To the Graduate Council:

I am submitting herewith a thesis written by Jessica Anne Mitchell entitled “Removing Acetic Acid from the UREX+ Process.” I have examined the final electronic copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Chemical Engineering.

Major Professor, Robert M. Counce

We have read this thesis and recommend its acceptance:

Professor, Jack S. Watson

Professor, Paul Bienkowski

Accepted for the Council:

Carolyn R. Hodges, Vice Provost and Dean of Graduate Studies

(Original signatures are on file with official student records.)
ACKNOWLEDGEMENTS

This work was supported by the U.S. Department of Energy, Nuclear Energy Research Initiative (NERI) program, under DOE Contract No. DE-PS07-05ID14713 with Oak Ridge National Laboratory. Their support makes this thesis possible. I would also like to thank my professors, Dr. Pete Counce and Dr. Jack Watson, and Oak Ridge National Laboratory Staff, Dr. Barry Spencer and Dr. Guillermo Del Cul, for their valuable insight and knowledge they shared with me throughout this project. I would also like to thank Dr. Paul Bienkowski for being on my thesis committee.

In addition to all my academic support, I received much support from my lab mates who made the journey that much easier. Ify and Christina especially made coming to the lab everyday a joy and the late nights eventful. Thank you both for giving me so many great memories. Thank you also to Susan Seymour for being my sounding board and my go to person for all things non-chemical engineering.

To save the best for last, I would like to thank my family. I am blessed to have an enormous support system—my parents, Sara and Alan Mitchell; my sister, Jacqueline Mitchell; my fiancé, Derick Hobby; my grandparents, John and Barbara Lane and Hays and Geneva Mitchell; my great-grandmother, Rachel Christine Lundgren Lane; and my aunts and uncles, Greg Lane, Alice Blankenship, and Cheryl Caruso. They all continually cheerlead for me. They are proud of all my accomplishments and encourage me to be the best I can be. Without them, I know I would not be as successful as I am today.
ABSTRACT

Acetic acid needs to be removed from a waste stream in the UREX+ process so that nitric acid can be recycled and possible interference with downstream steps can be avoided. Acetic acid arises from acetohydroxamic acid (AHA) used to suppress plutonium in the first step of the UREX+ process. Later, it is hydrolyzed into hydroxyl amine nitrate and acetic acid. Many common separation technologies were examined, and solvent extraction was determined to be the best choice under process conditions. Solvents already used in the UREX+ process were then tested to determine if they would be sufficient for the removal of acetic acid. The tributyl phosphate (TBP)-dodecane diluent, used in both UREX and NPEX, was determined to be a solvent system that gave sufficient distribution coefficients for acetic acid in addition to a high separation factor from nitric acid. This solvent system was tested under various TBP concentrations in the dodecane to create a concentration plot that can be used for further flow sheet development. Each step in the UREX+ process was examined to determine if there was any acetic acid interference in the performance of any step of the UREX+ flow sheet that would make it necessary to remove the acetic acid prior to that step. It was found that no interference with acetic acid was present. Therefore, the acetic acid removal step can be placed essentially anywhere in the process. For simplicity, it has been proposed to place the removal step at the end of the process after TALSPEAK where all desirable metals have already been extracted and the nitric acid waste stream is prepared to be recycled.
# TABLE OF CONTENTS

**CHAPTER I: INTRODUCTION** ............................................................................. 1

1. INTRODUCTION ......................................................................................... 2

   1.1. Background ..................................................................................... 2

   1.2. Objective ......................................................................................... 3

**CHAPTER II: REMOVING ACETIC ACID FROM A UREX+ WASTE STREAM: A REVIEW OF TECHNOLOGIES** .................................................. 4

   ABSTRACT ............................................................................................... 5

   1. INTRODUCTION ..................................................................................... 5

   2. BACKGROUND ..................................................................................... 7

   3. ACETIC ACID REMOVAL METHODS ..................................................... 8

      3.1. Membrane Separation and Ion Exchange ...................................... 8

      3.2. Crystallization ................................................................................. 9

      3.3. Distillation ...................................................................................... 14

      3.4. Adsorption ...................................................................................... 14

      3.5. Solvent Extraction ......................................................................... 17

      3.6. Destruction ..................................................................................... 25

4. RESULTS .................................................................................................... 27

5. CONCLUSIONS .......................................................................................... 29

6. ACKNOWLEDGEMENTS ......................................................................... 30

REFERENCES ................................................................................................. 31

**CHAPTER III: EXTRACTING ACETIC ACID FROM ACIDIC SOLUTIONS** .......... 34
ABSTRACT .......................................................................................................................... 35

1. INTRODUCTION/BACKGROUND .............................................................................. 35

1.1. Alternate Separation Methods Considered .......................................................... 37

1.2. Solvent Selection ................................................................................................. 38

2. EXPERIMENT ........................................................................................................ 39

3. RESULTS AND DISCUSSION .................................................................................. 41

3.1. Titration Curve Analysis .................................................................................... 41

3.2. Acetic Acid Extraction from Water-Acetic Acid Solutions .................................. 41

3.3. Nitric Acid Extraction from Water-Nitric Acid Solutions ................................... 44

3.4. Nitric and Acetic Acid Extraction from Water-Acetic Acid-Nitric Acid Solutions .... 46

3.5. 2.5M Tributyl Phosphate Mixed With Organic Diluents ..................................... 46

4. CONCLUSIONS ...................................................................................................... 50

5. ACKNOWLEDGEMENTS ....................................................................................... 50

REFERENCES .................................................................................................................. 51

CHAPTER IV: PLACING THE ACETIC ACID STEP INTO THE UREX+ PROCESS .54

ABSTRACT .................................................................................................................. 55

1. INTRODUCTION ...................................................................................................... 55

2. BACKGROUND ........................................................................................................ 56

2.1. UREX+ Process ................................................................................................ 56

2.2. Acetic Acid Removal Step ................................................................................ 58

2.3. Extraction Factors .............................................................................................. 59

3. ACETIC ACID INTERFERENCE ESTIMATES ......................................................... 62

3.1. UREX ................................................................................................................... 62
3.2. CCD-PEG (or FPEX) ................................................................. 63
3.3. NPEX ...................................................................................... 66
3.4. TRUEX .................................................................................... 67
3.5. TALSPEAK ............................................................................ 68

4. ANALYSIS/DISCUSSION .............................................................. 69

5. CONCLUSION ........................................................................... 71

6. ACKNOWLEDGEMENTS .............................................................. 71

REFERENCES .................................................................................. 72

CHAPTER V: CONCLUSIONS ............................................................ 75

1. FUTURE WORK .......................................................................... 76

1.1. Centrifugal Contactor Studies ............................................... 76

1.2. Replacing Acetohydroxamic Acid ......................................... 76

2. CONCLUSIONS ......................................................................... 76

REFERENCES .................................................................................. 77

VITA .................................................................................................. 79
## LIST OF TABLES

Table 2-1. Physical Properties .................................................................9

Table 2-2: Ranges of Equilibrium Distribution Coefficients for Dilute Acetic Acid between Classes of Organic Solvents and Water. [16] .................................................................19

Table 2-3: Equilibrium Distribution Coefficients of Acetic Acid between Diluents and Water. [16] *Chevron Solvent 25 is mostly C-8 and C-9 alkylated aromatics [17] .................................19

Table 2-4. Technology Comparisons ................................................................28

Table 3-1. Extraction of Acetic Acid in Experimental Organic Diluents. ..................44

Table 3-2. Extraction of Acetic Acid in Pure Organic Diluents..............................45

Table 3-4. Extraction of Acetic and Nitric Acids in Organic Diluents........................48

Table 3-5. Extraction of Acids in 2.5M TBP Mixtures ........................................49

Table 4-1. Distribution Coefficients for the TBP-dodecane Solvent System[1] ............59

Table 4-2. Acid Distribution in TRUEX Solvent ..................................................68
## LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-1</td>
<td>UREX+ Process Overview</td>
<td>6</td>
</tr>
<tr>
<td>2-2</td>
<td>Phase Diagram for Acetic Acid and Water. [5]</td>
<td>11</td>
</tr>
<tr>
<td>2-3</td>
<td>Phase Diagram for Nitric Acid and Water. [6]</td>
<td>12</td>
</tr>
<tr>
<td>2-4</td>
<td>Phase Diagram for Nitric Acid and Acetic Acid. [6]</td>
<td>13</td>
</tr>
<tr>
<td>2-5</td>
<td>$K_D$ as a function of Acetic Acid Concentration using 30% TBP-Dodecane Solvent with an Organic to Aqueous Ratio of 1. [21]</td>
<td>22</td>
</tr>
<tr>
<td>2-6</td>
<td>$K_D$ as a function of Acetic Acid wt% using TOPO (22 wt%) in Chevron Solvent 25. [17]</td>
<td>24</td>
</tr>
<tr>
<td>3-1</td>
<td>UREX+ Flowsheet with Proposed Acetic Acid Removal Step</td>
<td>36</td>
</tr>
<tr>
<td>3-2</td>
<td>Single Acid Titration Curves (Nitric Acid and Acetic Acid)</td>
<td>42</td>
</tr>
<tr>
<td>3-3</td>
<td>Mixed Acid Titration Curves (Both Nitric and Acetic Acid Together)</td>
<td>43</td>
</tr>
<tr>
<td>4-1</td>
<td>The UREX+ Process Used for this Study. [3]</td>
<td>57</td>
</tr>
<tr>
<td>4-2</td>
<td>Distribution Coefficients for Acetic Acid in Acetic Acid and Nitric Acid Mixtures vs. TBP Concentration</td>
<td>60</td>
</tr>
<tr>
<td>4-3</td>
<td>Acetic Acid Removal Flow sheet Step</td>
<td>60</td>
</tr>
<tr>
<td>4-4</td>
<td>Uranium Distribution Coefficients vs. Initial Uranium Concentrations at different Nitric Acid Feed Concentrations. [6]</td>
<td>64</td>
</tr>
<tr>
<td>4-5</td>
<td>Flowsheet Proposal</td>
<td>70</td>
</tr>
</tbody>
</table>
NOMENCLATURE

$K_D$ = Distribution Coefficient

$K_C$ = Degree of Ionization

pKa = Acid Dissociation Constant

$[\text{Solute}]$ = Concentration of the Solute (mol/L)

$[\text{H}^+]$ = Hydronium Concentration (mol/L)

$[\text{Ac}^-]$ = Acetate Concentration (mol/L)

$[\text{HAc}]$ = Acetic Acid Concentration (mol/L)

MIBK = Methyl isobutyl ketone

TBP = Tributylphosphate

TOPO = Trioctylphosphine oxide

TnOA = Tri-n-octylamine

AHA = Acetohydroxamic Acid
CHAPTER I: Introduction
1. INTRODUCTION

1.1. Background

This project is funded by the Advanced Fuel Cycle Initiative (AFCI) as part of the Nuclear Energy Research Initiative (NERI) and the Global Nuclear Energy Partnership (GNEP). The goals of these programs are to establish a fuel reprocessing system capable of recovering fissile materials from spent nuclear fuel for reuse in nuclear power reactors, inhibit the purification of plutonium through co-extraction with actinides, and create an alternative process for recycle of spent nuclear fuel rather than the current once through plutonium and uranium extraction (PUREX) method. The production of energy from uranium on an industrial level would create a substantial decrease in coal and petroleum dependence for our energy sources. The inhibition of plutonium purification makes it difficult for plutonium to be used in non-peaceful uses. The recycle of the spent fuel components creates much less waste for deposition into such repositories as Yucca Mountain.

