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EXTRACTION OF TECHNETIUM FROM SIMULATED HANFORD TANK WASTES*

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ABSTRACT

Aqueous biphasic separation systems are being developed for the treatment of liquid radioactive wastes. These extraction systems are based on the use of polyethylene glycols (PEGs) for the selective extraction and recovery of long-lived radionuclides, such as ^{129}I, ^{75}Se, and ^{99}Tc, from caustic solutions containing high concentrations of nitrate, nitrite, and carbonate. Because of the high ionic strengths of supernatant liquids in Hanford underground storage tanks, aqueous biphasic systems can be generated by simply adding aqueous PEG solutions directly to the waste solution. In the process, anionic species like I^- and TcO_4^- are selectively transferred to the less dense PEG phase. The partition coefficients for a wide range of inorganic cations and anions, such as sodium, potassium, alumi-

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num, nitrate, nitrite, and carbonate, are all less than one. We present experimental data on extraction of technetium from several simulated Hanford tank wastes at 25° and 50°C.

INTRODUCTION

High-level radioactive wastes generated during the years of fuel reprocessing activities at Hanford were placed in underground tanks for storage. To prevent tank corrosion, the wastes were made alkaline, thereby causing the bulk of the transuranic elements and fission products to precipitate and form a sludge. Also contained in the tanks are an aqueous supernatant and a low-density salt cake. The supernatant consists primarily of the soluble salts of nitrate, nitrite, and carbonate but also contains lesser amounts of sulfates and phosphates (1).

One disposal option for alkaline supernatant and salt cake involves their conversion to grout for long-term isolation as a low-level waste. Long-term risks to the environment arising from grout storage could be minimized by removal of cesium, strontium, and transuranics to concentrations below Class A designations of the Nuclear Regulatory Commission (2, 3). The destruction of nitrate and nitrite, along with the removal of technetium and iodine, would further minimize risks associated with grout disposal. All of these species would exhibit high degrees of mobility from grout in the event of its contact with groundwater. Cesium, iodine, strontium, and technetium are currently destined for disposal along with high level waste in a glass waste form. However, the volatility of cesium, iodine, and technetium at the temperatures encountered in glass melters (e.g. > 1000°C) would require off-gas treatment to prevent environmental release of these radionuclides.

One of the goals set forth in the "Clean Option" for tank waste treatment involves the removal of technetium and iodine to levels as low as reasonably achievable (2, 3). A recently published review identifies several solvent extraction and ion exchange processes that have been examined for technetium removal from acidic and basic radioactive wastes (4). The best available current technologies for removing iodine and technetium from basic solution involve (a) volatilization with off-gas scrubbing and (b) ion exchange (3). Uncertainties exist regarding the efficiency of iodine removal. Additionally, the use of a strong-base anion exchanger for the recovery of technetium would require relatively large volumes of wash and strip solutions to elute the technetium from the ion exchanger. Clearly, improved separation technologies are needed for recovering these radionuclides from basic solutions.

During FY 1993, we began to examine the ability of PEGs to selectively extract iodide (I^-) and pertechnetate (TcO_4^-) from simulated Hanford tank supernatants. This effort is based on the observation that TcO_4^- and I^- are selectively extracted from aqueous caustic solutions into an immiscible, aqueous PEG layer (5). Our work on technetium extraction is part of a joint effort between our laboratory and researchers at Northern Illinois University to develop aqueous biphasic systems for treatment of tank waste supernatants and dissolved salt cake.

EXPERIMENTAL METHODS

All reagents were purchased commercially and were used as-received. Extraction equilibrium measurements were performed at 25° and 50°C. Equal volumes of aqueous waste simulants and aqueous PEG solutions were equilibrated by mixing in plastic centrifuge tubes for one minute on a vortex mixer. They were thermally equilibrated for 5 min. at either 25° or 50°C. The samples were then centrifuged for 15 min. and the phases separated using plastic pipettes. Before sampling, the solutions were diluted four-fold (by weight) with distilled water. This dilution was necessary to eliminate errors arising from pipetting salt solutions and slightly viscous PEG solutions. Cation and anion concentrations in each phase were determined by ICP-AES (inductively coupled plasma-atomic emission spectrometry) and ion chromatography, respectively. Partition coefficients for pertechnetate, PEG, and carbonate were measured using ^{99}Tc, ^{3}H-labeled PEG-4000, and ^{14}C-labeled carbonate, respectively. The partition coefficients, or D values, for the radiotracer species were determined by counting the activity present in aliquots of each liquid phase by using a liquid scintillation spectrometer (Packard, Model 2500TR).

