

UNIVERSITY HONORS PROGRAM

SENIOR PROJECT - APPROVAL

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PROJECT TITLE: Precipitation of Enriched Lutetium By Direct Oxalate Extraction

I have reviewed this completed senior honors thesis with this student and certify that it is a project commensurate with honors level undergraduate research in this field.

Signed: Geo. K. Schweitzer, Faculty Mentor

Date: 06 May 1999

Comments (Optional):

- Very good lab work.
- Very good write-up.

Precipitation of Enriched Lutetium by Direct Oxalate Extraction

A Senior Honors Paper by Paul Dennis Campbell, Jr.

Experimentation by Paul D. Campbell, Jr., Wes H. Fellers, and Peter M. Smith

Project Under the Supervision and Direction of

Professor George K. Schweitzer, PhD., ScD.

ABSTRACT

Enriched lutetium is commonly transferred from an organic extractant to an aqueous phase by the addition of strong acid. After stripping, neutralization of the highly acidic aqueous medium and subsequent addition of an oxalate salt yields a lutetium oxalate precipitate. The goal of this project was to study the effect of direct oxalate stripping on the lutetium-containing organic medium without resorting to the common tactics of acid addition and base neutralization. The lutetium recovery efficiency was studied, attempting to achieve maximized recovery of lutetium. The best overall method for direct oxalate stripping of lutetium was found to be a 2M acetic acid solution saturated with oxalic acid. The addition of this combination of acids consistently yielded a lutetium recovery rate of 90% or better when used to strip lutetium from the organic extracting agent. The success of this project has the potential in practice to eliminate unnecessary work with acids and bases, reducing not only the danger of human contact with hazardous chemicals but also the danger posed to the environment by the amount of hazardous waste produced in the current method. The problem of lutetium enrichment is applicable on a broader scale to the production of a lutetium-based photoreceptor which is very effective in medical imaging applications, namely PET Scanning.

INTRODUCTION

The separation and purification of the heavy rare earths has been the topic of a vast amount of previous chemical experimentation. Due to the similar properties of the rare earth elements, the elements have non-advantageous separation coefficients and are thus very difficult to isolate from a mixture. Extraction by organic compounds has often been employed in the past using kerosene-based extractants. Until studies by Wu Zhenzhong et al., di-(2-

ethylhexyl)phosphoric acid, or DEHPA (P-204), was one of the most commonly used organic extractants. However, it has since been discovered that mono(2-ethylhexyl)2-ethylhexylphosphonate (P-507) is a more advantageous extractant because extraction is permitted at lower acidity. Studies with P-507 have been conducted in both hydrochloric and nitric acid systems, with higher separation factors being found between lutetium and its neighbor ytterbium in the nitric acid system. A better stripping efficiency between lutetium and ytterbium was found in the hydrochloric acid system.¹

Zhenzhong et al. suggested countercurrent liquid-liquid reflux as the best method for P-507 extraction of lutetium. A simulated test consisting of eleven extraction stages, a twenty stage impoverishing section, a thirty stage nitric acid stripping and phase transfer section, a seven stage hydrochloric acid stripping section, and a two stage washing section in a mixer-settler was in operation by Zhenzhong et al. for a long time. In the process, lutetium with a purity > 99.95 % and a yield of > 98 % was obtained from a heavy rare earth mixture consisting of only 8 % lutetium and about 89 % ytterbium. Ytterbium with a purity of 92 % was found in the raffinate. The process was found more advantageous overall instead of the old sodium amalgam and ion exchange purification processes because it gives a higher yield, lower cost, greater operating simplicity, and elimination of mercury pollution.²

Another conventional extractant of rare earth cations is di(2-ethylhexyl) phosphoric acid, or D2EHPA. Peppard et al. were the first to use D2EHPA, and found an average separation factor of 2.5 for two consecutive rare earth cations, which is a higher separation factor than that obtained in ion exchange systems.³

STRIPPING

How are rare earth oxalates obtained? Stripping of rare earths is usually done from loaded extractant streams using mineral acid, then precipitated with oxalates.⁴ This is difficult for a couple of reasons. Safety is an important factor to consider. The rare earth cations are taken out of the organic medium by high hydrogen ion concentration, which competes with the rare earth for binding on the organic extractant. Working with high concentrations of acid necessary for the stripping is very dangerous, and should be avoided if at all necessary. Additionally, once the rare earth has been stripped into an aqueous phase, precipitation conditions for the desired chemical compound are often not optimal due to low pH. This is the case with lutetium oxalate, as a pH of one or less actually retards precipitation. To combat this, a weak base is usually added to “adjust” the pH to an optimal condition for precipitation. This, however, is not always good practice either because this can produce additional waste, which can be hazardous to the environment.

The process would be improved by combining the stripping and precipitation steps. Lee and Doyle studied the case of carboxylic acids, extracting yttrium and stripping at rather high pH values. Lee and Doyle’s work prove to be a model for future studies. An organic : aqueous ratio of 5:1 was used in all experiments. Stripping was performed using a stirrer, creating an emulsion. Centrifugation was found useful in separating the organic solution, aqueous solution, and precipitate. The yttrium – D2EHPA complex is very strong, so a high concentration of acid is needed to strip yttrium from the organic solution. A D2EHPA concentration of 0.5 M was used initially. The acidity of oxalic acid was adjusted to 2 or 3 M H^+ , using hydrochloric acid. It was found that additional hydrochloric acid was needed due to the low solubility of oxalic acid and its low dissociation constants. The percentage precipitation of yttrium increased with

increasing aqueous phase acidity, oxalic acid concentration, and treatment time. Increasing acidity accelerated the stripping rate and yield. The systems studied appeared to reach equilibrium after sixty minutes. The best conditions found were 0.750 M oxalic acid, adjusted to 3 M H^+ .

