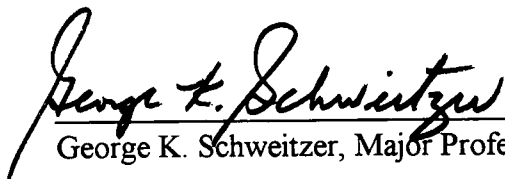
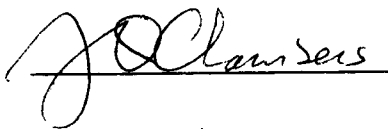


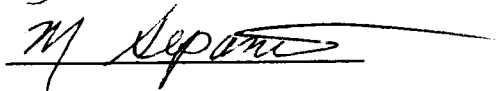
To the Graduate Council:

I am submitting herewith a thesis written by Wade Phillip Ivey entitled "Experimental Planning for Industrial Separation of Pure Lutetium." I have examined the final copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Chemistry.


George K. Schweitzer, Major Professor

We have read this thesis and
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J. O. Chambers


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Accepted for the Council:


Associate Vice Chancellor and
Dean of The Graduate School

EXPERIMENTAL PLANNING FOR
INDUSTRIAL SEPARATION
OF PURE LUTETIUM

A Thesis

Presented for the

Master of Science

Degree

The University of Tennessee, Knoxville

Wade Phillip Ivey

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ABSTRACT

Electrolytic reduction of Yb^{3+} at a Hg cathode to the somewhat unstable Yb^{2+} was performed in various aqueous media in an attempt to separate Yb^{3+} from Lu^{3+} by forming relatively insoluble YbSO_4 . The effects of the aqueous medium, current, and pH on the formation of Yb^{2+} and YbSO_4 were examined. The best experimental conditions for the reduction of Yb^{3+} to Yb^{2+} and the formation of YbSO_4 were found to be: 0.20-M Yb^{3+} , 0.40-M H_2SO_4 , and 0.50-M $(\text{NH}_4)_2\text{SO}_4$ in the aqueous phase, a direct current of 0.20-A, and a pH of 4.0-5.4(± 0.3). Under these conditions, approximately 90-95% of the Yb^{3+} in solution was removed as YbSO_4 .

Several experiments were conducted to determine suitable conditions for counter-current solvent extraction for the separation of Lu^{3+} from a mixed lanthanide ore. A mixer-settler type counter-current solvent extraction process was used. The effects of settling time between the aqueous and organic phases, chemical equilibrium time between the lanthanides and the extractant mono-(2-ethylhexyl)2-ethylhexyl-phosphonate (IQ-801) in kerosene, the load concentration of the aqueous phase, and the equilibrium acidity of the aqueous phase were studied. The experimental results indicated that an adequate settling time was approximately 30 sec, and a mixing time of 2 min was sufficient to reach chemical equilibrium. Furthermore, the aqueous load concentration of 0.15-M Ln^{3+} in 1.4-M to 2.2-M HCl along with an organic phase of 0.45-M IQ-801 in kerosene was satisfactory for limiting emulsion formation while properly utilizing the extractant. The optimum equilibrium acidity range in the aqueous phase was found to be 1.4-M to 1.9-M

HCl using a titration method and 1.6-M to 2.2-M HCl using inductively coupled plasma/mass spectrometry for analysis.

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CHAPTER I

BACKGROUND TO LANTHANIDE SEPARATIONS

A. INTRODUCTION

With recent applications of lanthanides and their compounds, there is a growing need for very pure metallic and oxide forms of the lanthanides. The lanthanides are increasingly being used in the electronic and steel industries as materials for applications such as: catalysts, ceramics, high temperature superconductors, phosphors, permanent magnets, and scintillation crystals^{1,2}. Many of these applications depend on very pure lanthanides. To obtain the purity of individual lanthanides required for such applications, a very good process is needed to separate the lanthanides from each other.

Group and individual separations of the lanthanides are very difficult for several reasons. First, the size and normal oxidation states of the lanthanides are very similar. The ionic radii of the lanthanides vary only approximately 1.5% from one element to the next and under normal conditions, all lanthanides possess an oxidation number of +3³. In addition to size and normal oxidation state, the structure of the electrons of the external shell is very similar for most of the 14 lanthanides. Finally, the electrochemical and complexation patterns of the lanthanides are quite similar. These factors make lanthanide separations among the most difficult separations in chemistry.

B. HISTORICAL METHODS

Two classical separation methods for the lanthanides are fractional crystallization

and precipitation methods. Both processes are rarely used today because of the time required and the tedium of the methods. For example, in 1907 Urbain prepared 99.9% Yb^{3+} by separating it from Lu^{3+} after 15,000 successive nitrate crystallizations. However, he was only able to produce microgram quantities³. Although these methods are very time consuming, modern methods can reduce the time considerably when comparing the same elements to be separated in both historic and modern methods.

C. ION EXCHANGE

One modern method in which elements, including the lanthanides, are separated is ion exchange. Cation exchange chromatography is one type of ion exchange used for separating the lanthanides. Two types of stationary phases used in cation exchange chromatography were developed in the 1940's for the Manhattan project. Cation exchange chromatography utilizes either natural zeolites or synthetic polymer resins as the stationary phase. Natural zeolites have all but been replaced by synthetic resins. Cation exchange chromatography involves adsorption of the lanthanide ions with an exchange for protons on the resin. The following equation shows the equilibrium process of the cation exchange mechanism,



where HR represents the protonated cation exchange resin and Ln^{3+} represents any lanthanide ion. Typically, the lanthanide ions exchange with protons on the cation resin to a slightly different extent in a non-complexing medium, but it is usually the elution process

that is the major factor in separating the ions³. Therefore, choosing an appropriate eluent for specific separations is very important for achieving high separation factors. Another variable in cation exchange separations is complexation of the lanthanide ions in the initial aqueous phase. Complexation of the lanthanide ions can change the resin/solution distribution of the lanthanides considered which may help or hinder separation.

Cation exchange resins can be categorized according to the functional groups of the polymer. One category of cation exchange resins is the sulfonate-containing polymers. Polystyrene cross-linked with divinylbenzene (1-16%) functionalized with sulfonic acid is a common sulfonate-containing resin. This type of resin has a high capacity (5 equivalents/kg dry resin) and the equilibrium and kinetics depend primarily on the percent cross-linking⁴. More cross-linking in the resin causes less swelling, higher selectivity, and less diffusion on the resin. The kinetics of the equilibria using sulfonate cation exchange resins are diffusion controlled.

Sulfonate cation exchange resins can be used with complexing or non-complexing aqueous media. When these cation exchange resins are used in complexing aqueous media, the ligands are usually anions of organic acids like α -hydroxyisobutyric acid⁴. Systems involving complexation of the lanthanides typically give better separation coefficients than other types of systems and thus are used more often in lanthanide separations, especially with the light lanthanides^{5,6}. Story et al. were able to separate all of the lanthanides using the resin Dowex 50W X8 with 2-hydroxyisobutyric acid as the eluent. However, the resolution between Yb^{3+} and Lu^{3+} was not complete⁷. Furthermore, the concentration of each lanthanide was only 5×10^{-4} M which is too low a concentration

for industrial separations.

A second group of cation exchange resins are those which do not contain sulfonate functional groups. Resins containing a carboxylate functional group make up one group of non-sulfonate cation exchange resin. A second group of non-sulfonate resins are those containing organophosphorus functional groups. Both types of resins typically give better separation coefficients (the ratio of the distribution coefficients of two elements) for the lanthanides than do the sulfonate resins, but the kinetics are slower.

Cation exchange resins can also be used in mixed aqueous-organic media. It has been demonstrated that in some systems alcohols have enhanced the separability of the lanthanides⁸. Separations are typically enhanced because Ln^{3+} ions are hydrated less due to the reduced water content in solution which increases the absorption of Ln^{3+} ions on the resin. Under these conditions, however, separation factors between certain Ln^{3+} ions have been shown to decrease.

Anion exchange chromatography is another method of ion exchange used for separating lanthanides. Faris⁸ demonstrated that the separation of lanthanides in the lactate form using the resin AG Dowex I X4 (100-200 mesh) was achievable, but the separation coefficients between the lanthanides were lower than using sulfonate cation exchange resins with alpha-hydroxyisobutyric as the eluent. He also determined that the use of mixed solvents, rather than only water, was needed for very good separations. De Corte⁹ et al. also found that anion exchange resins could be used for separating lanthanides in an oxalic acid medium. They concluded that only group separations occurred and that individual lanthanides could not be separated from each other under those conditions.

D. SOLVENT EXTRACTION

1. Background

The second modern lanthanide separation technique is solvent extraction. Solvent extraction is a technique in which a substance is transferred from one liquid phase to another liquid phase. The two liquid phases, therefore, should be immiscible. Typically, one of the liquid phases is aqueous and the second phase is organic in nature. Usually, the species to be separated are initially in the aqueous phase and partially distribute themselves into the organic phase. The organic phase contains an extractant, often dissolved in a proper organic diluent, which reacts with the lanthanides in one or more of several ways: solvation, chelation, ion-pairing, and ion exchange. Marcus¹⁰ discusses the details of each type in depth.

There are several applications of solvent extraction. Each application utilizes solvent extraction over other separation techniques, such as crystallization and distillation, because of the improved effectiveness and it is less time consuming. Some industrial applications of solvent extraction include:¹¹ separation of azeotropic mixtures (e.g., extraction of acetic and formic acid from aqueous media), separation of mixtures with high boiling points (e.g., vitamins), separation of analytes with similar boiling points (e.g., hydrocarbons from aromatics), extraction of metals from wastewater (e.g., copper), recovery of nuclear fuels (e.g., Purex process), and extraction of metals from ores (e.g., lanthanides).

Solvent extraction systems can be broadly defined by two concepts: 1) the nature of the extracted species and 2) the type of the extractant used. In general, the types of

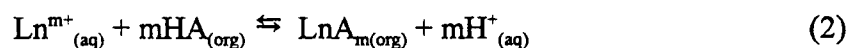
species which favor the organic phase over the aqueous phase are those which have a low charge density. Also, if a species is non-polar and does not contain a very electronegative atom, it favors the organic phase over the aqueous phase. Although these generalizations are typically true, the addition of aqueous phase modifiers and changes in solvent parameters such as dielectric constant and hydrogen bonding structure may cause the analyte to distribute itself more or less in the aqueous phase.

The second broad category for solvent extraction is the type of extractant used¹⁰⁻¹². One process is based using inert extractants. These extractants typically are used for non-polar species and thus are not favorable for lanthanide extraction because of the charge of the lanthanide in solution. Basic extractants are a second group of extractants. This type of system is based on the ability of the extractant to donate electrons which allow for solvation of a cation. The basic extractant tri-n-butylphosphate (TBP) is commonly used in the extraction for uranyl nitrate. Chelating agents make up a third class of extractants. Chelating agents typically form strong bonds with metal ions. An extractant of this type may be charged or neutral and can contain various numbers of displaceable hydrogens. The fourth group of extractants is the ionic extractants. These may extract cations (e.g., tetraphenyl arsonium) or anions (e.g., tetraphenylboride). The final class of extractants is the acidic extractants. The mechanism of the acidic extractants is an exchange reaction between metal ions and displaceable hydrogen ions on the extractant. The acidic extractants are the type usually used in lanthanide separations.

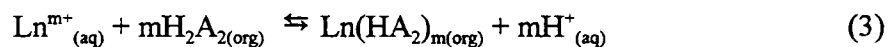
In 1957, Peppard et al.¹³ demonstrated that separation of the lanthanides using the acidic extractant di(2-ethylhexyl) phosphoric acid (DEHPA) had key advantages over TBP

which had been the most commonly used extractant for lanthanide separation. Since his work, several authors¹⁴⁻²¹ have used DEHPA for lanthanide separations. In fact, since Peppard's findings, DEHPA has been the most thoroughly studied and applied acidic extractant for lanthanide separations²². A second acidic extractant that has been investigated^{1,23-27} for lanthanide separations is mono-(2-ethylhexyl)2-ethylhexylphosphonate (IQ-801). It offers advantages over DEHPA including: less acid is needed for stripping, it is less susceptible to iron poisoning, and it shows reduced emulsion formation.

Extraction of the lanthanides from an aqueous phase to an organic phase using acidic extractants causes the extractant to lose hydrogen ions into the aqueous phase. The mechanism is very similar to cation exchange chromatography. The fundamental equation for extraction of lanthanides using acidic extractants is:



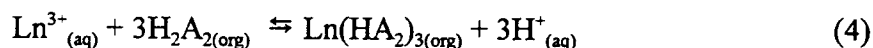
where Ln^{m+} represents any lanthanide and HA represents any acidic extractant. This equation is used if the extractant is in the monomer form. Many acidic extractants used in lanthanide separations form dimers. The equation that represents the separation for these extractants in the dimer form is:



Two important parameters used to describe the feasibility for the separation of elements are the distribution coefficient (D) and the separation coefficient, or separation factor (α). By definition, D is the ratio of the concentration of an element in the organic

phase to the concentration in the aqueous phase ($D = [\text{Ln}^{3+}]_{(\text{org})} / [\text{Ln}^{3+}]_{(\text{aq})}$). Values of D less than unity indicate the ion is more concentrated in the aqueous phase, whereas values of D greater than unity indicate the ion is more concentrated in the organic phase. For each system, every element has a specific value of D . Changing the conditions of the system changes the value of D for each element. The second important parameter used to indicate the feasibility of a system for separating elements is α . α is defined as the ratio of the distribution coefficients for two elements ($\alpha = D_{\text{Ln},1} / D_{\text{Ln},2}$). By definition, α is written so that it is always greater than unity. The greater the value of α , the greater separation there is between the two elements. It is evident that for the most efficient separation conditions for two elements, the conditions need to be such that the D value for one element is greater than unity and the D value for the other element is its reciprocal.

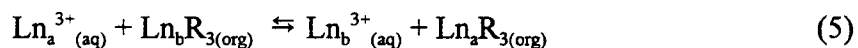
One condition in solvent extraction that can be regulated to increase separation is the load concentration of the lanthanides in the aqueous phase. From the following equation,



it can be demonstrated that if the initial concentration of lanthanides in the aqueous phase saturates the extractant, the optimum separation condition is not maintained. On the other hand, if the initial concentration of lanthanides in the aqueous phase is very low compared to the extractant, the optimum separation condition is maintained but the cost-effectiveness of the system is poor. For each system in solvent extraction, the initial load concentration is experimentally determined for optimum separation and cost-effectiveness.

The second major condition which must be met for effective separation in solvent extraction is the acidity in the aqueous phase. There is a twofold reason why the acidity in the aqueous phase is important. First, from equation (4), it can be shown that if the acidity in the aqueous phase is very low, the equilibrium favors the right. Under these conditions, the lanthanides to be separated are all extracted into the organic phase and the values of D for all of the lanthanides are high. Since the values of D for the lanthanides are quite similar, little to no separation occurs because there is little partial distribution of the lanthanides between the two phases. For optimum separation to take place, one lanthanide must have a D favoring the organic phase and the other lanthanide must have a D favoring the aqueous phase. Likewise, if the acidity in the aqueous phase is very high, little or no separation occurs since almost all of the lanthanides remain in the aqueous phase. Therefore, the acidity must be adjusted such that one element has a D which favors the organic phase and the other element has a D which favors the aqueous phase.

The second reason the acidity is important in solvent extraction is that under perfect acidic conditions, 50% of the total lanthanides extract into the organic phase and 50% remain in the aqueous phase. If this acidity is experimentally found for each specific system, then adjustments of the aqueous phase acidity are reduced to keep the system at optimum conditions. When there is a 50/50 ratio of lanthanides in each phase, there is no exchange of protons. Rather, the exchange is simply between the lanthanides. Reaction (3) simplifies to the following equation:



The reaction simplifies to a simple cation exchange reaction between two metals instead of the exchange between the metal and a proton.

