MN ONLY

PORTIONS OF THIS REPORT ARE ILLEGIBLE. It
has been prepared from the best available
copy to permit the broadest possible avail-
ability.

NOTICE
This report was prepared as an account of work
sponsored by the United States Government. Neither the
United States nor the United States Department of
Energy, nor any of their employees, nor any of their
contractors, subcontractors, or their employees, makes
any warranty, express or implied, or assumes any legal
liability or responsibility for the accuracy, completeness
or usefulness of any information, apparatus, product or
process disclosed, or represents that its use would not
infringe privately owned rights.

DYNAMIC PROCESS MODEL
OF A PLUTONIUM OXALATE
PRECIPITATOR

SAI Report No. SAI-78-696-WA

P.O. 55-32 703

Charles L. Miller
James E. Hammelman
Giancarlo M. Borgonovi

November, 1977

Final Report for
University of California Purchase Order 5532703

Prepared For
Lawrence Livermore Laboratory
University of California
Livermore, California 94550

Submitted by
Science Applications, Inc.
8400 Westpark Drive
McLean, Virginia 22101
(703) 821-4300

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

EXECUTIVE SUMMARY

In support of Lawrence Livermore Laboratory material safeguards program, SAI has developed a dynamic process model which simulates the performance of a plutonium (IV) oxalate precipitator. The plutonium oxalate precipitator is a component in the plutonium oxalate process for making plutonium oxide powder from plutonium nitrate. The model is based on state-of-the-art crystallization descriptive equations, the parameters of which are quantified through the use of batch experimental data. The dynamic model predicts performance very similar to general Hanford oxalate process experience. The utilization of such a process model in an actual plant operation could promote both process control and material safeguards control by serving as a baseline predictor which could give early warning of process upsets or material diversion.

The model has been incorporated into a FORTRAN computer program and is also compatible with the DYN SYS 2. computer code which is being used at LLL for process modeling efforts.

Table of Contents

<u>Chapters</u>		<u>Page</u>
1	INTRODUCTION.....	1-1
2	THE PLUTONIUM OXALATE PROCESS.....	2-1
	2.1 Process Description.....	2-1
	2.2 Operating Experience at Hanford.....	2-2
3	DEVELOPMENT OF THE PROCESS MODEL.....	3-1
	3.1 Introduction.....	3-1
	3.2 Establishment of the Precipitator Model.....	3-2
	3.3 The Particle Size Distribution and its Moments.....	3-6
	3.4 Conservation Equations for the Solid Phase.....	3-7
	3.5 Conservation Equation for Plutonium.....	3-11
	3.6 Conservation Equations for NO_3^- and $\text{C}_2\text{H}_4^{--}$ Ions.....	3-13
	3.7 Particle Size.....	3-14
	3.8 System of Differential Equations.....	3-15
	3.9 Transient Phase and Crystallizer Startup.....	3-16
	3.10 Zero-Flow Case.....	3-17
	3.11 Digestion Factor.....	3-19
4	DESCRIPTION OF THE COMPUTER PROGRAM.....	4-1
	4.1 Introduction.....	4-1
	4.2 Description of the Program.....	4-1
	4.3 Input Instructions.....	4-3

Table of Contents (Continued)

<u>Chapters</u>		<u>Page</u>
5	DETERMINATION OF PARAMETERS.....	5-1
	5.1 Introduction.....	5-1
	5.2 Solid Density from Crystallographic Data.	5-1
	5.3 Estimation of Model Parameters.....	5-2
6.	PARAMETER CHECK AND MODEL DEMONSTRATION.....	6-1
	6.1 Introduction.....	6-1
	6.2 Batch Testing of the Model.....	6-1
	6.3 Backmix Testing and Steady State Demonstration of the Model.....	6-3
	6.4 Dynamic Demonstration of the Model.....	6-13
7	CONVERSION TO DYNYSYS.....	7-1
	7.1 Introduction.....	7-1
	7.2 The DYNYSYS Modular Concept.....	7-1
	7.3 The Precipitator Module.....	7-2
	7.4 A Simple DYNYSYS System Including the Precipitator.....	7-6
	7.5 Numerical Example.....	7-8
8	CONCLUSIONS AND DISCUSSION	8-1
Appendix A	FORTTRAN PROGRAM OF MODEL.....	A-1
Appendix B	SUBROUTINE TYPE2.....	B-1
Appendix C	SUBROUTINE TYPE5.....	C-1
Appendix D	SUBROUTINE TYPE1.....	D-1
Appendix E	EQUILIBRIA MODEL.....	E-1
Appendix F	SOLUTION TECHNIQUE FOR LEAST SQUARES FIT TO DATA.....	F-1
References		R-1

List of Figures

<u>Figures</u>		<u>Page</u>
2.1	Plutonium Oxalate Process.....	2-3
3.1	Flow Model for Plutonium Precipitator.....	3-4
4.1	Flow-Chart for Precipitator Program.....	4-2
5.1	Kinetic Data for Batch Precipitation of Pu(C ₂ O ₄)·6H ₂ O - Short Times.....	5-5
5.2	Log-Log Plot of - dS/dt vs. S - Short Times	5-7
5.3	Kinetic Data for Batch Precipitation of Pu(C ₂ O ₄)·6H ₂ O - Long Times	5-11
5.4	Log-Log Plot of -dS/dt vs. S - Long Times ..	5-12
6.1	Model Fit to Data.....	6-2
6.2		6-5
to	Plutonium Precipitator Model.....	to
6.9		6-12
6.10		6-14
to	Response to a Step Decrease in Pu Concentration	to
6.13		6-19
7.1	Precipitator Module.....	7-3
7.2	Control Model for Precipitator.....	7-7
7.3	DYNSYS Input.....	7-9
7.4	DYNSYS Output.....	7-10
7.5	DYNSYS Model with No Control.....	7-12
7.6	DYNSYS Model with Proportional Integral Controller.....	7-13
E.1	Mechanistic Form of Equilibria Theory.....	E-2
E.2	Response Surface.....	E-8

List of Tables

<u>Tables</u>		<u>Page</u>
3.1	Solubility Rate Data.....	3-3
5.1	Graphical Differentiation of Figure 5.1.....	5-6
6.1	Limited Computer Output.....	6-4
7.1	DYNSYS Stream Elements.....	7-5
E.1	Stability Constants for Oxalate Complexes of Pu(IV) in 1M HNO ₃	E-1
E.2	Solubility Data.....	E-6
E.3	Specific Data Point Calculations.....	E-7

1. INTRODUCTION

Safeguarding of nuclear facilities against unauthorized diversion of special and source nuclear material continues to be an area of concern in the United States associated with nuclear power growth. A sound safeguards program includes aspects of both physical protection and material control, and employs the use of the best available scientific methods to each facet of the program. The Nuclear Regulatory Commission has assigned Lawrence Livermore Laboratory (LLL) the task of developing methods for material control systems. A specific program subtask is to develop process models of the systems that handle and process special nuclear material (SNM), with initial priority being assigned to the plutonium operations associated with lightwater power reactors. Irradiated fuel reprocessing was the first area examined.

A specific goal of the modeling effort is to produce mathematical simulation models of components of nuclear fuel reprocessing operations. These models must be capable of being linked together to form representations of an overall reprocessing facility. One of the parts of a fuel reprocessing facility that requires detailed modeling is the plutonium conversion process. The process is utilized for converting the purified plutonium nitrate produced in the separations section of the facility to plutonium oxide powder.

SAI has been contracted to provide LLL with a process description of the oxalate conversion process, and developing a detailed simulation process model for a component of the oxalate conversion process.

The component of the process that SAI has chosen to model is the continuous backmix precipitator which converts the plutonium nitrate to plutonium oxalate. This component was chosen because it presented an adequate technical challenge for process modeling due to the fact that there are input streams, output streams, chemical reactions, and phase changes occurring within. In addition, there were both operating data and equilibria/kinetic data available for the precipitation of plutonium oxalate.

The description of the oxalate process and remarks concerning the operating experience at Hanford are presented in the next section. Subsequent sections of the report present the model development. The model has been written as a FORTRAN program and also converted so that it is compatible with DYN SYS 2, which is the computer code used at LLL for linking the modeled components.

2. THE PLUTONIUM OXALATE PROCESS

2.1 PROCESS DESCRIPTION

In the oxalate process to produce PuO_2 , typical feeds consist of plutonium at concentrations from 100 to 400 g/l in nitric acid at concentrations from 2 to 8M. A small portion of the feed is in the Pu^{+6} valence state as plutonyl nitrate $\text{PuO}_2(\text{NO}_3)_2$, and the majority is in the Pu^{+4} valence state as plutonium nitrate $\text{Pu}(\text{NO}_3)_4$.

The plutonyl nitrate in the feed solution is reacted with hydrogen peroxide (H_2O_2) to reduce it to $\text{Pu}(\text{NO}_3)_4$ which has a much lower oxalate solubility. The reaction for this reduction is:

Excess H_2O_2 is used to assure full reaction before the H_2O_2 decomposes to H_2O and O_2 .

Following valence adjustment, the contents of the batch reactor are transferred to a pump tank to allow the excess H_2O_2 to fully decompose to H_2O before further processing.

The $\text{Pu}(\text{NO}_3)_4$ is then reacted with oxalic acid in a continuous backmix precipitator to obtain a plutonium oxalate hexahydrate precipitate according to the reaction:

The oxalate slurry is sent to a solid-liquid separator where the precipitate is separated from the supernatant liquid and washed with dilute oxalic acid to remove nitrate salts. The wet precipitate filter cake is then calcined at a temperature above 400°C to obtain the desired PuO_2 product.

The following reaction occurs in the calciner:

The supernate and the condensate from the cooled calciner off-gas are combined and sent to the receiver tank, where H_2O_2 and manganese nitrate ($\text{Mn}(\text{NO}_3)_2$) are used to kill the the excess oxalic acid according to the following series reactions:

The $\text{Mn}(\text{NO}_3)_2$ is a pseudo-catalyst which is regenerated. Keeping the concentration in the reaction vessel at .01M $\text{Mn}(\text{NO}_3)_2$ sustains the reaction to kill the excess oxalic acid. Figure 2.1 shows a schematic of the Process.

2.2 OPERATING EXPERIENCE AT HANFORD

Experiences at Hanford have found that the conditions under which plutonium nitrate and oxalic acid are contacted determine the quantity and particle size of the plutonium oxalate formed. The conditions which must be considered are: (1) H^+ ion concentration; (2) oxalic concentration in strike solution; (3) rate of agitation; (4) residence time in precipitator; and (5) temperature.

Stream	① Pc Feed	② Hydrogen Peroxide	③ Batch Reactor Off-Gas	④ Feed Stream	⑤ Oxalic Acid	⑥ Oxalate Slurry	⑦ Wash	⑧ Supernatant	⑨ Mtx Precipitate Cake	⑩ Air	⑪ Pc Oxide	⑫ Catalytic Off-gas	⑬ Cooling Catalyst Off-gas	⑭ Condensate	⑮ Supernatant Condensate	⑯ Hydroxyl Nitrate	⑰ Hydrogen Peroxide	⑱ Liquor Waste	⑲ Oxalic Acid Effluent Off-gas
Form	$\text{Pc}(\text{NO}_3)_6$ $\text{Pc}_2(\text{NO}_3)_8$	$4 \text{ H}_2\text{O}_2$	O_2	$\text{Pc}(\text{NO}_3)_6$	$1.0 \text{ M H}_2\text{C}_2\text{O}_4$	$\text{Pc}(\text{C}_2\text{O}_4)_2 \cdot 4 \text{ H}_2\text{O}$ $\text{Pc}(\text{NO}_3)_6$	Distilled H_2O	Solution	$\text{Pc}(\text{C}_2\text{O}_4)_2 \cdot 6 \text{ H}_2\text{O}$	100 H_2 215 O_2	PcO_2	Gas Mixture	Gas Mixture	H_2O	Solution	$12 \text{ H}(\text{NO}_3)_2$	$4 \text{ H}_2\text{O}_2$	Solution	CO_2

Figure 2.1 Plutonium Oxalate Process

The optimum H^+ concentration is between 2.5 and 3.5M. At acid concentrations below 1.5M, the co-precipitation of impurities is favored, and the precipitate is too finely divided for rapid settling or filtration. At slurry acid concentrations above 4.5M, plutonium (IV) oxalate solubility is high, and the precipitate is thixotropic.

The optimum range for the free oxalic acid concentration is 0.05 - 0.15M, depending on the purity of the solution. A large excess of oxalic acid increases the solubility of the plutonium in the strike solution.

The rate of agitation must be adequate to achieve uniform mixing of the precipitation reactants. However, excessive stirring results in a finely-divided precipitate which is difficult to filter. The best precipitations appear to occur at a temperature of 25° - 60°. Temperatures above 60°C have been found to produce a gummy precipitate. (20, 21)

3. DEVELOPMENT OF THE PROCESS MODEL

3.1 INTRODUCTION

A specific project subtask was to develop a system of equations describing the crystallization phenomena for $\text{Pu}(\text{C}_2\text{O}_4)_2 \cdot 6\text{H}_2\text{O}$. The specific goals of the system of equations were:

- 1) quantitative prediction of aqueous plutonium concentration exiting from the precipitator reactor
- 2) qualitative prediction of plutonium oxalate particle sizes exiting from the precipitator reactor.

In order to provide a sound base for the model development effort, a review of precipitation (crystallization) literature was conducted. The literature review was conducted with two objectives. The first objective was to gain a general understanding of the precipitation phenomena with its multi-phase/multi-component reactions. The second objective was to develop familiarity with state-of-the-art precipitation (crystallization) chemical process modeling.