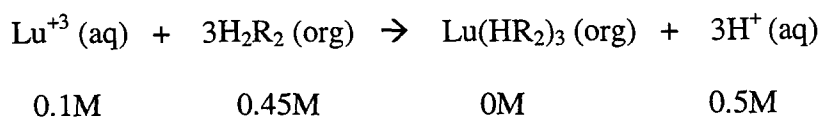
Concentration of D2EHPA appeared to be crucial because when it was increased to 1.0 M, rates were slowed and percentage precipitation dropped. Equilibrium was not obtained at sixty minutes using 1.0 M D2EHPA, and percentage precipitation decreased from 80 % to about 65 %. Thus, it appeared that the crucial factors were acidity, oxalic acid concentration, and D2EHPA concentration. Unfortunately, however, at high acidity and high oxalic acid concentration, oxalic acid crystallized before $Y_2(C_2O_4)_3$ precipitated. These conditions often led to poor precipitate characteristics, which led to difficulty in filtration, thus restricting some of the parameters that may be used in practice. Ultimately, however, the experiments showed that it might be possible to directly precipitate other rare earth complexes in a similar manner. Hopefully, with the adjustment of a few parameters, the efficiency in a lutetium oxalate precipitation can be found to be even greater than the yttrium oxalate efficiency. This investigation is what will comprise this paper.

PROPOSAL

Before the actual process of oxalate stripping can be examined, it is imperative to look at the extraction of lutetium into an organic phase. By understanding exactly how much lutetium is carried into organic medium, results of oxalate stripping procedures can be analyzed for efficiency. From the following equations and calculations it is hypothesized that direct oxalate

stripping is indeed a viable procedure for removal and precipitation of lutetium from organic media.

Trials to be performed consist of 0.1 M Lu^{+3} in aqueous media. Extraction is performed with 0.45 M H_2R_2 (commercial P-507, or “IonQuest”). The extraction is illustrated via the following reaction, with initial conditions underlying each species:



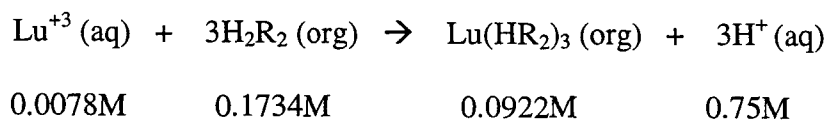
From various experimental procedures, the following equation for D was produced,

$$D = 50.56796 \times 0.142325^{[\text{H}^+]}$$

where D is $[\text{Lu}]_{\text{org}} / [\text{Lu}]_{\text{aq}}$.

After extraction, $[\text{H}^+]$ rises to 0.75M, which gives a $D=11.8$. A D value of 11.8 corresponds to 92.2% lutetium extraction into organic medium, with 7.8% residual lutetium in the aqueous phase. Granted, the countercurrent extraction mechanism proposed by Zhenzhong will bring about more complete lutetium extraction, but oxalate stripping experiments were conducted on organic media that had undergone one stage of extraction.

With the above D calculated for the specified conditions, the equilibrium constant K_{ex} can be calculated. Final conditions after the extraction equilibration are as follows:



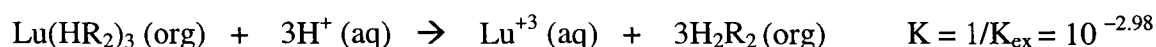
Lutetium species are in accordance with D, where $[\text{Lu}]_{\text{org}}$ is 0.0922 M and $[\text{Lu}]_{\text{aq}}$ is 0.0078M.

Since one lutetium displaces 3H^+ , final $[\text{H}_2\text{R}_2]$ is $0.45 - 3(0.0922) = 0.1734\text{M}$ H_2R_2 . All concentrations are known, so K_{ex} can be determined in the following manner:

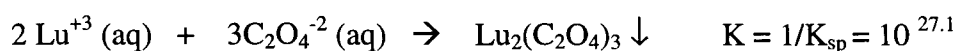
$$K = \frac{[\text{Lu}(\text{HR}_2)_3][\text{H}^+]^3}{[\text{Lu}^{+3}][\text{H}_2\text{R}_2]} = \frac{[0.0922][0.75]^3}{[0.0078][0.1734]^3} = 10^{2.98} = K_{\text{ex}}$$

Thus, the D of 11.8 leads to a favorable K_{ex} of $10^{2.98}$.

