Separation Science and Technology

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

Citrate-Based "TALSPEAK" Actindide-Lanthandide Separation Process

G. D. Del Cul[a]; L. M. Toth[a]; W. D. Bond[a]; G. D. Davis[a]; S. Dai[a]
[a] Chemical Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN, U.S.A.

To cite this Article Cul, G. D. Del , Toth, L. M. , Bond, W. D. , Davis, G. D. and Dai, S.(1997) 'Citrate-Based "TALSPEAK" Actindide-Lanthandide Separation Process', Separation Science and Technology, 32: 1, 431 — 446

To link to this Article: DOI: 10.1080/01496399708003208

URL: http://dx.doi.org/10.1080/01496399708003208

SEPARATION SCIENCE AND TECHNOLOGY, 32(1-4), pp. 431-446, 1997

CITRATE-BASED “TALSPEAK” ACTINIDE-LANTHANIDE SEPARATION PROCESS

G. D. Del Cul, L. M. Toth, W. D. Bond, G. D. Davis, and S. Dai
Chemical Technology Division, Oak Ridge National Laboratory
P.O. Box 2008, Oak Ridge, TN 37831-6181, U.S.A.

ABSTRACT

Lanthanide elements are produced in relatively high yield by fission of ^{235}U. Almost all the lanthanide isotopes decay to stable nonradioactive lanthanide isotopes in a relatively short time. Consequently, it is highly advantageous to separate the relatively small actinide fraction from the relatively large quantities of lanthanide isotopes.

The TALSPEAK process (Trivalent Actinide Lanthanide Separations by Phosphorus-reagent Extraction from Aqueous Complexes) is one of the few means available to separate the trivalent actinides from the lanthanides. Previous work based on the use of lactic or glycolic acid has shown deleterious effects of some impurity ions such as zirconium(IV), even at concentrations on the order of 10^{-4} *M*. Other perceived problems were the need to maintain the pH and reagent concentrations within a narrow range and a significant solubility of the organic phase at high carboxylic acid concentrations.

Our cold experiments showed that replacing the traditional extractants glycolic or lactic acid with citric acid eliminates or greatly reduces the deleterious effects produced by impurities such as zirconium. An extensive series of batch tests was done using a wide range of reagent concentrations at different pH values, temperatures, and contact times. The results demonstrated that the citrate-based TALSPEAK can tolerate appreciable changes in pH and reagent concentrations while maintaining an adequate lanthanide extraction.

Experiments using a three-stage glass mixer-settler showed a good lanthanide extraction, appropriate phase disengagement, no appreciable deleterious effects due to the presence of impurities such as zirconium, excellent pH buffering, and no significant loss of organic phase.

INTRODUCTION

One of the major problems resulting from the production of nuclear energy is the generation of highly radioactive spent fuel. Due to increased political and economic discussion regarding the future of nuclear energy production, there is renewed interest in partitioning, recycling, and destruction of long-lived radionuclides.[1]

The partitioning of the different groups of radionuclides can be accomplished using a variety of methods. One crucial aspect of the partitioning is the separation of the long-lived, highly radioactive actinides from the rather similar short-lived or nonradioactive lanthanides.

Because of their almost identical chemical behavior, the separation of actinide and lanthanide elements is a difficult process. A very promising treatment that can successfully and efficiently accomplish this difficult separation in aqueous systems is the so-called TALSPEAK[2] separative process (Trivalent Actinide-Lanthanide Separations by Phosphorus-reagent Extraction from Aqueous Complexes). Extensive laboratory-scale research and development on the TALSPEAK process has already been done.[2,3] Some limited closed-loop tests using high-level wastes generated from low-burnup spent fuel were also completed.[4,5] However, significant research and development is still needed before the method can be adequately implemented at either pilot or full industrial scale.

One area that needed to be evaluated was the effect of impurity ions on the lanthanide extraction and loading. Small amounts of zirconium(IV) reduce the lanthanide-actinide separation,[6] while higher concentrations can generate a third phase. The nature of this third phase has not been studied yet. In the absence of any concrete evidence, it can only be assumed to contain species that consist of three-dimensional layered structures with two or more phosphate groups per zirconium ion, similar to those in the third phase generated during the PUREX process.[7-13] Since the presence of a zirconium can seriously affect the separation process even at concentrations as low as 10^{-4} *M*, several experiments were conducted to determine the conditions under which zirconium will interfere with the actinide-lanthanide separation. Molybdenum is another impurity of concern because of its possible interference with the actinide-lanthanide separation. Hence, the concentration levels and conditions under which zirconium(IV) and molybdenum(VI) can be tolerated in the process stream needed to be determined.

