1 of 2

DETERMINATION OF VAPOR-LIQUID EQUILIBRIUM DATA AND DECONTAMINATION
FACTORS NEEDED FOR THE DEVELOPMENT OF EVAPORATOR TECHNOLOGY FOR USE
IN VOLUME REDUCTION OF RADIOACTIVE WASTE STREAMS

BY

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THESIS

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DECONTAMINATION FACTORS NEEDED FOR THE DEVELOPMENT OF EVAPORATOR
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ABSTRACT

A program is currently in progress at Argonne National Laboratory to evaluate and develop evaporator technology for concentrating radioactive waste streams. By concentrating radioactive waste streams, disposal costs can be significantly reduced. To effectively reduce the volume of waste, the evaporator must achieve high decontamination factors so that the distillate is sufficiently free of radioactive material. One technology that shows a great deal of potential for this application is being developed by LICON, Inc. In this program, Argonne plans to apply LICON's evaporator designs to the processing of radioactive solutions. Concepts that need to be incorporated into the design of the evaporator include, criticality safety, remote operation and maintenance, and materials of construction. To design an effective process for concentrating waste streams, both solubility and vapor-liquid equilibrium data are needed. The key issue, however, is the high decontamination factors that have been demonstrated by this equipment.

Two major contributions were made to this project. First, a literature survey was completed to obtain available solubility and vapor-liquid equilibrium data. Some vapor-liquid data necessary for the project but not available in the literature was obtained experimentally. Second, the decontamination factor for the evaporator was determined using neutron activation analysis (NAA).

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MASTER

DEDICATION

It has been said that behind every good man is a great woman. This is very true in my case. Without the continuing love and support of my wife, Becca, this work would never have been completed. Therefore, it is to her that I dedicate this thesis.

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CHAPTER 1

INTRODUCTION

1.1 Evaporator Technology Program Overview

Radioactive liquid waste streams are being produced at various DOE sites around the country, which have the potential to be concentrated by evaporation. Reducing the volume of these waste streams could help reduce the cost of storage and alleviate long and short term storage problems. To effectively reduce the volume of waste, the evaporator must achieve high decontamination factors so that the distillate is sufficiently free of radioactive material. One technology that shows a great deal of potential for this application is an evaporator-concentrator being developed by LICON, Inc. (Pensacola Florida).

Waste solutions that contain low concentrations of radioactive material are prime candidates for volume reduction by evaporation. Waste streams from the TRUEX process fit into this category. The TRUEX process, a program under development at Argonne National Laboratory, is a solvent extraction process capable of separating, with high efficiency, small quantities of transuranic (TRU) elements from aqueous nitrate or chloride solutions. The resulting solutions can be sufficiently separated from TRU elements to warrant disposal as non-TRU waste. Waste and product solutions generated by the TRUEX process are fairly dilute and contain recoverable quantities of nitric acid. By processing these solutions through an evaporator, nitric acid can be recovered for reuse, thus minimizing the volume of the waste produced.

Another potential solution that would likely benefit from volume reduction through evaporation is the water from commercial power plant spent fuel pools. When a reactor is decommissioned or if the pool develops a leak, it may be necessary to remove and store the pool water. This contaminated water could be processed in an evaporator to significantly reduce the volume of radioactive waste.

1.2 Design Considerations

An evaporator system capable of processing a wide variety of solution compositions, must be designed to withstand the worst potential conditions. When reducing the volume of radioactive waste streams by concentrating them, a solution initially relatively dilute in radioactive material will be concentrated to a solution of higher activity that occupies a smaller space. Similarly, solutions that are slightly acidic will concentrate to highly acidic solutions. Therefore, to process both water from reactor cooling pools as well as TRUEX waste streams, the evaporator must be designed to handle highly acidic, and highly radioactive solutions. Design considerations for this type of system include, nuclear criticality safety, solution self-heating due to radioactive decay, corrosion of potential materials of construction, and remote operation and maintenance. To design an evaporator system for processing a variety of solution compositions and for recovering nitric acid from process and product streams, it is necessary to be able to predict vapor phase compositions in equilibrium with complex aqueous solutions.

The key issue for the development of this evaporator technology is to have a high decontamination factor (DF). The DF is defined as the concentration of radioactive material in the liquid phase divided by that in the vapor phase. When processing TRUEX waste streams the high DF would allow recycling of acids from the evaporator, further reducing the volume of the waste generated and minimizing the need to purchase new chemicals. Similarly, when processing other solutions like waste water from spent fuel pools, the high DF would mean that the distillate could potentially be disposed of as non-radioactive waste.

1.3 The Scope of this Study

The Separation Science and Technology Section in the Chemical Technology Division (CMT) at Argonne National Laboratory is heading a multi-year program to apply LICON's evaporator designs

to the processing of radioactive solutions. All of the design considerations discussed above have or will be studied mainly by Argonne personnel. Two major contributions were made to this project.

First, fundamental parameters needed to design the evaporator were determined. One needed parameter is the solubility of metal salts in aqueous nitric acid solutions. Solubility data was obtained solely through a literature survey. A second needed parameter is the vapor-liquid equilibrium composition of both the liquid and vapor phases as a function of pressure, temperature and solution composition. Vapor-liquid equilibrium data were initially obtained through a literature survey. Some additional data needed for the program was obtained experimentally. The vapor-liquid equilibrium data will be used to verify the vapor phase prediction model discussed above. These topics are addressed in Chapter 2.

Second, we determined the decontamination factor of the evaporator using neutron activation analysis (NAA). This is very important to the evaporator program since it must be shown that high DF's are in fact achievable. Both neutron activation analysis and how it was used to obtain the evaporator decontamination factor is discussed in Chapter 3.

CHAPTER 2

DESIGN PARAMETERS

2.1 Introduction

To design a process for concentrating process streams, both solubility and vapor-liquid equilibrium data are needed. Solubility data are needed to determine the amount of solution concentration that can be achieved without precipitating any components from the solution. These data are needed to predict the vapor phase concentrations for any of the various solution compositions that will be processed. Both these measurements will be used in setting conditions of pressure and temperature, predicting effluent rates and compositions for the condensate and the bottoms, and knowing to what degree a stream can be concentrated. These results may also have an impact on the design of the evaporator.

To determine what information was available, an in depth literature survey was completed. In this survey, references on aqueous nitric, sulfuric, phosphoric and oxalic acids were obtained, as well as the effects of various metal salts in solution. A summary of the literature surveys is given in the two sections below. An overview of the solubility data is given in Section 2.2 while vapor-liquid equilibrium data are discussed in Section 2.3. The complete literature surveys are given in Appendix A (solubility data) and Appendix B (vapor-liquid equilibrium data). Some vapor-liquid equilibrium data, that were not available in the literature, were obtained experimentally.

2.2 Literature Survey Summary of Solubility Data

The composition at which solids precipitate from mixed acid-metal salt solutions as a function of temperature, pressure, and composition is important in designing a process for concentrating liquid waste streams. The evaporator being developed at Argonne has the ability to deal with small amounts of solids in solution. It is desirable, however, to operate the evaporator at a solution composition that would not precipitate solids. To accomplish this, it is essential to know the solubility of nitrate salts

as a function of temperature and solution composition. The nitrate salts of major importance in this project are aluminum, calcium, iron, lanthanum, nickel, samarium, sodium, and uranyl nitrate. Solubility data were obtained for each of these salts as a function of acid concentration at constant temperatures.

From the solubility data a few trends were noted. First, the solubility of a salt decreases with increasing nitric acid concentration. In some cases, such as with sodium nitrate, at very high acid concentrations solubility begins to increase after reaching a minimum. Second, solubility increases with increasing temperature. This effect, however, diminishes with increasing acid concentration. Third, the presence of more than one salt decreases the solubility of all salts compared to the single salt solubility. While the data were generally presented in units of weight percent, it is more useful to know the solubilities in units of molarity of the salt as a function of acid molarity. Solution densities, calculated at 25 °C, were used to convert the solubility data from weight percent to molar concentrations of salt and nitric acid. From plots of the data, it was found that aluminum nitrate had the lowest solubility of the nitrate salts studied. Solubility data at temperatures other than 25 °C were also collected for some of the salts.

2.3 Literature Survey Summary of Vapor-Liquid Equilibrium Data

To design the evaporator for concentrating specific waste streams, it is important to know the equilibrium composition of both the liquid and vapor phases as a function of temperature, pressure, and composition of aqueous solution. As discussed in Section 1.2, the evaporator should be designed for the worst potential operating condition. This will occur when processing TRUEX waste streams. The compositions of the TRUEX waste streams are mainly aqueous nitric acid solutions containing metal nitrate salts. Some solutions, however, may also contain other acids such as sulfuric, phosphoric, and oxalic. Thus, it is important to understand the effects of these acids on the system.

A literature survey was carried out to evaluate the effect that metal nitrate salts have on the vapor-liquid equilibria of aqueous solutions of HNO_3 . The most useful source of information was a set of five books by Wichterle et al. [WICHTERLE-1973, WICHTERLE-1976, WICHTERLE-1979, WICHTERLE-1982, WICHTERLE-1985] which gives a bibliography of almost 8500 vapor-liquid equilibrium systems studied from 1900 through 1984. Many applicable references were obtained from this source for both nitric acid-water and nitric acid-water-nitrate salt systems.

In the TRUEX waste streams, the nitrate salts present in the largest concentrations are Al, Ca, Fe, La, Na, Ni, and UO_2 nitrates. Therefore, these HNO_3 - H_2O -nitrate salts systems were studied. The review discussed the effect of that system pressure and salt concentration, in the liquid phase, had on the vapor phase composition and the boiling point of the system.

Several trends were evident from this survey. Based upon data at various pressures, reducing the pressure decreases the boiling point of the system, but has little effect on the vapor phase composition. The presence of salts, with the exception of potassium nitrate, tends to salt out the nitric acid into the vapor phase, thus enriching the vapor in nitric acid. The solution boiling point also tends to increase as the salt concentration increases.

Multiple acid systems, including nitric acid-water-sulfuric acid and nitric acid-water-phosphoric acid were also reviewed. Information on these systems was very limited. Based upon these data, the presence of the second acid tended to salt out the nitric acid into the vapor phase. No data were found on the nitric acid-water-oxalic acid system, nor was any found on multiple acid-water-salt systems. One multiple acid salt system important to the design of this project was studied using the laboratory still described in Section 2.4.

2.4 Laboratory Vapor-Equilibrium Still

The literature survey was also used to determine the experimental equipment needed to perform vapor-liquid equilibrium studies. Ten papers were found which used the circulation method to

determine the vapor liquid equilibrium for the nitric acid-water-nitrate salt system. The most common circulation apparatus used was the Bushmakín [BUSHMAKIN] still and modified versions of that apparatus such as the one described by Gorodetskii [GORODETSKII]. Hála [HALA-1967] compares 27 circulation vapor-liquid equilibrium stills. Among the stills compared are the stills by Bushmakín and Altsheler. The Bushmakín still is considered by Hála [HALA-1967] to be a simple still, reaches equilibrium in 2-3 hours, and does not measure the temperature accurately. The Altsheler [ALTSHELER] still is considered a very precise still, reaches equilibrium in about 40 minutes, but has no means of measuring temperature. This still, shown in Fig. 2-1, is currently manufactured by LUREX Scientific (South Vineland, NJ). It may be easily modified to measure the temperature of the vapor and liquid phases. Owensby [OWENSBY] inserted two thermocouples, one for the vapor and one for the liquid phase, through the top of the Altsheler still. With these considerations in mind, it appeared that Altsheler still would be adequate for collecting data of systems that were not available in the literature.

2.5 Vapor-Liquid Equilibrium Verification Studies

Experiments were conducted to reproduce literature data for the binary nitric acid-water system at atmospheric pressure. The experiments were carried out in a circulation type equilibrium still developed by Altsheler et al. [ALTSHELER], which was purchased from LUREX Scientific. The still was modified to measure equilibrium temperatures by replacing the glass stopper in the top of the still with an adapter that accepts two thermocouples. One thermocouple measured the liquid temperature and one the vapor. The thermocouples were coated with PFA Teflon to protect them from the corrosive acid environment. Data from the thermocouples were collected on a PC using a "White Box Interface System", purchased from Omega. The temperature resolution and accuracy of the data acquisition card for J-type thermocouples is given in Table 2-1.

Fig. 2-1. Section View of the Equilibrium Still

Table 2-1. Resolution and Accuracy of Data Acquisition Card for a J-type thermocouple

Range	Resolution	Accuracy
-80 to 100°C	0.3°C	±1.6°C
100 to 760°C	0.2°C	±1.2°C

Nitric acid solutions were prepared close to the desired equilibrium compositions from 15.8 M HNO₃ and DI water. In the first experiment 444 ml of solution were placed in the still. For all subsequent experiments 500 ml of solution were used. The stopcock at the bottom of the still was adjusted to allow fluid flow from the reflux line to the heating section of the still. The vapor sample began to collect in the vapor phase reservoir after 20-30 minutes of heating. Another 30 minutes was required before the vapor phase reservoir was filled and circulation began. The system was allowed to run for at least another hour.

Temperature data were collected every 5 seconds. For the first five runs, a 30.48 cm thermocouple was used to measure the liquid phase temperature and a 15.24 cm thermocouple was used for vapor phase temperatures. During these runs the vapor phase temperatures were about 100°C. In the last run a 38.10 cm thermocouple was used to measure the liquid temperature and a 30.48 cm thermocouple for the vapor phase. In this latter run the difference in equilibrium temperature between the two thermocouples was 0.9 °C, with the liquid phase having the higher temperature. Reported equilibrium temperature data were determined by averaging the liquid phase temperatures over the last hour of operation.

After the heating was terminated, the solution was allowed to cool in the still for approximately 15 hours. When collecting samples from the still, the first few milliliters of each phase was discarded. The concentration of the sample was determined by titrating with ≈ 0.5 M NaOH. Each titration was performed three times and the results were averaged. The density of the samples was found by weighing 5 ml of sample, except for the last data point where 1 ml of sample was used. From the density and molar concentration of acid, the wt% of HNO₃, wt% H₂O and mol% HNO₃ were calculated.

The concentration of the NaOH was standardized by titrating with potassium hydrogen phthalate (KHP). Again three titrations were performed. The average concentration was $0.498 \pm 0.0012 \text{ M}$ with a percent error of 2.3%. Before the last sample was analyzed, a new solution of NaOH was prepared and standardized with KHP. The average concentration was $0.512 \pm 0.0006 \text{ M}$.

The results of the experiments are presented in Table 2-2. The data in Table 2-2 were plotted in Fig. 2-2 and Fig. 2-3 with literature data. It can be seen from the figures that the data agree very well.

Table 2-2. Vapor Liquid Equilibrium Data for the Binary $\text{HNO}_3\text{-H}_2\text{O}$ System at Atmospheric Pressure

[HNO_3] M		density (g/ml)		wt% HNO_3		wt% H_2O		mol% HNO_3		Temp (°C)
Liquid	Vapor	Liquid	Vapor	Liquid	Vapor	Liquid	Vapor	Liquid	Vapor	
3.56	0.139	1.106	1.066	1.12	0.04	4.41	5.24	6.78	0.24	104.2
5.15	0.48	1.16	1.03	1.62	0.15	4.18	5.00	9.99	0.86	106.9
6.55	1.20	1.185	1.029	2.06	0.38	3.86	4.77	13.24	2.22	108.5
8.78	2.69	1.270	1.094	2.77	0.85	3.58	4.62	18.07	4.98	111.8
12.84	9.89	1.352	1.288	4.04	3.12	2.72	3.32	29.83	21.14	119.0
14.92	13.81	1.410	1.390	4.70	4.35	2.35	2.60	36.37	32.35	120.9

Fig. 2-2. Comparison of Vapor versus Liquid Phase Compositions with Literature Data for the $\text{HNO}_3\text{-H}_2\text{O}$ System

Fig. 2-3. Comparison of Equilibrium Temp. versus Liquid Phase Compositions with Literature Data for the $\text{HNO}_3\text{-H}_2\text{O}$ System

2.6 New Vapor-Liquid Equilibrium Data

From the verification study on the binary nitric acid - water system, it was shown that the experimental procedure for operating the equilibrium still as well as collecting and analyzing samples gave results that agreed well with literature. The next step then was to study a system for which data was not available in the literature. No data was available for multiple acid salt systems. A second acid likely to be present in solutions to be processed in the evaporator is sulfuric acid. From the literature review on the solubility of nitrate salts, it was found that aluminum nitrate had the lowest solubility of all the salts likely to be present in potential process streams. Sodium nitrate is also likely to be present in significant quantities and like aluminum has low solubility. Furthermore, sodium nitrate solutions have been studied extensively and present little difficulty to model thermodynamically. Therefore, it was decided to study the nitric acid-sulfuric acid-sodium nitrate system.

It is desirable to study this system using both low and high salt concentrations over a large range of nitric acid concentrations. While working with these solutions, however, it is necessary that the salt remain soluble at room temperature since samples will be collected and analyzed at this temperature. From solubility data, presented in Appendix A, it can be seen that 2 M NaNO_3 is soluble in solutions containing as much as 6 M HNO_3 . It was experimentally determined that the salt would remain completely soluble in a solution containing 5 M HNO_3 -1.5 M H_2SO_4 -2 M NaNO_3 , while some solid would form in a solution containing 5 M HNO_3 -2 M H_2SO_4 -2 M NaNO_3 . Therefore it was decided that the following solution compositions would be studied: 1,2,4,5 M HNO_3 - 0.5, 1, 1.5 M H_2SO_4 - 0.1, 1, 2 M NaNO_3 .

Solutions were prepared such that the equilibrium concentration of each component would be close to that listed above. Initially 500 ml of solution was placed into the equilibrium still. When equilibrium was achieved, approximately 400 ml of solution remained in the liquid phase. To ensure that all the salt remains in solution, it was assumed that this number could be as low as 390 ml. Since the activity of sulfuric acid is extremely low, virtually none is transferred to the vapor phase. Similarly,

sodium nitrate should also remain completely in the liquid phase. Therefore, the volume of sulfuric acid and mass of sodium nitrate needed to make one liter of solution, which resulted in the desired equilibrium composition, was found using the following equations:

$$vol (ml) H_2SO_4 = [FINAL H_2SO_4 (M)] \left[\frac{0.390}{0.5} \right] \left[\frac{1000}{18} \right] \quad (2-1)$$

$$Na (gr) = [FINAL Na (M)] \left[\frac{0.390}{0.5} \right] 84.99 \quad (2-2)$$

Using the above equations and the desired equilibrium solution compositions, it was determined that solutions should be prepared using combinations of 60, 125, 250, 315 ml of 15.8 M HNO₃, with 22, 44, 66 ml of 18.0 M H₂SO₄, and 6.65, 66.5, 135.0 g NaNO₃.

Temperature data for the liquid and vapor phases were recorded during the experiment using a 38.10 cm and 30.48 cm J-type thermocouple's, respectively. Approximately one hour was required for the solutions to reach equilibrium. The system was allowed to run for another two hours to allow sufficient reflux of the vapor phase. After shutting the heating off, the system was allowed to cool for about 15 hours. At this time the liquid and vapor samples were collected from the still and analyzed.

The concentrations of sulfuric and nitric acid in the liquid phase were obtained by an organic titration procedure using 0.5 M cyclohexylamine in methanol. This procedure was received from Brinkmann; Application Bulletin No. 39/1 e. According to the procedure, titrating sulfuric - nitric acid mixtures give two potential jumps. The first potential jump corresponds to the sum of HNO₃ + 1/2 H₂SO₄, and the difference between the first and second potential jump corresponds to the remaining half of the sulfuric acid. The bulletin points out that various titrating reagents; such as piperidine, alcoholic KOH, potassium methylate, and tetrabutylammonium hydroxide, have been used in the literature. Except for piperidine all the others are affected by atmospheric CO₂, which can cause difficulties in titration as well as produce serious errors in the results. As a titrating reagent, cyclohexylamine

maintains a constant titre, unaffected by atmospheric CO₂. Methanol usually gives a zero result on a blank control sample.

