

Research Article

Nano-Scale Hydroxyapatite: Synthesis, Two-Dimensional Transport Experiments, and Application for Uranium Remediation

S. R. Kanel,¹ T. P. Clement,² M. O. Barnett,² and M. N. Goltz¹

¹ Department of Systems and Engineering Management, Air Force Institute of Technology, 2950 Hobson Way, WPAFB, Fairborn, OH 45433, USA

² Department of Civil Engineering, Auburn University, Auburn, AL 36849, USA

Correspondence should be addressed to S. R. Kanel, sushil.kanel.ctr@afit.edu

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Synthetic nano-scale hydroxyapatite (NHA) was prepared and characterized using X-ray diffraction (XRD) and scanning electron microscopy (SEM) methods. The XRD data confirmed that the crystalline structure and chemical composition of NHA correspond to $\text{Ca}_5\text{OH}(\text{PO}_4)_3$. The SEM data confirmed the size of NHA to be less than 50 nm. A two-dimensional physical model packed with saturated porous media was used to study the transport characteristics of NHA under constant flow conditions. The data show that the transport patterns of NHA were almost identical to tracer transport patterns. This result indicates that the NHA material can move with water like a tracer, and its movement was neither retarded nor influenced by any physicochemical interactions and/or density effects. We have also tested the reactivity of NHA with 1 mg/L hexavalent uranium (U(VI)) and found that complete removal of U(VI) is possible using 0.5 g/L NHA at pH 5 to 6. Our results demonstrate that NHA has the potential to be injected as a dilute slurry for *in situ* treatment of U(VI)-contaminated groundwater systems.

1. Introduction

Groundwater systems can be contaminated by uranium discharged from ore mining and processing activities and from various nuclear weapons or fuel manufacturing activities. Uranium contamination can cause serious diseases including bone cancer, nonspecific malignant neoplasms, and lung cancer [1]. Therefore, the US Environmental Protection Agency (USEPA) standard for uranium in drinking water is set at 30 $\mu\text{g}/\text{L}$ [2].

A number of materials have been used as adsorbents or reductants for removing hexavalent uranium from groundwater. These include reactive sorbents such as activated carbon, zero-valent iron, phosphate rocks, zeolites, and various types of apatites [3]. Among available sorbent materials, apatites are one of the most promising candidates for adsorbing and immobilizing dissolved uranium from groundwater [4, 5]. This is because the apatite group of minerals have been found to be stable across a wide range of

geological conditions for hundreds of years [6, 7]. The solubility product of uranium-apatite minerals (K_{sp}) can vary from about 10^{-20} to 10^{-150} [7, 8]. Furthermore, apatite is an ideal material for long-term sequestration of metals due to its high affinity for actinides and heavy metals [9]. Therefore, apatite has been widely used for immobilizing heavy metals such as Pb [10], actinides such as plutonium [11] and U, Cr, Co, Ni, Al, Cu, Fe, Pu, Cd, Zn, As, Sb, and V [5, 12–14].

In the literature, several researchers have studied uranium removal by apatite using batch-scale [4, 5, 15–19] and column-scale experiments [20]. Several researchers have also attempted to apply hydroxyapatite (HA) to treat contaminant plumes at field sites. For example, commercial HA, $\text{Ca}_5(\text{PO}_4)_3\text{OH}$, has been used in a permeable reactive barrier (PRB) in a shallow alluvial aquifer at Fry Canyon, Utah to remove uranium [4]. However, almost all previous studies reported in the literature have focused on evaluating the feasibility for HA use in permeable reactive barrier (PRB)-type applications.

