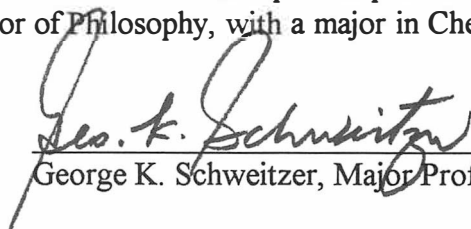


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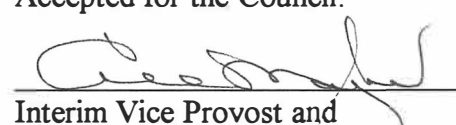
I am submitting herewith a dissertation written by Peter Michael Smith entitled "The Development of a Lutetium Recovery Plant." I have examined the final copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Chemistry.


George K. Schweitzer, Major Professor

We have read this dissertation
and recommend its acceptance:


Laurence Miller
Clifton Woods

Accepted for the Council:


Interim Vice Provost and
Dean of The Graduate School

THE DEVELOPMENT OF A LUTETIUM
RECOVERY PLANT

A Dissertation

Presented for the

Doctor of Philosophy

Degree

The University of Tennessee, Knoxville

Peter Michael Smith

August 2000

DEDICATION

The author would like to dedicate this work to his loving, enduring and beautiful wife, Erin, without whom he could never have reached his goals. This work is also dedicated to the author's parents, Duane and Dianna Smith, and his brother, Russ Smith, whose love and encouragement were a constant source of inspiration.

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ABSTRACT

This research project focused on the scale-up of an industrial facility for the continuous counter-current solvent extraction (CCCSX) separation of lutetium. CCCSX involves a multistage apparatus for the mixing in each stage of two immiscible liquid phases to transfer an analyte from one phase to the other. The two phases continuously flow in opposite directions in a CCCSX system. In this research, aqueous lutetium solutions, obtained from the acid leaching of lutetium oxyorthosilicate, were mixed with kerosene solutions of phosphorus based metal extractants (e.g. mono-2-ethylhexyl-(2-ethylhexyl) phosphonic acid, MEHEHP). This system extracted the lutetium from the aqueous phase, transferring the lutetium to the organic phase. The lutetium was stripped from the organic phase by mixing this phase with an aqueous solution of highly concentrated acid. The subsequent aqueous lutetium solution was processed to produce lutetium oxide.

Scale-up is a process which begins with bench-scale experiments and proceeds through pilot-scale experiments to the design of an industrial facility. Bench-scale experiments were performed to investigate the extraction characteristics of lutetium in a variety of systems. The information obtained from the bench-scale experiments was utilized in pilot-scale experiments. The pilot plant used for this research consisted of 15 interconnected mixer-settler units. This pilot plant was operated as a CCCSX system. The results of the pilot-scale experiments were used in the design of an industrial CCCSX facility with the capacity to produce 106 kg of 99.999% pure Lu_2O_3 from 127 kg of

lutetium oxyorthosilicate per day.

Research was also conducted on the industrialization of a technique known as precipitation stripping. Precipitation stripping involves the removal of a metal from a metal-loaded organic phase as a solid metal compound by mixing the organic phase with an aqueous solution of an appropriate precipitating agent. Precipitation stripping was applied to the lutetium CCCSX system to determine the effect of this technique of an industrial facility. It was determined that precipitation stripping can potentially reduce the volume of aqueous effluent generated by an industrial CCCSX facility by a considerable amount.

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CHAPTER 1

BACKGROUND

A. Introduction

The lanthanide elements have seen many technological applications over the years. Of these applications, the most important are their uses in phosphors, catalysts, ceramics and magnets.^{1,2} The light and middle lanthanides have been characterized extensively for use in these areas. The heavy lanthanides are now being used in these applications as well, and consequently the investigation of their properties has increased. A promising application of the heavy lanthanides is the use of lutetium in scintillation crystals. Lutetium oxyorthosilicate is the matrix for an excellent scintillator with a large γ -ray cross section and a very short decay time for the scintillation.

The majority of the industrial applications of the lanthanides require very high purity materials, typically 99.9% - 99.999% or higher. To achieve purities this high, the lanthanides must be rigorously separated from each other. This is not a trivial task. The lanthanides all have very similar physical and chemical properties. They all possess a +3 oxidation state and their ionic radii differ only by about 1.5% from one element to the next.³ The electronic structures in the outermost shell of the lanthanides are also very similar. Because of this, the electrochemical and complexing behavior of the lanthanides are almost identical. All of these factors make the separation of the lanthanides one of the most difficult separations to perform.

B. Lutetium Separation History

The discovery of lutetium has a controversial history. Lutetium was first separated from ytterbium in 1905 by Carl Auer von Welsbach. He used the fractional crystallization of double ammonium ytterbium oxalate. Fractional crystallization is a technique in which salts are separated based on their differing solubilities. A diagram of a fractional crystallization procedure is shown in Fig. 1.⁴ Auer did not report any quantitative data when he published his results in 1905-1906. His quantitative data, the atomic weights of lutetium and ytterbium and the emission spectrum of lutetium, were first reported on December 19, 1907 to the Vienna Academy. However, Georges Urbain had reported the atomic weight and spectral lines for lutetium one month earlier to the Paris Academy of Sciences. Urbain used the fractional crystallization of ytterbium nitrate to separate lutetium. Because Urbain reported numerical data before Auer, he was granted the priority of discovery by the International Committee on Atomic Weights in 1909. It is interesting to note that Urbain, himself, sat on this committee. Lutetium was also independently separated from ytterbium by Charles James at the University of New Hampshire in the summer of 1907. James separated lutetium by the fractional crystallization of double magnesium ytterbium nitrates. James did not report his findings and therefore his role in the discovery of lutetium has largely gone unnoticed.⁵

Fractional crystallization was the dominant separation technique for lutetium until the application of ion exchange to the lanthanides in the 1940's⁶. Ion exchange is a two-phase reaction in which ions are transferred from an aqueous solution to a solid resin and vice versa. A generalized equation for the cation exchange of lanthanide cations is:

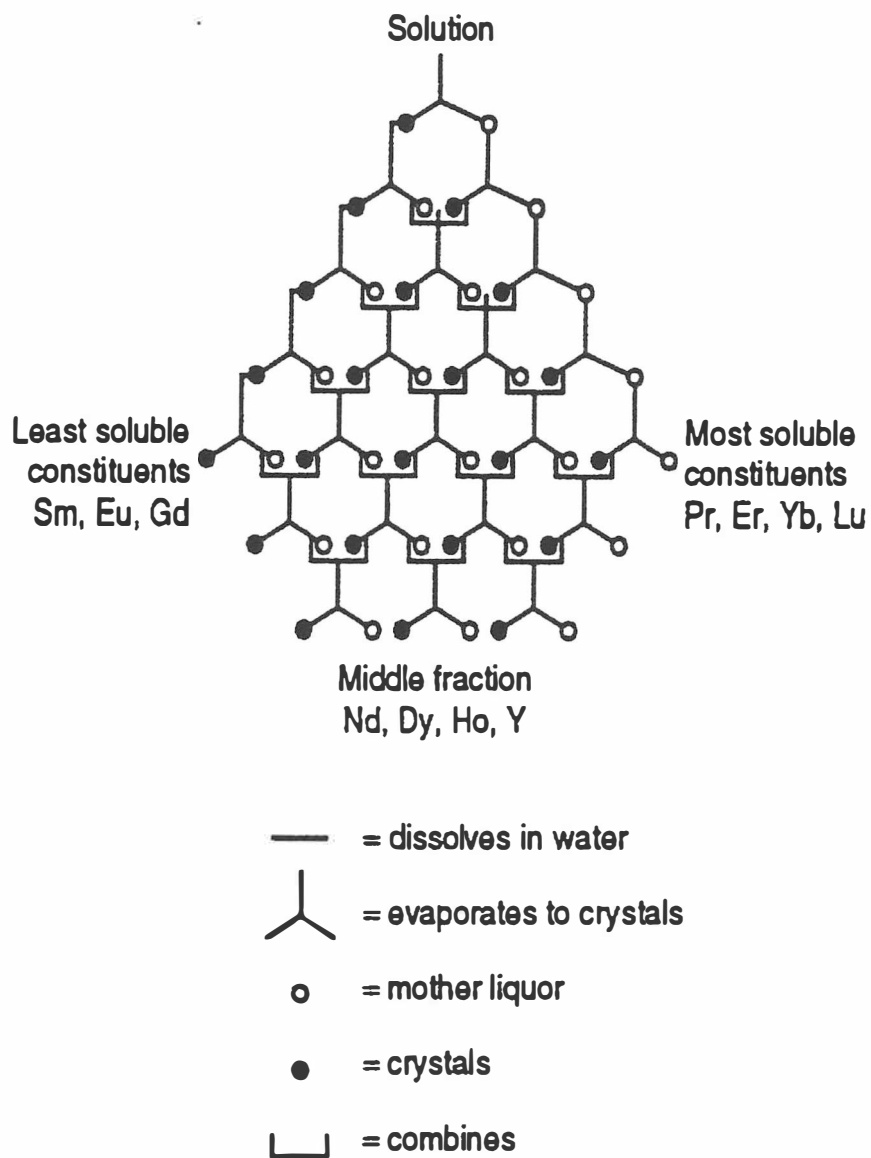


Fig. 1 Fractional Crystallization of the Salts of the Rare Earths

Source: F. Habashi, in "A Textbook of Hydrometallurgy," Métallurgie Extractive

Québec, Enr., Sainte Foy, Québec, Canada, 1993, pg. 559.



where Ln is the lanthanide, N is a univalent cation such as H^+ or NH_4^+ and R is the functionalized resin. Another type of ion exchange used in the separation of the lanthanides is anion exchange. A generalized equation for the anion exchange of a lanthanide anions is:



where X is the complexing anion for the lanthanide and Y is an exchangeable anion on the resin. Both cation and anion exchange have been employed to separate lutetium from the other lanthanides. Many different resins have been used in the cation exchange of lutetium. Among them are Ostion LG KS 0800⁷, Dowex 50 X2 - X16, KU-2⁶ and Diaion SK.⁸ The more common eluting agents used in the cation exchange of lutetium are α -hydroxyisobutyric acid (HIBA), α -hydroxy- α -methylbutyrate (HMB), citric acid, glycolic acid, lactic acid⁶ and mandelic acid.⁹ HIBA is the most frequently used eluting agent.¹⁰ Vobecký reports a separation factor of 1.3 for Lu/Yb, which is an average separation factor for adjacent lanthanides, using HMB as the eluting agent and Ostion LG KS 0800 as the resin.⁷ This separation factor is a representative value for the cation exchange separation of lutetium from ytterbium using common eluting agent and resins.

The anion exchange of lutetium has a more studied and diverse history. By far the most common anion exchange resin used is Dowex 1 X2-X16.^{6,11,12,13} A partial list of complexing reagents used to form the lutetium anion is: Cl^- , SCN^- , NO_3^- , PO_4^{3-} , HIBA, malonate, EDTA, CDTA (1,2-cyclohexanediamine-N,N,N',N'-tetraacetate)⁶, oxalate¹² and

lactate.¹⁴ Faris reports a Lu/Yb separation factor of 1.2 for the anion exchange separation of lutetium using 75/25 methanol/water solution as the eluting agent, Dowex 1 X4 as the resin and lactic acid as the complexing agent.¹⁴ This separation factor is a representative value for the anion exchange separation of lutetium from ytterbium using common anion exchange systems. Ion exchange dominated the industrial separation of lutetium from the 1940's until the 1960's. A new method was developed for the separation of lanthanides because the extent of dilution needed in the lanthanide solution to obtain high purity materials greatly reduced the amount of the lanthanides that could be processed. This factor prevented ion exchange from being economically preferable in industry.¹⁴ The new method that was developed for the separation of the lanthanides is another two-phase exchange process known as solvent extraction.

C. Solvent Extraction Separation of Lutetium

Solvent extraction is a separation technique that usually involves the partitioning of an ion or compound between two immiscible phases. In the solvent extraction of the lanthanides these immiscible phases are generally an aqueous solution and an organic based solution. The organic solution is comprised of an extractant, designed to preferentially attach to the lanthanides, and a diluent. Typical diluents include: chloroform, hexanol, benzene, toluene, xylene, hexanes and kerosene. The simplified generalized equation for the solvent extraction separation of the lanthanides is:



where HR is the extractant and the overbar indicates that the species is in the organic

phase. In a typical solvent extraction separation process for the lanthanides an aqueous solution of one or more lanthanide salts is mixed with an organic phase containing lanthanide extractant. The two phases are allowed to settle and then physically separated to undergo possible further treatment. The solvent extraction separation process transfers hydrogen ions from the organic phase into the aqueous phase thereby decreasing the pH of the solution. This indicates that the separation process described in (3) is pH dependent.

The efficiency of a solvent extraction system can be evaluated using three different numbers: extraction equilibrium constant (K_{ex}), distribution coefficient (D) and separation factor (α). K_{ex} is the equilibrium constant for equation (3):

$$K_{ex} = \frac{[LnR_3][H^+]^3}{[Ln^{+3}][HR]^3} \quad (4).$$

Solvent extraction system utilizing different extractants will have different K_{ex} values for a given lanthanide. If K_{ex} is large, then the extractant has a high affinity for the lanthanide and the solvent extraction process is efficient. The D of a solvent extraction system for a lanthanide is very closely related to K_{ex} and is defined as:

$$D = \frac{[Ln]_o}{[Ln]_a} \quad (5)$$

where $[Ln]_o$ is the concentration of the lanthanide in the organic phase and $[Ln]_a$ is the concentration of the lanthanide in the aqueous phase. It can be seen how D is abstracted from K_{ex} , and therefore, like K_{ex} , a large D indicates an efficient extraction. Both K_{ex} and

D apply to the extraction of a single element. The K_{ex} and D values of two elements can be combined to describe the separation efficiency of the two elements for a given solvent extraction system.

The separation selectivity of a solvent extraction process which separates lutetium from ytterbium is described by α , which is defined as:

$$\alpha = \frac{D_{Lu}}{D_{Yb}} \quad (6)$$

where D_{Lu} and D_{Yb} are the distribution coefficients of lutetium and ytterbium respectively.

The separation factor in a solvent extraction process is usually written such that it is greater than one and a large α indicates an efficient separation process. Many different extractants have been investigated for the solvent extraction separation of the lanthanides. These extractants can be grouped into two broad categories: those that contain phosphorus and those that do not. All of these extractants can be evaluated with either K_{ex} or D for the elements to be separated and the α of the separation.

1. Solvent extraction of lutetium with non-phosphorus based extractants

The solvent extraction separation of the lanthanides began in 1933 when it was determined that the lanthanide trichlorides would partition between an aqueous solution and an immiscible alcohol or ketone.¹⁵ These experiments are atypical for solvent extraction processes in that the alcohol or ketone is acting as both the extractant and the diluent. More conventional solvent extraction experiments have been performed using

solutions of carboxylic acids in a diluent to extract and separate the lanthanides. Long chain aliphatic carboxylic acids are primarily used because they tend to be hydrophobic and will extract the lanthanide from an aqueous solution into an immiscible organic solution. Some carboxylic acids that have been investigated are hexanoic, 2-ethylhexanoic, nonanoic, isononanoic, 3-cyclohexylpropanoic, heptadecanoic, stearic and eicosanoic acids.^{6,16} Carboxylic acids have been used in some commercial solvent extraction separation processes. These extractants are produced by Shell Chemical and are called Versatic 911 and Versatic 10. Versatic 911 is a mixture of aliphatic carboxylic acids which contain 9-11 carbon atoms. Versatic 10 is a mixture of aliphatic carboxylic acids containing 10 carbon atoms.¹⁷ Both Versatic 911 and Versatic 10 have been used to extract lutetium.^{16,18} Another type of carboxylic acids that have been used in the extraction of lutetium are the naphthenic acids which are substituted cyclopentylcarboxylic acids.^{19,20}

Extractants containing carbonyl substituents form an important class of extractants for lutetium. Chief among these extractants are the β -diketones, with the majority of the research being performed with acetylacetone (acac) and thenoyltrifluoroacetone (TTA)⁶ (Fig. 2). Nash reports a Lu/Yb separation factor of 1.77 for TTA in toluene.²¹ Manchanda used TTA and 1,7-diaza-4,10,13-trioxacyclopentadecane-N,N'-diacetic acid (DAPDA)(Fig. 3) in a synergistic lutetium extraction system.²² Research has also been conducted to study the extraction of lutetium by β -isopropyltropolone (HIPT) (Fig. 4) in chloroform.⁶ One final type of oxygen donor extractant for lutetium is the crown ether. The crown ether that exhibits the best extraction efficiency for lutetium is *sym*-dibenzo-16-

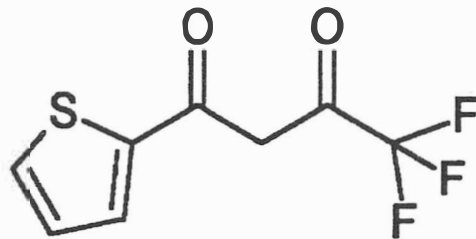


Fig. 2 Structure of TTA

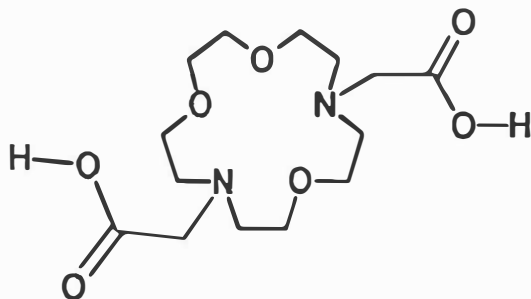


Fig. 3 Structure of DAPDA

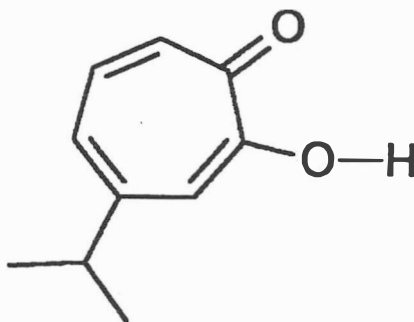


Fig. 4 Structure of HIPT

crown-5-oxyacetic acid.^{23,24} The acetic acid group on this crown ether is ionizable and therefore provides the counter anion needed to extract the lutetium into the organic phase.

Another class of extractants for lutetium is made up of those that contain nitrogen as donor atoms. The most useful of the nitrogen based extractants are the amines. Primary, secondary and tertiary amines have shown little promise for application to the solvent extraction separation of lutetium.²¹ Quaternary amines, however, have been used effectively for this purpose. This separation process is an anion exchange and is described by (2), where R is the positively charged quaternary amine instead of a resin. The commercial quaternary amine extractant Aliquat 336 (monomethyl-trioctyl-ammonium chloride) has been used to extract lutetium into xylene from an aqueous solution of lutetium thiocyanate.^{16,18}

2. Solvent extraction of lutetium with phosphorus based extractants

There are two basic types of phosphorus based extractants used for the solvent extraction of lutetium: neutral, solvating extractants and acidic extractants. The neutral, solvating extractants pull the lutetium from its aqueous salt solution into the organic phase by replacing the waters of hydration associated with the lutetium ion. A typical solvating extractant is tri-*n*-butyl phosphate (TBP). The structure of TBP can be seen Fig. 5. The extraction of lutetium with TBP can be represented by the following simplified equation:



A considerable amount of research has been conducted to study the behavior of lutetium in solvent extraction systems using neat TBP and solutions of TBP in various diluents.

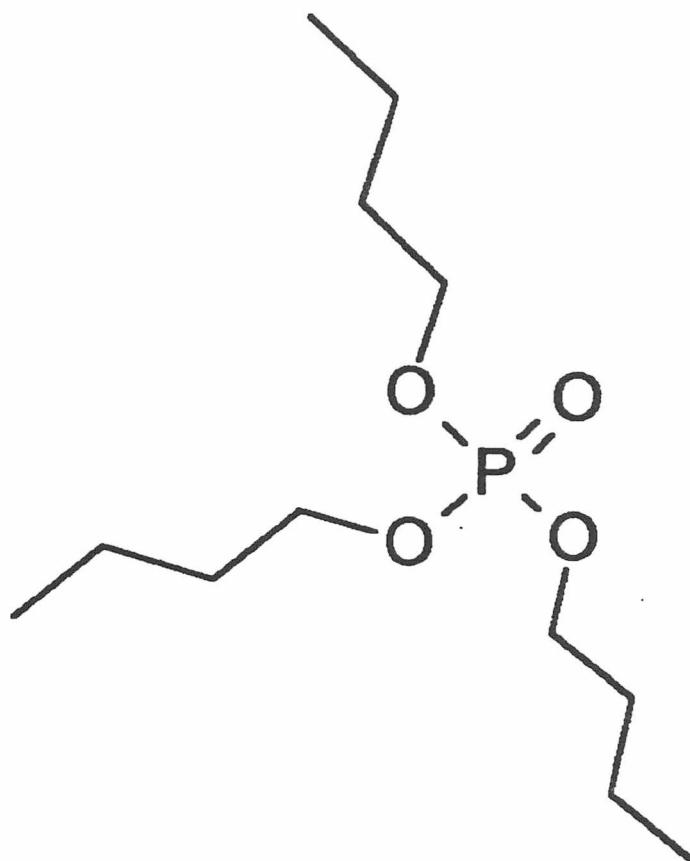
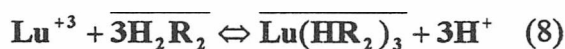


Fig. 5 Structure of TBP

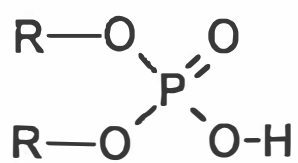
Peppard et al. demonstrated that lutetium nitrate can be extracted into 100% TBP.²⁵ It was also demonstrated that the D for the system increases with increasing nitric acid concentration. The D for this system was ~500 in 15.5M nitric acid and increased to ~3500 in 18.5M nitric acid. Solutions of TBP in carbon tetrachloride were also investigated. It was shown that the D for this system increased with increasing TBP concentration in the CCl₄. The results of this research have been confirmed by Hesford et al.²⁶ Much later, Preston and Du Preez studied the extraction behavior of lutetium nitrate from ammonium nitrate solutions.¹⁶ The system of 0.01M Lu(NO₃)₃ in 1M HNO₃ and 2M NH₄NO₃ gave 6% extraction of the lutetium nitrate into 2M TBP in toluene. The extraction of lutetium nitrate was increased to 26% by increasing the ammonium nitrate to 5M. The extraction of lutetium into TBP can also be increased by changing the anion of the lutetium salt. Yoshida demonstrated that the extraction of lutetium thiocyanate was much more efficient than the extraction of lutetium nitrate.²⁷ At a pH of 4 the D for Lu was ~60 from 3.0M NH₄SCN into 0.19M TBP in kerosene. The extraction of lutetium salts into TBP has been investigated by others with similar results.²⁸⁻³⁰

The second class of phosphorus based extractants for lutetium is the acidic extractants. As indicated by the name, the acidic extractants have an ionizable proton which can be exchanged for the lutetium in the solvent extraction process. The general reaction for the acidic extraction of lutetium can usually be described by the following equation:

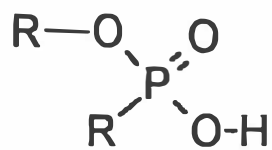


where H₂R₂ is the acidic extractant in its dimerized state. It is generally known that the

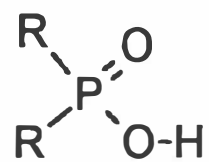
many acidic extractants form dimers in many organic solutions.⁶ The extraction of lutetium with acidic extractants is highly pH dependent, as indicated by (8). Within the class of acidic extractants there are three basic structural types: the phosphoric acids, the phosphonic acids and the phosphinic acids (Fig. 6). The earliest phosphorus-based acidic extractant to be used for the extraction of lutetium was di-2-ethylhexyl phosphoric acid (D2EHPA). Peppard et al., studying the extraction of lutetium with 0.75M D2EHPA in toluene, determined the D for lutetium from 0.5M HCl to be ~320.²⁵ Owens and Smutz extracted lutetium in the $\text{LuCl}_3\text{-H}_2\text{O-HCl-1M D2EHPA}$ in Amsco (mineral spirits) system.³¹ The D for lutetium from 5M HCl was shown to be 0.16. Sato used D2EHPA to extract lutetium from both hydrochloric acid and nitric acid.³² Kerosene solutions containing 0.05M D2EHPA were used in the experiments. The D_{Lu} from 0.1M HCl was shown to be ~25 and the D_{Lu} from 0.2M HNO_3 was ~65. More importantly, Sato reported a Lu/Yb α of 1.03 for the hydrochloric acid system. Lutetium extraction from sodium nitrate solutions was investigated by Preston and Du Preez.¹⁶ At a pH of 3, 100% of the lutetium was extracted from an aqueous solution of 0.02M Lu^{+3} and 0.4M NaNO_3 using 0.2M D2EHPA in kerosene. The extraction of lutetium from non-complexing media was studied by Pierce and Peck.³³ 20% solutions of D2EHPA in toluene were used to extract lutetium from perchloric acid. Again it was shown that D_{Lu} decreases as the acid concentration increases. Pierce and Peck reported a Lu/Yb α of 1.86 for their system. Sary confirmed the results of Peirce and Peck by using toluene solutions of D2EHPA and also reported a $\alpha = 1.86$.¹³ Bolshom and Pippel also used D2EHPA to extract lutetium.³⁴ Other phosphoric acids have been studied in the extraction of lutetium including: dibutyl



A.