The titrating reagent was standardized by titrating 2 ml of 1 M H₂SO₄ in 90 ml of methanol. From this titration two factors were calculated:

$$t_1 = \frac{4.000}{EP1} \quad (2-3)$$

$$t_2 = \frac{4.000}{EP2 - EP1} \quad (2-4)$$

where t_1 = reagent consumption up to the first endpoint (EP1)

t_2 = the difference between reagent consumption at the

first endpoint (EP1) and the second endpoint (EP2).

Unknown samples were prepared in the same manner as the standard by placing a small quantity of the sample in a beaker, and adding 90 ml of methanol. The concentrations of sulfuric and nitric acids were then found using the following equations:

$$H_2SO_4 \text{ (g/kg)} = \frac{(EP2 - EP1) \cdot C_1 \cdot t_2}{C_3} \quad (2-5)$$

$$HNO_3 \text{ (g/kg)} = \frac{(EP1 - (EP2 - EP1)) \cdot C_2 \cdot t_1}{C_3} \quad (2-6)$$

where C_1 = equivalent weight of sulfuric acid = 49038.8

C_2 = equivalent weight of nitric acid = 31506.5

C_3 = mg of sample titrated

The molar concentration of each acid was found using equations (2-7) and (2-8)

$$[H_2SO_4] (M) = [H_2SO_4] (g/kg) \frac{\rho}{98.0776} \quad (2-7)$$

$$[HNO_3] (M) = [HNO_3] (g/kg) \frac{\rho}{63.0130} \quad (2-8)$$

where ρ is the density of the solution in g/ml.

As mentioned above, virtually no sulfuric acid or sodium nitrate should transfer to the vapor phase. Therefore, the vapor phase should consist of only nitric acid and water. Thus, the concentration of nitric acid in the vapor phase was determined by titration with NaOH. As before the concentration of NaOH was standardized using KOH. The average concentration of NaOH was 0.509 M NaOH.

The experimental results for the HNO_3 - H_2SO_4 - $NaNO_3$ system at atmospheric pressure were organized in sets of constant sodium nitrate concentration and are given in Tables 2-3, 2-4 and 2-5. The data are plotted in Figs. 2-4, 2-5, 2-6, 2-7, 2-8 and 2-9. The convention used for the sample name is as follows. The number before the first M corresponds to the approximate equilibrium concentration of nitric acid in the liquid phase. The number between the first M and the second M corresponds to the approximate equilibrium concentration of sulfuric acid in the liquid phase. Similarly, the number between the second and the third M corresponds to the approximate equilibrium concentration of sodium nitrate in the liquid phase. Where the two numbers are used, a decimal place should be placed between them. For example the sample name 5M1.5M1M means that the equilibrium composition of the solution should be approximately 5 M HNO_3 -1.5 M H_2SO_4 -1 M $NaNO_3$.

It can be seen from the figures that the data follows expected trends. That is, the equilibrium composition of the vapor phase and the equilibrium temperature increase with increasing concentrations of nitric acid, sulfuric acid or sodium nitrate in the liquid phase. The data was also graphed for constant sulfuric acid concentrations. These graphs are given in Appendix C.

Table 2-3. Compositions of Prepared Solutions and Equilibrium Solutions as well as Equilibrium Temperatures for Solutions Containing HNO_3 - H_2SO_4 -0.09 M NaNO_3

Sample	Density of Liquid Phase (g/ml)	[H_2SO_4] (M)		[HNO_3] (M)		Vapor Phase [HNO_3] (M)	Temp (°C)
		Prepared	Liquid Phase	Prepared	Liquid Phase		
1M05M01M	1.064	0.39	0.45	0.94	1.05	0.014	102.4
2M05M01M	1.112	0.39	0.46	2.00	2.30	0.081	104.2
4M05M01M	1.178	0.39	0.46	3.90	4.47	0.446	107.4
5M05M01M	1.227	0.39	0.47	5.09	5.81	0.870	109.2
1M1M01M	1.100	0.79	0.96	0.95	1.14	0.030	102.9
2M1M01M	1.138	0.80	0.95	1.94	2.26	0.103	104.9
4M1M01M	1.203	0.79	0.93	3.90	4.47	0.593	108.6
5M1M01M	1.234	0.79	0.92	4.93	5.59	1.101	110.6
1M15M01M	1.130	1.19	1.38	0.97	1.10	0.038	103.9
2M15M01M	1.164	1.20	1.40	1.98	2.30	0.148	106.1
4M15M01M	1.235	1.20	1.39	3.97	4.46	0.804	110.0
5M15M01M	1.246	1.17	1.37	4.89	5.34	1.432	111.9

Table 2-4. Compositions of Prepared Solutions and Equilibrium Solutions as well as Equilibrium Temperatures for Solutions Containing HNO_3 - H_2SO_4 -0.92 M NaNO_3

Sample	Density of Liquid Phase (g/ml)	[H_2SO_4] (M)		[HNO_3] (M)		Vapor Phase [HNO_3] (M)	Temp (°C)
		Prepared	Liquid Phase	Prepared	Liquid Phase		
1M05M1M	1.148	0.39	0.46	0.95	1.16	0.029	103.9
2M05M1M	1.151	0.39	0.45	1.99	2.31	0.116	105.6
4M05M1M	1.218	0.40	0.46	4.04	4.53	0.606	109.0
5M05M1M	1.239	0.39	0.45	5.05	5.57	1.117	110.8
1M1M1M	1.142	0.80	0.93	0.96	1.11	0.049	104.3
2M1M1M	1.178	0.79	0.93	1.97	2.29	0.169	106.3
4M1M1M	1.236	0.78	0.92	3.95	4.42	0.778	110.1
5M1M1M	1.258	0.79	0.92	4.94	5.46	1.390	112.0
1M15M1M	1.167	1.19	1.40	0.95	1.12	0.078	105.1
2M15M1M	1.192	1.18	1.38	1.97	2.26	0.244	107.0
4M15M1M	1.257	1.17	1.38	3.88	4.36	0.998	110.5
5M15M1M	1.286	1.17	1.39	4.93	5.40	1.752	112.8

Table 2-5. Compositions of Prepared Solutions and Equilibrium Solutions as well as Equilibrium Temperatures for Solutions Containing HNO_3 - H_2SO_4 -1.86 M NaNO_3

Sample	Density of Liquid Phase (g/ml)	[H_2SO_4] (M)		[HNO_3] (M)		Vapor Phase [HNO_3] (M)	Temp ($^{\circ}\text{C}$)
		Prepared	Liquid Phase	Prepared	Liquid Phase		
1M05M2M	1.158	0.40	0.45	0.96	1.11	0.053	104.6
2M05M2M	1.196	0.39	0.45	1.97	2.28	0.177	106.4
4M05M2M	1.264	0.38	0.46	3.81	4.44	0.800	110.3
5M05M2M	1.287	0.39	0.45	4.99	5.51	1.401	112.1
1M1M2M	1.191	0.79	0.93	0.93	1.10	0.085	105.2
2M1M2M	1.228	0.79	0.94	1.97	2.28	0.272	107.2
4M1M2M	1.275	0.79	0.93	3.95	4.36	1.020	111.2
5M1M2M	1.307	0.79	0.91	4.96	5.41	1.703	113.2
1M15M2M	1.218	1.18	1.41	0.95	1.08	0.135	106.4
2M15M2M	1.247	1.17	1.39	2.00	2.25	0.360	108.2
4M15M2M	1.298	1.22	1.42	3.87	4.26	1.346	111.9
5M15M2M	1.344	1.18	1.41	4.93	5.36	2.244	114.2

Fig. 2-4. Concentration of Nitric Acid in the Vapor Phase versus the Liquid Phase for the HNO_3 - H_2SO_4 -0.09 M NaNO_3 system at 760 mmHg

Fig. 2-5. Equilibrium Temperature Versus Nitric Acid Concentration in the Liquid Phase for the HNO_3 - H_2SO_4 -0.09 M NaNO_3 system at 760 mmHg

Fig. 2-6. Concentration of Nitric Acid in the Vapor Phase Versus the Liquid Phase for the HNO_3 - H_2SO_4 -0.92 M NaNO_3 system at 760 mmHg

Fig. 2-7. Equilibrium Temperature Versus Nitric Acid Concentration in the Liquid Phase for the HNO_3 - H_2SO_4 -0.92 M NaNO_3 system at 760 mmHg

Fig. 2-8. Concentration of Nitric Acid in the Vapor Phase Versus the Liquid Phase for the HNO_3 - H_2SO_4 -1.86 M NaNO_3 system at 760 mmHg

Fig. 2-9. Equilibrium Temperature Versus Nitric Acid Concentration in the Liquid Phase for the HNO_3 - H_2SO_4 -1.86 M NaNO_3 system at 760 mmHg

Since neither sulfuric acid nor sodium nitrate transfer from the liquid to the vapor phase the ratio $([H_2SO_4]_L)/([H_2SO_4]_I)$ should equal the ratio $([Na]_L)/([Na]_I)$. Here L and I represent the liquid and initial (prepared) samples, respectively. To compare these ratios, it was necessary to have a means of measuring the sodium ion concentration. The sodium concentration was found using a Ross Sodium Ion Selective Electrode (ISE). The electrode was calibrated by obtaining mV readings from standard solutions of known sodium concentrations. Three known concentrations were used 0.001, 0.005, and 0.01 M Na. These were prepared by placing 0.1, 0.5 and 1.0 ml of 1 M Na standard, purchased from Orion, and 10 ml of Ionic Strength Adjustor (ISA), also purchased from Orion, into 100 ml volumetric flasks and filling with DI water. The ISA, consisting of 4 M NH_4OH and 4 M NH_4Cl , was used to adjust the pH of the sample to between 9-10. This is required for proper operation of the electrode. Calibration data were plot on a semi-log scale with the molar concentration of the standard on the log axis. A calibration curve was obtained by fitting the data with equation (2-9)

$$mV = A + B \ln ([Na] \text{ M}) \quad (2-9)$$

where A and B are fit constants. An example of calibration data is given in Table 2-6.

Table 2-6. Sample Calibration Data for the Sodium ISE

Standard Concentration [Na] (<u>M</u>)	mV
0.001	-100
0.05	-60
0.01	-43

The data from Table 2-6 is shown in Fig. 2-10 with the calibration curve. In this case the fit constants were $A=71.150$ and $B=24.772$ with $R^2=0.9999$.

Fig. 2-10. Sample Calibration Curve for the Sodium Ion Selective Electrode

Samples were prepared by placing a small amount of solution, from 0.25 to 3 ml, in a 100 ml volumetric flask adding 10 ml of ISA and filling with DI water. The volume of solution used was chosen such that the concentration of sodium, in the diluted sample, would fall between the high and low points on the calibration curve. The concentration of sodium in the sample was obtained by solving the calibration curve for the sodium concentration as a function of mV and multiplying by a term to correct for the dilution. This is shown in equation (2-10)

$$[Na] (M) = EXP \left(\frac{mV - A}{B} \right) \cdot \frac{100}{V} \quad (2-10)$$

where A and B are curve fit constants and V is the volume (ml) of solution placed in the 100 ml volumetric flask. The sodium concentration for the samples listed in Tables 2-3, 2-4, and 2-5 are given in 2-7, 2-8, and 2-9.

The initial concentration of sodium, [Na] I, and the equilibrium concentration of sodium, [Na] L, are less than they should be. This is likely do to the inaccuracy of the ISE. It was assumed that this

error would be approximately the same for both the initial and liquid phase samples. If this assumption is true, then the ratio $([\text{Na}] \text{ L})/([\text{Na}] \text{ I})$ should be accurate. A comparison between the ratios for sodium $([\text{Na}] \text{ L})/([\text{Na}] \text{ I})$ and sulfuric acid $([\text{H}_2\text{SO}_4] \text{ L})/([\text{H}_2\text{SO}_4] \text{ I})$, listed in Tables 2-7, 2-8 and 2-9, showed the percent difference to be less than 4%. As expected, the sulfuric acid and sodium have concentrated by the same factor.

Table 2-7. Comparison of the Ratio of Sodium Concentration in the Liquid and Initial Samples with the Same Ratio for Sulfuric Acid for Equilibrium Solutions of Approximately 0.09 M Na

Sample	Vol. (ml)	mV I	mV L	A	B	[Na] I	[Na] L	[Na]L/ [Na]I	[Acid] L/I	% Diff
1M05M01M	5	-69	-65	71.150	24.772	0.070	0.082	1.18	1.173	-0.21
2M05M01M	3	-82	-77	71.150	24.772	0.069	0.084	1.22	1.180	-3.67
4M05M01M	3	-82	-78	71.150	24.772	0.069	0.081	1.18	1.180	0.41
5M05M01M	3	-82	-78	71.150	24.772	0.069	0.081	1.18	1.200	2.08
1M1M01M	2	-90	-86	71.150	24.772	0.075	0.088	1.18	1.212	3.02
2M1M01M	2	-91	-87	71.150	24.772	0.072	0.084	1.18	1.184	0.75
4M1M01M	2	-91	-88	71.150	24.772	0.072	0.081	1.13	1.176	4.05
5M1M01M	2	-92	-89	71.150	24.772	0.069	0.078	1.13	1.167	3.26
1M15M01M	2	-92	-88	71.150	24.772	0.069	0.081	1.18	1.153	-1.92
2M15M01M	2	-91	-88	72.489	25.130	0.075	0.084	1.13	1.167	3.47
4M15M01M	2	-92	-88	72.489	25.130	0.072	0.084	1.17	1.155	-1.49
5M15M01M	2	-92	-88	72.489	25.130	0.072	0.084	1.17	1.171	-0.13

Table 2-8. Comparison of the Ratio of Sodium Concentration in the Liquid and Initial Samples with the Same Ratio for Sulfuric Acid for Equilibrium Solutions of Approximately 0.92 M Na

Sample	Vol. (ml)	mV I	mV L	A	B	[Na] I	[Na] L	[Na]L/ [Na]I	[Acid] L/I	% Diff
1M05M1M	0.5	-68	-64	72.489	25.130	0.747	0.875	1.17	1.187	1.25
2M05M1M	0.5	-68	-64	72.489	25.130	0.747	0.875	1.17	1.160	-1.06
4M05M1M	0.5	-68	-64	72.489	25.130	0.747	0.875	1.17	1.143	-2.63
5M05M1M	0.5	-68	-64	72.489	25.130	0.747	0.875	1.17	1.139	-2.98
1M1M1M	0.4	-74	-70	71.489	25.130	0.765	0.897	1.17	1.158	-1.22
2M1M1M	0.4	-74	-70	71.489	25.130	0.765	0.897	1.17	1.172	-0.07
4M1M1M	0.4	-74	-70	71.489	25.130	0.765	0.897	1.17	1.177	0.41
5M1M1M	0.4	-72	-68	73.489	25.130	0.765	0.897	1.17	1.162	-0.95
1M15M1M	0.3	-80	-75	73.489	25.130	0.742	0.905	1.22	1.179	-3.51
2M15M1M	0.3	-80	-76	73.489	25.130	0.742	0.870	1.17	1.170	-0.19
4M15M1M	0.3	-81	-77	73.489	25.130	0.713	0.836	1.17	1.173	0.06
5M15M1M	0.25	-85	-80	73.489	25.130	0.730	0.890	1.22	1.185	-2.96

Table 2-9. Comparison of the Ratio of Sodium Concentration in the Liquid and Initial Samples with the Same Ratio for Sulfuric Acid for Equilibrium Solutions of Approximately 1.86 M Na

Sample	Vol. (ml)	mV I	mV L	A	B	[Na] I	[Na] L	[Na]L/ [Na]I	[Acid] L/I	% Diff
1M05M2M	0.25	-67	-63	71.150	24.772	1.514	1.779	1.18	1.139	-3.18
2M05M2M	0.25	-67	-64	71.150	24.772	1.514	1.709	1.13	1.146	1.52
4M05M2M	0.25	-67	-63	71.150	24.772	1.514	1.779	1.18	1.210	2.90
5M05M2M	0.25	-68	-64	71.150	24.772	1.454	1.709	1.18	1.151	-2.14
1M1M2M	0.25	-67	-63	73.489	25.130	1.493	1.751	1.17	1.181	0.71
2M1M2M	0.25	-67	-63	73.489	25.130	1.493	1.751	1.17	1.189	1.42
4M1M2M	0.25	-67	-63	73.489	25.130	1.493	1.751	1.17	1.177	0.41
5M1M2M	0.25	-67	-63	73.489	25.130	1.493	1.751	1.17	1.151	-1.88
1M15M2M	0.25	-67	-63	73.435	25.239	1.533	1.796	1.17	1.191	1.59
2M15M2M	0.25	-68	-64	73.435	25.239	1.473	1.727	1.17	1.186	1.24
4M15M2M	0.25	-68	-64	73.435	25.239	1.473	1.727	1.17	1.162	-0.85
5M15M2M	0.25	-68	-63	73.435	25.239	1.473	1.796	1.22	1.192	-2.24

2.7 Suggestions for Future Work

In this study, data for only one system, which was not available the literature, were obtained at atmospheric pressure. If waste streams will contain other acids in significant quantities, then it may be useful to study systems containing those acids. Similarly, only one salt was studied in this system. Since potential solutions to be processed in the evaporator will likely contain many salts, it may be useful to study systems containing two or more salts. For TRUEX waste streams aluminum and sodium are present in the largest quantities. Therefore, it might be helpful to study a system containing both aluminum nitrate and sodium nitrate. Finally, this study was conducted at atmospheric pressure. Since the evaporator will operate under vacuum, it may be of use to obtain equilibrium data at pressures close to the evaporator operating pressure.

CHAPTER 3

DETERMINATION OF THE EVAPORATOR DECONTAMINATION FACTOR

3.1 Introduction

During normal operation of the evaporator a decontamination factor (DF) of 10^5 to 10^7 must be obtained in order to reuse distillate or dispose of it as non-radioactive waste. The decontamination factor is defined as follows

$$DF = \frac{[Radioactive\ Salts\ Liquid\ Phase]}{[Radioactive\ Salts\ Vapor\ Phase]} \quad (3-1)$$

A DF of 10^7 would mean that the vapor phase has 10^7 less radioactive salts than the liquid phase.

To measure decontamination factors of the evaporator, Argonne originally planned to use radioactive tracers. Detection limits for tracers are typically very low, so DF's of 10^4 to 10^5 are easily measured. The problem with tracers, however, is the equipment would be contaminated following their use. This complicates future work on the evaporator, and increases the cost associated with future tests. In addition, use of radioactivity at LICON (Pensacola Florida) is prohibited. Therefore, it was necessary to have a method to measure low concentrations of a material in a solution without introducing radioactivity into the evaporator. An analytical procedure called neutron activation is one such method that can be used to "measure" the concentration of a tracer element at low concentrations; and thus determine the DF of the evaporator.

3.2 Neutron Activation Analysis

Neutron activation is simply the creation of a radioactive element as a result of neutron interaction with a stable isotope. When a neutron collides with a nucleus, the following reactions may occur: elastic scattering (n,n), inelastic scattering (n,n'), radiative capture (n, γ), charge-particle reaction (n, α) or (n,p), neutron producing reaction (n,2n) and fission reactions (n,f). These reactions occur

according to their neutron interaction cross-section. This cross-section is simply the probability that a neutron will interact with the target. The most useful reaction in neutron activation analysis (NAA) is radiative capture, which can be denoted as

where $Z^{(A+1)*}$ is called the compound nucleus, which is usually in an excited state. It can de-excite with the emission of a gamma-ray called a prompt gamma. In many cases the $Z^{(A+1)}$ also decays emitting gamma rays called delayed gammas. These delayed gammas can be detected using a high resolution gamma sensitive detector.