The objectives of the literature review were achieved. References 1 - 8 provide the major sources of information that were used in this effort. For this particular modeling effort, the following assumptions have been made:

1. There are no significant heats of reaction associated with the oxalate complexing reactions and the precipitation process.
2. The specific crystal nucleation and growth phenomena can be adequately described by the following generally used empirical equations:

$$\frac{dN}{dt} = K_B S^{n_B}$$

$$\frac{dr}{dt} = K_G S^{n_G}$$

where,

N = particle population density

$\frac{dN}{dt}$ = volumetric particle birth rate

r = particle radius

$\frac{dr}{dt}$ = linear particle growth rate

K_G , K_B , n_B , and n_G = constants

$S = C_p - C^*$ = driving force (degree of supersaturation)

C = aqueous solute (Pu) concentration

C^* = equilibrium aqueous solute (Pu) concentration.

Additional theoretical expressions for the nucleation and crystal growth phenomena are unjustified because supporting experimental data is not available. In developing the process model, the only data available is that from some very early Manhattan project work at Clinton Labs.⁽¹³⁾ The data is for the batch precipitation of $\text{Pu}(\text{C}_2\text{O}_4)_2 \cdot 6 \text{H}_2\text{O}$, and is presented in Table 3.1.

3.2 ESTABLISHMENT OF THE PRECIPITATOR MODEL

The plutonium precipitator is modeled as a vessel of volume V , with two inputs and one output, as illustrated in Figure 3-1.

Table 3.1

Solubility Rate Data

Rate of Precipitation of Pu(IV) Oxalate from 1M HNO ₃ -0.1M Oxalic Acid	
Time after initial mixing, hr	Plutonium in supernate, g/liter
0	0.373
0+	0.22
0.5	0.070
1	0.036
2	0.031
4	0.028
7	0.027
78	0.025

Figure 3.1 Flow Model for Plutonium Precipitator

The following variables are used in the description of the process.

To define the plutonium nitrate input stream:

F_P = input Pu flow rate (liters/hour)

C_P = input Pu concentration (g/liter)

C_N = input NO_3^- concentration (moles/liter)

To define the oxalic acid input stream:

F_O = input oxalic acid flow rate (liters/hour)

C_O = input oxalic acid concentration (moles/liter)

To define the output stream:

F_f = output flow rate of the filtrate (liters/hour)

C_P' = output Pu concentration in the filtrate (g/liter)

C_N' = output NO_3^- concentration in the filtrate (moles/liter)

C_O' = output oxalic ion concentration in the filtrate (moles/liter)

F_S = output flow rate of the solid (liters/hour)

In addition, the following variables are used:

V = total volume of the precipitator (liters)

V_L = volume of the liquid phase (liters)

V_S = volume of the solid phase (liters)

ρ_P = density of Pu in the crystals (g/liter)

ρ_O = density of oxalic ion in the crystals (moles/liter)

The average residence time is defined as:

$$\tau = (\text{residence time}) = \frac{V}{F_P + F_0} \quad (1)$$

Since the crystallizer is well mixed,

$$\frac{V_L}{F_f} = \frac{V_S}{F_S} = \frac{V}{F_P + F_0} \quad (2)$$

In addition, there is no change of total volume during the precipitation process. This means

$$V_L + V_S = V \quad (3)$$

or, because of (2)

$$F_f + F_S = F_P + F_0 \quad (4)$$

3.3 THE PARTICLE SIZE DISTRIBUTION AND ITS MOMENTS

At any time t , crystals of different size and shape will be present in the precipitator. If we assume that the crystals have all the same shape, they can be described by a linear dimension only, and we can introduce a distribution function $n(r, t)$, such that $n(r, t)dr$ gives the number of crystals at time t , per unit volume, in the size interval $r, r+dr$.

The first few moments of the distribution have simple physical meaning. For example

$$\mu_0(t) = \int_0^{\infty} n(r, t)dr \quad (5)$$

represents the total number of crystals per unit volume at time t .

Similarly, the three moments

$$\begin{aligned}\mu_1(t) &= \int_0^{\infty} r n(r,t) dr \\ \mu_2(t) &= \int_0^{\infty} r^2 n(r,t) dr \\ \mu_3(t) &= \int_0^{\infty} r^3 n(r,t) dr\end{aligned}\tag{6}$$

can be related to the total crystal length, total crystal surface, and total crystal volume, respectively (per unit volume). In particular, the third moment can be written as

$$\mu_3 = \frac{1}{K} \frac{V_S}{V}\tag{7}$$

where K is a shape factor (for spherical crystals $K = \frac{4}{3}\pi$).

3.4 CONSERVATION EQUATIONS FOR THE SOLID PHASE

The conservation equations for the solid phase are derived from a balance equation on the total number of crystals. The balance states that the number of crystals entering a size interval dr must be equal to the number of crystals leaving that interval (because of growth or because of outflow). Using the $n(r,t)$ distribution introduced previously, the balance equation is written as follows:

$$\frac{\partial n(r,t)}{\partial t} = -G \frac{\partial n(r,t)}{\partial r} + B\delta(r-r_0) \frac{V}{V} - \frac{n(r,t)}{\tau}\tag{8}$$

The three terms on the right of Eq. 8 represent the variation of the number of crystals per unit volume, per unit size, due respectively to growth, nucleation, and outflow. The first term contains G , the rate of linear growth of the crystals, and is written assuming that G is independent of r . The second term contains B , the number of particles produced, because of nucleation, per unit volume of solution per unit time. B is multiplied by the Dirac delta function $\delta(r-r_0)$ to signify that the nuclei appear in the precipitator with the same size r_0 . The third term (outflow) indicates that all the particles, independently of their size, have the same probability of surviving for an average time t in the precipitator. The quantities G and B depend on the Pu concentration in the liquid (C_p') according to a kinetic model. Therefore, an equation for C_p' will have to be developed later.

At steady state, Eq. 8 becomes

$$\frac{dn(r)}{dr} + \frac{n(r)}{G\tau} = \frac{B}{G} \frac{V_l}{V} \delta(r-r_0) \quad (9)$$

and has the solution

$$n(r) = \frac{B}{G} \frac{V_l}{V} e^{-\frac{r-r_0}{G\tau}} H(r-r_0) \quad (10)$$

where $H(r-r_0)$ is the Heaviside step function.

It is not necessary to solve the partial differential Eq. 8, since the complete knowledge of the distribution $n(r,t)$ is not necessary for the dynamic description of the

crystallizer. Since the third moment of the distribution is simply related to F_S and F_L through Eqs. 7 and 2, a differential equation in μ_3 would be sufficient. As it will be shown next, a differential equation for μ_k , where k is any integer, can be obtained from Eq. 8, and contains μ_k and μ_{k-1} . Therefore, a system of four differential equations, involving μ_0 , μ_1 , μ_2 and μ_3 is, for our purposes, equivalent to Eq. 8.

We start from Eq. 8, multiply each term by r^k and integrate over r between 0 and ∞ , obtaining

$$\begin{aligned} \frac{d}{dt} \int_0^{\infty} r^k n(r, t) dr &= -G \int_0^{\infty} r^k \frac{\partial n(r, t)}{\partial r} dr \\ &+ B \frac{V_L}{V} \int_0^{\infty} r^k \delta(r - r_c) dr \\ &- \frac{1}{\tau} \int_0^{\infty} r^k n(r, t) dr \end{aligned} \quad (11)$$

Using the moment definition

$$\mu_k = \int_0^{\infty} r^k n(r, t) dr, \quad (12)$$

the property of the Dirac delta function (for any function $f(x)$)

$$\int f(x) \delta(x - x_0) dx = f(x_0), \quad (13)$$

and observing that

$$\begin{aligned} \int_0^{\infty} r^k \frac{\partial n(r,t)}{\partial r} dr &= n(r,t) r^k \Big|_0^{\infty} - k \int_0^{\infty} n(r,t) r^{k-1} dr \\ &= -k \mu_{k-1}, \end{aligned} \quad (14)$$

Eq. 11 becomes

$$\frac{d\mu_k}{dt} = kG\mu_{k-1} + B\frac{V}{V} r_0^k - \frac{\mu_k}{\tau} \quad (15)$$

The first four conservation equations are then:

$$\begin{aligned} \frac{d\mu_0}{dt} &= B\frac{V}{V} - \frac{\mu_0}{\tau} \\ \frac{d\mu_1}{dt} &= G\mu_0 + B\frac{V}{V} r_0 - \frac{\mu_1}{\tau} \\ \frac{d\mu_2}{dt} &= 2G\mu_1 + B\frac{V}{V} r_0^2 - \frac{\mu_2}{\tau} \\ \frac{d\mu_3}{dt} &= 3G\mu_2 + B\frac{V}{V} r_0^3 - \frac{\mu_3}{\tau} \end{aligned} \quad (16)$$

We have chosen to use, instead of the variable μ_3 , the variable F_f . Using Eqs. 3, 4, and 7 we have

$$\mu_3 = \frac{1}{K} \left(1 - \frac{F_f \tau}{V} \right) = \frac{1}{K} \left(1 - \frac{F_f}{F_P + F_O} \right) \quad (17)$$

and also

$$\frac{V_l}{V} = \frac{F_f}{F_P + F_O} \quad (18)$$

In terms of the variable F_f (note that F_P and F_O are in general functions of time), the conservation equations (14) can now be written:

$$\begin{aligned} \frac{dF_f}{dt} = & \frac{F_f}{F_P + F_O} \left(\frac{dF_P}{dt} + \frac{dF_O}{dt} \right) \\ & + (F_P + F_O) \left\{ \frac{F_P + F_O}{V} - \frac{F_f}{V} - 3K\mu_2 G - \frac{F_f}{F_P + F_O} r_o^3 B \right\} \end{aligned}$$

$$\begin{aligned} \frac{d\mu_0}{dt} = & B \frac{F_f}{F_P + F_O} - \frac{\mu_0}{V} (F_P + F_O) \\ \frac{d\mu_1}{dt} = & G\mu_0 + B \frac{F_f}{F_P + F_O} r_o - \frac{\mu_1}{V} (F_P + F_O) \end{aligned} \quad (19)$$

$$\frac{d\mu_2}{dt} = 2G\mu_1 + B \frac{F_f}{F_P + F_O} r_o^2 - \frac{\mu_2}{V} (F_P + F_O)$$

3.5 CONSERVATION EQUATION FOR PLUTONIUM

The terms G and B are strongly nonlinear functions of the concentration C_p' . As stated earlier, the equations used in this effort are described by the exponential forms:

$$\begin{aligned}
 G &= \frac{dr}{dt} = K_G (C_P' - C^*)^{n_G} \\
 B &= \frac{dN}{dt} = K_B (C_P' - C^*)^{n_B}
 \end{aligned}
 \tag{20}$$

where K_G , K_B , n_G , and n_B are constants, and C^* is the Pu equilibrium solubility. We need, therefore, a way of calculating C_P' .

If we call m the mass of Pu contained in the precipitator, this is given by

$$m = C_P' V_\ell + \rho_P V_S \tag{21}$$

so that (the density in the solid is a constant)

$$\frac{dm}{dt} = C_P' \frac{dV_\ell}{dt} + V_\ell \frac{dC_P'}{dt} + \rho_P \frac{dV_S}{dt} \tag{22}$$

$$\text{Since } V_\ell = V \frac{F_f}{F_P + F_0}, \quad \frac{dV_\ell}{dt} = \frac{V}{F_P + F_0} \frac{dF_f}{dt} - V \frac{F_f}{(F_P + F_0)^2} \left(\frac{dF_P}{dt} + \frac{dF_0}{dt} \right)$$

and also, because of Eq. 3, $\frac{dV_S}{dt} = - \frac{dV_\ell}{dt}$. Eq. 22 can then be written

$$\begin{aligned}
 \frac{dm}{dt} &= \frac{dC_P'}{dt} \frac{V}{F_P + F_0} F_f \\
 &+ (C_P' - \rho_P) \frac{V}{F_P + F_0} \left[\frac{dF_f}{dt} - \frac{F_f}{F_P + F_0} \left(\frac{dF_P}{dt} + \frac{dF_0}{dt} \right) \right]
 \end{aligned}
 \tag{23}$$

At the same time, the balance equation for the mass of Pu gives:

$$\frac{dm}{dt} = F_P C_P - F_S \rho_P - F_f C_P' \quad (24)$$

Eliminating $\frac{dm}{dt}$ between Eqs. 23 and 24, using for $\frac{dF_f}{dt}$ the first equation in 19, and solving with respect to $\frac{dC_P'}{dt}$, we obtain the additional differential equation

$$\begin{aligned} \frac{dC_P'}{dt} = \frac{F_P + F_O}{V F_f} \left\{ (C_P - C_P') F_P - C_P' F_O + (C_P' - \rho_P) \right. \\ \left. \cdot \left[3\mu_2 KVG + K \frac{V}{F_P + F_O} F_f r_O^3 B \right] \right\} \quad (25) \end{aligned}$$

3.6 CONSERVATION EQUATIONS FOR NO_3^- and $\text{C}_2\text{H}_4^{--}$ IONS

The expressions for G and B contain the equilibrium solubility C^* . An equilibrium model has been developed in Appendix E which determines the value of C^* as a function of the molar concentrations $[\text{C}_2\text{O}_4^{--}]$ and $[\text{H}^+]$, or, equivalently, of $[\text{C}_2\text{O}_4^{--}]$ and $[\text{NO}_3^-]$. According to our notation, C^* is a function of C_N' and C_O' . We need, therefore, differential equations for C_N' and C_O' .

The balance equations for these components are

$$\frac{d}{dt}(V_L C_N') = F_P C_N - F_f C_N' \quad (26)$$

for the NO_3^- ion, and

$$\frac{d}{dt}(V_L C_O' + V_S \rho_O) = F_O C_O - F_f C_O' - F_S \rho_O \quad (27)$$

for the oxalic ion. Notice that for the oxalic ion there is a term for the solid, with ρ_0 representing the density of the oxalic ions in the oxalate crystals.

