

**Theoretical Consideration in Designing a Sediment-Packed Column for Phosphate and Polyphosphate Transport Study under Saturated Flow Conditions Relevant to the DOE-Hanford Site- 10489**

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**ABSTRACT**

Uranium occurs in high concentrations in groundwater at several contaminated sites in the United States. Due to the potential threat of uranium radionuclides on human health, different techniques have been developed in order to control the spread of this contaminant in the environment. In this regard, *in situ* stabilization of uranium by polyphosphate amendments has been found to be quite useful. As a part of the uranium remediation work at the DOE Hanford Site, a study was designed to look into the interactions of phosphate and polyphosphate with sediments and other ionic constituents (e.g., calcium and iron), and later evaluate the cumulative effects of these interactions in the transport of phosphate and polyphosphate through a saturated sediment column. This paper presents the findings from the investigation that focused on the theoretical and the design aspects of the sediment-packed column. Some of the important design criteria that were considered in this study were: *i*) to be able to simulate groundwater flow at the Hanford Site using the saturated column, *ii*) to have a sufficient column length in order to observe significant changes that occur in phosphate concentration with respect to time and distance, and *iii*) to have a proper placement of the sampling ports along the column length with appropriate spacing, in order to collect the water samples with varying concentrations of phosphate and polyphosphate. Due to the high adsorption capacity of the Hanford sediments, it was found that the required length of column was smaller for wider columns. The lowest concentration of phosphate in this study, 100 mg/L, required a 226.81 cm sediment-packed column length with a diameter of 2.54 cm (1 inch) to reduce the phosphate concentration at the outlet by 90%. A higher initial concentration of phosphate (5000 mg/L), on the other hand, required a 627.19 cm column length with the same diameter to achieve the same results. Some of the relevant factors that were identified to be applicable in the design of the sediment-packed column were the saturation capacity of the sediment-packed column, the rate of removal of the phosphate and the polyphosphate by the sediment inside the column, and the adsorption capacity of the Hanford sediments.

**INTRODUCTION**

Uranium is a radioactive substance occurring naturally. It exists in the form of minerals in rocks, soil, air, and water. By mining these natural resources, a large quantity of uranium is produced globally. During both production and utilization processes, large quantities of uranium may be released into the environment. This kind of release took place at some of the nuclear facilities in

the United States, contaminating large areas that included soil, ground- and surface-water systems. It has been reported that uranium occurs in high concentrations at several of these contaminated sites in the United States [1]. Due to the potential threat on human health, the U.S. Environmental Protection Agency (USEPA) has set a maximum contaminant level of 30  $\mu\text{g/L}$  for uranium concentration in groundwater [2]. Once released, uranium (radionuclides) persists in the environment and can have toxic effects on living organisms. Uranium can be hazardous due to its ability to produce radiation and its chemical toxicity at high concentrations. The radiation can be carcinogenic and mutagenic, and similar to other heavy metals, it may also damage internal organs (e.g., kidneys) and impact reproductive health.

Among several other uranium contaminated areas in the United States, DOE's Hanford Site in Washington State was included on the National Priorities List (NPL) in 1989. The Hanford Site covers approximately 586 square miles and was established to produce nuclear material for national defense. This site was further divided into 4 NPL sites, including the 100 Area, 200 Area, 300 Area, and 1100 Area. The 300 Area consists of a 0.25-square-mile industrial complex area that was used for uranium fuel fabrication and research and development activities [3]. During its operation beginning in 1943, large amounts of waste containing uranium were discharged to unlined surface ponds and trenches. This types of disposal contaminated both soil and groundwater in the Hanford area.

