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Use of Extractive Distillation to Produce Concentrated Nitric Acid

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ABSTRACT

Concentrated nitric acid (>95 wt %) is needed for the treatment of off-gases from a fuels-reprocessing plant. The production of concentrated nitric acid by means of extractive distillation in the "two-pot" apparatus was studied to determine the steady-state behavior of the system. Four parameters, EDP volume (V_{EDP}) and temperature (T_{EDP}), acid feed rate, and solvent recycle, were independently varied. The major response factors were percent recovery (CPRR) and product purity (CCP). Stage efficiencies also provided information about the system response. Correlations developed for the response parameters are:

$$\mathrm{CPRR} = 0.02(V_{EDP} - 800\ \mathrm{cc}) + 53.5$$

$$\mathrm{CCP} = -0.87\ (T_{EDP} - 140°\mathrm{C}) + 81$$

$$\eta_{V,EDP} = 9.1(F_{feed} - 11.5\ \mathrm{cc/min}) - 0.047(V_{EDP} - 800\ \mathrm{cc}) - 2.8(F_{Mg(NO_3)_2} - 50\ \mathrm{cc/min}) + 390$$

$$\eta_{L,EDP} = 1.9(T_{EDP} - 140°\mathrm{C}) + 79$$

A computer simulation of the process capable of predicting steady-state conditions was developed, but it requires further work.

Contents

1. SUMMARY

The Consolidated Fuel Reprocessing Program is currently developing the Iodox Process for the scrubbing of iodine compounds from effluent gases of the Hot Engineering Facility (HEF). The Iodox Process consists of contacting off-gases with a countercurrent stream of concentrated nitric acid. It is economically desirable to reconcentrate and then recycle the dilute aqueous nitric acid bottoms stream. Simple distillation cannot be used to dehydrate the acid because of an azeotrope at 68.5 wt % nitric acid. However, extractive distillation with magnesium nitrate solution as a solvent can be used to produce hyperazeotropic acid. A novel method, the "two-pot" concept for this extractive distillation was developed and studied.

The two-pot apparatus consists of an extractive distillation pot (EDP) and a solvent-recovery pot (SRP). A factorial design was used to investigate the effect of EDP volume, EDP temperature, feed acid flow rate, and solvent recycle rate on the steady-state response of the two-pot system. The response parameters studied were the concentrated product recovery ratio (CPRR), the concentration of concentrated product (CCP), and several Hansen stage efficiencies. The experimental results showed that CPRR and CCP were the most useful response factors for design and scaleup of the two-pot system. The stage efficiencies indicated that the EDP could be better studied as a mass transfer problem. Such a study would require significant modifications to the experimental apparatus. Nevertheless, the analysis of results and the development of the mathematical model were based on the assumption that the two pots were near-equilibrium contactors.

The computer model was developed to predict the steady-state behavior of the system. The two pots were simulated as equilibrium stages, which were connected for stage efficiency in a separate step.

Recommendations for further study include the investigation of additional controlled variables as well as a greater range for those already studied. It is also recommended that the EDP be studied from a mass transfer perspective. Finally, more work will be required before the computer simulation of the system is fully functional.

2. INTRODUCTION

2.1 Background

The Iodox Process is designed to scrub iodine compounds from effluent gases from the Hot Engineering Facility (HEF), thereby preventing the release to the atmosphere of the radioactive isotopes ^{129}I and ^{131}I, which concentrate in the thyroid gland.

Highly concentrated HNO_3 contacts fuel reprocessing off-gases in a countercurrent column and converts the volatile iodides, such as HI, to nonvolatile iodic acid (HIO_3). Water is added near the top of the column to facilitate the absorption of nitrous oxide. The diluted nitric acid bottoms stream is evaporated to produce a solid metaiodic acid waste (HI_3O_8) and near-azeotropic aqueous nitric acid vapor (68.5 wt %). The solid is stored as a radioactive waste. Figure 1 is a schematic diagram of the system. More detail is given by Counce *et al.* (1).

To make the Iodox Process economically feasible and to contain the nitric acid, it is necessary to reconcentrate and recycle the nitric acid. An azeotrope at 68.5 wt % nitric acid precludes dehydration by simple distillation.

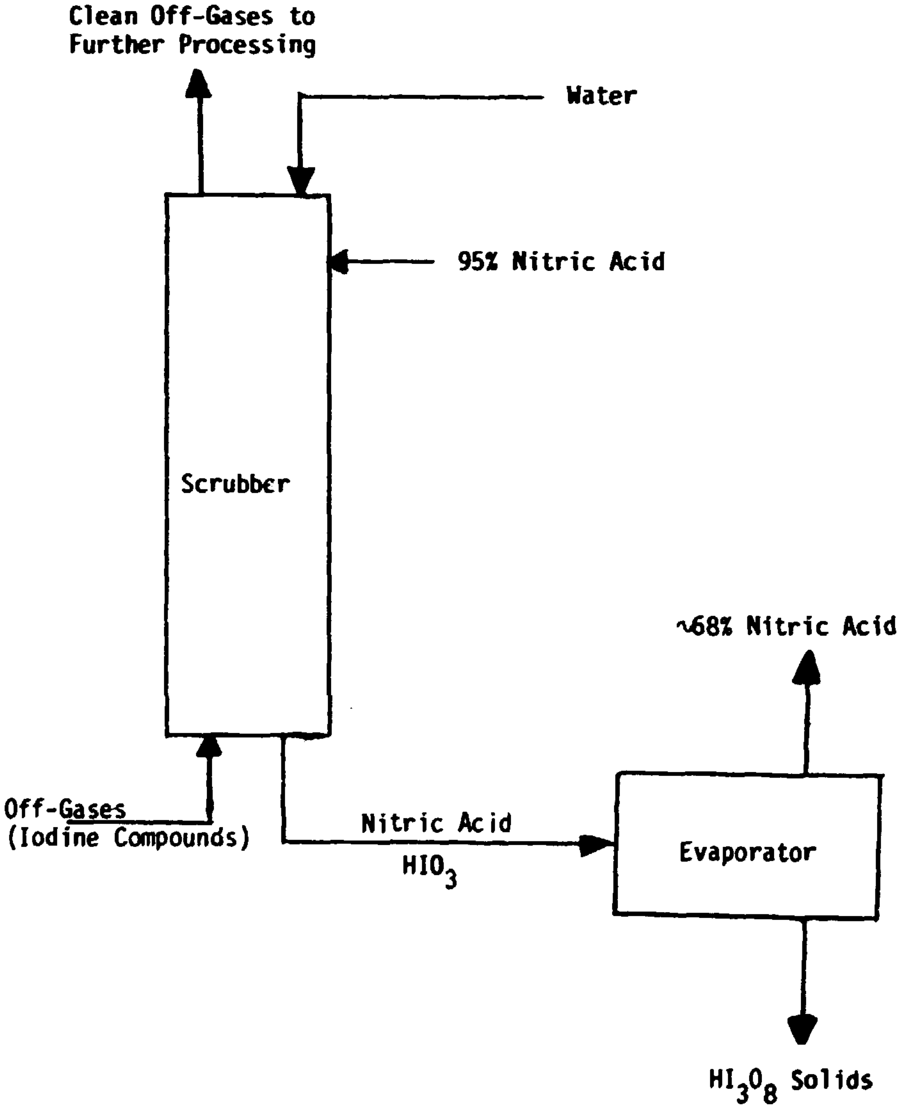
Extractive distillation techniques are used commercially for the processing of hypoazeotropic acid to hyperazeotropic concentrations (10). A particularly effective solvent for this application is an aqueous solution of magnesium nitrate [$Mg(NO_3)_2$], which lowers the activity of water with respect to that of nitric acid, thereby shifting the azeotrope toward pure water and ultimately toward high magnesium nitrate concentrations, causing the azeotrope to disappear completely. The separation includes three steps: production of hyperazeotropic HNO_3 vapor, rectification of the vapor to greater than 95 wt % acid, and reconcentration of the magnesium nitrate for recycle.

Two schemes being considered for this process are a continuous column design and the two-pot concept (1), which uses a single vessel for contacting feed HNO_3 with the magnesium nitrate and another for reconcentrating the $Mg(NO_3)_2$ solution. The latter proposal is shown schematically in Fig. 2. In the extractive-distillation pot (EDP) the acid is contacted at high temperature (∿150°C) with the solvent, immediately vaporized, and concentrated by the absorption of water into the $Mg(NO_3)_2$ solution as the acid vapor bubbles upward. In the solvent-recovery pot (SRP) the $Mg(NO_3)_2$ is reconcentrated by boiling off water and nitric acid. Two rectifying columns are then used to concentrate both HNO_3 streams, one to 95% HNO_3 and the other to remove water and recycle acid.

Possible advantages of the two-pot system include ease of control (since remote operation will be required) and a savings in material cost (less titanium and tantalum may be required). Evaluation of the alternatives will require a pilot-plant scale study. Such a unit will also facilitate the development of elements of a control scheme and the selection of structural materials.

2.2 Objectives

The two major objectives were to experimentally study the behavior of the two-pot system and to use these data in the development of a computer simulation of the system. The experimental program was keyed to investigate the effects of critical parameters on the response variables. The goal was to rank the parameters and to develop expressions for the response parameters as functions of the key parameters.



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IODOX PROCESS

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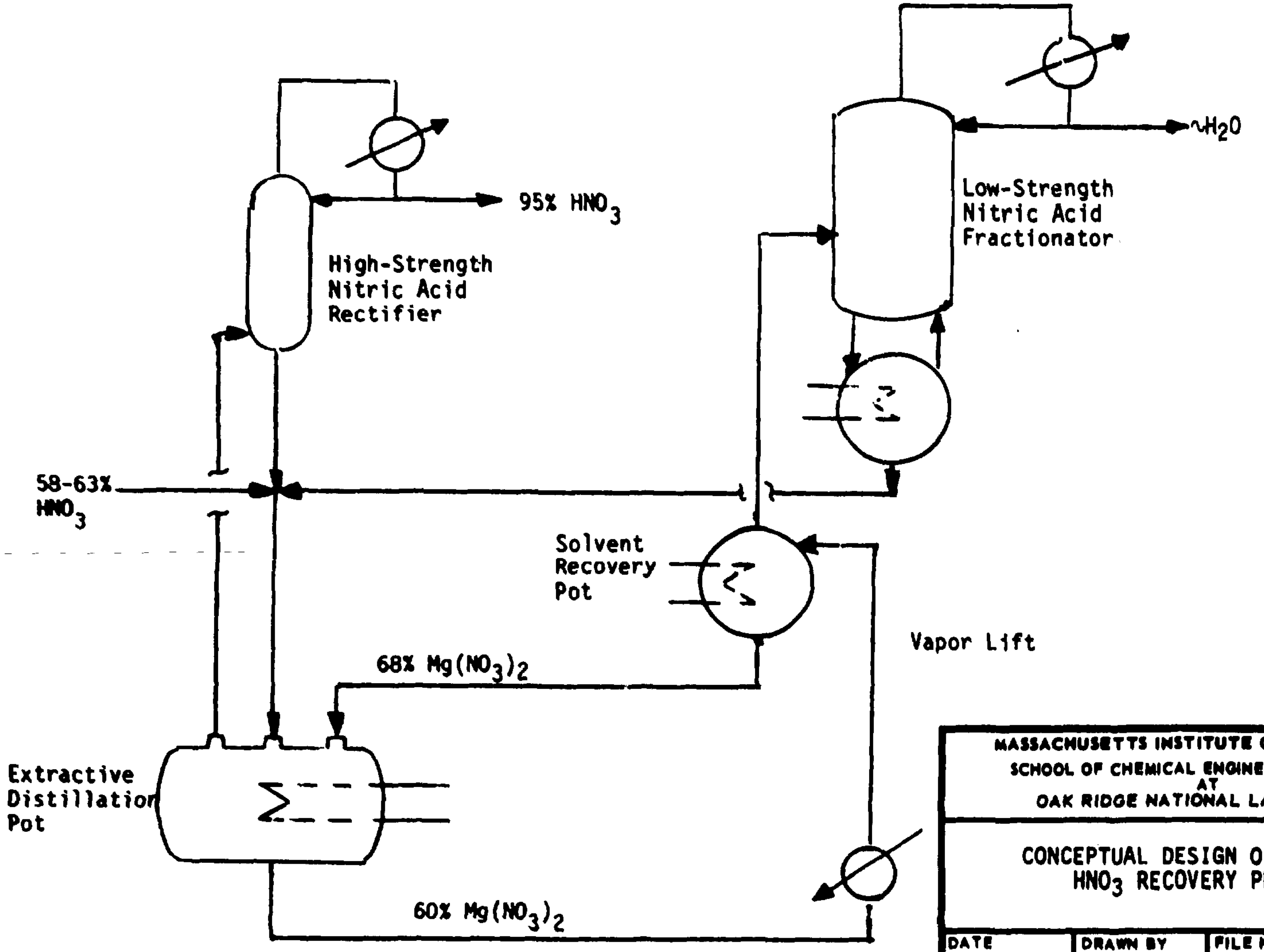

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CONCEPTUAL DESIGN OF TWO-POT
HNO_3 RECOVERY PROCESS

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11-24-80	PCC	CEPS-X-325	2

The objective of the mathematical modeling was to develop a method for predicting the steady-state performance of the two-pot system for a specified set of operating conditions. Such a model can be used to design a pilot-plant-scale, two-pot system and to serve as a basis for future simulation and experimental work.

2.3 Method of Attack

Previous work on the two-pot system indicates that extractive separation, equilibrium data for the three-component system, and other physical-property data are all relevant to this study. The studies of Counce *et al.* (1) gave insight into suitable ranges of operating conditions and expected system behavior, and also led to the consideration of a factorial design in the current study.

The factorial experimental design, which maximized the amount of information available from a limited number of experiments, was developed. The design consisted of eight runs, each comprising a unique set of operating parameter levels. The varied parameters were: EDP temperature and volume, feed acid flow rate, and magnesium nitrate flow rate. The experimental results and equilibrium data (2, 3) were used to calculate stage efficiencies for both pots. Factorial statistical analysis was used to determine the effects of the main operating parameters and two interactions on the concentrated-product recovery ratio (CPRR), concentration of concentrated product (CCP), and the stage efficiencies.

The mathematical model was developed by treating each pot as an equilibrium flash stage, with a modification of exit stream compositions and flow rates with the stage efficiencies.

3. PREVIOUS WORK/LITERATURE REVIEW

3.1 Previous Work

Counce *et al.* conducted a preliminary study on the two-pot apparatus, in which they explored the effect of EDP volume, EDP temperature, and feed-acid flow rate on the Murphree stage efficiency, the CPRR, and the CCP. EDP temperature and feed-acid flow rate had the strongest effects on the response factors, while EDP volume had little or no effect. As temperature was increased, CPRR increased, CCP decreased, and Murphree stage efficiency decreased. When the acid feed rate was increased, CPRR increased, CCP stayed nearly constant, and Murphree stage efficiency increased. The experimental error observed in this preliminary study was unusually large. Counce recommended that more studies be conducted to completely determine the effect of the controlled variables on the response parameters.

