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Development of an integrated process simulation system model for spent fuel treatment facility (Sftf) design

Matthew S Hodges
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DEVELOPMENT OF AN INTEGRATED PROCESS SIMULATION SYSTEM
MODEL FOR SPENT FUEL TREATMENT FACILITY (SFTF) DESIGN

by

Matthew S. Hodges

Bachelor of Science in Engineering, Chemical Engineering, 2003
Arizona State University, Tempe, Arizona

A thesis submitted in partial fulfillment
of the requirements for the

Master of Science Degree in Mechanical Engineering
Department of Mechanical Engineering
Howard R. Hughes College of Engineering

Graduate College
University of Nevada, Las Vegas
August 2006

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Matthew S. Hodges

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Development of an Integrated Process Simulation System Model for

Spent Fuel Treatment Facility (SFTF) Design

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Master of Science in Mechanical Engineering

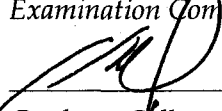

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ABSTRACT

Development of an Integrated Process Simulation System Model for Spent Fuel Treatment Facility Design (SFTF)

by

Matthew S. Hodges

Dr. Yitung Chen, Examination Committee Chair
Associate Professor of Department of Mechanical Engineering
University of Nevada, Las Vegas

Major issues concerning nuclear waste storage at Yucca Mountain are that of safety and long term disposal. Approximately one percent of the content of spent nuclear fuel is that which is responsible for nearly all the long-term associated health risks. The removal and transmutation of this content will render the toxicity of the remaining waste to that of natural uranium within a few hundred years. The research contained in this thesis details several simulations that are involved in the overall removal process. The first objective was to test the feasibility of the design of a distillation column that will separate an acid waste stream used in a recycle loop used throughout the spent fuel treatment facility. The second objective was to design an ASPEN PLUS model that will simulate the plutonium metal production process used in the spent nuclear fuel recycling processes.

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CHAPTER 1

INTRODUCTION AND BACKGROUND

The opening chapter of this thesis serves as an introduction to the reader regarding the background information, project objective and the content contained within the thesis.

1.1 Nuclear Power

Nuclear power accounts for nearly 16% of the global and 20% of the domestic electricity production. In the United States, energy production due to nuclear technology is second only to that produced by fossil fuel combustion. A distinct advantage over fossil fuel energy, “nuclear energy is the most "eco-efficient" of all energy sources because it produces the most electricity in relation to its minimal environmental impact. There are no significant adverse effects to water, land, habitat, species and air resources [1].” Furthermore, “Nuclear energy is the world's largest source of emission-free energy. Nuclear power plants produce no controlled air pollutants, such as sulfur and particulates, or greenhouse gases. The use of nuclear energy in place of other energy sources helps to keep the air clean, preserve the Earth's climate, avoid ground-level ozone formation and prevent acid rain [2].” In addition to being environmentally friendly, nuclear power is

considered a reliable energy source. It is “not subject to unreliable weather or climate conditions, unpredictable cost fluctuations, or dependence on foreign suppliers [3]”

However, despite the great number of benefits in using nuclear generated power, public opinion of the nuclear industry has remained low. The most common public perceived application of nuclear technology is of course, that of nuclear weapons development and use. This negative connotation coupled with that of several popular nuclear power plant disasters (Chernobyl, Three Mile Island) has led to a halt in production of new nuclear facilities. Recently, the U.S. has added another potential problem to the list – nuclear waste disposal.

1.2 Nuclear Waste Concerns

In 2003, the Department of Energy (DOE) launched the Advanced Fuel Cycle Initiative (AFCI) to address nuclear issues facing the United States. Amongst the major issues as identified by the AFCI were energy and waste management concerns. This thesis work deals primarily with the issue of nuclear waste management and secondarily with that of energy management.

There are several types of nuclear waste, each classified by their origin and toxicity. This thesis deals with spent nuclear fuel (SNF) wastes as well as transuranic (TRU) wastes. SNF waste is fuel that has been discharged from a nuclear reactor after being used for at least one cycle or a reactor operation. TRU wastes are those that contain alpha-bearing radionuclides with atomic numbers greater than uranium (greater than 92

protons). There are many proposed disposal methods for nuclear waste ranging from deep sea disposal to outer space disposal to transmutation and geological disposal. This thesis deals with research pertaining to geologic disposal as well as transmutation.

Currently, the U.S. plans to store its SNF and radioactive high level waste (HLW) in a deep geologic disposal repository located at Yucca Mountain, NV. Figure 1.1 depicts the current locations of all domestic SNF and HLW storage sites.

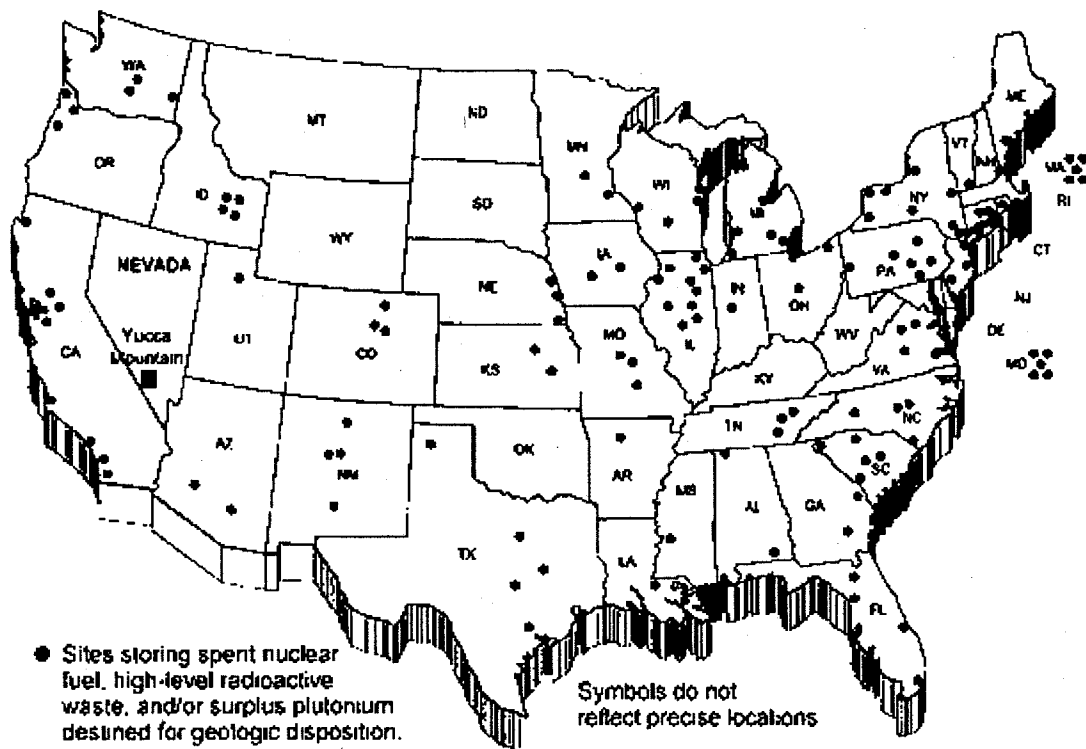


Figure 1.1 – Domestic SNF/HLW Storage Sites [4]

There are many questions regarding safety issues about the adverse health effects of long term storage of nuclear waste. Yucca Mountain has a finite capacity to which it can store

spent nuclear waste. The limiting factor for determining this capacity is the temperature rise of the rock caused by the decay of the SNF. The majority of this heat comes from the transuranic elements. If these elements are removed from the waste, the storage capacity of the mountain would increase five times before the temperature would again become a problem. Specifically, the removal of cesium-137 (^{137}Cs) and strontium-90 (^{90}Sr) from the waste streams would allow for a one hundred fold increase in storage capacity.

“Nearly all issues related to risks to future generations arising from long-term disposal of such spent nuclear fuel are attributable to approximately one percent of its content [5].” The chemical species responsible for the high toxicity can be broken down into two main groups: the transuranic elements - plutonium (Pu), neptunium (Np), americium (Am), and curium (Cm); and the long-lived isotope products from the fission process during power reaction, namely iodine-129 (I) and technetium-99 (Te). Upon successful separation and removal of the transuranic species from the spent fuel, the toxicity falls to that of naturally occurring uranium (U) ore within several hundred years.

“The removal of neptunium, technetium, and iodine render negligible the possibility of radioactive material penetration into the biosphere far in the future. Finally, removal of plutonium negates any incentive for future intrusion into repositories driven by overt or covert recovery of material for nuclear proliferation [6].”

1.3 Previous Work

The development of a process model to simulate the separation of nuclear waste is considered to be phase two of a two phase project. Phase one consisted of “the development of a systems engineering model and the refinement of the Argonne code AMUSE (Argonne Model for Universal Solvent Extraction). The detailed systems engineering model is the start of an integrated approach to the analysis of the materials separations associated with the AFCI Program. A second portion of the project is to streamline and improve an integral part of the overall systems model, which is the software package AMUSE. AMUSE analyzes the UREX process and other related solvent extraction processes and defines many of the process streams that are integral to the systems engineering model [7]” Phase one was completed by former UNLV mechanical engineering masters student Lijian Sun.

1.4 Project Objective

While the opening of Yucca Mountain has been marred in political red-tape, it has not prevented the U.S. government from funding research projects throughout the country’s national labs and universities. The University of Nevada, Las Vegas has entered into a partnership with the national laboratories through the Transmutation Research Program (TRP). The central theme and purpose of this program is to involve UNLV students in research on the economically and environmentally sound refinement of spent nuclear fuel. A long-term goal of the program is to address one of the nation's most pressing

technological and environmental problems [8].” This project is in accordance and in conjunction with Argonne National Laboratory (ANL). ANL wishes to simulate the Light Water Reactor (LWR) Spent Fuel Treatment Facility (SFTF) using the Argonne Model for Universal Solvent Extraction (AMUSE) code and ASPEN PLUS commercial process simulation software.

The overall project consists of three main components – a systems engineering model, AMUSE code and process engineering software. The purpose of such implementation is to interact with both chemical separation calculation (AMUSE) and process engineering software (ASPEN PLUS) to generate an optimized solution. As shown in Figure 1.2, ASPEN PLUS generated data can be passed to AMUSE, while AMUSE separation results can feed through the interface as input information for the ASPEN PLUS. An iterative processing is expected between and within modules.

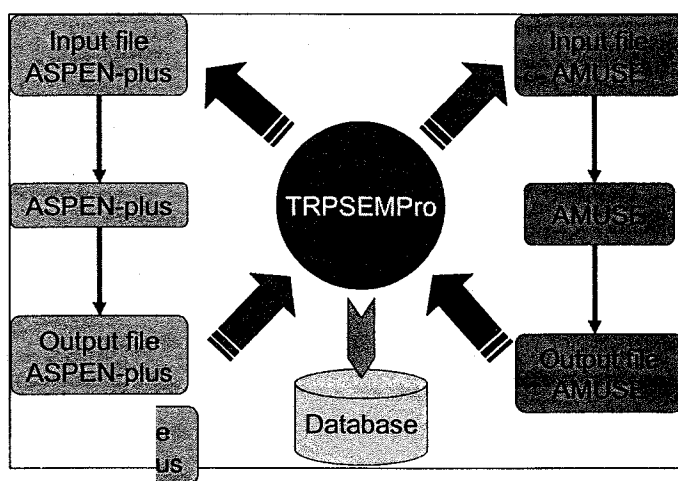


Figure 1.2 – Information Flow between ASPEN PLUS and AMUSE

The complete SFTF contains many operations and processes designed to separate the necessary chemical species from the spent fuel. This thesis deals with the simulation of two of the processes – an acid separations process and a plutonium metal production process. The overall chemical separation process envisioned by ANL researchers can be seen in Figure 1.3 (highlighted process are those that this project is concerned with).

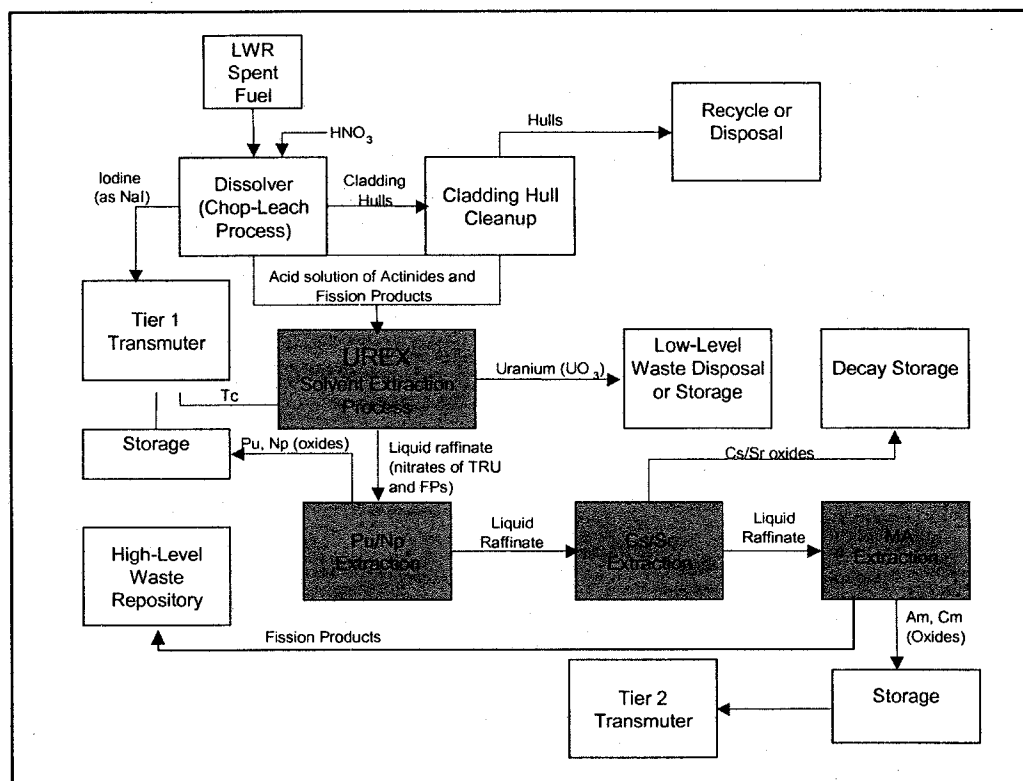


Figure 1.3 Overall Chemical Separations Process [5]

1.5 Thesis Overview

The first chapter served as the motivation for the project. The second chapter of the thesis discusses processes analysis and control. It will also introduce the software used in

the research. Chapter three will detail the chemical separations and processes used in the spent fuel treatment facilities. Chapter four will discuss the first simulation performed, that of the acid separations. Chapter five will discuss the second simulation - that of the plutonium metal production. Chapter six will wrap up the research and give conclusions, as well as give any recommendations for future research objectives.

CHAPTER 2

PROCESS CONTROL AND ANALYSIS

Process modeling is a tool by which engineers study the dynamic behavior of a system. Process engineers use mathematical models to properly design process equipment for a desired production rate. For example, it is of great importance for a chemical engineer to understand how an increase in flowrate temperature will affect the reaction kinetics (and thus product generation) in a reactor. Process analysis is the tool that engineers use in an attempt to answer such questions. In process analysis, the engineer will define the system to be that of a specific process or unit operation.

Scientifically accepted physical-chemical relationships are used as the cornerstone of the mathematical models that engineers use in process analysis. A general accounting balance (as seen in equation 2.1) is the first step of all process models.

$\text{accumulation} = \text{input} - \text{output} + \text{generation}$	2.1
--	-----

From this equation, the principles of mass and energy conservation can be applied.

When combined with the aforementioned conservation laws, equation 2.1 becomes equation 2.2 (conservation of mass) and 2.3 (conservation of energy) [21].

$\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial x_j}(\rho u_j) = s_m$	2.2
--	-----

Where:

t = time
 x_i = Cartesian coordinate
 u_j = velocity components
 p = pressure
 ρ = density
 s_m = mass source

$\frac{\partial \rho h}{\partial t} + \frac{\partial}{\partial x_j}(\rho h u_j + F_{h,j}) = \frac{\partial p}{\partial t} + u_j \frac{\partial p}{\partial x_j} + \tau_{ij} \frac{\partial u_i}{\partial x_j} + s_h$	2.3
--	-----

Where:

$h = \bar{c}_p T - c_p^0 T_0 + \sum Y_m H_m = h_t + \sum Y_m H_m$	2.4
---	-----

τ_{ij} = stress tensor components
 T = temperature
 Y_m = mass fraction of mixture constituent m
 H_m = heat of formation of constituent m
 c_p = mean constant – pressure specific heat at T
 c_p^0 = reference specific heat at temperature T_0
 $F_{h,j}$ = diffusional energy flux in direction x_j

s_h = energy source

s_i = momentum source components

h_t = thermal enthalpy

The above equations can be solved analytically or through use of a process simulator commercial application. For this thesis, the commercial simulator ASPEN PLUS was used in process analysis.

2.1 Process Analysis using ASPEN PLUS

ASPEN PLUS is a commercially available chemical process simulator developed by ASPEN Tech. It is used as a “process modeling tool for steady state simulation, design, performance monitoring, optimization and business planning for chemicals, specialty chemicals, petrochemicals and metallurgy industries [9].” In this project, ASPEN PLUS was used to simulate the various unit operation processes as requested by ANL in an attempt to simulate several operations in the SFTF. The calculations that have taken place in this simulation have been performed in ASPEN PLUS.

CHAPTER 3

CHEMICAL SEPARATIONS PROCESS

In a chemical reaction, unique atomic species/compounds come together to react with one another to produce a product with different chemical characteristics than that which originally reacted. A generic example of chemical reaction can taken to be as follows



This reaction is read as: component A plus component B yields component C. The species/compounds on the left side of the reaction arrow are known as reactants while those on the right side of the arrow are called products. There are a great number of different types of reactions. The study of chemistry is present in our everyday lives, yet is almost certainly overlooked by all. The plastic of our electronic devices, the rubber on our tires, the fuel that enables our cars to run...all are products of desired specified chemical reactions. Scientists and engineers harness and control these reactions to achieve a specific yield of product.

Unfortunately, many chemical reactions participate in side reactions or produce unwanted product. For example, take the following; Component D is the desired product of a chemical reaction between components A and B. In addition to D, undesirable component C is produced in the reaction. Similarly component B takes place in a side

reaction with component D to form component E. Factors such as conversion and kinetics often make the yield of desired product less than suitable. The product stream from the chemical reactor (called the effluent) may consist of several undesirable species. Because the chemical industry depends upon the purity of products, it is necessary to separate the unwanted species from those that are ultimately desired.

Chemical separations are a large part of the chemical industry. There are many ways to separate chemicals. Perhaps the simplest separation methods occur when chemicals exist in two phases of matter. A liquid and a solid may be separated simply by filtration or by centrifugation. A gas may be removed from a liquid by the presence of a vacuum overhead. It is possible to separate chemicals even if they exist in the same phase. Common methods of this type of separation are based upon the engineer's ability to exploit the different phase change temperatures of the chemicals in question. For example, a flash is used to separate chemicals that have a large difference in boiling points. Similarly, distillation is a process used when there exists a difference in boiling points that is not quite as large. Another method of separation, called crystallization, is one that exploits the difference in chemical freezing points.

