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Title: Mini-columns for Conducting Breakthrough Experiments: Design and Construction

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Mini-columns for Conducting Breakthrough Experiments: Design and Construction

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Abstract

Experiments with moderately and strongly sorbing radionuclides (i.e., U, Cs, Am) have shown that sorption between experimental solutions and traditional column materials must be accounted for to accurately determine stationary phase or porous media sorption properties (i.e., sorption site density, sorption site reaction rate coefficients, and partition coefficients or K_d values). This report details the materials and construction of mini-columns for use in breakthrough columns to allow for accurate measurement and modeling of sorption parameters. Material selection, construction techniques, wet packing of columns, tubing connections, and lessons learned are addressed.

Keywords: breakthrough experiments, Teflon® syringes, column set-up, construction

1. Introduction

Small breakthrough columns (mini-columns) constructed by the EES-14 radiogeochemistry team at Los Alamos National Laboratory before 2013 were constructed from 6.5 cm lengths of 1 cm diameter polyethylene tubing (Figure 1) and are described in other publications (Dittrich and Reimus, 2015, Wang reports, AGU/ACS presentations).

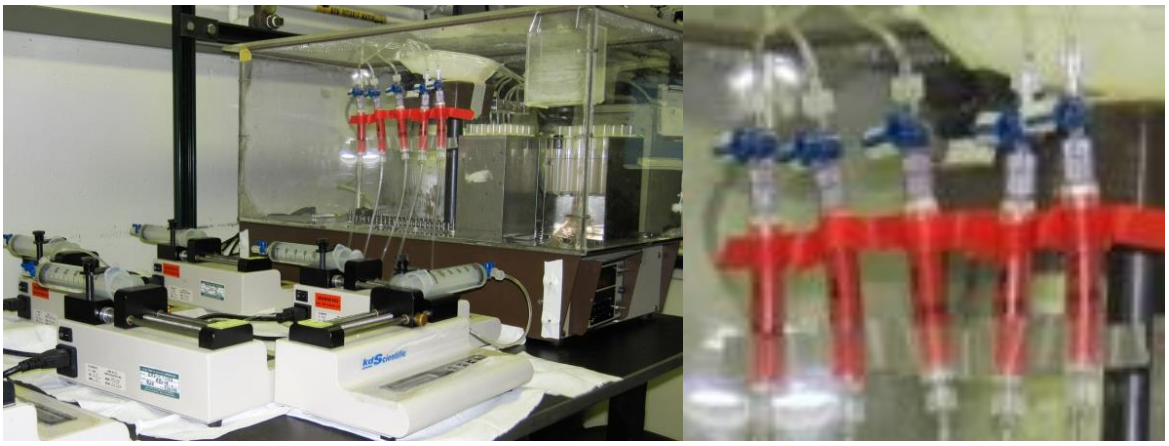

Figure 1. Image of column setup with 5 columns running in parallel.

We define a mini-column in this report as a column with a diameter equal to or less than 1 cm with a length of 1.5-10 cm. Mini-columns were devised to allow rapid and economical evaluation of sorption/desorption behavior under flowing conditions (and in duplicate or triplicate). These breakthrough experiments have been shown to be useful in elucidating sorption parameters with the advantages of requiring only small amounts of porous media material and by minimizing waste that requires disposal (Dittrich, 2014; Dittrich and Reimus, 2014; Dittrich and Reimus, 2013a; Dittrich and Reimus, 2013b; Dittrich and Reimus, 2014; Dittrich and Reimus, 2015; Dittrich et al., 2014; Dittrich et al., 2015, Dittrich et al., in review; Reimus et al., 2014; Wang et al., 2013; Wang et al., 2014). One of the limitations of the first generation of LANL mini-columns were experimental artifacts due to sorption of radionuclides

from the experimental solution to column materials (e.g., polypropylene columns, Tygon® tubing, glass wool, polyethylene test tubes) was observed, especially with uranium and americium (Dittrich and Reimus, 2015).