3.2 Equilibrium Data

Vapor-liquid equilibrium (VLE) data for the ternary system were reported by several researchers (2, 3, 4). Typically, the data were presented as constant nitric acid vapor-composition curves and constant boiling-point curves as a function of the ternary liquid composition. Empirical correlations for the isonitrate curves were developed by Cigna *et al.* (2). However, no correlations were found for the isotherms.

The data found for isonitrate curves are in good agreement, but the isotherms are not nearly so consistent. Figure 3 is a comparison of the three sources for a 140°C boiling point as a function of system concentration. The isotherm data presented by Sloan (3) were chosen because this source is most often used by other workers in the field. The equilibrium data base used in the computer model can be easily changed to accommodate other isotherms.

3.3 Density Data

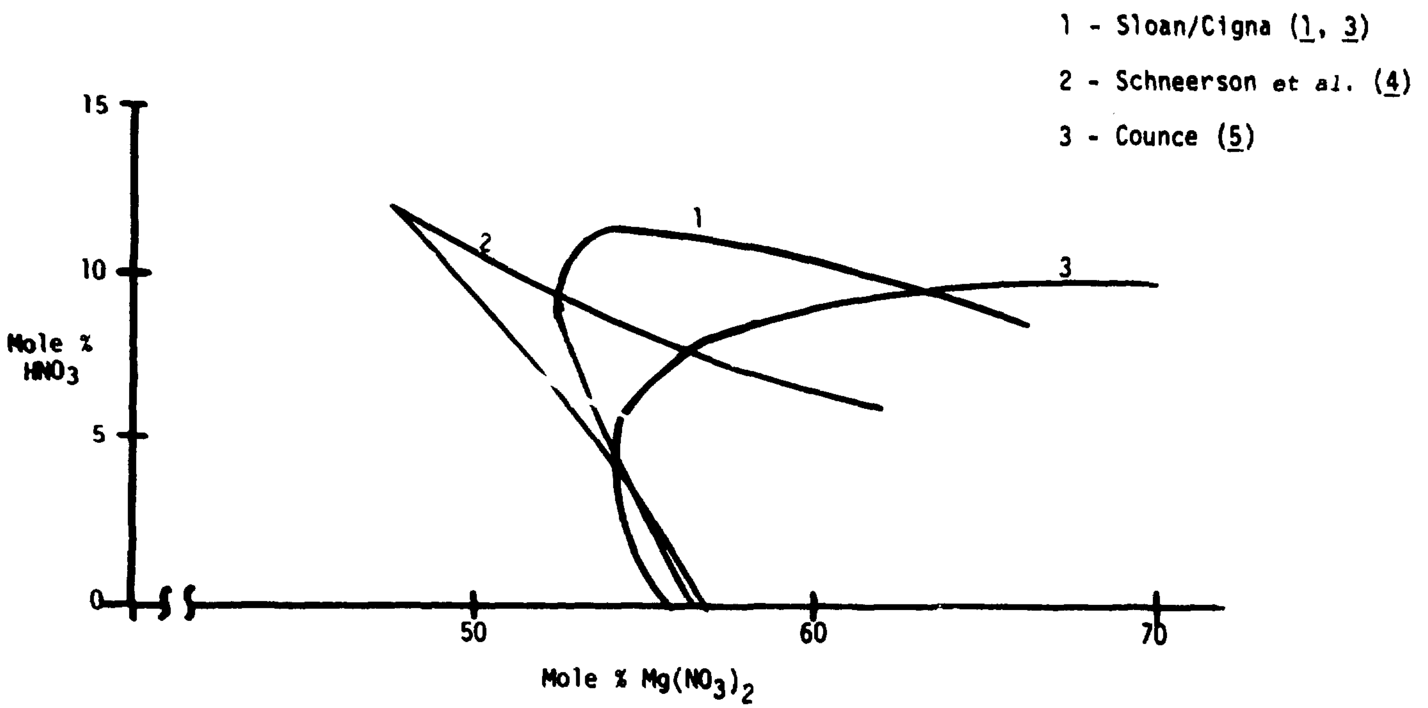
Density data were required for the ternary and HNO_3-H_2O systems to determine mass balances for the two-pot apparatus. Data for the binary mixtures $Mg(NO_3)_2$-H_2O and HNO_3-H_2O are available. The densities of the streams containing three components were initially determined experimentally (see Sect. 4.2), and then approximated from binary data (see Appendix 11.2).

4. EXPERIMENTAL

4.1 Apparatus

The two-pot bench-scale apparatus (Fig. 4) is located in Bldg. 7601, Laboratory 2. The main units are a 1500-ml extractive-distillation pot (EDP) and a 1500-ml solvent-recovery pot (SRP). Both are enclosed in heated cabinets and are typically operated at 150-170°C. Feed acid flows by gravity from an elevated tank into the EDP solvent, 2 cm from the bottom of the pot. Because of the elevated temperature of the magnesium nitrate solution, the acid leaving the feed tube vaporizes and bubbles through the solvent, becoming more concentrated in nitric acid. The vapor product is condensed and collected for analysis. The EDP solvent is pumped continuously into the SRP, where excess water and residual nitric acid are boiled off. The reconcentrated solvent is recycled to the EDP while the overhead dilute acid product is condensed.

The feed acid flow rate is manually controlled and observed by a rotameter, which is calibrated for the feed acid concentration studied.



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140°C EQUILIBRIUM ISOTHERMS FOR HNO_3-H_2O-$Mg(NO_3)_2$ MIXTURES

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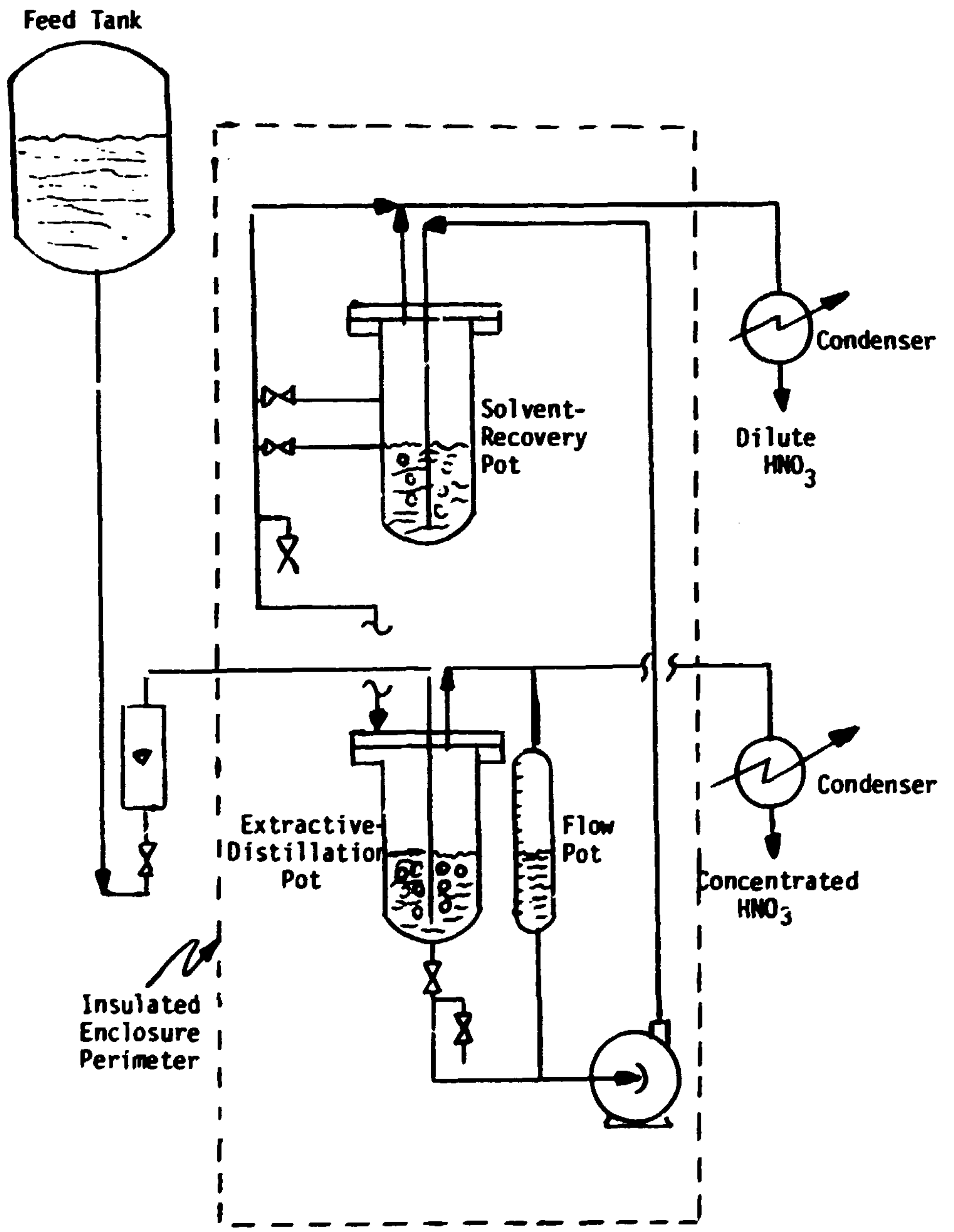

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TWO-POT BENCH-SCALE APPARATUS

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11-24-80	PCC	CEPS-X-325	4

The magnesium nitrate recycle flow rate is controlled by a variable speed pump and measured with a burette (flow pot) connected in parallel with the EDP.

Heat inputs are controlled by use of a Honeywell controller. Both pots have heating mantles; heating tapes on the recycle line between the EDP and SRP provide additional heating. Temperatures throughout the system are measured with thermocouples and monitored on a strip-chart recorder.

4.2 Procedure

At the start of an experiment, magnesium nitrate solution is charged to the two-pot system through a funnel at the top of the SRP. The volume of the SRP is controlled by a valve on the lower of the two-level arms attached to this pot. The EDP volume is fixed by either draining or adding solvent to obtain the required liquid height. The feed acid and solvent recycle flow rates are then fixed at the desired levels.

The system is allowed to reach steady state at the desired operating conditions. It is usually necessary to adjust the heat inputs through the mantles and heating tapes. Flow rates and temperature are continuously monitored. Three to four hours are required to reach steady state, because the pots have relatively long residence times (>20 min) and are very sensitive to changes in each other due to the recycle stream. When steady state is reached, the system is monitored for an additional hour to ensure that no fluctuations persist. When steady state is confirmed, final operating conditions are recorded and samples are collected from the overhead and bottoms streams of both pots and from the acid feed. The densities of the two bottoms streams can be determined by taking a sample in a pycnometer jar.

The samples are then analyzed in the analytical laboratory. The acid concentrations in all samples are determined by thermometric titration with NaOH, while the magnesium nitrate concentrations in the bottoms samples are measured by colorimetric titration. The analytical procedure is discussed further in Appendix 11.6. An estimate of analytical experimental error is given in Appendix 11.3. In summary, the estimated error in overall material balance is approximately 20%, while stage-efficiency estimates are in the range of 15%. Obviously this points out a need for improved analytical techniques.

4.3 Design of Experimental Program

4.3.1 Factors

The factors which can be directly controlled are the EDP temperature and volume, SRP temperature and volume, acid feed concentration, and flow rates of the acid feed and the solvent recycle. Setting these factors in each experiment fixes the compositions of all the streams (see Sect. 4.3.2). Of these factors, only four were studied: EDP temperature and volume, acid feed flow rate, and solvent recycle flow rate.

The response variables that illustrate the effects of the controlled factors on these compositions are the concentrated product recovery ratio (CPRR), the concentration of the concentrated product (CCP), and several stage efficiencies (η). CPRR, defined as

$$\text{CPRR} = \frac{\text{g/s concentrated acid product}}{\text{g/s feed acid}} \qquad (1)$$

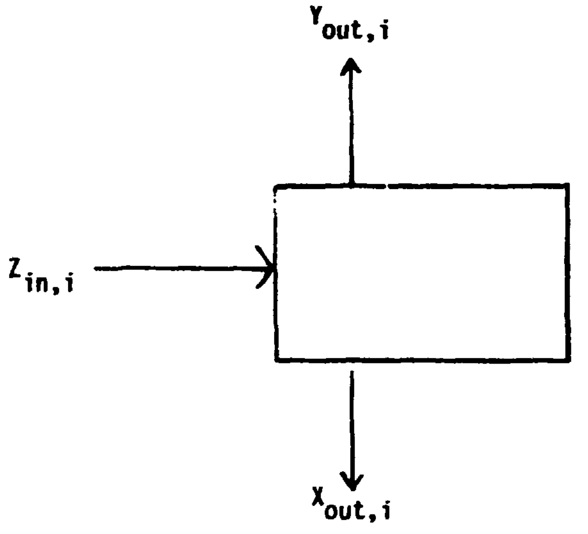
is a measure of recovery, while the CCP is the purity of the primary separation product. Optimization of the two-pot system design will include maximizing CPRR while exceeding a minimum CCP.

The stage efficiency indicates the degree to which equilibrium is achieved in a given pot by comparing the actual exit composition with an equilibrium exit composition, as shown in Fig. 5. The equilibrium exit composition may be defined in several ways, each definition corresponding to a different stage efficiency. For example, in a Murphree stage efficiency, Y^*_{out} is defined as the vapor-phase composition that would be in equilibrium with the actual X_{out} at constant pressure. Alternately, if Y^*_{out} is defined as the vapor-phase composition resulting from a constant temperature and pressure equilibrium flash of the total feed stream, then the stage efficiency is called a Hansen stage efficiency. King (8) gives a detailed discussion of the Hansen and Murphree stage efficiencies.

The Hansen stage efficiency is the more appropriate response factor for this experiment, since the EDP and SRP are operated at constant temperature and pressure. The equilibrium stream compositions, required to calculate the efficiency, are determined by a flash calculation based on a combined total liquid feed stream. One feature of a computational scheme involving Hansen efficiencies is that product compositions may be directly calculated. On the other hand the Murphree efficiency will necessarily involve an iterative process. Two efficiencies are necessary to describe the behavior of each pot since there are three components; liquid and vapor nitric acid efficiencies were selected.