With the same substitutions as before for the V_k , V_S , and F_S , and some algebra, Eqs. 26 and 27 are transformed into:

$$\begin{aligned} \frac{dC_N'}{dt} = & \left[-\frac{1}{F_f} \frac{dF_f}{dt} + \frac{1}{F_P+F_O} \left(\frac{dF_P}{dt} + \frac{dF_O}{dt} \right) \right] C_N' \\ & + \frac{F_P+F_O}{V} \left(\frac{F_P C_N}{F_f} - C_N' \right) \end{aligned} \quad (28)$$

$$\begin{aligned} \frac{dC_O'}{dt} = & \frac{\rho_0 - C_O'}{F_f} \frac{dF_f}{dt} - \frac{\rho_0 - C_O'}{F_O+F_P} \left(\frac{dF_P}{dt} + \frac{dF_O}{dt} \right) \\ & + \frac{(F_P+F_O) [F_O C_O - (F_P+F_O) \rho_0 - F_f C_O' + F_f \rho_0]}{V F_f} \end{aligned} \quad (29)$$

3.7 PARTICLE SIZE

The average particle size is commonly obtained from a weight distribution rather than from a particle number distribution.

The weight distribution $W(r,t)$ is related to the number distribution $n(r,t)$ by

$$W(r,t) = \rho K r^3 n(r,t) \quad (30)$$

where ρ is the crystal density, and the average particle size with respect to the weight distribution is given by

$$\bar{r}(t) = \frac{\int_0^\infty rW(r,t)dr}{\int_0^\infty W(r,t)dr} = \frac{\int_0^\infty r^4 n(r,t)dr}{\int_0^\infty r^3 n(r,t)dr} = \frac{\mu_4(t)}{\mu_3(t)} \quad (31)$$

In order to compute the particle size we therefore need μ_4 , and for this purpose only we have added an additional moment equation, as follows:

$$\frac{d\mu_4}{dt} = 4G\mu_3 + B\frac{F_f}{F_P+F_0} r_0^4 - \frac{\mu_4}{V}(F_P + F_0) \quad (32)$$

or, in terms of F_f

$$\frac{d\mu_4}{dt} = 4\frac{G}{K}(1 - \frac{F_f}{F_P+F_0}) + B\frac{F_f}{F_P+F_0} r_0^4 - \frac{\mu_4}{V}(F_P + F_0) \quad (33)$$

3.8 SYSTEM OF DIFFERENTIAL EQUATIONS

Using mass and particle conservation, we have written a system of eight first order differential equations for the variables C_P' , F_f , C_N' , C_0' , μ_0 , μ_1 , μ_2 , and μ_4 . This is the system of equations (19), (25), (28), (29), and (33).

For numerical reasons, in order to work with more balanced numbers, it is convenient to use, instead of μ_0 , μ_1 , μ_2 , and μ_4 the variables:

$$\begin{aligned} \mu_0' &= r_0^3 \mu_0 \\ \mu_1' &= r_0^2 \mu_1 \\ \mu_2' &= r_0 \mu_2 \\ \mu_4' &= \mu_4 / r_0 \end{aligned} \quad (34)$$

With this substitution, our final system of differential equations has the form:

$$\begin{aligned}
 \frac{dC_p'}{dt} &= \frac{F_p+F_0}{VF_f} \left\{ (C_p-C_p') F_p - C_p' F_0 + (C_p'-\rho_p) \left[3\mu_2' KVG/r_0 + K \frac{V}{F_p+F_0} F_f r_0^3 B \right] \right\} \\
 \frac{dF_f}{dt} &= \frac{F_f}{F_p+F_0} \left(\frac{dF_p}{dt} + \frac{dF_0}{dt} \right) + \left(\frac{F_p+F_0}{V} - \frac{F_f}{V} - 3K \frac{\mu_2'}{r_0} G - \frac{KF_f}{F_p+F_0} r_0^3 B \right) \\
 \frac{dC_N'}{dt} &= \left[-\frac{1}{F_f} \frac{dF_f}{dt} + \frac{1}{F_p+F_0} \left(\frac{dF_p}{dt} + \frac{dF_0}{dt} \right) \right] C_N' + \frac{F_p+F_0}{V} \left(\frac{F_p C_N}{F_f} - C_N' \right) \\
 \frac{dC_0'}{dt} &= \frac{\rho_0-C_0'}{F_f} \frac{dF_f}{dt} - \frac{\rho_0-C_0'}{F_p+F_0} \left(\frac{dF_p}{dt} + \frac{dF_0}{dt} \right) + \frac{(F_p+F_0)(F_0 C_0 - (F_p+F_0)\rho_0 - F_f C_0' + F_f \rho_0)}{VF_f} \\
 \frac{d\mu_0'}{dt} &= Br_0^3 \frac{F_f}{F_p+F_0} - \frac{\mu_0'}{V} (F_p+F_0) \\
 \frac{d\mu_1'}{dt} &= G \frac{\mu_0'}{r_0} + Br_0^3 \frac{F_f}{F_p+F_0} - \frac{\mu_1'}{V} (F_p+F_0) \\
 \frac{d\mu_2'}{dt} &= 2G \frac{\mu_1'}{r_0} + Br_0^3 \frac{F_f}{F_p+F_0} - \frac{\mu_2'}{V} (F_p+F_0) \\
 \frac{d\mu_4'}{dt} &= 4G \frac{\mu_3'}{r_0} + Br_0^3 \frac{F_f}{F_p+F_0} - \frac{\mu_4'}{V} (F_p+F_0)
 \end{aligned} \tag{35}$$

3.9 TRANSIENT PHASE AND CRYSTALLIZER STARTUP

The system of differential equations (35) can be solved numerically, and the computational details are given in the next chapter. For the solution, we need, of course, initial values for all the variables. It is not clear, a priori,

whether it is possible to obtain complete mixing before crystallization starts, so that one can have a known, finite Pu concentration at time $t = 0$. It is important, therefore, to describe with system (35), the transient phase during which the operation of the crystallizer starts up. This can be done, provided that care is taken in computing the proper limits (for $t = 0$) in the right members of (35).

First of all, we note that, for $C_0' = 0$, the equilibrium solubility C^* becomes infinite. We assume therefore that, at $t = 0$, the crystallizer is full of oxalic acid at some finite concentration. At $t = 0$, we turn on the flow of plutonium nitrate and oxalic acid. We note that, although $F_p(0) = F_0(0) = F_f(0) = 0$, we must have:

$$\lim_{t \rightarrow 0} \frac{F_f(t)}{F_p(t) + F_0(t)} = 1 \quad (36)$$

At $t = 0$, taking into account the limiting values, system (35) reduces to:

$$\begin{aligned} \frac{dC_p'}{dt} &= -K_p Br_o^3 & \frac{d\mu_o'}{dt} &= Br_o^3 \\ \frac{dF_f}{dt} &= \frac{dF_p}{dt} + \frac{dF_0}{dt} & \frac{d\mu_1'}{dt} &= Br_o^3 \\ \frac{dC_N'}{dt} &= 0 & \frac{d\mu_2'}{dt} &= Br_o^3 \\ \frac{dC_0'}{dt} &= 0 & \frac{d\mu_4'}{dt} &= Br_o^3 \end{aligned} \quad (37)$$

3.10 ZERO-FLOW CASE

Another possibility to be considered, especially for fitting the model parameters (K_B , K_G , r_o) to experimental data, is the no-flow case. At time $t = 0$, the precipitator is suddenly filled with plutonium nitrate and oxalic acid solution.

If we assume that complete mixing takes place before precipitation begins, the time behavior of the system can be described by a modified version of system (35). Since there is no flow, the variable F_f is replaced by the variable

$$\epsilon = \frac{V_s}{V} \quad (38)$$

the volume fraction of the solid in the precipitator.

The system of differential equations for this case is:

$$\begin{aligned} \frac{dC_p'}{dt} &= \frac{K(C_p' - \rho_p)}{1 - \epsilon} - \left[3\mu_2' G/r_o + (1 - \epsilon)r_o^3 B \right] \\ \frac{d\epsilon}{dt} &= 3KG \frac{\mu_2'}{r_o} + (1 - \epsilon)Br_o^3 K \\ \frac{dC_N'}{dt} &= 0 \\ \frac{dC_o'}{dt} &= \frac{C_o' - \rho_o}{1 - \epsilon} \frac{d\epsilon}{dt} \\ \frac{d\mu_o'}{dt} &= Br_o^3 (1 - \epsilon) \\ \frac{d\mu_1'}{dt} &= G \frac{\mu_o'}{r_o} + Br_o^3 (1 - \epsilon) \\ \frac{d\mu_2'}{dt} &= 2G \frac{\mu_1'}{r_o} + Br_o^3 (1 - \epsilon) \\ \frac{d\mu_4'}{dt} &= 4G \frac{\epsilon}{Kr_o} + Br_o^3 (1 - \epsilon) \end{aligned} \quad (39)$$

A subsequent section of this report will illustrate how these equations can be used to estimate values of the model parameters.

3.11 DIGESTION FACTOR

The digestion factor, defined as

$$D_F = 1 - \frac{F_f C_p'}{F_p C_p} \quad (40)$$

describes the yield from the crystallizer, or fraction of plutonium which precipitates. At $t = 0$, since $F_f = 0$, $C_p' = 0$, $F_p = 0$

$$\lim_{t \rightarrow 0} D_F = 1 \quad (41)$$

This should not be interpreted, of course, to mean that at $t = 0$, 100% of the plutonium precipitates. It simply represents the dilution effect on the first plutonium atoms entering the precipitator. If there were no precipitation, D_F would decrease rapidly to zero (when the condition $F_f C_p' = F_p C_p$ is reached). The beginning of crystallization has the effect of turning around the initial drop of the digestion factor, as can be seen from the numerical examples described in subsequent sections of this report.

4. DESCRIPTION OF THE COMPUTER PROGRAM

4.1 INTRODUCTION

A computer program has been written to solve the system of differential equations (35). The program is written in FORTRAN IV and has been compiled using the CDC-7600 machine at the Lawrence Berkeley Laboratory. The actual solution of the differential equations is performed by the routine DIFSUB, which uses the Gear's method^(15,16). This choice was determined by the fact that a modified version of DIFSUB is used in the modular executive system DYNSSYS⁽¹⁷⁾, and the final objective is to write a routine for the precipitator in the form of a DYNSSYS module.

The following sections describe briefly the routines in the program and the input instructions.

4.2 DESCRIPTION OF THE PROGRAM

Figure 4.1 is a flow chart of the program, showing the order of calls to the different subroutines.

The main program calls the following routines.

READ Reads and echoes the input data. Several cases can be stacked.

INPUT Computes the input flowrates of plutonium nitrate and oxalic acid, and their derivations. If these values are not constant, functional forms must be inserted in this routine, which is the only one that needs to be modified.

DIFSUB This is the routine stored in library SOURCE, subset DIFSUB, at Berkeley. Some of the arguments for DIFSUB

Figure 4.1. FLOW-CHART FOR PRECIPITATOR PROGRAM

have been introduced as constants in the main program. Values of $H = .001$, $HMIN = .00001$, and $HMAX = .02$ have been found to be adequate in all cases considered. The quantity EPSO, which determines the criterion of convergence on the corrector, is introduced by input, although a value of .001 has been found to be adequate in most cases.

OUT Prints and, optionally, plots the output data on the Stromberg-Carlson 4020 microfilm recording device. The plotting part uses routine PLOJB, from the graphics package stored at Berkeley on library MISSION, subset BIN.

Subroutine DIFSUB calls the following routines:

DIFFUN This routine contains the coefficients for the system of differential equations for the precipitator. It is this routine which will be transformed into a DYNYSYS module.

PEDERV This is a routine required by DIFFUN to compute the partial derivatives, if the calculation of the Jacobian is necessary. We did not find the system to be stiff, so that the Jacobian was not required, and this routine was inserted as a dummy.

Subroutine DIFFUN calls INPUT, previously described, and SOLUB.

SOLUB Computes the equilibrium solubility as a function of the concentration $[NO_3^-]$ and $[C_2O_4^{--}]$. This routine uses the trigonometric form to solve a cubic algebraic equation.

The listing of the FORTRAN program can be found in Appendix A.