Based on previous experiments, it was also expected that the pH and reagent concentrations had to be controlled within a narrow range to maintain an adequate separation. Another potential problem was a significant aqueous solubility of the organic phase at high buffer (i.e., carboxylic acid) concentrations.[2,4] Using 2-ethylhexyl phenylphosphoric acid and 6 *M* lactic acid concentration, Weaver[2] reported a 20% volume loss of the organic phase at pH 2.5. However, a high carboxylic acid concentration has several advantages, which include a highly buffered aqueous phase with increased diethylenetriaminepentaacetic acid (DTPA) solubility (DTPA precipitation particularly at low pH can be a problem), faster extraction kinetics, and better phase disengagement. A

0.8–1.5 *M* carboxylic acid concentration appears to be a good compromise between good separation and low organic extractant loss.[2,4,5,14]

The primary emphasis of this work was to determine the best set of conditions for TALSPEAK processing, particularly with respect to the reduction or elimination of the deleterious effects of impurity ions such as zirconium and molybdenum. These were compared with the traditional fluoride complexant for zirconium. "Cold" batch tests were conducted to identify the range of conditions for acceptable separations and adequate rates of extraction. Reagent concentrations were varied, and rates of extraction and separation factors were determined. Also, methods of purifying the extractants (from the radiolytic degradation products) for recycling and reuse were examined. Considerable concern regarding radiolytic changes in the pH values warranted closer examination of the organic/aqueous-phase behavior and solvent/extractant degradation. Also, the solubility of the organic phase under different conditions, such as varied carboxylic acid concentration, pH, etc., was studied to determine the best conditions for a good separation and a low loss of extractant. As batch tests reached their completion, the initiation of mixer-settler tests was pursued on laboratory-scale quantities of solutions in order to optimize conditions for multistage operations.

RESULTS AND DISCUSSION

Glycolic Acid Systems

Previous work done by B. Weaver[15] indicated that the extraction kinetics and phase disengagement were improved by the use of glycolic acid instead of lactic acid. For this reason, our initial work was conducted using glycolic acid for comparative purposes.[16]

Preliminary tests were conducted to determine the levels of zirconium that can be tolerated without third-phase formation. A 0.80 *M* di-(2-ethylhexyl) phosphoric acid (HDEHP) solution in diisopropylbenzene (DIPB) was contacted with an aqueous solution of 1.0 *M* glycolic acid and 0.1 *M* DTPA. The pH was adjusted to 3.0 using sodium hydroxide. These reagent concentrations and pH were chosen because previous work showed these conditions to be satisfactory.

Zirconium concentrations ranged from 0.01 to 1.0 mg/mL (aq), while the initial neodymium concentrations ranged from 0.01 to 20 mg/mL (aq). Visual observation indicated the formation of a third phase at zirconium concentrations ≥0.05 mg/mL (aq) and no apparent third phase for concentrations ≤0.01 mg/mL (aq). For the samples containing zirconium in concentrations >0.01 mg/mL, there is an initial stage where a globular phase occupies a significant volume of the aqueous phase. This globular phase breaks down slowly (several hours to a day or two) if left undisturbed. Time or centrifugation transforms the globular phase into a relatively thin layer located between the organic and the aqueous phases. Higher neodymium concentrations seem to stabilize the globular stage.

Tests conducted with different levels of zirconium and neodymium, all at concentrations higher than trace level, showed no appreciable change in the neodymium distribution ratio due to the presence of zirconium. As observed before, higher neodymium concentrations seem to stabilize the third phase.

The addition of fluoride ions, as sodium fluoride, along with the neodymium and zirconium in a 1:1 $F^-/Zr(IV)$ ratio, largely prevented the formation of the third phase. Instead, a single cloudy aqueous phase was present. The neodymium distribution remained unchanged. The organic and aqueous phases disengaged as quickly in the presence of 1:1 fluoride as in the absence of zirconium (about 2 min by natural settling).

Using a lower (0.5:1) $F^-/Zr(IV)$ ratio helped only marginally in limiting the third-phase formation. The use of a higher ratio such as 2:1 $F^-/Zr(IV)$ produced a different kind of third phase (more like a reticular pattern, not the cotton-like structure as noted in the absence of fluoride). This third phase broke down and disappeared in about 30 min of natural settling, leaving a clear aqueous phase. Again, neodymium distribution remained unchanged.

The addition of fluoride at a 1:1 $F^-/Zr(IV)$ ratio into a system with an already existent third phase was also studied. It was observed that the third phase slowly disappeared (about 15–20 min), leaving the aqueous phase cloudy in appearance.

It was also noted that the addition of zirconium into the same kind of system (0.80 *M* HDEHP in DIPB and 1.0 *M* glycolic acid) but without DTPA resulted in an even more extended third phase that occupied almost the entire aqueous phase and could not be eliminated even by prolonged centrifugation (about 20–30 min at the maximum speed of the lab centrifuge).

The use of fluoride ions, however effective, requires a knowledge of the zirconium concentration to adjust the fluoride doses. Additionally, the presence of fluoride even at very low concentrations ($\sim 10^{-4}$ *M*) is problematic because of the known corrosivity of fluoride solutions. For these reasons, several other alternatives were tried, including the addition of known zirconium complexants such as hydrogen peroxide and citric acid. While hydrogen peroxide was not useful, the use of citric acid proved to be very effective.

