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A SIMPLE MODEL OF A PLUTONIUM NITRATE CONCENTRATOR

R. B. Rozsa
S. J. Underwood

February 2, 1979

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R. B. Rozsa

S. J. Underwood

Now at University of California, Chemical Engineering Department

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NOMENCLATURE

- a_i - Empirical constants in equation B-1
- b_i - Empirical constants in equation B-2
- c_i - Empirical constants in equation B-4
- d_i - Empirical constants in equation B-6
- $f()$ - Functional relationship involving ()
- H - Enthalpy of tank solution J/g mol
- H_s - Enthalpy of feed, J/g mol
- H_s - Enthalpy of steam, J/g mol
- H_v - Enthalpy of vapor, J/g mol
- H^* - dH/dt , derivative with respect to time
- M_f - Feed flow rates, g mol/h
- M_o - Overflow rate, g mol/h
- M_s - Steam rate, g mol/h
- M_v - Vapor flow rate, g mol/h
- P - Pressure, Pa
- P_s - Steam pressure, Pa
- Q - Steam heat flow rate, J/h
- t - time, h
- T - Temperature, $^{\circ}\text{C}$
- U_N - Mole fraction HNO_3 in feed
- U_p - Mole fraction $\text{Pu}(\text{NO}_3)_4$ in feed
- V - Volume, m^3
- V_o - Volume of tank at overflow, m^3
- X_N - Mole fraction HNO_3 in tank, product
- X_p - Mole fraction $\text{Pu}(\text{NO}_3)_4$ in tank, product
- Y_N - Mole fraction HNO_3 in vapor
- ρ - Density of tank solution, g mol/ m^3
- ρ^* - $d\rho/dt$, derivative with respect to time
- $(^{\circ})$ - $d()/dt$, derivative of state variable with respect to time

ABSTRACT

A simple mathematical model of a plutonium nitrate evaporator/concentrator is described and computer code calculations are tested against results from a more complex model. The computer code is capable of computing transient responses of the system to arbitrary stimuli input by the user in an interactive mode. The model is described in detail including mass and energy conservation equations as well as boundary conditions and other system constraints. A closed form solution which is valid under restricted conditions is also described. The results show agreement within a few percent between the simple and complex model calculations.

INTRODUCTION

Lawrence Livermore Laboratory (LLL) is conducting a safeguards program for the Nuclear Regulatory Commission. One task of the Material Control Project of this program is to develop a methodology for assessing material control and accounting methods (MCA) in chemical plants that handle special nuclear material (SNM). As part of this task, we have undertaken mathematical modeling of some of the chemical process operations that typically take place in these plants. The objective is twofold: (1) To simulate experimental data and (2) to provide simple estimator models for simulating on-line process monitors. The first objective is motivated by the lack of pertinent data and the expense of obtaining many different sets of experimental data for studying material diversion scenarios. The second objective is due to the need for reduced-order models for studying on-line estimator/detector applications. The latter model must necessarily be simple since the estimator algorithms use it repetitively during their functioning. (See Candy and Rozsa¹ for an example.)

In this report we describe a simple model of a plutonium nitrate evaporator/concentrator and contrast it with a more complex detailed model of a unit similar to one at the Barnwell, S.C. Plant of Allied General Nuclear Services (AGNS). Although this work is discussed in the context of a plutonium nitrate evaporator/concentrator, it is representative of a class of thermosiphon concentrator components that are generic to any fuel cycle involving chemical separations/purifications

DISCUSSION

CONCENTRATOR (COMPLEX MODEL)

The plutonium nitrate evaporator/concentrator (sometimes called thermosiphon reboiler) is depicted in Fig. 1. The unit increases the concentration of plutonium nitrate in an aqueous acid liquid phase by evaporating the water and acid out of solution. Low concentrate $\text{Pu}(\text{NO}_3)_4$ enters the feed line in solution with water and nitric acid and mixes with the process stream in the reboiler (heat exchanger). The reboiler heats and partially vaporizes the solution which then flows to the vapor separator. The vapor exits at the top after passing through a demister and the liquid settles to the bottom. The demister prevents liquid from being drawn off with the vapor. Periodically, the demister is washed with nitric acid to eliminate plutonium nitrate buildup. The major fraction of the liquid in the separator is recycled through the reboiler loop. Recirculation of the process stream occurs because of the difference in effective density in the reboiler and separator. The liquid level in the separator is essentially the same height as the overflow pipe. The flow rate through the reboiler adjusts by natural circulation to a level such that the pressure drop due to the density difference is equivalent to the frictional drop.

A detailed model of this evaporator/concentrator was developed by Frogner and Randell² under contract to LLL. This complex 10-state or more* nonlinear dynamic model with nonlinear algebraic constraint equations includes two-phase mass and heat transfer and accounts for temperature and pressure variations throughout the system. The number of state variables coupled with the small time constant of the recirculation loop causes the code calculations to run slowly in certain cases (many minutes for simulating hours of real time). For

*The reboiler was partitioned into nodes that increase the number of state equations depending on the grid desired.

