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A Field Trial of Novel Bifunctional Resins for Removing Pertechnetate (TcO_4^-) from Contaminated Groundwater

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EXECUTIVE SUMMARY

A field trial using a custom-designed bifunctional synthetic resin prepared at the University of Tennessee and designed to selectively remove pertechnetate (TcO_4^-) from groundwater was conducted in summer 1997 at the Northwest Plume Pump-and-Treat Facility at the U.S. Department of Energy's Paducah Gaseous Diffusion Plant (PGDP) site. The bifunctional resin, RO-02-119, was a copolymer of vinylbenzylchloride and divinylbenzene that had been functionalized with trihexylamine and triethylamine. The experiment was a parallel test of our synthetic resin and a commercial resin, Purolite A-520E, to directly compare the performance of the two resins. Purolite resin is currently used by the treatment facility to remove Tc-99 from the contaminated groundwater containing ~1000 pCi/L TcO_4^-. A total of ~692,000 bed volumes of groundwater was passed through the column containing the synthetic resin (RO-02-119) whereas only ~205,000 bed volumes of groundwater were passed through the Purolite resin column because of reduced hydraulic conductivity and clogging within the latter column. Despite less groundwater passing through the Purolite resin column, however, the breakthrough of TcO_4^- occurred earlier in the Purolite column than in the RO-02-119 column .

The resin beads from both columns after treatment were examined by means of scanning electron microscopy, which revealed significant amounts of surface precipitates, particularly on the Purolite beads. The Purolite beads appeared to be smooth and rigid, and the buildup of surface precipitates may have quickly filled the void spaces between the resin beads, causing a rapidly decreased hydraulic conductivity for the Purolite column. The synthetic resin beads, however, appeared to be porous spheres and the formation of mineral deposits appeared evenly distributed in the inner and on the external surfaces. These deposits appeared to be primarily silicate minerals, probably coprecipitated with Al, Ca, and Mg, as determined by energy

dispersive X-ray (EDX) analysis. An acid extraction analysis further indicated that a substantially higher amount of SO_4^{-2} was retained by the Purolite than by the synthetic resin. This higher retention of SO_4^{-2} may have also contributed to the transformation of surface precipitates on the Purolite beads. The overall results of the parallel test demonstrated that our synthetic resin (RO-02-119) was more selective for pertechnetate sorption and had hydraulic characteristics superior to those of the commercial Purolite A-520E resin. Our synthetic resin was observed to be less susceptible to clogging than the Purolite resin in part because of improved selectivity and in part because of the bead morphology. However, the synthetic resin (RO-02-119) is not yet commercially available. Negotiations are in progress with a commercial vendor to manufacture the resin to our specifications for further testing.

ACKNOWLEDGMENTS

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INTRODUCTION

Groundwater at the U.S. Department of Energy's (DOE's) Paducah Gaseous Diffusion Plant (PGDP) site is contaminated with the radionuclide technetium (Tc-99). In oxygenated and suboxygenated environments this radionuclide is in the form of the pertechnetate anion, TcO_4^-, and is mobile in most underground aquifers (Pourbaix, 1966; Gu and Schulz, 1991; Gu et al., 1994; 1996). The concentration of this anion is 4 to 5 orders of magnitude less than the concentrations of other anions commonly found in groundwater, such as chloride, sulfate, and nitrate, thus the separation techniques used for pertechnetate removal need to be highly selective (Brown et al., 1995; 1996; 1997; Ashley et al., 1994; Liang et al., 1996). The pertechnetate anion has been shown to be strongly adsorbed on commercially available strong base ion exchange resins, but in view of the extremely low concentration of Tc involved, enhanced selectivity for this species will have a favorable impact on the economics of groundwater treatment. We designed and tested novel bifunctional resins that have enhanced selectivity and good kinetics for the removal of Tc-99 from groundwater. From our resins, we chose the most promising synthetic resin for field trial along with the most promising commercial resin.

A pertechnetate selective resin was selected by measuring the distribution coefficient for TcO_4^- sorption in a series of over 80 new resins prepared in our laboratories (from different batches) and compared with 6 commercially available resins (including Purolite A-520E, Sybron Ionac SR-6, Reillex HPQ, Dowex 1-X8, Amberlite, and IRA-904). Pertechnetate selectivity was measured following systematic variations of the microenvironment of the exchange site; these results provided a scientific basis for developing pertechnetate selectivity. An environment favorable to TcO_4^- was created within a poly(vinylbenzylchloride)-based resin by reacting trialkylamines having long hydrocarbon chains with the reactive benzylchloride group to create the quaternary ammonium ion exchange sites. The base poly(vinylbenzylchloride) resin had also been crosslinked by the addition of 5% divinylbenzene. These and other modifications of the physical and chemical properties of the macroreticular resin were made so that the sorptive affinity for pertechnetate ion over the other anions commonly found in groundwater was greatly enhanced (Brown et al., 1995; 1996; 1997). A consideration of the rate of approach to equilibrium in time-dependent, batch-equilibrium distribution ratio measurements led us to prepare bifunctional resins that have exchange sites comprised of large quaternary ammonium groups for high selectivity and small alkyl groups for improved kinetics. Laboratory studies indicated that a bifunctional resin with trihexylamine and triethylamine exchange sites in an optimal engineering bead size (+40/-60 mesh) gave the best performance in a column test. Thus, this synthetic resin, RO-02-119, was chosen for this small-scale field demonstration.