3.1 – Spent Fuel Treatment Facility Processes

The spent fuel treatment facility has many individual processes that make up the overall separations processes. The overall process flowsheet can be seen in Figure 3.1 [10].

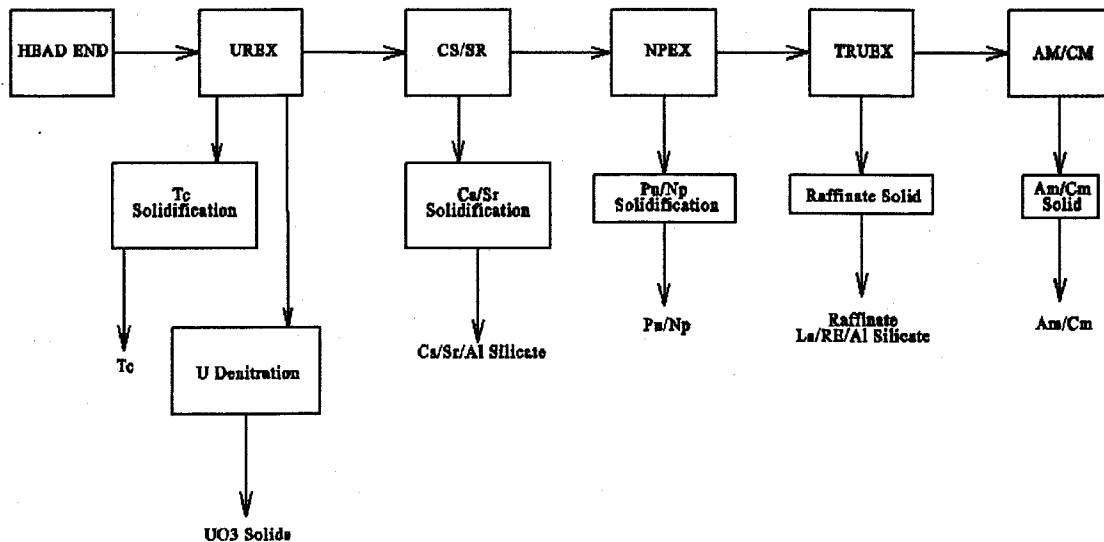


Figure 3.1 – Overall Process Flowsheet

The purpose of the head end process is to prepare the chemicals for separation elsewhere in the plant. Specifically, this is where the chopped fuel pellets are first received by the recycle plant. The fuel undergoes voloxidation (process used for the removal of volatile fission products from irradiated fuel) and then enters a dissolver/leach vessel. After the fuel passes through the dissolver, it is centrifuged and passed to the UREX process.

Each block in the overall process flowsheet represents a unique process that carries out an individual chemical separation. Each individual process block contains many operations that are responsible for the chemical separation. Figures 3.2 through 3.6 detail the individual process flowsheets that compose the overall process SFTF.

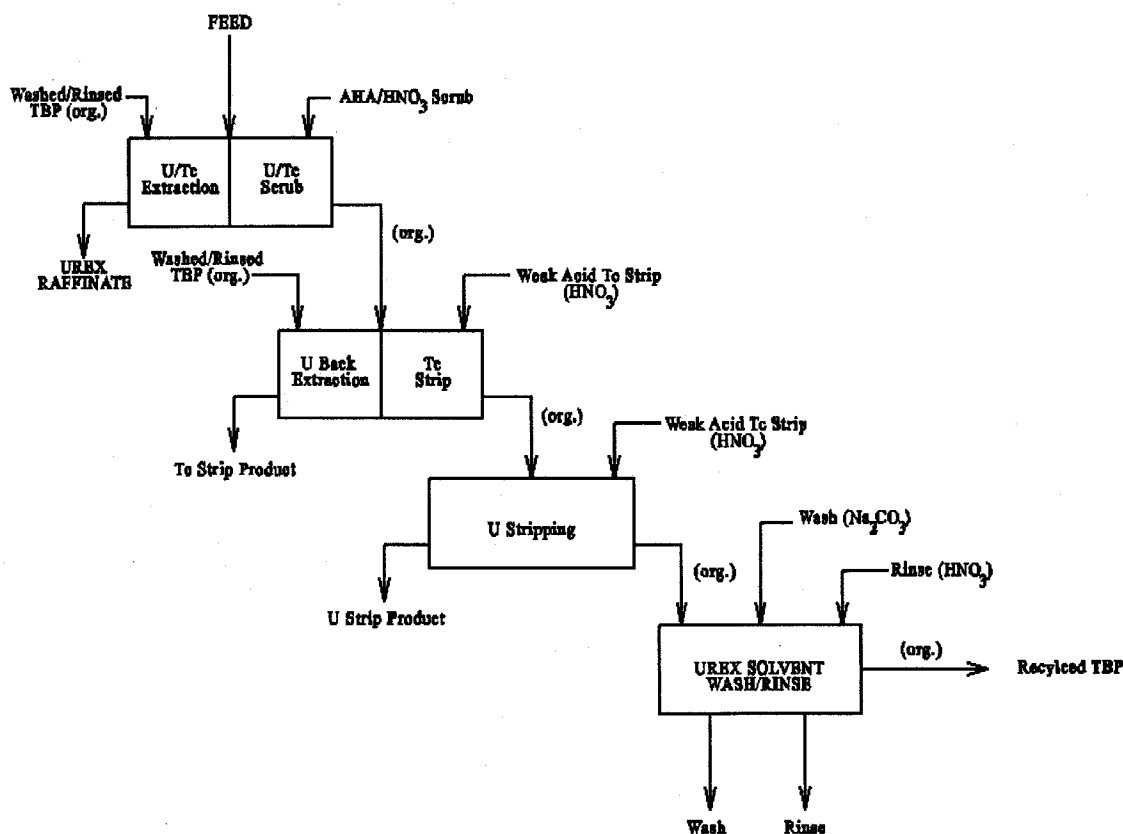


Figure 3.2 – UREX Process

The uranium extraction (UREX) process is the process by which Uranium and Technetium are removed from the spent fuel. Removing the U (which is the primary constituent by mass and volume of spent fuel) enables more waste to be able to be stored

at geologic repositories. UREX is often the first removal process in the overall scheme of spent fuel recycling. After the U and Tc have been removed from the spent fuel, the washed and rinsed effluent (Cs/Sr raffinate) enters the second separations operation as shown in Figure 3.3.

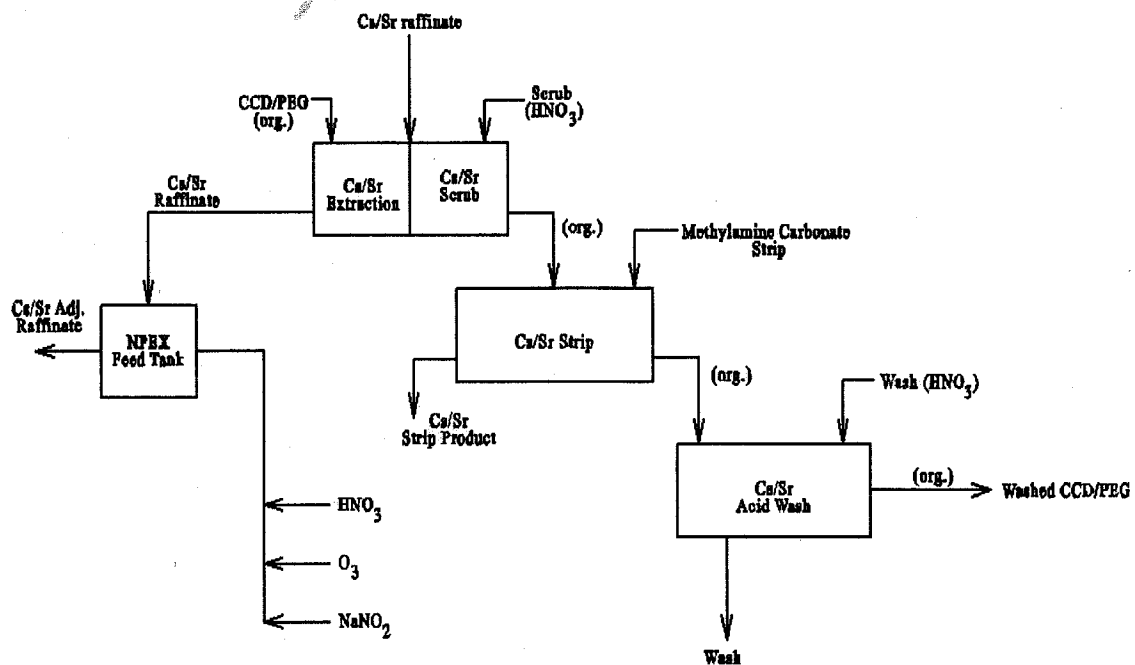


Figure 3.3 – Cs/Sr Removal Process

In the second stage of the chemical separation operation, cesium and strontium are removed from the liquid spent fuel stream. After the appropriate scrubbing and extraction, the adjusted raffinate is fed to the vitrification process elsewhere in the plant and the spent fuel backbone stream is washed and further cleansed before being fed to the third process as seen in Figure 3.4.

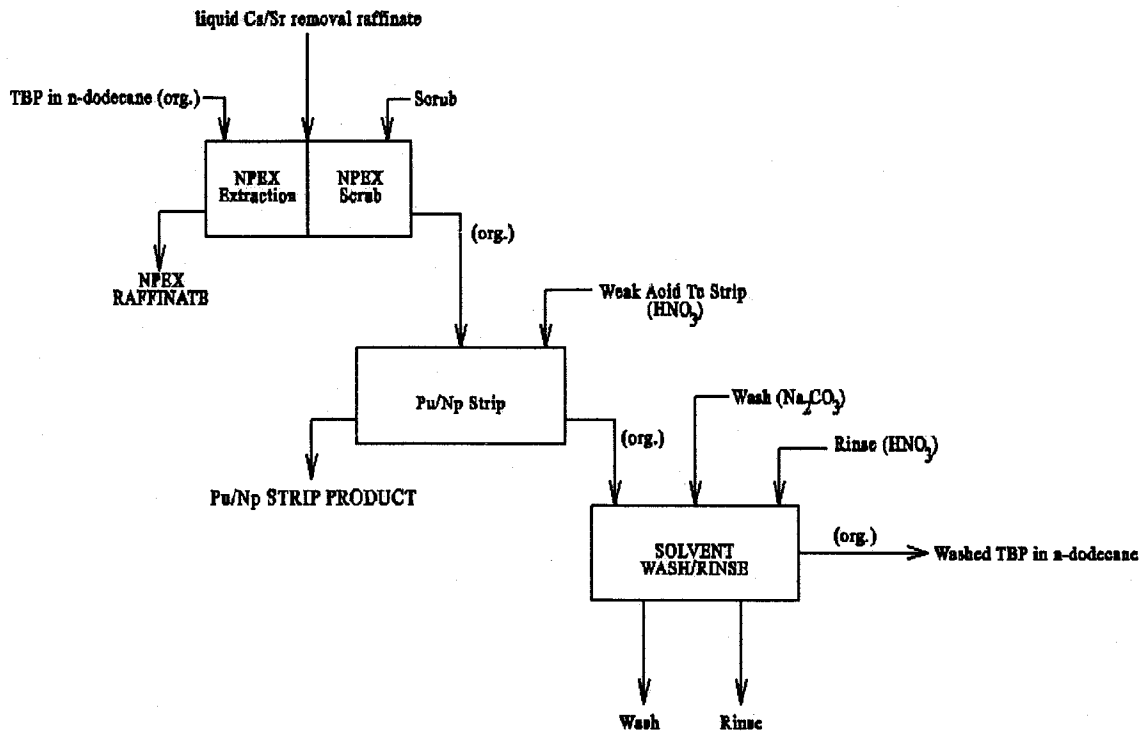


Figure 3.4 – NPEX process

The NPEX process shown in Figure 3.4 is used to recover the plutonium (Pu) and neptunium (Np) present in the spent fuel. After the Pu and Np have been removed from the fuel, the remaining liquid is considered HLW due to its primary constituency of the minor actinides, americium (Am) and curium (Cu). These actinides are highly radioactive and thus continue to generate a lot of heat from decay.

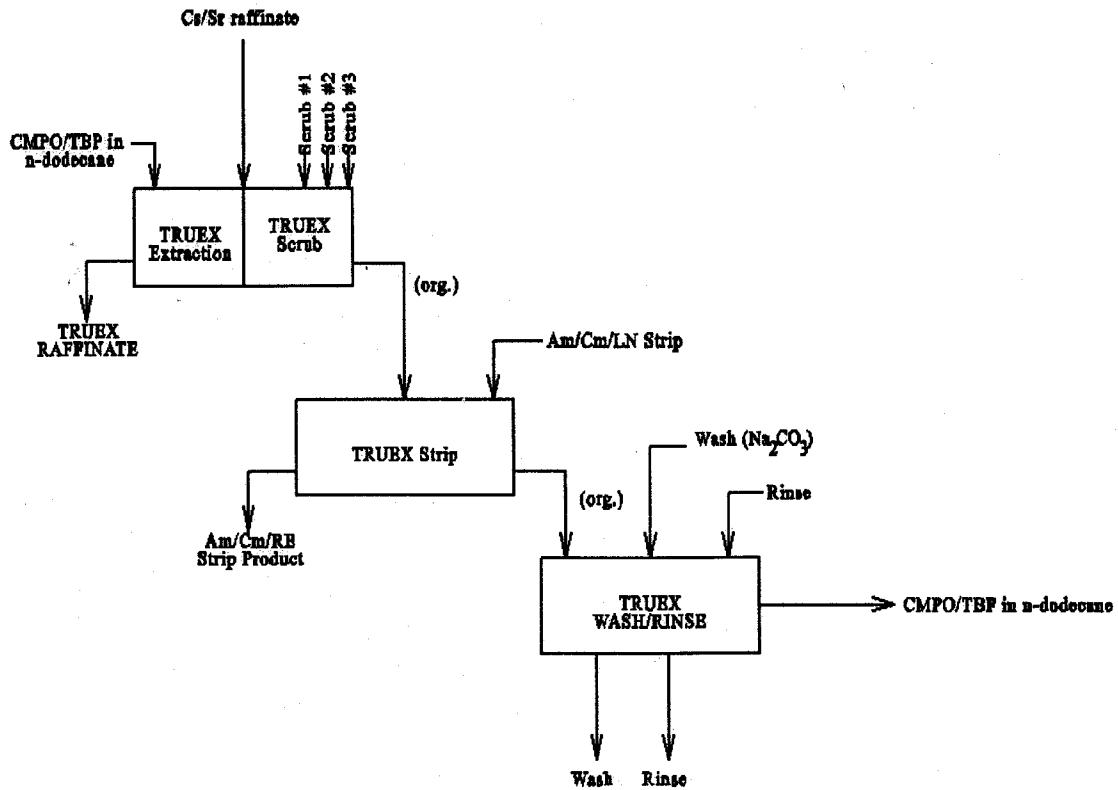


Figure 3.5 – TRUEX Process

The TRUEX process shown in Figure 3.5 is used to remove the transuranic elements (TRU elements) from the spent fuel. TRU elements include those with atomic numbers greater than that of 92 (uranium).

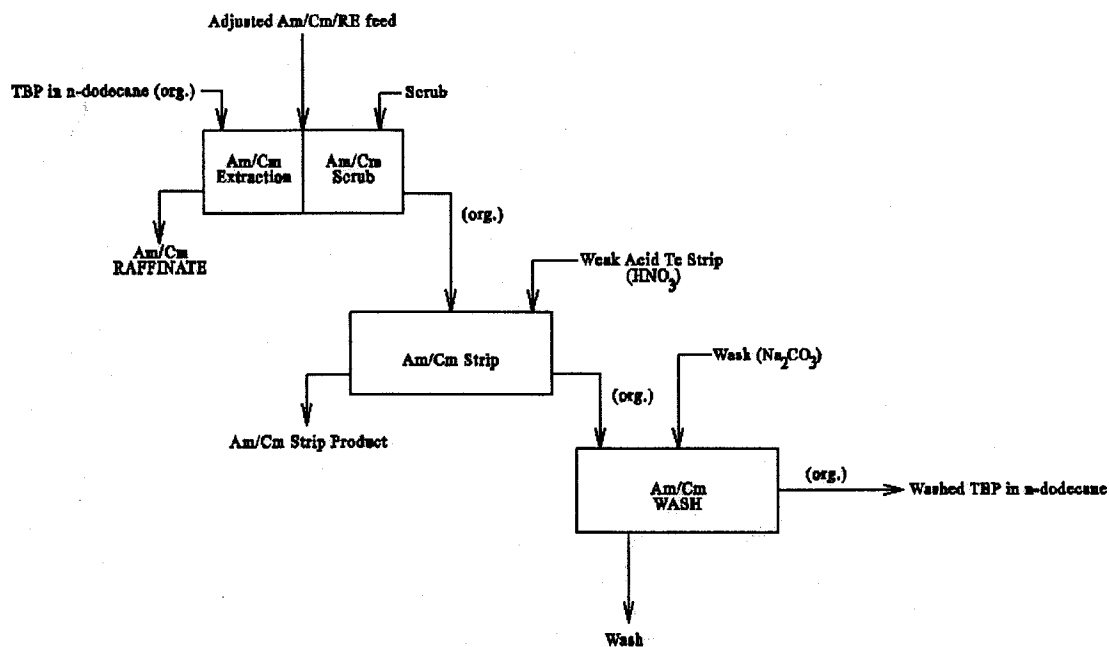


Figure 3.6 – Am/Cm removal

Figure 3.6 details the final separation, that of americium and curium from the TRUEX effluent. Product streams from this process include the americium and curium stripped product as well as the associated raffinate product from the scrub process. The raffinate streams from each of the individual processes are collected and fed to the vitrification processes elsewhere in the plant. The vitrification process takes the process raffinates from across the plant and solidifies them into a glass like product, suitable for transport and storage.

CHAPTER 4

ACID SEPARATION

The first research objective was that of the simulation of a process vital to the acid separation.

4.1 Nitric Acid Recycle

A key concept in the SFTF plant design is the recycle of nitric acid. The purpose of the nitric acid recycle system is to concentrate the spent nitric acid to a desired molarity that in turn can be recycled back to the process. The spent nitric acid streams from the many processes are collected and sent to a distillation column where it is separated from the impurities collected in the various separation processes. The feed to the separation column contains acetic acid and water as well as the desired nitric acid. Figure 4.1 depicts an example of a process using nitric acid (which is needed to be recycled throughout the overall spent fuel process).