One process utilizing these objectives is the Uranium Extraction (UREX+) process. The first step in this flow sheet is the Uranium Extraction (UREX) step. This step has an added complexant, acetohydroxamic acid (AHA), which suppresses the extraction of both plutonium and neptunium. The downstream steps of this process vary from flow sheet to flow sheet, but a later step in the process extracts plutonium and neptunium together with minor actinides making plutonium much less attractive for undeclared uses. At the end of this process, the nitric acid waste stream is reconcentrated, most likely through distillation, for reuse. This recycle of nitric acid requires acetic acid to be removed from the system prior to or during this step to prevent accumulation of acetic acid in the process.
Acetic acid is created from the decomposition of AHA after the UREX step. This hydrolysis is necessary so that plutonium and neptunium can be extracted in later step, and will probably be accomplished by heating the stream to accelerate the hydrolysis rate. The acetic acid needs to be removed to prevent potential problems in the recycle of nitric acid and downstream steps.

1.2. Objective

The objective of this thesis is to determine a way to remove acetic acid from the raffinate stream of the UREX+ process or downstream in the UREX+ process. This will be done in three chapters. The goal of Chapter II is to evaluate the most promising technology through literature review that will remove acetic acid in these process conditions. In Chapter III, the experimental evaluation of the selected technology will be explored. Finally, Chapter IV will determine the placement of this removal step in the UREX+ process.
CHAPTER II: Removing Acetic Acid from a UREX+ Waste Stream: A Review of Technologies

Chapter II of this thesis is a slightly revised version of an article by the same name will be published in the journal *Nuclear Technology* in 2009 by Jessica Mitchell, Robert M. Counce, Jack S. Watson, Barry B. Spencer, and G.D. Del Cul:


This article is reproduced with permission from the journal. This work is in total the effort of Jessica Anne Mitchell.
ABSTRACT

This study explores different technologies for removing acetic acid from a UREX+ waste stream. The waste stream contains both nitric and acetic acids, and the acetic acid must be removed from the waste stream to prevent potential problems in the downstream steps as well as affecting the recycle of nitric acid. The acetic acid is formed after the UREX step of the process as a result of hydrolytic degradation of acetohydroxamic acid used to suppress plutonium extraction. Of the available technologies, the two most attractive approaches are solvent extraction and distillation. In industry, solvent extraction is used for more dilute concentrations of acetic acid while distillation is used for concentrated acetic acid. If a liquid-liquid extraction is viable, this would be the best option with the addition of an extractant, like tributyl phosphate or tri-n-octyl amine, if needed. However, if acetic acid removal can be delayed until the end of the UREX+ process when the nitric acid may be concentrated for recycle, distillation may remain an option, though not necessarily a better option than solvent extraction.

1. INTRODUCTION

The objective of this study is to identify and evaluate the most attractive approach to removing acetic acid from the UREX+ process (Figure 2-1). The evaluation includes consideration of acceptability of the approach in nuclear material processing, the effects of the approach on the UREX+ process and downstream process steps, as well as factors that affect costs of the approach. Technologies including solvent extraction, destruction, absorption, distillation, and crystallization for the removal/destruction of acetic acid are studied, based on available literature. The objective of this study is to determine the most appropriate method for
Figure 2-1. UREX+ Process Overview
(1) effective removal of acetic acid without removal of other key components in the process, and
(2) the removal step must not interfere with other downstream steps or the recycling of nitric acid.
Once chosen, this method will be experimentally verified at UREX+ process conditions. The
degree/percent of removal remains a variable in this study since no specific limit for residual
acetic acid was available.

2. BACKGROUND

The UREX+ process, as presented in Figure 2-1, is a series of solvent extraction steps
designed to treat spent nuclear fuel by separating its various components for reuse and disposal.
Since this process is still under development, there are many different flow sheet scenarios. The
flow sheet presented in Figure 2-1 is used in this study.

The first step in Figure 2-1 is the UREX step; nuclear fuel dissolved in aqueous nitric
acid is treated with an organic solvent to remove uranium and technetium. The solvent consists
of tributyl phosphate dissolved in n-dodecane with acetohydroxamic acid (AHA) added to the
aqueous stream to prevent the extraction of plutonium. Both uranium and technetium are
extracted into this solvent.\(^1\) The downstream steps of this process, CCD-PEG (or FPEX), NPEX,
TRUEX, and TALSPEAK, are discussed at length in papers on the UREX+ process. [1-4]

The source of the acetic acid, which is the focus of this study, is a degradation product of
acetohydroxamic acid. In the acid environment, most of the acetohydroxamic acid hydrolyzes to
produce acetic acid and hydroxylamine nitrate. Acetic acid and residual AHA are assumed to
leave the UREX segment of the process in the raffinate. The complexant will be completely
destroyed prior to the plutonium removal step (NPEX) so that the plutonium will no longer be
suppressed. The acetic acid must be separated and/or destroyed because it has potential to interfere with downstream steps and with the recycling of the nitric acid for reuse in the UREX+ process. [3]

The raffinate stream of interest was modeled as an aqueous mixture of nitric acid and acetic acid in an approximate 10:1 concentration ratio (0.5M nitric acid and 0.05M acetic acid). This is believed to be close to the acid concentrations in the raffinate streams, but, of course, the concentrations will depend upon where the acetic acid removal step is placed in the UREX+ process. There will also be numerous salts in the raffinate stream, but those are assumed to be at low concentrations and are not expected to affect the acetic acid removal or destruction step. However, the behavior of those salts during the separation and destruction will be an important consideration throughout this analysis of removal options since many of these salts are (1) highly radioactive, (2) desired products to be recovered in downstream steps, or (3) may affect the disposal of any wastes from the acetate removal step.

Relevant physical properties for acetic acid, nitric acid, and water are shown in Table 2-1. Additionally, nitric acid and water form a maximum boiling azeotrope at about 68 weight percent nitric acid. The following section summarizes the result of the literature study of potential acetic acid removal methods.

3. ACETIC ACID REMOVAL METHODS

3.1. Membrane Separation and Ion Exchange

Technologies such as membrane separation and ion exchange were eliminated early in the literature review. No membrane was found to be sufficiently selective to remove acetic acid
<table>
<thead>
<tr>
<th>Properties</th>
<th>Acetic Acid (CH₃COOH)</th>
<th>Nitric Acid (HNO₃)</th>
<th>Water (H₂O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boiling Point (°C)</td>
<td>118</td>
<td>122</td>
<td>100</td>
</tr>
<tr>
<td>Freezing Point (°C)</td>
<td>16.6</td>
<td>-42</td>
<td>0</td>
</tr>
<tr>
<td>Vapor Pressure (mm Hg @20°C)</td>
<td>11</td>
<td>48</td>
<td>17.5</td>
</tr>
<tr>
<td>pKa</td>
<td>4.8</td>
<td>-1.5</td>
<td>15.74</td>
</tr>
</tbody>
</table>

Table 2-1. Physical Properties

in a single pass, and multistage membrane operation was not thought to be an attractive option. Also organic membranes are not normally used in high radiation fields because of potential radiation degradation; so the membrane selection may be limited to inorganic membranes.

Ion exchange was also eliminated as a possible technology because no ion exchange material was identified with sufficient selectivity for acetate ions over nitrate ions at conditions of this study. Ion exchange occurs primarily through adsorption onto a resin with exchangeable ions, anions in this case. For the raffinate stream of interest, nitric acid depresses the dissociation of the acetic acid, i.e. it lowers the acetic acid uptake and reduces the selectivity of anion resins for acetate ions.

3.2. Crystallization

Crystallization is the formation of a solid phase from a homogeneous liquid phase. It is of possible interest due to the high freezing point of acetic acid compared to water. Crystallization first requires a saturated solution so that further changes in solution conditions cause solid formation (crystallization). Currently, solubility data are available only for binary systems, water-nitric acid, water-acetic acid, and nitric acid-acetic acid. Information on ternary systems of nitric acid-acetic acid-water are not available, so evaluations were made on three binary systems.
The acetic acid-water phase diagram (Figure 2-2) shows for dilute acetic acid solutions (to the left of the eutectic) the crystallizing specie is water. Substantial concentration of the aqueous acetic acid-water system must occur before acetic acid becomes the crystallizing specie (to the right of eutectic). The freezing points for nitric acid and water are quite a bit lower than for acetic acid and water (Figure 2-3). Since the solution of interest contains substantial quantities of nitric acid and nitrate salts in addition to acetic acid and water, the presence of this species lead to additional changes in the freezing point. In general, the addition of various salts as well as nitric acid to aqueous acetic acid solutions results in an increase in activity for the acetic acid and a decrease in water activity. [7,8] Applying such information, the freezing point curves will likely shift some for the solution of interest from that shown for the aqueous acetic acid binary system. Other pertinent information comes from Linke and Seidell (1965) who indicate for the acetic acid-nitric acid binary system there is a nitric acid-acetic acid specie with an estimated freezing point of about -23.9 degrees Celsius. While this does not rule out the possibility of a useful acetic acid-nitric acid compound for crystallization, it indicates that considerable concentration of the acetic acid and nitric acid is likely to be necessary, and the eventual solid phase that removes acetic acid is likely to contain some nitric acid. Also, the behavior of dissolved salts during crystallization may be important if crystallization is used for acetic acid removal. Multistage crystallization equipment was noted to usually involve considerable mechanical equipment for washing and redissolving the crystals. The primary conclusion from Figures 2-2, 2-3, and 2-4 is that considerable concentration of acetic acid appears to be necessary before crystallization can be a viable candidate technology for acetic acid removal. Thus crystallization was not considered further in this study. It is noted, however,
Figure 2-2. Phase Diagram for Acetic Acid and Water. [5]
Figure 2-3. Phase Diagram for Nitric Acid and Water. [6]
Figure 2-4. Phase Diagram for Nitric Acid and Acetic Acid. [6]
that in activities where nitric acid is concentrated for recycle crystallization of acetic acid may again be of interest.

3.3. Distillation

Acetic acid and water have been separated industrially by simple, azeotropic, and extractive distillation. [9,10] The purpose of these industrial uses is to concentrate the acetic acid starting with concentrations higher than 5 wt% of acetic acid not present in the UREX+ process. At these concentrations, the most volatile component is water; so distillation would initially remove water and concentrate the nitric and acetic acids. If distillation is employed for another purpose like nitric acid concentration in the recycle stream, then it may be useful to consider this option more seriously for acetic acid removal. For this reason, further discussion of distillation is needed.

Acetic acid gas-liquid distribution coefficients at 13.3 kBar for the three-component system of nitric acid, water, and acetic acid from Nagahama and Jiang (1989) vary from relative volatilities ($K_{\text{Acetic}}/K_{\text{water}}$) of 0.594 at a temperature of 329.6K to 0.975 at a temperature of 343.8K. Using the UREX model stream of 0.5M nitric acid with 0.05M acetic acid, there is very little change in the vapor-liquid equilibrium data from the binary acetic acid-water system to the ternary acetic acid-nitric acid-water system. [7] Thus, distillation would continue to be attractive for higher concentrations of acetic acid, but not so attractive for low concentrations.