RESULTS AND DISCUSSION

A. RESIN PERFORMANCE—BREAKTHROUGH OF Tc-99

A small-scale field demonstration of one of our best synthetic resins (RO-02-119, trihexylamine/triethylamine, +40/-60 mesh) was conducted from July 17 to October 15, 1997, at the Northwest Plume Pump-and-Treat Facility at the PGDP site. Two columns approximately 1 inch in diameter by 4 inches in length, each with a bed volume (BV) of ~50 cm^3, were set up to run in parallel at the treatment facility. One column contained our synthetic resin RO-02 119, and the other column contained commercially available Purolite A-520E resin (sieved to +40/-60 mesh). Each of these anion exchange resins was initially in chloride form. The two columns were configured for upward flow of groundwater in parallel so that we could determine the relative effectiveness of the two resins in removing TcO_4^- from the contaminated groundwater under field conditions. The contaminated groundwater was diverted through a ½" pipe from the main treatment facility (South wells) through the resin columns at an initial flow rate of ~300 mL/min (or ~6 BV/min) per column. Once the flow passed through the resin columns, it was diverted back to the equalization tank for treatment by the process system so that no liquid waste was generated from the field trial. Concentrations of TcO_4^- in the influent and the effluent were monitored periodically and analyzed at Oak Ridge National Laboratory. The detection limit for TcO_4^- is approximately 1 pCi/L (or ~$6x10^{-5}$ parts per billion).

Results (Fig. 1) indicated that the column containing the synthetic resin (RO-02-119) performed extremely well with respect to both Tc-99 removal and hydraulic flow characteristics. Less than 3% breakthrough of Tc-99 was observed after approximately 3 months of operation. The breakthrough of Tc-99 appeared to increase relatively fast after ~600,000 BV groundwater had passed through the synthetic resin column. However, we had difficulty in maintaining a good hydraulic flow through the Purolite A-520E column. The flow was reduced from an initial flow rate of 300 mL/min to approximately 50–60 mL/min after about 5 weeks of operation; the column became clogged and flow stopped on September 15, 1997. The maximum in-line pressure was approximately 12 psi, which varied slightly from 10–12 psi throughout the test. Although less groundwater was passed through the Purolite column than the synthetic column, an early breakthrough of Tc-99 was observed in the Purolite column. At 1% breakthrough of Tc-99, approximately 580,000 BVs of groundwater had been treated by the synthetic resin whereas about 105,000 BVs of groundwater was treated by the Purolite resin.

Results of TcO_4^- breakthrough from this field trial were consistent with our previous laboratory and field studies using Purolite A-520E resin and the same or related synthetic resins (Brown et al., 1995; 1996; 1997). Table 1 lists the laboratory determined *K'd* values for sorption of pertechnetate (6 •M) from a solution matrix containing NaCl, $NaNO_3$, and Na_2SO_4 (each at 0.06 M) for some previously tested synthetic resins and the Purolite resin. The synthetic resins exhibited ~3–5 times higher batch equilibrium *K'd* values and were therefore more selective for TcO_4^- than the Purolite resin. Laboratory column tests conducted with this same solution matrix at constant flow rate conditions also indicated a substantially retarded breakthrough (>10 times) of TcO_4^- in these synthetic resin columns than in the Purolite column (Fig. 2). To achieve a 10% TcO_4^- breakthrough, ~1540 BV test solution was passed through trihexylamine/tripropylamine (VP-02-217) resin whereas only ~ 50 BV test solution was passed through the Purolite column. In a small-scale field trial conducted in 1996 with groundwater from a monitoring well (MW 106) at DOE's Oak Ridge Reservation, columns containing VP-02-217 resin exhibited 10% pertechnetate breakthrough at about 127,000 BV in comparison with ~1500 BV in columns containing Purolite A-520E (Fig. 3). Note that a positive displacement pump was used in the

1996 small-scale field trial so that a constant flow rate (at ~30 mL/min or ~11 BV/min) was maintained throughout the experiment. Therefore, our previous laboratory studies and field trials indicated that the performance of our synthetic resins (RO-02-119 and VP-02-217) are superior to the commercial Purolite resin in terms of both TcO_4^- selectivity and hydraulic characteristics.

Currently, PGDP is running two Purolite treatment columns (~65 ft^3 or ~478 gal per column) at a flow rate of ~125 gal/min per column. At this flow rate, ~137,400 BVs of groundwater are treated per column per year. We estimated that, by using the same configuration, our synthetic resin column would operate for ~4.2 years before a breakthrough of 1% TcO_4^- would occur, while the Purolite resin column would operate for ~0.8 years (or 9–10 months) to achieve 1% breakthrough of TcO_4^-. A significant cost saving may therefore be anticipated by using our synthetic resin assuming the resin cost is about twice as much as the Purolite resin. Other cost savings may be indirectly related to the operational and maintenance costs.

