Separation Science and Technology

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Beneficiation of Pu Residues by Ultrafine Grinding and Aqueous Biphasic Extraction

D. J. Chaiko[a]; R. Mensah-Biney[a]; C. J. Mertz[a]; A. Rollins[b]
[a] Chemical Technology Division, Argonne National Laboratory, Argonne, IL [b] Chemistry Department, Northern Illinois University, DeKalb, IL

To cite this Article Chaiko, D. J. , Mensah-Biney, R. , Mertz, C. J. and Rollins, A.(1993) 'Beneficiation of Pu Residues by Ultrafine Grinding and Aqueous Biphasic Extraction', Separation Science and Technology, 28: 1, 765 — 780

To link to this Article: DOI: 10.1080/01496399308019519

URL: http://dx.doi.org/10.1080/01496399308019519

SEPARATION SCIENCE AND TECHNOLOGY, 28(1-3), pp. 765-780 (1993)

BENEFICIATION OF Pu RESIDUES BY ULTRAFINE GRINDING AND AQUEOUS BIPHASIC EXTRACTION*

D. J. Chaiko, R. Mensah-Biney, C. J. Mertz
Chemical Technology Division
Argonne National Laboratory
Argonne, IL 60439

and

A. Rollins
Chemistry Department
Northern Illinois University
DeKalb, IL 60115

ABSTRACT

Aqueous biphase systems are heterogeneous liquid/liquid systems that result from appropriate combinations of inorganic salts and water-soluble polymers such as polyethylene glycol. Colloid-size particles that are suspended in an aqueous biphase system will partition to one of the phases, depending on a complex balancing of particle interactions with the surrounding solvent. With regard to waste treatment applications, aqueous biphase systems are similar to conventional solvent extraction but do not utilize an organic diluent, which may itself become a source of pollution. In addition, the water-soluble polymers that have been used in biphase formation are inexpensive, nontoxic, and biodegradable. The application of aqueous biphasic extraction to the beneficiation of plutonium residues will be discussed.

INTRODUCTION

Current beneficiation strategies for plutonium residues include the incineration of combustibles, such as wood, paper, plastics, and oils; particle-size

---

*Work supported by the U. S. Department of Energy, Office of Basic Energy Sciences, under Contract No. W-31-109-ENG-38

reduction where necessary; and washing, leaching, or dissolution with acid. The pregnant solutions are then further processed to yield either PuO_2 or PuF_4. Metal oxides (both reactive and high-fired) and impure plutonium metal are processed by either direct oxide reduction, molten salt extraction, or electrorefining (1).

Both hydrometallurgical and pyrometallurgical processing of plutonium residues have historically been carried out with little or no physical beneficiation prior to chemical processing. Notable exceptions include the recent attempts at using magnetic separation techniques to produce a uranium concentrate from magnesium fluoride (2,3) and plutonium concentrates from various pyrochemical residues (4).

Many of the plutonium residues are heterogeneous materials, with the plutonium being distributed as discrete grains within a larger particle matrix. Some examples include pyrochemical residues, such as sand, slag, and crucibles; graphite; and chloride salts. Ultrafine grinding to an average particle size of about one micron should effectively liberate the plutonium from the particle matrix. Selective partitioning in an aqueous biphasic extraction process could then produce a plutonium concentrate.

In this paper, we discuss the scientific and engineering principles of this extraction technology and its application to nuclear waste treatment.

BACKGROUND

Aqueous Biphase Formation

Aqueous biphase systems were originally developed by Albertsson in the mid-1950s for the separation of microbial cells, cell organelles, and viruses (5). In recent years, interest in aqueous biphasic systems has broadened to applications in commercial scale protein separations (6,7), separation of metal ions (8), ultrafine particles (9), and organics (10,11). Aqueous biphasic extraction involves the selective partitioning of either solutes or colloid-size particles between two immiscible aqueous phases. These aqueous/aqueous systems form spontaneously from mixtures of aqueous solutions of unlike polymers, typically a straight-chain polymer such as polyethylene glycol (PEG) and a highly branched polymer such as dextran. Aqueous/aqueous systems may also be generated from mixtures of organic polymers and inorganic salt solutions. For example, combining equal volumes of a 15-wt% solution of sodium sulfate and a 30-wt% solution of PEG-3400 produces a turbid mixture that will separate after a few minutes, with the sodium sulfate concentrated in the bottom layer and the PEG concentrated in the top layer.