3.3 NAA Facilities

Neutron activation analysis is readily available for use at the University of Illinois. The operating TRIGA reactor can provide a thermal neutron flux of $3.3 \times 10^{12} \text{ n cm}^{-2} \text{ sec}^{-1}$ at 1.5 MW, using the "lazy-susan" facility, and is capable of irradiating upwards to eighty samples simultaneously. For higher neutron fluxes an in core facility for thermal ($1.2 \times 10^{13} \text{ n cm}^{-2} \text{ sec}^{-1}$ at 1.5 MW) and epithermal ($1.0 \times 10^{12} \text{ n cm}^{-2} \text{ sec}^{-1}$ at 1.5 MW) irradiation positions are also available. The neutron activation analysis facility, located in the Materials Research Laboratory, is equipped with three distinct counting systems. These include a 19% efficient germanium detector in conjunction with a Compton Suppression system, a 13% efficient Gamma-X detector capable of detecting both x- and gamma- rays and a 24% efficient germanium detector in conjunction with a sample changer. All data collection and analysis routines incorporate ORTEC hardware and software with three personal computers.

3.4 Radioisotope for Determining the Evaporator DF

To use neutron activation for measuring decontamination factors in the evaporator, it is necessary to find a stable, inexpensive element with a large cross-section for radiative capture.

Therefore, a review of elements was initiated. Based on this review, samarium is one such element that may be suitable for our application. Samarium-152 has a radiative capture cross-section of $\sigma_r=208$ barns. The radiative capture reaction produces ^{153}Sm , which has a half-life of 1.929 d, and emits a 103.2 keV gamma. This gamma-ray falls within the region of highest resolution for the detector. Furthermore, the 2-day half-life allows sufficient time for analysis and relatively rapid decay for radioactive waste production not to be of concern.

3.5 Calculations to Convert Counts to Concentration

The number of radioactive atoms produced during irradiation is measured in terms of the rate of decrease or decay of the induced radioactivity. The law of radioactive decay states that the number of atoms which disintegrate per unit time (dN/dt) is proportional to the total number of radioactive atoms, N , present. Hence

$$\frac{dN}{dt} = -\lambda N \quad (3-3)$$

where λ is the radioactive decay constant, which represents the probability that an atom will decay in a unit time. Integration of (3-3) yields

$$N(t) = N_0 e^{-\lambda t} \quad (3-4)$$

where

N_0 = the number of radioactive atoms present at some original time, $t=0$,

N = the number present at time t .

The decay constant is related to the half-life as follows

$$t_{\frac{1}{2}} = \frac{0.693}{\lambda} \quad (3-5)$$

Since half-life data is readily available one can easily determine the decay constant by equation (3-5).

Equation (3-3) described radioactive decay. During irradiation, radioactive nuclei are being produced and equation (3-3) can be modified to include this production. Assuming that a single radionuclide is produced, the increase in number of radionuclides is the product of the neutron flux, ϕ , the neutron activation cross-section, σ_{act} , and the number of target nuclei, N^* . Incorporating the production term into equation (3-3) gives

$$\frac{dN}{dt} = \sigma_{act}\phi N^* - \lambda N \quad (3-6)$$

Thus the first term in equation (3-6) accounts for production and the second term for decay (Again this assumes that only one radionuclide is being produced during irradiation which is described by equation (3-2)). Integrating equation (3-6) gives

$$N(t_i) = \frac{\sigma_{act}\phi N^*}{\lambda} (1 - e^{-\lambda t_i}) \quad (3-7)$$

As activation proceeds, there is an increase in activity, but the rate of growth of the activity diminishes with time. Thus, irradiation times are usually limited to one half-life since eight times as much activation only doubles the activity. For irradiation times less than one half-life, the amount of induced activity is nearly proportional to the activation time.

At the end of irradiation the number of radioactive nuclei present is a constant for that moment in time, since production has ceased. Thus, for a set irradiation time, t_i , N in equation (3-7) could be "thought" of as the N_0 in the decay equation (3-4). So after a fixed irradiation time t_i the number of radioactive nuclei present, N_{decay} , for some decay time, t_d , is given by equation (3-8)

$$N_{decay}(t_d) = \frac{\sigma_{act}\phi N^*}{\lambda} (1 - e^{-\lambda t_i}) e^{-\lambda t_d} \quad (3-8)$$

Now the number of radioactive nuclei that will be available for counting are those which decay during the counting time, t_c . Just as before, for some irradiation time t_i and decay time t_d , N_{decay} will be a constant and equation (3-8) can be "thought" of as the N_0 in the decay equation (3-4). Remember, however, that equation (3-4) describes the number of radioactive nuclei present at some time t . The number of radioactive nuclei that decay during a time t is simply $(N_0 - \text{equation (3-4)})$.

Therefore, the number of radioactive nuclei available for counting during the counting time, t_c , is given by

$$N_{ac}(t_c) = \frac{\sigma_{act}\phi N^*}{\lambda} (1 - e^{-\lambda t_i}) e^{-\lambda t_d} (1 - e^{-\lambda t_c}) \quad (3-9)$$

Of the radioactive nuclei available for counting only a fraction may decay by a given mode (in the case of ^{151}Sm the radiation of interest is the 103.2 keV photon). The fraction of the radionuclides that decay by a given mode is given by the probability of a radionuclide decaying by that mode and is known as the intensity, i_γ for gamma intensities. Furthermore, only a fraction of the radiation emitted by the source is "visible" to the detector. This is due to two factors. First, is the fact that radiation is emitted isotropically and the detector can only see the radiation which is within the solid angle subtended by the source to detector geometry. Second, in some cases only a fraction of gammas that enter the active volume of the detector will interact with the detector material in such a way as to record a count. The fraction of radiation "visible" to the detector is accounted for by the detector efficiency, ϵ_γ for gamma efficiency.

Therefore for some irradiation time t_i , decay time t_d , and counting time t_c , the number of counts measured, C , is the product of N_{ac} , the gamma intensity, i_γ , and the detector efficiency, ϵ_γ , and is given by equation (3-10)

$$C = \frac{\sigma_{act}\phi N^*}{\lambda} (1 - e^{-\lambda t_i}) e^{-\lambda t_d} (1 - e^{-\lambda t_c}) i_\gamma \epsilon_\gamma \quad (3-10)$$

Neutron activation has proven to be a very accurate comparative method. That is, the concentration of a sample can be determined by comparing its activity to that of a known standard which was irradiated at the same time, in the same flux, and counted on the same detector using the same counting geometry. The number of counts obtained for the standard and sample is obtained from equation (3-10) and is denoted as C_{st} and C_{spl} respectively. Taking the ratio of C_{spl} and C_{st} gives

$$\frac{C_{spl}}{C_{st}} = \frac{N_{spl}^* \cdot e^{-\lambda(t_{d,spl})} \cdot (1 - e^{-\lambda(t_{c,spl})})}{N_{st}^* \cdot e^{-\lambda(t_{d,st})} \cdot (1 - e^{-\lambda(t_{c,st})})} \quad (3-11)$$

where N_{spl}^* = the number of target nuclei present in the sample

N_{st}^* = the number of target nuclei present in the standard

$t_{d,spl}$ = the decay time, time from end of irradiation to start of count, for the sample

$t_{d,st}$ = the decay time, time from end of irradiation to start of count, for the standard

$t_{c,spl}$ = the counting time for the sample

$t_{c,st}$ = the counting time for the standard

Note that the flux, neutron absorption cross-section, gamma intensity, and detector efficiency all drop out of the equation since they are the same for the sample and the standard. Note also that the decay constant for the two are also the same. The decay times are different since one is still decaying while the first is being counted.

Generally it is useful to know the concentration of the radionuclide in the sample instead of the number of nuclei present. Since the standards are readily available in concentration units of parts per million, ppm, this unit will be used. The number of atoms in a sample, N^* , can be written as a function of concentration as follows

$$N^* = (ppm) \left(\frac{10^{-6}g}{\mu g} \right) \left(\frac{1}{MW} \right) (W)(Av) \quad (3-12)$$

where ppm = μg element per gram of sample solution

MW = The molecular weight of the desired element (ie. Sm)

W = The weight of the sample solution that contains the desired element

Av = Avogadro's number

Now note that when N' , in equation (3-12), is substituted into equation (3-11) for N'_{sp} and N'_{st} , then the following equation is obtained

$$\frac{C_{sp}}{C_{st}} = \frac{(ppm_{sp})(W_{sp})}{(ppm_{st})(W_{st})} \cdot \frac{e^{-\lambda(t_{sp})}}{e^{-\lambda(t_{st})}} \cdot \frac{(1 - e^{-\lambda(t_{sp})})}{(1 - e^{-\lambda(t_{st})})} \quad (3-13)$$

Rearranging equation (3-13) to solve for the concentration of the sample, ppm_{sp} , gives

$$ppm_{sp} = (ppm_{st}) \cdot \frac{(W_{st})}{(W_{sp})} \cdot \frac{C_{sp}}{C_{st}} \cdot \frac{e^{-\lambda(t_{sp})}}{e^{-\lambda(t_{st})}} \cdot \frac{(1 - e^{-\lambda(t_{sp})})}{(1 - e^{-\lambda(t_{st})})} \quad (3-14)$$

Equation (3-14) represents the concentration of the sample in ppm as a function of known and measurable quantities.

3.6 NAA Data Analysis

Elemental concentrations, uncertainty and detection limits for a sample were determined using a neutron activation analysis code (NADA92) developed in-house [LANDSBERGER]. This code employs the equations described in Section 3.5 and corrects for the counter dead time using the P-factor method [LINDSTROM]. Detection limits in radiochemistry are fully described by Currie [CURRIE].

3.7 System Detection Limit for Samarium

To obtain a given DF using as little samarium as possible, it is necessary to know the minimum detectable concentration of samarium for our system. To this end experiments were conducted to using

solutions of a 10, 0.001, and 1×10^{-7} ppm samarium in nitric acid and water prepared from a samarium standard. The standard used was samarium atomic absorption standard solution consisting of 995 $\mu\text{g/ml}$ of samarium in 1 wt% HNO_3 , purchased from Aldrich Chemical Company. The 10 ppm solution was prepared by placing 1 ml of the Aldrich 1000 ppm samarium standard in a 100 ml volumetric flask adding 1 ml of Baker Ultra Pure concentrated nitric acid and then filling to 100 ml with distilled water. A 0.1 ppm solution was then prepared by diluting 1 ml of the 10 ppm solution in another 100 ml volumetric flask. The same procedure was followed to produce the 1×10^{-7} ppm solution. A one milliliter sample of each concentration was then placed in polyethylene vials. The vials were then heat sealed to prevent leaking. The samples were irradiated in the lazy susan facility for 5 hours at 1500 kW. The 10, 0.001 and 1×10^{-7} ppm samples were each counted twice. The first 10 ppm solution was counted for 30 minutes and the second for 5 minutes. The other samples were counted for 10 hours. In NAA one normally compares a known reference standard to samples of unknown concentration. In this case one of the 10 ppm solutions was considered the reference standard. The concentration of the other samples was then calculated from the experimental data. The results of the calculations are given in Table 3-1

Table 3-1. Calculated and Actual Concentrations of Samarium Standards

Actual Concentration (ppm)	Calculated Concentration (ppm)	Percent Error	Detection Limit (ppm)
10	9.9497 ± 0.995	0.5	0.013
$1.0\text{E-}3$	$1.07\text{E-}3 \pm 1.0\text{E-}3$	7.0	$1.4\text{E-}5$
$1.0\text{E-}3$	$1.06\text{E-}3 \pm 1.0\text{E-}3$	6.0	$2.1\text{E-}5$
$1.0\text{E-}7$	$2.0\text{E-}5 \pm 3\text{E-}6$	-	-
$1.0\text{E-}7$	$2.3\text{E-}5 \pm 9\text{E-}6$	-	-

The results were good for the 10 and 0.001 ppm solutions. The other sample may have been cross-contaminated during sample preparation or handling.

To verify that the data can be reproduced the experiment was conducted a second time. In the second experiment samarium solutions of 10, 0.1, 0.001, and 1×10^{-5} ppm were prepared using the same method described above. The volume of sample irradiated was 5 ml instead of 1 ml. The vials were then heat sealed to prevent leaking. The samples were irradiated in the lazy susan facility, which has a thermal flux of $3.3 \times 10^{12} \text{ cm}^{-2} \text{ sec}^{-1}$, for 4 hours at 1500 kW. One milliliter of each sample was counted on a 19% efficient germanium detector. The 10, 0.1 and 0.001 ppm solutions were each counted twice and the 0.00001 ppm solution was counted once. As was done for the first run, one of the 10 ppm solutions was used as a reference to calculate concentrations of the other solutions. The results of the calculations are given in Table 3-2.

Table 3-2. Calculated and Actual Concentrations of Samarium Standards for Second Run Counted

Actual Concentration (ppm)	Calculated Concentration (ppm)	Percent Error	Detection Limit (ppm)
10	9.8257 ± 0.983	1.74	0.010
0.1	$0.1013 \pm 1.0\text{E-}2$	1.27	4.93E-4
0.1	$0.0992 \pm 1.0\text{E-}2$	0.78	6.57E-4
1.0E-3	$1.05\text{E-}3 \pm 1.1\text{E-}4$	5.20	1.3E-5
1.0E-3	$9.9\text{E-}4 \pm 9.9\text{E-}5$	1.50	2.1E-5
1.0E-5	$1.3\text{E-}5 \pm 2\text{E-}6$	30.0	-

The results are good for the 10 0.1 and 0.001 ppm solutions. The 30% error in the 0.00001 ppm solution may indicate that this concentration is close to the detection limit.

From the data it appears that the minimum detectable concentration of samarium for our system is 2×10^{-5} ppm. This suggests that a concentration of 0.001 ppm can be detected and it is likely that a 0.0001 ppm solution could be detected. It should be noted, however, that these results are good for the samarium nitrate - nitric acid - water system. If other salts or impurities are introduced into the system, then the minimum detectable concentration may increase.

3.8 Interferences with NAA for Samarium

Several interferences may occur, when using NAA, which cause analytical error. Interferences of importance in this study were, gamma-ray spectral interference, shelf-shielding of gamma rays, and shelf-shielding of neutrons. Gamma-ray spectral interferences will be discussed in this Section while shelf-shielding of gamma-rays and neutrons will be discussed in the next two Sections.

Gamma-ray spectral interference occurs when two radionuclides emit gamma-rays very close to the same energy or when a single radionuclide emits gamma-rays of energies too close to one another to resolve. As mentioned in Section 3.4, ^{151}Sm , from the $^{152}\text{Sm}(n,\gamma)^{153}\text{Sm}$, emits a gamma-ray at 103.2 keV with a half-life of 1.929 d. Another reaction, the $^{154}\text{Sm}(n,\gamma)^{155}\text{Sm}$, emits a gamma-ray at 104.3 keV with a half-life of 22.2 m. These two gamma-rays could not be fully resolved on our system. The 104.3 keV gamma-ray dies off fairly quickly compared with the 103.2 keV gamma but does introduce significant activity, in the first few hours after irradiation, to cause a large analytical error. This error can be significantly reduced, if not eliminated, by allowing the sample to decay at least ten half-lives of the 104.3 keV gamma before counting.

3.9 Correction Factors for NAA

In a comparative analysis, such as NAA, situations may arise when the calculations described in Section 3.6 need to be modified to give accurate results. For example, if the sample and standard do not have the same matrix, then gamma rays may be attenuated differently across the sample. Likewise neutron shelf-shielding may occur in samples containing large concentrations of an element that has a large cross-section for neutron capture. In this case neutrons may be attenuated across the sample.

To determine if neutron self-shielding is a problem for samarium, a series of samarium standards ranging from 0.01 mg to 10 mg of samarium was prepared and irradiated. The samples from 0.5 mg to 10 mg were prepared by pipetting correct quantities of a 10.0 mg/ml samarium standard, from the

National Bureau of Standards (NBS) standard #3147, into polyethylene vials. The vials were filled to one milliliter with DI water. The 0.01 - 0.1 mg standards were prepared by diluting 0.1 to 1 ml, of the same 10.0 mg/ml samarium NBS standard, in a 100 ml volumetric flask. Again one milliliter of these solutions was placed into polyethylene vials. All sample vials were heat sealed prior to irradiation. Each standard was prepared in duplicate. These standards were irradiated at 500 kW for 6 seconds, and allowed to decay for at least the 3.67 hr before counting. The 0.01 mg standard was used as a reference to calculate the concentration of samarium (mg) in the other standards. The results are given in Table 3-3 and Fig. 3-1.

Table 3-3. Actual and Experimental Concentrations of Samarium to Determine Neutron Self-Shielding in NAA

Actual [Sm] (mg)	Ave [Sm] (mg) from NAA
0.05	0.0502 $\pm$ 1.22E-03
0.06	0.0615 $\pm$ 1.10E-03
0.08	0.0821 $\pm$ 4.52E-03
0.10	0.1030 $\pm$ 5.41E-03
0.50	0.4985 $\pm$ 1.12E-02
0.60	0.5950 $\pm$ 1.10E-02
0.70	0.6860 $\pm$ 1.60E-02
0.80	0.7735 $\pm$ 2.66E-02
0.90	0.8760 $\pm$ 1.97E-02
1.00	0.9570 $\pm$ 9.78E-02
2.00	1.7815 $\pm$ 5.29E-02
3.00	2.4800 $\pm$ 1.89E-01
4.00	3.3050 $\pm$ 6.04E-02
5.00	3.8800 $\pm$ 9.00E-02
6.00	4.3250 $\pm$ 3.55E-01
7.00	5.2950 $\pm$ 1.62E-01
8.00	5.7150 $\pm$ 1.02E-01
9.00	6.1350 $\pm$ 2.56E-01
10.00	6.9100 $\pm$ 1.27E-01

Fig. 3-1. Correction Curve for Neutron Self-Shielding in Samarium Samples

It is apparent from Fig. 3-1 that neutron self-shielding does occur in samples with large concentrations of samarium. The data was fit to a second order linear equation to obtain a relation to correct NAA results for neutron self-shielding. The relation is as follows

$$[Sm](mg) = 1.044 \cdot \left(\frac{[Sm](mg)NAA}{T} \right) + 0.062 \cdot \left(\frac{[Sm](mg)NAA}{T} \right)^2 \quad (3-15)$$

where

T = the transmission coefficient

Since the matrix for these standards was the same the transmission coefficient was assumed to be 1. If samples have a different matrix than the standard, then the transmission coefficient should be determined.

3.10 Results for the Evaporator Decontamination Factor

To obtain the evaporator DF two evaporator runs were conducted on the LICON lab-scale evaporator. In the first run the feed was $6.7\text{E-}4 \text{ M Sm(NO}_3)_3$. The feed for the second run was $0.5 \text{ M Al(NO}_3)_3$, and $6.7\text{E-}3 \text{ M Sm(NO}_3)_3$. Three samples of both the distillate and concentrate as well as one sample of the feed were received at the University of Illinois for use in (NAA).