The Purolite treatment columns at PGDP have been in service since the Northwest Plume Groundwater System plant operations began in August 1995. Operational and analytical data have shown that the Purolite is the most effective commercial resin when compared with four other commercially available resins that were tested for removal of Tc-99 to levels that meet plant effluent requirements. Analysis of influent Tc-99 concentrations, system flow rates, and effluent Tc-99 concentrations at one of the columns over a 13-month period indicated that the Tc-99 loading on the 65 ft^3 of Purolite resin was ~0.19 Ci. No significant operational problems have been experienced while using the Purolite resin. However, analysis of spent resin removed during the last changeout revealed scaling and plugging of the resin surface. The materials responsible for the fouling were composed of such elements as calcium, silica, and manganese.

B. ANALYSIS OF RESINS

After the field trial at PGDP was completed, the resin columns were sectioned, and the amount of Tc-99 sorbed was analyzed as a function of column depth. These analyses were performed by directly adding the resin beads into a scintillation cocktail (Packard Ultima-Gold) and analyzing by means of liquid scintillation counting. However, it must be noted that TcO_4^- was so strongly adsorbed on the resin beads that we have not yet identified a good technique to desorb TcO_4^- from the bead surfaces. Thus, this analytical technique may have substantially underestimated the Tc-99 activity, particularly for those pertechnetate anions adsorbed in the internal surface areas of the synthetic resin beads. Therefore, results presented in Fig. 4 should be regarded as a minimum estimate of Tc-99 activity, which showed a general distribution of TcO_4^- adsorbed along the column. The actual amount of TcO_4^- retained by the synthetic resin could be much higher because it has a larger internal surface area than that of Purolite. As expected, a much higher Tc-99 activity was observed at the influent to the resin column on the bottom. The Tc-99 activity decreased rapidly from bottom to the top (or along the flow path).

The resin beads were also examined by scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) analyses in an attempt to identify any surface adsorbed species or surface precipitates. SEM analysis (Fig. 5) indicated that the synthetic resin RO-02-119 appeared to be very porous and have a large internal surface area as expected for a macroreticular resin. On the other hand, the commercial Purolite A-520E resin beads appeared to have a smooth and relatively nonporous surface without a large internal surface area (Fig. 6). To further evaluate these differences, we also examined the untreated Purolite resin beads as shown in Fig. 7. Results with untreated beads were quite similar to results with resin beads that had been exposed to the contaminated groundwater. They also appeared to be rigid, and the surface was smooth. Literature from Purolite indicates the A-520E resin is a macroreticular material, but a high magnification SEM (75,000X) is required to see the secondary morphology of the beads. EDX analysis indicated that chloride was the only element that was detected on the untreated Purolite bead surfaces (since the resin was initially in chloride form).

SEM analysis revealed some obvious precipitates on the external surfaces of both the Purolite and the synthetic resin beads, but with more precipitates on the Purolite beads (Fig. 5,6). This difference is probably due to the fact that the RO-02-119 beads have a higher internal surface area, so the precipitates were dispersed onto a relatively larger surface area of the RO-02-119 beads. Furthermore, the Purolite bead surfaces appeared to be smooth and rigid so that the precipitates may have accumulated between the void spaces of the resin beads. Subsequently the flow channels between the beads became clogged. This may offer an explanation why the flow rate decreased rapidly and eventually stopped in the column containing the Purolite A-520E resin after being in the field for ~6 weeks. One of the Purolite columns in use at the PGDP Northwest Plume Treatment Facility also experienced a pressure drop during operation, and the facility personnel found it necessary to backflush the resin column once a year.

Our EDX analysis showed that the precipitates on the two types of resin beads composed primarily of silicate minerals. Some other minor constituents such Ca, Fe, and Mg were also identified by EDX analysis. These constituents could have co-precipitated along with the silicate minerals; however, they may also result from an accumulation of colloidal clay particles that were present in the groundwater. An acid extraction analysis of both types of resin beads (Table 2) indicated the presence of the Ca, Fe, and Mg metal cations. Silica in the acid extractant was not determined because dilute acid could not give a complete extraction of Si. However, it is of great significance to note that the Purolite resin column retained 3 times more sulfate (SO_4^{-2})

than did the RO-02-119 column although about three times less groundwater was passed through the Purolite resin column. These results indicate that the Purolite resin has a higher affinity for SO_4^{-2} than the synthetic resin RO-02-119 does and the TcO_4^-/SO_4^{-2} selectivity afforded by Purolite A520-E is lower than that afforded by RO-02-119. The presence of large quantities of SO_4^{-2} in the Purolite resin (or an enhanced surface concentration of SO_4^{-2}) was important because the presence of this anion (as well as dissolved silica) may have facilitated the formation of mineral precipitates (with Al, Ca, or Mg). The hypothesis that SO_4^{-2} anions are preferentially retained by the Purolite resin was independently tested by conducting the SO_4^{-2} breakthrough experiments in the laboratory with both resins used in the field trial. These laboratory experiments (with 1 mM sodium sulfate) revealed that SO_4^{-2} breakthrough occurred much earlier with the synthetic resin (240 BVs to produce 50% breakthrough) than with the Purolite resin (460 BVs to produce 50% breakthrough). However, RO-02-119 resin adsorbed more NO_3^- anions than did the Purolite (Table 2) because NO_3^- is similar to TcO_4^-, both of which are less hydrated than SO_4^{-2} anions.