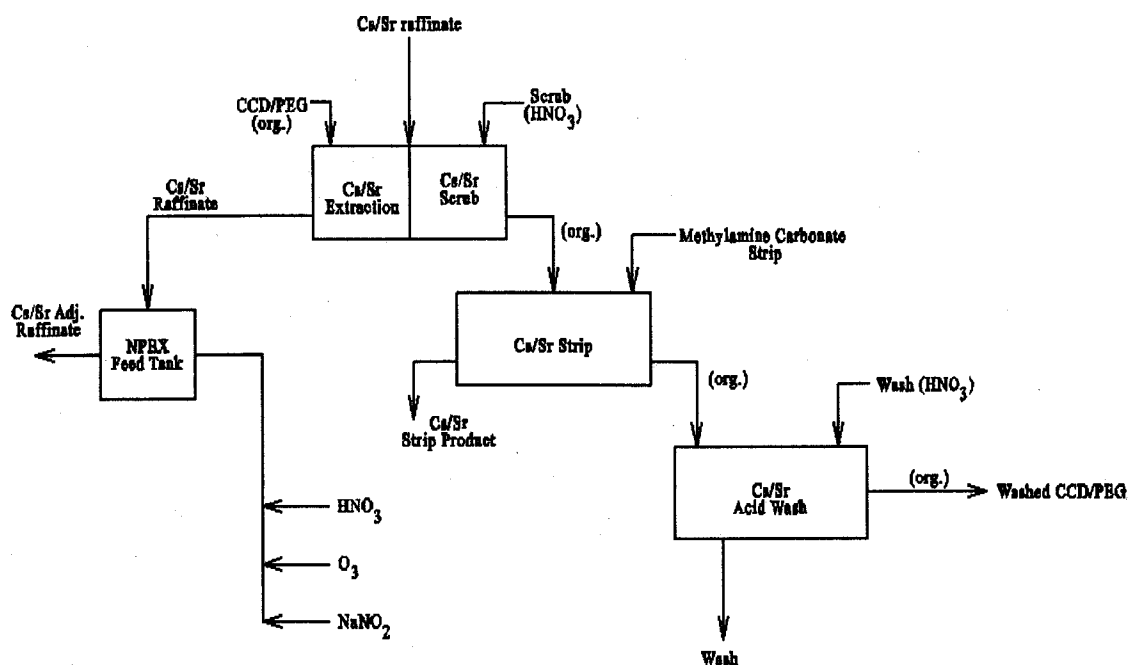


Figure 4.1 – Nitric acid example

4.2 Distillation

Distillation is a separations method that is used to separate chemicals based on relative volatilities. Distillation takes place in what is commonly called a distillation column. Solids cannot be separated by distillation, rather only substances in the vapor and liquid phases can be separated via this method.

4.2.1 Column General Principles

The distillation column is a cylindrical shell filled with a specified number of stages (also known as bubble trays), stacked one above another so as to bring the liquid and vapor phase in contact with one another. The feed enters the column and separates according to density. The vapor phase (having the lighter density) flows up the column,

while the liquid phase (greater density) runs down the column and trays. The contact between the liquid and vapor phases allow for heat and mass transfer. The liquid will flow down the column until it reaches the reboiler. The temperature of the column is highest in the reboiler and generally speaking, this is the temperature which the operator normally controls. The high temperature in the reboiler will cause one or more components to vaporize. The newly vaporized component(s) is/are sent up the column while the liquid component(s) exit the column in what is known as a 'bottoms' product stream. The vapor stream flows up the tower where it eventually meets a condenser and is cooled to a liquid. This stream is known as the 'tops' product stream. An operator set fraction of this tops stream (known as the reflux ratio) is recycled back to the tower so as to allow for further separation. The remainder of the condensed stream is taken off the tower and is known as the distillate. Due to the counter current flow of the liquid and vapor phases; the individual column stages approach thermal, pressure and compositional equilibrium. Species with low boiling points (called the light keys or LK) end up in the vapor phase while those with the high boiling points (heavy keys or HK) end up in the liquid phase. With this knowledge, the engineer usually operates the tower at a temperature large enough to vaporize one component and low enough to keep the remaining component in the liquid phase. Varying the number of stages, reflux ratio, and operating temperature will affect the resulting separation of the stream. There are a number of different ways to customize and operate a column so as to provide for the desired separation.

4.3 Research Purpose

The main purpose of the research on the acid recycle is twofold. ANL requested to test the feasibility of having a tower separate nitric acid, acetic acid and water, with nitric acid leaving as bottoms product. In the instance where this is not an acceptable design, ANL wishes to know under what conditions can a stream of 0.6M nitric acid be concentrated to 4.5M.

4.4 Simulation 1

The separation simulated for this thesis assumes a liquid feed with ternary composition. Nitric acid, water and acetic acid are all present in the stream. In addition, traces of the fission products will be present but are minute and are not included in the study. It was desired to simulate a separation of the feed and have the nitric acid leave the column as a bottoms product. While this is not the desired separation (the easiest separation would have nitric acid leaving in the tops stream), ASPEN PLUS will come up with a solution to the scenario posed. It is the purpose of this first simulation to accumulate results which show that this tower design will fail in its intended goal of sufficient removal of nitric acid. A molar flowrate of arbitrary number was chosen in an effort to test the hypothesis that having nitric acid be removed off the bottom tower is infeasible.

Based on the findings, a recommendation will be made as to the feasibility of nitric acid being taken off in the bottoms product. Because the process developed is not of

ideal simplicity, a more rigorous ASPEN PLUS distillation block must be used in the simulation. ASPEN PLUS has a variety of different distillation blocks for the user to choose from when performing a separation. Each block is used under different circumstances and has differing inputs. For example; petroleum processes will use the Petrofrac block and vacuum towers will use the SCFrac block. For this initial simulation, the Radfrac block will be used as it is recommended for a rigorous, 2 to 3 phase system within a single column. The ASPEN PLUS flowsheet used in the initial simulation can be seen in Figure 4.2.

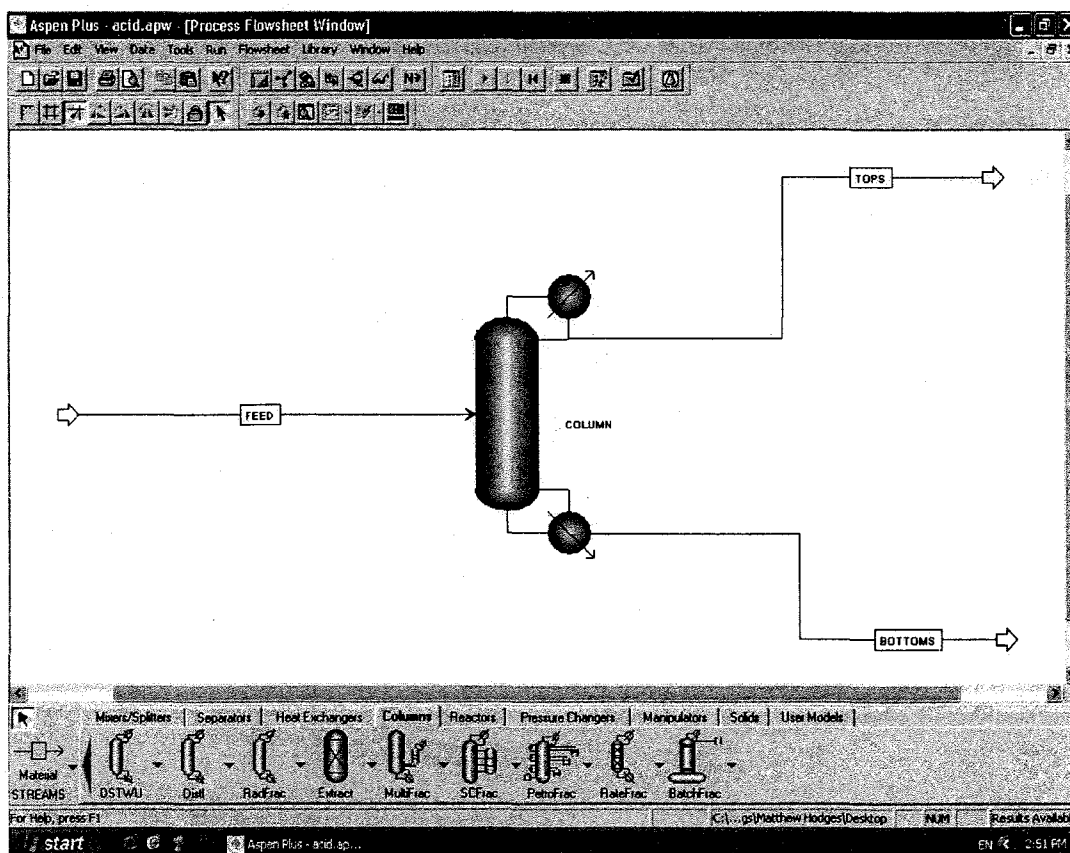


Figure 4.2 – ASPEN PLUS Process Flowsheet, Acid Separation

The feed stream conditions entering the distillation column can be seen in Table 4.1 while the distillation tower parameters can be seen in Table 4.2

Table 4.1 – Feed Stream Conditions, Simulation 1

Components	Flowrate (kmol/hr)	T (K)	P (atm)
Acetic Acid	10	298.15	1
Nitric Acid	100		
Water	10		

Table 4.2 – Column Operating Conditions, Simulation 1

Distillate Rate (kmol/hr)	Reflux Ratio	Number of Stages	Feed Stage
25	10	15	2

For this first simulation, it was desired to test the feasibility of adequately separating the feed stream using a single column. Furthermore, it was desired to study the effects of changing the operating parameters and observe the resulting change in behavior for the outlet mol flow rate (in an effort to achieve the desired separation of nitric acid in the bottoms). There were three parametric studies conducted for this distillation simulation. The first parametric study was to observe the effects of varying the reflux ratio on the outlet flowrates. The second study examined the effect of varying the number of stages on outlet flowrate. The third study was concerned with the effect of varying feed stage on product flowrates.

4.4.1 Parametric Study 1 – Varying Reflux Ratio

With the temperature, pressure, feed concentration, distillate rate and number of stages held constant (as described in section 4.4); it was desired to study how changing the reflux ratio in the column affected the product flowrates. Figure 4.3 depicts the results of the study for the bottoms product stream, nitric acid.

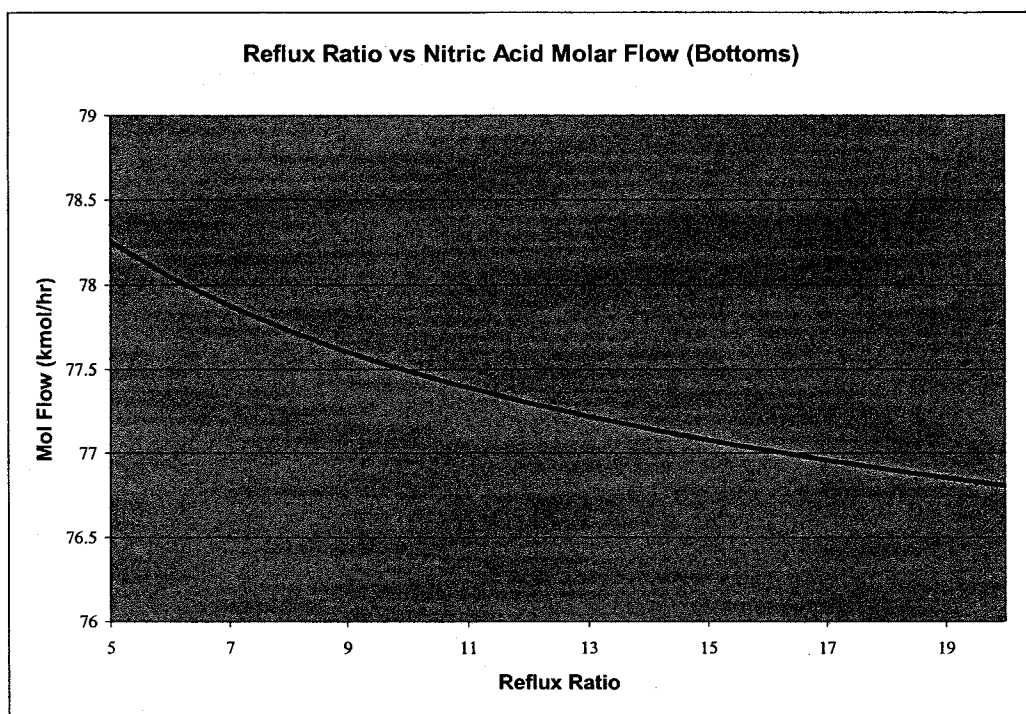


Figure 4.3 – Effects of Varying Reflux Ratio on Nitric Acid, Bottoms

In general, it can be seen that an increase in the reflux ratio gives an overall decrease of nitric acid flowrate in the bottoms stream (and thus an increase in flow in the tops stream as seen in Figure 4.4). Conversely, an increase in reflux ratio leads to a decrease in acetic acid and water flow in the tops and an increase in bottoms (as shown in Figures

4.5 and 4.6). This is explained simply by component boiling point and density. Reflux ratio is a molar ratio of the amount of distillate product (tops stream) that is recycled back into the tower. Reflux is used to further separate the desired distillate component from those undesired. The separation is increased due to the fact that the heavy components are denser than the light ones. As they are denser, they will flow down the tower while more of the vaporized light components are brought to the top of the tower. With that said, an increase in the reflux ratio allows for more of the light components to leave the tower in the tops stream and more of the heavy components to leave as bottoms product. Figures 4.3 through 4.6 reflect this understanding.

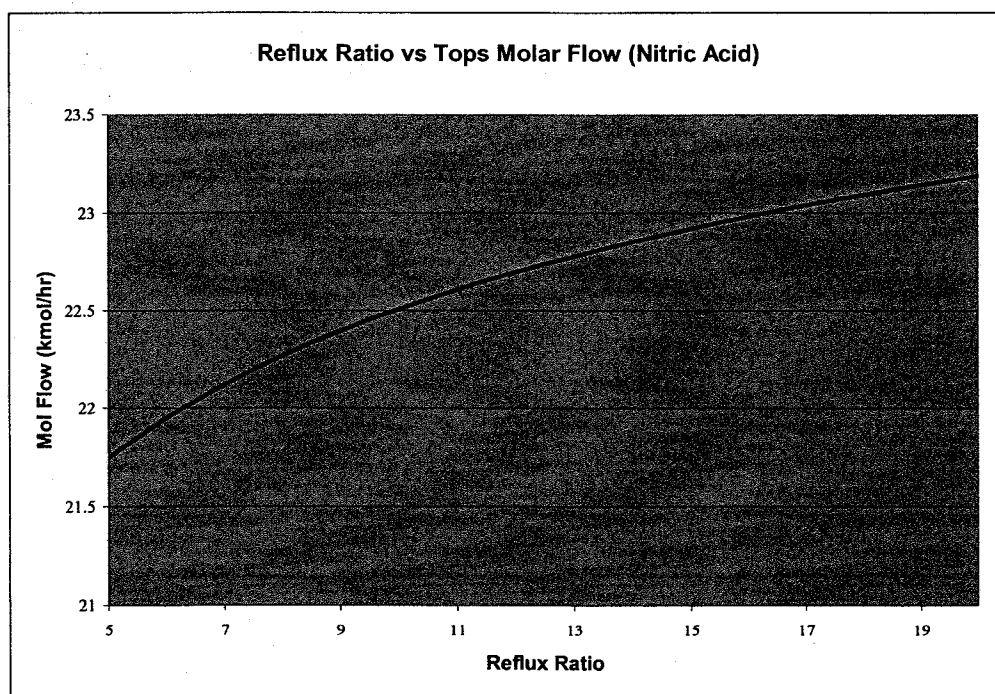


Figure 4.4 – Effects of Varying Reflux Ratio on Nitric Acid, Tops

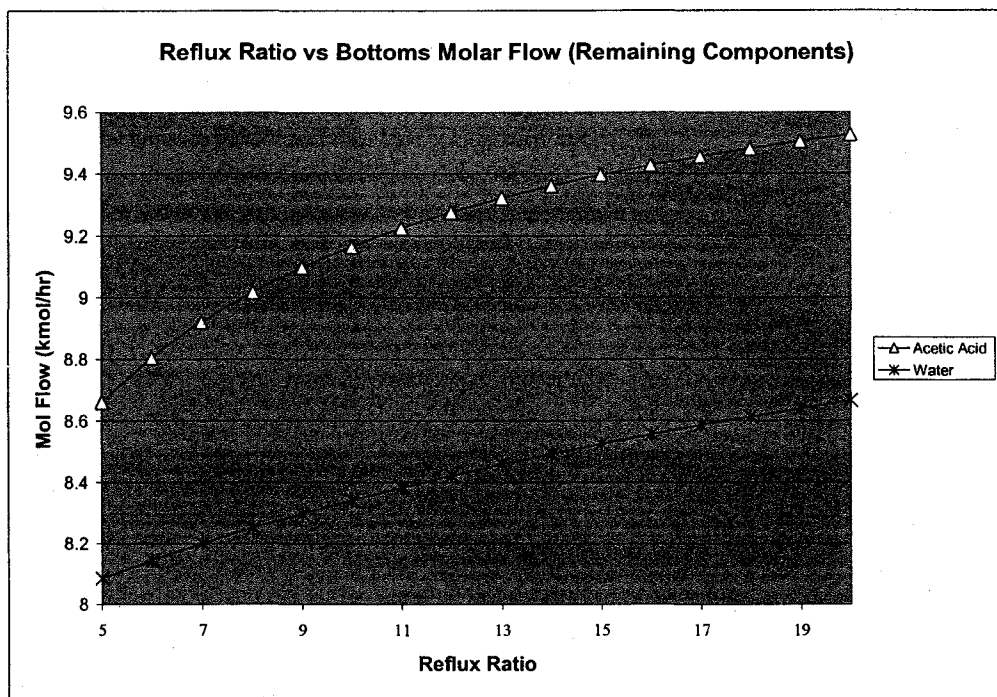


Figure 4.5 – Effects of Varying Reflux Ratio on Acetic Acid and Water, Bottoms

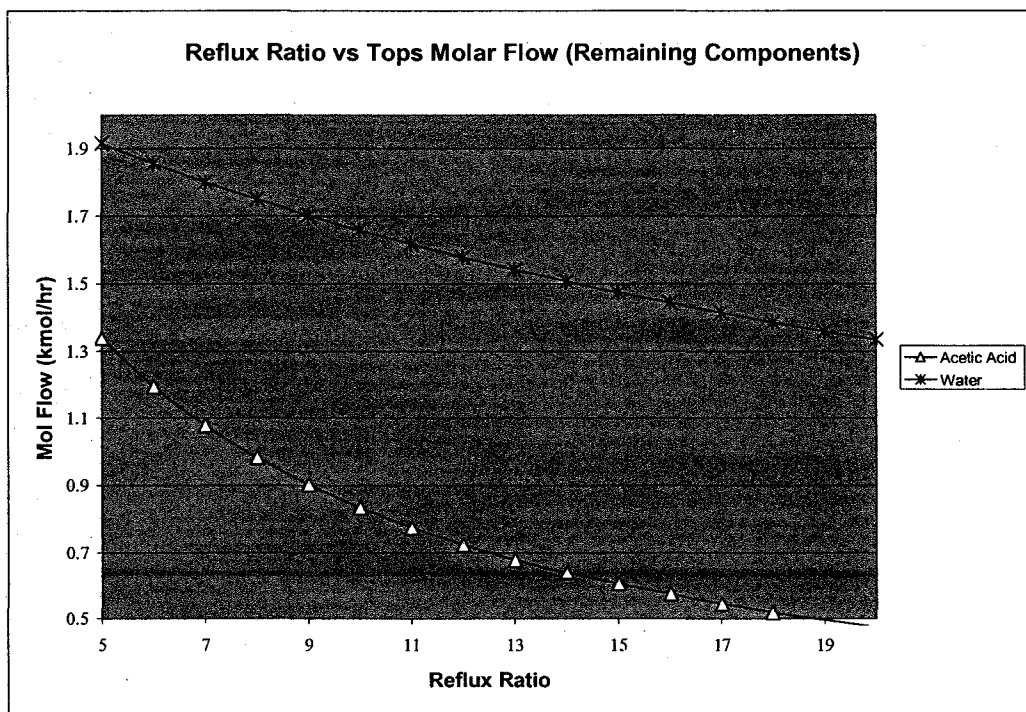


Figure 4.6 – Effects of Varying Reflux Ratio on Acetic Acid and Water, Tops

A quick glance at the results shows that for this simulation, it is best to run the tower at a low reflux ratio in an effort to have the majority of nitric acid come off the tower in the bottoms product. Table 4.3 gives the separation efficiency for this parametric study.