Similar tests using molybdenum(VI) (as sodium molybdate), zirconium(IV), and neodymium(III) showed that molybdenum causes no additional problems, even at the highest concentration tested (1.0 mg/mL, initial aq).

Selection of Citric Acid Systems

Previous work[2] indicated that citric acid solutions containing DTPA also gave large separations between the lanthanides and the americium-curium pair. It was also reported[2] that citric acid increased the solubility of DTPA. Since our preliminary tests indicated that the addition of citric acid to the glycolic acid largely prevented the formation of the third phase in the presence of zirconium, a series of experiments was conducted using citric acid alone as the buffer/complexant additive.[16]

A solution of 0.8 *M* HDEHP in DIPB was contacted with an aqueous solution containing 1.0 *M* citric acid and 0.1 *M* DTPA. The pH was adjusted to 3.0 using sodium hydroxide. From each phase, aliquots were drawn and transferred to separatory funnels. The appropriate volume of zirconyl nitrate and neodymium nitrate solutions was added, using micropipettes, to the aqueous phase in each funnel.

The initial zirconium concentration ranged from 0.01 to 5 mg/mL, while the initial neodymium concentration ranged from 0.01 to 20 mg/mL (initial aq). Each funnel was agitated for 3 min and allowed to settle. Absorption spectra for the aqueous and organic phase were obtained from each sample in the visible range (400–830 nm).[17,18]

Tests conducted with different levels of zirconium and neodymium, all at concentrations higher than trace levels, showed no appreciable change in the neodymium distribution ratio due to the presence of zirconium. Only experiments at the highest zirconium concentration tested, 1.0 mg/mL (initial aq), showed a third phase in the organic phase, and this third phase was like a haze or emulsion with large bubbles. At 0.5 mg/mL, the organic phase was hazy and had few bubbles. At zirconium concentrations of ≤0.25 mg/mL, no effects were visible. Similar tests using molybdenum, zirconium, and neodymium showed that molybdenum causes no additional problems even at the highest concentration tested (1.0 mg/mL, initial aq).

In order to measure the distribution of lanthanide(III) ions between the aqueous and organic phases at different lanthanide concentrations with and without zirconium and molybdenum, three samples—containing all the lanthanides from lanthanum through lutetium, except promethium and yttrium—were prepared. The experimental concentrations were determined using inductively coupled plasma/mass spectrometry (ICP/MS).

One solution had a total lanthanide concentration of 0.001 *M* ($\sim 7 \times 10^{-5}$ *M* for each lanthanide, initial aq), another was 0.01 *M* ($\sim 7 \times 10^{-4}$ for each lanthanide, initial aq), and the third was 0.04 *M* ($\sim 2.5 \times 10^{-3}$ *M* for each lanthanide, initial aq).

The results, displayed as the ratio of the concentration in the organic to the concentration in the aqueous phase, are shown Figure 1. The distribution coefficients for

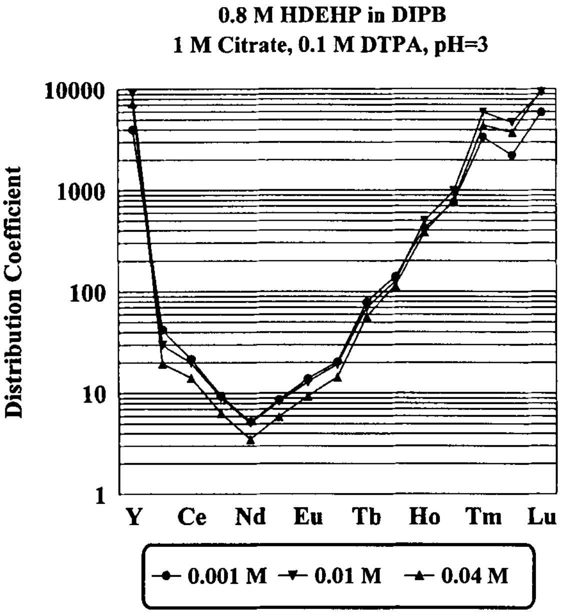

Figure 1. Distribution coefficients for citrate TALSPEAK lanthanide extraction at different loadings. The axis label does not include all lanthanides in the series.

the first two solutions are almost identical; however, for the most concentrated solution, the values are somewhat lower for the early lanthanides (lanthanum to gadolinium). There was no visual difference between the three samples.