B.



C.

Fig. 6 Structure of Acidic Organophosphorus Extractants

(A) Dialkylphosphoric acid (B) Alkyl-(alkyl)phosphonic acid (C) Dialkylphosphinic acid

phosphoric acid HDBP(in dibutyl ether)^{13,35}, 2-ethylhexyl-phenyl phosphoric acid HEH ϕ P (in diethyl benzene)¹³, di(butoxyethyl) phosphoric acid HDBEP³⁶, mono-*n*-octyl phosphoric acid H₂MOP³⁶ and di[para(1,1,3,3-tetramethyl-butyl)phenyl] phosphoric acid HDO ϕ P.³⁷

As seen in Fig. 6, the phosphonic acids contain one less oxygen atom than the phosphoric acids. This makes the phosphonic acids weaker acids than the phosphoric acids which indicates that the extraction of lutetium with phosphonic acids will occur at higher pH values. The most commonly studied phosphonic acid for the extraction of lutetium is mono-2-ethylhexyl-(2-ethylhexyl) phosphonic acid (MEHEHP). Sato used 0.2M solutions of MEHEHP in kerosene to extract lutetium from 0.1 M HCl.³² He reported a D_{Lu} of ~ 25 and a Lu/Yb $\alpha = 1.13$, which is better than the reported D2EHPA α . Enxin et al. extracted lutetium from 0.01M solutions of lutetium in 1 M (Na, H)NO₃ using 0.25M MEHEHP in *n*-dodecane.³⁸ As before, the D_{Lu} decreased as the acid concentration was increased. A Lu/Yb α of 1.83 was reported for this system. Wu et al. investigated the extraction of lutetium from both chloride and nitrate solutions.³⁹ It was determined that nitrate solutions gave a more efficient extraction in MEHEHP-kerosene systems. While MEHEHP is the most common of the phosphonic acid extractants it is not the only one to be studied. Other phosphonic acids that have been investigated for the extraction of lutetium are: mono-*n*-octyl-(*n*-octyl) phosphonic acid HO[OP], mono-*n*-octyl-(phenyl) phosphonic acid HO[ϕ P], mono-*n*-octyl phosphonic acid H₂[OP], mono-*n*-octyl-(dichloromethyl) phosphonic acid HO[Cl₂MP]³⁶ and mono-(1-hexyl-4-ethyl)octyl-(isopropyl) phosphonic acid.⁴⁰

The third class of phosphorus based acidic extractants are the phosphinic acids. As seen in Fig. 6, the phosphinic acids contain two fewer oxygen atoms than the phosphoric acids and are, therefore, the weakest acids of the phosphorus-based acidic extractants. Again, just like the phosphoric and phosphonic acids, the most common phosphinic acid used in the extraction of lutetium is di-2-ethylhexyl phosphinic acid (D2EHPinA). However, the quantity of research that has been conducted to study the extraction of lutetium with the phosphinic acids is considerably less than that for the phosphoric and phosphonic acids. The majority of the lutetium extraction research is tied up in patents or reported in Asian language journals.⁴¹ A few accounts of research have been recorded in English language journals. Preston and Du Preez reported 100% extraction of lutetium from a 0.02M Lu^{+3} in 0.40M NaNO_3 at a pH of 3 using 0.20M D2EHPinA in toluene.¹⁶ Nagaosa and Binghua determined that the D_{Lu} was $\sim 10^{1.5}$ for an aqueous solution of 0.01M Lu^{+3} in 0.1M sodium perchlorate at a pH of 0.1 ($\sim 0.8\text{M H}^+$) using 0.32M D2EHPinA in heptane.⁴² Nagaosa and Binghua also compare the K_{ex} of Lu^{+3} for its extraction with D2EHPA, D2EHPinA and diphenyl phosphinic acid (HDPP). It was determined that the HDPP-Lu system has the largest K_{ex} followed by D2EHPinA and D2EHPA respectively.

One final class of phosphorus-based extractant for lutetium are the carbamoylmethyl phosphonates. The carbamoylmethyl phosphonates are ionizing extractants similar to the β -diketones. Horwitz et al. studied the extraction of lutetium with 0.817M solutions of dihexyl-N,N-diethyl-carbamoylmethyl phosphonate (DHDECMP, Fig. 7) in p-diisopropyl benzene. The D_{Lu} from 1 M lithium nitrate was 0.18

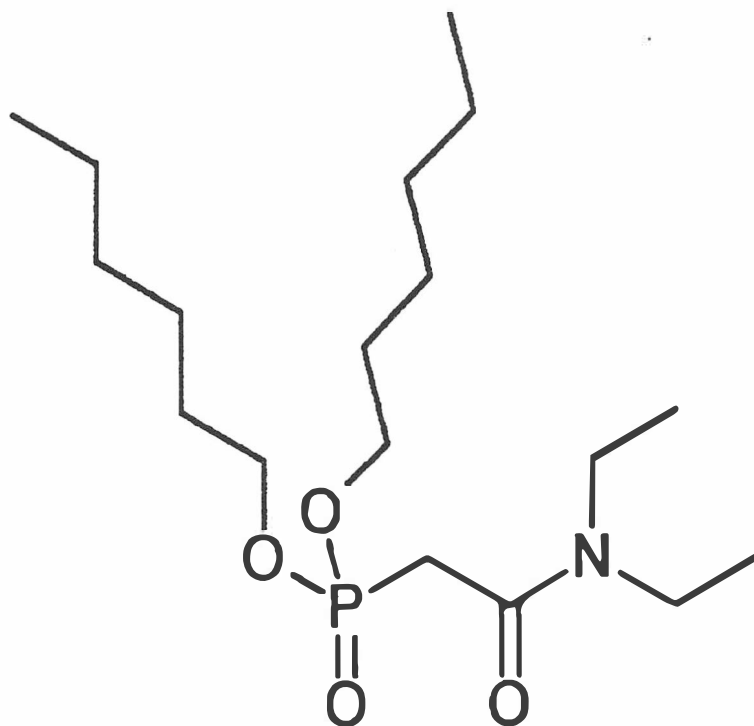


Fig. 7 Structure of DHDECMP

and it was 0.0558 from 1M HNO₃.⁴³

3. Stripping of lutetium from the lutetium-loaded organic phase

As indicated many times above, the extraction efficiency of lutetium by an acidic extractant into an immiscible organic phase is strongly pH dependent. This fact can be utilized in removing, or stripping, the lutetium from a lutetium-loaded organic phase. As the pH of the aqueous system decreases the D_{Lu} also decreases. This can be recognized by applying Le Chatelier's principle to (8). At some pH the D_{Lu} will become less than one and the lutetium will be concentrated in the aqueous phase. This is how lutetium is conventionally removed from a loaded organic phase. The loaded organic phase is mixed with an aqueous acid phase in which the pH is sufficiently low to concentrate the lutetium in the aqueous phase. When the phases separate, all or a portion of the lutetium will have been removed from the organic phase. Hydrochloric and/or nitric acid have been traditionally used to strip lutetium. Very little research has been reported for the stripping of lutetium from loaded organic phases. Owens and Smutz report that five double portions of 6M HCl stripped only 70% of the lutetium from the loaded organic phase in the LuCl₃-H₂O-HCl-1M D2EHPA (in Amsco mineral spirits) system.³¹ This difficulty in stripping lutetium, and the other heavy lanthanides, from D2EHPA is one of the contributing factors that led researchers to begin investigating MEHEHP and D2EHPinA. Wu et al. performed extensive stripping studies for lutetium from D2EHPA and MEHEHP.³⁹ Four portions of 5.00M HNO₃ stripped 99.7% of the lutetium from MEHEHP but only stripped 29.5% of the lutetium from D2EHPA. Four portions of

6.05M HCl stripped 100% of the lutetium from MEHEHP but only 61.0% from D2EHPA. They also determined that HCl was better at stripping than HNO_3 from both MEHEHP and D2EHPA.

D. Industrial Separation of Lutetium by Solvent Extraction

The industrial separation of lutetium from the other lanthanides is carried out through a process known as continuous counter-current solvent extraction (CCCSX). CCCSX involves joining many stages of extraction together in sequence to produce a system in which the aqueous and organic phases continuously move in opposite directions. Each stage in the CCCSX system acts like an individual separatory funnel and the reaction occurring in each stage is described by (8). The physical processes of mixing and settling of the two phases in an individual stage of a CCCSX system are also very similar to the separatory funnel processes. After the phases are mixed, they are allowed to settle and then the settled phases are transferred in opposite directions to the respective adjacent stage where further extraction takes place. A simple schematic diagram of a CCCSX system is shown in Fig. 8.⁴⁴

The lutetium is introduced into the CCCSX system in the aqueous phase. This introduction usually occurs in the middle of the CCCSX system. During the mixing of the aqueous phase with the organic phase, a portion of the lutetium, along with a portion of the impurities, transfers into the organic phase. As stated before, this extraction is strongly pH dependent. The pH of the aqueous solution can be optimized to provide maximum extraction of lutetium and minimum extraction of the impurities. Once the

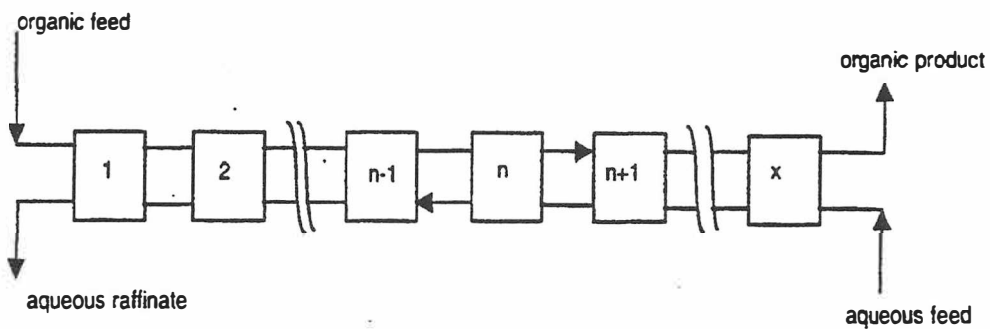


Fig. 8 Countercurrent Contact of Aqueous and Organic Phases in Multi-Stage Solvent

Extraction (x = total number of stages)

Source: Doyle, F.M., M.G. Benz, J.C. Shei, D.S. Bao, H.X. Ku and N.D. Zhen, in "Rare Earths and Actinides: Science, Technology and Applications IV," Bautista, R.G. and B.

Mishra, Eds., TMS, Warrendale, PA, 2000, pp. 31-44.

partially depleted aqueous phase has settled, it is transferred to be mixed with fresh organic phase. This fresh organic phase extracts another portion of the lutetium and its impurities. The aqueous phase is transferred again any number of times to ensure that the all of the lutetium has been extracted into the organic phase. As the aqueous phase is being treated and transferred in one direction, the organic phase is being transferred in the other direction to be mixed with fresh aqueous in order to remove the impurities.

The typical apparatus used in CCCSX systems is known as a mixer-settler system (see Fig. 9).⁴⁵ Mixer- settlers are usually plastic boxes comprised of two chambers, a mixing chamber and a settling chamber. The mixer always contains some type of agitation appliance, usually an impeller attached to a stirring motor. The aqueous and organic phases are pumped into the mixer and agitated by the impeller. The mixed phases are drained into the settler which can either be a simple chamber or it can contain baffles (to increase settling time). In CCCSX the individual mixer-settlers are the stages of extraction mentioned above. To produce high purity lutetium (99.99% - 99.999%), many stages are required. However, not all of the stages in a CCCSX system have the same function.

A general CCCSX system for lutetium contains three sections of stages: extraction, scrubbing and stripping. The extraction stages involve the mixing of an aqueous lanthanide solution with the organic phase to extract the lutetium and any impurities. In the scrubbing stages, the lanthanide loaded organic solution is mixed with fresh aqueous phase which removes the impurities and leaves only lutetium in the organic phases. The purity of the lutetium in the organic phase is dictated by the number of

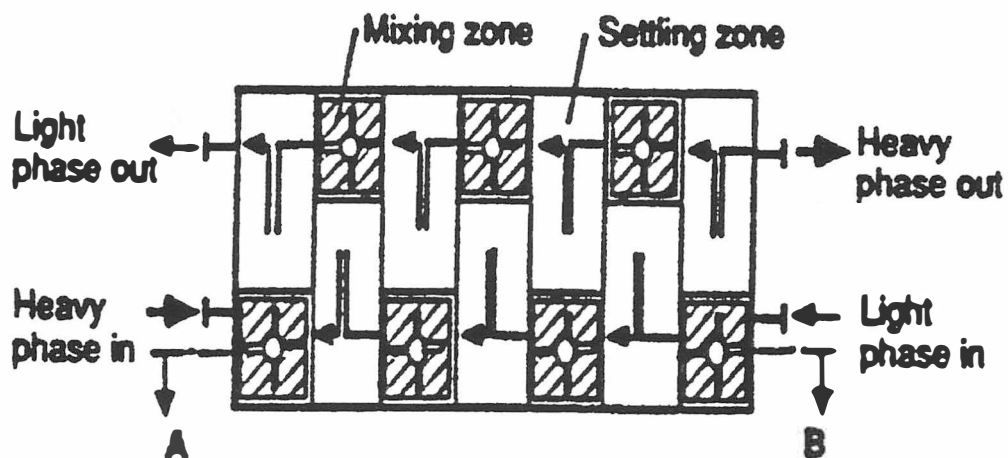


Fig. 9 Diagram of Simple Mixer-Settler

Source: Muller, E., R. Berger, W.C.G. Koster and M. Cox, in "Ullmann's Encyclopedia of Industrial Chemistry," Vol. B3, Gerhartz, W., Ed., VCH Publishers, Deerfield Beach,

FL, 1988, pg. 6-20.

scrubbing stages in the CCCSX system. A good rule of thumb to determine the number of stages needed for a desired purity is:

$$\alpha^x = N \quad (9)$$

where N is the desired purity and x is number of stages needed. An example of this calculation for the separation of lutetium from ytterbium to obtain 99.999% lutetium is:

$$1.5^x = 99999, \quad x \approx 29. \quad (10)$$

Therefore, if the separation factor between lutetium and ytterbium is 1.5, then 29 stages of scrubbing are necessary to obtain 99.999% lutetium. The stage into which the lutetium is introduced determines the separation of extraction stages from the scrubbing stages. All of the stages in the direction of the aqueous flow, from the point of lutetium introduction, will be extraction stages. The stages in the direction opposite of the aqueous flow, from the point of lutetium introduction to the stripping stages, will be scrubbing stages.

Finally, in the stripping stages, the organic phase loaded with pure lutetium is mixed with a highly concentrated aqueous acid solution to strip the lutetium from the organic phase. This process transfers the lutetium back into an aqueous phase where it can undergo any final processing to produce a lutetium compound. General overviews on the use of mixer-settler technology in CCCSX can be found in many good review articles.⁴⁶⁻⁵¹ Wu et al. investigated the industrial separation of lutetium from a lanthanide concentrate using MEHEHP. They reported an increase of lutetium purity from 8% to 99.99% after 60 scrubbing stages. The CCCSX system described also employed 20 extraction stages and 37 stripping stages, 30 using 5.0M HNO₃ and 7 using 6.0M HCl. This system had the capacity to produce 170g of 99.95% Lu₂O₃ per day.⁵²

Two major industrial producers of lutetium exist in the world at this time: Rhône-Poulenc (Rhodia) in France and The Yao Lung Chemical Co. in The Peoples Republic of China.⁵³ However, both companies receive their lutetium ore from the Baotou bastnaesite (lutetium containing lanthanide ore) deposit in Inner Mongolia (Northern China). A very simplified flowsheet of the Yao Lung Chemical Plant is shown in Fig. 10.⁵³ This flowsheet is based on the general Rhône-Poulenc flowsheet for the solvent extraction separation of the lanthanides. The Rhône-Poulenc flowsheet is the standard which the vast majority of all industrial producers of the lanthanides follow. Fig. 11 shows the Rhône-Poulenc flowsheet.⁵⁴

E. Precipitation Stripping for the Removal of Lutetium from a Loaded Organic Phase

The acid stripping of lutetium, from a lutetium-loaded organic phase, back into a aqueous phase has been described above. This resultant aqueous lutetium phase contains highly concentrated acid. In order to further treat this aqueous phase, the acid must first be neutralized. Oxalic acid is then generally added to the neutralized lutetium solution to precipitate the lutetium as lutetium oxalate, $\text{Lu}_2(\text{C}_2\text{O}_4)_3$. Lutetium oxalate is then calcined to the oxide, which is the starting material for most lutetium compounds. In an industrial facility this process generates a considerable quantity of neutralized acid waste (concentrated salt solutions). Disposal of these waste salt solutions is not only potentially hazardous to the environment, but it can also be very costly.

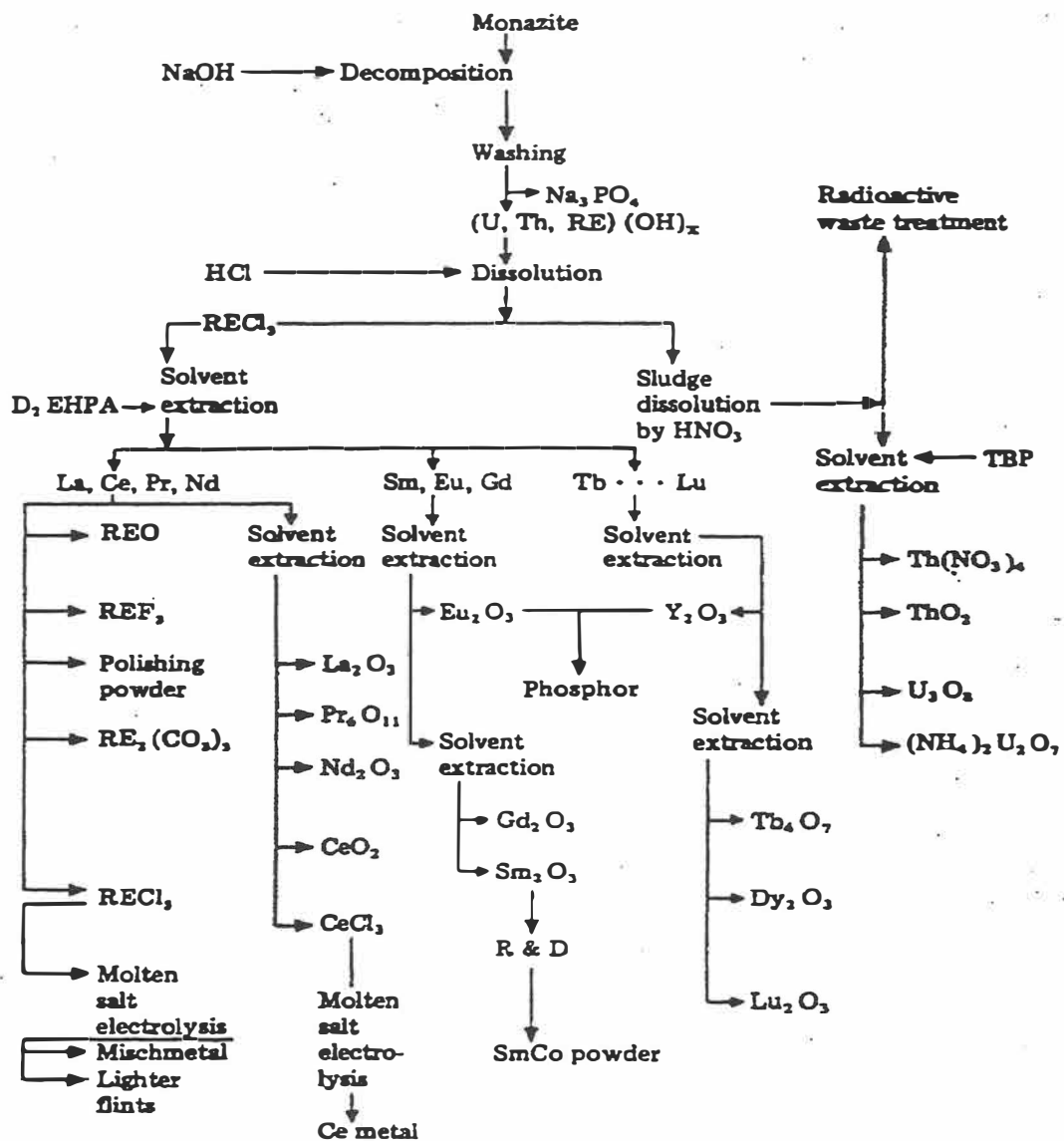


Fig. 10 Yao Lung Chemical Plant Flowsheet

Source: Zhang, Z.B., K.Y. Lu, K.C. King, W.C. Wei and W.C. Wang, Hydrometallurgy,

9, 1982, pp. 205-210.