Various efforts were made to contain the radioactive and chemical effects of uranium at the Hanford Site. Different activities related to the cleanup in the 300 Area included removal of contaminated soils and debris, treatment of the material to reduce the toxicity and mobility of the contaminants, and disposal of the material in an appropriate long-term waste management facility. Also, uranium levels in groundwater are monitored on a routine basis. However, in spite of all these remedial measures, groundwater containing uranium still discharges into surface water bodies, mainly into the Columbia River. It has been reported that by changing the chemical speciation of uranium, toxic and mobile species can be converted to nontoxic and immobile species [4]. In this regard, in situ stabilization of uranium by polyphosphate amendments has been tried at different DOE sites, including the Hanford Site [4, 5].

The polyphosphate technology utilizes different types of polyphosphates as a source of phosphate ions, which in turn bind uranium ions to form uranium phosphate. So, formed uranium phosphate is largely a precipitate of uranyl phosphate, such as autunite, metaautunite, or other complexes, which are very much desired in the case of polyphosphate mediated uranium stabilization methods. Uranium phosphate is relatively insoluble in water, and hence uranium can be made immobile within the aquifer. However, phosphate has an affinity towards the aquifer sediments and other groundwater components. The efficacy of this technology to stabilize uranium in the groundwater at the Hanford Site depends on the degree of interaction of phosphate with the groundwater constituents other than uranium. A study was designed to look into the interactions of phosphate and polyphosphate with sediments and other ionic constituents (e.g., calcium and iron), and later evaluate the cumulative effects of these interactions in the transport of phosphate and polyphosphate through a saturated sediment column. Laboratory column experiments using Hanford sediment and groundwater can be very helpful in understanding the nature and extent of the interactions between the phosphate compounds and the aquifer materials. The contaminant studies using columns require the proper selection and

design of the columns, in order to meet the objectives of the study in an accurate and timely way. This might not be possible through an ad hoc selection of the columns. This paper presents the findings from the investigation that was focused on the theoretical and the design aspects of the sediment-packed column.

## COLUMN DESIGN CRITERIA

The design of the sediment packed column was aimed at meeting the following basic criteria:

- i) to be able to simulate groundwater flow at the Hanford Site using the saturated column,
- ii) to have a sufficient column length in order to observe significant changes that occur in phosphate concentration with respect to time and distance, and
- iii) to have a proper placement of the sampling ports along the column length with appropriate spacing, in order to collect the water samples with varying concentrations of phosphate and polyphosphate. For this theoretical study, only phosphate has been considered, as it is the product of the hydrolysis of polyphosphate in an aquatic environment.

## ESTIMATING COLUMN PARAMETERS

Two factors are necessary in order to initiate the column design process. The first one is the aqueous concentration of the chemical being studied, which in this case is phosphate. Knowledge of the initial concentration at the inlet and the desired concentration at the outlet leads to the calculation of the amount of phosphate that needs to adsorb in the sediment. The relationship between the adsorption capacity of the sediment and the mass of the sediment helps in determining the required amount of sediment in the column to achieve the desired reduction in phosphate concentration at the outlet. Once the amount and its equivalent volume are found, then the length and the width of the column can be determined. Modifying the calculations provided by Kuo [6], important relationships between the column parameters can be derived as follows.

The amount of the sediment required in the column can be given as:

$$M_{sed} = \frac{M_{Pr}}{C_{ad\_actual}} \quad (1)$$

Where,

$M_{sed}$  is the amount of the sediment in the column to be designed

$M_{Pr}$  is the maximum amount of phosphate removed by the sediment in the column

$C_{ad\_actual}$  is the actual adsorption capacity of the sediment for phosphate, and is taken as 25-50% of the theoretical value ( $C_{ad}$ ). In this study, we will take 50% of the theoretical value, i.e.:

$$C_{ad\_actual} = 50 \% C_{ad} \quad (2)$$

Equation (1) can be re-written as:

$$M_{sed} = \frac{2 \times M_{Pr}}{C_{ad}} \quad (3)$$

Also, the mass of the sediment is related to the volume of the sediment ( $V_{sed}$ ) and bulk density of the sediment ( $\rho_b$ ) as shown below (equation 4):

$$M_{sed} = V_{sed} \times \rho_b \quad (4)$$

Where  $V_{sed}$  is equivalent to the internal volume of the column to be used:

$$V_{column} = \pi r^2 h \quad (5)$$

Where,

$V_{column}$  is the internal volume of the column

$\pi$  is equal to  $\frac{22}{7}$ ,  $r$  and  $h$  are the radius and height (length) of the column, respectively.