FIG. 1. Plutonium nitrate evaporator/concentrator.

simulating experimental data, the code is quite adequate; in fact, this level of detail allows sophisticated diversion scenarios to be investigated involving the recirculation loop response to upsets. However, for inclusion in simulation codes such as DYN SYL³ (a complex process simulator) or DYNEST⁴ (an estimator) this version is too complicated.

CONCENTRATOR (SIMPLE MODEL)

A simpler model that retains many of the important features of the unit is shown in Fig. 2. Here, we lump the separator and the recirculation loop into one volume and assume instantaneous head and mass transfer (well-mixed tank assumption). We also assume a constant pressure in the unit and include the nitric acid wash effects in the feed stream composition. From an overall mass and energy balance view, these assumptions are reasonable since the high rate of recirculation ensures rapid mixing and heat transfer in the system. The time constant of the simple model is dominated by the mass capacity of the unit and is much larger than that of the more complex model thereby allowing larger integration time steps to be taken.

MODEL EQUATIONS:

We describe the system in terms of species' mass balances, an energy balance, and several empirical relationships of density, temperature, and composition. These are similar to those used by Frogner and Randall² and are shown in detail in Appendix B.

The final form for the $\text{Pu}(\text{NO}_3)_4$ and HNO_3 mole fractions is as follows:

$$X_p = \frac{(M_v - M_f) X_p + M_f U_p}{\rho V} \quad (1)$$

$$X_N = \frac{(M_v - M_f) X_N + M_f U_N - M_v Y_N}{\rho V} \quad (2)$$

where

FIG. 2. Reduced plutonium nitrate evaporator/concentrator model.

$$\dot{(\quad)} = \frac{d(\quad)}{dt}$$

t = time, h

ρ = the liquid density in the vessel (g mol/m³)

V = the volume of the vessel (m³)

M_f, M_v = the feed and vapor flow rates (g mol/h)

U_p, X_p = the feed and product mole fraction of $\text{Pu}(\text{NO}_3)_4$ in the liquid phase

U_N, X_N = the feed and product mole fraction of HNO_3 in the liquid phase

Y_N = the mole fraction of HNO_3 in the vapor phase.

The overflow pipe constrains the volume $V \leq V_0$ where V_0 is the maximum or overflow volume. If the level is less than the overflow height another description for volume is needed:

$$\dot{V} = \frac{M_f - M_v - \rho^* V}{\rho} \quad \begin{array}{l} \text{for } V < V_0 \text{ or} \\ \text{for } V = V_0 \text{ and } \dot{V} < 0 \end{array} \quad (3)$$

The above system [Eqs. (1-3)] is a two-state model when overflow is occurring and a three-state model when there is no overflow.

M_f, U_p and U_N are input values normally. M_v is determined by the energy balance (Appendix A), ρ is determined through an empirical relationship in X_p and X_N (Appendix B), and ρ^* is calculated by formally differentiating the expression for ρ (Appendix C). These algebraic relationships for M_v, ρ , and ρ^* are complex and nonlinear and are solved

SOLUTION TECHNIQUE

The three ordinary differential equations are nonlinear by virtue of the above M_v, ρ , and ρ^* relationships. We use solution techniques incorporated in a code version developed at LLL.⁵ This version has several options which include solution of stiff systems using techniques pioneered by Gear. Our set

is not stiff under normal conditions and will allow calculation of simulation times of 10-20 h in 2-5 s for overflowing cases and 5-20 s for nonoverflowing cases using a simple Adams⁵ method with functional iteration.

CLOSED FORM SOLUTION

Under certain conditions the equations for plutonium nitrate may be integrated directly. If the system is overflowing ($V = V_0$) and ρ and M_V do not vary significantly, direct integration of Eq. 1 is possible:

$$\frac{\left(X_p + \frac{M_f U_p}{M_V - M_f} \right)}{\left(X_p + \frac{M_f U_p}{M_V - M_f} \right) @ t = t_0} = \text{Exp} \left[\left(\frac{M_f - M_V}{\rho V_0} \right) t \right] . \quad (4)$$

The above expression is identical to the one that Frogner and Randall² found by fitting their numerical results to an exponential curve. They obtained three different time constants depending on whether they perturbed the initial plutonium feed composition (U_p) or the steam rate (changes M_V) or feed flow rate (M_f). They thought this was due to nonlinearities in the model. The above time constant, $(M_f - M_V/\rho V_0)^{-1}$ is indeed different for the three perturbations, but is still basically a turnover time (capacity/net outflow).

SAMPLE CALCULATIONS

To compare the results of the complex, simple, and closed form models, we calculated three cases where steady state conditions were perturbed about 10% in certain boundary or input conditions. Figure 3 compares the results calculated using the models for three cases perturbed from nominal steady state conditions. Table 1 gives the steady state conditions used in the calculation of the three cases. The agreement between all three models is excellent (within 2%). The density variation for the complex and simple models during these runs was about 2% for case A and about 10% for cases B and C. We should also note that the $\text{Pu}(\text{NO}_3)_4$ mole fraction from

Case A: $\text{Pu}(\text{NO}_3)_4$ mole fraction in feed changed to 0.005
 $\rho \sim 4.5 \times 10^4 \text{ mol/m}^3$

Case B: Feed flow rate changed to 1804 mol/h
 $\rho \sim 4.2 \times 10^4 \text{ mol/m}^3$

Case C: Vaporization rate changed to 1729 mol/h
 $\rho \sim 4.3 \times 10^4 \text{ mol/m}^3$

FIG. 3. Perturbations from steady-state conditions.