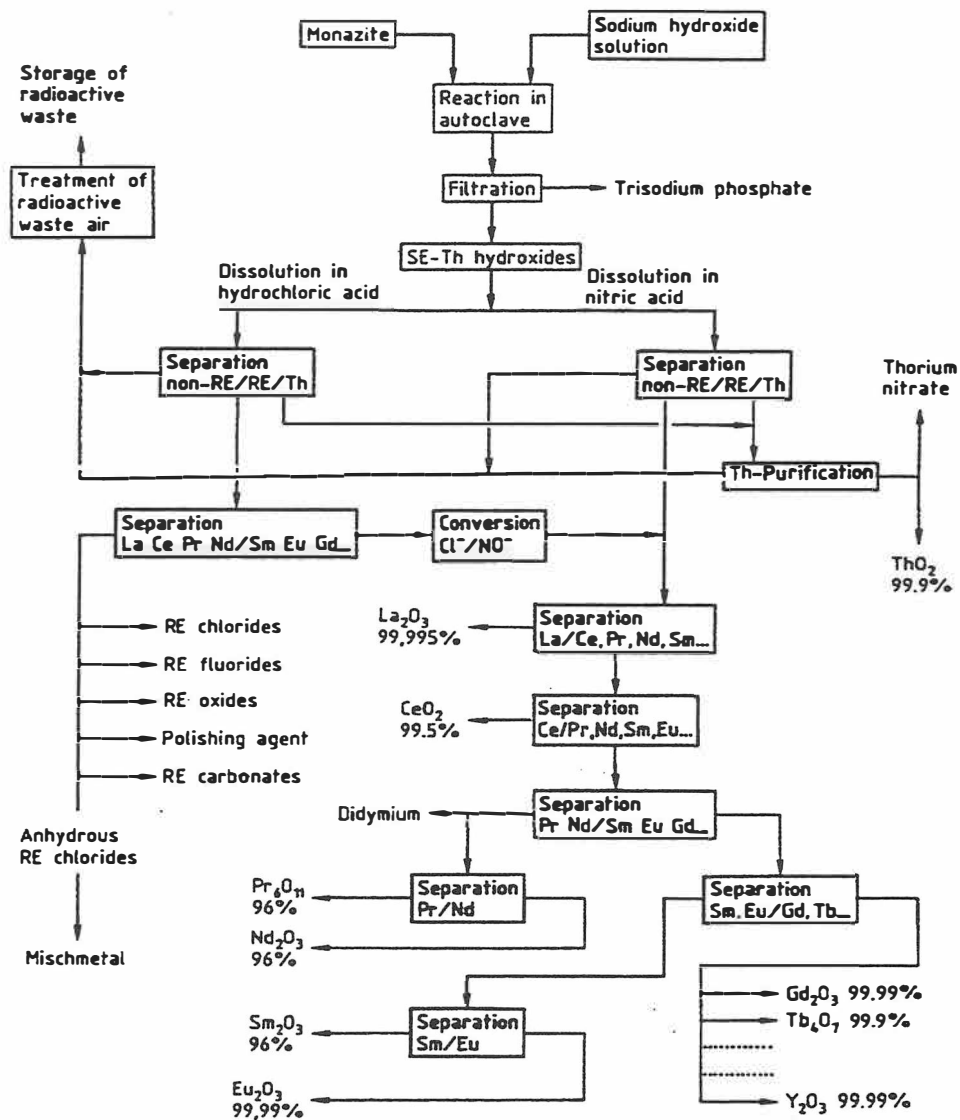
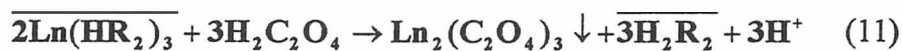


Fig. 11 The Rhône-Poulenc Flowsheet

Source: I. McGill, in "Ullmann's Encyclopedia of Industrial Chemistry," Vol. A22, Elvers, B., S. Hawkins, W. Russey and G. Schulz, Eds. VCH Publishers, Weinheim, FRG, 1993, pg. 631.

A potential remedy to the problem of salt solution disposal has been proposed by Lee and Doyle.⁵⁵ The remedy is precipitation stripping. Precipitation stripping is a technique in which a metal ion is removed from an organic phase by mixing that phase with an immiscible aqueous phase containing a selective precipitating agent for the metal. This process directly precipitates the metal out of the organic phase, depositing it as an insoluble salt in the aqueous phase. Precipitation stripping can be described as the combination of acid stripping and aqueous precipitation. An excellent example of precipitation stripping is the removal of a lanthanide ion from an organophosphorus solution using aqueous oxalic acid:



where the overbar indicates the species is in the organic phase, H_2R_2 is the lanthanide extractant, Ln is the lanthanide being extracted and the down arrow indicates that the species is insoluble.

The applicability of precipitation stripping to a particular CCCSX system can be estimated by combining the extraction equilibrium constant (K_{ex}) of the CCCSX system, the solubility product (K_{sp}) of the insoluble metal salt to be produced and the protonation constants of the precipitating agent (K_{p}). For example, this analysis can be performed on the system represented by (11):

$$K_{\text{ex}} = \frac{[\overline{\text{Ln}(\text{HR}_2)_3}][\text{H}^+]^3}{[\text{Ln}^{+3}][\text{H}_2\text{R}_2]^3} \quad (12)$$

$$K_{sp} = \frac{[Ln^{+3}]^2 [C_2O_4^{-2}]^3}{[Ln_2(C_2O_4)_3]} \quad (13)$$

$$K_{p1} \times K_{p2} = K_p = \frac{[H_2C_2O_4]}{[C_2O_4^{-2}][H^+]^2} \quad (14)$$

therefore if

$$K_{strip} \equiv (2K_{ex})^{-1} \times (K_{sp})^{-1} \times (3K_p)^{-1} > 1 \quad (15)$$

then the lanthanide should be precipitated as the insoluble oxalate. This general analysis can be applied to solvent extraction systems in which precipitation stripping could substitute for acid stripping and subsequent precipitation.

Some research has been conducted on the precipitation stripping of lanthanide ion from organic solutions. Yoon and Doyle have prepared yttrium and lanthanum oxalate powders by precipitation stripping from carboxylate based extractants using aqueous solutions of oxalic acid and dimethyloxalate.^{56,57} Konishi, Noda and Asai also precipitated yttrium oxalate from a carboxylate extractant using oxalic acid.⁵⁸ Precipitation stripping with oxalic acid has been used by Lee and Doyle to remove yttrium and lanthanum from D2EHPA.⁵⁵ Iglesias et al. also studied the precipitation stripping of yttrium oxalate from D2EHPA⁵⁹, as did Combes et al.⁶⁰ Neodymium oxalate has been precipitated with oxalic acid from MEHEHP by Konishi, Asai and Murai.^{61,62} Konishi and Asai also extended their research on precipitation stripping from MEHEHP to include yttrium and cerium.⁶³

Other anions have been studied in the precipitation stripping of the lanthanides.

Perhaps the earliest, and only, researchers to use precipitation stripping to remove lutetium from an organic phase were Owens and Smutz.³¹ Aqueous solutions of 20% HF were used to completely strip lutetium from D2EHPA as lutetium fluoride. Zieliński et al. precipitated lanthanum and neodymium fluorides from D2EHPA using phosphoric and sulfuric acid solutions containing ammonium bifluoride.⁶⁴ Lanthanum and neodymium have been stripped from D2EHPA as the double sulfates by Zieliński, Buca and Szczepanik by using sulfuric acid solutions of potassium, sodium and ammonium sulfate.⁶⁵ This work was continued by Zieliński and Szczepanik and it included europium, dysprosium and erbium.⁶⁶

All of the research that has been conducted on the precipitation stripping of the lanthanides using oxalic acid has been carried out to regulate the oxalate particle size and particle morphology. Plus, this research has been carried out solely on the light lanthanides. The only precipitation stripping studies involving the middle and heavy lanthanides have produced the fluorides or sulfates, which are more difficult to convert to the oxides than the oxalates. Not one of the accounts of research on precipitation stripping reports application of this technique to the industrial separation of the lanthanides by CCCSX. The industrial application of precipitation stripping to the CCCSX of the lanthanides is an area ripe with research possibilities.

F. Summary of Proposed Research

CTI, Inc. of Knoxville, Tennessee is a major producer of positron emission tomography (PET) scanners. PET scanners work by detecting γ -rays emanating from a patients body. The γ -ray detectors used in the most sensitive of CTI's PET scanners are made of lutetium oxyorthosilicate (Lu_2OSiO_4 or LSO) containing 0.2 atom% cerium dopant. LSO is prepared as a single crystal by the Czochralski growth method. This growth method has the potential to concentrate the other heavy lanthanides in the bottom of a crystal. As the crystal is pulled out of the Lu_2O_3 - SiO_2 - CeO_2 melt, the solidification process will eliminate the impurities from the LSO matrix, thereby concentrating the impurities in the bottom of the crystal. This process is known as zone refining.

After the growing process is completed, the LSO crystals are cut and shaped into the proper detector configuration. At the present time, CTI is only ~34% efficient in their LSO production. This indicates that ~66% of the LSO that is prepared ends up as unusable scrap. Because of the high cost of lutetium oxide, CTI is very interested in developing a system which will treat their scrap LSO and return to them 99.999% pure lutetium oxide.

The research that will be performed for CTI involves four aspects: bench scale counter-current solvent extraction experiments for lutetium, experimental scale-up to a pilot plant, the design of a factory for the CCCSX of lutetium and the application of precipitation stripping to the CCCSX of lutetium.

The bench scale solvent extraction experiments will be used to determine the optimum conditions for lutetium extraction into MEHEHP. These conditions include: pH

of extraction for desired D_{Lu} , organic to aqueous volume ratio, lutetium and MEHEHP concentrations, equilibrium mixing time, and settling time. The results of these bench scale experiments will subsequently be used to scale up the system to the pilot-plant level.

The pilot scale experiments will focus on operating a continuous counter-current solvent extraction system. The pilot scale experiments will include: determination and maintenance of proper flow rates of all solutions, adjustment of the acid and base concentrations to maintain the proper conditions for the desired D_{Lu} and identification of the number of stages necessary to provide 99.999% pure Lu_2O_3 .

The design of the CCCSX factory to produce 99.999% pure Lu_2O_3 will use all of the results from the bench scale and pilot scale experiments. Many factors will be considered in the design of the CCCSX factory in order to ensure maximum cost effectiveness. Storage and disposal of all reagents and waste stream will be very important considerations even though they are generally not a concern in a laboratory setting.

Finally, experiments will be performed to test the utilization of precipitation stripping in the CCCSX facility. The steps of aqueous acid stripping and oxalic acid precipitation will be combined to directly remove the lutetium from the MEHEHP as the oxalate. The purity of the Lu_2O_3 produced by precipitation stripping will also be determined.

CHAPTER 2

MATERIALS, APPARATUS AND TECHNIQUES

A. Materials and Reagents

1. General and bench-scale experiments

All of the lanthanides, except lutetium, used in the bench-scale solvent extraction studies were obtained as the oxides with a purity of 99.9% from Alfa Aesar. The lutetium oxide used for these studies was provided by CTI, Inc. of Knoxville, TN. The purity of the Lu_2O_3 was 99.99%. The lanthanide oxides were dissolved in either hydrochloric acid or nitric acid (both Fisher A.C.S. Reagent Grade) to produce an acidic aqueous solution of the lanthanide ion. Extractions were carried out into kerosene solutions of MEHEHP or D2EHPA. The kerosene that was used was Calumet 400-500 (<1% aromatics) which is a product of Calumet Lubricants, Inc. of Cotton Valley, LA. Both phosphorus-based extractants were obtained from Albright & Wilson Americas, Inc. of Richmond, VA. Albright & Wilson markets MEHEHP and D2EHPA under the trade names Ionquest 801 (IQ 801) and DEHPA respectively. All water used in this project was both distilled and deionized.

2. Pilot-scale experiments

A different source of lutetium, other than that used in the bench-scale experiments, was used in the pilot-scale CCCSX studies. This lutetium was leached with nitric acid from scrap LSO (lutetium oxyorthosilicate) provided by CTI, Inc. All leaching and

dissolution work performed on LSO to obtain acidic aqueous solutions of lutetium was conducted by Mr. Wes Fellers in Dr. George Schweitzer's laboratory. Basic neutralization solutions, required for efficient CCCSX, were made, by either Wes Fellers or Peter M. Smith, by diluting concentrated ammonium hydroxide from J.T. Baker (Baker Analyzed Low Sodium CMOS Electronic Grade).

3. Precipitation stripping experiments

The dicarboxylic acid used in the precipitation stripping studies was oxalic acid (Fisher Technical Grade and/or Pacific Century Enterprises, Inc., 99.6%). The acetic acid that was used for the precipitation stripping studies was Fisher A.C.S. Reagent Grade glacial acetic acid. Several different low molecular weight organic solvents were investigated to rinse the precipitated lutetium carboxylates. A list of these solvent is: acetone, ethanol, *n*-propanol, isopropanol, *n*-butanol and isobutanol. All of the above solvents were obtained from Fisher Scientific and were Electronic Grade or better. The spectrophotometric complexing agent Arsenazo I (Acros indicator grade) was used in some of the lanthanide concentration analyses.

B. Apparatus

1. Bench-scale experiments

All bench-scale solvent extraction studies were performed in separatory funnels with a capacity of 125 mL or larger. All mixing of the phases was accomplished by placing the separatory funnels into a rotary mixer. This mixer was constructed in the lab

and consisted of a bar connected to a rotary motor. The separatory funnels were secured to the bar prior to mixing.

2. Pilot-scale experiments

The pilot-scale CCCSX studies were performed in custom made glassware obtained from SX Kinetics of Peterborough, Ontario, Canada. Fifteen solvent extraction stages were purchased from SX Kinetics. Each stage consists of a mixer, a settler and a jackleg. The jackleg is a movable component that compensates for the difference in density of the two phases and allows for adjustment of the phase interface level in the settler. A diagram of this glassware can be seen in Fig. 12. The counter-current flows of the aqueous and organic phases were generated and maintained by mixing impellers and peristaltic pumps (Masterflex L/S 7523-20). The mixing impellers were also obtained from SX Kinetics. The components of the mixing impellers are an Arrow 1750 stirring motor and a specially designed plastic impeller, a diagram of which can be seen in Fig. 13. All of the mixer/settler stages were connected via Viton tubing. Figure 14 is a picture of the completely assembled pilot-scale system.

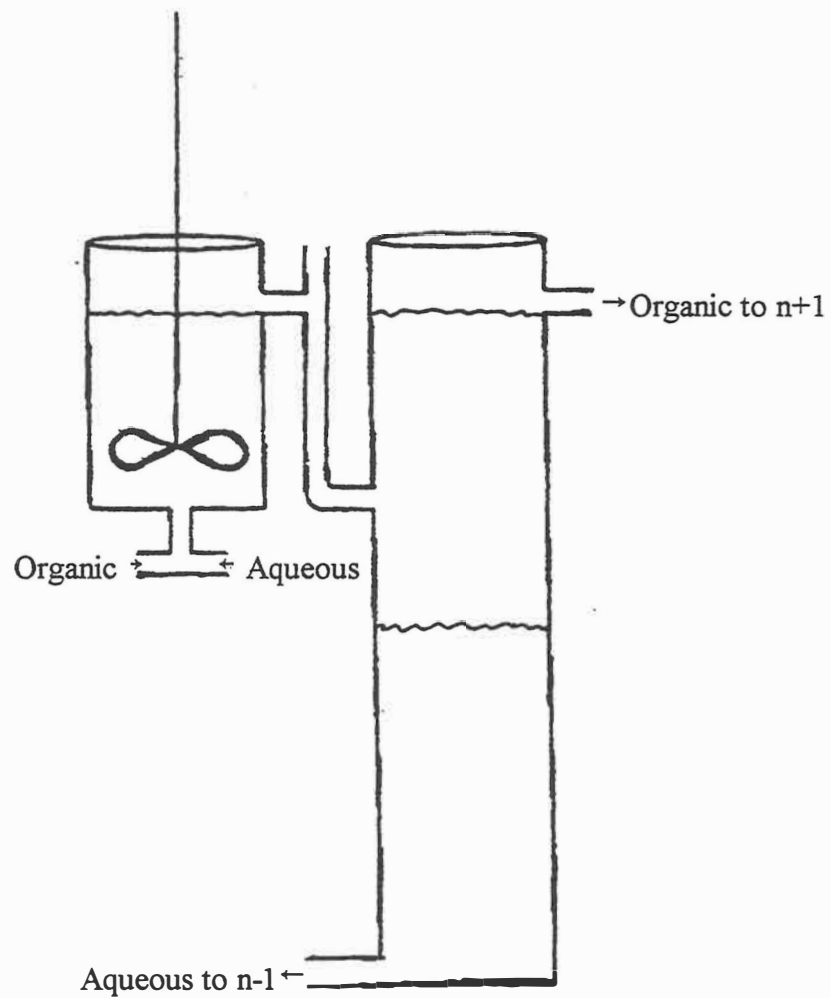


Fig. 12 Diagram of Pilot-Scale Mixer/Settler Stage

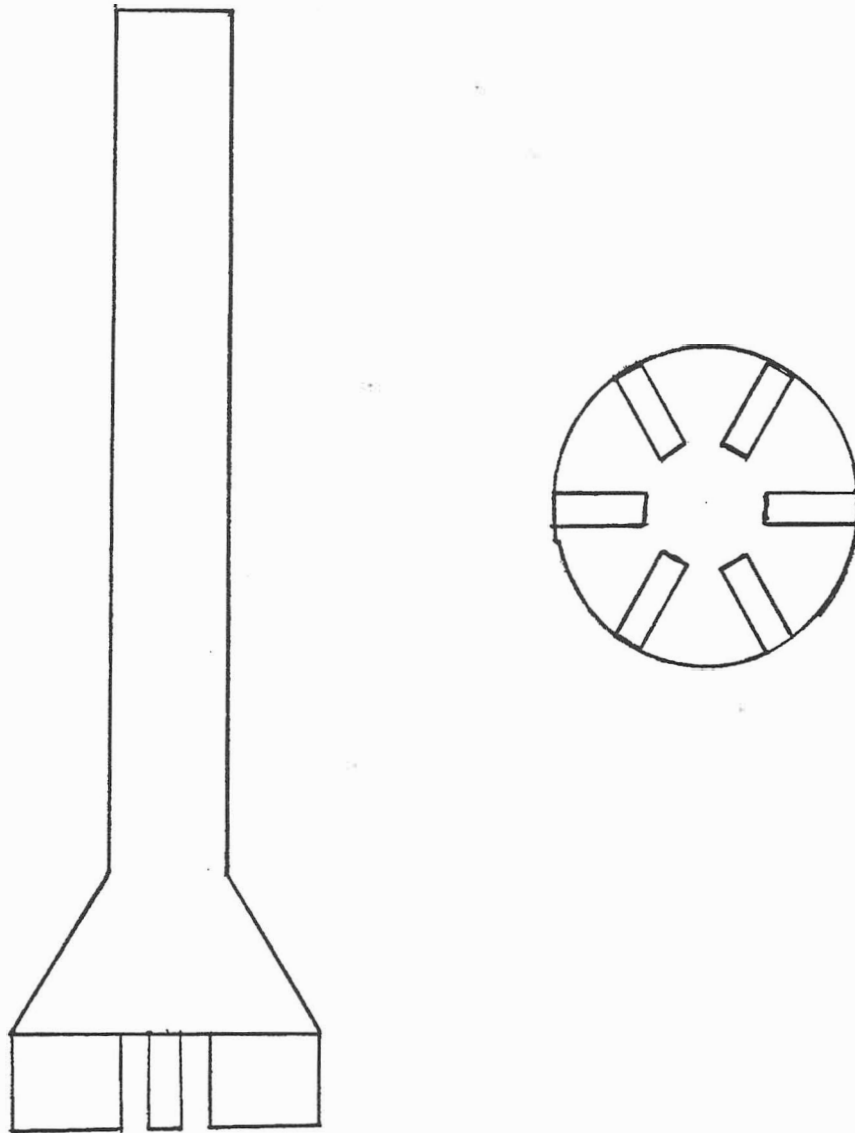


Fig. 13 Diagram of Mixer Impeller
(Side View and Bottom View)



Fig. 14 Complete Pilot-Scale CCCSX System

3. Precipitation stripping experiments

The precipitation stripping experiments were all performed in 125 mL or larger capacity separatory funnels. The immiscible phases were mixed in the separatory funnels by attaching the funnels to the previously described rotary mixer. Physical separation of the solid lanthanide salts from the aqueous solution was accomplished with vacuum filtration through a Buchner funnel.

C. Techniques

1. Bench-scale experiments

The bench-scale solvent extraction and stripping experiments involved mixing predetermined volumes of the organic phase and the aqueous phase in a separatory funnel. The acid concentration of the aqueous phase prior to extraction was determined by titration to the bromophenol blue endpoint with standardized sodium hydroxide. The mixing was carried out in a rotary mixer which rotated the separatory funnels at approximately 65 rpm. After a certain length of time the mixer was stopped and the phases were allowed to settle. The acid concentration of the aqueous phase after extraction was determined by titration as described above. The lanthanide concentrations in the aqueous phase prior to and after extraction were determined by inductively-coupled plasma mass spectrometry (ICP-MS) at the Y-12 Union Valley Sample Prep Facility in Oak Ridge, TN. These analyses were performed by Ms. Juli Miranda. The lanthanide concentration in the organic phase was taken as the difference in the aqueous phase lanthanide concentration prior to and after extraction.

2. Pilot-scale experiments

The pilot-scale CCCSX experiments focused on determining and maintaining proper flow rates and acid concentrations for the most efficient extraction and separation of lutetium from ytterbium and cerium. Experiments were performed on both 7 stage and 15 stage mixer-settler systems. Aqueous nitric acid was pumped through the system right to left, entering the system at the right-most mixer and exiting the system at the left-most settler. The kerosene solution of Ionquest 801 was pumped through the system left to right, entering the system at the left-most mixer and exiting the system at the right-most settler. An aqueous lutetium solution, obtained from the nitric acid leaching of LSO, was pumped into the system at various stages in the system. An aqueous ammonium hydroxide solution was pumped into the system at various stages in order to neutralize the acid transferred into the aqueous phase during the extraction of lutetium. The aqueous phase was sampled at each of the stages, at timed intervals, to analyze for lanthanide concentration and acid concentration. Lanthanide concentrations were measured by ICP-MS by Juli Miranda and acid concentrations were measured by titration to the bromophenol blue endpoint.

3. Precipitation stripping experiments

The precipitation stripping of select lanthanides from kerosene solutions of phosphorus-based extractants was carried out in 125 mL or larger separatory funnels. A volume of lanthanide-loaded organic phase, with a known lanthanide concentration, was mixed with a volume of an aqueous solution of oxalic acid. The mixing was accomplished

by attaching the separatory funnel, containing the two phases, to a rotary mixer which rotated the funnels at approximately 65 rpm. After a certain period of time, the mixing was stopped and the phases were allowed to settle. If precipitation stripping occurred then the lanthanide oxalate settled in the aqueous phase. This three phase phenomenon can be seen in Fig. 15. The solid was separated from the aqueous solution by vacuum filtration. The lanthanide oxalate was then stirred in a large volume of a low molecular weight organic solvent in order to remove any adsorbed organic contaminants. The solid was again separated from the liquid by vacuum filtration and allowed to air dry in the Buchner funnel. The oxalate was transferred to a ceramic high-form crucible and calcined over a Bunsen burner. The resulting lanthanide oxide was subsequently weighed in order to measure the precipitation stripping efficiency of the system. The extent of phosphorus contamination was measured by dissolving the lanthanide oxide in aqua regia and analyzing the resulting solution with a CHEMets orthophosphate detector. This kit uses molybdenum blue and stannous chloride as the colorimetric reagents for the analysis of orthophosphate.

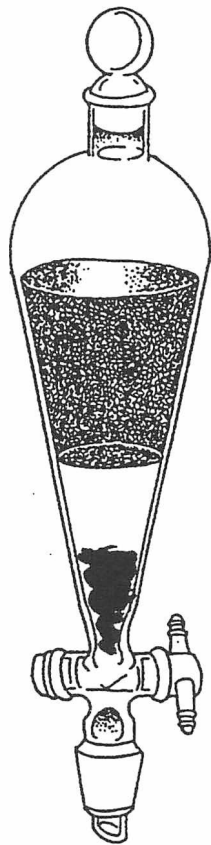


Fig. 15 Three Phase System of Precipitation Stripping

CHAPTER 3

EXPERIMENTAL RESULTS

The design of an industrial facility for the separation of the lanthanides involves many steps. This process generally begins with small-scale experiments and then incrementally builds to full production scale. In order to properly plan the facility, the extraction characteristics of the lanthanides must be determined. The first step in this characterization is bench-scale experiments using test tubes and separatory funnels. The information obtained from the bench-scale experiments is then used to design and conduct pilot-scale experiments. The pilot-scale experiments generally provide enough information to plan and operate a full scale industrial facility. This whole process is known as scale-up. Scale-up is one of the most important factors in the design of an industrial production plant. The main focus of the following accounts of research is the scale-up of a CCCSX facility for the recovery of highly pure lutetium oxide from scrap lutetium oxyorthosilicate (LSO).

A. Bench-Scale Solvent Extraction Experiments

1. Extraction of lutetium and other heavy lanthanides

All research on the extraction of lutetium and the other heavy lanthanides was performed in cooperation with Mr. Wes Fellers. Mr. Fellers is a Research Associate in the chemistry laboratory of Dr. George K. Schweitzer.

The extraction behavior of the heavy lanthanides lutetium, ytterbium, thulium,

erbium and yttrium has previously been studied and reported.⁶⁶ The source of these lanthanides was a heavy lanthanide concentrate obtained from bastnaesite from Baotou, Inner Mongolia, China. The composition of this concentrate was: 70% Yb_2O_3 , 13% Tm_2O_3 , 10% Lu_2O_3 , 6% Er_2O_3 and 1% Y_2O_3 . This concentrate was dissolved in nitric acid and extracted with a kerosene solution of IQ 801. A Lu/Yb separation factor of 1.7 was reported.