Integrating equations (4) and (5) together yields:

$$M_{sed} = \pi r^2 h \times \rho_b \quad (6)$$

Combining equations (3) and (6) gives an equation where both the radius and the height of the column can be related to the adsorption and the sediment parameters:

$$r^2 h = \frac{2M_{Pr}}{\pi \rho_b C_{ad}} \quad (7)$$

$$h = \frac{2M_{Pr}}{\pi r^2 \rho_b C_{ad}} \quad (8)$$

$$r = \sqrt{\frac{2M_{Pr}}{\pi h \rho_b C_{ad}}} \quad (9)$$

As stated earlier, the desired reduction in phosphate concentration at the outlet, which is represented by parameter  $M_{Pr}$  in equations (8) and (9), can be assigned based on the need of the experiments and instrumental requirements (detection limit, etc.). Similarly, the bulk density of the sediment can be calculated as the weight of the sediment per unit volume ( $\text{lb}/\text{ft}^3$ ). Adsorption capacity ( $C_{ad}$ ) can be most appropriately determined through simple batch experiments (explained later) and the relevant equations.

Adsorption is the process of accumulating substances that are in solution on a suitable interface. Adsorption is a mass transfer operation in that a constituent in the liquid phase is transferred to the solid phase [7]. Adsorption is best described by sorption isotherms, which are developed by

exposing a given amount of adsorbate (phosphates in this study) in a fixed volume of liquid to varying amounts of adsorbent (sediment). In order to describe adsorption characteristics, the Freundlich isotherm model and the Langmuir isotherm model are most commonly used. The Freundlich and the Langmuir isotherm models for phosphate adsorption can be given as:

$$C_{ad} = K_F C_{aq}^{\frac{1}{n}} \quad (\text{Freundlich Model}) \quad (10)$$

$$C_{ad} = \frac{C_m K_L C_{aq}}{1 + K_L C_{aq}} \quad (\text{Langmuir Model}) \quad (11)$$

Where,

$C_{ad}$  is an adsorbed phosphate concentration (adsorption capacity), mg/gm

$K_F$  is the Freundlich capacity factor

$C_{aq}$  is an equilibrium phosphate concentration in the aqueous phase, mg/mL

$1/n$  is the Freundlich intensity parameter

$C_m$  is the maximum sorption capacity, mg/gm

$K_L$  is the Langmuir empirical constant

The constants in equation (10) can be determined by plotting  $\log C_{ad}$  versus  $\log C_{aq}$  values and equation (10) can be rewritten as:

$$\log C_{ad} = \frac{1}{n} \log C_{aq} + \log k_F \quad (12)$$

The constants in equation (11) can be determined by plotting  $1/C_{ad}$  versus  $1/C_{aq}$  values, and equation (11) can be rewritten as:

$$\frac{1}{C_{ad}} = \frac{1}{C_m} + \frac{1}{K_L C_m C_{aq}} \quad (13)$$

In the above equations,  $C_{ad}$  (adsorbed phosphate concentration, mg/gm) is an equilibrium value that can be considered as the theoretical adsorption capacity of the sediments. In the continuous unidirectional flow column that is being designed in this study, equilibrium is not achieved that easily and thus adsorption is less than the theoretical values. For designing purposes, it is a common practice to accept 25-50% of the theoretical value as the actual adsorption capacity ( $C_{ad\_actual}$ ) of the sediments.