RESULTS AND DISCUSSION

Biphase Formation

Three tank waste simulants (nonradioactive) were used in this study: NCAW (Neutralized Current Acid Waste), SST (Single-Shell Tank) supernatant, and Hanford 101-SY supernatant. The compositions of the waste simulants are given in Tables 1-3.

While nitrate and nitrite salts do not promote aqueous biphase formation with PEGs, the concentration of hydroxide in the three waste simulants was sufficient to support biphase formation with PEGs ranging in molecular weight from 1500 to 3400. Representative binodial curves for the PEG/101-SY system at 25° and 50°C, are shown in Fig. 1. The concentration of the waste simulant is expressed in terms of the weight percent of undiluted waste simulant added. For example, partition coefficients were routinely measured in biphase systems generated using equal volumes of a 30 wt.% PEG solution and the undiluted waste simulant. This gives a biphase composition of 15 wt.% PEG/50 wt.% 101-SY.

The general features of the curves in Fig. 1 are typical of the curves that we obtained with the other two waste simulants. That is, the volume of PEG and waste solutions required to form a biphase did not vary appreciably from one waste simulant to the other. Due to self-heating from radioactive decay, tank waste temperatures of about 50°C are expected (8). Figure 1 shows that increasing temperature promotes biphase formation at lower salt and PEG concentrations.

The partition coefficients, or D values, for all major inorganic species present in the waste simulants were measured as a function of temperature and PEG molecular weight. These data are summarized in Tables 4 and 5. In general, the D values for inorganic electrolyte species are depressed by either

TABLE 1. COMPOSITION OF NCAW[a]

Reagent	Concentration, M
Sodium Nitrate	0.31
Sodium Sulfate	0.18
Potassium Nitrate	0.14
Rubidium Nitrate	0.00013
Sodium Carbonate Monohydrate	0.24
Sodium Nitrite	0.52
Sodium Phosphate Dibasic	0.03
Aluminum Nitrate	0.52
Sodium Fluoride	0.107
Sodium Hydroxide	4.08

[a] Recipe obtained from Bray (6).

TABLE 2. COMPOSITION OF SST-SUPERNATANT[a]

Reagent	Concentration, M
Sodium Nitrate	2.94
Sodium Aluminate	0.46
Sodium Nitrite	0.20
Sodium Sulfate	0.05
Sodium Bicarbonate	0.60
Citrate (Trisodium Salt)	0.0394
EDTA (Disodium Salt)	0.0244
Potassium Nitrate	0.0771
Sodium Phosphate (Tribasic)	0.0058
Sodium Fluoride	0.031
Sodium Hydroxide	1.96
Cesium Nitrate	7.4×10^{-5}

[a] Recipe obtained from Colton (7).

TABLE 3. COMPOSITION OF HANFORD TANK 101-SY SUPERNATANT[a]

Reagent	Concentration, M
Sodium Hydroxide	2.00
Sodium Aluminate	1.54
Sodium Nitrate	2.59
Sodium Nitrite	2.24
Sodium Carbonate	0.42
Citrate (Trisodium Salt)	0.06439
HEDTA (Trisodium Salt)	0.03753
EDTA (Tetrasodium Salt)	0.03141
IDA (Disodium Salt)	0.18732

[a] Recipe obtained from Colton (7).

HEDTA: N-(2-Hydroxyethyl) ethylenediamine triacetic acid.

EDTA: Ethylenediamine tetraacetic acid.

IDA: Iminodiacetic acid.

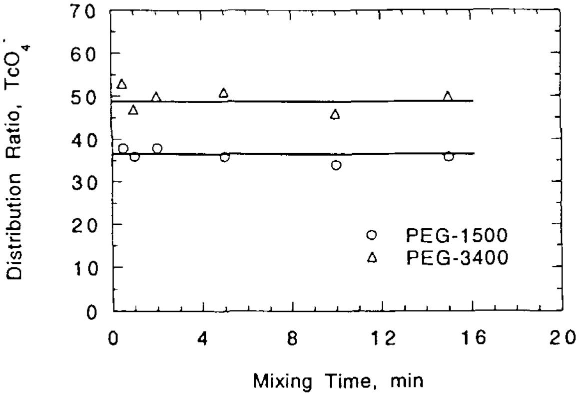

Figure 1. Effect of mixing time on the extraction of pertechnetate from 101-SY at 25°C.

