Bi-functional Resin for Removal of Contaminants from Groundwater

Efficient Separations and Processing Crosscutting Program and Subsurface Contaminants Focus Area

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Bi-functional Resin for Removal of Contaminants from Groundwater

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Efficient Separations and Processing Crosscutting Program and Subsurface Contaminants Focus Area

Demonstrated at Paducah Gaseous Diffusion Plant Site Paducah, Kentucky
Purpose of this document

Innovative Technology Summary Reports are designed to provide potential users with the information they need to quickly determine whether a technology would apply to a particular environmental management problem. They are also designed for readers who may recommend that a technology be considered by prospective users.

Each report describes a technology, system, or process that has been developed and tested with funding from DOE’s Office of Science and Technology (OST). A report presents the full range of problems that a technology, system, or process will address and its advantages to the DOE cleanup in terms of system performance, cost, and cleanup effectiveness. Most reports include comparisons to baseline technologies as well as other competing technologies. Information about commercial availability and technology readiness for implementation is also included. Innovative Technology Summary Reports are intended to provide summary information. References for more detailed information are provided in an appendix.

Efforts have been made to provide key data describing the performance, cost, and regulatory acceptance of the technology. If this information was not available at the time of publication, the omission is noted.

All published Innovative Technology Summary Reports are available on the OST Web site at www.em.doe.gov/ost under “Publications.”
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Technology Summary

Groundwater used for processing uranium or plutonium at U.S. Department of Energy (DOE) sites is frequently contaminated with the technetium radionuclide $^{99}\text{Tc}$, with half-life of 213,000 years. At DOE’s Paducah and Portsmouth sites, contaminated solutions were poured into lagoons and burial pits, creating a plume that has seeped into the sandy aquifers below the vadose zone. Technetium is the principal radioactive contaminant in Paducah site groundwater where it is present at a concentration of 170 to 250 ng/L in a plume that covers 2 square miles and extends several miles off-site. Concentrations as high as 400 ng/L have been reported at the Portsmouth site, with the average concentration being 26 ng/L in a 14-acre plume.

The chemical form of the technetium in oxygen-rich groundwater is the pertechnetate anion, $\text{TcO}_4^-$. This water-soluble species is highly mobile, and transport of the $^{99}\text{Tc}$ into the biosphere is of great concern. Removal by sorption onto strong-base ion exchange resins has become the accepted method of treatment, but enhanced selectivity for the pertechnetate anion is needed over other anions commonly found in groundwater such as chloride, sulfate and nitrate.

New bifunctional anion-exchange resins that were designed to be highly selective for pertechnetate have been prepared and tested as part of this research project at Oak Ridge National Laboratory (ORNL) and the University of Tennessee (UT). Features that enhance selectivity while maintaining favorable exchange kinetics and good capacity were identified in a testing program involving more than 90 new resins. The optimum resin identified in this program in turn has been compared with the commercial Purolite A-520E resin in current use at the Paducah Gaseous Diffusion Plant (PGDP). Figure 1 illustrates the column setup used for the field demonstration at PGDP.

Field Demonstration for $\text{TcO}_4^-$ Treatment

*Paducah Gaseous Diffusion Plant site, Kentucky (FY 99).*

![Figure 1. Column Setup.](image-url)
Demonstration Summary

This report covers the period of 10/94-9/00. One of the new bifunctional resins (nicknamed BiQuat) was evaluated in a field demonstration conducted at the Northwest Plume Treatment Facility at Paducah Gaseous Diffusion Plant (PGDP), Kentucky, in 1999. Approximately 840,000 gal of $^{99}$Tc-contaminated groundwater were passed through a resin-filled column 5.25 inches in diameter and 12 inches in length. The BiQuat resin performed about 5-times better than the Purolite A-520 E resin. Less than 3% of pertechnetate breakthrough was observed when the 600,000 bed volumes (BV) were treated at a flow rate of 2.2 BV/min (2.5 gal/min) over the 8-month continuous test.

A regeneration process for perchlorate ($\text{ClO}_4^-$) loaded resins has recently been developed at ORNL (Brown 2000b) to allow these anion exchange resins to be used repeatedly over a long-term operation (patent pending). The BiQuat resins have also been demonstrated to be selective and efficient in removing perchlorate ion, $\text{ClO}_4^-$, from contaminated groundwater, and a licensing agreement has been made with Purolite Corporation to develop and market the resins for use in perchlorate remediation. The regeneration process will be applicable to pertechnetate-loaded resin as well. Figure 2 is a photograph of the column, flow meter, and pressure gages used at PGDP.