C. FURTHER FIELD DEMONSTRATIONS

The resin RO-02-119, that was used in this field trial at PGDP, was prepared in the laboratory of Professor Spiro Alexandratos at The University of Tennessee in Knoxville. While the performance of this resin looks promising in relation to the resin in current use, this material is not commercially available. At present, we can only estimate the cost of this resin in the quantities that would be required for practical applications. We would like to conduct a larger pilot-scale field demonstration (at ~1 gal/min flow rate with a 0.5 ft by 1.5 ft column) using a bifunctional resin similar to RO-02-119 (made to our specifications by a commercial vendor). This demonstration would begin in the spring of 1998 and run for six or more months. This field demonstration would reveal practical processing information needed for the design of an ideal TcO_4^--selective anion exchange resin. Furthermore, the pilot synthesis by a commercial vendor would help us better estimate the cost of the synthetic resin in bulk. Our synthetic resin RO-02-119 is at least five times more selective for Tc_4^- and has better hydraulic characteristics than the Purolite resin. These features of the synthetic resin should significantly increase the life time of the treatment columns by as much as five times longer and reduce the overall operational and waste management costs.

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APPENDIX

TABLES AND FIGURES

Table 1. Sorption of TcO_4^- by Purolite A-520E and three synthetic resins[a]

Resin	**TAEC[b]** (meq/g)	**1 h *K'd*** (mL/g)	**24 h *K'd*** (mL/g)	**168 h *K'd*** (mL/g)	**Comment**
Purolite A-520E (-16/+50 mesh)	2.8	9,400	12,800	10,400	As purchased
Purolite A-520E (-40/+60 mesh)	2.8	ND[c]	13,600	13,600	Sieved
RO-02-119 (-40/+60 mesh)	2.53	14,400	38,500	50,100	Hexyl/Ethyl
VP-02-217 (-60/+200 mesh)	2.06	17,900	48,400	56,300	Finer size Hexyl/propyl
RO-02-74 (-40/+60 mesh)	3.04	14,600	37,800	46,000	Hexyl/Ethyl
RO-03-124 (-40/+60 mesh)	3.15	18,300	27,200	30,800	Hexyl/Ethyl Improved

[a] The groundwater test solution contained 0.06M NaCl, $NaNO_3$, and Na_2SO_4; all *K'd* values have a ±5% uncertainty.

[b] TAEC = total anion exchange capacity.

[c] ND = not determined.

Table 2. Analysis of major cations and anions (milligrams per gram resin) following the acid extraction of resin beads[a]

Cation/Anion	Synthetic resin RO-02-119	Commercial resin Purolite A-520E
Sulfate (SO_4^{-2})	10.20	32.84
Nitrate (NO_3^-)	15.52	10.68
Calcium (Ca)	0.201	0.103
Iron (Fe)	0.031	0.029
Magnesium (Mg)	0.037	0.013
Manganese (Mn)	0.003	0.002

[a] Synthetic resin column = 18.8 g; Purolite resin column = 18.3 g.