Aqueous biphase systems behave similarly to conventional solvent extraction systems but are particularly attractive for waste treatment applications because they do not utilize an organic diluent, which may itself become a source of pollution. In addition, the water-soluble polymers that have been used in biphase formation are inexpensive, nontoxic, and biodegradable. They can also be removed from the process effluents for recycle by ultrafiltration (12) or electrodialysis (13). Alternatively, suspended solids can be removed by high-speed centrifugation (5), allowing the aqueous phases to be recycled.

For large-scale applications, the polymer/salt biphase systems are generally more commercially attractive than polymer/polymer systems because of their lower cost and higher phase-separation rates. Using commodity prices of PEG-3350 and Na_2SO_4, the estimated cost per kilogram for a 15% PEG/7.5% Na_2SO_4 system is about \$0.47. By contrast, the cost per kilogram of the two-polymer system 4% PEG 8000/7% Dextran 500 is about \$7. There are, however, some low-cost substitutes for the fractionated dextrans. The system proposed by Szlag et al. would cost only \$0.20/kg and uses maltodextrans at \$0.59/kg in place of the more expensive size-fractionated dextrans costing \$500/kg (14). To put these solvent costs in perspective, they can be compared with those for more conventional oil/water systems that have been proposed for the extraction and purification of transuranic elements such as the PUREX and TRUEX solvents. The PUREX solvent contains 30% tributyl phosphate (TBP), and the TRUEX solvent has 1.4M TBP and 0.2M octyl(phenyl)-N-N-diisobutylcarbamoylmethylphosphine oxide (CMPO). These solvents have estimated costs of \$0.36 and \$240 per kg, respectively.

EXPERIMENTAL

Materials

Technical grade sodium silicate (37%) was purchased from Fisher Scientific. Colloidal suspensions of SiO_2 and CeO_2 (average particle size, 20nm) were purchased from Fisher Scientific and Johnson Matthey, respectively. All other chemicals were reagent grade or better. PEG-3400 and graphite (1- to 2 μm particle size) were purchased from Aldrich. Powdered TiO_2 (99+% rutile, 1.7 μm average particle size) was purchased from Johnson Matthey. The polymeric Pu(IV) was supplied by H. Diamond, Chemistry Division (ANL). The details of its preparation are given elsewhere (15).

Methods

Powdered metal oxides such as Al_2O_3, Fe_2O_3, and SiO_2 were ground wet in 0.1- to 0.5g batches to an average particle size of about 0.5- to 2 μm using a McCrone Micronising mill with grinding times of 2 to 5h. Sodium hexametaphosphate was used as a dispersant and grinding aid at a concentration of 0.1-wt%. Submicron particle-size distributions were measured by dynamic laser light scattering using a Malvern 4700c photon correlation spectrometer fitted with a 35mW HeNe laser. Samples for light scattering analysis were diluted to a solids concentration of 10^{-4} wt%. At this dilution, a slight cloudiness was just barely visible to the eye.

Estimates for partition coefficients of individual metal oxides in aqueous biphasic extractions were were derived from the fact that in each case the upper PEG containing phase was crystal clear with no trace of cloudiness. At the same time the lower, sulfate phase contained 2-wt% metal oxide solids. The fact that the upper PEG phase was clear suggests that the solids concentration in that phase was less than 10^{-4} wt%. This is based on the observation that light scattering samples of the ground metal oxides at a solids concentration of 10^{-4} wt% were slightly cloudy. In a similar manner, the partitioning of ground SiO_2 at a total solids concentration of 2-wt% produced a bottom, sulfate phase with no trace of cloudiness. The partition coefficients of colloidal PuO_2, on the other hand, were determined by measuring alpha activity in the aqueous PEG and sodium sulfate phases using liquid scintillation counting. The use of radiotracers permits routine measurement of partition coefficients $\geq 10^3$ or $\leq 10^{-3}$.