Normally, liquid samples in NAA should have a pH close to 1. This prevents the metal ion from adhering to the plastic vial and thus allows complete transfer of the ion from the irradiated vial to a non-irradiated vial for analysis. Therefore, the pH of the samples received from Argonne was checked using litmus paper. The distillate samples from both runs and the feed and concentrate samples from run 1 had a pH of 5 while the feed and concentrate samples from run 2 had a pH of 1. The pH of each sample was adjusted to 1 by adding $20 \mu\text{L}$ of concentrated HNO_3 .

Distillate samples were prepared for irradiation by placing five milliliters of each sample in small polyethylene vials. These vials were heat sealed and placed in larger vials, which were also heat sealed, for irradiation. Due to the expected low concentrations of samarium in the distillate samples, a 4-hr irradiation at full power, 1.5 MW, was used. An 0.1 ppm atomic absorption samarium standard was also irradiated with the samples. After irradiation, the samples were transferred to non-irradiated vials for counting. The samples were counted on a 19% efficient germanium counter. The 0.1 ppm atomic absorption standard was used to determine the concentration of samarium in the samples. The results are presented in Table 3-4. The molar concentration of samarium was determined from equation (3-16).

$$[\text{Sm}] \text{ M} = ([\text{Sm}] \text{ (ppm)}) (\rho) (6.65 \times 10^{-6}) \quad (3-16)$$

The feed and concentrate samples from run #2 have a different matrix from that of the samarium standard. This is due to the presence of aluminum nitrate. To determine the self-shielding of the 103.2 keV gamma-ray, small quantities, $100 \mu\text{L}$, of the irradiated 1000 ppm Sm Atomic

Absorption standard were added to 0.5 ml of non-irradiated feed and concentrate samples from run #2. An 0.5 ml sample of DI water was also spiked in the same manner. These spiked samples were then counted on the 13% Gamma-X detector in position 1. The results are given in Table 3-5.

Table 3-4. Samarium Concentrations in the Distillate Samples from Run 1 and 2 Determined by NAA

Sample	density (g/ml)	[Sm] (ppm)	[Sm] (M)
Sm 3-2 0.1 ppm Std.	-	0.1013 $\pm$ 0.0052	-
D12-1	1.006	3.96E-4 $\pm$ 2.1E-5	2.65E-9
D14-1	0.987	3.25E-4 $\pm$ 1.7E-5	2.13E-9
D15-1	0.993	2.82E-4 $\pm$ 1.5E-5	1.86E-9
D22-1	0.994	1.025E-3 $\pm$ 5.2E-5	6.78E-9
D22-2	0.994	1.117E-3 $\pm$ 6.1E-5	7.38E-9
D24-1	1.004	4.06E-4 $\pm$ 2.1E-5	2.71E-9
D24-2	1.004	3.93E-4 $\pm$ 2.0E-5	2.62E-9
D26-1	0.995	4.78E-4 $\pm$ 2.5E-5	3.16E-9
D26-2	0.995	7.36E-4 $\pm$ 3.8E-5	4.87E-9

Table 3-5. Percentage of Gamma-Ray Attenuation for the Feed and Concentrate Samples from Evaporator Run #2 Compared to DI Water

Sample	Net Counts	Gamma Transition (T)	% Gamma Attenuation
DI Water	8735	1.0000	0
F-2-1	8696	0.9955	0.003
C-2-2	8349	0.9558	4.42
C-2-4	8295	0.9496	5.04
C-2-7	8124	0.9301	6.99

The transmission coefficient in Table 3-5 may be used in equation (3-15) to correct for gamma-ray self-shielding.

Feed and concentrate samples from both evaporator runs were prepared for irradiation by placing 1 ml of sample in polyethylene vials. The vials were heat sealed prior to irradiation. They were irradiated at 500 kW for 6 seconds, and allowed to decay for at least the 3.67 hr before counting. The concentration of samarium (mg) in the samples was determined by using an 0.01 mg NBS standard as a reference. Equation (3-15) was used to correct NAA results for neutron self-shielding. For samples from run #1 the transmission coefficient was assumed to be one and for run #2 the values listed in Table 3-5 were used. The results are given below in Table 3-6 and 3-7. As before, the molar concentration of samarium was found using equation (3-16).

Table 3-6. Samarium Concentrations Determined by NAA for the Feed and Concentrate Samples from Evaporator Run #1

Sample	Density (g/ml)	[Sm] (mg) NAA	[Sm] (mg) Corr.	[Sm] (M) NAA	Concent. Factor
F-1-1	1.003	0.0940	0.099	6.56E-04	1
C-1-2	0.9587	0.1780	0.188	1.25E-03	1.91
C-1-4	1.006	0.2382	0.252	1.68E-03	2.56
C-1-7	1.005	0.4565	0.489	3.25E-03	4.95

Table 3-7. Samarium Concentrations Determined by NAA for the Feed and Concentrate Samples from Evaporator Run #2

Sample	Density (g/ml)	[Sm] (mg) NAA	[Sm] (mg) Corr.	[Sm] M NAA	Concent. Factor
F-2-1	1.086	0.954	1.057	7.03E-03	1
C-2-2	1.143	1.551	1.857	1.23E-02	1.76
C-2-4	1.200	2.263	2.839	1.89E-02	2.69
C-2-7	1.315	3.295	4.474	2.98E-02	4.23

A concentration versus density correlation for solutions containing $\text{Al}(\text{NO}_3)_3$ at 35°C was developed by Argonne personnel. The correlation is

$$[\text{Al}(\text{NO}_3)_3] = \frac{\rho - 0.99473}{0.1486} \quad (3-17)$$

where ρ is the density of the solution. A density meter was used to measure the density of the samples, from evaporator run #2 and the concentration of aluminum in these samples was calculated using the correlation. From these concentrations concentration factors were determined by dividing each sample concentration by the concentration of the feed. The expected samarium concentration for each concentrate sample was then calculated by multiplying the concentration of samarium in the feed by each concentration factor. The results from Argonne's calculations for samarium in these samples were compared with the results from NAA in Table 3-8. It appears that the results agree well.

Table 3-8. Comparison of Samarium Concentrations Determined by NAA with Expected Concentration Based on the Aluminum Concentration Calculated from the Density Correlation

Sample Name	Density (g/ml) 35°C	[ANN], calc. (M)	Concen. Factor (from Feed)	[Sm], calc. (M)	Density (g/ml) 25°C	[Sm], NAA (M)	% Diff (ANN-NAA)
F-2-1		0.5	1	6.70E-03	1.086	7.03E-03	-4.93
C-2-2		0.85*	1.7	1.14E-02	1.143	1.23E-02	-7.89
C-2-4	1.19	1.314	2.6	1.76E-02	1.200	1.89E-02	-7.39
C-2-7	1.3145	2.152	4.3	2.88E-02	1.315	2.98E-02	-3.47

*this value was estimated using the solution density at 25°C.

The decontamination factors for the evaporator were calculated by dividing the molar concentration of samarium in the concentrate by that in the distillate. The results are given in Table 3-9.

Table 3-9. Decontamination Factor for the LICON Lab-scale Evaporator

Samples	[Sm] M (in the Vapor Phase)	Decontamination Factor
C-1-2/D-1-2	2.65E-09	4.71E+05
C-1-4/D-1-4	2.13E-09	7.87E+05
C-1-6/D-1-5	1.86E-09	1.75E+06
C-2-2/D-2-2	7.08E-09	1.74E+06
C-2-4/D-2-4	2.67E-09	7.07E+06
C-2-7/D-2-6	4.02E-09	7.40E+06

3.11 Summary of NAA Study

It can be seen from the data, in Table 3-9, that a DF of 10^3 to 10^6 has been achieved. This finding is significant because it shows that the distillate is sufficiently free of radioactive material so that it can be reused or disposed of as non-radioactive material. Thus, it appears that volume reduction of radioactive waste streams can be realized with this evaporator system.

Furthermore, it was found that samarium could be used well as a tracer but two correction factors must be incorporated into calculations to obtain accurate results. First, it was found that when samarium is present in large concentration that significant neutron self-shielding occurs across the sample. Second, it was shown that gamma-ray self-shielding was important in samples with a different matrix from that of the standard. A correlation was developed to correct NAA results for both these factors. It was also found that the 104.3 keV gamma-ray, from the decay of ^{152}Sm , fell within the 103.2 keV photopeak and could not be sufficiently resolved and caused significant error if the sample was counted within the first few hours after irradiation. If the sample was allowed to decay for at least ten half-lives, of the 104.3 keV gamma-ray, then little error was introduced.

CHAPTER 4

SUMMARY AND CONCLUSIONS

This study provided useful information in two areas. First, data were obtained which will be useful in the design of an evaporator to be used in volume reduction of radioactive liquid waste streams. The vapor-liquid equilibrium study provided data which were unavailable in the literature but important to the design of the evaporator. Both the data obtained in the literature survey and the experimental data obtained in this study may be used by Argonne National Laboratory to validate their computer code which predicts vapor phase compositions in equilibrium with complex aqueous solutions. This is essential to design the evaporator to process a wide range of solution compositions. Similarly, the decontamination factor for the evaporator was shown to be 10^4 to 10^6 . A DF of this magnitude should leave the distillate sufficiently free of radioactive material so that it may be reused or disposed of as non-radioactive material. This finding is essential to the success of the evaporator program since a high DF is needed to achieve waste minimization.

Second, experimental procedures for vapor-liquid equilibrium studies were improved, and an experimental process was designed, using NAA, to determine decontamination factors of evaporator systems. The equilibrium still, discussed in Section 2.4, did not have the capability to measure equilibrium temperatures. While Owensby [OWENSBY] used thermocouples in this still, it was not apparent what type of apparatus he used to read the temperature data from the thermocouples. In this study, thermocouples were attached to a data acquisition system which recorded and saved temperature data, on a computer, every five seconds. In so doing, it was possible to verify that equilibrium had in fact been achieved in each experiment. Furthermore, temperature data could be averaged over hundreds of data points to give potentially more accurate results. If no data acquisition system is used, then the temperature data recorded is only instantaneous. This may give an error of a few degrees due to fluctuations in thermocouple readings.

While improving the data collection process, used in the vapor-liquid equilibrium studies, was helpful, it was not as significant as the development of the experimental procedure for determining decontamination factors for evaporator systems. In developing this latter experiment, it was shown that large decontamination factors could be measured using a non-radioactive tracer. Using a non-radioactive tracer prevented radioactive contamination of the evaporator and protected personnel from unnecessary exposure. In this study samarium was used as the tracer. Stable samarium was introduced into evaporator feed samples in trace quantities. The evaporator was run and samples collected from the liquid and vapor phases. The concentration of samarium in the feed, liquid phase and vapor phase was determined by NAA. The decontamination factor was then determined by taking the ratio of the samarium concentration in the liquid phase with that in the vapor phase. Despite the problems with neutron self-shielding, it was found that samarium could be measured accurately. Furthermore, the low detection limit, 2×10^{-4} ppm, relatively short half-life, which minimizes the generation of radioactive waste, and gamma-ray energy, which falls within the region of highest detector efficiency, makes samarium ideal for non-destructive, non-radioactive, tracer work. Using samarium as a tracer could potentially be useful in studies where either trace quantities of material need to be measured or where large concentration difference, such as decontamination factors, need to be determined.

APPENDIX A

SOLUBILITY OF NITRATE SALTS IN AQUEOUS NITRIC ACID

The LICON evaporator has the ability to operate smoothly with small amounts of solids in solution. It is desirable, however, to operate the evaporator at a solution composition that does not precipitate solids. To accomplish this it is essential to know the solubility of salts as a function of solution composition. Some of the nitrate salts important to concentrating solutions from treatment of Hanford tank wastes are aluminum, calcium, iron, lanthanum, nickel, samarium, sodium, and uranyl nitrate. Solubility data were obtained for each of these salts as a function of acid concentration at constant temperatures. Solubility data for other nitrate salts (such as other rare earths and bismuth) and fluoride, sulfate, oxalate, and phosphate salts will be collected in the future. To aid the reader in locating information in this appendix, the following two tables were generated. Table A-1 lists the nine figures that show solubility data for various nitrate salts. Table A-2 lists the specific tables that contain these data. For clarity, all of the data tables were moved to the end of the appendix. The data presented in the various figures were taken from these tables.

Table A-1. List of Systems Presented in Figure Format in Appendix A

Number	Title	Page
A-1.	Solubility of Al^{3+} , Ca^{2+} , Fe^{3+} , La^{3+} , Na^{+} , Ni^{2+} , Sm^{3+} , and UO_2^{2+} Nitrate Salts in Aqueous Nitric Acid at 25°C	45
A-2.	Solubility of Al^{3+} , Ca^{2+} , La^{3+} , Na^{+} , and Sm^{3+} Nitrate Salts in Aqueous Nitric Acid at 25°C	46
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A-5.	Solubility of $La(NO_3)_3$ in Aqueous Nitric Acid at 25 and 50°C	48
A-6.	Solubility of $NaNO_3$ in Aqueous Nitric Acid at 25, 35, 50, and 75°C	49
A-7.	Solubility of $Sm(NO_3)_3$ in Aqueous Nitric Acid at 25 and 50°C	49
A-8.	Solubility of $UO_2(NO_3)_2$ in Aqueous Nitric Acid at 25, 49.1 and 50°C	50
A-9.	Solubility of $UO_2(NO_3)_2$ in the Presence of a Second Nitrate Salt in 1.5M HNO_3 at 25°C	51

Table A-2. List of Systems Presented in Table Format in Appendix A

No.	Title	Page
A-3.	Apparent Molar Volumes (AMV) for Selected Ions	52
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A-6.	Solubility Data for $\text{Fe}(\text{NO}_3)_3$ in Nitric Acid - Water at 25°C	54
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A-8.	Solubility Data for NaNO_3 in Nitric Acid - Water at 25°C	55
A-9.	Solubility Data for $\text{Ni}(\text{NO}_3)_2$ in Nitric Acid - Water at 25°C	56
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A-13.	Solubility data for $\text{Al}(\text{NO}_3)_3$ in Nitric Acid - Water at 40°C	59
A-14.	Solubility data for $\text{Al}(\text{NO}_3)_3$ in Nitric Acid - Water at 60°C	59
A-15.	Solubility Data for NaNO_3 - KNO_3 -Water-Nitric Acid at 25 °C	60
A-16.	Solubility Data for $\text{Ca}(\text{NO}_3)_2$ - $\text{Sr}(\text{NO}_3)_2$ in Nitric Acid-Water at 25°C	61
A-17.	Solubility data for $\text{Fe}(\text{NO}_3)_3$ - $\text{Th}(\text{NO}_3)_4$ in Nitric Acid - Water at 20°C	62
A-18.	Solubility data for $\text{UO}_2(\text{NO}_3)_2$ - $\text{Mg}(\text{NO}_3)_2$ in Nitric Acid - Water at 25°C	62
A-19.	Solubility Data for $\text{UO}_2(\text{NO}_3)_2$ - $\text{Ca}(\text{NO}_3)_2$ in Nitric Acid - Water at 25°C	63
A-20.	Solubility data for $\text{UO}_2(\text{NO}_3)_2$ - $\text{Cu}(\text{NO}_3)_2$ in Nitric Acid - Water at 25°C	63
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A-24.	Solubility Data for $\text{Ca}(\text{NO}_3)_2$ in Nitric Acid-Water at 60°C	66
A-25.	Solubility Data for $\text{La}(\text{NO}_3)_3$ in Nitric Acid-Water at 25°C	66
A-26.	Solubility Data for $\text{La}(\text{NO}_3)_3$ in Nitric Acid-Water at 50°C	67
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A-29.	Solubility Data for NaNO_3 in Nitric Acid-Water at 75°C	68
A-30.	Solubility Data for $\text{Sm}(\text{NO}_3)_3$ in Nitric Acid-Water at 25°C	69
A-31.	Solubility Data for $\text{Sm}(\text{NO}_3)_3$ in Nitric Acid-Water at 50°C	69
A-32.	Solubility Data for $\text{UO}_2(\text{NO}_3)_2$ in Nitric Acid-Water at 25°C	70
A-33.	Solubility Data for $\text{UO}_2(\text{NO}_3)_2$ in Nitric Acid-Water at 49.1°C	71
A-34.	Solubility Data for $\text{UO}_2(\text{NO}_3)_2$ in Nitric Acid-Water at 50°C	72

The data reported in the literature were generally presented as grams of salt, acid, and water per 100 grams of saturated solution. It is more useful, however, to know the solubilities in units of molarity. To convert the literature data to molarity, the density of the solution must be known. If the solution density was not given in the literature, it was calculated. Assuming a total solution weight of 100 grams, the solution density could be estimated using Eq. A-1.

$$d = \frac{100}{V} \quad (\text{A-1})$$

The solution volume was calculated using Eq. A-2, the same equation used in the Generic TRUEX Model (GTM).

$$V = V_{\text{H}_2\text{O}} + \sum n_i V_{\phi,i} \quad (\text{A-2})$$

where $V_{\text{H}_2\text{O}}$ is the volume of water, n is the moles of solute and V_{ϕ} is the apparent molar volume (AMV) of the solute. Note that the volume of water was determined by dividing the mass of water, for a given solution, by the density of water at 25 °C (0.99707 g/mL (WEAST)). The product nV_{ϕ} is the volume of the solute. For the nitric acid-water-nitrate salt system, water is considered the solvent and the salt and acid the solutes. Values for apparent molar volumes of cations and anions at 25 °C are listed in Table A-3. The AMV for H^+ was set to zero as the reference AMV. Since the AMV's were only available for 25°C, only the solubility data at 25°C were converted to molar concentrations. The experimental data, weight percent of nitric acid and nitrate salt, calculated densities, and molar concentrations of nitric acid plus salts are listed in the various data tables.

For comparison purposes, the salt concentration, in molarity, for various salts are plotted as a function of nitric acid concentration in Fig. A-1 and Fig. A-2. It is evident from the data in these two figures that aluminum nitrate has the lowest solubility of the salts under consideration. Aluminum and sodium nitrate salts are present in many raffinate streams from the TRUEX process in concentrations that range between 0.1-1M. These streams also contain high concentrations of nitric acid (0.5-8M). For this stream, the solubility of aluminum will likely limit the degree to which the solution can be concentrated in the evaporator. Other TRUEX process and waste streams are dilute in both nitric acid (0.02-0.2M) and nitrate salts (10^{-10} - 10^{-3} M), so large volume reductions can be expected.

Fig. A-1. Solubility of Al^{3+} , Ca^{2+} , Fe^{3+} , La^{3+} , Na^{+} , Ni^{2+} , Sm^{3+} , and UO_2^{2+} Nitrate Salts in Aqueous Nitric Acid at 25°C

Fig A-2. Solubility of Al^{3+} , Ca^{2+} , La^{3+} , Na^{+} , Sm^{3+} Nitrate Salts in Aqueous Nitric Acid 25°C

Solubility data with solution densities for aluminum nitrate were also available at 20, 40 and 60°C. These data, including the 25°C data for aluminum and sodium nitrate plotted in Figs. A-1 and A-2 are plotted in Fig. A-3. From this figure it can be seen that the solubility of aluminum nitrate is less than sodium nitrate for nitric acid concentrations less than 7M. These data also show that solubility increases as the solution temperature increases.

Fig. A-3. Comparison of Solubilities for Aluminum and Sodium Nitrate in Nitric Acid

Solubility data for many of the nitric acid-water-nitrate salt system were obtained at several temperatures. The data for these systems are plotted in Figs A-4 through A-8. Note that the remaining data have been plotted as weight percent of salt versus mole percent of salt-free nitric acid. This was done so that comparisons could easily be made between the acid concentrations for solubility data and corresponding acid concentrations presented in Appendix B for the vapor-liquid equilibrium data. The mole percent nitric acid was calculated from the given solubility data.