4.3.2 Reproducibility

The description rule (8) for separation processes was used to specify the problem. In this analysis all the system variables and relationships were compared to determine the number of variables that must be specified to completely and uniquely fix the system. Figure 6 is a simplified block diagram of the two-pot system and its individual units. Table 1 is a summary of the analysis.



$$\eta_i = \left[\frac{Y_{out} - Z_{in}}{Y^{*}_{out} - Z_{in}}\right]_i \qquad (2)$$

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DEFINITION OF STAGE EFFICIENCY
FOR COMPONENT i, η_i

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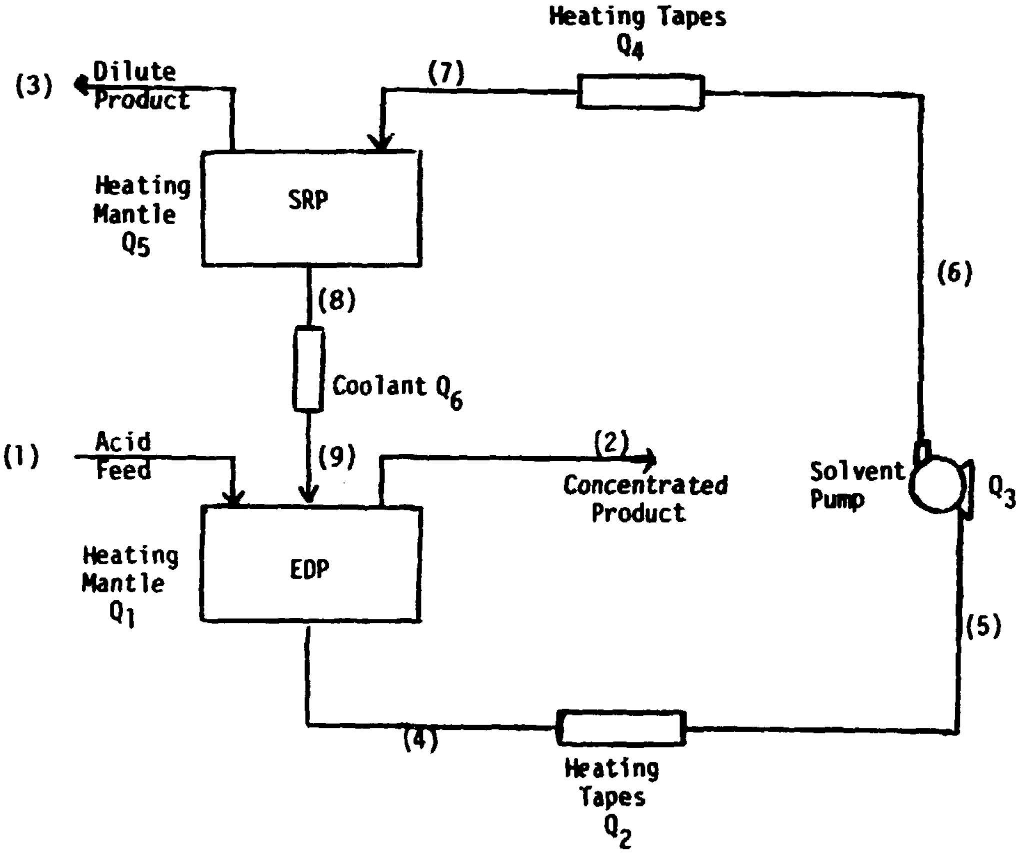

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SYSTEM DIAGRAM FOR
DESCRIPTION RULE ANALYSIS

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11-24-80	PCC	CEPS-X-325	6

Table 1. Two-Pot System Specification

Variables

Composition (C) (independent)	8(2) + 1	=	17
Flow rate (F)	9		9
Temperature (T)	9		9
Pressure (P)	9		9
Heat input (Q)	6		6
			50

Relationships

Mass Balances		
Pots	3(2)	6
Heaters	3(3)	9
Pump	3	3
Vapor-Liquid Equilibrium		
Y-X relationships in pots		6
$T_{vapor} = T_{liquid}$ in pots		2
$P_{apor} = P_{liquid}$ in pots		2
Enthalpy Balances		6
		34

50 - 34 = 16 variables that must be specified to uniquely describe the system.

Specified Variables

T in pots	2
P in pots	2
C, F, T, and P in acid feed	4
F in Stream 6	1
P in Stream 9	1
Q in pots, heaters, and pump	6
	16

In brief, sixteen variables must be specified. When this is done, every experiment should be reproducible within experimental error. To determine experimental reproducibility, one experiment was a duplicate of a previous run. Good agreement was obtained (see project calculation file).

4.3.3 Factorial Design

A factorial design was developed to maximize the information gained from the limited number of experiments. Beyond the initial practice run only eight experiments could be performed due to time restraints and several experimental setbacks. To minimize the number of main effects and the number of required runs, only four controllable factors (T_{EDP}, V_{EDP}, F_{feed}, and $F_{Mg(NO_3)_2}$) were varied; the remaining factors (T_{SRP}, V_{SRP}, and C_{feed}) were held constant.

Two values for each controlled factor were chosen for study (see Table 2). Several considerations influenced their selection (9). The values must be in a region of experimental interest and sufficiently separated so that the response parameter can exhibit a significant response. However, the two levels must lie on a planar region, as a linear correlation is intended and cannot be infinitely separated. The results of Counce *et al.* aided in this factor-level selection.

Table 2. Factor Levels

Factor	Units	Lower Level	Upper Level
V_{EDP}	ml	800	1500
T_{EDP}	°C	140	155
F_{acid}	cc/min	11.5	16
$F_{Mg(NO_3)_2}$	cc/min	50	65

For an experimental program of eight runs and four controlled factors (two levels each), two factorial designs are recommended (9). The first is a two-level 2^{4-1} design which consists of eight different experiments. This design yields a ranking of the main effects and no estimate of experimental error. The second design is a two-level 2^{4-2} program of eight runs, four runs with each duplicated once. From this design a good estimate of experimental error is obtained, but the main effects are confounded with each other and cannot be isolated.

The two-level 2^{4-1} design was chosen because it was felt by the investigators that the ranking of main effects and important interactions, in order of importance, was of more immediate interest than an estimate of experimental error. Less important factors can then be eliminated from future studies, which can easily include an experimental-error analysis. The complete factorial design program, including constant factors, is shown in Table 3 (see Sect. 6). A more detailed discussion of factorial design theory is given in Box, Hunter, and Hunter (9).

5. THEORETICAL MODEL

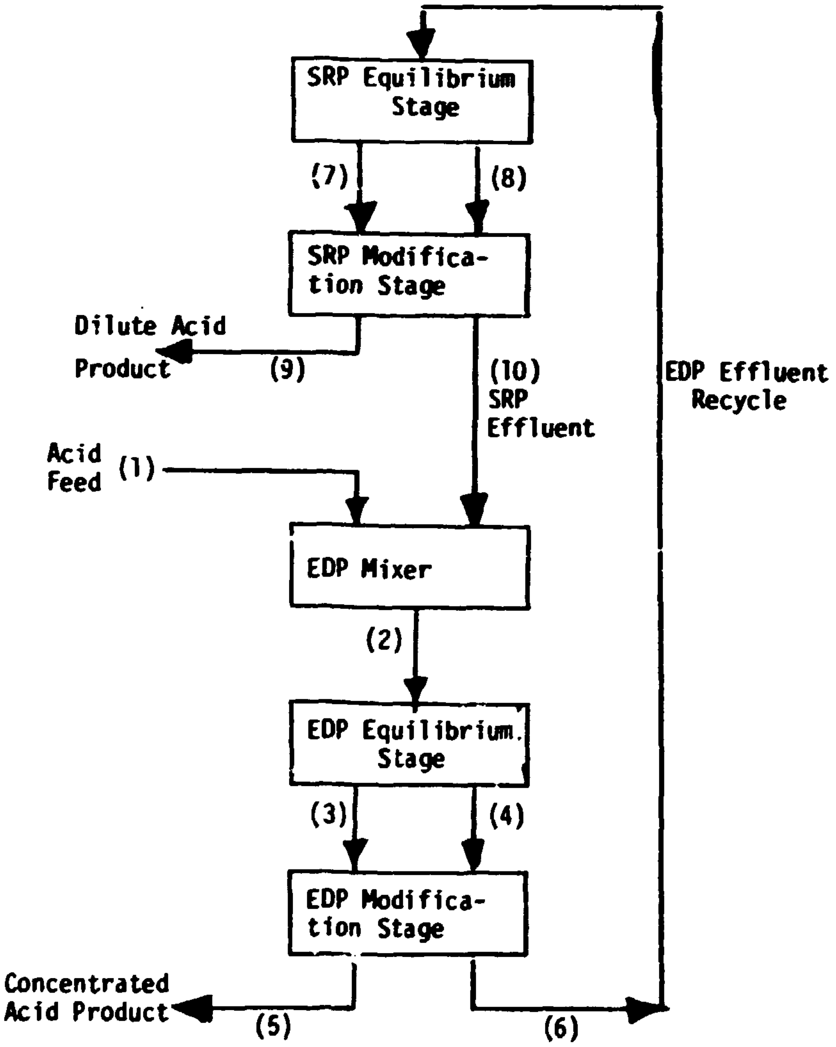
5.1 Approach

A mathematical model capable of predicting the steady-state behavior of the two-pot nitric acid dehydration apparatus was implemented on the PDP-10 system. The two-pot apparatus can be modeled as a mass-transfer problem or as an equilibrium system. In the former, the mass exchanged as the bubble rises through the magnesium nitrate system is determined by use of mass transfer coefficients. Physically the process is complicated by the fact that the acid feed is heated as it flows down the inlet pipe (which is in contact with the contents of the pot) and probably partially vaporizes. Then the two liquid phases mix at the exit point of the pipe and further flashing occurs, this time with $Mg(NO_3)_2$ present. Finally, the vapor phase rises through the liquid medium, providing further opportunity for mass transfer. In an equilibrium model, the vapor and liquid streams from an isothermal and isobaric flash of the combined feed are corrected for non-equilibrium with Hansen stage efficiencies. The latter model was selected because correlation of stage efficiency as a function of controlled factors can be more easily obtained from the experimental apparatus than from the mass transfer coefficients.

5.2 Equilibrium Model

A schematic diagram for the equilibrium model is presented in Fig. 7. The EDP is divided into three imaginary stages: a mixing stage, an equilibrium stage, and an equilibrium modification stage. In the mixer, the acid feed and the SRP effluent are combined to form an imaginary total liquid feed stream (No. 2). This stream is then flashed, at constant temperature and pressure, to imaginary streams No. 3 (vapor) and No. 4 (liquid). The actual EDP effluent streams (5 and 6) are determined by adjusting the composition and flow rates of streams 3 and 4 for nonequilibrium with the Hansen stage efficiencies. The stage efficiencies are calculated from correlations expressing the efficiency as a function of the controlled factors (see Sect. 6).

The SRP is modeled similarly. In this case, a mixing stage is not required as the SRP receives only one liquid feed. Two imaginary equilibrium streams (7 and 8) are determined by an equilibrium flash calculation, as in the EDP. These streams are then modified with two Hansen stage efficiencies to determine the SRP effluent streams 9 and 10.



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SCHEMATIC DIAGRAM OF EQUILIBRIUM MODEL

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6. RESULTS

The experimental design and factor levels are presented in Table 3. Values to the left of the slash are upper levels; values to the right are lower levels. The raw data from each run (stream compositions, densities, and flow rates) are presented in Appendix 11.1. The mass flow rate is the product of the volumetric flow rate and density. (Sample calculations are given in Appendix 11.2.)

Table 3. Experimental Design

Run	Experiment	V_{EDP} (cc)	F_{feed} (cc/min)	$F_{Mg(NO_3)_2}$ (cc/min)	T_{EDP} (°C)
1	ACR-42	/800	/11.5	65/	155/
2	ACR-43	/800	16/	/50	155/
3	ACR-44	1500/	/11.5	/50	155/
4	ACR-45	/800	16/	65/	/140
5	ACR-46	/800	/11.5	/50	/140
6	ACR-47	1500/	16/	65/	155/
7	ACR-48	1500/	16/	/50	/140
8	ACR-49	1500/	/11.5	65/	/140

Note: Values to the left of the slash represent upper levels; values to the right of the slash represent lower levels.

Process constants: T_{SRP} = 165°C, V_{SRP} = 1500 ml, and $C_{feed\ acid}$ = 65%

Calculated response factors for each run are summarized in Table 4. The CPRR is the ratio of the concentrated-product mass flow rate (g/s) to the feed-acid mass flow rate (g/s). CCP is the concentration of the concentrated product (weight fraction HNO_3). The efficiencies are for nitric acid in the vapor and liquid streams from each pot; two efficiencies are required for each pot. The equilibrium exit-stream compositions were determined by a constant T,P flash calculation. This is discussed in more detail in Appendices 11.4 and 11.7.

Table 5 shows the results of mass balance calculations used to check for error. A sample calculation is given in Appendix 11.2. The results are analyzed and discussed in the following section.

Table 4. Response Factors

Run ACR-	CPRR	CCP	Percent Efficiencies $\eta_{V,EDP}$	 $\eta_{L,EDP}$	 $\eta_{V,SRP}$	 $\eta_{L,SRP}$
42	0.756	0.692	594	107	2391	100
43	0.565	0.676	322	113	2136	(-20)
44	0.756	0.668	245	107	763	86
45	0.900	0.675	239	105	781	100
46	0.570	0.779	281	94	366	106
47	0.469	0.817	510	65	760	113
48	0.311	0.810	381	78	429	100
49	0.401	0.828	379	80	378	122

Table 5. Mass Balance Check of Results

Component Run ACR-	Percent Deviations HNO_3 Overall	 SRP	 EDP	 H_2O Overall	 SRP	 EDP
42	2.8	-2.9	3.5	9.1	3.3	-24.0
43	22.8	-76	33	21.4	-3.8	43
44	12.0	-6.0	19.0	7.0	0.3	5.0
45	-3.4	2.2	-3.8	-9.3	-3.6	17.7
46	-3.7	-14.5	2.3	-3.4	-13.4	10.0
47	4.6	27.0	13.6	1.4	4.4	-44
48	10.9	17.9	21.3	8.0	4.3	11.8
49	-4.3	5.6	1.0	1.4	-1.1	9.1

7. ANALYSIS AND DISCUSSION OF RESULTS

7.1 Statistical Analysis

The experimental results were analyzed by Yates' algorithm (9) to determine the main effects (V_{EDP}, F_{feed}, $F_{Mg(NO_3)_2}$, and T_{EDP}) and the contributions of two interactions (V_{EDP} x F_{feed} and V_{EDP} x $F_{Mg(NO_3)_2}$) for each of the four response factors. The percentage change of a response parameter for a change in the factor level is determined by dividing the effects by the average low value of the response variable itself (Appendix 11.5). The results of this analysis are used to rank the effects of the factors on the response parameters (see Table 6).