RESULTS AND DISCUSSION

Hydrodynamic Performance

Preliminary data reported below suggest that aqueous biphase extractions can be carried out using conventional contacting equipment such as mixer/settlers, pulsed columns, and centrifugal contactors. Others have reported satisfactory performance of mixer/settlers (16), Schiebel columns (17,18), and spray columns (19) for carrying out aqueous biphasic extractions.

The dispersion number (N_{Di}) is an indicator of the rate of phase separation from an agitated liquid/liquid system. This parameter has been used for centrifugal contactor design and as a guide in estimating hydraulic performance of contactor equipment in general (20, 21). It is a dimensionless number defined as follows:

$$N_{Di} = \left[\frac{1}{t_{Di}}\right]\sqrt{\Delta Z / g} \qquad (1)$$

where t_{Di} is the time required for phase separation under the earth's gravitational field, ΔZ is the total height of the two-phase liquid column in cm, and g is the gravitational constant in cm sec^{-2}. The test is conveniently carried out using a stoppered, 100-mL graduated cylinder which gives the proper ratio of column height to column diameter necessary to ensure reproducible measurements. After thoroughly mixing the phases, the time required for a distinct, liquid/liquid interface of constant vertical position to appear in the column is recorded. The results of N_{Di} measurements for several aqueous biphase systems at 22° and 80°C are reported in Table 1.

The N_{Di} values in Table 1 compare favorably with typical values of oil/water solvent extraction systems. For example, the N_{Di} values of PUREX and TRUEX solvents in contact with dilute nitric acid solutions are typically in the range of 1-15 x 10^{-4}, with separation times of 1.5 - 22.4 min (22). Based on their dispersion numbers, the aqueous biphase systems in Table 1 would be compatible with centrifugal contactors and pulsed columns. It should also be pointed out that the dispersion numbers were not appreciably affected by the

TABLE 1. DISPERSION NUMBERS OF SOME AQUEOUS BIPHASE SYSTEMS

System Composition	Temp., °C	Separation Time, min	N_{Di} ($\times 10^4$)
14.5% PEG-10000 6.5% Na_2SO_4	22	3.2	6.9
15% PEG-3400 7.5% Na_2SO_4	22	8.5	2.6
15% PEG-3400 7.5% Na_2SO_4	80	1.0	22.4
9% PVA-40000[a] 7.5% Na_2SO_4	80	2.2	10.1

[a] PVA refers to polyvinylpyrrolidone.

presence of ultrafine solids like hematite or silica at an average particle size of 0.5μm and a solids concentration of 2-wt%. Additionally, the Argonne centrifugal contactors have been designed and demonstrated to operate with feed solutions containing finely divided solids (23).

Particle Characterization

Many of the plutonium residues are heterogeneous and, therefore, would be amenable to physical beneficiation techniques. An example of the segregation of plutonium within a larger non-actinide matrix is shown in Fig. 1. The plutonium appears as bright, discrete grains about 1 μm in diameter imbedded in a matrix of copper and aluminum oxides. The particle shown in Fig. 1 is from a LECO crucible. These ceramic crucibles are used in the analytical determination of carbon in plutonium samples. After use, the crucibles retain small amounts of refractory PuO_2 imbedded in the ceramic along with a catalyst that may be either Cu, Fe, or Sn. In a large majority of the particles obtained from crushed crucibles, only silica can be detected. In others, only Si and Al, together with traces of Ca and Cr, are present. Interestingly, plutonium was

