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INCINERATOR ASH DISSOLUTION MODEL FOR THE SYSTEM: PLUTONIUM, NITRIC ACID AND HYDROFLUORIC ACID

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A THESIS
Presented to
The Faculty of the Division of Graduate Studies
By
Eric Vincent Brown

In Partial Fulfillment
of the Requirements for the Degree
Master of Science in Chemical Engineering

Georgia Institute of Technology
June 1988

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DEDICATION

I dedicate this entire work to my parents, the late Martha Walters Brown and the late Charlie Bunion Brown. This is being done because most of the credit for the accomplishments and goals that I have achieved and will achieve in the future should be given to them. Although they are gone, they are truly not forgotten. May they always live through my actions and behavior as a person.

ACKNOWLEDGEMENTS

The first line of thanks is given to the good Lord who has provided me with the courage and the inspiration to see this research to its conclusion. Next, I would like to thank Dr. Leonard W. Gray of the Savannah River Laboratory (SRL) and Dr. Daniel W. Tedder of the Georgia Institute of Technology for their valuable assistance in this research. Many thanks also go to the members of the Actinide Technology Division of SRL for allowing me to work on this project in their facilities as well as providing both direct and indirect assistance to my work. A special word of appreciation goes to the GEM Consortium, Notre Dame, IN, the U.S. Department of Energy[1], and the Georgia Tech Foundation for their financial support of my graduate education. A special word of thanks goes to Beverly Adams and Don Morgan for their contributions to the success of this work.

Because it is impossible to name each and every individual who made a contribution to this work, I would like to thank all for their help in this very important chapter of my life.

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

NOMENCLATURE

Abbreviations

A_c = cross sectional area of draft tube
a = conversion factor
aa = submergence ratio
a_j, b_j, c_j, d_j, e_j = empirical constants for the heat capacity equations

B = activation energy for the viscosity dependence on temperature

C_d = drag coefficient
$C_{p,j}$ = heat capacity at constant pressure of the jth species
CMD = count mean diameter

dH/dx = change in the total head of liquid, feet H_2O per foot
dH_f/dx = change in the head of liquid due to friction, feet H_2O per foot
dH_h/dx = change in the head of liquid due to hydrostatic pressure, feet H_2O per foot
dH_s/dx = change in the head of liquid in single phase flow, feet H_2O per foot

D = diffusion coefficient
D_c = diameter of the draft tube
D_o = outer diameter of the dissolver

D_1 = distance between the bottom of the air sparge line and the bottom of the dissolver
d_p = average particle diameter
d_s = diameter of average surface area
d_v = diameter of average volume

E = activation energy for PuO_2 dissolution
E' = activation energy for the dissolution of silica

f = Fanning friction factor
$F_{Buoyant}$ = buoyant force on a spherical particle
F_{Drag} = drag force on a spherical particle
F_{HF} = molar flow rate of fluoride into the dissolver
$F_{j,i}$ = molar flow rate of the jth species into the ith dissolver
$F_{j,(i+1)}$ = molar flow rate of the jth species into the $(i+1)th$ dissolver
F_{PuO_2} = molar flow rate of PuO_2 into the dissolver
F_{SiO_2} = molar flow rate of silica into the dissolver
FRF = flow rate of incinerator ash feed

g = gravitational constant
g_c = Newton's law proportionality factor
G_A = volumetric flow rate of the gas inside the draft tube

ΔH = overall enthalpy change for the dissolver
H_j = specific enthalpy of the jth species
$[HF]_B$ = concentration of undissociated HF in solution
$[HF]_o$ = molarity of HF in the dissolver feed stream
$[HF]_S$ = surface concentration of undissociated HF

i = dissolver number i, $i.e.$ the ith dissolver

j = component number j, *i.e.* the jth component

K = constant for use in equation II.17
k' = reaction rate constant for the dissolution of silica by HF
k_m = mass transfer coefficient
k_m^v = mass transfer coefficient based upon dissolver volume considerations
k'_o = frequency factor for the dissolution of silica
k_{oa} = overall reaction rate constant
k_r = surface reaction rate constant for PuO_2 dissolution
k_{ro} = frequency factor for the PuO_2 reaction rate equation

L = height of liquid in the dissolver
L' = volumetric flow rate of liquid inside the draft tube

M = mass of a spherical particle
M_{HNO_3} = molecular weight of nitric acid

N = number of dissolver stages
N_{Re} = Reynolds number for flow of liquid inside draft tube, $\frac{\rho_L D_t V_N}{\mu_M}$
$N_{Re,p}$ = particle Reynolds Number, $\frac{\rho_L d_t V_{Rel}}{\mu_M}$
N_{Sc} = Schmidt Number, $\frac{\mu_M}{\rho_L D}$
N_{Sh} = Sherwood Number, $\frac{k_m d_t}{D}$
N_{PuO_2} = number of PuO_2 particles

PD_{PuO_2} = particle density of PuO_2

Q = rate of heat input

R = ideal gas constant

R_p = radius of a spherical particle
r_j = reaction rate of the jth species
r_k = reaction rate by kinetic considerations
r_m = reaction rate by mass transfer considerations
r_{PuO_2} = rate of dissolution of plutonium oxide
r_{SiO_2} = rate of dissolution of silica

S = surface area of PuO_2 per unit volume of dissolver fluid
S_{SiO_2} = exposed surface area of silica
S_{SiO_2} = surface area of silica per unit volume of dissolver fluid
S_{AP} = surface area per particle

T = temperature
$TVOL$ = total volume of solids in dissolver

u_c = minimum spouting velocity

V = volume of liquid in dissolver
V_{HF} = molar volume of undissociated HF
V_{HNO_3} = molar volume of nitric acid
V_L = velocity of liquid inside of draft tube
$V_{L,Ave.}$ = average liquid velocity in the dissolver
V_N = instantaneous average velocity of the liquid inside the draft tube
V_o = velocity of liquid in the annulus space
V_p = velocity of the particle
$V_{Rel.}$ = relative velocity of the particle

$VFRL$ = volumetric flow rate of liquid being pumped to a dissolver stage
$VOLP$ = volume per particle

W = weight of a spherical particle

X_{SiO_2} = fraction of silica dissolved
X_{HF} = fraction of fluoride consumed
x_1 = distance between the top of the dissolver fluid and the bottom of the air sparge line
x_2 = distance between the top of the draft tube and the bottom of the air sparge line

Greek

ϵ = void fraction

μ_L = viscosity of liquid mixture without any suspended solids
μ_{Lo} = frequency factor for viscosity calculations
μ_M = viscosity of liquid mixture

ϕ_s = volume fraction of solids in the dissolver

ρ_L = density of the dissolver fluid
ρ_S = density of PuO_2
ρ_{ash} = density of the incinerator ash

σ_g = geometric standard deviation for the particle size distribution

τ = residence time of solids

SUMMARY

This research accomplished two goals. The first was to develop a computer program to simulate a cascade dissolver system. This program would be used to predict the bulk rate of dissolution of plutonium oxide (PuO_2) in incinerator ash. The other was to verify the model in a single-stage dissolver system using dysprosium oxide (Dy_2O_3) as a surrogate.

The assumption was made that PuO_2 (and all of the species in the incinerator ash) exists as spherical particles. A model using the spherical particle assumption was incorporated to derive a rate equation. This rate equation was used to calculate the bulk rate of plutonium oxide dissolution using fluoride as a catalyst. Once the bulk rate of PuO_2 dissolution and the dissolution rate of all soluble species (using the PuO_2 bulk dissolution rate as an estimate) were calculated, mass and energy balances were written. A computer program simulating the cascade dissolver system was subsequently developed by using the mass and energy balances.

The experimental work consisted of conducting tests on a single-stage dissolver. A simulated incinerator ash mixture was made and added to the dissolver. Calcium fluoride (CaF_2) was added to the mixture to provide fluoride as a catalyst. A nine molar nitric acid solution was pumped at 20 liters per hour into the dissolver system. Samples of the dissolver effluent were analyzed for dissolved dysprosium and fluoride concentrations. This data was used as a basis for model verification.

The computer program proved satisfactory in predicting the fluoride concentrations in the dissolver effluent. The sparge air flow rate in the experimental work was predicted by the computer program to within 5.5 percent. The experimentally determined percentage of solids dissolved (51.34 percent) compared favorably to the percentage of incinerator ash dissolved (47 percent) in previous work. No

general conclusions on model verification could be reached by examining the experimentally determined dissolved dysprosium concentrations and comparing to the computer predicted plutonium concentrations. This is because rate data for PuO_2 dissolution is dependent upon the preparative history of the oxide. The only way that the correct rate data can be used in the model is to conduct a kinetic study on a sample of representative PuO_2. This PuO_2 would have the same preparative history as the PuO_2 in the incinerator ash.

CHAPTER I

INTRODUCTION

Plutonium, a member of the actinide series, is a metal with atomic number 94. Plutonium was discovered in 1941 at the University of California at Berkeley by Glenn T. Seaborg and colleagues[1]. Since its discovery, isotopes of mass numbers 232 through 246 have been identified with the most important isotopes being plutonium-238 and plutonium-239. All isotopes of plutonium are radioactive.

Plutonium was the first element to be synthesized. Because of its unique properties, the availability of plutonium has increased from microgram to tonnage quantities. The most useful characteristic of plutonium-239 is the large energy release associated with its fission. Upon fission, one gram of plutonium has the energy equivalent of that produced by the complete combustion of three metric tons of coal[2]. This energy has been used in the generation of electricity via nuclear reactors. It also has been used to provide the necessary power needed for military and industrial explosives.

One important characteristic of plutonium-238 is that it has a power density of 6.8-7.3 Watts/cm^3. Because of this, plutonium-238 has been used as a heat source. The heat is converted to electrical power through the use of thermocouples to provide power for deep-space probes and long-term space exploration experiments. An example of this use can be found in the Apollo-11 expedition to the moon. A package of instruments and support equipment, called the Apollo Lunar Surface

Experiments Package (ALSEP) was placed on the lunar surface. The power for this system was supplied by a thermoelectric generator that contained $^{238}PuO_2$ microspheres producing about 1480 Watts of thermal power. The amount of electrical power produced by such a generator is about 63 Watts. It was expected at the time that the resulting power decay for this system would be less than 1% per year[3].

Although plutonium is useful for science and technology, it is also a very toxic material. The main health hazard associated with plutonium is its tendency to accumulate and concentrate in the blood-forming tissues of the bones. The radioactive decay of plutonium-239 produces alpha particles. An alpha particle is a helium atom which has been stripped of its two electrons, thus producing a charged particle. Because alpha particles have a very low ability to penetrate through matter, alpha particles lodged inside the bone marrow tend to stay localized. They destroy the bone marrow cells through gene mutations and chromosome breakage. Gene mutations and chromosome breakage occur when the cell is "hit" by the charged (alpha) particles[4]. Because of this, work being done with plutonium is either performed remotely or in hermetically sealed gloveboxes having an air pressure slightly less than that inside the laboratory itself.

Plutonium metal is also very expensive. The cost of plutonium depends a great deal on its isotopic content. According to information given in the Kirk-Othmer Encyclopedia of Chemical Technology (Volume 18, p. 283, 1982 ed.), this cost ranges from about $40/kilogram[2] for weapons grade (eg. high 239 and 241 fissile-content material) to about $10,000/kilogram for advanced weapons grade (low fissile-content material). Thus, it is desirable that plutonium be recovered and recycled from any by-product or waste stream of the plutonium-processing operations. Another reason for the recovery of plutonium is that there are many enviromental concerns surrounding the handling and disposal of waste containing appreciable amounts of plutonium.

When plutonium is processed, a wide variety of plutonium-bearing residues are generated. Some of these residues include incinerator ash (ash resulting from the burning of gloves, absorbent wipes, tissue paper, etc. that has been contaminated with plutonium)[5] and glovebox floor sweepings (plutonium-containing powders that have been inadvertently dropped to the floor of a glovebox).

To recover the plutonium, aqueous processes typically are used. One attractive industrial operation consists of a continuous-flow cascade dissolver system, using an air-lift pump for the circulation and suspension of solid particles[6,7]. This system operates by gravity flow, where the liquid effluent stream from one dissolver stage is the feed stream to the next stage. As the solid particles are suspended in the solvent, dissolution will be achieved by mass transfer and a reaction at the surface of the suspended particles. Once the plutonium has been dissolved, it can be isolated and purified by either ion exchange or solvent extraction.

Another common method of dissolving plutonium has been to use a batch dissolver. A charge of incinerator ash contaminated with plutonium (in the form of PuO_2) is introduced to the dissolver. The solvent typically has consisted of nitric acid with fluoride ion introduced in the form of KF, CaF_2, or HF as a catalyst. Heat for the process has been supplied by electrical immersion heaters in the 1000 watt range, hot plate-type heaters, or steam coils. To agitate the mixture, the boiling action of the electric heaters, air sparge, mechanical agitation, or some combination of the three methods has been utilized.

Dissolvers used to process plutonium or any other fissile material on a full-scale operation must be sized so that a nuclear criticality will always be avoided. This can be done by making allowances so that the neutrons being given off by the fission of the radioactive compounds can escape from the dissolvers instead of entering back into the fission process. One way to accomplish this is to pay close attention to the geometric dimensions of the dissolvers, vessels, tanks, etc. that may be used to hold fissile material. This means that any cylindrical vessels must have small diameters and all slab tanks must be thin. As an example, consider an infinite, water-reflected slab that contains $Pu(NO_3)_3$ in a two normal nitric acid solution. For a two percent by weight plutonium-240 solution at a concentration of 90 grams of plutonium per liter, the critical slab thickness is 2.46 inches[8]. There are other methods combined with the process tank geometry criterion that can be used to prevent criticality from occurring. Some of these methods have included placing operating limits on fissile material concentrations and making available fixed neutron poisons. By using a combination of criticality control methods, one will have a two-error criterion in which it would take the application of at least two or more simultaneous and independent error conditions to cause nuclear criticality[9].

Despite its simplistic design and mode of operation, using the batch dissolvers in a full-scale operation has presented many problems. The acid in the off-gases corrodes the electrical heater connections. Working with the batch systems is labor-intensive and requires much handling inside the glovebox. Solids are difficult to keep in suspension in the batch dissolver, resulting in a very poor dissolution efficiency. To help solve the problem of the agitation of solids, mechanical agitators were incorporated into the batch dissolvers. Although this increased the bulk dissolution rate of plutonium, this method had its drawbacks as well. For example, using a propeller mixer required glovebox shaft seals, metal propeller blades and other parts that failed at an unacceptable rate[6] during the production process.

After much research, attention was focused on the air-lift cascade dissolver. The use of the air-lift cascade dissolver system provided many immediate advantages compared to the batch dissolvers. One of these advantages is in the proper choice of the materials of construction[6]. The use of the cascade dissolver system eliminated the need to use glovebox shaft seals, propeller blades, and other metal parts which would be in contact with the acid solution and/or the corrosive nitric acid vapor inside the glovebox. Use of the cascade dissolver system resulted in a higher percentage of plutonium being dissolved. Thus, in the same time, a larger bulk of plutonium would be recovered by using the cascade dissolver system.