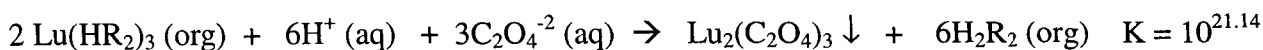
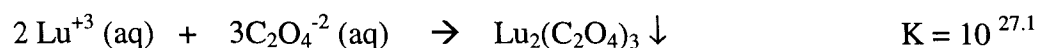
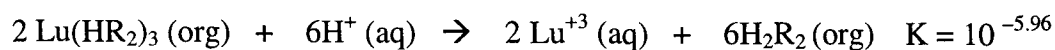
Since the lutetium in the organic medium after extraction is quantitated, oxalate stripping efficiency can be determined. The stripping equation is



and the precipitation equation is

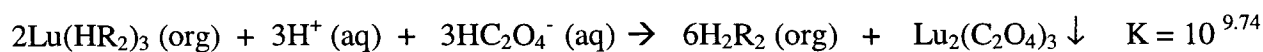
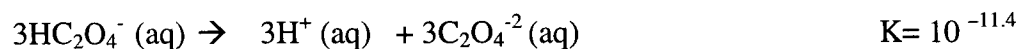
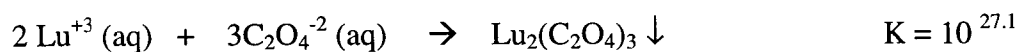
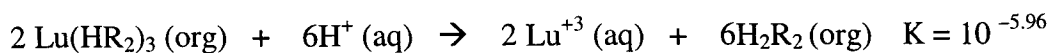


The K_{sp} for $\text{La}_2(\text{C}_2\text{O}_4)_3$ is approximately 10^{-25} ; the lanthanides each exhibit about a $10^{-0.15}$ K_{sp} difference as one progresses toward the heavier elements, so a K_{sp} of roughly 10^{-27} is assumed of $\text{Lu}_2(\text{C}_2\text{O}_4)_3$. After combining the above equations and combining K values, we have



$$\text{where } K = \frac{[\text{H}_2\text{R}_2]^6}{[\text{Lu}(\text{HR}_2)_3]^2[\text{H}^+]^6[\text{C}_2\text{O}_4]^{-3}}$$

Recognizing, however, that $\text{H}_2\text{C}_2\text{O}_4$ is the prominent species in solution only at pH values below 1, the reaction equations must be addressed by looking at the HC_2O_4^- ion, which is the prominent species between pH values of 1 and 3.8, the main pH region of investigation.



Thus, it follows that a favorable stripping reaction will be permitted due to the overall K above.

The ultimate test of relative efficiency is seen in the D ratio. A 90% product yield will be used in the following example calculations.

$$0.0922\text{M Lu}(\text{HR}_2)_3 \times 90\% \text{ stripping} = 0.08298\text{M Lu}_2(\text{C}_2\text{O}_4)_3$$

This leaves 0.00922 M $\text{Lu}(\text{HR}_2)_3$ remaining in the organic phase. The distribution ratio

$[\text{D}]_{\text{aq}}/[\text{D}]_{\text{org}}$ comes to 9.

The D=9 in one stage of oxalate stripping will be compared with direct 5M nitric acid stripping, as described in results by Zhenzhong.

INITIAL	0.0922M	5.0M	0	0.1734M
	$\text{Lu}(\text{HR}_2)_3 (\text{org}) + 3\text{H}^+ (\text{aq}) \rightarrow \text{Lu}^{+3} (\text{aq}) + 3\text{H}_2\text{R}_2 (\text{org})$			
FINAL	0.036M	4.83M	0.056M	0.342M

61% of the lutetium is stripped in one extraction, so $[\text{Lu}^{+3}] = (0.0922\text{M}) \times (.61) = 0.056 \text{ M}$.

$[\text{Lu}(\text{HR}_2)_3] = 0.0922\text{M} - 0.056 = 0.036\text{M}$. $D = [\text{Lu}^{+3}] / [\text{Lu}(\text{HR}_2)_3] = 1.56$. $[\text{H}_2\text{R}_2]$ is thus $0.45\text{M} - 3(0.036) = 0.342\text{M}$. $[\text{H}^+] = 5\text{M} - 3(0.056) = 4.83\text{M}$. From the above equation, K can again be calculated in the nitric acid stripping reaction:

$$K = \frac{[\text{H}_2\text{R}_2]^3 [\text{Lu}^{+3}]}{[\text{H}^+]^3 [\text{Lu}(\text{HR}_2)_3]} = 1.56 \frac{[\text{H}_2\text{R}_2]^3}{[\text{H}^+]^3} = 1.56 \frac{[0.342]^3}{[4.83]^3} = 10^{-3.26}$$

It is interesting to calculate exactly what concentration of nitric acid must then be used to obtain a $D = 9$ as in the oxalate stripping described above.

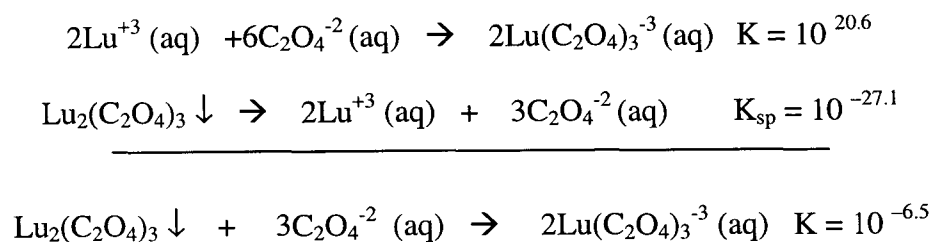
$$10^{-3.26} = 9 \frac{[\text{H}_2\text{R}_2]^3}{[\text{H}^+]^3} \rightarrow 0.0393 = \frac{[\text{H}_2\text{R}_2]}{[\text{H}^+]} = \frac{0.42234}{[\text{H}^+]}$$

$[\text{H}^+] = 10.75 \text{ M}$, so stripping concentration of HNO_3 must then be