Table 6. Ranking of Effects

	Response Variable			
	CPRR	CPP	$\eta_{V,EDP}$	$\eta_{L,EDP}$
Factor (percent change)	T (76.6)	T (-16.2) - - - - - -	F_{feed} (40.1)	T (36.3) - - - - -
	V (26.2) - - - - - -	F_{feed} (2.7)	F_{Mg} (-29.4)	F_{Mg} (9.8)
	$F_{Mg(NO_3)_2}$ (10.4)	V (-2.2)	V (-23.9) - - - - - - -	F_{feed} (-9.0)
↓	V x F_{Mg} (10.4)	V x F_{Mg} (-1.1)	T (-9.7)	V x F_{feed}(6.7)
decreasing importance	V_{feed} (9.5)	F_{Mg} (-1.0)	V x F_{feed}(-3.1)	V x F_{Mg}(5.2)
	V x F_{feed}(-5.6)	V x F_{feed}(0.1)	V x F_{Mg} (2.7)	V (-1.9)
Estimated Experimental Error (%)	± 14.7	± 3.0	± 21.6	± 21.6

To determine which effects are insignificant, the percentage changes are compared with an estimate of minimum experimental error, which is usually determined by comparing results from duplicate experiments. Since this experimental program gave no error estimate, the "best" estimate of this error is obtained by multiplying the analytical error by 1.5 to allow for additional systematic error (Appendix 11.5). If the percentage change in a response parameter is less than the estimated error, the effect of the factor is considered insignificant. The dashed lines drawn across each response parameter in Table 6 separate the significant factors (above the line) from those that are insignificant.

The following relations (see Appendix 11.5) express the response parameters as functions of the remaining factors, over the range of the factor levels:

$$\mathrm{CPRR} = 0.01\,(V_{\mathrm{EDP}} - 800\ \mathrm{cc}) + 1.1\,(T_{\mathrm{EDP}} - 140°\mathrm{C}) + 49 \tag{3}$$

$$\mathrm{CCP} = 81 - 0.87(T_{\mathrm{EDP}} - 140°\mathrm{C}) \tag{4}$$

$$\begin{aligned}\eta_{V,\mathrm{EDP}} &= 9.1(F_{\mathrm{feed}} - 11.5\ \mathrm{cc/min}) - 0.047(V_{\mathrm{EDP}} - 800\ \mathrm{cc})\\ &\quad - 2.8(F_{\mathrm{Mg(NO_3)_2}} - 50\ \mathrm{cc/min}) + 390\end{aligned} \tag{5}$$

$$\eta_{L,\mathrm{EDP}} = 1.9(T - 140°\mathrm{C}) + 79 \tag{6}$$

Stage-efficiency correlations for the SRP are discussed in Appendix 11.5.

The use of the factorial design for data analysis involves several assumptions. First, the levels chosen for the parameters are assumed to result in a linear model, i.e., the significant effects are linear over the range studied. Second, the effects are assumed to be additive such that additive response-factor expressions may be developed. Finally, it is assumed that all effects (second- and third-order interactions) other than those directly studied are insignificant and therefore the possibility of confounding is eliminated.

7.2 Qualitative Discussion

CPRR and CCP both depend strongly on the EDP temperature. As temperature increases, CPRR (vapor product recovery) increases as more water is retained in the vapor phase. Similarly, CCP (product purity) decreases with increasing temperature. Unexpectedly, volume, acid feed rate, and solvent recycle rate have little effect on CPRR and CCP. One explanation for this result is that the chosen values for these factors are not in the most suitable range. Therefore, the full effects are not elicited.

The liquid-phase stage efficiency for the EDP ($\eta_{L,\mathrm{EDP}}$) depends most strongly on temperature. This is expected because the vapor-liquid equilibrium and vapor pressures are highly temperature-dependent. The other factors did not significantly affect $\eta_{L,\mathrm{EDP}}$.

The EDP vapor-phase stage efficiency ($\eta_{V,\mathrm{EDP}}$) is independent only of T_{EDP}. This is not expected, in light of the previous results. It is suspected that this efficiency is a poor choice of response parameter: all values of $\eta_{V,EDP}$ are much greater than 100%; and the feed composition is that of a liquid, not a vapor, as should be used. This latter approximation is necessitated by the lack of a vapor feed. Nevertheless, vapor efficiencies greater than 100% may be possible due to the poor mixing in the EDP. Mass transfer limitations may then cause more nitric acid to remain in the vapor than predicted by the vapor-liquid equilibrium.

The system mass balances indicate that the experiment was running smoothly. In six of eight cases, all the deviations were within the range of experimental error. The only significant discrepancies were in run ACR-43, where deviations as high as 76% were observed. This is due to operator error in determining the acid product flow rates.

Some possible sources of error were introduced in the execution of the experimental design. The acid feed concentration was specified as 65 wt % but did not remain constant throughout the experiments. Analytical results showed that this concentration ranged from 63.8 to 68.0%. Furthermore, the "randomization" plan for the order of the eight runs was not adhered to because of time limitations. This deviation from random order may have contaminated the results with additional systematic error.

7.3 Anomalies Observed

The only unexpected stream compositions were observed in ACR-43, in which the exit liquid stream from the SRP was more concentrated in acid than the EDP bottoms (2.8 vs 2.5%). This violates the law of conservation of mass and results in the liquid-phase efficiency $\eta_{L,SRP}$ having a negative value.

There are several possible explanations for this "inverted mass balance." First, the composition values are fairly close, and might lie within the range of true experimental error (especially at the low acid level). Alternatively, the shift could be due to a real effect. Perhaps the azeotropic composition is not 0% HNO_3, but actually is above the SRP composition. [Cigna *et al.* (2) reported that 45 wt % $Mg(NO_3)_2$ is required to completely eliminate the azeotrope.] This would cause water to be boiled off before nitric acid, producing the observed effect.

7.4 Computer Model

The program was implemented onto the PDP-10 system and was believed to be completely debugged. Several tasks still remain before the program may be used, however. It must be shown that the model will actually converge (see Appendix 11.7) on a unique SRP effluent flow rate and composition for any set of operating conditions. When this convergence is proved, the ability of the computer model to duplicate observed conditions must be evaluated. Only then can the simulation be used with confidence.

8. CONCLUSIONS

1. The effects of four controlled factors, EDP temperature, EDP volume, acid feed rate, and solvent recycle rate, on several response variables were ordered. Linear expressions for the response parameters as functions of the controlled factors were developed.

2. The CPRR and CCP are the most important response parameters in scaleup. CPRR increases with EDP volume and temperature, while CCP decreases with EDP temperature.

3. Stage efficiencies are not as useful in scaleup but are used in the theoretical model to predict the CPRR and CCP. The liquid-phase efficiency is an increasing function of EDP temperature while the vapor-phase efficiency increases with acid flow rate and decreases with EDP volume and solvent recycle rate.

4. A greater range of controlled factors must be studied to fully determine their effect on the system.

5. The two-pot system may be better represented as a mass transfer problem.

9. RECOMMENDATIONS

Recommendations for further study on the two-pot nitric acid dehydration proposal are:

1. Obtain an estimate of overall experimental error for the two-pot system by conducting a series of duplicate runs. Use this error analysis to determine whether the observed effects are statistically significant.

2. Study the effect of other variables, especially SRP temperature and volume, on the response variables.

3. Study extended variable ranges. In particular, investigate lower EDP temperatures (∿130°C) and much lower magnesium nitrate flow rates (<25 cc/min).

4. Redesign the system to permit a direct study of the mass transfer aspects. Other feed-tube designs and baffles to produce smaller bubbles are suggested.

5. Improve and extend existing equilibrium data with a complete literature search. An experimental study may be necessary to accurately determine isotherms.

6. Refine computer model by:

    a) developing more complete correlations for the SRP efficiencies after relevant factors are studied;

    b) improving the data base;

    c) developing a convergence routine that can determine the optimal values for the SRP effluent stream;

    d) verifying the model by comparing its predictions to observed steady-state operating conditions.

10. ACKNOWLEDGMENTS

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11. APPENDIX

11.1 Experimental Data

Table 7 is a compilation of the data which were collected in the eight runs of the factorial design. From this basic information all response factors were calculated.

Table 7. Experimental Results

Conditions for Run ACR-42

T_{EDP} = 155°C
V_{EDP} = 800 cc
$F_{Mg(NO_3)_2}$ = 65 cc/min
F_{feed} = 11.5 cc/min

	Stream Parameters (wt %)			F	ρ	G
	HNO_3	H_2O	$Mg(NO_3)_2$	(cc/min)	(g/cc)	(g/min)
Feed	64.8	35.2	0.0	11.5	1.389	16.0
Concentrated product	69.2	30.8	0.0	8.7	1.395	12.1
Dilute product	55.1	44.9	0.0	2.3	1.331	3.1
SRP bottoms	1.0	53.5	45.5	*	*	100.6
EDP bottoms	2.5	54.1	43.4	65.0	[1.623]	105.5

Conditions for Run ACR-43

T_{EDP} = 155°C
V_{EDP} = 800 cc
$F_{Mg(NO_3)_2}$ = 16 cc/min
F_{feed} = 50 cc/min

Feed	65.1	34.9	0.0	16.0	1.390	22.1
Concentrated product	67.6	32.4	0.0	10.5	1.397	14.7
Dilute product	49.5	50.5	0.0	2.0	1.298	2.6
SRP bottoms	2.8	53.5	43.7	*	*	82.0
EDP bottoms	2.5	53.5	44.0	50.0	[1.629]	81.4

[ ] = experimentally determined density.
* = not measured

Table 7 (continued)

Conditions for Run ACR-44

T_{EDP} = 155°C
V_{EDP} = 1500 cc
$F_{Mg(NO_3)_2}$ = 5.0 cc/min
F_{feed} = 11.5 cc/min

	Stream Parameters (wt %)			F	ρ	G
	HNO_3	H_2O	$Mg(NO_3)_2$	(cc/min)	(g/cc)	(g/min)
Feed	65.5	34.5	0.0	11.5	1.389	16.0
Conc. product	66.8	33.2	0.0	8.7	1.392	12.1
Dilute product	45.1	54.9	0.0	2.0	1.276	2.6
SRP bottoms	1.7	52.9	45.4	*	*	78.9
EDP bottoms	2.9	53.1	44.0	50.0	1.629	81.5

Conditions for Run ACR-45

T_{EDP} = 155°C
V_{EDP} = 1500 cc
$F_{Mg(NO_3)_2}$ = 65 cc/min
F_{feed} = 16 cc/min

Feed	65.5	34.5	0.0	16.0	1.380	22.1
Conc. product	67.5	32.5	0.0	14.3	1.390	19.9
Dilute product	45.2	54.8	0.0	2.7	1.270	3.4
SRP bottoms	1.5	54.2	44.3	*	*	104.3
EDP bottoms	3.0	53.3	43.7	65.0	1.626	105.7

Conditions for Run ACR-46

T_{EDP} = 140°C
V_{EDP} = 1500 cc
$F_{Mg(NO_3)_2}$ = 50 cc/min
F_{feed} = 16 cc/min

Feed	66.1	33.9	0.0	16.0	1.396	22.3
Conc. product	77.9	22.1	0.0	8.8	1.445	12.7
Dilute product	51.8	48.2	0.0	7.9	1.321	10.4
SRP bottoms	2.2	53.6	44.2	*	*	71.5
EDP bottoms	7.6	52.9	39.5	50.0	1.600	80.0

Table 7. (continued)

Conditions for Run ACR-47

T_{EDP} = 140°C
V_{EDP} = 1500 cc
$F_{Mg(NO_3)_2}$ = 65 cc/min
F_{feed} = 11.5 cc/min

	Stream Parameters (wt %)			F	ρ	G
	HNO_3	H_2O	$Mg(NO_3)_2$	(cc/min)	(g/cc)	(g/min)
Feed	68.0	32.0	0.0	11.5	1.405	16.2
Conc. product	81.7	18.3	0.0	5.2	1.458	7.6
Dilute product	53.5	46.5	0.0	6.0	1.331	8.0
SRP bottoms	1.3	53.6	45.1	*	*	91.7
EDP bottoms	7.2	53.1	39.7	65.0	1.602	104.1

Conditions for Run ACR-48

T_{EDP} = 140°C
V_{EDP} = 800 cc
$F_{Mg(NO_3)_2}$ = 50 cc/min
F_{feed} = 11.5 cc/min

Feed	67.1	32.9	0.0	11.5	1.400	16.1
Conc. product	81.0	19.0	0.0	3.5	1.456	5.0
Dilute product	58.7	41.3	0.0	7.0	1.360	9.5
SRP bottoms	2.5	53.2	44.3	*	*	72.2
EDP bottoms	7.8	52.4	39.8	50.0	1.602	80.2

Conditions for Run ACR-49

T_{EDP} = 140°C
V_{EDP} = 800 cc
$F_{Mg(NO_3)_2}$ = 65 cc/min
F_{feed} = 16 cc/min

Feed	63.8	36.2	0.0	16.0	1.386	22.2
Conc. product	82.8	17.2	0.0	6.1	1.458	8.9
Dilute product	53.5	46.5	0.0	10.2	1.331	13.6
SRP bottoms	1.4	53.6	45.6	*	*	91.9
EDP bottom	7.5	52.8	39.7	65.0	1.602	104.1

Early in the experimental program an experiment was performed in which the objective was to reproduce one of the runs which had been performed by Counce *et al.* (1). Of particular interest was a comparison of stream compositions. The feed compositions of the two runs were slightly different; run ACR-38 contained more water. Overhead streams which contained only HNO_3 and H_2O agreed within the analytical error of the experiment (Appendix 11.3). The bottoms concentrations showed rather large discrepancies in the H_2O and $Mg(NO_3)_2$ concentrations. This is possibly attributable to differences in feed compositions. More likely however is the possibility that one or both runs had not attained steady state or that a measurement or sampling error was made. This comparison is given in Table 8.

Table 8. Comparison of Performance Results from Runs ACR-10* and ACR-38

Operating Conditions - Both Runs

T_{EDP} = 140°C

T_{SRP} = 170°C

V_{EDP} = 1000 cc

$V_{SRP} \simeq$ 1500 cc

$F_{Mg(NO_3)_2}$ = 65 cc/min

F_{feed} = 17.3 cc/min

	Stream Concentrations (wt %)					
	HNO_3		H_2O		$Mg(NO_3)_2$	
Stream Run No.	ACR-10	ACR-38	ACR-10	ACR-38	ACR-10	ACR-38
Feed	70.0	66.0	30.0	34.0	-	-
EDP						
overhead	81.0	83.0	19.0	17.0	-	-
bottoms	6.5	6.1	33.4	52.6	60.1	41.3
SRP						
overhead	53.0	51.0	47.0	49.0	-	-
bottoms	0.6	0	31.7	52.7	67.7	47.3

*Data from Counce *et al.* (1).

11.2 Sample Set of Analytical Calculations for Run ACR-48

1. Calibration of Nitric Acid Titration

$$\text{mmol } HNO_3 = (0.0173 \times \text{chart mm}) - 0.0207 \qquad (7)$$

See project calculation file for thermographs used in the calibration.