TABLE 1. Steady-state conditions.

Feed rate = 1988 mol/h

$\text{Pu}(\text{NO}_3)_4$ mole fraction	= 0.0043
HNO_3 mole fraction	= 0.0098
H_2O mole fraction	= 0.9869

Vaporization rate = 1603 mol/h

Tank vol = 0.048 m³

$\text{Pu}(\text{NO}_3)_4$ mole fraction	= 0.0223
HNO_3 mole fraction	= 0.0377
H_2O mole fraction	= 0.9400

the detailed model has not been averaged to reflect the fluid in the recirculation loop--about 20% of the total. In Fig. 3 we only compare the $\text{Pu}(\text{NO}_3)_4$ mole fraction. Other variables of interest such as density, temperature and vaporization rate, and vapor composition are also in good agreement between the simple and detailed model. The closed form solution does not give these other variables.

To illustrate most of the options available to the user in the interactive mode, we ran the simple model code for a series of operational changes. Table 2 gives the startup conditions.

TABLE 2. Startup conditions.

Tank conditions:	$V = 0.0025 \text{ M}^3$
	$X_p = 0.005$
	$X_n = 0.063$
Feed conditions:	$M_f = 2000 \text{ mol/h}$
	$U_p = 0.005$
	$U_n = 0.063$
Steam conditions:	$P_s = 0.2 \text{ MPa}$
	$M_s = 1750. \text{ mol/h}$
	$(M_v \sim 1600 \text{ mol/h})$

Step 1: Startup--filling the unit while evaporating water and acid.
Time: 0-6 h. Figure 4 shows the results for $\text{Pu}(\text{NO}_3)_4$ and HNO mole fraction, density, temperature, product flow, and level. (Note that most variables reach equilibrium rapidly even though the tank itself takes about 5 h to fill and reach final conditions.)

Step 2: Feed rate increased for 2 h. Time: 6-8 h.

Step 3: Feed composition changed for 2 h. Time: 8-10 h.

Step 4: Steam rate changed for 2 h. Time: 10-12 h.

Step 5: Tank level reduced instantly. Time: 12-14 h.

Step 6: Feed rate and composition changed to drop tank level. Time: 14-16 h.

Figure 5 shows steps 1 through 6 for selected variables vs time. Table 3 lists the time/feature relationships at 6, 8, 10, 12, and 14 h.

FIG. 4. Plot of selected variables vs time for startup conditions 0-6 h ($V_0 = 0.050 \text{ M}^3$, Feed temp = 30°C).

FIG. 5. Plot of selected variables vs time for various input parameters changes at 6, 8, 10, 12, and 14 h.*

* (Refer to Table 4 for exact conditions.)

TABLE 3. Time/feature relationships.

Time, h	Feature
0-5	Start up from 5% tank volume
6-8	Feed rate increased 5%
8-10	$\text{Pu}(\text{NO}_3)_4$ feed comp increased 20%
10-12	Steam rate decreased 8%
12-14	Tank level reduced 20% at $t = 12$ h
14-16	Feed rate and composition changed to drop tank level

Table 4 summarizes the graphical results calculated for a series of operational steps. These steps do not necessarily represent actual operating procedures but are intended to show the types of parameter changes allowed in the code.

TABLE 4. Tank, feed, and steam conditions for the results in Figs. 4 and 5.

Time, h	Tank conditions			Feed conditions ($T = 30^\circ\text{C}$)			Steam condition
	x_p	x_n	$V(\text{m}^3)$	U_p	U_N	$M_f(\text{mol/h})$	$M_s(\text{mol/h})$
0	0.005	0.063	0.0025	0.005	0.063	2000.0	1750.0
6	0.024	0.138	0.050	0.005	0.063	2100.0	1750.0
8	0.023	0.135	0.050	0.006	0.061	2099.0	1750.0
10	0.024	0.132	0.050	0.005	0.063	2100.0	1600.0
12	0.020	0.128	0.040	0.005	0.063	2000.0	1750.0
14	0.022	0.138	0.050	0.0001	0.024	1508.0	1750.0

The user has the option of changing feed rate, composition, steam flow, volume of liquid in the tank or any combination of these. In addition, graphics may be generated for any increment of time. Figure 4 is for 0-6 h and Fig. 5 is 0-16 h. Time increments such as 0-8 h or 10-14 h can also be selected. This feature allows the user to selectively magnify certain effects or restart problem conditions at will. (See Appendix E for a detailed example of multiple case generation.)