Subsequent improvements were made to the LANL mini-column system in 2013-2015. Polyethylene column material was replaced with Teflon® and all Tygon® tubing (R-3606) was replaced with Teflon® tubing. Teflon® syringes were purchased and modified to allow use with syringe pumps and replaced polypropylene syringes. Column fittings were switched from polyethylene fittings (threaded end into column and barb fitting) to Teflon® compression fittings that threaded into the column. Glass wool that was used to prevent column material from entering the tubing was replaced with 75 µm polyetheretherketone (PEEK) screen. Polyethylene test tubes were also replaced with polystyrene test tubes, which reduced sorption while allowing for more accurate transfer of liquid (polyethylene becomes slightly hydrophilic after being in contact with a sample for >12 hours which makes removal of all liquid difficult and adds experimental error). Syringes and syringe pumps are used to inject experimental solutions through a column at a predetermined flow rate and effluent samples are collected in test tubes in a fraction collector.

2. Materials and Methods

2.1. Teflon® syringe modification for syringe pump use

Although 60 mL polypropylene syringes (Becton Dickinson or BD) have been used in many applications, sorption of uranium to the inside of polypropylene syringes at pH below 8.0 required us to seek a Teflon® alternative. The only Teflon® syringes we could locate were not made to use with syringe pumps (KD scientific, Model 100). The modification described in this report allows for 50 mL Teflon® syringes (Torviq, TS-50) to be used with a syringe pump.

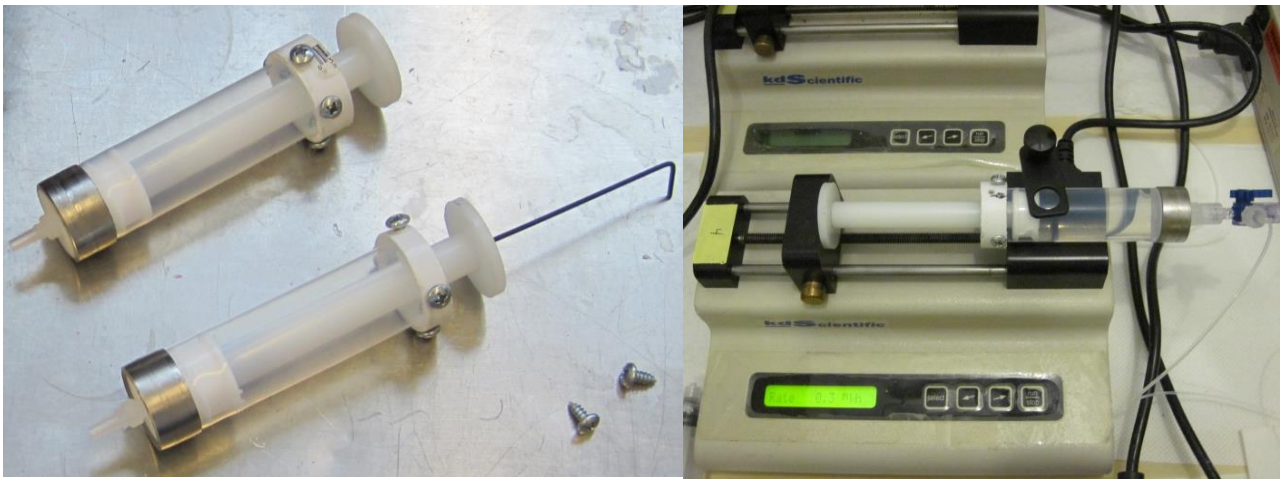

Figure 2. Image of support ring attached to top of Teflon® syringe with screws and reattachment of the plunger top with hex key (left) and syringe in syringe pump (right).

A support ring must be attached to the base of the syringe to allow it to work with a syringe pump. This support ring is cut (either with a band saw or hack saw) from a 1" Schedule 40 PVC coupling. Cut a ¾" piece from both ends of the coupling (each coupling proves two support rings). The top of the plunger must be removed with a hex wrench or allen key before the support ring can be installed. Care must be taken to not strip the material. Once the top is removed, slide the support ring with the factory end facing down toward the tip of the syringe to ensure correct operation since uneven pressure from even a slightly uneven cut can cause the syringe to leak. Predrill four holes through the support ring, ensuring the ring is perpendicular to the body of the syringe. Screw four 1 cm screws through the predrilled holes in the support ring and syringe body (Figure 2). Make sure the screws do not go too deep and touch the plunger support.