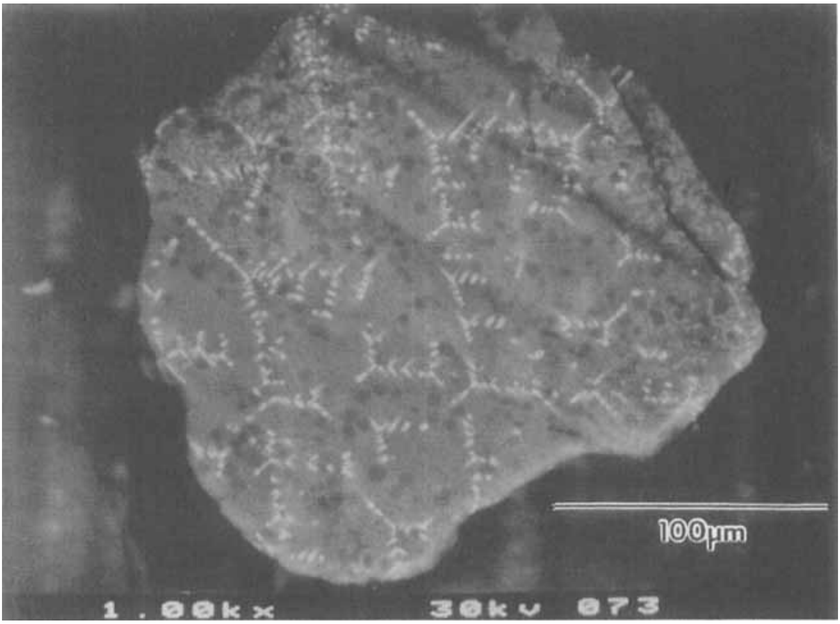

FIGURE 1. Backscattering electron micrograph of a Pu-containing particle from a crushed LECO crucible. The brighest spots contain Pu, the gray matrix contains Cu, and the dark spots contain Al.

observed only in particles that also contained significant amounts of Cu and Al, as shown in Fig. 1.

This liberation of the plutonium from the ceramic matrix suggests that preferential breakage of the ceramic had occurred during grinding. High-fired PuO_2 is known to be extremely abrasive, with a Moh's hardness greater than 9 (24). The PuO_2 can therefore be expected to be much more resistant to fracture than the surrounding ceramic matrix. The extreme hardness of high-fired PuO_2 should not present a problem during grinding since the plutonium in this and other residues is present as one-micron grains. It is not expected that the PuO_2 grains would require any further size reduction.

Silica/Metal Oxide Separations

The ability to quantitatively separate silica from a wide range of metal oxides is a particularly attractive feature of aqueous biphasic extraction. For example, in preliminary separations that we carried out using nonradioactive materials, an estimated separation factor of $>6\times10^3$ was obtained for 2-wt% mixtures of nanometer sized SiO_2 and CeO_2 in a biphase system consisting of 15% PEG-3400/7.5% Na_2SO_4 at a pH of 3. When separating 0.5µm amorphous SiO_2 particles from 0.5µm hematite (Fe_2O_3), the upper PEG phase containing the silica was white without any trace of red color. The amount of each solid added corresponded to 2-wt%. In separate experiments, the addition of 0.5µm sized hematite particles to 1-2wt% silica suspensions imparted a visually detectable red coloration even at hematite concentrations as low as 1 to 10 ppm. Based on the lack of color in the upper PEG layer, we estimate the partition coefficient of hematite in SiO_2/Fe_2O_3 mixtures to be in the range of 10^{-4} or less.

Attempts to determine the concentrations of suspended solids by digesting the solids in either HF or HNO_3 followed by analysis of dissolved Si and metal ions by inductively coupled plasma-atomic emission spectrometry (ICP-AES) were unsuccessful due to the extreme range of the partition coefficients. Even with 1-2 wt% metal oxide loading in the sulfate phase, the metal oxide concentration in the upper PEG phase was to close to the detection limit for accurate estimation of the partition coefficients.

The partitioning behavior just described is based on surface chemical properties and not on bulk phase properties like density. Consequently, those factors that influence surface characteristics can, in principle, be used to selectively control partitioning behavior. Many of the same chemical reagents used in mineral flotation to promote or suppress particle attachment at the air/water interface can be used in aqueous biphasic systems for promoting separations between metal oxides, phosphates, carbonates, silicates, sulfides, etc. (9). Some examples of surface-modified phase transfer are listed in Table 2.