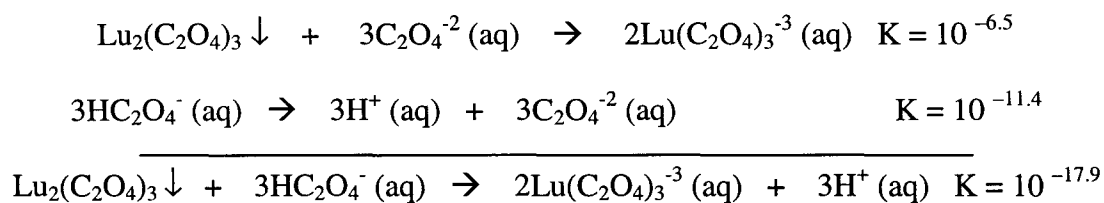
$$10.75 + 3(0.08298) = 11\text{M HNO}_3$$

From this concentration, oxalate stripping obviously looks like the better choice. 11M acid is extremely dangerous to work with. In addition, a neutralization step must occur when stripping with nitric before precipitating lutetium oxalate. If such a strong acid is used, neutralization will require either a stronger base or a larger quantity of a weaker base.

Yet another factor to regard is the complexation of oxalate to lutetium, which has a β_3 constant of $10^{10.3}$. However, this does not appear to be a competition that will cause any net effect.



Again realize, however, that HC_2O_4^- is a more accurate representation of the ion species present.



This is an unfavorable K_{complex} , so complexation does not appear to be an obstacle.

For each of the above equations and calculations, it follows that direct oxalate precipitation may be a viable alternative to nitric acid stripping. K_{rxn} and D for the oxalate strip both appear to be more favorable than their counterparts in the 5M nitric acid strip. The following experiments attempt to test this hypothesis.

EXPERIMENTS

A. The first stripping experiment performed involved the addition of an oxalate salt, in the form of a saturated solution of $\text{Na}_2\text{C}_2\text{O}_4$, to loaded IonQuest which has extracted lutetium from an aqueous phase. After a fifteen-minute equilibration which included vigorous shaking of the system to ensure adequate contact between the two phases, an aqueous phase with a distinct precipitate was seen. This precipitate was probably $\text{Lu}_2(\text{C}_2\text{O}_4)_3$. The remaining organic medium was then subjected to different experiments.

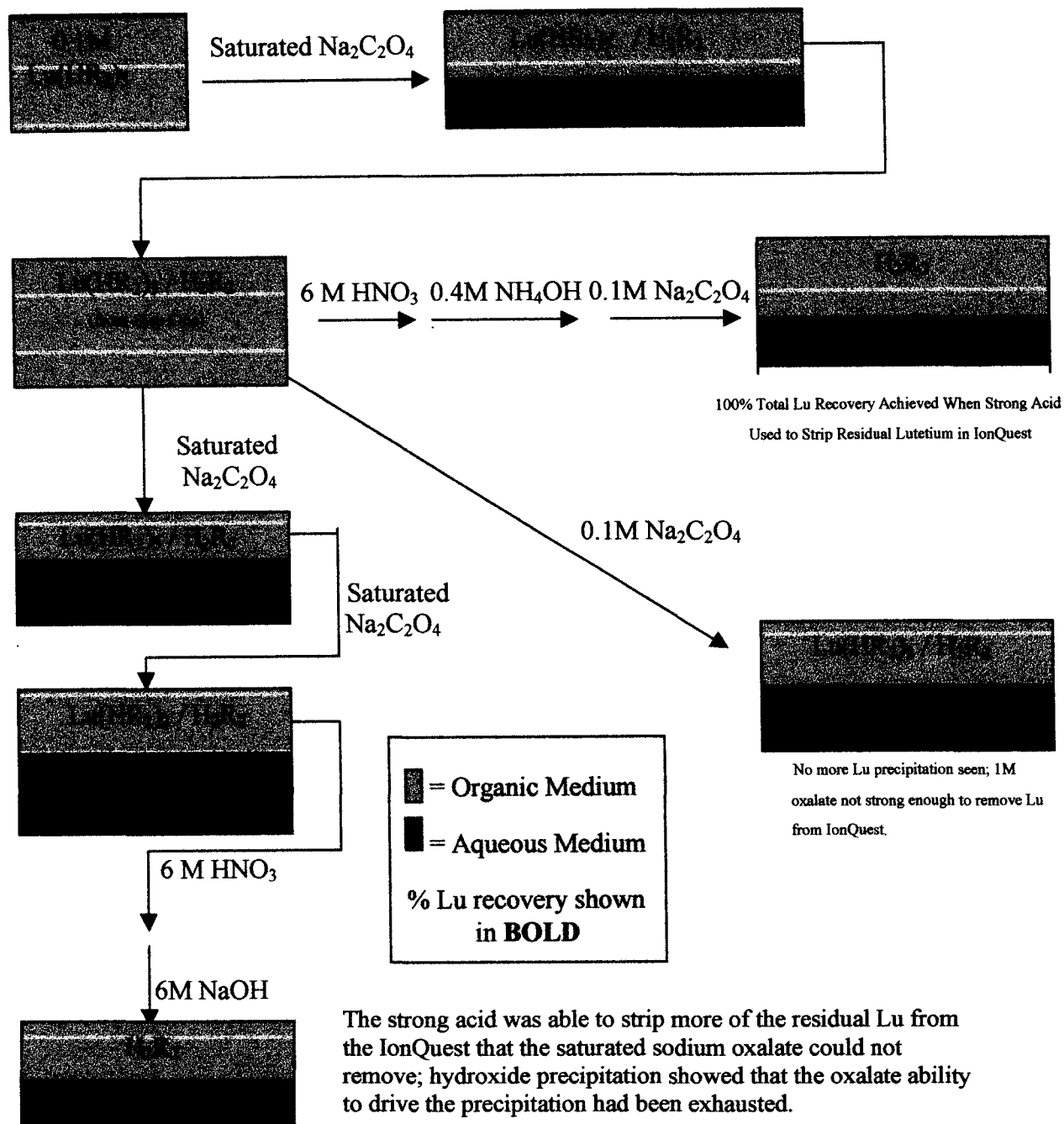
The initial experiments performed on the residual organic phase were the traditional stripping procedures. Nitric acid of 6M concentration was added to the organic phase to attempt to strip all of the remaining lutetium from the IonQuest. The stripped aqueous phase was then neutralized with 0.4 M NH_4OH to a pH of approximately 3-4, which was found in separate experiments to be the optimal pH for lutetium oxalate precipitation. Addition of various different oxalate salts, usually $\text{Na}_2\text{C}_2\text{O}_4$ or $\text{K}_2\text{C}_2\text{O}_4$, to the neutralized aqueous media yielded a substantial amount of $\text{Lu}_2(\text{C}_2\text{O}_4)_3$ precipitate, indicating that the initial $\text{Na}_2\text{C}_2\text{O}_4$ strip had failed to remove all of the lutetium from the IonQuest.