3.4. Adsorption

Adsorption involves the transfer of a solute from a fluid phase to a solid surface where it is bound by intermolecular forces. The solute being concentrated on a surface is defined as the adsorbate, and the material on which the adsorbate accumulates is defined as the adsorbent.
The amount of material that can be accumulated on a unit area of a surface is small; so useful adsorbents are typically porous material such as activated carbon or other materials with large internal surface areas. The term adsorption as used in this review includes any form of bulk uptake by solids, but only one term is used for the sake of simplicity. The design of adsorption equipment requires selection of an adsorbent and information on the equilibrium loading of the adsorbate on the adsorbent (the isotherm), the rate of transport of the adsorbate to the surface during adsorption and away from the surface during regeneration, and equilibrium loading of the adsorbate under regeneration conditions. As part of the process for selection of the adsorbent, the following information is necessary on the characteristics of the adsorbent: (1) the equilibrium capacity of the adsorbent, (2) the selectivity of the adsorbent, (3) physical and chemical characteristics of the adsorbent and (4) the regeneration characteristic of the adsorbent.

Generally the adsorption of weak electrolytes from aqueous solutions occurs through the association of the undissociated molecule with the hydrophobic surface. At conditions where the pH is lower than the pKa of the ionizable solute, the equilibrium loading will be greater than that expected at conditions where the pH is higher than the pKa. Acetic acid in the stream of interest will be largely associated, not ionized, at the expected pH, due to the presence of nitric acid, and the pKa of the acetic acid (see Table 2-1) thereby favors the adsorption of acetic acid in the conditions of this study.

Equilibrium adsorption capacity for acetic acid on various carbons and polymeric adsorbents is widely reported in the literature. In a study utilizing activated carbon with a surface area of 1080 m²/g, it was determined that the equilibrium capacity for a 0.0333 molar aqueous acetic acid to be 0.081 grams acetic acid per gram of carbon. [11] In a similar study of
commercially-available activated carbons with specific surface areas ranging from 390 to 2350 m$^2$/g found capacities for 1 weight percent aqueous solutions of acetic acid to be 0.05 to 0.18 g acetic acid per g carbon. [12] Several different mathematical forms for expressing the equilibrium data have been used such as the Langmuir isotherm, [13] Frueundlich-type isotherms, [14] and the Radke/Praunsnitz type isotherm. [15]

The term “polymeric adsorbents” is used in this report for synthetic organic adsorbents without functional groups. Adsorption onto polymeric adsorbents without functional groups is a surface-based phenomena similar to that of activated carbon; surface areas of 400 to 1000 m$^2$/g are common. The uptake mechanism shifts from surface based phenomena to that of bulk uptake at surface areas of about 500 m$^2$/g. Kuo et al. (1987) found equilibrium capacities for 1 wt% acetic acid of up to 0.12 g acetic acid per g of adsorbent for several commercial non-functionalized adsorbents; this is somewhat lower than similar equilibrium capacities of activated carbon but are comparable when expressed on the basis of specific surface area.

Nitric acid is not likely to be adsorbed to a significant extent on activated carbon or other non-functionalized adsorbents. The possibility of nitration reactions of nitric acid with polymeric adsorbents deserves careful investigation. For activated carbon adsorbents, nitration of carbon could occur after many cycles and possibly lead to the formation of compounds which not only would be unfavorable but could also be a safety concern. The low nitric acid concentration is a favorable factor in reducing the likelihood of significant nitration. Nevertheless, it is likely to be desirable to restrict the useful life of any carbon or polymer based adsorbent to reduce the potential for accumulation of excessive nitration products.
The usual methods of adsorbent regeneration include stripping at a higher temperature (usually with steam), desorption with a reactive solution (such as an aqueous base), or leaching with an appropriate solvent (such as acetone, various acetates, and methanol). The commercial non-functionalized adsorbents are generally more easily regenerated by solvents than activate carbon. [16] Since acetic acid will be adsorbed as the un-ionized molecule, it may be possible in this case to strip with either a dilute basic (caustic) solution that would ionize the acetic acid or an organic solvent that has favorable acetic acid solubility.

3.5. Solvent Extraction

The removal of a solute from a liquid solution using another immiscible liquid is referred to as liquid-liquid or solvent extraction. Most investigations of solvent extraction express that the degree to which a solute is extracted in terms of the distribution coefficient of the solute between the two liquids. The distribution coefficient is defined as

$$K_D = \frac{[\text{Solute}]_{\text{Organic}}}{[\text{Solute}]_{\text{Aqueous}}}$$  \hspace{1cm} (1)

where $[\text{Solute}]_{\text{Organic}}$ and $[\text{Solute}]_{\text{Aqueous}}$ are equilibrium concentrations of solute in the organic and aqueous phases. Coefficients of this type are a strong function of the degree of ionization of the solute. Non-ionized solutes tend to produce higher distribution coefficients into solvents with non-ionized extractants (non-ion exchange extractants) than into ionizing solutes since the extractant removes the neutral solute molecule rather than an individual ion, as in ion exchange.

A great deal of research has been done into the extraction of dilute acetic acid from aqueous waste or product streams. In industrial processes, the preferred method of removal for
dilute concentrations of acetic acid is solvent extraction. [9] In many cases, the aqueous waste or product streams are contacted with an organic diluent to extract acetic acid. In some cases an extractant must be added to the diluent to aid in the extraction. These extractants form weak complexes with the solute to be extracted that are insoluble in water but are soluble in the organic phase. [17] Wardell and King (1978) determined the distribution coefficients displayed in Tables 2-2 and 2-3 for several types of organic solvents. Distribution coefficients were measured for acetic acid-water solutions only (no nitric acid present). Wardell and King (1978) state the equilibrium distribution coefficients of phosphoryl compounds as extractants in diluents follow the following trend phosphates < phosphonate < phosphine oxide. Data presented by Wardell and King (1978) examines the relationship between basicity, extractant concentration, and molecular weight for the distribution of carboxylic acids in various solvent systems. Some of the data indicate acetic acid distribution coefficients for trioctylamines as high as 9.9 while the distribution coefficient of tributyl phosphate (TBP) was found to be typically 2.3 at 100% TBP with no diluent. [18]

The degree of ionization for aqueous acetic acid solutions can be estimated as follows:

$$K_c = 1.77 \times 10^{-5} = 10^{-\rho K_a} = \frac{[H^+][Ac^-]}{[HAc]}$$

(2a)

Or

$$\frac{[Ac^-]}{[HAc]} = 1.77 \times 10^{-5}$$

(2b)
Table 2-2: Ranges of Equilibrium Distribution Coefficients for Dilute Acetic Acid between Classes of Organic Solvents and Water. [16]

<table>
<thead>
<tr>
<th>Solvents</th>
<th>Range of Distribution Coefficients</th>
</tr>
</thead>
<tbody>
<tr>
<td>ethers (C₄-C₈)</td>
<td>0.63-0.14</td>
</tr>
<tr>
<td>acetates (C₄-C₁₀)</td>
<td>0.89-0.17</td>
</tr>
<tr>
<td>ketones (C₄-C₁₀)</td>
<td>1.20-0.61</td>
</tr>
<tr>
<td>alcohols (C₄-C₈)</td>
<td>1.68-0.64</td>
</tr>
</tbody>
</table>

Table 2-3: Equilibrium Distribution Coefficients of Acetic Acid between Diluents and Water. [16]  
*aChevron Solvent 25 is mostly C-8 and C-9 alkylated aromatics [17]*

<table>
<thead>
<tr>
<th>Diluents</th>
<th>Distribution Coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chevron Solvent 25&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.009</td>
</tr>
<tr>
<td>Chloroform</td>
<td>0.028</td>
</tr>
<tr>
<td>n-Hexanol</td>
<td>0.88</td>
</tr>
<tr>
<td>n-Heptanol/n-Hexanol (2:1)</td>
<td>0.30</td>
</tr>
<tr>
<td>Nitrobenzene</td>
<td>0.06</td>
</tr>
<tr>
<td>n-Heptane</td>
<td>0.02</td>
</tr>
</tbody>
</table>
Thus, using a concentration of approximately 0.05M acetic acid, the percent ionized (degree of ionization multiplied by 100) is 1.86% in a solution of only water and acetic acid. With the addition of 0.5M nitric acid, the percent ionized decreased further. This also relates to the distribution coefficient since with nitric acid present, most acetic acid will be molecular and therefore more easily extracted into the organic phase. This does not mean that the increase in the distribution coefficient to the organic will be directly related to the fraction of acetic acid to the total acetic acid concentration, but it does give some insight into the distribution of acetic acid in aqueous solutions of interest. A possible contradicting effect is the presence of a mineral acid, if strong enough, could protonate the acetic acid and causes it to be in an ionic form, therefore suppressing extraction. [20]

In discussing potential solvent extraction options for this application, solvent options will be divided into two main groups, solvents that are partially miscible in aqueous solutions and solvents that are essentially immiscible in water. The first group includes the De Dietrich process which uses solvents such as ethyl acetate or methyl isobutyl ketone (MIBK) to remove acetic acid during manufacture of pharmaceutical products or cellulose acetate. Although this is a relatively mature technology, it is not likely to be attractive for removing acetic acid from nuclear spent fuel reprocessing streams due to the miscibility of the solvent that would leave some residual solvent after the acetate is removed. Thus, an additional process step is likely to be required to remove the remaining solvent. With a relatively volatile solvent, the additional removal step may be a reasonable choice, but in general, the use of miscible solvents makes solvent extraction much less advantageous.

Immiscible solvents usually include a diluent and an active extractant, much like the
systems used in fuel processing to remove actinides, fission products, and other metals. The diluent is likely to be a hydrocarbon such as kerosene or dodecane, and a variety of extractants can be used. The extractant, as well as the diluent, should be essentially insoluble in the aqueous phase. At least three extractants have been tested for removing acetic acid from aqueous phase, trioctylphosphine oxide (TOPO), tri-n-octylamine (TnOA), and tributylphosphate (TBP). The diluent only case was also considered.