Two similar samples were prepared but with the addition of zirconium and molybdenum. The first sample had a total lanthanide concentration of 0.01 *M* (~7 × 10^{-4} *M* for each lanthanide, initial aq) and 0.5 mg/mL (~5 × 10^{-3} *M*) of zirconium and molybdenum. The second sample had a total lanthanide concentration of 0.03 *M* (~2 × 10^{-3} *M* for each lanthanide, initial aq) and 1.0 mg/mL (~10^{-2} *M*) of zirconium and molybdenum. The results, along with those for the previously described 0.01 *M* sample prepared without zirconium or molybdenum, are displayed in Figure 2. The distribution coefficients for the first two solutions (0.01 *M* with and without zirconium and molybdenum) are almost identical; however, for the most concentrated solution, 0.03 *M*, the values are somewhat lower for all lanthanides. Only traces of molybdenum were found in the organic phase. The distribution coefficient for zirconium was between 0.2 and 0.6. In contrast, reported

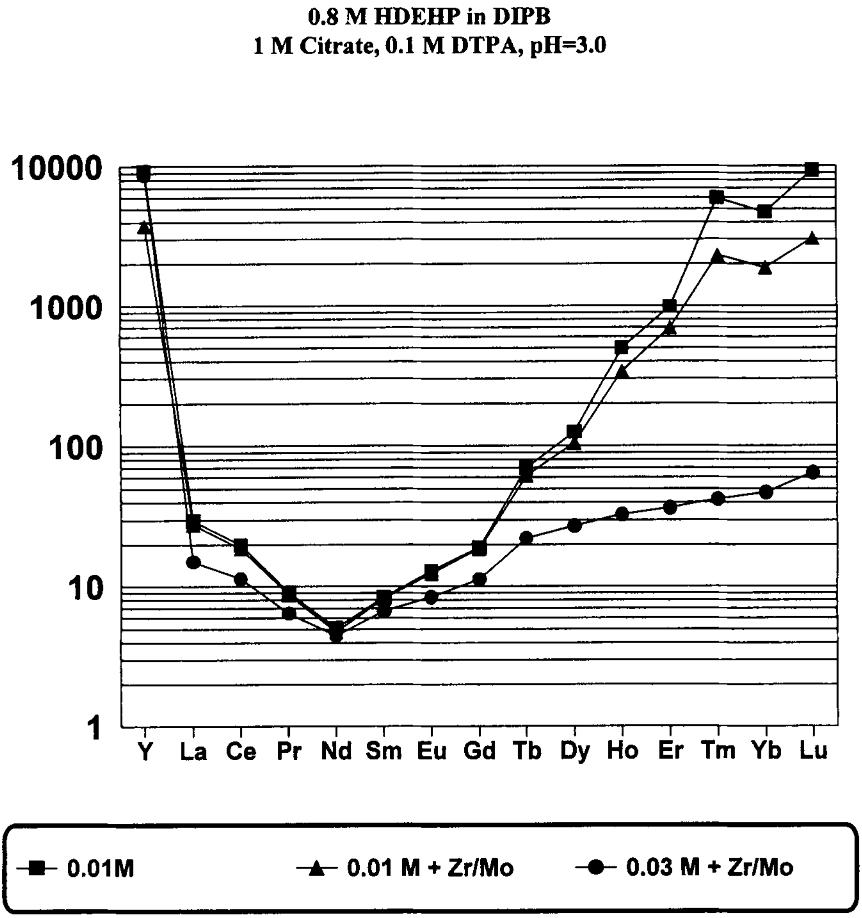

Figure 2. Distribution coefficients for citrate TALSPEAK lanthanide extraction at different loadings in the presence of 10^{-3} M zirconium(IV) and molybdenum(IV).

experiments[2] using glycolic acid and zirconium showed that the zirconium activity remained almost completely in the aqueous phase.

It was noted that the organic phase (0.80 *M* HDEHP in DIPB) contacted with the glycolic/DTPA aqueous phase turns yellow with time. The same organic phase contacted with the citric/DTPA aqueous phase remained colorless. It was noted that the yellow color appears even when the ampoule containing the organic solution was covered with aluminum foil to eliminate any possible photoreaction. This color is produced by the tail of a broad absorption band centered at about 400 nm. Since DIPB is known to form peroxides, it is possible that the yellow color is due to a DIPB peroxide and that the citric acid is preventing the formation of peroxide precursors. There is no apparent effect on the extraction chemistry due to the yellowish coloration of the organic phase.

Scoping Extraction Tests of Citrate-Based TALSPEAK

The primary emphasis of this work was to determine the best set of conditions for TALSPEAK processing, particularly with respect to the reduction or elimination of the deleterious effects of impurity ions such as zirconium and molybdenum. Preliminary tests indicated that the use of citric acid as the buffer/complexant was preferable to the usage of glycolic acid. For this reason, an extensive series of small-volume batch extraction experiments (15–30 mL), using a wide range of reagent concentrations at different pH values, temperatures, and contact times, was examined to scope the citrate-based TALSPEAK extraction process.