Table 4.3 – Separation Efficiency of Various Reflux Ratios

Reflux Ratio	Fraction of Feed Stream in Bottoms Stream			Fraction of Feed Stream in Bottoms Stream		
	Acetic Acid	Nitric Acid	Water	Acetic Acid	Nitric Acid	Water
5	0.8661	0.7825	0.8086	0.1339	0.2175	0.1914
6	0.8805	0.7805	0.8145	0.1195	0.2195	0.1855
7	0.8921	0.7788	0.8200	0.1079	0.2212	0.1800
8	0.9017	0.7773	0.8250	0.0983	0.2227	0.1750
9	0.9098	0.7760	0.8298	0.0902	0.2240	0.1702
10	0.9166	0.7749	0.8342	0.0834	0.2251	0.1658
11	0.9225	0.7739	0.8383	0.0775	0.2261	0.1617
12	0.9276	0.7730	0.8422	0.0724	0.2270	0.1578
13	0.9321	0.7722	0.8458	0.0679	0.2278	0.1542
14	0.9360	0.7715	0.8493	0.0640	0.2285	0.1507
15	0.9396	0.7708	0.8525	0.0604	0.2292	0.1475
16	0.9427	0.7702	0.8556	0.0573	0.2298	0.1444
17	0.9456	0.7696	0.8586	0.0544	0.2304	0.1414
18	0.9481	0.7691	0.8614	0.0519	0.2309	0.1386
19	0.9505	0.7686	0.8640	0.0495	0.2314	0.1360
20	0.9526	0.7681	0.8665	0.0474	0.2319	0.1335

4.4.2 Parametric Study 2 – Varying the Number of Stages

The second study was concerned with observing the effects on product flowrate caused by varying the number of the stages in the column. Again, the main concern is the flow of nitric acid in the bottoms stream. As with the study in 4.4.1, it is necessary to remove all of the nitric acid in the bottoms stream. Figure 4.7 shows the effects on nitric acid in the bottoms stream.

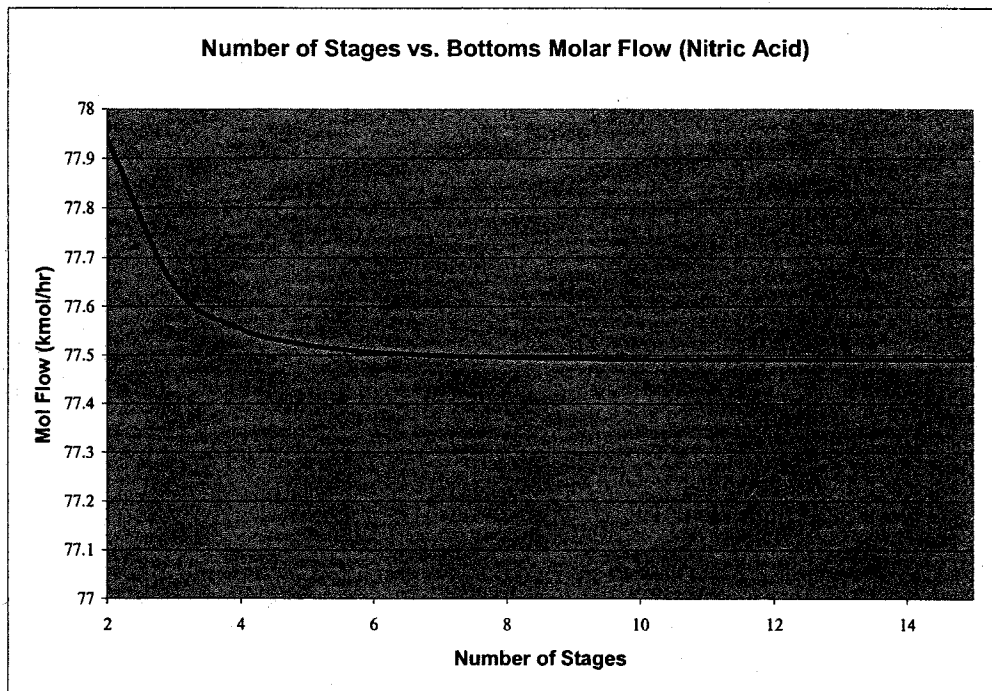


Figure 4.7 – Effects of Varying Stages on Nitric Acid, Bottoms

From this chart, it is easily enough seen that increasing the number of column trays decreases the molar flowrate of nitric acid in the bottoms stream. It can also be seen that once the number of stages reaches approximately 6, the flowrate can be considered constant. Figure 4.8 depicts the effects of varying stage number for both acetic acid and water in the bottom stream.

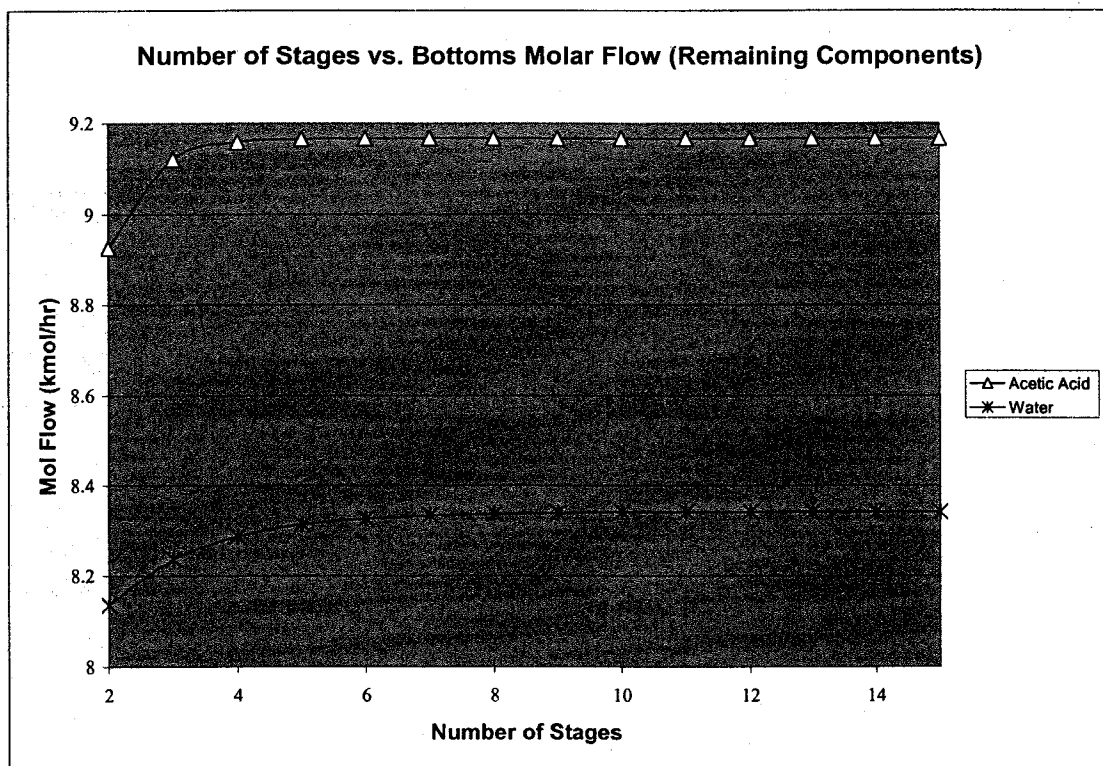


Figure 4.8 – Effects of Varying Stages on Acetic Acid and Water, Bottoms

It can be observed that an increase in the number of stages leads to a slight increase in the production of both acetic acid and water. Similar to the nitric acid stream, increasing the number of stages beyond 8 has no effect on the change of flowrates. Figures 4.9 and 4.10 respectively depict the results for the tops stream concerning nitric acid as well as acetic acid and water.

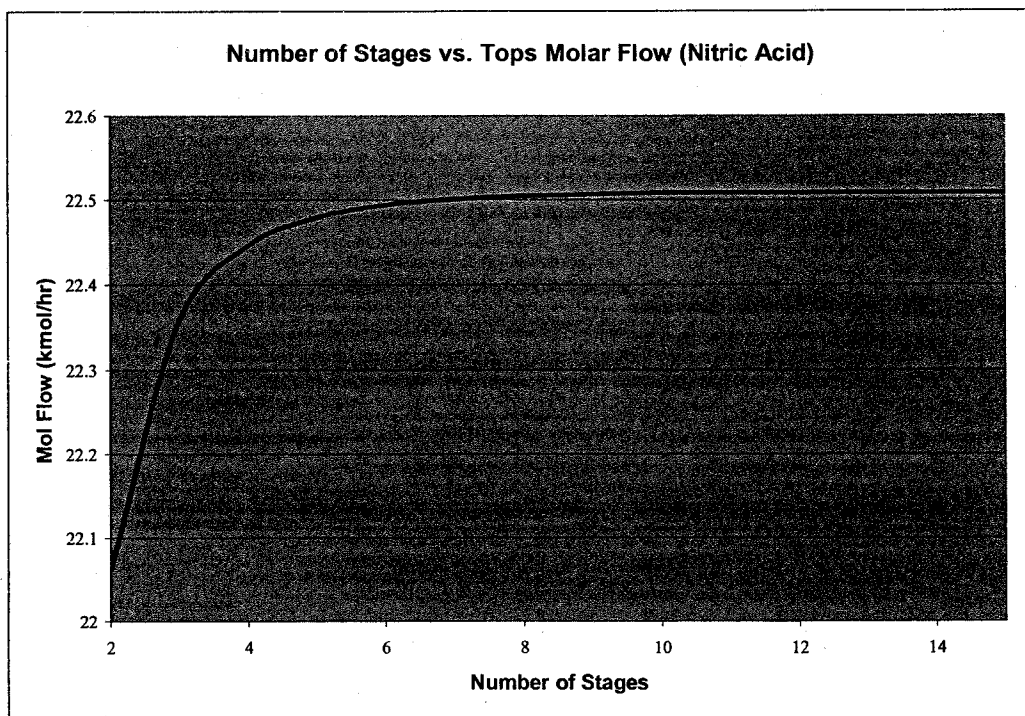


Figure 4.9 – Effects of Varying Stages on Nitric Acid, Tops

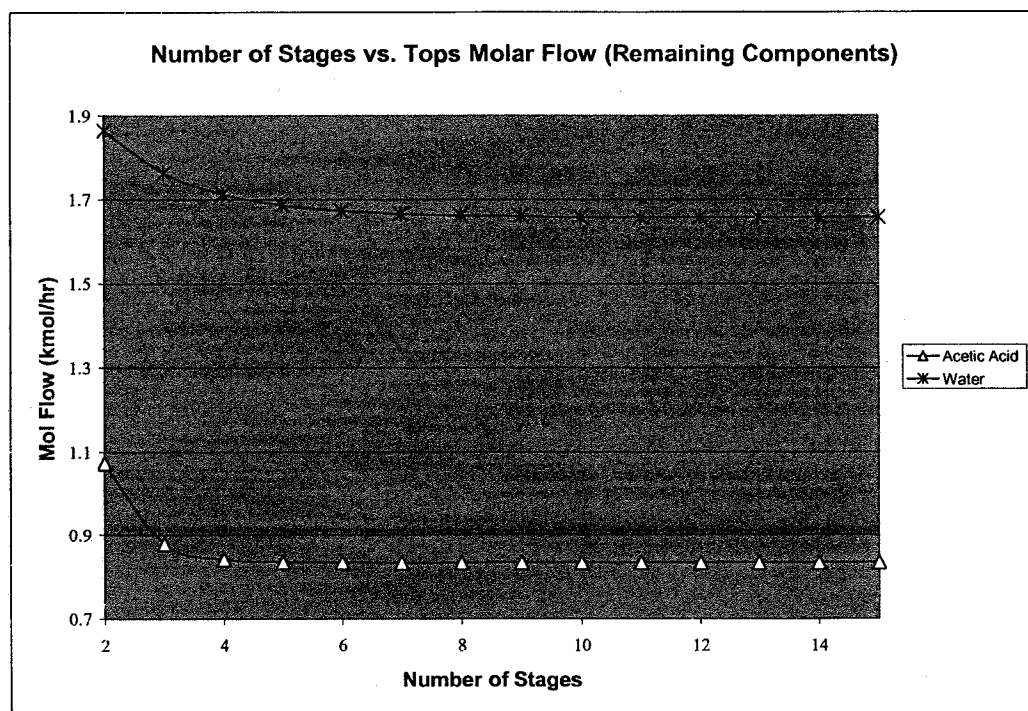


Figure 4.10 – Effects of Varying Stages on Acetic Acid and Water, Tops

Table 4.4 displays the separation efficiency achieved by varying the number of stages in the column.

Table 4.4 – Separation Efficiency of Various Numbers of Stages

# of Stages	Fraction of Feed Stream in Bottoms Stream			Fraction of Feed Stream in Bottoms Stream		
	Acetic Acid	Nitric Acid	Water	Acetic Acid	Nitric Acid	Water
2	0.8926	0.7794	0.8136	0.1074	0.2206	0.1864
3	0.9122	0.7764	0.8236	0.0878	0.2236	0.1764
4	0.9159	0.7755	0.8287	0.0841	0.2245	0.1713
5	0.9166	0.7752	0.8313	0.0834	0.2248	0.1687
6	0.9167	0.7751	0.8327	0.0833	0.2249	0.1673
7	0.9167	0.7750	0.8334	0.0833	0.2250	0.1666
8	0.9167	0.7750	0.8338	0.0833	0.2250	0.1662
9	0.9167	0.7749	0.8340	0.0833	0.2251	0.1660
10	0.9167	0.7749	0.8342	0.0833	0.2251	0.1658
11	0.9167	0.7749	0.8342	0.0833	0.2251	0.1658
12	0.9167	0.7749	0.8342	0.0833	0.2251	0.1658
13	0.9167	0.7749	0.8342	0.0833	0.2251	0.1658
14	0.9167	0.7749	0.8342	0.0833	0.2251	0.1658
15	0.9167	0.7749	0.8342	0.0833	0.2251	0.1658

4.4.3 Parametric Study 3 – Varying the Location of the Feed Stage

The above studies were performed with the feed stream entering the tower at stage two. That is, the feed stream enters the tower at the stage second from the top. The third parametric study was concerned with examining the effects of having the feed stream enter at differing stages. Figure 4.11 displays the impact of varying the feed location has on the bottoms stream.

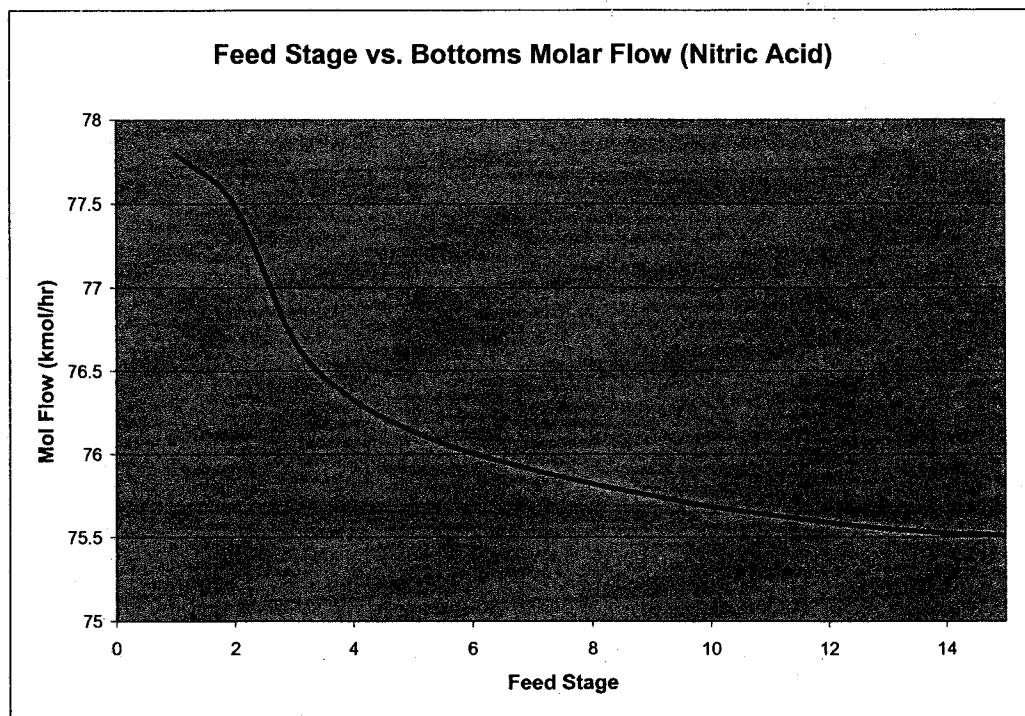


Figure 4.11 - Effects of Varying Feed Location on Nitric Acid, Bottoms

It is easily enough seen that having the feed stream enter the tower at a higher stage number (lower in the tower) will result in less nitric acid being brought off the tower in the bottoms flowrate. As more nitric acid is allowed to rest in the bottom of the tower (and thus near the heat of the reboiler), more nitric acid will be vaporized and fed up the tower (to be removed in the tops stream). Figure 4.12 shows the effects of varying feed stage on the nitric acid in the tops stream.