The distribution coefficient using TBP is of particular interest for this investigation because TBP is already used as a solvent during the UREX, NPEX, and TRUEX segments of the UREX+ process. This makes it a leading candidate for use as an extractant with an appropriate organic diluent. TBP is a highly polar compound with its phosphoryl group acting as a Lewis base. This allows TBP to create an acid-base complex with acetic acid and gives a high equilibrium distribution coefficient. [20] The system used in the UREX+ process is a 30% TBP-dodecane organic solvent with acetic acid-nitric acid-water. Data has already been measured for 30% TBP-dodecane in a 1:1 organic to aqueous ratio with acetic acid-water. This data is shown in Figure 2-5 which shows as the initial concentration of the acid increases, the distribution coefficient decreases. [21] When a strong mineral acid is added to an acetic acid-water-TBP system, like nitric acid in this case, the acetic acid may be protonated and may be in an ionic state that will be difficult to extract to the organic stream. [20]

Much like TBP, tri-n-octyl amine (TnOA) will also have the same protonation result with the addition of a strong mineral acid to an acetic acid-water mixture. The distribution coefficient may also decrease because of competition of the strong mineral acid for TnOA since it has a higher affinity for the TnOA than its weaker acetic acid counterpart.
Figure 2-5. $K_D$ as a function of Acetic Acid Concentration using 30% TBP-Dodecane Solvent with an Organic to Aqueous Ratio of 1. [21]
Trioctylphosphine Oxide (TOPO) can be used in the extraction of acetic acid. TOPO’s ability to extract acetic acid at various concentrations is shown in Figure 2-6. TOPO has been proposed as a possible extractant to be used in nuclear processes, however, the UREX+ processes do not include this solvent. Also, TOPO is a very expensive extractant when compared to TBP or TnOA. Therefore, TOPO will be used only if these other extractants prove ineffective.

Another option that was considered was the diluent-only case. That is, the use of the diluent used throughout the fuel process system without the use of an extractant. Although something of a long-shot, this option can be evaluated experimentally very quickly. If one can use the same diluent as elsewhere in the fuel processing system, there would be minimal risk of undesirable effects from entrainment of diluent through the nitric acid product into other process steps. Also the diluent would not be likely to extract any metal ions (fission products, actinides, etc.), so the acetic acid should be relatively free of radioactivity. The principal path for radioactivity to reach the acetic acid probably would be via entrainment. Although, Table 2-3 shows that Chevron Solvent 25 does not appear to extract acetic acid alone, it possibly will extract some additional acetic acid in highly acidic solutions where a substantial portion of the acetic acid will not be ionized. There is also the rather remote possibility that other diluents such as dodecane will give somewhat higher distribution coefficients. However, the diluent-only option will be attractive only if the distribution coefficient for dodecane or a similar satisfactory diluent gives much higher distribution coefficients than that reported for Chevron Solvent 25. There is no hard limit for the value of the distribution coefficient that would be necessary for the diluent-only option to be viable, but we would like for the distribution coefficient to be 0.1 or larger. Smaller distribution coefficients require increasingly larger solvent flow rates and make operation of
Figure 2-6. $K_D$ as a function of Acetic Acid wt\% using TOPO (22 wt\%) in Chevron Solvent

25. [17]
some liquid-liquid contactors difficult. Even if extraction could be practical with diluent-only, it
will also be necessary to strip the acetic acid. The preferential approach would be to strip with
water alone since the pH of the strip could be close to neutral, with hydrogen ion concentrations
approaching values as low as $10^{-7}$ molar. However, if one wanted to improve the strip and/or
concentrate the acetate, a slightly alkaline strip could be used. The best option for solvent
extraction would be to use an immiscible solvent. If the diluent only case can yield sufficient
extraction, it would be the most attractive approach. If not, the addition of TBP to any diluent
would be second choice. The use of a TBP-dodecane system would be most favorable for this
choice because of its expected use in UREX+ processes. For any choice, the stripping of the
acetic acid once it has been extracted into the organic will be needed.

3.6. Destruction

This study assumed that there are limitations on the nature of reagents that can be added
to the UREX+ process. So, there are limitations on how the acetic acid in the raffinate can be
destroyed. Some methods thought to be potentially acceptable are Supercritical Water Oxidation,
Wet-Air Oxidation, using a Corona Discharge Reactor, and using Hydrogen Peroxide. Other
oxidation methods require adding a salt or other reagent that leaves a residue in the solution, and
those residues may complicate downstream process steps and hinder reuse of the nitric acid,
and/or could increase the amount of mass in the waste streams.

Using Supercritical Water Oxidation, under high temperature and pressure, the water
molecule will become a non-polar solvent. This makes it a very good environment for oxidizing
organic compounds. The process requires oxygen or hydrogen peroxide at temperatures higher
than 647.3K and pressures higher than 22.12 MPa to maintain supercritical conditions. Either of
these two oxidizing agents can completely breakdown the acetic acid into carbon dioxide and water. This process occurs in four main steps: (1) raising the pressure of the oxidizing agents, (2) the reaction, (3) separating the salt, and (4) depressurization and heat recovery. [22] While this method is expected to efficiently destroy acetic acid, the required high temperature and pressure conditions seem too extreme for a unit operation processing radioactive materials as part of the UREX+ process.

Consideration of wet-air oxidation to destroy acetic acid results in similar concerns as supercritical oxidation. A high temperature and a high pressure—though not as high as supercritical conditions—are required. This is so that the oxygen molecules are sufficiently reactive to interact with small carboxylic acids like acetic acid. The small size of the acetic acid molecule is unfavorable for oxidation under normal conditions. Also wet air oxidation is less efficient than supercritical oxidation at destroying acetic acid. A favorable approach to oxidize small acetic acid molecules may be to add a metal catalyst. Even so, there is no guarantee for complete oxidation of acetic acid unless the temperature is raised to 200°C or higher. [23]

Hydrogen Peroxide is a strong oxidant, and a mixture of ozone and hydrogen peroxide makes even stronger hydroxyl radicals. Hydroxyl radicals create acetate radicals from acetic acid. These radicals will be very active and will oxidize effectively to carbon dioxide and water. However, high temperatures—unfavorable to the UREX+ process—and a low pH are needed for this process to be able to operate optimally. [24]

Another possible destruction method is a corona discharge reactor. With this method, oxygen radicals can be produced from three different electron energy levels. Using this process
with oxygen radicals and raising the pH will degrade the acetic acid to 75 ppm from 100 ppm at pH 1 with the largest effect at pH 14 where it is degraded down to 20 ppm. [25] A base would have to be added to raise the pH to 14. Obviously a higher pH would require adding sodium ions or other neutralizing reagent, affect downstream processing, and makes nitric acid reuse impractical. The higher pH is also undesirable because plutonium is reduced at higher pH’s and may inappropriately precipitate from solution. Therefore, the corona discharge reactor is a non-viable option for acetic acid destruction in the UREX+ process.

Upon considering each of these destruction technologies, three constraints are considered: (1) nitric acid not being destroyed, (2) no new chemicals being added, and (3) no extreme equipment specifications for radioactive removal. It is desirable to recover and recycle nitric acid, so technology which destroys nitric acid or does not selectively destroy acetic acid over nitric acid is rejected. Likewise, no new chemicals are to be added without careful consideration. Also, the size of the equipment and pressure requirements of supercritical and wet air oxidation tend to cause these options to be severely discounted. No appropriate destruction technology is identified.

4. RESULTS
Each of the technologies discussed have some potential for the UREX+ process, but some prove to be more favorable than others. The potential advantages and disadvantages for these technologies are summarized in Table 2-4. Crystallization is a simple process but requires a preliminary concentration step to create conditions where the acetic acid will crystallize from solution; this technology would be considered if one needed to remove acetic acid from the recovered and concentrated nitric acid solution prior to its recycle. Distillation does not seem to
<table>
<thead>
<tr>
<th>Technology</th>
<th>Pros</th>
<th>Cons</th>
</tr>
</thead>
</table>
| Crystallization         | • Used with distillation  
• Feasible  
• Favors acetic acid over nitric acid | • Requires concentration  
• Some mechanical operation needed |
| Distillation            | • Feasible  
• Used with Crystallization | • Removes water first which concentrates nitric acid  
• Multiple towers required to remove acetic acid |
| Adsorption/Ion Exchange | • Uncertain Feasibility                                             | • No highly attractive adsorbent found                              |
| Solvent Extraction      | • Similar to other UREX+ operations  
• Could use extractant and diluent already in process  
• Data exist on similar systems | • Restricted to solvents in UREX+  
• Strip step required  
• Possibly wash and/or solvent scrub step required |
| Destruction             | • Could possibly eliminate acetic acid  
• Creation of hydroxyl radicals will completely breakdown acetic acid | • Mainly need high temperature and pressure  
• High pH needed for corona discharge  
• Could also destroy nitric acid |
offer any advantage for acetic acid removal due to the dilute concentration used unless coupled with crystallization or another unit operation. Adsorption is a technically feasible option with similar concerns for additional process complexity as those for solvent extraction. Solvent extraction appears to be technically feasible, is a similar technology to that used elsewhere in the UREX+ system, and is a preferred method of removal for dilute acetic acid-water systems in industry; regeneration of the solvent and removal of the acetic acid adds complexity to the process however. No destruction technology for acetic acid in the UREX+ process was identified.

Overall, solvent extraction, probably using TBP extractant in dodecane (materials already used in UREX+), appears to be the most promising approach to acetic acid removal. Distillation was not considered superior to solvent extraction except for higher concentrations of acetic acid than those expected in UREX+. However, if acetic acid removal can be delayed until the end of the UREX+ process when the nitric acid may be concentrated for recycle, distillation may remain an option, though not necessarily a better option than solvent extraction. Distillation to remove acetic acid selectively from nitric acid would be more complex than distillation simply to concentrate the nitric acid. As noted earlier, this would be a ternary distillation system that is expected to involve an acetic acid-nitric acid azeotrope.

5. CONCLUSIONS

The primary method that seems the most feasible is solvent extraction, and the next efforts should focus on solvent extraction options. With no assurance that a practical solvent extraction technology can be found, other options should be considered if in the future solvent
extraction proves to be less attractive. These alternate options are distillation, a combined distillation and crystallization, or carbon or polymer-based adsorption.

By careful selection of a solvent, acetic acid may be preferentially extracted from the aqueous phase. With the selection of the most promising technologies, further investigation through literature research and experimentation will lead to the most appropriate technology for the UREX+ process. The studies will need to cover the behavior of selected metal ions (metals used to simulate the fission products and actinides in the UREX raffinate) as well as acetic acid.

6. ACKNOWLEDGEMENTS

This work was supported by the U.S. Department of Energy, NERI program, under DOE Contract No. DE-PS07-05ID14713 with Oak Ridge National Laboratory.
REFERENCES
REFERENCES


CHAPTER III: Extracting Acetic Acid from Acidic Solutions

Chapter III of this thesis is a slightly revised version of an article by the same name originally published in the journal *Separation Science and Technology* in 2008 by Jessica Mitchell, Jared Johnson, Robert M. Counce, Jack S. Watson, Barry B. Spencer, and G.D. Del Cul:


This article is reproduced with permission from the journal. This work is in total the effort of Jessica Anne Mitchell.
ABSTRACT

In the UREX+ process, acetic acid must be removed from the raffinate stream to avoid interference with the recovery and recycle of nitric acid solutions. Solvent extraction was selected to be the most promising approach to accomplish this cleanup. Acetic acid partitioning into pure diluents used in the UREX+ process were found to be too low for an effective separation. Of the solvents tested, the most promising solvents for the extraction of acetic acid were found to be TBP in dodecane and TBP in FS-13.

