0.662	**93.4**	1.2	0.480	**93.4**	1.8	0.662	**93.4**	1.2	0.480	**93.4**
	2	1.2	0.480	**93.4**	0.6	0.297	**93.4**	1.2	0.480	**93.4**	1.2	0.480	**93.4**
	3	1.2	0.480	**93.4**	1.2	0.480	**93.4**	3.0	1.027	89.7	1.2	0.480	**93.4**

Table A-11: Test Matrix for Powdered Clinoptilolite Batch Experiment

Solution	Replicate	Powdered Mass(g)											
		1			2.5			5			7.5		
		α	nCi/L	% Removal	α	nCi/L	% Removal	α	nCi/L	% Removal	α	nCi/L	% Removal
4 Med IC (1)	1	1.8	1.475	**74.3**	0.6	0.125	**74.3**	0.6	0.125	**74.3**			
	2	2.4	2.150	**74.3**	1.8	1.475	**74.3**	1.2	0.800	**74.3**			
	3	1.8	1.475	**74.3**	1.2	0.800	**74.3**	1.8	1.475	**74.3**			
3 Low IC (.5)	1	1.8	1.869	**81.3**	0.6	0.935	**81.3**	0.6	0.935	**81.3**	0.6	0.935	**81.3**
	2	1.8	1.869	**81.3**	1.2	1.402	**81.3**	0.6	0.935	**81.3**	1.2	1.402	**81.3**
	3	1.8	1.869	**81.3**	0.6	0.935	**81.3**	1.2	1.402	**81.3**	0.6	0.935	**81.3**
1 Zero IC (0)	1	1.2	0.480	**93.4**	0.6	0.297	**93.4**	0.6	0.297	**93.4**	1.8	0.662	**93.4**
	2	1.2	0.480	**93.4**	0.6	0.297	**93.4**	0.6	0.297	**93.4**	2.4	0.845	91.6
	3	0.6	0.297	**93.4**	2.4	0.845	91.6	0.6	0.297	**93.4**	-	-	-

Table A-12: Test Matrix for DOWEX Batch Experiments

Solution	Replicate	DOWEX Mass(g)								
		1			2.5			5		
		α	nCi/L	% Removal	α	nCi/L	% Removal	α	nCi/L	% Removal
4 Med IC (1)	1	3.6	3.499	65.0	2.4	2.150	**74.3**	4.2	4.174	58.3
	2	3.0	2.824	71.8	2.4	2.150	**74.3**	3.6	3.499	65.0
	3	3.6	3.499	65.0	2.4	2.150	**74.3**	3.0	2.824	71.8
3 Low IC (.5)	1	1.8	1.869	**81.3**	6.0	5.138	48.6	3.6	3.270	67.3
	2	2.4	2.336	76.6	3.0	2.803	72.0	3.6	3.270	67.3
	3	5.4	4.671	53.3	3.6	3.270	67.3	3.6	3.270	67.3
1 Zero IC (0)	1	1.2	0.480	**93.4**	1.2	0.480	**93.4**	0.0	0.115	**93.4**
	2	1.8	0.662	**93.4**	1.8	0.662	**93.4**	1.2	0.480	**93.4**
	3	1.2	0.480	**93.4**	1.8	0.662	**93.4**	1.2	0.480	**93.4**

Table A-13: Test Matrix for Barium Sulfate Batch Experiments

Solution	Replicate	$BaSO_4$ Mass(g)								
		1			2.5			5		
		α	nCi/L	% Removal	α	nCi/L	% Removal	α	nCi/L	% Removal
4 Med IC (1)	1	3.0	2.824	71.8	0.0	-0.549	**74.3**	1.2	0.800	**74.3**
	2	3.0	2.824	71.8	0.6	0.125	**74.3**	0.0	-0.549	**74.3**
	3	2.4	2.150	**74.3**	0.6	0.125	**74.3**	0.0	-0.549	**74.3**
3 Low IC (.5)	1	1.2	1.402	**81.3**	0.6	0.935	**81.3**	0.0	0.468	**81.3**
	2	3.6	3.270	67.3	0.6	0.935	**81.3**	0.6	0.935	**81.3**
	3	2.4	2.336	76.6	1.2	1.402	**81.3**	0.6	0.935	**81.3**
1 Zero IC (0)	1	0.6	0.297	**93.4**	0.6	0.297	**93.4**	0.6	0.297	**93.4**
	2	0.0	0.115	**93.4**	0.6	0.297	**93.4**	0.0	0.115	**93.4**
	3	0.6	0.297	**93.4**	0.6	0.297	**93.4**	0.6	0.297	**93.4**