4.3 INPUT INSTRUCTIONS

The following data are required as input instructions to the FORTRAN program:

ARD	ITEM	SYMBOL IN PROGRAM	SYMBOL IN EQUATIONS	FORMAT	MEANING
1	1	TITLE	-	7A10	Title card
2	1	AKG	K_G	E12.5	Coefficient for growth (cm/hr)/(g/l) ^{n_G}
	2	ANG	n_G	E12.5	Exponent for growth
	3	AKB	K_B	E12.5	Coefficient for nucleation (hr ⁻¹ l ⁻³)/(g/l) ^{n_B}
	4	ANB	n_B	E12.5	Exponent for nucleation
	5	RZRO	r_o	E12.5	Radius of nuclei at formation (cm)
3	1	RO	ρ	E12.5	Density of plutonium oxalate hexahydrate (the densities of ρ_p and ρ_o are calculated internally in the code from the chemical formula)(g/cm ³)
	2	V	V	E12.5	Volume of the precipitator (l).
4	1	KPLØT	-	I4	Plotting option KPLØT = 0 No plots requested KPLØT = 1 Plots requested
5	1	TMAX	-	E12.5	Maximum integration time
	2	EPSO	-	E12.5	Relative error for convergence
6	1	FP	F_p	E12.5	Input flowrate of plutonium nitrate (l/hr)
	2	FO	F_o	E12.5	Input flowrate of oxalic acid (l/hr)
	3	DFPDT	$\frac{dF_p}{dt}$	E12.5	Time derivative of F_p (lhr ⁻²)
	4	DFODT	$\frac{dF_o}{dt}$	E12.5	Time derivative of F_o (lhr ⁻²)
	5	CP	C_p	E12.5	Input concentration of plutonium nitrate (g/l).
	6	CO	C_o	E12.5	Input concentration of oxalic acid (moles/l).
	7	CN	C_N	E12.5	Input concentration of NO ₃ ⁻ in plutonium stream (moles/l) Note: All the values in card 6 will be, if they are not constant, overridden by the functions in subroutine INPUT.
7	1	Y1	$C_p'(0)$	E12.5	Pu concentration in filtrate at t = 0 (g/l)
	2	Y2	$F_f(0)$	E12.5	Filtrate flowrate at t = 0 (l/hr)

CARD	ITEM	SYMBOL IN PROGRAM	SYMBOL IN EQUATIONS	FORMAT	MEANING
	3	Y3	$C_N'(0)$	E12.5	NO_3^- concentration in filtrate at $t = 0$ (moles/l)
	4	Y4	$C_O'(0)$	E12.5	$C_2O_4^{--}$ concentration in filtrate at $t = 0$ (moles/l)
	5	Y5	$\mu_0'(0)$	E12.5	Zero moment $\times r_o^3$
	6	Y6	$\mu_1'(0)$	E12.5	First moment $\times r_o^2$
	7	Y7	$\mu_2'(0)$	E12.5	Second moment $\times r_o$
	8	Y8	$\mu_4'(0)$	E12.5	Fourth moment $/r_o$

at $t = 0$
(dimensionless)

5. DETERMINATION OF PARAMETERS

5.1 INTRODUCTION

The dynamic theory for the precipitator contains a number of parameters which are vital to quantitative prediction. The following section describes the estimation of these parameters.

5.2 SOLID DENSITY FROM CRYSTALLOGRAPHIC DATA

The densities ρ_p and ρ_o appear in the system of equations (35). From the chemical formula of $\text{Pu}(\text{C}_2\text{O}_4)_2 \cdot 6\text{H}_2\text{O}$ we obtain:

$$\rho_p = 457 \rho_s$$

$$\rho_o = 3.82 \rho_s$$

where ρ_p is the Pu density in the solid (g/liter), ρ_o is the oxalic ion density in the solid (moles/liter), and ρ_s is the density of plutonium oxalate (g/cm^3).

The density of the solid can be obtained from x-ray powder crystallographic data. Jenkins et al. ⁽¹⁸⁾ analyzed the diffraction pattern of several plutonium oxalates. For $\text{Pu}(\text{C}_2\text{O}_4)_2 \cdot 6\text{H}_2\text{O}$ they concluded that the crystal belongs to the triclinic system with the following parameters:

$$\begin{array}{lll} a = 6.377 \text{ \AA} & b = 6.377 \text{ \AA} & c = 7.931 \text{ \AA} \\ \alpha = 91.74^\circ & \beta = 91.74^\circ & \gamma = 89.26^\circ \end{array}$$

The volume of the triclinic cell is given by ⁽¹⁹⁾:

$$V_c = 2abc\sqrt{\sin s \cdot \sin(s-\alpha)\sin(s-\beta)\sin(s-\gamma)}$$

with

$$2s = \alpha + \beta + \gamma$$

Therefore, in our case

$$V_c = 322.202 \times 10^{-24} \text{ cm}^3$$

The mass in the cell (one molecule per unit cell) is

$$M_c = (239 + 4 \times 12 + 8 \times 16 + 6 \times 18) \times 1.66 \times 10^{-24} \text{ g} = 868.18 \times 10^{-24} \text{ g.}$$

Therefore, the density of the oxalate crystals is estimated to be:

$$\rho_s = \frac{M_c}{V_c} = 2.694 \text{ g/cm}^3$$

5.3 ESTIMATION OF MODEL PARAMETERS

The empirical equations describing crystal birth and growth were incorporated into the theoretical model that was developed in Chapter 3. The model contains five parameters of interest, these being K_B , n_B , K_G , n_G , and r_o . Due to the scarcity of experimental data, the estimation of these parameters is a very difficult task. However, by approaching the problem gradually, and making use of all the information that is available, reasonable engineering estimations of these parameters can be made.

We start by noting that in all of the equations describing precipitation (Chapter 3 systems of equations 35 and 39), only the combinations " K_G/r_o " and " $K_B r_o^3$ " appear. This means that none of the three parameters K_G , K_B and r_o can be estimated by simply fitting experimental data to the results of the model. Estimates for these parameters must be determined by including other information as well.

We start by examination of the data in Table 3.1. The assumption is made that crystal growth is negligible for relatively short time periods. This assumption is reasonable from a physical standpoint because for short reaction times there are not an adequate number of crystals present to account for significant growth. The first equation in the system of equations(39) in Chapter 3, illustrates this point.

$$\frac{dC_p'}{dt} = \frac{K(C_p' - \rho_p)}{1-\epsilon} \left[3\nu_2' G/r_o + (1-\epsilon)r_o^3 B \right]$$

For early times ν_2' and ϵ will be small, since the number of crystals per unit volume (N) is small, and can be neglected. Also, noting that for the experimental data that is being considered

$$C_p' \leq .373\text{g/l} \ll (\rho_p = 1231 \text{ g/l}).$$

Therefore, in this situation, the above equation reduces to

$$\frac{dC_p'}{dt} = -K\rho_p r_o^3 B = -\frac{4}{3}\pi\rho_p K_B (C_p' - C^*)^{n_B}$$

or using $S = (C_p' - C^*)$

$$\frac{dS}{dt} = -\psi K_B r_o^3 S^{n_B} \quad (42)$$

where $\psi = \frac{4\pi\rho_p}{3}$

let,

$$Y = \ln \left(-\frac{dS}{dt} \right)$$

$$X = \ln S$$

Using these definitions equation (42) can be transformed into the following linear equation:

$$Y = \ln (\psi K_B r_o^3) + n_B X \quad (43)$$

A reasonable approximation of the terms $\psi K_B r_o^3$ and n_B can be made if the data in Table 3.1 for short reaction times (≤ 1.5 hours) reasonably fits equation (43). To test the fit, a basic kinetic data evaluation technique of plotting $-dS/dt$ vs S on log-log paper can be used. If the data falls on a straight line, the slope of the line is n_B and the value of $-dS/dt$ at $S = 1$ is $\psi K_B r_o^3$.

In preparing the plot, the following data manipulation has been performed:

1. plotting the original "S" vs "t" data from Table 3.1.
2. Graphical differentiation of the "S" vs "t" plot to obtain " dS/dt " vs "S" data.
3. Plotting of the data from step 2 in order to obtain " n_B " and " $\psi K_B r_o^3$ ".

These are shown in Figure 5.1, Table 5.1 and Figure 5.2 respectively.

Figure 5.2 shows that the plotted data produces a straight line, therefore, the following approximations can be made:

$$n_B \approx 1.4$$

$$\psi K_B r_o^3 \approx 8$$

Figure 5.1
Kinetic Data for Batch Precipitation of $\text{Pu}(\text{C}_2\text{O}_4) \cdot 6\text{H}_2\text{O}$ - Short Times

Table 5.1 Graphical Differentiation of Figure 5.1

<u>S_i (g/l)</u>	<u>S_j (g/l)</u>	<u>Δt (hr)</u>	<u>$-\Delta S / \Delta t$ (g/l-hr)</u>	<u>S_m (g/l)</u>
.348	.09	.25	1.032	.219
.09	.044	.25	.184	.067
.044	.021	.25	.092	.0325
.021	.014	.25	.028	.0175
.014	.008	.5	.012	.011

Figure 5.2
Log-Log Plot of $-dS/dt$ vs. S - Short Times

Now, ψ was defined as

$$\psi = \frac{4\pi\rho_p}{3}.$$

$$\text{So, } \rho_p = \rho_s \left[\frac{239}{239 + 2(24+64) + 6(18)} \right].$$

In Section 5.2, ρ_s was determined to be 2.69 g/cc, therefore,

$$\rho_p = 1.23 \text{ kg/l} \quad \text{and } \psi = 5.15 \text{ kg/l}^2$$

Yielding,

$$K_B r_o^3 = 1.55.$$

To quantify the crystal growth rate constant, K_G , the data in Table 3.1 after long reaction times ($t \geq 6$ hours), can be examined in a manner similar to that for short times. However, at these long time periods, the assumption will be made that crystal birth is negligible and only growth occurs. Again the first equation in the system of equations (39) can be used to illustrate the point. At long times, the value of $(C_p' - C^*)$ is very small for the data under consideration. Therefore, the value of B will be small, and the second term in the equation can be neglected. This is reasonable from a physical standpoint. For a small $(C_p' - C^*)$, there is not an abundance of molecules of Pu available (relatively speaking). Since it takes many molecules to form stable crystals, crystal birth will be negligible and any Pu that is precipitated will attach to existing crystals. Again, $C_p' \ll \rho_p$ and $\epsilon \ll 1$, and using previously defined definitions, the first equation in series (39) reduces to:

$$\frac{dC_p'}{dt} = -3K \rho_p \mu' G/r_o = -4\pi\mu_2 K_G (C_p' - C^*)^{n_G} \quad (44)$$

If we assume that the distribution of crystal sizes is concentrated a size $\bar{r}$, by conservation we have:

$$\frac{4}{3} \pi \bar{r}^3 N \rho_p = (C_p^{o'} - C_p') \quad (45)$$

Where $C_p^{o'}$ is the initial concentration of Pu (.373 g/l in the experiment considered) and N is the number of crystals per unit volume.

Also, by definition:

$$\mu_2 = \bar{r}^2 N \quad (46)$$

Combining equations (44), (45) and (46) gives

$$\frac{dC_p'}{dt} = -3 \frac{K_G}{\bar{r}} (C_p^{o'} - C_p') (C_p' - C^*)^{n_G}$$

Or

$$\frac{dS}{d\tau} = -3 \frac{K_G}{\bar{r}} (C_p^{o'} - C_p') S^{n_G}$$

For the data under consideration, $(C_p^{o'} - C_p')$ can be considered constant at long times:

$$(C_p^{o'} - C_p') \approx .373 - .025 \approx .348$$

Now,

$$\frac{dS}{d\tau} = -1.044 \frac{K_G}{\bar{r}} S^{n_G} \quad (47)$$

In analyzing the batch data for long reaction times, a problem arises because there were no measurements made between 7 and 78 hours. To overcome this problem, a curve was fitted by trial and error techniques until it produced a straight line on a log-log plot of dS/dt vs S . The straight line then has a slope of n_G . The value of dS/dt at S equal to 1 is equal to $(-1.044 K_G/\bar{r})$. Figures 5.3 and 5.4 are the plots of S vs t and dS/dt vs S . From Figure 5.4, it can be seen that

$$n_G = 1$$

$$\frac{K_G}{\bar{r}} = 7.95 \times 10^{-2}$$

A value of n_G equal to one is in reasonable agreement with the findings that are published in the literature. ^(2,3,4,5,6)

As a final step in the parameter quantification effort, some estimate of r_0 must be made. Review of literature shows that stable crystals usually contain 10 - 1000 molecules. ⁽⁷⁾

The molecular weight of plutonium oxalate hexahydrate is 523 g/g-mole. Assuming spherical crystals with a density of 2.69 g/cc and making use of the Avagadro number, the following expression can be written for the radius of a crystal at birth.

$$r_0 (\text{cm}) = \sqrt[3]{\frac{3}{4\pi} \times \frac{523 \left(\frac{\text{g}}{\text{g-mole}}\right) \times m (\text{molecules})}{6.02 \times 10^{23} \left(\frac{\text{molecules}}{\text{g-mole}}\right) \times 2.69 \frac{\text{g}}{\text{cm}^3}}}$$

$$= 4.26 \times 10^{-8} \sqrt[3]{m}$$

Where m is the number of molecules per crystal.

From this equation, we can see that r_0 is of the order of magnitude of 10^{-7} cm when the number of molecules per crystal range from 10 to 1000.

Figure 5.3
Kinetic Data for Batch Precipitation of $\text{Pu}(\text{C}_2\text{O}_4) \cdot 6\text{H}_2\text{O}$ - Long Times
5-11

Figure 5.4 Log-Log Plot of $-dS/dt$ vs. S - Long Times

6. PARAMETER CHECK AND MODEL DEMONSTRATION

6.1 INTRODUCTION

The parameter estimates that were determined in the previous section were put into the model to check how well actual experience was duplicated. The model was used to simulate the operation of the precipitator in both the batch and backmix modes.

The following values of the parameters were used:

$$K_B = 1.55 \times 10^{21}$$

$$n_B = 1.4$$

$$K_G = 7.95 \times 10^{-9}$$

$$n_G = 1.0$$

$$r_o = 10^{-7}$$

The results are presented below. Also, the results for the operation of the model in the backmix mode serve to demonstrate the model's capability to simulate the steady state and dynamic operation of the precipitator.

6.2 BATCH TESTING OF THE MODEL

As a check on the parameter estimation effort, the nominal values were inserted into a "no-flow" version of the model in an attempt to reproduce the experimental batch data presented in Table 3.1. Figure 6.1 shows the predicted versus experimental performance. Agreement is good considering the limited amount of data reported.

Figure 6.1 Model Fit to Data

6.3 BACKMIX TESTING AND STEADY STATE DEMONSTRATION OF THE MODEL

A second check is performed by using the nominal parameter values in the flow model. The results are checked against Hanford experience. Reported Hanford operating experience shows that for a precipitator volume of 3.7 liters, a residence time of about an hour and an input Pu concentration of 260 g/l that a digestion factor in excess of .9 was achieved. (20,21)

The model was used to see how well the Hanford experience could be duplicated. The flow model was tested by using transient functions for the plutonium and oxalic acid input flowrates.