1. INTRODUCTION/BACKGROUND

The UREX+ process is a proposed new approach to separating the components of spent nuclear fuels. It has 5 steps all utilizing solvents to extract various components of the spent fuel. The current steps considered for the UREX+ process are shown in Figure 3-1. The first step is called the UREX step and uses tributylphosphate (TBP) with dodecane and acetohydroxamic acid to selectively extract uranium and technetium. The purpose of the acetohydroxamic acid is to prevent the extraction of plutonium in the UREX step. The next step uses polyethylene glycol (PEG) with phenyltrifluoromethyl sulfone, FS-13, and cobalt dicarbollide to extract both strontium and cesium. An alternative to CCD-PEG step is the FPEX step uses a BOB Calix solvent in order to extract Sr and Cs. The NPEX step is next and uses the same TBP-dodecane solvent system as UREX without the acetohydroxamic acid so that plutonium and neptunium are co-extracted with any remaining uranium. During the TRUEX segment of the process, americium, curium, the rare earth elements(lanthanides), and any remaining plutonium and neptunium are extracted by a solvent containing octyl(phenyl)-N, N-di-isobutyl carbamoylmethyl phosphine oxide (CMPO) and TBP with n-dodecane. The final step is the
Figure 3-1. UREX+ Flowsheet with Proposed Acetic Acid Removal Step
TALSPEAK step that extracts the lanthanides from the TRUEX product using diethylene triamine pentaacetic acid (DTPA) and a complexing agent (e.g. citric or lactic acid) to hold the actinides (e.g. americium and curium) in the aqueous solution.[1,2].

In the first step of the UREX+ process, acetohydroxamic acid is added to suppress extraction of plutonium when TBP-dodecane extracts uranium and technetium. Plutonium forms a complex with acetohydroxamic acid so that TBP is unable to extract it from aqueous solution. After uranium and technetium are extracted, this complexing agent hydrolyzes to form acetic acid and hydroxylamine. While the hydroxylamine will break down in strong acid solutions and/or at elevated temperatures, the acetic acid degradation product needs to be removed or destroyed so it will not interfere in the recycling of nitric acid [2]. The acetic acid removal is shown in Figure 3-1 occurring just after the UREX step. The optimum location of the acetic acid removal step is not established, but it should be used after the acetohydroxamic acid has decomposed. The extraction of acetic acid is also needed for many non-nuclear manufacturing processes, and the results from this study could also be useful to those processes.

1.1. Alternate Separation Methods Considered

Many technologies were examined as possible acetate removal and/or destruction methods, but some proved more favorable than others for the UREX+ process. Technologies such as membrane separation and ion exchange were eliminated early in the literature review. No membrane was found that was sufficiently selective to remove acetic acid effectively in a single pass, and multistage membrane operations did not appear attractive. Ion exchange was eliminated because no ion exchange material was identified with sufficient selectivity for acetate ions over higher concentrations of nitrate ions in a mixed stream. Crystallization is a simple
process but requires a preliminary concentration step to create conditions where the acetic acid could crystallize from solution [5-7]. Distillation does not seem to offer any advantage for acetic acid removal unless coupled with crystallization or another unit operation [6]. Adsorption was considered, but no adsorbent was found with sufficient selectivity for acetic acid [3,4]. Destruction methods could completely destroy the acetic acid. However, the extreme conditions required to destroy acetic acid are likely to destroy all or most of the nitric acid as well [8-10].

It was decided that solvent extraction would be the most promising method to pursue further. Solvent extraction appears to be technically feasible and is a similar technology to that used elsewhere in the UREX+ system. A few solvent mixtures (diluent and extractant) have been shown to remove acetic acid from nitric acid [11,12], however, these mixtures are also capable of extracting some of the radioactive components in spent fuel solutions and add unwanted complexity to the process being developed. In addition, there appeared to be further opportunities for considering alternative solvents. The focus of this study is to identify an agent capable of extracting acetic acid without co-extraction of other radioactive components, or with minimal extraction of radioactive components. Ideally, the solvent selected would be commonly used in the UREX+ process.

1.2. Solvent Selection

The three solvents/diluents discussed, dodecane, dichloroethane, and FS-13 were chosen because dodecane is already present in the UREX+ process and dichloroethane is comparable in some ways to phenyltrifluoromethyl sulfone, also known as FS-13 solvent, utilized in the PEG-CCD step [13]. Dodecane is used in the UREX, NPEX, and TRUEX steps of the process, and FS-13 solvent is used during the PEG/CCD step. It was decided that the most probable place to
extract the excess acetic acid was after the UREX step and before the PEG/CCD step (Figure 3-1). At this point, the acetohydroxamic acid is hydrolyzed into acetic acid and hydroxylamine nitrate (HAN). Since FS-13 was not readily available early in this study, dichloroethane was used initially as an analogue for FS-13 solvent [13]. Dichloroethane is not a suitable solvent for the UREX+ process due to its flammability. A limited quantity of FS-13 became available during the experimental trials and was also tested. These solvents were also run through the experiment with tributyl phosphate (TBP) at a 2.5M concentration.

2. EXPERIMENT

The distribution coefficients for a number of solvents and conditions were measured to determine the amount of acid transferred into the organic phase from solutions similar to those found in the UREX+ process. Solutions of various acidic concentrations were prepared ranging from 0.01M to 1M of both nitric and acetic acids to serve as the reference aqueous solutions for this study. Organic solvents (diluents) dichloroethane, dodecane, and FS-13 were the first solvents tested. Dodecane 99% was obtained from ACROS Chemicals, ACS grade dichloroethane was obtained from Fisher Scientific, and FS-13 was obtained from Marshallton Reasearch Laboratories. Using a 250 mL separatory funnel, 10 mL of aqueous and 10 mL of organic solvent were added. The funnel was hand-shaken for approximately one minute and settling was allowed for full separation of the layers. The aqueous layer was drawn off into a small beaker and analyzed using a Mettler-Toledo SevenEasy pH meter and a Brinkmann 765 Dosimat set on dose mode containing 1M caustic solution. Using the amount of caustic required to obtain the equivalence point of the aqueous solution, the concentration of acid in the aqueous phase was determined by equation 1.
\[ [AQ] = \frac{[Base] \times V_{Base}}{V_{Sample}} \]  

(1)

[Base] represents the standardized concentration of the solution used to titrate, \( V_{Base} \) is the amount of base needed to reach the equivalence point, \( V_{Sample} \) is the sample size, and \([AQ]\) is the calculated concentration of the aqueous phase after mixing with the organic phase. The amount of acid in the organic phase is then found by mass balance.

\[ [AQ]_{Original} \times V_{Original} - [AQ]_{Sample} = [ORG] \times V_{ORG} \]  

(2)

\([AQ]_{Original}\) represents the initial concentration of the aqueous phase when put into the separatory funnel. \( V_{Original} \) is the volume put into the separatory funnel. \([ORG]\) is the concentration of acid in the organic phase calculated by the difference of the initial aqueous acid concentration and aqueous concentration after equilibration, and \( V_{ORG} \) is the volume of organic initially in the separatory funnel. The distribution coefficient was then calculated using equation 3.

\[ K_D = \frac{[ORG]}{[AQ]} \]  

(3)

When using a mixture of nitric and acetic acids with equal volumes, the amount of caustic required to reach equivalence must be read from the titration plot with two equivalence points and calculated as shown in equations 4 and 5 and Figure 3-2.

\[ V_2 - V_1 = V_{Base\text{--Acetic}} \]  

(4)

\[ V_1 = V_{Base\text{--Nitric}} \]  

(5)
$V_2$ is the second equivalence point and $V_1$ is the first equivalence point. The calculations result in
the volume of base required to reach the end point for equal volume acetic and nitric acids,
respectively.

3. RESULTS AND DISCUSSION

3.1. Titration Curve Analysis

For the single acid case, the procedure is simple. The steepest point of the curve where the
concavity changes is the equivalence point reading (Figure 3-2). The volume of base required is
then simply read from the x-axis. Using this value, the above calculations can be completed.

For the mixed acid case, the procedure becomes slightly more complicated. The titration curve is
similar to that of a diprotic acid analysis with two equivalence points. In the case of nitric and
acetic acids, the first curve is completion of nitric acid neutralization while the difference
between the endpoints of the first curve and the second curve is the completion of acetic acid
neutralization (Figure 3-3) [14,15]. Using equations 4 and 5, the volume of base needed to
neutralize each acid can be found and then inserted into equations 1-3 to obtain a distribution
coefficient for each acid.

3.2. Acetic Acid Extraction from Water-Acetic Acid Solutions

Tests were run to determine the distribution coefficient for acetic acid between aqueous and
diluent phases (Table 3-1). The distribution coefficients found in this study for dodecane was
small, but generally comparable to those reported by Judd King using several diluents with acetic
acid (Table 3-2). The distribution for the other two solvents, dichloroethane and FS-13 were also
small. A plausible explanation of the significant negative numbers for FS-13 is that there may
Figure 3-2. Single Acid Titration Curves (Nitric Acid and Acetic Acid)
Figure 3-3. Mixed Acid Titration Curves (Both Nitric and Acetic Acid Together).
Table 3-1. Extraction of Acetic Acid in Experimental Organic Diluents.

<table>
<thead>
<tr>
<th>Acetic Acid Concentration</th>
<th>$K_D$</th>
<th>Standard Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Dodecane</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.01M</td>
<td>-0.00397</td>
<td>0.022258</td>
</tr>
<tr>
<td>0.05M</td>
<td>0.006039</td>
<td>0.003788</td>
</tr>
<tr>
<td>0.5M</td>
<td>0.050085</td>
<td>0.01119</td>
</tr>
<tr>
<td>1M</td>
<td>0.010973</td>
<td>0.034771</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.01M</td>
<td>0.041742</td>
<td>0.020909</td>
</tr>
<tr>
<td>0.05M</td>
<td>0.01898</td>
<td>0.008563</td>
</tr>
<tr>
<td>0.5M</td>
<td>0.03064</td>
<td>0.024639</td>
</tr>
<tr>
<td>1M</td>
<td>0.05004</td>
<td>0.01795</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.01M</td>
<td>-0.83036</td>
<td>0.00089</td>
</tr>
<tr>
<td>0.05M</td>
<td>-0.25364</td>
<td>0.2257</td>
</tr>
<tr>
<td>0.5M</td>
<td>-0.0696</td>
<td>0.04424</td>
</tr>
<tr>
<td>1M</td>
<td>-0.00995</td>
<td>0.023845</td>
</tr>
</tbody>
</table>
Table 3-2. Extraction of Acetic Acid in Pure Organic Diluents.

<table>
<thead>
<tr>
<th>Diluent</th>
<th>$K_D$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chevron Solvent 25</td>
<td>0.009</td>
<td>[3]</td>
</tr>
<tr>
<td>n-Hexanol</td>
<td>0.88</td>
<td>[3]</td>
</tr>
<tr>
<td>Nitrobenzene</td>
<td>0.06</td>
<td>[3]</td>
</tr>
<tr>
<td>Chloroform</td>
<td>0.028</td>
<td>[3]</td>
</tr>
<tr>
<td>n-Heptane</td>
<td>0.02</td>
<td>[3]</td>
</tr>
</tbody>
</table>
have been some transfer of an acidic contaminant from the organic phase to the aqueous phase.

3.3. Nitric Acid Extraction from Water-Nitric Acid Solutions

The next tests involved determining the distribution coefficient for nitric acid between aqueous and diluent phases. When contacting aqueous nitric acid with the three diluents tested, a low distribution coefficient was obtained similar to those measured with acetic acid solutions (Table 3-3). This was expected since nitric acid almost completely dissociates in water.