The information obtained from this experiment was inadequate for scale-up considerations. The industrial CCCSX facility for the recovery of lutetium oxide from LSO involves the extraction of essentially pure lutetium solutions. LSO is manufactured with >99.99% pure lutetium oxide. It also contains a 0.2 atom% cerium dopant. This cerium is the major impurity in the aqueous lutetium solution. Very minor traces of the other heavy lanthanides may be present in the solutions as well. As the LSO crystals are grown, they are pulled from a SiO_2 - Lu_2O_3 - CeO_2 melt which has a temperature of 2200 °C. The process of pulling has the potential of concentrating the heavy lanthanide impurities in the bottom of the LSO crystals. This concentrating effect is known as zone refining. However, since the starting materials for the LSO were all >99.99% pure, the concentrations of the heavy lanthanides in the leached lutetium solutions will be very low. Because of this, the extraction behavior of pure lutetium solutions will provide more reliable information for the scale-up of the facility.

The extraction characteristics of lutetium from pure lutetium solutions were investigated by extracting 0.100M aqueous Lu^{+3} solutions in varying concentrations of nitric acid with 0.45M solutions of IQ 801 in kerosene. An appropriate amount of

lutetium oxide of 99.99% purity was dissolved in enough nitric acid to produce solutions of 0.100M Lu^{+3} with nitric acid concentrations of: 0.5M, 0.75M, 1.0M, 1.25M and 1.5M. A 25 mL aliquot of each of these five solutions was mixed in 125 mL separatory funnels with a 25 mL aliquot of a 0.45M kerosene solution of IQ 801. The mixing time for each of these extractions was 15 minutes. After the mixing was completed the phases were allowed to settle and the aqueous phase was titrated with a KHP standardized solution of sodium hydroxide. This titration established the equilibrium acid concentration for the lutetium extraction. The results of this titration can be seen in Table I. The distribution of the lutetium between the aqueous and organic phases was obtained by measuring the lutetium concentration in the aqueous phases before and after extraction. This measurement was done by ICP-MS. The difference between the two concentrations was taken as the concentration of lutetium in the organic phase. The distribution of lutetium was then calculated using Eq. 5. These results can also be seen in Table I. Graphical representation of this data is shown in Fig. 16. The relationship between the log of $[\text{H}^+]$ and the log of D is linear. The equation of the line in Fig. 16 is:

$$\log D = -2.298 \times \log[\text{H}^+] + 0.850 \quad (16)$$

This equation allows for the calculation of the equilibrium acid concentration required for a desired distribution. For a $D = 4.5$, the equilibrium acid concentration is 1.18M. This value of D was chosen as an important value because the implications it would have on the CCCSX facility. This implication is discussed in section B.

This experiment was repeated and the results are reported in Table II and Fig. 17. The equation for the line in Fig. 17 is:

Table I

Bench-Scale Solvent Extraction of Lutetium from Various HNO_3 Concentrations Using
0.45M IQ 801 in Kerosene

Trial 1

Sample	Initial $[\text{H}^+]$	Equilibrium $[\text{H}^+]$	D_{Lu}
Lu-1	0.49M	0.76M	13.5
Lu-2	0.74M	1.01M	6.7
Lu-3	1.00M	1.25M	4.3
Lu-4	1.24M	1.44M	3.1
Lu-5	1.51M	1.67M	2.2

Table II

Bench-Scale Solvent Extraction of Lutetium from Various HNO_3 Concentrations Using
0.45M IQ 801 in Kerosene

Trial 2

Sample	Initial $[\text{H}^+]$	Equilibrium $[\text{H}^+]$	D_{Lu}
Lu-1	0.48M	0.76M	13.5
Lu-2	0.75M	1.01M	6.8
Lu-3	0.99M	1.21M	4.3
Lu-4	1.23M	1.44M	3.1
Lu-5	1.49M	1.68M	2.2

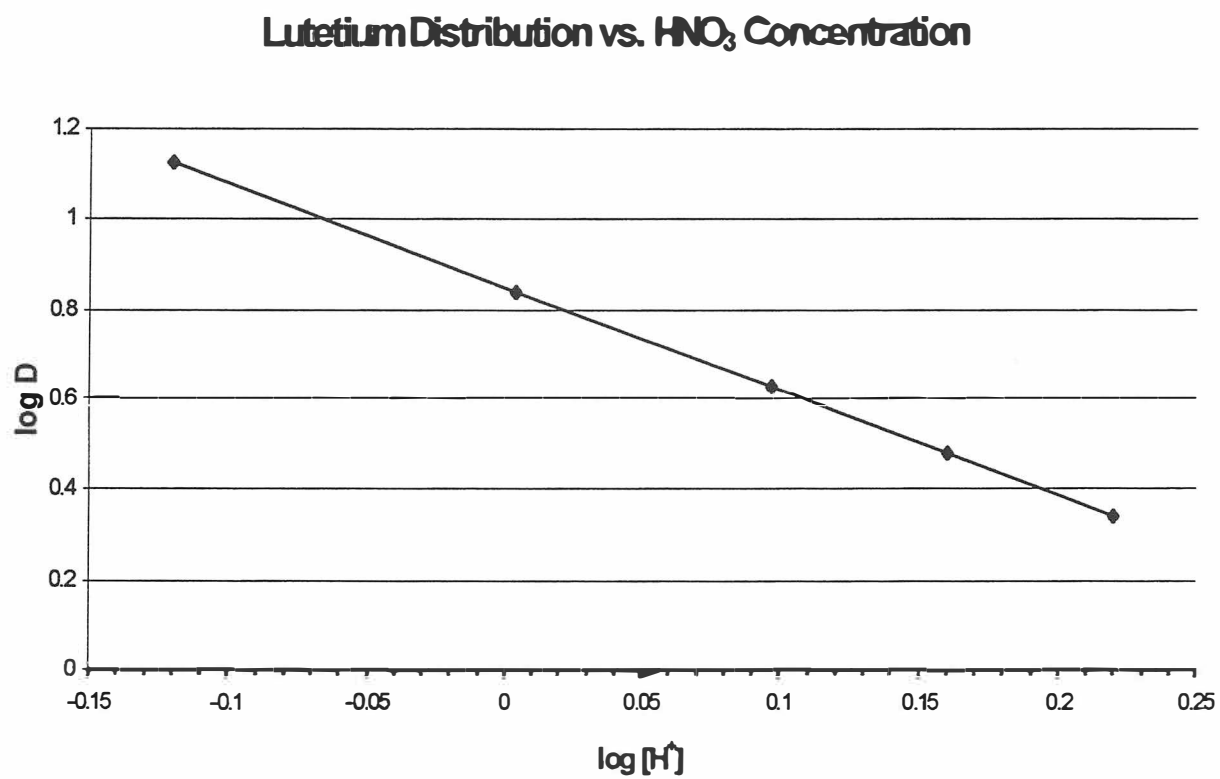


Fig. 16 Graph of Lutetium Distribution, Trial 1

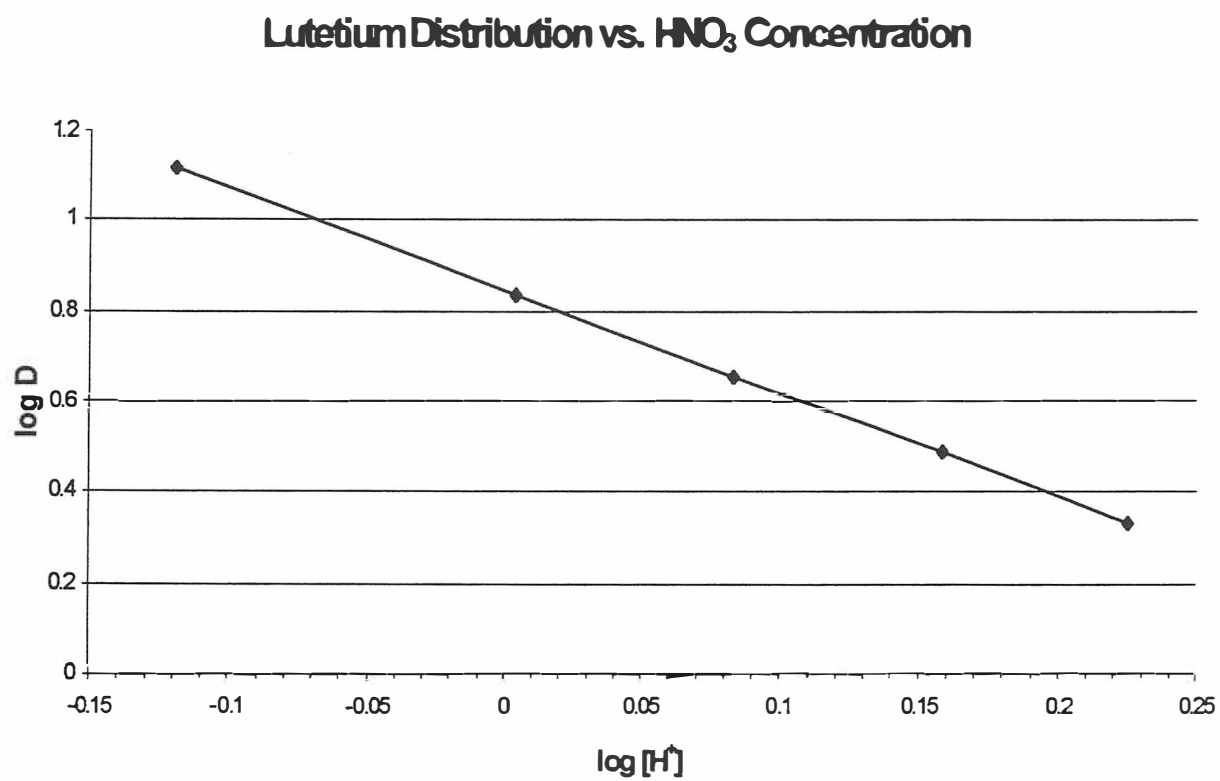


Fig. 17 Graph of Lutetium Distribution, Trial 2

$$\log D = -2.274 \times \log[H^+] + 0.846 \quad (17)$$

The results of this experiment indicate that an equilibrium acid concentration of 1.22M is required for a D of 4.5.

The lutetium extractions in both Trial 1 and Trial 2 can be described by equation (8). The extraction of the lutetium into the organic phase causes the release of hydrogen ions from the IQ 801 into the aqueous phase, thereby increasing the acidity of that phase. The difference between the initial acid concentrations and the equilibrium acid concentrations is, on average, ~0.3M for Trials 1 and 2. This is exactly the concentration increase that is expected, because the lutetium concentration was 0.10M and equation (8) indicates that the acid concentration increase should be triple the lanthanide concentration. If the equilibrium acid concentration has increased by less than three times the lanthanide concentration, then the extraction of lanthanide was not complete. This is seen in the extraction of lutetium from the 1.25M and 1.5M nitric acid solutions in Trials 1 and 2.

The extraction kinetics of lutetium in the HNO_3 /IQ 801 system were studied in order to determine the optimum time that the organic and aqueous phases need to be mixed to ensure equilibrium. The experiment was performed by mixing 1 mL of 0.45M IQ 801 in kerosene with 1 mL of 0.100M Lu^{+3} in 1.2M HNO_3 in a test tube for various lengths of time. Table III and Fig. 18 show the results of this experiment. Equilibrium was reached in less than 2 minutes. Therefore a mixing time of 3 to 5 minutes would be enough time, in a CCCSX facility, to reach equilibrium in a stage.

Table III

Extraction Kinetics of Lutetium in the HNO₃/IQ 801 System

Time (sec.)	Aq. [Lu ⁺³] (g/L)	Aq. [Lu ⁺³] (g/L)
	Trial 1	Trial 2
0	17.9	17.2
15	5.6	4.6
30	3.7	4.1
45	3.5	4.8
60	3.3	3.9
90	3.6	3.7
120	3.1	3.6
180	3.5	3.7
360	3.6	4.9

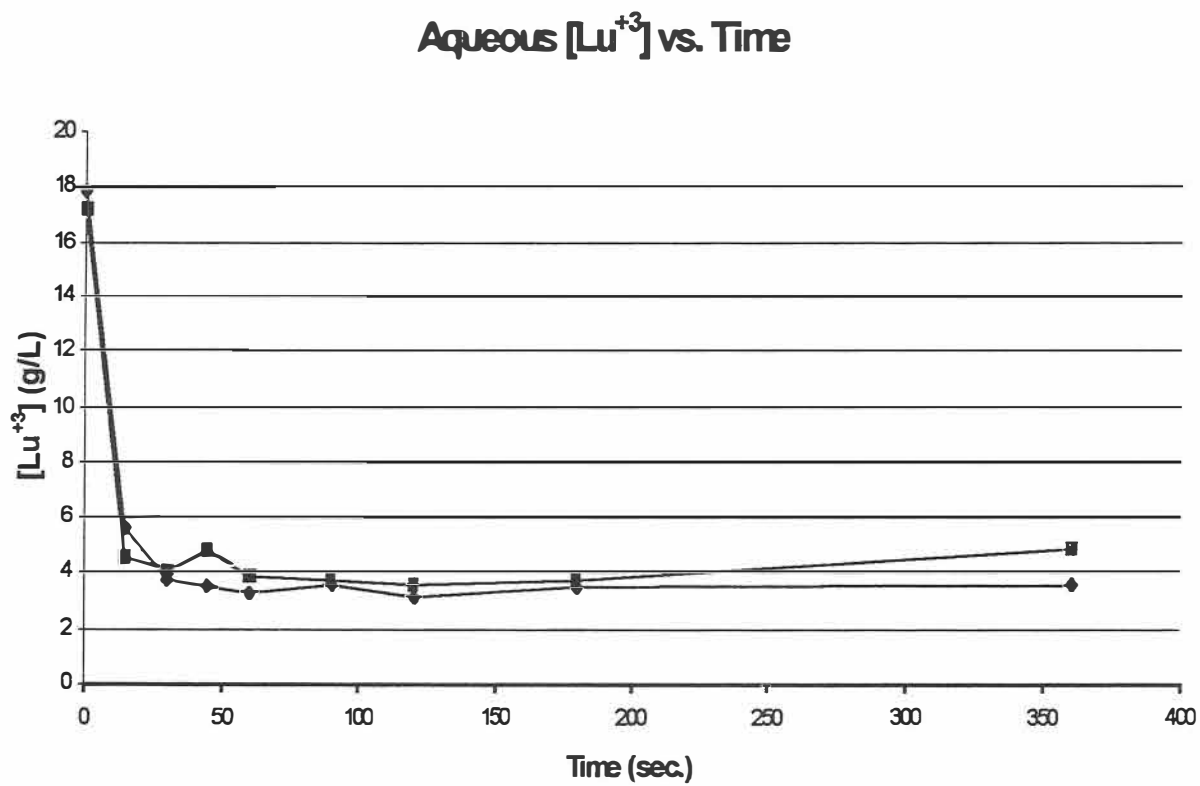


Fig. 18 Lutetium Extraction versus Time

2. Acid stripping experiments

All of the bench-scale acid stripping experiments were performed with the cooperation of Mr. Wes Fellers.

The first nitric acid stripping experiments were performed using the heavy lanthanide concentrate as the source of lutetium. This concentrate was dissolved in nitric acid to produce a solution that was 0.15M in total lanthanides and 1.85M HNO_3 . The lanthanides were extracted from the resulting aqueous solution with 0.45M solution of IQ 801 in kerosene. 20 mL of the lanthanide-loaded organic phase was stripped five times with successive 20 mL aliquots of 5M nitric acid. Only lutetium and ytterbium concentrations were measured in this experiment. The lanthanide concentrations in the organic phase were taken as the difference in the aqueous lanthanide concentrations before and after equilibrium. The results of the stripping experiment can be seen in Table IV. Essentially complete stripping of the heavy lanthanides from a kerosene solution of IQ 801 can be accomplished in 5 stages using 5M nitric acid. As expected, the ytterbium was stripped from the organic phase more efficiently than the lutetium, although the behaviors are very similar.

Other nitric acid stripping experiments were performed to investigate the stripping behavior of pure lutetium solutions. More accurate information for the scale-up to the desired CCCSX facility can be obtained using pure lutetium solutions. Internal documents from the chemistry laboratory of Dr. George Schweitzer to CTI, Inc. of Knoxville, TN indicate that complete stripping of lutetium from a lutetium-loaded organic phase (0.45M IQ 801 in kerosene) can be accomplished in 6 stages using 6M nitric acid. In this

Table IV

Nitric Acid Stripping of Heavy Lanthanide-Loaded Organic Phase (0.45M IQ 801 in Kerosene)

Ln	Initial [Ln⁺³]_a	Equil. [Ln⁺³]_o	[Ln⁺³]_o Strip 1	[Ln⁺³]_o Strip 2	[Ln⁺³]_o Strip 3	[Ln⁺³]_o Strip 4	[Ln⁺³]_o Strip 5
Lu	2.89 g/L	1.58 g/L	0.63 g/L (60.1%) ¹	0.37 g/L (76.6%)	0.15 g/L (90.7%)	0.06 g/L (96.3%)	0.02 g/L (98.5%)
Yb	21.0 g/L	9.08 g/L	3.63 g/L (60.0%)	1.45 g/L (84.0%)	0.58 g/L (93.6%)	0.24 g/L (97.4%)	0.09 g/L (99.0%)

¹ All percentages are percent stripping from organic phase.

procedure a 50 mL aliquot of lutetium-loaded organic phase was stripped with six 10 mL aliquots of 6M HNO₃ creating an organic to aqueous volume ratio of 5:1.⁶⁶ All previous experiments have utilized an organic to aqueous volume ratio of 1:1. The results of this experiment provide an economic benefit to the design of the CCCSX facility, in that the stripping circuit can be designed to consume less concentrated nitric acid.

3. Aqueous precipitation studies

All experiments designed to investigate the aqueous precipitation of lutetium oxalate were performed independently.

Once a lanthanide has been stripped from the organic phase it is present in an aqueous solution of high acid concentration. This aqueous solution is generally neutralized and the lanthanide is precipitated as the oxalate by adding either oxalic acid or an oxalate salt to the neutralized solution. In order to properly design the CCCSX facility, the precipitation characteristics of lutetium oxalate must be investigated.

The first precipitation characteristic to be studied was the extent of neutralization that would be necessary for optimum precipitation. Four 100 mL aliquots of a solution of 0.100M Lu⁺³ in 5.0M HNO₃ was neutralized to different pH values with concentrated ammonium hydroxide. An excess of oxalic acid was added, in the form of a saturated aqueous solution of oxalic acid (1.0M), to these solutions to precipitate the lutetium oxalate. The precipitated lutetium oxalate was then filtered, rinsed and calcined to produce lutetium oxide. The results of these precipitations are seen in Table V. It was shown that neutralizing the aqueous solutions to pH values higher than 2 was unnecessary.

Table V

Neutralization Experiments for the Aqueous Precipitation of Lutetium Oxalate

pH	Amount Lu_2O_3 Produced	% Lu_2O_3 Recovery ¹
-0.69 (5M)	1.76 g	88%
1	1.87g	94%
2	1.94g	97.5%
3	1.93g	97.2%

¹100% recovery would be 1.99g from the 0.100M Lu^{+3} solution.

The incomplete recovery of the lutetium oxide can most likely be attributed to transfer losses. The 2.5% of the lutetium oxide that was not recovered is equivalent to 0.05g. Because Lu_2O_3 is such a dense powder, 0.05g is an exceedingly small amount of material. This amount is easily left in the filter or any of the precipitation vessels.

The effects of heat on the precipitation of lutetium oxalate was studied next. A 10 mL aliquot of 1.00M Lu^{+3} in 5M HNO_3 was neutralized to a pH of ~2 with concentrated ammonium hydroxide. This solution was kept a temperature of 80 °C using a water bath. 30 mL of a saturated solution of oxalic acid (50% stoichiometric excess) was slowly added to the heated lutetium solution. The oxalic acid solution was added slowly to ensure that the temperature of the solution did not drop past 75 °C. The resulting precipitate was filtered, rinsed and calcined to produce Lu_2O_3 . A total of 1.91g of lutetium oxide was recovered from this experiment. This represents a 96% recovery. Therefore, heating the solution above room temperature does not produce a better precipitation environment.

Another important consideration for the precipitation of $\text{Lu}_2(\text{C}_2\text{O}_4)_3$ is the amount of oxalic acid that is needed to yield quantitative precipitation. A stoichiometric excess of oxalic acid was always added to keep the reaction kinetics as fast as possible. An experiment was performed to determine the optimum amount of stoichiometric excess of oxalic acid needed in the precipitation. Lutetium oxalate was precipitated from a lutetium solution by adding a saturated solution of oxalic acid in 10%, 20%, 30% and 50% stoichiometric excess. The precipitate from all four solutions was filtered, rinsed and dried overnight at 110 °C. Drying the precipitate removes both water and oxalic acid from the

solid by evaporation. The solution in which 30% excess oxalic acid was added yielded 100% recovery of lutetium oxalate.

Two final experiments were performed to study the precipitation characteristics of lutetium oxalate. These experiments were designed to measure the percent solids of various lutetium oxalate slurries and the moisture content of a lutetium oxalate filter cake. The percent solids of a slurry is a critical consideration in acquiring both pumps and filters for the CCCSX facility. The moisture content of a filter cake is an important factor in the type of oven used to dry the cake and the length of time provided for adequate drying. To measure the percent solids of a lutetium oxalate slurry, 100 mL of 0.400M Lu^{+3} in 5.0M HNO_3 was neutralized to a pH of ~ 3 and 78 mL (30% excess) of a saturated solution of oxalic acid was added to precipitate the lutetium oxalate. The slurry was poured into a 250 mL graduated cylinder and allowed to settle. The total volume of the slurry was 213 mL and the volume of the settled precipitate (thickened slurry) was 50 mL. The dry weight of the lutetium oxalate that was produced was 12.3g. Lutetium oxalate has a density of 2.5 g/cm^3 , therefore the volume of the $\text{Lu}_2(\text{C}_2\text{O}_4)_3$ was 4.9 cm^3 .⁶⁷ The percent solids of a slurry is defined as:

$$\% \text{ Solids} = \text{Dry Weight of Solids} \div \text{Total Weight of Slurry}. \quad (18)$$

The total weight of the lutetium oxalate slurry was taken as 220.4g. This value was obtained by subtracting the volume of the solids (4.9 cm^3) from the total volume of the slurry (213 mL) to get the volume of the aqueous solution (208.1 mL). Assuming that the density of the aqueous solution is approximately 1 g/mL, the weight of the solution was taken as 208.1g. Therefore the total weight of the solution was: the weight of the solution

plus the weight of the solids ($208.1\text{g} + 12.3\text{g} = 220.4\text{g}$). Using equation (18), the percent solids in the lutetium oxalate slurry was calculated as 5.6%. The percent solids in the thickened slurry is also an industrially important parameter. The percent solids in the thickened slurry was calculated in the same way as the percent solids of the lutetium oxalate slurry, except that the volume of the thickened slurry was now 50 mL. The percent solids of the thickened slurry was calculated as 21.4%.

The moisture content of a lutetium oxalate filter cake was measured by precipitating a quantity of lutetium oxalate and filtering this precipitate in a Buchner funnel. Air was drawn through the filter cake by aspiration and the cake was allowed dry for 5 minutes. This wet filter cake was weighed and the wet weight was measured as 70.0g. The filter cake was then dried in an oven overnight at $110\text{ }^{\circ}\text{C}$. The dry weight of the filter cake was measured as 31.0g. Therefore, the moisture content of the lutetium oxalate was calculated as 39.0g or 55.7%.

4. Calcination of lutetium oxalate to lutetium oxide

All experiments designed to investigate the calcination of lutetium oxalate to produce lutetium oxide were performed independently.