Although the optimum load concentration of the lanthanides and the acidity of the aqueous phase can be experimentally found, there is a need for successive extractions because the separation coefficients between adjacent lanthanides are very small. The separation factors for neighboring lanthanides are typically only 1.5-2.5²⁸. To produce relatively pure lanthanides (99.9% or greater), the extraction process theoretically needs to be repeated 17 or more times, depending on the desired element and purity. To produce 99.99% pure Lu theoretically requires approximately 23 stages because the separation factor between Lu^{3+} and Yb^{3+} is roughly 1.5 under good separation conditions. One way to perform the required number of stages is to bring the organic and aqueous phase to equilibrium by shaking the phases in a vessel (e.g., a separatory funnel), and then removing the aqueous layer and extracting it with a fresh organic phase. One disadvantage of using this method is the amount of the desired lanthanide in the organic phase after a number of stages is extremely small compared to the initial amount in the aqueous phase. For example, if the initial concentration in the aqueous phase of the desired Ln^{3+} was 1.00-M and the separation coefficient between the desired Ln^{3+} and the adjacent Ln^{3+} was such that 30 stages were needed for the desired purity, and half of the desired Ln^{3+} was extracted into the organic phase in each stage, then only 9.31×10^{-10} M of the pure Ln^{3+} would be in the organic phase. A second major disadvantage using successive solvent extractions is the need for large quantities of solvent and extractant. This problem is a major concern for those wishing to make large quantities of pure

lanthanides. Although the desired purity of the lanthanides is achieved using successive extractions, a continuous successive extraction method is needed for large-scale production of pure lanthanides to give a high degree of recovery and a considerably concentrated extract.

One way to reduce the time and solvent waste needed in singly successive solvent extractions is the use of continuous counter-current solvent extraction. This is a method in which the organic and aqueous phases are moved in opposite directions from one another after the initial extraction. This method is ideal for lanthanide separations since the separation factors of the lanthanides are so small. The practice of continuous counter-current solvent extraction is fairly simple. Regardless of the type of system used, the two phases are moved in opposite directions from each other. Some systems (columns) use differences in density of the two phases to move the phases in opposite directions, and some systems (mixer-settlers) use pumps and/or gravity to move the two phases in opposite directions. Figure 1 (p. 12) is a diagram of a general counter-current apparatus.

There are two types of counter-current extraction apparatuses used in the purification of lanthanides. The first is the use of different types of columns and the second is the use of separated mixing and settling chambers (mixer-settlers).

2. Counter-Current Columns

There are several types of columns used for continuous counter-current solvent extraction. The first types are those based on columns without energy input. The simplest design is when the light phase (usually the organic phase) is added to the bottom of the column and the heavy (usually the aqueous phase) phase is added to the top of the

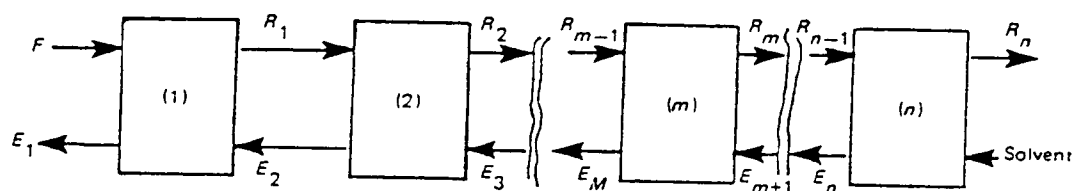


FIGURE 1

DIAGRAM OF A GENERAL COUNTER-CURRENT SET-UP

column. The two phases mix in the column as they pass each other. The contact time between the two phases in this type of column is minimal and thus is only used for simple separations in which only a few stages are required. Columns utilizing no energy input are improved if they are packed, contain baffles, or have sieve plates within the column because they increase non-axial mixing and thereby mass transfer is increased. However, packing, baffles, or sieve plates within a column reduce the overall throughput per unit cross-sectional area and larger diameter columns are needed for the same throughput as the columns without packing, baffles, or sieve plates.

The mass transfer and efficiency of counter-current columns are improved if a supply of energy is given to the column. The first type of these columns involves mixing the two phases within the column by some type of mechanical device. Often with these columns, there are baffles inside the column to permit separation of the two phases between the mixing zones. The simplest is the rotating disc contactor (RDC) in which a disc is placed through the center of the column and is rotated to mix the two phases. The RDC is a very effective extractor which is used for difficult separations. However, the loading limits of lanthanides in a RDC are fairly small. A second type of mechanically mixed column is the Rushton column which utilizes turbine agitators which cause more shear in the mixing zones. Both the RDC and Rushton columns are subject to axial mixing which reduces separation efficiency. Therefore, the Asymmetric Rotating Disc Extractor (ARD) was developed. This column has the mixing shaft off-center and utilizes a vertical sheet which separates the mixing and transport zones. This column decreases back-mixing and axial mixing which increases the efficiency. Two other mechanically mixed columns

are the self stabilizing high efficiency extractor and the Graesser contractor. All mechanically mixed columns show a decreased separation efficiency with increasing column diameter. These columns have been constructed to 3.5-cm in diameter and can handle medium to large throughputs. These mechanically mixed columns are quite complex and expensive to construct.

The second type of column which utilizes energy input is the pulsed-type column. Unlike the mechanically mixed columns which mix the two phases using an agitating device, the pulsed-type columns promote phase mixing using some form of oscillating pulse. Two types include the pulsed-packed and pulsed-sieve plate columns. Both use a piston pump or diaphragm pump to cause the entire liquid inside the column to vibrate. These pulses cause the mass transfer to increase and the droplet size of the two phases to decrease which increases the number of theoretical plates per unit length. Although systems which tend to emulsify easily cannot be used with pulsed columns, systems which require high throughputs are favorable in these columns. Another way the phases can be mixed is to pulse the plates inside the column instead of pulsing the entire liquid. Such columns are termed reciprocating plate columns. Two commercially available reciprocating plate columns are the Karr and Prochazka columns. In both types, sieve plates with small holes inside the column are pulsed. The advantage of pulsing the plates instead of the entire volume of liquid is the energy requirement to operate such a column is reduced. A second advantage of reciprocating plate columns is the larger throughput and the larger possible diameters of the column. Berger²⁹ and Bailes et al.³⁰ discuss specific details for these types of columns.

Although columns can be used to separate lanthanides, they usually lack high efficiencies. All columns have two features which decrease the overall efficiency. First, there is always some back-mixing of the continuous phase which decreases separation efficiency. Second, the velocity distribution of the dispersed phase cannot be completely controlled. These two parameters may distort the concentration profiles of the aqueous phase and extractant. Without the complete absence of back-mixing and complete control of phase velocities, the system is not truly counter-current. Without true counter-current flow, the mixing of the two phases is not 100% efficient and the mass transfer is less efficient. True counter-current conditions are needed to separate the lanthanides in high purity. The industrial method of choice is the mixer-settler system.

3. Mixer-Settlers

Mixer-settlers consist of a series of mixing stages each of which is immediately followed by a settling stage. Many mixer-settlers are of an integral-box design. Figure 2 (p. 16) displays the simplest type designed by Denver Mineral Company in which the mixing and separating chambers are combined into a single unit in which the two phases move counter-current to each other.

The two phases are placed into the mixing stage and are agitated by rotating discs inside the chamber. Several box-type mixer-settlers have been designed which differ only in the type of pump used to mix the two phases in the mixing chamber. These mixer-settlers include the Davy McKee and the IMI turbine pump-mix unit²⁹. After the appropriate mixing time, the two phases flow into a settling chamber and separate from each other. The two phases are then mechanically pumped in opposite directions into

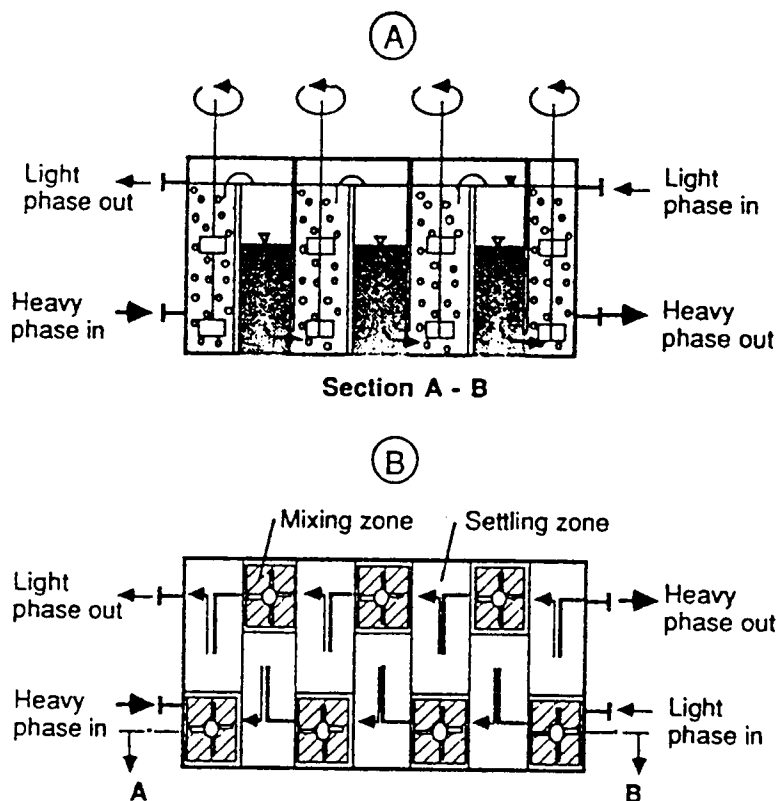


FIGURE 2

DIAGRAM OF A BOX-TYPE MIXER-SETTLER

succeeding mixing stages. The process is continued until the appropriate number of stages for the separation is attained.

The major advantages of mixer-settlers over existing columns are: 1) there is more nearly complete mixing of the two stages, 2) there is more nearly complete phase transfer, 3) mixing and settling efficiencies of near 100% are possible, 4) there are very large throughputs possible because the system can be made very large, 5) the system can be stopped at each stage, 6) scale-up from pilot plant operations to industrial plants is fairly easy, and 7) there can be higher load rates of the aqueous phase. Although the use of mixer-settlers is the most widely used method to separate lanthanides, they do have some disadvantages. First, they are very complex and there is a need for accurate calculations and experimentation for optimum efficiency. Second, the mixer-settlers are large and take up a lot of space. Third, they require large inputs of energy and solvent. Several references³¹⁻³⁶ give detailed insight into the engineering aspect of mixer-settlers, including selection of solvent, estimation of the mixer-volume, estimation of the settler area required, flow rates, and solvent requirements. Slater's³⁷ review of solvent extraction processes in industry gives specific lanthanide separations using mixer-settlers.

The most difficult aspect of producing large quantities of pure Lu is the separation of Lu from Yb, the lanthanide adjacent to Lu. It is proposed that if Yb could be completely removed from the mixture of lanthanides prior to the solvent extraction, the number of stages to produce the pure Lu would be dramatically reduced. Not only would the number of stages required be reduced but the quantity of raw lanthanide ore would be reduced to produce large quantities of pure Lu.

CHAPTER II

ELECTROLYTIC REDUCTION OF YTTERBIUM (III)

A. INTRODUCTION

Although very pure Lu is obtained using ion exchange or solvent extraction methods, both processes can be simplified considerably if Yb, the lanthanide adjacent to Lu, is removed completely prior to each process. The separation methods would be simplified because the separation "gap" for Lu is much larger between the other lanthanides than it is between Yb. In other words, the separation "gap" between Lu and Tm, the lanthanide adjacent to Yb, is much larger than the separation "gap" between Lu and Yb which allows for both shorter columns in ion exchange and fewer stages in solvent extraction for the same purity of Lu.

B. METHODS FOR REMOVING YTTERBIUM FROM SOLUTION

1. Amalgam Displacement

One classical method for the removal of metal ions from aqueous solution is displacement by a less noble metal in the form of an amalgam. The metal ions separated using amalgam formation usually are limited to those with oxidation states of (III) or lower³⁸. It has been demonstrated³⁸⁻⁵² that lanthanides which form somewhat stable +2 oxidation states in water can be separated from lanthanides which do not form stable +2 oxidation states in water. One theory is the electrostatic charge of the +3 ions is very high and the water molecules are so tightly bound to the +3 ion that the electrons from an

electrode surface break the oxygen-hydrogen bond of the water molecule rather than penetrate the solvent sphere to reduce the lanthanide by a three-electron reduction.

Reduction of lanthanides which have only a +3 oxidation state is achieved using amalgam displacement, but the relative rate of reduction in comparison to the lanthanides which also have a +2 oxidation state is much slower³⁸. Since Yb has a marginally stable +2 oxidation state in an aqueous medium, amalgam displacement may be one method of separating Lu from Yb.

Historically, amalgam displacement has been the most widely used reduction method for the separation of aqueous lanthanides. Several papers demonstrate the use of alkali metal amalgams for the separation of lanthanides which exhibit aqueous divalency from lanthanides which do not^{39-45,53}. The most commonly used medium for the reduction and separation of lanthanides by this method is either an acetate or citrate containing solution. The use of these media allows for higher pH values which helps retard the oxidation of +2 to +3 which is more likely under more acidic conditions.

Marsh⁴¹ states that it is impossible to remove the last 0.01% Yb^{3+} from a solution containing only Yb^{3+} . However, he demonstrated that with the addition of samarium acetate to the Yb^{3+} containing solution, only 0.001% Yb^{3+} remained in solution if the samarium amalgam was removed periodically during the experiment. To achieve this purity, however, several extractions with the sodium amalgam were necessary. Barrett et al.⁴⁵ tried to improve on existing techniques by using a dropwise extraction procedure. A column was filled with a lanthanide citrate solution and a sodium amalgam was introduced dropwise to the top of the column. The sodium amalgam reacted with some of the

lanthanides and the produced lanthanide amalgam fell to the bottom of the column. The authors found that only 90% of Yb^{3+} was removed from a solution containing a mixture of lanthanides.

2. Electrolysis Using Amalgam Cathodes

Not only can partial separation of Yb from Lu be achieved using alkali amalgams, but the combination of electrolysis and amalgam formation can also partially separate the two elements. It has been demonstrated^{44,53} that the combination of electrolysis and lithium amalgams allows partial separation of lanthanides, particularly Eu, Sm and Yb from the others. The rate of electrolysis for lanthanide-amalgam formation is $\text{Eu} > \text{Yb} > \text{Sm}$ and then the remaining lanthanides in increasing atomic number. However, it was shown that the combination of electrolysis and amalgam formation was much better for the separation of the lanthanides if an organic solvent, usually methanol, was used⁵³.

3. Electrolysis Using Mercury Cathode

The third classical method for the separation of aqueous lanthanides is direct electrolysis using a mercury cathode. Both direct amalgam formation and the formation of somewhat stable lanthanide (II) salts, for those lanthanides which possess a stable (II) oxidation state, have been studied. It has been shown⁴⁷⁻⁵⁰ that relatively pure (90-95%) lanthanides with a stable (II) oxidation state can be prepared using electrolysis. A current was passed through an aqueous solution of mixed lanthanides, and the lanthanides which possessed a +2 oxidation state had the potential to form insoluble +2 salts. By this method both insoluble chloride and sulfate salts were prepared for Eu^{2+} , Sm^{2+} , and Yb^{2+} . The sulfate salts are more insoluble than the chloride salts and thus are more promising for

separating Lu^{3+} from Yb^{3+} . However, the best separation of Yb^{3+} from Lu^{3+} by this method from a mixture with a high Yb^{3+} content was found to be 90%-95% Lu^{3+} ^{49,50}.

C. PROPOSAL

It has been shown that relatively pure Lu (90%) can be made using either alkali amalgams, direct electrolysis, or a combination of the two. However, alkali amalgams in aqueous media are very dangerous and the need to eliminate them is crucial for industrial preparation of pure Lu. Therefore, direct electrolysis seems to be a more favorable method to eliminate Yb from a lanthanide mixture. Removal of 90% Yb from lanthanide ores has been achieved in the past using electrolysis in H_2SO_4 but no other medium has been examined⁵⁴. It is proposed that removal of Yb may be improved using direct electrolysis for the formation of insoluble YbSO_4 in different chemical media. Listed below are various aqueous media to be electrolyzed to determine the optimum conditions for the reduction of Yb^{3+} to Yb^{2+} and in some cases to produce a simultaneous formation of insoluble YbSO_4 .