It was decided after examining the cascade dissolver system that a computer model of it would be valuable. A satisfactory model would predict the total dissolution rate of PuO_2 in a nitric acid-fluoride mixture. The model would incorporate mechanical variables (such as the diameter of the draft tube and the height of liquid in the dissolver) as well as the effect of the fluoride concentration on the bulk dissolution rate of plutonium oxide. It would also incorporate the effects of certain process variables such as average particle size and size distribution of the ash, flow rate of the liquid species, working dissolver volume, number of dissolver stages, temperature, and the rate of sparge gas on the bulk dissolution rate. By combining these input data with material and energy balances around the dissolver(s), the amount of PuO_2 that can be dissolved per unit time could be calculated. Other quantities that could be determined would be the heat input rate to the dissolver(s) and the flow rates of the liquid and gas effluent streams from the dissolver(s). A model fulfilling these criteria has been constructed as the major product of this work.

The modeling approach assumed that the plutonium oxide and the other particles in the incinerator ash were spherical. This assumption simplified the equations describing the size distribution of incinerator ash being fed to the dissolver(s) (See Appendix A). It also helped simplify the particle terminal velocity equation that is obtained when writing a force balance around the particle (see Appendix B). This allowed the calculation of an average particle velocity inside the dissolver. A second key assumption was that the dissolution reaction can be described by a shrinking sphere model.

Using these assumptions and others listed in Appendix C, a computer model of the cascade dissolver system was constructed. This model can now predict the rate of bulk dissolution of PuO_2 inside a dissolver. A further assumption that the plutonium oxide and the ash dissolve at about the same rate was then used to predict the rate of bulk dissolution of all other soluble species in the incinerator ash. This allowed an estimate to be made of the quantity of other material[10] being dissolved. A listing of the components that can be found in incinerator ash is given in Appendix D.

CHAPTER II

LITERATURE REVIEW

II.1 Reaction Kinetics and Mechanisms for the Dissolution of PuO_2

In most chemical engineering texts, two different categories of chemical reactions are usually discussed – homogeneous and heterogeneous. As defined by Levenspiel[11]:

> A reaction is homogeneous if it takes place in one phase alone. A reaction is heterogeneous if it requires the presence of at least two phases to proceed at the rate that it does. It is immaterial whether the reaction takes place in one, two, or more phases, or at an interface, or whether the reactants and products are distributed among the phases or all are contained within a single phase. All that counts is that at least two phases are necessary for the reacton to proceed as it does.

Thus, based on this definition, the dissolution of plutonium oxide in nitric acid is a special type of heterogeneous reaction.

Now consider a heterogeneous reaction of the following form:

$$A(\text{solid}) + B(\text{in some fluid}) \rightarrow \text{Product(s)} \tag{II.1}$$

where the word fluid could describe either a liquid or a gas. In a heterogeneous reaction with no formation of an ash layer (known as the shrinking sphere model), the total rate of reaction depends upon three steps[11]

Step 1. Diffusion of B through a film layer to the surface of A.
Step 2. Reaction of A and B to form some product or products.
Step 3. Diffusion of the product(s) back through the film layer into the fluid.

A reaction describing the dissolution of PuO_2 can be written as follows:

$$PuO_2 + 6HNO_3 \rightarrow H_2Pu(NO_3)_6 + 2H_2O \tag{II.2}$$

In this reaction, undissociated HF serves as a catalyst for this dissolution. The desired product is the hexanitrato complex of plutonium in nitric acid solution. Brothers, Hart, and Mathers[12] proved by extraction studies that in nitric acid solutions above eleven molar, plutonium exists predominantly in the following molecular formula: $H_2Pu(NO_3)_6$. Others such as Lipis, Pozharskii, and Fomin[13] showed through spectrophotometric studies that this complex is found in nitric acid solutions in concentrations as low as seven molar. In the range of nitric acid concentrations between nine and eleven molar, the hexanitratoplutonitrate(IV) anion is the predominant species. For the purposes of this computer modeling, it was assumed that the plutonium in the nitric acid solution will exist as $H_2Pu(NO_3)_6$.

Reaction (II.2) can be rewritten as a series of six intermediate steps as seen in Figure II.1[14,15,16]. In this sequence of steps, it is proposed that reaction (II.3) written as

$$Pu(OH)^{3+} + HF \rightarrow PuF^{3+} + H_2O \tag{II.3}$$

is the rate limiting step[16]. According to the shrinking sphere model, the following sequence of steps will occur (Figure II.2):

Step 1. Diffusion of undissociated HF through the film layer to the oxide surface, which has been previously hydrated.
Step 2. Reaction between the HF and the hydrated oxide surface, forming a water molecule and a plutonium fluoride complex.
Step 3. Diffusion of the water molecule and the plutonium fluoride complex away from the surface of the sphere.

$$6HNO_3 \longrightarrow 6H^+ + 6NO_3^- \tag{1}$$

$$PuO_2 + 3H^+ \longrightarrow PuOH^{3+} + H_2O \tag{2}$$

$$PuOH^{3+} + HF \longrightarrow PuF^{3+} + H_2O \tag{3}$$

$$PuF^{3+} + H^+ \longrightarrow Pu^{4+} + HF \tag{4}$$

$$Pu^{4+} + 6NO_3^- \longrightarrow Pu(NO_3)_6^{2-} \tag{5}$$

$$2H^+ + Pu(NO_3)_6^{2-} \longrightarrow H_2Pu(NO_3)_6 \tag{6}$$

$$PuO_2 + 6HNO_3 \longrightarrow H_2Pu(NO_3)_6 + 2H_2O$$

Figure II.1: Sequence of Steps for the Dissolution of Plutonium Oxide

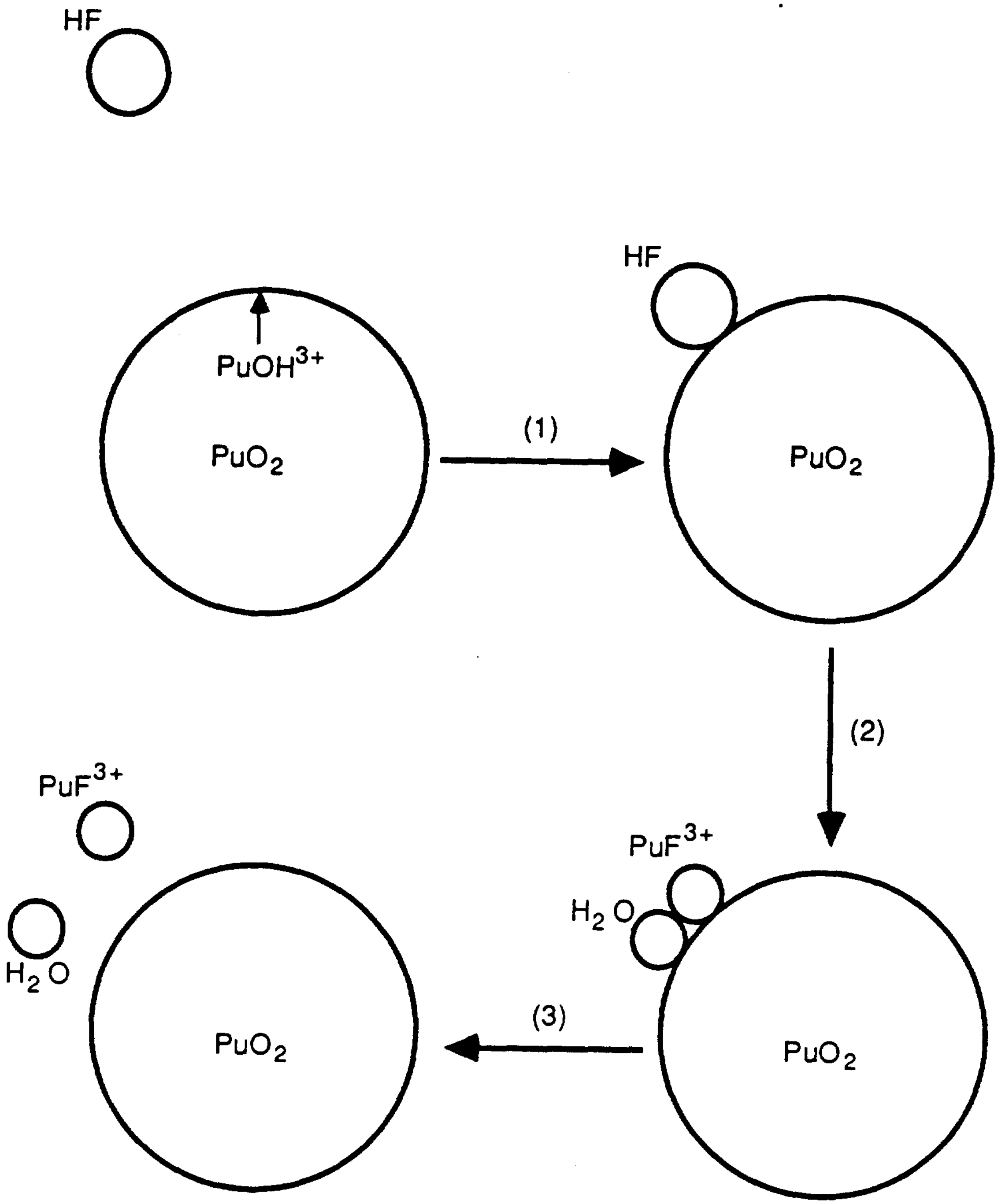

Figure II.2: Schematic Picture of the Dissolution of Plutonium Oxide

Based upon these steps, the rate of dissolution of PuO_2 can be viewed as a function of two forms of resistance. One is due to diffusion of the undissociated HF through the film layer. The other type of resistance is due to the surface reaction. A rate law to describe this dissolution can be written as follows:

$$r_{PuO_2} = k_{oa}[HF]_B \tag{II.4}$$

where:

r_{PuO_2} - rate of dissolution of plutonium oxide, g-moles/(length^3-time)
k_{oa} - overall reaction rate constant, time^{-1}
$[HF]_B$ - concentration of undissociated HF in solution, g-moles/length^3

The diffusional and surface reaction effects can be incorporated into the overall rate constant. An equation to describe these effects has been derived in Appendix E and can be written as follows:

$$\frac{1}{k_{oa}} = \frac{1}{k_m a} + \frac{1}{k_r S} \tag{II.5}$$

where:

k_m - mass transfer coefficient, length/time
k_r - reaction rate constant for the dissolution of PuO_2, length/time
a - conversion factor, length^{-1}
S - surface area of PuO_2 per unit volume of dissolver fluid, length^2/length^3

The first term on the right hand side of equation (II.5) describes the resistance due to mass transfer. The second term describes the resistance as a result of the surface reaction. An evaluation of each resistance term will give an idea of the overall rate constant.

II.2 Mass Transfer Resistance

An equation that describes mass transfer from a sphere has been used in the calculation of the mass transfer coefficient. This equation[17] is

$$N_{Sh} = 2 + 0.6 N_{Sc}^{1/3} N_{Re,p}^{1/2} \tag{II.6}$$

where:

N_{Sh} - Sherwood Number, $\frac{k_m d_p}{D}$, dimensionless
N_{Sc} - Schmidt Number, $\frac{\mu_M}{\rho_L D}$, dimensionless
$N_{Re,p}$ - particle Reynolds Number, $\frac{\rho_L d_p V_{Rel.}}{\mu_M}$, dimensionless

In equation II.6, the constant, 2, describes a system where pure molecular diffusion of a single component is occurring at steady-state conditions outward from a spherical surface into an infinite stagnant medium. The second term in equation (II.6) describes the effect of fluid motion on the Sherwood number. Thus, any movement of fluid around the particle will increase the Sherwood number to some value greater than two. The particle Reynolds number is based upon a relative velocity, that is, the difference between the velocity of the fluid and the velocity of the particle. To ensure that equation (II.6) remained dimensionally consistent, a conversion factor has been introduced to the mass transfer term. The calculation and derivation of this term is also described in Appendix E.

II.3 Reaction Rate Resistance

Barney[16] presents data listed in Table II.1 describing the reaction rate constants as a function of temperature for the dissolution of plutonium oxide in nitric/hydrofluoric acid solutions. In order that a temperature dependence may be incorporated into the rate of dissolution, Arrhenius' Law is used to develop an expression for the reaction rate constant:

$$k_r = k_o \exp(\frac{-E}{RT}) \qquad \text{(II.7)}$$

where:

k_r - reaction rate constant, length/time
k_o - frequency factor, length/time
E - activation energy, energy/g-mole
R - ideal gas constant, energy/(g-mole-abs. temp.)
T - temperature, absolute units.

The data in Table II.1 can be interpolated to determine the values of k_o and -(E/R). To do this, first equation (II.7) was rewritten in a linear form. Next, a linear regression analysis was incorporated to solve for k_o and (E/R) in the modified equation. The results are shown in Table II.2.

In this dissolution, one of the most important variables is the amount of exposed surface area of PuO_2. According to the shrinking sphere model, as the exposed surface area of PuO_2 decreases, the rate will decrease as well. However, for this problem, it was assumed that the average particle diameter of the ash feed could be used to estimate the exposed surface area of PuO_2 in the dissolver. This was done by using the Hatch-Choate equations[18]. The only requirement for valid use of the Hatch-Choate equations is that the particle size distribution in the incinerator ash be lognormal (i.e., plot out as a straight line on a log-probability graph). Figures II.3—II.5 show a log-probability graph of three incinerator ash samples[19]. Since the figures indicate that the mass distribution is nearly a straight line, it was assumed that the lognormal size distribution assumption was valid.

