Use of Novel Reactive Barrier Materials for Treatment of Strontium, Uranium, Nitrate and Perchlorate in Groundwater

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Abstract: Reactive barrier technology has been under investigation at Los Alamos National Laboratory for remediation of contaminated groundwater. The presence of multiple contaminants, including $^{85,\ 87}Sr$, ^{235}U, NO_3^- and ClO_4^-, has prompted investigation of novel types of reactive media to remediate groundwater. Contaminants have been contacted with media utilizing batch techniques, kinetically limited one-dimensional (1-D) columns, and a 2-D box packed with reactive porous materials. Two materials have shown significant propensity to remove aqueous phase metals, NO_3^- and ClO_4^- from groundwater: Apatite®II and pecan shells. Apatite II effectively sorbs ^{238}U (92 mg ^{238}U/kg Apatite II) and provides sustenance for microorganisms that continuously reduce NO_3^- and ClO_4^- (undetected during experiments). Since Apatite II contains significant amounts of naturally abundant Sr, its capacity to sorb anthropogenic $^{85,\ 87}Sr$ is limited. Pecan shells provide a long-term carbon source for microorganisms that form biofilm on the surface of the shells. The biofilm and shells sorb ^{87}Sr (42 mg ^{87}Sr/kg shells) and microorganisms reduce NO_3^- and ClO_4^-, although it is necessary to stimulate microorganisms with a supplemental carbon source such as dog food to reduce NO_3^- and ClO_4^- to undetectable levels. When placed in series, Apatite II followed by pecan shells, these materials effectively eliminate multiple contaminants from groundwater.

Permeable reactive barrier (PRB) technology is an emerging alternative to traditional pump-and-treat groundwater remediation. PRB research at Los Alamos National Laboratory (LANL) has focused on the use of various reactive media arranged in sequential layers to react with multiple contaminants including $^{85,87}Sr$, ^{238}U, NO_3^- and ClO_4^-. Apatite II was investigated for its potential to induce the precipitation of heavy metals and radionuclides on the Apatite II surface. Recently, Conca et al. (2000) documented the utility of Apatite II to immobilize Pb according to the following reactions:

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1) dissolution: $Ca_5(PO_4)_3(OH)$ (c) + $7H^+ \rightarrow 5Ca^{2+} + 3H_2PO_4^- + H_20$
2) precipitation: $5Pb^{2+} + 3H_2PO_4^- + H_20 \rightarrow Pb_5(PO_4)_3(OH)$ (c) + $7H^+$

To reduce NO_3^- and ClO_4^- concentrations in groundwater, a biologically active barrier material was sought. Pecan shells were utilized as the carbon-based support material for proliferation of biofilm. Experiments were conducted with and without dog food, which served as a supplemental carbon source for developing microbial populations.

Equilibrium batch study results showed that sorption coefficients (K_d = sorbed phase concentration/aqueous phase concentration) for Apatite II and pecan shells contacted with ^{85}Sr were 453 and 163, respectively. Although significant sorption of ^{85}Sr was observed by the Apatite II, microwave digestion and ICP analysis of Apatite II indicated that 1146 (+/-144) mg/kg of ^{87}Sr was naturally abundant in the material. It was clear from batch results that Apatite II would preferentially exchange ^{87}Sr, and other naturally abundant cations (Ca^{2+}, K^+, Mg^{2+}, Na^+), in its phosphate structure for radioactive Sr.

Batch studies were also conducted to evaluate the capability of pecan shells, with and without dog food as a micronutrient source, to reduce NO_3^- and ClO_4^- concentrations. In the absence of dog food, 600 mg L^{-1} NO_3^- was reduced to below detection in 14 days, whereas with dog food the concentration was undetectable after 7 days. Perchlorate concentrations (350 μg L^{-1}) were reduced below detection in 7 days in the systems containing dog food (Strietelmeier et al., 2001).