- | | |
|--|--|
| 1) H_2SO_4 | 7) $\text{H}_2\text{SO}_4/(\text{NH}_4)_2\text{SO}_4$ |
| 2) $\text{H}_2\text{SO}_4/\text{Na}_2\text{SO}_4$ | 8) HCl |
| 3) $\text{HC}_2\text{H}_3\text{O}_2$ | 9) $\text{HCl}/\text{HC}_2\text{H}_3\text{O}_2$ |
| 4) $\text{HC}_2\text{H}_3\text{O}_2/\text{NaC}_2\text{H}_3\text{O}_2$ | 10) $\text{HC}_2\text{H}_3\text{O}_2/\text{NH}_4\text{Cl}$ |
| 5) $\text{HC}_2\text{H}_3\text{O}_2/\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ | 11) $\text{HC}_2\text{H}_3\text{O}_2/(\text{NH}_4)_2\text{SO}_4$ |
| 6) $\text{HC}_2\text{H}_3\text{O}_2/\text{H}_2\text{SO}_4$ | |

A more detailed understanding for the formation of +2 lanthanides using electrolysis was needed. Therefore, electrolysis on Eu^{3+} was first attempted because the

formation of Eu^{+2} is much easier than the formation of Yb^{2+} since Eu^{3+} has a lower reduction potential. Secondly, Eu^{3+} was used first because Eu is much less expensive than Yb. Attempts to form EuSO_4 were tried under various conditions. After successful reduction of Eu^{3+} to Eu^{2+} and formation of EuSO_4 was completed, reduction of Yb^{3+} was attempted.

D. REAGENTS AND APPARATUS

All chemicals used were reagent grade or better and the purity of the Eu_2O_3 and Yb_2O_3 were 99.9%. The basic electrolytic set-up was quite simple and represented the one used by Yntema, Pearce, and Prantl^{147-49,54} (Figure 3, p. 23). Both Heathkit and Sargent-Slomin DC power supplies were used for the electrolysis to control the current through the cell. Mercury (99.99%) was used as the cathode and enough was placed in a 150-ml beaker to allow connection to the negative wire. The solution to be electrolyzed was placed in the beaker along with a small stir bar. The solution was purged with nitrogen during the electrolysis to remove oxygen. The beaker was placed on a magnetic stirrer and the solution was slowly stirred. The anode was separated from the cathode in one of two ways. The first was by placing a small, porous clay pot (Mayo, Knoxville, TN) with a capacity of 60-ml directly into the beaker and filling it with a solution similar to the cathode solution but without the Eu^{3+} or Yb^{3+} . The anode was then placed directly into the clay pot. The second method was to use a second 150-ml beaker for the anode and the electrolytic connection was made using a salt bridge containing either saturated KCl or agar. After some experimentation, it was found that the first method of separating the

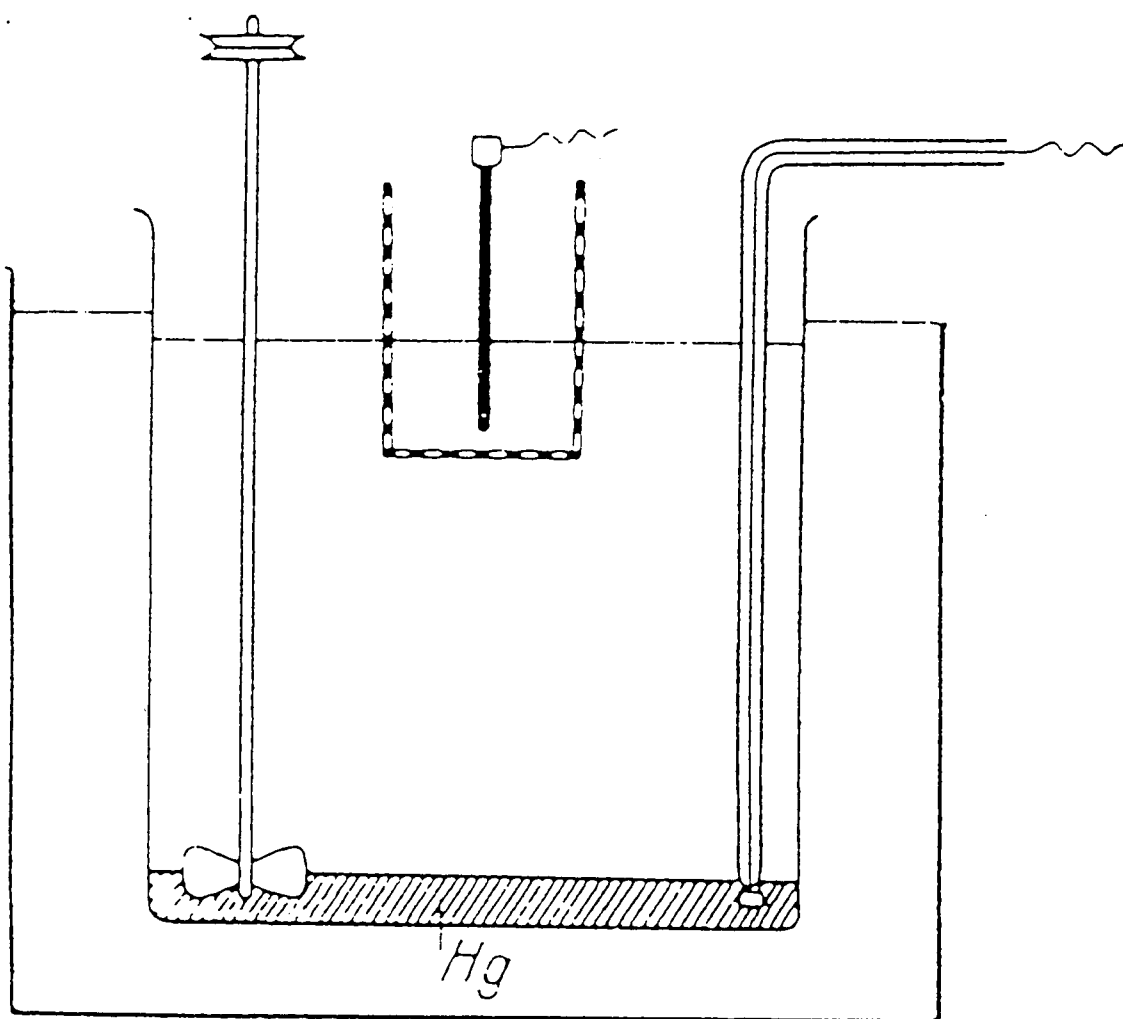


FIGURE 3

DIAGRAM OF ELECTROLYTIC SET-UP

cathode and anode was better since the KCl salt bridge either was blocked by H_2 production or the agar would decompose.

Different cathode wires and two anodes (all 99.9% pure) were tested for feasibility and durability. Ni, Cu, and Pt wire were used as connections to the Hg. These were constructed by sealing the metal in suitable glass in which only 2-3 mm of one end could be in contact with the Hg. Experimentation showed that the Ni cathode was the most feasible in that it produced the best electrolytic current and current density. Both graphite-type C and Pt were used as anodes. The C was not very durable and began to deteriorate after about 24 hr of electrolysis. Also, after short electrolysis times, the cathode solution turned black and it was suspected that the black precipitate was either C and/or MnO_2 contamination. Therefore, Pt was used as the anode for most of the experiments.

E. EXPERIMENTS AND RESULTS

The first attempt to reduce Eu^{3+} to Eu^{2+} was performed in 1.0-M H_2SO_4 and 0.50-M Eu^{3+} in the cathode compartment and 0.10-M H_2SO_4 in the anode compartment. The Eu^{3+} was made by dissolving 4.40-g Eu_2O_3 in 50.00-ml of 1.0-M H_2SO_4 using low heat. The dissolution process typically took 8-24 hr because the oxides of the lanthanides were often refractory. The initial electrolysis experiments were run with a current of 0.5A. After 80 min of electrolysis, reduction of Eu^{3+} to Eu^{2+} occurred and approximately 30% of the total Eu in solution precipitated as $EuSO_4$. Longer electrolyses were performed. The formation of $EuSO_4$ was seen in 1 hr, but even after a 24 hr electrolysis, no further $EuSO_4$

had formed. Also, under longer electrolysis, Hg compounds developed, particularly $\text{HgSO}_4\text{-HgO}$ and the formation of gelatinous Eu(OH)_3 began to appear since the pH increased to 7. Therefore, shorter electrolysis times seemed to be better for the production of EuSO_4 .

It has been demonstrated that the presence of high acidity can cause a decrease of the amount of EuSO_4 precipitated. With this in mind, attempts were made for the reduction of Eu^{3+} to Eu^{2+} using the electrolytic reduction in the presence of $\text{HC}_2\text{H}_3\text{O}_2$, a weak acid. Half-M (0.50-M) Eu^{3+} was electrolyzed for 24 hr in 1.0-M $\text{HC}_2\text{H}_3\text{O}_2$. The solution was removed from the cell and placed into a saturated Na_2SO_4 solution in hopes EuSO_4 would form. However, no white EuSO_4 formed which indicated that Eu^{2+} needs to be removed from solution as it is formed. The presence of H^+ in the cell probably assists in the oxidation of Eu^{2+} back to Eu^{3+} , thus no accumulation of the +2 species was obtained. This was shown as the electrolyzed solution did not reduce dilute KMnO_4 to Mn^{2+} .

Attempts were made to reduce Yb^{3+} to Yb^{2+} and form YbSO_4 using the various media listed above. The cathode was Ni/Hg while the anode was Pt. All of the chemical media were first electrolyzed without the presence of Yb^{3+} to observe how each would behave under electrolytic conditions. Several observations were made. The media which contained Na^+ ions tended to form Na amalgams after extended electrolysis. Although Na amalgams have been used for the reduction of Yb^{3+} to Yb^{2+} , it was not the method of reduction that the author wanted to pursue. Another observation made was the differences in pH for each medium. It has been proposed that the reduction of Yb^{3+} is pH

dependent and the media listed above displayed a wide range of acidities.

The preparation of the Yb^{3+} from Yb_2O_3 was different for the various media. For experiments containing H_2SO_4 , the appropriate amount of Yb_2O_3 was simply dissolved with heat in the amount of H_2SO_4 needed to give the desired concentration of H_2SO_4 . If other salts were added, the appropriate amount was dissolved directly into the solution. The procedure was the same for the experiments using HCl except the H_2SO_4 was replaced by HCl . For the $\text{HC}_2\text{H}_3\text{O}_2$ experiments, the Yb_2O_3 was first dissolved in HCl and the solution was made basic using NH_4OH until gelatinous $\text{Yb}(\text{OH})_3$ formed. The precipitate was dissolved in the appropriate concentration of $\text{HC}_2\text{H}_3\text{O}_2$.

Electrolysis of Yb^{3+} was started in 0.50-M H_2SO_4 with a Ni/Hg cathode and a Pt anode. After several hr of electrolysis with a current of $>1.0\text{A}$, green Yb^{2+} never formed. However a white, gelatinous precipitate formed in the cathode compartment. The solid formed was probably $\text{Yb}(\text{OH})_3$ since the pH had risen to 6. Subsequent experiments were run under similar conditions but the pH was maintained by the addition of H_2SO_4 to the cathode compartment. Again, after 4.0 to 24 hr no reduction of Yb^{3+} had taken place. It was determined that the current used was too high and that at lower currents ($<1.0\text{A}$) the reduction to Yb^{2+} was possible. The effect of current on the production of green Yb^{2+} was investigated to determine what was the best current to use for the fastest reduction. The reductions were run with 0.50-M H_2SO_4 and 0.70-M Yb^{3+} from currents from 1.00A down to 0.08A. As the current decreased the rate of reduction increased until 0.20A. Lower currents resulted in longer reduction times. It was found that the optimum operating current was 0.10A to 0.20A.

The electrolysis time was extended to determine if solid YbSO_4 would form in the cathode compartment. Using 0.70-M Yb^{3+} and 0.50-M H_2SO_4 , the Yb^{3+} was reduced to Yb^{2+} within 1.5 (± 0.2) hr but no YbSO_4 formed in a 7.0 hr electrolysis period. After 12 (± 1) hr the precipitate finally formed. The amount of the crystalline, very light green YbSO_4 was minimal. Qualitatively, it was evident that only a small fraction of the original Yb^{3+} had been precipitated as YbSO_4 . Similar experiments were run in 0.50-M H_2SO_4 with varying amounts of Yb^{3+} . Although the time needed to reduce Yb^{3+} to the +2 state was longer with less concentrated Yb^{3+} , the amount of YbSO_4 that formed was greater. Therefore, most of the remaining experiments were run with an initial Yb^{3+} concentration of 0.10-M to 0.30-M. Regardless of the initial concentration of Yb^{3+} used, the pH always increased as the electrolysis continued. The pH was lowered as necessary with the addition of the appropriate acid.

The other media (listed above) were then electrolyzed in the presence of Yb^{3+} . In every medium tested the reduction of Yb^{3+} to Yb^{2+} was evident. Table 1 (p. 28) provides the results of the electrolysis of Yb^{3+} in the various chemical media. The pH range in which Yb^{2+} was stable is under the pH column and the time that it took to form the Yb^{2+} and YbSO_4 is shown. The last column details the media in which a Yb/Hg amalgam formed under electrolysis.

F. CONCLUSIONS

Although every medium electrolyzed produced Yb^{2+} , only four media produced solid YbSO_4 . It appeared as though H_2SO_4 must be present to form YbSO_4 . The best

TABLE 1

RESULTS OF YTTERBIUM ELECTROLYSIS EXPERIMENTS

Medium	[Yb ³⁺]	Current, A	pH	Yb ²⁺ / time	YbSO ₄ / time	Yb/ Hg
0.50-M H ₂ SO ₄	0.70	0.40	1.0-2.0 (±0.3)	1.5(±0.2)hr	no	no
0.50-M H ₂ SO ₄	0.70	0.20	1.0-2.0 (±0.3)	30(±5)min	12(±2)hr	no
0.50-M H ₂ SO ₄	0.20	0.20	1.3-5.4 (±0.3)	3.0(±0.2)hr	12(±2)hr	no
0.50-M H ₂ SO ₄	0.20	0.08	1.3-5.4 (±0.3)	20(±2)hr	12(±2)hr	no
0.50-M H ₂ SO ₄ / 0.50-M Na ₂ SO ₄	0.30	0.20	4.4-5.3 (±0.3)	2.0(±0.5) min	6.0(±1.0) min	yes
0.40-M H ₂ SO ₄ / 0.25-M (NH ₄) ₂ SO ₄	0.20	0.20	4.0-5.3 (±0.3)	<1 min	4.5(±0.5) hr	yes

TABLE 1 (CONTINUED)

Medium	[Yb ³⁺]	Current, A	pH	Yb ²⁺ / time	YbSO ₄ / time	Yb- Hg
0.40-M H ₂ SO ₄ / 0.50-M (NH ₄) ₂ SO ₄	0.20	0.20	4.0-5.3 (±0.3)	2.0(±0.5) min	15(±2) min	yes
0.40-M H ₂ SO ₄ / 0.50-M (NH ₄) ₂ SO ₄	0.10	0.15	4.0-5.3 (±0.3)	2.0(±0.5) min	3.5(±0.5)hr	yes
0.40-M H ₂ SO ₄ / 1.0-M (NH ₄) ₂ SO ₄	0.10	0.20	4.0-5.3 (±0.3)	15(±3)sec	1.5(±0.2)hr	yes
0.40-M H ₂ SO ₄ / 2.0-M (NH ₄) ₂ SO ₄	0.10	0.20	4.0-5.3 (±0.3)	25(±3)min	3(±0.5)hr	yes

TABLE 1 (CONTINUED)