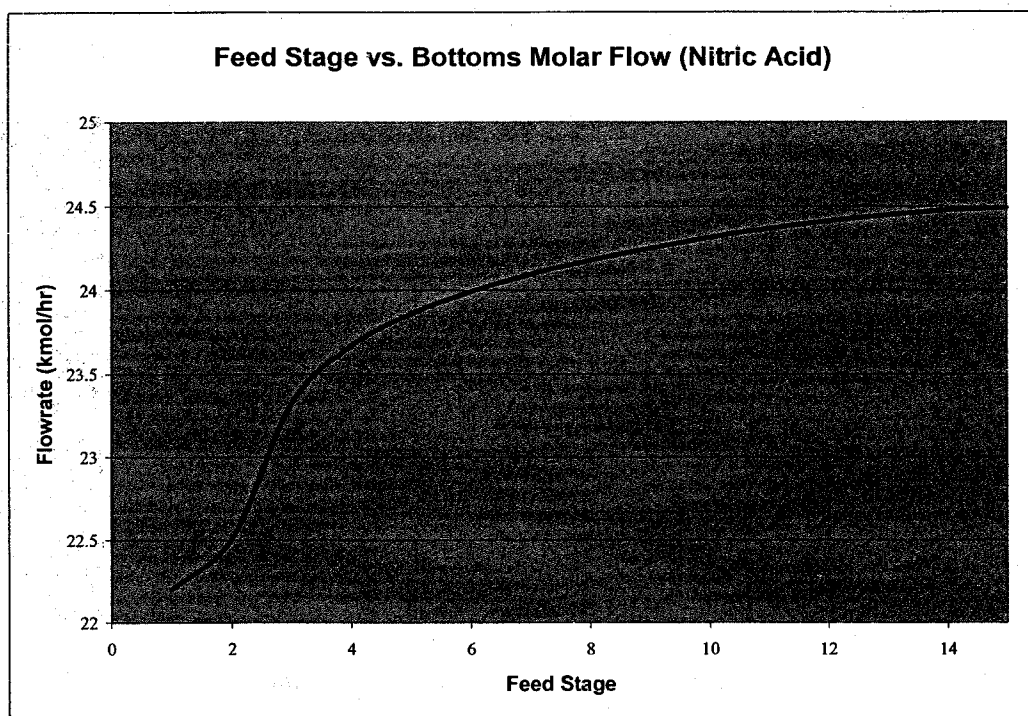


Figure 4.12 - Effects of Varying Feed Location on Nitric Acid, Tops

Figures 4.13 and 4.14 depict the results of the same study on water and acetic acid in both the bottoms and tops stream, respectfully.

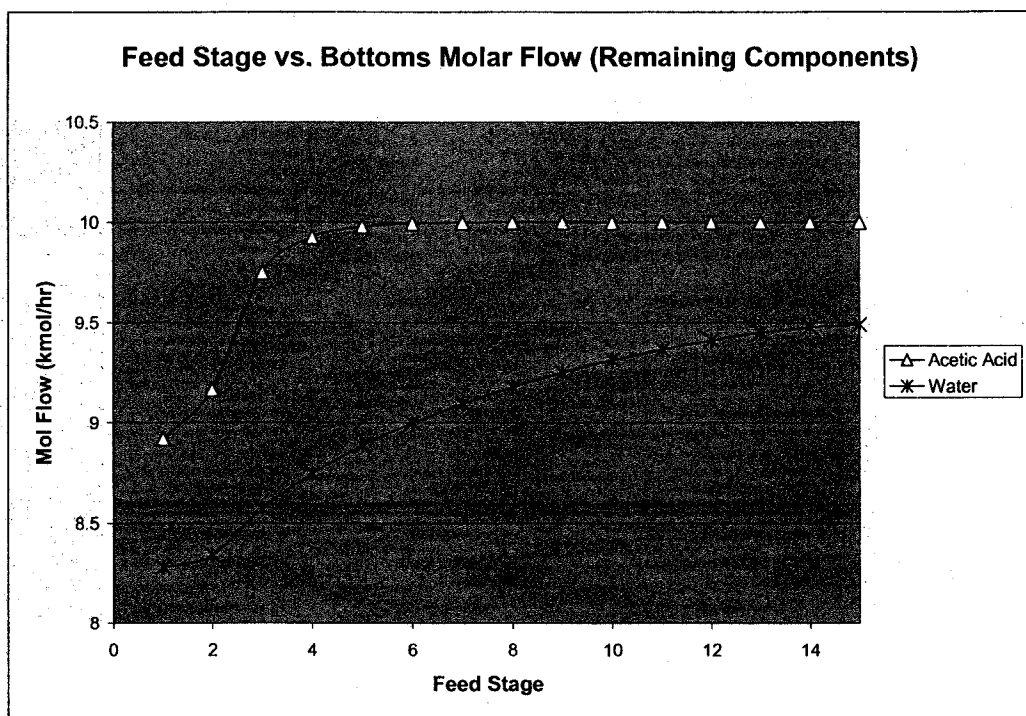


Figure 4.13 - Effects of Varying Feed Location on Acetic Acid and Water, Bottoms

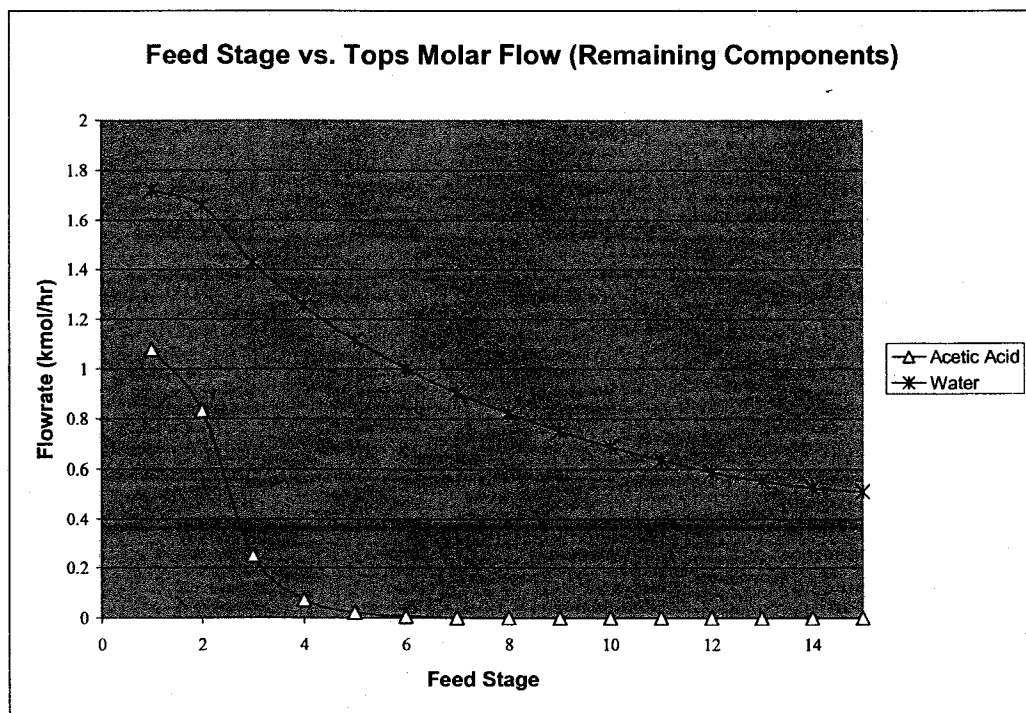


Figure 4.14 - Effects of Varying Feed Location on Acetic Acid and Water, Tops

The water and acetic acid streams both increase in molar flowrate in the bottoms stream as the feed stage is lowered in the column. As the feed stage is moved closer and closer to the bottom of the tower, the bottom of the tower will fill quicker with water and acetic acid. As the energy is not enough to vaporize a majority of these components, they will be taken out the tower as bottoms product. This is expected however, as they are the heavy components in the tower. There will be more mols of acetic acid and water in the bottoms stream because there are more mols of water and acetic acid in the bottom of the tower. Conversely, this same understanding provides explanation for why there is a decrease in both components in the tops stream. Table 4.5 provides the separation efficiency for this parametric study.

Table 4.5 – Separation Efficiency of Varying Feed Stage Location

Feed Stage Location	Fraction of Feed Stream in Bottoms Stream			Fraction of Feed Stream in Bottoms Stream		
	Acetic Acid	Nitric Acid	Water	Acetic Acid	Nitric Acid	Water
2	0.8921	0.7780	0.8280	0.1079	0.2220	0.1720
3	0.9167	0.7749	0.8342	0.0833	0.2251	0.1658
4	0.9750	0.7668	0.8572	0.0250	0.2332	0.1428
5	0.9925	0.7633	0.8745	0.0075	0.2367	0.1255
6	0.9978	0.7614	0.8884	0.0022	0.2386	0.1116
7	0.9993	0.7601	0.8999	0.0007	0.2399	0.1001
8	0.9998	0.7591	0.9096	0.0002	0.2409	0.0904
9	0.9999	0.7582	0.9179	0.0001	0.2418	0.0821
10	1.0000	0.7575	0.9250	0.0000	0.2425	0.0750
11	1.0000	0.7569	0.9312	0.0000	0.2431	0.0688
12	1.0000	0.7563	0.9365	0.0000	0.2437	0.0635
13	1.0000	0.7559	0.9411	0.0000	0.2441	0.0589
14	1.0000	0.7555	0.9448	0.0000	0.2445	0.0552
15	1.0000	0.7553	0.9475	0.0000	0.2447	0.0525

4.4.4 Simulation 1 – Discussion.

In an effort to determine the most important factor in designing the desired distillation column, the separation factors (percentage of feed stream components present in the respective product streams) were calculated and presented in tables 4.3 through 4.5. Examining the resulting separation efficiencies from the parametric studies, it can be seen that the desired goal of increasing the molar flow of nitric acid in the bottoms is not achieved in any study. The nitric acid separation efficiency decreases in each study as the respective independent parameter (reflux ratio, number of stages, feed stage location) is increased. It would be advisable to keep these parameters low so as to maximize nitric acid separation efficiency, however; because the value of the nitric acid efficiency is so low to begin with; the studies have only served to show the infeasibility of tower design under the given constraint of having nitric acid leave as bottoms product.

The overall conclusion that can be drawn from the study of increasing the number of stages in the column is that the optimal number of stages for the column will be around 8. To have more than 8 stages will be an unnecessary expense that will not aid in further separation of products. While the studies performed have shown that the manipulation of reflux ratio, number of stages and feed location affects the separation of feed components, the changes are so minimal they can be considered negligible. The greatest conclusion that is to be drawn from this first simulation is however, that it is not feasible to design a tower that removes nitric acid as a bottoms product from a feed of nitric acid, acetic acid and water. While a majority of the acid can be removed as a bottoms product;

it is not a high enough concentration to be considered successful. A successful separation should yield more than 80% of the molar content. In this case, more than 20% of the molar concentration would have to be separated further (in another tower) or discarded. The addition of such processes would add greatly to the cost, and is unnecessary when there are other more cost efficient methods exist (as will be discussed in the proceeding section).

4.5 Simulation 2

It was found that the design for a column to separate a ternary mixture of nitric acid, acetic acid and water with nitric acid leaving in the bottoms product would be infeasible. The main error in this design is simple chemistry. Because the boiling point of nitric acid is less than that of acetic acid (see Table 4.6); it will vaporize at first and flow up the column to the condenser.

Table 4.6 – Component Boiling Points

Component	Boiling Point (K)
Acetic Acid	391.05
Nitric Acid	356.15
Water	373.15

The previous simulation has shown that it is not possible to remove a high enough quantity nitric acid from the column as a bottoms product to be successful. With that said,

if it is desired to separate and obtain a high purity nitric acid stream there is only one choice – to have the nitric acid leave the column as distillate. In this scenario, it is no longer necessary to have a rigorous separation model as it is no longer of interest to determine the feasibility of performing the separation with nitric acid coming off as a bottoms product. This new simulation follows the most physically likely scenario, thus, a more crude method of calculation was used. The ASPEN PLUS distillation block DSTWU will be used for this new simulation.

The distillation block enables the user to enter a number of parameters different than that available in the block used in the first simulation. Whereas the Radfrac block used in the first simulation called for the user to enter the distillate rate and reflux rate, in addition to the number of stages; the DSTWU block calls for either the number of stages or reflux rate (and thus calculates the option not chosen).

Furthermore, the component percent recovery is specified by the user. That is to say, the user will specify what percent of the light and heavy key is to be recovered in the distillate stream. This block is useful when a desired separation percent is known and it is of interest to study the amount of energy required by the column. Also, ASPEN PLUS will calculate the number of stages and reflux ratio based on the engineer's desired separation efficiency.

4.6 Tower Design

The purpose of the second simulation was twofold. The first goal is to gain an understanding of what factors influence separation within a column when near perfect product purity is desired. The second goal is more concrete, and that is to determine the correct tower conditions that will concentrate a 0.6M feed of nitric acid (in water) to a 4.5 M solution (in the tops stream). As before, there exists a small amount of acetic acid (arbitrarily chosen to be half that of the nitric acid). For this simulation it is necessary to choose a basis of nitric acid before we begin working. Using the basis as a starting point, we can determine the required composition of water in the feed stream.

$M = \frac{n}{V}$	4.1
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Where M = molarity

n = number of mols

V = volume (in liters)

To find the number of mols of water, it is first necessary to find the volume of water. Solving the above equation for V (with $M = .6$ and $n = 100$ kmol), gives a volume of water equal to 166.66 L. Multiplying the volume of water by the density of water (1 kg/L) will give the mass of water that occupies 166.66L. Dividing this mass of water by the molecular weight of water (18 kg/kmol) will yield the moles of water. This procedure

leads to the calculation of 9258.88 kmols of water. The feed conditions are summarized in Table 4.7

Table 4.7 – Feed Stream Conditions, Simulation 2

Components	Flowrate (kmol/hr)	T (K)	P (atm)
Acetic Acid	50	298.15	1
Nitric Acid	100	298.15	1
Water	9,258.88	298.15	1

The new scenario explored the feasibility of complete removal of nitric acid (as distillate) in a single tower. The ASPEN PLUS flowsheet for this second separation simulation can be seen below.

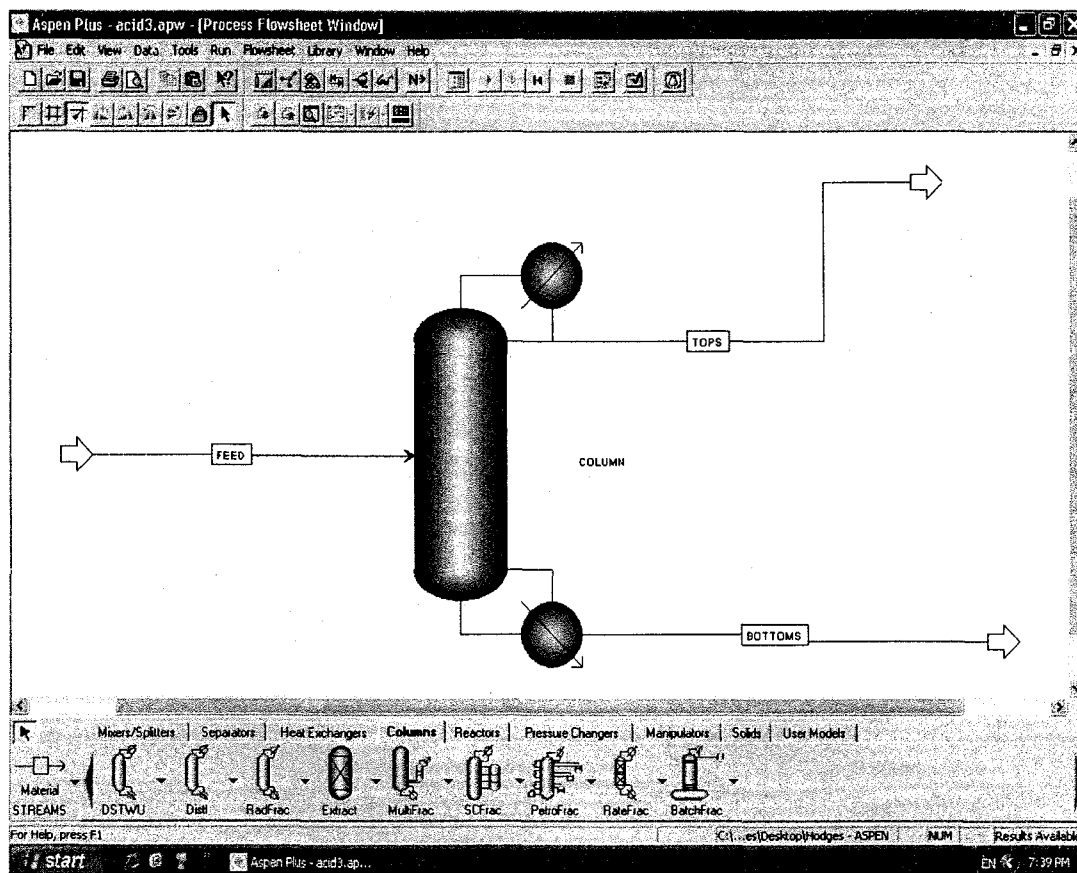


Figure 4.15 – Column Distillation Flowsheet

The DSTWU distillation block chosen for this separation has a few new user inputs that the engineer must specify. The most important of these is the recovery fraction of two components in the tops stream must be specified. Further, this DSTWU block does allow the user to decide where the feed stage is placed. From the data the user enters, the feed stage will be calculated. Since it is desired to have all the nitric acid be removed in the tops stream, the simulation was run with the light key recovery sent to .999 (or 99.9%). The light key to be specified must be the lightest component in the system. In this case, it is nitric acid. The heavy key must be chosen from the remaining two

components. In our simulation, the heavy key can be either water or acetic acid (as both are 'heavier' than nitric acid). From the principle of evaporation, it is known that nitric acid will boil before water which will boil before acetic acid. If the heavy key is chosen to be the component with the middle boiling point, and it is specified that relatively none of this material is to be recovered in the tops stream; then it is assumed that none of the heaviest component will be recovered as well. With this said, choosing water to the heavy key and specifying the recovery to be practically nothing (0.01%) ensures that the tops stream will consist of only nitric acid; that is, a pure nitric acid recovery stream. The pressure was assumed to be atmospheric at the reboiler. However, a slight pressure drop is needed or no flow would take place in the column. Table 4.8 summarizes the column operating conditions.

Table 4.8 – Column Operating Conditions, Simulation 2

Number of Stages	15
LK: Nitric Acid	0.999
HK: Water	0.00001
Reboiler P (atm):	1.1
Condenser P (atm):	1

With the feed and column operating conditions entered as discussed above, the simulation was performed. The results are discussed in the next section.

4.6.1 Tower Design Results

The simulation was performed as expected. 99.9% of the nitric acid in the feed stream was recovered in the tops stream. In addition, 0.01% of water was recovered. Because the tower was operated so as to ensure so little of the 'medium' key was recovered in the distillate; all of the heavy material was found in the bottoms stream. Table 4.9 summarizes the stream results from this simulation.

Table 4.9 – Stream Conditions, Simulation 2

	Feed	Bottoms	Tops
Temperature K	298.15	373.26	356.05
Pressure atm	1.00	1.00	1.00
Vapor Frac	0.00	0.00	0.00
Mole Flow kmol/hr	9408.88	9308.88	100.00
Mass Flow kg/hr	176105.23	169808.35	6296.88
Volume Flow l/min	2929.35	3088.19	76.33
Enthalpy MMBtu/hr	-2545.44	-2479.46	-15.43
Mole Flow kmol/hr			
Acetic Acid	50.00	50.00	0.00
Nitric Acid	100.00	0.10	99.90
Water	9258.88	9258.79	0.09

The data collected from the streams shows exactly what was expected. The tops stream is almost entirely nitric acid (99.91% pure), which was the intent of the simulation. The bottoms stream contains all of the acetic acid and 99.999% of the water. The stream results show in fact that it is possible to obtain a 99.91% stream of nitric acid

that is to be removed off of the top of a column. To understand the feasibility of such a separation, it is necessary to study the results of the column. Table 4.10 presents the data collected on the column.