The functions had the form

$$F_p = F_p^0 [(1-e^{-At}) + B \sin \omega t e^{-Ct}]$$

$$F_0 = F_0^0 [(1-e^{-At}) + B \sin \omega t e^{-Ct}]$$

with F_p^0 , F_0^0 , A, B, ω , and C Constants.

This functional form gives a flow rate which starts at zero and reaches an asymptotic value. It is used to simulate startup conditions. Other functional forms could be chosen at the user's discretion.

For illustration, Table 6.1 shows a limited amount of computer output. The full results have been illustrated graphically in Figure 6.2 through 6.9 which show the behavior of the input plutonium flowrate; the input oxalic acid flowrate; the concentration of Pu in the liquid (C_p); the filtrate flowrate (F_f); the NO_3^- ion concentration; the oxalic ion concentration; the mean particle size with respect to a weight distribution; and the digestion factor, respectively.

[illegible]

Figure 6.2 Plutonium Precipitator Model

Figure 6.3. Plutonium Precipitator Model

Figure 6.4 Plutonium Precipitator Model

Figure 6.5. Plutonium Precipitator Model

Figure 6.6. Plutonium Precipitator Model

Figure 6.7 Plutonium Precipitator Model

Figure 6.8. Plutonium Precipitator Model

Figure 6.9. Plutonium Precipitator Model

The curves illustrate the initial transient behavior of the input, the ultimate reaching of steady state, and the response of the output variables until steady state is obtained.

6.4 DYNAMIC DEMONSTRATION OF THE MODEL

The model can be used to simulate the dynamic operation of the precipitator. For demonstration purposes, results from a sample case are presented. The sample case consists of taking the output conditions from the case presented earlier and making a step change from 260 g/l to 200 g/l in the input concentration of plutonium nitrate.

Figures 6.10 through 6.16 show the response of the plutonium concentration in the filtrate; the filtrate flowrate; the NO_3^- concentration; the oxalic ion concentration; the mean particle size with respect to a weight distribution; and the digestion factor, respectively. After the step change, all the output variables reach a new equilibrium value.

Figure 6.10 Response to a Step Decrease in Pu Concentration

Figure 6.11 Response to a Step Decrease in Pu Concentration

97-9

Figure 6.12 Response to a Step Decrease in Pu Concentration

Figure 6.13 Response to a Step Decrease in Pu Concentration

Figure 6.14 Response to a Step Decrease in Pu Concentration

61-9

Figure 6.15 Response to a Step Decrease in Pu Concentration

7. CONVERSION TO DYNSSYS

7.1 INTRODUCTION

The plutonium precipitator equations have been re-programmed to be compatible with the modular executive system DYNSSYS 2.0. In such a form, the precipitator model can be used in conjunction with other DYNSSYS modules to simulate part or all of the plutonium conversion process. In what follows, a brief summary of the DYNSSYS 2.0 modular system is given. Subsequently, the DYNSSYS module for the precipitator is described, pointing out the arrangement of the precipitator variables in the DYNSSYS stream matrix.

A system was then set up by adding to the precipitator a positional, proportional-integral controller, and a valve regulating the input flow of oxalic acid. DYNSSYS calculations for this system show the effectiveness of the controller in maintaining a constant digestion factor.

7.2 THE DYNSSYS MODULAR CONCEPT

The DYNSSYS 2.0⁽¹⁷⁾ executive system is a program which permits the analysis of time dependent phenomena in complex systems, like chemical plants, using a modular approach. In real life, the system is usually a collection of process units, related to each other by process streams. In the DYNSSYS representation, to each physical unit corresponds a unit of computation, and to each process stream corresponds a stream of information.

The unit of computation, which is a subroutine, modifies the incoming information and passes it on to the following computational units. In this way, DYNSSYS permits a very direct representation of a physical system. The units of computation

can be either algebraic or differential, with differential units representing those processes which, in general, contain capacity.

The heart of the DYNSSYS executive is a modified version of subroutine DIFSUB which uses a multistep method to solve automatically the differential equations. The order in which the different computational units are called is important, the differential units being usually processed before the algebraic units. For each successful integration step, the program steps through the sequence of modules twice, the first time using a predictor formula, and the second time a corrector formula. A criterion on the convergence of predicted and corrected values determines whether the step is successful. If not, the step size will be automatically reduced.

The advantage of the modular approach is that, once a library of modules is available, a system can be set up and modified without the need for rewriting every time the differential equations for the entire system. Only the information (process matrix) describing how the different units are interconnected needs to be given, together with the initial values of the variables i. the streams.

Although the version of DYNSSYS that we have been using is specifically intended for chemical systems, the concept can be applied to any system which modifies information and is conveniently described in terms of modular units.

7.3 THE PRECIPITATOR MODULE

As shown in Fig. 7.1, the precipitator consists of a box with two input streams and one output stream. For our present purpose, we model the precipitator as a box with three material streams (plutonium nitrate, oxalic acid, and slurry) and one information stream (signal). The graphical representation, according to DYNSSYS conventions, is illustrated in Fig. 7.1 and shows the variables carried in each stream.

Figure 7.1 Precipitator Module

We note that the two input streams carry the derivative of the flow rate with respect to time, and that the four dimensionless moments of the particle distribution are carried in the slurry stream.

The signal stream contains the fraction of plutonium in the liquid phase, or $1 - D_F$.

In DYNSSYS, the stream information is contained in a matrix $S(L, I, J)$, where

L = time indicator (1 for present value of time, 2 for past value of time)

I = stream number

J = stream element

In the version of DYNSSYS we have been using, J can have a maximum value of 11, and the recommended arrangement for J is:

$J = 1$ - stream number

2 - stream flag (1 for material stream, 2 for information stream)

3 - total molar flow

4 - temperature

5 - pressure

6 - through 11 - molar fraction of components 1 through 6

As seen in Fig. 7.1, we want the slurry stream to carry 9 elements. Therefore, we keep $J = 1$ and $J = 2$ as stream number and flag respectively, but use J from 3 through 11 to store different information, like the moments of the particle distribution. This in no way affects the computation in DYNSSYS, but in the printout of the process variables, headings like TEMPERATURE, PRESSURE, COMPONENTS will of course be meaningless. We have chosen to represent the stream elements for the precipitator as listed in Table 7.1.

TABLE 7.1

I \ J											
	1	2	3	4	5	6	7	8	9	10	11
1	1	1	F_p	$\frac{dF_p}{dt}$	-	C_p	-	C_N	-	-	-
2	2	1	F_o	$\frac{dF_o}{dt}$	-	C_o	-	-	-	-	-
3	3	1	$F_f + F_s$	μ_o'	μ_1'	C_p'	F_f	C_N'	C_o'	μ_2'	μ_4'
4	4	2	$\frac{F_f C_p'}{F_p C_p}$	-	-	-	-	-	-	-	-

It may be worthwhile to point out that the DYNSSYS output is, for this particular problem, a bit awkward. This is due to the nature and values of the variables carried in the slurry stream from the precipitator. The awkwardness refers to the headings as well as the printout formats used.

The equations for the precipitator contain a number of microscopic parameters (like K_G , K_B , r_o , etc.). We have chosen to include these values, as well as the plutonium oxalate density, as data in the module, rather than as equipment parameters. The rationale for this is that these numbers would not be usually changed in a macroscopic rearrangement of the system being simulated. The only equipment parameter (in a DYNSSYS sense) is the volume of the precipitator, which is read in as EP(IM,1), where IM is the number assigned to the precipitator unit in the process matrix. With the above conventions, a module has been written for the precipitator, using the same equations as described in Chapter 3. The listing of the module, which has been identified as TYPE 2, is given in Appendix B. Since this module requires subroutine SOLUB to compute the equilibrium solubility, this routine should be compiled together with the DYNSSYS executive and library.

7.4 A SIMPLE DYNSSYS SYSTEM INCLUDING THE PRECIPITATOR

Figure 7.2 shows a system which involves three components, namely the precipitator, a controller, and a valve. The fraction of plutonium in the liquid stream is sampled, and if an error from the set point is detected, a signal is sent to the valve which controls the flow of oxalic acid. The controller is a positional, proportional-integral module, which means that the signal P from the controller is obtained as

$$P = K_p \left(e + \frac{1}{K_I} \int_0^t e dt \right) \quad (1)$$

where the error e is defined as

$$e = \text{measured variable} - \text{set point} \quad (2)$$

and K_p and K_I are the proportional constant and integral time constant of the controller respectively.

The module for the controller was taken from the library of DYNSSYS modules, subroutine CONT1 or TYPE 30. Since we have used a limited library of modules, we have relabeled this TYPE5. The listing for this routine is given in Appendix C.

The module for the valve which controls the flow of oxalic acid was also taken from the library of DYNSSYS modules, subroutine VALV2 or TYPE 1, with a minor modification. Since the equations for the precipitator require the derivative $\frac{dF_0}{dt}$, which varies because of the action of the valve, the statement

$$S(1,OUT,4) = (S(1,OUT,3) - S(2,OUT,3))/H$$

was added in subroutine TYPE 1, together with the COMMON block GEAR2 which contains the variable H , the present time step. The listing for the modified routine TYPE 1 is given in Appendix D.

Figure 7.2 Control Model for Precipitator

We note that, if the signal from the precipitator increases, this is an indication that less plutonium is precipitating. With our type of control, to keep the yield constant, the residence time has to be increased, and for this, the flow of oxalic acid must be reduced. The valve must therefore have reverse action.

The process matrix for the system of Fig. 7.2 is, according to DYNSSYS conventions, as follows

UNIT NO.	TYPE	ASSOCIATED STREAMS			
1	TYPE 2	1	2	-3	-4
2	TYPE 5	4	-5		
3	TYPE 1	5	-2		

The DYNSSYS input data for a simulation are shown in Fig. 7.3 and a limited part of the output is shown in Fig. 7.4. As mentioned previously, the headings should be disregarded and the meaning of the variables in the streams should be found from Table 7.1.

7.5 NUMERICAL EXAMPLE

An example of the effect of the controller on the precipitator will now be given.

Suppose that the system is at steady state, with input conditions:

$$F_p = 7 \text{ liters/hour}$$

$$F_0 = 20 \text{ liters/hour}$$

$$C_p = 280 \text{ g/liter}$$

$$C_0 = 1 \text{ mole/liter}$$

$$C_N = 5.33 \text{ moles/liter}$$


```

$$$$$ PROGRESS VARIABLES AT TIME = .13471E+01 $$$$$
STEP#  FLOW  TEMP  PRES  COMPONENTS
1  0.0000  0.0000  0.0000  290.00000  0.00000  5.33000  0.00000  0.0000
    0.00000
2  20.4471  .1227  0.0000  1.00000  0.00000  0.00000  0.00000  0.0000
    0.00000
3  20.4471  .1227  .0000  7.67989  26.95482  1.59187  .11404  .0000
    11.47499
4  .0124  0.0000  0.0000  0.00000  0.00000  0.00000  0.00000  0.0000
    0.00000
5  49.1543  0.0000  0.0000  0.00000  0.00000  0.00000  0.00000  0.0000
    0.00000

$$$$$ PROGRESS VARIABLES AT TIME = .15874E+01 $$$$$
STEP#  FLOW  TEMP  PRES  COMPONENTS
1  0.0000  0.0000  0.0000  290.00000  0.00000  5.33000  0.00000  0.0000
    0.00000
2  20.4554  .1000  0.0000  1.00000  0.00000  0.00000  0.00000  0.0000
    0.00000
3  20.6641  .0000  .0000  7.68500  26.97720  1.54058  .13482  .0000
    11.33173
4  .0225  0.0000  0.0000  0.00000  0.00000  0.00000  0.00000  0.0000
    0.00000
5  49.1177  0.0000  0.0000  0.00000  0.00000  0.00000  0.00000  0.0000
    0.00000

$$$$$ PROGRESS VARIABLES AT TIME = .16374E+01 $$$$$
STEP#  FLOW  TEMP  PRES  COMPONENTS
1  0.0000  0.0000  0.0000  290.00000  0.00000  5.33000  0.00000  0.0000
    0.00000
2  20.6212  .1227  0.0000  1.00000  0.00000  0.00000  0.00000  0.0000
    0.00000
3  20.4700  .0000  .0000  7.67403  26.97697  1.57941  .13551  .0000
    11.30700
4  .0126  0.0000  0.0000  0.00000  0.00000  0.00000  0.00000  0.0000
    0.00000
5  49.1450  0.0000  0.0000  0.00000  0.00000  0.00000  0.00000  0.0000
    0.00000

$$$$$ PROGRESS VARIABLES AT TIME = .17471E+01 $$$$$
STEP#  FLOW  TEMP  PRES  COMPONENTS
1  0.0000  0.0000  0.0000  290.00000  0.00000  5.33000  0.00000  0.0000
    0.00000
2  20.5912  .1221  0.0000  1.00000  0.00000  0.00000  0.00000  0.0000
    0.00000
3  20.5936  .0000  .0000  7.68089  27.01422  1.57812  .13611  .0000
    11.30000

```

Figure 7.4 DYNSSYS Output

By running the precipitator model through the transient phase, we found that the output variables at steady state are:

$$C_p' = 7.155 \text{ g/liter}$$

$$F_f' = 25.557 \text{ liters/hour}$$

$$C_N' = 1.4599 \text{ moles/liter}$$

$$C_o' = .2013 \text{ moles/liter}$$

$$\mu_o' = .27363 \times 10^{-9}$$

$$\mu_1' = .54388 \times 10^{-7}$$

$$\mu_2' = .21512 \times 10^{-4}$$

$$\mu_4' = .10096 \times 10^2$$

and that the signal (fraction of Pu in the liquid) is .0933.