SUMMARY AND CONCLUSIONS

We have developed a simple model of a plutonium nitrate concentrator and graphically compared its calculated results with both a more complex model and a closed form solution. Agreement within 2% between all three is shown in predicting $\text{Pu}(\text{NO}_3)_4$ mole fractions. The complex model permits a more exhaustive examination of the internal fluid flow and heat transfer at the expense of computer time. The simple model calculates the essential features of the unit (plutonium inventory) in very short computer times and is suitable as either a stand alone interactive code or in special purpose master codes such as process simulators or estimator/detector codes.

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APPENDIX A

CONVERTING THE CONSERVATION EQUATIONS TO STATE VARIABLE EQUATIONS

We start formulating our solution for the simple unit shown in Fig. 2 by writing two species' mass balances, an overall mass balance, and an energy balance around the tank volume: See nomenclature for symbols.

$$\left[\text{Pu}(\text{NO}_3)_4 \right] \quad (\rho \dot{V} X_p) = M_f U_p - M_o X_p \quad (\text{A-1})$$

$$\left[\text{HNO}_3 \right] \quad (\rho \dot{V} X_N) = M_f U_N - M_o X_N - M_v Y_N \quad (\text{A-2})$$

$$\left[\text{overall} \right] \quad (\rho \dot{V}) = M_f - M_o - M_v \quad (\text{A-3})$$

$$\left[\text{energy} \right] \quad (\rho \dot{V} H) = M_f H_f - M_o H - M_v H_v + Q \quad (\text{A-4})$$

We also have some auxiliary relationships (Appendix B) for equilibrium liquid-vapor mole fractions:

$$Y_N = f_1(X_p, X_N) \quad , \quad (\text{A-5})$$

liquid density:

$$\rho = f_2(X_p, X_N, T) \quad , \quad (\text{A-6})$$

atmospheric boiling temperature:

$$T = f_3(X_p, X_N, \rho) \quad , \text{ and} \quad (\text{A-7})$$

enthalpy:

$$H = f_4(X_p, X_N, T) \quad . \quad (\text{A-8})$$

With this set, we have nine unknowns:

$\rho, V, X_p, X_N, Y_N, H, T, M_o, M_v$, and the above eight independent relationships plus the overflow constraint on M_o and V . To arrive at a more compact form, we first differentiate the left hand sides of Eqs. A-1, A-2, and A-4 and eliminate (ρV) using Eq. A-3. M_o , an unknown, also drops out and we have, after dividing by ρV :

$$\dot{X}_p = \frac{M_f U_p - (M_f - M_v) X_p}{\rho V}, \quad (A-9)$$

$$\dot{X}_N = \frac{M_f U_N - (M_f - M_v) X_N - M_v Y_N}{\rho V}, \text{ and} \quad (A-10)$$

$$\dot{H} = \frac{M_f H_f - (M_f - M_v) H - M_v H_v + Q}{\rho V}. \quad (A-11)$$

Differentiating the left hand side of Eq. A-3 and substituting the derivative of Eq. A-6 (Appendix C) to eliminate ρ , we obtain:

$$\dot{V} = \frac{M_f - M_v - M_o - V f_2}{\rho}. \quad (A-12)$$

From the overflow constraint, we see that if $V < V_o$, $M_o \equiv 0$ and

$$\dot{V} = \frac{M_f - M_v - V f_2}{\rho}. \quad (A-13)$$

If $V = V_o$, $\dot{V} \equiv 0$ and the overflow rate is

$$M_o = M_f - M_v - V f_2. \quad (A-14)$$

Equations A-9, A-10, and A-13 give state variables as function of known variables with the exception of M_V . We use Eq. A-11 to solve for M_V by substituting the derivative of Eq. A-8 (Appendix C) to eliminate H and Eq. A-8 and similar relationships to eliminate H_V , H_F and H . M_V is a complicated function of X_p , X_N , T and their derivatives. Using Eqs. A-6 and A-7 and the derivative of Eq. A-7 (Appendix C), M_V is finally given as a function of X_p , X_N and their derivatives:

$$M_V = \frac{\rho V_f \dot{4} - M_f(H_f - H) - Q}{(H - H_V)} \quad (A-15)$$

We now have our final set of equations:

STATE VARIABLES	EQUATION
-----------------	----------

$\dot{X}_p = \frac{M_f U_p - (M_f - M_V) X_p}{\rho V}$	(A-9)
--	-------

$\dot{X}_N = \frac{M_f U_N - (M_f - M_V) X_N - M_V Y_N}{\rho V}$	(A-10)
--	--------

$\dot{V} = \frac{M_f - M_V - V \dot{f}_2}{\rho}$	(A-13)
--	--------

AUXILIARY RELATIONSHIPS

$Y_N = f_1(X_p, X_N)$	(A-5)
-----------------------	-------

$\rho = f_2(X_p, X_N, T)$	(A-6)
---------------------------	-------

$T = f_3(X_p, X_N, \rho)$	(A-7)
---------------------------	-------

$H = f_4(X_p, X_N, T)$	(A-8)
------------------------	-------

$M_V = f_5(\rho, V, M_f, H_f, H_V, Q)$	(A-15)
--	--------

The auxiliary relationships are nonlinear and implicit in many of the variables. This requires iteration to find the solutions. For instance, Eqs. A-6 and A-7 are iterated to find the correct density and temperature for a given X_p , and X_N . M_v is a function of both variables and derivatives of variables, and so Eqs. A-6 through A-10 and A-15 are iterated until a solution for X_p , X_N and M_v is found. Fortunately, many of the relationships are weak and direct substitution during iterations allows convergence to the correct values in just a few cycles.