During the calculation of the amount of exposed surface area of PuO_2, an estimate was also made of the number of PuO_2 particles in suspension in the dissolver

Table II.1: Reaction Rate Constants as a Function of Temperature

Temperature, T, Deg. C	Rate Constant, $k_r * 10^6$, liter/(second-meter^2)
35	3.0
45	4.7
55	9.2
75	30

Table II.2: Least-Squares Fit of Table II.1 Data to Equation (II.7)

Temperature T, K	Rate constant k_r*10^6	(1/T)*10^3 K^{-1}	lnk_r
308.16	3.0	3.2451	-12.7169
318.16	4.7	3.1431	-12.2679
328.16	9.2	3.0473	-11.5963
348.16	30.	2.8722	-10.4143

Linear form of equation (II.7): $\ln k_r = \ln k_o - (E/R)(1/T)$

slope = -(E/R) = -6293.8748 K

intercept = $\ln k_o$ = 7.6169307

k_o = 2032.3148 liter/(second-meter^2) = 24004.172 feet/hour

correlation = -0.9963461

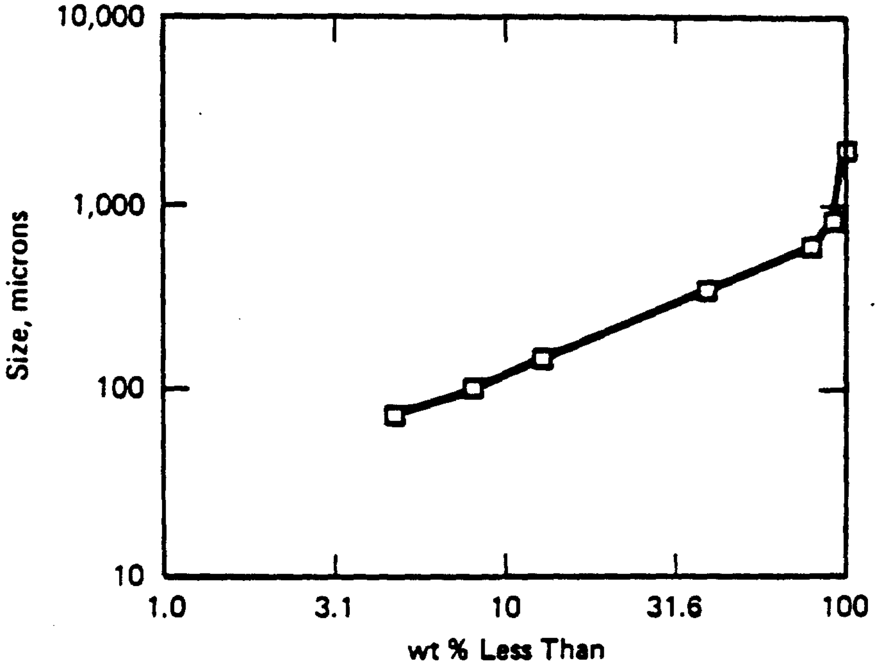

Figure II.3: Log-Probability Graph of Incinerator Ash Sample 1

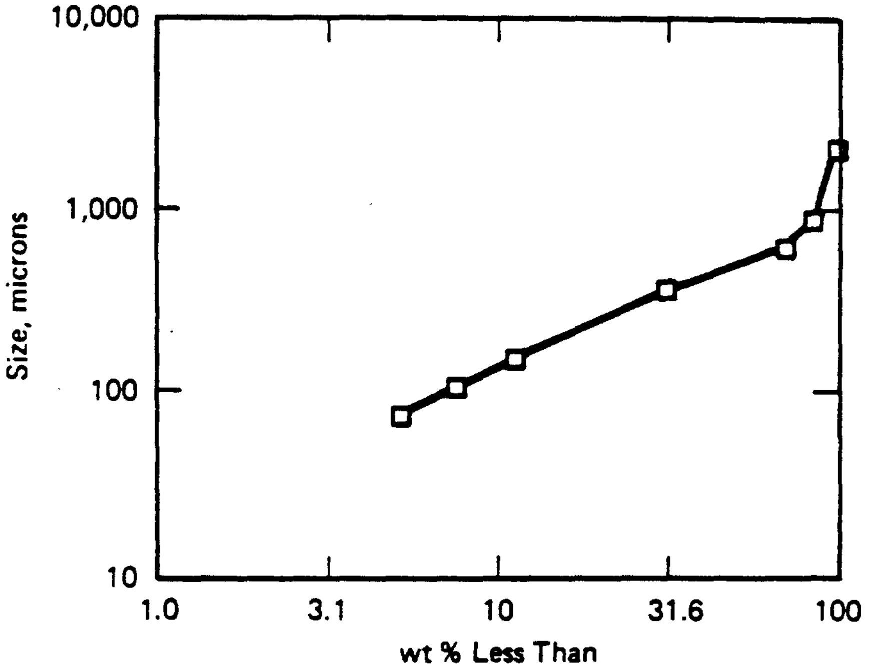

Figure II.4: Log-Probability Graph of Incinerator Ash Sample 2

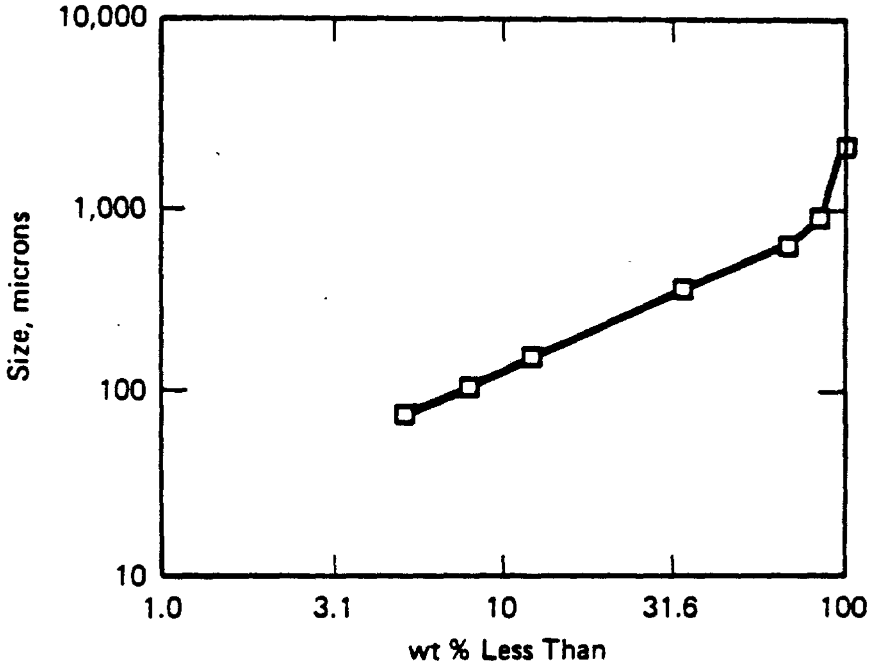

Figure II.5: Log-probability Graph of Incinerator Ash Sample 3 fluid. This estimate was based upon the residence time of the dissolver fluid as well as the molar flow rate of PuO_2 into the dissolver. Thus, it was postulated that the number of PuO_2 particles leaving the dissolver in the effluent stream were being replaced by the same number of PuO_2 particles entering the dissolver in the influent stream. Because of this, the number of PuO_2 particles and the total exposed surface area of PuO_2 in the dissolver would remain constant. These assumptions were used in conjunction with the Hatch-Choate equations as described above to estimate the number of particles in the dissolver.

The following equations are used to estimate the amount of exposed surface area of PuO_2 in the dissolver:

$$d_p = CMD\exp(3[\ln\sigma_g]^2) \tag{II.8}$$

$$d_s = CMD\exp([\ln\sigma_g]^2) \tag{II.9}$$

$$d_v = CMD\exp(1.5[\ln\sigma_g]^2) \tag{II.10}$$

$$SAP = \pi d_s^2 \tag{II.11}$$

$$VOLP = (\pi/6)d_v^3 \tag{II.12}$$

$$\tau = V/VFRL \tag{II.13}$$

$$N_{PuO_2} = \frac{\tau F_{PuO_2}}{\rho_S(VOLP)} \tag{II.14}$$

$$PD_{PuO_2} = N_{PuO_2}/V \tag{II.15}$$

$$S = SAP * PD_{PuO_2} \tag{II.16}$$

where:

d_p - average particle diameter, length
CMD - count median diameter, length
σ_g - geometric standard deviation for the particle size distribution, dimensionless
d_s - diameter of average surface area, length
d_v - diameter of average volume, length
SAP - surface area per particle, length^2
$VOLP$ - volume per particle, length^3
τ - residence time of solids, time
V - volume of liquid in the dissolver, length^3
$VFRL$ - volumetric flow rate of liquid being pumped to a dissolver stage, length^3/time
N_{PuO_2} - number of PuO_2 particles
F_{PuO_2} - molar flow rate of PuO_2 into the dissolver, g-moles/time
ρ_S - density of PuO_2, mass/length^3
PD_{PuO_2} - particle density of PuO_2, length^{-3}

Once the rate of dissolution of PuO_2 was calculated, the assumption of uniform dissolution of the ash and plutonium oxide was used to predict the dissolution rate of all other soluble components. The reaction stoichiometry for the soluble incinerator ash species as well as all of the other important reactions is shown in Section F of the Appendix.

II.4 Calculation of the Minimum Spouting Velocity

A typical dissolver design is shown in Figure II.6 along with some key dimensions. The dimensions of the dissolvers being used in actual production are limited to avoid criticality. To provide agitation and suspension of the solid material, sparge air is introduced into the center of the dissolver. The amount of sparge air required has been found to be a function of the dissolver geometry, particle size, particle density and liquid density[20]. Based upon these factors, Ghosh[21] derived an equation that predicts the minimum spouting velocity of air that is needed to suspend a system of solid particles:

$$u_c = K(\frac{d_p}{D_1})(\frac{D_1}{D_o})^2\sqrt{2gL\frac{\rho_S - \rho_L}{\rho_L}} \tag{II.17}$$

where:

u_c - minimum spouting velocity, length/time
K - dimensionless constant
D_o - outer diameter of the dissolver, length
g - gravitational constant, length/time^2
L - height of liquid in dissolver, length
ρ_S - density of PuO_2, mass/length^3
ρ_L - density of the dissolver fluid, mass/length^3

When using the English system of pounds, feet, and seconds, the value of K is 38.173. This equation thus defines the minimum air velocity that is needed to suspend a system of solid particles with an average diameter of d_p. Equation (II.17) was used just to give an idea of what spouting velocity may be sufficient to suspend the solid particles. This value may or may not be adequate to provide the necessary lift to transport a liquid up the draft tube for a particular dissolver design. If the calculated value of u_c was insufficient to provide the necessary lift to cause fluid movement, a new and arbitrary value of u_c was chosen by the computer program.

II.5 Miscellaneous

II.5.1 Reaction of HF with SiO_2

One of the main problems with the cascade dissolver system is the consumption of HF by silica in the ash[22]. This occurs via the reaction

$$SiO_2 + 4HF \rightarrow SiF_4 + 2H_2O \tag{II.18}$$

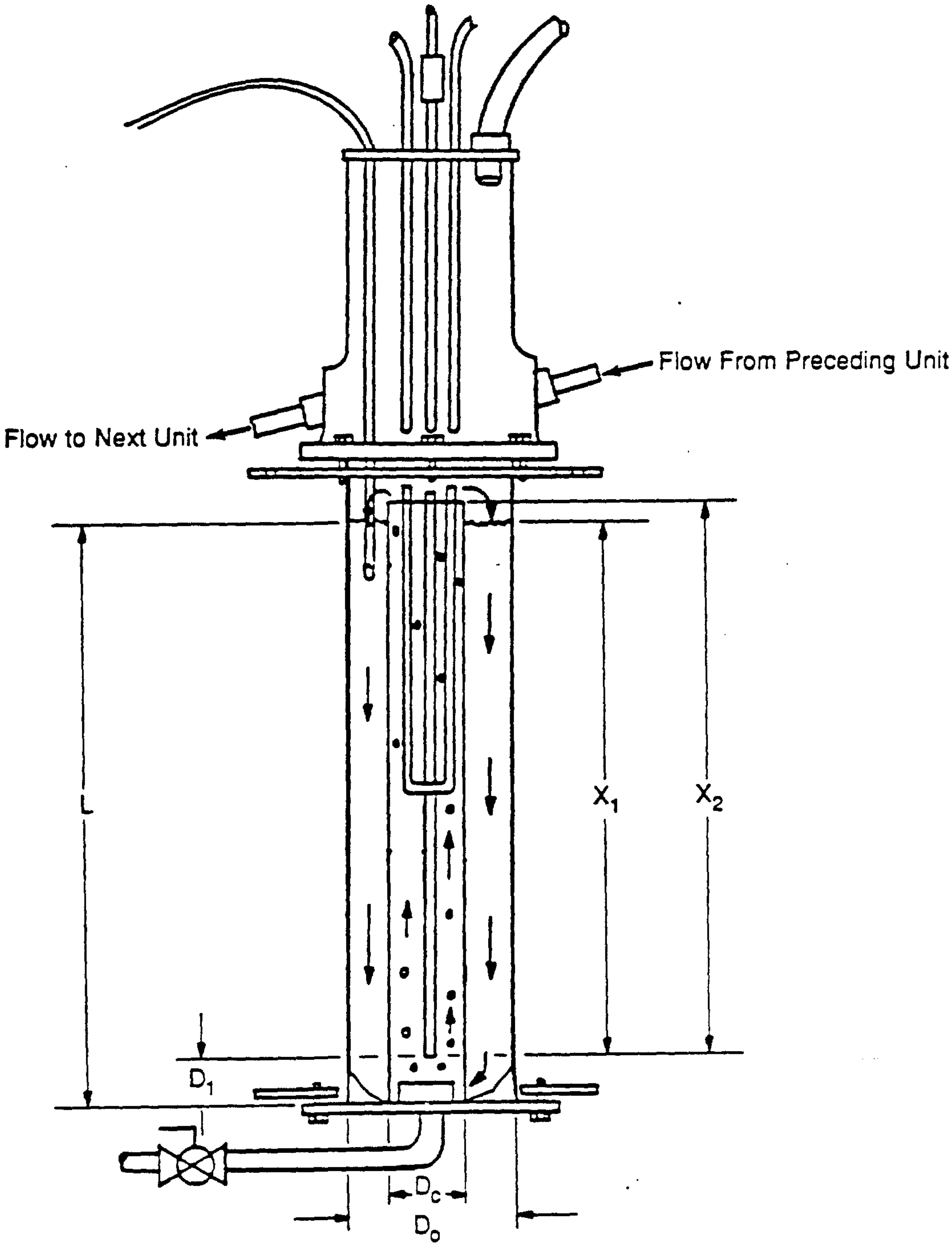

Figure II.6: Schematic of a Typical Incinerator Ash Dissolver

This reaction can be written as the sum of two intermediate reactions[23,24]:

$$SiO_2 + 6HF \rightarrow H_2SiF_6 + 2H_2O \tag{II.19}$$

$$H_2SiF_6 + aq \rightarrow SiF_4 + 2HF + aq \tag{II.20}$$

The rate law for Equation (II.19) is written as[24]:

$$r_{SiO_2} = -k'_o \exp(\frac{-E'}{RT}) S_{SiO_2}[HF]_B \tag{II.21}$$

where

r_{SiO_2} - rate of dissolution of SiO_2, mass/(time-length^2)
k'_o - frequency factor, mass/(time-length^2-HF molarity)
E' - activation energy, energy/g-mole
S_{SiO_2} - exposed surface area of SiO_2, length^2

For equation (II.21) the value of k'_o is 0.120 and the value of E' is 9 kcal/g-mole.

Assume that equation (II.21) in its current form can totally describe the dissolution of silica. This means equation (II.19) is also the rate limiting step for the consumption of HF with silica in the ash. Thus, in the computer model, equation (II.21) was used to predict the amount of silica consumed by HF.

There are two reasons why it is important to know about the effects of silica on the HF concentration. The first is that the HF concentration has a direct effect on the bulk rate of dissolution of PuO_2. The other reason is silicon tetrafluoride (SiF_4) gas is formed. When this gas forms, it is transported out of the dissolver(s) via the off-gas stream. The SiF_4 will then react with water in the off-gas stream, reforming hydrated silica. The hydrated silica plates out on the condenser, causing pluggage and other equipment problems[10,22].

To overcome the reduction of the bulk dissolution rate of PuO_2 as a result of HF being consumed by silica, it is possible that an excessive amount of fluoride could be added to the solvent. Although this would indeed increase the bulk dissolution rate of PuO_2, this proposal has its drawbacks. One problem is the corrosive nature of the fluoride. A higher fluoride concentration in the dissolver solution would increase the amount of maintenance required, decrease the expected equipment lifetime, and require additional aluminum nitrate ($Al(NO_3)_3$) to mask the fluoride before the leachant is sent to the ion exchange equipment for plutonium removal. The other problem in using an excessive amount of fluoride is that it would increase the possibility of forming plutonium tetrafluoride (PuF_4). Plutonium tetrafluoride is a solid that will precipitate out of the acid solution[25]. This solid would have to be redissolved to recover the plutonium. In addition, an excessive number of neutrons would be formed by the reaction of fluoride with alpha particles. The additional neutrons in the dissolver would increase the probability of a nuclear criticality.