At $t=0$ we make a step change in the Pu input flow from 7 liters/hour to 8 liters/hour.

Because the volume of the precipitator remains constant, the filtrate flowrate increases instantaneously from 25.557 liters/hour to 26.557 liters/hour. For the same reason, the signal from the precipitator drops suddenly from the value .0933 to the value

$$\frac{26.557 \times 7.155}{8 \times 280} = .0848$$

After this sudden drop, all the variables change smoothly and their behavior can be computed with DYNSSYS. Figure 7.5 shows the response of the signal when the controller is not inserted. After the sudden drop directly attributable to the variation in input, the fraction of Pu in the liquid increases and then decreases, to reach a new equilibrium value at .0890. The oxalic flowrate remains, obviously, constant.

Figure 7.6 shows the response of the system to the same step change when the controller is inserted. The flowrate

NO CONTROL

Figure 7.5. DYNSYS Model with No Control

WITH PROPORTIONAL INTEGRAL CONTROLLER

Figure 7.6. DYN SYS Model with Proportional Integral Controller

of oxalic acid is increased by the valve to reach a new equilibrium level and the fraction of plutonium in the liquid returns to its original value of .0933.

The action of the controller has been kept deliberately slow. Because of the peculiar nature of the signal, which changes rapidly after the perturbation has been made, a too fast corrective action of the controller would result in convergence problems in routine DIFSUB.

8. CONCLUSIONS AND DISCUSSION

The plutonium oxalate precipitator model that has been developed serves to demonstrate that mathematical (simulation) process modeling efforts can be useful as in plant aids for material and process control. The model shows that performance of the precipitator can be predicted, with a reasonable amount of accuracy so that advanced notice could be given of process malfunctions or material diversions.

It should be noted that the accuracy of the model at this time is data limited. Model improvement could be made only by setting up experiments and taking more data. This would allow verification of parameter estimates and key assumptions that were used in the model development.

FORTTRAN PROGRAM OF MODEL

APPENDIX A

[illegible]

```

35 YFP(NPL)=FP
   YFD(NPL)=FD
   YCP(NPL)=CP
   YCN(NPL)=CN
   YCD(NPL)=CD
   IF (FP,LT,1,F=20) GO TO 45
   FRAC(4PL)=1.-YF(NPL)*YF(NPL)/(YFP(NPL)*YCP(NPL))
   GO TO 55
45 FRAC(NPL)=1,
55 IF (NPL,EQ,1000) GO TO 40
   I= (KFLAG,ML,1) GO TO 40
   IF (T,LT,THAX) GO TO 30
40 CALL DNT
   WRITE (6,75) KFLAG
75 FORMAT (1H0,7H KFLAG =,I3)
   GO TO 10
END
SUBROUTINE INHIT(T)
DOUBLE PRECISION I
COMMON/INP/II,FP,DFDNT,DFPDT,CP,CN,CD
PI=3.141592

C
C
C
C THIS SECTION COMPUTES THE INPUT VARIABLES
C ANALYTIC FUNCTIONS SHOULD BE GIVEN
C IF NO FUNCTIONS ARE GIVEN, THE CONSTANT VALUES READ
C AS DATA WILL BE USED
C
ARG1=EXP(-10.*T)
ARG2=EXP(-30.*T)
ARG3=EXP(-1.*T)
C INPUT FLOWRATE OF PU NITRATE (LITERS/HOUR)
FP=7.*(1.-ARG1)+1750.*STL(ARG)*ARG2
C INPUT FLOWRATE OF OXALIC ACID (LITERS/HOUR)
FD=20.*(1.-ARG1)+5000.*SLC(ARG)*ARG2
C TIME DERIVATIVE OF PU NITRATE FLOWRATE
VAR1=.1*PI*(1.-ARG1)-50.*STL(ARG)
DFPDT=70.*ARG1+1750.*VART*ARG2
C TIME DERIVATIVE OF OXALIC ACID FLOWRATE
DFDNT=200.*ARG1+5000.*VAR1*ARG2
C CONCENTRATION OF PU IN INPUT STREAM (G/LITER)
CP=CP
C CONCENTRATION OF UHS IN INPUT STREAM (MMOL/LITER)
CN=CN
C CONCENTRATION OF H2CPO4 IN INPUT STREAM (MMOL/LITER)
CD=CD
C
C
C
RETURN
END
SUBROUTINE DTEFUN(T,V,XY)
DOUBLE PRECISION T,V,XY
DIMENSION Y(4,1),XY(4)
COMMON/OUT/PI,ARG,ARGC,1H0,RIID,QH0,V,R7RI,VK,THAX
COMMON/INP/II,FP,DFDNT,DFPDT,CP,CN,CD
CALL INHIT(T)
IF R=FP
TDS=DFDNT+DFPDT
CALL SOLUH(Y(1,3),Y(1,4),CSTAR,CH)

```

```

CSTAR=CSTAR*239,
S=1,
IF (Y(1,1).LE.CSTAR) S=0,
G=AKG*S*(ABS(Y(1,1)-CSTAR))**ANG
B=AKB*S*(ABS(Y(1,1)-CSTAR))**ANB
IF (Y(1,2).EQ.0.) GO TO 50
P1=3.*Y(1,7)*VK*VG/RZR0+V*VK*Y(1,2)*B+RZR0**3/TFR
P2=(CP-Y(1,1))*FP-Y(1,1)*FO+(Y(1,1)-RDP)*P1
DY(1)=P2*TFH/(V*Y(1,2))
X1=TFH/V-Y(1,2)/V-3.*VK*Y(1,7)*G/RZR0-Y(1,2)*VK*RZR0**3
1*H/TFH
X2=Y(1,2)*TDFR/TFR
DY(2)=X2+TFH*X1
Z1=-DY(2)/Y(1,2)+TDFR/TFR
Z2=(FP*(4/Y(1,2)-Y(1,3))*TFR/V
DY(3)=Z1+Y(1,3)+Z2
T1=(P-R0-Y(1,4))*TDFR/TFR
T2=TFH*(F0*(4-Y(1,2)*Y(1,4)+Y(1,2)*R00)/(V*Y(1,2))
T3=(R00-Y(1,4))*DY(2)/Y(1,2)
DY(4)=-T1+T2+T3
TRAV=R*Y(1,2)*RZR0**3/TFR
DY(5)=TRAV-Y(1,4)*TFH/V
DY(6)=G*Y(1,5)/RZR0+TRAV-Y(1,6)*TFH/V
DY(7)=2.*G*Y(1,6)/RZR0+TRAV-Y(1,7)*TFH/V
AMU3=(1.-Y(1,2)/TFH)/VK
DY(8)=G.*AMU3/RZR0+TRAV-Y(1,8)*TFH/V
RETURN
50 D0=H*GZR0**3
DY(1)=RDP*AKG*D0
DY(2)=RDP1*TFHDT
DY(3)=0.
DY(4)=0.
DY(5)=0.
DY(6)=0.
DY(7)=0.
DY(8)=0.
R1=0.
END
SUBROUTINE READ
DIMENSION TITLE(7)
COMMON/DA1/P1,AKG,AKB,ANG,ANB,RDP,R00,RZR0,VK,TRAV
COMMON/DA2/PEPDT,TITLE,EMSA
COMMON/DA3/FP,FO,RDP1,DEPDT,CP,CN,C
COMMON/IN1/Y1,Y2,Y3,Y4,Y5,Y6,Y7,Y8
READ (5,1) TITLE
IF (FEOFILF 5) 100,30
READ (5,2) AKG,ANG,AKB,ANB,RZR0
READ (5,2) RDP,V
RDP=457.*D0
R00=3.*RZR0
READ (5,3) RDP1
READ (5,2) TRAV,EMSA
READ (5,2) FP,FO,DEPDT,DEPDT,CP,CN,
READ (5,2) Y1,Y2,Y3,Y4,Y5,Y6,Y7,Y8
1 FORMAT (7A10)
2 FORMAT (6E12,5)
3 FORMAT (14)
WRITE (6,4)
4 FORMAT (14),30X,40NDYNAMIC MODE FOR IONIUM PRECIPITATION )
WRITE (5,5) TITLE

```

```

5  FORMAT (1H0,5X,7A10)
   WRITE (6,6)
6  FORMAT (1H0,30X,26HCRYSTALLIZATION PARAMETERS)
   WRITE (6,7) AKG
7  FORMAT (1H0,25X,13HCOEFFICIENT =,E10,4,10H (CM/MR))
   WRITE (6,8)
8  FORMAT (1H ,10X,6HGHOWTH)
   WRITE (6,9) ANG
9  FORMAT (1H ,25X,10HEXPOWENT =,F5,2)
   WRITE (6,10) AKB
10 FORMAT (1H0,25X,13HCOEFFICIENT =,E10,4,
122H (MICELI/MICRALI/FH))
   WRITE (6,11) ANG
11 FORMAT (1H ,10X,10HCOEFFICIENT,5X,10HEXPOWENT =,F5,2)
   WRITE (6,12) HZD
12 FORMAT (1H ,25X,18HADIUS OF NUCLEI =,E10,4,7H (CM),/)
   WRITE (6,13) RHP
13 FORMAT (1H0,10X,30HCONDENSITY OF PU IN PRECIPITATE =,
1F10,4,10H (G/LITER))
   WRITE (6,14) RHP
14 FORMAT (1H0,10X,30HCONDENSITY OF OXALIC ION IN PRECIPITATE =,
1F10,4,12H (MOLES/L))
   WRITE (6,15) V
15 FORMAT (1H0,10X,20HOLUME OF PRECIPITATOR =,F5,2,
111H (LITER))
   WRITE (6,16) RHP
16 FORMAT (1H0,10X,11HPRINTING OPTION =,I3,15H (0=NO,1=YES) )
   WRITE (6,17) FDSF
20 FORMAT (1H0,10X,16HRELATIVE ERROR =,E10,4)
   WRITE (6,17) MAX
17 FORMAT (1H0,10X,20HMAXIMUM INTEGRATION TIME =,
1F5,2,10H (MINUS),/)
   WRITE (6,18)
18 FORMAT (1H0,20X,14HINITIAL VALUES)
   WRITE (6,19) Y1
19 FORMAT (1H0,10X,10HPU CONCENTRATION =,E10,4,12H (G/LITER))
   WRITE (6,20) Y1
20 FORMAT (1H ,10X,13HPU FLOWRATE =,E10,4,16H (LITERS/MIN))
   WRITE (6,21) Y1
21 FORMAT (1H ,10X,14HPU CONCENTRATION =,E10,3,
116H (MOLES/LITER))
   WRITE (6,22) Y1
22 FORMAT (1H ,10X,22HAXALIC CONCENTRATION =,E10,4,
111H (MOLES/LITER))
   WRITE (6,23) Y1
23 FORMAT (1H ,10X,30H2ND MOMENT OF DISTRIBUTION (Y5) =,E10,4)
   WRITE (6,24) Y6
24 FORMAT (1H ,10X,30H1ST " " " " (Y6) =,E10,4)
   WRITE (6,25) Y7
25 FORMAT (1H ,10X,30H3RD MOM " " " " (Y7) =,E10,4)
   WRITE (6,26) Y8
26 FORMAT (1H ,10X,30H4TH " " " " (Y8) =,E10,4)
   AKG=AKG/10,
   RHP=RHP/10,
   RETURN
100 CALL EXIT
END

```

[illegible]

```

ILABX,50,LYFR,501
CALL STOPF(6,TAPE10)
RETURN
END
SUBROUTINE PEDFRV(T,Y,PW,N)
DOUBLE PRECISION T,Y
RETURN
END
SUBROUTINE S0119(C1,C2,CHCN,CSTAR,CH)
DIMENSION X(3)
C2=.0443051
B=-C1/3/4.
C=-5.39E+2*CHCN/3.
D=-5.58E+6*CHCN
O=C+H**2
R=(3.+H*(C=0))/2.-H**3
DELT=7*+3+H**2
IF (DELT,1,0.) GO TO 10
SD=SQRT(DELT)
S1=(H+SD)**0.33333333
S2=(H-SD)**0.33333333
CH=S1+S2-H
GO TO 50
10 S=R/A1*(H)
T1=2.*S+SQRT(-O)
T2=ACOS(S+H/SQRT(-O**3))/3.
X(1)=T1*COS(T2)-H
X(2)=T1*COS(T2+H)-H
X(3)=1+*COS(T2+2.*H)-H
DO 100 I=1,3
II(X(I),1,0.) GO TO 100
CH=X(1)
END
C1=111111
50 A1=4.840473E+05
H1=6.124450E+11
C1=4.944701E+04
CSTAR=H+H1*C1**4/CHCN**2+C1*CHCN
RETURN
END