2.2. Column construction

Mini-column experiments are conducted by injecting radionuclide solutions or radionulide-equilibrated colloidal suspensions through columns packed with porous media. Columns can be

constructed at any length; however, 1.2 cm must be added to the desired packing length to account for the 0.6 cm necessary for each threaded fitting inside the ends of the columns. For example, a 6.2 cm length column that will be described here will allow for 5 cm of material, 0.6 cm for the top fitting, and 0.6 cm for the bottom fitting.

The first step is to cut a section length of 0.95 cm diameter tubing slightly to ~6.5 cm using either a band saw or tin snips. The snips will distort the end of the tubing making it necessary to reshape the ends and make them round again. The ends will still be slightly misshapen with rough cuts, and the remaining 0.3 cm should be removed with very shallow (0.5 mm) cuts until the final column length is 6.2 cm and the ends are smooth and perpendicular to the tubing walls (Figure 3).

The next step is to add threads to the inside of both ends of the tube by tapping them with a 1/8" #27 NPT tap. The tubing is soft and this can be done by hand with care being given to ensure the tap is threaded into the hole perpendicular to the side walls. Thread the tap into the end of the tubing roughly ½ turn, then reverse ¼ turn. This will limit the stretching of the tubing and ensure the fitting secures properly and limits drips. The red line visible on the tap in Figure 3 shows the depth to thread for the fittings described below.

Before the compression fittings are threaded into the column ends, the inside opening is covered with a small disk of 75 µm polyetheretherketone (PEEK) screen to retain the column material while providing minimum resistance to flow and causing negligible straining of colloids in experimental solutions. A small disk (~0.75 cm diameter circle) is cut from a large disk and a ring of silicone adhesive is thinly spread between the opening and the edge of the compression fitting. Care should be given to ensure no silicone is blocking the opening. Carefully place the

PEEK disk onto the silicone and press in place with the flat end of a thin wooden dowel (Figure 4). Let dry before installing into column openings and packing column.

Figure 3. Image of 1/8" #27 NPT tap, Teflon® tube used for column, and Teflon compression fitting (left) and red line on tap for depth indicator (right).

Figure 4. Image of small PEEK disk being attached to the top of a Teflon® compression fitting with silicone adhesive. and packaging for PTFE tubing (right).

Cut two lengths of polytetrafluoroethylene (PTFE) #20 thin walled tubing (0.032" or 1.59 mm ID and 0.056" OD) to connect as the inlet and outlet tubing for the column (Figure 5). In our setup, the outlet tube was 30 cm long and the inlet tube was 80 cm long. One end of the tubing

must be inserted into the opening of a suitably sized polyethylene barb fitting to allow for a snug fit. Epoxy or super glue should be used to ensure the tube is sealed and securely fastened to the fitting (Figure 5). Once cured, thread the fitting onto the male end of a polycarbonate 3-way stopcock and thread the male end of the stopcock into the female end of a syringe. The 3-way stopcock provides a means of refilling the syringes during experiments and switching experimental solutions while minimizing pressure disturbances. Insert the inlet tubing into the compression fitting by unscrewing the fitting, sliding the ferrule over the tubing, sliding the tubing through the opening in the fitting, then screwing the top of the fitting into the base (Figure 6). Adjust the tubing before screwing into the base to ensure the tubing doesn't enter too far and push on the PEEK screen or the PEEK screen will need to be reattached with silicone. The top fitting is assembled in the same manner.

Figure 5. Epoxy seal to attach PTFE tubing inside barb end of polyethylene female Luer lock fitting.

The bottom fitting is installed in the column first. Add a layer of silicone to the threads of the bottom (inlet) fitting with a wooden dowel or toothpick and screw into one end of the column

(what will become the bottom). Allow the silicone to cure before proceeding with the wet-packing step.