Fig. A-4. Solubility of $\text{Ca}(\text{NO}_3)_2$ in Nitric Acid at 25, 50, and 60°C

Fig. A-5. Solubility of $\text{La}(\text{NO}_3)_3$ in Nitric Acid at 25 and 50°C

Fig A-6. Solubility of NaNO₃ in Nitric Acid at 25, 35, 50, and 75 °C

Fig. A-7. Solubility of Sm(NO₃)₃ in Nitric Acid at 25 and 50 °C

Fig. A-8. Solubility of $\text{UO}_2(\text{NO}_3)_2$ in Nitric Acid at 25, 49.1 and 50°C

According to Yakimov [SILOCK-B], the discrepancy between the data at 49.1 and 50°C above 60 mol% nitric acid, as shown in Fig. A-8, is probably due to the presence of NO_2 in solution [SILOCK-J]. Yakimov suggested that the use of fuming nitric acid by Gaunt (data at 49.1°C) allowed $\text{UO}_2(\text{NO}_2)_2$ solids to form. This compounds solubility is much lower than $\text{UO}_2(\text{NO}_3)_2$.

Since most of the waste streams to be concentrated will contain multiple salts in aqueous nitric acid, it would be helpful to know how the solubility of a salt changes with the presence of additional salts. Solubility data, however, were very limited for multiple salt systems in aqueous nitric acid. Multiple salt systems included NaNO_3 - KNO_3 , $\text{Ca}(\text{NO}_3)_2$ - $\text{Sr}(\text{NO}_3)_2$, $\text{Fe}(\text{NO}_3)_3$ - $\text{Th}(\text{NO}_3)_4$, $\text{UO}_2(\text{NO}_3)_2$ - $\text{Mg}(\text{NO}_3)_2$, $\text{UO}_2(\text{NO}_3)_2$ - $\text{Ca}(\text{NO}_3)_2$, and $\text{UO}_2(\text{NO}_3)_2$ - $\text{Cu}(\text{NO}_3)_2$. The data from the first two systems were not very useful since the concentration of both salts and the acid were varied for each data point. The other 4 systems maintained the nitric acid concentration at 1.5M and only varied the salt concentrations. The data for the UO_2^{2+} systems, are plotted in Fig. A-9. The solution densities were also reported, allowing the conversion to molarity units.

Fig. A-9. Solubility of $\text{UO}_2(\text{NO}_3)_2$ in the Presence of a Second Nitrate Salt in 1.5M HNO_3 at 25°C

From Fig. A-9 it is apparent that when two salts are present in solution, the solubility of both salts is lower than it would be for the single salt in solution. This effect is called the common ion effect.

From the solubility data presented here in this report, a few trends can be noted. First solubility of a salt decreases with increasing nitric acid concentration. In some cases, such as sodium nitrate, at very high acid concentrations solubility begins to increase after reaching a minimum. Second, solubility increases with increasing temperature. This effect diminishes with increasing acid concentration. Third, the presence of more than one salt decreases the solubility of all salts compared to the single salt solubility.

Table A-3. Apparent Molar Volumes (AMV)
for Selected Ions

Ion	AMV (mL/mol)
Al ³⁺	-45.3
Ca ²⁺	-17.8
Fe ³⁺	-43.7
La ³⁺	-39.1
Na ⁺	-1.2
Ni ²⁺	-29.5
Sm ³⁺	-42.33
UO ₂ ²⁺	15.91
NO ₃ ⁻	29.5

Table A-4. Solubility Data for Al(NO₃)₃ in Nitric Acid - Water at 25°C^a

[HNO ₃] (wt%)	[HNO ₃] (mol%)	[Al(NO ₃) ₃] (wt%)	Calculated Density (g/mL)	[HNO ₃] (M)	[Al(NO ₃) ₃] (M)
0.00	0.00	39.00	1.45	0.00	2.65
10.00	4.58	30.50	1.42	2.25	2.03
20.00	9.05	22.60	1.40	4.44	1.48
30.00	13.59	15.50	1.39	6.63	1.01
40.00	18.31	9.00	1.39	8.85	0.59
50.00	23.66	3.90	1.42	11.27	0.26
60.00	30.86	1.60	1.49	14.23	0.11
65.10	35.50	1.10	1.55	15.99	0.08
68.50	39.09	1.00	1.59	17.30	0.07
72.50	44.06	1.20	1.65	19.00	0.09
75.00	46.76	0.60	1.67	19.94	0.05
80.00	53.58	0.20	1.74	22.14	0.02
85.00	61.98	0.10	1.83	24.64	0.01
90.00	72.71	0.35	1.93	27.53	0.03

^a[LINKE-1958A]

Table A-5. Solubility Data for $\text{Ca}(\text{NO}_3)_2$ in Nitric Acid - Water at 25 °C^a

$[\text{HNO}_3]$ (wt%)	$[\text{HNO}_3]$ (mol%)	$[\text{Ca}(\text{NO}_3)_2]$ (wt%)	Calculated Density (g/mL)	$[\text{HNO}_3]$ (M)	$[\text{Ca}(\text{NO}_3)_2]$ (M)
0.00	0.00	57.98	1.76	0.00	6.23
3.33	2.22	54.82	1.75	0.92	5.83
5.87	3.91	52.96	1.74	1.63	5.63
7.21	4.76	51.58	1.73	1.98	5.45
11.27	7.30	47.82	1.71	3.07	5.00
13.71	8.78	45.59	1.70	3.71	4.73
19.65	12.40	40.70	1.69	5.27	4.19
22.80	14.30	38.17	1.68	6.09	3.92
28.81	18.31	34.46	1.70	7.75	3.56
32.63	21.26	32.84	1.72	8.91	3.44
33.52	21.99	32.50	1.73	9.18	3.42
35.63	24.76	33.44	1.78	10.08	3.63
41.66	28.90	29.05	1.78	11.77	3.15
45.70	32.93	27.70	1.82	13.18	3.07
40.56	29.02	31.09	1.81	11.66	3.43
45.70	31.63	26.07	1.78	12.89	2.82
55.48	36.90	17.41	1.74	15.30	1.84
62.05	40.82	12.25	1.73	17.01	1.29
65.69	42.91	9.34	1.72	17.93	0.98
67.20	44.16	8.52	1.73	18.40	0.90
71.12	46.04	5.06	1.71	19.31	0.53
74.77	48.48	2.53	1.71	20.32	0.26
78.56	52.40	1.05	1.74	21.69	0.11
80.83	55.35	0.54	1.76	22.64	0.06
85.83	63.97	0.36	1.85	25.17	0.04
90.90	74.07	0.01	1.93	27.92	0.00
96.86	89.81	0.00	2.06	31.70	0.00

^a[LINKE-1958B]

Table A-6. Solubility Data for $\text{Fe}(\text{NO}_3)_3$ in Nitric Acid - Water at 25°C^a

$[\text{HNO}_3]$ (wt%)	$[\text{HNO}_3]$ (mol%)	$[\text{Fe}(\text{NO}_3)_3]$ (wt%)	Calculated Density (g/mL)	$[\text{HNO}_3]$ (M)	$[\text{Fe}(\text{NO}_3)_3]$ (M)
53.48	35.01	18.15	1.76	14.93	1.32
53.79	39.24	22.41	1.88	16.05	1.74
54.23	46.61	28.02	2.07	17.79	2.39
57.03	52.30	28.11	2.14	19.34	2.48

^a[SILLOCK-A]

Table A-7. Solubility Data for $\text{La}(\text{NO}_3)_3$ in Nitric Acid - Water at 25°C^a

$[\text{HNO}_3]$ (wt%)	$[\text{HNO}_3]$ (mol%)	$[\text{La}(\text{NO}_3)_3]$ (wt%)	Calculated Density (g/mL)	$[\text{HNO}_3]$ (M)	$[\text{La}(\text{NO}_3)_3]$ (M)
0.00	0.00	60.27	2.04	0.00	3.78
0.80	0.57	59.30	2.02	0.26	3.69
15.50	9.71	43.30	1.81	4.46	2.42
22.40	13.45	36.40	1.74	6.20	1.95
35.10	21.88	29.10	1.76	9.81	1.58
36.80	23.10	28.20	1.77	10.32	1.53
38.50	24.55	27.70	1.78	10.89	1.52
38.80	25.49	28.80	1.82	11.19	1.61
39.60	26.36	28.80	1.83	11.51	1.62
40.50	26.74	27.80	1.82	11.69	1.56
41.10	27.60	28.10	1.84	11.99	1.59
52.50	35.55	20.30	1.82	15.17	1.14
57.00	40.03	18.60	1.85	16.76	1.06
58.40	42.36	18.90	1.89	17.49	1.10
60.20	43.11	17.10	1.87	17.84	0.98
62.10	45.91	17.00	1.90	18.73	0.99
62.90	47.58	17.30	1.93	19.22	1.03
62.50	49.80	19.50	1.99	19.73	1.19

^a[SIEKIERSKI-A]

Table A-8. Solubility Data for NaNO₃ in Nitric Acid - Water at 25°C^a

[HNO ₃] (wt%)	[HNO ₃] (mol%)	[NaNO ₃] (wt%)	Calculated Density (g/mL)	[HNO ₃] (M)	[NaNO ₃] (M)
0.00	0.00	47.90	1.47	0.00	8.26
4.30	2.24	42.10	1.43	0.98	7.10
9.20	4.56	35.80	1.40	2.05	5.90
10.80	5.26	33.60	1.39	2.38	5.49
11.90	5.73	32.20	1.38	2.61	5.24
14.90	7.06	29.10	1.37	3.25	4.70
16.10	7.55	27.60	1.37	3.49	4.44
19.90	9.14	23.60	1.35	4.28	3.76
25.70	11.59	18.30	1.35	5.49	2.90
30.90	13.88	14.30	1.35	6.61	2.27
36.40	16.48	10.90	1.36	7.86	1.74
42.20	19.52	8.10	1.38	9.26	1.32
47.90	22.89	6.00	1.42	10.76	1.00
52.70	26.16	4.80	1.45	12.14	0.82
57.80	29.96	3.60	1.49	13.70	0.63
63.87	35.52	3.00	1.56	15.81	0.55
71.90	44.71	2.70	1.67	19.01	0.53
76.20	51.26	3.10	1.74	21.04	0.63
81.40	62.26	4.50	1.86	24.04	0.98
84.90	71.43	5.40	1.95	26.28	1.24
90.00	98.09	9.50	2.18	31.19	2.44

^a[YAKIMOV]

Table A-9. Solubility Data for $\text{Ni}(\text{NO}_3)_2$ in Nitric Acid - Water at 25°C^a

$[\text{HNO}_3]$ (wt%)	$[\text{HNO}_3]$ (mol%)	$[\text{Ni}(\text{NO}_3)_2]$ (wt%)	Calculated Density (g/mL)	$[\text{HNO}_3]$ (M)	$[\text{Ni}(\text{NO}_3)_2]$ (M)
7.60	4.25	43.50	1.68	2.02	3.99
13.20	7.30	38.90	1.65	3.46	3.52
19.10	10.48	34.30	1.63	4.95	3.07
24.10	13.09	30.20	1.61	6.17	2.67
32.10	17.51	24.70	1.60	8.17	2.17
40.00	22.27	20.10	1.61	10.24	1.77
52.00	31.71	16.00	1.69	13.98	1.48
60.20	36.52	9.90	1.67	15.99	0.91
65.20	40.47	7.40	1.69	17.48	0.68
70.50	46.05	5.90	1.74	19.42	0.56
73.90	50.37	5.30	1.78	20.83	0.52
78.60	58.09	5.20	1.86	23.15	0.53
80.50	61.33	5.00	1.89	24.09	0.52
81.60	61.98	4.10	1.88	24.34	0.42
84.30	64.95	2.70	1.89	25.27	0.28
89.80	74.25	1.30	1.95	27.85	0.14
95.30	86.09	0.30	2.04	30.82	0.03
99.50	98.44	0.05	2.13	33.57	0.01

^a[LINKE-1965A]

Table A-10. Solubility Data for $\text{Sm}(\text{NO}_3)_3$ in Nitric Acid - Water at 25°C^a

$[\text{HNO}_3]$ (wt%)	$[\text{HNO}_3]$ (mol%)	$[\text{Sm}(\text{NO}_3)_3]$ (wt%)	Calculated Density (g/mL)	$[\text{HNO}_3]$ (M)	$[\text{Sm}(\text{NO}_3)_3]$ (M)
0.00	0.00	61.14	2.11	0.00	3.84
3.40	2.43	57.60	2.06	1.11	3.52
8.90	6.09	51.90	1.98	2.79	3.05
15.80	10.01	43.60	1.85	4.64	2.40
38.80	21.87	21.60	1.64	10.12	1.06
40.70	22.97	20.30	1.64	10.60	0.99
46.60	26.73	16.90	1.65	12.18	0.83
51.50	30.21	14.50	1.66	13.58	0.72
52.10	30.83	14.50	1.67	13.81	0.72
52.20	30.93	14.50	1.67	13.85	0.72
52.50	31.32	14.60	1.68	13.99	0.73
56.60	34.43	12.60	1.69	15.20	0.63
59.20	36.44	11.30	1.70	15.97	0.57
62.30	39.47	10.40	1.72	17.06	0.53
64.10	41.70	10.30	1.75	17.82	0.54
66.90	45.71	10.40	1.80	19.13	0.56
67.00	50.06	13.90	1.91	20.28	0.79
66.00	49.16	14.50	1.91	19.97	0.82
66.00	50.61	15.60	1.94	20.34	0.90
66.30	51.00	15.50	1.94	20.46	0.90
65.00	51.49	17.50	1.98	20.48	1.03
66.70	52.13	15.80	1.96	20.78	0.92
68.10	52.79	14.50	1.95	21.06	0.84
68.50	56.61	16.50	2.02	22.02	0.99
69.70	59.78	16.90	2.07	22.86	1.04
69.70	62.40	18.30	2.12	23.45	1.15
70.00	65.57	19.50	2.17	24.16	1.26
71.00	65.89	18.50	2.16	24.33	1.19
73.90	70.11	17.10	2.17	25.51	1.11
78.50	72.99	13.20	2.13	26.57	0.84
80.10	72.92	11.40	2.10	26.71	0.71
84.70	75.63	7.50	2.06	27.71	0.46
88.70	81.12	5.40	2.08	29.21	0.33
90.30	81.39	3.80	2.05	29.42	0.23
94.20	91.19	3.20	2.12	31.71	0.20
95.60	91.92	2.00	2.11	31.98	0.13
98.30	99.65	1.60	2.16	33.66	0.10

^a(SIEKIERSKI-B)

Table A-11. Solubility Data for $\text{UO}_2(\text{NO}_3)_2$ in Nitric Acid - Water at 25°C^a

$[\text{HNO}_3]$ (wt%)	$[\text{HNO}_3]$ (mol%)	$[\text{UO}_2(\text{NO}_3)_2]$ (wt%)	Calculated Density (g/mL)	$[\text{HNO}_3]$ (M)	$[\text{UO}_2(\text{NO}_3)_2]$ (M)
0.00	0.00	55.95	1.82	0.00	2.59
3.80	2.34	50.90	1.76	1.06	2.27
7.20	4.25	46.40	1.70	1.95	2.01
9.10	5.30	44.40	1.69	2.43	1.90
15.20	8.56	38.40	1.64	3.96	1.60
22.40	12.50	32.80	1.62	5.77	1.35
29.90	19.31	34.40	1.77	8.42	1.55
38.40	26.98	31.90	1.86	11.32	1.50
38.40	26.71	31.50	1.85	11.25	1.48
39.60	26.93	29.70	1.82	11.43	1.37
48.00	35.15	26.70	1.89	14.40	1.28
50.70	40.03	27.60	1.97	15.86	1.38
52.30	43.64	28.40	2.03	16.86	1.46
52.50	44.38	28.70	2.05	17.04	1.49
54.50	46.11	27.30	2.04	17.67	1.41
55.70	47.49	26.70	2.05	18.11	1.39
59.10	51.19	24.80	2.06	19.33	1.30
63.40	57.66	23.30	2.11	21.21	1.25
66.00	61.31	22.10	2.13	22.27	1.19
68.90	68.39	22.00	2.19	24.00	1.23
70.50	73.94	22.40	2.25	25.21	1.28
71.10	75.48	22.30	2.26	25.56	1.28
71.60	83.64	24.40	2.37	26.95	1.47
68.20	89.44	29.50	2.51	27.17	1.88
68.20	91.12	29.90	2.53	27.39	1.92
64.70	92.03	33.70	2.61	26.81	2.23
61.60	95.65	37.60	2.72	26.57	2.59
62.70	96.76	36.70	2.71	26.94	2.52
63.40	97.31	36.10	2.70	27.16	2.47

^a(SILCOCK-B)

Table A-12. Solubility data for $\text{Al}(\text{NO}_3)_3$ in Nitric Acid - Water at 20°C^a

$[\text{HNO}_3]$ (wt%)	$[\text{Al}(\text{NO}_3)_3]$ (wt%)	Density (g/mL)	$[\text{HNO}_3]$ (M)	$[\text{Al}(\text{NO}_3)_3]$ (M)
0	40.00	1.383	0.000	2.597
10	31.00	1.368	2.171	1.991
20	23.00	1.354	4.298	1.462
30	16.00	1.345	6.405	1.010
40	9.00	1.34	8.508	0.566
50	4.00	1.345	10.675	0.253
60	1.50	1.364	12.990	0.096
70	0.75	1.405	15.611	0.049

^a[LINKE-1958C]

Table A-13. Solubility data for $\text{Al}(\text{NO}_3)_3$ in Nitric Acid - Water at 40°C^a

$[\text{HNO}_3]$ (wt%)	$[\text{Al}(\text{NO}_3)_3]$ (wt%)	Density (g/mL)	$[\text{HNO}_3]$ (M)	$[\text{Al}(\text{NO}_3)_3]$ (M)
0.00	44.00	1.430	0.000	2.954
10.00	36.00	1.402	2.225	2.370
20.00	29.00	1.386	4.400	1.887
30.00	21.00	1.377	6.557	1.358
40.00	15.00	1.370	8.698	0.965
50.00	9.50	1.375	10.913	0.613
60.00	5.50	1.392	13.257	0.359
70.00	3.00	1.430	15.889	0.201

^a[LINKE-1958C]

Table A-14. Solubility data for $\text{Al}(\text{NO}_3)_3$ in Nitric Acid - Water at 60°C^a

$[\text{HNO}_3]$ (wt%)	$[\text{Al}(\text{NO}_3)_3]$ (wt%)	Density (g/mL)	$[\text{HNO}_3]$ (M)	$[\text{Al}(\text{NO}_3)_3]$ (M)
0.00	47.50	1.461	0.000	3.258
10.00	40.50	1.457	2.313	2.770
20.00	34.50	1.457	4.625	2.360
30.00	29.00	1.460	6.952	1.988
40.00	24.00	1.468	9.321	1.654
50.00	20.00	1.480	11.746	1.390

^a[LINKE-1958C]

**Table A-15. Solubility Data for NaNO_3 - KNO_3 -Water-
Nitric Acid at 25°C^a**

$[\text{HNO}_3]$ (wt%)	$[\text{HNO}_3]$ (mol%)	$[\text{NaNO}_3]$ (wt%)	$[\text{KNO}_3]$ (wt%)
0.00	0.00	40.26	19.17
5.20	3.43	35.26	17.68
10.66	6.57	30.01	16.04
16.17	9.42	23.64	15.74
21.18	12.21	19.24	16.06
32.65	19.12	11.20	16.70
38.98	23.07	7.15	16.74
42.61	23.35	5.75	11.68
54.04	30.41	4.10	6.52
58.62	32.95	3.82	3.48
62.59	35.10	3.32	1.02

^a[SILOCK-C]