TABLE 4. PARTITION COEFFICIENTS FOR ELECTROLYTES IN BIPHASIC SYSTEMS WITH AQUEOUS PEG SOLUTIONS AT 25°C

Biphase System	Na^+	K^+	Al^{3+}	NO_2^-	NO_3^-	SO_4^{2-}	PO_4^{3-}	F^-	CO_3^{2-}
PEG-1500/101-SY	0.26	--	0.02	0.49	1.00	--	--	--	0.005
PEG-1500/SST	0.37	0.65	0.13	0.91	0.69	0.06	<0.13	0.13	0.063
PEG-1500/NCAW	0.39	0.63	0.17	0.69	0.86	0.09	0.51	0.14	0.084
PEG-3400/101-SY	0.24	--	0.01	0.45	0.73	--	--	--	0.004
PEG-3400/SST	0.32	0.60	0.07	0.55	0.72	0.03	<0.13	0.11	0.030
PEG-3400/NCAW	0.32	0.59	0.07	0.61	0.83	0.03	<0.02	0.13	0.031

TABLE 5. PARTITION COEFFICIENTS FOR ELECTROLYTES IN BIPHASIC SYSTEMS WITH AQUEOUS PEG SOLUTIONS AT 50°C

Biphase System	Na^+	K^+	Al^{3+}	NO_2^-	NO_3^-	SO_4^{2-}	PO_4^{3-}	F^-	CO_3^{2-}
PEG-1500/101-SY	0.24	--	0.02	0.50	0.68	--	--	--	0.004
PEG-1500/SST	0.32	0.56	0.10	0.54	0.71	0.05	<0.13	0.13	0.041
PEG-1500/NCAW	0.33	0.56	0.10	0.59	0.83	0.06	0.03	0.13	0.043
PEG-3400/101-SY	0.20	--	0.01	0.36	0.67	-	--	--	0.002
PEG-3400/SST	0.30	0.56	0.05	0.48	0.65	0.02	<0.13	0.07	0.025
PEG-3400/NCAW	0.30	0.53	0.05	0.52	0.76	0.03	<0.02	0.11	0.019

increasing temperature or increasing PEG molecular weight. The largest D values were obtained for nitrate and nitrite -- anions that do not support biphase formation with PEGs.

Partition coefficients for PEG were measured using ^{3}H-labeled PEG-3400. For 101-SY, SST, and NCAW, the D values of PEG-3400 were 59, 39, and 31, respectively. These values were obtained at both 25° and 50°C, indicating that the partitioning behavior of PEG is not significantly affected by temperature between 25° and 50°C.

Ideally, the partition coefficient of PEG should be in the range of 1000 or higher to minimize PEG losses due to dissolution into the aqueous waste stream. It should be pointed out that the affinity between PEG and both nitrate and nitrite, leads to low D values for PEG and enhances the partitioning of these anions into the PEG layer. This has the undesirable result of reducing the separation factor between TcO_4^- and NO_3^-/NO_2^-.

We are currently examining alternatives to address these problems and thereby improve extraction performance. One approach involves immobilizing the PEG onto an inorganic support. This would completely eliminate polymer losses via dissolution. Another approach involves the use of a PEG-PPG (polypropylene glycol) copolymer. We have found that low molecular weight PPGs (e.g., PPG-420) form immiscible phases with nitrate salts and the waste simulants. Presumably, the D values for nitrate and nitrite will be significantly lower for PPG or PEG-PPG copolymers. If this is indeed the case, we would expect to see higher D values for the polymers and thereby reduce polymer losses due to dissolution into the waste stream.

Partitioning of Pertechnetate

To establish the mixing time necessary to achieve extraction equilibrium, we measured D values of pertechnetate as a function of mixing time at 25° and 50°C. The partitioning data for the PEG/101-SY system at 25°C are shown in Figure 2. These data indicate that the forward extraction of pertech-