Prolonged use of the sediment packed column may give rise to the low adsorption of phosphate, especially when the sediment is near saturation. Hence, the experiment cannot continue forever using the same column. The duration of time the column can be utilized in studying phosphate

transport and interaction can be calculated by dividing the maximum amount of phosphate that can be removed by the sediment in the column ( $M_{Pr}$ ) with the rate of phosphate removal from the aqueous solution ( $R_{Pr}$ ) as given in equation (14).

$$Time = \frac{M_{Pr}}{R_{Pr}} \quad (14)$$

$R_{Pr}$  can be calculated as:

$$R_{Pr} = (C_{in} - C_{out})Q \quad (15)$$

Where,  $C_{in}$  and  $C_{out}$  are the concentrations of phosphate at the inlet and outlet of the column and  $Q$  is the water flow rate in the column.

## CHARACTERISTICS OF HANFORD SEDIMENT

### Physical Characteristics

During a physical examination of the Hanford sediment, it was found that the majority of the soil weight was due to particle sizes greater than 500  $\mu\text{m}$ , which contributed to 45.32% of the total weight of the soil. Table I lists the amount of particles determined in the laboratory after sieving 200 g of Hanford soil and Fig. 1 shows the particle size fraction distribution (%) observed in the Hanford sediment. Based on the soil texture analysis, the Hanford soil was found to be sandy with very little clay (0.5%). Sand and silt were 93.5% and 6.0%, respectively. The pH for this soil was determined to be 6.90 (n=3) and the soil showed very poor organic matter content (2.05%, n=3). The bulk density for these sediments was determined to be 1.57 g/cc (weight/volume).

Table I. Soil Particle Size Distribution in 200 g of Soil

Particle Size ( $\mu\text{m}$ )	Weight (g)
> 500	90.65
< 500 - > 250	44.88
< 250 - > 125	31.12
< 125 - > 63	20.93
< 63	10.8

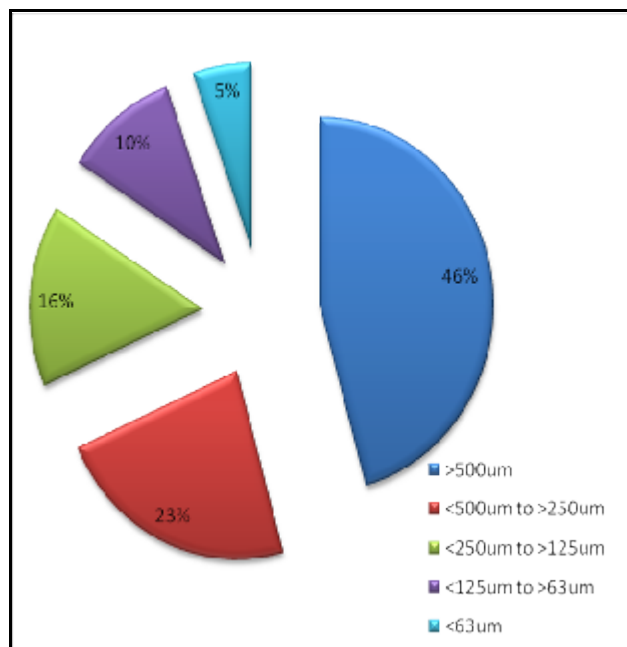


Fig. 1 Particle size fraction distributions in Hanford sediment samples

### Adsorption Characteristics

In order to determine the adsorption potential of the Hanford sediments, five sets 40-mL vials were prepared in triplicate with 2 gm sterilized (autoclaved) sediment (<1 mm particle size) and 10 ml deionized water. The vials were capped and placed on a magnetic shaker (100 rpm) for 24 hours to homogenize the mixture. To each set, a different concentration of phosphate (100, 250, 500, 1000, and 5000 mg/liter) was added. Each concentration was run in triplicate for a total of 15 vials (5 x 3 = 15). The final volume of water was made to 20 mL. The vials were placed on a magnetic shaker at 150 rpm for the 48-hour experiment to achieve equilibrium. Later, the experimental vials were centrifuged and the aqueous phase was filtered through PTFE filter (0.2  $\mu$ m) for the analysis of phosphate concentration. The vanadomolybdophosphoric acid calorimetric method was used in the analysis of phosphate and the absorbance was recorded at  $\lambda=470\text{nm}$  using a UV-spectrophotometer [8].