In the PEG/sodium sulfate system, the metal oxides listed in Table 2 reported quantitatively to the sulfate-containing phase, regardless of pH. The affinity of the metal oxides for the sulfate phase is understandable given the fact that sulfate is known to be surface-active towards a number of metal oxides including TiO_2 and Al_2O_3 (25). In general, the ionic interaction of electrolyte ions

TABLE 2. SURFACE-MODIFIED PHASE TRANSFER IN AQUEOUS BIPHASIC EXTRACTION[a]

Solid	Reagent	Partition Coefficient
TiO_2, Fe_2O_3, Al_2O_3	None	<0.0001
TiO_2, Fe_2O_3, Al_2O_3	0.1% Sodium Silicate, pH 3	>200
Fe_2O_3, TiO_2	0.01% Oleic Acid	>200
$CaCO_3$	None	<0.005
$CaCO_3$	0.01% Oleic Acid	>200

[a] Biphase System: 15% PEG-3400/7.5% Na_2SO_4 at a pH of 6.

at a metal oxide surface would be expected to inhibit the adsorption of PEG, which occurs through a much weaker hydrogen bond. In addition, PEG must compete with the water of hydration for surface adsorption sites. Measurements of the heat of immersion (ΔH_i) can give an indication of the energy of interaction between solid surfaces and the surrounding water molecules. A large exothermic heat of immersion indicates very strong adsorption of water. The partitioning of SiO_2 and the metal oxides between the sodium sulfate and PEG phases can be qualitatively related to the heat of immersion. Solids having low values of ΔH_i, such as graphite and silica, partition into the PEG layer, while those solids with large ΔH_i values, such as the metal oxides, partition into the sulfate phase. Some values of the heat of immersion are listed in Table 3.

To obtain a separation between metal oxides, selective adsorption of water soluble surfactants onto the desired metal oxide surfaces can be used to render the solids sufficiently hydrophobic to cause them to partition into the PEG phase (9). However, we have found that surfactants which adsorb through physical interactions, such as electrostatic attraction and hydrophobic bonding, tend to be ineffective phase transfer agents.

TABLE 3. HEATS OF IMMERSION FOR SEVERAL SOLIDS IN WATER[a]

Solid	$-\Delta H_i$ (ergs/cm^2)
Graphite	26
Amorphous Silica	165 - 220
Quartz	260 - 370
Fe_2O_3 (hematite)	530
TiO_2 (rutile)	550
Al_2O_3	650 - 900

[a] Data Obtained From Ref 26.

For example, the adsorption of sodium dodecyl sulfate (NaSDS) and sodium dodecyl benzene sulfonate (NaDBS) onto TiO_2, Al_2O_3, and Fe_2O_3 at a pH below the Point-of-Zero-Charge (PZC) of each solid is known to take place through electrostatic attraction between the anionic surfactant and the positively-charged metal oxide surface (27). In the aqueous biphase system, partition coefficients <0.005 were obtained with each of the metal oxides listed in Table 2, even in the presence of NaSDS and NaDBS. Varying the NaDBS concentration from 10^{-6} to 10^{-1} wt% had no effect on the partitioning of 0.25% TiO_2 suspensions. In the high ionic strength environment of the PEG/sodium sulfate system, the electrolyte ions, by virtue of their high concentration, are able to exclude ionic surfactants from surface adsorption sites on metal oxide surfaces. Thus, there is insufficient coverage of these sites for phase transfer to occur.

In contrast to the poor performance of physically adsorbed collectors, we have found that surfactants which chemisorb through covalent bonding can be quite effective at promoting solids partitioning from aqueous sulfate solutions into PEG phases. As shown in Table 2, oleic acid promotes the transfer of Fe_2O_3 and TiO_2 into the PEG-rich phase. The chemisorption of oleic acid onto hematite and rutile has been demonstrated by infrared spectroscopy, which shows surface hydroxyl displacement by oleate (25).

As indicated in Table 2, calcite ($CaCO_3$) also partitions into the PEG layer when 0.01% oleic acid is added to the aqueous biphase system. This is another example of phase transfer brought about by chemisorption of the collector at the mineral surface.

Activation of insoluble oxides can be brought about by the adsorption of monosilicic acid and polysilicic acids. The addition of 0.1-wt% sodium silicate to a particle suspension at a pH 9-10 was used to deposit a silica coating on the metal oxide surfaces. At a pH range of about 8 to 10, mono- and polysilicic acids are rapidly adsorbed onto insoluble metal oxides via a base catalyzed reaction (28) as follows:

$$\text{Me-OH} + \text{Si(OH)}_4 \xrightarrow{OH^-} \text{Me-O-Si(OH)}_3 + H_2O \qquad (2)$$