The second experiment on a portion of the residual organic medium from the initial $\text{Na}_2\text{C}_2\text{O}_4$ strip involved the addition of a 0.1M $\text{Na}_2\text{C}_2\text{O}_4$ solution. No precipitate was seen in this procedure, suggesting that a 0.1M concentration of oxalate is not adequate to bring the remaining lutetium held by the IonQuest into an aqueous phase.

Another portion of the residual organic medium from the initial strip was also subjected to a third series of experiments in which another solution of saturated $\text{Na}_2\text{C}_2\text{O}_4$ was added. After a fifteen-minute equilibration, more $\text{Lu}_2(\text{C}_2\text{O}_4)_3$ precipitate was recovered. The remaining organic phase after this second equilibration was treated with yet another saturated $\text{Na}_2\text{C}_2\text{O}_4$

solution; no more precipitate could be recovered in this case, suggesting that either all of the Lu had been removed from the IonQuest in two saturated $\text{Na}_2\text{C}_2\text{O}_4$ strips or that some of the Lu could not be precipitated with any further addition of saturated $\text{Na}_2\text{C}_2\text{O}_4$ solution. A sample of the second residual organic phase was subjected to a 6M HNO_3 strip, neutralized with a strong base, and a small amount of gelatinous precipitate, $\text{Lu}(\text{OH})_3$, was observed. These results showed that even with subsequent additions of saturated $\text{Na}_2\text{C}_2\text{O}_4$ solution, all of the lutetium was not being stripped from the IonQuest because the stripping power of the $\text{Na}_2\text{C}_2\text{O}_4$ solution seemed to be exhausted. By roasting the $\text{Lu}_2(\text{C}_2\text{O}_4)_3$ to Lu_2O_3 , gravimetric analysis showed that the saturated $\text{Na}_2\text{C}_2\text{O}_4$ strips were inferior in their ability to remove the lutetium from the IonQuest as compared to the stripping efficiency of 6M HNO_3 . Thus, it could be that something other than the oxalate ion was the driving force of the strip, possibly the concentration of H^+ . The process and gravimetric results of the experiments are shown in Figure I. The percent total lutetium recovery for a given step is shown in parentheses.

B. Previous experiments by Schweitzer et al. compared the driving force in a strip using saturated oxalic acid to that in a strip using saturated $\text{Na}_2\text{C}_2\text{O}_4$ (as described above). The lutetium recovery of a saturated $\text{H}_2\text{C}_2\text{O}_4$ was still found to be inferior to the recovery of lutetium in a 6M HNO_3 strip. However, the lutetium recovery in a strip using saturated $\text{H}_2\text{C}_2\text{O}_4$ was found to be slightly better than a strip using saturated $\text{Na}_2\text{C}_2\text{O}_4$; thus, the hydrogen ion may be the driving force in the stripping procedure.

Figure I

To test the power of H^+ in stripping compared to $C_2O_4^{-2}$, a qualitative comparison was performed. When saturated $K_2C_2O_4$ was added to an organic IonQuest solution loaded with lutetium, little white precipitate formed compared to the amount of precipitate that was seen when 0.2M oxalic acid was added to the same organic solution. Addition of another equivalent volume (1:1 organic: aqueous ratio) of 0.2M oxalic acid yielded more white precipitate, whereas another addition of saturated $K_2C_2O_4$ yielded almost no more precipitate. By adding saturated oxalic acid to the latter organic phase, even more white precipitate was seen. The results show that the H^+ in the oxalic acid is performing a role in the stripping procedure that is not achieved by the potassium oxalate solution; the hydrogen ion appears to be a much greater driving force in the stripping mechanism at the molecular level than the oxalate ion. The qualitative procedure is shown in Figure II.