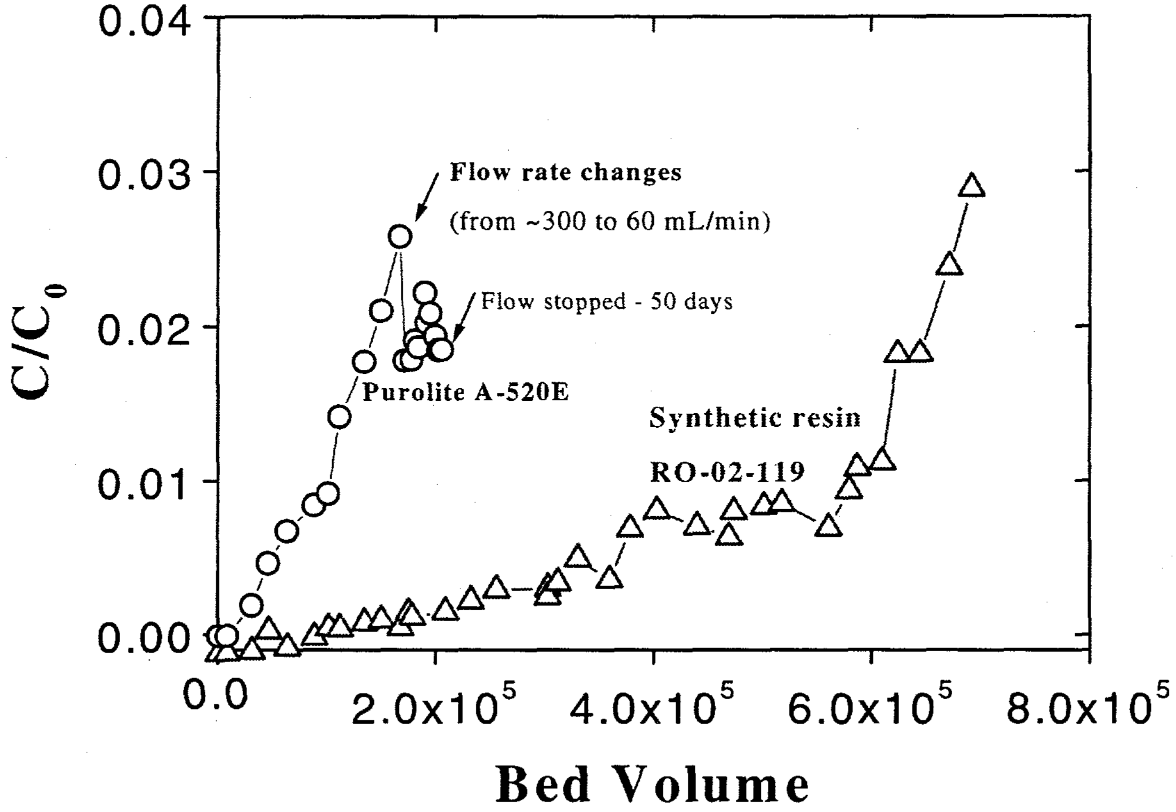

Fig. 1. TcO_4^- breakthrough curves for the synthetic resin RO-02-119 and Purolite A-520E resin using PGDP groundwater. C/C_0 is the ratio between the effluent TcO_4^- concentration and the inlet TcO_4^- concentration.

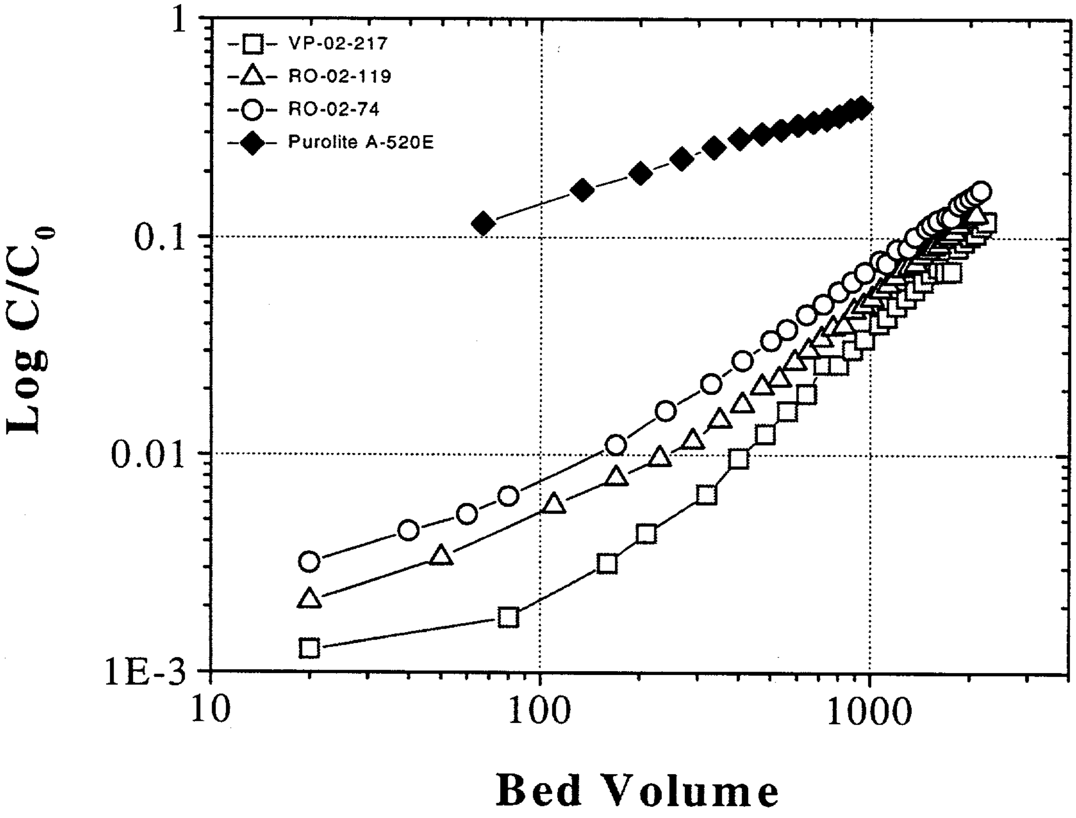

Fig. 2. TcO_4^- breakthrough for selected resins using groundwater test solution (with 0.06M NaCl, $NaNO_3$, and Na_2SO_4) at about 33 mL/min (or ~11 BV/min) flow rate.