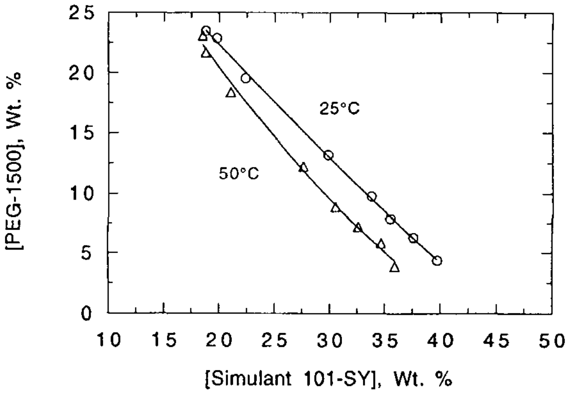

Figure 2. Phase diagram for the PEG-1500/101-SY system. The biphase region lies to the right of the curves.

netate from the salt phase to the PEG phase is rapid, and equilibrium partitioning is obtained with mixing times as short as 30 s. At 50°C, the curves were displaced slightly toward higher D values. Additional evidence in support of rapid pertechnetate partitioning is the finding that identical D values were obtained regardless of whether the pertechnetate was spiked into the PEG phase or the salt phase. Data for the extraction of pertechnetate from the three waste simulants by PEG-1500 and PEG-3400 at 25° and 50°C are given in Table 6. The pertechnetate D values in Table 6 are more than an order of magnitude lower than those obtained previously in PEG/Na_2CO_3 systems (5). We believe that this large variance in pertechnetate partitioning is directly related to the partitioning behavior of PEG. For example, we obtained D values of about 1000 for PEG in PEG/Na_2CO_3 systems, compared with 30-60 for the PEG/waste simulant systems. Additionally, the trend in pertechnetate partitioning evident in Table 6 mirrors the trend in PEG partitioning discussed earlier. That is, the partition coefficients of PEG follow the order 101-SY > SST ~ NCAW, as do the partition coefficients of pertechnetate. Interestingly, the D values of pertechnetate are relatively insensitive to temperature

TABLE 6. EXTRACTION OF PERTECHNETATE FROM WASTE SIMULANTS BY PEG

Biphase System	D Value, TcO_4^- 25°C	D Value, TcO_4^- 50°C
PEG-1500/101-SY	40	42
PEG-1500/SST	7	9
PEG-1500/NCAW	8	10
PEG-3400/101-SY	50	53
PEG-3400/SST	10	12
PEG-3400/NCAW	12	14

variations. We have also found this to be the case with PEG partitioning behavior.

The D values for pertechnetate in Table 6 and the D values of other anions in Tables 4 and 5 were used to calculate separation factors (Table 7). It is evident that fairly high single-stage separation factors can be attained. In general, the separation factors for pertechnetate and multivalent anions are greater than those between pertechnetate and monovalent anions. The best separation is obtained between TcO_4^- and CO_3^{2-}. The separation factors for pertechnetate and nitrate/nitrite are substantially lower. Nevertheless, with multi-stage, countercurrent extraction, it should be possible to achieve technetium decontamination factors well above 10^3.

It is well-known that uranyl ion can form complexes with pertechnetate. Small amounts of uranium in the real tank wastes might lead to complexation of TcO_4^- and thereby significantly alter the partitioning of pertechnetate. We decided to investigate this possibility by measuring the D values of technetium in the presence of comparable concentrations of uranium. The concentration of ^{99}Tc used in the D value measurements was approximately 9 x 10^{-4}M. There-

TABLE 7. SEPARATION OF PERTECHNETATE FROM OTHER WASTE SIMULANT ANIONS USING PEG-3400 AT 50°C

Ionic Species	Separation Factor[a]
F^-	171
NO_3^-	79
NO_2^-	147
SO_4^{2-}	600
CO_3^{2-}	26,500
PO_4^{3-}	>700

[a] Calculated by dividing the D value for $Tc0_4^-$ by that for the other anions.

fore, a uranium concentration of 10^{-4}<u>M</u> was used to study the effect of uranium on pertechnetate extraction. Under these conditions, we found that the presence of uranyl had no significant effect on the partitioning of pertechnetate. Representative extraction data are shown in Table 8.

Effect of Irradiation

When real tank supernatants and dissolved salt cake are treated, the solvent will be exposed to significant radiation levels. To simulate this condition, we exposed aqueous solutions of PEG-1500, -2000, and -3400 to between 14 and 75 Mrad of γ radiation, using the ^{60}Co source at Argonne. Continuous solvent exposure to the 101-SY supernatant for one year would result in an estimated $\beta + \gamma$ dose of approximately 5 Mrad (8). Cesium and strontium account for >99% of the $\beta + \gamma$ source in the supernatant. Their removal from the supernatant prior to technetium extraction would significantly reduce the radiation exposure to the polymer-rich phase.