There are two important factors in the calcination of lutetium oxalate to produce lutetium oxide: the temperature of calcination and the length of time for calcination. Complete calcination to the oxide is determined by visual inspection and an acid test. During calcination the lutetium oxalate, which originally is white, turns dark gray, presumably due to the formation of elemental carbon. As the calcination continues and

the oxalate and carbon are oxidized, the powder returns to the pristine white color which is indicative of lutetium oxide. However, there is a slight potential that the decomposition of lutetium oxalate can form lutetium carbonate, which also is white. The calcined powder is tested for carbonate by wetting it with dilute aqueous acid. If the product is the carbonate, the acid will decompose it with great effervescence. If the product is the oxide, no visible reaction will occur.

A sample of oven dried lutetium oxalate, in a high-form ceramic crucible, was placed in a Thermolyne 1400 portable muffle furnace. The temperature of the furnace was then set to 1000 °C and the furnace was allowed to reach this temperature. When the furnace reached 500 °C, the door of the furnace was opened for 30 seconds to allow the atmosphere inside the furnace to exchange with the atmosphere outside the furnace. This procedure ensured that sufficient oxygen was present in the furnace for complete calcination. Starting from the ambient temperature, the furnace required approximately 20 minutes to reach 1000 °C. Once the furnace reached 1000 °C, the door of the furnace was opened again to exchange the atmosphere. However, the lutetium oxalate had visually decomposed (reduced in volume by ~75%) and the powder in the crucible was white. The product was allowed to cool and subsequently tested for carbonate. The acid test was negative and the product was determined to be lutetium oxide.

A second sample of lutetium oxalate was prepared and calcined at 800 °C. When the furnace reached 800 °C, the product was examined for decomposition and found to be light gray in color. The powder was calcined for an additional 20 minutes at 800 °C. After such time, the calcination was complete, passing both the visual inspection and acid

tests. A third sample of lutetium oxalate was calcined at 700 °C. Repeating the same procedure as before, the decomposition of lutetium oxalate to lutetium oxide required 25 minutes. No lower temperature were investigated. It was determined that 700 °C - 800 °C is an easily controllable temperature in an industrial facility and lower temperature may have required inordinately long periods of time for complete calcination.

B. Pilot-Scale Solvent Extraction Experiments

All of the pilot-scale solvent extraction experiments were designed using the information obtained from the bench-scale experiments. The pilot-scale experiments were all performed using the cerium-contaminated aqueous lutetium solutions attained from the nitric acid leaching of LSO. The main focus of the pilot-scale solvent extraction experiments was to investigate the separation of gross amounts of lutetium from the minor contaminant cerium. All of the LSO leach solutions were prepared so that they were approximately 1.2M HNO₃. Lutetium will have a distribution (D) of 4.5 at this acid concentration.

All of the bench-scale experiments were performed with an organic to aqueous volume ratio of 1:1. However, all of the pilot-scale experiments were operated with an organic to aqueous volume ratio of about 2:1. This ratio was introduced to double the production rate of purified lutetium and to reduce the amount of aqueous waste generated by the pilot plant. The distribution (D) of lutetium will also be 4.5 in the 2:1 volume ratio, provided that the acid concentration is 1.2M. Distribution is independent of volume, as indicated by equation (5). The value 4.5 was chosen as an appropriate lutetium

distribution because, in the 2:1 volume ratio system, 90% of the lutetium in the aqueous phase will extract in each stage. This extraction value (E) is defined as:

$$E = \frac{V_o}{V_a} D = \frac{V_o [\text{Lu}^{+3}]_o}{V_a [\text{Lu}^{+3}]_a} = \frac{\text{Mol}(\text{Lu}^{+3})_o}{\text{Mol}(\text{Lu}^{+3})_a} \quad (19)$$

where V_o is the volume of the organic phase and V_a is the volume of the aqueous phase.

In the 2:1 volume ratio system, E is equal to 2D. Therefore, since D is 4.5, E must be 9.0 and the total moles of Lu^{+3} in the organic phase is 9 times the total moles of Lu^{+3} in the aqueous phase (or 90% extraction). It can be seen that 4 stages of extraction should transfer 99.99% of the lutetium from the aqueous phase into the organic phase.

All of the pilot-scale solvent extraction experiments were performed in cooperation with Mr. Wes Fellers.

1. Pilot Plant Test 1

Pilot Plant Test 1 utilized 8 mixer-settler stages comprised of 5 extraction stages and 3 scrubbing stages. An aqueous stream of 1.2M nitric acid was pumped through the system at a flow rate of 20 mL/min. The aqueous stream entered the system in the last stage of scrubbing (Sc3) and exited the system at the last stage of extraction (E5). An organic stream of 0.45M IQ 801 in kerosene was pumped through the system at flow rate of 40 mL/min. The organic stream entered the system at E5 and exited the system at Sc3. An LSO leach solution was prepared as the aqueous lutetium feed by Mr. Wes Fellers. This lutetium feed was 409 g/L (2.3M) Lu^{+3} and 0.96 g/L (0.007M) Ce^{+3} in 1.2M HNO_3 .

This lutetium feed was introduced, with a flow rate of 2 mL/min., into the aqueous stream of the pilot plant immediately before the first stage of extraction (E1). In order to neutralize the acid that was transferred from the organic phase to the aqueous phase, thus maintaining the ~1.2M acid concentration, a solution of 5.4M ammonium hydroxide was fed into the aqueous stream immediately after E1. The flow rate of the ammonium hydroxide was also 2 mL/min. The ammonium hydroxide was mixed with the aqueous stream in a separate mixer to ensure that no solid lutetium hydroxide would enter the extraction circuit. All of the mixing motors were operated at 900 rpm. Pilot Plant Test 1 was conducted for 8 hours.

The lutetium and cerium were removed from the organic phase for analysis by stripping them with 3 portions of 8.0M HCl and combining the aqueous strip solutions. The concentrations of lutetium and cerium were measured by ICP-MS. The results of Pilot Plant Test 1, including lutetium, cerium and acid concentrations are presented in Table VI. The lutetium to cerium ratio in the feed solution was 425. In the organic phase of Sc3, the lutetium to cerium ratio was 32,850. This represents a considerable purification of the lutetium. The aqueous phase of E5 contained the bulk of the cerium from the feed. In fact, the concentration of the cerium in E5 was greater than the lutetium concentration and the lutetium to cerium ratio was 0.007. This indicates that the pilot plant functioned as expected.

Table VI
Results of Pilot Plant Test 1

Element	Conc. In E5	Conc. In E4	Conc. In E3	Conc. In E2	Conc. In E1	Conc. In Sc1	Conc. In Sc2	Conc. In Sc3
Lu ⁺³ (o)	0.004 ¹	0.013	0.39	14.10	47.00	44.40	32.43	21.75
Ce ⁺³ (o)	—	—	—	—	0.096	—	—	0.0007
Lu ⁺³ (a)	0.0004	0.0007	0.017	1.04	19.60	4.62	3.62	3.26
Ce ⁺³ (a)	0.095	—	—	—	—	—	—	—
H ⁺ (a)	1.08 ²	1.10	1.13	1.11	1.37	1.09	1.10	1.13

¹All [Lu⁺³] and [Ce⁺³] are reported in g/L

²[H⁺] is reported in M

Aqueous Feed = 1.2M HNO₃ @ 20 mL/min.

Organic Feed = 0.45M IQ 801 in kerosene @ 40 mL/min.

Lu Feed = 409g/L (2.3M) Lu⁺³ and 0.96g/L (0.007M) Ce⁺³ in 1.2M HNO₃ @ 2 mL/min.

NH₄OH Feed = 5.4M @ 2 mL/min.

2. Pilot Plant Test 2

Pilot Plant Test 2 was conducted to replicate the results of Pilot Plant Test 1. An aqueous stream of 1.2M HNO_3 was pumped through the system from Sc3 to E5 at 20 mL/min. An organic stream of 0.45M IQ 801 in kerosene was pumped through the system from E5 to Sc3 at 40 mL/min. A lutetium feed solution containing 322 g/L (1.84M) Lu^{+3} and 0.70 g/L (0.005M) Ce^{+3} in 1.32M HNO_3 was introduced into the aqueous stream immediately before E1 at a flow rate of 2 mL/min. A 4.97M ammonium hydroxide solution was fed into the aqueous stream immediately after E1 at a flow rate of 2 mL/min. The mixing motors in each stage were operated at 900 rpm. Pilot Plant Test 2 was conducted for 8.5 hours.

The concentrations of lutetium and cerium were not measured for Pilot Plant Test 2. In Pilot Plant Test 1 the separation of lutetium from cerium occurred exactly as expected, therefore it was determined that the measurement of the concentrations of lutetium and cerium for Pilot Plant Test 2 was not necessary, based on the high cost of ICP-MS analysis. The aqueous acid concentrations in each stage was measured as before. These results are reported in Table VII. The behavior of the acid in Pilot Plant Test 2 was very comparable to that of Pilot Plant Test 1. It was determined that the extraction of lutetium occurred as expected in Pilot Plant Test 2.

3. Pilot Plant Test 3

Encouraged by the results of Pilot Plant Tests 1 and 2, a third test was performed with higher flow rates. This test was Pilot Plant Test 3. The pilot plant was operated with

Table VII

Results of Pilot Plant Test 2

$[H^+]$ in E5	$[H^+]$ in E4	$[H^+]$ in E3	$[H^+]$ in E2	$[H^+]$ in E1	$[H^+]$ in Sc1	$[H^+]$ in Sc2	$[H^+]$ in Sc3
1.04M	1.03M	1.03M	1.05M	1.52M	1.19M	1.16M	1.15M

Aqueous Feed = 1.2M HNO_3 @ 20 mL/min.

Organic Feed = 0.45M IQ 801 in kerosene @ 40 mL/min.

Lu Feed = 322g/L (1.8M) Lu^{+3} and 0.70g/L (0.005M) Ce^{+3} in 1.3M HNO_3 @ 2 mL/min.

NH_4OH Feed = 4.97M @ 2 mL/min.

higher flow rates in order to increase the production of the plant. Because the pilot plant would be operating with higher flow rates, more stages of extraction and scrubbing were added to the system. More stages in the system would require a longer time for the system to reach equilibrium, thereby compensating for the increased flow rates. Pilot Plant Test 3 was conducted on a 14 stage system with 6 stages of extraction and 8 stages of scrubbing.

An organic stream of 0.45M IQ 801 in kerosene was pumped through the system from the last stage of extraction (E6) to the last stage of scrubbing (Sc8) at a flow rate of 60 mL/min. An aqueous stream of 1.2M HNO_3 was pumped through the system from Sc8 to E6 with a flow rate of 30 mL/min. A lutetium feed consisting of 196 g/L (1.1M) Lu^{+3} and 0.25 g/L (0.002M) Ce^{+3} in 1.2M HNO_3 was fed into the system immediately before E1 at a flow rate of 6.6 mL/min. This flow rate diluted the lutetium feed 5.5 times as opposed to the 11 fold dilution in Pilot Plant Tests 1 and 2. The dilution factor was halved for Pilot Plant Test 3 because the lutetium concentration in the feed solution was essentially half that of the feed solutions used in the previous tests. A 3.9M ammonium hydroxide solution was introduced into the system immediately before E1 at a non-continuous flow rate of 6.3 mL/min. This procedure is also different from the procedure used in the previous tests. The ammonium hydroxide was fed into the aqueous stream prior to extraction so that the acid concentration would be initially lowered and subsequently brought back to the desired 1.2M during extraction. The pilot plant was operated for 11 hours. The results of Pilot Plant Test 3, including Lu^{+3} , Ce^{+3} and H^+ concentrations, are presented in Table VIII and Table IX. The acid concentration profile

Table VIII

Results for the Extraction Stages of Pilot Plant Test 3

Element	Conc. In E6	Conc. In E5	Conc. In E4	Conc. In E3	Conc. In E2	Conc. In E1
Lu ⁺³ (o)	8.8 ¹	—	—	—	25.8	25.3
Ce ⁺³ (o)	2.2·10 ⁻⁵	—	—	—	1.8·10 ⁻⁵	1.5·10 ⁻⁵
Lu ⁺³ (a)	2.2	15.2	36.1	46.7	47.1	52.1
Ce ⁺³ (a)	0.040	0.039	0.039	0.039	0.033	0.033
H ⁺ (a)	1.71M	1.50M	1.23M	1.08M	1.02M	0.99M

¹All [Lu⁺³] and [Ce⁺³] are reported in g/L

Table IX

Results for the Scrubbing Stages of Pilot Plant Test 3

Element	Conc. In Sc1	Conc. In Sc2	Conc. In Sc3	Conc. In Sc4	Conc. In Sc5	Conc. In Sc6	Conc. In Sc7	Conc. In Sc8
Lu ⁺³ (o)	24.4 ¹	—	—	—	—	—	—	17.2
Ce ⁺³ (o)	2.1·10 ⁻⁵	—	—	—	—	—	—	2.1·10 ⁻⁵
Lu ⁺³ (a)	14.5	11.8	9.3	8.6	7.0	4.7	4.2	3.3
Ce ⁺³ (a)	1·10 ⁻⁴	4·10 ⁻⁵	3·10 ⁻⁵	2·10 ⁻⁵	2.5·10 ⁻⁵	1.9·10 ⁻⁵	1.7·10 ⁻⁵	1.8·10 ⁻⁵
H ⁺ (a)	0.96M	1.00M	1.00M	1.05M	1.06M	1.09M	1.08M	1.12M

¹All [Lu⁺³] and [Ce⁺³] are reported in g/L

Organic Feed = 0.45M IQ 801 in kerosene @ 60 mL/min.

Aqueous Feed = 1.2M HNO₃ @ 30 mL/min.

Lu Feed = 196g/L(1.1M) Lu⁺³ and 0.25g/L(0.002M) Ce⁺³ in 1.2M HNO₃ @ 6.6 mL/min.

NH₄OH Feed = 3.9M @ 6.3 mL/min. (not continuous)

for Pilot Plant Test 3 does not resemble the profiles of Pilot Plant Test 1 and 2. The acid concentrations in E5 and E6 are much too high and the acid concentrations in E1, E2 and E3 are too low. The organic and aqueous lutetium concentrations in E6 are also much too high. Therefore, the system did not extract the lutetium efficiently. The inefficient extraction is most likely due to the overloading of the organic phase with lutetium. The organic phase contained an 0.15M excess of IQ 801. However, because the acid concentration was so low in E1, this excess IQ 801 extracted additional lutetium thereby saturating the organic phase with lutetium. Once the organic phase in E1 became saturated with lutetium, the first stage of actual extraction shifted to E2. The acid concentration was also too low in E2 and the organic phase became saturated with lutetium. This process continued down the system, such that, at the end of the test, the extraction of lutetium was taking place in E5 and E6. This explains the high concentration of lutetium and the high acid concentration in E6. If the system was operating properly, the concentration of lutetium in E6 should have been a fraction of a percent of the initial concentration.

The scrubbing section of Pilot Plant Test 3 operated correctly, in that the separation of lutetium from cerium occurred as expected. The initial lutetium feed had a lutetium to cerium ratio of 784 whereas the lutetium to cerium ratio in Sc8 was 820,000. This represents a purity increase from 99.87% to 99.9999% (assuming cerium is the only impurity).

4. Pilot Plant Test 4

Pilot Plant Test 4 was conducted with the same parameters as Pilot Plant Test 3 except that the ammonium hydroxide concentration was lowered from 3.9M to 3.0M. This procedure was adopted to test the hypothesis that the acid concentration was too low in the extraction circuit, thus saturating the organic phase with lutetium. During Pilot Plant Test 3, the measurement and maintenance of the acid concentration in each stage became very difficult and time consuming. Therefore, the pilot plant was operated with only 7 stages (4 stages of extraction and 3 stages of scrubbing) for Pilot Plant Test 4.

An organic stream of 0.45M IQ 801 in kerosene was pumped through the system from E4 to Sc3 with a flow rate of 60 mL/min. An aqueous stream of 1.2M HNO_3 was pumped through the system from Sc3 to E4 with a flow rate of 30 mL/min. The same lutetium feed from Pilot Plant Test 3 was used in Pilot Plant Test 4. It was fed into the system immediately before E1 with a flow rate of 6.6 mL/min. An ammonium hydroxide solution was also introduced immediately before E1 with an initial concentration of 3.0M and a flow rate of 6.3 mL/min. The flow of the ammonium hydroxide was not continuous and half way through the test the concentration of the NH_4OH was lowered to 2.1M. Pilot Plant Test 4 was conducted for 7.5 hours. The results are reported in Table X. The extraction characteristics of lutetium in Pilot Plant Test 4 were the same as Pilot Plant Test 3. Over the whole run, the extraction of lutetium transferred from E1 all the way to E4. However, the acid concentrations in Pilot Plant Test 4 were closer to the expected 1.2M than in Pilot Plant Test 3. Therefore, the inefficiency in the extraction of lutetium can not be attributed to the saturation of the organic phase. It is more likely that the flow

Table X

Results of Pilot Plant Test 4

Element	Conc. In E4	Conc. In E3	Conc. In E2	Conc. In E1	Conc. In Sc1	Conc. In Sc2	Conc. In Sc3
Lu ⁺³ (o)	12.7 ¹	20.3	22.6	24.2	20.7	19.5	20.4
Ce ⁺³ (o)	—	—	—	—	—	—	<1·10 ⁻⁵
Lu ⁺³ (a)	8.2	27.6	40.8	46.8	22.9	7.2	4.2
Ce ⁺³ (a)	0.052	0.051	0.050	0.048	0.017	2.7·10 ⁻⁵	1·10 ⁻⁵
H ⁺ (a)	1.73M	1.41M	1.20M	1.06M	1.00M	1.06M	1.09M

¹All [Lu⁺³] and [Ce⁺³] are reported in g/L

Organic Feed = 0.45M IQ 801 in kerosene @ 60 mL/min.

Aqueous Feed = 1.2M HNO₃ @ 30 mL/min.

Lu Feed = 196g/L(1.1M) Lu⁺³ and 0.25g/L(0.002M) Ce⁺³ in 1.2M HNO₃ @ 6.6 mL/min.

NH₄OH Feed = 3.0M for 3.25 hours then 2.1M for 3.25 hours @ 6.3 mL/min.

rates of the organic and aqueous phases were too high and the phases were not in contact for sufficient time for equilibrium to occur. If equilibrium did not occur in E1, then the extraction of lutetium would have been incomplete and would transfer to E2. The same non-equilibrium process could have occurred in E2, thus transferring the extraction of lutetium to E3 and so on. The extraction circuit of Pilot Plant Test 4 did not operate efficiently. The lutetium concentration in E4 should have been a fraction of a percent of the original concentration, not half of that concentration. The scrubbing section of Pilot Plant Test 4 did operate as expected, by purifying the lutetium feed considerably. In fact, the cerium concentration in the organic phase of Sc3 was below the detection limit of ICP-MS (~200 ppb, factoring in dilution).

5. Pilot Plant Test 5

Because the organic and aqueous flow rates were too high in Pilot Plant Test 4, the system did not reach equilibrium in each stage. Therefore, Pilot Plant Test 5 was conducted with flow rates three times slower than Pilot Plant Test 4. This procedure was implemented to allow the system to reach equilibrium. An organic stream of 0.45M IQ 801 was pumped through the system from E4 to Sc3 with a flow rate of 20 mL/min. An aqueous stream of 1.18M HNO_3 was pumped through the system from Sc3 to E4 with a flow rate of 10 mL/min. A lutetium feed consisting of 240 g/L (1.37M) Lu^{+3} was introduced into the system immediately before E1 with a flow rate of 2 mL/min. The cerium concentration of the lutetium feed was not measured because the separation of lutetium from cerium had been demonstrated in the previous Pilot Plant Tests. A 3.9M

ammonium hydroxide was fed into the system immediately after E1 with a non-continuous flow rate of 2.2 mL/min. The introduction point of the base was placed after E1 to replicate Pilot Plant Tests 1 and 2. Pilot Plant Test 5 was conducted for 10.5 hours. The concentrations of lutetium and cerium were not measured because ICP-MS analysis is very expensive and the extraction characteristics of lutetium can be interpolated from the acid concentrations in each stage. The results of Pilot Plant Test 5 are presented in Table XI. The extraction of lutetium in Pilot Plant Test 5 was not efficient in that it required 2 stages for complete extraction. The extraction of lutetium increased the acid concentration approximately 0.6M. If the extraction was efficient, then the acid concentration should have increased by 0.54M in E1 and 0.06M in E2. However, the acid concentration increase was ~0.3M in both E1 and E2. This inefficiency was attributed to the low concentration of the ammonium hydroxide feed. The extraction in E1 increased the acid concentration to a point at which the extraction of lutetium became unfavorable. This increase in acid should have been neutralized by the ammonium hydroxide feed bringing the acid concentration back to 1.2M. This was not accomplished because the ammonium hydroxide feed was not concentrated enough and, therefore, the acid concentration in the aqueous stream was too high and the extraction of lutetium in Pilot Plant Test 5 was not efficient.

6. Pilot Plant Test 6

When Pilot Plant Test 5 was completed, the system was shut down but all of the solutions were left in the mixers and settlers. All of the conditions of Pilot Plant Test 5

Table XI
Results of Pilot Plant Test 5

$[H^+]$ E4	$[H^+]$ E3	$[H^+]$ E2	$[H^+]$ E1	$[H^+]$ Sc1	$[H^+]$ Sc2	$[H^+]$ Sc3
1.56M	1.53M	1.53M	1.31M	1.10M	1.07M	1.10M

Organic Feed = 0.45M IQ 801 in kerosene @ 20 mL/min.

Aqueous Feed = 1.18M HNO_3 @ 10 mL/min.

Lu Feed = 240 g/L (1.37M) Lu^{+3} in 1.2M HNO_3 @ 2 mL/min.

NH_4OH Feed = 3.9M @ 2.2 mL/min. (not continuous)

were repeated for Pilot Plant Test 6 except for the organic and ammonium hydroxide feeds. In Pilot Plant Test 6, no NH_4OH was fed into the system. This was done to investigate the acid characteristics of the system. The flow rate of the organic feed was varied throughout the test to attempt to control the acid concentration without feeding base into the system. Pilot Plant Test 6 was performed to see if the acid concentrations would regulate and reach a steady-state. The test was conducted for 13.5 hours. The acid concentrations in each stage are reported in Table XII. Just as in Pilot Plant Test 5, the extraction of lutetium required 2 stages. The acid increase from Sc1 to E1 is the same increase from E1 to E2. The acid concentration in the extraction circuit continued to run high throughout Pilot Plant Test 6. Varying the flow rate of the organic phase did not help control the acid concentrations in the extraction circuit. However, the acid concentrations in the scrubbing section were all very near the desired 1.2M. As in all previous Pilot Plant Tests, the scrubbing section of Pilot Plant Test 6 operated according to design.

7. Pilot Plant Test 7

One final Pilot Plant Test was performed to attempt to control the acid concentrations in the extraction circuit of the pilot plant. At the end of Pilot Plant Test 6, the system was shut down and every stage was drained and cleaned. The same feed solutions from Pilot Plant Test 5 and 6 were used in Pilot Plant Test 7. However, in Pilot Plant Test 7, an ammonium hydroxide feed was combined with the aqueous stream immediately prior to E1. This was done to drop the acid concentration of the aqueous

Table XII
Results of Pilot Plant Test 6

$[H^+]$ E4	$[H^+]$ E3	$[H^+]$ E2	$[H^+]$ E1	$[H^+]$ Sc1	$[H^+]$ Sc2	$[H^+]$ Sc3
1.96M	1.93M	1.89M	1.51M	1.14M	1.13M	1.14M

Organic Feed = 0.45M IQ 801 in kerosene @ 25 mL/min. for 5.5 hours and 30 mL/min.

for 6 hours

Aqueous Feed = 1.18M HNO_3 @ 10 mL/min.

Lu Feed = 240 g/L (1.37M) Lu^{+3} in 1.2M HNO_3 @ 2 mL/min.