Rate-limited 1-D column experiments were conducted by filling borosilicate glass columns (6 cm long, 4.8 cm inside diameter) with Apatite II or pecan shells. Groundwater collected from a local well at LANL was spiked with ^{87}Sr (5 mg L^{-1}) and flushed through the first Apatite II column with a contact residence time of 0.2 days. ICP analysis of ^{87}Sr from column effluent revealed that concentrations of ^{87}Sr continuously increased from 0.87 to 2 mg L^{-1} over the course of collecting 2 L of effluent. These results validated batch results, which indicated that Apatite II would not effectively sorb ^{87}Sr. In fact, the column effluent was leaching 0.87 mg L^{-1} ^{87}Sr before influent waters replaced Nanopure® water that initially saturated the column. An identical column experiment was conducted to measure the capacity of Apatite II to sorb ^{238}U (5 mg L^{-1}). Figure 1 illustrates the Apatite II column used in the study and the concentrations of ^{238}U detected in effluent water. Concentrations of ^{238}U were undetected for the first 1.2 L resulting in a capacity of 92 mg ^{238}U per kg Apatite II.

A single pecan shell column study was flushed with groundwater containing 2 mg L^{-1} ^{87}Sr, 150 mg L^{-1} NO_3^- and 350 μg L^{-1} ClO_4^- with a contact time of 0.25 days. Concentrations of ^{87}Sr were undetected for 1.4 L (42 mg ^{87}Sr per kg pecan shells), while NO_3^- and ClO_4^- concentrations were not substantially reduced. Acetate (10 mM) was introduced as a readily available carbon source with influent water resulting in complete reduction of NO_3^- and ClO_4^-. This experiment proved that pecan shells could sorb ^{87}Sr leached from Apatite II and produce a biofilm that could reduce NO_3^- and ClO_4^- granted a substantial carbon source was available for microorganisms.

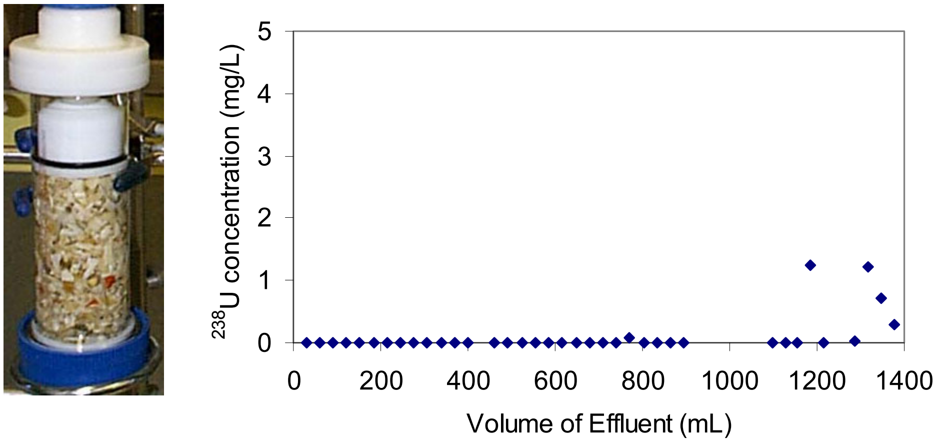

Figure 1. Apatite II column used to assess ^{238}U sorption, and ^{238}U effluent concentrations from Apatite II column study.

The final experiment, a 2-D box experiment, demonstrated the capability of Apatite II to completely reduce NO_3^- and ClO_4^- concentrations. Apatite II and pecan shells were arranged sequentially in a 60 x 31 x5 cm^3 box. Flow in the vertical and horizontal dimensions can be monitored in the box, and sampling at the Apatite II/pecan shell interface was accomplished via ports located on the exterior of the box. Concentrations of contaminants in the groundwater were 2 mg L^{-1} ^{87}Sr, 125 mg L^{-1} NO_3^-, 300 μg L^{-1} ClO_4^-. After 100 days of continuous contaminant injection, concentrations of NO_3^- and ClO_4^- remained undetected following contact with the Apatite II. The Apatite II contains enough organic matter to provide a substantial micronutrient source for microbial proliferation. The background concentration of ~0.87 mg L^{-1} ^{87}Sr was continuously leached from the Apatite II, however ^{87}Sr concentrations did not increased above that level. Pecan shells were not provided the opportunity to reduce NO_3^- and ClO_4^- concentrations, however the shells sorbed ^{87}Sr leached from the Apatite II. For the suite of contaminants evaluated in this research, Apatite II followed by pecan shells cooperate in a synergistic fashion to completely remove ^{87}Sr, NO_3^- and ClO_4^- from contaminated groundwater.

References

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