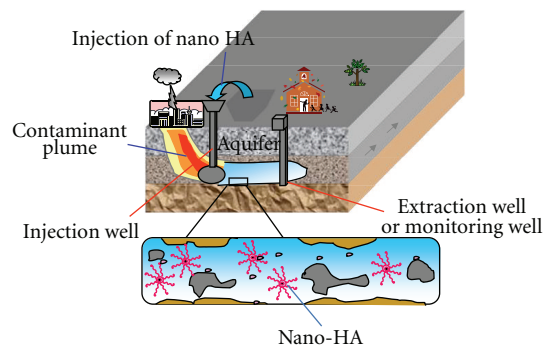


FIGURE 1: Schematic diagram of *in situ* groundwater remediation by injection of nano-HA.

The focus of this study is to demonstrate the feasibility of a novel *in situ* remediation technology that can treat uranium using nano-scale HA that can be directly delivered *in situ* and transported to the contaminated zone via injection wells. HA reacting with hexavalent uranium (U(VI)) has been shown to produce stable minerals such as chernikovite and autunite [5]. Use of injection wells would help avoid construction of expensive barriers, and also the method can target deep plumes at locations where trenching to construct a PRB is infeasible or cost prohibitive. Furthermore, a methodology that involves injection of HA would allow for repetitive treatments to ensure that sufficient quantities of U(VI) were immobilized to protect the environment.

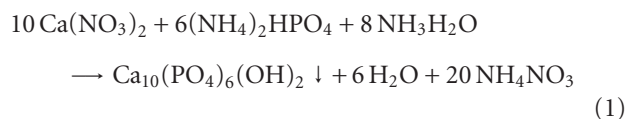
A conceptual schematic diagram illustrating the concept of injecting nano-HA to remediate a dissolved contaminant plume is shown in Figure 1. The overall goal of this study is to develop experimental datasets to investigate the feasibility of the remediation methodologies illustrated in this figure. The specific objectives of this study are to (1) synthesize and characterize nano-scale HA particles in laboratory, (2) investigate the transport characteristics of the synthesized nano-scale HA, and (3) demonstrate the reactivity of the nano-HA for treating U(VI) at different pH conditions.

2. Experimental

2.1. Material and Methods. All the chemicals used in the experiments were reagent grade. Chemicals used in this study, which include O-phosphoric acid, sodium nitrate, sodium bicarbonate, sodium hydroxide, and nitric acid, were purchased from Fisher Chemical Company (Fisher Scientific, Fairlawn, NJ, USA). Calcium nitrate ($\text{CaN}_2\text{O}_6 \cdot 4\text{H}_2\text{O}$) was purchased from Acros Organic (Morris Plains, NJ, USA). Ammonium hydroxide (6N) was purchased from Ricca Chemical Company (Arlington, TX, USA). The acids were trace metal grade, and the uranium standards and stock solutions were prepared from plasma-grade uranium standard (using depleted uranium).

2.2. Nano-HA Synthesis. Nano hydroxyapatite (NHA) was synthesized by reacting $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (0.1 M), and $(\text{NH}_4)_2\text{HPO}_4$ (0.06 M) with ammonium hydroxide (1 M).

The $\text{Ca}(\text{NO}_3)_2$ solution was vigorously stirred at room temperature and phosphate solution was added dropwise to the solution. The NH_4OH was then slowly added dropwise to this mixture for about 30 min to produce a milky gelatinous hydroxyapatite precipitate ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$), which was washed with deionized water three times. The overall precipitation reaction for synthesizing hydroxyapatite can be written as



The reaction process described above is a modified version of an HA synthesis method described in previous studies [21, 22].