Table 4.10 – Design Specifications, Simulation 2

Minimum reflux ratio:	72.34891
Actual reflux ratio:	80.75802
Minimum number of stages:	63.27878
Number of actual stages:	126.5576
Feed stage:	116.9886
Number of actual stages above feed:	115.9886
Reboiler heating required (kW):	86920.53
Condenser cooling required (kW):	72108.75
Distillate temperature (K):	356.0455
Bottom temperature (K):	373.2601
Distillate to feed fraction:	0.010628

When determining feasibility of a distillation process, it is important to look at two main factors, the reflux ratio and the number of actual stages. In general, it is beneficial to keep both values low. It is desired to keep the reflux ratio low in an effort to minimize the energy required by the condenser to cool the distillate. Perhaps more obvious (and more important) is the need to keep the number of stages low. More stages in a column lead to a larger column. Larger columns face many points of difficulty. A tall column presents many issues involving possible worker falls, difficult tower maintenance at large heights and perhaps most important, difficulty of safe storage indoors. According to Price [11], a column should not exceed 175 feet tall. Typical tray spacing is 2 ft. in

between trays. Further, 15% of the total tray spacing is added for the top and bottom of the tower. With these heuristics, a tower containing approximately 127 trays would be a little over 290 feet tall, over 100 feet taller than safety limits call for. When tower designs call for such a large tower, it is often recommended that two towers be used. Before that is done however, it is necessary to modify the tower parameters in hopes that more desirable operating conditions might be found. Modifying the heavy key and light key recovery fractions will indeed have an effect on the required trays.

4.6.2 Parametric Study 4 - Varying LK Recovery

It is desired to see how much of an impact the LK recovery plays on the number of stages. Figure 4.16 displays the results found for this study.

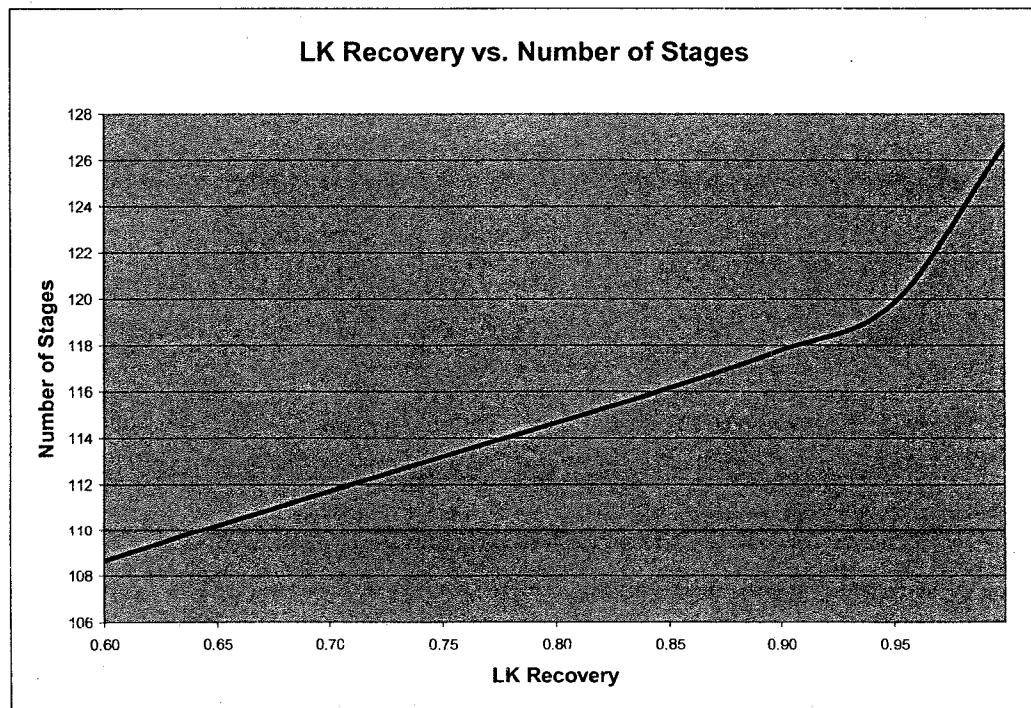


Figure 4.16 – Effect of Varying LK Recovery on Number of Stages

The chart shows that as the LK recovery is increased from 60.0% to 99.9%, the number of stages increases. This is expected when looking at the physics of the unit operation. A distillation column is able to more efficiently separate chemicals by providing more surface area for the mass and energy transfer. This surface area is added by the placement of more trays. It serves to make sense that adding more trays will increase the separation rate. Perhaps more important though, is the fact that this study has shown that decreasing the LK recovery rate a great deal (by nearly 40%) has a relatively small effect on decreasing the number of stages. While it is true that a pure product stream of nitric acid is desired, reduction of the LK recovery (and thus a decrease in the product purity) rate leads to a decrease of only about 14% of the column trays. If it is desired to decrease the number of stages in the column, reduction of the LK recovery is not the way to achieve it.

4.6.3 Parametric Study 5 - Varying HK Recovery

A second study was performed to observe what effect varying the HK (water) recovery rate would have on the number of stages. For the second study, the HK recovery rate was varied from .1% to .001%. The tray change resulting from a varying HK recovery rate can be seen in Figure 4.17.

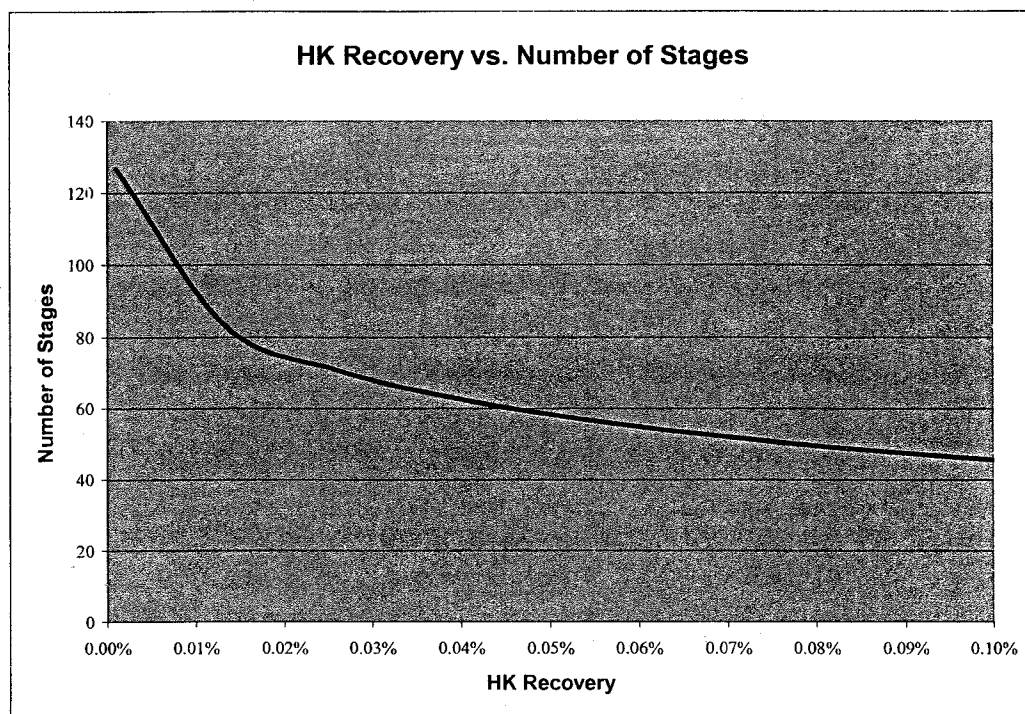


Figure 4.17 – Effect of Varying HK Recovery on Number of Stages

This new relationship is much more promising than the one found by varying the HK recovery rate (Figure 4.16). As can be seen in the figure, an increase in the HK recovery causes a decrease in the number of stages. While this at first appears to be the desired solution, it must be noted that an increase in HK recovery means that more of the HK will be present in the distillate stream. An increase of the HK in the distillate stream leads to a decrease in the desired component purity (nitric acid) of the stream (and thus compromises the overall goal). The extent of this compromise needs to be studied if a recommendation concerning the usefulness of varying the HK recovery rate is to be given. Figure 4.18 reveals the relationship that helps to address this concern.

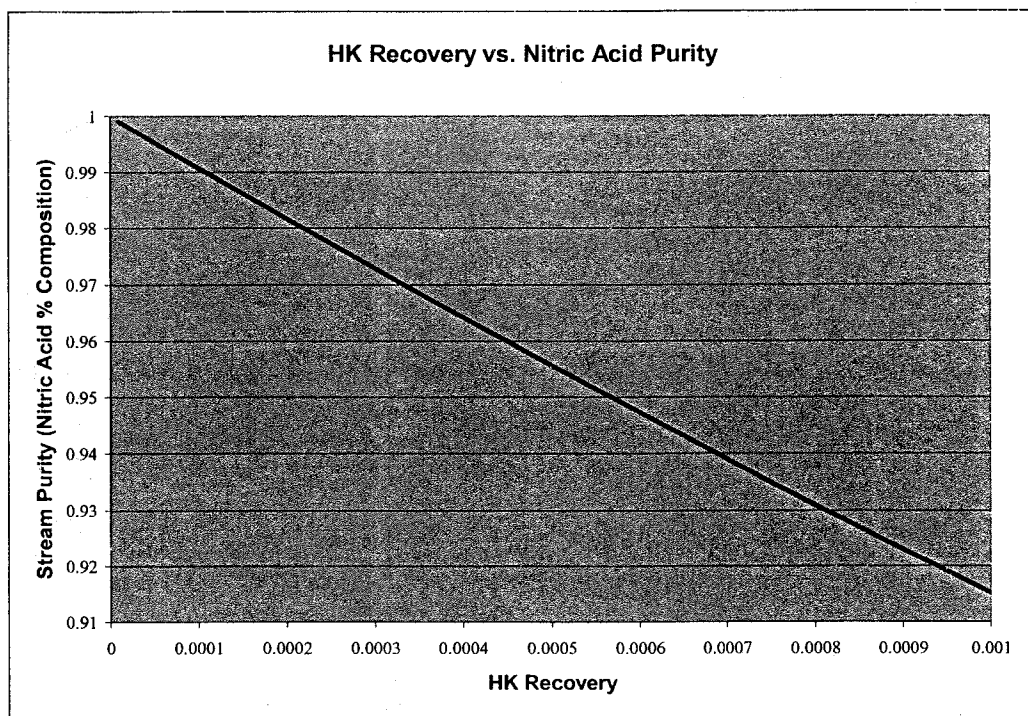


Figure 4.18 – Effect of Varying HK Recovery on Stream Purity

As expected, an increase in the HK recovery fraction leads to a decrease in stream purity with respect to nitric acid. The extent of impurity however, is minor when compared to the benefit of the decreased number of trays. The study managed to decrease the number of trays from 127 to 46. This huge decrease in the number of required trays came only at the expense of about 8.4% stream purity (from 99.9% to 91.5%). Depending on the level of purity desired, changing the HK recovery rate can drastically reduce the number of trays needed for the desired separation. Figure 4.15 depicts a similar relationship, that of HK recovery to the mols of water in the distillate.

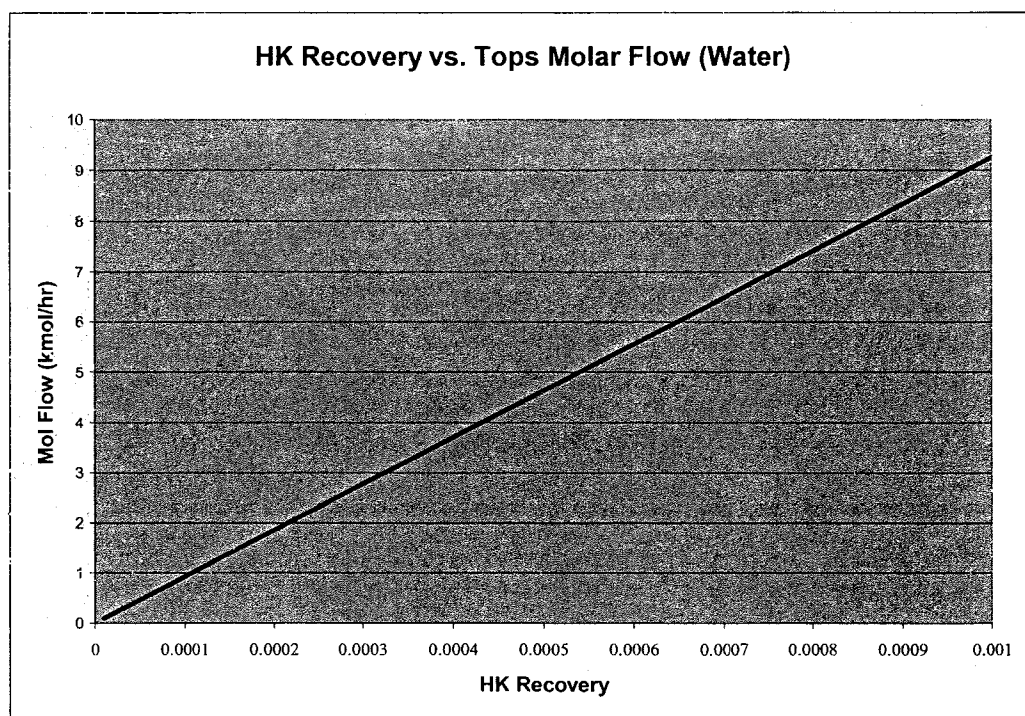


Figure 4.19 – Effect of Varying HK Recovery on Water Flowrate, Tops

As can be observed above; as HK recovery increases, the amount of water in the distillate also increases. This is of course, straight from the meaning of component recovery and can be calculated by a simple mass balance over the column. As water is defined to be the HK, it is expected that it will reappear in the tops stream. If this did not happen, there would be something wrong with ASPEN PLUS. What is quite useful about this tendency however, is its apparent linear relationship. Performing a linear regression on the data presented in Figure 4.19; results in equation 4.2.

$y = 9258.9x + 3E-5$	4.2
----------------------	-----

Where y = mols of water collected in the distillate
 x = HK (water) recovery

Recall from section 4.7 that the secondary goal of this research was to determine the correct operating conditions of a tower required to concentrate 0.6 M acetic acid to 4.5 M (in the presence of acetic acid and water). Assuming this relationship to be constant throughout the process, the value of HK recovery which yields the desired amount of water necessary to produce a 4.5 M nitric acid solution can be calculated. Using the approach outlined in section 4.7, the number of mols of water can be used to solve equation 4.2 to come up with the respective HK recovery value.

A 4.5M nitric acid solution will contain 1234.6 mols of water per every 100 mols of nitric acid. With y equal to 1234.6 mols, solving equation 4.2 for the HK recovery yields a value of 0.13334. If this linear relationship between HK recovery and mols of water is in fact correct, an ASPEN PLUS simulation should give results that agree with the estimate. Table 4.11 displays the stream information as yielded by ASPEN PLUS.

Table 4.11 – Parametric Study 5 Stream Conditions

	Feed	Bottoms	Tops
Temperature K	298.15	375.97	368.50
Pressure atm	1.00	1.10	1.00
Vapor Frac	0.00	0.00	0.00
Mole Flow			
kmol/hr	9408.88	8074.39	1334.49
Mass Flow kg/hr	176105.23	147568.08	28537.15
Volume Flow			
l/min	2929.35	2692.80	488.54
Enthalpy			
MMBtu/hr	-2545.44	-2150.07	-343.36
Mole Flow			
kmol/hr			
Acetic Acid	50.00	49.99	0.01
Nitric Acid	100.00	0.10	99.90
Water	9258.88	8024.30	1234.58

The ASPEN PLUS simulation data yields what was expected mathematically.

Practically all of the nitric acid is removed in the tops and 1234.58 mols of water have been removed as well. This ratio of mols of nitric acid to the volume occupied by 1234.58 mols of water yields the desired stream concentration of 4.5M. While ASPEN PLUS has now shown that it is possible for such a separation to occur, it is now of great interest to study the feasibility of such a design. For this, we again focus our attention to the column characteristics as solved for by ASPEN PLUS.

Table 4.12 – Parametric Study 5 Design Specifications

Minimum reflux ratio:	0.46469719
Actual reflux ratio:	0.60144517
Minimum number of stages:	6.5845354
Number of actual stages:	15
Feed stage:	4.50291027
Number of actual stages above feed:	3.50291027
Reboiler heating required (kW):	39113.7538
Condenser cooling required (kW):	23872.8776
Distillate temperature (K):	368.497691
Bottom temperature (K):	375.970329
Distillate to feed fraction:	0.14183342

It can be seen that the number of stages required for such a column is only 15. Further, the actual reflux ratio is a mere 0.60. These numbers are well below that suggested by Price [11]. Now that it has been shown that it is feasible to build a tower for our desired separation, it is of interest to make the tower as energy efficient as possible.

4.6.4 Parametric Study 6 – Varying Reboiler Pressure

To gain an understanding of this, a parametric study was performed in an attempt to minimize the amount of heating required by the reboiler and condenser. The driving force behind the mass transfer in the tower is the pressure drop between the reboiler and condenser. The reboiler pressure has to be greater than that of the condenser so as to initiate vapor flow upward. The effects of increasing reboiler pressure on the energy needs for the tower can be seen in Figure 4.20.

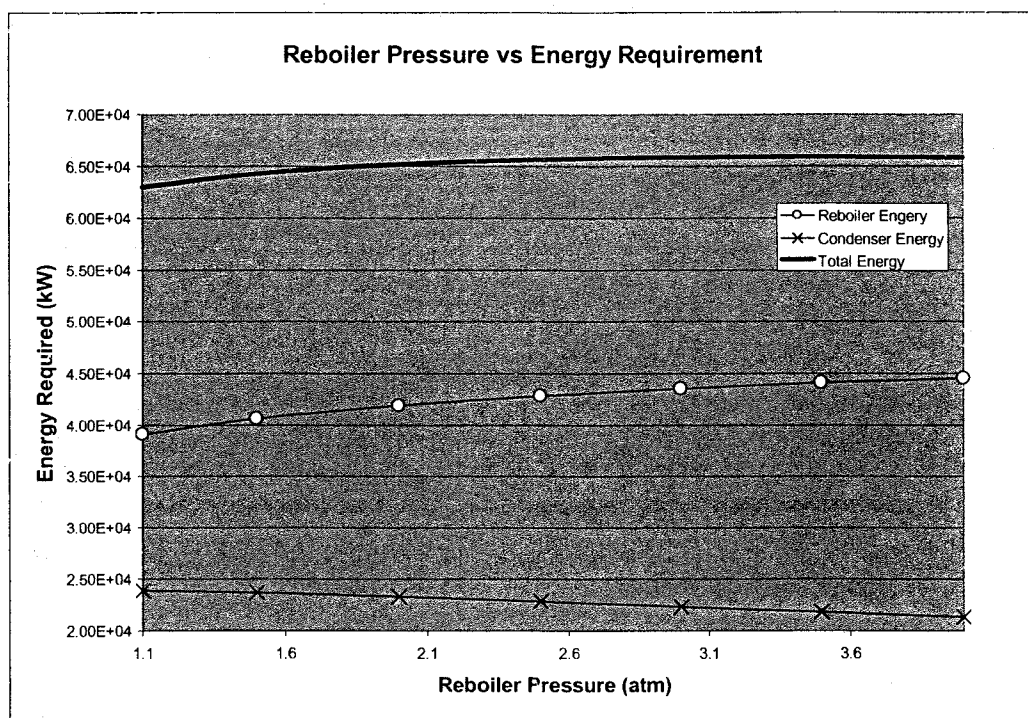


Figure 4.20 – Effect of Varying Reboiler Pressure on Energy Requirement

The figure shows that as the pressure is increased at the bottom of the tower, the overall energy needed by the tower increases. Individually, the energy needed by the reboiler increases and the energy needed by the condenser decreases. This relationship can be understood by studying the phase diagram of water as shown in Figure 4.21.