APPENDIX B

MATERIAL PROPERTIES

We use empirical expressions typical of those of Frogner and Randell,² modified slightly to conform with our variables.

EQUILIBRIUM LIQUID-VAPOR MOLE FRACTION⁶

$$y_N = \frac{A}{1 - (x_N + x_p)^2 + A} \quad , \quad (B-1)$$

where

$$A = x_N(x_N + x_p) \left(10^{(a_1 + a_2(x_N + x_p)^{1/2} + a_3(1 - 2x_N - x_p) + a_4x_p)} \right)$$

and

$$a_1 = 1.3723$$

$$a_2 = -0.7936$$

$$a_3 = -1.3705$$

$$a_4 = 9.0$$

DENSITY OF THE LIQUID SOLUTION⁷

$$\rho^2 (b_1 x_p x_N + b_2 x_p^2) + \rho (b_3 x_p + b_4 x_N + b_5 x_p T + b_6) + a_7 + a_8 T = 0 \quad , \quad (B-2)$$

where

$$b_1 = 1.856E-6$$

$$b_2 = -3.628E-5$$

$$b_3 = -2.028E-2$$

$$b_4 = -1.862E-2$$

$$b_5 = -5.569E-4$$

$$b_6 = -1.802E-2$$

$$b_7 = 1.005E+3$$

$$b_8 = -3.158E-1$$

from the quadratic formula:

$$\rho = \frac{-B - \sqrt{B^2 - 4AC}}{2A}, \quad (B-3)$$

where

$$A = b_1 X_p X_N + b_2 X_p^2$$

$$B = b_3 X_p + b_4 X_N + b_5 X_p T + b_6$$

$$C = b_7 + b_8 T$$

The other root is extraneous.

THE ONE ATMOSPHERE BOILING TEMPERATURE

$$T = C_1 + C_2 \rho X_p + C_3 \rho X_N + C_4 \rho^2 X_N X_p + C_5 \rho^2 X_p^2 + C_6 \rho^2 X_N^2, \quad (B-4)$$

where

$$C_1 = 1.0E+2$$

$$C_2 = 5.025E-3$$

$$C_3 = 1.223E-3$$

$$C_4 = 4.119E-7$$

$$C_5 = 2.079E-7$$

$$C_6 = 6.042E-8$$

ENTHALPY AS A FUNCTION OF TEMPERATURE

The enthalpy of any phase is the sum of the individual species' enthalpies:

$$H = \sum_{i=1}^n X_i H_i \quad (B-5)$$

and each specie's enthalpy is given by

$$H_i = d_{1,i} + d_{2,i}T + d_{3,i}T^2, \quad (B-6)$$

where the d_i 's are given below.

<u>Species</u>	d_1	d_2	d_3
Liquids {	Pu(NO ₃) ₄	0.	110.8
	HNO ₃	0.	75.54
	H ₂ O	0.	75.54
Vapor {	HNO ₃	5.936E+4	55.51
	H ₂ O	4.506E+4	33.23
			3.855E-3

ENTHALPY RELEASED FROM STEAM

As a function of saturation pressure we assume

$$H_{SAT} = e_1 + e_2 P_s + e_3 P_s^2 + e_4 P_s^3 \quad (B-7)$$

$$\text{for } (1.45E+5 \leq P_s \leq 3.8E5),$$

where P_s = saturation pressure (N/M²)

$$\begin{aligned} \text{and } e_1 &= 2.331E+6 \\ e_2 &= -0.896 \\ e_3 &= 1.484E-6 \\ e_4 &= 1.209E-12 \end{aligned}$$

The energy delivered to the unit at a fixed P_s is then

$$Q = (H_{SAT}) M_s. \quad (B-8)$$

APPENDIX C

DERIVATIVES OF ρ , H AND T

As described in Appendix A, we need the derivatives of ρ , H, AND T in order to complete our auxiliary expressions. To calculate these, we formally differentiate the appropriate equations in Appendix B. (See Appendix B for the appropriate constants.)