Table A-14: Test Matrix for Additional Powdered Clinoptilolite Batch Experiments

Solution	Replicate	Powdered Mass(g)								
		0.1			0.5			1		
		α	nCi/L	% Removal	α	nCi/L	% Removal	α	nCi/L	% Removal
3 Low IC (.5)	1	4.2	2.766	72.3	1.8	0.359	96.4	1.8	1.869	**81.3**
	2	5.4	3.970	60.3	3.0	1.563	81.3	1.8	1.869	**81.3**
	3	4.8	3.368	66.3	2.4	0.961	81.3	1.8	1.869	**81.3**
1 Zero IC (0)	1	1.8	0.181	98.2	1.8	0.181	98.2	1.2	0.480	**93.4**
	2	0.6	-0.241	**100.0**	3.6	0.813	91.9	1.2	0.480	**93.4**
	3	2.4	0.391	96.1	1.2	-0.030	**100.0**	0.6	0.297	**93.4**

Solution	Replicate	Powdered Mass(g) - pH 4								
		0.1			0.5			1.0		
		α	nCi/L	% Removal	α	nCi/L	% Removal	α	nCi/L	% Removal
3 Low IC (.5)	1	5.4	4.671	53.3	3.0	2.803	72.0	1.2	1.402	**81.3**
	2	4.2	3.737	62.6	1.8	1.869	**81.3**	1.8	1.869	**81.3**
	3	3.6	3.270	67.3	2.4	2.336	76.6	0.6	0.935	**81.3**
1 Zero IC (0)	1	1.2	0.480	**93.4**	1.2	0.480	**93.4**	1.8	0.662	**93.4**
	2	0.6	0.297	**93.4**	1.8	0.662	**93.4**	4.8	1.575	84.3
	3	0.6	0.297	**93.4**	1.2	0.480	**93.4**	0.6	0.297	**93.4**

Solution	Replicate	Powdered Mass(g) - pH 10								
		0.1			0.5			1.0		
		α	nCi/L	% Removal	α	nCi/L	% Removal	α	nCi/L	% Removal
3 Low IC (.5)	1	4.8	4.204	58.0	1.8	1.869	**81.3**	1.2	1.402	**81.3**
	2	4.8	4.204	58.0	1.8	1.869	**81.3**	1.2	1.402	**81.3**
	3	4.8	4.204	58.0	1.8	1.869	**81.3**	1.8	1.869	**81.3**
1 Zero IC (0)	1	1.2	0.480	**93.4**	1.8	0.662	**93.4**	0.6	0.297	**93.4**
	2	1.2	0.480	**93.4**	1.8	0.662	**93.4**	1.2	0.480	**93.4**
	3	0.6	0.297	**93.4**	1.2	0.480	**93.4**	1.8	0.662	**93.4**

Table A-15: Test Matrix for Additional DOWEX Batch Experiments

Solution	Replicate	DOWEX Mass(g) - pH 6.5								
		0.1			0.5			1.0		
		α	nCi/L	% Removal	α	nCi/L	% Removal	α	nCi/L	% Removal
3 Low IC (.5)	1	6.6	5.174	48.3	5.4	3.970	60.3	1.8	1.869	**81.3**
	2	7.2	5.776	42.2	4.8	3.368	66.3	2.4	2.336	76.6
	3	6.6	5.174	48.3	5.4	3.970	60.3	5.4	4.671	53.3
1 Zero IC (0)	1	4.2	1.024	89.8	1.8	0.181	98.2	1.2	0.480	**93.4**
	2	1.8	0.181	98.2	1.8	0.181	98.2	1.8	0.662	**93.4**
	3	1.8	0.181	98.2	2.4	0.391	96.1	1.2	0.480	**93.4**