A Freundlich plot of  $\log [C_{aq}]$  vs.  $\log [C_{ad}]$  gave  $R^2 = 0.97$ , and  $K_F=6.61$  with  $1/n = 0.74$  (Fig. 2). A Langmuir plot of  $1/C_{aq}$  vs.  $1/C_{ad}$  gave a correlation coefficient  $R^2= 0.85$ , with  $K_L= 6.59$  (Fig. 3). It was found that the best fit for the experimental results were provided by the Freundlich model, and thus the same model was used in the calculation of adsorption capacity ( $C_{ad}$ ). Using equation (10) and the Freundlich parameters described above, the adsorption capacity ( $C_{ad}$ ) for the Hanford sediment was calculated as 199.62 mg/kg for the initial aqueous phosphate concentration 100 mg/L.

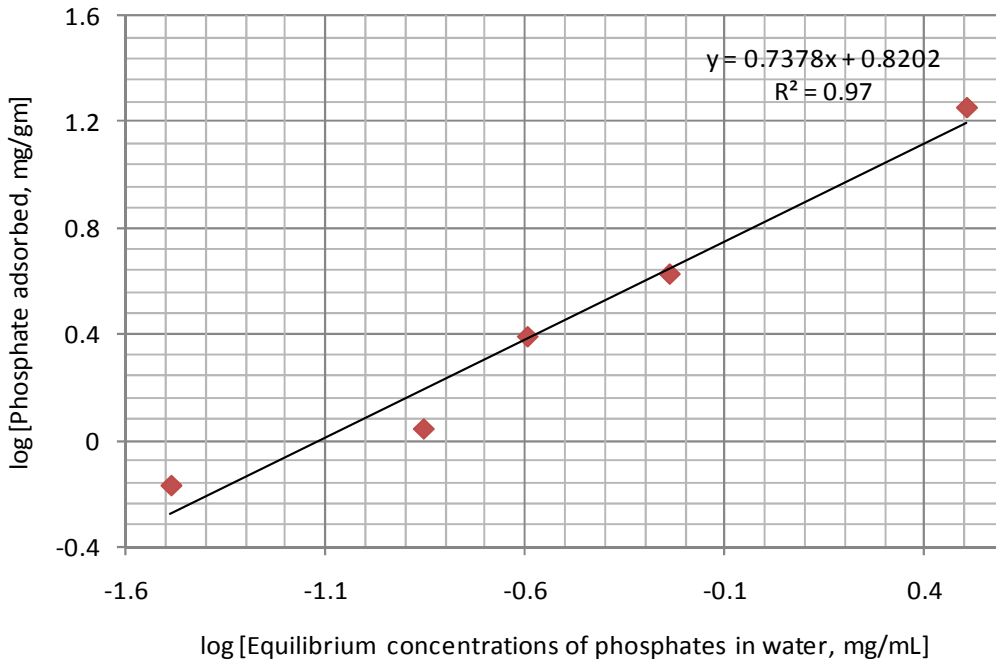


Fig. 2 A plot for  $\log C_{ad}$  versus  $\log C_{aq}$  in order to determine Freundlich parameters