DENSITY DERIVATIVE

$$\begin{aligned}
 2\rho\dot{\rho}(b_1\dot{x}_p x_N + b_2\dot{x}_p^2) &+ \rho^2(b_1(\dot{x}_p x_N + x_p \dot{x}_N) + 2b_2\dot{x}_p \dot{x}_p) \\
 &+ \dot{\rho}(b_3\dot{x}_p + b_4\dot{x}_N + b_5\dot{x}_p T + b_6) \\
 &+ \rho(b_3\dot{x}_p + b_4\dot{x}_N + b_5(\dot{x}_p T + T\dot{x}_p)) + a_8\dot{T} = 0
 \end{aligned}$$

Collecting the terms we obtain:

$$\dot{\rho} = \frac{-\rho^2(b_1(\dot{x}_p x_N + x_p \dot{x}_N) + 2b_2\dot{x}_p \dot{x}_p) - \rho(b_3\dot{x}_p + b_4\dot{x}_N + b_5(\dot{x}_p T + T\dot{x}_p))}{2\rho(b_1\dot{x}_p x_N + b_2\dot{x}_p^2) + (b_3\dot{x}_p + b_4\dot{x}_N + b_5\dot{x}_p T + b_6)} \quad (C-1)$$

TEMPERATURE DERIVATIVE

$$\begin{aligned}
 \dot{T} &= C_2(\dot{\rho}x_p + \rho\dot{x}_p) + C_3(\dot{\rho}x_N + \rho\dot{x}_N) + C_4(2\rho\dot{x}_N x_p + \rho^2\dot{x}_N x_p + \rho^2 x_N \dot{x}_p) \\
 &+ C_5(2\rho\dot{x}_p^2 + \rho^2 2\dot{x}_p \dot{x}_p) + C_6(2\rho\dot{x}_N^2 + \rho^2 2\dot{x}_N \dot{x}_N) \quad (C-2)
 \end{aligned}$$

ENTHALPY DERIVATIVE

$$H = \sum_{i=1}^n x_i H_i$$

$$\dot{H} = \sum_{i=1}^n \left[x_i \left(d_{2,i} \dot{T} + 2d_{3,i} \dot{T} \right) + \dot{x}_i H_i \right] \quad (C-3)$$

APPENDIX D

USER'S GUIDE TO THE CODE

The present version of the code is running at LLL on the 7600 Octopus system. It was compiled under CHAT using TV80LIB and ORDERLIB in December 1978. It still has a few bugs in certain options but runs most of the cases attempted in several seconds. The code is written in FORTRAN and can be modified easily and recompiled. Since the code was built up by several people, some "deadwood" areas remain. The present controllee is CT5 which immediately creates a drop file, + CT5. This may be referenced by either DBUG or DDT if needed (these are LLL "debug" codes). The teletype interaction and graphics output are specific to LLL and must be modified if used elsewhere. (See Appendix E for complete listing of the code.)

The code is set up to receive input data and instructions via teletype. Upon first entry, the code asks for input feed rate, composition, timing information and some boundary conditions (tank volume, feed temperature, height of overflow, steam pressure, and overflow rate). The overflow rate is used along with steady state assumptions to then compute the calculated steady state conditions pertaining to the input values. The present version of the code assumes that the feed is composed of HNO_3 , H_2O , $\text{Pu}(\text{NO}_3)_4$, N_2H_4 , NH_2OH , and $\text{Pu}(\text{NO}_3)_3$ which reacts instantaneously to form HNO_3 , $\text{Pu}(\text{NO}_3)_4$ and H_2O with the generation of heat. We duplicated this scenario to match that of Frogner and Randall.² This calculation is done in subroutine FEEDXH and may be modified if one desires to input directly the $\text{Pu}(\text{NO}_3)_4$ and water compositions. The reactions proposed also result in a total mole change and the feed rate is modified accordingly. The code prints out the 6 component model fractions and then the total mole factor plus the calculated $\text{Pu}(\text{NO}_3)_4$, H_2O and HNO_3 mole fractions. The code next asks if you want to start with these conditions or input new tank conditions. The user can also request another steady state calculation. If the steady state condition is not valid for the input values or the total time increments >100, the code prints a message and recycles for new input.

After the user specifies the tank conditions, the code asks for new perturbed input values (feed rate, composition-- $\text{Pu}(\text{NO}_3)$ and H_2O --and steam flow rate). A title is then asked for (up to 50 characters allowed--do not put a "1" in column 1) and the code calculates the problem from TINL to TEND in increments of TINC (up to 100 increments allowed). The code then asks for plots desired. Up to 10 plots with arbitrary mapping may be calculated. If all 10 are wanted, input "-99.", otherwise the plot number followed by the map number should be input. The plot numbers correspond to variables vs times:

<u>Plot #</u>	<u>Variable</u>
1	Plutonium mole fraction in product
2	Nitric acid mole fraction in product
3	Water mole fraction in product
4	Density (mol/m^3) of product
5	Temperature, $^{\circ}\text{C}$
6	Product level in tank, m
7	Nitric acid mole fraction in vapor
8	Water mole fraction in vapor
9	Density (Kg/m^3) of product
10	Liquid product volume flow rate m^3/h

The mapping number may be 1-12 and corresponds to the following:

<u># Y, X coord, grid</u>	<u># Y, X coord, grid</u>
1 linear, linear, no grid	7 linear, log, full grid
2 log, log, no grid	8 log, linear, full grid
3 linear, log, no grid	9 linear, linear, partial grid
4 log, linear, no grid	10 log, log, partial grid
5 linear, linear, full grid	11 linear, log, partial grid
6 log, log, full grid	12 log, linear, partial grid

Care must be used in selecting the log options since no check for legal values is made. The present system scales according to maximum and minimum values in the plot array and may not be appropriate for log scaling. The current default value of the map number is 9.