```


APPENDIX B

```

SUBROUTINE TYPE2
C
C SUBROUTINE PPREC2
C
C THIS MODULE DESCRIBES THE PLUTONIUM OXALATE PRECIPITATOR
C
C THE FOLLOWING PARAMETER IS REQUIRED
C EP(14,1) = VOLUME OF PRECIPITATOR (LITERS)
C
COMMON/MAT/MP(35,13),EP(35,10),S(7,45,11),EY(50)
COMMON/COMP/IG,SCOMP,NC5,N7,NS,TMAX
COMMON/UNIT/UNIT,UNIT
COMMON/GEAR2/JSTART,ISTIFF,TIME,H,KFLAG,ICOMV
COMMON/MODULE/IDEP1,ITER,ITRI,NZERO
DIMENSION Y(6),DEPY(6)
C
C THE MICROSCOPIC QUANTITIES IN THE DATA STATEMENT HAVE TWO UNITS
C AYG(DP/HR), AYG(1./LITER*HOUR), F2PO(UM), RL(G/CC)
C DATA AYG,AYG,AYG,AYG,AYG,AYG/1.5E-04,1.1E-03,1.4,1.E-06/
C DATA PD,VK/2.594,4.188/902/
C
C VOLUME OF PRECIPITATOR
C V=EP(14,1)
C
C ITLU=0
C FIND STREAMS
C INPU=MP(14,3)
C INDX=MP(14,4)
C STUT=145*(EP(14,5))
C ASIG=145*(EP(14,6))
C
C NUMBER OF DIFFERENTIAL EQUATIONS
C NRQ=8
C
C DENSITY OF PU IN OXALATE (G/LITER)
C DENSITY OF O2.14 IN OXALATE (MOLES/LITER)
C
C ROP=457.*PU
C ROP=1.82*PU
C
C IF (JSTART.NE.0.DP.IG.EQ.1) GJ TO 1
C
C CALCULATE INITIAL CONDITIONS
C Y(1)=S(7,UNIT,6)
C Y(2)=S(7,UNIT,7)
C Y(3)=S(7,UNIT,8)
C Y(4)=S(7,UNIT,9)
C Y(5)=S(7,UNIT,10)
C Y(6)=S(7,UNIT,11)
C
C 1 CONTINUE
C
C COMPUTE INPUT VARIABLES
C 3 DEINT=S(1,INPU,4)
C DEINT=S(1,INDX,4)
C FP=S(1,INPU,3)
C FP=S(1,INDX,3)
C CP=S(1,INPU,6)

```

```

CN=S(1,INPU,3)
CO=S(1,INX,6)
TFP=FD*FB
TDFR=DFDDT+DFPDY
C
C COMPUTE PLUTONIUM EQUILIBRIUM SOLUBILITY
CALL SOLUB(V(3),V(4),CSTAR,CH)
CSTAR=CSTAR*239.
C
Z=1.
IF (V(1).LE.CSTAR) Z=0.
C
C COMPUTE GROWTH AND NUCLEATION COEFFICIENTS
G=AVG*Z*(1+S(V(1)-CSTAR))**ANG
B=AFB*Z*(1+S(V(1)-CSTAR))**ABR
C
IF (V(2).EQ.0.0.OR.TFR.EQ.0.) GO TO 50
C
C SYSTEM OF DIFFERENTIAL EQUATIONS
P1=3.*V(7)*VK*V*G/RZRO+V*VK*V(2)*R*PZPO**3/TFR
P2=(CP-V(1))*FV-V(1)*FQ+(V(1)-ROP)*P1
DERV(1)=P2*TFP/(V*V(2))
X1=TFP/V-V(2)/V-3.*VK*V(7)*G/RZPO-V(2)*VK*RZLO**3*P2/TFR
X2=V(2)*TDFR/TFP
DERV(2)=X2+TFR*X1
Z1=-DERV(2)/V(2)+TDFR/TFR
Z2=(FPC/V*(2)-V(7))*TFP/V
DERV(3)=Z1*V(3)+Z2
T1=(1.0-V(4))*TFR/V
T2=TFP*(FV*CO-1FV*PZLO-V(2)*V(4)+V(2)*PZD)/(V*V(2))
T3=(FQ)-V(4))*V(2)/V(4)
DERV(4)=-T1+T2+T3
THAV=V*V(2)*RZL**3/TFR
DERV(5)=THAV-V(5)*FV/V
DERV(6)=V(4)/V(2)+THAV-V(5)*TFP/V
DERV(7)=2.*V(4)/V(2)+THAV-V(7)*TFP/V
A*U=(1.-V(2)/V(1))/V
DERV(8)=4.*G*ABR/RZLO+THAV-V(8)*TFP/V
C
GO TO 60
C
C LIMIT OF SYSTEM OF DIFFERENTIAL EQUATIONS
FOR VARIOUS INPUT FLUX
50
DERV(1)=-3.0*V*V*G
DERV(2)=CP-V(1)+DFPDY
DERV(3)=0.
DERV(4)=0.
DERV(5)=0
DERV(6)=0
DERV(7)=0
DERV(8)=0
60
CONTINUE
C
C CALL TO DIFSUB
CALL DIFSUB(NEQ,V,DERV)
C
C EVALUATION OF DERIVATIVES
IF (IDBY.NE.0) GO TO 3

```

```

C
C      COMPUTE OUTPUT SIGNAL
IF (CP.LE.1.0E-70.UP.FP.LE.1.E-20) GO TO 30
SIGNAL=Y(1)*Y(2)/(CP*FP)
GO TO 40
30  SIGNAL=0.
C
C      COMPUTE OUTPUT VARIABLES
40  S(1,NSIG,3)=SIGNAL
S(1,NOUT,3)=FF*FU
S(1,NOUT,4)=Y(1)
S(1,NOUT,7)=Y(2)
S(1,NOUT,8)=Y(3)
S(1,NOUT,9)=Y(4)
S(1,NOUT,4)=Y(5)
S(1,NOUT,6)=Y(6)
S(1,NOUT,10)=Y(7)
S(1,NOUT,11)=Y(8)
C
      RETURN
      END

```

APPENDIX C

```

SUBROUTINE TYPES
SUBROUTINE CONT1
COMMON/UNIT/10,11,12
COMMON/PAT/MP(35,13),EP(35,10),S(2,45,11),ZX(50)
COMMON/CTN/10,11,12,13,14,15,16,17,18,19,20,21,22,23,24,25,26,27,28,29,30,31,32,33,34,35,36,37,38,39,40,41,42,43,44,45,46,47,48,49,50
COMMON/TEAR2/JSTART,ISTIFF,TIME,H,KFLAG,ICOMPV
COMMON/ID/INID,OUTID,NEPR,NPOINT
COMMON/CTP/NCTP,NSK
DIMENSION SIGMA(10),OLD(10,2)
INTEGER OUT
DATA SIGMA,OLD/10*0.0,20*0.0/
IF (ICFLAG.EQ.1) RETURN
NTR=EP(1,10)
IF (NTR.EQ.1) WRITE (NOUT,10)
NCT=NCT+1
IN=MP(1,3)
OUT=MP(1,4)
K=EP(1,1)
RANGE=EP(14,2)-EP(14,3)
IF (OUT.LT.0) GO TO 1
STEP=EP(14,4)*50./RANGE
GO TO 3
1 IN2=-OUT
OUT=-MP(14,5)
IF (S(1,1,2,2).GT.11.) GO TO 2
IN=IN2
IN2=MP(14,3)
2 STEP=5/(1,1,2,3)
3 SIGMA=5/(1,1,1,1)
IF (SIGMA.GT.EP(14,2)) GO TO 4
IF (SIGMA.LT.EP(14,3)) GO TO 5
WRITE (NOUT,11) IN
SIGMA=EP(14,3)
GO TO 5
4 WRITE (NOUT,12) IN
SIGMA=EP(14,2)
5 ERR=(SIGMA-OLD(1,1))/STEP
OLDERR=OLD(NCT,NSK)
PD=0.
PI=0.
R=EP(14,6)
GO TO (7,8,9,10),R
6 PD=EP(14,9)*(ERR-OLDERR)/R
GO TO 9
7 PD=EP(14,9)*(ERR-OLDERR)/R
8 SIGMA(NCT)=SIGMA(NCT)+(R*(ERR+OLDERR)/2.)
PI=SIGMA(NCT)/R
9 S(1,OUT,10)=PI(1,6)*(EP(14,7)*(ERR+PI*PD))
OLD(NCT,1)=OLD(NCT,NSK)
OLD(NCT,2)=PD
IF (NTR.EQ.1) WRITE (NOUT,13) ERR,OLDERR,PI,PD
RETURN
10 PRINT (204 EXTENDING CONTROLLING)
11 PRINT (204 WARNING- VARIABLE UNDER RANGE,17)
12 PRINT (204 WARNING- VARIABLE OVER RANGE,12)
13 PRINT (10X,4F14.7)
END

```

APPENDIX D

```

C      SUBROUTINE TYPE1
      SUBROUTINE VALV2
      COMMON/VALV/IV,NMP
      COMMON/VALV/FP(35,11),S(2,45,11),EX(50)
      COMMON/CD/IG,ICONV,ACO
      COMMON/GEAR2/JSTART,1STIFF,TIME,H,AFLAG,ICONV
      INTEGER OUT
      IN=NP(IV,2)
      OUT=ABS("P(1",4))
      V=S(1,IV,3)
      IF (V.LT.0.0) V=0.0
      IF (V.GT.100.0) V=100.0
      A=EP(IN,2)
      IF (A.LT.0.0) S(1,OUT,3)=FP(IV,1)*(100.0-V)**2
      IF (A.GE.0.0) S(1,OUT,3)=FP(IV,1)*V**2
      S(1,OUT,4)=(S(1,OUT,3)-S(2,OUT,3))/"
      RETURN
      END

```

APPENDIX L

Equilibria Model

An equilibria model for calculating C^* is developed recognizing that several oxalate ($C_2O_4^{2-}$) complexing phenomena are possible. This is illustrated in Table E.1 which shows data from Cleveland. (8) A slightly simplified mechanism for the system is used and is summarized diagrammatically in Figure E.1.

Table E.1 Stability Constants for Oxalate Complexes of
Pu(IV) in 1M HNO_3

Reaction	Equilibrium Constant (20.0 ± 0.2°C)
$Pu^{4+} + C_2O_4^{2-} \rightleftharpoons Pu(C_2O_4)^{2+}$	5.6×10^8
$Pu(C_2O_4)^{2+} + C_2O_4^{2-} \rightleftharpoons Pu(C_2O_4)_2$	1.5×10^8
$Pu(C_2O_4)_2 + C_2O_4^{2-} \rightleftharpoons Pu(C_2O_4)_3^{2-}$	3.0×10^6
$Pu(C_2O_4)_3^{2-} + C_2O_4^{2-} \rightleftharpoons Pu(C_2O_4)_4^{4-}$	1.3×10^4

Where the equilibrium constant is defined as:

$$\frac{[\text{Product}]}{[\text{Reactant 1}] [\text{Reactant 2}]}$$

Figure E.1 MECHANISTIC FORM OF EQUILIBRIA THEORY

Since the only available equilibria data (8,12) for $\text{Pu}(\text{C}_2\text{O}_4)$ solubility is reported as a function of equilibrium nitrate (NO_3) and oxalate ($\text{H}_2\text{C}_2\text{O}_4$) concentrations, the overall equilibrium relationship will have to be developed in terms of these variables.

Referring to Figure E.1, the development of the equilibrium relationship is as follows:

$$K1 = \frac{[\text{Pu}(\text{C}_2\text{O}_4)_2]_1}{[\text{Pu}(\text{C}_2\text{O}_4)_2 \cdot 6\text{H}_2\text{O}]_s}$$

where the bracket, [] designate the concentration of the species contained within them. By conventional definition⁽⁹⁾, $[\text{Pu}(\text{C}_2\text{O}_4)_2 \cdot 6\text{H}_2\text{O}]_s = 1$ and, therefore, $[\text{Pu}(\text{C}_2\text{O}_4)_2]_1 = K1$.

Now,

$$K2 = \frac{[\text{Pu}^{+4}] [\text{C}_2\text{O}_4^{=}]^2}{[\text{Pu}(\text{C}_2\text{O}_4)_2]_1} = \frac{[\text{Pu}^{+4}] [\text{C}_2\text{O}_4^{=}]^2}{K1}$$

and,

$$K3 = \frac{[\text{Pu}(\text{C}_2\text{O}_4)_3 \cdot \text{H}_2]}{[\text{Pu}(\text{C}_2\text{O}_4)_2]_1 [\text{H}_2\text{C}_2\text{O}_4]} = \frac{[\text{Pu}(\text{C}_2\text{O}_4)_3 \cdot \text{H}_2]}{K1 [\text{H}_2\text{C}_2\text{O}_4]}$$

Use of these relationships allow the soluble plutonium concentration Pu to be expressed in a quantitative manner using the following equation:

$$[\text{Pu}] = [\text{Pu}^{+4}] + [\text{Pu}(\text{C}_2\text{O}_4)_2] + [\text{Pu}(\text{C}_2\text{O}_4)_3 \cdot \text{H}_2] =$$

$$\frac{K1K2}{[\text{C}_2\text{O}_4^{=}]^2} + K1 + K1K3 [\text{H}_2\text{C}_2\text{O}_4]$$

An additional relationship may be derived based on the knowledge of the dissociation constants for oxalic acid^(9,10)

$$K_A = \frac{[H^+][HC_2O_4^-]}{[H_2C_2O_4]} = 5.38 \times 10^{-2}$$

$$K_B = \frac{[H^+][C_2O_4^{=}] }{[HC_2O_4^-]} = 5.18 \times 10^{-5}$$

combining these,

$$[H_2C_2O_4] = \frac{[H^+]^2 [C_2O_4^{=}] }{K_A K_B} = \frac{[H^+]^2 [C_2O_4^{=}] }{2.78 \times 10^{-6}}$$

This expression can be substituted back into the equation for [Pu] to yield a single equation.

$$[Pu] = K_1 + \frac{K_1 K_2 [H^+]^4}{(2.78 \times 10^{-6})^2 [H_2C_2O_4]^2} + K_1 K_3 [H_2C_2O_4]$$

which has the form,

$$[Pu] = A + \frac{B[H^+]^4}{[H_2C_2O_4]^2} + C [H_2C_2O_4]$$

where $A = K_1$

$$B = \frac{K_1 K_2}{(2.78 \times 10^{-6})^2}$$

$$C = K_1 K_3$$

Existing solubility data has been collected from open literature sources^(8,12). The data that is used in this study is presented in Table E.2, columns 1, 2 and 3 as collected from the sources. In order to fit the data for the [Pu] equation, $[H^+]$ must be derived from the HNO_3 , $H_2C_2O_4$ data. $[H^+]$ can be determined making use of the following relationship:

$$\begin{aligned} [H^+] &= [NO_3^-] + [HC_2O_4^-] + 2[C_2O_4^{2-}] \\ &= [NO_3^-] + (5.38 \times 10^{-2}) \frac{[H_2C_2O_4]}{[H^+]} + (2)(2.79 \times 10^{-6}) \frac{[H_2C_2O_4]}{[H^+]^2} \end{aligned}$$

Use of this equation and columns 1, 2 and 3 of Table E.2 yields column 4 of the Table which are values for $[H^+]$.