2. HNO_3 in Feed and Product Streams

$$\underline{M}\ HNO_3(\text{moles/liter}) = \text{mmol } HNO_3 \div \text{aliquot volume (ml)} \qquad (8)$$

Stream	Sample		Aliquot ($\lambda\ell$)	Chart (mm)	HNO_3 (mmole)	$\underline{M}$ HNO_3	X_{HNO_3}(%)
Feed	488	a)	50	42.2	0.7396	14.79	66.7
		b)	50	42.9	0.7524	15.05	67.5
Concentrate	480	a)	50	52.4	0.9253	18.51	80.3
		b)	50	53.5	0.9243	18.91	81.7
Dilute	482	a)	50	36.1	0.6286	12.57	58.2
		b)	50	36.6	0.6377	12.75	59.2

Weight fractions (X_{HNO_3}) were found from molarities ($\underline{M}$ HNO_3) using tables from Dean (6).

Average values for feed, product stream (wt %):

feed acid = 67.1
concentrated product = 81.0
dilute product = 58.7

3. Solution Makeup from Recycle Stream Samples

Stream	Sample	Total Weight (g)	Tared Weight (g)	Net Weight (g)	Volume (ml)
SRP bottoms	484	47.3246	30.1073	17.2173	200
EDP bottoms	486	41.7085	29.9991	11.7094	100

4. HNO_3 in Recycle Streams

Stream	Sample	Aliquot (ml)	Spike Volume (ml)	Chart (mm)	Total HNO_3 (mmol)	Spike HNO_3 (mmol)	Net HNO_3 (mmol)	X_{HNO_3}
SRP bottoms	484 a)	5.0	500	40.8	0.6851	0.5016	0.1835	0.0269
	b)	5.0	500	39.5	0.6626	0.5016	0.1610	0.0236
EDP bottoms	486 a)	5.0	500	72.9	1.2405	0.5016	0.7389	0.0796
	b)	5.0	500	71.4	1.2145	0.5016	0.7129	0.0768

$$HNO_3(\text{mmol}) = (0.0173 \times \text{chart mm}) - 0.0207 - \text{spike(mmol)}$$

$$X_{HNO_3} = HNO_3(\text{mmol})\left[\frac{63.1\ \text{g/mole} \times \text{solution volume } (\ell)}{\text{aliquot(ml)} \times \text{sample weight(g)}}\right] \qquad (9)$$

Average values for HNO_3 weight percents in recycle streams are:

SRP bottoms = 2.5%
EDP bottoms = 7.8%

5. Standardization of EDTA Solution for Titration of $Mg(NO_3)_2$

	Aliquot of Mg Standard	EDTA Volume (ml)	M (moles/liter)
a)	5.0	9.84	0.05036
b)	5.0	9.86	0.05025

Standard: 2.4088 M

$$\text{EDTA concentration } \underline{M} = 2.4088\ \text{g}/\ell \div 24.307\ \text{g/mole} \times \text{aliquot (ml)} \div \text{EDTA volume (ml)} \qquad (10)$$

$$= 0.0503$$

6. $Mg(NO_3)_2$ in Recycle Streams

Stream	Sample	Aliquot (ml)	EDTA Volume (ml)	EDTA M	$Mg(NO_3)_2$ M	$X_{Mg(NO_3)2}$
SRP bottoms	484 a)	1.0	7.57	0.0503	0.3808	0.4437
	b)	2.0	15.07	0.0503	0.3790	0.4417
EDP bottoms	486 a)	1.0	9.25	0.0503	0.4653	0.3986
	b)	1.0	9.20	0.0503	0.4628	0.3965

$$\underline{M},\ Mg(NO_3)_2 = \frac{\text{EDTA Volume (ml) x EDTA } \underline{M}\text{(mol/liter)}}{\text{aliquot (ml)}} \qquad (11)$$

$$X_{Mg(NO_3)_2} = \frac{\underline{M}Mg(NO_3)_2\text{(mol/liter) x 130.32 g/mole x solution volume } (\ell)}{\text{sample weight (g)}} \qquad (12)$$

Average $Mg(NO_3)_2$ composition of recycle streams are:

SRP bottoms = 44.3%
EDP bottoms = 39.8%

7. Stream Flow Rates

Stream	F (cc/min)	ρ (g/cc)	G (cc/min)
Feed	11.5	1.400	16.1
Concentrated product	3.5	1.456	5.0
Dilute product	7.0	1.360	9.5
SRP bottoms	*	*	72.2
EDP bottoms	50.0	1.602	80.2

Density data for acid streams (feed and products) were taken from Dean (6). For recycle streams, a correlation based on Rainey's work (7) for the dependences of density on temperature and on $Mg(NO_3)_2$ concentration was used:

$$\rho \text{ (g/cc)} = 1.6288 - (T - 155°C)(8 \times 10^{-4}) + (X_3 - 0.440)(0.90) \qquad (13)$$

8. Concentrated-Product Recovery Ratio:

$$CPRR = \frac{G_{HNO_3}\text{ (concentrate)}}{G_{HNO_3}\text{ (feed)}} = \frac{5.0}{16.1} = 0.31$$

9. Concentration of Concentrated Product, X_{HNO_3} (concentrate)

CCP = 0.810

---

*Not measured.

10. Mass Balance Check on Results for Run ACR-48

a) HNO_3

$$\text{overall: \% deviation} = 100\left[\frac{G_1W_{1,1} - G_2W_{2,1} - G_3W_{3,1}}{G_1W_{1,1}}\right] \tag{14}$$

$$\text{SRP: \% deviation} = 100\left[\frac{G_4W_{4,1} - G_3W_{3,1} - G_5W_{5,1}}{G_4W_{4,1}}\right] \tag{15}$$

$$\text{EDP: \% deviation} = 100\left[\frac{G_1W_{1,1} + G_5W_{5,1} - G_2W_{2,1} - G_4W_{4,1}}{G_1W_{1,1}}\right] \tag{16}$$

b) H_2O

Same as above, with weight fractions for water.

Streams: 1 - feed
2 - concentrate
3 - dilute
4 - EDP bottoms
5 - SRP bottoms

Components: 1 - HNO_3
2 - H_2O
3 - $Mg(NO_3)_2$

Results

	% Deviation		
	Overall	EDP	SRP
HNO_3	10.9	21.3	17.9
H_2O	8.0	11.8	4.3

11.3 Estimation of Experimental Error

This section presents an estimation of experimental error for both measured and calculated quantities. Errors for volumetric flow rates and temperature measurements were made in operating the equipment. The analytical error in determining compositions was made by consultation with the analytical chemist of CFRF. From these estimates, the error in the mass flow rates, response factors, and mass balances was calculated by using standard methods shown below.

1. Directly Measured Quantities

a) Compositions (weight fractions) - ε_W = 2% error

b) Volumetric flow rates (cc/min) - ε_F = 5% error

c) Densities (g/cc) - $\varepsilon_\rho = 1\%$ error

Mass flow rates (g/min) (ε_G) may be calculated from the relationship:

$$(100 - \varepsilon_G) = (100 - \varepsilon_\rho)(100 - \varepsilon_F) = (99)(95) \qquad (17)$$

Therefore, $\varepsilon_G = 5.9\%$

2. Response Factor

a) CPRR

$(100 - \varepsilon_{CPRR}) = (100 - \varepsilon_G)^2$. Therefore $\varepsilon_{CPRR} = 11.5\%$.

b) CCP

$\varepsilon_{CCP} = 2.0\%$

c) Stage efficiencies are defined as follows:

$$\eta = \frac{W_1 - Z_1}{W_1^* - Z_1} \qquad (18)$$

Therefore the error in the stage efficiencies is:

$$100 - \varepsilon_\eta = [100 - \sqrt{2}\,\varepsilon_W][100 - \sqrt{\varepsilon_W^2 + \varepsilon_*^2}] \qquad (19)$$

The error in equilibrium data is:

$\varepsilon_* = 4.0\%$ (average deviation)

Therefore,

$\varepsilon_\eta = 14.4\%$

3. Mass Balances

a) Overall

$$\%\text{ deviation} = \frac{G_1W_{1,1} - G_2W_{2,1} - G_3W_{3,1}}{G_1W_{1,1}}$$

$$100 - \epsilon_{G,W} = (100 - \epsilon_G)(100 - \epsilon_W) = (100 - 5.9)(100 - 2.0) \quad (20)$$

$$\epsilon_{G,W} = 7.8\%$$

$$100 - \epsilon_{d,o} = [100 - \sqrt{3(\epsilon_{G,W})^2}][100 - \epsilon_{G,W}] = [100 - 13.5][100 - 7.8] \quad (21)$$

$$\epsilon_{d,o} = 20.2\%$$

b) SRP

SRP is the same as overall mass balance:

$$\epsilon_{d,s} = 20.2\%$$

c) EDP

$$\%\text{ deviation} = \frac{G_1W_{1,1} + G_5W_{5,1} - G_2W_{2,1} - G_4W_{4,1}}{G_1W_{1,1}} \quad (22)$$

$$100 - \epsilon_{d,E} = [100 - \sqrt{4(\epsilon_{G,W})^2}][100 - \epsilon_{G,W}] = [100 - 15.6][100 - 7.8] \quad (23)$$

$$\epsilon_{d,E} = 22.2\%$$

11.4 Calculation of Stage Efficiencies

1. Combined Feed: EDP

G (g/min)	Weight Fractions
Feed acid	X_1, X_2
SRP bottoms	X_1, X_2, X_3
Combined feed	Z_1, Z_2, Z_3

The feed compositions for run ACR-48 with the temperature at 140°C is:

	G (g/min)	$X_1(Z_1)$	X_2	X_3
Feed acid	16.1	0.671	0.329	0
SRP bottoms	72.0	0.025	0.532	0.443
Combined feed	88.1	0.143	0.495	0.362

2. Calculation of Equilibrium Vapor-Phase Composition

A computer routine called EQCALC was written to calculate the equilibrium vapor-phase composition if a liquid-phase composition is given. It is discussed in detail in Appendix 11.7. Using EQCALC, the equilibrium composition of the vapor phase exiting the EDP was calculated. This was done by inputting the combined feed (SRP bottoms and feed acid) and EDP temperature, and using the appropriate equilibrium data file (see Sect. 5). The results of this calculationare given in Table 9.

Table 9. Equilibrium Product Composition - EDP Feeds
Run ACR-48

	Weight Fraction		
Stream	1 - HNO_3	2 - H_2O	3 - $Mg(NO_3)_2$
Combined feed	0.143	0.495	0.362
Equilibrium vapor product	0.318	0.682	0.00
Equilibrium liquid product	0.060	0.406	0.534

3. Calculation of Hansen Stage Efficiencies for the Extractive-Distillation Pot ($\eta_{V,EDP}$, $\eta_{L,EDP}$)

$$\eta_{V,EDP} = \frac{Y_1 - Z_1}{Y_1^* - Z_1}(100\%) = \frac{0.810 - 0.143}{0.318 - 0.143}(100) = 381\% \qquad (24)$$

$$\eta_{L,EDP} = \frac{X_1 - Z_1}{X_1^* - Z_1}(100\%) = \frac{0.078 - 0.143}{0.060 - 0.143}(100) = 78\% \qquad (25)$$

It should be stressed that both stage efficiencies were defined by using the combined feed stream (Z_1). It is customary to define an efficiency for a single phase, but this was not possible for the vapor efficiency. Therefore, the combined feed was used to calculate both efficiencies although it is actually at least partially liquid.

4. Feed to SRP (EDP Bottoms) and Computer Calculation of Flash Compositions

The calculation of the compositions at equilibrium of the streams associated with the SRP was performed in an analogous manner to the calculation technique used in the preceding section. Table 10 gives a summary of the results. In this case there is a single feed to the pot.

$$100 - \varepsilon_{G,W} = (100 - \varepsilon_G)(100 - \varepsilon_W) = (100 - 5.9)(100 - 2.0) \qquad (20)$$

$$\varepsilon_{G,W} = 7.8\%$$

$$100 - \varepsilon_{d,o} = [100 - \sqrt{3(\varepsilon_{G,W})^2}][100 - \varepsilon_{G,W}] = [100 - 13.5][100 - 7.8] \qquad (21)$$

$$\varepsilon_{d,o} = 20.2\%$$

b) SRP

SRP is the same as overall mass balance:

$$\varepsilon_{d,s} = 20.2\%$$

c) EDP

$$\%\ \text{deviation} = \frac{G_1W_{1,1} + G_5W_{5,1} - G_2W_{2,1} - G_4W_{4,1}}{G_1W_{1,1}} \qquad (22)$$

$$100 - \varepsilon_{d,E} = [100 - \sqrt{4(\varepsilon_{G,W})^2}][100 - \varepsilon_{G,W}] = [100 - 15.6][100 - 7.8] \qquad (23)$$

$$\varepsilon_{d,E} = 22.2\%$$

11.4 Calculation of Stage Efficiencies

1. Combined Feed: EDP

G (g/min)	Weight Fractions
Feed acid	X_1, X_2
SRP bottoms	X_1, X_2, X_3
Combined feed	Z_1, Z_2, Z_3

The feed compositions for run ACR-48 with the temperature at 140°C is:

	G (g/min)	$X_1(Z_1)$	X_2	X_3
Feed acid	16.1	0.671	0.329	0
SRP bottoms	72.0	0.025	0.532	0.443
Combined feed	88.1	0.143	0.495	0.362

2. Calculation of Equilibrium Vapor-Phase Composition

A computer routine called EQCALC was written to calculate the equilibrium vapor-phase composition if a liquid-phase composition is given. It is discussed in detail in Appendix 11.7. Using EQCALC, the equilibrium composition of the vapor phase exiting the EDP was calculated. This was done by inputting the combined feed (SRP bottoms and feed acid) and EDP temperature, and using the appropriate equilibrium data file (see Sect. 5). The results of this calculationare given in Table 9.

Table 9. Equilibrium Product Composition - EDP Feeds
Run ACR-48

	Weight Fraction		
Stream	1 - HNO_3	2 - H_2O	3 - $Mg(NO_3)_2$
Combined feed	0.143	0.495	0.362
Equilibrium vapor product	0.318	0.682	0.00
Equilibrium liquid product	0.060	0.406	0.534

3. Calculation of Hansen Stage Efficiencies for the Extractive Distillation Pot ($\eta_{V,EDP}$, $\eta_{L,EDP}$)

$$\eta_{V,EDP} = \frac{Y_1 - Z_1}{Y_1^* - Z_1}(100\%) = \frac{0.810 - 0.143}{0.318 - 0.143}(100) = 381\% \qquad (24)$$

$$\eta_{L,EDP} = \frac{X_1 - Z_1}{X_1^* - Z_1}(100\%) = \frac{0.078 - 0.143}{0.060 - 0.143}(100) = 78\% \qquad (25)$$

It should be stressed that both stage efficiencies were defined by using the combined feed stream (Z_1). It is customary to define an efficiency for a single phase, but this was not possible for the vapor efficiency. Therefore, the combined feed was used to calculate both efficiencies although it is actually at least partially liquid.

4. Feed to SRP (EDP Bottoms) and Computer Calculation of Flash Compositions

The calculation of the compositions at equilibrium of the streams associated with the SRP was performed in an analogous manner to the calculation technique used in the preceding section. Table 10 gives a summary of the results. In this case there is a single feed to the pot.