![Column, Flow Meter, Pressure Gages](image)

Figure 2. Column, Flow Meter, Pressure Gages.
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Permitting

Other
All published Innovative Technology Summary Reports are available on the OST Web site at www.em.doe.gov/ost under “Publications.” The Technology Management System (TMS), also available through the OST Web site, provides information about OST programs, technologies, and problems. The Tech ID for Bi-functional Resin for Removal of Contaminants from Groundwater is 255.
SECTION 2
TECHNOLOGY DESCRIPTION

Overall Process Definition

The radionuclide $^{99}$Tc is a fission product of $^{235}$U and $^{239}$Pu, and it has been found as a contaminant in groundwater at DOE sites where uranium and plutonium have been processed. Because of the low (typically nanomolar) concentration of pertechnetate in groundwater, the development of resins with enhanced selectivity for this anion over other ions commonly found in groundwater such as chloride, sulfate and nitrate will have a favorable impact on the economics of groundwater treatment.

**Ion characteristics** that increase the affinity of an anion for a sorptive resin include
- large size
- small charge-to-size ratio
- low hydration energy

Because pertechnetate is larger and has a lower hydration energy than most other groundwater anions, there is a natural bias for the sorption of pertechnetate on a resin in comparison to anions commonly found in groundwater.

**Resin selectivity** for pertechnetate can be enhanced by
- increasing the size of the resin cation
- maintaining an environment of low polarity at the exchange site

In developing their resins, the ORNL/UT research team enhanced pertechnetate sorption by choosing
- poly(vinylbenzylchloride) as the polymer backbone
- partial crosslinking of the polymer using known amounts of divinylbenzene
- quaternary ammonium ion exchange sites of large and variable size

The ion exchange sites were created by reacting trialkyl amines with the benzyl chloride groups on the resin. Pertechnetate sorption selectivity increased with size of the alkyl group, but sorption rate decreased with size. Greatest 24-hr batch sorption by mono-functional resin was achieved with the tributyl and tripropyl amines.

An important innovation made by the ORNL/UT team was based on the recognition that sorption rates and sorption selectivities for pertechnetate could both be increased by having two different anion exchange sites on the resin. The larger site, derived from trialkyl amines having three identical alkyl groups, each with 5-8 carbon atoms, would enhance selectivity for pertechnetate sorption. The smaller sites, made with alkyl groups containing 2-4 carbon atoms, would enhance sorption kinetics. In comparison to resins prepared from single trialkyl amines, the bi-functional resins were found to have
- superior selectivity for pertechnetate
- equal or better exchange capacity
- equal or faster exchange kinetics

Column tests at higher flow rates indicated the optimum resin is a bifunctional material with triethyl and trihexyl quarternary ammonium cations, hence the nickname BiQuat.

US Patent No. 6,059,975 (Alexandratos et al. 2000) has been awarded to Lockheed Martin for these resins, and the technology has been licensed by Purolite and Lockheed Martin. Purolite has worked with ORNL/UT to develop a commercial version of the bifunctional resin.
System Operation

Ion Exchange is a familiar technology for selectively removing cations or anions from aqueous solution, either for commercial recovery or environmental cleanup. Removal of pertechnetate (or perchlorate) from ground water using BiQuat resin is operationally similar to water softening, but resin regeneration by backwashing was not required during the 8-month field test. Regeneration of the resin is economically desirable given the relatively high cost of the resin (currently at least $1000 per cubic foot from Purolite.)

The pilot test discussed in this report operated at 2.5 gal/min. Scale-up to 100 gal/min for pertechnetate removal from groundwater contaminated at a level of 1500 pCi/L could be accomplished in a column 2.76 ft in diameter of 1 ft depth or more likely a series of smaller diameter columns run in parallel. The 6 cubic feet of resin would process 600,000 BV in 187 days before needing regeneration.
SECTION 3
PERFORMANCE

Demonstration Plan

The bifunctional resin chosen for the PGDP field test had trihexylammonium and triethylammonium exchange sites (6- and 2-carbon alkyl groups, respectively.) The resin was produced by Purolite International and designated D3696 by Purolite. Resin D3696 is –25/+40 mesh, and the total anion exchange capacity is approximately 2.0 meq/g.