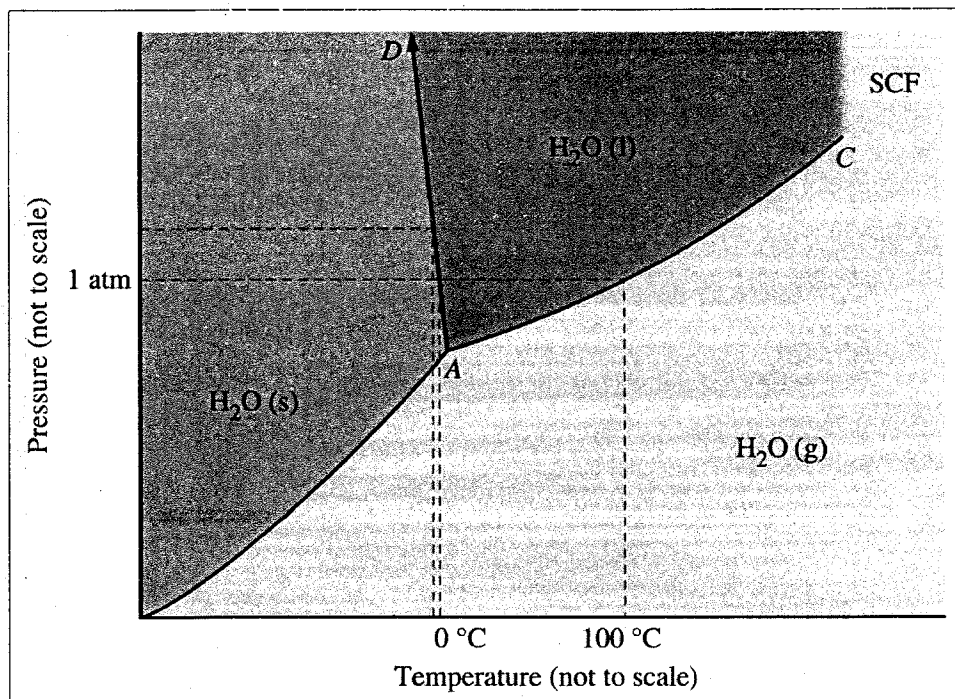


Figure 4.21 – Phase Diagram of Water [12]

As the pressure is increased at a constant temperature, the water tends towards the liquid phase. The production rate of nitric acid and water in the tops stream is constant as set by the engineer. The reboiler will vaporize any amount of liquid present in an effort to achieve the desired amount in the tops stream. This new liquid phase water must be vaporized until the required mol flowrate is achieved in the distillate stream. More liquid phase water at the bottom means more energy is needed for the reboiler to vaporize it.

As pressure is increased at the bottom of the tower, the pressure gradient increases and as such, the velocity of the vapor flow upward increases. As the velocity flow increases, a small amount of the liquid water maybe adversely pushed upwards in the tower. Upon reaching the top of the tower, being already in the liquid state, the

condenser will not have to use energy to cool the stream. As can be seen, because the increase in the energy required by the reboiler is greater than the decrease in the energy required by the condenser, the overall energy required by the tower will increase

CHAPTER 5

PLUTONIUM METAL PRODUCTION

The second of the major objectives of this thesis is to simulate several operations in the plutonium metal production process. The plutonium metal production process takes the product from the NPEX process as its feed.

5.1 NPEX Process

The NPEX process is used by ANL scientists to remove plutonium and neptunium from spent fuel [10, 16, and 20]. The overall NPEX process can be seen in Figure 5.1.

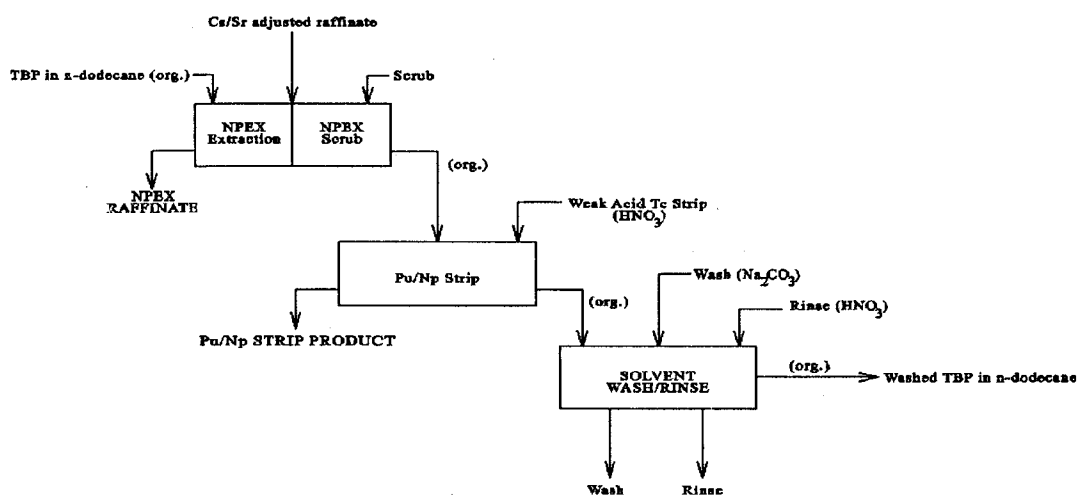


Figure 5.1 – NPEX Process

In the NPEX process, tri-butyl-phosphate (TBP) in n-dodecane is used to extract the plutonium/neptunium from the cesium/strontium solvent extraction raffinate. A slight nitric acid scrub is used to remove the fission products, americium/curium and lanthanides. These species are collected in the NPEX raffinate stream and fed to the vitrification process elsewhere in the plant (beyond the scope of this thesis). Once the Pu/Np has been removed from the spent fuel, it needs to be further separated and eventually processed into a purer form of plutonium metal. The work contained in this project is the simulation of the process following the removal of the plutonium/neptunium strip product (shown in red in the above figure). There are a variety of methods of producing plutonium metal each with their own individual strengths and weaknesses.

5.2 Research Purpose

While it was first desired to perform a complete simulation of the process and perform several parametric studies exploring the variable effects on molar flowrates; it is now of interest to construct a “skeletal backbone” of the plutonium metal production process for delivery to ANL. The difficulty of acquiring the plutonium metal production process simulation parameters (as will be discussed in Sections 5.6 and 5.7) for thermodynamic data as well as reaction specifics have led to the purpose of the research changing. Once received, ANL engineers can enter the “sensitive” missing data and explore the results.

5.3 Methods of Plutonium Metal Production

Previous research has shown that there are multiple ways to produce plutonium metal.

Table 5.1 shows the various processes, as well as the locations they are practiced [13].

Table 5.1 – Plutonium Metal Production Process Options

Conversion Processes

Type of Process	Steps	Facilities Practiced At
Direct Denitration	Evaporation, Calcination	Argonne National Lab (ANL) Hanford Site
Peroxide Precipitation	Precipitation, Calcination	Los Alamos National Lab (LANL) Rocky Flats Plant (RFP)
Pu (III) Oxalate Precipitation	Valence adjustment, Precipitation, Calcination	Savannah River Plant (SRP) Los Alamos National Lab (LANL)
Pu (IV) Oxalate Precipitation	Valence adjustment, Precipitation, Calcination	Hanford Site
Sol-gel process	Dilution, n-hexanol contact Calcination	Oak Ridge National Lab (ORNL)

Developed at ANL and the Hanford Site, plutonium metal production by direct denitration is the simplest, most straightforward process. There are relatively few processes required for this option, resulting in a simple equipment operation. However,

this process has been shown to have high corrosion rates due to nitric acid fumes; which results in extensive clean-up steps. Furthermore, direct denitration provides no decontamination from impurities. Oxide production via this method is severely limited and it is not known if the plutonium oxide would meet the required fuel specifications.

The plutonium peroxide precipitation method was originally developed at LANL but has been practiced at the SRP as well as at RFP [14]. Advantages of this method include excellent decontamination from impurities as well as feasible methods of remote operation and maintenance. Disadvantages of this option include a presence of excess peroxide in the filtrate as well as a surge in pressure caused by the potential decomposition of hydrogen peroxide.

Precipitation of plutonium (III) oxalate is the main process by which LANL scientists use for concentrating plutonium during recovery operations. Advantages of this process are numerous. The plutonium precipitate is easily enough handled and filtered in addition to having low decontamination from impurities. Furthermore, losses of plutonium to the filtrate are low.

The Sol-gel process developed by ORNL takes the plutonium nitrate feed and reacts it with n-hexanol to produce a sol-gel (colloidal suspension of silica particles). The major drawback of this option is that the process is quite complex and has not been demonstrated on an engineering scale [15].

The most successfully proven option is that of Pu (IV) oxalate precipitation. In general, this process provides a good yield of easily enough filterable precipitate which

can be calcined to an oxide powder which meets product specifications. The work contained in this thesis uses the Pu (IV) oxalate precipitation method as the backbone for plutonium metal production.

5.4 Production by Precipitation-Calcination-Fluorination-Reduction

This plutonium metal production process that is the motivation for the simulation is that which is in operation at the Department of Energy's Hanford Site. This process follows the commonly used method to produce plutonium metal, namely precipitation-calcination-fluorination-reduction. In this thesis, precipitation, calcination and fluorination are to be simulated in ASPEN PLUS. The reduction operations are beyond the scope of this project.

5.4.1 Feed Preparation

The plutonium nitrate product stream from the NPEX process is received in product receiver (PR) cans. The PR cans are manually loaded into staging tanks where they are blended and sampled. The solution batches are vacuum transferred to a preparation tank. In this preparation tank, the solution acidity, plutonium concentration, and valence of the nitrate feed are operator adjusted in an effort to guarantee optimal performance for the conversion of nitrate-to-oxalate in the first reactor [16]. Concentrated solutions of 12M and 2M nitric acid are used to adjust the acidity and overall plutonium concentration in the PR. Hydrogen peroxide is used to adjust the plutonium valence via reduction-

oxidation. Samples of the solution are taken after the adjustments have been made in an effort to ensure the correct feed conditions.

5.4.2 Precipitation-Calcination-Fluorination-Reduction

The chemical processes detailed in this section are those discussed by Gibson and Nyman in “Recent Plutonium Metal Production Experience at Hanford” [16]. The first operation in the plutonium metal production process is the reaction of the plutonium nitrate feed with oxalic acid to produce brown plutonium oxalate solids. The oxalate solids are then converted to plutonium oxide in a screw calciner. This reaction is performed through countercurrent contact with an air stream of near 450 °C. After the plutonium oxide has been produced, it enters a fluorinator where it becomes plutonium tetrafluoride by reaction with hydrogen fluoride and oxygen at 525 °C. The conversion of plutonium to the fluoride compound is the final step in the simulation. From here, the plutonium tetrafluoride is collected and reduced to plutonium metal by reaction with calcium. This project takes the feed stream of plutonium nitrate and follows the above process to produce plutonium metal. This flowsheet can be seen in Figure 5.2.

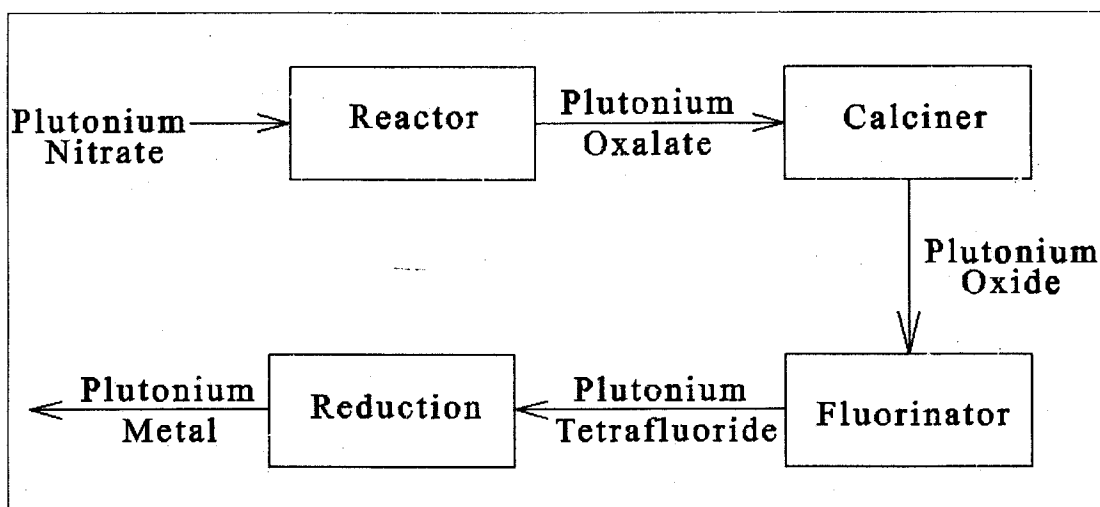
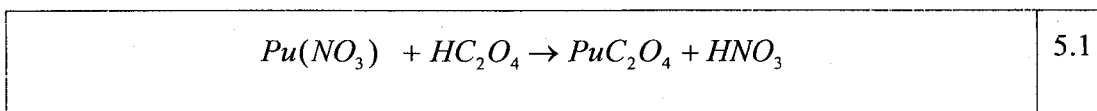


Figure 5.2 – Plutonium Production Flowsheet

5.5 ASPEN PLUS Design

The above process is simulated in ASPEN PLUS with a variety of assumptions. The first of these assumptions is that the only plutonium ion of interest is Pu (IV). For that reason, only the Pu (IV) ion is present in the feed. The process can be separated into four distinct unit operations. The first of these is the reaction of plutonium nitrate with oxalic acid in the reactor to produce plutonium oxalate (as seen in Equation 5.1)



The second unit operation is the calcination of plutonium oxalate into plutonium oxide. Figure 5.3 depicts the calciner in use at the Rocky Flats Plant in Golden Colorado (photo taken 4/29/65).

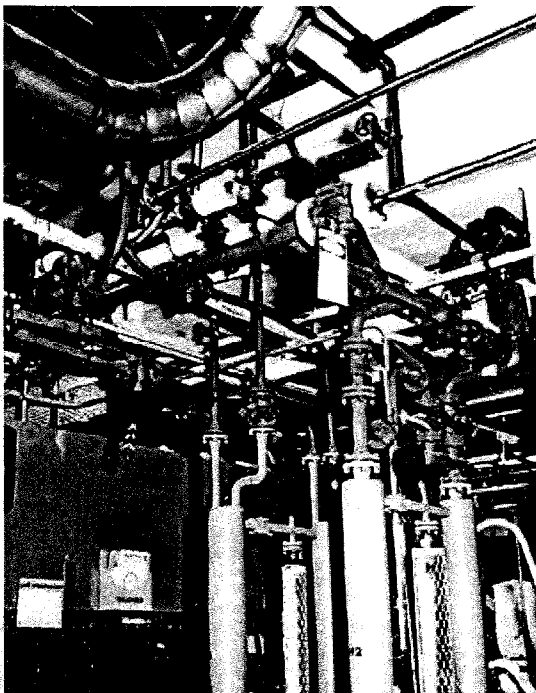
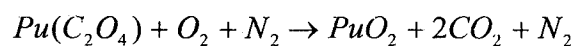


Figure 5.3 – Screw Calciner, Golden, CO [17]

In the calciner, the plutonium oxalate is converted to plutonium oxide (green powder). The oxalate is reacted with air in a countercurrent fashion at around 450 °C. The calciner has a length of 7 feet, an outside diameter of 10 inches and has a pitch of 1 inch [16]. ASPEN PLUS does not have a block dedicated to a calciner therefore the process will be simulated as a reactor. The reaction between plutonium oxalate and air can be seen in Equation 5.2.



5.2

The third step in the plutonium metal production process is the fluorination of plutonium oxide. The plutonium oxide from the calciner is fed to the fluorinator and allowed to react with a gaseous stream of hydrogen fluoride (HF) at 525 °C [16]. Figure 5.4 depicts the fluorinator which was used at the Rocky Flats Plant in Golden Colorado (photo taken 1/11/62).

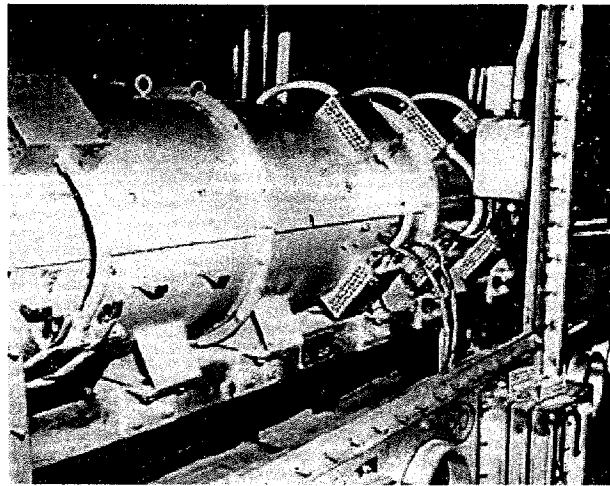
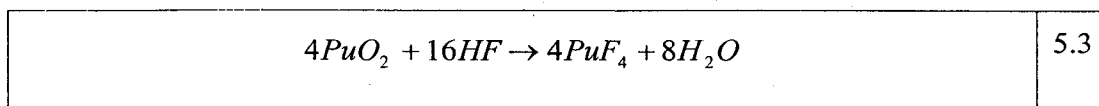
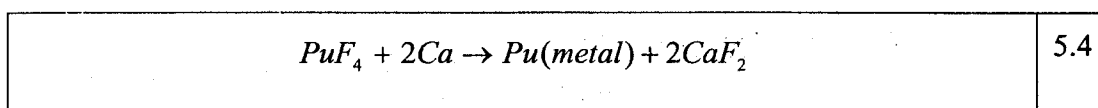


Figure 5.4 – Fluorinator, Golden, CO [18]

In the fluorinator, the countercurrent stream of HF reacts with the PuO_2 to form plutonium tetrafluoride (PuF_4) in accordance with the following reaction.



The temperature in the fluorinator is kept at 525 °C. The fluorinator is about 5 feet long and has six heating elements for which to keep the internal temperature at the desired warmth. The PuF₄ product is collected in powder pans and transferred to the process responsible for reduction. Calcium is the reducing agent used to separate plutonium from PuF₄ [19]. The reaction can be seen below in Equation 5.4.



Equation 5.4 is the last reaction that takes place in the simulation. The flowsheet for the ASPEN PLUS simulation can be seen in Figure 5.5.