Table 10. Equilibrium Product Compositions - SRP Feed
Run ACR-48

Stream	Weight Fraction (1) HNO_3	 (2) H_2O	 (3) $Mg(NO_3)_2$
SRP feed	0.078	0.528	0.398
Equilibrium vapor product	0.197	0.803	0
Equilibrium liquid product	0.025	0.322	0.653

From these results one can compute stage efficiencies for the nitric acid:

$$\eta_{V,SRP} = \frac{Y_1 - Z_1}{Y_1^* - Z_1}(100) = \frac{0.587 - 0.078}{0.197 - 0.078}(100) = 429\% \qquad (26)$$

The liquid-phase Hansen efficiency for the SRP is defined as:

$$\eta_{L,SRP} = \frac{X_1 - Z_1}{X_1^* - Z_1}(100) = \frac{0.025 - 0.078}{0.025 - 0.078}(100) = 100\% \qquad (27)$$

11.5 Statistical Analysis

For each experimental run the adjustable parameters were set to the low or high values (-, +) as specified by the factorial design. The effect of each parameter on the response factors was determined by taking the average difference of the factors corresponding to the high and low levels. The average results of this analysis for each response factor and parameter are presented in Table 11. The average effect for a typical response factor (CPRR, V_{EDP}) is:

$$\text{net effect} = \left[\frac{(\Sigma+) - (\Sigma-)}{4}\right] = \frac{270 - 214}{4} = 14.0 \qquad (28)$$

Table 11. Net Effect of Parameter Effects on Response Factors

Response Factor	V_{EDP}	F_{feed}	$F_{Mg(NO_3)_2}$	T_{EDP}	$V_{EDP}\cdot F_{feed}$	$V_{EDP}\cdot F_{Mg(NO_3)_2}$
CPRR	14.0	5.5	6.0	33.5	-3.5	6.0
CCP	-1.7	2.0	-0.7	-13.1	0.3	-0.8
$\eta_{V,EDP}$	-100	123	-127	-38	-11.8	9.8
$\eta_{L,EDP}$	-1.8	-8.8	8.8	28.8	6.8	4.8
$\eta_{V,SRP}$	-666	154	-171	1043	52	-17.5
$\eta_{L,SRP}$	25.7	40.7	-22.7	-43.7	-30.2	26.2

To determine whether an observed change indicated a significant effect, the changes in response factors were expressed in percentage form as given in Table 12. Error estimates were made for each factor as shown in Table 13. These were based solely on uncertainties incurred in analytical work; provision for additional system error was made with a multiplication factor of 1.5. The 50% factor which attempts to account for the experimental system error is arbitrary. Inherent in our design is a forsaking of any ability to estimate experimental error. This is an area in which further work is indicated. By comparing the error estimated with the response factor changes shown in Table 12, the parameters that had significant effects on each factor could be determined. These are tabulated in order of decreasing importance to the respective variables.

Table 12. Percentage Changes in Response Factors

Parameter	CPRR	CCP	$\eta_{V,EDP}$	$\eta_{L,EDP}$	$\eta_{V,SRP}$	$\eta_{L,SRP}$
V_{EDP}	26.2	-2.2	-23.9	-1.9	-49.9	34.4
F_{feed}	9.5	2.7	40.1	-9.0	16.7	59.8
$F_{Mg(NO_3)_2}$	10.4	-1.0	-29.4	9.8	-15.7	-22.8
T_{EDP}	76.6	-16.2	-9.7	36.3	-214	-39.6
$V_{EDP}\cdot F_{feed}$	-5.6	0.1	-3.1	6.7	5.3	-29.2
$V_{EDP}\cdot F_{Mg(NO_3)_2}$	10.4	-1.1	2.7	5.2	-1.7	34.8

Table 13. Error Estimates and Significant Effects

Response	Analytical Error (%)	Total Error (%) (1.5 x analytical)	Significant Effects (in order of importance)
CPRR	±9.8	±14.7	T_{EDP}, V_{EDP}
CCP	2.0	3.0	T_{EDP}
$\eta_{V,EDP}$	14.4	21.6	F_{feed}, $F_{Mg(NO_3)_2}$, V_{EDP}
$\eta_{L,EDP}$	14.4	21.6	T_{EDP}
$\eta_{V,SRP}$	14.4	21.6	T_{EDP}, V_{EDP}
$\eta_{L,SRP}$	14.4	21.6	F_{feed}, T_{EDP}, $V_{EDP} \cdot F_{Mg(NO_3)_2}$, V_{EDP}, $V_{EDP} \cdot F_{Mg(NO_3)_2}$

Expressions were developed for each response factor as a linear function of the corresponding significant parameters:

$$\text{CPRR} = 0.010(V_{EDP} - 800\text{ cc}) + 1.1(T_{EDP} - 140°\text{C}) + 49 \qquad (29)$$

$$\text{CCP} = -0.87(T_{EDP} - 140°\text{C}) + 81 \qquad (30)$$

$$\eta_{V,EDP} = 9.1(F_{feed} - 11.5\text{ cc/min}) - 0.047(V_{EDP} - 800\text{ cc}) -2.8(F_{Mg(NO_3)_2} - 50\text{ cc/min}) + 390 \qquad (31)$$

$$\eta_{L,EDP} = 1.9(T_{EDP} - 140°\text{C}) + 79 \qquad (32)$$

$$\eta_{V,SRP} = 69(T_{EDP} - 140°\text{C}) - 0.95(V_{EDP} - 800\text{ cc}) + 1800 \qquad (33)$$

$$\eta_{L,SRP} = -2.9(T_{EDP} - 140°\text{C}) + 0.040(V_{EDP} - 800\text{ cc}) + 9.0(F_{feed} - 11.5\text{ cc/min}) - 1.5(F_{Mg(NO_3)_2} - 50\text{ cc/min}) - 0.002 \times (V_{EDP}F_{feed} - V^{\circ}_{EDP}F^{\circ}_{feed}) - 0.0004(V_{EDP}F_{Mg(NO_3)_2} - V^{\circ}_{EDP}F^{\circ}_{Mg(NO_3)_2}) + 530 \qquad (34)$$

Obviously the data allow no more than a linear relationship in each variable. Therefore a simple graphical analysis was performed.

11.6 Analytical Laboratory Procedures

Composition determination of samples included titrations for HNO_3 and $Mg(NO_3)_2$ content. The HNO_3 titrations were of the thermometric type, while those for $Mg(NO_3)_2$ were calorimetric.

The acid feed and overhead products were assumed to be binaries and were analyzed for HNO_3 only. This was done with a thermometric titrator that mechanically pumps NaOH solution (0.5 M) into the acid sample. The temperature rise of reaction was monitored on a strip chart; this change was sharp as the neutralization began, followed a roughly linear path, then stopped abruptly as the reaction endpoint was reached. Samples were transferred to the reaction beaker by micropipetting and were diluted to about 1 cc. Approximately 20 cc of potassium fluoride solution (4.5 M) was added to form complexes with Mg^{++} ions, permitting true determination of free acid concentration.

The titrator was calibrated with a nitric acid standard of known concentration. The amount of base added was related to distance on the strip chart. As the moles of base added is equivalent to the moles of acid present, this calibration gives a linear relation between strip-chart distance and moles of acid in solution. Standard samples of 1.0 and 0.5 mmoles were usually used; product acid samples of 50-100 microliters were used to lie within the calibration region.

The EDP and SRP bottoms streams include significant amounts of $Mg(NO_3)_2$ and are solids at room temperature. Solutions of known volume must be diluted with distilled water. These were analyzed for HNO_3 as before. However, acid content was low (<5%) and an aliquot of standardized HNO_3 (about 0.5 mmoles) had to be added before titration. This kept the total determination in the range of the calibration points, where the linear fit is most reliable.

These variations were analyzed further for $Mg(NO_3)_2$ concentration by calorimetric methods. Disodium ethylenediaminetetraacetate (EDTA) of 0.05 M concentration was used to titrate the Mg^{++} ions. Samples were poured into a beaker, diluted to about 80 ml, and treated with about 5 ml of a NH_4^+ buffer solution to a pH 10.5, where the Mg^{++} EDTA complex is most stable.

One or two drops of Black T (Erichrome Black) was used as the indicator. The initially rose-colored solution turned violet as the endpoint was approached, and it became royal blue when the reaction went to completion. This procedure was most reliable for a content of Mg^{++} ions not greater than 25 mg; this corresponds to 20 ml of EDTA required for titration. (If this level was exceeded, the analysis was repeated with a smaller aliquot.)

Stream densities are required for mass flow rate determinations and system mass balances. As the flow rates read from the experimental apparatus are volumetric for the acid streams, 1.0 ml of each sample was drawn and weighed on an analytical balance.

Pycnometers were initially used to draw samples for density determinations of the ternary system at operating temperature. Several data points were taken and reported in Appendix 11.1; however, a complete set of data were not taken because the technique required new jars for each test and the laboratory's supply was exhausted. In cases where density data were not measured directly, they were estimated from existing ternary data and some extrapolations based on known binary information. Appendix 11.1 gives detail on the required calculations.

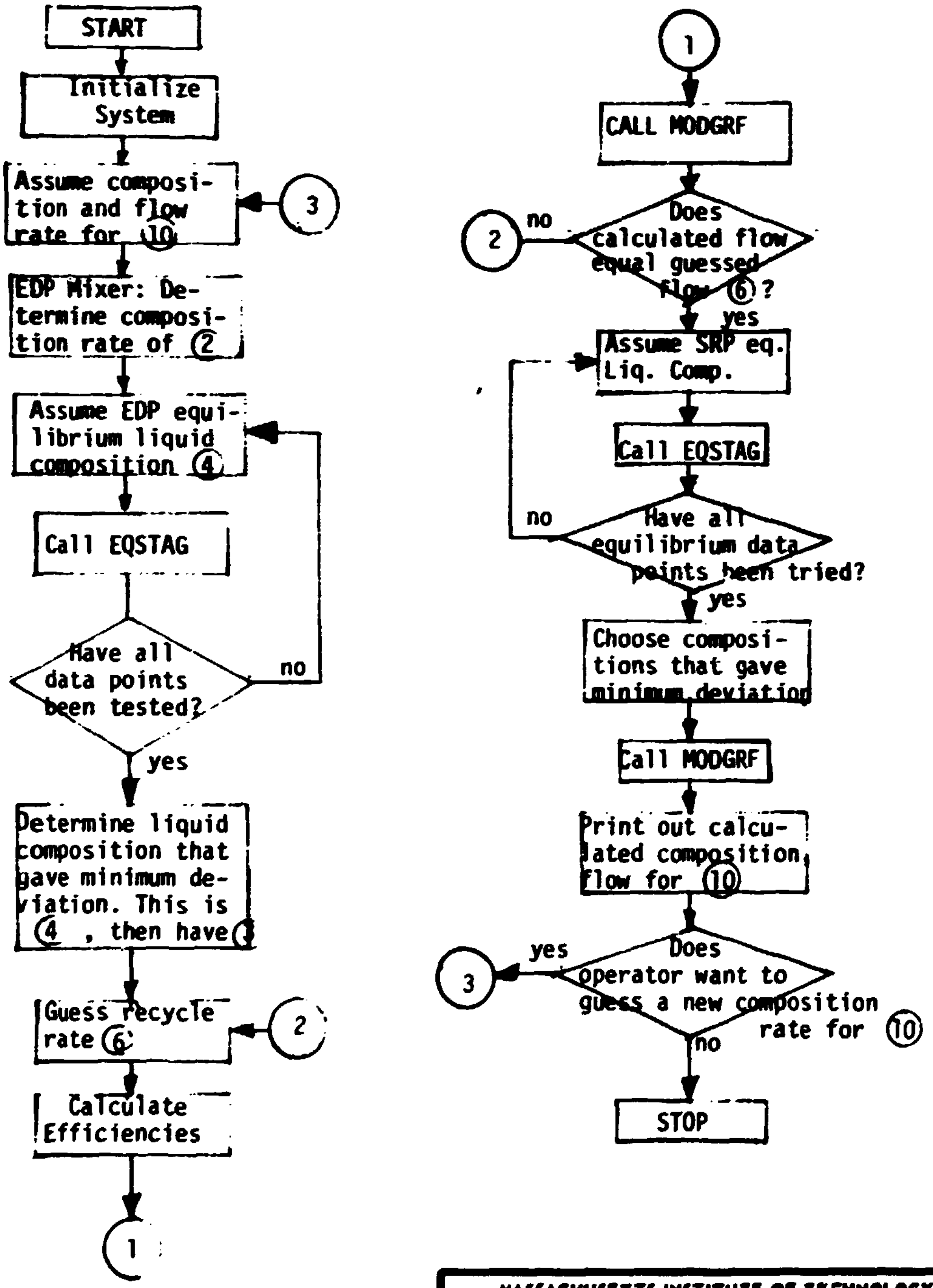
11.7 Computer Model

Section 7.4 was devoted to a discussion of a Fortran program which was written and implemented on the ORNL PDP-10 computer system. The computer flowsheet is presented in Fig. 8, and a list of the program along with the subroutines is given on the following pages.

The calculations required to determine the steady-state conditions for a given set of controllable parameters (see Sect. 4.3.2) are highly iterative due to the large number of unknowns. Initially, values for the mass flow rate and composition of stream 10 (the SRP effluent of Figs. 7 and 8) are assumed, permitting the straightforward calculation of all flow rates and compositions, including new values for stream 10. The original guess is then modified by the operator until (1) the recycle mass flow rate (stream 6) equals the desired value, and (2) the calculated composition and mass flow rate for stream 10 equals the guessed values.

The first step in the main program (TWOPOT) is initialization, in which the controllable parameters are specified, and points lying on equilibrium isotherms for the ternary system are read into the equilibrium-data matrices (EQDAT1 and EQDAT2). A listing also follows of the points for three isotherms (140, 155, and 165°C) stored in data files (FORXX.DAT) 40, 55, and 60, respectively.