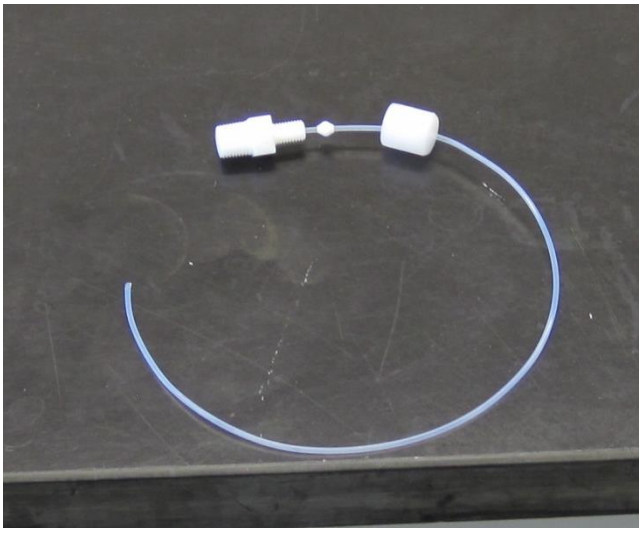

Figure 6. Installation of tubing into compression fitting (right).

2.3. Wet-packing column procedure

The first step is to weight the necessary amount of porous media for the column you wish to pack. The columns shown in this report are 5.0 g columns. Fold a square of wax paper in half to leave a crease in the middle. This will make transferring the media to the column easier. Add 5.0 g of material onto the paper square (Figure 7). With the same squares of paper, make 2 or 3 paper funnels by twisting into a cone, sizing the ends appropriately, and taping them in place with masking tape. If the tips get wet during the last phase of packing, the funnels can be unwrapped and the grains of media can be removed and added to the column to minimize weighing error. An appropriately sized glass funnel would work well; however, plastic funnels tend to have static charges that scatter grains and add to measurement errors.

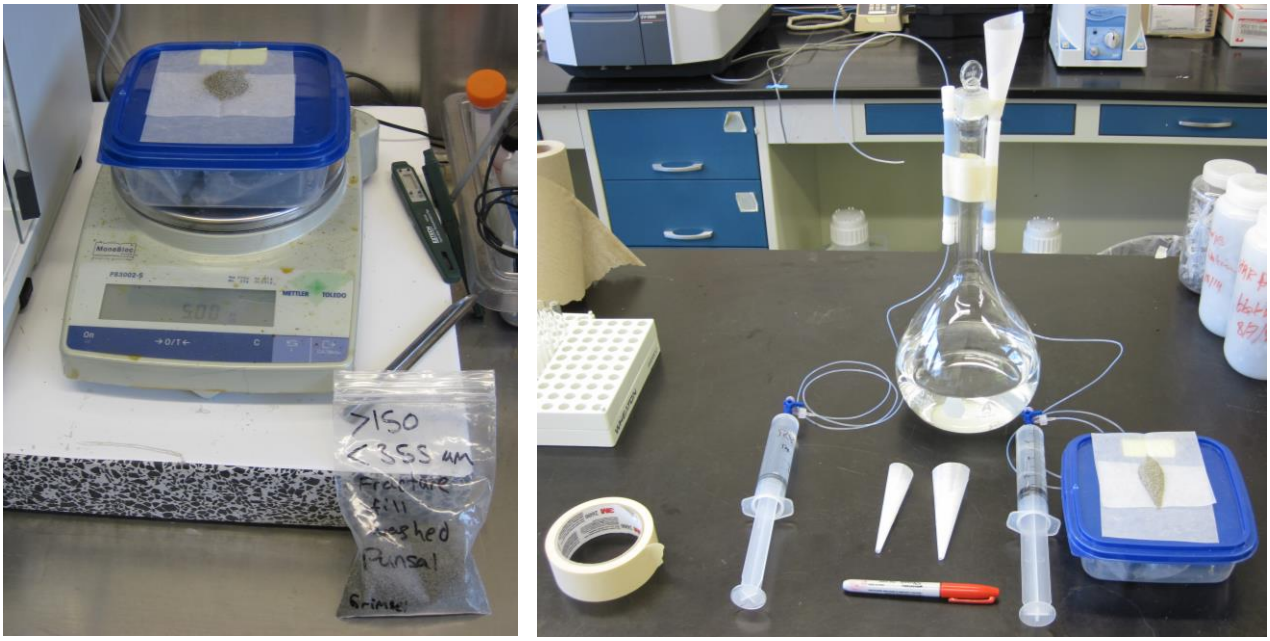

Figure 7. Images of weighing 5.0 grams of porous media (left) and preparing to pack columns with paper funnels in the foreground (right).