Medium	[Yb ³⁺]	Current, A	pH	Yb ²⁺ / time	YbSO ₄ / time	Yb- Hg
0.10-M H ₂ SO ₄ / 3.0-M (NH ₄) ₂ SO ₄	0.01	0.20	4.0-5.3 (±0.3)	5(±0.5)min	no	yes
0.50-M HC ₂ H ₃ O ₂	0.30	0.20	3.5- 5.4(±0.3)	<1min	no	yes
0.50-M HC ₂ H ₃ O ₂	0.10	0.20	3.5- 5.4(±0.3)	1.0(±0.2)hr	no	yes
0.50-M HC ₂ H ₃ O ₂	0.30	0.08	3.5- 5.4(±0.3)	1.0(±0.2)hr	no	yes
0.50-M HC ₂ H ₃ O ₂ / 0.50-M NH ₄ C ₂ H ₃ O ₂	0.30	0.20	3.8-5.4 (±0.3)	<1min	no	yes
0.50-M HC ₂ H ₃ O ₂ / 0.50-M NaC ₂ H ₃ O ₂	0.30	0.20	3.8-5.4 (±0.3)	<1min	no	yes

TABLE 1 (CONTINUED)

Medium	[Yb ³⁺]	Current, A	pH	Yb ²⁺ / time	YbSO ₄ / time	Yb- Hg
0.50-M HC ₂ H ₃ O ₂ / 0.50-M H ₂ SO ₄	0.10	0.20	1.3-5.0 (±0.3)	10(±1)min	100(±10) min	yes
0.50-M HC ₂ H ₃ O ₂ / 0.50-M (NH ₄) ₂ SO ₄	0.10	0.20	4.4-5.4 (±0.3)	10(±1)min	no	yes
0.50-M HCl	0.10	0.10	0.7-5.4 (±0.3)	24(±2)hr	no	yes
0.50-M HCl/ 0.50-M HC ₂ H ₃ O ₂	0.10	0.10	0.7- 5.4(±0.3)	24(±2)hr	no	yes
0.50-M HC ₂ H ₃ O ₂ / 0.50-M NH ₄ Cl	0.10	0.10	0.7- 5.4(±0.3)	24(±2)hr	no	yes

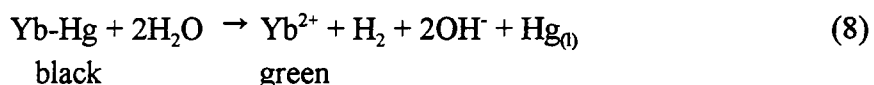
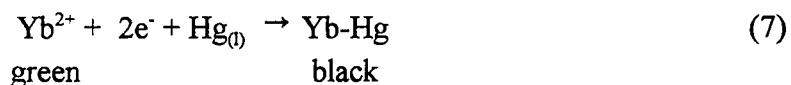
condition found was using 0.20-M Yb^{3+} , 0.40-M H_2SO_4 , and 0.50-M $(\text{NH}_4)_2\text{SO}_4$. The reduction of Yb^{3+} to Yb^{2+} and subsequent precipitation of YbSO_4 took only $2.0(\pm 0.5)$ and $15(\pm 2)$ min respectively while using a current of 0.20A. The pH range in which reduction took place was 4.0-5.4(± 0.3). This solution was also the only one in which YbSO_4 could be produced more than once re-electrolyzing the same starting solution. This was achieved by filtering the YbSO_4 once it formed and re-electrolyzing the solution. The precipitate was formed three times using this method. It was estimated that 90-95% of the initial Yb^{3+} was removed by using a qualitative NaOH precipitation method.

Precipitation of YbSO_4 also occurred using only H_2SO_4 but the time needed was much longer. Two benefits of using only H_2SO_4 were the wide range of pH and the absence of the formation of a Yb-Hg amalgam. The use of H_2SO_4 and Na_2SO_4 also produced YbSO_4 but the formation of a Na-Hg amalgam was always present and thus this system was avoided. The only other medium which favored the production of YbSO_4 was a combination of $\text{HC}_2\text{H}_3\text{O}_2$ and H_2SO_4 . Although the pH range for this medium was wide, the time for the reduction to take place was considerably longer.

The reduction of Yb^{3+} to Yb^{2+} in $\text{HC}_2\text{H}_3\text{O}_2$ or combinations with $\text{HC}_2\text{H}_3\text{O}_2$ was the fastest but YbSO_4 did not form because of the absence of sulfate. Likewise reduction occurred using HCl or HCl in combination with $\text{HC}_2\text{H}_3\text{O}_2$ but the time needed was very long.

In every medium except those using only H_2SO_4 , the initial green Yb^{2+} which formed would disappear and a grey to black suspension would appear. The black suspension was hypothesized to be a Yb-Hg amalgam. The black suspension would

usually disappear and the green Yb^{2+} would return after 30-60 min. The cause of this black suspension is not completely known, however, a hypothesis for the mechanism for its development and disappearance follows.



It appears as though the Yb temporarily formed an amalgam with the mercury cathode and was subsequently oxidized to Yb^{2+} .

Although electrolysis has been demonstrated to reduce Yb^{3+} to Yb^{2+} , and YbSO_4 has been formed and isolated, the method has its limitations. The major disadvantage is that it does not seem as though 100% of the Yb can be removed, and thus obtaining 99.99% Lu cannot be achieved. However, if electrolysis can remove 90-95% Yb from a mixture of lanthanides, it may be a method to use to reduce the bulk material needed for solvent extraction. For example, suppose a lanthanide mixture containing 10% Lu^{3+} , 80% Yb^{3+} , and 10% other lanthanides is used in solvent extraction. To produce 10-kg Lu, a total of 100-kg of the lanthanide mixture would be needed. If, by using electrolysis, 90% of the Yb was removed from the mixture, only 28-kg of the mixture would be needed to produce 10-kg of Lu.

There are other possibilities to remove the Yb^{2+} from solution other than to

precipitate it as the sulfate. One may be to use a resin specific for +2 ions. The resin could be placed in the electrolytic cell to remove the Yb^{2+} as it is formed. Another method may be to use a +3 specific resin in the cell. In this case the remaining +3 ions would be removed leaving the +2 ions in solution. This may be a more appropriate choice for this application since the Lu^{3+} is the minor constituent. One other method of removing the Yb^{2+} is to use a co-precipitation method. BaSO_4 is often used as a co-precipitating agent in many applications, including actinide separations.

Other disadvantages of electrolysis include the use of Hg and the formation of amalgams. Mercury is one of the most toxic materials known and its use in manufacturing is heavily regulated. For large-scale production of Lu, a large amount of Hg would be needed and environmental agencies, particularly the EPA, would not allow its use in this country. The formation of very reactive amalgams is another drawback to electrolysis. Alkali amalgams can react violently with water and thus electrolysis would not be appropriate for large-scale production of Lu.

One alternative method for the reduction of Yb^{3+} may be to use a reactive metal, such as Mg or Mg alloys. It has been demonstrated that Mg can be activated under certain conditions, typically in organic media. The use of Mg to reduce Yb^{3+} would be more environmentally safe and less dangerous. Another metal which may be used is Al. The problem with Al is that it has a very protective oxide coating and thus is typically non-reactive in water. However, if the Al can be activated, its use for the reduction of Yb^{3+} may be possible. One way in which to activate it may be to coat the Al with liquid Ga. The Ga could act as a transport mechanism for the electrons through the oxide coating.

CHAPTER III

SOLVENT EXTRACTION STUDIES

A. INTRODUCTION

There are several key factors in solvent extraction that need to be optimized for the best separation between the lanthanides. One factor to be determined is the settling time needed between the aqueous phase and the organic phase. The settling time between the aqueous and organic phases is important for a couple of reasons. First, the settling time should be as brief as possible so that relatively fast separations can occur. For industrial separations of the lanthanides, the amount of time it takes for the two phases to settle is a cost concern and should be fast enough for profitable results. Secondly, the settling time between the aqueous and organic phase is important because it may help determine if the organic phase is becoming too concentrated with the lanthanides which may cause an emulsion of the two phases. If an emulsion occurs, adjustments must be made in the concentration of the lanthanides in the aqueous phase to enhance the settling time between the two phases.

A second important factor in optimizing separations of lanthanides using solvent extraction is the time it takes for chemical equilibrium to be reached between the lanthanides and the extractant. For industrial lanthanide separations, the time for the lanthanides and extractant to reach equilibrium is critical. The faster the equilibrium is reached while the two phases are mixed, the more cost-effective and efficient the process. Therefore, it is necessary to find the equilibrium time between the two phases.

The load concentration of the aqueous phase is another important factor in optimizing the industrial separation of the lanthanides. The desired concentration of lanthanides in the aqueous phase is such that the extractant is being properly utilized while not being saturated. The major reason this aspect of optimization is important is for cost-effectiveness and efficiency. If the load concentration of the lanthanides is very low, the majority of the extractant is not being used and thus is being wasted. On the other hand, if the extractant is saturated with lanthanides, the values of the distribution coefficients of the lanthanides are more similar to each other than if the extractant is not saturated. Also, as mentioned above, if the extractant is saturated, the organic and aqueous phases may form an emulsion which increases the settling time between the two phases and thus the efficiency of the system is decreased.

A fourth important factor to consider for industrial separations of the lanthanides using an acidic extractant is the aqueous phase acidity. The equilibrium acidity of the aqueous phase needs to be at a value that allows for more than half of the Lu^{3+} and less than half of all other lanthanides to be extracted into the organic phase. If the aqueous phase acidity is too low, the heavy lanthanides to be separated almost all extract into the organic phase and little to no useful separation occurs. Likewise, if the aqueous phase acidity is too high, the lanthanides almost all remain in the aqueous phase and again a useful separation does not occur. In fact, using very high acidity in the aqueous phase is how the lanthanides are removed or stripped from the organic phase. Although there is a range of aqueous phase acidities that allows concentration and eventually separation of pure Lu^{3+} from the other lanthanides, there is a single aqueous phase acidity in which the

extraction mechanism follows a simple metal-metal exchange rather than a metal-proton exchange mechanism. The extraction mechanism does not follow the exchange of protons from the extractant, rather lanthanides in the aqueous phase exchange for other lanthanides in the organic phase. The reason the acidity is important to determine is that the adjustment of the aqueous phase acidity during the counter-current process may be reduced or eliminated. The acidity in which this mechanism occurs is when 50% of the total amount of lanthanides in solution are extracted into the organic phase. Once this acidity is found, there is a need to test to see if the acidity remains relatively constant in successive extractions as well as in counter-current extractions.

B. REAGENTS AND APPARATUS

The ore containing the heavy lanthanides was obtained from CTI-Siemens (Knoxville, TN) and contained five lanthanide oxides in the following proportions: Y_2O_3 (1%), Er_2O_3 (5%), Tm_2O_3 (10%), Yb_2O_3 (75%), and Lu_2O_3 (9%). The extractant used was mono-(2-ethylhexyl)2-ethylhexyl-phosphonate (IQ-801) and was obtained from Albright and Wilson. Yb_2O_3 (99.9%), Lu_2O_3 (99.9%), and the ICP/MS standards ($99.9\%\text{Y}^{3+}$, Er^{3+} , Tm^{3+} , Yb^{3+} , and Lu^{3+}) were purchased from Alfa chemicals. Low odor kerosene was used as the organic diluent and was purchased from Aldrich chemical. Reagent grade HCl and NaOH were purchased from Fischer chemical. The water used in every experiment was both distilled and deionized.

C. EXPERIMENTS AND RESULTS

1. Settling Times

The time needed for the organic and aqueous phases to physically separate from each other after mixing is the settling time between the two phases. The settling time was determined by adding a quantity of known concentration of each phase to a separatory funnel, vigorously shaking the funnel for a known amount of time, and then recording the time needed for the two phases to separate from each other. The first experiment was performed by hand shaking 15.00-ml of 0.60-M HCl and 15.00-ml of 0.45-M IQ-801 in kerosene in a 125-ml separatory funnel. After 5.0 minutes of shaking, the funnel was placed in a ring stand and the time needed for the two phases to settle was recorded. Within 30 sec, the two phases usually had separated from one another. However, both phases, particularly the organic phase, appeared to have a formation of a slight emulsion. Within 15.0 min the top 2-mm of the organic phase had cleared completely, and after 1.0 hr approximately the top one-third of the organic phase was clear. The two phases had cleared completely after 4 hr. This experiment was modified by shaking the two phases for 10.0 and 15.0 min. The results were practically identical to those with a 5.0 min shaking time. Longer shaking times did not seem to influence the rate of settling between the two phases.

A second type of settling time experiment was conducted to determine if the settling times were influenced if the same two phases were mixed several times. The aqueous phase consisted of 15.00-ml of 0.60-M HCl and the organic phase consisted of 15.00-ml of 0.45-M IQ-801 in kerosene. The mixture was hand shaken for 30 sec and the

time for the phases to settle was recorded. After the phases had settled, the same mixture was re-shaken for an additional 30 sec and the time was recorded for separation of the phases. This process was repeated 15 times and the settling time between the two phases was recorded for each trial. The results of each trial are shown in Table 2 (p. 40).

Another experiment was conducted to determine the settling time needed for the organic and aqueous phases. The experiment was conducted similarly to the one with the results listed in Table 2 (p. 40), except that the aqueous and organic phases were reduced from 15.00-ml to 10.00-ml. The volumes were reduced to determine if volume had a role in the settling times. The results of the thirteen trials are shown in Table 3 (p. 41).

The 0.60-M HCl and 0.45-M IQ-801 were used in the settling time study based on results of an emulsion study conducted to determine the concentrations of the aqueous and organic phases in which an emulsion forms. Various concentrations of HCl and IQ-801 in kerosene (15.00-ml each) were shaken for 5.0 min in separatory funnels and allowed to settle for 1.0 min. The degree of emulsion formation for each mixture was qualitatively evaluated. These qualitative emulsion observations for the various concentrations of HCl and IQ-801 in kerosene are shown in Table 4 (p. 42).

2. Chemical Equilibrium

Not only is the time needed for phase separation important in solvent extraction, but also the time needed for the lanthanides to reach chemical equilibrium with the extractant is important. To determine the time needed to reach chemical equilibrium, known amounts and concentrations of Yb^{3+} in the aqueous phase and IQ-801 in kerosene in the organic phase were placed in small test tubes and shaken for various time periods.

TABLE 2
AQUEOUS/ORGANIC SETTLING TIMES (15-ml)

Trial	Settling Time, sec	Trial	Settling Time, sec	Trial	Settling Time, sec
1	29	6	30	11	30
2	28	7	30	12	35
3	24	8	30	13	30
4	32	9	25	14	30
5	28	10	30	15	32

TABLE 3
AQUEOUS/ORGANIC SETTLING TIMES (10-ml)

Trial	Settling Time, sec	Trial	Settling Time, sec	Trial	Settling Time, sec
1	25	6	27	11	56
2	30	7	30	12	60
3	30	8	50	13	55
4	30	9	47		
5	32	10	55		

TABLE 4
EMULSION FORMATION

IQ-801, M	0.15	0.25	0.35	0.45	0.55	0.65
HCl, M						
0.5	none	v little	little	little	little	moderate
1.0	none	v little	v little	v little	little	much
1.5	none	v little	little	little	moderate	much

After the specified amount of shaking time, the test tubes were quickly placed in a centrifuge and spun to separate the two phases as quickly as possible. An aliquot of the aqueous phase was removed, diluted with HCl to an appropriate concentration and analyzed for Yb^{3+} using atomic emission spectroscopy (AES). Yb was chosen to be the lanthanide in the aqueous phase because it is much cheaper than the other heavy lanthanides and it was assumed that it would behave similarly to the other lanthanides. Three separate trials were conducted, each having an aqueous phase consisting of 0.33-M Yb^{3+} and 0.60-M HCl and an organic phase consisting of 0.45-M IQ-801 in kerosene. The 0.33-M Yb^{3+} was prepared by dissolving 12.79-g $\text{YbCl}_3 \cdot 6\text{H}_2\text{O}$ in 0.60-M HCl to a total volume of 100.00-ml. The 0.45-M IQ-801 was prepared by dissolving 300.00-ml pure (1.50-M) IQ-801 in kerosene to a total volume of 1.00-L.

The first trial consisted of 15 separate samples each containing 1.00-ml of each phase. The first sample was shaken for 1.0 min and each successive sample was shaken in 1.0 min increments. After the appropriate shaking time, each sample was centrifuged for 15 sec, and after an additional 15 sec, a 0.50-ml aliquot of the aqueous phase was removed. The aqueous aliquot was diluted to an appropriate concentration by adding 4.50-ml of 0.60-M HCl. The samples were mixed well and 1.00-ml was removed and again diluted to 100.00-ml with 0.60-M HCl. Again, the samples were mixed well and analyzed for Yb^{3+} using AES. The relative intensity of all 15 samples were virtually the same indicating that chemical equilibrium had been reached within the first minute.