In this test, pertechnetate-contaminated groundwater (nominally <1500 pCi/L $^{99}$Tc) was passed through a column 5.25 inches in diameter by 12 inches in length filled with the resin. Water flowed from bottom to top in the column as shown schematically in Figure 1, and the system had a nominal flow rate of 2.5 gal/min. A contingent pump was used to maintain a constant flow through the column during the duration of the test, and pressure gages at the inlet and outlet monitored the pressure drop across the column. The resin beads are supported on a stainless steel screen and a plexiglas plate that serve the dual functions of support plate and water flow distributor. An analogous plate and screen confined the resin at the top of the column.

Figure 2 shows a picture of the actual column and associated hardware before it was filled with resin. The column was fitted with sampling ports at the inlet, the outlet, and at two intermediate positions within the column. Samples were taken twice a week for the duration of the test that began in early February, 1999, and concluded in mid-September, 1999. Samples were shipped to ORNL for $^{99}$Tc analysis by scintillation counting. The test was stopped to allow time for site cleanup and return of the resin-filled column to ORNL before the end of FY 1999.

Results

This column was used in the treatment of approximately 600,000 BV (840,000 gal) of $^{99}$Tc contaminated groundwater. The breakthrough curve is shown in Figure 3, where $C/C_0$ represents the ratio of pertechnetate concentrations at the sampling ports (C) compared to pertechnetate concentration in the groundwater ($C_0$). Figure 3 shows that breakthrough was not observed for the column effluent. However complete breakthrough was observed at the first port (1/3 of column length), and 20% breakthrough occurred at the second port (2/3 of column length.) One bed volume is 1.12 gal, and at a nominal flow rate of 2.5 gal/min, the flow rate is 2.2 BV/min. This corresponds to a residence time of approximately 27 seconds, a remarkably short time for complete capture of the pertechnetate. The results also demonstrate that the new resin is particularly effective in removing low levels of pertechnetate (e.g., at nmol/L range.) These results are discussed in a recently published journal article (Gu et al. 2000b.)
Figure 3. Pilot Scale Test for $^{99}$Tc Removal.

Pilot Scale Test for Tc-99 Removal

Purolite D-3696 Resin
Column 5.25" x 12"
(Flow: ~2.5 gal/min)

Stage #2
Outlet

Bed Volume

C/C₀
SECTION 4
TECHNOLOGY APPLICABILITY AND ALTERNATIVES

Competing Technologies

Current treatment processes for the decontamination of wastewater usually involve the removal of the radionuclides by ion exchange on organic resins or inorganic zeolites. One of the drawbacks in using these technologies is that they are not adequately selective for the removal of these particular radionuclides in the presence of larger concentrations of alkaline and alkaline-earth chlorides, sulfates, bicarbonates and nitrates typically found in wastewater. Consequently, the sorbents are quickly exhausted and generate large amounts of solid secondary waste. Because the handling and disposal of these secondary wastes can be very expensive, new processes are needed that will minimize the volume of secondary waste produced during wastewater treatment. In addition to the disposal issue, the location of contaminated groundwater sites generally is remote and not easily accessible to treatment and disposal systems. Methods for isolation and on-site treatment of groundwater are needed that can be implemented at these remote sites.

Despite the problems noted above, ion exchange is the compelling choice for wastewater treatment, offering
• simplicity of operation in modular units of equipment
• high waste concentration factors
• well-understood principles of operation
• an acceptable solid waste form

The ion exchange treatment process now used at PGDP incorporates Purolite A-520E resin into two 64 cu ft beds in a lead and lag configuration. The pilot demonstration of BiQuat resin has shown that a single column with a much smaller volume of resin could be used, leading to a proportionally smaller volume of solid waste.

Technology Applicability

The BiQuat anion-exchange resin was also evaluated in both laboratory and field experiments for sorption of the perchlorate anion. Perchlorate is a contaminant in ground and surface waters at sites where perchlorate salts were manufactured or used. Perchlorate salts are highly soluble in water, and the physical and chemical properties of the perchlorate anion make it difficult to remove by conventional environmental treatment methods.