NH_4OH Feed = none

stream to approximately 0.5M. With the acid concentration so low in E1, it was hoped that the extraction of lutetium would have been essentially complete in one stage. The extraction of lutetium should have increased the acid concentration to the desired 1.2M. Because the extraction should have been complete, the acid concentration should not have increased as dramatically in the rest of the extraction circuit. The pilot plant was reduced to 5 stages, 3 extraction and 2 scrubbing, in order to more efficiently measure and control the acid concentration in the system. Pilot Plant Test 7 was conducted for 7 hours. The results are presented in Table XIII. At the end of Pilot Plant Test 7, the acid concentrations in each stage were much closer to 1.2M than the concentrations in Pilot Plant Tests 5 and 6. The introduction of the ammonium hydroxide before extraction worked as planned in lowering the acid concentration in the extraction circuit. In fact, the acid concentration was lowered too much, so the concentration of the ammonium hydroxide had to be lowered, from 4.0M to 3.7M, in the middle of the test. Based on the acid concentrations in each stage, it was determined that the system in Pilot Plant Test 7 operated with good efficiency.

In order to quantitatively test the separation of lutetium from cerium in the pilot plant, a sample lutetium oxide was prepared from the organic phase from Sc2 of Pilot Plant Test 7. The organic phase was stripped with 3 portions of 8.0M HCl. The 3 aqueous solutions were combined and neutralized with ammonium hydroxide. A saturated solution of oxalic acid was added to the neutralized strip liquor in order to precipitate lutetium oxalate. The lutetium oxalate was filtered, rinsed and calcined to produce lutetium oxide. This lutetium oxide was analyzed by glow discharge mass spectrometry at

Table XIII

Results of Pilot Plant Test 7

$[H^+]$ E3	$[H^+]$ E2	$[H^+]$ E1	$[H^+]$ Feed	$[H^+]$ Sc1	$[H^+]$ Sc2
1.12M	1.12M	1.00M	0.44M	1.13M	1.14M

Organic Feed = 0.45M IQ 801 in kerosene @ 28 mL/min.

Aqueous Feed = 1.18M HNO_3 @ 10 mL/min.

Lu Feed = 240 g/L (1.37M) Lu^{+3} in 1.2M HNO_3 @ 2 mL/min.

NH_4OH Feed = 4.0M for 3 hours and 3.7M for 4 hours @ 1.9 mL/min.

Northern Analytical Laboratory, Inc. A sample of 99.999% virgin Lu_2O_3 was also analyzed for reference. The results of this analysis are presented in Table XIV. The cerium concentration in the Lu_2O_3 from the pilot plant was greatly reduced compared to the 99.999% virgin Lu_2O_3 . However, the concentrations of dysprosium, thulium and ytterbium are higher in the recycled Lu_2O_3 than in the virgin Lu_2O_3 . This indicates that the heavy lanthanides are concentrated in the bottom of a LSO crystal. This concentration is due to the zone refining process. The concentrations of the heavy lanthanides could be reduced to more acceptable levels by adding extra stages of scrubbing to the system.

C. Industrial CCCSX Plant for the Recovery of Lu_2O_3 from Lutetium

Oxyorthosilicate.

All of the results of the bench-scale and pilot-scale experiments were utilized in the planning of an industrial continuous counter-current solvent extraction (CCCSX) facility for the recovery of lutetium oxide from lutetium oxyorthosilicate (LSO). This facility was designed and modified in complete cooperation with Mr. Wes Fellers, a research associate in the chemistry labs of Dr. George Schweitzer, and Mr. Steve Webster, a chemical engineer specializing in hydrometallurgy for SX Kinetics in Peterborough, Ontario, Canada. The design of the CCCSX facility is centered around 30 mixer-settler stages: 10 stages of each of extraction, scrubbing and stripping. This CCCSX facility includes all of the necessary equipment to dissolve the LSO, separate the lutetium from the other lanthanides, precipitate the lutetium oxalate and produce the 99.999% pure lutetium oxide. The designed capacity of the facility is 106 kg of 99.999% Lu_2O_3 from 127 kg of

Table XIV

Lu₂O₃ Purity

Element	Conc. in 99.999% (ppm)	Conc. in pilot (ppm)
La	0.12	0.028
Ce	1.1	0.15
Pr	0.14	0.11
Nd	0.12	0.006
Sm	0.039	0.007
Eu	0.015	0.005
Gd	0.085	0.008
Tb	0.023	0.002
Dy	0.004	0.008
Ho	0.065	0.002
Er	0.012	0.008
Tm	0.002	0.071
Yb	1.5	12

LSO per day. At this capacity, the chemical consumption of the facility is: 634 L/day of concentrated HNO_3 , 600 L/day of concentrated NH_4OH and 79 kg/day of oxalic acid. Each mixer-settler has a capacity of 440 L divided into a 105 L mixer and a 335 L settler. The organic to aqueous volume ratio in this facility is 2:1, therefore, the total volume of the organic phase in all the mixer-settlers is 8800 L. The organic phase to be used in the CCCSX facility is 0.45 M (30 volume %) IQ 801 in kerosene, which indicates that 2640 L of IQ 801 and 6160 L of kerosene are needed to fill the mixer-settlers. This organic phase is re-used in the facility and, therefore, it is not considered a consumed chemical.

The estimated cost for this facility is \$1,100,000. This estimate can be divided into four categories: pre-extraction, extraction, post-extraction and chemical laboratory/quality control. The pre-extraction circuit includes solution make-up tanks and LSO digestion equipment. The cost of the pre-extraction circuit is estimated at \$275,000. The extraction circuit includes the mixer-settlers, pumps, holding tanks and process control. The estimated cost of the extraction circuit is \$160,000. The post-extraction circuit includes solution make-up tanks, precipitation tanks, filter presses, an oven and a furnace. The estimated cost of the post-extraction circuit is \$275,000. The chemical laboratory for quality control includes an ICP-MS instrument, an atomic absorption spectrometer and general laboratory wares. The estimated cost of the quality control lab is \$390,000.

The complete schematic drawings of the CCCSX facility for the production of 99.999% pure lutetium oxide from lutetium oxyorthosilicate are presented in the appendix. Included in the appendix is the mass balance flowsheet of the CCCSX facility. The flow rates of every stream, solid or liquid, are presented in the mass balance flowsheet.

D. Precipitation Stripping

Precipitation stripping experiments were performed to investigate the feasibility of applying this technique to a CCCSX facility for the separation of the heavy lanthanides. This technique is attractive for an industrial plant because it has the potential to greatly reduce the amount of acid required in a CCCSX system, thereby reducing the quantity of aqueous waste generated by that system. Conventional CCCSX systems utilize concentrated acids in a stripping circuit to remove the purified lanthanide from the organic phase. The resulting aqueous lanthanide solution is then subjected to further treatment generally partial or complete neutralization. This process can generate large quantities of aqueous salt and/or acid effluent. If the lanthanide can be removed from this organic phase as a solid, by direct contact of this phase with an aqueous solution of a precipitating agent, then concentrated acid will not be required in a stripping circuit.

The typical end product of a CCCSX system for the separation and purification of the lanthanides is a lanthanide oxide. The oxides are produced by the calcination of the lanthanide oxalate. Therefore, the precipitation stripping experiments for the heavy lanthanides should focus on using precipitating agents which will precipitate salts that can be readily calcined to the oxide.

The following accounts of research describe the precipitation stripping of various heavy lanthanides from kerosene solutions of IQ 801 and DEHPA using aqueous solutions of oxalic acid. All heavy lanthanide concentrations, except ytterbium, were measured with a spectrophotometer using Arsenazo I as the indicator. Ytterbium concentrations were measured by atomic emission spectrometry.

Also described are experiments which investigated the feasibility of using precipitation stripping in an industrial CCCSX facility. All of the experimentation conducted on the precipitation stripping of the heavy lanthanides was performed independently. Portions of this research have previously been published.⁶⁹

1. Precipitation stripping of lutetium from kerosene solutions of IQ 801 using aqueous solutions of oxalic acid

Precipitation stripping experiments were performed on the IQ 801 system first because it was the chosen extractant in for use in the industrial CCCSX facility. In all of the following precipitation stripping experiments, a solution of 0.45M IQ 801 in kerosene was loaded with lutetium by mixing the organic phase with an aqueous 0.100M lutetium solution. The concentration of the lutetium in the organic phase was taken as the difference in the lutetium concentration in the aqueous phase before and after extraction. The lutetium-loaded organic phase was then mixed with a saturated aqueous oxalic acid solution.

A typical experiment involved mixing 25 mL of a lutetium-loaded organic phase with a predetermined volume of a saturated aqueous solution of oxalic acid for 15 minutes in a 125 mL separatory funnel. The phases were allowed to settle and the precipitate was filtered from the aqueous phase using a Buchner funnel and quantitative filter paper. The precipitate was rinsed on the filter paper with aliquots of deionized water and acetone. The precipitate was then transferred to a high form crucible and roasted over a Bunsen burner. This roasting converted the precipitate from the lutetium oxalate to lutetium

oxide. The oxide was subsequently weighed and this weight was compared to the theoretical value to obtain the percent stripping of lutetium. The theoretical oxide weight was calculated from the lutetium concentration in the organic phase. The percentage of stripping for lutetium was generally in the range of 70% to 85%. Higher recoveries were always obtained when greater care was taken in the transfers of solutions and the product. As stated before, the oxides of the heavy lanthanides are very dense and therefore, the loss of very small amounts of the oxide can significantly affect the calculated percent stripping. The percent stripping values of representative experiments using lutetium are reported in Table XV. It can be seen that stripping with an equal volume of a saturated oxalic acid solution produces the largest stripping efficiency. Two possible explanations for the decrease in the stripping of lutetium when using larger volumes of a saturated oxalic acid solution are: 1) the increased volume can potentially increase the solubility of the lutetium oxalate or 2) the increase in the amount of the oxalate anion can potentially increase the concentration of soluble lutetium oxalato complexes. Therefore all subsequent experiments were designed to strip the loaded organic phase with an equal volume of an oxalic acid solution.

An important variable in the optimization of the precipitation stripping of lutetium is the mixing time. In order for the maximum amount of lutetium to be stripped from the organic phase, equilibrium must be established between the two phases. In order to determine the optimum mixing time the following experiment was performed. In a test tube, 30 mL of lutetium-loaded organic phase was mixed with 30 mL an aqueous solution of oxalic acid for increasing amounts of time. The precipitated lutetium oxalate was

Table XV

Percent Stripping Values for Representative Lutetium Systems

Vol. of Org. Phase	Vol. of Oxalic Acid Soln.	Mixing Time	Percent Stripping
25 mL	25 mL	15 min.	82%
25 mL	50 mL	15 min.	71%
25 mL	75 mL	15 min.	50%

filtered, rinsed and calcined. The lutetium oxide was weighed to calculate the percent stripping. The results of this experiment are presented in Fig. 19. It can be seen in the results that the maximum amount of lutetium was not stripped from the organic phase at less than 6 hours. This would not be an efficient process for an industrial facility. To make precipitation stripping industrially feasible, the time required to reach equilibrium must be shortened.

2. Precipitation stripping of lutetium using aqueous oxalic acid solutions containing acidic additives

Aqueous oxalic acid solutions probably strip the lutetium from the organic phase using two mechanisms: 1) direct combination of the lutetium cations and the oxalate anions to form the lutetium oxalate precipitate and 2) the hydrogen ions from the oxalic acid strip the lutetium, as in conventional acid stripping, and the lutetium oxalate is subsequently precipitated. Since it is not possible to increase the concentration of the oxalate ion in a saturated oxalic acid solution, experiments were performed to investigate the effects of increased acid concentration in the stripping solution. It was decided that the addition of a strong, mineral acid to the stripping solution would not be appropriate within the scope of the studies. Precipitation stripping was investigated as a method to eliminate the use of strong mineral acids in an industrial CCCSX plant. Therefore, the acids used to increase the total acid concentration in the stripping solutions were weak, organic acids. Stripping solutions were prepared by saturating 2.0M organic acid

Percent Stripping of Lu vs. Time

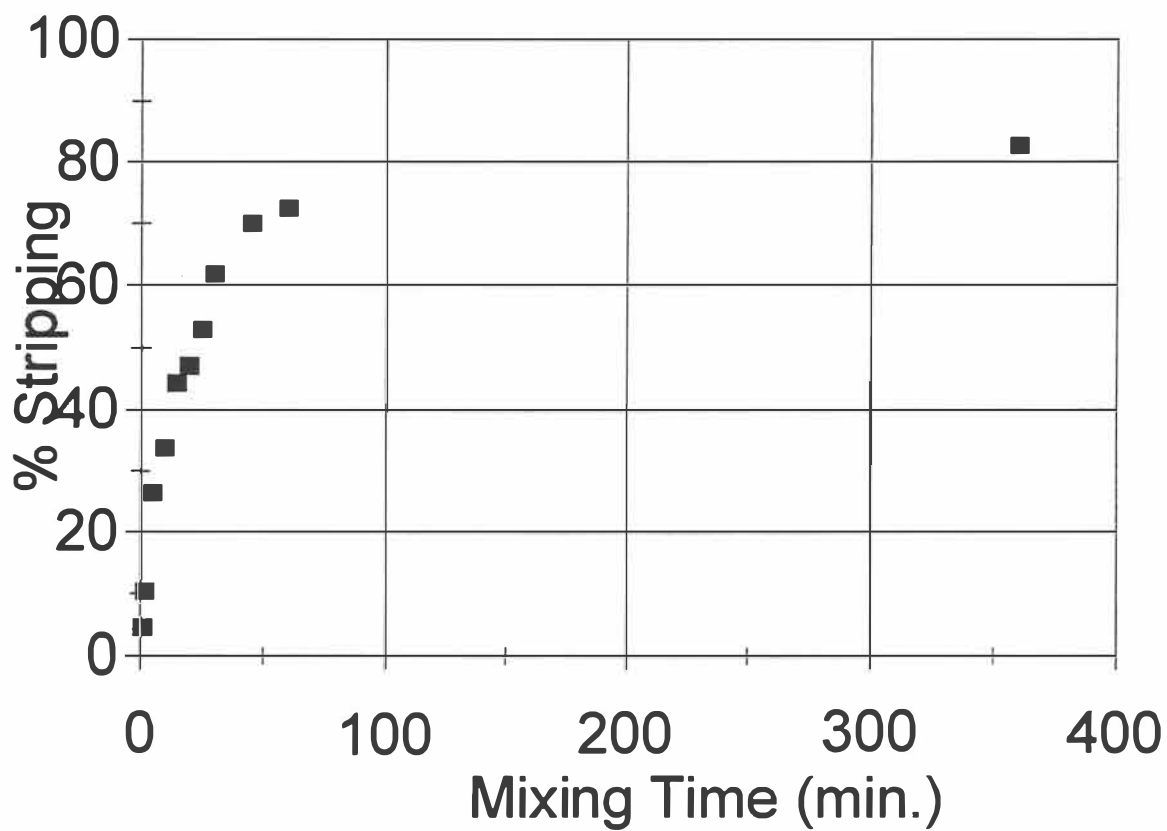


Fig. 19 Equilibrium Mixing Time for the Precipitation Stripping of Lutetium

solutions with oxalic acid. These solutions were mixed with an equal volume of lutetium-loaded organic phase using the general procedure described above. The percent stripping values achieved using these solutions are presented in Table XVI. The maximum amount of lutetium was stripped by the chloroacetic/oxalic acid solution. However, chloroacetic acid is a hazardous chemical and would not be safe for use in bulk in the CCCSX plant. The disposal of chloroacetic acid solutions would also present a problem since it cannot be introduced to the drainage system and it cannot be burned to produce environmentally acceptable compounds. Therefore, further experiments were performed using acetic/oxalic acid solutions exclusively. Acetic acid is not hazardous to either humans or the environment and it can be burned to CO_2 and H_2O which can be introduced to the atmosphere.

The optimum acetic acid concentration in the stripping solution was determined by saturating 1.0M, 2.0M, 3.0M and 6.0M solutions of acetic acid with oxalic acid. These stripping solutions were used in the general precipitation stripping procedure. The results of this experiment are presented in Fig. 20. The stripping solution consisting of 2.0M acetic acid saturated with oxalic acid stripped more lutetium than any of the other solutions tested.

The stripping kinetics of the 2.0M acetic acid stripping solution were investigated to determine the time required for the system to reach equilibrium. The same procedure as the previous kinetics experiment, using saturated oxalic acid, was used in this experiment. The results of this experiment are presented in Fig. 21. Equilibrium was established in this system in less than one hour. Therefore, precipitation stripping using

Table XVI

Percent Stripping Using Oxalic Acid Solutions Containing Organic Acid Additives

Organic Acid	Org. Acid Conc.	% Stripping of Lu
Acetic acid	1.0M	83%
Acetic acid	2.0M	90%
Chloroacetic acid	1.0M	91%
Formic acid	2.0M	73%
Propionic acid	2.0M	85%

Percent Stripping of Lu vs. Acetic Acid Conc.

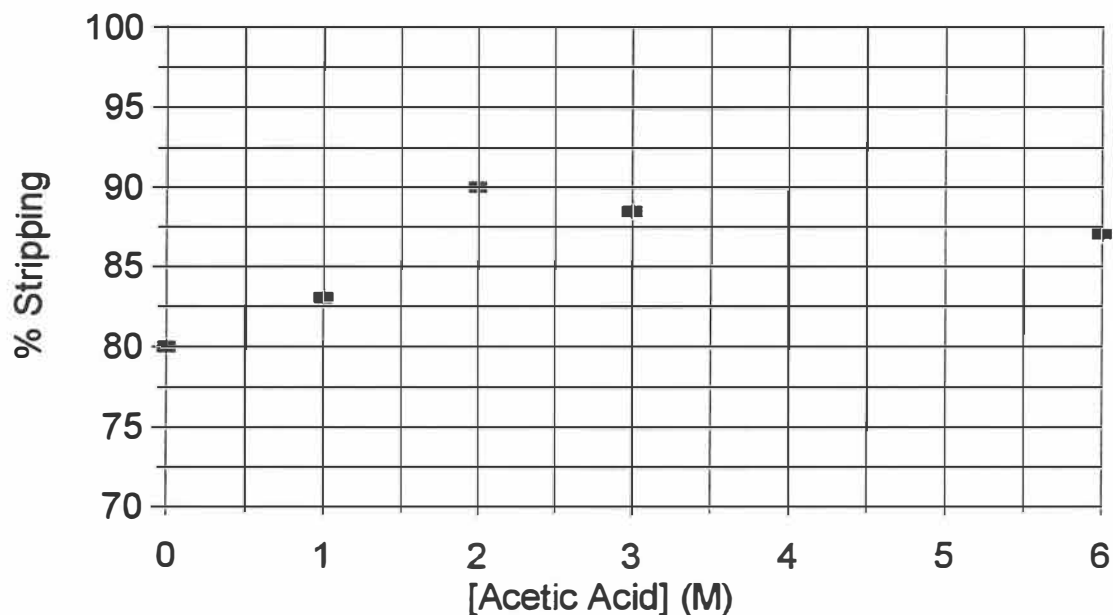


Fig. 20 Effect of Acetic Acid Concentration on the Precipitation Stripping of Lutetium

Percent Stripping of Lu vs. Mixing Time

Using 2.0M Acetic Acid Saturated with Oxalic Acid

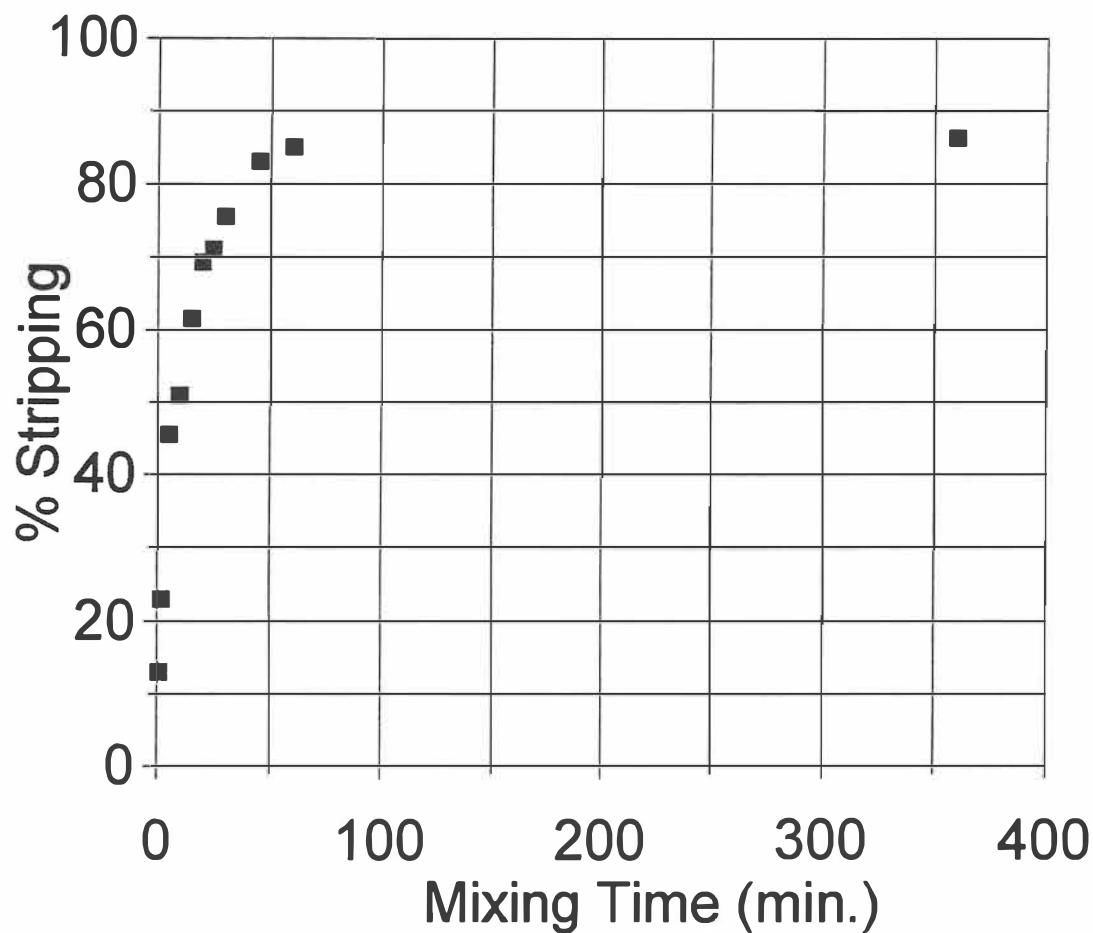


Fig. 21 Equilibrium Mixing Time Using 2.0M Acetic Acid Saturated with Oxalic Acid

2.0M acetic acid saturated with oxalic acid could be adapted into an industrial process for the removal of lutetium from an organic phase.

3. Precipitation stripping of the heavy lanthanides from solutions of 0.45M DEHPA in kerosene

Experiments were performed to investigate the precipitation stripping of the heavy lanthanides from organic phases containing DEHPA. These experiments were conducted to test the hypothesis that the percent stripping should be less in this system because it is more difficult to strip the heavy lanthanides from DEHPA than from IQ 801. An experiment was performed in which a 0.45M DEHPA solution in kerosene was loaded with lutetium and then equilibrated with an equal volume of 2.0M acetic acid solution saturated with oxalic acid. There was no precipitation in this system. The experiment was repeated with the same results. This procedure was then carried out on an ytterbium-loaded organic phase. After equilibration, 19.6% of the ytterbium had been stripped as the oxalate. A correlation between the precipitation stripping efficiency and the atomic number of the lanthanides was made for the DEHPA system. The experiment was carried out using Sm^{+3} , Gd^{+3} , Dy^{+3} , Er^{+3} , Tm^{+3} , Yb^{+3} and Lu^{+3} . The results of this experiment can be seen in Fig. 22. These experiments confirm the hypothesis that the precipitation stripping efficiency is lower in DEHPA solutions.