2.3. Batch Experiments. Batch adsorption experiments were conducted at room temperature ($\sim 295 \text{ K}$) in 50 mL polycarbonate centrifuge tubes, each tube yielding one data point. Experiments were performed in duplicates to verify the reproducibility of the results. The samples are prepared by mixing an appropriate amount of the HA, ionic strength adjuster (0.01 M NaNO_3), acidified U(VI) stock solution ($\text{UO}_2(\text{NO}_3)_2$), and distilled deionized water. In all the batch experiments, the pH of the solution was adjusted using 1 M NaOH or HNO_3 . The reacted samples were removed from the shaker and centrifuged to aid in filtration. The samples were opened and an aliquot of the supernatant was withdrawn and immediately filtered with a $0.45 \mu\text{m}$ syringe filter, and the pH of the remaining suspension was measured. The filtrate was analyzed to measure the values of aqueous U(VI) concentration levels using a kinetic phosphorescence analyzer (KPA) (model KPA-11, Chemchek Instruments, Richland, WA) after acidifying the filtrate to a pH value of 1. The level of uncertainty associated with the U(VI) analysis method is $\pm 3\%$ [23, 24].

2.4. Details of Porous Media Transport Experiments. A two-dimensional aquifer model packed with A-110 silica beads (Potters Industries, USA) was used in this study. A uniform flow field was established by maintaining a constant hydraulic gradient across the flow tank. Experimental details of the two-dimensional experiments are summarized in our previous work [25, 26]. Briefly, the dimensions of the flow container were 41 cm (length) \times 1.1 cm (width) \times 30 cm (height). Two chambers (each 5.5 cm wide) were situated at the left and right ends of the tank. A series of overflow orifices were used to control the water level (head) at either side of the flow tank. In all the transport experiments the ambient freshwater flowed by establishing a head difference of 0.7 cm across the chamber. The flow field was allowed to reach steady state for a period of 10 min before starting the nanoparticle injection experiments.

The freshwater supply source was marked with a small amount of nonsorbing red dye, and hence the entire tank appeared red prior to any injection. After establishing steady-state flow conditions, 20 mL of uncolored freshwater was

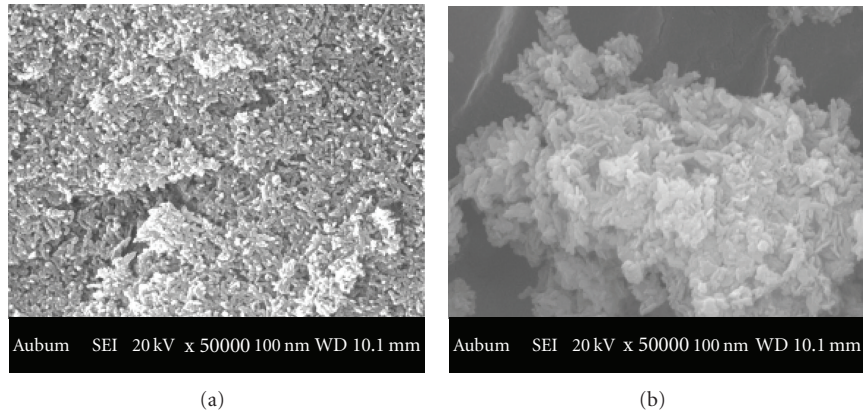


FIGURE 2: SEM images of (a) lab synthesized nano-HA and (b) commercial Aldrich-HA.

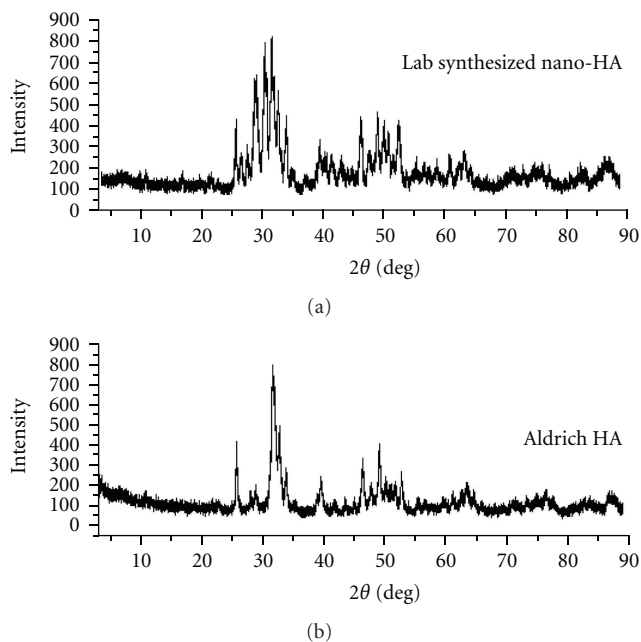


FIGURE 3: Lab synthesized nano-HA and Aldrich HA.