Perchlorate and pertechnetate are both large and poorly hydrated anions of approximately the same size, and the same resins that are selective for pertechnetate were expected to have good selectivity for perchlorate sorption as well. Test results (Brown et al. 2000a; Gu et al. 2000a) showed that the BiQuat resins again performed about 5 times better than Purolite A-520E and were particularly effective in removing trace quantities of perchlorate in groundwater. Performance did not rely solely on the inherent anion exchange capacity but rather on the exchange kinetics and the adsorption selectivity of the resins.

Advantages of BiQuat resins include:
• capable of processing 5 times more water than the best competing resins
• operate at a high flow rate of 2-4 BV/min
• require no pretreatment
• require no addition or removal of unwanted organic or inorganic components in the water

It is anticipated that the BiQuat resin loaded with pertechnetate can be regenerated using the same technology developed to remove perchlorate ion from the resin (Gu, et al 2001). The agent stripping anions from the resin is tetrachloroferrate (FeCl₄⁻) anion, formed in equilibrium amounts in a ferric chloride and hydrochloric acid solution, and this solution was found to effectively displace ClO₄⁻ anions that were sorbed on the resin. Approximately 10 BV of strip should be sufficient to remove pertechnetate from 1 BV of resin, and another 10 BV of solution would be needed to convert the resin from the FeCl₄⁻ form to the Cl⁻ form. If
12 cu ft of resin treats a 100 gpm stream for 1 year, sorption on the resin followed by stripping represents a $^{99}\text{Tc}$ volume concentration factor of 30,000. The resin could be considered for *in situ* funnel and gate applications as well as for traditional column operations.

Some problems remain with waste disposal of the ferric chloride-hydrochloric acid regenerant solution, particularly in the state of California, and these problems will need to be solved before the BiQuat resin can be applicable for large scale use. This regeneration technology does not reduce the perchlorate anion to the more innocuous chloride ion, a process needed for release to the environment. For regeneration of pertechnetate loaded resins, the decision to regenerate would be determined by the requirements for disposition of the radionuclide $^{99}\text{Tc}$.

**Patents/Commercialization/Sponsor**

A patent has been issued to Lockheed-Martin covering the design and use of BiQuat resins (Alexandratos et al. 2000), and another patent is pending that covers the regeneration process for the resins (Brown et al. 2000b). The Purolite Co. has licensed the resin technology and is actively collaborating with the ORNL/UT team in developing a commercial synthesis and market for the resin.

This work was sponsored by the Efficient Separations and Processing Crosscutting Program of DOE.
SECTION 5
COST

Methodology

A cost comparison of using BiQuat resin in place of the commercial Purolite A-520E resin for Tc removal at PGDP is limited by the proprietary nature of cost information from the PGDP subcontractor doing the cleanup work. Therefore, the capital costs of the demonstration, the operating and maintenance costs, and the costs of scale up are not available. The only data available are the relative costs of the resins, where Purolite A-520E is approximately five times less expensive than BiQuat ($200/cu ft vs >$1000/cu ft).

(Cost of the BiQuat resin is highly dependent on the size of the commercial market for the material. One of the major starting materials for BiQuat synthesis, trihexylamine, is not produced commercially because of low market demand, but could be made at reasonable cost if demand was sufficient—say, ten tons per year. Purolite would now charge about $2000/cu ft for BiQuat resin, with a minimum order size of 90 cu ft. However, if BiQuat was adopted for large scale use in the treatment of water contaminated with perchlorate, the price would drop to approximately $600/cu ft.)

Cost Analysis

According to the PGDP Procurement Representative (Jolly 2001) PGDP has no interest in converting their existing operation to incorporate a more efficient resin. Several factors contribute to this decision:
• influent $^{99}$Tc levels at PGDP have decreased significantly in recent years; e.g., one primary column of Purolite A-520E resin has not been changed in four years
• hardening and solidification of the resin (probably due to mineral deposits within the resin) can occur over long periods of use, making changeout very difficult. PGDP operators fear that less frequent changeout of the more efficient BiQuat resins could worsen this problem.
• system shutdown is scheduled for 2007, making new capital investment difficult to justify

If the resin itself is the waste form, the disposal cost will be related to the volume of material, and a smaller volume of BiQuat will be required to sorb the same quantity of $^{99}$Tc.