The mass flow rate and composition of stream 10 is then specified by the operator. Stream 10 is then combined with stream 1 (feed acid) with sample component mass balances, resulting in stream 2. The vapor and liquid streams resulting from an isothermal and isobaric equilibrium flash of stream 2 are then determined by subroutine EQSTAG. This calculation is iterative; liquid-phase product compositions are assumed, permitting the determination of the vapor-phase composition by using the correlations developed by Cigna *et al.* (2). A linear fit in the region of 35-45 wt % $Mg(NO_3)_2$ is used to calculate the azeotropic HNO_3 mole fraction, which is no longer zero if $Mg(NO_3)_2$ wt % drops below 45. Unfortunately, there exist no correlations for solution temperature as a function of composition. Consequently, trial liquid-phase compositions must lie on the



MASSACHUSETTS INSTITUTE OF TECHNOLOGY
SCHOOL OF CHEMICAL ENGINEERING PRACTICE
AT
OAK RIDGE NATIONAL LABORATORY

TWO-POT NITRIC ACID DISTILLATION
PROGRAM ALGORITHM FLOWSHEET

DATE	DRAWN BY	FILE NO.	FIG.
11-23-80	PCC	CEPS-X-325	8

```
C        MAIN PROGRAM -"TWOPOT"
C        MAIN PROGRAM FOR STEADY-STATE SIMULATION OF TWO-POT
C        NITRIC ACID DEHYDRATION APPARATUS.
C        WRITTEN BY C F IRWIN, 11/80
C        \\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\
         DIMENSION FLOW(12),WFRAC(12,3),EQDAT1(100,5),EQDAT2(100,5),
     C   GWFRAC(3),FWFRAC(3),LWFRAC(3),VWFRAC(3),E(15),
     C   EFFEDP(2),EFFSRP(2),VOLDWF(3),LOUTWF(3),DEVWGT(3),VOUTWF(3)
         REAL LWFRAC,LOUTWF
C********INPUT THE FACTOR LEVELS
         READ(45,*)(E(I),I=1,14)
         READ(46,*)TEMEDP,VOLEDP,TEMSRP,VOLSRP,FLOW(1),WFRAC(1,1),
     C   FLOREC, IDATA1,IDATA2,IPRINT,LREP1,LREP2
         WFRAC(1,2)=1.-WFRAC(1,1)
         WFRAC(1,3)=0.0
C********INPUT THE EQUILIBRIUM DATA
         READ(IDATA1,*)LLIST1
         READ(IDATA1,*)((EQDAT1(I,J),J=1,5),I=1,LLIST1)
         READ(IDATA2,*)LLIST2
         READ(IDATA2,*)((EQDAT2(I,J),J=1,5),I=1,LLIST2)
C********DOUBLE THE SIZE OF THE EQUILIBRIUM DATA BASE BY LINEARLY
C********INTERPOLATING BETWEEN THE PROVIDED POINTS.
         IF (LREP1.EQ.1)GOTO 10
         DO 15 NPOS=1,LLIST1-1
         EQDAT1(NPOS+LLIST1,1)=NPOS+LLIST1
         EQDAT1(NPOS+LLIST1,2)=EQDAT1(1,2)
         DO 15 J=3,5
15       EQDAT1(NPOS+LLIST1,J)=(EQDAT1(NPOS,J)+EQDAT1(NPOS+1,J))/2.
10       IF(LREP2.EQ.1)GOTO 11
         DO 16 NPOS=1,LLIST2-1
         EQDAT2(NPOS+LLIST2,1)=NPOS+LLIST2
         EQDAT2(NPOS+LLIST2,2)=EQDAT2(1,2)
         DO 16 J=3,5
16       EQDAT2(NPOS+LLIST2,J)=(EQDAT2(NPOS,J)+EQDAT2(NPOS+1,J))/2.
C********PRINT OUT THE DATA TO CHECK ON IT
11       WRITE(05,2010)TEMEDP,VOLEDP,TEMSRP,VOLSRP,FLOW(1),WFRAC(1,1),FLOREC
         IF(LREP1.EQ.1)LSTOP1=LLIST1
         IF(LREP2.EQ.1)LSTOP2=LLIST2
         IF(LREP1.EQ.2)LSTOP1=LLIST1*LREP1-1
         IF(LREP2.EQ.2)LSTOP2=LLIST2*LREP2-1
         IF(IPRINT.NE.1)GOTO 20
         WRITE(05,2014)
         WRITE(05,2015)
         WRITE(05,2020)((EQDAT1(I,J),J=1,5),I=1,LSTOP1)
         WRITE(05,2021)((EQDAT2(I,J),J=1,5),I=1,LSTOP2)
```

```
C*******INITIALIZE THE PROCESS BY GUESSING A FLOW AND COMP FOR SRP EFFLUENT
20      WRITE(U5,210A)
        READ(05,*)GFLOW,GWFRAC(1),GWFRAC(2),IENUF
        IF(IENUF.EQ.0)GOTO 1000
        GWFRAC(3)=1.-GWFRAC(1)-GWFRAC(2)
C*******MIXER SECTION FOR THE EDP
        FLOW(2)=FLOW(1)+GFLOW
        DO 40 I=1,3
        WFRAC(2,I)=(FLOW(1)*WFRAC(1,I)+GFLOW*GWFRAC(I))/FLOW(2)
40      FWFRAC(I)=WFRAC(2,I)
C*******FEED THIS FLOW INTO THE EQUILIBRIUM STAGE FOR THE EDP
        DO 100 NLIST=1,LSTOP1
        DO 110 I=1,3
110     LWFRAC(I)=EQDAT1(NLIST,I+2)/100.
        CALL EQSTAG(FLOW(2),CFLOW3,CFLOW4,FWFRAC,VWFRAC,LWFRAC,DEV)
        IF(NLIST.EQ.1)DEVOLD=DEV
        IF(DEV.GT.DEVOLD)GOTO 100
        DEVOLD=DEV
        DO 120 I=1,3
        WFRAC(3,I)=VWFRAC(I)
120     WFRAC(4,I)=LWFRAC(I)
        FLOW(3)=CFLOW3
        FLOW(4)=CFLOW4
100     CONTINUE
C*******BEGIN EDP MODIFICATION STAGE SECTION
        DO 200 I=1,3
        VWFRAC(I)=WFRAC(3,I)
        LWFRAC(I)=WFRAC(4,I)
200     VOLDWF(I)=WFRAC(2,I)
        EXXX=.1
        KID=1
        DO 300 J=1,100
        GUESS=10.*ZEROTH(KID,EXXX)
        FLOW(6)=GUESS*FLOW(4)
        IF(KID.LT.0)GOTO310
C*******CALSULATE EFFICIENCIES
        EFFEDP(1)=E(1)*TEMEDP+E(2)*VOLEDP+E(3)*FLOW(1)+E(4)*FLOW(6)+E(5)
        EFFEDP(2)=E(6)*TEMEDP+E(7)*VOLEDP+E(8)*FLOW(1)+E(9)*FLOW(6)+E(10)
C*******CALL SUBROUTINE TO CALC EXIT FLOWS AND COMPOSITIONS
        CALL MODARF(EFFEDP,FLOW(3),VWFRAC,FLOW(4),LWFRAC,FLOW(2),
      C VOLDWF,CFLOW6,LOUTWF,FLOW(5),VOUTWF)
300     EXXX=(FLOW(6)-CFLOW6)/FLOW(4)
310     DO 330 I=1,3
        WFRAC(5,I)=VOUTWF(I)
        FWFRAC(I)=LOUTWF(I)
330     WFRAC(6,I)=LOUTWF(I)
```

```
C********DO EQUILIBRIUM STAGE CALC FOR SRP
         DO 400 NLIST=1,LSTOP2
         DO 410 I=1,3
410      LWFRAC(I)=EQDAT2(NLIST,I+2)/100.
         CALL EQSTAG(FLOW(6),CFLOW7,CFLOW8,FWFRAC,VWFRAC,LWFRAC,DEV)
C********COMPARE DEVIATIONS
         IF(NLIST.EQ.1)DEVOLD=DEV
         IF(DEV.GT.DEVOLD)GOTO 400
         DEVOLD=DEV
         DO 420 I=1,3
         WFRAC(7,I)=VWFRAC(I)
420      WFRAC(8,I)=LWFRAC(I)
         FLOW(7)=CFLOW7
         FLOW(8)=CFLOW8
400      CONTINUE
         DO 450 I=1,3
         FWFRAC(I)=WFRAC(6,I)
         VWFRAC(I)=WFRAC(7,I)
450      LWFRAC(I)=WFRAC(8,I)
C********SRP EQ MODIFICATION STAGE
C********CALCULATE EFFICIENCIES
480      EFFSRP(1)=E(11)*FLOW(6)+E(12)
         EFFSRP(2)=E(13)*FLOW(6)+E(14)
         CALL MODGRF(EFFSRP,FLOW(7),VWFRAC,FLOW(8),LWFRAC,FLOW(6),
       C FWFRAC,FLOW(10),LOUTWF,FLOW(9),VOUTWF)
         DO 530 I=1,3
         WFRAC(10,I)=LOUTWF(I)
530      WFRAC(9,I)=VOUTWF(I)
         WRITE(05,2050)
         DO 600 I=1,10
         AAAA=I
600      WRITE(05,2060)AAAA,FLOW(I),WFRAC(I,1),WFRAC(I,2),WFRAC(I,3)
         DEVREC=((FLOREC-FLOW(6))/FLOREC)*100.
         DEVMAG=(GFLOW-FLOW(10))/GFLOW*100.
         DO 610 I=1,3
610      DEVWGT(I)=(GWFRAC(I)-WFRAC(10,I))/GWFRAC(I)*100.
         WRITE(05,2070)
         WRITE(05,2080)DEVREC,DEVMAG,DEVWGT(1),DEVWGT(2),DEVWGT(3)
         GOTO 20
C********FORMAT STATEMENTS
2010     FORMAT(7F9.1)
2005     FORMAT('  EDP TEMP'T15,'EDP VOL'T25,'SRP TEMP'T35,'SRP VOL'
       C T45,'FEED RATE'T55,'HNO3 PER'T65,'REC RATE'/)
2015     FORMAT('  ENTRY #'T10,'TEMP'T20,'HNO3 WGT'T35,'H2O WGT'
       C T50,'MAG NIT WGT'/)
2014     FORMAT('  EQUILIBRIUM DATA',//)
2020     FORMAT(5F8.2)
2021     FORMAT(5F10.4)
2050     FORMAT('  STREAM#'T13,'FLOW RATE'T25,'HNO3 WGT'T35,'H2O WGT'
       C T45,'MAG NIT WGT',//)
2060     FORMAT(5F10.4/)
2070     FORMAT('  REC RATE DEV'T15,'SRP EFF FLOW DEV'T30,'SRP HNO3 DEV'
       C T45,'SRP H2O DEV'T60,'SRPMAG NIT DEV',//)
2080     FORMAT(5F10.4/)
2100     FORMAT(16H  GUESS AGAIN...)
1000         STOP
         END
```

```
C          \\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\
C          SUBROUTINE "EQSTAG"
C          EQUILIBRIUM STAGE SUBROUTINE - CALCULATES THE COMPOSITION
C          OF THE VAPOR PHASE THAT WOULD BE IN EQUILIBRIUM WITH THE
C          GIVEN LIQUID PHASE. WRITTEN BY CF IRWIN, 11/80.
C          \\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\
           SUBROUTINE EQSTAG(FFLOW,VFLOW,LFLOW,FWFRAC,VWFRAC,LWFRAC,DEV)
           DIMENSION FWFRAC(3),VWFRAC(3), LWFRAC(3),LMFRAC(3),LMFRSF(3)
           DIMENSION VMFRAC(3)
           REAL LFLOW, LWFRAC,LMFRAC,LMFRSF
C********CALCULATE CONSTANTS A AND B
           A=10**(-2.97*LWFRAC(3)+0.648)
           B=10**(2.81*LWFRAC(3)-0.523)
C********CONVERT ALL WEIGHT FRACTIONS TO MOL FRACTIONS
           TOTWGT=LWFRAC(1)/63.1+LWFRAC(2)/18.02+LWFRAC(3)/100.32
           LMFRAC(1)=LWFRAC(1)/63.1/TOTWGT
           LMFRAC(2)=LWFRAC(2)/18.02/TOTWGT
C********CALCULATE SALT-FREE MOLE FRACTIONS FOR LIQ STRAM
           DO 500 I=1,2
500        LMFRSF(I)=LMFRAC(I)/(LMFRAC(1)+LMFRAC(2))
           AZLMFR=-0.689*LWFRAC(3)+0.315
           IF(AZLMFR.LT.0.0)AZLMFR=0.0
C********CALCULATE RELATIVE VOLATILITY
           IF((LMFRSF(1).EQ.0.).AND.(AZLMFR.NE.0.))RELVOL=10**(-A-B*AZLMFR)
           IF((LMFRSF(1).NE.0.).AND.(AZLMFR.EQ.0.))RELVOL=10**(A+B*LMFRSF(1))
           IF((LMFRSF(1).EQ.0.).AND.(AZLMFR.EQ.0.))RELVOL=10**A
           IF((LMFRSF(1).NE.0.).AND.(AZLMFR.NE.0.))RELVOL=10**((A/(LMFRSF(1)
      C    +AZLMFR)+B)*(LMFRSF(1)-AZLMFR))
C********CALCULATE VAPOR COMP IN EQ WITH THE GIVEN LIQ COMP
           IF (LMFRSF(1).EQ.0.0)VMFRAC(1)=0.0
           IF (LMFRSF(1).EQ.0.0)GOTO 600
           VMFRAC(1)=1./(1.+LMFRSF(2)/RELVOL/LMFRSF(1))
600        VMFRAC(2)=1.-VMFRAC(1)
           VMFRAC(3)=0.0
C********CONVERT THESE MOLE FRACTIONS TO WEIGHT FRACTIONS
           TOTWGT=VMFRAC(1)*63.1+VMFRAC(2)*18.02+VMFRAC(3)*100.32
           VWFRAC(1)=VMFRAC(1)*63.1/TOTWGT
           VWFRAC(2)=VMFRAC(2)*18.02/TOTWGT
           VWFRAC(3)=0.0
C********CALCULATE THE VAPOR AND LIQUID FLOW RATES VIA MASS BALANCESC
           IF(LMFRAC(1).EQ.0.)GOTO 700
           VFLOW=FFLOW*(FWFRAC(1)*LWFRAC(2)-FWFRAC(2)*LWFRAC(1))/
      C     (VWFRAC(1)*LWFRAC(2)-VWFRAC(2)*LWFRAC(1))
           LFLOW=(FFLOW*FWFRAC(1)-VFLOW*VWFRAC(1))/LWFRAC(1)
           GOTO 800
700        LFLOW=FFLOW*FWFRAC(3)/LWFRAC(3)
           VFLOW=(FFLOW*FWFRAC(2)-LFLOW*LWFRAC(2))/VWFRAC(2)
800        CONTINUE
C********CALCULATE THE DEVIATION FROM PERFECT M.B.
           DEV=ABS((VFLOW+LFLOW-FFLOW)/FFLOW)
           RETURN
           END
```

```
C         \\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\
C         SUBROUTINE "MODGRF"
C         MODIFICATION STAGE SUBROUTINE - CALCULATES PRODUCT VAPOR AND
C         LIQUID FLOW RATES AND COMPOSITIONS USING THE HAUSEN BASED
C         GRIFFIN STAGE EFFICIENCY. WRITTEN BY CF IRWIN, 11/23/80.
C         \\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\
          SUBROUTINE MODGRF(EFF,VIN,VINWFR,LIN,LINWFR,FFLOW,FWFRAC,
     C    LOUT,LOUTWF,VOUT,VOUTWF)
          DIMENSION VINWFR(3),LINWFR(3),FWFRAC(3),LOUTWF(3),VOUTWF(3),
     C    EFF(3)
          REAL LIN,LINWFR,LOUT,LOUTWF
C*********CALCULATE THE ACTUAL FLOWS THAT ARE USED TO DEFINE THE EFFICIENCY
          VOUTWF(1)=EFF(1)*(VINWFR(1)-FWFRAC(1))+FWFRAC(1)
          VOUTWF(2)=1.0-VOUTWF(1)
          VOUTWF(3)=0.0
          LOUTWF(1)=EFF(2)*(LINWFR(1)-FWFRAC(1))+FWFRAC(1)
C*********CALCULATE THE UNKNOWNS BY GUESSING LOUTWF(2), AND MODIFYING THE
C*********GUESS UNTIL THE MASS BALANCES GENERATE THE SAME NUMBER.
          EXXX=.1
          KID=1
          DO 50 J=1,100
          LOUTWF(2)=ZERUF(KID,EXXX)
          IF(KID.LT.0)GOTO 60
          LOUTWF(3)=1.-LOUTWF(1)-LOUTWF(2)
          LOUT=LIN*LINWFR(3)/LOUTWF(3)
          VOUT=(FFLOW*FWFRAC(1)-LOUTWF(1)*LOUT)/VOUTWF(1)
          CLWFPC=(FFLOW*FWFRAC(2)-VOUT*VOUTWF(2))/LOUT
50        EXXX=LOUTWF(2)-CLWFPC
60        RETURN
          END
```

```
      FUNCTION ZEROTH(KID,TRY)
C KEEPS VALUE OF ZEROTH BETWEEN ZERO AND ONE
C   ***ZEROTH BY M.E.WHATLEY***
C   ***   MODIFIED DEC 1973    ***
C   ***  MAJOR MODIFICATION  FEB 2,1977   ***
C   ***  CHANGED TO ZEROTH FROM MULONE AUG 1,1977
      DIMENSION XCF(4),YCF(5)
      IF(KID)3,1,2
    1 YCF(4)=TRY
      IF(ABS(YCF(4)-YCF(3))-1.E-30)30,30,40
   40 IF(TRY*YPOS*YNEG) 6,41,5
   41 IF(TRY*YPOS) 5,42,44
   42 IF(TRY) 43,30,6
   43 IF(YNEG) 45,5,33
   44 IF(YPOS-TRY) 46,33,6
   45 IF(TRY-YNEG) 46,33,5
   46 XCF(2) = XCF(4)
      YCF(2) = TRY
      BS=1.0
      GOTO 9
    5 XNEG=XCF(4)
      YNEG=TRY
      BS =BS*.85-1.
      GOTO 7
    6 XPOS=XCF(4)
      YPOS=TRY
      BS=BS*.85+1.
    7 DO8J=1,3
      YCF(J)=YCF(J+1)
    8 XCF(J)=XCF(J+1)
    9 DBS= ABS(BS)
      IF(XPOS*XNEG.GT. 0.) GOTO 11
      IF(YCF(2).EQ. 0.) GOTO 31
C  ***  BEFORE BOTH  XPOS AND XNEG ARE ESTABLISHED ***
      IF(XCF(3)*(1.-XCF(3)).LE.0.) GOTO 33
      XCF(4) = XCF(3)-DBS *(XCF(2)-XCF(3))*YCF(3)/(YCF(2)-YCF(3))
      DO12 J=1,10
      IF(XCF(4)*(1.-XCF(4)))12,12,36
   12 XCF(4)=(XCF(4)+XCF(3))/2.
      GOTO 33
   11 CUT = CUT+1.
C  ***  THIS IS THE WAY WE RUN ***
      IF(CUT.LT. 1.9 .OR. DBS.GT. 4.0) BS=0.
      IF(DBS .GT.3.5) GOTO 22
      IF(DBS .GT.2.3) GOTO 27
C  ***  SIMPLE LINEAR INTERPOLATION  ***
   14 NBS= (BS-.8)*(BS+.8)
      AAA = NBS*EXP(-CUT)
      IF(NBS*BS)24,26,25
   24 YPOS= YPOS*2.**(1.-DBS)
```

```
      GOTO 26
   25 YNEG = YNEG*2.**(1.-DBS)
   26 XCF(4) = XPOS-(XNEG-XPOS)*(YPOS-AAA*YNEG)/(YNEG-YPOS)/(1.+AAA)
      GOTO 29
C  ***  TRIES A PARABOLIC FIT ***
   27 AAA=0.
      CCC=0.
      BBB=0.
      XCF(4)=XCF(1)
      YCF(4)=YCF(1)
      YCF(5)=YCF(2)
      DO28J=1,3
      AAA=AAA+XCF(J)*YCF(J+1)-YCF(J)*XCF(J+1)
      BBB=BBB+YCF(J)*XCF(J+1)*XCF(J+1)-YCF(J+1)*XCF(J)*XCF(J)
   28 CCC=CCC+YCF(J+2)*(XCF(J)*XCF(J+1)*XCF(J+1)-XCF(J+1)*XCF(J)*XCF(J))
      RAD= BBB*BBB-4.*AAA*CCC
      IF(RAD.LE.0. .OR. ABS(AAA).LT. 1.E-25) GOTO 22
      RAD= 0.5*SQRT(RAD)/AAA
      BBB= -0.5*BBB/AAA
      XCF(4)= BBB+RAD
      IF((XCF(4)-XNEG)*(XCF(4)-XPOS).LT.0.) GOTO 36
      XCF(4)= BBB-RAD
   29 IF((XCF(4)-XNEG)*(XCF(4)-XPOS).LT.0.) GOTO 36
C  ***  BISECTS INTERVAL  ***
   22 XCF(4)=(XPOS+XNEG)/2.
C  THIS WAY OUT
   36 IF(ABS((XPOS-XNEG)/(XPOS+XNEG)) -DEL)30,30,3
   30 KID = -1
    3 ZEROTH= XCF(4)
      RETURN
C  ***  INITIALIZES WHEN KID .GT. ZERO  ***
    2 XCF(4)= TRY
      CUT = 0.
      XPOS= 0.
      XNEG= 0.
      YPOS= 0.
      YNEG= 0.
      YCF(3)= 0.
      DEL = KID* .0000001
      DEL = ABS(DEL)
      KID = 0
      IF((1.-TRY)*TRY)33,33,3
C  FIRST STEP
   31 XCF(4)= 0.9*XCF(3)
      BS= 0.
      IF(XCF(3)*(1.-XCF(3)).GT.0.) GOTO 36
   33 WRITE(6,133)
      GOTO 30
  133 FORMAT(' VIOLATION OF ZEROTH')
      END
```

```
C         \\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\
C         MAIN PROGRAM "EQCALC"
C         EQUILIBRIUM FLASH - CONSTANT T AND P - CALC PROGRAM
C         FOR TERNARY HNO3-H2O-MG(NO3)2 SYSTEM.  WRITTEN BY CF IRWIN,11/80.
C         \\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\
          DIMENSION FWFRAC(3),LWFRAC(3),VWFRAC(3),TLWFRC(3),TVWFRC(3),
     C    EQDATA(50,5)
          REAL LFLOW,LWFRAC
C********INPUT FLOW RATE FEED AND FEED COMPOSITION DATA
          READ(05,*)FFLOW,FWFRAC(1),FWFRAC(2),IDATA,IPRINT,LREP
          FWFRAC(3)=1.-FWFRAC(1)-FWFRAC(2)
          WRITE(05,1000)FFLOW,FWFRAC(1),FWFRAC(2),FWFRAC(3)
C********REAL IN EQUILIBRIUM DATA BASE - POINTS FROM EQ. ISOTHERM
          READ(IDATA,*)LLIST
          READ(IDATA,*)((EQDATA(I,J),J=1,5),I=1,LLIST)
C********DOUBLE SIZE OF DATA BASE BY INTERPOLATING LINEARLY
C********BETWEEN THE PROVIDED DATA POINTS.
          IF(LREP.EQ.1)GOTO 150
          DO 110 NPOS=1,LLIST-1
          EQDATA(NPOS+LLIST,1)=(NPOS+LLIST)
          EQDATA(NPOS+LLIST,2)=EQDATA(1,2)
          DO 100 J=3,5
100       EQDATA(NPOS+LLIST,J)=(EQDATA(NPOS,J)+EQDATA(NPOS+1,J))/2.
110       CONTINUE
150       IF(LREP.EQ.1) LSTOP=LLIST
          IF(LREP.EQ.2) LSTOP=LLIST*LREP-1
          IF(IPRINT.EQ.0)WRITE(05,1010)((EQDATA(I,J),J=1,5),I=1,LSTOP)
          WRITE(05,1050)
C********BEGIN LOOP THAT TESTS EACH DATA POINT TO SEE HOW WELL IT
C********SATISFIES THE MASS BALANCE AT EQ CONDITIONS.
          DO 200 NLIST=1,LSTOP
          DO 210 I=1,3
210       TLWFRC(I)=EQDATA(NLIST,I+2)/100.
          IF(TLWFRC(1).EQ.0.)DEVOLD=100.
          IF(TLWFRC(1).EQ.0.)GOTO 200
          CALL EQSTAG(FFLOW,TVFLOW,TLFLOW,FWFRAC,TVWFRC,TLWFRC,DEV)
          IF(NLIST.EQ.1)DEVOLD=DEV
          WRITE(05,*)NLIST,DEV
          IF(DEV.GT.DEVOLD)GOTO 200
          DEVOLD=DEV
          VFLOW=TVFLOW
          LFLOW=TLFLOW
          DO 230 I=1,3
          VWFRAC(I)=TVWFRC(I)
230       LWFRAC(I)=TLWFRC(I)
200       CONTINUE
C********PRINT THE RESULTS OF THE SEARCH
          WRITE(05,1040)
          WRITE(05,1020)FFLOW,FWFRAC(1),FWFRAL(2),FWFRAC(3)
          WRITE(05,1021)VFLOW,VWFRAL(1),VWFRAC(2),VWFRAC(3)
          WRITE(05,1022)LFLOW,LWFRAC(1),LWFRAC(2),LWFRAC(3)
          WRITE(05,1030)DEVOLD
C********FORMAT STATEMENTS
1000      FORMAT(///4F10.4///)
1010      FORMAT(5F8.2)
1020      FORMAT(11H FEED       4F10.4)
1021      FORMAT(11H VAPOR      4F10.4)
1022      FORMAT(11H LIQUID     4F10.4)
1040      FORMAT(55H                  FLOW      W HNO3    W H2O      W MG(NO3)2)
1030      FORMAT(F10.4)
1050      FORMAT(29H  TRIAL POINTS AND DEVIATIONS)
          STOP
          END
```

```
TECO FOR40.DAT
        17
        1,140.,0.0,43.8,56.2
        2,140.,2.0,42.8,55.2
        3,140.,4.0,41.7,54.3
        4,140.,6.0,40.6,53.4
        5,140.,8.0,39.3,52.7
        6,140.,10.0,37.7,52.3
        7,140.,11.0,36.0,53.0
        8,140.,11.2,35.0,53.8
        9,140.,11.2,34.0,54.8
        10,140.,11.1,33.0,55.9
        11,140.,11.0,32.0,57.0
        12,140.,10.8,31.0,58.2
        13,140.,10.4,30.0,59.6
        14,140.,10.1,29.0,60.9
        15,140.,9.6,28.0,62.4
        16,140.,9.1,27.0,63.9
        17,140.,8.4,25.4,66.2

TECO FOR55,DAT
                    13
        1,155.,0.0,38.2,61.8
        2,155.,1.0,37.2,61.8
        3,155.,2.0,36.2,61.8
        4,155.,3.0,35.0,62.0
        5,155.,4.0,33.8,62.2
        6,155.,4.2,32.8,63.0
        7,155.,4.4,31.6,64.0
        8,155.,4.5,30.5,65.0
        9,155.,4.5,29.5,66.0
        10,155.,4.5,28.5,67.0
        11,155.,4.5,27.5,68.0
        12,155.,4.5,26.5,69.0
        13,155.,4.5,25.5,70.0

TECO FOR60.DAT

                                  11
        1,165.,0.0,34.8,65.2
        2,165.,1.0,33.6,65.2
        3,165.,2.0,32.8,65.2
        4,165.,3.0,31.5,65.5
        5,165.,3.3,30.7,66.0
        6,165.,3.5,29.5,67.0
        7,165.,3.6,28.4,68.0
        8,165.,3.7,27.3,69.0
        9,165.,3.7,26.3,70.0
        10,165.,3.7,25.3,71.0
        11,165.,3.7,24.3,72.0
```