II.5.2 Calculation of the Viscosity of the Dissolver Fluid

In the absence of mixture data, a correlation described by Gambill[26] was used to estimate the viscosity of the nitric acid solution with the suspended solids:

$$\frac{\mu_M}{\mu_L} = 1 + \frac{1.56\phi_S}{0.52 - \phi_S} \tag{II.22}$$

where:

μ_M - viscosity of liquid mixture, $\mathrm{lb_m/(feet\text{-}hour)}$
μ_L - viscosity of liquid without any suspended solids, $\mathrm{lb_m/(feet\text{-}hour)}$
ϕ_S - volume fraction of solids in the dissolver, $\mathrm{feet^3 solids/feet^3}$ dissolver fluid

The viscosity of a liquid is a function of temperature and for most liquids, it can be described by Arrhenius' Law in a form similar to equation (II.7):

$$\mu_L = \mu_{L_o} \exp\left(\frac{B}{RT}\right) \tag{II.23}$$

where

μ_{Lo} - frequency factor for viscosity calculations, $lb_m/(hour\text{-}feet)$

B - activation energy, kcal/g-mole

To determine the values of μ_{Lo} and (B/R), equation (II.23) was written in a least squares form and used in a linear regression program. This manner was similar to that used to fit the parameters in equation (II.7). The values of μ_L vs. T were determined by experiment[27] for a nine molar nitric acid solution. Tables II.3 and II.4 show the results of this data analysis.

II.5.3 Particle Surface Temperature Considerations

In this study, it was assumed that the surface of the plutonium oxide particles and the dissolver fluid are at the same temperature. For liquids in general, the thermal conductivity is relatively high, therefore the heat transfer coefficient at the surface of the particle would be large. Thus, there is little temperature difference between the particle and the liquid[28]. Therefore, the possibility of temperature gradients was neglected in conducting this modeling operation.

II.5.4 Precedence Order for Calculating the Bulk Dissolution Rate of PuO_2

One of the most important calculations in the computer model is the calculation of the bulk dissolution rate of plutonium oxide. However, due to the number of equations required to calculate this quantity, some means was necessary to organize all the equations and variables for the computer modeling.

Rudd and Watson[29] developed a design variable selection algorithm that can be used to determine the precedence order for solving a system of equations. In

Table II.3: Viscosity vs. Temperature Data for a Nine Molar Nitric Acid Solution

Temp., T, Deg. C	Viscosity, centipoise
90	0.64
80	0.76
70	0.86
60	0.98

Table II.4: Least-Squares Fit of Table II.3 Data to Equation (II.23)

Temp. T Deg. C	viscosity, μ_L $lb_m/(\text{feet-hour})$	$(1/T)*10^3$ K^{-1}	$\ln\mu_L$
363.16	1.5488	2.7536	0.4375
353.16	1.8392	2.8316	0.6093
343.16	2.0812	2.9141	0.7329
333.16	2.3716	3.0016	0.8636

Linear form of equation (II.23): $\ln\mu_L = \ln\mu_{Lo} + (B/R)(1/T)$

slope = (B/R) = 1692.2528 K

intercept = $\ln\mu_{Lo}$ = -4.2048

$\mu_{Lo} = 1.4924 * 10^{-2}$ $lb_m/(\text{feet-hour})$

correlation = 0.995101

this case, their strategy has been used to set up the equations in the proper order to determine the bulk rate of dissolution of plutonium oxide.

Section G of the Appendix shows the structural array for these equations. As a result of this chart, a precedence order for solving these equations has been determined with the degrees of freedom for this system being calculated as follows:

No. of Variables	61
No. of Equations	43
Degrees of Freedom	18

It was noted that two different situations occurred where a system of equations was solved simultaneously to obtain a final answer. These equations were solved iteratively as described in Chapter III.

CHAPTER III

DISSOLVER STAGE MODELING

Given certain particle characteristics, dissolvent characteristics, and dissolver specifications, a gas velocity u_c can be calculated using equation (II.17). This is the minimum gas velocity needed to keep a particle suspended in a liquid. The next sections trace the sequence of steps used to model the rest of a typical single-stage dissolver.

III.1 Air-Lift Equations

Nicklin[7] suggested that an air-lift pump can be interpreted as a problem in two-phase flow if the frictional losses entering and leaving the riser tube are neglected. As a result the following equations were used to model the air-lift section of the draft tube (see Figure II.6 in Chapter II and Figure III.1):

$$\frac{u_c}{\epsilon} = 1.2u_c + 1.2\frac{L'}{A_c} + 0.35\sqrt{gD_c} \tag{III.1}$$

$$G_A = A_c u_c \tag{III.2}$$

$$x_1 = L - D_1 \tag{III.3}$$

$$aa = \frac{x_1}{x_2} \tag{III.4}$$

$$\frac{dH_h}{dx} = 1 - \epsilon \tag{III.5}$$

$$V_N = \frac{G_A + L'}{A_c} \tag{III.6}$$

$$N_{Re} = \frac{D_c V_N \rho_L}{\mu_M} \tag{III.7}$$

$$f = 0.0014 + 0.125 N_{Re}^{-0.32} \tag{III.8}$$

$$\frac{dH_s}{dx} = \frac{4f}{D_c} \frac{V_N^2}{2g_c} \rho_L \tag{III.9}$$

$$\frac{dH_f}{dx} = (1 - \epsilon) \frac{dH_s}{dx} \tag{III.10}$$

$$\frac{dH}{dx} = \frac{dH_h}{dx} + \frac{dH_f}{dx} \tag{III.11}$$

$$\frac{dH}{dx} = aa \tag{III.12}$$

where:

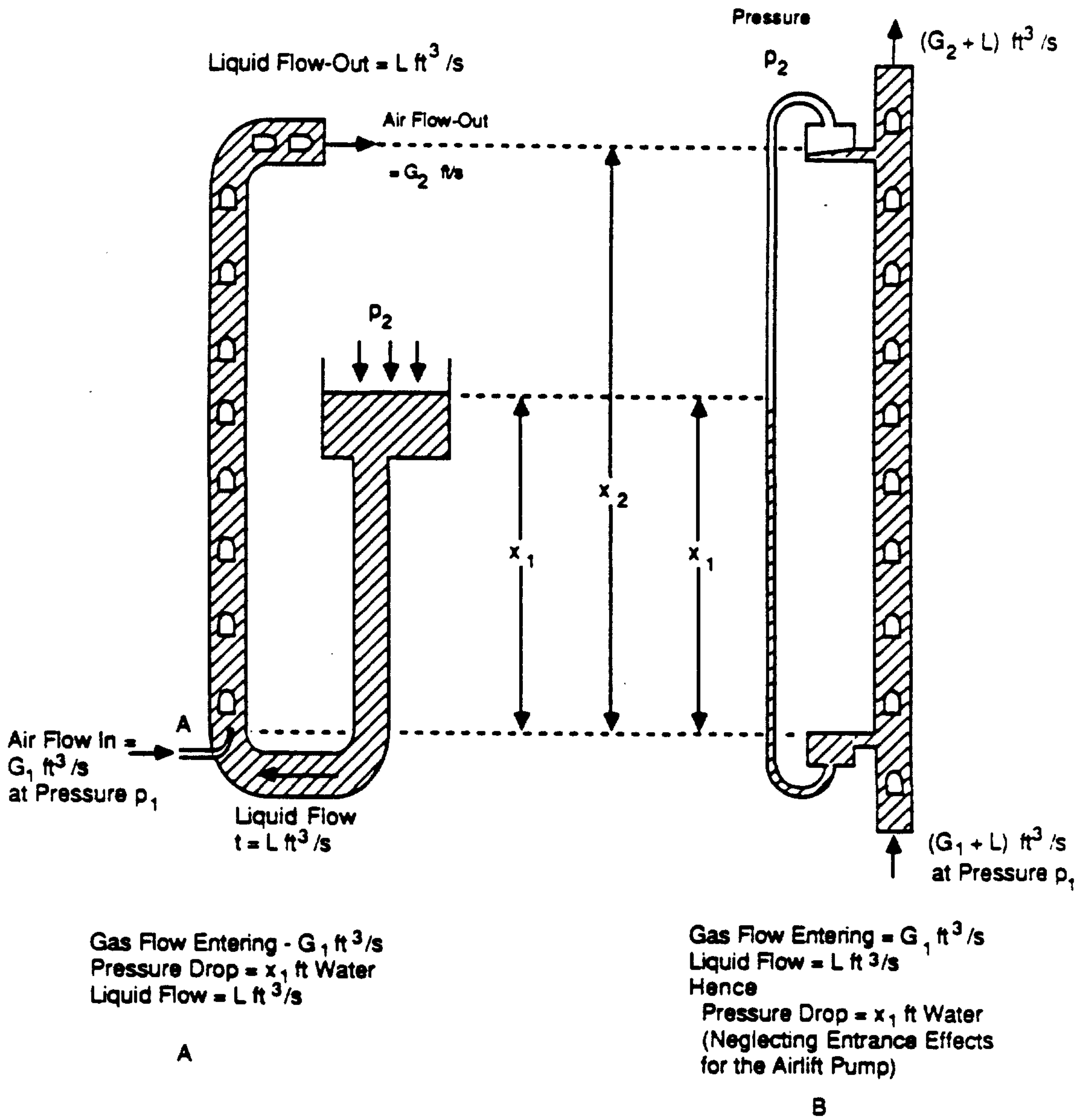

Figure III.1: The Airlift Pump, A, and the Equivalent Two-Phase Flow System, B. (The pressure at the top of the test length is p_2 in both cases) (Taken from Nicklin[7])

ϵ - void fraction, dimensionless

L' - volumetric flow rate of liquid inside draft tube, feet^3/sec

A_e - cross sectional area of draft tube, feet^2

D_e - diameter of draft tube, feet

G_A - volumetric flow rate of gas inside the draft tube, feet^3/sec

x_1 - distance between the top of the dissolver and the air sparge line, feet

D_1 - distance between the bottom of the air sparge line and the bottom of the dissolver, feet

aa - submergence ratio, dimensionless

x_2 - distance between the top of the draft tube and the bottom of the air sparge line, feet

$\frac{dH_h}{dx}$ - change in the head of liquid due to hydrostatic pressure, feet H_2O/foot

V_N - instantaneous average velocity of the liquid inside the draft tube, feet/sec

N_{Re} - Reynolds number for flow of liquid inside draft tube, dimensionless

f - Fanning friction factor[30], dimensionless

$\frac{dH_s}{dx}$ - change in the head of liquid in single phase flow[30], feet H_2O/foot

g_c - Newton's law proportionality constant, 32.2 foot-lb$_f$/(lb$_m$-second^2)

$\frac{dH_f}{dx}$ - change in the head of liquid due to friction, feet H_2O/foot

$\frac{dH}{dx}$ - change in the total head of liquid, feet H_2O/foot

By using equations (III.1) through (III.12), an iterative strategy was employed to determine the performance of an air-lift pump. Given the values of D_c, G_A, and aa, the proper value of L' was calculated by using a numerical method such as the method of false position. A description of this method is given later in this chapter.

III.2 Force Balance

An equation to calculate the velocity of a spherical particle as it moves though a fluid was derived by using a force balance. The equation was written so that at steady state, the sum of the buoyant and the drag forces acting on the particle is equal to the weight of the particle (see Section B in the Appendix for a complete derivation). As a result, an equation to calculate the velocity of the particle was written as follows:

$$\frac{\pi}{8} C_d \rho_L d_s^3 (V_{L,Ave.} - V_p)^2 + \frac{\pi}{6} d_v^3 \rho_L g - \frac{\pi}{6} \rho_S d_v^3 g = 0 \tag{III.13}$$

where:

C_d - drag coefficient, dimensionless

$V_{L,Ave.}$ - average liquid velocity in the disssolver, length/time

V_p - velocity of the particle, length/time

ρ_S - density of the solid particle, mass/length^3 (in this case, solid PuO_2, which is 140.4 pound-mass/foot^3 or 2.25 grams per cubic centimeter[31])

The drag coefficient, C_d, is a function of the particle Reynolds number, $N_{Re,p}$. For $N_{Re,p} < 0.2$, Holland[32] stated that

$$C_d = \frac{24}{N_{Re,p}} \tag{III.14}$$

For $0.2 < N_{Re,p} < 500$, Schiller and Naumann[33] found that

$$C_d = \frac{24}{N_{Re,p}}(1 + 0.15N_{Re,p}^{0.667}) \qquad \text{(III.15)}$$

If $N_{Re,p} > 500$, then

$$C_d = 0.44 \qquad \text{(III.16)}$$

In all cases

$$N_{Re,p} = \frac{d_s V_{Rel.} \rho_S}{\mu_M} \qquad \text{(III.17)}$$

and

$$V_{Rel} = V_{L,Ave} - V_p \qquad \text{(III.18)}$$

A method that is used to solve an equation such as equation (III.13) is to assume that equation (III.16) is valid and calculate V_p. Next, equations (III.17) and (III.18) were used to determine $N_{Re,p}$. If $N_{Re,p} < 500$, then an iterative method was used employing equations (III.13) — (III.15), (III.17), and (III.18). Eventually the proper value of $N_{Re,p}$ was determined. This is the particle Reynolds number that is used in the calculation of the mass transfer coefficient.

III.3 Mass Transfer Coefficients and Reaction Rate Constants

Equation (II.6) show that the mass transfer coefficient k_m can be calculated from three dimensionless groups. These three groups are the Sherwood number, N_{Sh}, the Reynolds number for particles, $N_{Re,p}$, and the Schmidt number, N_{Sc}. The defining equations for N_{Sh} and N_{Sc} are as follows:

$$N_{Sh} = \frac{k_m d_s}{D} \tag{III.19}$$

$$N_{Sc} = \frac{\mu_M}{\rho_L D} \tag{III.20}$$

where:

D - Diffusion coefficient for the movement of HF in HNO_3, length^2/time

Reddy and Doraiswamy[34] proposed an equation that can be used to estimate liquid diffusivity. This equation is taken from a modified form of the Wilke-Chang equation:

for the ratio $\frac{V_{HNO_3}}{V_{HF}} > 1.5$,

$$D = \frac{3.29 * 10^{-7} * M_{HNO_3}^{0.5} * T}{\mu_M * V_{HNO_3}^{0.333} * V_{HF}^{0.333}} \tag{III.21}$$

where:

M_{HNO_3} - molecular weight of nitric acid, grams/g-mole

V_{HNO_3} - molar volume of nitric acid, cubic centimeters/g-mole

V_{HF} - molar volume of hydrofluoric acid, cubic centimeters/g-mole

Due to a lack of data, the molar volumes of HNO_3 and HF for equation (III.21) had to be estimated. The molar volume of HNO_3 was estimated by using the specific gravity for a 46 weight percent solution of acid at 85 degrees Celsius[35]. In the case of the HF, the specific gravity for a 5 weight percent solution was used[35]. For equation (II.5) to remain dimensionally consistent, the mass transfer coefficient, k_m^v in the equation

$$r_{PuO_2} = k_m^v([HF]_B - [HF]_S) \tag{III.22}$$

where:

$[HF]_S$ - surface concentration of fluoride,
g-moles/liter

must be written in the units of time^{-1}. This can be done by using the following equations:

$$k_m^v = k_m a \tag{III.23}$$

$$a = \frac{\pi N_{PuO_2} d_s^2}{V} \tag{III.24}$$

A complete derivation of equations (III.23) and (III.24) can be found in Section E of the Appendix.

As described in Chapter II, the reaction rate constant is only dependent on the temperature at the surface of the particle. Thus, Equation (II.7) was used by itself to calculate the value of k_r. The reaction rate constant in combination with the exposed surface area of plutonium oxide was used to calculate the resistance due to surface area considerations. Once this is completed, the overall reaction rate constant k_{oa} was calculated from equation (II.5).