Vertically attach columns to a large vessel (volumetric flask with water for stability, in this case) with making tape. Fill syringes with the experimental background solution and open 3-way stopcock to allow flow. Push the plunger to fill the empty column approximately 0.75 cm of solution. This procedure limits differential settling of grains by adding material in small increments. Tape a paper funnel with bottom end inserted into top of column (or place glass funnel in top of column. Pick up the paper with the porous media on it and pour a small amount (~0.25-.50 g or 0.25-0.50 cm in column). Tap column gently with a marker or screwdriver handle 5 times to settle grains. Push plunger slowly to reestablish 0.75 cm layer of water to bottom of column (pushing too fast will create pressure at the bottom of the media, lifting the media and creating a void at the bottom of the column). Add 0.25-0.50 g of material to column. Stir grains with a metal rod to disrupt layer between media in column and media just added, then tap column 5 times. Reestablish water level, add more media, stir column, tap column, and

repeat this process until the column is filled with only 0.6 cm remaining in the top for the top compression fitting. A test column may need to be packed to determine the correct column length for the desired amount of fill material. Before and after weights of tubing, fittings, and the column are also very useful for determining porosity, pore volumes, bulk density, and tubing volumes of the system. Carefully remove the funnel and dry threads with a paper towel. Add silicone sealant to the threads of the top compression fitting and screw in until slight resistance if felt, the bottom of the fitting appears to be in contact with the top of the media, and a small amount of solution is observed in the top tube leaving the column. Allow sealant to dry before using column in experiments.

2.4. Experimental design

The final step after all silicone adhesive is dry is to set up the syringe pumps and fraction collector (Figure 8). We used a chain driven Gilson FC-200 fraction collector filled with 13 × 100 mm polystyrene test tubes. This fraction collector has metal racks that allow for 5 columns to be run in parallel at the same time and also has an enclosed box that minimizes evaporation when used with an evaporation pan filled with distilled water. Columns are tapped to the side of the fraction collector box and the syringes are mounted into syringe pumps (KD Scientific, Model 100). KD Scientific syringe pumps have preprogrammed settings for 60 mL BD syringes. When Teflon® syringes are used, the 60 mL BD syringe setting was used; however, the diameter was adjusted from 26.7 mm to 28.4 mm (or the specific diameter of the Teflon® syringe being used). We used a 0.30-0.60 mL h^{-1} flow rate and this adjustment allowed for the flow to be set on the main screen of the syringe pump. The modified Teflon® syringe pumps must also be filled by connecting a tube and pulling the plunger back to fill the chamber, instead of filled by removal of the plunger (Figure 9). The screws for the support ring prevent easy plunger

removal. The fill tube can be constructed by cutting a 20 cm length of #20 PTFE tubing, inserting one end into the barb end of a polyethylene Luer lok fitting and applying super glue or epoxy to hold the connection together.