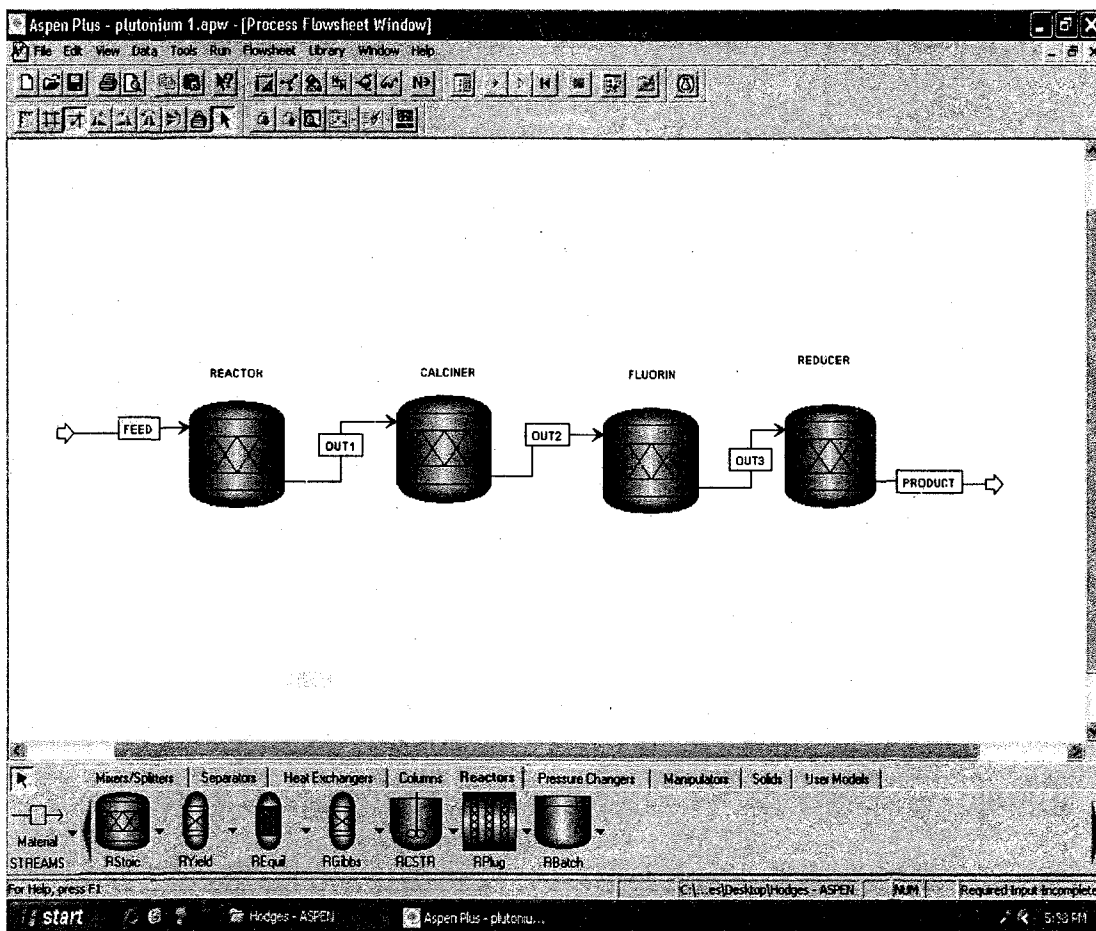


Figure 5.5 – ASPEN PLUS Process Flowsheet, Plutonium Metal Production

The feed to the first reactor contains water, plutonium nitrate and oxalic acid. Of these components, only water and oxalic acid are contained in the ASPEN databanks. Plutonium nitrate is not contained in the databank and as such must be defined by the user. The process of adding a user defined component is discussed in the next section.

5.6 User Defined Components

ASPEN PLUS contains over 15,000 compounds in its thermodynamic databank. If a process contains a component not listed within the databank, it must be defined by the user. There are a number of parameters that the user may input in an effort to define the component, but for the simulation desired in this thesis, only four are required and are discussed below.

- Molecular weight
- Standard normal boiling point
- Standard enthalpy of formation
- Standard Gibbs energy of formation

Proper values for the above parameters are vital if the simulation is to be accurate and successful. For the research contained in this simulation, the required components are listed in Table 5.2.

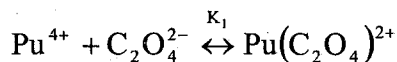
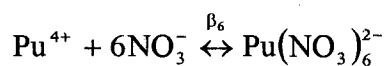
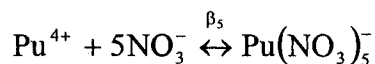
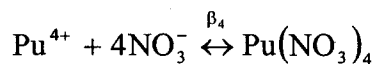
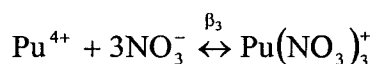
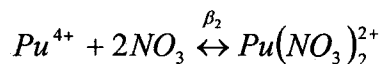
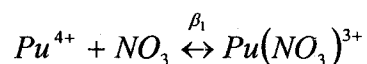
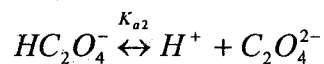
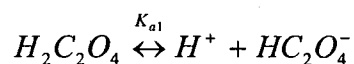
Table 5.2 – Simulation Components

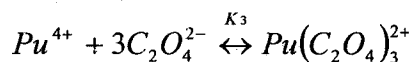
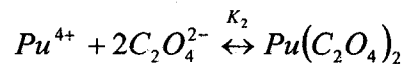
Name	Molecular Formula	Contained in ASPEN PLUS
Carbon Dioxide	CO ₂	Yes
Nitrate Ion	NO ₃ ⁻	Yes
Oxalic Acid	C ₂ H ₂ O ₄	Yes
Oxalate Ion	C ₂ O ₄ ²⁻	No
Plutonium (IV) Ion	Pu ⁴⁺	No
Plutonium Nitrate	Pu(NO ₃) ₄	No
Plutonium Nitrate Ion	Pu(NO ₃) ₄ ²⁻	No
Plutonium Nitrate Ion	Pu(NO ₃) ₄ ⁻	No
Plutonium Nitrate Ion	Pu(NO ₃) ₄ ⁺	No
Plutonium Nitrate Ion	Pu(NO ₃) ₄ ²⁺	No
Plutonium Nitrate Ion	Pu(NO ₃) ₄ ³⁺	No
Plutonium Oxalate	Pu(C ₂ O ₄) ₂	No
Plutonium Oxalate Ion	Pu(C ₂ O ₄) ₂ ²⁺	No
Plutonium Oxalate Ion	Pu(C ₂ O ₄) ₃ ²⁺	No
Water	H ₂ O	Yes

As can be seen from the above table, very few of the components that take place in the process are contained within the ASPEN databanks and as such, all missing components must be entered manually by the user. Unfortunately, most of these components are not well documented and, furthermore, are difficult to come by due to the fact that they are predominantly used in the processes that involve nuclear reactions. Information regarding such processes is considered to be proprietary and viewed by certain persons only. For this reason, the data for these components can not be entered into the ASPEN simulation by anyone other than those qualified to view such data, namely, the ANL scientists.

5.7 Electrolytic Reactions

Equations 5.1 through 5.4 detail the primary reactions needed for the production of plutonium metal. There are however, many dissociation reactions that occur also. In addition to the dissociation reactions, there are secondary reactions that take place between the dissociated ions. The dissociation and secondary reactions are seen below [20].





The dissociation reactions must be specified in the ASPEN PLUS blocks. Not only must the user enter the detailed reaction, but the values of the solubility constants (K_i and β_i) must be entered as well. While most textbooks and handbooks list the values for common solubility constants, because these reactions involve species that have are relatively not well studied (and can be considered “sensitive” as in section 5.5), values for these constants must come from the lab. Scientists at ANL have these values and upon delivery of the model, can enter them manually.

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

The research performed in this study contains two main sections; the nitric acid recycle process and the plutonium metal production process. At the completion of this project; the conclusions and recommendations for future work follow.

6.1 Simulation 1 - Acid Separation

Recall that the purpose of the acid separation was twofold. The first purpose was to test the feasibility of the design of a column where a feed of nitric acid, acetic acid and water were separated with nitric acid and water leaving as bottoms product and acetic acid leaving in the distillate stream. While the chemistry involved suggests that the lightest component (nitric acid) will leave in the distillate, it was desired to see if any a variation in tower operating conditions would allow nitric acid to leave as a bottoms product. The original simulation (without alteration of operating conditions) produced results as expected, with only about 77% (by mol) of the nitric acid leaving the tower as bottoms. The first parametric study showed that an increase in reflux ratio resulted in slight decrease (~2%) in nitric acid leaving the tower as bottoms product. The second study showed that an increase in the number of stages decreased the mol flow of nitric

acid in the bottoms stream but as the number of stages increased past 6, the flow was relatively constant. The first simulation showed that no matter what the operating conditions of the tower, it was not feasible to go through with a design that removed nitric acid as a bottoms product.

The second goal was to design a tower that would take 0.6 M nitric acid and remove it as distillate with a concentration of 4.5M. Early results were promising. It was found that in order to achieve the desired separation, the heavy (water) and light key (nitric acid) recovery needed to be set at .999 and .133 respectively. The tower operating conditions were found to be quite acceptable with a reflux ratio of 0.6 and number of stages equal to 15. This tower would be approximately within the size recommendations as given by Price [11]. A study was performed to observe the relationship between pressure drop and energy needs of the tower. It was found that increasing the pressure drop (by increasing the pressure of the reboiler) resulted in an increase of energy needed by the tower. Recommendations for future work with regards to the acid separation are as follows

- Perform a variety of other simulations using the other distillatory options and observe their effect on the chemical separation.
- Use exact values of feed flowrates to determine the actual specifications of the tower.

6.2 – Simulation 2 - Plutonium Metal Production

The second part of this study was the simulation of the plutonium metal production process as used at the DOE's Hanford site. This process consisted of four main operations - precipitation, calcination, fluorination and reduction. Due to the sensitivity of values of thermodynamic data for the components not contained in the ASPEN PLUS databanks, only a skeletal backbone of the process could be produced. Upon receiving the model developed in this research, ANL scientists will be able to use the laboratory values and enter them into the model. Recommended future work on this plutonium metal process is as follows

- Enter required sensitive data as described in Section 5.5
- Connect backbone to AMUSE software
- Run simulation to test accuracy of model
- Perform parametric studies to observe effect of temperature, pressure, and reaction constant on production rate of plutonium metal.

APPENDIX A

Study 1 –Reflux Ratio Parametric Data

Feed					
acetic acid	nitric	water	# stages	T (K)	P (atm)
10	100	10	15	298	1

reflux ratio	Bottoms			Tops		
	acetic acid	nitric	water	acetic acid	nitric	water
5	8.66095812	78.2535	8.085537	1.339042	21.746496	1.914463
6	8.80479855	78.05029	8.144909	1.195201	21.949708	1.855091
7	8.92130529	77.87903	8.199661	1.078695	22.120966	1.800339
8	9.0174014	77.73221	8.250386	0.982599	22.267787	1.749614
9	9.09792273	77.6045	8.29758	0.902077	22.395503	1.70242
10	9.166321	77.49202	8.341654	0.833679	22.507975	1.658346
11	9.22511404	77.39194	8.38295	0.774886	22.608064	1.61705
12	9.2761761	77.30207	8.42175	0.723824	22.697926	1.57825
13	9.32092838	77.22078	8.458295	0.679072	22.779224	1.541705
14	9.36046663	77.14674	8.492791	0.639533	22.853257	1.507209
15	9.39564844	77.07894	8.525414	0.604352	22.921062	1.474586
16	9.42715415	77.01653	8.556319	0.572846	22.983473	1.443681
17	9.4555301	76.95883	8.585643	0.54447	23.041173	1.414357
18	9.48121989	76.90527	8.613507	0.51878	23.094727	1.386493
19	9.50458733	76.85539	8.640018	0.495413	23.144606	1.359982
20	9.52593355	76.80879	8.665274	0.474066	23.191208	1.334726

Study 2 – Number of Stages Parametric Data

Feed					
acetic acid	nitric	water	T (K)	P (atm)	R. Ratio
10	100	10	298	1	15

number of stages	Bottoms			Tops		
	acetic acid	nitric	water	acetic acid	nitric	water
2	8.92590247	77.93858	8.135518	1.074098	22.061421	1.864482
3	9.12179584	77.64199	8.236212	0.878204	22.358008	1.763788
4	9.15901913	77.55383	8.287152	0.840981	22.446171	1.712848
5	9.16566479	77.52094	8.313393	0.834335	22.479058	1.686607
6	9.16673947	77.50625	8.327015	0.833261	22.493755	1.672985
7	9.16685557	77.49904	8.334107	0.833144	22.500963	1.665893
8	9.16683356	77.49536	8.337802	0.833166	22.504636	1.662198
9	9.16680674	77.49346	8.339729	0.833193	22.506536	1.660271
10	9.16677018	77.4914	8.341827	0.83323	22.508597	1.658173
11	9.16677018	77.4914	8.341827	0.83323	22.508597	1.658173
12	9.16677018	77.4914	8.341827	0.83323	22.508597	1.658173
13	9.16677018	77.4914	8.341827	0.83323	22.508597	1.658173
14	9.16677018	77.4914	8.341827	0.83323	22.508597	1.658173
15	9.16677018	77.4914	8.341827	0.83323	22.508597	1.658173

Study 3 – Feed Stage Location Parametric Data

Feed Stage Location	Percent of Feed Stream in Bottoms Stream			Percent of Feed Stream in Bottoms Stream		
	Acetic Acid	Nitric Acid	Water	Acetic Acid	Nitric Acid	Water
2	0.8921	0.7780	0.8280	0.1079	0.2220	0.1720
3	0.9167	0.7749	0.8342	0.0833	0.2251	0.1658
4	0.9750	0.7668	0.8572	0.0250	0.2332	0.1428
5	0.9925	0.7633	0.8745	0.0075	0.2367	0.1255
6	0.9978	0.7614	0.8884	0.0022	0.2386	0.1116
7	0.9993	0.7601	0.8999	0.0007	0.2399	0.1001
8	0.9998	0.7591	0.9096	0.0002	0.2409	0.0904
9	0.9999	0.7582	0.9179	0.0001	0.2418	0.0821
10	1.0000	0.7575	0.9250	0.0000	0.2425	0.0750
11	1.0000	0.7569	0.9312	0.0000	0.2431	0.0688
12	1.0000	0.7563	0.9365	0.0000	0.2437	0.0635
13	1.0000	0.7559	0.9411	0.0000	0.2441	0.0589
14	1.0000	0.7555	0.9448	0.0000	0.2445	0.0552
15	1.0000	0.7553	0.9475	0.0000	0.2447	0.0525

Study 4 – LK Recovery Parametric Data

Column Data

Minimum reflux ratio:	72.34891
Actual reflux ratio:	80.75802
Minimum number of stages:	63.27878
Number of actual stages:	126.5576
Feed stage:	116.9886
Number of actual stages above feed:	115.9886
Reboiler heating required (kW):	86920.53
Condenser cooling required (kW):	72108.75
Distillate temperature (K):	356.0455
Bottom temperature (K):	373.2601
Distillate to feed fraction:	0.010628

Number of Stages	15
LK: Nitric Acid	0.999
HK: Water	0.00001
Reboiler P (atm)	1.1
Condenser P (atm)	1

Stream Data

	Feed	Bottoms	Tops
Temperature K	298.15	373.26	356.05
Pressure atm	1.00	1.00	1.00
Vapor Frac	0.00	0.00	0.00
Mole Flow kmol/hr	9408.88	9308.88	100.00
Mass Flow kg/hr	176105.23	169808.35	6296.88
Volume Flow l/min	2929.35	3088.19	76.33
Enthalpy MMBtu/hr	-2545.44	-2479.46	-15.43
Mole Flow kmol/hr			
Acetic Acid	50.00	50.00	0.00
Nitric Acid	100.00	0.10	99.90
Water	9258.88	9258.79	0.09

LK Recovery	# Stages	mol water	mol acetic acid	mol nitric acid	% purity
0.00001	126.68928	0.0925888	0.00378375	99.9	0.999036
0.00013375	83.00154	1.2383752	0.00374135	99.9	0.987719
0.0002575	70.93	2.3841616	0.0036999	99.9	0.976655
0.00038125	63.50	3.529948	0.00365937	99.9	0.965837
0.000505	58.16	4.6757344	0.00361972	99.9	0.955255
0.00062875	54.03	5.8215208	0.00367768	99.9	0.944902
0.0007525	50.69	6.9673072	0.00354298	99.9	0.934773
0.00087625	47.92	8.1130936	4.05E-05	99.9	0.924888
0.001	45.58	9.25888	4.05E-05	99.9	0.915179

Study 5 – HK Recovery Parametric Data

Streams

HK Recovery	Bottoms			Tops		
	acetic acid	nitric	water	acetic acid	nitric	water
1.00%	9.9	0.1	0.358631	0.1	99.9	9.641369
2.00%	9.8	0.1	0.325732	0.2	99.9	9.674268
3.00%	9.7	0.1	0.30748	0.3	99.9	9.69252
4.00%	9.6	0.1	0.294835	0.4	99.9	9.705165
5.00%	9.5	0.1	0.285127	0.5	99.9	9.714873
6.00%	9.4	0.1	0.277992	0.6	99.9	9.722008
7.00%	9.3	0.1	0.271195	0.7	99.9	9.728805
8.00%	9.2	0.1	0.265275	0.8	99.9	9.734725
9.00%	9.1	0.1	0.260009	0.9	99.9	9.739991
10.00%	9	0.1	0.255247	1	99.9	9.744753

Study 6 – Reboiler Pressure Parametric Data

Column

Minimum reflux ratio:	0.46469719
Actual reflux ratio:	0.60144517
Minimum number of stages:	6.5845354
Number of actual stages:	15
Feed stage:	4.50291027
Number of actual stages above feed:	3.50291027
Reboiler heating required (kW):	39113.7538
Condenser cooling required (kW):	23872.8776
Distillate temperature (K):	368.497691
Bottom temperature (K):	375.970329
Distillate to feed fraction:	0.14183342

Number of Stages	15
LK: Nitric Acid	0.999
HK: Water	0.13334
Reboiler P (atm)	1.1
Condenser P (atm)	1

Streams

	Feed	Bottoms	Tops
Temperature K	298.15	375.97	368.50
Pressure atm	1.00	1.10	1.00
Vapor Frac	0.00	0.00	0.00
Mole Flow kmol/hr	9408.88	8074.39	1334.49
Mass Flow kg/hr	176105.23	147568.08	28537.15
Volume Flow l/min	2929.35	2692.80	488.54
Enthalpy MMBtu/hr	-2545.44	-2150.07	-343.36
Mole Flow kmol/hr			
Acetic Acid	50.00	49.99	0.01
Nitric Acid	100.00	0.10	99.90
Water	9258.88	8024.30	1234.58

Reboiler Pressure (atm)	Reb. Energy (kW)	Cond. Heat Energy (kW)	Total Heat (kW)
1.1	39113.75	23872.88	62986.63
1.5	40613.81	23694.98	64308.79
2	41901.90	23304.76	65206.65
2.5	42826.71	22837.34	65664.05
3	43530.62	22339.03	65869.65
3.5	44087.78	21830.45	65918.23
4	44541.24	21321.55	65862.79

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