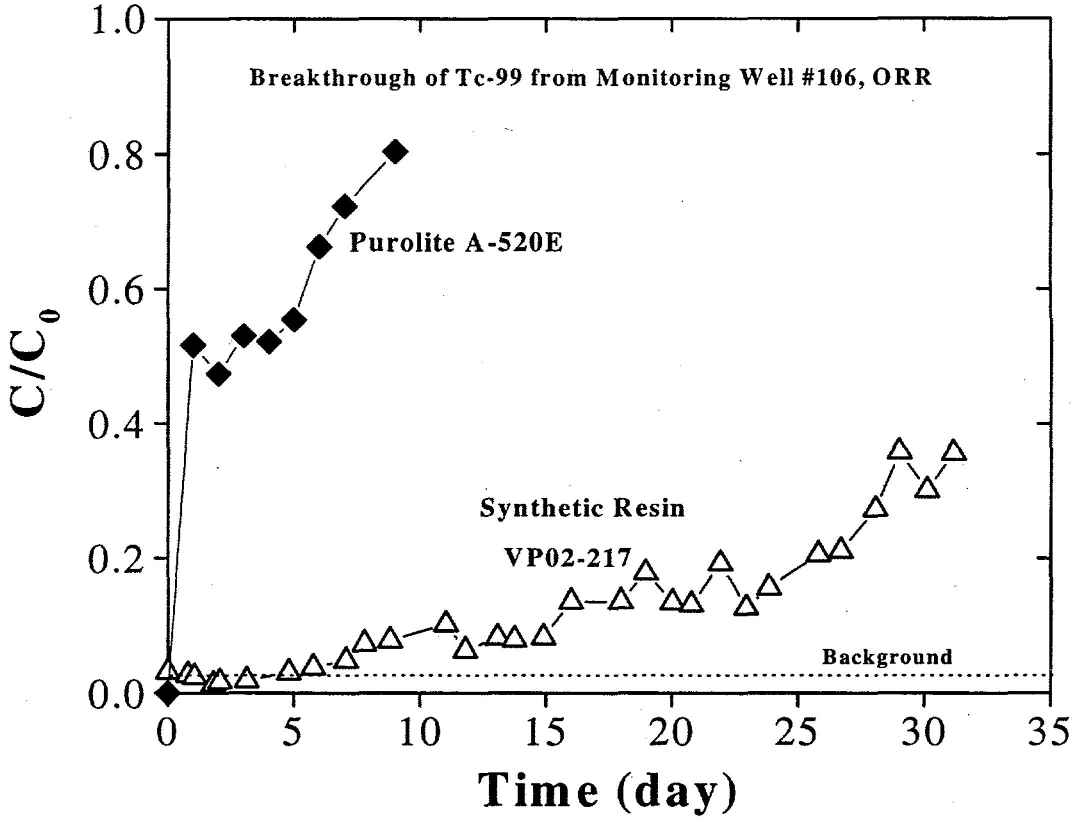

Fig. 3. TcO_4^- breakthrough curves for the synthetic resin RO-02-217 and Purolite A20E resin in a test using groundwater from monitoring well 106 on the Oak Ridge Reservation.