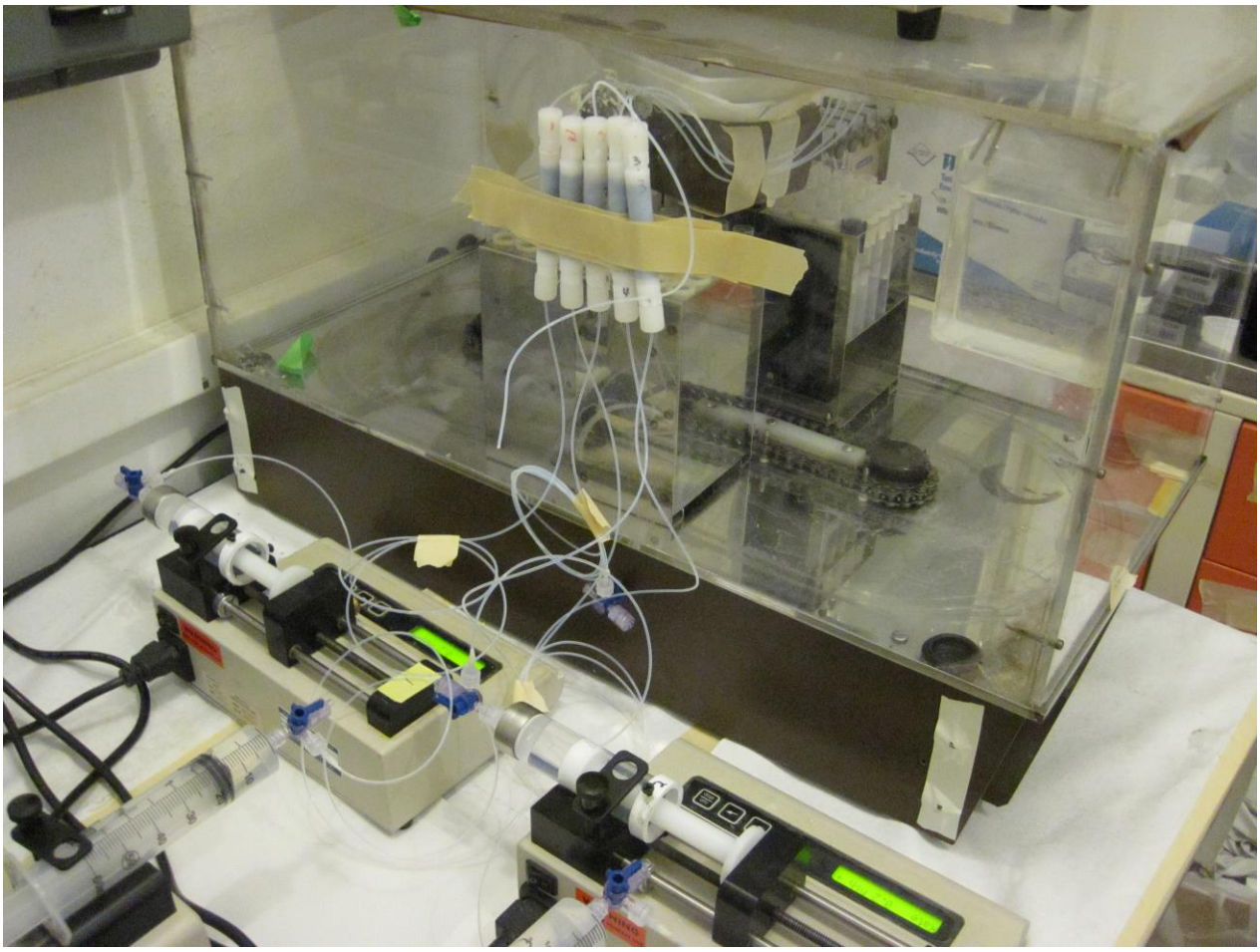

Figure 8. Modified Teflon® syringes mounted in syringe pumps in foreground, enclosed fraction collector with polystyrene test tubes is back, and Teflon® columns mounted to fraction collector with masking tape.

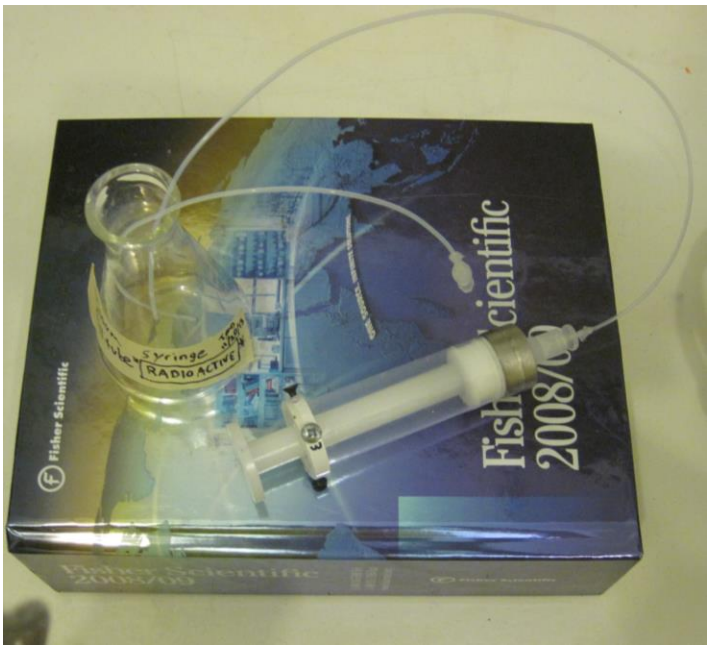

Figure 9. Modified Teflon® syringe and constructed fill tube.

