

Selective Sorption of Technetium from Groundwater

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EM Focus Area: contaminant plume containment and remediation

Technology Needs

Groundwater at DOE sites in which uranium or plutonium has been processed is frequently contaminated with the radionuclide Tc-99. DOE's Paducah and Portsmouth sites are typical of the contamination problem. Solutions contaminated with radionuclides were poured into lagoons and burial pits, which created a plume that has seeped into the sandy aquifers below the vados zone. Technetium is the principal radioactive metal-ion contaminant in the groundwater at the Paducah site, and it is present at a concentration of about 25 ng/L. Tc is present in the groundwater at Portsmouth at a concentration which varies a great deal with distance from the source, and concentrations of >400 ng/L have been reported. Under the oxidizing conditions of near-surface groundwater, the principal form of the element Tc is expected to be the pertechnetate anion, TcO_4^- [1]. Pertechnetate salts are highly water-soluble and quite mobile in underground aquifers, and, when coupled with the long half-life of Tc-99 (213,000 years), the resulting probable transport into the biosphere makes the presence of this radioisotope in groundwater a great concern. A related problem exists at other DOE sites where the processing of uranium or plutonium resulted in the release of technetium to the surrounding groundwater. Commercially available anion-exchange resins are capable of removing TcO_4^- ion in the presence of typical anions found in groundwater, but improving the selectivity will result in substantial cost savings in terms of the quantity of resin needed and the scale of the equipment required to treat huge flow rates.

Technology Description

The pertechnetate anion is strongly sorbed on commercially-available strong-base anion-exchange resins, but in view of the low (typically nanomolar) concentrations of Tc involved, enhanced selectivity for the pertechnetate anion over other anions commonly found in groundwater such as chloride, sulfate, and nitrate will be needed. We have prepared and evaluated new anion-exchange resins which were designed to be highly selective for pertechnetate. The technology involves building those features which are known to enhance the selectivity of pertechnetate over other anions into the exchange sites of the resin (hydrophobicity), while at the same time maintaining favorable exchange kinetics.

A resin bed of this material will be used either as part of a coupled treatment-recirculation system for the in situ remediation of groundwater contaminated with technetium or in a once-through treatment scheme.

Benefits to DOE/EM

While commercially available strong-base anion-exchange resins are effective in removing pertechnetate from groundwater, improvements in selectivity can result in substantial cost savings

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due to less resin required to treat a given volume of groundwater. The use of exchangeable resin modules is expected to lead to a low-maintenance easily-cared-for technology for technetium removal.

Technology Transfer/Collaborators

Collaborators: Department of Chemistry, University of Tennessee, Knoxville; Environmental Sciences Division, ORNL.

Technology Transfer: Eichrom Industries, Inc., Darien, IL

Scientific Background

Strong base anion exchange resins can remove TcO_4^- ion with varying degrees of selectivity from waste streams containing an excess of other competing anions. Ashley et al. [2] at LANL have demonstrated that ReillexTM-HPQ resin is effective in removing pertechnetate from tank waste simulants that have high concentrations of nitrate ion. At ORNL, DowexTM 1-X8 resin has been shown to be effective in removing pertechnetate in the presence of typical anions found in groundwater at Paducah.

Other schemes have been proposed for removing technetium from groundwater. One method under examination will reduce the technetium to a lower oxidation state that is insoluble or that precipitates from solution. This method may not be effective if oxygen in the aquifer or from other sources can oxidize the technetium back to the soluble TcO_4^- ion. Use of a resin to sorb the anion will have advantages over reductive schemes if the resin can be made selective. Air stripping is the currently favored technology to remove trichloroethylene and other volatile organic compounds from groundwater, and this process necessarily puts a high concentration of oxygen in the aquifer.

We are developing resins to selectively sorb technetium from groundwater that can be used with a remediation scheme involving recirculation of the water through a decontamination station within the aquifer. These resins will also be effective with once-through treatment schemes such as that being demonstrated at Paducah.

Technical Approach

The pertechnetate anion has a high affinity for strong-base anion-exchange resins such as those made from quaternary amines. Most commercially-available strong-base resins do not have as high a selectivity for TcO_4^- over chloride, sulfate, or nitrate ion as is desirable or attainable. These latter anions can be present in the groundwater at concentrations 10^6 times that of pertechnetate.

On theoretical grounds, the microenvironment of the exchange sites within the resin is expected to play a major role in ionic selectivity, and the synthesis of a new series of resins in which the properties of the resin were systematically varied was undertaken. These resins were part of a program to modify the microenvironment of the exchange sites and to thus enhance the selectivity for pertechnetate ion over the other anions commonly found in groundwater. During the past two years, we have prepared and evaluated over 80 laboratory resins. These were tested along with 7 commercial resins for sorption of pertechnetate from a "Groundwater Test Solution" consisting of pertechnetate at a concentration of 6.0 micromolar in a matrix of sodium chloride, sodium nitrate, and sodium sulfate (each at 60 millimolar), as previously described [3]. The affinity of a resin for

pertechnetate was determined by measuring the batch distribution coefficient (K'_d) for TcO_4^- sorption on the resin following a given equilibration period (e.g., 1, 4, 24, and 168 hour time periods). The batch equilibrium testing method for measuring pertechnetate uptake provided a useful means for comparing the affinity of a resin for pertechnetate as a function of time. Early results were instrumental in alerting us to the key structural and chemical properties of the resin that enhanced both the overall pertechnetate selectivity and the rate of pertechnetate uptake.