A mix of lanthanides— neodymium, praseodymium, europium, and erbium (each added at a concentration of ~ 10^{-3} *M*), with and without zirconium and molybdenum—was used as a cold surrogate. This mix was chosen because the individual absorption spectra of these elements do not overlap significantly in the region 340–900 nm,[17,18] and hence, the lanthanide concentrations could be spectrophotometrically monitored in the near UV/visible/near IR (340- to 900-nm) range. The appearance of interfacial precipitates and the phase disengagement process were visually followed.

The citrate concentration was varied between 0.5 and 2.0 *M*, while the concentration of added DTPA was in the range of 0–0.1 *M*. The organic and aqueous phases were preequilibrated at a pH value between 2.5 and 4.4 using sodium hydroxide. Molybdenum(VI) and zirconium(IV) were added as sodium molybdate and zirconyl nitrate at concentrations ranging from 0 to 1.0 mg of metal/mL.

The results indicate that good lanthanide extraction can be accomplished under a relatively wide range of pH values and changes in concentrations. The lanthanide extraction kinetics and phase disengagement were acceptable from pH 2.5 to 4.1. The phase disengagement was good under most conditions but was somewhat better at the higher pH values. Extraction of all lanthanides was more effective at the lower pH values tested; however, the distribution factors do not change significantly from pH 3 to 4. Higher concentrations of DTPA and citrate anions somewhat diminish the lanthanide extraction because of the increased complexing power of both reagents. The solubility of DTPA decreases at lower pH values. Deposits of DTPA were observed at the lower pH values when the solution was stored for prolonged periods (a few days).

At lower pH values (near pH 2), the lanthanide extraction by the organic phase is higher. However, the actinide extraction by the organic phase, although very low, is also higher. As a result, a low-pH separation will produce an aqueous phase that is essentially free of lanthanides but that contains most of the actinides. At the same time, the organic phase will contain all the lanthanides and a small fraction of the actinides. Because of the increased concentration of DTPA and citrate anions (higher complexing power in the aqueous phase) at higher pH values (near pH 4), the actinide extraction is expected to be extremely low. However, the lanthanide extraction by the organic phase, although still high, will also diminish. As a result, a high-pH separation will produce an organic phase that is essentially free of actinides but that contains most of the lanthanides and an aqueous phase that contains all the actinides and a small residual concentration of lanthanides.

Similarly, the zirconium(IV) concentrations that can be tolerated increase at higher pH values, probably due to the same increased complexing power of the free DTPA and citrate anions. No significant losses of organic extractant were observed. The lanthanide extraction kinetics in absence of DTPA was a significantly slower process.

In order to test the extraction of impurity ions from TALSPEAK aqueous solutions, a 200-mL aqueous solution containing 39 elements in concentrations ranging from 10^{-3}–10^{-4} *M* was prepared. Citric acid and DTPA were added to produce concentrations of 1.0 *M* citrate and 0.1 *M* DTPA in the solution. Four 15-mL aliquots of the aqueous phase were contacted with an equal volume of 0.8 *M* HDEHP in DIPB. Sodium hydroxide was added to the four aliquots to achieve pH values of 2.6, 3.0, 3.6, and 3.9. The results indicated that Al^{3+} and Mn^{2+} are extracted into the organic phase and Pb^{+}, Cs^{+}, Sr^{2+}, Ba^{2+}, Fe^{3+} are partially extracted. The partial extraction of Rb, Cs, Sr, and Ba increased with increased pH. Other ions tested—Cr, Co, Ni, Cu, Zn, Mo, Ru, Rh, Pd, Ag, Cd, In, Sn, Sb, and Pb—were not extracted.

Extraction and Stripping from Nitric Acid Solution

The reverse TALSPEAK process can be a very convenient way of connecting the TALSPEAK partitioning process with other separative schemes. In the reverse TALSPEAK process,[3] the organic phase is first loaded with the actinides and lanthanides, usually from a diluted acidic solution (0.05–0.1 *M* nitric acid), and then contacted with the aqueous phase to strip the actinides.

In order to test the loading and stripping of lanthanides and impurity ions from diluted nitric acid solutions, a 200-mL aqueous solution containing 39 elements in concentrations ranging from 10^{-3}–10^{-4} *M* was prepared. The solution was contacted with an equal volume of 0.8 *M* HDEHP in DIPB and stirred for about 10 min. Aliquots of the organic phase were contacted with an equal volume (15 mL) of nitric acid solutions of varying concentrations (0.1, 0.3, 0.6, 1, 2, 4, and 6 *M*) and analyzed using ICP/MS.

The results for the 0.1 *M* nitric acid indicated that aluminum, tin, and molybdenum are extracted into the organic phase and that Rb^+, Sr^{2+}, Ba^{2+}, Fe^{3+}, Mn^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, and In^{3+} are partially extracted. No significant extraction of Cs, Co, Ni, Zr, Ru, Rh, Pd, Ag, Sb, and Pb took place.