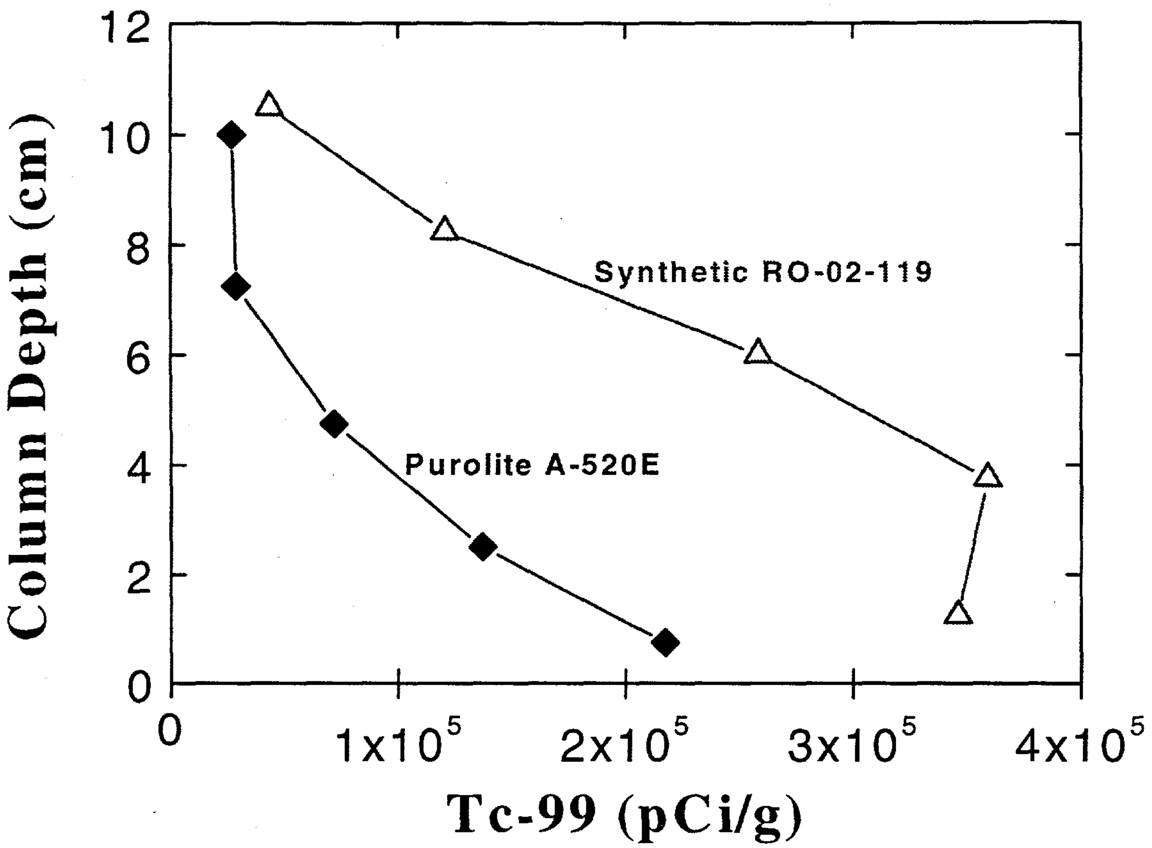

Fig. 4. Retention of Tc-99 at different depths of the resin columns.

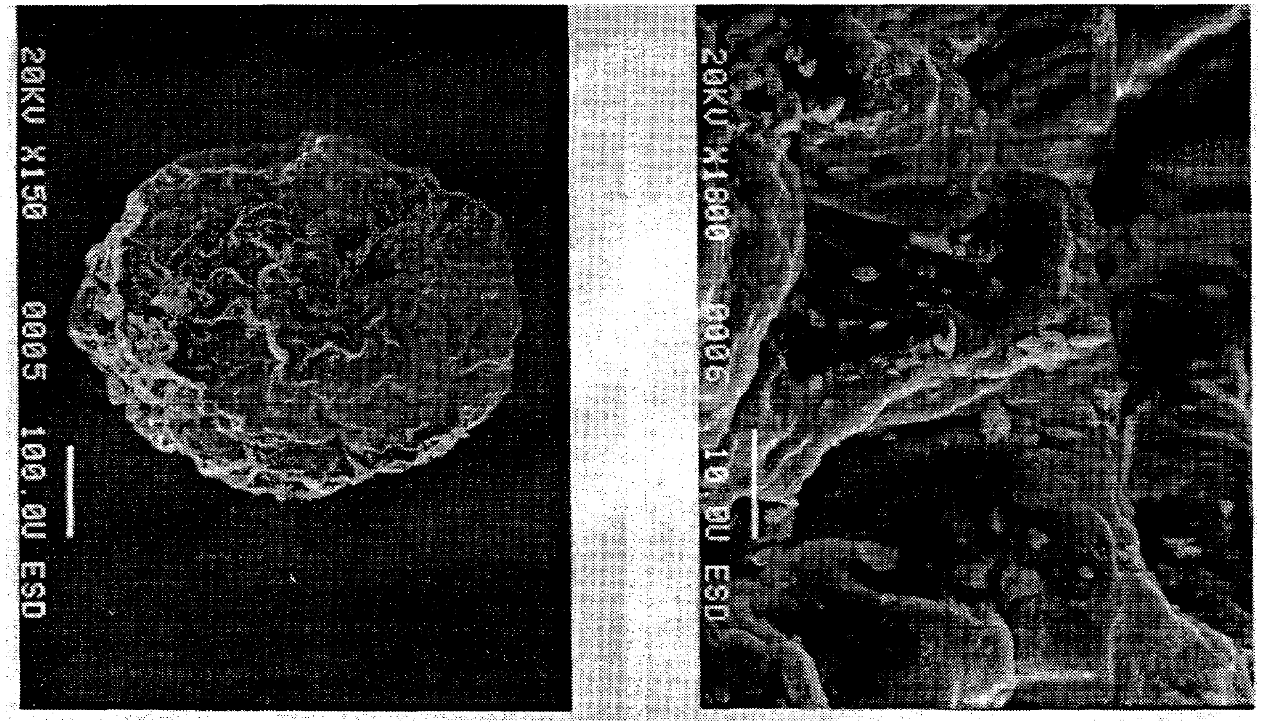

Fig. 5. Synthetic resin RO-02-119 beads after treatment with PGDP groundwater.