Cost Conclusions

Because BiQuat is approximately five times more effective than Purolite A-520E but also costs about five times as much, the total cost of needed material would be approximately the same for the two resins. If a new facility had to be built today, BiQuat would presumably be the better choice based on the need for fewer columns and associated hardware, less frequent changeout, and smaller volumes of spent resin needing disposal. For in situ processing, BiQuat is the resin of choice because of the higher capacity per unit volume.
SECTION 6
OCCUPATIONAL SAFETY AND HEALTH

Required Safety and Health Measures

Substitution of BiQuat resin for the commercial Purolite resin now used at PGDP for removing technetium from groundwater would not introduce any new concerns for safety and health. Resin is changed when the effluent concentration of Tc$^{99}$ reaches 50% of the influent level. The greater absorption capacity of BiQuat would permit less frequent changeout, thereby reducing the frequency of worker exposure to the radioactive resin. The higher concentration of Tc$^{99}$ in the loaded BiQuat resin makes it more radioactive than the loaded Purolite resin, but no new handling or disposal procedures would be required.

Safety and Health Lessons Learned from Demonstrations

No problems relating to safety or health arose during this demonstration.

Comparison with Baseline and Alternative Technologies

Health and safety are not significantly affected by changing to a more selective, higher capacity resin.
SECTION 7
REGULATORY AND POLICY ISSUES

Regulatory Considerations

Ion exchange technology is well understood and widely used for wastewater cleanup. Regulatory issues therefore are limited to waste discharge and safe practice, and should require no special permits related to the adoption of a new technology. PGDP has not been required to seek any special permits associated with its Tc removal operation. This is a Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) interim remedial action operating under an approved Record of Decision (ROD) and subsequent operations and maintenance plan. Change in the resin would have to be documented to the regulators but no approval or modification to the ROD would be required. (Jolly 2001)

The technetium-loaded ion exchange materials must be managed as a low-level radioactive waste. Management of radioactive waste is addressed by DOE Order 5820.21 (to be replaced by DOE Order 435.1.) The revised directive will call for performance-based and risk-based requirements.

The CERCLA evaluation criteria for this technology are addressed as follows:

- **Overall Protection of Human Health and the Environment.** The technology removes radioactive $^{99}$Tc from wastewater to achieve acceptable levels for water discharge to the environment. The radioactive technetium is sorbed onto solid organic polymer pellets and safely disposed in an approved repository.
- **Compliance with Applicable or Relevant and Appropriate Requirements (ARARs).** Compliance with ARARs is required when waste is disposed on site. Loaded ion-exchange solids would be sent to an off-site repository for disposal.
- **Long-term Effectiveness and Permanence.** The low-activity solid waste will be appropriately packaged for safe transport and long-term disposal. Incursion of saline water into the disposal site would create only a minor risk for release of $^{99}$Tc, given the high affinity of BiQuat resin for Tc.
- **Reduction of Volume, Mobility or Toxicity.** $^{99}$Tc is concentrated and immobilized as sorbed pertechnetate ion in solid organic resin, with loaded BiQuat resin volume being about 1/5 that of loaded Purolite A-520 E.
- **Short-term Effectiveness.** No significant difference in effectiveness between Purolite A-520 E and BiQuat resins is forecast during construction and implementation of the ion-exchange treatment system.
- **Implementability.** Full-scale implementation is straightforward. Equipment and reagents are commercially available except for the trihexyamine needed to make commercial quantities of BiQuat resin. Skilled personnel are familiar with the ion exchange process.
- **Costs.** These have been addressed in Section 5.
- **State and Community Acceptance.** Citizens and regulators are familiar and comfortable with ion exchange sorption technology.

Risks, Benefits, and Community Reaction

- **Worker Risks.** Change-out of the loaded ion exchange materials can be hazardous to unprotected workers, but safe procedures have been established and implemented for this periodic task.

- **Community Risks.** Transportation of low-activity waste solids poses some risk to the community, but accidents are of low probability, and shielded trucks and canisters protect the public from radiation.
SECTION 8
LESSONS LEARNED

Implementation Considerations

A large-scale application of this technology is needed in order to make commercialization viable. Trihexylamine (needed to make the functionalized BiQuat resin) is not a commodity chemical due to lack of demand. It could be made at reasonable cost in bulk quantities: $186,000 for 22,000 pounds. The cost of the BiQuat resin will be less if it is utilized on a large scale for removal of perchlorate from water.
APPENDIX A

REFERENCES

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