injected into the porous media tank to characterize tracer transport through the physical system. The location of the injection point was approximately 11.2 cm from the left end and 17 cm from the bottom of the flow container. It took approximately 10 s to manually inject the 20 mL tracer slug. The movement of the tracer was recorded for about 15 min by taking high-resolution digital pictures at regular intervals. After completing the tracer study, we injected similar volume of nano-HA and recorded its migration patterns and compared it with the tracer data.

3. Results and Discussion

3.1. Characterization of NHA. SEM images of synthesized nano-HA particles and commercial HA powder purchased

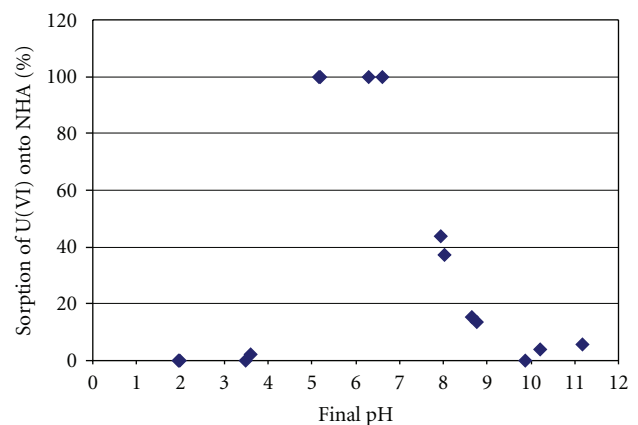


FIGURE 4: Influence of pH on U(VI) removal by synthetic NHA; experimental conditions: U(VI): 1 mg/L and NHA: 0.5 g/L.

from Aldrich Chemicals are shown in Figure 2. The image confirms that the particles are on the order of 20 to 50 nanometers and are needle shaped.

The XRD data for nano-HA and a commercial HA powder are shown in Figure 3. The XRD data confirm that the lab synthesized nano-HA has peaks that correspond to the peaks of commercial crystalline HA.

3.2. Reactivity of Nano-HA with U(VI). The percent removal of U(VI) by NHA was investigated using 1 mg L^{-1} of the U(VI) at different pH values, and the results are presented in Figure 4. The data show that almost 100% of U(VI) (at a concentration of 1 mg/L) can be removed by 0.5 g/L NHA at pH 5 to 6 (see Figure 4). The U(VI) removal capacity and the pH dependence pattern of the synthesized NHA were comparable to the commercial HA (data not shown here).

3.3. Transport of NHA in Porous Media Systems. The transport patterns of the tracer and NHA observed at different times are shown in Figure 5. The pictures at 0 min present