Other experiments were performed that demonstrated the relative weakness of the oxalate ion by itself as a driving force in lutetium oxalate precipitation. An attempt was made to precipitate lutetium oxalate from a lutetium-containing aqueous solution by the addition of excess oxalate. Excess oxalate was known to be required because earlier experiments had shown that addition of an equimolar amount of oxalate ion did not precipitate all of the lutetium in the aqueous phase. Various amounts of excess oxalate in the form of saturated oxalic acid were investigated, with the results shown below. The lutetium was contained in a 5.0M HNO_3 aqueous phase; because of this, neutralization to the optimal pH was imperative. It required 50% excess oxalic acid to adequately precipitate all of the lutetium, as shown in Figure III.

Figure II

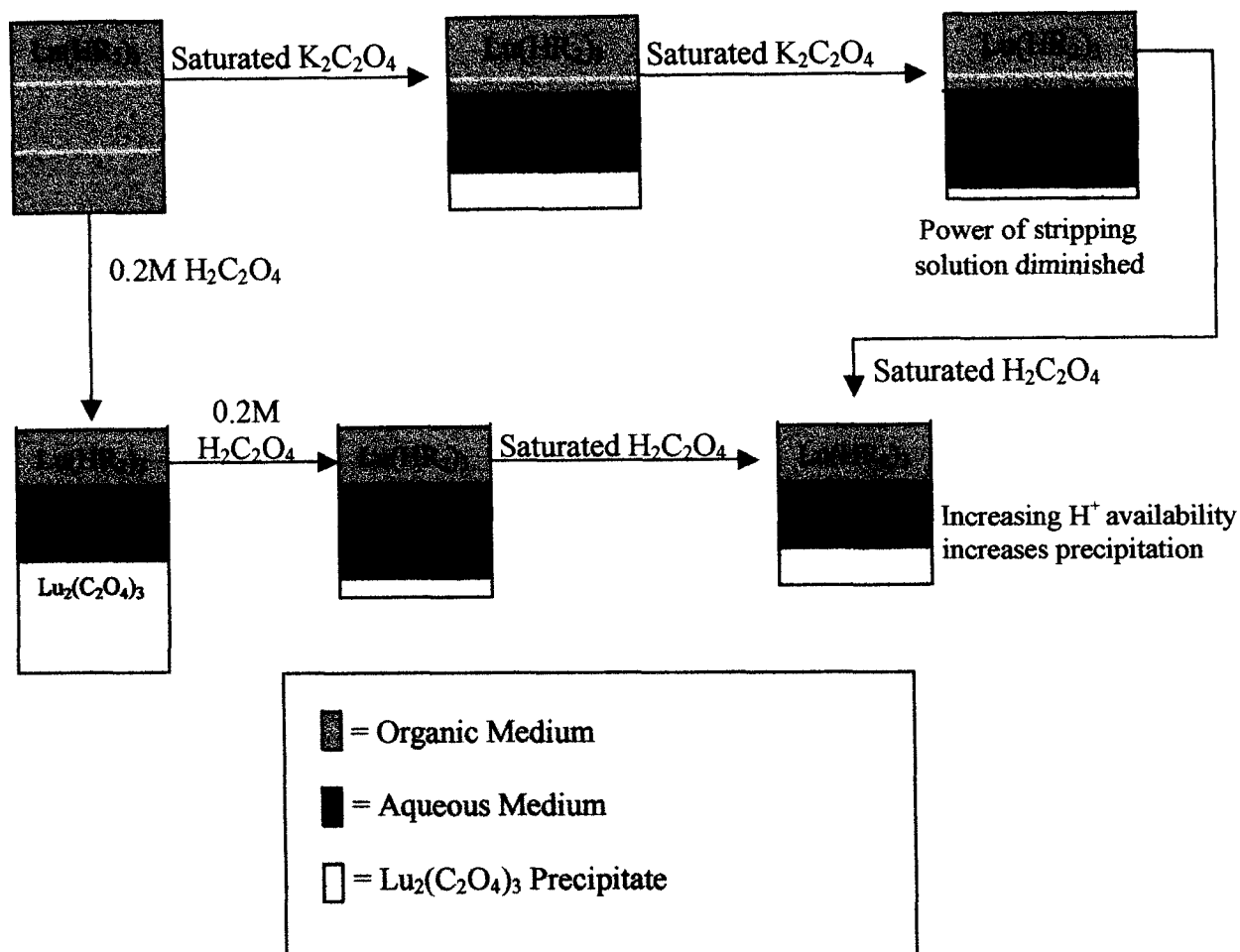
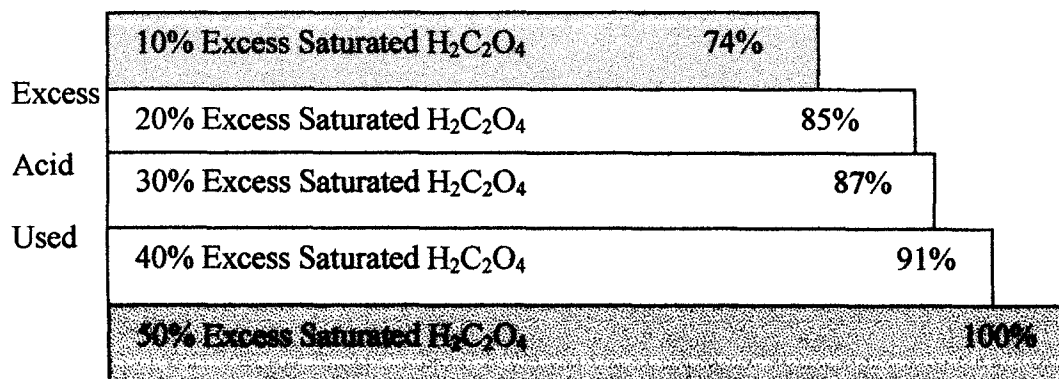