equilibrium isotherm of interest. Isotherms were available in Sloane (3).

Two of the component mass balances are then used to determine the equilibrium vapor and liquid mass flow rates, the sum of which is compared with the feed mass flow rate. This mass-balance deviation is calculated for points over the entire isotherm; the liquid composition and calculated vapor composition that give the smallest deviation are taken to be the actual products of an equilibrium flash.

The equilibrium-stage effluent streams (3 and 4) are corrected for nonequilibrium by using Hansen stage efficiencies in subroutine MODGRF. Two efficiencies are required because there are three components. Expressions for these efficencies as functions of system parameters (T_{EDP}, V_{EDP}, F_{feed}, $F_{Mg(NO_3)_2}$) are developed in Sect. 7 (The vapor stage efficiency is defined using a combined liquid feed.) The modification-stage calculation is also iterative, since the efficiency is a function of the recycle flow rate [$F_{Mg(NO_3)_2}$]. Function ZEROTH is used as the convergence routine.

The EDP effluent (6) is then flashed in the SRP, again at constant temperature and pressure. The same algorithm (EQSTAG) is employed to determine the composition and flow rates of the equilibrium streams. A second isotherm data base is required as the SRP is operated at a higher temperature than the EDP. An isotherm at the normal SRP temperature (165°C) was estimated because no experimental equilibrium data are available for such elevated temperatures. A noniterative modification stage using SRP efficiency relations developed in Appendix 11.5 yields the SRP effluent and dilute acid flow rates and compositions.

A detailed list of the variables used in the program and their definitions is located in the calculation file.

11.8 Location of Data

The data are on file with the MIT School of Chemical Engineering, Bldg. 1505, ORNL.

11.9 Nomenclature

C	composition of a stream, mole %
CCP	concentration of concentrated product, %
CPRR	concentrated product recovery ratio (%)
F	volumetric flow rate, cm^3/min
G	mass flow rate, g/min

P	pressure, qualitative
Q	heat input, qualitative
T	temperature, °C
V	volume, ml
W	weight percent, wt %
X	liquid mole fraction
Y	vapor mole fraction
Z	combined feed mole fraction

Greek Symbols

η	stage efficiency, %
ε	error, %
ρ	density, g/cm^3

Subscripts

F, G, W, ρ,η	refer to the quantities defined above
d	material balance direction
EDP	extractive distillation pot
E	EDP
feed	acid feed
i	component i
L	liquid
$Mg(NO_3)_2$	magnesium nitrate
o	overall
S	SRP
SRP	solvent recovery pot
V	vapor
*	equilibrium; also a superscript
1, 2, 3	see tabulation mid-page 31

11.10 Literature References

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