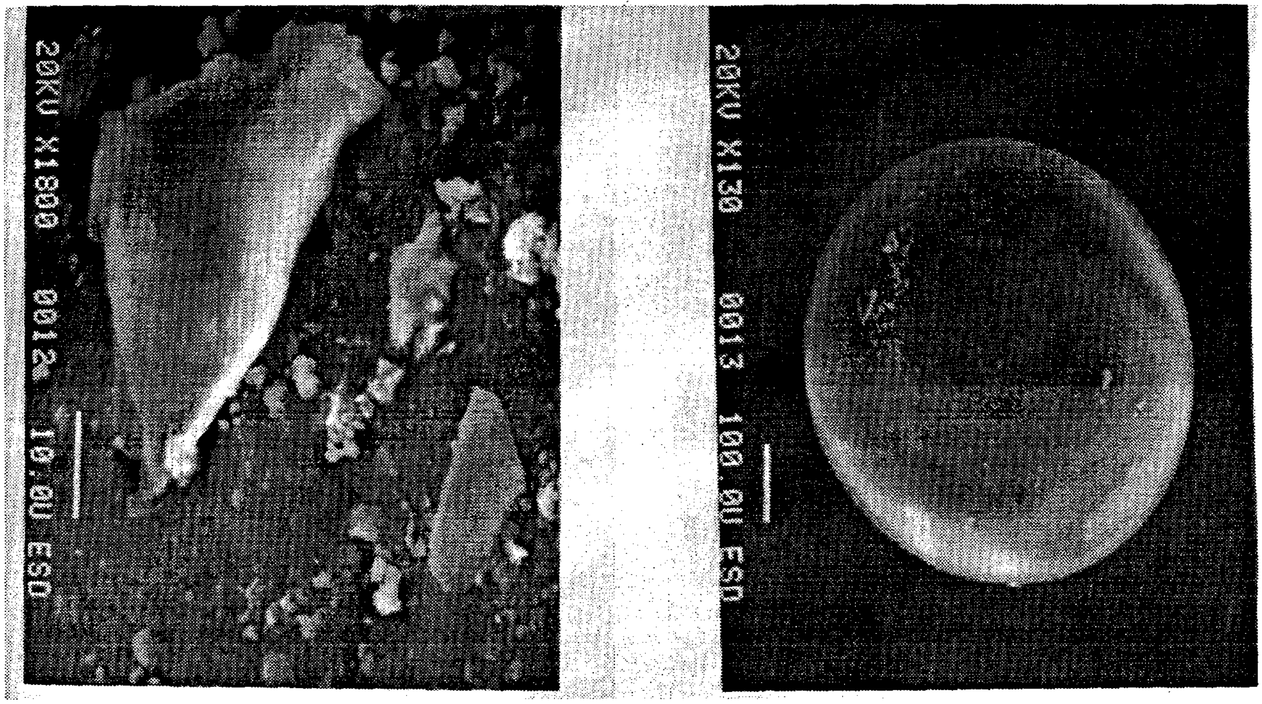

Fig. 6. Purolite A-520E resin beads after treatment with PGDP groundwater.

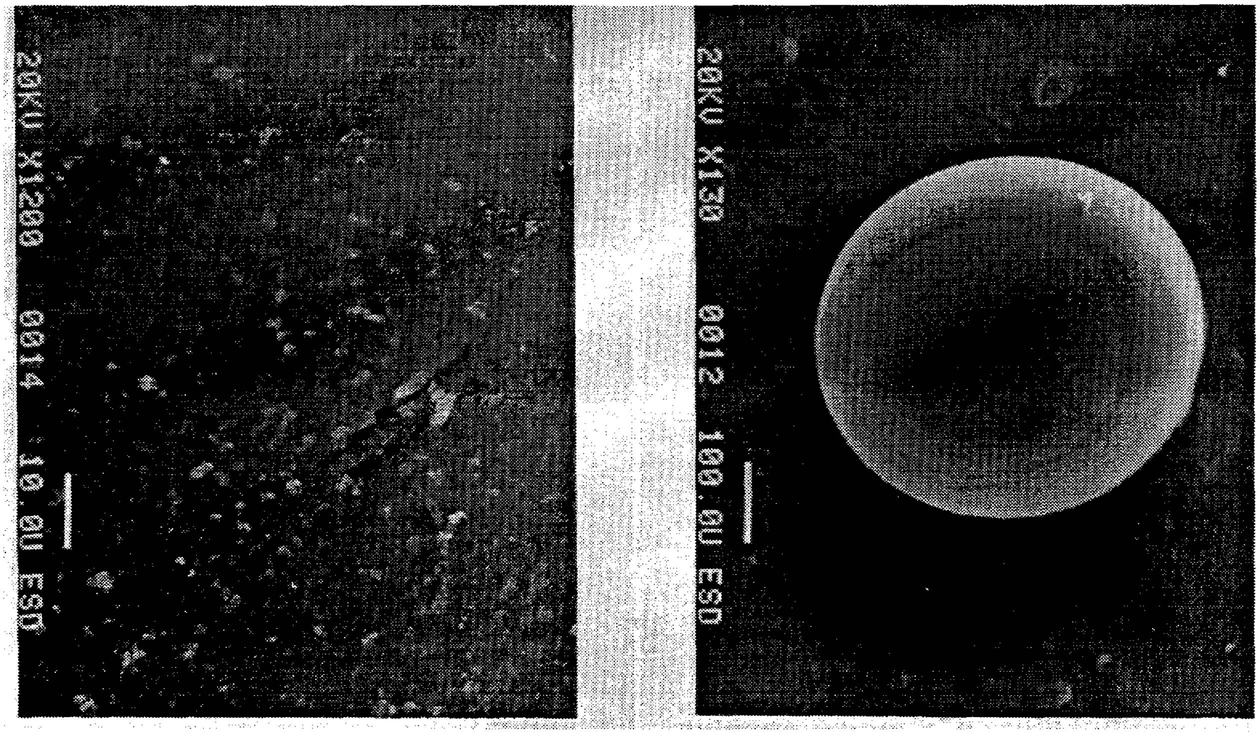

Fig. 7. Untreated Purolite A-520E resin beads.