The code next asks if you want another run. If yes, it asks for new input conditions and time and increment values. The user may then continue the problem from the end time of the previous problem or start from the same initial conditions again. If starting from the last problem's state, the user may ask also for continuous plots which means the subsequent graphics will contain the data from the previous run. This way, a series of problems or conditions may be strung together to show many changes. Up to 10 problems may be done this way--each one with up to 100-data increments. When picking the new time and increment, it is assumed that the start time for the new problem is that of the old problem ending time for continuation problems and the old initial time otherwise. If more than 100-time increments are asked for or bad data is input, the code recycles to the appropriate input area and again requests input.

The graphics data is put into an FR80 file type, FX035/TIME and contains a title page with tank and input conditions and the users title, followed by the plotted variables vs time. A final plot is also given of $\log(\text{Pu}(\text{NO}_3)_N$ --equilibrium value) vs time. This corresponds to the closed form solution and should yield a straight line with a slope equal to the time constant, if applicable.

The code also generates a file called CANDY1 which is a data file for use in an estimator code. It contains the state variables and time values similar to those plotted in the graphics file.

The code has its own nomenclature, the more important of which are shown below in the order the code asks for them.

Code variable	Nomenclature variable	Comments
MFIN	= M_f	
XIPU	= U_p	These are actually the $Pu(NO_3)_3$ and water mole fractions of an assumed 6 component mixture. The code calculates the appropriate U_p and U_N and prints out the above components and total mole factor which is the multiplied by MFIN to get M_f .
XIW	= $1 - U_p - U_N$	
TINL	= Start time	
TEND	= End time	
TINC	= Time increment	$\left(\frac{TEND - TINL}{TINC} \leq 100 \right)$
MOUT	= M_o	
PSTM	= P	
VOL	= V_o	
OVERFLOW HT	= Height of overflow pipe (graphics plotting purposes)	
MFIN TEMP	= Feed temperature	
XTPU	= X_p	
XTNA	= X_N	

Code variable	Nomenclature variable	Comments
XTW	= $1 - X_P - X_N$	
CTVP	= Temperature of liquid, T	
DMLL	= ρ	
MVAP	= M_V	
V	= Vol conditions in tank	
MSTM	= Steam flow rate, M_S	

The following is the teletype output/input for the run that generated the graphics shown in Figs. 4 and 5. Only the first three cases are shown for brevity, but the remainder are similar.

User	Code output	Comments
CTS	Plutonium (IV) Nitrate evaporator. Please provide the following steady state information in the units specified. If you have the variable sequence at hand, type yes, linefeed, and type in values as shown in the manual.	Controllee start
Yes	Type in MFIN, XIPU, XIW, TINL 1966.5, 0.005, 0.9, 0. Type in TEND, TINC, MOUT, PSTM 6., 0.1, 400., 202660. Type in VOL, OVERFLOW HT, MFIN TEMP, 3F10.5 0.05, 2., 30.	
	6 COMPS ARE 0.07988 0.90000 0. 0.00524 0.00988 0.00500	6 Feed comps assumed
	TMOL factor, XIPU, XIW and XINA are 1.002 0.00499 0.93209 0.06292 You have input the following steady-state and initializing parameters for this job: Overall feed rate = 2000.0072 mol/h Mole fraction PU in feed = 0.00499 Mole fraction H ₂ O in feed = 0.93209 Starting time = 0. h Ending time = 6.0000 h	Calculated 3 comp feed

(Continued)

User	Code Output	Comments
	Time increment = 0.10000 h Out flow rate = 400.0000 mol/h Steam pressure = 202660.0000 N/M2	
	Are these input values satisfactory?	
Yes	***** 15 ***** The steam flow rate is 1751.4140 mol/h XTPU = 0.02496 XTW = 0.83875 XTNA = 0.13629 CTVP = 116.2280 DMLL = 41465.7939 MOUT = 400.0000 MVAP = 1600.0072	} 15 iterations to find SS } SS conditions
	If you want another SS condition - type AS If you want SS as input condition - type SS If you want to input conditions - type IN	
IN	XTPU, XTW, VOL conditions in tank, please 0.005, 0.932, 0.0025	} Case 1 Initial condition
	Now that the tank conditions are set, please provide the pertrubed boundary values in the same units as above. MFIN, XTPU, XTW, MSTM?	
1996.5, 0.005, 0.9, 1750.		Case 1 Feed and steam
	6 Comps are 0.07988 0.90000 0. 0.00524 0.00988 0.00500 TMOL Factor, XIPU, XIW and XINA are 1.002 0.00499 0.93209 0.06292	} 6 Feed comps to 3 Feed comps conversion
	Feed Rate = 2000.0072 mol/h Mole fraction of plutonium compound in Feed = 0.00499	

(Continued)