Solution	Replicate	DOWEX Mass(g) - pH 4								
		0.1			0.5			1.0		
		α	nCi/L	% Removal	α	nCi/L	% Removal	α	nCi/L	% Removal
3 Low IC (.5)	1	7.8	6.539	34.6	5.4	4.671	53.3	6.0	5.138	48.6
	2	8.4	7.006	29.9	6.6	5.605	43.9	3.0	2.803	72.0
	3	9.6	7.940	20.6	4.2	3.737	62.6	3.6	3.270	67.3
1 Zero IC (0)	1	1.2	0.480	**93.4**	1.8	0.662	**93.4**	1.2	0.480	**93.4**
	2	1.2	0.480	**93.4**	1.2	0.480	**93.4**	1.8	0.662	**93.4**
	3	1.8	0.662	**93.4**	2.4	0.845	91.6	1.8	0.662	**93.4**

Solution	Replicate	DOWEX Mass(g) - pH 10								
		0.1			0.5			1.0		
		α	nCi/L	% Removal	α	nCi/L	% Removal	α	nCi/L	% Removal
3 Low IC (.5)	1	7.8	6.539	34.6	4.8	4.204	58.0	6.6	5.605	43.9
	2	8.4	7.006	29.9	3.6	3.270	67.3	9.0	7.473	25.3
	3	8.4	7.006	29.9	4.2	3.737	62.6	6.6	5.605	43.9
1 Zero IC (0)	1	1.2	0.480	**93.4**	1.2	0.480	**93.4**	1.8	0.662	**93.4**
	2	0.6	0.297	**93.4**	3.0	1.027	89.7	0.6	0.297	**93.4**
	3	1.2	0.480	**93.4**	1.8	0.662	**93.4**	1.8	0.662	**93.4**

Table A-16: Column Experiment Data Using 5.0g DOWEX Resin in a 0.5" Reaction Vessel, Solution 1 at 25 mL/min (1)

5.0 g DOWEX Resin Solution 1		β	α	Average α
Time (min)	Pretreatment	63.6	31.2	30.8
	Pretreatment	59.4	30.0	
	Pretreatment	57.6	31.2	
	0	51.6	1.2	
	4	52.2	1.8	
	8	52.8	1.8	
	12	57.0	1.2	
	16	55.2	1.2	
	20	52.2	0.6	
	24	53.4	0.6	
	28	52.2	1.2	
	32	52.8	1.2	
	36	53.4	0.6	

Table A-17: Column Experiment Data Using 2.5g DOWEX Resin in a 0.5" Reaction Vessel, Solution 1 at 25 mL/min

2.5 g DOWEX Resin Solution 1		β	α	Average α
	Pretreatment	71.4	33.0	31.4
	Pretreatment	66.0	31.8	
	Pretreatment	60.0	29.4	
Time (min)	0	55.2	3.0	
	4	56.4	3.6	
	8	57.0	2.4	
	12	58.2	3.6	
	16	55.2	4.2	
	20	56.4	3.6	
	24	60.0	4.8	
	28	54.6	3.6	
	32	56.4	3.0	
	36	55.2	3.0	

Table A-18: Column Experiment Data Using 5.0g DOWEX Resin in a 0.5" Reaction Vessel, Solution 1 at 25 mL/min (2)

5.0 g DOWEX Resin Solution 1		β	α	Average α
Time (min)	Pretreatment	78.8	39.6	36.6
	Pretreatment	69.9	34.8	
	Pretreatment	63.6	35.4	
	0	55.2	1.2	
	30	55.8	0.6	
	60	60.6	3.6	
	90	58.2	1.8	
	120	55.8	1.2	
	150	60.0	1.2	

Table A-19: Column Experiment Data Using 2.5g DOWEX Resin in a 0.5" Reaction Vessel, Solution 3 at 25 mL/min

2.5 g DOWEX Resin Solution 3		β	α	Average α
Time (min)	Pretreatment	75.6	17.4	14.8
	Pretreatment	66.6	14.4	
	Pretreatment	60.0	12.6	
	0	53.4	4.2	
	10	62.4	10.8	
	20	70.8	16.7	
	30	72.6	18.6	
	40	73.8	21.6	
	50	70.8	18.0	
	60	71.4	18.0	
	70	72.6	18.6	