Results for the more concentrated nitric acid solutions indicated that lanthanides are not significantly extracted at acid concentrations above 0.1 *M*. Acid concentrations as low as 0.3–0.6 *M* can be used to strip the lighter lanthanides from the organic extractant. The heavy lanthanides, which represent only a small fraction of the lanthanides produced as a result of fission, require the use of more concentrated nitric acid (2–4 *M*) and display a slower kinetics.

Purification of the Organic Extractant

One of the major by-products of the radiolytic damage of the monoacid HDEHP is the diacid monosubstituted 2-ethylhexyl phosphoric acid (MEHPA).[19–27] The dibasic character of the 2-ethylhexyl-phosphate ion makes this species a very strong organic-phase complexant for both actinides and lanthanides. This characteristic interferes with the TALSPEAK separative process, which succeeds in the absence of such universal complexants as a result of subtle differences in complexation between lanthanides and actinides. The net result is the co-extraction of lanthanides and actinides and a less-than-satisfactory separation. For this reason, it is necessary to continuously remove the MEHPA as it is formed by radiolysis of the organic extractant to maintain an efficient separation.

Several methods described in the literature could be used to purify the HDEHP,[23–32] including the precipitation of the copper salt of the HDEHP, liquid-liquid partition of the HDEHP and MEHPA between ethylene glycol and petroleum ether, vacuum distillation, and caustic washing.

The need to continuously purify HDEHP dissolved in an organic solvent such as the DIPB precludes most of the methods except for the caustic washing. The monobasic disubstituted HDEHP is not water soluble; however, the monosubstituted dibasic MEHPA is highly soluble. This difference in solubilities can, in principle, be used to purify the organic extractant by caustic washing.

Our tests showed that the caustic washing using sodium carbonate solutions produced gel-type precipitates that were very difficult to handle. The use of ammonium carbonate, however, proved to be effective and did not cause any precipitates to form. The caustic washing must be preceded by stripping of the organic extractant. The caustic washing of partially laden organic extractant produced total gelation of the organic phase when sodium carbonate was used and partial gelation when ammonium carbonate was used.

In our tests, a single-step washing of the organic extractant with an equal volume of 0.5 *M* ammonium carbonate solution almost completely removed the MEHPA, as determined by titration of the treated solution.

Multistage Testing

A three-stage glass mixer-settler apparatus was assembled to test the general behavior of the citrate-based TALSPEAK separative process. The organic extractant and the lanthanide-laden aqueous phase were fed countercurrently.

The experiments showed the pH to be highly constant, even when there was significant loading of the organic phase. In fact, the pH was essentially constant before and after reaching steady state in all three stages. The lanthanide extraction and phase disengagement were acceptable in the entire pH range (2.5–4.0). No significant losses of organic extractant and no appreciable effects due to impurities such as zirconium were observed.

Extensive "cold" runs using a three-stage mixer-settler showed good lanthanide extraction, appropriate phase disengagement, and excellent pH buffering. In order to test the recycling of the extractant, stripping and washing runs were also performed with very favorable results.

Mechanistic Factors that Influence the TALSPEAK Separation Process

Association of organophosphoric acids due to hydrogen bonding is stronger than that of monocarboxylic acids.[33] The monobasic phosphoric acids, such as the HDEHP, and the phosphonic acids form dimers as a result of intermolecular bonding. The dimerization constant of these acids is large ($\sim 10^4\ M^{-1}$). Polymerization increases and the kinetics of extraction decreases at higher solute concentrations and lower solvent polarities. A higher degree of dimerization-polymerization appears to be associated with a slower extraction process. It has been reported[2] that the extractive power of the phosphoric acids, such as

HDEHP, is higher when they are dissolved in aliphatic solvents (less polar, higher degree of dimerization-polymerization) than when they are dissolved in aromatic solvents such as DIPB. However, it has also been reported that better separation of lanthanides and actinides is achieved when aromatic solvents are used.[2]

It was previously determined[2,14,34] that when lactic acid is used as the buffer reagent, the lanthanide or actinide species extracted into the organic phase is the monolactate complex ($MeLact^{2+}$, where Me is a lanthanide or actinide). The following experimental evidence suggests that the extraction mechanism is different when using glycolic or citric acid because carboxylic acids are found in the aqueous strip only when lactic acid is used.

Three 15-mL aqueous samples with respective concentrations of 1.0 *M* lactic acid, glycolic acid, or citric acid were prepared. After adding 0.1 *M* DTPA to the samples, they were preequilibrated with an equal volume of 0.8 *M* HDEHP in DIPB and adjusted to pH 3.0. Then Nd^{3+} was then added to the samples to achieve a 10^{-3} *M* concentration. Extraction of the preequilibrated organic solutions was accomplished by vigorous stirring for 10 min. The samples were allowed to settle and then stripped using 1 *M* nitric acid. The stripped samples had the typical purplish color attributable to the presence of Nd^{3+}.

Using ^{13}C NMR, the aqueous samples were analyzed to determine the presence of carboxylic acids. Only the sample stripped from the lactic acid extraction contained lactic acid. The ^{13}C NMR testing is not adequate for trace analysis, but it is possible to conclude that neither citric or glycolic acid is significantly co-extracted, as is the case for the lactic acid.