The precipitation stripping efficiency of lutetium systems in which the organic phase contains both DEHPA and IQ 801 was investigated next. Organic solutions were prepared with a DEHPA to IQ 801 ratio of: 100:0, 80:20, 60:40, 50:50, 40:60, 20:80 and

Percent Stripping of Some Heavy Lanthanides

From DEHPA Solutions Using 2.0M Acetic Acid Saturated with Oxalic Acid

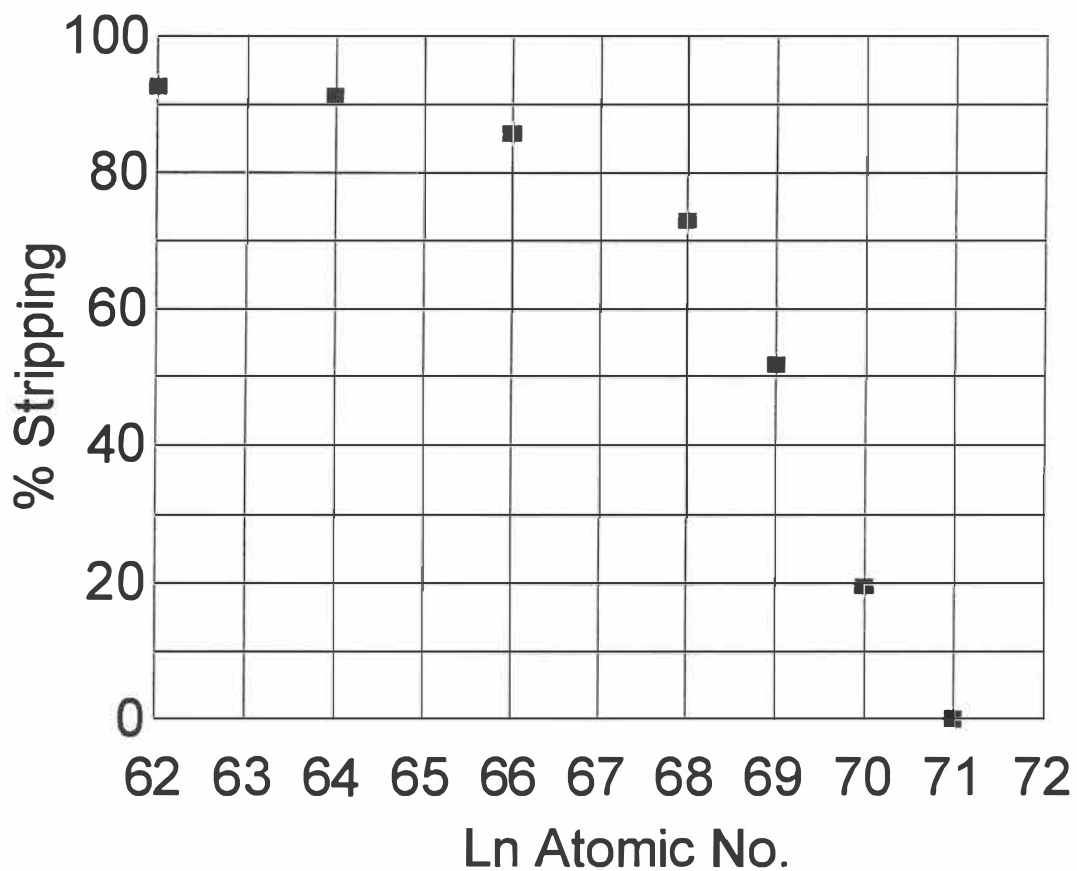


Fig. 22 Precipitation Stripping of Some Heavy Lanthanides from DEHPA Solutions

0:100. These solutions were loaded with lutetium and then equilibrated with a saturated aqueous solution of oxalic acid. The precipitation stripping efficiencies of each system are presented in Fig. 23. This experiments indicates an essentially linear relationship between the concentration of IQ 801 in an organic phase and the precipitation stripping efficiency for lutetium.

4. Experiments on the industrialization of precipitation stripping for a CCCSX plant

Once it had been determined that ~90% of the lutetium in a lutetium-loaded IQ 801 organic phase could be stripped by precipitation stripping, experiments were designed to test the industrial feasibility of this process. One of the most important features of an industrial CCCSX facility is the recycling of the organic phase. During the stripping of the lutetium from the organic phase the IQ 801 is regenerated as H_2R_2 . This regenerated organic phase is sent back into the extraction circuit of the plant to be re-loaded with lutetium. The most important consideration in the feasibility studies for precipitation stripping was this extractant regeneration.

A 0.45M solution of IQ 801 in kerosene was equilibrated with an aqueous solution of 0.100M Lu^{+3} in 0.50M HNO_3 . Since the initial acid concentration was so low 97% of the lutetium was extracted into the organic phase. This lutetium-loaded organic phase was then equilibrated with an equal volume of 2.0M acetic acid saturated with oxalic acid. The precipitate was processed to the oxide and weighed to calculate the precipitation stripping efficiency of the system. After this first cycle of precipitation stripping, the organic phase was re-equilibrated with a fresh portion of the lutetium solution. The organic phase did

Precipitation Stripping of Lu vs. IQ 801 Conc.

In Organic Solutions of DEHPA and IQ 801 in Kerosene

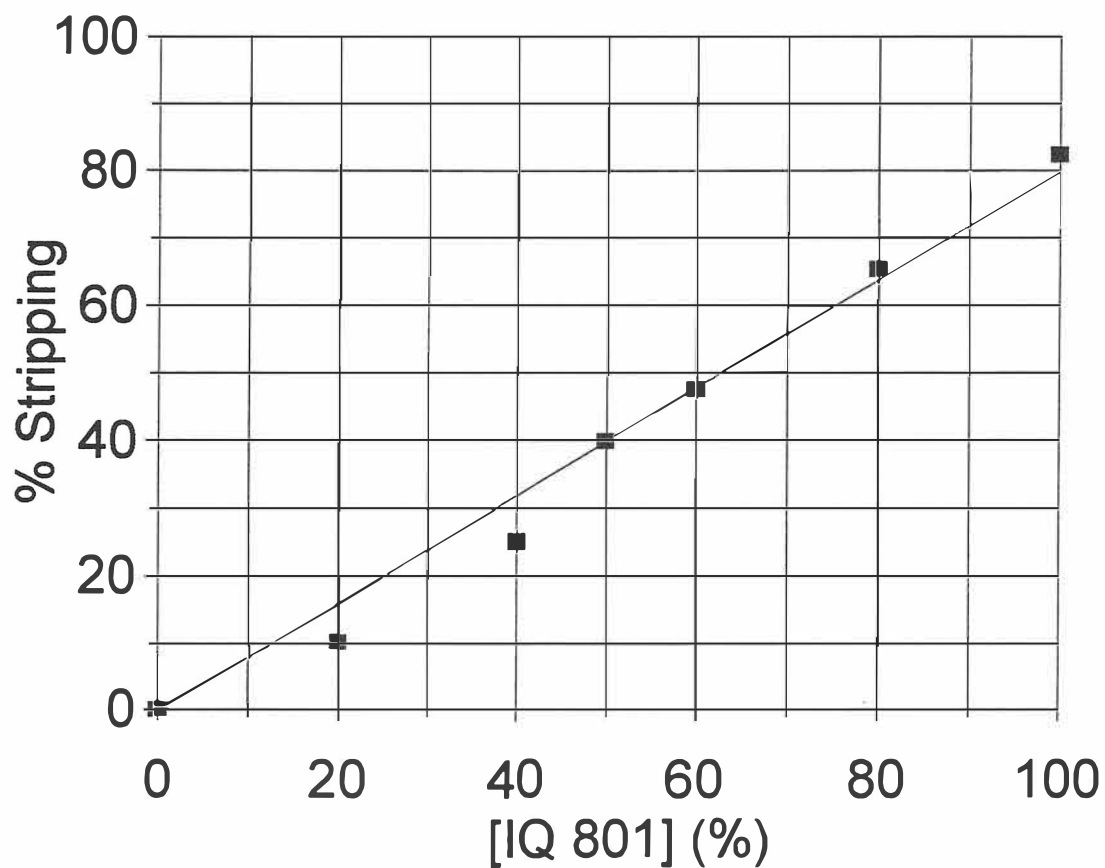


Fig. 23 Precipitation Stripping Efficiency in DEHPA/IQ 801 Organic Solutions

not undergo any additional treatment before this second cycle. Since the precipitation stripping of lutetium is not 100% efficient, the remaining portion of the lutetium was tied up in the organic phase and carried back into the second extraction cycle. This hold up is reflected in a lower loading capacity of the organic phase. This first extraction cycle extracted 97% of the lutetium, whereas the second extraction cycle extracted 93% of the lutetium. The organic phase, which had been re-loaded with lutetium, was equilibrated with a fresh aliquot of the acetic/oxalic acid stripping solution. Again, the precipitate was processed as the oxide and weighed as to calculate the precipitation stripping efficiency of the second cycle. This process was repeated four more times and the results are displayed in Fig. 24. The results of this first experiment were not satisfactory because the initial stripping cycle was very inefficient.

The experiment was repeated and the process was refined based on the experiences during the first trial. The results of the second trial are presented in Fig. 25. The initial stripping cycle was much more efficient in the second trial in that 88% of the lutetium was removed from the organic phase. Approximately 100% of the loaded lutetium was stripped in each of the five following cycles. Also, the amount of lutetium held up in the system did not appear to increase past the initial cycle. The complete stripping of the lutetium from the organic phase indicates that precipitation stripping could be a feasible industrial process.

After demonstrating that the precipitation stripping process did not adversely affect the loading characteristics of the IQ 801 solutions, experiments were performed to investigate the possibility of recycling the stripping solution after each cycle. This

Precipitation Stripping Efficiency in the Organic Phase Regeneration Tests, Trial 1

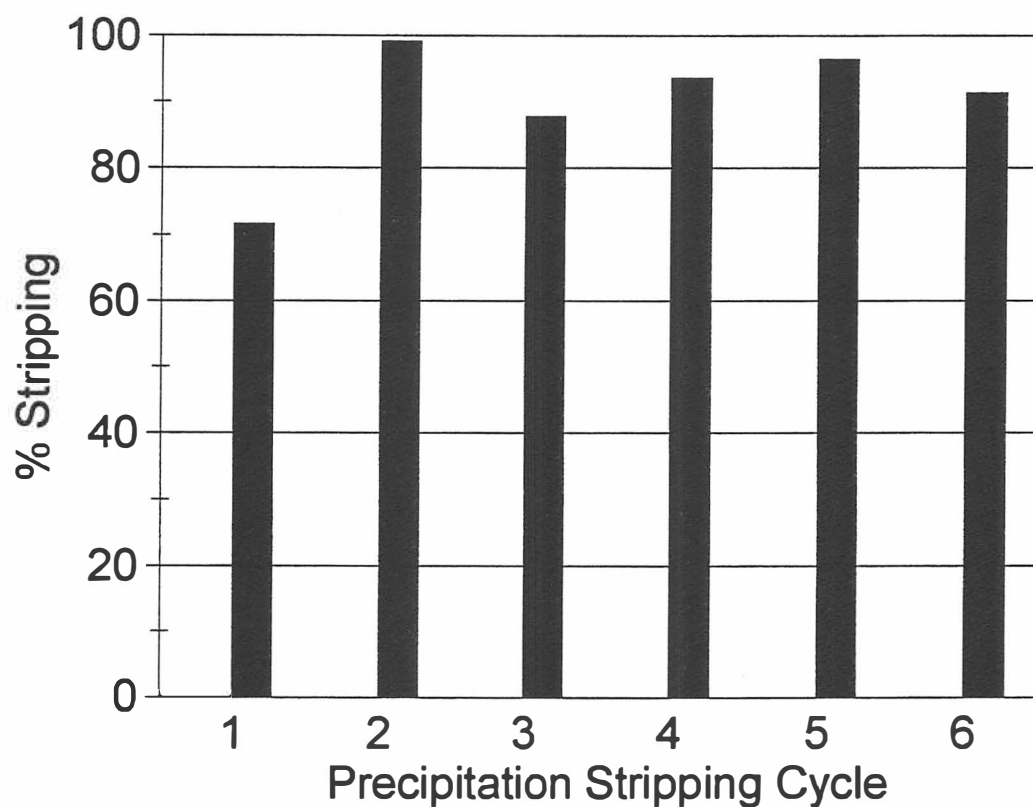


Fig. 24 Precipitation Stripping Efficiency in Organic Phase Regeneration Tests Using
Fresh Stripping Solution Each Cycle, Trial 1

Precipitation Stripping Efficiency in the Organic Phase Regeneration Tests, Trial 2

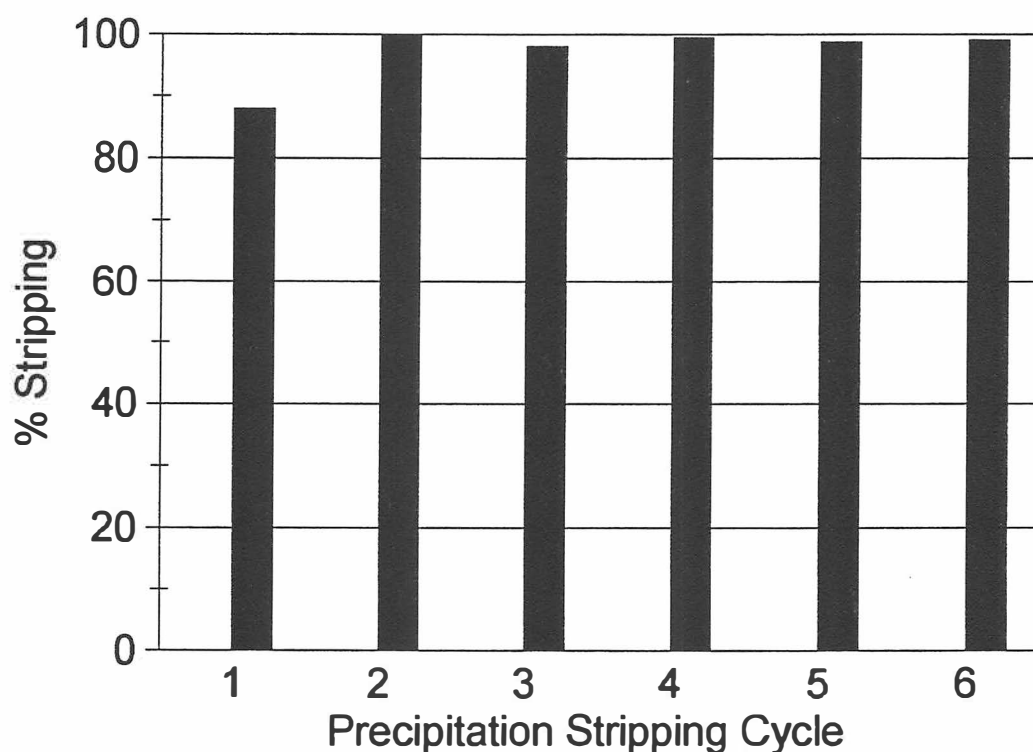


Fig. 25 Precipitation Stripping Efficiency in Organic Phase Regeneration Tests Using
Fresh Stripping Solution Each Cycle, Trial 2

experiment was conducted in the same manner as described above. However, in this procedure, the stripping solution was recovered after filtration and re-saturated with oxalic acid for use in the next cycle. The lutetium oxalate precipitate was rinsed with 2.0M acetic acid instead of deionized water so that the acetic acid concentration in the stripping solution would not be diluted. The results of the stripping solution recycling test can be seen in Fig. 26. The initial precipitation stripping cycle in this experiment was very inefficient. This inefficiency was ascribed to transfer losses because the loading capacity of the regenerated organic phase was not significantly lower in the second cycle. Approximately 95% of the lutetium was stripped in each of the following cycles. While this process does not appear to be as efficient as the process using fresh stripping solution in each cycle, it could be industrially feasible. The recycling of the stripping solution could potentially create considerable cost savings for the CCCSX facility because the amount of oxalic acid consumed by the plant would be drastically reduced.

One final experiment was performed to investigate the feasibility of using saturated oxalic acid solutions without acetic acid and thereby generating even more cost savings. The experiment was performed exactly as before, except the stripping solution used was saturated oxalic acid. Fig. 27 displays the results of this experiment. Clearly it can be seen that this system is not nearly as efficient as the acetic/oxalic acid system and therefore, would not be as feasible for use in the industrial CCCSX facility.

Precipitation Stripping Efficiency in the Stripping Solution Recycling Test

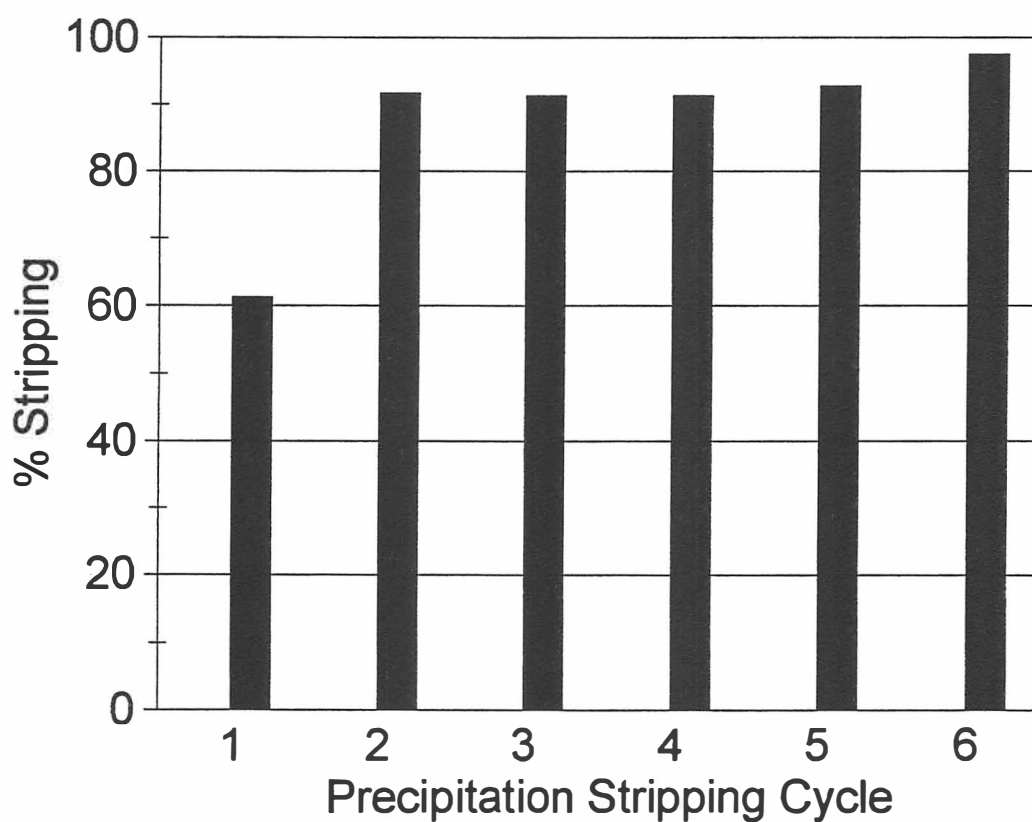


Fig. 26 Precipitation Stripping Efficiency in the Stripping Solution Recycling Test Using
2.0M Acetic Acid Saturated with Oxalic Acid as the Stripping Solution

Precipitation Stripping Efficiency in the Saturated Oxalic Acid Solution Recycling Test

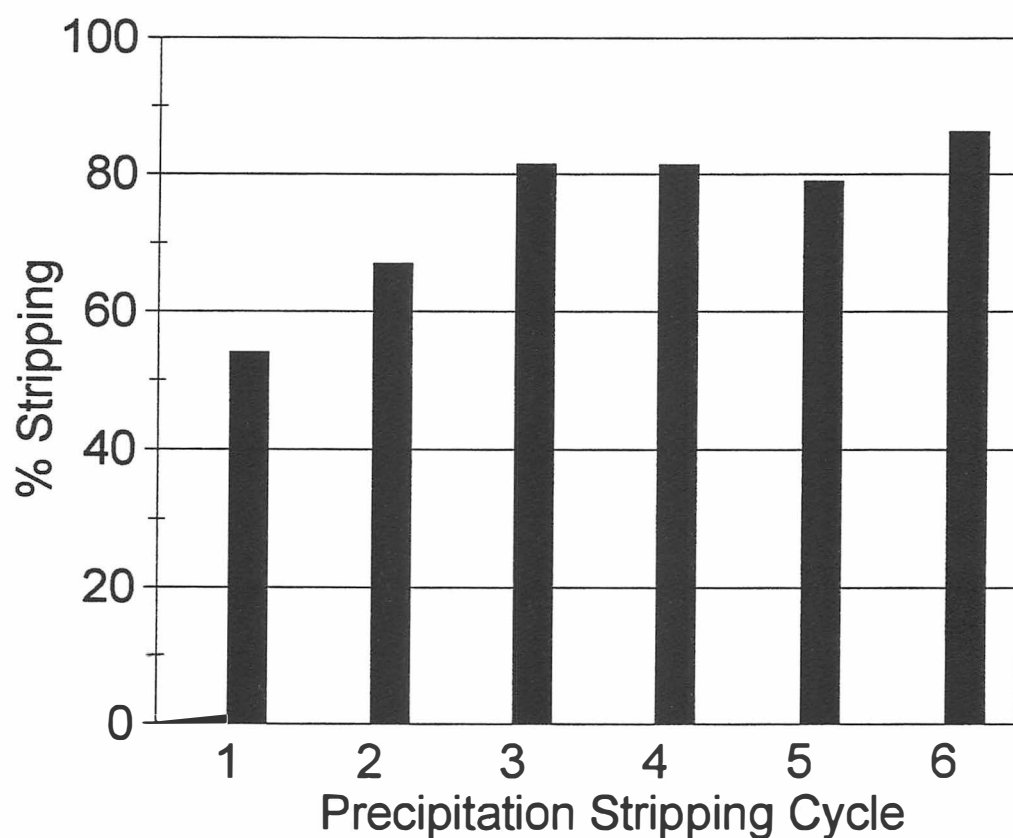


Fig. 27 Precipitation Stripping Efficiency in the Stripping Solution Recycling Tests Using
Saturated Oxalic Acid as the Stripping Solution

5. Purity of the lutetium oxide produced by precipitation stripping

The CCCSX facility was designed to produce >99.999% pure lutetium oxide. This dictates that the purity of the lutetium oxide produced by precipitation stripping must be carefully measured and controlled. Precipitation stripping is used to remove the 99.999% pure lutetium from the organic phase. Therefore, if the oxide which is produced is not equally as pure, then the precipitation stripping process introduced a contaminant. The purity of a sample of lutetium oxide produced by precipitation stripping was analyzed by glow discharge mass spectrometry (by Northern Analytical Laboratory, Inc.) and compared to a sample of 99.999% pure virgin Lu_2O_3 . The only element that did not have a comparable concentration in each sample was phosphorus. The concentration of phosphorus in the virgin oxide was measured at 4.1 ppm, whereas the phosphorus concentration in the lutetium oxide produced by precipitation stripping was measured at 7×10^2 ppm. The only plausible source of this phosphorus contamination was the IQ 801. The standard procedure of rinsing the lutetium oxalate precipitate in the Buchner funnel with two aliquots of acetone was not sufficient to completely remove all of the extractant which was adsorbed onto the oxalate. A new rinsing procedure needed to be developed.

Before new rinsing techniques could be implemented, an analytical method for phosphorus needed to be developed. The analytical method, used for the measurement of the phosphorus concentration in all of the rinsing experiments, was a colorimetric method based on the formation of a phosphomolybdate complex known as molybdenum blue. The phosphorus contamination in the lutetium oxide prepared by the standard precipitation stripping method was measured at 6×10^2 ppm by this colorimetric method. This

concentration is very close to the concentration measured by glow discharge mass spectrometry.

A variety of organic solvents were used for the rinsing of the lutetium oxalate. In each experiment, an approximately 2.0g sample of lutetium oxalate was stirred for one hour in ~500 mL of the organic solvent. It was hoped that during the dissolution and re-precipitation of the lutetium oxalate, the organic solvent would dissolve the adsorbed extract. After stirring the precipitate for one hour, it was filtered and calcined to the oxide. The lutetium oxide was then analyzed for phosphorus contamination. The phosphorus concentration in the lutetium oxide after rinsing with the various organic solvents is reported in Table XVIII. Ethanol, n-propanol and 2-propanol each rinsed the lutetium oxalate equally effectively. All three solvents are highly volatile and flammable, so safety would not be the deciding factor in which solvent to use in an industrial facility. The cost of each solvent would be the main deciding factor.