Table A-16. Solubility Data for $\text{Ca}(\text{NO}_3)_2$ - $\text{Sr}(\text{NO}_3)_2$ in Nitric Acid-Water
at 25°C^a

$[\text{HNO}_3]$ (wt%)	$[\text{HNO}_3]$ (mol%)	$[\text{Ca}(\text{NO}_3)_2]$ (wt%)	$[\text{Sr}(\text{NO}_3)_2]$ (wt%)	$[\text{H}_2\text{O}]$ (wt%)
10.05	4.51	0.00	29.20	60.75
9.76	4.39	0.95	28.55	60.74
9.89	4.45	1.49	27.92	60.70
9.57	4.35	7.66	22.65	60.12
9.88	4.59	15.53	15.92	58.67
9.98	4.77	22.11	10.94	56.97
10.03	5.25	33.98	4.26	51.73
10.35	6.62	47.47	0.48	41.70
9.91	6.42	48.41	0.41	41.27
10.19	6.63	48.84	0.00	40.97
20.13	8.22	0.00	15.62	64.25
19.74	8.15	3.87	12.86	63.53
20.50	8.62	7.99	9.40	62.11
20.31	8.69	10.41	8.31	60.97
19.86	8.67	13.37	7.03	59.74
19.62	8.79	16.48	5.75	58.15
19.58	9.22	21.71	3.66	55.05
20.25	10.83	30.48	1.62	47.65
19.96	12.61	40.28	0.23	39.53
19.88	12.54	40.52	0.00	39.60
30.15	11.98	0.00	6.55	63.30
30.67	12.34	2.68	4.42	62.23
29.91	12.61	7.54	3.32	59.23
29.51	13.47	14.21	2.10	54.18
30.03	15.87	23.70	0.78	45.49
30.83	19.47	32.66	0.07	36.44
30.00	18.97	33.38	0.00	36.62
40.00	16.37	0.00	1.61	58.39
39.73	16.88	3.39	0.98	55.90
39.33	19.24	12.97	0.53	47.17
40.83	27.37	28.20	0.01	30.96
50.00	22.30	0.00	0.22	49.78
48.89	24.24	7.30	0.15	43.66
48.95	30.20	18.72	0.01	32.32

^a[SILOCK-D]

Table A-17. Solubility data for $\text{Fe}(\text{NO}_3)_3\text{-Th}(\text{NO}_3)_4$ in Nitric Acid - Water at 20°C^a

Density (g/mL)	[HNO ₃] (wt%)	[HNO ₃] (mol%)	[Fe(NO ₃) ₃] (wt%)	[Th(NO ₃) ₄] (wt%)
1.92	4.93	4.35	0.00	64.06
1.81	5.23	4.33	11.82	49.88
1.70	5.57	4.33	21.22	38.01
1.59	5.96	4.54	26.33	31.90
1.53	6.17	4.13	26.89	25.99
1.49	6.33	4.09	29.58	21.66
1.44	6.54	3.98	33.95	14.44
1.39	6.81	3.78	39.45	4.26
1.37	6.92	3.65	40.93	0.00

^a[SILOCK-E]

Table A-18. Solubility data for $\text{UO}_2(\text{NO}_3)_2\text{-Mg}(\text{NO}_3)_2$ in Nitric Acid - Water at 25°C^a

Density (g/mL)	[UO ₂ (NO ₃) ₂] (wt%)	[Mg(NO ₃) ₂] (wt%)	[UO ₂ (NO ₃) ₂] (M)	[Mg(NO ₃) ₂] (M)
1.409	0.00	38.94	0.000	3.699
1.415	4.18	35.74	0.150	3.410
1.448	8.21	34.34	0.302	3.353
1.485	12.12	33.00	0.457	3.304
1.527	16.07	30.19	0.623	3.108
1.543	17.73	29.88	0.694	3.109
1.547	17.91	29.20	0.703	3.046
1.549	18.25	29.31	0.717	3.061
1.548	18.29	28.67	0.719	2.992
1.548	18.37	27.38	0.722	2.858
1.536	18.85	26.71	0.735	2.766
1.532	19.49	25.26	0.758	2.609
1.538	21.39	22.93	0.835	2.378
1.533	23.14	20.98	0.900	2.169
1.538	23.90	19.46	0.933	2.018
1.555	26.27	17.02	1.037	1.784
1.560	27.69	16.24	1.096	1.708
1.563	29.41	13.91	1.167	1.466
1.578	31.96	11.52	1.280	1.226
1.618	38.09	7.01	1.564	0.765
1.657	41.60	3.56	1.749	0.398
1.684	48.49	0.00	2.072	0.000

^a[SILOCK-E]

Table A-19. Solubility Data for $\text{UO}_2(\text{NO}_3)_2\text{-Ca}(\text{NO}_3)_2$ in Nitric Acid - Water at 25°C^a

Density (g/mL)	$[\text{UO}_2(\text{NO}_3)_2]$ (wt%)	$[\text{Ca}(\text{NO}_3)_2]$ (wt%)	$[\text{UO}_2(\text{NO}_3)_2]$ (M)	$[\text{Ca}(\text{NO}_3)_2]$ (M)
1.508	0.00	48.72	0.000	4.477
1.551	5.96	45.36	0.235	4.287
1.582	10.18	41.68	0.409	4.018
1.590	10.35	40.80	0.418	3.953
1.604	10.69	40.80	0.435	3.988
1.604	11.28	40.29	0.459	3.938
1.576	12.21	38.94	0.488	3.740
1.578	16.80	32.58	0.673	3.133
1.584	22.03	25.87	0.886	2.497
1.604	29.05	18.18	1.183	1.777
1.626	33.92	13.42	1.400	1.330
1.650	38.72	8.15	1.621	0.820
1.648	39.35	6.80	1.646	0.683
1.684	48.79	0.00	2.085	0.000

^a[SILOCK-E]

Table A-20. Solubility data for $\text{UO}_2(\text{NO}_3)_2\text{-Cu}(\text{NO}_3)_2$ in Nitric Acid - Water at 25°C^a

Density (g/mL)	$[\text{UO}_2(\text{NO}_3)_2]$ (wt%)	$[\text{Cu}(\text{NO}_3)_2]$ (wt%)	$[\text{UO}_2(\text{NO}_3)_2]$ (M)	$[\text{Cu}(\text{NO}_3)_2]$ (M)
1.709	0.00	56.43	0.000	5.142
1.732	5.05	49.56	0.222	4.577
1.770	10.06	47.12	0.452	4.447
1.806	13.94	45.29	0.639	4.361
1.804	13.77	44.00	0.630	4.232
1.785	13.00	43.02	0.589	4.094
1.745	12.63	41.63	0.559	3.873
1.716	11.97	41.60	0.521	3.806
1.676	12.27	38.71	0.522	3.459
1.672	13.26	38.50	0.563	3.432
1.657	13.07	37.85	0.550	3.344
1.641	14.88	34.20	0.620	2.992
1.619	21.68	24.87	0.891	2.147
1.624	32.72	13.07	1.349	1.132
1.670	40.40	6.52	1.712	0.581
1.684	48.79	0.00	2.085	0.000

^a[SILOCK-E]

Table A-21. Solubility Data for $\text{Ca}(\text{NO}_3)_2$ in Nitric Acid-Water at 25°C^a

$[\text{HNO}_3]$ (wt%)	$[\text{HNO}_3]$ (mol%)	$[\text{Ca}(\text{NO}_3)_2]$ (wt%)
0.00	0.00	57.40
11.63	7.37	46.61
21.30	13.21	38.70
21.72	13.48	38.44
34.33	22.52	31.93
33.13	22.91	35.02
33.94	23.37	34.27
33.82	23.31	34.39
39.69	27.11	29.82
44.55	30.78	26.83
48.70	33.02	23.08
57.46	37.89	15.63
64.80	42.58	10.23
74.39	48.42	2.97
86.39	64.61	0.09
99.99	100.00	0.01

^a[LINKE-1958D]

Table A-22. Solubility Data for $\text{Ca}(\text{NO}_3)_2$ in Nitric Acid-Water at 50°C^a

$[\text{HNO}_3]$ (wt%)	$[\text{HNO}_3]$ (mol%)	$[\text{Ca}(\text{NO}_3)_2]$ (wt%)
0.00	0.00	77.90
1.46	1.81	75.93
4.19	5.18	73.90
5.91	7.18	72.25
9.83	11.09	67.65
17.26	17.22	59.03
25.91	23.22	49.61
48.89	36.09	26.37
64.79	44.51	12.13
75.77	51.07	3.49
78.76	53.78	1.90
97.57	91.98	0.00

^a[LINKE-1958E]

Table A-23. Solubility Data for $\text{Ca}(\text{NO}_3)_2$ in Nitric
Acid-Water at 50°C^a

$[\text{HNO}_3]$ (wt%)	$[\text{HNO}_3]$ (mol%)	$[\text{Ca}(\text{NO}_3)_2]$ (wt%)
0.59	0.71	75.80
0.89	1.07	75.70
1.19	1.46	75.80
1.52	1.74	73.90
1.61	1.79	73.20
1.64	1.92	74.40
1.87	2.15	73.80
2.98	3.52	73.70
7.51	8.18	68.40
12.32	12.66	63.40
19.20	18.29	56.30
23.85	21.66	51.50
23.85	21.39	51.10
30.35	25.71	44.60
30.80	26.19	44.40
30.90	26.02	44.00
42.70	32.62	32.10
57.60	39.99	17.70
76.40	51.57	3.10

^a[LINKE-1958F]

Table A-24. Solubility Data for $\text{Ca}(\text{NO}_3)_2$ in Nitric
Acid-Water at 60°C^a

$[\text{HNO}_3]$ (wt%)	$[\text{HNO}_3]$ (mol%)	$[\text{Ca}(\text{NO}_3)_2]$ (wt%)
0.00	0.00	78.16
0.91	1.17	77.19
3.62	4.48	74.32
6.86	8.01	70.63
8.48	9.73	69.05
14.22	14.95	62.67
19.71	19.44	56.96
28.50	25.24	47.38
38.66	30.87	36.60
50.94	37.08	24.36
58.66	39.88	16.07
67.63	45.25	8.99
77.67	52.65	2.37
83.20	59.22	0.43

^a[SILOCK-F]

Table A-25. Solubility Data for $\text{La}(\text{NO}_3)_3$ in Nitric
Acid-Water at 25°C^a

$[\text{HNO}_3]$ (wt%)	$[\text{HNO}_3]$ (mol%)	$[\text{La}(\text{NO}_3)_3]$ (wt%)
0.00	0.00	59.00
3.06	2.11	56.42
11.95	7.58	46.42
34.69	21.49	29.10
40.17	27.53	29.62
41.14	28.06	28.73
54.41	43.24	25.18
58.36	45.43	21.61
70.70	43.25	2.79
87.85	68.41	0.56
90.00	72.00	0.00

^a[LINKE-1965B]

Table A-26. Solubility Data for $\text{La}(\text{NO}_3)_3$ in
Nitric Acid-Water at 50°C^a

$[\text{HNO}_3]$ (wt%)	$[\text{HNO}_3]$ (mol%)	$[\text{La}(\text{NO}_3)_3]$ (wt%)
0.00	0.00	66.65
2.59	2.00	61.21
5.29	4.40	61.85
12.05	9.92	56.70
14.93	12.93	56.34
27.73	22.03	44.23
44.48	33.52	30.31
50.53	42.06	29.58
78.31	57.99	5.48
85.51	65.08	1.38
91.15	75.52	0.41
90.00	72.00	0.00

^a[LINKE-1965B]

Table A-27. Solubility Data for NaNO_3 in Nitric
Acid-Water at 35°C^a

$[\text{HNO}_3]$ (wt%)	$[\text{HNO}_3]$ (mol%)	$[\text{NaNO}_3]$ (wt%)
0.00	0.00	50.13
1.40	0.79	48.20
4.80	2.59	43.60
8.80	4.57	38.70
12.70	6.35	33.80
16.40	8.01	29.80
23.50	11.06	22.50
31.90	14.77	15.50
39.20	18.39	11.10
47.60	23.17	7.30
55.40	28.61	5.10
65.30	37.27	3.30
70.10	42.86	3.20
73.40	47.26	3.20
81.80	63.04	4.50
84.10	69.39	5.30
89.90	97.72	9.50

^a[YAKIMOV]

Table A-28. Solubility Data for NaNO₃ in Nitric Acid-Water at 50°C

[HNO ₃] (wt%)	[HNO ₃] (mol%)	[NaNO ₃] (wt%)
0.00	0.00	53.60
10.00	5.50	40.90
18.40	9.65	32.40
28.50	14.05	21.70
37.90	18.73	15.10
49.00	25.04	9.10
59.80	32.99	5.50
72.80	47.17	3.90
79.60	58.55	4.30
87.90	81.77	6.50
90.20	98.47	9.40

^a[YAKIMOV]

Table A-29. Solubility Data for NaNO₃ in Nitric Acid-Water at 75°C^a

[HNO ₃] (wt%)	[HNO ₃] (mol%)	[NaNO ₃] (wt%)
0.00	0.00	58.30
17.20	9.99	38.50
30.50	16.56	25.60
38.00	20.42	19.70
41.70	22.47	17.20
63.70	38.16	6.80
70.80	46.79	6.20
78.30	58.61	5.90
87.00	81.61	7.40
87.70	84.49	7.70
88.90	89.44	8.10

^a[SILOCK-G]

Table A-30. Solubility Data for $\text{Sm}(\text{NO}_3)_3$ in
Nitric Acid-Water at 25°C^a

$[\text{HNO}_3]$ (wt%)	$[\text{HNO}_3]$ (mol%)	$[\text{Sm}(\text{NO}_3)_3]$ (wt%)
0.00	0.00	58.95
6.15	4.04	52.08
11.34	7.14	46.52
44.38	24.43	16.40
48.40	26.99	14.20
51.58	29.76	13.64

^a(SILOCK-H)

Table A-31. Solubility Data for $\text{Sm}(\text{NO}_3)_3$ in Nitric
Acid-Water at 50°C^a

$[\text{HNO}_3]$ (wt%)	$[\text{HNO}_3]$ (mol%)	$[\text{Sm}(\text{NO}_3)_3]$ (wt%)
0.00	0.00	64.81
2.12	1.71	62.97
7.53	5.81	57.57
22.38	16.41	45.05
36.40	23.49	33.20
47.52	37.89	30.22
46.21	33.76	27.89

^a(SILOCK-H)

Table A-32. Solubility Data for $\text{UO}_2(\text{NO}_3)_2$ in Nitric Acid-Water at 25°C^a

$[\text{HNO}_3]$ (wt%)	$[\text{HNO}_3]$ (mol%)	$[\text{UO}_2(\text{NO}_3)_2]$ (wt%)
0.00	0.00	56.08
12.35	6.94	40.36
25.14	13.88	30.29
28.67	16.43	29.65
29.84	17.98	31.27
30.43	20.93	36.72
30.15	21.28	37.99
32.31	22.71	36.28
46.12	33.04	27.18
50.43	37.73	25.79
53.20	43.15	26.77
53.71	44.94	27.49
55.24	47.39	27.24
60.38	51.93	23.65
66.71	63.41	22.29
68.83	69.38	22.49

^a(SILOCK-1)

Table A-33. Solubility Data for $\text{UO}_2(\text{NO}_3)_2$ in
Nitric Acid-Water at 49.1°C^a

$[\text{HNO}_3]$ (wt%)	$[\text{HNO}_3]$ (mol%)	$[\text{UO}_2(\text{NO}_3)_2]$ (wt%)
5.10	4.24	62.00
3.20	2.64	63.10
5.40	4.59	62.50
11.30	9.80	59.00
10.70	9.88	61.40
10.90	8.79	56.80
12.40	11.71	60.90
13.10	12.54	60.80
19.70	17.97	54.60
19.70	18.44	55.40
25.50	22.57	49.50
27.20	24.01	48.20
28.20	25.13	47.80
30.80	27.76	46.30
30.00	26.64	46.40
33.40	31.55	45.90
34.10	32.43	45.60
35.80	34.06	44.40
36.30	36.56	45.70
37.90	34.35	41.40
40.60	38.28	40.70
48.60	48.24	36.50
49.50	49.20	35.90
52.30	54.06	35.00
63.50	63.34	26.00
80.20	75.09	12.20
80.70	77.75	12.70
83.00	77.97	10.30
85.50	81.16	8.83

^a[SILOCK-J]

Table A-34. Solubility Data for $\text{UO}_2(\text{NO}_3)_2$ in Nitric
Acid-Water at 50°C^a

$[\text{HNO}_3]$ (wt%)	$[\text{HNO}_3]$ (mol%)	$[\text{UO}_2(\text{NO}_3)_2]$ (wt%)
0.15	0.14	69.15
0.60	0.54	68.10
3.30	3.01	66.00
5.20	4.84	65.60
8.10	7.95	65.10
8.40	8.48	65.70
10.40	10.29	63.70
10.60	10.47	63.50
13.10	12.76	61.30
13.00	12.54	61.10
15.40	14.29	58.20
24.00	21.66	51.20
27.60	24.73	48.40
30.10	27.56	47.30
30.10	27.39	47.10
32.10	29.33	45.80
35.50	34.80	45.50
36.40	35.62	44.80
38.00	37.49	43.90
38.90	38.04	43.00
41.80	40.56	40.70
44.60	43.28	38.70
50.50	49.03	34.50
60.00	61.79	29.40
63.80	70.03	28.40
65.00	72.91	28.10
64.40	74.49	29.30
62.50	83.61	34.00
57.00	89.06	41.00
54.40	90.67	44.00
53.00	88.85	45.10
53.20	92.12	45.50
55.30	98.75	44.50

^a(SILOCK-B)

APPENDIX B

VAPOR-LIQUID EQUILIBRIUM DATA

The composition of the TRUEX waste streams is mainly aqueous nitric acid solutions containing metal nitrate salts. Therefore, to design the evaporator for concentrating specific TRUEX waste streams it is important to know the concentration of water and nitric acid in the liquid and vapor phases as a function of temperature, pressure, and composition of the aqueous solution. However, some solutions may also contain other acids such as sulfuric, phosphoric, hydrofluoric, and oxalic. Thus it is important to understand the effects of these acid on the system.

A literature survey was carried out to evaluate the effect the presence of metal nitrate salts have on the vapor-liquid equilibria of aqueous solutions of HNO_3 . The most useful source of information was a set of five books by Wichterle et al. (WICHTERLE-1973, WICHTERLE-1976, WICHTERLE-1979, WICHTERLE-1982, WICHTERLE-1985) which give a bibliography of almost 8500 vapor-liquid equilibrium systems studied from 1900 through 1984. Many applicable references were obtained from this source for both nitric acid-water and nitric acid-water-nitrate salt systems.

In the Hanford waste streams, the nitrate salts present in the largest concentrations are Al^{3+} , Ca^{2+} , Fe^{3+} , La^{3+} , Na^+ , Ni^{2+} , and UO_2^{2+} nitrates. Therefore these HNO_3 - H_2O -nitrate salts systems were studied.

To aid the reader in locating information in this appendix, the following two tables were generated. Table B-1 summarizes the systems displayed in each figure. Table B-2 contains a list of the systems reported in each table. For clarity, all of the tables were moved to the end of this appendix.