A second trial was conducted to determine the equilibration time between the aqueous and organic phases. The two phases used in the second trial were prepared in the

same way as in the first trial. The first sample was shaken for 15 sec and the two phases were separated the same way described for trial one. The second sample was shaken for 30 sec while the third, fourth, and fifth were shaken for 1.0, 1.5, and 2.0 min, respectively. Samples 6-9 were shaken in 1.0 min increments until 6.0 min had been reached. Each sample was diluted for AES by sampling 0.50-ml of the aqueous phase and diluting it to 5.00-ml with 0.60-M HCl. The samples were well shaken and 0.50-ml was diluted to 5.00-ml using 0.60-M HCl. Again, the samples were shaken well and 0.25-ml of the sample was diluted to 10.00-ml using 0.60-M HCl. The total dilution was 4000 which was an appropriate amount for good AES results. The results of this equilibrium study are shown in Figure 4 (p. 45). It appears that chemical equilibrium was reached within 2.0 min of shaking time.

A third trial was conducted to ascertain reproducibility of the equilibrium times. The experiment was run exactly as the one in trial 2 except a 6.0 min shaking time was not included. The results are shown in Figure 5 (p. 46).

3. Acid Concentration Studies

Since the reaction between the lanthanides and IQ-801 is a cation exchange reaction, the equilibrium concentration of H^+ in the aqueous phase is not the same as the initial H^+ concentration since protons are released from IQ-801 to the aqueous phase. It is the equilibrium acid concentration that is important for determining the distribution coefficient for each lanthanide in a mixture since distribution coefficients are values at equilibrium. The optimum equilibrium acid concentration in the aqueous phase is when 50% of the total lanthanides remain in the aqueous phase after extraction and 50%

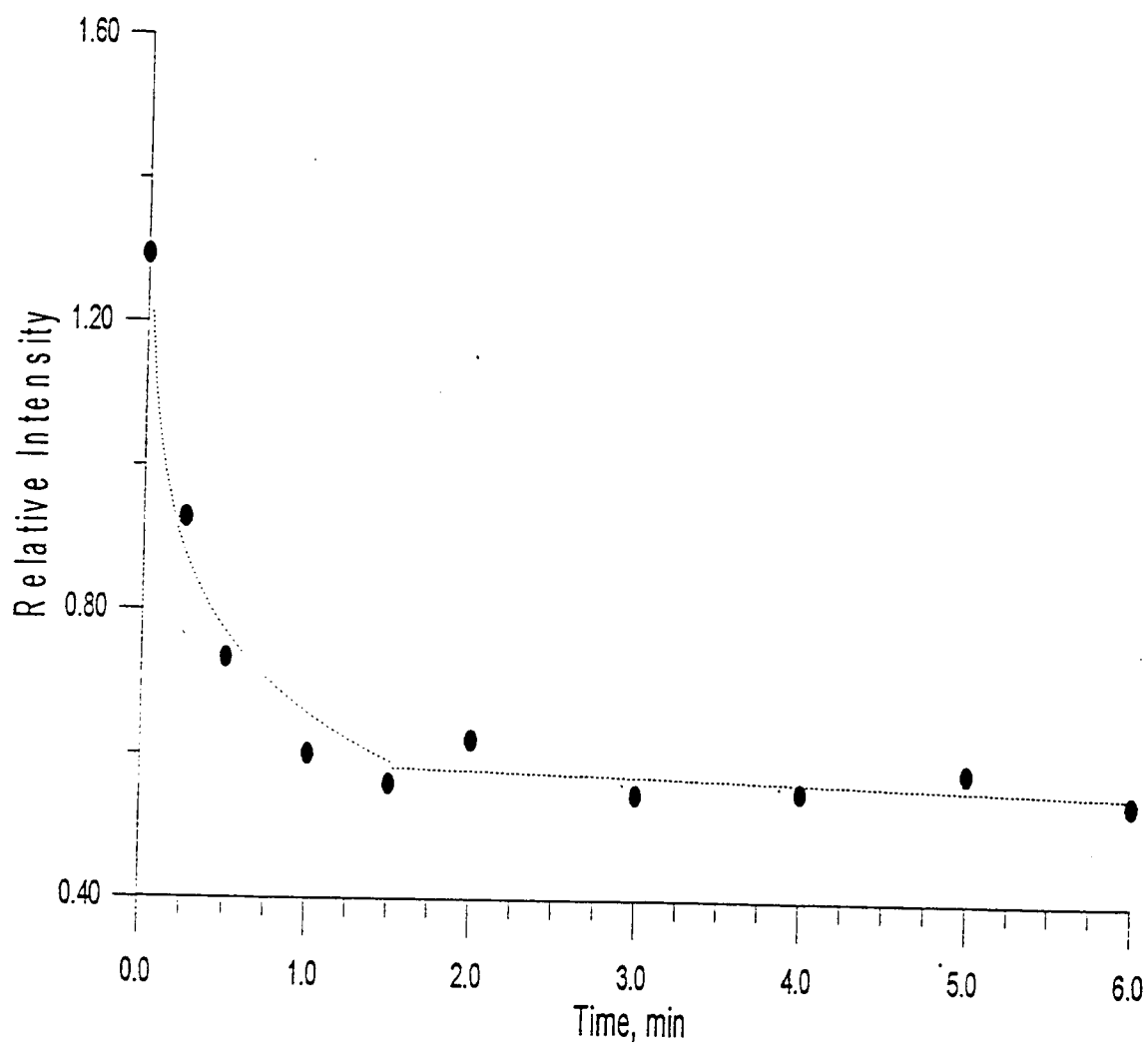


FIGURE 4

CHEMICAL EQUILIBRIUM TIMES
BETWEEN Yb^{3+} AND IONQUEST 801 (TRIAL 1)

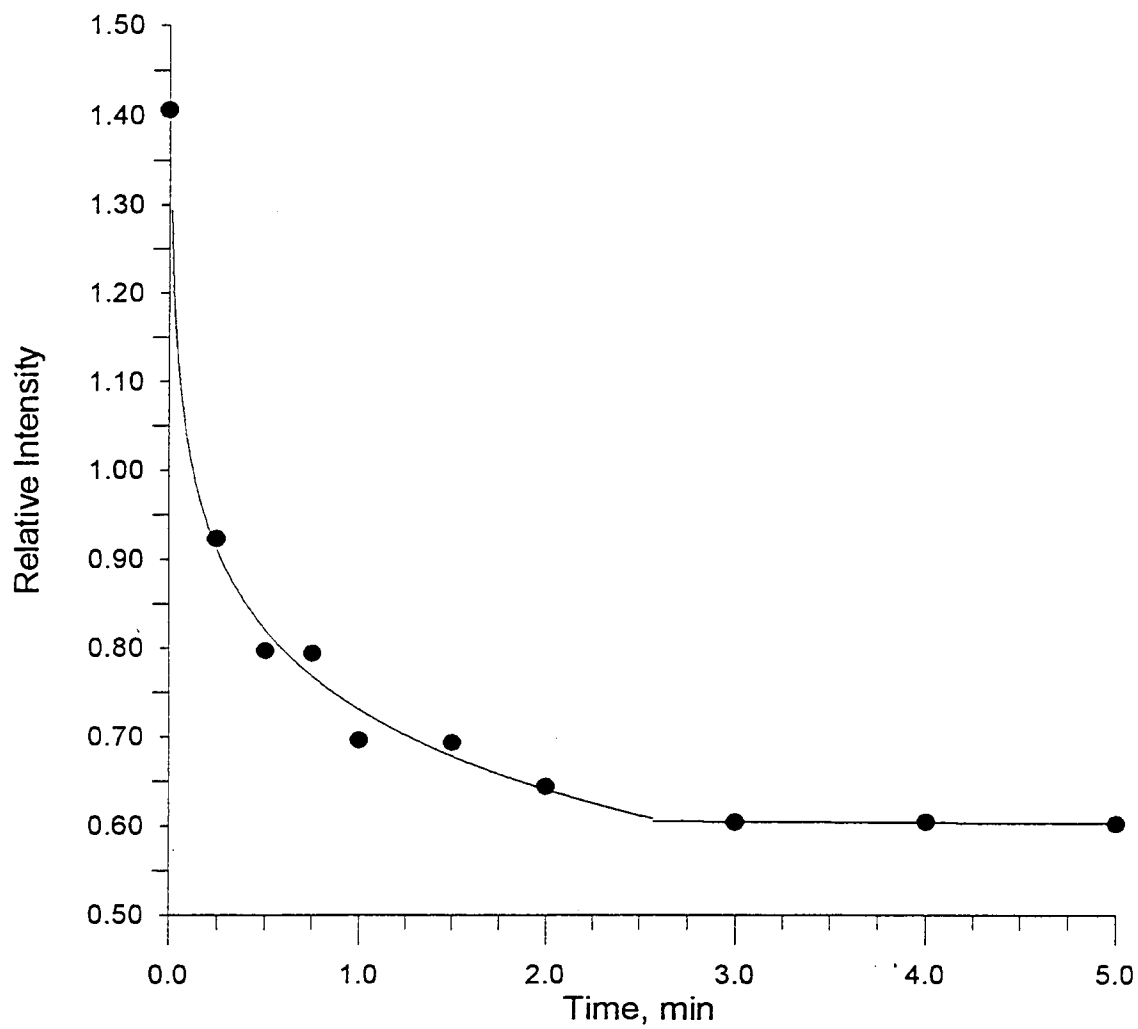
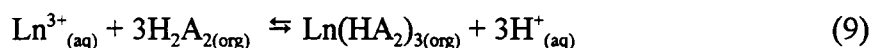


FIGURE 5

CHEMICAL EQUILIBRIUM TIMES
BETWEEN Yb^{3+} AND IONQUEST 801 (TRIAL 2)

of the total lanthanides are extracted into the organic phase. It is this optimum acid concentration that allows the chemistry to become a simple metal-metal exchange instead of a metal-proton exchange. A second reason for knowing the equilibrium acid concentration in the aqueous phase is important is that there is a narrow range of acidities in which greater than 50% Lu^{3+} will extract into the organic phase and greater than 50% Yb^{3+} will remain in the aqueous phase. Since Yb^{3+} is the most difficult lanthanide to separate from Lu^{3+} , this acid range is sufficient for separating Lu^{3+} from all other lanthanides. In other words, this acidity range provides good separation of Lu^{3+} .

An experiment was conducted to determine the range of acidities in the aqueous phase which provides >50% extraction of Lu^{3+} and <50% extraction of Yb^{3+} . In order to determine this range, the distribution coefficients (D) were calculated based on the following reaction:



where Ln^{3+} represents any lanthanide in the aqueous phase and H_2A_2 represents IQ-801. Initial experiments to determine the value of D for Lu^{3+} and Yb^{3+} were conducted based on titrating the aqueous phase before and after extraction to determine the change in acid concentration after extraction. The determination of the distribution coefficient using this titration method was based on the knowledge of the initial concentration of the lanthanide and initial concentration of the acid in the aqueous phase. After extraction the aqueous phase was again titrated with standardized base to determine the change in acid concentration. From the stoichiometry of the reaction, the amount of lanthanide which

was extracted into the organic phase was calculated. Once the amount of lanthanide which was extracted into the organic phase was determined, the distribution coefficient was calculated ($D = \frac{Ln^{3+}_{(org)}}{Ln^{3+}_{(aq)}}$).

Once the equilibrium acid concentration and the distribution coefficients for Lu^{3+} and Yb^{3+} were found, a plot of $\log D$ vs $\log [H^+]$ was made and the range of acidities which allow $>50\%$ Lu^{3+} and $<50\%$ Yb^{3+} to be extracted was found. The plot was made in log-log form to give a straight line with a slope of negative 3. The equilibrium expression from equation 9 is:

$$K = \frac{[Ln(HA_2)_3]_{(org)} [H^+]^3_{(aq)}}{[H_2A_2]^3_{(org)} [Ln^{3+}]_{(aq)}} \quad (10)$$

By taking the log and rearranging the expression, the equation for a straight line with a slope of -3 is:

$$\log D = -3 \log [H^+]_{(aq)} - \log K [H_2A_2]^3_{(org)} \quad (11)$$

After the equation of the line was determined, the optimum equilibrium acid concentration range in which $>50\%$ Lu^{3+} and $<50\%$ Yb^{3+} is extracted into the organic phase was calculated. The separation coefficient at this optimum acid concentration range was also calculated and was used to estimate the number of stages needed for separating 99.99% pure Lu^{3+} . The number of stages was calculated by the equation:

$$(\alpha)^n = 10^4 \quad (12)$$

where 10^4 represents the desired 99.99% Lu , and n represents the number of stages needed to obtain this purity from the experimentally determined separation coefficient.

The first experiment using the titration method was composed of five separate

solutions of 0.15-M Lu^{3+} and four separate solutions of 0.15-M Yb^{3+} . Each solution was adjusted so that the acidity was different for each sample. The organic phase consisted of 0.45-M IQ-801 in kerosene. Prior to extraction, the aqueous phases for both Lu^{3+} and Yb^{3+} were titrated with standardized NaOH using bromphenyl blue as the indicator. Once the initial acid concentration was determined, 20.00-ml of the Lu^{3+} containing aqueous phase was placed in a 125-ml separatory funnel along with 20.00-ml of 0.45-M IQ-801 in kerosene. The two phases were hand shaken for 15.0 min to ensure equilibrium and the phases were allowed to settle for 10.0 min. The same procedure was used for the four Yb^{3+} containing aqueous phases. A portion of each aqueous phase was taken and titrated with standardized NaOH to determine the equilibrium acid concentrations. Finally, the distribution coefficients for both Lu^{3+} and Yb^{3+} were calculated and a plot of $\log D$ vs $\log [\text{H}^+]$ for both lanthanides was made. Table 5 (p. 50) summarizes the initial and equilibrium acid concentrations as well as the distribution coefficients for both Lu^{3+} and Yb^{3+} . Figure 6 (p. 51) is a plot of $\log D$ vs $\log [\text{H}^+]$ for Lu^{3+} and Yb^{3+} .