Table A-20: Column Experiment Data Using 1.0g Glass Wool in a 0.5" Reaction Vessel, Solution 1 at 25 mL/min

Time (min)	β CPM	α CPM	avg.
Initial	62.4	34.2	32.7
Initial	57.0	31.2	
0	52.8	15.6	
2	57.6	31.8	
4	55.8	30.6	
6	57.6	31.2	
8	55.8	30.6	

Table A-21: Column Experiment Data Using 1.0g Powdered Clinoptilolite in a 0.25" Reaction Vessel, Solution 1 at 10 mL/min

1.0 g Powder Clino Solution 1 1/4" RV, 10 mL/min		β	α	Average α
Time (min)	Pretreatment	68.4	34.8	32.7
	Pretreatment	63.0	33.0	
	Pretreatment	59.4	31.8	
	Pretreatment	59.4	33.0	
	Pretreatment	64.8	30.0	
	Pretreatment	58.2	33.0	
	Pretreatment	66.0	33.6	
	0	55.8	2.4	
	20	53.4	3.0	
	40	56.4	4.2	
	60	59.4	4.8	
	80	55.2	6.0	
	100	51.0	6.6	
	120	49.2	5.4	
	140	54.6	7.8	
	160	52.2	8.4	
	170	56.4	10.2	
	170	54.0	10.2	
	180	52.8	7.8	
	200	50.4	6.6	
	220	52.2	7.8	
	240	52.2	9.6	
	250	54.6	8.4	
	250	44.4	7.8	
	260	48.0	10.8	
	280	49.8	13.8	
	300	48.6	13.8	
	320	50.4	12.6	

Table A-22: Column Experiment Data Using 1.0g DOWEX Resin in a 0.25" Reaction Vessel, Solution 1 at 10 mL/min

1.0 g DOWEX Solution 1 1/4" RV, 10 mL/min		β	α	Average α
Time (min)	Pretreatment	69.6	28.8	32.7
	Pretreatment	62.4	34.2	
	Pretreatment	58.8	36.0	
	Pretreatment	56.4	31.2	
	Pretreatment	55.2	33.0	
	Pretreatment	51.0	33.0	
	Pretreatment	60.0	31.2	
	Pretreatment	57.0	34.2	
	0	48.6	3.6	
	20	49.2	3.6	
	40	46.8	3.6	
	60	46.8	1.8	
	80	50.4	4.2	
	100	48.0	3.6	
	120	48.0	4.2	
	140	48.6	3.6	
	160	49.2	4.2	
	160	48.0	6.0	
	180	42.6	2.4	
	200	43.8	3.6	
	220	44.4	3.6	
	240	47.4	8.4	
	250	45.6	4.8	
	250	50.4	5.4	
	260	45.0	2.4	
	280	43.8	4.2	
	300	42.6	3.0	
	320	42.6	2.4	
	340	45.0	2.4	

Table A-23: Column Experiment Data Using 1.0g Sorbent in a 0.25" Reaction Vessel, Solution 3 at 10 mL/min

	α Activity (CPM)	
Time	Clino	DOWEX
Influent	15.0	12.6
Influent	13.2	14.4
Influent	12.0	13.8
Influent	12.6	-
Inf Avg	13.4	
0	6.6	6.0
15	10.8	10.2
30	11.4	10.8
45	11.4	12.0
60	12.6	12.6
75	13.2	13.8
90	12.6	13.2
105	11.4	10.8
120	10.2	12.6
135	12.0	14.4
150	12.0	9.6
165	11.4	12.6
180		11.4
195		10.8
210		12.6

Table A-24: Ion Breakthrough Data Using 1.0g Powdered Clinoptilolite in a 0.25" Reaction Vessel, Solution 3 at 10 mL/min