Figure III



Percent of Lutetium Precipitating From Aqueous Phase

The results show that a 50% excess of saturated oxalic acid is required for complete lutetium precipitation from the aqueous phase. By increasing the amount of excess of oxalic acid, the hydrogen ion concentration is not markedly changed; the availability of oxalate is changed, however. The increase in oxalate required for complete precipitation of lutetium shows that even by utilizing LeChatelier's principle, oxalate would not be very beneficial to strip lutetium from an organic phase for which it has a very strong affinity. For this reason, hydrogen ion is believed to be the main driving force in the direct oxalate stripping of lutetium from IonQuest rather than the oxalate ion itself.

C. Since the H^+ concentration was shown to be important in the stripping reaction, the efficiency of the strip should increase with increasing availability of hydrogen ion. However, the increased presence of the hydrogen ion is usually associated with a stronger acid, causing a drop in pH which is not beneficial to oxalate precipitation. A way to get around this fact is to use saturated oxalic acid in an acidic medium, rather than pure water. A weak acid aqueous solution was selected as a solvent for investigation, because if a strong acid were used the pH would be too low and neutralization steps would have to be performed for optimal precipitation conditions. A solution of 1M acetic acid was saturated with oxalic acid and used to perform a strip. The 1M acetic acid / sat'd oxalic acid solution was mixed with loaded IonQuest organic medium. After equilibration, gravimetric analysis showed that 83% of the lutetium had been recovered in one strip, a great improvement over the 60% that had been achieved by oxalate salt addition. Further experiments showed that by increasing the equilibration time to 30 minutes rather than the normal fifteen minutes increased lutetium recovery efficiency in some instances, but at most by 2-3 percent. Additionally, a 1:1 organic:aqueous ratio was found to be the optimal condition for

the strip to occur; any substantial deviation from this equal ratio of volumes subsequently decreased the lutetium recovery efficiency. Various other acid combinations were tested in experiments; up to 91% lutetium recovery was seen in some instances. Solvent acids were chosen that had pKa values between 2.5 and 4, the optimal pH of lutetium oxalate precipitation. Unless otherwise noted, the strips were performed under conditions of fifteen-minute equilibration and a 1:1 organic:aqueous ratio. The results are shown in Figure IV.

Figure IV

Acid Used	1 M acetic acid / saturated oxalic acid	83%
	2 M acetic acid / saturated oxalic acid	90%
	2 M acetic acid / saturated oxalic acid, 2:1 org:aq	88%
	3 M acetic acid / saturated oxalic acid	87%
	2 M formic acid / saturated oxalic acid	72%
	1 M chloroacetic acid / saturated oxalic acid	91%

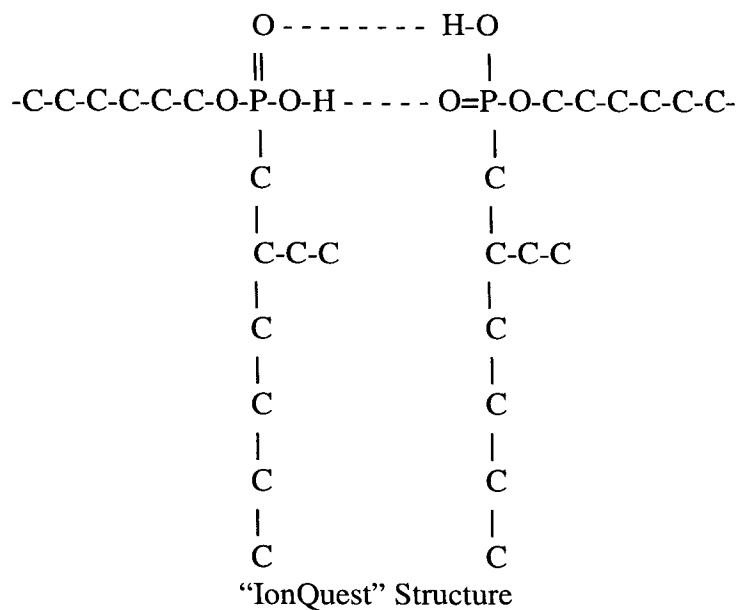
Percent Lutetium Recovered In Process Using Organic Extractant

The mechanism of this “dual acid” addition is at the heart of its unique performance. The addition of only oxalic acid to a loaded organic media is not as effective in removing as much lutetium as an acetic/oxalic solution because of the hydrogen driving force it possesses. For each oxalate that is used to precipitate $\text{Lu}_2(\text{C}_2\text{O}_4)_3$, three hydrogen ions are transferred from the aqueous to the organic phase. This causes a drastic reduction in the hydrogen ion driving force which the aqueous phase uses to power the strip of lutetium from the IonQuest. As this driving force is diminished, so is the stripping ability of the aqueous phase; the lutetium recovery is

compromised as a result. However in the acetic acid/saturated oxalic acid system, the pH is held relatively constant and thus the hydrogen driving force is greatly increased by the presence of a second weak acid. As the aqueous phase loses hydrogen to the IonQuest, the hydrogen ion is replaced by the second weak acid; the pH stays constant, the driving force does not decrease, and the ability to precipitate $\text{Lu}_2(\text{C}_2\text{O}_4)_3$ is not depleted. The beauty of the system is that since a weak acid is used so there is no need to resort to traditional neutralization procedures before precipitation can occur.