Table B-1. List of Systems Displayed in Figures

No.	System	Pressure (mmHg)	Page
B-1.	Nitric Acid-Water	760	76
B-2.	Nitric Acid-Water	760	77
B-3.	Nitric Acid-Water	50, 100, & 760	78
B-4.	Nitric Acid-Water System	Various Pressures	78
B-5.	La, Ni, & Na Salting-out Capacity	400	79
B-6.	Nitric Acid-Aluminum Nitrate	130	81
B-7.	Nitric Acid-Sodium Nitrate	760	81
B-8.	Nitric Acid-Sodium Nitrate	760	82
B-9.	$\text{HNO}_3\text{-H}_2\text{O-UO}_2(\text{NO}_3)_2$		83
B-10.	Nitric Acid-Water-Sodium Nitrate		84
B-11.	Nitric Acid - Water - Sulfuric Acid	760	86
B-12.	Nitric Acid - Water - Sulfuric Acid	760	86
B-13.	Sulfuric Acid - Water		87
B-14.	Phosphoric Acid vs. Water Activity		88

Table B-2. List of Systems Described in Tables

No.	System	Pressure (mmHg ^a)	Page
B-3.	Nitric Acid-Water	760	89
B-4.	Nitric Acid-Water	760	90
B-5.	Nitric Acid-Water	760	90
B-6.	Nitric Acid-Water	760	91
B-7.	Nitric Acid-Water	50	92
B-8.	Nitric Acid-Water	100	93
B-9.	Nitric Acid-Water	200	93
B-10.	Nitric Acid-Water	400	94
B-11.	Nitric Acid-Water	450	95
B-12.	Nitric Acid-Water	600	96
B-13.	Comparison of Salting Out Capacity of 6 mol%La, Ni, & Na	400	97
B-14.	Aluminum Nitrate	30	98
B-15.	Sodium Nitrate	760	99
B-16.	HNO ₃ -H ₂ O-UO ₂ (NO ₃) ₂	180, 360, 720	100
B-17.	Nitric Acid - Water - Sulfuric Acid	760	101
B-18.	Sulfuric Acid		103
B-19.	Constants for Water-Sulfuric Acid Fit		105
B-20.	Water Activity Over Aqueous Phosphoric Acid at 25°C		106

1. Conventions

The following two conventions will be used in presenting data in the literature survey.

- (1) When data are plotted as a function of mol% of nitric acid this will be mol% of nitric acid in solution with the salt removed. This is described by Eq. B-1:

$$\text{mol\% HNO}_3 \text{ (Salt Free)} = \frac{\text{mol HNO}_3}{\text{mol HNO}_3 + \text{mol H}_2\text{O}} \cdot 100 \quad (\text{B-1})$$

For example, a solution containing 10 mol nitrate salt, 30 mol HNO₃, and 60 mol H₂O would have an actual 10 mol% salt 30 mol% mol HNO₃, and 60 mol% H₂O. The mol% HNO₃ (Salt Free) = 33.33 mol%.

- (2) Additionally, the variables x and y will be used to represent the concentration of nitric acid in the liquid and vapor phases respectively.

2. Binary Systems

To understand the effects that salts have on H_2O - HNO_3 -salt systems, it is useful to first understand the binary system. According to Ellis and Thwaites [ELLIS], at atmospheric pressure the azeotropic composition of nitric acid-water system is 38.65 mol% HNO_3 with a boiling temperature of 120.1°C . Data from three additional authors, Boolik et al., Potier & Alger, and Prosek [HALA-A, HALA-B, HALA-C] were also obtained for this system at atmospheric pressure. The data from these four authors are listed in Table B-3 through Table B-6. The boiling temperature versus the nitric acid concentration in the liquid phase is plotted in Fig. B-1 and the concentration of nitric acid in the vapor phase versus the concentration of nitric acid in the liquid phase is plotted in Fig. B-2.

It can be seen from Figs. B-1 and B-2 that all the data agree very well at this pressure.

Fig. B-1. Comparison of Boiling-Temperature Data for Nitric Acid-Water System at 760 mmHg

Fig. B-2. Comparison of Vapor and Liquid Composition Data for the Nitric Acid-Water System at 760 mmHg

Boolik et al. [HALA-D, HALA-E, HALA-F, HALA-G] also conducted experiments at pressures of 50, 100, 200, 400, and 450 mmHg and Potier & Alger [HALA-H, HALA-I] conducted an experiment at 600 mmHg. From these data, plotted in Fig B-3 and B-4 and listed in Table B-7 through B-12, it is evident that decreasing the pressure only reduces the temperature at which the system will boil for a given acid concentration. Note that for clarity, only data for 3 different pressures are plotted in Fig. B-3. This was sufficient to show the trends as pressure changed.

Fig. B-3. Comparison of Binary Nitric Acid-Water System at 50, 100, & 760 mmHg

Fig. B-4. Comparison of Binary Nitric Acid-Water System at Various Pressures

3. Ternary Systems (Effect of Salts)

For multi-component systems, such as nitric acid-water-nitrate salt, the vapor-liquid equilibrium is affected by two variables. One is the composition of the aqueous solution, which effects the activities of water and nitric acid. The second is the pressure of the system, which effects primarily boiling temperature.

The presence of salts, with the exception of potassium nitrate, in the nitric acid-water system tends to salt out the nitric acid into the vapor phase, thus enriching the vapor phase in nitric acid. In terms of thermodynamics, salting out is equivalent to increasing the activity of HNO_3 and decreasing the activity of water. Barnov et al. [BARNOV] investigated the vapor-liquid equilibrium of 13 nitric acid-water-nitrate salt systems at atmospheric pressure. Nitrate salts included potassium, sodium, lithium, barium, strontium, calcium, magnesium, mercury, cadmium, zinc, manganese, cobalt, and nickel. He concluded that the salting out capacity of salts can be related to the square root of the charge to radius ratio. Polovnikova et al. [POLOVNIKOVA] studied 16 ternary systems of nitric acid-water-sulfates at atmospheric pressure. Sulfates salts included lithium, sodium, potassium, zinc, cadmium, mercury, copper, manganese, cobalt, nickel, lanthanum, yttrium, scandium, indium, gallium, and aluminum. Polovnikova et al. suggest that the salting out capacity of sulfates show trends similar to the nitrates. Using the information from Barnov et al. and Polovnikova et al. it can be shown that the salting out capacity of the salts, of interest in this project, is as follows: $\text{Al} > \text{La} > \text{Ni} > \text{Ca} > \text{Na}$. This trend can be verified for La, Ni, and Na by plotting experimental data from Efimov et al. [EFIMOV-1974, EFIMOV-1975]. The plot is shown in Fig. B-5, and the data are listed in Table B-13.

Fig. B-5. Comparison of Salting-out Capacity for 6 mol % La, Ni, & Na at 400 mmHg

Although data were available for other salt systems, it was not possible to make similar comparisons since data were either obtained at different pressures or for different salt concentrations.

According to Efimov et al. [EFIMOV-1970], the salting out of the nitrates is basically the result of two factors. First is the hydration of the salts (equivalent to decreasing the activity of H_2O). Second is the shift of the ionic equilibrium of the nitric acid under the influence of the common ion, NO_3^- , introduced with the salt (increasing the activity of nitrate and, therefore nitric acid). Both factors lead to an increase in the effective concentration of nitric acid in the liquid, and consequently in the equilibrium vapors.

While it is important to understand the relative salting-out capacities of different salts it is also important, if not more so, to know how the vapor-liquid equilibrium for nitric acid-water-nitrate salt system changes as the concentration of the salt increases. With all the salts studied, it was found that increasing the salt concentration, while maintaining a constant pressure, increases both the concentration of acid in the vapor phase and the solution boiling point while decreasing the azeotropic point. The change in vapor phase composition of nitric acid is illustrated in Fig. B-6 for aluminum nitrate at 130 mmHg [EFIMOV-1975] and in Fig. B-7 for sodium nitrate at 760 mmHg [EFIMOV-1974]. The data are listed in Table B-14 and Table B-15 respectively.

Fig. B-6. Concentration of Nitric Acid in the Vapor Phase as a function of the Concentration in the Liquid Phase of Aluminum Nitrate at 130 mmHg

Fig. B-7. Concentration of Nitric Acid in the Vapor Phase as a function of the Concentration in the Liquid Phase of Sodium Nitrate at 760 mmHg

Shneerson et al. [SHNEERSON] of nitric acid and water showed that the azeotropic composition (the point at which the liquid and vapor-phase concentrations are equal) of the nitric acid-water-salt system decreased with increasing concentration of magnesium nitrate or calcium nitrate. In other words, the azeotropic point occurred at lower concentrations of nitric acid in the liquid phase as the salt concentration increased. This is also observed in Fig. B-6 with aluminum nitrate. The diagonal line in Fig. B-6 represents equal compositions in the liquid and vapor phases. Thus the points of intersection between this line and the curves from the data are azeotropes for that concentration of salt.

As mentioned earlier, the boiling point of the system increases with increasing salt concentration. The effect is illustrated in Fig. B-8 for sodium nitrate at 760 mmHg [EFIMOV-1974]. The data are listed in Table B-15.

Fig. B-8. Boiling Temperature vs. Concentrations of Nitric Acid and Sodium Nitrate

4. Pressure Effects

The system pressure for nitric acid-water-nitrate salt systems affects both the concentration of nitric acid in the vapor phase and the system boiling point. Efimov et al. [EFIMOV-1970, EFIMOV-1973] reported that at low nitric acid concentrations in the vapor phase (y), the concentration of nitric acid in the vapor phase decreased as the system pressure decreased. The region of low concentration was reported as $y < 15$ mol% when they studied the $\text{H}_2\text{O}-\text{HNO}_3-\text{UO}_2(\text{NO}_3)_2$ system and $y < 25$ mol% when they studied the $\text{H}_2\text{O}-\text{HNO}_3-\text{Be}(\text{NO}_3)_2$ and $\text{H}_2\text{O}-\text{HNO}_3-\text{Cu}(\text{NO}_3)_2$ systems. For higher vapor concentrations, y , the affect is the opposite. This is illustrated in Fig. B-9 for the $\text{H}_2\text{O}-\text{HNO}_3-\text{UO}_2(\text{NO}_3)_2$ system [EFIMOV-1970]. The data are listed in Table B-16.

Fig B-9. Change in Nitric Acid Concentration in the Vapor Phase [log (mol %)] with Change in System Pressure [log (mmHg)] for the $\text{HNO}_3-\text{H}_2\text{O}-\text{UO}_2(\text{NO}_3)_2$ at Constant Salt Concentration of 3 mol%

The temperature at which a system will boil is affected by both the composition of the system as well as the system pressure. Decreasing the pressure of the system, while maintaining a constant solution composition, reduces the boiling point of the solution. An example of this is shown in Fig. B-10 for 3 mol% sodium nitrate (using data from Table B-15) [EFIMOV-1974].

Fig. B-10. Effect of Change in System Pressure on the Boiling Temperature of the Nitric Acid-Water- 3 mol% Sodium Nitrate System

5. Multiple Salts Systems

Since the evaporator will operate with solutions containing more than one salt, it is advantageous to understand the effect of multiple salts on the nitric acid-water-salt system. Both Zhikharev et al. [ZHIKAREV] and Shneerson et al. [SHNEERSON] suggest that the presence of two or more salts is approximately additive. Zhikharev et al. studied ternary systems of $\text{HNO}_3\text{-H}_2\text{O-Fe(NO}_3)_3$, and $\text{HNO}_3\text{-H}_2\text{O-Cu(NO}_3)_2$. From the results of these systems they used Eq. B-2 to predict the acid concentration in the vapor phase for the system $\text{HNO}_3\text{-H}_2\text{O-Cu(NO}_3)_2\text{-Fe(NO}_3)_3$.

$$\log \frac{Y}{100-Y} = \sum_i \frac{C_i}{C_S} \log \frac{Y_i}{100-Y_i} \quad (\text{B-2})$$

where Y = concentration of nitric acid in the vapor phase for the multi-component system when X is constant.

Y_i = concentration of nitric acid in the vapor phase as a result of the i th salt from a ternary system.

C_i = concentration of the i th salt.

C_S = total concentration of the salting-out agent.

They found the calculated results to compare well with experimental results for the four component system. They concluded that equation B-2 could be used to predict, within experimental error, the nitric acid concentration in the vapor phase for systems containing multiple salts from ternary system data.

6. Other Data Available

Additional data was collected during this literature search but was not presented in this report. Vapor-liquid equilibrium data for nitric acid-water-nitrate salt systems, at various pressures, not listed above include system with Be, Ca, Cr, Cu, Fe, Fe + Cu, La, La + Mg, Ni, and UO₂ nitrate salts. Furthermore, for the Al and Na nitrate salt systems, data were also collected for pressures not presented above. The data tables and plots are recorded in a Laboratory Notebook for later access.

7. Multiple Acid Systems

Information on systems containing nitric acid-water and some other acid, such as sulfuric, phosphoric or oxalic acid, was very limited. One paper, by Flatt and Bonnet [FLATT], was obtained for the nitric acid-water-phosphoric acid system. This paper appears to give some useful information and is in the process of being translated from French. Another paper, by Berl et al. [BERL] discussed both the nitric acid-water-phosphoric acid and the nitric acid-water-sulfuric acid systems. This reference is written in German and contains no data but does contain a few figures. A decision to translate this paper has not yet been made. Ellis and Thwaites [ELLIS] studied the nitric acid-water-sulfuric acid system and Petrov et al. [PETROV] studied the nitric acid-water-phosphoric acid system (only the abstract is currently available for this paper). Both authors found that the presence of the second acid tended to salt out the nitric acid into the vapor phase. Ellis and Thwaites [ELLIS] also showed that the equilibrium temperature increased with increasing concentration of sulfuric acid. These phenomena are illustrated Fig. B-11 and Fig. B-12 using data from Ellis and Thwaites [ELLIS] for the nitric acid - sulfuric acid -water system. The data in is listed in Table B-17.

Fig. B-11. Concentration of Nitric Acid in the Vapor Phase Above Solutions of Nitric Acid - Water - Sulfuric Acid at 760 mmHg

Fig. B-12. Temperature Versus Nitric Acid in the Liquid Phase for Nitric Acid - Water - Sulfuric Acid Systems at 760 mmHg

Fig. B-13. Vapor Pressure of Water over Aqueous Sulfuric Acid solutions as a Function of Absolute Temperature

Three trends are evident from the data. First, the vapor pressure of water decreases as acid concentration increases. Second, the vapor pressure of water increases with increasing temperature. Note that temperature in Fig. B-13 decreases from left to right. Third, the relationship between the log of the vapor pressure and the inverse of the absolute temperature, °K, is nearly linear. This may be expressed fairly accurately by the following equation

$$\log(p) = A + B(1/T) \quad (B-3)$$

For most acid concentrations the data were fit by minimizing the sum of the squares of the difference between the experimental vapor pressure and the calculated vapor pressure to obtain values for the constants A and B. The constants obtained are given in Table B-19.

Only two references were available on phosphoric acid - water systems. Fontana (FONTANA) studied systems with 86.5% to almost 100% phosphoric acid. As was done for the sulfuric acid-water system, he showed a linear relationship between the log of the pressure and the inverse of the absolute temperature. This concentration range, however, is not likely to occur in the evaporator and therefore the data are not presented here. Elmore et al. (ELMORE) studied the activity of aqueous phosphoric acid systems at 25°C from 1 to 75 molal H_3PO_4 . Sulfuric acid was used as a reference standard. The activity of water is plotted as a function of phosphoric acid concentration in Fig. B-14. The data are presented in Table B-20. As was noted for sulfuric acid systems, the activity of water decreases with increasing concentration of phosphoric acid for a constant temperature.

Fig. B-14. Activity of Water over Aqueous Phosphoric Acid Solutions

Due to the limited information on the systems containing phosphoric acid and sulfuric acid it might be useful to study these systems further.

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Table B-3. Comparison of Data for Binary $\text{HNO}_3\text{-H}_2\text{O}$
Systems at 760 mmHg^a

Mol % HNO_3		Temp (°C)
Liquid	Vapor	
6.10	0.36	104.0
9.60	0.95	106.4
11.70	1.50	107.8
13.90	2.11	109.4
17.50	4.23	111.8
18.30	5.10	112.3
22.50	8.95	114.8
26.60	13.60	116.9
27.70	15.99	117.5
34.10	25.90	119.4
37.40	36.50	119.9
38.32	37.45	120.1
48.50	73.00	116.1
52.10	81.08	113.4
54.70	85.00	110.8
65.10	94.20	102.9
71.90	97.20	96.1
76.50	98.75	92.0
81.60	99.30	88.4
100.0	100.00	83.4

^a[ELLIS]

Table B-4. Comparison of Data for Binary HNO₃-H₂O
Systems at 760 mmHg^a

Mol % HNO ₃		Temp (°C)
Liquid	Vapor	
8.88	8.00	106.50
9.00	1.10	106.50
11.70	1.70	108.50
14.50	2.60	110.70
25.80	13.80	117.80
35.50	32.40	120.60
36.10	34.00	120.60
39.80	44.00	120.30
40.30	44.50	120.10
51.60	70.50	113.50
66.80	89.30	98.20
69.80	91.20	96.00
85.80	97.80	85.80

^a[HALA-A]

Table B-5. Comparison of Data for Binary HNO₃-H₂O
Systems at 760 mmHg^a

Mol % HNO ₃		Temp (°C)
Liquid	Vapor	
17.85	4.39	111.15
23.91	10.27	114.80
34.84	29.85	119.85
39.95	43.00	119.35
41.83	47.46	119.05
47.08	61.19	117.20
47.61	62.61	117.20
49.51	67.60	116.10

^a[HALA-B]

Table B-6. Comparison of Data for Binary HNO₃-H₂O
Systems at 760 mmHg^a

Mol % HNO ₃		Temp (°C)
Liquid	Vapor	
6.70	0.25	104.00
7.20	0.25	104.50
10.20	1.03	106.50
10.20	1.05	106.70
11.00	1.20	107.00
13.50	2.00	108.50
14.10	2.30	109.50
16.20	3.50	110.50
18.10	4.20	111.50
18.10	4.20	112.00
21.70	8.20	114.50
23.30	9.60	115.50
28.20	16.50	117.50
30.00	19.10	118.00
33.70	21.10	119.00
34.80	29.70	119.20
45.00	56.40	118.50
47.40	65.10	117.00
51.50	76.20	115.00
51.50	73.60	114.90
53.00	76.40	113.00
54.00	76.80	112.60
55.70	85.70	111.50
57.40	86.40	108.80
60.60	93.60	106.00
64.90	94.50	102.00
70.00	96.00	97.50
72.30	98.40	95.80
73.80	98.60	95.50
75.50	98.30	92.00
80.20	98.30	91.00
85.30	98.40	87.20
87.80	98.80	86.90
99.10	99.70	82.80

^a[HALA-C]

Table B-7. Data for Nitric Acid-Water System at P = 50 mmHg^a

Mol% HNO ₃		Temp (°C)
Liquid	Vapor	
9.30	0.60	43.00
15.30	1.00	48.20
24.00	9.00	55.00
28.30	16.50	56.90
35.30	34.50	57.80
35.70	35.80	57.90
38.50	43.90	57.60
39.20	45.80	57.10
54.60	79.50	50.40
55.10	80.40	50.20
57.60	84.80	47.40
66.40	92.30	38.50
68.10	91.90	36.60
71.30	94.10	32.60
72.70	95.00	32.50
88.70	99.00	24.60

^a[HALA-D]

Table B-8. Data for Nitric Acid-Water System at P = 100 mmHg^a

Mol% HNO ₃		Temp (°C)
Liquid	Vapor	
14.90	1.20	61.60
21.90	5.40	65.60
25.00	10.60	68.10
31.00	22.40	71.60
35.40	34.30	72.60
38.90	44.30	71.70
39.80	46.30	71.50
43.30	57.60	70.10
55.20	81.70	61.90
62.90	88.10	55.60
65.40	90.40	54.00
68.30	92.60	50.80

^a[HALA-E]