We have applied our knowledge of the properties of existing anion-exchange resins in making both the chemical and physical modifications necessary to improve both the K'_d and the $K'_d(\text{eq})$ (the K'_d per exchange site) for pertechnetate. The iterative process of resin synthesis, evaluation of Tc selectivity, and further resin synthesis in a close collaboration allowed us to rapidly converge on a novel class of resins with superior selectivity for the pertechnetate ion. These resins were studied more thoroughly under flow-through column conditions using our Groundwater Test Solution, with the objective of determining selectivity under conditions of solution flow in a column where mass-transport limitations become important. The best resin from this study was then tested using actual Paducah groundwater, followed by a field test, in which pertechnetate-contaminated groundwater from monitoring well #106 in the Pits and Trenches area of ORNL at the DOE Oak Ridge Reservation was pumped through a column containing the resin for a month. We are presently evaluating different methods of preparing the best resins, to determine the most economical synthetic procedures that can be used for preparing bulk quantities of the best resins, while maintaining optimum pertechnetate sorptive performance.

Accomplishments

Best Candidate Resins Identified. A new class of anion exchange resins with improved selectivity and sorptive capacity for the pertechnetate anion as compared to commercially available resins have been prepared and evaluated, both in batch-equilibrium and flow-through column testing conditions using a groundwater test solution. When evaluated in column flow-through experiments, the best laboratory resin, code-named VP02-217, can process more than 30 times the volume of groundwater test solution before reaching the same level of break-through as the commercial resin Purolite® A-520E (see Table 1), which is currently being used to remove pertechnetate from groundwater at DOE's Paducah, KY facility.

Invention Disclosure Submitted. An invention disclosure was submitted describing the synthesis and characterization of the new class of anion exchange resins. Eichrom Industries, Inc., has expressed interest in this resin to complement other Tc-selective materials in their product lines.

Field Tests at Monitoring Well #106 in the Pits and Trenches area of ORNL at the DOE Oak Ridge Reservation. Evaluation of the Tc selectivity of our synthetic resin under actual field conditions using contaminated groundwater was begun during late July and continued into August, 1996. This small-scale field test was designed for the optimization and eventual engineering scale-up for a pilot-scale or a full-scale field demonstration in FY 1997 and FY 1998. We determined the breakthrough of Tc-99 using our best synthetic resin VP02-217 at a relatively high flow rate which is representative of the rate that may be used in field pump-and-treat operations. In this test, the system fouling, clogging, and hydraulic head loss during the experiment were also evaluated. The test was performed with the VP02-217 resin contained in a small column (10 x 40 mm) at a constant flow rate of 17.8 mL/min. The volume of the resin bed ("bed volume") was 3.1 mL, with an effective void fraction for the resin of ~31% (making the "pore volume" for this resin bed equal to 0.96 mL). Therefore, the interstitial linear velocity was

Table 1. Column break-through data for pertechnetate sorption from Groundwater Test Solution for Purolite® A-520E and VP02-217 resins at two different flowrates, and break-through data for VP02-217 field trial at monitoring well #106 for comparison.

Property	Purolite® A-520E "slow" flowrate	Purolite® A-520E "fast" flowrate	VP02-217 Laboratory "slow" flowrate	VP02-217 Laboratory "fast" flowrate	VP02-217 Field Trial "intermediate" flowrate
24 hr Batch-equilibrium K'd (mL/g) ($\pm 5\%$)	12800		48400		
Resin Bed Volume (mL)	3.0	3.0	3.0	3.0	3.1
Void fraction (interstitial volume in mL/mL resin)	0.31	0.31	0.31	0.31	0.31
Resin Pore Volume Bed Vol x Void fraction (mL)	0.93	0.93	0.93	0.93	0.96
Actual Flowrate (BV/min)	3.26 ± 0.10	10.84 ± 0.44	3.52 ± 0.06	11.12 ± 0.09	5.7
Interstitial velocity (cm/min)	40 ± 1	134 ± 5	43 ± 1	136 ± 1	73
Bed Volumes at 0.1% Break-through	<10	<<10	400	80	Not determined*
Bed Volumes at 1.0% Break-through	33	<10	1250	330	40,000
Bed Volumes at 2.0% Break-through	90	<10	1800	500	56,000
Bed Volumes at 10.0% Break-through	550	50 est. (11.5% at 67 BV)	3700-4000 est. (4% at 2440 BV)	1540	143,000

* Not determined due to the variation of the background data.

calculated to be ~73 cm/min, which is comparable to the value (~80 cm/min) in use at the Northwest Plume pump-and-treat facility at DOE's Paducah Gaseous Diffusion Plant (PGDP) site.

This field test was conducted in the Pits and Trenches area at the DOE Oak Ridge Reservation. Groundwater in this area is contaminated with Tc-99 (as TcO_4^-). Monitoring well #106 was selected as our test site because the groundwater contains a relatively high Tc-99 concentration but relatively low concentrations of other contaminants such as Co-60, H-3, Sr-90, and Cs-137. However, the groundwater contains a relatively high concentration of NO_3^- and SO_4^{2-} (>100 mg/L). The TcO_4^- concentration in the groundwater varied from ~1000 to 5000 pCi/L during the test period because of rainfall events.

Results indicated that no significant breakthrough of Tc-99 was observed during the first 5 days of operation. At day 7 (or after ~56,000 bed volumes of groundwater passed through the column), we observed ~2% breakthrough of TcO_4^- . The column was continuously operated for 31 days, and by an observed color change, the column appeared to pick up a coating of organic materials on the resin which did not appear to significantly reduce the performance of the synthetic resin. The performance of this resin in this test (see data in Table 1) indicates that it is at least an order of magnitude more selective than any other sorbant which has been tested for Tc sorption including iron filings [4], other resins, and activated carbon [5].

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