III.4 Fluoride Balance Constraints

In the computer program, the mixed reactor assumption was used to derive a set of equations that relates the amount of fluoride consumed to the amount of silica dissolved. This derivation is based upon reaction (II.18) and the rate law given as equation (II.21). The complete derivation of these equations can be found in Section H of the Appendix, therefore only the end results are given here:

$$X_{SiO_2} = \frac{k'[HF]_o S'_{SiO_2} V F_{HF}}{F_{SiO_2} F_{HF} + 4k'[HF]_o S'_{SiO_2} V F_{HF}} \tag{III.25}$$

$$X_{HF} = \frac{4F_{SiO_2} X_{SiO_2}}{F_{HF}} \tag{III.26}$$

where:

X_{SiO_2} - fraction of silica dissolved, g-moles SiO_2 consumed/g-moles SiO_2 fed

k' - reaction rate constant for the dissolution of SiO_2 by HF, mass/(time-length^2-HF molarity)

$[HF]_o$ - molarity of HF in the dissolver feed stream, g-moles/liter

S'_{SiO_2} - surface area of silica per unit volume of dissolver fluid, length^2/length^3

F_{HF} - molar flow rate of fluoride into the dissolver, g-moles/time

F_{SiO_2} - molar flow rate of silica into dissolver, g-moles/time

X_{HF} - fraction of fluoride consumed, g-moles fluoride consumed/g-mole fluoride fed

Equation (III.25) relates the fraction of silica dissolved to system variables that are either known or estimated. In equation (III.26), the fraction of silica dissolved is used to determine the fractional amount of fluoride consumed.

III.5 Mass and Energy Balances

Before the mass and energy balances around one dissolver could be written, a determination of the components in the influent and effluent streams around one dissolver was done. These results along with a description of the component numbering system used in the computer program can be found in Appendix I.

The steady-state mass balance equation for continuous flow systems was used for the writing of the material balances:

$$\text{Input} + \text{Generation} = \text{Output} + \text{Consumption} \qquad \text{(III.27)}$$

For example, the mass balance for the dissolution of plutonium oxide around the first dissolver stage will read as follows:

$$F_{PuO_2,1} + 0 = F_{PuO_2,2} + r_{PuO_2}V_1 \qquad \text{(III.28)}$$

where:

$F_{PuO_2,1}$ - molar flow rate of plutonium oxide into the first dissolver stage, g-moles/time
$F_{PuO_2,2}$ - molar flow rate of plutonium oxide out of the first dissolver stage, g-moles/time

A general mass balance for any species, j, that enters the ith dissolver stage in the influent stream, reacts and leaves in the effluent stream with no generation of species j can be written as follows:

$$F_{j,i} + 0 = F_{j,(i+1)} + r_jV_i \qquad \text{(III.29)}$$

where:

$F_{j,i}$ - molar flow rate of the jth species into the ith dissolver stage, g-moles/time

$F_{j,(i+1)}$ - molar flow rate of the jth species into the $(i+1)th$ dissolver stage or out of the ith stage, g-moles/time

r_j - reaction rate of the jth species, g-moles/(time-length^3). It will be assumed that the plutonium oxide and the incinerator ash will dissolve uniformly[36].

Figures III.2 and III.3 indicate use of the subscripts that allowed an expansion of all variables from a single dissolver stage to a cascade dissolver system with N stages. For clarity, the dissolver draft tube is not shown in Figure III.3.

Stoichiometric considerations were used to write mass balances for all species. The reactions that are thought to occur in this system are listed in Section F of the Appendix. Mass balances for the gaseous species in this dissolution system were handled by applying equation (III.27) accordingly.

The energy balance equation was used to estimate the net rate of heat input to the dissolver. An energy balance equation was formed by considering the first law of thermodynamics for a steady-state flow process. By neglecting the kinetic and potential energy terms and assuming that the amount of mechanical work done by the air sparge on the dissolver fluid is negligible, the following equation was obtained:

$$Q = \Delta H \qquad \text{(III.30)}$$

where:

Q - rate of heat input, energy/time

ΔH - overall enthalpy change for the dissolver, energy/time

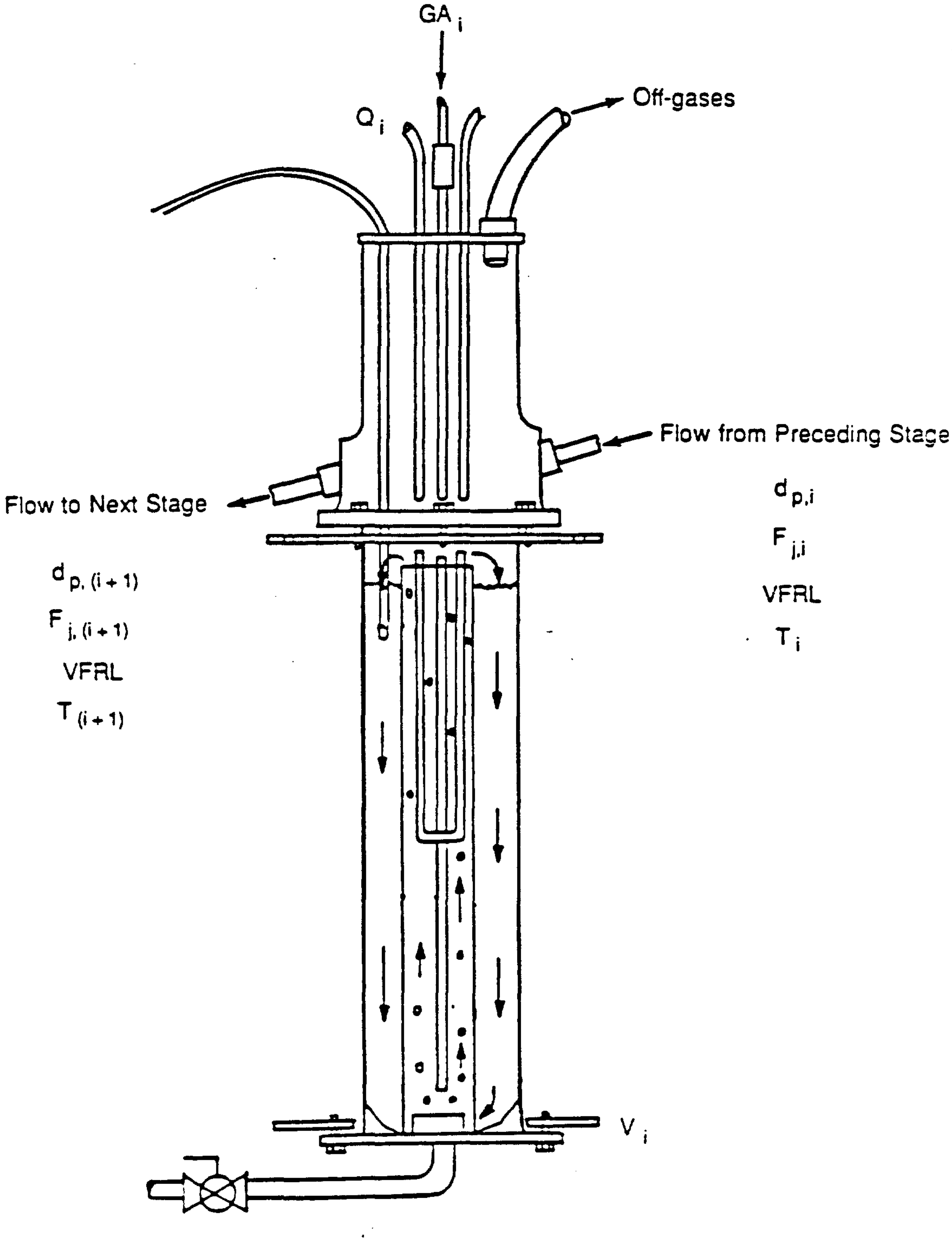

Figure III.2: A Description of the Variables Around the *ith* Dissolver Stage

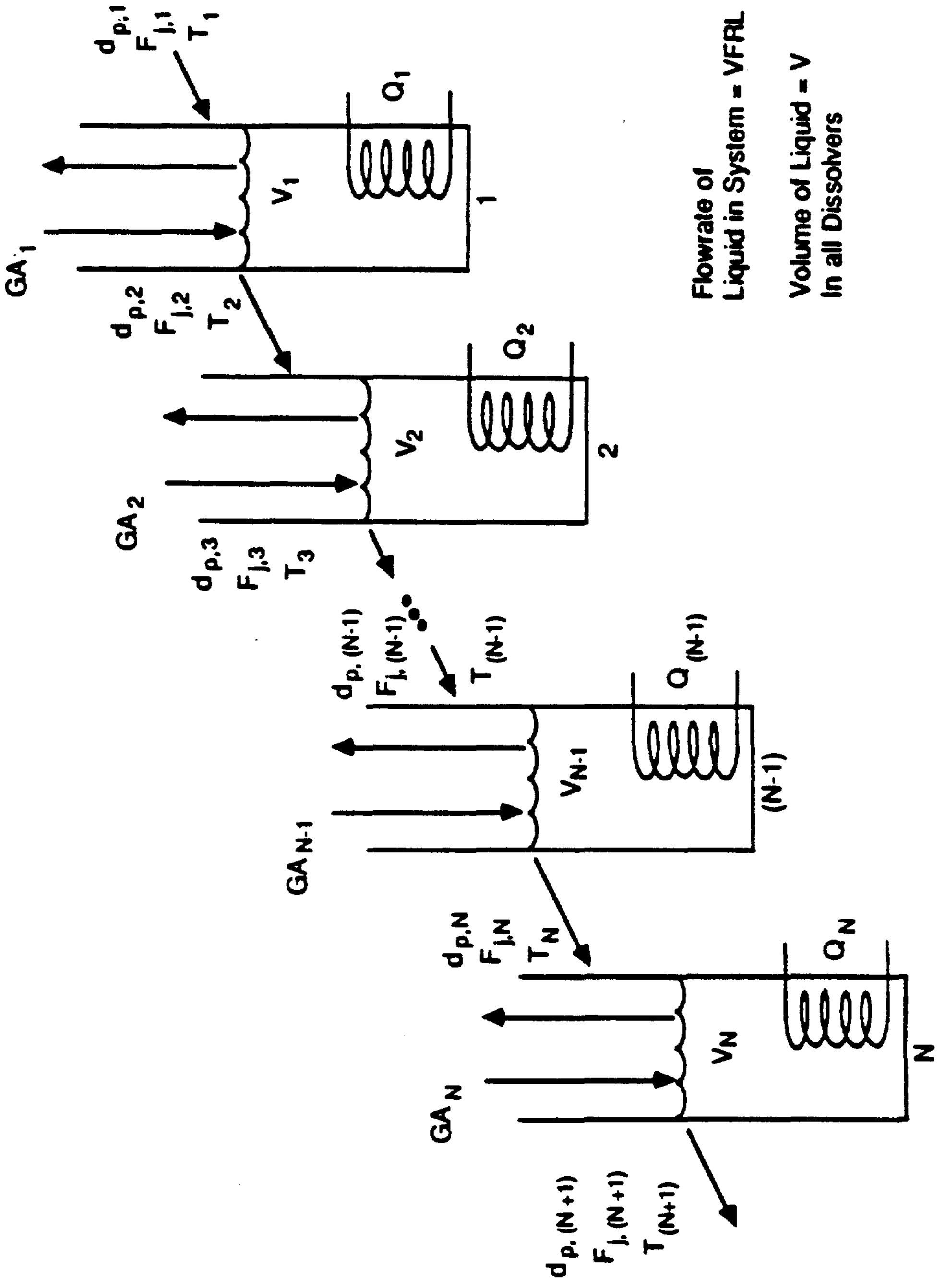

Figure III.3: Extension of Figure III.2 to a Cascade Dissolver System

The second term in equation (III.30) can be calculated from the following equation:

$$\Delta H = \sum F_{j,(i+1)} H_j - \sum F_{j,i} H_j \tag{III.31}$$

where:

H_j - specific enthalpy of the jth species, energy/g-mole

The second term in equation (III.31) represents the summation of the enthalpy of all components leaving the dissolver. The third term in equation (III.31) represents the summation of the enthalpy of all components entering the dissolver. To determine H_j, the following expression needed to be integrated:

$$dH_j = C_{p,j}\, dT \tag{III.32}$$

where:

$C_{p,j}$ - heat capacity of component j at constant pressure, energy/(g-mole-degree)

dH_j - differential change in the specific enthalpy of component j, energy/g-mole

dT - differential change in the temperature, temperature units

An integration of equation (III.32) gave the specific enthalpy of component j at a temperature T. This value of H_j is calculated based on reference state being defined as the atomic species of all components at 25 degrees Celsius. Appendix J describes the two forms of $C_{p,j}$ used in the modeling operation. Included in Appendix J are a list of the coefficients for each value of $C_{p,j}$. Also in this section is the heat of formation of each component. It is generally understood that the heat of formation is the constant of integration that results from the integration of equation (III.32).

Once all of the mass and energy balances have been constructed, a complete computer model of a single-stage dissolver can be finalized. A computer model for a single-stage dissolver can be found in Appendix K. This computer model has been written so that it can be expanded to a cascade dissolver system by varying the input data to the program.

III.6 Numerical Methods

Carnahan and Wilkes[37] describes one of the many known methods available for solving an equation of one root. This particular method is known as the regula-falsi method or the method of false position. The derivation of the equation used in this iterative scheme can be found in the original text; therefore, it is not shown here. Instead, the final equation is:

$$x_2 = \frac{x_{L1} f(x_{R1}) - x_{R1} f(x_{L1})}{f(x_{R1}) - f(x_{L1})} \tag{III.33}$$

where x_{L1} and x_{R1} are picked in such a way that $f(x_{L1})$ and $f(x_{R1})$ are opposite in signs. It is hoped that x_2 will be a value so that $f(x_2) = 0$. If the calculated value of x_2 is not within a specified tolerance, the corresponding value of either x_{L1} or x_{R1} along with its functional value $f(x)$ was changed and replaced with x_2 and $f(x_2)$. Which value is changed depended upon the sign of $f(x_2)$. In the computer program, this method was used to solve the air-lift equations and the particle force balance equation.

CHAPTER IV

EXPERIMENTAL PROGRAM

IV.1 Equipment Description and Operating Procedure

To verify the computer model, a single-stage, air lift dissolver system was designed and fabricated (See Figure IV.1 and Table IV.1). The dissolver (total liquid holdup volume 13.4 liters) had a diameter of six inches with a three inch diameter draft tube at its center. The parts for the dissolver shell consisted of a six-inch high glass cap attached to a 30-inch piece of glass pipe by a flange. To prevent leakage, a teflon gasket was positioned between the glass cap and pipe. A 33-inch length of three inch diameter glass pipe was fused to the inside of the glass cap. This glass pipe served as the draft tube for the dissolver. Four one-inch diameter holes were drilled in the draft tube. These holes were located one inch from the dissolver bottom. These holes allowed the dissolvent to flow from the annulus space into the draft tube. A 1/4-inch piece of glass tubing with a drain valve was attached to the side of the glass cap. This valve was used for draining the dissolver and removing some of the undissolved solids. In lieu of a steam coil, three 1000-watt glass immersion heaters were used to heat the dissolver. One heater was placed in the center of the draft tube. The other two were positioned in the annular space between the draft tube and the dissolver wall.