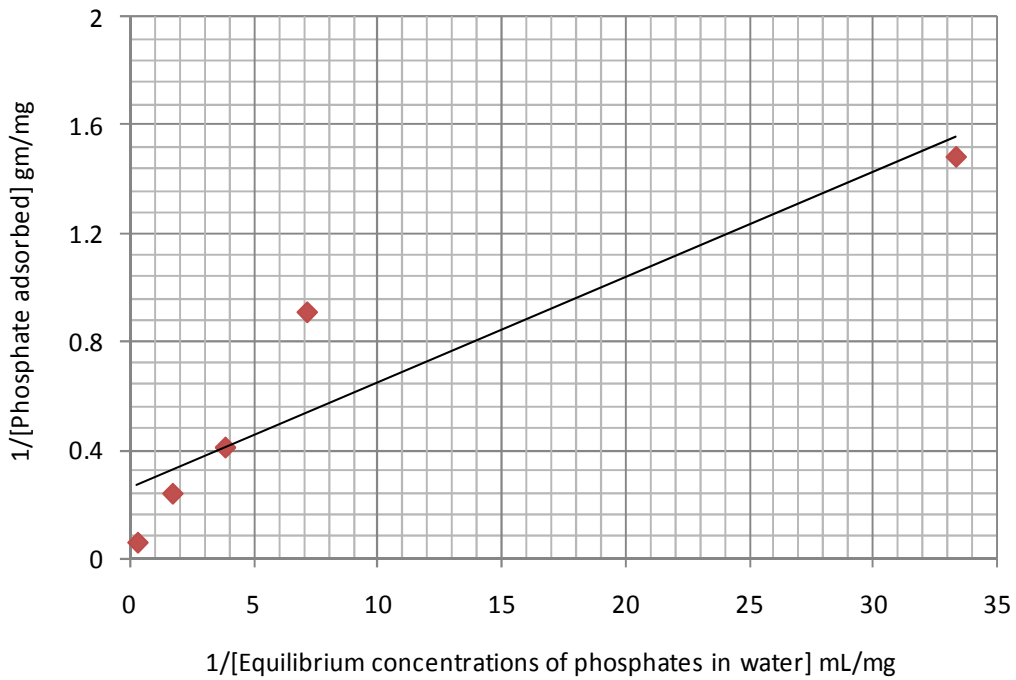


Fig. 3 A plot for  $1/C_{ad}$  versus  $1/C_{aq}$  in order to determine Langmuir parameters



## ESTIMATING COLUMN SIZE FOR HANFORD ENVIRONMENTAL CONDITIONS

Earlier, equations (8) and (9) were derived in order to calculate the height (length) and the radius of the required column to pack a given amount of Hanford sediment. From this relationship, the required radius of the column will decrease with an increase in the height of the column and vice versa. Often, the raw materials for column construction are obtained from commercial sources, and thus the users must select from only those materials that are available from the suppliers. Fig. 4 shows a curve generated for the selection of the column size for this particular study. The curve was generated for the standard radii of the tubing materials that are commercially available. Equation (8) was used to calculate the corresponding height of the column based on the 90% reduction in aqueous phosphate concentration ( $M_{Pr}$ ), for the initial phosphate concentrations of 100, 500, 1000, and 5000 mg/L. Experimental adsorption capacity and the bulk density of the sediments, as determined earlier, were also utilized. As can be seen in Fig. 4, the required column length (sediment filled) is higher for the smaller radii as well as for the higher initial phosphate concentrations. Working with the lowest concentration of phosphate in this study, 100 mg/L, required a 226.81 cm column length with a diameter of 2.54 cm (1 inch). On the other hand, the higher initial concentration of phosphate (5000 mg/L) required a 627.19 cm column length with the same diameter. Various other diameters that were tested based on their availability through the commercial sources were 3.81 cm (1.5"), 5.08 cm (2"), 7.62 cm (3"), 10.16 cm (4"), 12.7 cm (5"), and 15.24 cm (6").