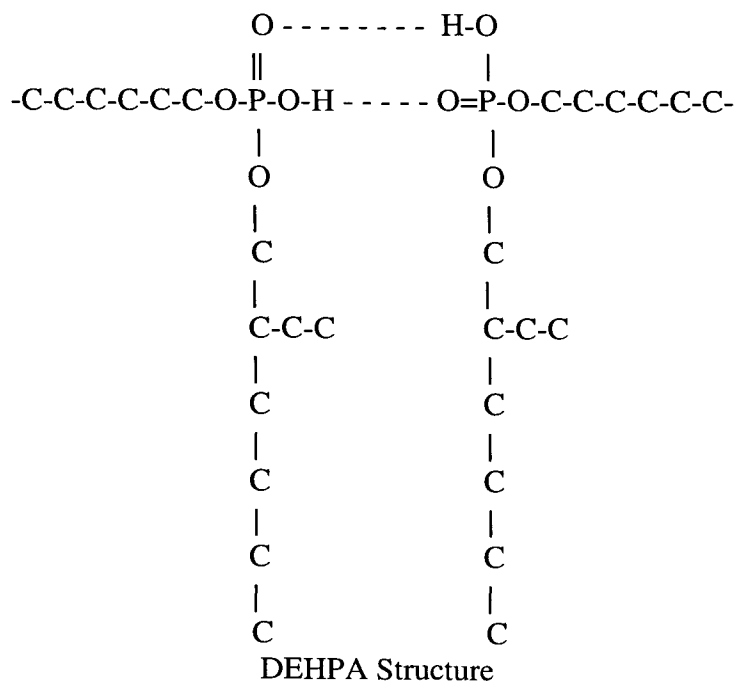
Why, then, is 100% of the lutetium not recovered from the IonQuest with the constant hydrogen driving force? The reason is perhaps found in the composition of the IonQuest extractant. The structure of the dimerized IonQuest that is involved in lutetium binding is shown in Figure V. The site of lutetium binding is the “ring” which is formed by hydrogen bonds. Three of these “rings” are used as binding sites for each lutetium atom.

Figure V



There is a DEHPA impurity present in the IonQuest. DEHPA holds lutetium much more strongly than IonQuest; the structure of DEHPA is shown in Figure VI. The additional oxygen atom in the ethylhexyl side chain results in an even greater affinity for lutetium than is present in IonQuest. Experiments showed that lutetium in loaded DEHPA could not be precipitated by the addition of oxalate or a weak acid /saturated oxalic acid solution due to lutetium's strong affinity for DEHPA; the method of effective lutetium removal from DEHPA was very strong acid addition. Thus, the DEHPA impurity in IonQuest is in effect locking up some of the lutetium so that it can not be precipitated by weak acid addition.

Figure VI



CONCLUSIONS

A viable alternative to the traditional lutetium stripping method from an organic extractant has been found. The expected decrease in $[H^+]$ during oxalate precipitation is offset by the presence of a second weak acid. The second weak acid's contribution to the system stabilizes the pH and increases the driving force of the stripping reaction. It is believed that any aqueous solution weak acid with a pK_a between 2.5 and 4 will suffice as a solvent for saturated oxalic acid; chloroacetic acid, while it produced slightly better lutetium recovery, is not a good alternative to acetic acid because of its hazards.

While a 90% lutetium recovery was achieved in the 2M acetic acid/saturated oxalic acid system, the yield still did not approach the 100% lutetium recovery that could be achieved by strong acid stripping. It appears that the ten percent of lutetium that could not be recovered serves a "loading capacity," as it is locked up in IonQuest impurities. If a stripped organic phase still containing ten percent of the original lutetium is used to extract lutetium from a mixture of rare earths again, a subsequent 2M acetic acid/saturated oxalic acid strip will again achieve 90% lutetium recovery. Even though ten percent of the lutetium can not be recovered without resorting to strong acid addition, the new method proves beneficial because an organic extractant can be reused over and over again, producing 90% lutetium recovery each time, keeping a constant ten percent of the lutetium locked in the Ionquest which is never really lost. Reuse of IonQuest extractant thus serves as a vehicle for lutetium extraction from mixtures of rare earths, and allows efficient removal with the addition of a weak acid/saturated oxalic acid solution.

Thus, the hypotheses of the project are confirmed. Direct oxalate extraction is indeed a viable alternative to the traditional methods used for removal of the lutetium from the organic

phase. Without resorting to strong acid stripping, base neutralization, and oxalate addition, these three steps are reduced to one. With the decreased complexity of the new process, the hazards of working with dangerous chemicals are lessened, as strong acids and bases are no longer employed. In addition, the dangerous ammonium nitrate side product that is produced in the neutralization step of traditional method is not produced in the new procedure. The new procedure for direct oxalate extraction discussed in this paper is so beneficial that the company which subsidized this project, a manufacturer of PET Scanning machines, is considering the pursuit of a United States patent so that it can secure the use of the method for the production of a lutetium-based photoreceptor used in the PET instruments.

Works Cited

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