Once the filled columns are secured in place and syringe pumps and fraction collectors have been programmed, the columns should be flushed with background experimental solution for at least 48 h and the effluent measured for parameters if interest (i.e., pH, colloid concentration, etc.) to ensure stability before the injection of experimental solution is started. Test tube racks should be filled with pre-weighed test tubes if an accurate flow rate or evaporation correction is desired.

To begin a breakthrough experiment, turn the 3-way stopcock to the "off" position in the outlet connected to the syringe and replace with a syringe filled with experimental solution. Mount the syringe into the syringe pump and ensure the pump is on. By pressing the on button continuously and pulsing the "fast forward" button, maximum control can be exerted to minimize a flow disturbance while ensuring the syringe plunger is in contact with the syringe pump push plate. It is advisable to manually push and pull on the syringe pump push plate to

ensure that the push plate is licked (and the lock button is fully in the outward position), otherwise the push plate may adjust after pushing for an hour, and a flow rate error will result due to the push plate taking more time to re-contact the plunger before injection resumes.

3. Lessons Learned

The most important consideration that we observed is that maximum care and preliminary experimentation are required to ensure the best materials are chosen for syringes, tubing, and test tubes to minimize artifacts and error. We noticed that uranium solutions (pH 6.9) left a red coating in Tygon® (R-3606) tubing which was believed to be a uranium phthalate complex (Figure 10). The plasticizer in most PVC tubing is phthalate, and some of the softer PVC tubing can use up to 40% plasticizer. Caution and material compatibility tests should be performed with all system components to ensure stability.

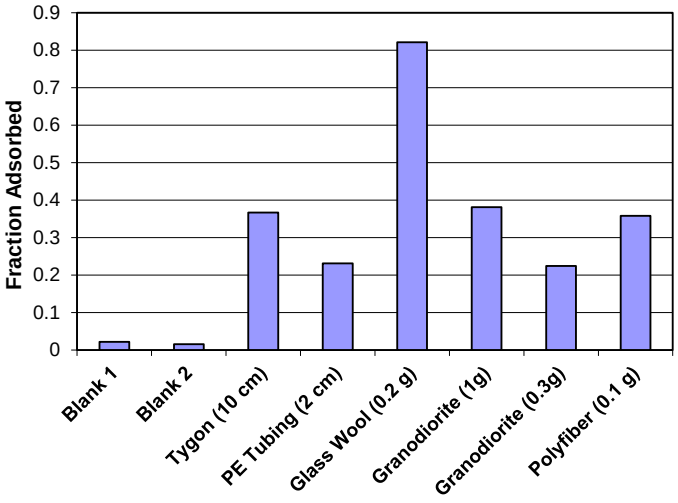

Figure 10. Uranium interactions with column components in batch experiments (144 hrs, 10 ml solution).

Polypropylene syringes can be refilled at least 5 times without problem, however, the plunger becomes increasingly more difficult to slide with each addition pass and it is recommended that polypropylene syringes are not used more than 5 times (or are at least monitored). When using modified Teflon® syringes as described in this report, care must be taken to ensure the plunger is perpendicular to the syringe walls. Some syringes were slightly askew and let to leaking between the plunger and the syringe wall, which subsequently let to flow rate errors.

Polyethylene test tubes were used in early experiments; however, liquid at the air-water interface was found to stay attached to the interface after samples sat in the tubes for more than 24 h. Polystyrene tubes were found to be much more hydrophilic and nearly all of the sample could be poured from the test tubes into liquid scintillation vials for measurement. This was important to ensure accurate mass balances for experiments.

Minimizing the length and diameter of inlet and outlet tubing can ensure additional accuracy, especially for very small mini-columns. Empty columns should also be run in parallel with columns filled with media to serve as control columns and to monitor and account for any system artifacts. Duplicate columns are recommended to ensure accuracy and to justify reproducibility. Glasswool (and polyfiber fill) were found to sorb radionuclides and the use of the PEEK disks with zero headspace minimized experimental error.

Acknowledgments

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