When the aqueous biphase system is adjusted to a pH of about 10 or greater, the metal oxides continue to report to the bottom phase, just as they do in the absence of sodium silicate. But when the pH is reduced to between 8.5 to 3, the metal oxides transfer quantitatively to the top PEG phase. This pH dependence parallels the ionization behavior of silicic acid which has a pK at 9.8

When PEG adsorbs onto a silica surface, the oxygens are oriented toward the SiOH surface and the hydrocarbon groups are oriented outward, away from the silica surface, as shown in Fig. 2. The hydrophobic surface regions generated by this preferred spatial orientation thus promote the partitioning of silica into the PEG layer. In going from pH 2 to 4, there is only a slight increase in surface charge, but at a pH ≥5 the surface charge becomes increasingly negative much more rapidly (28). As the pH is raised, counter-cation adsorption at the silica surface increases in proportion to surface charge. Because of the relatively large size of hydrated cations such as $Na(H_2O)_6^+$, surface ionization also prevents polymer adsorption to neutral silanol groups that are in the immediate vicinity of SiO^- surface sites (28).

Plutonium Partitioning

Graphite and silica are the major constituents of certain foundry residues and incinerator ash, respectively. Separations of PuO_2/graphite and

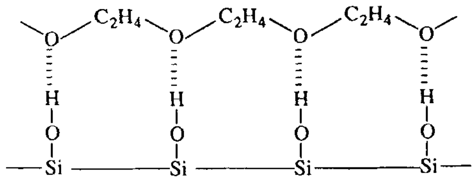

FIGURE 2. Oriented adsorption of ethylene oxide segments on a silica surface gives rise to hydrophobic surface regions. The remainder of the PEG molecule extends into solution, away from the surface.

PuO_2/SiO_2 mixtures are therefore of interest, and were attempted using a PEG/sodium sulfate biphase system. In these experiments, polymeric Pu(IV) was used as a stand-in for particulate PuO_2. Data from x-ray diffraction measurements have shown that the aged plutonium polymer has a PuO_2 crystal lattice structure, while small-angle neutron scattering measurements indicate that the polymer is approximately 22Å in diameter and 120Å long (23).

As with other metal oxides, polymeric Pu(IV) partitions quantitatively to the sulfate layer. Its partition coefficient in the PEG-3400/Na_2SO_4 system at pHs from 3 to 6 is approximately 0.001. During the extraction of polymeric Pu(IV) in the presence of ground amorphous silica, the silica partitioned into the top phase, leaving the bottom phase with no trace of cloudiness (see Table 4). The size distribution of the ground silica was between 0.2 and 1.0 μm, and since the bottom phase was clear, the silica concentration in that phase can be estimated as less than 10^{-4} wt%. Based on the total amount of silica added, slightly greater than 99.99% of the silica had partitioned into the top phase. With greater than 99% of the polymeric Pu(IV) remaining in the bottom phase, a separation factor greater than 10^6 is estimated to have been obtained in a single stage.

It is expected that the surface properties of the plutonium polymer and PuO_2 particles found in the plutonium residues are similar. The surfaces of both contain hydrated Pu-OH sites and should therefore display similar partitioning behavior. Efforts to correlate the partitioning of polymeric PuO_2 and micron-size PuO_2 particles are currently underway.

TABLE 4. PARTITIONING OF COLLOIDAL PuO_2 IN BINARY SYSTEMS[a]

System	Reagent	Partition Coeff.		
		PuO_2	SiO_2	Graphite
PuO_2/SiO_2	None	0.009	$>10^4$	
PuO_2/Graphite	None	4.0		$>10^3$
PuO_2/Graphite	0.01% AOT[b]	0.04		$>10^3$

[a] Aqueous biphase system: 15% PEG-3400/7.5% sodium sulfate at pH 3.
[b] AOT: sodium bis(2-ethylhexyl)sulfosuccinate, Aerosol OT.