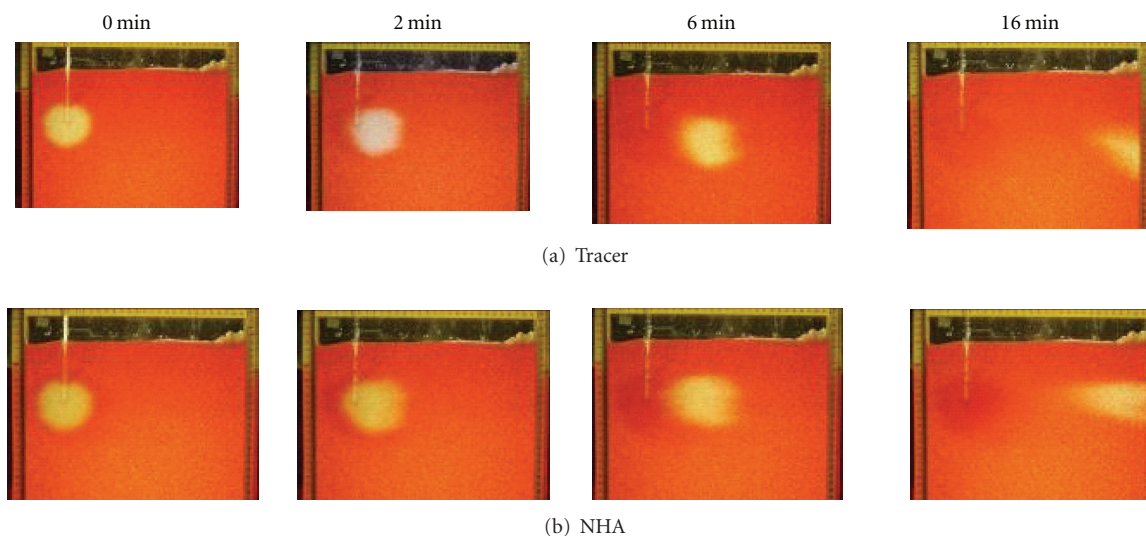


FIGURE 5: Transport of (a) tracer (uncolored deionized water) and (b) NHA plumes in the two-dimensional flow container.

the location of the plumes immediately after injection. Other pictures shown in the figure were taken at 2, 6, and 16 minutes. The data indicate that the freshwater tracer (deionized water) plume dispersed and moved horizontally and reached the right boundary after approximately 16 minutes of transport (see Figure 5(a)). The NHA plume also moved horizontally toward the right boundary at a rate nearly identical to the tracer transport rate (see Figure 5(b)).

Colloidal suspensions can be removed by the porous medium due to various physical and chemical processes including charge interaction, filtration, diffusion, interception, and/or sedimentation [27]. However, in the case of NHA, the transport was observed to be similar to that of a tracer plume. This implies that the transport of dilute NHA solutions will be controlled primarily by advection and dispersion processes. A mass balance analysis that compared the mass of injected NHA with the mass recovered in the effluent indicated that about 85% of NHA was transported through the system. The mass balance discrepancy of 15% is attributed to experimental errors; however, it is possible that an unrecoverable fraction of NHA particles remain trapped in the porous medium. Extraction of porous media samples obtained near the injection zone did not yield any recoverable amount of NHA.

In the published literature, no datasets are available that document the transport patterns of NHA in a two-dimensional (2D) flow tank packed with porous media. In an earlier report we studied the 2D transport of stabilized and unstabilized zero-valent iron nanoparticles through porous media [26] and found that density effects can play a significant role in transporting surface-modified iron nanoparticles. Such density effects were not observed in these NHA transport experiments. Since NHA moved like a tracer, this material could be used either for extracting contaminants or for *in situ* stabilization of contaminants, depending on site-specific needs and conditions.

4. Conclusions

The findings of this study demonstrate that nano-scale hydroxyapatite (NHA) materials could be used for developing treatment approaches for removing and/or immobilizing highly toxic radionuclides such as U(VI) in subsurface groundwater systems. These approaches would allow remediation of U(VI) without the need to excavate. Since HA has the potential to immobilize U(VI) to stable minerals such as autunite and chernikovite [5, 6], this process has important implication for *in situ* U(VI) remediation. Our flow tank data indicate that the transport characteristics of NHA are similar to tracer transport characteristics. The reactivity data show that NHA has a strong affinity to efficiently remove U(VI) around pH 5 to 6. More studies are, however, needed to further understand and scale up these processes to field-specific transport conditions.

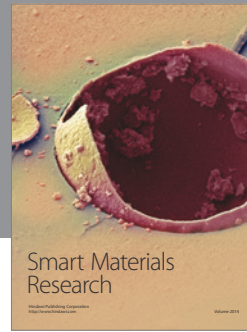
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