A least squares fit of the data in Table E.2 to the equation for Pu yielded the followed values for the coefficients:

$$\begin{aligned} A &= 4.89 \times 10^{-5} \\ B &= 6.12 \times 10^{-11} \\ C &= 4.98 \times 10^{-4} \end{aligned}$$

The least squares solution technique is presented in Appendix F. Specific data point calculations are presented in Table E.3. A response surface, showing the effect of H^+ and $H_2C_2O_4$ on Pu oxalate solubility using the postulated equilibrium reaction mechanisms function is shown in Figure E.2. The area above the surface is the region where precipitation of plutonium oxalate takes place. The area below the surface is the soluble

Table E.2

$\text{NO}_3^- (\text{M})$	$\text{H}_2\text{C}_2\text{O}_4$	$\text{Pu}^+ (\text{M})$	$\text{H}^+ (\text{M})$
1.000E+00	2.000E-01	2.200E-04	1.011E+00
2.000E+00	2.000E-01	1.300E-04	2.005E+00
1.000E+00	1.000E-01	1.000E-04	1.005E+00
2.000E+00	1.000E-01	6.000E-05	2.003E+00
4.000E+00	1.000E-01	1.100E-04	4.001E+00
6.000E+00	1.000E-01	2.100E-04	6.001E+00
1.000E+00	5.000E-02	5.000E-05	1.003E+00
2.000E+00	5.000E-02	6.000E-05	2.001E+00
1.000E+00	5.000E-02	5.565E-05	1.003E+00
1.000E+00	2.500E-01	1.544E-04	1.013E+00
1.000E+00	6.000E-01	5.565E-04	1.031E+00
1.180E+00	7.100E-03	6.820E-05	1.180E+00
1.610E+00	2.000E-03	2.753E-04	1.610E+00
1.610E+00	1.500E-02	6.276E-05	1.611E+00
2.000E+00	5.000E-02	4.059E-05	2.001E+00
2.000E+00	2.500E-01	6.318E-05	2.007E+00
2.340E+00	1.000E-02	6.402E-05	2.340E+00
2.340E+00	5.000E-03	1.042E-04	2.340E+00
2.520E+00	2.500E-02	6.987E-05	2.521E+00
3.520E+00	5.000E-03	3.854E-04	3.520E+00
3.520E+00	1.000E-02	1.916E-04	3.520E+00
3.520E+00	5.000E-02	7.531E-05	3.521E+00
3.520E+00	1.000E-01	7.615E-05	3.522E+00
3.520E+00	5.000E-01	8.954E-05	3.528E+00

Table E.3

Results of Least Squares Fit to

$$Pu = A + B \frac{[H^+]^4}{[H_2C_2O_4]^2} + C[H_2C_2O_4]$$

$H_2C_2O_4$ (M)	H^+ (M)	Pu^+ (M)	Fit Pu^+ (M)
2.000E-01	1.011E+00	2.200E-04	1.486E-04
2.000E-01	2.005E+00	1.300E-04	1.486E-04
1.000E-01	1.005E+00	1.000E-04	9.877E-05
1.000E-01	2.003E+00	6.000E-05	9.886E-05
1.000E-01	4.001E+00	1.100E-04	1.003E-04
1.000E-01	6.001E+00	2.100E-04	1.067E-04
5.000E-02	1.003E+00	5.000E-05	7.386E-05
5.000E-02	2.001E+00	6.000E-05	7.423E-05
5.000E-02	1.003E+00	5.565E-05	7.386E-05
2.500E-01	1.013E+00	1.544E-04	1.736E-04
6.000E-01	1.031E+00	5.565E-04	3.481E-04
7.100E-03	1.180E+00	6.820E-05	5.481E-05
2.000E-03	1.610E+00	2.753E-04	1.528E-04
1.500E-02	1.611E+00	6.276E-05	5.822E-05
5.000E-02	2.001E+00	4.059E-05	7.423E-05
2.500E-01	2.007E+00	6.318E-05	1.736E-04
1.000E-02	2.340E+00	6.402E-05	7.227E-05
5.000E-03	2.340E+00	1.042E-04	1.249E-04
2.500E-02	2.521E+00	6.987E-05	6.533E-05
5.000E-03	3.520E+00	3.854E-04	4.276E-04
1.000E-02	3.520E+00	1.916E-04	1.479E-04
5.000E-02	3.521E+00	7.531E-05	7.760E-05
1.000E-01	3.522E+00	7.615E-05	9.971E-05
5.000E-01	3.528E+00	8.954E-05	2.982E-04

Figure E-2. Response Surface

region. In chapter 2 of the report, it was stated that Hanford operating experience found the stable operating regions to be between 0.05 and 0.15M oxalic acid and between 2.5 - 3.5M H^+ , and that H^+ concentrations above 4.5M, yielded high plutonium oxalate solubilities. Examination of Figure E.2 shows that the equilibrium data can be used to give a sound reasoning for this experience.

Appendix F

Solution Technique for Least Squares Fit to Data (14)

The function form for the data fit is:

$$f(X,Y) = A + B \frac{X^4}{Y^2} + CY$$

Define the quantity ϕ^2 such that,

$$\frac{1}{\sigma^2} \sum_{i=1}^N \left[A + B \frac{X_i^4}{Y_i^2} + CY_i - f(X_i, Y_i) \right]^2 \equiv \phi^2(A, B, C)$$

where $X_i, Y_i, f(X_i, Y_i)$ are data points, and σ^2 is the uncertainty in the data.

In order to find the values of A, B, and C that yield a minimum value for ϕ^2 , the following relationship must hold.

$$\frac{\partial \phi^2}{\partial A} = 0 = 2 \sum_{i=1}^N \left[A + B \frac{X_i^4}{Y_i^2} + CY_i - f(X_i, Y_i) \right]$$

or rearranging

$$NA + B \sum_{i=1}^N \frac{X_i^4}{Y_i^2} + C \sum_{i=1}^N Y_i = \sum_{i=1}^N f(X_i, Y_i) \quad \dots (F-1)$$

$$\frac{\partial \phi^2}{\partial B} = 0 = 2 \left\{ \sum_{i=1}^N \left[A + B \frac{X_i^4}{Y_i^2} + CY_i - f(X_i, Y_i) \right] \cdot \left[\frac{X_i^4}{Y_i^2} \right] \right\}$$

or rearranging

$$A \sum_{i=1}^N \frac{X_i^4}{Y_i^2} + B \sum_{i=1}^N \frac{X_i^8}{Y_i^4} + C \sum_{i=1}^N \frac{X_i^4}{Y_i} = \sum_{i=1}^N f(X_i, Y_i) \cdot \frac{X_i^4}{Y_i^2} \quad \dots (F-2)$$

$$\frac{\partial \phi^2}{\partial C} = 0 = 2 \sum_{i=1}^N \left\{ \left[A + B \frac{X_i^4}{Y_i^2} + CY_i - f(X_i, Y_i) \right] \cdot Y_i \right\}$$

or rearranging

$$A \sum_{i=1}^N Y_i + B \sum_{i=1}^N \frac{X_i^4}{Y_i} + C \sum_{i=1}^N Y_i^2 = \sum_{i=1}^N (f(X_i, Y_i) \cdot Y_i) \dots (F-3)$$

Solving Equations (F-1), (F-2), and (F-3) simultaneously yields a least squares solution for the coefficients A, B, and C.

From Equation (F-1)

$$NA + S_{11}B + S_{12}C = S_{13} \dots (F-4)$$

From Equation (F-2)

$$S_{21}A + S_{22}B + S_{23}C = S_{24} \dots (F-5)$$

From Equation (F-3)

$$S_{31}A + S_{32}B + S_{33}C = S_{34}$$

or

$$A = (S_{34} - S_{32}B - S_{33}C) / S_{31} \dots (F-6)$$

Where $S_{ij} = \sum_{i=1}^N$ (respective terms of Equations (F-1), (F-2),

(F-3). Plugging Equation (F-6) into (F-5) yields

$$\frac{S_{21}}{S_{31}} (S_{34} - S_{32}B - S_{33}C) + S_{22}B + S_{23}C = S_{24}$$

$$B = \underbrace{\left[\left(-\frac{S_{32}S_{21}}{S_{31}} + S_{22} \right) \right]^{-1}}_{Z_1} \left[S_{24} + \underbrace{\left(-S_{23} + \frac{S_{33}S_{21}}{S_{31}} \right)}_{Z_2} C - \underbrace{\left[\frac{S_{21}S_{34}}{S_{31}} \right]}_{Z_3} \right]$$

.... (F-7)

Plugging Equation (F-7) into Equation (F-4) yields

$$-\frac{N}{S_{31}} \left(S_{34} - S_{32} \left\{ \frac{S_{24} + Z_2 C - Z_3}{Z_1} \right\} - S_{33} C \right) + S_{11} \left\{ \frac{S_{24} + Z_2 C - Z_3}{Z_1} \right\}$$

$$+ S_{12} C = S_{13}$$

$$\left[\left(\frac{N}{S_{31}} \left(\frac{-S_{32} Z_2}{Z_1} - S_{33} \right) + \frac{S_{11} Z_2}{Z_1} + S_{12} \right) C = S_{13} - \frac{N}{S_{31}} \left(S_{34} - \frac{S_{32}}{Z_1} (S_{24} - Z_3) \right) \right. \\ \left. \frac{Z_4}{\frac{-S_{11}}{Z_1} (S_{24} - Z_3)} \right]$$

$$C = \left\{ \frac{S_{13}}{Z_4} - \frac{N}{S_{31}} \left(S_{34} - \frac{S_{32}}{Z_1} (S_{24} - Z_3) \right) - \frac{S_{11}}{Z_1} (S_{24} - Z_3) \right\} \dots (F-8)$$

Once C is solved plugging back into Equations (F-7) and (F-6) yield the values for B and A respectively.

REFERENCES

1. Chapman, R. F., Separation Processes in Practice, Reinhold Publishing Co., New York, 1961.
2. Sherwin, M. B., et al, "Dynamic Behavior of the well-Mixed Isothermal Crystallizer", Crystallization From Solutions and Melts, Chemical Engineering Progress Symposium Series, p.59-74, No. 95, Vol. 65.
3. Becker, G. W. Jr., and Larson, M. A., "Mixing Effects in Continuous Crystallization", Crystallization From Solutions and Melts, Chemical Engineering Progress Symposium Series, p.14-23, No. 95, Vol. 65.
4. Randolph, A. D., "Comments on Recent Advances in the Analysis of Crystallization Processes", Crystallization from Solution: Factors Influencing Size Distribution, Chemical Engineering Progress Symposium Series, p.1-5, No. 110, Vol. 67.
5. Larson, M. A. and Randolph, A. D., "Size Distribution Analysis in Continuous Crystallization", Crystallization From Solutions and Melts, Chemical Engineering Progress Symposium Series, p. 1-13, No. 95, Vol. 65.
6. Moyers, C. G. Jr., and Randolph, A. D., "Crystal-Size Distribution and Its Interaction with Crystallizer Design", AIChE Journal, Vol. 19, No.6, p.1089-1103, Nov. 1973.
7. McCabe, W. L. and Smith, J. C., Unit Operations of Chemical Engineering, 2nd Ed., McGraw-Hill Book Co., Inc. New York, 1967.
8. Cleveland, J. M., The Chemistry of Plutonium, Gordon and Breach Science Publishers, New York, 1970.
9. Nordman, J., Qualitative Testing and Inorganic Chemistry, John Wiley and Sons, Inc., New York, 1957.
10. Harned, Herbert S. and Owen, Benton B., The Physical Chemistry of Electrolytic Solutions, Reinhold Publishing Corp., New York, 1958.
11. Estach, Ovid W., and Souders, Mott., Handbook of Engineering Fundamentals, Third Edition, John Wiley and Sons, New York, 1975.

12. Stoller, S. M., Richards, R. B., Reactor Handbook, Vol. II, Fuel Reprocessing, Interscience Publishers, Inc. New York, 1961.
13. O'Connor, P. R., in USAEC Report CN-1702, 1944.
14. Bevington, Philip R., Data Reduction and Error Analysis for the Physical Sciences, McGraw Hill Book Company, New York, 1969.
15. C. W. Gear, "Numerical Initial Value Problems in Ordinary Differential Equations", Prentice Hall, 1971.
16. C. W. Gear, Comm. A.C.M., 14, 176, 1971.
17. J. R. Barney, R. S., Ahluwalia, and A. I. Johnson, "DYN SYS 2.0 Users Manual", University of Western Ontario, 1975.
18. I. L. Jenkins, F. H. Moore, and M. J. Waterman, J. Inorg. Nucl. Chem. 27, 81, 1965.
19. International Tables for X-Ray Crystallography, Volume II, Birmingham, 1967.
20. Doto, P. C., "Production of Ceramic Grade Plutonium Dioxide", ARH-SA-213, Atlantic Richfield Hanford Co., Richland, Washington, April, 1975.
21. Pease, R. A., "Proposed Flowsheet - Processing of High Exposure Plutonium at the Purex Plant", ARH-2765, Atlantic Richfield Hanford Co., Richland, Washington, March, 1973.

NOTICE

"This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately-owned rights."