The system was agitated by blowing process air through a 1/8-inch diameter

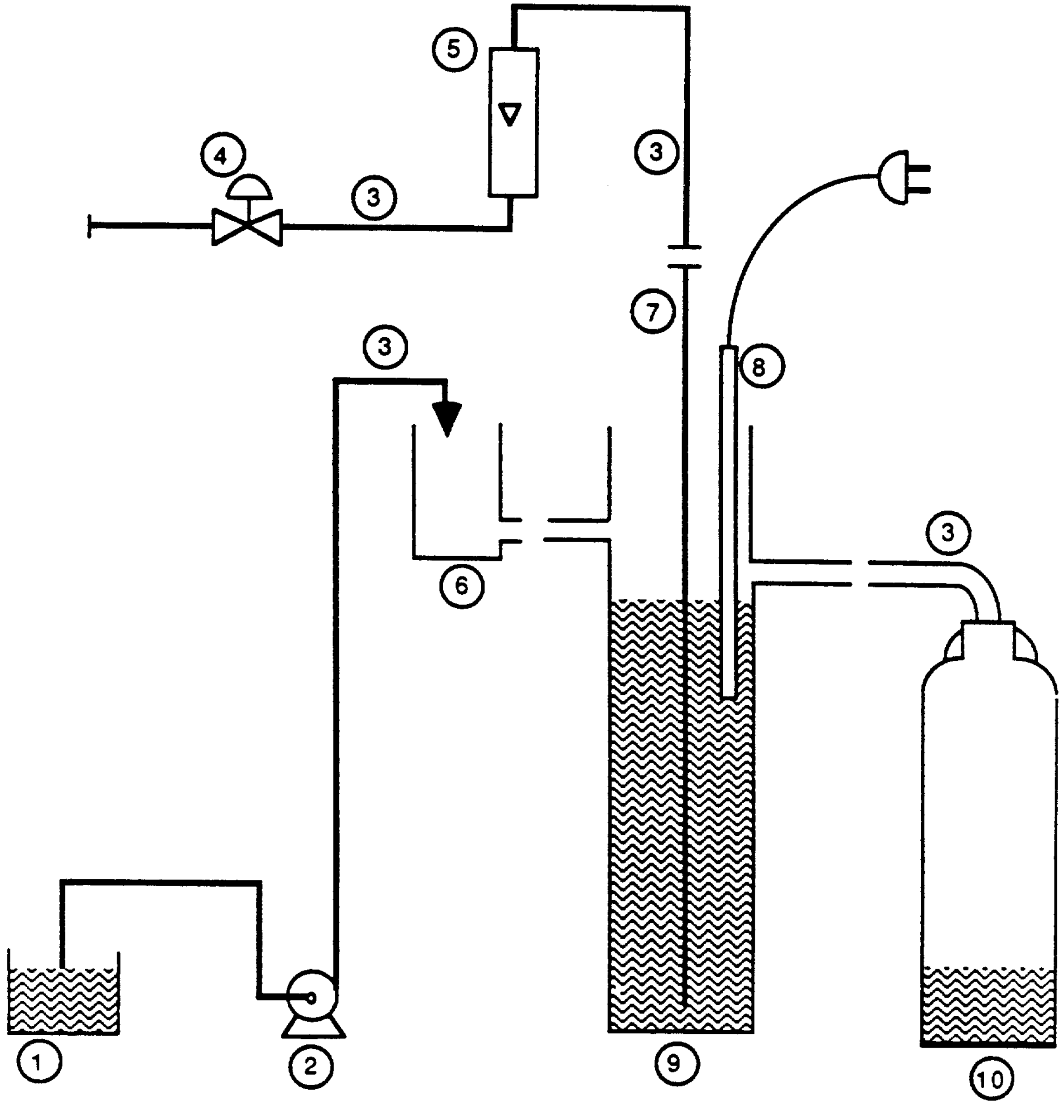

Figure IV.1: Schematic Drawing of the Experimental Dissolver System

Table IV.1: Key to the Schematic in Figure IV.1

Part No.	Equipment Name
1	Acid Feed Beaker
2	Acid Feed Pump
3	Sparge Air and Acid Feed Lines (Excelon Tubing)
4	Sparge Air Flow Control Valve
5	Sparge Air Rotameter
6	Solids Feed Beaker
7	Sparge Air Line (Stainless Steel)
8	Dissolver Immersion Heater (Note: Only One of Three Shown)
9	Experimental Dissolver (Draft Tube Not Shown)
10	Effluent Catch Bottle

stainless steel tubing. This tube was positioned in the center of the draft tube with its end one inch from the bottom of the dissolver. A rotameter was used to measure the flow rate of sparge air. Both the sparge air line and immersion heaters were held in place by laboratory clamps. These clamps were attached to three laboratory stands. These stands provided extra support for the dissolver.

The acid feed beaker and the solids feed beaker were made of Pyrex glass. These beakers had liquid capacities of 2000 ml and 1000 ml respectively. The effluent catch bottles were made of polypropylene plastic and had a liquid capacity of 26 liters each. Excelon plastic tubing was used to transport acid solutions and sparge air through the dissolver system. The stainless steel air sparging tube in the dissolver was the exception.

The dissolver was initially filled with 13.4 liters of nine molar nitric acid. The sparge air flow control valve was turned on. The sparge air flow was adjusted as needed to avoid splattering solution through the top of the dissolver. Once this was done, the three immersion heaters were energized for about 20 minutes to raise the solution temperature to 85 degrees Celsius. Then the experimental run was started by energizing the acid feed pump.

A nine molar nitric acid solution was pumped at a rate of 20 liters per hour into the solids feed beaker. This liquid was then gravity-fed into the dissolver. A non-radioactive surrogate material was also added to the solids feed beaker. This material consisted of the following: (1) incinerator ash from previous waste incinerator test work, (2) dysprosium oxide (Dy_2O_3) as a surrogate for plutonium oxide, (3) silica (SiO_2), and (4) calcium fluoride (CaF_2). The dysprosium oxide, silica and the calcium fluoride were blended together and blended into the ash. The following quantities of material were mixed together: (1) ash — 178.7 grams, (2) dysprosium oxide — 14.4 grams, (3) silica — 181.9 grams, and (4) calcium fluoride — 100 grams.

This mixture was added in increments of 475 grams to the solids feed beaker. To avoid foaming of the dissolvent, the solid mixture was added very slowly. The total amount of material added is shown in Tables IV.2 and IV.3. The flow of the nitric acid solution washed the solids into the dissolver. A judicious effort was made to ensure that the dissolver received a continuous flow of solid material throughout the experimental run. A difficulty encountered was pluggage of the solids feed beaker. Forceps were used when necessary to ensure that the solids feed beaker did not plug.

The overflow from the dissolver was collected in a series of effluent catch bottles. These bottles were removed and replaced as they filled with the dissolver effluent. The dissolver effluent was sampled 30 minutes after the introduction of the first solid material to the dissolver. Additional samples were taken at 30 minute intervals for four and one-half hours. Sampling was done by collecting a 250 ml volume of the effluent from the dissolver. The sample was submitted to the Analytical Development Division for chemical determination of dissolved dysprosium and fluoride concentrations.

IV.2 Results and Comparisons to the Computer Model

The verification process for the computer model was done by calculating the percent difference between the experimental data and the computer data. This comparison consisted of first conducting experimental work and gathering the results either through direct measurements or laboratory analysis. The computer program was then run for a single-stage dissolver. The input variables to the computer program were the same variables and operating conditions that existed during the experimental work. The differences between the results as given by the computer program and the experimental work were analyzed and interpreted.

Table IV.2: Flow Rates of All Materials to the Experimental Dissolver for the First Run

Material	Total Amount Added, Grams	Average Mass Flow Rate Grams/Hour	Average Molar Flow Rate G-Moles/Hour
ash	1250.0	277.8	—
Dy_2O_3	101.1	22.5	0.060
SiO_2	1273.1	282.9	4.707
CaF_2	700.0	155.6	1.992

9 M Nitric Acid Flow Rate (Liters/Hour)	20
Total Time for Run (Hours)	4.5
Average Dissolver Temperature (Deg. Celsius)	86.5
Feed Stream Temperature (Deg. Celsius)	22

Table IV.3: Flow Rates of All Materials to the Experimental Dissolver for the Second Run

Material	Total Amount Added, Grams	Average Mass Flow Rate Grams/Hour	Average Molar Flow Rate G-Moles/Hour
ash	1608.1	338.5	—
Dy_2O_3	130.0	27.4	0.074
SiO_2	1636.9	344.6	5.743
CaF_2	900.0	189.5	2.429

9 M Nitric Acid Flow Rate (Liters/Hour)	20
Total Time for Run (Hours)	4.75
Average Dissolver Temperature (Deg. Celsius)	88.3
Feed Stream Temperature (Deg. Celsius)	23

In addition, a set of Rocky Flats Plant (RFP) data is presented along with the computer and experimental results. This plant data is taken from an experimental run carried out during February 1987. The data is based upon a four-stage cascade dissolver system. The known operating conditions for this particular dissolver system are given in Table IV.4[38]. These operating conditions were necessary for this particular plant study.

An inductively coupled plasma-emission spectroscopy (ICP) method was used to determine the composition of the surrogate incinerator ash. The ICP method consisted of dissolving 100 grams of incinerator ash in a sodium peroxide (Na_2O_2) solution. The liquid solution was then injected into the plasma which is maintained at a temperature of approximatly 6000 degrees Kelvin. At these temperatures, the atoms in the dissolved ash sample were "excited" and thus "jumped" to a higher energy level. Since the higher energy level is not a stable level, the atoms returned to the lower energy levels and released energy in the form of photons. By measuring the energy of the photons, the presence of certain elements was detected. The amount of each element present was also measured with an uncertainty of ten percent. The results[39] are shown in Table IV.5. All components being fed to the dissolver were then calculatable.

It was assumed that the metallic elements in the surrogate incinerator ash existed as an oxide. Therefore, the data in Table IV.5 were used to calculate the molar flow rate of the respective oxide compounds. As an example, consider the compound M_xO_y where M is the element with a molecular weight of MW, x and y represent the subscripts in the molecular formula of the compound. The equation used to calculate the molar flow rate of M_xO_y is as follows:

$$\text{Molar Flow Rate of } M_xO_y = \frac{\text{Mass Flow Rate of } M/MW \text{ of } M}{x \text{ g-moles of } M}, \quad \text{(IV.1)}$$

Table IV.4: Rocky Flats Plant Operating Data for a Cascade Dissolver System Experimental Run

Total Amount of Ash Fed (Kg)	3.388
Total Amount of Plutonium Fed (Kg)	0.914
Total Run Time (Hours)	3.083
9 M Nitric Acid Flow Rate (Liters/Hour)	20
Amount of Calcium Fluoride (Grams CaF_2/Kg Ash)	235
Total Residence Time for Dissolvers (Hours)	1.2
Size of Dissolvers (Inches)	4
Number of Dissolvers in Cascade	4

Table IV.5: Elemental Composition of the Incinerator Ash using ICP Analysis

Element	Elemental Weight %	Calculated Oxide Weight %
Al	2.09	3.95
B	< 0.00096	< 0.0031
Ba	0.189	0.211
Be	< 0.00057	< 0.0016
Ca	4.88	6.83
Cd	< 0.0019	< 0.0022
Co	0.572	0.805
Cr	0.458	0.599
Cu	0.00711	0.00890
Fe	1.25	1.787
La	0.00489	0.00573
Li	0.00181	0.00390
Mg	0.307	0.509
Mn	< 0.0019	< 0.0030
Mo	0.00395	0.00595
P	0.125	0.286
Pb	0.224	0.241
Ru	< 0.0096	< 0.013
Si	29.5	63.1
Sn	0.0125	0.0142
Sr	0.00999	0.0118
Ti	1.19	1.98
U	< 0.096	< 0.109
V	0.00447	0.00657
Zn	< 0.0019	< 0.0024
Zr	< 0.00096	< 0.0013
Total Weight Percentages	40.99	80.49

A composite mass balance was drawn up for the components being introduced to the dissolver for each experimental run. This was done by using equation (IV.1) and the information given in Tables IV.2 and IV.3. Calculated results are shown in Tables IV.6 and IV.7. Included in the tables are the estimated molar flow rates of amorphous graphitic carbon. In lieu of a direct analysis, the amount of carbon in the ash was estimated by subtracting the metal oxide percentages from 100 percent. For example, by looking at Table IV.5, the calculated percent of oxides in this sample was 80.49 percent. Therefore there was (100–80.49) or 19.51 percent carbon by weight in the ash sample. This compares to 22 percent by weight that Johnson[10] reports in his work. Any compound that consisted of an elemental composition of less than 10^{-2} weight percent as given in Table IV.5 was considered negligible in the composite mass balance.

An important part of the data is the size parameters that describe the dissolver and the solid feed. These numbers are shown in Table IV.8.

A Neutron Activation Analysis (NAA) was used to determine the concentration of dissolved dysprosium and fluoride in the samples. The NAA was done by taking a 10 ml liquid sample and placing it in a small container called a "rabbit." The rabbit was placed in a neutron field and the sample irradiated by neutrons. Irradiating the sample caused the dysprosium and fluoride atoms to become radioactive. By counting the gamma rays from the activation products, the amounts of dissolved dysprosium and fluoride were determined. The accuracy of the analysis is plus or minus 10 percent at the 95 percent confidence level. The dissolved dysprosium concentrations are measured to within one percent at the 95 percent confidence level. The results of both experimental runs are shown in Tables IV.9 and IV.10[40].