It was calculated that the equilibrium acid concentration range in which $>50\%$ Lu^{3+} and $<50\%$ Yb^{3+} extracts into the organic phase was 1.38-M to 1.68-M HCl. The acid concentration in which there was the most partition between Lu^{3+} and Yb^{3+} was 1.52-M HCl. At this concentration the separation coefficient was calculated to be 1.5. With this separation coefficient, the theoretical number of solvent extraction stages needed to produce 99.99% pure Lu^{3+} is approximately 23. A second attempt was made to determine the optimum acid concentration range in the aqueous phase using the titration method. The only difference was that a mechanical shaker was used instead of hand shaking. The

TABLE 5
DATA FOR SINGLE EXTRACTIONS OF Lu^{3+} AND Yb^{3+} USING
TITRATION METHOD (TRIAL 1)

Sample	$[\text{H}^+]_{\text{initial}}$	$[\text{H}^+]_{\text{equilibrium}}$	$\log [\text{H}^+]_{\text{equilibrium}}$	$\log D$
Lu^{3+} -1	0.958	1.245	0.095	0.250
Lu^{3+} -2	1.280	1.540	0.188	0.140
Lu^{3+} -3	1.389	1.758	0.245	-0.086
Lu^{3+} -4	1.640	1.834	0.263	-0.119
Lu^{3+} -5	2.268	2.440	0.389	-0.396
Yb^{3+} -1	1.018	1.273	0.105	0.114
Yb^{3+} -2	1.160	1.381	0.140	-0.013
Yb^{3+} -3	1.397	1.584	0.200	-0.149
Yb^{3+} -4	1.512	1.685	0.227	-0.201

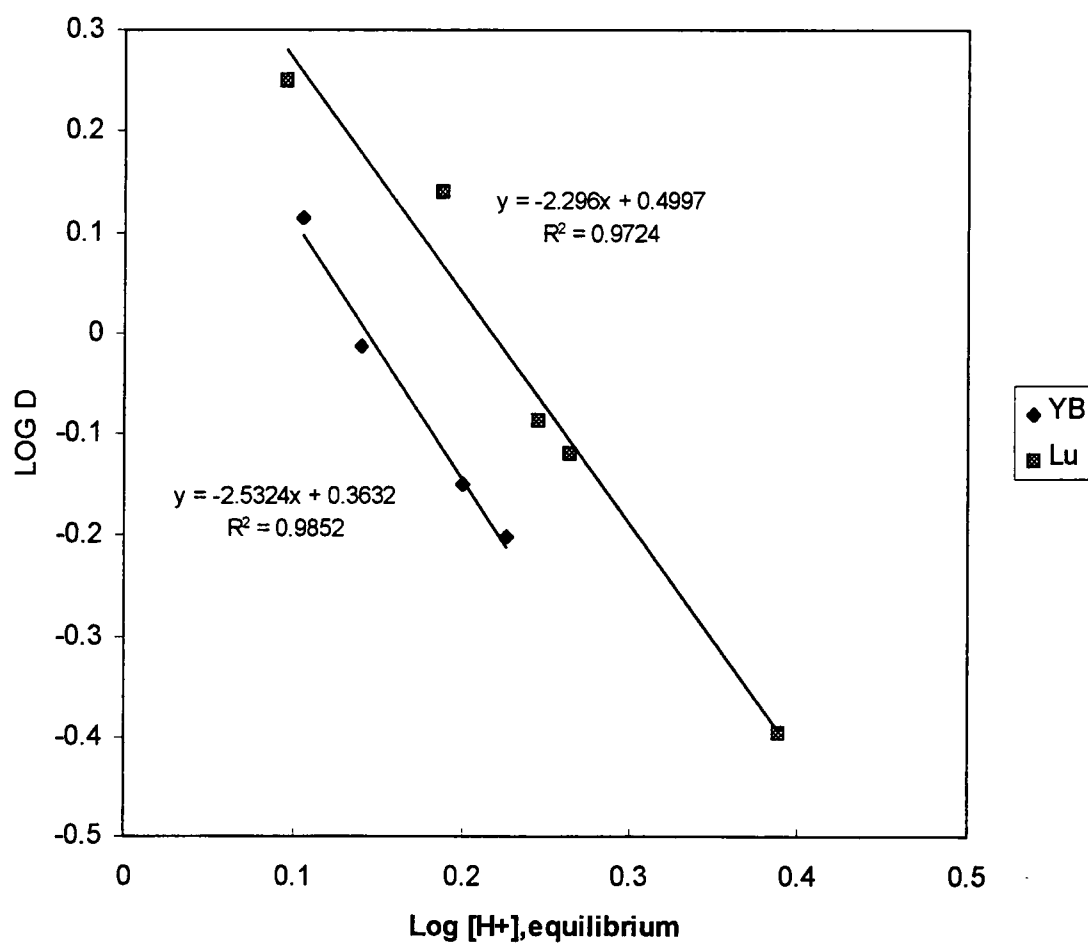


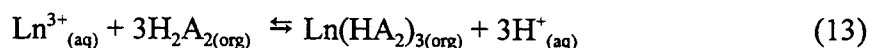
FIGURE 6

PLOT OF LOG D VS LOG [H⁺] FOR Lu³⁺ AND Yb³⁺ USING
TITRATION METHOD (TRIAL 1)

results were very similar to those with the hand shaken samples. The results are shown in Table 6 (p. 53) and Figure 7 (p. 54). From this second extraction the optimum acid concentration range to provide >50% Lu^{3+} and <50% Yb^{3+} to be extracted was calculated to be 1.44-M to 1.64-M. The acid concentration for the best partition of Lu^{3+} from Yb^{3+} was found to be 1.53-M. The results are very similar to the first extraction and provided confirmation for the equilibrium acid concentration range. An experiment was conducted in which an attempt was made to obtain equilibrium acid concentrations of approximately 1.50-M. Separate Lu^{3+} and Yb^{3+} aqueous phases, at various acid concentrations, were extracted in 0.45-M IQ-801 in kerosene using a mechanical mixer. The samples were shaken for 15.0 min and allowed to settle for 10.0 min. The results of this experiment in which the aqueous phase acidities were kept closer to 1.50-M are shown in Table 7 (p. 55) and Figure 8 (p. 56).

Under these conditions the optimum acid concentration range for the partition of Lu^{3+} from Yb^{3+} was found to be 1.56 to 1.93-M HCl, whereas the best partition condition was calculated to be 1.68-M HCl.

Although an optimum acid concentration range for the aqueous phase was determined using the titration method, the method depends on the assumption that the equation



is exactly correct. In some solvent extraction mechanisms, the above equation does not hold exactly true and there is not a 1:3 ratio of lanthanide to the extractant and thus three

TABLE 6
DATA FOR SINGLE EXTRACTIONS OF Lu^{3+} AND Yb^{3+} USING
TITRATION METHOD (TRIAL 2)

Sample	$[\text{H}^+]_{\text{initial}}$	$[\text{H}^+]_{\text{equilibrium}}$	$\log [\text{H}^+]_{\text{equilibrium}}$	$\log D$
Lu^{3+} -1	0.493	0.853	-0.069	0.602
Lu^{3+} -2	0.790	1.083	0.035	0.364
Lu^{3+} -3	1.022	1.298	0.113	0.199
Lu^{3+} -4	1.265	1.518	0.181	0.104
Lu^{3+} -5	1.497	1.698	0.230	-0.081
Yb^{3+} -1	0.490	0.829	-0.079	0.485
Yb^{3+} -2	0.781	1.063	0.027	0.225
Yb^{3+} -3	1.016	1.268	0.103	0.105
Yb^{3+} -4	1.257	1.472	0.168	-0.035
Yb^{3+} -5	1.505	1.703	0.231	-0.105

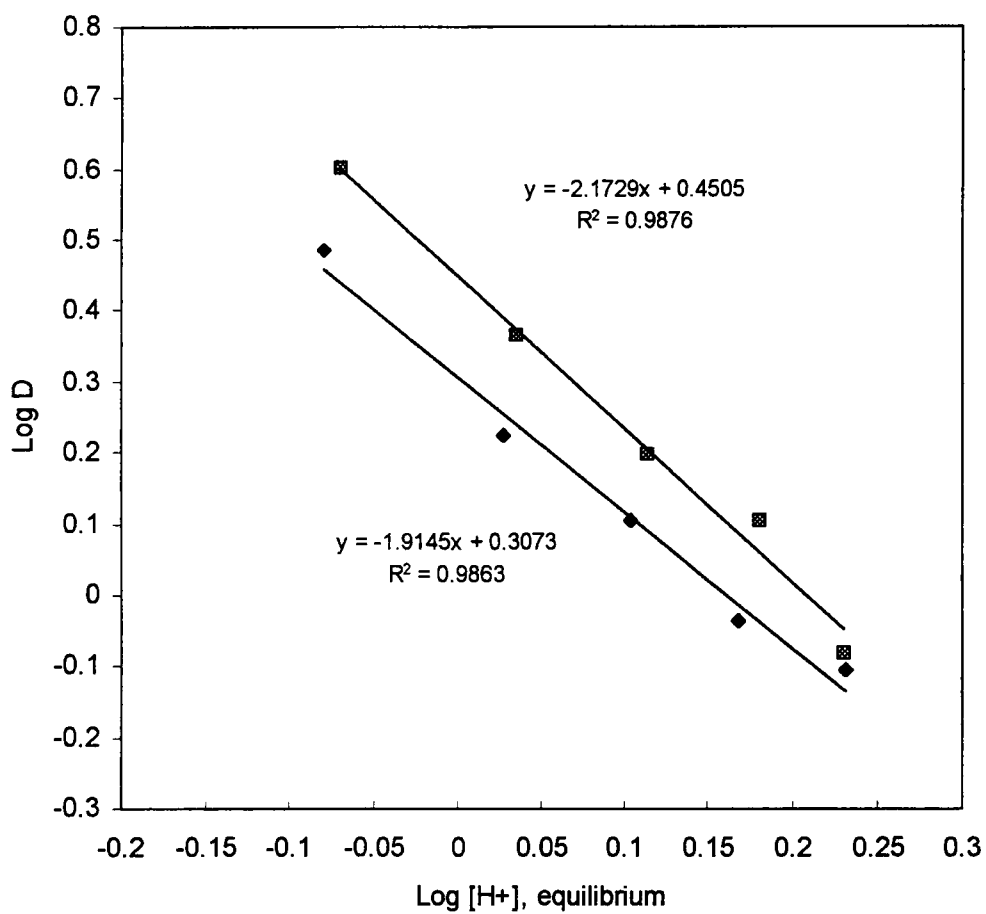


FIGURE 7

PLOT OF LOG D VS LOG [H⁺] FOR Lu³⁺ AND Yb³⁺ USING
TITRATION METHOD (TRIAL 2)

TABLE 7
DATA FOR SINGLE EXTRACTIONS OF Lu^{3+} AND Yb^{3+} WITH
NARROWER ACID CONCENTRATION RANGE USING
TITRATION METHOD

Sample	$[\text{H}^+]_{\text{initial}}$	$[\text{H}^+]_{\text{equilibrium}}$	$\log [\text{H}^+]_{\text{equilibrium}}$	$\log D$
Lu^{3+} -1	1.134	1.413	0.150	0.204
Lu^{3+} -2	1.233	1.492	0.174	0.159
Lu^{3+} -3	1.255	1.519	0.182	0.152
Lu^{3+} -4	1.324	1.578	0.198	0.109
Lu^{3+} -5	1.433	1.675	0.224	0.066
Yb^{3+} -1	1.126	1.374	0.138	0.093
Yb^{3+} -2	1.225	1.466	0.166	0.058
Yb^{3+} -3	1.268	1.500	0.176	0.023
Yb^{3+} -4	1.315	1.538	0.187	-0.012
Yb^{3+} -5	1.416	1.637	0.214	-0.023

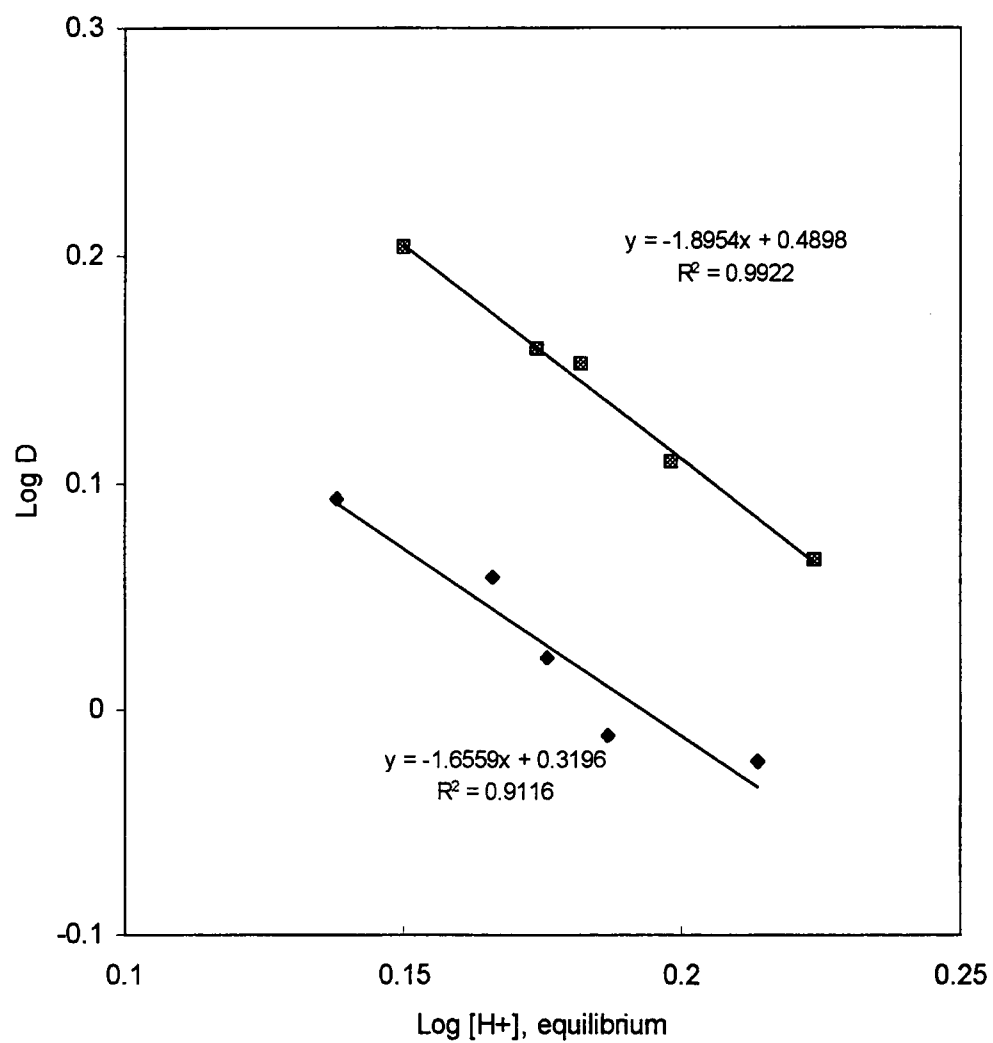


FIGURE 8

PLOT OF LOG D VS LOG [H⁺] FOR Lu³⁺ AND Yb³⁺ WITH A NARROWER ACID CONCENTRATION RANGE USING TITRATION METHOD

protons are not released from the extractant into the aqueous phase. Therefore, a more reliable method in determining the optimum acid concentration range is to directly measure the amount of lanthanides that are extracted into the organic phase. One such direct measurement of the lanthanides may be made using inductively coupled plasma/mass spectrometry (ICP/MS). This direct measurement of the amounts of lanthanides that were extracted into the organic phase and the determination of the equilibrium acid concentration in the aqueous phase allows for more reliable information regarding the distribution coefficients for the lanthanides. Another key reason ICP/MS is a better method for calculating of the distribution coefficients is it allows for a mixture of the lanthanides to be present in the aqueous phase whereas the titration method does not. Using the titration method, a mixture of lanthanides in the aqueous phase cannot be used because the method cannot distinguish between different lanthanides. Using ICP/MS, analysis of a mixture of the elements in the aqueous phase is possible.

An experiment using ICP/MS to trace the path of Lu^{3+} and Yb^{3+} during the extraction process was conducted from a lanthanide ore obtained from CTI-Siemens (Knoxville, TN). The ore contained approximately 70% Yb_2O_3 , 10% Lu_2O_3 , and the remaining being other lanthanide oxides. The formula weight was estimated to be 395-g/mol. Six separate solutions of approximately 0.15-M Ln^{3+} (where Ln^{3+} represents lanthanide) were made in various concentrations of HCl. After the six solutions were prepared, each aqueous phase was titrated with standardized NaOH to determine the initial acidity prior to extraction. The knowledge of the initial acidity was important because once the optimum acidity range at equilibrium was found, the change in acidity

after equilibrium was calculated. Knowing the change in acidity, the initial aqueous phase could be prepared at the appropriate acidity for extraction.

Prior to extraction, the initial concentration of each lanthanide was determined by taking a small portion (2.00 to 5.00-ml) of each sample and diluting each with 1.00-M HCl to give an appropriate concentration of the lanthanides needed for ICP/MS. The best concentrations were found to be in the range of 1-200 ppb where the linear dynamic range of the standards was very good. For each extraction, 15.00-ml of each of the 0.15-M Ln^{3+} solutions was placed in a 125-ml separatory funnel along with 15.00-ml 0.45-M IQ-801 in kerosene. The mixtures were mechanically shaken for 15.0 min and allowed to settle for 10.0 min. The aqueous phases were drawn off and a small portion of each sample was removed and diluted to give a concentration of around 1-200 ppb of each lanthanide. The initial and equilibrated aqueous phases were subsequently analyzed for Lu^{3+} and Yb^{3+} using ICP/MS.