3.4. Nitric and Acetic Acid Extraction from Water-Acetic Acid-Nitric Acid Solutions

A two equivalence point titration curve was produced using both nitric and acetic acids in the aqueous layer. (Figure 3-3) The distribution coefficients of acetic acid and nitric acid separately both yield little extraction. When combined, the distribution coefficients of acetic and nitric acid are still very small (See Table 3-4). As shown in Table 3-4, n-dodecane extracts nitric acid at a higher ratio than acetic acid. With dichloroethane, acetic extracts more strongly than nitric acid. The negative extraction values probably mean the very small extent of extraction is within the experimental error. This case is represented by the larger negative values in the FS-13 results. In either case, all the distribution coefficients show that there is a need for another approach to the extraction of acetic acid.

3.5. 2.5M Tributyl Phosphate Mixed With Organic Diluents

The addition of tributyl phosphate (TBP) to the system can be used to enhance the extraction of either acid when using Chevron Solvent 25 [11]. Addition of tributyl phosphate to these diluents also improves the extraction of both acetic and nitric acids as shown in Table 3-5. Tests were made with aqueous solutions of 0.05M acetic acid only and 0.5M nitric acid only. Then an equal-volume mixture of 0.05M acetic acid and 0.5M nitric acid was tested. While the TBP in
Table 3-3. Extraction of Nitric Acid in Pure Organic Diluents.

<table>
<thead>
<tr>
<th>Nitric Acid Concentration</th>
<th>$K_D$</th>
<th>Standard Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Dodecane</td>
<td></td>
</tr>
<tr>
<td>0.01M</td>
<td>0.050017</td>
<td>0.022206</td>
</tr>
<tr>
<td>0.05M</td>
<td>0.061638</td>
<td>0.050059</td>
</tr>
<tr>
<td>0.5M</td>
<td>0.027958</td>
<td>0.00172</td>
</tr>
<tr>
<td>1M</td>
<td>-0.00474</td>
<td>0.009551</td>
</tr>
<tr>
<td></td>
<td>Dichloroethane</td>
<td></td>
</tr>
<tr>
<td>0.01M</td>
<td>0.020709</td>
<td>0.032938</td>
</tr>
<tr>
<td>0.05M</td>
<td>0.020515</td>
<td>0.016487</td>
</tr>
<tr>
<td>0.5M</td>
<td>-0.02579</td>
<td>0.030955</td>
</tr>
<tr>
<td>1M</td>
<td>0.015247</td>
<td>0.002282</td>
</tr>
<tr>
<td></td>
<td>FS-13</td>
<td></td>
</tr>
<tr>
<td>0.01M</td>
<td>-0.83136</td>
<td>0.00016</td>
</tr>
<tr>
<td>0.05M</td>
<td>-0.51616</td>
<td>0.021645</td>
</tr>
<tr>
<td>0.5M</td>
<td>-0.10366</td>
<td>0.018025</td>
</tr>
<tr>
<td>1M</td>
<td>-0.03877</td>
<td>0.048026</td>
</tr>
<tr>
<td>Ratio of Concentrations (Acetic:Nitric)</td>
<td>Nitric Acid</td>
<td>Acetic Acid</td>
</tr>
<tr>
<td>----------------------------------------</td>
<td>------------</td>
<td>------------</td>
</tr>
<tr>
<td></td>
<td>$K_D$</td>
<td>$K_D$</td>
</tr>
<tr>
<td></td>
<td>Standard</td>
<td>Standard</td>
</tr>
<tr>
<td></td>
<td>Deviation</td>
<td>Deviation</td>
</tr>
<tr>
<td>Dodecane</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.5:0.025</td>
<td>0.030</td>
<td>0.012</td>
</tr>
<tr>
<td>0.5:0.25</td>
<td>0.026</td>
<td>0.024</td>
</tr>
<tr>
<td>0.5:0.5</td>
<td>0.008</td>
<td>0.010</td>
</tr>
<tr>
<td>0.25:0.5</td>
<td>-0.003</td>
<td>0.001</td>
</tr>
<tr>
<td>0.025:0.5</td>
<td>-0.011</td>
<td>0.000</td>
</tr>
<tr>
<td>Dichloroethane</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.5:0.025</td>
<td>0.058</td>
<td>0.098</td>
</tr>
<tr>
<td>0.5:0.25</td>
<td>0.024</td>
<td>0.017</td>
</tr>
<tr>
<td>0.5:0.5</td>
<td>0.021</td>
<td>0.002</td>
</tr>
<tr>
<td>0.25:0.5</td>
<td>0.013</td>
<td>0.012</td>
</tr>
<tr>
<td>0.025:0.5</td>
<td>0.037</td>
<td>0.007</td>
</tr>
<tr>
<td>FS-13</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.5:0.025</td>
<td>-0.588</td>
<td>0.010</td>
</tr>
<tr>
<td>0.5:0.25</td>
<td>-0.200</td>
<td>0.079</td>
</tr>
<tr>
<td>0.5:0.5</td>
<td>-0.048</td>
<td>0.022</td>
</tr>
<tr>
<td>0.25:0.5</td>
<td>-0.065</td>
<td>0.024</td>
</tr>
<tr>
<td>0.025:0.5</td>
<td>0.060</td>
<td>0.010</td>
</tr>
<tr>
<td>Concentration of Acid</td>
<td>Nitric Acid</td>
<td>Acetic Acid</td>
</tr>
<tr>
<td>-----------------------</td>
<td>-------------</td>
<td>-------------</td>
</tr>
<tr>
<td></td>
<td>K</td>
<td>Standard Deviation</td>
</tr>
<tr>
<td>Dodecane</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.05M Acetic Acid</td>
<td>---</td>
<td>1.408</td>
</tr>
<tr>
<td>0.5M Nitric Acid</td>
<td>0.404</td>
<td>0.021</td>
</tr>
<tr>
<td>0.025M:0.25M Mixture</td>
<td>0.308</td>
<td>0.161</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Concentration of Acid</th>
<th>Nitric Acid</th>
<th>Acetic Acid</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>K</td>
<td>Standard Deviation</td>
</tr>
<tr>
<td>Dichloroethane</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.05M Acetic Acid</td>
<td>---</td>
<td>1.255</td>
</tr>
<tr>
<td>0.5M Nitric Acid</td>
<td>0.193</td>
<td>0.100</td>
</tr>
<tr>
<td>0.025M:0.25M Mixture</td>
<td>0.134</td>
<td>0.124</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Concentration of Acid</th>
<th>Nitric Acid</th>
<th>Acetic Acid</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>K</td>
<td>Standard Deviation</td>
</tr>
<tr>
<td>FS-13</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.05M Acetic Acid</td>
<td>---</td>
<td>0.530</td>
</tr>
<tr>
<td>0.5M Nitric Acid</td>
<td>0.259</td>
<td>0.063</td>
</tr>
<tr>
<td>0.025M:0.25M Mixture</td>
<td>0.133</td>
<td>1.083</td>
</tr>
</tbody>
</table>
dodecane has the largest distribution coefficient for acetic acid out of the three diluents, the solvent with dichloroethane has the largest separation factor. The separation factor is the ratio of acetic acid to nitric acid distribution coefficients in the mixtures. FS-13 also shows a high separation factor and might be suitable in the UREX+ process since, as noted earlier, dichloroethane is unsuitable. FS-13 also shows the highest jump between the distribution coefficients of the single acids and the mixture. This is favorable for the UREX+ process and will be explored in further research as a method to extract acetic acid from the waste stream.

4. CONCLUSIONS
The diluent results confirm the results by King and coworkers [3] that neither acetic acid nor nitric acid is extracted effectively by simple hydrocarbon solvents. All of the solvents and extractants used by King were partially soluble in water or able to extract salts, including radioactive compounds present in the UREX+ process. FS-13 is not soluble in water and is already used in one proposed step of the UREX+ process. The most promising solvents for the extraction of acetic acid are TBP in dodecane and TBP in FS-13. Each solvent system exhibits a distribution coefficient greater than one with a sufficiently large separation factor.

5. ACKNOWLEDGEMENTS
The authors are grateful to Dean Peterman, Joseph Birdwell, George Vandegrift, Catherine Mattus, and Matthäus Siebenhofer for their support and advice during the course of this work. This work was supported by the U.S. Department of Energy, NERI program, under DOE Contract No. DE-PS07-05ID14713 with Oak Ridge National Laboratory.
REFERENCES


Chapter IV of this thesis has been submitted as a journal article to Solvent Extraction and Ion Exchange in 2008 by Jessica Mitchell, Robert M. Counce, Jack S. Watson, Barry B. Spencer, and G.D. Del Cul titled *Placing the Acetic Acid Removal Step into the UREX+ Process*. It is awaiting review.
Abstract

In the UREX+ process, acetohydroxamic acid is used to suppress plutonium extraction in the first process step (known as the UREX step). However, acetohydroxamic acid hydrolyzes during the UREX+ process into acetic acid and hydroxyl amine nitrate. Solvent extraction was determined to be the most suitable method for removing acetic acid from the UREX+ process streams. Experimental data have shown sufficient extraction values for acetic acid into the solvent system of tributyl phosphate and dodecane and favorable separation factors between acetic acid and nitric acid in this solvent system. Using this experimental data, worst-case estimates of acetic acid concentration, and literature information on each of the steps of the UREX+ process, it was determined acetic acid will not cause a problem in the UREX+ process. A process flow sheet is proposed for the selective removal of acetic acid.

1. Introduction

Acetic acid is a degradation product of acetohydroxamic acid (AHA) that is used in the UREX process to suppress plutonium extraction. The acetic acid must eventually be removed from the UREX+ process stream to purge acetic acid and recycle nitric acid. Previous work done by these authors has shown that solvent extraction using a TBP-dodecane organic solvent system is suitable to remove this acid from an aqueous nitric acid stream. [1] Since similar solvent mixtures are used throughout the UREX+ process, some acetic acid is expected to be extracted as long as acetic acid is present in the aqueous stream. The purpose of this paper is to estimate any likely deleterious effects of acetic acid on the process steps of the UREX+ process and suggest the most appropriate location of the acetic acid removal step. Each process step
within the process will be examined, and data obtained in this activity on acetic acid extraction will be used to estimate the concentrations of acetic acid in each raffinate and extractant stream. This allows determination of the fate of the acetic acid if it is introduced to each process step via the aqueous stream and the potential for problems from acetic acid presence. This extraction provides insight into the potential that acetic acid extraction could affect the extraction of desired components in each step of the UREX+ process. The easiest placement of the acetic acid removal step would be at the end of the process steps just before the nitric acid is concentrated for recycle. That would be after the more valuable components have been removed. In that case, there would be fewer components present with the acetic acid removed to complicate its disposal. This paper investigates the affect that acetic acid has on the extraction of desired components in any of the UREX+ process steps. This work is necessary to determine if acetic acid requires earlier removal, before any affected process step.

2. Background

2.1. UREX+ Process

The UREX+ process used in this study is shown in figure 4-1. The UREX+ process has been under development for many years, and throughout those years, many flow sheets have developed. For this study, the flow sheet presented in figure 4-1 is being used, a slightly modified UREX+3 flow sheet to include two replacement possibilities—TALSPEAK in place of Cyanex-301 and FPEX as a possible alternative to CCD-PEG.