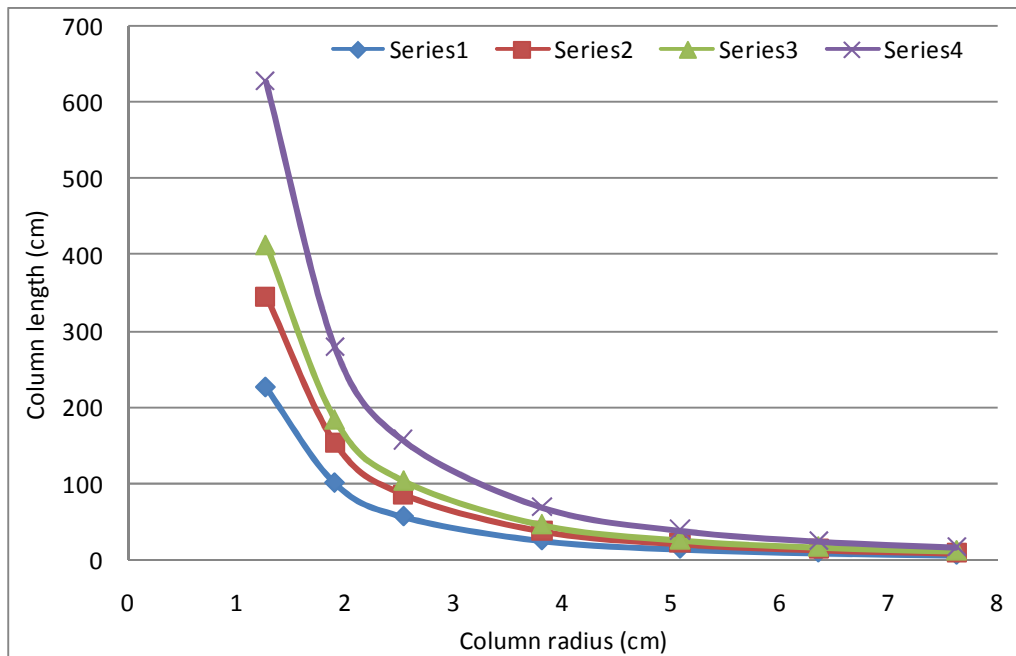


Fig. 4 Relationship between the column lengths & radii for the initial phosphate concentrations: 100 (series1), 500 (series2), 1000 (series3), & 5000 mg/L (series4)

From Fig.4 it becomes clear that most of the radii tested (> 5.08 cm), showed a requirement for smaller column lengths (<40 cm), compared to those with the smaller radii (<5.08 cm). Given that the flow rate of water inside the column will be adjusted to that of the Hanford Site

groundwater conditions (63.4 cm/h), most of the columns with a higher diameter may not provide sufficient retention time for the phosphate-containing water. In addition, low retention time is not helpful for placing the sampling ports along the column in order to generate time series data, especially with a manual method of sampling.

## **SIGNIFICANCE AND CONCLUSIONS**

FIU's Applied Research Center (ARC) is supporting the Hanford Site of the U.S. Department of Energy in developing a strategy to improve the efficiency of uranium stabilization processes through polyphosphate injection technology. Polyphosphate can precipitate uranium in the groundwater by making it immobile, thus preventing its release into the surface water system. However, this technology is relatively new, and very little information is available regarding the physical and chemical factors that govern the process of uranium immobilization in the groundwater environment. Batch and column studies may be quite useful in providing valuable information to the scientific community and in furthering the development of this technology. The contaminant studies using columns require a proper selection and design of the columns in order to meet the objectives of the study in an accurate and timely manner. This might not be possible through an ad hoc selection of the columns. The theoretical outputs and derivations relevant to sediment-packed columns that are provided in this study are expected to be useful in column selection and designing procedures.

From this study, it was found that if the working concentration of phosphate at the inlet and the desired concentration at the outlet are known, then amount of sediment required to bring about the expected change in phosphate concentration can be determined mathematically. The required amount of sediment, when expressed in terms of volume, helps in determining the size of the column needed. The required length of the column is inversely proportional to its radius. Looking at the flow rate of water inside the column (63.4 cm/h), the longer the column the better it is for the sampling of water along the column length through the installed sampling ports. Alternatively, shorter columns (with wider diameters) can also be used in series to obtain the time series data. Using longer and wider columns will require additional sediment and a change in the initial concentration of phosphate to get the desired concentration at the outlet.

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