The determination of the distribution coefficients for both lanthanides were calculated at each of the six acidities. Since $D = \text{Ln}^{3+}_{(\text{org})} / \text{Ln}^{3+}_{(\text{aq})}$ at equilibrium, the value of $\text{Ln}^{3+}_{(\text{aq})}$ was simply the amount of lanthanide in the aqueous phase after extraction determined from the ICP/MS results. Calculation of the amount of lanthanide in the organic phase was determined from a knowledge of the initial and equilibrium amounts of the lanthanides in the aqueous phases. The amount of lanthanides in the organic phase was calculated by taking the difference of the two ($\text{Ln}^{3+}_{(\text{org})} = \text{Ln}^{3+}_{(\text{aq, initial})} - \text{Ln}^{3+}_{(\text{aq, equilibrium})}$). Once these values were calculated, the distribution coefficients of each lanthanide at each acidity were calculated. Finally, a plot of $\log D$ vs $\log [\text{H}^+]$ was made to determine the

optimum range of acidities using this method of tracing the lanthanides. Table 8 (p. 60) displays the change in acidity for each sample along with the calculated value of $\log [H^+]$ and $\log D$. Figure 9 (p. 61) is a plot of $\log D$ vs $\log [H^+]$.

The optimum equilibrium acid concentration range in the aqueous phase for partitioning Lu^{3+} and Yb^{3+} under these conditions was found to be approximately 1.63-M to 2.22-M HCl. The acid concentration for the best partitioning conditions was calculated to be around 1.95-M which corresponds to a Lu^{3+}/Yb^{3+} separation coefficient of 1.8.

A final experiment was conducted to determine the equilibrium acid concentration which would provide for 50% of the lanthanides to be extracted into the organic phase and 50% of the lanthanides to remain in the aqueous phase. The same lanthanide ore was used as in the previous experiment, but in this experiment Lu^{3+} , Yb^{3+} , Tm^{3+} , Er^{3+} , and Y^{3+} were all analyzed using ICP/MS. The experimental conditions were identical to those used in the extraction where only Lu^{3+} and Yb^{3+} were analyzed. Six samples of 0.15-M Ln^{3+} were made in different acid concentrations. The organic phase was 0.45-M IQ-801 in kerosene. Prior to the extraction, the acid concentration for each sample was determined by titrating a portion of the aqueous phases with standardized NaOH. Next, a portion of each aqueous phase was sampled and diluted with 1.00-M HCl to an appropriate concentration for ICP/MS analysis to determine the initial amounts of each lanthanide in the aqueous phase. The two phases were mixed for 15.0 min using a mechanical mixer and allowed to settle for 10.0 min. After the phases settled, a portion was sampled from the aqueous phases and diluted with 1.00-M HCl for analysis, and another portion of the aqueous phases was titrated with standardized NaOH to determine

TABLE 8
DATA FOR SINGLE EXTRACTIONS OF Lu^{3+} AND Yb^{3+} USING
ICP/MS ANALYSIS

Sample	$[\text{H}^+]_{\text{initial}}$	$[\text{H}^+]_{\text{equilibrium}}$	$\log [\text{H}^+]_{\text{equilibrium}}$	$\log D_{\text{Lu}^{3+}}$	$\log D_{\text{Yb}^{3+}}$
1	0.735	0.989	-0.005	0.642	0.452
2	0.965	1.194	0.077	0.555	0.331
3	1.214	1.414	0.150	0.429	0.193
4	1.474	1.639	0.215	0.250	0.029
5	1.702	1.852	0.268	0.196	-0.071
6	1.927	20.60	0.314	0.043	-0.216

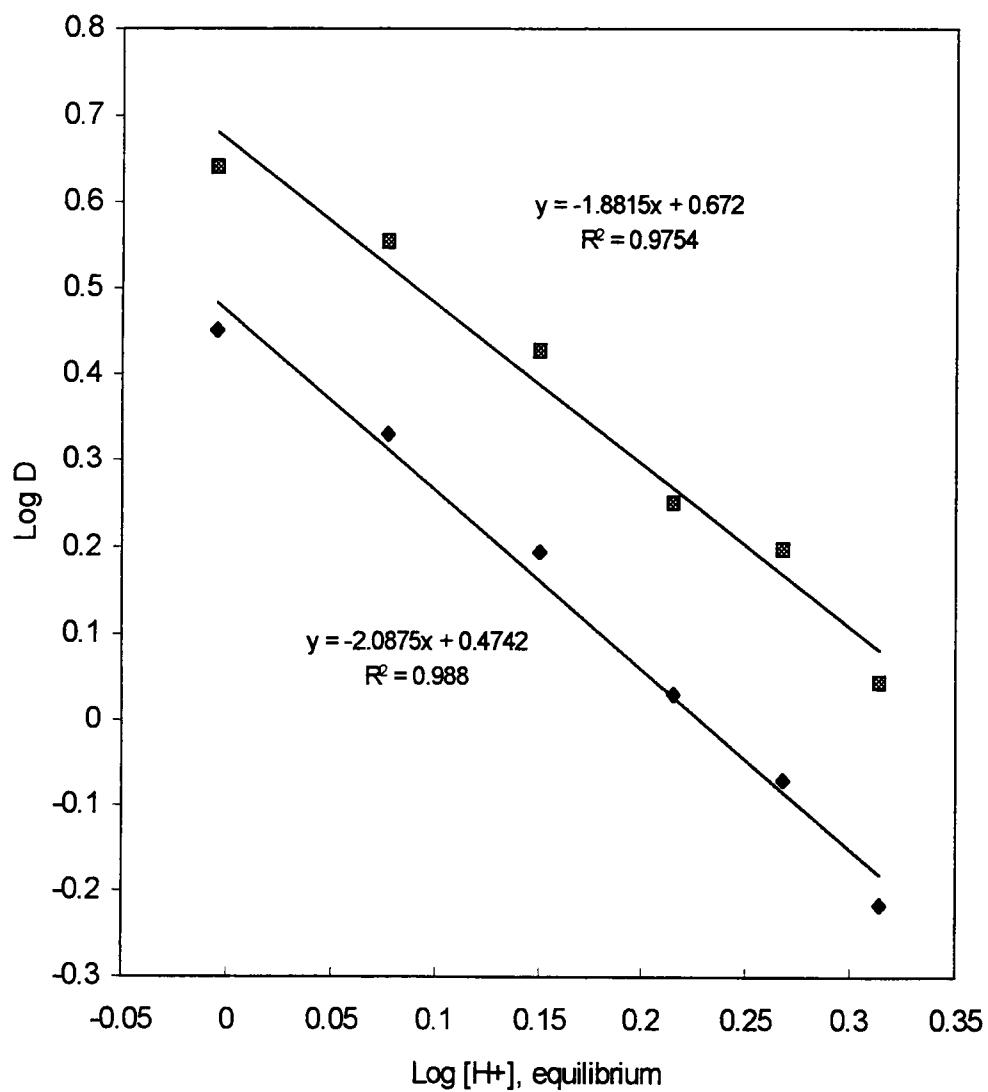


FIGURE 9

PLOT OF LOG D VS LOG [H⁺] FOR Lu³⁺ AND Yb³⁺ USING ICP/MS ANALYSIS

the equilibrium acid concentration. The results of this experiment are shown in Table 9 (p. 63) and Figure 10 (p. 64). Table 9 (p. 63) shows the initial and equilibrium acid concentrations for each sample along with the distribution coefficient for each lanthanide. Figure 10 (p. 64) shows how the distribution coefficient for each lanthanide varies with the equilibrated acid concentration.

From the knowledge of the initial amounts of each lanthanide, and assuming there were no other elements present in the ore, the percentage of each lanthanide in the ore was calculated. The calculated percentages of Lu^{3+} , Yb^{3+} , Tm^{3+} , Er^{3+} , and Y^{3+} in the ore were 10.1, 72.0, 11.9, 5.1, and 0.8 respectively. These percentages are very close to the original estimate. Knowing the percentages of each lanthanide in the ore, the equilibrium acid concentration which provides 50% of the total amount of lanthanides to be extracted into the organic phase was calculated to be 1.56-M HCl. The separation coefficient between Lu^{3+} and Yb^{3+} was 1.76 and that between Lu^{3+} and Tm^{3+} was 5.9.

4. Successive Solvent Extractions

An experiment was conducted to determine if the equilibrium acid concentration and the separation coefficient between Lu^{3+} and Yb^{3+} would remain relatively stable after three successive extractions. A 0.30-M lanthanide stock solution was prepared from the lanthanide ore. The stock solution was made by dissolving 29.6-g of the ore in 1.00-M HCl to a volume of 500.00-ml. The solution was titrated with NaOH to determine the acid concentration which was found to be 0.82-M HCl. Fifteen and a half ml (15.50-ml) of concentrated HCl was added to 100.00-ml of the stock solution and the mixture was diluted to 200.00 ml with water. The final solution was 0.15 M in Ln^{3+} and was 1.33 M in

TABLE 9
DATA FOR SINGLE EXTRACTIONS OF Lu^{3+} , Yb^{3+} , Tm^{3+} , Er^{3+} ,
AND Y^{3+} USING ICP/MS ANALYSIS

Sample	$[\text{H}^+]_{\text{initial}}$	$[\text{H}^+]_{\text{equil}}$	$\log [\text{H}^+]_{\text{equil.}}$	$\log D_{\text{Lu}^{3+}}$	$\log D_{\text{Yb}^{3+}}$	$\log D_{\text{Tm}^{3+}}$	$\log D_{\text{Er}^{3+}}$	$\log D_{\text{Y}^{3+}}$
1	0.748	1.016	0.007	0.633	0.433	-0.083	-0.631	-0.794
2	1.01	1.244	0.095	0.460	0.246	-0.251	-0.744	-0.816
3	1.239	1.455	0.163	0.351	0.103	-0.430	na	na
4	1.497	1.680	0.225	0.256	-0.003	-0.534	-1.046	-1.169
5	1.735	1.916	0.282	0.136	-0.136	-0.693	-1.314	-1.593
6	1.977	2.112	0.324	0.028	-0.233	-0.754	-1.310	na

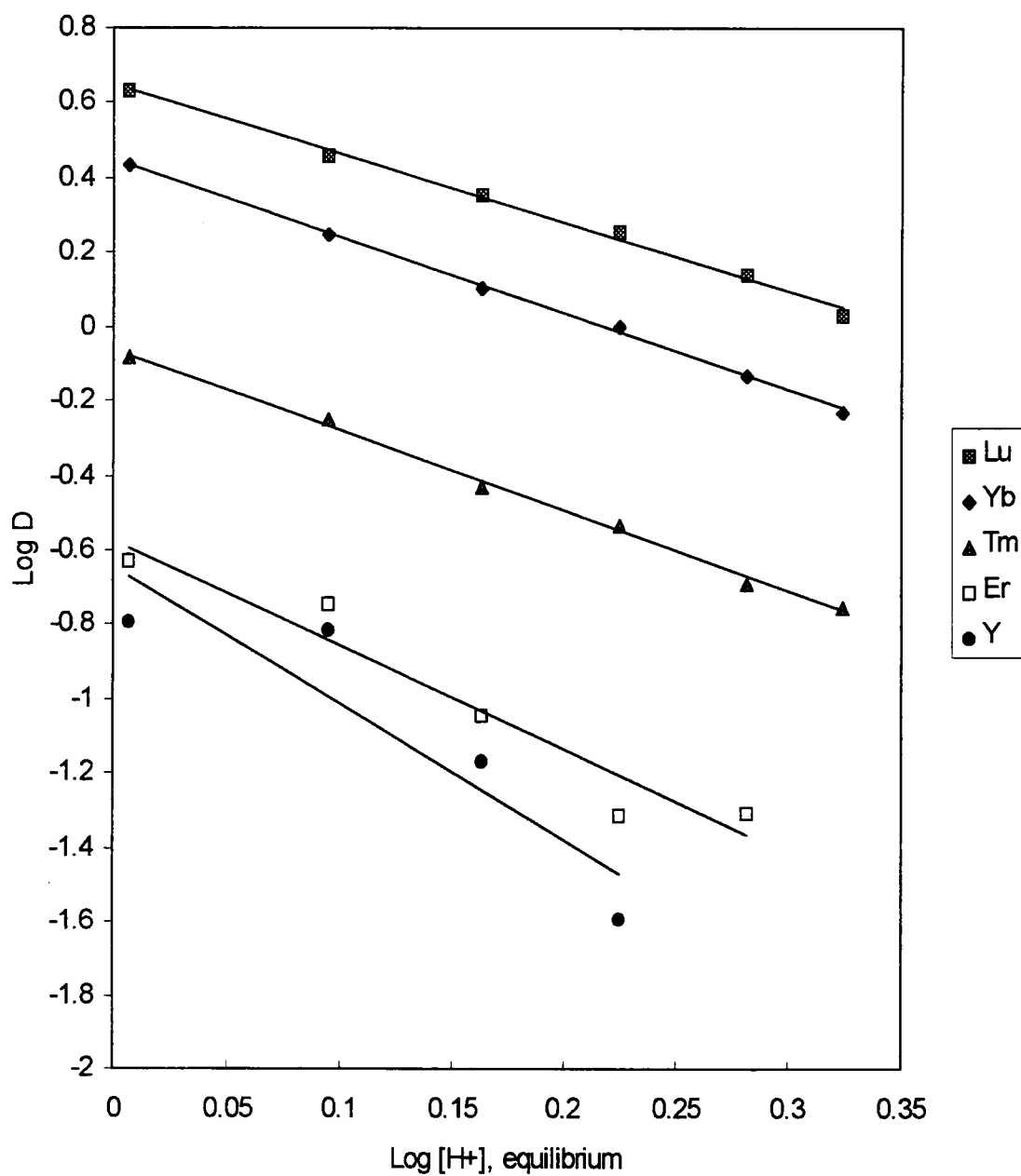


FIGURE 10

PLOT OF LOG D VS LOG [H⁺] FOR Lu³⁺, Yb³⁺, Tm³⁺, Er³⁺,
AND Y³⁺ USING ICP/MS ANALYSIS

HCl.

The first stage of the extraction was performed with 50.00-ml of the 0.15-M Ln^{3+} and 50.00-ml 0.45-M IQ-801 in kerosene in a 125-ml separatory funnel. The two phases were mechanically shaken for 15.0 min and allowed to settle for 10.0 min. After the settling period, 10.00-ml of the aqueous phase was removed and titrated with standardized NaOH to determine the equilibrium acid concentration. One tenth of a ml (0.10-ml) of the aqueous phase was also removed and diluted to 100.00-ml with 1.00-M HCl. Two ml (2.00-ml) of this solution was diluted to 100.00-ml with 1.00-M HCl and analyzed by ICP/MS for Lu^{3+} and Yb^{3+} .

The second stage in the successive solvent extraction was performed with 45.00-ml of the organic phase from the first stage and 45.00-ml of 1.52-M HCl. Again, the phases were mixed for 15.0 min and allowed to settle for 10.0 min. After settling, 10.00-ml of the aqueous phase was titrated to determine the equilibrium acid concentration and 0.10-ml of the aqueous phase was diluted the same way as was done for the first stage.

The third and final stage consisted of 40.00-ml of the organic phase used in stages one and two and 40.00-ml of 1.52-M HCl as the aqueous phase. The solution was shaken for 15.0 min and allowed to settle for 10.0 min. Again, 10.00-ml of the aqueous phase was titrated with standardized NaOH and a portion was diluted accordingly for ICP/MS analysis. Table 10 (p. 66) shows how the equilibrium acid concentration and the separation coefficients for Lu^{3+} and Yb^{3+} varied between the three stages.

Although the separation coefficient between Lu^{3+} and Yb^{3+} did vary to some extent, the acid concentration between each stage remained relatively constant which

TABLE 10
RESULTS FOR SUCCESSIVE SOLVENT EXTRACTIONS

Stage	$[\text{H}^+]_{\text{equilibrium}}$	$\text{Lu}^{3+}/\text{Yb}^{3+}$ Separation
		Coefficient
1	1.52	1.80
2	1.45	1.77
3	1.49	1.54

indicated that the extraction process is close to a metal-metal extraction rather than metal-proton extraction. Although the information found in this successive solvent extraction experiment was useful, a better understanding on how a counter-current solvent extraction system would behave was needed since this type of extraction is much more efficient than the successive stages in terms of solvent use and overall cost.