Table XVIII

Phosphorus Concentration in the Lutetium Oxide After the Organic Rinse

Organic Solvent	[P] in the Lu_2O_3
acetone	11.4 ppm
ethanol	0.0033 ppm (3.3 ppb)
n-propanol	below detection limit (<3 ppb)
2-propanol	below detection limit
n-butanol	0.160 ppm (160 ppb)
2-butanol	0.030 ppm (30 ppb)

CHAPTER 4

CONCLUSIONS

A. Continuous Counter-Current Solvent Extraction for the Separation and Purification of Lutetium

The preceding chapters have described the experimentation performed to investigate the use of continuous counter-current solvent extraction (CCCSX) for separation and purification of lutetium from scrap lutetium oxyorthosilicate (LSO). LSO is a scintillating γ -ray detector used in positron emission tomography. The LSO must contain a 0.2 atom% cerium dopant in order to scintillate. Therefore, the cerium must be separated from the lutetium if highly pure lutetium oxide is to be produced by CCCSX. The final goal of the research described herein was the design of an industrial CCCSX facility with the capacity to recycle 127 kg of scrap LSO and produce 106 kg of 99.999% pure Lu_2O_3 per day.

1. Bench-scale experiments

The standard industrial procedure for the scale up to the industrial plant was followed. First, bench-scale experiments were performed to thoroughly investigate the extraction behavior of lutetium from an aqueous HNO_3 solution into an immiscible organic phase consisting of 0.45M IQ 801 in kerosene. The extraction of lutetium is highly dependent on the acid concentration in the aqueous phase. As the aqueous acid concentration approaches 2.0M, the extraction of lutetium becomes a thermodynamically

unfavorable process. Therefore, the acid concentration in the aqueous phase must be carefully monitored and controlled in an industrial CCCSX plant.

Bench-scale experiments were also conducted to investigate the acid stripping of lutetium from the organic phase. When a lutetium-loaded organic phase was mixed with 6 portions of 6.0M HNO_3 essentially all of the lutetium was removed from the organic phase and was present in the aqueous acid phase. Since the desired final product of the CCCSX facility is lutetium oxide, the aqueous lutetium solution was processed to produce the oxide. The process involved neutralizing the aqueous solution to a pH of approximately 3 or 4. After neutralization, lutetium oxalate was precipitated from the solution by adding a 50% stoichiometric excess of oxalic acid in the form of a saturated aqueous solution of oxalic acid. The precipitated lutetium oxalate was filtered, rinsed and calcined to convert it to lutetium oxide.

2. Pilot-scale experiments

Based on the encouraging results obtained in the bench-scale experiments, the second step of the scale up was carried out. This second step was the pilot-scale experiments. The pilot-scale experiments were performed in a pilot plant containing 15 mixer-settlers. The pilot plant was operated by pumping an organic solution of 0.45M IQ 801 in kerosene through system. The organic phase entered the pilot plant at the last stage of extraction and exited the plant at the stage of scrubbing. An aqueous 1.20M aqueous HNO_3 phase was pumped through the system counter-current to the organic phase. The aqueous phase entered the pilot plant at the last stage of scrubbing and exited

the plant at the last stage of extraction. A lutetium feed solution obtained from the acid leaching of scrap LSO was introduced into the aqueous stream approximately at the midpoint of the system. The mixer-settler stage immediately to the left of the lutetium introduction point became the first stage of extraction and consequently, the stage immediately to the right of the introduction point became the first stage of scrubbing.

Many parameters were adjusted throughout the course of the pilot plant studies and it was determined that the most important parameters in the operation of the pilot plant were the flow rates of the two phases. The extraction of the lutetium depended very heavily on the flow rates of the organic and the aqueous phases. If the flow rates were too high, then the system was not able to reach equilibrium in each stage. This non-equilibrium condition caused the extraction of lutetium to transfer from the first stage of extraction to the second, third or even fourth stage of extraction. In one experiment, the flow rates were so high that the extraction of lutetium was not complete after six extraction stages. The transfer of the lutetium extraction creates a very inefficient CCCSX process.

The scrubbing of the lutetium-loaded organic phase was very efficient in every experiment performed. The scrubbing circuit of the pilot plant removes the impurities which contaminate the lutetium. In one experiment, the lutetium to cerium ratio was increased from 784 to 820,000. This represents a purity increase from ~99.9% to >99.9999%, if cerium is considered the only contaminant. However, purity analyses indicated that the heavy lanthanides were also contaminating the lutetium oxide produced from scrap LSO. The purity of the Lu_2O_3 could be increased with respect to the other

heavy lanthanides by simply adding more scrubbing stages.

3. Design of industrial CCCSX facility

Using the information obtained from the pilot-scale experiments, an industrial CCCSX facility was designed. The design of this plant included the pre-extraction section, the CCCSX circuit and the post-extraction section. The pre-extraction section consisted of the equipment to leach the lutetium from scrap LSO and prepare a clarified lutetium solution. The CCCSX circuit contained 30 mixer-settler stages, 10 each of extraction, scrubbing and stripping. The post-extraction section included all of the equipment necessary for the neutralization, precipitation, filtration and calcination of the final product, 99.999% pure Lu_2O_3 . This facility was designed to have the capacity to convert 127 kg of scrap LSO into 106 kg of lutetium oxide per day. The volume of aqueous effluent generated per day would be 9126 L. This effluent would contain 582 kg of ammonium nitrate and 11.3 kg of ammonium oxalate. Experiments were performed to investigate the possibility of reducing this amount of aqueous effluent generated by the CCCSX plant.

B. Precipitation Stripping of Lutetium

The precipitation stripping of lutetium is a technique in which the lutetium is removed from an organic phase as the insoluble oxalate. This is accomplished by mixing the lutetium-loaded organic phase with an aqueous solution of oxalic acid. The precipitation stripping of lutetium from an organic phase containing IQ 801 using a saturated solution of oxalic acid is not a highly efficient process. It was determined that

the total acid concentration of the saturated solution of oxalic acid was too low. The acid concentration in the stripping solution was increased by using a 2.0M acetic acid solution saturated with oxalic acid for the precipitation stripping of lutetium. This increased the stripping efficiency from ~80% to >90%.

The feasibility of using precipitation stripping in an industrial facility was investigated by recycling both the organic phase and the stripping solution. After stripping the lutetium from the organic phase as the oxalate, the organic phase was re-loaded with lutetium. The precipitation stripping process did not adversely affect the loading characteristics of the organic phase. The stripping solution was also re-used after each precipitation stripping cycle. The stripping solution was re-saturated with oxalic acid and mixed with the re-loaded organic phase. The recycling the of the stripping solution did not adversely affect the precipitation stripping efficiency of lutetium. In fact, the stripping efficiency remained essentially constant after the initial precipitation stripping cycle.

Precipitation stripping appears to be industrially viable. If the precipitation stripping process were to be added into the previously designed industrial CCCSX facility, considerable savings could be affected. The volume of the aqueous effluent generated per day would be decreased from 9126 L to 3402 L (63%) and the amount of NH_4NO_3 produced would be cut in half. This makes precipitation stripping very attractive for industrial CCCSX processes.

C. Future Work

Listed below are items that may increase the efficiency of an industrial CCCSX facility for the separation and purification of lutetium from the other lanthanides. These suggestions are based on observations made during the course of investigation and would require additional experimentation.

1. The separation of lutetium from ytterbium might be improved by adding a complexing agent into the aqueous phase which complexes more strongly with ytterbium. This complexation would increase the effective number scrubbing stages in a facility. The organic phase complexes more strongly with lutetium and therefore, concentrates the lutetium in that phase in each stage. The concentration of lutetium in the organic phase would also be increased because the extraction of ytterbium would be retarded by the aqueous complexing agent. Based on this principle, the number of stages required to produce a desired purity of lutetium could be reduced, thus generating cost savings in the facility. However, the possibility of finding such complexing agents will most likely be very difficult. The hardness of the lanthanide ions increases with increasing atomic number. Therefore, a complexing agent which would bond more strongly to ytterbium would be a soft complexing agent. Soft complexing agent generally do not bond to the lanthanides.

2. Some literature reports indicate that the separation factor between the lanthanides are larger in solvent extraction processes which have non-equilibrium conditions. The pilot

plant described in Chapter 3 was operated under non-equilibrium conditions during two experiments. It was found that these conditions did not adversely affect the scrubbing circuit of the system. Therefore, experiments could be performed to investigate the possibility of reducing the number of stages required to produce a desired purity of lutetium oxide by operating a facility with non-equilibrium conditions.

3. All of the precipitation stripping experiments described in the previous accounts of research involved batch production of lutetium oxide. Experiments could be conducted to study the feasibility of making the precipitation stripping process a continuous process. A continuous precipitation stripping process would reduce the amount of labor required to produce the lutetium oxide. Batch-wise processes require the storing and transferring of large quantities of solutions. This would be eliminated in a continuous process in which the lutetium-loaded organic phase was taken directly from the scrubbing circuit and introduced into the precipitation stripping circuit.

A continuous precipitation stripping circuit might also be used to separate the lanthanides. Previous precipitation stripping experiments demonstrated that lutetium could not be stripped from DEHPA by oxalic acid. However, the other lanthanide could be stripped. In fact, the separation factors between the adjacent heavy lanthanides are quite large. The Yb/Tm separation factor was ~ 4 and the Tm/Er separation factor was ~ 3 . This technique could be a novel separation technique for the lanthanides.

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APPENDIX

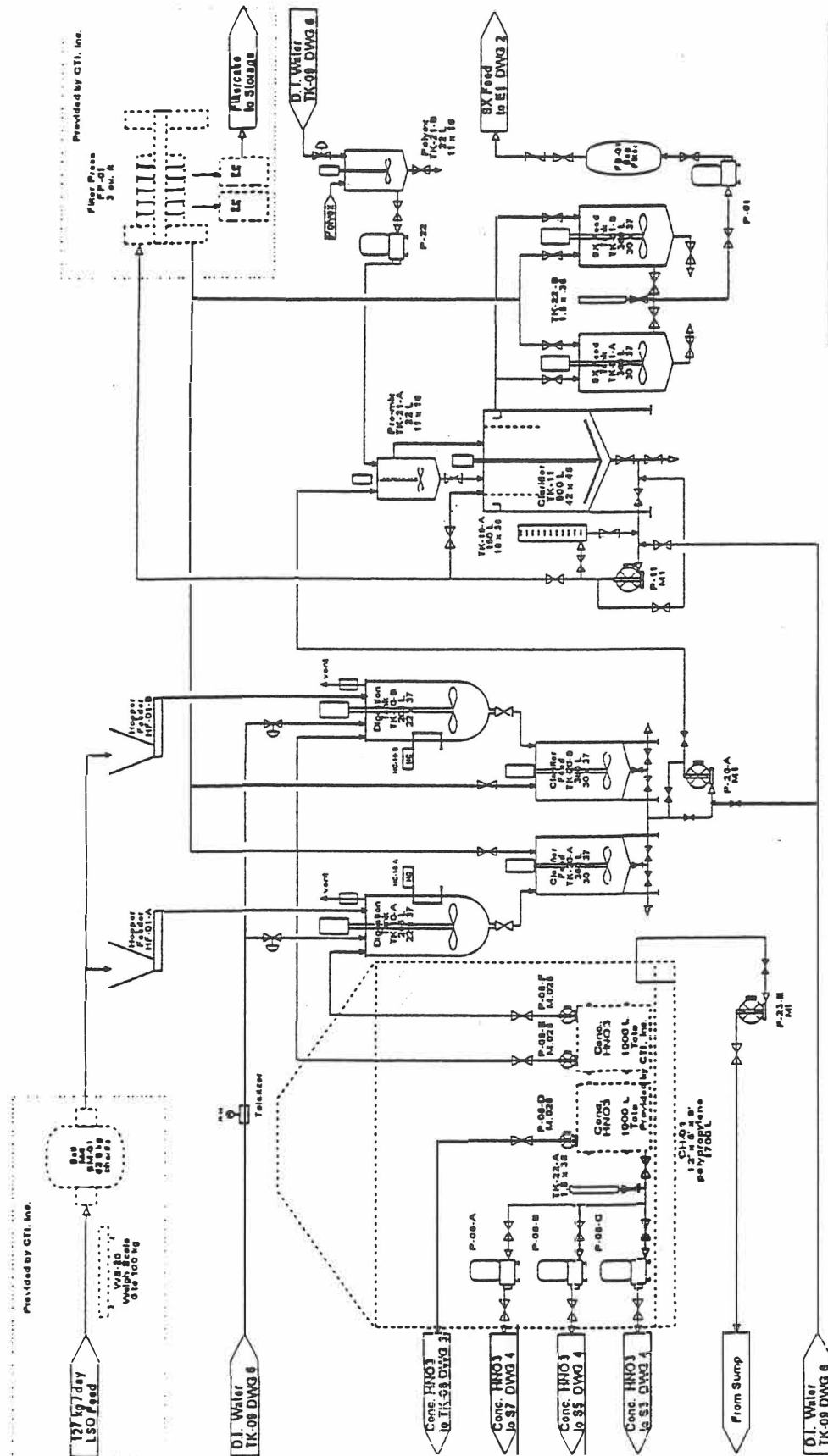


Fig. 28 Pre-Extraction Circuit of Industrial CCCSX Plant

CTI Lutetium Recycle Project:	Digestion Circuit
REV A	DWG 1
Feb 01 04 0000	Feb 01 04 0000

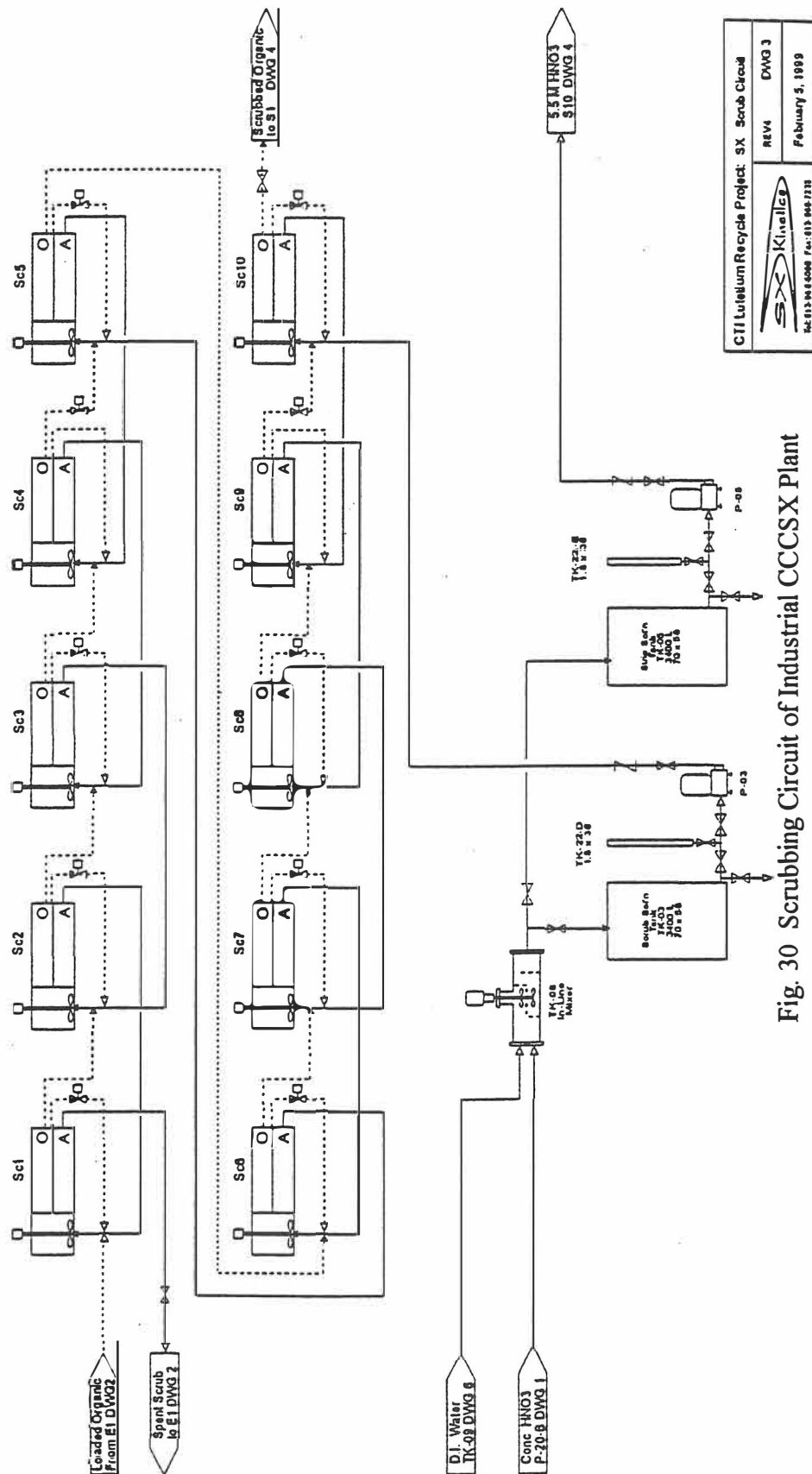
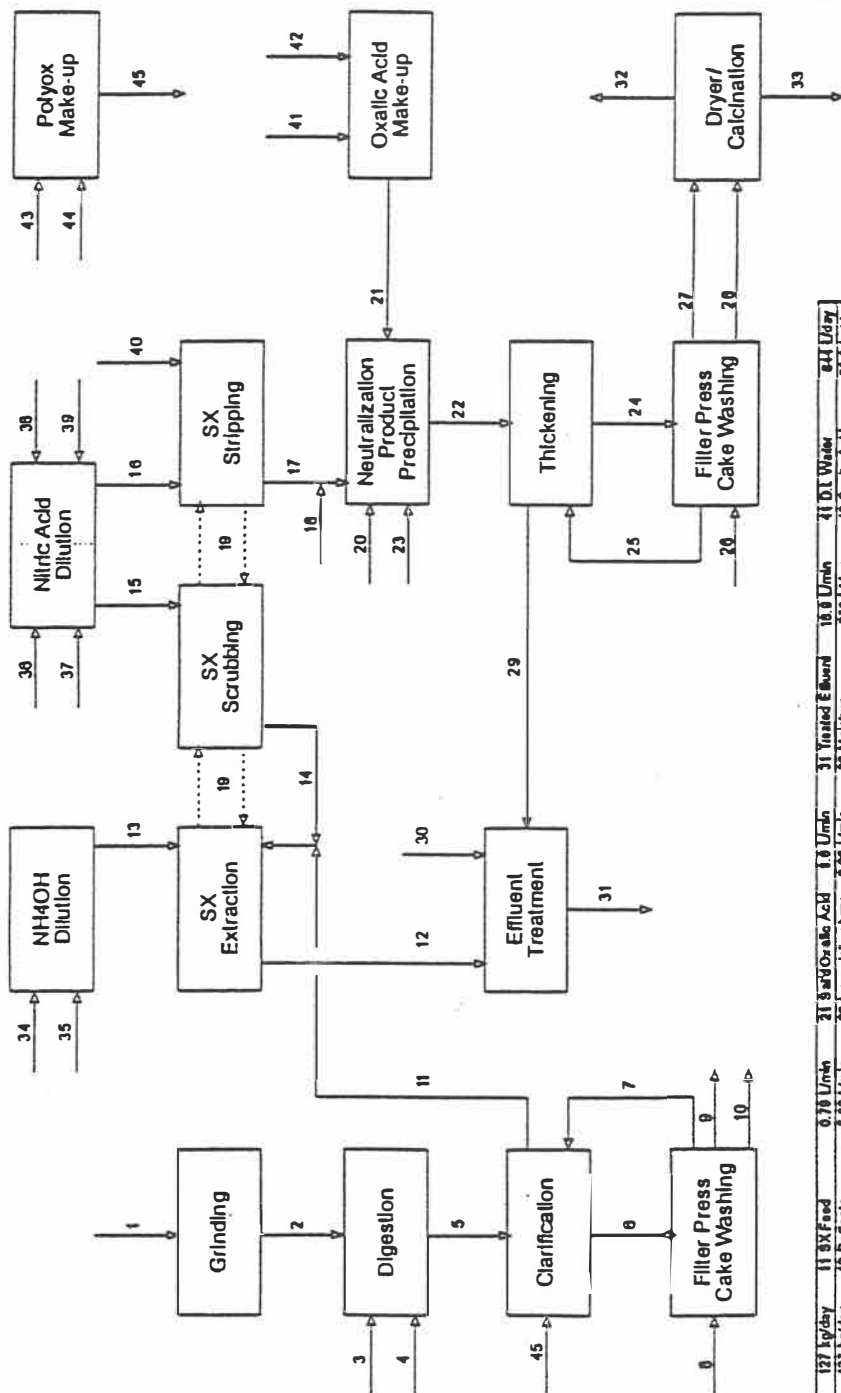


Fig. 30 Scrubbing Circuit of Industrial CCCSX Plant



1 LSO Feed	127 kg/day	11 SX Feed	0.78 U/min	21 3rd Oxalic Acid	1.8 U/min	31 Treated Effluent	18.8 U/min	41 D.I. Water	244 U/day
2 Ground Feed	127 kg/day	12 Raffinate	9.82 U/min	22 1st Wash Water	8.74 U/min	32 Mother	378 U/day	42 Oxalic Acid	78.8 U/day
3 Digestion Water	138 U/day	13 NH4OH (8M)	0.48 U/min	23 D.I. Wash Water	2.00 U/min	33 Lu2O3 product	108 kg/day	43 Water	
4 HNO3 (15.8M)	138 U/day	14 Spent Scrub	8.0 U/min	24 Thickener UF	1.11 U/min	34 NH4OH (14.7M)	109 U/day	44 Polyox	
5 Digest Discharge	278 U/day	15 Spent Scrub	8.0 U/min	25 Filtrate	2.41 U/min	35 D.I. Water	137 U/day	45 Flocculant Feed	
6 Clarifier UF	278 U/day	16 Strip Sol'n	1.0 U/min	26 D.I. Wash Water	2.00 U/min	36 HNO3 (15.8M)	205 U/day	46	
7 Filtrate	428 U/day	17 Strip Liquor	1.2 U/min	27 Cake Moisture	378 U/day	37 D.I. Water	2485 U/day	47	
8 Wash Water	236 U/day	18 D.I. dilution water	4.0 U/min	28 Filter Cake	163 kg/day	38 HNO3 (15.8M)	188 U/day	48	
9 Cake Moisture	63 U/day	19 Organic phase	10.0 U/min	29 Thickener O/F	10.8 U/min	39 D.I. Water	332 U/day	49	
10 Filter Cake SiO2	22 kg/day	20 NH4OH (14.7M)	0.44 U/min	30 NH4OH (14.7M)	0.41 U/min	40 HNO3 (15.8M)	0.19 U/min	50	

CTI Lutetium Recycle Project: Mass Balance & Flow	
	REV 3
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	February 5, 1999

Fig. 34 Mass Balance Flowsheet of Industrial CCCSX Plant

VITA

Peter Michael Smith was born in Indianapolis, Indiana on June 14, 1974. He was the second son of Duane and Dianna Smith. Peter graduated from Stewart County High School of Dover, Tennessee in May 1992. After attending Rose-Hulman Institute of Technology in Terre Haute, Indiana and Tennessee Technological University in Cookeville, Tennessee, Peter settled down at the University of Tennessee at Knoxville. He experimented with majors in education and physics but finally decided on chemistry and received his Bachelor of Science degree in May 1997.

Shortly after graduation, Peter married the love of his life, Erin Tieman. Four days after the wedding, he started his graduate career at the University of Tennessee at Knoxville. He has been working in the chemistry labs of Dr. George K. Schweitzer since starting graduate school. Peter has become an active member of both the American Chemical Society and The Mineral, Metals and Materials Society by presenting papers at each society's meetings.

In his spare time during his graduate career, Peter served as an interim youth minister at Seymour Heights Christian Church in Seymour, Tennessee where he received more blessings than any one man deserves.