SUMMARY AND CONCLUSIONS

Citrate-based TALSPEAK is a preferred process since interference by impurity ions such as zirconium is eliminated or minimized. Because the citric acid is a tricarboxylic acid, its buffering capacity is very high relative to the lactic or glycolic acids. In fact, all our batch and mixer-settler experiments showed a highly constant pH, even when there was significant loading of the organic phase. Relatively wide variations in pH values and concentrations changes can be tolerated with good lanthanide extraction. The lanthanide extraction kinetics and phase disengagement were acceptable, and no significant losses of organic extractant were observed.

Extensive "cold" runs using a three-stage mixer-settler showed good lanthanide extraction, appropriate phase disengagement, no appreciable effects due to impurities such as zirconium, and excellent pH buffering (0.5–1.0 *M*).

Stripping of the lanthanides can be accomplished using diluted nitric acid. Stripping of neodymium, praseodymium, and europium was almost complete in the three-stage mixer-settler tested. Only partial stripping of erbium was achieved.

Purification of the organic extractant HDEHP diluted in DIPB to remove MEHPA can be accomplished by washing with 1 *M* ammonium carbonate. After a three-stage washing with the ammonium carbonate solution, titration of the organic extractant spiked with 3–5% MEHPA showed the neutralization of only one proton. In all cases, the organic extractant must be stripped before the washing treatment to avoid the formation of gel-like third phases. Washing with sodium carbonate solutions causes the gelation of the entire organic phase and, hence, cannot be done.

REFERENCES

1. M. Srinivasan and M. V. Dingankar, "Long Lived Fission Reactor Waste Problem: Fact or Fiction," *Waste Manage.*, **12**, 313–322 (1992).

2. B. Weaver and F. A. Kappelmann, *Talspeak: A New Method of Separating Americium and Curium from Lanthanides by Extraction from an Aqueous Solution of Aminopolyacetic Acid Complex with a Monoacidic Phosphate or Phosphorate*, ORNL-3559, August 1964.

3. G. Koch, *Recovery of By-product Actinides from Power Reactor Fuels*, KFK-976, 1969.

4. I. Svantesson, I. Hangström, G. Persson, and J. O. Liljenzin, "Separation of Americium and Neodymium by Selective Stripping and Subsequent Extraction with HDEHP Using DTPA–Lactic Acid Solutions in a Closed Loop," *Radiochem. Radioanal. Lett.*, **37**, 4–5, 215–222 (1979).

5. G. Persson, I. Svantesson, S. Wingefors, and J. O. Liljenzin, "Hot Test of a Talspeak Procedure for Separation of Actinides and Lanthanides Using Recirculating DTPA–Lactic Acid Solution," *Solvent Extr. Ion Exch.*, **2**, 1, 89–113 (1984).

6. R. E. Leuze, W. D. Bond, and A. D. Lyon, ORNL, personal communication, January 1979.

7. L. Maya and C. D. Bopp, "Extraction of Zirconium from Nitric Acid Media by Butyl Lauryl Phosphoric Acid in Dodecane," *J. Inorg. Nucl. Chem.*, **40**, 1147–1151 (1978).

8. L. Maya, "Structure and Chromatographic Applications of Crystalline Zirconium(OPO$_3$R)$_2$ R= Butyl, Lauryl and Octylphenyl," *Inorg. Nucl. Chem. Lett.*, **15**, 207–212 (1979).

9. L. Maya and P. O. Danis, "Bis(octadecyl phosphate)zirconium(IV), Novel Support for Reversed-Phase Chromatography," *J. Chromatogr.*, **190**, 145–149 (1980).

10. L. Maya, "Zirconium Behavior in the System HNO$_3$–30% Tributyl Phosphate–Dodecane in the Presence of Monobutyl Phosphoric Acid," *J. Inorg. Nucl. Chem.*, **43**, 379–384 (1981).

11. C. Miyake, M. Hirose, T. Yoshimura, M. Ikeda, S. Imoto, and M. Sano, "'The Third Phase'of Extraction Processes in Fuel Reprocessing (I), Formation Conditions, Compositions and Structures of Precipitates in Zirconium-Degradation Products of TBP Systems," *J. Nucl. Sci. Technol.*, **27**, 2, 157–166 (1990).

12. C. Miyake, M. Hirose, and Y. Yoneda, "'The Third Phase' of Extraction Processes in Fuel Reprocessing (II), EXAFS Study of Zirconium Monobutylphosphate and Zirconium Dibutylphosphate," *J. Nucl. Sci. Technol.*, **27**, 3, 256–261 (1990).

13. M. Hirose, C. Miyake, and M. Iida, "'The Third Phase' of Extraction Processes in Fuel Reprocessing (III), ^{31}P-NMR Study of the Coordination Behavior of Zirconium Dibutylphosphates," *J. Nucl. Sci. Technol.*, **30**, 3, 232–238 (1993).