TABLE 8. EXTRACTION OF PERTECHNETATE IN THE PRESENCE OF U(VI) AT 50°C

Biphase System	D Value, TcO_4^-	
	No U(VI)	10^{-4} M U(VI)
PEG-1500/101-SY	46	42
PEG-1500/SST	9	9
PEG-1500/NCAW	9	9
PEG-3400/101-SY	58	56
PEG-3400/SST	12	13
PEG-3400/NCAW	15	15

The only noticeable physical effect of the 14 Mrad irradiation dose was that a slight yellow color developed in the polymer phase after it was later contacted with the waste simulants. At the higher dose of 75 Mrad, on the other hand, a gel began to form in the PEG-2000 and -3400 solutions. The partition coefficients of PEG-3400 after irradiation at 14 Mrad increased slightly, as shown in Table 9. This increase in D values suggests that a slight increase in PEG molecular weight had occurred as a result of radiation-induced polymer cross-linking. The viscosity of the irradiated PEG-1500 solutions, however, was not noticeably different from fresh PEG stock solutions, suggesting that only minimal cross-linkage had occurred. We will be measuring solution viscosities and polymer molecular weight distributions in the near future to confirm this observation.

The partition coefficients for pertechnetate and ^{14}C-labeled sodium carbonate were measured at 25°C and 50°C with each of the waste simulants and PEG irradiated at 14 Mrad. In each case, irradiation had little effect on the D values (see Table 10 for 50°C data). The results indicate that the PEGs exhibit little susceptibility toward radiation damage under doses at least as high

TABLE 9. EFFECT OF 14 MRAD GAMMA IRRADIATION ON THE PARTITIONING OF PEG-3400

Waste Simulant	D-Value, PEG-3400	
	Pre-Irradiation	Post-Irradiation
25° C		
101-SY	59	92
SST	39	52
NCAW	31	43
50° C		
101-SY	56	96
SST	35	52
NCAW	32	50

TABLE 10. EFFECT OF GAMMA IRRADIATION ON THE EXTRACTION OF PERTECHNETATE AT 50°C

Biphase System	D Value, TcO_4^-	
	No Irradiation	14 Mrad Dose
PEG-1500/101-SY	46	42
PEG-1500/SST	9	9
PEG-1500/NCAW	9	9
PEG-3400/101-SY	58	56
PEG-3400/SST	12	13
PEG-3400/NCAW	15	15

as that expected after three years of process exposure. In the near future, we plan to carry out another set of irradiation experiments using biphasic PEG/waste simulant systems. This will enable us to evaluate the resistance of PEGs to the combined effects of radiolysis and hydrolysis.

CONCLUSIONS

We have demonstrated that aqueous biphase systems can be generated by combination of aqueous PEG solutions with simulated Hanford tank waste supernatants. Partition coefficients for all of the major cationic and anionic species in the wastes were measured and found to be less than one at 50°C. The extraction of pertechnetate was found to be rapid, with single-stage separation factors as high as 10^4 achieved between TcO_4^- and CO_3^{2-}.

We have collected pertechnetate partition data at 25° and 50°C with fresh PEG and with PEG solutions gamma irradiated at a dose level of 14 Mrad. This irradiation represents a 3 year equivalent dose for processing supernatant solutions from tank waste 101-SY. The partition coefficients for PEG ranged from 30 to 60 with no irradiation and 50 to 100 with irradiation. For PEG-1500, we found that irradiation up to 14 Mrad had no effect on the D values for pertechnetate. With PEG-2000 and -3400, physical changes in the polymer solution became apparent only after 70-75 Mrad doses. However, partition coefficients for pertechnetate were unaffected by 14-18 Mrad doses with these polymers.

Work is now underway to measure the extraction behavior of iodine and selenium. We will also be evaluating various options for the back extraction of radionuclides from polymer phases. The most direct approach involves the use of electrodialysis for stripping all ions from the polymer phase. Another approach that we will be investigating involves the use of immobilized PEG or PEG/PPG copolymers. This approach is based on our previous small angle neutron scattering measurements, which indicate that biphase formation with PEGs is accompanied by extensive polymer aggregation (9). We believe that this aggregation phenomenon plays a key role in the selective extraction of pertechnetate. Radionuclide stripping from immobilized polymers, therefore, may be as simple as inhibiting these polymer/polymer interactions. This could be brought about by simply washing the immobilized polymer with distilled water at low temperatures.

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