User	Code Output	Comments
	Mole fraction of water in feed = 0.93209 Steam flow rate = 1750.0000 mol/h Are these values correct?	
Yes	Type in identification line, please Start-up from 5% tank volume--1/31/79 Type in number--NN-of plot wanted, 1-10, >10 to exist	} Title of case
	Also MM--the * of the map wanted--2F5.1 format	
-99.	Time used = 4 s--015:82:01	} Do all plots option Run time IO:CPU:SYS
	Would you like to consider another case?	
Yes	MFIN, XIPU, XIW, MSTM, VOL? 2096.5, 0.005, 0.9, 1750., 0.05	} Change feed rate (case 2)
	6 comps are 0.07988 0.9000 0. 0.00524 0.00988 0.00500 TMOL FACTOR, XIPU, XIW AND XINA are 1.002 0.00499 0.93209 0.06292 TEND, TINC?	
8., 0.05	Feed rate = 2100.1829 mol/h Mole fraction of plutonium compound in feed = 0.00499 Mole fraction of water in feed = 0.93209 Steam flow rate = 1750.0000 mol/h End of complete time period = 8.0000 Time increment = 0.0500 h Are these values correct?	} 8.0-h final time

(Continued)

User	Code Output	Comments
Yes	Would you like to start from the initial state conditions (SS), or would you like to start where the last case (LC) ended or last case with cont plots (LP)?	
LP		} Include data from 1st case when plotting results
	Type in identification line, please	
Feed rate increase by 5%--run to 8.0 h		} Title of case
	Type in number--NN-of plot wanted, 1-10, >10 to exist	
	Also MM--the * of the map wanted--2F5.1 format	
-99.	Time used = 2 s--025:74:00	
	Would you like to consider another case?	
Yes	MFIN, XIPU, XIW, MSTM, VOL?	
2096.5, 006, 0.9, 1750., 0.05		} Change PU(NO ₃) ₄ value (Case 3) ⁴
	6 comps are	
	0.07888 0.90000 0.	
	0.00524 0.00988 0.00600	
	TMOL factor, XIPU, XIW and XINA are	
	1.001 0.00599 0.93337 0.06063	
	TEND, TINC?	
10., 0.05		} 10.0-h final time
	Feed rate = 2098.7852 mol/h	
	Mole fraction of plutonium compound in feed = 0.00599	
	Mole fraction of water in feed = 0.93337	

(Continued)

User	Code Output	Comments
	Steam flow rate = 1750.0000 mol/h End of complete time period = 10.0000 Time increment = 0.0500 h Are these values correct?	
Yes	Would you like to start from the initial state conditions (SS), or would you like to start where the last case (LC) ended or last case with Cont Plots (LP)?	
LP	Type in identification line, please Feed composition changed 20%--run to 10 h Type in number--NN--of plot wanted, 1-10, >10 to exit	} include all previous data in graphics } Title of case
	Also MM--the * of the map wanted--2F5.1 format	
-99.	Time used = 2 s--024:75:00	
	Would you like to consider another case?	
	...etc	

APPENDIX E

CODE LISTING

The code consists of several subroutines. Some important ones are:

- MAIN:** Initialization and control of all case calculations. Computes steady state values and calls the Gear driver and plot subroutine.
- PLOTDR:** Plotting subroutine--entered to ask for title line and plots graphics as directed. (Called by MAIN.)
- VPSH:** Calculates overflow condition and resets volume if needed. (Called by DRIVE.)
- DIFFUN:** Heart of calculation of state derivatives. Produces current value of derivative based on state variables and present boundary conditions. (Called by DRIVE.)
- ENTHCAL:** Computes the enthalpy of liquid and vapor.
- FEEDXH:** Computes the feed composition and heat effects for six component feed. (See Appendix D)
- GMLQDN:** Computes the liquid density and boiling temperature.
- PEDERV:** Dummy subroutine needed by Gear package.
- VAPCOMP:** Computes vapor mole fractions
- DRIVE:** Main control and driver for the Gear package.

The code listing is in the attached fiche.

REFERENCES

1. J. V. Candy and R. B. Rozsa, Nonlinear Estimators, etc., Lawrence Livermore Laboratory, Livermore, Ca. (to be published).
2. B. Frogner and K. Randall, Final Report: Characterization and Modeling of a Plutonium Concentrator, Lawrence Livermore Laboratory, Livermore, Ca., UCRL-13864 (1978).
3. G. K. Patterson and R. B. Rozsa, DYNSYL: A General Purpose Dynamic Simulator for Chemical Processes, Lawrence Livermore Laboratory, Livermore, Ca., UCRL-52561 (1978).
4. R. Castleton and J. V. Candy, DYNESL, A Dynamic Estimator Calculation Program, Lawrence Livermore Laboratory, Livermore, Ca., UCRL-52573 (1978).
5. A. C. Hindmarsh, GEAR, Ordinary Differential Equation System Solver, Lawrence Livermore Laboratory, Livermore, Ca., UCID-30001, Rev. 3, (1974).
6. A. Maimoni, Lawrence Livermore Laboratory, private communication (1977).
7. R. A. daRoza, Lawrence Livermore Laboratory, private communication (1977).

EHB:mab