Table B-9. Data for Nitric Acid-Water System at P = 200 mmHg^a

Mol% HNO ₃		Temp (°C)
Liquid	Vapor	
8.50	1.00	71.70
13.20	1.10	75.40
14.40	1.50	77.20
19.20	4.00	79.50
28.40	17.10	84.80
35.60	34.10	86.50
39.70	47.00	86.30
43.20	55.00	85.10
55.80	79.90	73.40
65.30	89.30	64.60
68.60	93.10	61.90
71.60	94.00	58.20
93.30	98.60	49.80

^a[HALA-F]

Table B-10. Data for Nitric Acid-Water System at P= 400 mmHg^a

Mol% HNO ₃		Temp (°C)
Liquid	Vapor	
13.50	1.60	91.90
18.10	4.50	96.00
29.60	20.50	102.40
35.70	32.10	103.20
39.80	45.50	102.80
43.50	54.40	101.60
53.30	73.90	94.10
53.70	74.90	94.00
54.60	77.00	92.70
71.80	93.10	78.50
88.00	98.80	68.50
88.90	98.80	67.80

^a[HALA-G]

Table B-11. Data for Nitric Acid-Water System at P= 450 mmHg^a

Mol% HNO ₃		Temp (°C)
Liquid	Vapor	
5.20	0.00	88.60
6.90	0.01	89.70
8.90	0.22	92.00
9.60	0.24	92.40
18.10	3.20	100.00
24.10	8.10	102.00
30.00	11.40	103.80
30.20	8.70	104.40
32.20	23.80	104.70
31.60	21.60	105.00
32.20	24.90	105.20
34.10	27.10	105.30
36.80	36.70	106.00
45.70	60.70	104.00
49.80	72.60	101.00
53.70	82.30	97.50
63.00	88.60	91.50
72.50	96.30	81.90
75.90	96.10	79.50
82.40	96.30	74.60
87.50	97.00	73.10
90.10	96.80	72.20
91.40	97.90	71.40
93.80	96.75	70.60
96.10	97.40	70.00

^a[HALA-H]

Table B-12. Data for Nitric Acid-Water System at P= 600 mmHg^a

Mol% HNO ₃		Temp (°C)
Liquid	Vapor	
1.70	0.01	94.20
2.90	0.08	96.00
5.10	0.10	96.90
4.20	0.07	97.00
4.30	0.08	97.10
4.80	0.08	97.30
7.90	0.29	98.60
7.20	0.20	99.20
8.40	0.30	100.00
10.80	1.05	102.00
13.90	1.80	103.50
16.40	2.90	105.00
18.70	4.00	106.20
18.70	5.90	108.20
25.90	9.50	110.80
33.80	26.70	113.50
36.90	36.80	113.70
39.20	42.30	113.60
43.90	56.30	112.80
53.30	72.70	108.00
52.80	74.20	107.90
54.60	82.30	105.00
58.90	91.30	102.10
60.00	94.50	99.10
63.30	92.90	97.00
70.60	98.00	93.30
69.10	96.00	91.70
72.80	98.00	99.20
72.20	98.40	87.80
89.10	98.40	79.50
96.10	99.80	76.80

^a[HALA-I]

Table B-13. Comparison of Salting Out Capacity of 6 mol%La, Ni, & Na at 400 mmHg

La(NO ₃) ₃ ^a		Ni(NO ₃) ₂ ^a		NaNO ₃ ^b	
Mol % HNO ₃		Mol % HNO ₃		Mol % HNO ₃	
Liquid	Vapor	Liquid	Vapor	Liquid	Vapor
6.00	2.59	6.00	3.50	0.00	0.00
9.00	5.03	15.00	16.11	3.00	0.22
15.00	15.25	24.00	35.30	6.00	0.62
24.00	40.83			9.00	1.23
				12.00	2.34
				15.00	4.18
				18.00	6.82
				21.00	10.28
				24.00	14.28
				27.00	19.11
				30.00	25.30

^a[EFIMOV-1975].

^b[EFIMOV-1974].

Table B-14. Aluminum Nitrate Data at 130 mmHg^a

Wt% Salt	Mol% HNO ₃	
	Liquid	Vapor
10	3.08	0.11
	6.67	0.40
	10.91	1.13
	16.00	4.57
	22.23	14.19
20	3.08	0.20
	6.67	0.91
	10.91	3.39
	16.00	11.24
	22.23	27.13
30	3.08	0.61
	6.67	2.60
	10.91	8.84
	16.00	20.45
40	3.08	2.48
	6.67	8.30
	10.91	23.12
50	3.08	9.47
	6.67	24.84

^a[EFIMOV-1975]

Table B-15. Sodium Nitrate Data at 760 mmHg^a

mol% salt	Mol% HNO ₃		Temp (°C)
	Liquid	Vapor	
3.00	0.00	0.00	101.40
	3.00	0.21	103.60
	6.00	0.54	105.70
	9.00	1.13	107.80
	12.00	2.17	109.90
	15.00	3.60	111.90
	18.00	5.80	113.70
	21.00	8.63	115.60
	24.00	12.42	117.30
	27.00	17.23	118.80
	30.00	22.00	119.80
	0.00	0.00	103.10
	3.00	0.33	105.40
	6.00	0.85	107.60
6.00	9.00	1.60	109.70
	12.00	2.93	111.70
	15.00	4.91	113.50
	18.00	7.70	115.30
	21.00	11.10	117.00
	24.00	15.03	118.60
	27.00	19.54	120.00
	30.00	25.30	120.50
	0.00	0.00	104.80
	3.00	0.50	107.20
	6.00	1.21	109.40
	9.00	2.15	111.50
	12.00	3.79	113.00
	15.00	6.16	115.40
9.00	18.00	9.25	117.00
	21.00	13.15	118.60
	24.00	17.76	120.00
	27.00	22.23	120.70
	30.00	28.00	121.20
	0.00	0.00	106.60
	3.00	0.67	109.20
	6.00	1.55	111.30
	9.00	2.88	113.40
	12.00	4.85	115.20
	15.00	7.57	116.90
	18.00	10.95	118.50
	21.00	15.10	120.00
	24.00	19.53	121.00

(contd.)

Table B-15. Contd.

Mol% HNO ₃			
mol% salt	Liquid	Vapor	Temp (°C)
15.00	27.00	25.61	121.50
	30.00	30.86	121.80
	0.00	0.00	108.50
	3.00	0.81	111.10
	6.00	1.92	113.30
	9.00	3.51	115.20
	12.00	5.85	116.90
	15.00	8.90	118.60
18.00	18.00	12.65	120.00
	21.00	17.20	121.50
	0.00	0.00	110.60
	3.00	1.02	113.10
	6.00	2.40	115.30
	9.00	4.40	117.10
	12.00	7.15	118.80
	15.00	10.60	120.30
21.00	0.00	0.00	112.70
	3.00	1.23	115.00
	6.00	2.90	117.20
	9.00	5.18	119.00

^a[EFIMOV-1974]Table B-16. Vapor-Liquid Equilibrium Data for HNO₃-H₂O-UO₂(NO₃)₂ System at 3 Pressures for a Constant Salt Concentration of 3 mol%^a

mol% HNO ₃ , x	System Pressure					
	180		360		720	
	y	log y	y	log y	y	log y
6	0.40	-0.40	0.55	-0.26	0.77	-0.11
12	2.10	0.32	2.42	0.38	2.91	0.46
18	7.32	0.86	7.86	0.90	8.51	0.93
24	15.11	1.18	15.24	1.18	14.94	1.17
30	26.38	1.42	24.36	1.39	21.98	1.34

^a[EFIMOV-1970]

Table B-17. Equilibrium Data for the Nitric Acid - Water - Sulfuric Acid System at 760
mmHg^a

Weight % Liquid		Mol% Liquid		Mol% Vapor	Temp. (°C)
H ₂ SO ₄	HNO ₃	H ₂ SO ₄	HNO ₃	HNO ₃	
7.45	40.80	2.10	18.20	7.00	114.30
7.38	43.40	2.16	19.60	8.75	115.50
7.51	59.50	2.70	33.10	35.20	120.20
6.80	64.00	2.50	37.50	46.50	120.00
6.90	74.00	3.00	51.00	85.60	110.00
19.70	15.81	5.00	6.22	0.15	109.90
20.10	22.60	5.47	9.57	3.11	112.80
20.10	29.50	5.90	13.50	7.03	115.80
20.50	35.50	6.52	17.50	14.70	118.70
19.80	41.30	6.69	21.71	26.58	121.25
19.50	46.70	7.06	26.30	44.50	122.20
19.80	53.20	7.93	33.16	74.74	117.40
38.20	6.74	10.96	3.01	1.89	115.30
37.50	9.53	11.00	4.35	3.96	116.90
37.00	12.60	11.20	5.93	5.26	118.50
37.60	16.40	11.97	8.13	9.80	121.30
37.70	21.60	12.86	11.47	20.02	123.10
37.00	24.90	13.10	13.50	26.20	125.10
38.10	29.25	14.57	17.41	48.46	125.70
37.20	33.30	14.90	20.75	63.61	125.25
37.60	41.20	17.40	29.40	92.50	112.50
49.80	2.38	15.90	1.17	1.93	124.10
48.75	4.50	15.70	2.26	3.84	124.95
50.10	9.12	17.50	4.96	13.50	129.50
49.75	13.55	18.37	7.79	29.50	132.30
50.00	15.90	18.15	9.50	42.96	131.20
50.00	18.40	20.00	11.40	57.50	130.10
50.60	26.20	23.40	18.80	93.70	123.00
51.00	30.15	24.90	22.80	97.70	115.90
59.80	0.81	21.70	0.45	2.08	140.50
59.00	1.67	21.39	0.94	4.58	138.00
60.50	2.59	22.80	1.51	7.90	141.50
60.40	3.94	23.35	2.37	13.30	142.20
60.00	6.04	23.70	3.70	25.20	141.35
59.95	9.18	25.00	5.94	45.10	137.60
59.10	11.72	25.10	7.72	59.30	134.40
60.00	14.72	27.20	10.38	84.45	129.40
70.10	0.29	30.20	0.19	2.58	161.40
69.25	0.68	29.60	0.45	5.86	163.00
70.43	0.93	30.91	0.62	9.47	165.00

(contd)

Table B-17. (contd)

Weight % Liquid		Mol% Liquid		Mol% Vapor	Temp. (°C)
H ₂ SO ₄	HNO ₃	H ₂ SO ₄	HNO ₃	HNO ₃	
70.00	1.30	30.70	0.87	13.30	165.80
69.90	2.02	31.00	1.39	21.00	164.60
69.80	3.05	31.38	2.13	34.66	162.00
69.40	4.28	32.80	3.10	53.00	152.20
68.80	7.20	32.70	5.30	77.30	144.50
70.00	8.46	34.90	6.60	95.60	137.50
80.50	0.19	43.30	0.15	4.70	198.30
79.55	0.44	41.60	0.32	10.00	196.60
80.40	0.65	43.60	0.54	19.73	197.90
81.00	0.95	44.80	0.81	29.55	196.60
80.20	1.15	43.50	0.96	34.60	193.90
80.70	1.31	44.60	1.12	53.80	195.60

a[ELLIS]

Table B-18. Vapor Pressure Above Aqueous Sulfuric Acid Solutions vs. Temperature and wt % Sulfuric Acid^a

Temp. °C	1/T (1/°K)	10.02 wt%		20.4 wt%		29.84 wt%		34.74 wt%		39.90 wt%		48.44 wt%	
		P (mmHg)	log P	P (mmHg)	log P	P (mmHg)	log P	P (mmHg)	log P	P (mmHg)	log P	P (mmHg)	log P
0	0.00366	4.08	0.6107	3.4	0.5340	2.9	0.4639	3.05	0.4843	1.8	0.2529	1.4	0.1584
10	0.00353	8.17	0.9122	7.2	0.8591	6.1	0.7825			4.1	0.6096	3.0	0.4742
20	0.00341	15.82	1.1992	15.3	1.1853	12.7	1.1048	10.99	1.0410	7.6	0.8808	7.0	0.8451
25	0.00336	21.80	1.3385	20.8	1.3181	17.4	1.2405			10.9	1.0374	9.5	0.9791
30	0.00330	28.60	1.4564	27.1	1.4330	21.9	1.3404			15.2	1.1810	12.3	1.0906
35	0.00325	38.80	1.5888	37.3	1.5717	31.3	1.4955			21.5	1.3324	16.8	1.2251
40	0.00319	50.30	1.7016	47.4	1.6758	39.9	1.6010	36.30	1.5599	29.8	1.4742	21.5	1.3324
45	0.00314	66.60	1.8235	62.0	1.7924	53.5	1.7284			39.8	1.5999	29.2	1.4654
50	0.00310	85.60	1.9325	79.7	1.9015	68.9	1.8382			52.5	1.7202	37.4	1.5729
55	0.00305	110.90	2.0449	102.4	2.0103	89.4	1.9513			68.4	1.8351	49.1	1.6911
60	0.00300	139.00	2.1430	130.0	2.1139	111.5	2.0473	101.00	2.0043	88.3	1.9460	62.7	1.7973
65	0.00296	175.40	2.2440	163.9	2.2146	143.2	2.1559			112.2	2.0500	80.1	1.9036
70	0.00292	217.00	2.3365	204.1	2.3098	179.0	2.2529			141.1	2.1495	101.0	2.0043
75	0.00287	273.00	2.4362	256.2	2.4086	227.0	2.3560			178.2	2.2509	129.7	2.1129
80	0.00283	334.00	2.5237	313.8	2.4967	277.0	2.4425			220.0	2.3424	159.6	2.2030
85	0.00279	408.00	2.6107	385.0	2.5855	337.0	2.5276			272.0	2.4346	197.5	2.2956
90	0.00275	502.00	2.7007	469.9	2.6720	415.0	2.6180			332.0	2.5211	243.0	2.3856
95	0.00272	608.00	2.7839	566.5	2.7532	502.0	2.7007			411.0	2.6138	296.0	2.4713
100	0.00268	718.00	2.8561	662.2	2.8210	591.0	2.7716			525.0	2.7202	346.0	2.5391

(contd)

Table B-18. (contd)

Temp. °C	54.62 wt%		56.06 wt%		62.70 wt%		68.34 wt%		71.63 wt%		74.35 wt%		77.83 wt%	
	P (mmHg)	log P	P (mmHg)	log P	P (mmHg)	log P	P (mmHg)	log P	P (mmHg)	log P	P (mmHg)	log P	P (mmHg)	log P
0	1.1	0.0531	0.98	-0.0110	0.53	-0.2798	0.23	-0.6478	0.13	-	0.07	-1.1871	0.03	-1.4949
10	2.2	0.3424							0.9031					
20	4.2	0.6243	4.20	0.6232	2.18	0.3385	1.05	0.0212	0.58	-	0.33	-0.4868	0.18	-0.7545
25	6.2	0.7938	5.55	0.7443					0.2388					
30	8.3	0.9206	7.43	0.8710										
35	11.2	1.0492	9.61	0.9827										
40	15.3	1.1836	13.40	1.1271	7.71	0.8871	3.80	0.5798	2.19	0.3404	1.28	0.1072	0.73	-0.1367
45	20.1	1.3032	17.66	1.2470										
50	26.8	1.4281	23.70	1.3747										
55	34.7	1.5403	31.00	1.4914										
60	44.8	1.6513	40.10	1.6031	23.50	1.3711	11.98	1.0785	7.06	0.8488	4.50	0.6532	2.55	0.4065
65	57.7	1.7612	51.60	1.7126										
70	72.8	1.8621	65.20	1.8142										
75	91.6	1.9619	82.20	1.9149										
80	114.4	2.0584	103.70	2.0158	60.00	1.7782	31.50	1.4983	21.00	1.3222	13.49	1.1300	7.89	0.8971
85	142.5	2.1538	127.90	2.1069										
90	175.9	2.2453	160.30	2.2049										
95	214.0	2.3304	196.60	2.2936										
100	258.0	2.4116	231.80	2.3651	146.40	2.1655	2.1655	1.9025	54.10	1.7332	35.50	1.5502	22.00	1.3424

a[TARASENKOV]

Table B-19. Constants Determined by Least Square Method to fit
Vapor Pressure of Water Data in Table B-16 to Eq.
B-3

Concentration of H ₂ SO ₄ wt %	A	B
10.02	9.004	-2286.68
20.40	9.030	-2305.15
29.84	9.070	-2339.20
39.90	9.406	-2490.37
48.44	9.026	-2408.30
54.62	8.938	-2428.66
56.06	9.174	-2525.74
62.70	8.838	-2489.16
68.34	8.835	-2585.68
71.63	8.920	-2683.44
74.55	9.026	-2788.50
77.83	9.053	-2877.21
83.28	9.230	-3100.02

Table B-20. Activity of Water Over Aqueous
Phosphoric Acid at 25°C^a

[H ₃ PO ₄], Molal	Activity of Water	[H ₂ SO ₄], Molal
1.0675	0.9782	0.5973
1.7602	0.9633	0.9694
2.9858	0.9331	1.6192
4.3541	0.8962	2.3082
5.1875	0.8690	2.7320
9.1862	0.7367	4.5628
9.5130	0.7231	4.7401
10.2840	0.6999	5.0404
10.9030	0.6774	5.3309
11.0700	0.6720	5.4010
11.1970	0.6669	5.4660
11.9380	0.6452	5.7441
12.6470	0.6237	6.0190
13.5500	0.5915	6.4432
14.0570	0.5765	6.6349
15.6850	0.5323	7.2422
15.9120	0.5237	7.3646
18.0340	0.4677	8.1749
19.0060	0.4432	8.5554
20.7080	0.4084	9.1841
21.3270	0.3937	9.3940
21.6080	0.3874	9.5043
23.5240	0.3528	10.1460
24.8540	0.3289	10.6190
28.2020	0.2778	11.7460
28.7680	0.2732	11.8610
28.9950	0.2649	12.0680
31.0440	0.2470	12.5360
31.9820	0.2366	12.8270
33.3050	0.2230	13.2240
34.0990	0.2167	13.4140
35.7730	0.1963	14.0640
37.8240	0.1857	14.4280
41.1840	0.1625	15.2830
43.0350	0.1518	15.7330
50.0100	0.1202	17.2680
57.2650	0.0957	18.7660
64.4200	0.0791	20.0240
64.6590	0.0786	20.0640
74.7260	0.0627	21.6600

^a[ELMORE]

APPENDIX C

ADDITIONAL VAPOR-LIQUID EQUILIBRIUM GRAPHS

Fig. C-1. Concentration of Nitric Acid in the Vapor Phase versus the Liquid Phase for the HNO_3 -0.46 M H_2SO_4 - NaNO_3 system at 760 mmHg

Fig. C-2. Equilibrium Temperature Versus Nitric Acid Concentration in the Liquid Phase for the HNO_3 -0.46 M H_2SO_4 - NaNO_3 system at 760 mmHg

Fig. C-3. Concentration of Nitric Acid in the Vapor Phase versus the Liquid Phase for the HNO₃-0.93 M H₂SO₄-NaNO₃ system at 760 mmHg

Fig. C-4. Equilibrium Temperature Versus Nitric Acid Concentration in the Liquid Phase for the HNO₃-0.93 M H₂SO₄-NaNO₃ system at 760 mmHg

Fig. C-5. Concentration of Nitric Acid in the Vapor Phase versus the Liquid Phase for the HNO₃-1.39 M H₂SO₄-NaNO₃ system at 760 mmHg

Fig. C-6. Equilibrium Temperature Versus Nitric Acid Concentration in the Liquid Phase for the HNO₃-1.39 M H₂SO₄-NaNO₃ system at 760 mmHg

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