Table IV.6: Molar Flow Rates of all Species to the Dissolver for the First Experimental Run

Component	Molar Flow Rate G-Moles/Hour
Al_2O_3	0.1075
BaO	0.003822
CaO	0.3382
Co_2O_3	0.01348
Cr_2O_3	0.01223
Fe_2O_3	0.03109
MgO	0.03507
P_2O_5	0.005608
PbO	0.003003
SiO_2	7.6254
SnO	0.0002925
TiO_2	0.06904
$H_2O(l)$	743.
HNO_3	180.
CaF_2	1.992
Dy_2O_3	0.060
C	4.5165

Table IV.7: Molar Flow Rates of all Species to the Dissolver for the Second Experimental Run

Component	Molar Flow Rate G-Moles/Hour
Al_2O_3	0.1311
BaO	0.004658
CaO	0.4121
Co_2O_3	0.01643
Cr_2O_3	0.01491
Fe_2O_3	0.03788
MgO	0.04274
P_2O_5	0.006831
PbO	0.003659
SiO_2	9.299
SnO	0.0003564
TiO_2	0.08409
$H_2O(l)$	743.
HNO_3	180.
CaF_2	2.429
Dy_2O_3	0.074
C	5.5034

Table IV.8: Dissolver Stage and Incinerator Ash Size Parameters for the Computer Program

$$L = 2.41667 \text{ feet}$$

$$D_1 = 0.08333 \text{ feet}$$

$$D_c = 0.25 \text{ feet}$$

$$x_2 = 2.6667 \text{ feet}$$

$$D_o = 0.5 \text{ feet}$$

$$d_p(1) = 1.586 \text{ x } 10^{-3} \text{ feet}$$

$$\sigma_g = 2.56$$

with:

L - height of liquid in dissolver

D_1 - distance between the bottom of the air sparge line and the bottom of the dissolver

D_c - diameter of the draft tube

x_2 - distance between the top of the draft tube and the bottom of the air sparge line

D_o - outer diameter of the dissolver

$d_p(1)$ - average particle diameter of the solids entering the first dissolver stage

σ_g - geometric standard deviation for the particle size distribution

Table IV.9: Dissolved Dysprosium and Fluoride Concentrations for the First Experimental Run

Sample Time Hour:Min	Dysprosium Conc., (PPM) mass basis	Moving Average Dysprosium Conc.	Fluoride Conc. (M)	Moving Average Fluoride Conc.
0:30	790	790	0.11	0.11
1:00	1275	1033	0.14	0.125
1:30	1205	1090	0.11	0.12
2:00	1123	1098	0.10	0.115
2:30	965	1072	0.089	0.110
3:00	878	1039	0.11	0.110
3:30	825	1009	0.09	0.107
4:00	1205	1033	0.12	0.109
4:30	1223	1054	0.11	0.109

	Dissolved Dysprosium	Fluoride
Cumulative Average For All Samples	1054 PPM	0.109 M
Population Standard Deviation (PSD)	179 PPM	0.0146 M
PSD * 2	358 PPM	0.0292 M
Variance	32041 PPM^2	0.000213 M^2

Table IV.10: Dissolved Dysprosium and Fluoride Concentrations for the Second Experimental Run

Sample Time Hour:Min	Dysprosium Conc., (PPM) mass basis	Moving Average Dysprosium Conc.	Fluoride Conc. (M)	Moving Average Fluoride Conc.
0:30	921	921	0.18	0.18
1:00	862	892	0.14	0.16
1:30	1119	967	0.16	0.16
2:00	1435	1084	0.18	0.165
2:30	1005	1068	0.15	0.162
3:00	1003	1058	0.15	0.16
3:30	1045	1056	0.11	0.153
4:00	1239	1079	0.17	0.155
4:30	1655	1143	0.24	0.164

	Dissolved Dysprosium	Fluoride
Cumulative Average For All Samples	1143 PPM	0.164 M
Population Standard Deviation (PSD)	244 PPM	0.0337 M
PSD * 2	488 PPM	0.0674 M
Variance	59536 PPM^2	0.00114 M^2

Equilibrium in the single-stage dissolver was assumed to occur within one liquid volume residence time. The residence time for the dissolver was (13.4/20) hours or 40.2 minutes. The dissolver appeared to be well mixed, so the assumption was made that 40.2 minutes was the maximum time required for equilibrium. Thus the concentrations of dissolved dysprosium and fluoride for each sample were used to compute an average concentration. These average concentrations were used as a basis for model verification.

The computer results, the experimental results and the plant results are presented in Tables IV.11 and IV.12[40,41]. The results presented are the sparge air flow rate, the effluent fluoride concentrations, the dysprosium and plutonium concentrations, and the percentage of the solids dissolved. The purpose of listing results about the RFP dissolvers is to provide information about RFP operations. Model verification is done by calculating the percent difference between the experimental data and the computer data.

The sparge gas flow rate was used to enhance the rate of dissolution of PuO_2 by keeping the PuO_2 particles suspended in the solvent. Therefore, it is important that the gas flow rate is neither too high nor too low. Roman[41] reports that an excessive sparge gas flow rate will prevent the particles from circulating inside the dissolver. A excessive flow rate will cause the particles to bounce back and forth around the same spot in the annulus of the dissolver.

The comparisons between the sparge air flow as predicted by the computer model and the experimental sparge air flow was excellent (5.5 percent difference). An accurate comparison between the computer predicted sparge air flow and the RFP sparge air flow was not possible. The sparge air flow in the computer model is dependent upon the dissolver geometry, particle size, and dissolvent characteristics. At RFP, the dissolvers were operated on a fixed sparge air flow rate. The sparge

Table IV.11: Comparison Between the Experimental Results and the Computer Results

	Experimental Results		Computer Results	
Measurement	Run No. 1	Run No. 2	Run No. 1	Run No. 2
Sparge Air Flow Rate (Feet^3)/Hour)	39.13	39.13	41.41	41.41
Fluoride Conc. (M)	0.109	0.164	0.1764	0.2080
Plutonium Conc. (Grams/Liter)	N.A.	N.A.	0.036	0.058
Dysprosium Conc. (Grams/Liter)	1.054	1.143	N.A.	N.A.
Amount of Solids Dissolved, Wt. Percent	26.44 (Est.)	51.34	2.23	2.51

N.A. - Not Applicable or Unattainable

Table IV.12: Rocky Flats Plant Results For A Cascade Dissolver Run

Sparge Air Flow Rate (Feet^3/Hour) 12.7

Fluoride Concentration (M) 0.33*

* Theoretical concentration of fluoride going into the RFP dissolvers. This is based upon actual production conditions.

Operating Time Hours	Pu Concentration** Grams/Liter
1.5	2.25
2.0	3.38
3.0	3.4

** Pu concentrations are for samples taken from the last dissolver stage at the time indicated since the feed was first introduced to the dissolver system.

air flow rate used depended only upon the amount of ash fed to the first dissolver stage. This sparge air flow rate was 32.2 standard cubic feet per hour (SCFH) per kilogram of ash fed to the dissolver system (This quantity was the total amount of sparge air fed to a three-stage cascade dissolver system)[41]. Assuming that each dissolver receives the same quantity of sparge air, dividing 32.2 by three gives 10.7 SCFH of sparge air per kilogram of ash fed to the dissolver system. The feed rate of ash in the plant data was 1.098 kilograms per hour; therefore multiplying 1.098 times 10.7 gives 11.8 SCFH of sparge air. If room temperature was assumed to be 70 degrees Fahrenheit, then 11.8 multiplied by (530 degrees Rankine/492 degrees Rankine) or 1.077 gives 12.7 cubic feet per hour of sparge air. This sparge air flow rate is not necessarily the optimum flow rate at which the dissolver(s) should be operated.

Samples of the dissolver effluent were taken so that the concentration of fluoride could be determined. In the first experimental run, the percent difference is 38.7 percent between the computer predicted fluoride concentration (0.1764 M) and the average experimental concentration (0.109 plus or minus 0.0146 M). The percent difference is deceiving because the numbers being compared are small. The same applies for the second experimental run. The difference here is only 21.1 percent between the average experimental concentration (0.164 plus or minus 0.0337 M) and the computer results (0.208 M).

Assuming a normal distribution, the probability is 95.44 percent the true average fluoride concentration is within two standard deviations of the cumulative average. Therefore, for the first experimental run, the likelihood is the actual average fluoride concentration lies between 0.0798 M and 0.1382 M. Thus, the percent difference between the computer results (0.164 M) and the actual average concentration lies within a range from +51.3 percent to +15.7 percent (the plus sign represents an overestimate of the true fluoride concentration by the computer program). The range for the actual average fluoride concentration in the second experimental run is from 0.0966 M to 0.2314 M. The range of percent differences between the computer results (0.208 M) and the average fluoride concentration is from +53.6 percent to -11.2 percent. Notice the computer predicted fluoride concentration lies within the 95.44 percent confidence interval. This fact means there is the probability the actual average fluoride concentration would be similar to the concentration as predicted by the computer program.

In examining the plant fluoride concentrations, the concentrations leaving the first dissolver stage or any of the other three stages was not known. The only available data was the theoretical concentration of fluoride in the feed stream of the first dissolver. This concentration was calculated based upon a ratio of 235 grams of calcium fluoride per kilogram of ash fed to the dissolver system. Since the ash was fed to the first dissolver stage at a rate of 1.098 kilograms per hour, multiplying 235 times 1.098 gave 258.03 grams of calcium fluoride per hour (3.308 gram-moles of calcium fluoride per hour). At a liquid flow rate of 20 liters per hour, the calculated calcium fluoride concentration is 0.1654 gram-moles per liter; or a fluoride concentration of 0.33 gram-moles per liter.

A scale factor (239 grams plutonium/162.5 grams dysprosium) was used to convert the dissolved dysprosium concentrations to approximate plutonium concentrations. The scale factor was multiplied by 1.054 grams of dysprosium per liter giving 1.550 grams of plutonium per liter for the first experimental run. This scale factor multiplied by 1.143 grams of dysprosium per liter gave a plutonium concentration of 1.681 grams of plutonium per liter for the second experimental run. In both cases the approximate plutonium concentrations are higher than the computer predicted plutonium concentrations (0.036 and 0.054 grams of plutonium per liter).

One reason why is the dysprosium oxide was added to the ash after the ash had been burned. Thus the dysprosium oxide would not be encapsulated in the ash matrix. Another difficulty was that the rate constants used in the computer program were for plutonium oxide which had been made by burning plutonium metal. This metal was used to prepare the oxide for the original kinetic study[16] under preparative conditions (burning temperature, pressure, etc.) which are not known. These preparative conditions and the type of plutonium metal used will determine the magnitude of any rate constants obtained in a kinetic study. A third difficulty is that the concentration of dissolved plutonium spilling out of the first dissolver stage at RFP is not known. Therefore, no conclusions about model verification can be made based upon the predicted plutonium concentrations and experimental dysprosium concentrations.

The total amount of solid material dissolved was also found. This consisted of first collecting the undissolved solids out of the dissolver and dissolver effluent. These solids were then dried at 100 degrees Celsius for one hour and weighed to determine the percentage of solids dissolved.

The first run consisted of estimating the amount of solids undissolved based upon the collection of 29 liters of effluent. This estimate was done by measuring the weight of dried undissolved solids recovered from 15 and 14 liters of dissolver effluent. These quantities were 248.3 grams and 226.0 grams respectively. The ratio of undissolved solids to dissolver effluent was determined for each quantity of effluent. These quantities were 16.55 and 16.14 grams of solids per liter of effluent. An average of these two numbers gave 16.34 grams of solids per liter of effluent. This number was multiplied by 90 liters of effluent (20 liters per hour times 4.5 hours), giving a total of 1470.6 grams of undissolved solids. Next the weight of dried solids recovered from the dissolver (459.8 grams) was added to the 1470.6

grams of solids recovered. This sum was 1930.4 grams of solids. Since four sheets of filter paper (weight, 0.5 grams each) were used to filter the solids, two grams was subtracted from 1930.4 grams. This difference gave 1928.4 grams of solids. This number represents the estimated amount of undissolved dried solids. Thus for the first run, the estimated percent of solids dissolved was [((2624.2-1928.4)/2624.2) * 100] or 26.44 percent solids dissolved.

The second run consisted of collecting all of the effluent and allowing the solids to settle. Most of the liquid was removed before filtering the remaining solids. After filtering, these solids were dried at 100 degrees Celsius for one hour and weighed. The total amount of undissolved solids collected from the dissolver and dissolver effluent was 1646.35 grams. Since eight sheets of filter paper (weight, 0.5 grams) were used for filtering, four grams was subtracted from 1646.35 grams. This difference was 1642.35 grams of undissolved solids. This analysis gave a percentage of solids dissolved of [((3375-1642.35)/3375) * 100] or 51.35 percent solids dissolved. The second run gave a more reliable percentage of solids dissolved because this is based upon collection of all of the dissolver effluent.

The percentage of ash dissolved in the second experimental run as compared to the computer results was very poor (95 percent difference). Because of this, a more accurate assessment of the ash dissolution rate would be needed in the program. However, Johnson[10] claims a 47 percent total solids dissolved for virgin incinerator ash in a four-stage cascade dissolver system. This is favorable as compared to the experimental results (51.34 percent for the second run) that was found in this work.

CHAPTER V

CONCLUSIONS

In the computer model, the sparge air flow rates and the fluoride concentrations were found to be in excellent agreement with experimental results. The difference between the sparge air flow rates calculated in the computer model and the experimental data was 5.5 percent. A statistical analysis of the fluoride concentrations indicated the computer model could predict the actual average fluoride concentrations leaving the dissolver.

Using air to sparge the dissolver is important for many reasons. The sparge air provides agitation for the dissolvent. This agitation increases the bulk rate of dissolution of PuO_2 by suspending the PuO_2 in the dissolver. Using sparge air eliminates the need for metal propeller blades, glovebox shaft seals, etc., which would be corroded by acid vapors.

The sparge air flow as calculated by the computer program is a function of a number of variables. These variables are the ones describing the dissolver geometry, particle sizes and dissolvent characteristics. Using multiple variables will give a better estimate of the sparge air flow required than a single variable.

The percent difference between the computer predicted sparge air flow and the experimental results were 5.5 percent for both experimental runs. Therefore, it was concluded all equations and assumptions used to model the draft tube of the dissolver were valid.

A catalyst is provided to enhance the bulk rate of dissolution of plutonium oxide by using fluoride. Without the fluoride, the PuO_2 will hardly dissolve at all. Thus, it is important some fluoride be provided in the form of HF, CaF_2 or KF. It is just as important an excessive amount of fluoride is not used in the dissolver. Too much fluoride will decrease equipment lifetime, precipitate out unwanted plutonium tetrafluoride (PuF_4) and increase the amount of fluoride that must be complexed in the dissolvent.

The probability the true average fluoride concentration lie within two standard deviations of the average experimental concentrations is 95.44 percent. An analysis of experimental run two indicated the computer predicted fluoride concentration (0.208 M) was within a range of two standard deviations (0.0966 M to 0.2314 M) of the average experimental fluoride concentration (0.164 M). The analysis thus pointed out the probability the program may calculate the actual fluoride concentration present in the dissolver effluent. Therefore, it is concluded the assumptions and equations used in the model to predict fluoride concentrations are valid.

The agreement between the total amount of solid material dissolved in this work (51.34 percent) and that found by Johnson[10] (47 percent) was excellent. These results are based upon a single-stage dissolver used in this work and a four-stage dissolver system used by Johnson. The conclusion here is that most of the soluble material in the ash is probably dissolved in the first stage of a cascade dissolver system.

Based upon the criterion used, it is indicated the computer model does have some application to the RFP dissolvers. These applications are in estimating sparge air flow rates and fluoride concentrations. The main conclusion is the model should be used only under the conditions and assumptions for which it was developed and subsequently tested. If this rule is followed, the model has the potential to become a useful simulation tool.

CHAPTER VI

RECOMMENDATIONS

This summary provides some of the reasons for the discrepancies and difficulties that were observed in this research. The analysis of these problems will open other aspects of research that can be done with the cascade dissolver system.

An important factor is the ability to use rate data that is representative of the plutonium oxide being dissolved. Barney[16] states that the rate at which plutonium oxide can be dissolved depends a great deal upon its preparative history. This history includes both the temperature at which the oxide was formed and the temperature which the oxide may have been reheated or reburned. Christensen and Maraman[42] indicate that, in general, oxides which have been heated to temperatures less than 600 degrees Celsius are considered to be easy to dissolve. Any oxides heated to temperatures between 600 and 1000 degrees Celsius require more stringent procedures. Oxides that have been fired at temperatures of greater than 1000 degrees Celsius require more extreme measures. This assessment was proven in part experimentally by Molen and Wing[43]. They found that redrying ash heels at temperatures of greater than 650 degrees Celsius drastically reduced the effectiveness of a 12.5 M HNO_3-0.2 M CaF_2 solvent system.

Rate data should be determined for each type of feed before the computer model can be used for dissolution studies. This rate data should be based upon the plutonium oxide in the specific feed. Only then would the oxide used have a preparative history based upon the conditions of the incinerator that produced the ash.

The only way the correct rate data can be used is to actually measure the dissolution rate of PuO_2. The oxide would be a sample taken from the incinerator ash. This oxide would be representative of the material that is actually being dissolved. Only under these conditions where the actual material being used is PuO_2 (and not a surrogate) can the correct rate data be gathered and used.