During the UREX step, uranium and technetium are extracted and purified using a TBP-dodecane solvent system. Plutonium extraction is suppressed in this step by adding AHA to the aqueous feed. AHA is hydrolyzed slowly under the acid conditions of the aqueous phase. CCD-PEG performance is not affected significantly by AHA. [2] However, if the second step is FPEX,
Figure 4-1. The UREX+ Process Used for this Study. [3]
all AHA must be hydrolyzed prior to the FPEX step. This hydrolysis can be achieved by heating the stream containing AHA to increase the hydrolysis rate. Both the FPEX and CCD-PEG steps remove cesium and strontium but use different solvent systems to achieve the same result. FPEX is said to be more efficient in removing both cesium and strontium simultaneously, thereby requiring fewer stages and less equipment. By the NPEX step, all AHA must be hydrolyzed to allow plutonium to be extracted. NPEX uses the same solvent system (TBP-dodecane) as UREX. TRUEX follows NPEX and recovers lanthanides and lanthanides rejecting the fission products using a CMPO-TBP-n-dodecane solvent. [2] The last step of the process is TALSPEAK, replacing Cyanex-301; it removes rare earth metals leaving the americium and curium and a nitric acid waste stream as product streams. In the most likely form of TALSPEAK, the organic stream from TRUEX will be stripped into aqueous, then treated with 0.8M di-(2-ethylhexy) phosphoric acid (HDEHP) dissolved in diisopropylbenzene (DIPB) that is capable of removing both actinides and lanthanides. This new organic stream will then be treated with diethylene triamine pentaacetic (DTPA) in aqueous solutions of either lactic or citric acid to remove actinides from the lanthanides. [4]

2.2. Acetic Acid Removal Step

Previous work by the authors was done to study the removal of acetic acid from a solution of acetic acid, nitric acid, and water—important components in the UREX+ process waste stream. [1] In an earlier study, solvent extraction was determined to be the best method to explore further. Tributyl phosphate-dodecane solvent was selected as a solvent system which provided both sufficient distribution coefficients and separation factors with an aqueous system of nitric acid at 0.5M and acetic acid at 0.05M. [1] In addition, more tests were run at various
TBP concentrations in dodecane as well as adjustments to the aqueous phase of 1M nitric acid with 0.1M acetic acid to prepare samples for analysis. A summary of all results for the selected solvent system of TBP-dodecane are shown in Table 4-1 and figure 4-2. This figure shows that distribution coefficients are directly related to the concentration of TBP in the solvent. The higher the concentration of the TBP, the higher the distribution coefficient and the higher the separation factor between acetic and nitric acids. Typically, TBP is a very viscous liquid non-ideal for a centrifugal contactor used for solvent extraction steps in the UREX+ process. However, dilute mixtures of TBP in dodecane can be used in the contactors since the presence of dodecane creates a much less viscous phase. A flow sheet of a proposed acetic acid removal step can be seen in figure 4-3.

2.3. Extraction Factors

Extraction factors are a way to compare distribution coefficients of two separate solutes to determine which is extracted more effectively. Since no testing has been done on UREX+ process demonstrations to determine the amount of acetic acid being extracted in each of the

<table>
<thead>
<tr>
<th>AQUEOUS SYSTEM</th>
<th>ORGANIC SYSTEM</th>
<th>KD Nitric Acid</th>
<th>KD Acetic Acid</th>
<th>Separation Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5M Nitric Acid 0.05M Acetic Acid Water</td>
<td>Dodecane</td>
<td>0.022</td>
<td>-0.021</td>
<td>N/A</td>
</tr>
<tr>
<td></td>
<td>1M TBP in dodecane</td>
<td>0.049</td>
<td>0.183</td>
<td>3.73</td>
</tr>
<tr>
<td></td>
<td>1.5M TBP-dodecane</td>
<td>0.098</td>
<td>0.878</td>
<td>8.96</td>
</tr>
<tr>
<td></td>
<td>2.5M TBP-dodecane</td>
<td>0.308</td>
<td>1.481</td>
<td>4.81</td>
</tr>
<tr>
<td></td>
<td>TBP</td>
<td>0.62</td>
<td>2.573</td>
<td>4.15</td>
</tr>
<tr>
<td>1M Nitric Acid 0.1M Acetic Acid Water</td>
<td>Dodecane</td>
<td>-0.003</td>
<td>-0.043</td>
<td>N/A</td>
</tr>
<tr>
<td></td>
<td>1M TBP-dodecane</td>
<td>0.078</td>
<td>0.342</td>
<td>4.38</td>
</tr>
<tr>
<td></td>
<td>1.5M TBP-dodecane</td>
<td>0.15</td>
<td>0.525</td>
<td>3.50</td>
</tr>
<tr>
<td></td>
<td>2.5M TBP-dodecane</td>
<td>0.299</td>
<td>1.038</td>
<td>3.47</td>
</tr>
<tr>
<td></td>
<td>TBP</td>
<td>0.66</td>
<td>1.751</td>
<td>2.65</td>
</tr>
</tbody>
</table>
Figure 4-2. Distribution Coefficients for Acetic Acid in Acetic Acid and Nitric Acid Mixtures vs. TBP Concentration.

\[ y = 0.6376x \]
\[ y = 0.4419x \]
\[ y = 0.397x \]

Figure 4-3. Acetic Acid Removal Flow sheet Step.
process steps, equation 1 will be used to compare the extraction of acetic acid in experimental tests including nitric acid and water to extraction of radioactive metals being extracted in each step of the UREX+ process.

\[ E = K_D \cdot \frac{\text{ORG}}{\text{AQ}} \]  

(1)

In this equation, \( K_D \) is the distribution coefficient, relating the equilibrium concentration (mol/L) of the extracted component (solute) in the organic phase to the concentration (mol/L) of the solute in the aqueous phase. The ORG/AQ is the organic to aqueous ratio of the volumetric flow rates. Therefore, the extraction factor (E) is a measure of moles of acid in the organic divided by moles of acid in the aqueous feed. The extraction factor multiplied by the concentration in the aqueous feed is simply the concentration of acetic acid in the organic phase. For example, in the NPEX step, plutonium and neptunium are the main components extracted. To evaluate the quantities of acetic acid extraction, a distribution coefficient will be needed, along with an organic to aqueous phase ratio. The product of the two values gives the extraction factor. If the organic to aqueous ratio to be used in UREX+ is not given in literature, an extraction factor of 1 will be assumed to calculate the organic to aqueous ratio. The actual values used are expected to be only slightly more than this, but not a large multiple of this. Thus an estimate of the extraction can be obtained, even if it may be a little low. Using the same organic to aqueous ratio for extraction of the metals, an extraction factor can be found for acetic acid using the distribution coefficients found for acetic acid at the same concentration of TBP. The extraction factor for acetic acid is the fraction of acid extracted if the organic coming from the first stage is in equilibrium with the acetic acid in the feed. Therefore, for these calculations, it is assumed a large number of stages are used (i.e. infinite) thus giving generous values as maximum amounts
that acetic acid will interfere with each step of the UREX+ process. Using the distribution coefficients found from figure 4-2 and the organic to aqueous ratios from the metal extraction calculations, these extraction factors will determine how much acetic acid is expected to be extracted during each metal extraction step and, thus, an estimate of whether acetic acid will extract sufficiently to cause interference in the extraction of these metals.

3. Acetic Acid Interference Estimates

Each step in the UREX+ process is examined closely to determine if any problems are expected to arise with acetic acid being present in that step. Since no data have been obtained for the acetic acid content in actual test runs of the UREX+ process, the authors rely on related work to estimate the acetic acid extraction and see if that amount of acetic acid is likely to consume (or bind to) a significant fraction of the extractant.

3.1. UREX

The two main factors in this step of the process to be examined are AHA concentration and uranium extraction. Acetohydroxamic acid is added in two places within the UREX step. First, it is added in the feed to suppress extraction of plutonium. Additional AHA is then added to a scrub step, so AHA from both additions will be present for the feed in the CCD-PEG step. AHA is not expected to hydrolyze significantly in this step since most will be bound to plutonium, however small amounts of hydrolyzation could occur. Acetohydroxamic acid forms acetic acid and hydroxylamine nitrate, and has the rate equation shown in equation 2.

\[
-k[AHA][H^+] = \frac{d[AHA]}{dt}
\]  

(2)
This equation has been tested at 25°C with various nitric acid concentrations (0 to 4M) and shows increased hydrolysis as the nitric acid concentration increases. The rate equation has a $k = 0.0015$ mol/L•min and an activation energy of 81.4 kJ/mol. [5]

The uranium extraction values versus the concentration of the feed are shown in figure 4-4. These values are for a system of 0.726M TBP-kerosene and 0.5M nitric acid with 0.126M uranium initially. Kerosene is very similar to dodecane and is assumed to behave similarly. If we use equation 1 and assume an extraction factor of 1.0 and a $K_D$ of 1.33, then the organic to aqueous feed ratio will be from 0.752. Using this same equation, the data for acetic acid distribution in 0.5M nitric acid, and the organic to aqueous feed ratios, the extraction factor for acetic acid from figure 4-2 is 0.241. That is, only approximately 24% of the small concentration of acetic acid in the UREX process stream will be removed. Since the acetic acid concentration is expected to be much smaller than the uranium concentration, the acetic acid is not likely to “tie-up” a significant fraction of the TBP and hinders the extraction of uranium. If the uranium is purified further by other steps, the role of acetic acid may be eliminated completely. Note also that much of the small quantity of acetic acid extracted during UREX will be washed out in the scrub step; so the impact of the traces of acetic acid should be even less than indicated above.

3.2. CCD-PEG (or FPEX)

Two options are available for the removal of cesium and strontium—CCD-PEG and FPEX. The CCD-PEG step uses a 0.08M chlorinated cobalt dicarbollide (CCD) to remove cesium, and 0.016M polyethylene glycol (PEG-400) to remove strontium. These extractants are in a phenyltrifluoromethyl sulfone (FS-13) diluent. Distribution coefficients for both Cs and Sr are extremely high and favorable for an aqueous system of nitric acid concentrations ranging
Figure 4-4. Uranium Distribution Coefficients vs. Initial Uranium Concentrations at different Nitric Acid Feed Concentrations. [6]
from 0.1M up to about 10M. However, the distribution coefficients are inversely proportional to
the nitric acid concentration. As nitric acid concentration increases, the distribution coefficient
decreases over the range of two orders of magnitude. The effect of AHA on this system is
explored in the paper by Law, et. al. [7] Since AHA is added to the feed and scrub step in the
UREX for the feed to the subsequent CCD-PEG step, this analysis is necessary to identify any
problems in the extraction of cesium or strontium. Both fresh AHA and decomposed AHA—a
mixture of AHA and hydrolysis components of acetic acid and hydroxyl amine nitrate—were
tested. In the case of fresh AHA, there was little to no difference in cesium or strontium
distribution coefficients. However, in the case of decomposed AHA, the cesium distribution
coefficients were unchanged while the strontium distribution coefficients decreased significantly.
Decomposed AHA could be AHA, acetic acid, or hydroxyl amine nitrate interfering with the
strontium extraction. During this study, it could not be determined which of the three was
interfering. [7] Therefore, acetic acid can possibly cause interference at this step if acetic acid is
responsible for the strontium extraction decrease. Thus, if little decomposition occurs before the
CCD-PEG step, there will be little effect on strontium extraction. On the other hand and more
likely, if HAN (and not acetic acid) is responsible for the decrease in strontium extraction, it may
be worthwhile to decompose the AHA all the way to acetic acid prior to the CCD-PEG step.
Determining the component responsible for reducing strontium extraction was beyond the scope
of this study. It will be assumed acetic acid does not interfere with this step in further analysis.