The other binary system studied consisted of polymeric Pu(IV)/graphite mixtures. Regardless of pH, the naturally hydrophobic graphite was quantitatively extracted into the upper PEG phase, leaving no visible trace of color or cloudiness in the bottom sulfate layer. Given a particle size of 1 to 2 μm, the graphite concentration in the lower phase was therefore estimated to be less than 10^{-4} wt%. The partition coefficient of the polymerized Pu(IV) was 4 in this case. This large partition coefficient for plutonium is probably due to adsorption of the plutonium polymer onto the graphite particles. Whether or not this adsorption is mediated by the presence of the PEG is not known; but polymeric Pu(IV) adsorption onto hydrophobic polyethylene in the absence of PEG has been observed (29).

By adding 100 ppm Aerosol OT to the biphase system, the partition coefficient of plutonium was reduced to 0.04. It is possible that the partition coefficient could be reduced even further by optimizing the choice of dispersing agent and its concentration. Interestingly, the Aerosol OT was effective only when it was added as a dodecane solution. Using an aqueous Aerosol OT stock solution actually resulted in Pu partition coefficients larger than 4. Its possible that adsorption of the hydrocarbon, alone, at the graphite surface is responsible for blocking Pu polymer adsorption. In fact, when adding 100ppm dodecane to the biphase system, the partition coefficient of plutonium dropped to 0.02. However, in the absence of Aerosol OT, the dodecane also caused the graphite to agglomerate and then partition to the top, PEG phase. A few large graphite agglomerates settled to the bottom of the test tube. Otherwise, the bottom, sulfate phase remained clear as before. Surface modification of activated and graphitic carbons with additives such as kerosene is commonly used in gold beneficiation as a means of reducing gold adsorption in carbonaceous ores (30). The mechanism by which organic compounds inhibit gold uptake by the carbonaceous material is not fully understood, but is believed to involve both hydrophobic and electrostatic interactions (30). It is possible that in the present situation, the dodecane acts to block sites on both the graphite surface and the plutonium polymer.

CONCLUSIONS

Aqueous biphasic extraction offers the potential for obtaining extremely high separation factors between metal oxides and silica. In principle, the selective adsorption of phase-transfer agents can be used to obtain separations between different metal oxides. The ability of this extraction technique to separate particles that are ≤ 1 µm makes it feasible to use ultrafine grinding as a means of liberating PuO_2 from plutonium-containing residues. In preliminary tests with model systems containing polymeric Pu(IV), estimated single-stage separation factors of $\geq 10^4$ were obtained with PuO_2/graphite and PuO_2/SiO_2 mixtures, respectively. Polymeric Pu(IV) is known to be highly surface-active with an ability to adsorb to practically any solid surface (31). The fact that such high separation factors were obtained in the presence of high surface area particulates represents a significant separations achievement.

Work is underway to evaluate separation capabilities of aqueous biphasic extraction using actual plutonium residues. Grinding studies are being carried out concurrently to evaluate the extent of plutonium liberation during particle-size reduction. The residues will be ground wet to an average particle size of 1 µm or less using a vibratory ball mill. If separation factors as large as those obtained with the model systems reported here are attainable with actual plutonium residues, a significant portion of the residue volume would become discardable. The plutonium concentrates could then be processed more economically by chemical means to recover highly purified plutonium as either the metal or the oxide.

ACKNOWLEDGEMENT

The authors would like to thank F. Mrazek (CMT) for helpful suggestions on preparing samples for SEM analysis and Dr. J. K. Bates (CMT) for taking the electron micrographs.