	Ion Concentration (ppm)				
Time	Barium	Calcium	Magnesium	Sodium	Strontium
Influent	655.1	2801	300.1	6798	455.2
Influent	790.7	3332	362.8	8384	552.4
Influent	690.5	2780	304.9	6754	442.4
Influent	663.1	2671	290.6	6632	425.5
Inf Avg	699.9	2896	314.6	7142	468.9
0	307.1	1469	154.3	3267	222.2
5	645.6	2749	302.3	6734	452.8
10	853.5	3621	393.0	9116	601.7
15	646.9	2723	298.6	6783	452.3
20	808.6	3392	375.1	8469	565.0
25	671.6	2818	303.8	6995	468.0
30	668.6	2798	306.0	7063	465.4
35	653.3	2700	298.8	6776	447.3
40	912.0	3780	419.1	9341	627.3
45	661.5	2733	307.7	6878	453.9
50	671.8	2775	305.4	6822	461.2
55	662.4	2758	302.8	6957	454.0
60	679.2	2813	310.8	7037	465.6
65	690.7	2856	314.4	7195	470.0
70	678.4	2795	307.2	6949	457.6
75	727.4	3033	335.1	7575	497.2
80	664.0	2743	299.6	6806	448.8
85	672.4	2774	299.9	6994	452.6
90	736.9	3053	326.9	7913	495.9
95	784.6	3243	354.0	7957	529.4
100	706.0	2913	321.2	7552	476.3
105	680.0	2808	304.0	7042	458.0
110	672.8	2779	302.3	6971	452.8
115	673.6	2781	305.1	6901	454.1
120	675.0	2791	303.7	6897	455.8
125	674.1	2785	304.3	7030	455.4
130	759.5	3144	343.7	7782	514.6
135	674.5	2811	303.0	6987	455.3
140	670.5	2775	306.9	6878	452.2
145	743.7	3082	337.3	7840	501.3
150	682.3	2831	307.3	7107	459.5
155	691.3	2862	307.4	7290	464.9
160	675.2	2807	304.5	6953	454.3
165	696.3	2899	312.3	7160	468.5
170	685.7	2843	305.7	7067	459.7
175	683.2	2841	302.3	6935	457.6

Table A-25: Ion Breakthrough Data Using 1.0g DOWEX Resin in a 0.25" Reaction Vessel, Solution 3 at 10 mL/min

	Ion Concentration (ppm)				
Time	Barium	Calcium	Magnesium	Sodium	Strontium
Influent	715.9	3077	344.7	7836	486.6
Influent	728.1	3127	351.0	7719	493.7
Influent	730.2	3110	352.7	7695	487.3
Influent	730.4	3115	355.8	7954	489.4
Inf Avg	726.2	3107	351.1	7801	489.3
0	114.6	1158	206.1	4673	150.0
5	522.0	2862	335.3	7665	432.5
10	632.8	3072	348.3	7520	477.0
15	672.3	3131	349.1	7746	489.1
20	695.6	3180	354.0	7741	497.1
25	700.7	3165	359.7	7841	495.8
30	704.3	3115	359.4	7746	491.9
35	728.4	3208	366.7	7610	506.0
40	701.7	3075	359.0	7798	485.0
45	715.6	3158	346.7	7911	493.6
50	710.9	3096	344.3	7675	489.3
55	725.6	3142	352.2	7655	496.4
60	726.3	3160	352.2	7727	496.5
65	724.5	3142	353.9	7699	493.4
70	758.4	3287	375.0	8237	517.6
75	726.9	3146	364.8	7722	495.8
80	725.9	3113	342.2	7529	493.1
85	721.1	3100	347.0	7522	491.5
90	721.4	3096	348.4	7630	489.1
95	733.7	3136	348.5	7719	499.0
100	734.8	3155	354.2	7654	499.6
105	730.8	3121	356.6	7513	495.2
110	757.1	3234	359.2	7976	512.7
115	734.3	3140	349.0	7717	498.9
120	731.2	3120	345.7	7482	495.5
125	741.5	3159	351.0	7811	500.0
130	728.7	3114	349.0	7677	492.3
135	747.8	3195	364.7	7860	506.5
140	725.2	3101	354.7	7636	490.3
145	727.9	3109	342.7	7577	491.0
150	733.5	3140	352.7	7613	497.2
155	726.8	3106	347.6	7484	491.0
160	741.4	3179	352.7	7568	502.6
165	740.2	3176	366.1	7448	502.3
170	805.6	3443	376.4	8255	545.0
175	746.4	3195	349.8	7572	505.7
180	747.4	3209	355.0	7670	507.0
185	745.5	3207	354.9	7677	505.7
190	747.5	3210	353.8	7548	509.5
195	754.7	3259	362.7	7600	515.5