Another possibility for removal of cesium and strontium is the FPEX step. This step
involves a cooperative extraction of strontium and cesium using 4,4′,(5′)-di-(t-butyldicyclo-
hexano)-18-crown-6 (DtBuCH18C6), calix[4]arene-bis-(tert-octylbenzo-crown-6)
(BOBCalixC6), 1-(2,2,3,3-tetrafluoropropoxy)-3-(4-sec-butylphenoxy)-2-propanol (Cs-7SB modifier), and Isopar® L solvent. The DtBuCH18C6 extracts strontium while the BOBCalixC6 extracts cesium. The Cs-7SB modifier is the component which makes it possible to extract strontium and cesium in one step rather than two (SREX and CSSX) steps. The BOBCalixC6 has a very high affinity for cesium and, since acetic acid is a much smaller molecule, it is not expected to bind in cesium’s place. There was nothing found in literature to suggest acetic acid present in the FPEX process will cause any problems with the extraction of cesium or strontium. Therefore, it will be assumed there is no problem with acetic acid’s presence in FPEX. [3]

3.3. NPEX

The two components being extracted in this step are neptunium and plutonium. Both neptunium and plutonium distribution coefficients are higher than those for acetic acid in a TBP-dodecane solution. In 30 vol% TBP-dodecane with 1M nitric acid and a 1:1 organic to aqueous ratio, the $K_D$ for Np(VI) is given as 6.4 while Np(IV) is given as 1.0. At an organic to aqueous ratio of 1, the extraction factors for these two components are 6.4 and 1.0 respectively. [8] Since it is assumed that nitric and acetic acid has a 10:1 molar ratio, [9] the distribution coefficient for acetic acid at 0.1M in the presence of 1M nitric acid is 0.437 based on the correlation in figure 4-2. Using the organic to aqueous ratio of 1, the extraction factor of acetic acid is 0.437. Based on the previous discussion of extraction factors, this extraction factor means about 44% of acetic acid is removed from the aqueous phase into the organic stream. Since acetic acid binds with TBP in a 1:1 ratio [10], it will only use 4% of the TBP in the stream. This is not expected to affect the neptunium or plutonium extraction more than slightly.

In several papers [11] [12] [13], the concentration of Pu used in various fuel cycle experiments ranges from 0.02 g/L to 34 g/L. The distribution coefficient most recently obtained
is from a 2007 flow sheet test. The NPEX step was simulated with a distribution coefficient of 6.5 for Np and approximately 11 for Pu. [14] Since distribution coefficients depend highly on the nitric acid concentration, it can be assumed that the nitric acid concentration is near the same as for the above experiments ran with Neptunium at 1M nitric acid. With this assumption, acetic acid distribution coefficients can also be compared to the Pu distribution coefficient. Using the same O/A ratio as used for neptunium, 1, the Pu extraction factor is 11. Using this same O/A ratio for acetic acid, the extraction factor for acetic acid is 0.4367. This means 44% of acetic acid present at this point of the process will be extracted. The amount of TBP used by acetic acid is estimated to be 4% of TBP. Even though this small amount of TBP could be used by acetic acid, acetic acid is not expected to cause a substantiating effect on plutonium extraction.

3.4. TRUEX

The purpose of this step is to remove essentially all transuranic elements from the spent nuclear fuel. The main elements removed in this step are americium and curium. However, for these studies, only americium will be considered since curium is more easily extracted. These two components are removed by the TRUEX solvent made up of 0.2M CMPO-1.4M TBP-dodecane solution. We know that the TBP extracts acetic acid, but the effects of CMPO on the extraction were not known; so acetic acid distribution coefficient measurements were made with the TRUEX solvent. The model aqueous solution used consisted of 0.5M nitric acid and 0.05M acetic acid. Higher concentrations were not tested due to a possible third phase formation. The results of these tests are shown in Table 4-2. In the literature, americium extraction is tested in a system of 0.2M CMPO-1.4M TBP-Conoco (C12-C14). Data at 30°C and about 0.5M nitric acid give a distribution coefficient of 8.9 for americium. [15] Assuming an extraction factor of 1 and
Table 4-2. Acid Distribution in TRUEX Solvent.

<table>
<thead>
<tr>
<th>Acid</th>
<th>$K_D$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetic Acid 0.05M</td>
<td>0.952</td>
</tr>
<tr>
<td>Nitric Acid 0.5M</td>
<td>0.328</td>
</tr>
</tbody>
</table>

using equation 2 for calculation of the flow ratios, the organic to aqueous ratio can be determined. The O/A ratio is found to be 0.112. Utilizing this ratio and the distribution coefficient correlated for acetic acid using a comparable diluent dodecane from figure 4-2, the extraction factor for acetic acid is 0.107. This corresponds to 10.7% of acetic acid extracted and only a maximum of 0.38% of TBP consumed in acetic acid extraction reaction. With this small value, the extraction of americium should not be affected by acetic acid to any substantial amount.

3.5. TALSPEAK

TALSPEAK separates the lanthanides from the actinides that are extracted by the TRUEX process. The process is done in a two steps. The organic solvent system is made up of 0.8M di-(2-ethylhexyl) phosphoric acid (HDEHP) dissolved in diisopropylbenzene (DIPB). This extracts both lanthanides and actinides. The aqueous system of diethylene triamine pentaacetic acid mixed with either lactic or citric acid is added to strip the actinides from the organic, thereby sufficiently separating the actinides from the lanthanides. [4] The organic stream from the TRUEX step is treated to strip actinides and lanthanides into the aqueous phase. Then lanthanides and actinides are both extracted into the organic stream by the HDEHP solvent system. DTPA then extracts the actinides from the organic phase. This process can also be done by treating the aqueous stream (treated TRUEX organic stream) with the DTPA solution to hold
the actinides in the aqueous stream and then extracting lanthanides by HDEHP-DIPB. To
determine if acetic acid would interfere if it were to be at all present, acetic acid extraction tests
were done for the system of 0.8M HDEHP in DIPB and for 0.3M HDEHP-0.2M TBP-dodecane.
For both tests, no extraction of acetic acid or nitric acid occurred. Therefore, there is no expected
interference with acetic acid being in the streams during the TALSPEAK process if any were
present in this step.

4. Analysis/Discussion

A flow sheet is proposed from the results of the literature review. (figure 4-5) The
literature review and experimental data on acetic acid extraction in the process solvents suggests
no likely interference of acetic acid in the process. The flow sheet reflects this finding with the
acetic acid removal placed at the end of the process when nitric acid is concentrated for the
recycle.

While ideally one would like the option to place the acetic acid removal step anywhere in
the process with no interference on its part, there are complications with using TBP-dodecane
solvent for extracting acetic acid at some positions in the UREX+ process because the solvent
would extract metals (radioactivity) as well as acetic acid if the acetic acid removal step were
placed prior to the step in the UREX+ process where the metals are to be removed. For example,
placing the TBP-dodecane base acetic acid removal step just after the UREX step would result in
extraction of plutonium and neptunium as well as acetic acid. As shown in the literature review,
these metals are favored for extraction by TBP over acetic acid so they will be the first to be
removed. Therefore, placing this step before neptunium and plutonium extraction (NPEX) would
not be an efficient option. Placing the removal step after NPEX may be suitable because
Figure 4-5. Flowsheet Proposal.
americium and curium are mainly extracted by CMPO and not the TBP, other fission products will be extracted with the acetic acid. Placing the removal step between TRUEX and TALSPEAK would be a possible method since the aqueous stream is fission products plus acetic acid and nitric acid. The fission products were not extracted by CMPO-TBP-dodecane system, therefore, they will most likely not be affected by the TBP-dodecane solvent used to treat acetic acid. Therefore, the simplest model is the flow sheet proposed in figure 5 which shows the acetic acid removal step after all metal extraction steps have taken place to eliminate concern for extraction of metals in the same process.

5. Conclusion

After literature review of each process step and analysis of acetic acid extraction compared with radioactive metal extraction, it is determined that acetic acid should not pose a problem for any step of the UREX+ process. Thus, acetic acid is principally a problem for recycle of the nitric acid. Hypothetically, the acetic acid solvent extraction removal step can be placed anywhere in the process. However, there is cause for concern that metals will extract with the removal step if placed before these metals are removed. Therefore, due to simplicity, the authors feel the removal step should go after TRUEX where distillation may be a viable removal option in the combination of re-concentrating nitric acid for recycle.

6. Acknowledgements

This work was supported by the U.S. Department of Energy, NERI program, under DOE Contract No. DE-PS07-05ID14713 with Oak Ridge National Laboratory.
REFERENCES
REFERENCES


7. L. Nunez and G.F. Vandegrift. ANL-00/35. (2001)


11. V.E. Vereshchagin, and E.V. Renard., Atomnaya Energiya, 45, 45. (1978)

CHAPTER V: CONCLUSIONS
1. FUTURE WORK

1.1. Centrifugal Contactor Studies

Solvent extraction equilibrium data presented in this thesis will be further explored by Travis Russell. He will test the efficiencies of the solvent system selected in this thesis—1.5M TBP-dodecane—in a centrifugal contactor and create a quantitative flow sheet based on these results. [1]

1.2. Replacing Acetohydroxamic Acid

Savannah River National Laboratory is examining new ways to suppress plutonium extraction in the UREX step of the UREX+ process. This is a preventative approach to the removal of acetic acid. Instead of using acetohydroxamic acid which breaks down into acetic acid and hydroxyl amine nitrate, this study plans to find a new complexant/extractant that will accomplish the same goal, but break down into gaseous compounds eliminating the need for a removal step of the hydrolysis products. [2]

2. CONCLUSIONS

In conclusion, the acetic acid solvent extraction removal step should be placed at the end of the UREX+ process after TALSPEAK. Use of a TBP-dodecane solvent will lead to the best distribution coefficients and separation factors for acetic acid and should be further explored.
REFERENCES

1. Travis Russell, University of Tennessee, Personal Correspondence. 2008

2. Tracy Rudisill, Savannah River National Lab, Personal Correspondence, 2008.
VITA

Jessica Anne Mitchell was born in Knoxville, TN on September 8, 1983. She graduated from Bearden High School in Knoxville, TN in 2001. From there, she attended the University of Tennessee at Martin majoring in chemistry. She received her Bachelor’s of Science degree in Chemistry in May 2006. She then came back to Knoxville to continue school at the University of Tennessee-Knoxville, and began a Master’s of Science degree in Chemical Engineering in January 2007. She graduated in December 2008.