5. Counter-Current Solvent Extractions

An initial counter-current solvent extraction experiment was run using five stages. The initial aqueous phase consisted of 10.00-ml 0.90-M Ln^{3+} mixture (assuming the ore had a MW of 395-g/mol) in 1.45-M HCl and 50.00-ml 1.55-M HCl. The initial organic phase was 0.45-M IQ-801 in kerosene. Five separatory funnels were assembled next to each other and labeled A, B, C, D, and E. The two initial phases were placed in the 125-ml separatory funnel C and mechanically shaken for 15.0 min and allowed to settle for 10.0-min. After the settling period, the aqueous phase was removed and moved left to separatory funnel B and the organic phase was moved right to separatory funnel D. To both separatory funnels B and C 50.00-ml of “fresh” organic phase (0.45-M IQ-801 in kerosene) was added while 50.00-ml of “fresh” aqueous phase (1.55-M HCl) was added to separatory funnels C and D. To funnel D, 10.00-ml of the 0.90-M Ln^{3+} mixture was added. The three separatory funnels were shaken for 15.0-min and allowed to settle for 10.0-min. Again, the aqueous phases were removed and transferred to the separatory funnels to the left and the organic phases were removed and moved to the separatory funnels to the right. Both phases were now in separatory funnel C, while separatory funnels A and B contained only the aqueous phase and funnels D and E contained only the

organic phase. Fifty ml (50.00-ml) of fresh aqueous phase was added to funnels D and E while 50.00-ml of fresh organic phase was added to funnels A and B. To funnel C, 10.00-ml of 0.90-M Ln^{3+} was added. The five funnels were shaken for 15.0-min and allowed to settle for 10.0-min.

After settling, 5.00-ml of each of the aqueous phases was removed and titrated with standardized NaOH to determine the acid concentration after equilibrium. Another portion of each of the aqueous phases was removed and diluted with 1.00-M HCl to an appropriate concentration for analysis using ICP/MS. Figure 11 (p. 69) shows the theoretical (assuming a $\text{Lu}^{3+}/\text{Yb}^{3+}$ separation coefficient of 1.75) and experimental distribution for Lu^{3+} and Yb^{3+} after the final equilibrium. The units in the figure are in g/L.

Although the experimental results differ from theoretical calculations, there is separation of Lu^{3+} and Yb^{3+} occurring throughout the five stages. It appears as though the calculated distribution coefficients for Yb^{3+} using this method are higher than the results determined using the titration method for calculating distribution coefficients. The aqueous phase acidity in stage A was found to be 1.69-M, in stage B 1.62-M, in stage C 1.57-M, in stage D 1.48-M, and in stage E 1.51-M HCl.

A second counter-current solvent extraction experiment was conducted in which the aqueous phase was sampled after each equilibrium. The experimental conditions were identical to those performed in the first counter-current solvent extraction experiment. After each equilibrium, 0.10-ml of the aqueous phase was sampled and diluted with 1.00-M HCl for analysis using ICP/MS. After the third equilibrium, the organic phases were placed in contact with 50.00-ml 6.0-M HCl to strip the lanthanides from the organic

Org. Phase Lu Yb	Org. Phase Lu Yb	Org. Phase Lu Yb	Org. Phase Lu Yb	Org. Phase Lu Yb
0.33 Lu	0.69 Lu	2.14 Lu	0.82 Lu	0.47 Lu
1.30 Yb	7.01 Yb	16.62 Yb	4.93 Yb	2.12 Yb
Aq. Phase	Aq. Phase	Aq. Phase	Aq. Phase	Aq. Phase

(A)

Org. Phase Lu Yb	Org. Phase Lu Yb	Org. Phase Lu Yb	Org. Phase Lu Yb	Org. Phase Lu Yb
0.12 Lu	0.28 Lu	1.65 Lu	0.34 Lu	0.32 Lu
1.57 Yb	4.20 Yb	16.0 Yb	3.10 Yb	1.87 Yb
Aq. Phase	Aq. Phase	Aq. Phase	Aq. Phase	Aq. Phase

(B)

FIGURE 11

THEORETICAL (A) AND EXPERIMENTAL (B) DISTRIBUTIONS
FOR Lu^{3+} AND Yb^{3+} FOR COUNTER-CURRENT SOLVENT
EXTRACTION (TRIAL 1)

phase. The stripped organic phase was properly diluted and analyzed for Lu^{3+} and Yb^{3+} using ICP/MS. Again the theoretical and experimental distribution for Lu^{3+} and Yb^{3+} are shown in Figure 12 (p. 71). The theoretical values are placed in parenthesis next to the experimental values. The units in the figure are g/L.

The experimental results for the second counter-current solvent extraction are fairly similar to the theoretical calculations. The difference may be because the aqueous phase equilibrium acidities for stages A, B, C, D, and E were found to be 1.80, 1.73, 1.51, 1.41, and 1.44, respectively whereas the theoretical calculations were based on constant equilibrium acidities.

A third counter-current solvent extraction experiment was performed in order to try to keep the aqueous phase acidity more constant. Since previous experiments indicated that the optimum aqueous phase acidity for the separation of the lanthanide mix was around 1.5 to 1.6-M HCl, and since the second counter-current solvent extraction experiment showed a range of equilibrium acidities, the initial aqueous phase was lowered in attempt to correct for these problems. The initial (Stage C) aqueous phase consisted of 10.00-ml 0.90-M lanthanide mixture dissolved in 1.33-M HCl and 50.00-ml of 1.55-M HCl. The initial (Stage C) organic phase consisted of 0.45-M IQ-801 in kerosene. The experiment was conducted the same way as the second counter-current extraction experiment with the equilibrium aqueous phases being sampled for analysis of Lu^{3+} and Yb^{3+} using ICP/MS. The final equilibrium organic phase was stripped with 6.0-M HCl and analyzed for Lu^{3+} and Yb^{3+} . The final aqueous phase also was titrated with standardized NaOH to determine the equilibrium acidities of the five stages. The results

Stage A	Stage B	Stage C	Stage D	Stage E
Org. Phase Lu Yb Lu Yb Aq. Phase	Org. Phase Lu Yb Lu Yb Aq. Phase	Org. Phase 0.0(0.0)Lu 0.0(0.0)Yb 2.60(2.60)Lu 19.72(19.72)Yb Aq. Phase	Org. Phase Lu Yb Lu Yb Aq. Phase	Org. Phase Lu Yb Lu Yb Aq. Phase
Start				
Org. Phase Lu Yb Lu Yb Aq. Phase	Org. Phase Lu Yb Lu Yb Aq. Phase	Org. Phase (1.63) Lu (9.16) Yb 1.10(1.24) Lu 11.08(12.09)Yb Aq. Phase	Org. Phase Lu Yb Lu Yb Aq. Phase	Org. Phase Lu Yb Lu Yb Aq. Phase
Equilibrium 1				
Org. Phase Lu Yb Lu Yb Aq. Phase	Org. Phase (0.78) Lu (5.61) Yb 0.41(0.59) Lu 5.81(7.41)Yb Aq. Phase	Org. Phase (1.63) Lu (9.16) Yb 1.14(1.24) Lu 11.32(12.09)Yb Aq. Phase	Org. Phase (0.93) Lu (3.73)Yb 0.29(0.70)Lu 2.63(4.93)Yb Aq. Phase	Org. Phase Lu Yb Lu Yb Aq. Phase
Equilibrium 2				
Org. Phase 0.28(0.37) Lu 3.40(3.44)Yb 0.22(0.28)Lu 2.65(4.54)Yb Aq. Phase	Org. Phase 0.62(0.78)Lu 5.06(5.61)Yb 0.40(0.59) Lu 5.80(7.41)Yb Aq. Phase	Org. Phase 1.80(2.41) Lu 10.52(13.24)Yb 1.71(1.82) Lu 18.36(17.47)Yb Aq. Phase	Org. Phase 1.16(0.93) Lu 6.03(3.95)Yb 0.30(0.70)Lu 2.67(5.21)Yb Aq. Phase	Org. Phase 1.09(0.53) Lu 4.84(1.61)Yb 0.21(0.40)Lu 1.63(2.12)Yb Aq. Phase
Equilibrium 3				

FIGURE 12
THEORETICAL AND EXPERIMENTAL DISTRIBUTIONS
FOR Lu^{3+} AND Yb^{3+} FOR COUNTER-CURRENT SOLVENT
EXTRACTION (TRIAL 2)

are shown in Figure 13 (p. 73) with the theoretical calculations in parenthesis.

The results of the third counter-current solvent extraction are very similar to those in the second experiment including the equilibrium aqueous acidities after the five extractions. The equilibrium acidities for stage A, B, C, D, and E were 1.78, 1.72, 1.51, 1.42, and 1.44-M respectively.

D. CONCLUSIONS

There are many key factors which influence the feasibility and control of separating the heavy lanthanides using counter-current solvent extraction. Some of these factors include:

- 1) Settling times between the aqueous and organic phases,
- 2) Equilibrium times between the lanthanides and extractant,
- 3) Load concentration of the lanthanides in the aqueous phase, and
- 4) Equilibrium acidity of the aqueous phase.

1) The settling time required for the organic phase and aqueous phase was determined by shaking 10.00 to 15.00-ml of each phase for 5 min and recording the time needed for the two phases to settle. Using 0.60-M HCl and 0.45-M IQ-801, the time required for adequate settling for the 15.00-ml samples was 30 sec, while the 10.00-ml samples settled within 1 min. Samples shaken several separate times did not require more time to settle than the samples shaken only once.

2) The time required for chemical equilibrium to be reached between 0.33-M Yb^{3+} and 0.45-M IQ-801 was determined by measuring the disappearance of the Yb^{3+} in the

Stage A	Stage B	Stage C	Stage D	Stage E
Org. Phase Lu Yb Lu Yb Aq. Phase	Org. Phase Lu Yb Lu Yb Aq. Phase	Org. Phase 0.0(0.0)Lu 0.0(0.0)Yb 2.58(2.58)Lu 18.93(18.93)Yb Aq. Phase	Org. Phase Lu Yb Lu Yb Aq. Phase	Org. Phase Lu Yb Lu Yb Aq. Phase

Start

Org. Phase Lu Yb Lu Yb Aq. Phase	Org. Phase Lu Yb Lu Yb Aq. Phase	Org. Phase (1.62) Lu (8.79) Yb 1.04(1.23) Lu 10.46(11.60)Yb Aq. Phase	Org. Phase Lu Yb Lu Yb Aq. Phase	Org. Phase Lu Yb Lu Yb Aq. Phase
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Equilibrium 1

Org. Phase Lu Yb Lu Yb Aq. Phase	Org. Phase (0.77) Lu (5.39) Yb 1.58(0.59) Lu 6.32(7.11)Yb Aq. Phase	Org. Phase (1.62) Lu (8.79) Yb 2.08(1.23) Lu 11.14(11.60)Yb Aq. Phase	Org. Phase (0.92) Lu (3.79)Yb 0.36(0.70)Lu 2.90(5.00)Yb Aq. Phase	Org. Phase Lu Yb Lu Yb Aq. Phase
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Equilibrium 2

Org. Phase 0.28(0.37) Lu 3.11(3.30)Yb 0.18(0.28)Lu 2.31(4.36)Yb Aq. Phase	Org. Phase 0.82(0.77)Lu 6.05(5.39)Yb 0.42(0.59) Lu 5.12(7.11)Yb Aq. Phase	Org. Phase 1.65(2.39) Lu 9.62(12.81)Yb 1.59(1.81) Lu 15.38(16.91)Yb Aq. Phase	Org. Phase 1.16(0.92) Lu 5.72(3.79)Yb 0.30(0.70)Lu 2.42(5.00)Yb Aq. Phase	Org. Phase 0.88(0.52) Lu 3.92(1.63)Yb 0.22(0.40)Lu 1.58(2.16)Yb Aq. Phase
--	--	--	--	--

Equilibrium 3

FIGURE 13
THEORETICAL AND EXPERIMENTAL DISTRIBUTIONS
FOR Lu^{3+} AND Yb^{3+} FOR COUNTER-CURRENT SOLVENT
EXTRACTION (TRIAL 3)

aqueous phase at various mixing times. From the AES measurements, it was found that chemical equilibrium was reached within 2 min.

3) The load concentration of the aqueous phase was determined qualitatively. It was found that an aqueous phase 0.15-M Ln^{3+} in approximately 1.5-M HCl and an organic phase of 0.45-M IQ-801 were good concentrations to use in order to limit emulsion formation and to properly utilize the extractant. It was determined that higher concentrations of extractant tended to cause a higher degree of emulsion formation.

4) The optimum equilibrium aqueous acidity range was determined in two ways. Using the titration method, the optimum equilibrium acidity range in the aqueous phase was found to be from 1.4-M to 1.9-M HCl. This method, although fairly straightforward, gave similar results obtained using ICP/MS. The optimum equilibrium acidity range using ICP/MS was found to be 1.6-M to 2.2-M HCl. From these equilibrium acidities, the separation coefficient between Lu^{3+} and Yb^{3+} was calculated to be 1.5 to 1.8. The theoretical number of stages needed to produce 99.99% Lu with a $\text{Lu}^{3+}/\text{Yb}^{3+}$ separation coefficient of 1.5 was calculated to be 23, while a $\text{Lu}^{3+}/\text{Yb}^{3+}$ separation coefficient of 1.8 would theoretically require 16 stages.

CHAPTER IV

CONCLUSIONS AND SUMMARY

With recent applications of Lu in modern technology, a good separation technique is needed for the production of large quantities of Lu at high purities. Two modern separation methods for this application are ion exchange chromatography and solvent extraction. Solvent extraction has been used in both column-type separations and mixer-settler apparatus, with the latter having several key advantages over the former.

Prior to the solvent extraction studies, Yb^{3+} was electrolytically reduced at a Hg cathode in attempt to completely remove it from solution. This was attempted because Yb is the adjacent lanthanide to Lu and if it can be completely removed from a mixture of lanthanides, then the number of stages in the solvent extraction process can be considerably reduced. In other words, if Yb can be completely removed from a mixture of lanthanides, the separation "gap" between Lu and the rest of the lanthanides is considerably increased.

Under the best experimental conditions, it was found that only 90-95% of the Yb^{3+} was removed as YbSO_4 . Since Yb^{3+} was not removed completely, the number of stages in the solvent extraction process needed to produce 99.99% Lu would not be reduced. However, the amount of the lanthanide mixture needed to produce a given amount of Lu would decrease dramatically.

Although most of the Yb^{3+} was removed from solution, electrolytic reduction of Yb^{3+} has its drawbacks. The major problem with the method is that Hg was used as the

cathode. Since Hg is a very toxic metal, the method can not be used for industrial enrichment of Lu. Secondly, the method requires careful maintenance to control optimum conditions. One alternative to the electrolytic reduction of Yb^{3+} may be to use an activated metal (e.g., Mg or Al) in an aqueous or organic medium for the reduction of Yb^{3+} . If the reduction of Yb^{3+} to Yb^{2+} is possible using this method, perhaps the Yb^{2+} can be removed from solution using resins which are specific to +2 ions or precipitating insoluble Yb (II) salts.

Several factors that influence the effectiveness of the solvent extraction separation of Lu^{3+} from the other lanthanides were studied. It was determined that the settling time between the organic and aqueous phases and the time needed to reach chemical equilibrium between the lanthanides and IQ-801 were reached within 30 sec and 2 min, respectively. The optimum load concentration of the aqueous phase was found to be approximately 0.15-M Ln^{3+} in 1.4-M to 2.2-M HCl. The optimum equilibrium aqueous acidity was found to be 1.4-M to 2.2-M HCl using an organic concentration of 0.45-M IQ-801 in kerosene. The first three factors can easily be maintained in an industrial separation process. The equilibrium aqueous phase acidity, however, is not as easy to maintain. Although, a theoretical acidity was calculated based on distribution coefficients, it was found that the stages in the counter-current extraction did not behave theoretically. Therefore, the acidity in the aqueous phase needs to be monitored and adjusted during the extraction process.

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