14. B. Weaver and F. A. Kappelman, "Preferential Extraction of Lanthanides or Trivalent Actinides by Monoacidic Organophosphonates from Carboxylic Acids and from Carboxylic and Aminopolyacetic Acids," *J. Inorg. Nucl. Chem.* **30**, 263–72 (1968).

15. B. Weaver, ORNL, personnel communication, December 1974.

16. T. Moeller and J. C. Brantley, "Spectrophotometric Estimation of Certain Rare Earth Elements," *Anal.Chem.*, **22**, 3, 433–441 (1950).

17. C. V. Banks and D. W. Klingman, "Spectrophotometric Determination of Rare Earth Mixtures," *Anal. Chim. Acta*, **15**, 356–363 (1956).

18. S. F. Marsh and S. L. Yarbro, *Comparative Evaluation of DHDECMP and CMPO as Extractants for Recovering Actinides from Nitric Acid*, LA-11191, 1988.

19. S. Tachimori and H. Nakamura, "Radiation Effects on the Separation of Lanthanides and Transplutonides by the Talspeak-Type Extraction.," *J. Radioanal. Chem.*, **52**, 2, 343–354 (1979).

20. S. Tachimori, "Effects of Radiolysis of Di(2-ethylhexyl)phosphoric Acid upon the Extraction of Strontium(II)," *J. Radioanal. Chem.*, **44**, 25–35.(1978).

21. S. Tachimori, "Radiation Damage of Organic Extractant in Partitioning of High-Level Liquid Waste (I)," *J. Nucl. Technol.*, **16**, 1, 49–56 (1979).

22. N. E. Bibler, "Gamma and Alpha Radiolysis of Aqueous Solutions of Diethylenetriaminepentaacetic Acid," *J. Inorg. Nucl. Chem.*, **34**, 1417–1425 (1972).

23. W. J. McDowell and P. T. Perdue, "Purification of Di(2-ethylhexyl)-Phosphoric Acid," *J. Inorg. Nucl. Chem.*, **38**, 2127–2129 (1976).

24. J. A. Partridge and R. C. Jensen, "Purification of Di(2-ethylhexyl)-Phosphoric Acid by Precipitation of Copper(II) Di-(2-Ethylhexyl)Phosphate," *J. Inorg. Nucl. Chem.*, **31**, 2587–2589 (1969).

25. D. C. Stewart and H. W. Crandall, "The Separation of Mixtures of Mono- and Di-Substituted Alkyl Phosphoric Acids," *J. Am. Chem. Soc.*, **73**, 1377–1378 (1951).

26. G. W. Mason and D. F. Peppard, "Types of Acidic Organophosphorus Extractants and Their Applications to Transuranic Separations," *Nucl. Sci. Eng.*, **17**, 247–251 (1963).

27. D. F. Peppard, J. R. Ferraro, and G. W. Mason, "The Preparation and Infrared Spectra of Several New Organophosphonates," *J. Inorg. Nucl. Chem.*, **12**, 60–70 (1959).

28. J. M. Schmitt and C. A. Blake, *Purification of Di(2-Ethylhexyl)-Phosphoric Acid*, ORNL-3548, February 1964.

29. R. E. Leuze, R. D. Baybarz, and B. Weaver, "Application of Amine and Phosphonate Extractants to Transplutonium Element Production," *Nucl. Sci. Eng.*, **17**, 252–258 (1963).

30. C. A. Blake, K. B. Brown, and C. F. Coleman, *The Extraction and Recovery of Uranium (and Vanadium) from Acid Liquors with Di(2-ethylhexyl) Phosphoric Acid and Some Other Organophosphorus Acids*, ORNL-1903, May 1955.

31. D. E. Horner, D. J. Crouse, K. B. Brown, and B. Weaver, "Solvent Extraction Chemistry Symposium, Part II: Fission Product Recovery from Waste Solutions by Solvent Extraction," *Nucl. Sci. Eng.*, **17**, 234–246 (1963).

32. F. Kubota, M. Goto, and F. Nakashio, "Extraction of Rare Earth Metals with 2-Thylhexyl Phosphonic Acid Mono-2-ethylhexyl Ester in the Presence of Diethylentriaminepentaacetic Acid in Aqueous Phase," *Solvent Extr. Ion Exch.*, **11**, 3, 437–453 (1993).

33. D. J. Peppard, J. R. Ferraro, and G. W. Mason, "Hydrogen Bonding in Organophosphoric Acids," *J. Inorg. Nucl. Chem.*, **7**, 231–244 (1958).

34. V. N. Kosyakov and E. A. Yerin, "On the Mechanism of Trivalent Actinide Extraction in the System HDEHP–Lactic Acid with DTPA," *J. Radioanal. Chem.*, **56**, 1–2, 93–104 (1980).