REFERENCES

1. D. C. Christensen, D. F. Bowersox, B. J. McKerley, and R. L. Nance, Waste From Plutonium Conversion and Scrap Recovery Operations, U. S. DOE Report LA-11-69-MS (1988).
2. J. M. Hoegler and W. M. Bradshaw, Magnetic Separation of Department of Energy Wastes, U. S. DOE Report ORNL -TM-11117 (1989).
3. R. P. Wichner, A. A. Khan, and J. M. Hoegler, Separation of Depleted Uranium Fragments from Gun Test Catchments, U. S. DOE Report ORNL-TM-11141 (1989).
4. L. R. Avens, U. F. Gallegos, and J. T. McFarlan, Sep. Sci. Technol. 25, 1967 (1990).
5. P.-Å. Albertsson, Partition of Cell Particles and Macromolecules, 3rd ed., Wiley-Interscience, New York (1986).
6. M.-R. Kula, in Enzyme Technology, Applied Biochemistry and Bioengineering, Vol. 2, L. B. Wingard, Jr., E. Katchalski-Katzler, and L. Goldstein, Eds., Academic Press, New York, p. 74 (1979).
7. H. Walter, D. E. Brooks, and D. Fisher, Eds., Partitioning in Aqueous Two-Phase Systems, Academic Press, New York (1985).
8. T. I. Zvarova, V. M. Shkinev, G. A. Vorob'eva, B. Ya. Spivakov, and Yu. A. Zolotov, Mikrochimica Acta [Wien] 3, 449 (1984).
9. K. P. Ananthapadmanabhan and E. D. Goddard, "Process for the Separation of Solid Particulate Matter," U. S. Patent 47,225,358 (1987).
10. N. D. Gullickson, J. F. Scamehorn, and J. H. Harwell, in Surfactant-Based Separation Processes, J. F. Scamehorn and J. H. Horwell, Eds., Surfactant Science Series Vol. 33, Marcel Dekker, New York, p. 305 (1989).
11. D. J. Chaiko et al., in Proceedings 14th Annual Army Environmental R&D Symposium, USATHAMA Report CETHA-TE-TR-90055, p. 305 (1989).
12. K. D. Ingham and T. F. Busby, Chem. Eng. Comm. 7, 315 (1980).
13. H. Hustedt, K. H. Kroner, and M.-R. Kula, in Partitioning in Aqueous Two-Phase Systems, Academic Press, New York , p. 529 (1985).

14. H. Hustedt, K. H. Kroner, U. Menge, and M.-R. Kula, Enzyme Eng. 5, 45 (1980).

15. G. Bloomquist and P.-Å. Albertsson, J. Chromatogr. 73, 125 (1972).

16. M.-R. Kula and H. Hustedt, Adv Biochem. Eng. 24, 73 (1982).

17. S. B. Sawant, S. K. Sikdar, and J. B. Joshi, Biotechnol. Bioeng. 36, 109 (1990).

18. D. C. Szlag, K. A. Giuliana, and S. M. Snyder, in Downstream Processing and Bioseparation, J.-F. Hamel, J. B. Hunter, and S. K. Sikdar, Eds., ACS Symposium Series 413, ACS, Washington, DC, Ch. 4 (1990).

19. P. Thiyagarajan, H. Diamond, L. Sonderholm, E. P. Horwitz, L. M. Toth, and L. K. Felder, Inorg. Chem. 29, 1902 (1990).

20. R. A. Leonard, G. J. Bernstein, R. H. Pelto, and A. A. Ziegler, AIChE J. 27, 495 (1981).

21. R. A. Leonard, G. J. Bernstein, R. H. Pelto, and A. A. Ziegler, Sep. Sci. Technol. 18, 1568 (1983).

22. R. A. Leonard, Argonne National Laboratory, personal communication (1991).

23. G. J. Bernstein, D. E. Grosvenor, J. F. Lenc, and N. M. Levity, Nucl. Technol. 20, 200 (1973).

24. R. E. Skavdahl and T. D. Chikalla, in Plutonium Handbook, Vol. 1, O. J. Wick Ed., Gordon and Breach, New York, Ch. 8 (1967).

25. D. W. Fuerstenau, Pure Appl. Chem. 24, 135 (1970).

26. D. W. Fuerstenau and S. Roghaven, in Flotation, M. C. Fuerstenau, Ed., AIME, New York, p. 33 (1976).

27. J. Leja, Surface Chemistry of Froth Flotation, Plenum Press, New York (1982).

28. R. K. Iler, The Chemistry of Silica, John Wiley, New York, Ch. 3 (1979).

29. D. J. Chaiko, Argonne National Laboratory, Argonne, IL, unpublished data, 1991.

30. K. Osseo-Asare, P. M. Afenya, and G. M. K. Abotsi, "Carbonaceous Matter in Gold Ores: Isolation, Characterixation and Adsorption Behavior in Aurocyanide Solutions," in Precious Metals: Mining, Extraction, and Processing, V. Kudryk, D. A. Corrigan, and W. W. Liang, TMS, Warrenville, PA, p. 125(1984).

31. D. W. Ockenden and G. A. Welch, J. Chem. Soc., p. 3358 (1956).