It would be incorrect to take one set of rate data and use it to model the dissolution of every form of plutonium oxide. If the ash consisted of oxides from different and various sources, even an attempt to model this particular system would be impractical.

One assumption was that the plutonium oxide and the other solids dissolve at the same rate. This assumption may not be true if the plutonium oxide was formed at a temperature of above 600 degrees Celsius. It would be more useful to measure the rates of dissolution of the solid species that is soluble in nitric acid. Rate laws can then be formed for these species.

The usefulness of this computer model could be enhanced if these comments and suggestions for future work could be implemented. Another area of possible research would be to examine the model by adjusting a particular set of variables and/or assumptions. This would provide the opportunity to examine which of these factors are more important in the modeling of the cascade dissolver system.

APPENDIX A

DESCRIPTION OF THE HATCH-CHOATE EQUATIONS

In particle statistics, use is made of many types of distributions for analyzing particle sizes. The most common distribution, however, is the lognormal distribution. The real power of this type of distribution is that any number of properties describing a particular particle distribution can be determined from just two parameters. These two parameters in this case are the mass median diameter, d_p and the geometric standard deviation, σ_g. An equation to relate these two variables are as follows:

$$d_p = CMD \exp(3\,[\ln \sigma_g]^2) \tag{A.1}$$

where

CMD - count median diameter, length
σ_g - the ratio of the diameters at the 84% and the 50% cumulative size points (eg. $d_{84\%}/d_{50\%}$), dimensionless

Once the count median diameter is determined, the diameter of average surface, d_s and the diameter of average volume, d_v can be calculated. This is done by using the following equations:

$$d_s = CMD \exp([\ln \sigma_g]^2) \tag{A.2}$$

$$d_v = CMD \exp(1.5\,[\ln \sigma_g]^2) \tag{A.3}$$

Therefore, d_s is that size particle whose surface area multiplied by the total number of particles will give the total surface area. Likewise, d_v represents that size particle whose volume multiplied by the total number of particles will give the total volume. A further description of these equations, known as the Hatch-Choate equations, can be found in the literature[18].

APPENDIX B

DERIVATION OF AN AVERAGE VELOCITY EQUATION USING A FORCE BALANCE

To calculate the mass transfer coefficient for matter diffusing from a spherical particle, some means must be used to determine the velocity of the particle as it is being suspended in a fluid. The way to do this is to derive an equation that can be used to calculate the velocity of the particle as it is being suspended.

Consider a spherical particle of diameter d_p being suspended in some fluid moving upwards at an average velocity, $V_{L,Ave}$. Under these conditions, a force balance can be written on the particle as follows:

$$M\frac{dV_p}{dt} = F_{Buoyant} + F_{Drag} - W \tag{B.1}$$

where

M - mass of the particle
V_p - velocity of the particle
$F_{Buoyant}$ - buoyant force acting on the particle
F_{Drag} - drag force acting on the particle[44]
W - weight of the particle

The three quantities on the right hand side of equation (B.1) can be written in terms of the particle and the fluid properties:

$$F_{Buoyant} = (\frac{\pi}{6})d_p^3\rho_L g \tag{B.2}$$

$$F_{Drag} = C_d(\frac{\pi}{8})\rho_L d_s^2 (V_{L,Ave.} - V_p)^2 \tag{B.3}$$

$$W = Mg = (\frac{\pi}{6}) d_v^3 \rho_S g \tag{B.4}$$

where

ρ_L - density of the liquid
ρ_S - density of the solid
g - acceleration of gravity

Assume steady-state conditions so that equation (B.1) is equal to zero, or

$$\frac{dV_p}{dt} = 0 \tag{B.5}$$

Substituting equations (B.2) through (B.5) into (B.1), one then obtains

$$C_d(\frac{\pi}{8})\rho_L d_s^3 (V_{L,Ave.} - V_p)^2 + (\frac{\pi}{6}) d_v^3 \rho_L g - (\frac{\pi}{6}) d_v^3 \rho_S g = 0 \tag{B.6}$$

Now equation (B.6) can then be solved for V_p, the particle velocity.

APPENDIX C

MODELING ASSUMPTIONS

The following list indicates the assumptions that have been made in the computer model of the cascade dissolver system. Any assumptions that need further explanation are described either in other sections of the Appendix or are referred to in the literature as indicated.

1. The incinerator ash and the plutonium oxide in the cascade dissolver system can be thought of as a system of spherical particles.
2. Steady-state conditions exist throughout the system. In other words, all time derivatives are equal to zero.
3. There is complete mixing of the dissolver fluid which allows the use of the mixed reactor assumption.
4. The rate of reaction inside the dissolver is equal to the rate of reaction of the particles when the particles first enter the dissolver at an average diameter of d_p.
5. There is an equal residence time for all particles in suspension in the dissolver fluid.
6. The particle size distribution is lognormal.

7. The rate of dissolution of the soluble species in the incinerator ash is the same as that of the plutonium oxide.

8. The concentration of PuO_2 for surface area determination is based upon the particle size of the feed that is entering the dissolver (Same with SiO_2) as well as a particle residence time.

9. The fluoride in the dissolvent will react only with the SiO_2 in the incinerator ash.

10. The rate of dissolution of SiO_2 by HF is based only upon the rate law as found in the literature[24].

11. This is a constant density system (eg., volume of fluid in the dissolver is constant).

12. The entrance and exit effects of the fluid entering and leaving the draft tube can be neglected so that $aa = x_1/x_2 = dH/dx$[7]. See Figure III.1.

13. The equation for the drag coefficient in the transition region is given as defined below[33]:
$$C_d = [\frac{24}{N_{Re,p}}][1 + 0.15(N_{Re,p})^{0.68}] \qquad \text{(C.1)}$$

14. All species in the incinerator ash exist in the oxide forms as given in the Rocky Flats Report listing (See Table D.1, Appendix D).

15. The stoichiometry of the reactions occurs as given in Appendix F. For modeling purposes, it will be assumed that the products will leave the dissolver(s) in the forms as given in Appendix F.

16. Calcium fluoride (CaF_2) is used as the fluoride (HF) source and it reacts completely with nitric acid yielding $Ca(NO_3)_2$and HF[45].

17. The dissolution of PuO_2 conforms to the shrinking sphere model. Thus, the fractional amount of PuO_2 dissolved can be used to determine the diameter of the unreacted core as follows:

$$1 - X_{PuO_2} = \frac{\text{volume of unreacted core}}{\text{initial particle volume}} \tag{C.2}$$

APPENDIX D

INCINERATOR ASH COMPOSITION

A representative composition of incinerator ash is shown on Table D.1. All elements are shown in the form that is thought to exist immediately after incineration[10]. A check was made of other sources of ash as well to verify the forms that will be assumed in the modeling operation[46,47,48].

Table D.1: Rocky Flats Plant Incinerator Ash Composition

Constituent	Ash weight %
Aluminum Oxide(Al_2O_3)	3.3
Barium Oxide(BaO)	0.9
Boron Oxide(B_2O_3)	1.8
Calcium Oxide(CaO)	4.0
Chromium Oxide(Cr_2O_3)	0.7
Copper Oxide(CuO)	1.0
Iron Oxide(Fe_2O_3)	5.7
Lead Oxide(PbO_2)	0.8
Magnesium Oxide(MgO)	4.6
Manganese Oxide(MnO_2)	0.1
Nickel Oxide(NiO)	0.5
Potassium Oxide(K_2O)	0.7
Plutonium Oxide(PuO_2)	2.8
Silicon Oxide(SiO_2)	48.5
Sodium Oxide(Na_2O)	1.2
Tantalum Oxide(Ta_2O_5)	0.4
Tin Oxide(SnO)	0.1
Titanium Oxide(TiO_2)	1.4
Carbon(C)	22.0
Total	100.5

APPENDIX E

DERIVATION OF THE REACTION RATE CONSTANT EQUATION

The derivation of the reaction rate constant equation is based upon two factors. These two factors are the resistance due to the surface reaction and the resistance due to mass transfer considerations. A knowledge of how both of these factors relate to one another will lead to an equation that will describe the net result when both of these factors are working at the same time.

Consider a spherical particle of plutonium oxide being dissolved in nitric acid with undissociated HF as a catalyst. The equations to describe the reaction rates of PuO_2 by kinetic and mass transfer considerations are as follows:

$$r_k = k_r S[HF]_S \tag{E.1}$$

$$r_m = k_m^v([HF]_B - [HF]_S) \tag{E.2}$$

where

r_k - reaction rate by kinetic considerations, g-moles/(time-length^3)

r_m - reaction rate by mass transfer considerations, g-moles/(time-length^3)

$[HF]_S$ - fluoride concentration at the surface of the PuO_2 sphere, g-moles/length^3

$[HF]_B$ - fluoride concentration in the dissolver fluid, g-moles/length^3

k_m^v - mass transfer coefficient based upon dissolver volume considerations, time^{-1}

At steady-state, equation (E.1) is equal to (E.2), therefore an expression can be derived to determine the surface concentration of HF which is:

$$[HF]_S = \frac{k_m^v}{k_r S + k_m^v}[HF]_B \tag{E.3}$$

Place (E.3) into (E.1) and obtain

$$r = \frac{d[Pu]}{dt} = \frac{k_m^v k_r S}{k_r S + k_m^v}[HF]_B \tag{E.4}$$

or

$$r_{PuO_2} = (\frac{1}{V})\frac{dN_{Pu}}{dt} = k_{oa}[HF]_B \tag{E.5}$$

with

$$\frac{1}{k_{oa}} = \frac{1}{k_m^v} + \frac{1}{k_r S} \tag{E.6}$$

In equation (E.6), the value of k_m^v must be defined. Therefore consider a spherical particle with a radius R_p. In this case, the total amount of PuO_2 dissolved is as follows: based upon a surface area consideration:

$$\frac{\text{moles } PuO_2 \text{ dissolved}}{\text{time}} = k_m([HF]_B - [HF]_S)(4\pi R_p^2)(N_{PuO_2}) \tag{E.7}$$

Likewise, a similar statement can be made based upon a dissolvent volume consideration:

$$\frac{\text{moles } PuO_2 \text{ dissolved}}{\text{time}} = k_m^v([HF]_B - [HF]_S)V \tag{E.8}$$

Equating (E.7) and (E.8), it is seen that

$$(4\pi R_p^2)(N_{PuO_2})k_m = k_m^v V \tag{E.9}$$

or

$$k_m^v = \frac{k_m(N_{PuO_2})(4\pi R_p^2)}{V} = k_m a \tag{E.10}$$

Since

$$R_p = d_s/2 \tag{E.11}$$

then by combining (E.10) and (E.11) and rearranging, one notices that

$$a = \frac{(N_{PuO_2})(\pi d_s^2)}{V} \tag{E.12}$$

Finally, one can define the overall reaction rate constant by using the following equation:

$$\frac{1}{k_{oa}} = \frac{1}{k_m a} + \frac{1}{k_r S} \tag{E.13}$$

APPENDIX F

STOICHIOMETRY FOR THE REACTIONS IN THE CASCADE DISSOLVER SYSTEM

Table F.1 gives a list of the reactions that will be used in the modeling of the cascade dissolver system. These are the reactions that are thought to occur among the various species in the dissolvers.

To predict whether or not a particular reaction will occur, a check was made of the literature to establish some basis for writing the reaction. Then the stoichiometry was written for the reaction with the assumption that its rate was the same as that for the bulk dissolution of plutonium oxide if it is a component of the incinerator ash. Last of all, the general mass balance equation was used to incorporate the reaction into the dissolver model.

An example of the above can be seen by considering reaction (F.4). On page 3-10 in Perry's Chemical Engineers' Handbook (5th ed.), it is noted that calcium oxide (CaO) is soluble in acids. Thus, reaction (F.4) is written with the products being calcium nitrate ($Ca(NO)_3)_2$) and water (H_2O).

In the case of reactions (F.9) through (F.12), the assumption was made that potassium oxide and sodium oxide first will dissolve in water. The resulting potassium hydroxide and sodium hydroxide then reacts with the nitric acid in the dissolver to form a salt and water.

Table F.1: Stoichiometric Relations for Modeling the Cascade Dissolver System

Reactions	Ref. No.	Equ. Number
$CaF_2 + 2HNO_3 \rightarrow Ca(NO_3)_2 + 2HF$	[45]	(F.1)
$PuO_2 + 6HNO_3 \rightarrow H_2Pu(NO_3)_6 + 2H_2O$		(F.2)
$SiO_2 + 4HF \rightarrow SiF_4 + 2H_2O$	[22]	(F.3)
$CaO + 2HNO_3 \rightarrow Ca(NO_3)_2 + H_2O$	[35]	(F.4)
$MgO + 2HNO_3 \rightarrow Mg(NO_3)_2 + H_2O$	[35]	(F.5)
$NiO + 2HNO_3 \rightarrow Ni(NO_3)_2 + H_2O$	[35]	(F.6)
$CuO + 2HNO_3 \rightarrow Cu(NO_3)_2 + H_2O$	[35]	(F.7)
$PbO + 2HNO_3 \rightarrow Pb(NO_3)_2 + H_2O$	[49]	(F.8)
$K_2O + H_2O \rightarrow 2KOH$		(F.9)
$KOH + HNO_3 \rightarrow KNO_3 + H_2O$		(F.10)
$Na_2O + H_2O \rightarrow 2NaOH$		(F.11)
$NaOH + HNO_3 \rightarrow NaNO_3 + H_2O$		(F.12)

APPENDIX G

STRUCTURAL ARRAY FOR SOLVING A SYSTEM OF EQUATIONS TO FIND THE BULK RATE OF DISSOLUTION OF PLUTONIUM OXIDE

To solve a system of equations when the proper order of solution is not readily apparent, a table that describes the structure of the equations can be prepared. This is called a structural array, where the columns correspond to all of the variables that enter into the design problem and the rows correspond to the equations. For an example of the use of a structural array for design purposes, see Rudd and Watson[29] pp. 45-49.

In this case, a structural array has been prepared to assist in the solution of the bulk dissolution rate of plutonium oxide (see Table G.1). This table is set up so that the equations are numbered by rows and the columns correspond to the variables.

Tables G.2–G.4 are listings of the equations that correspond to the numbers in the structural array of Table G.1. In this listing, the number of the equation for the table is given, the equation itself is listed and the equation number for this section is given respectively. In Table G.5, the variables are listed along with a corresponding key for Table G.1. In this table, the first letter corresponds to the letter indicated for each column in Table G.1 while the variable that the letter represents is placed after the letter itself.

Also included in the table are either a plus (+) or a circle (o) written over some of the columns. The plus signs indicate variables that are design parameters. These can be adjusted to study different situations (for example, the volume (V) of dissolvent in the dissolver(s) or the volumetric flow rate of liquid (VFRL) being pumped through the system). A circle over a variable means that a variable is fixed by nature, and generally can not be adjusted (example, the molecular weight of nitric acid, M_{HNO_3}).

To read the structural array, consider as an example equation (1) and the variables D_o, L, and V which represent the diameter of the dissolver, the height of liquid in the dissolver, and the volume of liquid in the dissolver respectively. An examination of the table will show that the variables D_o and L are design parameters and therefore are known quantities. Substitution of these variables into equation (1) will reveal the value of V. All subsequent variables are determined by reading the table from left to right and taking advantage of the fact that the variables to the left are either known or have already been solved for previously. By looking at the plus signs and the circles, one can determine if the variable in question has a predetermined numerical value. If it does, then the number can be substituted directly into the equation.

In the structural array, there are two areas that are shaded. These indicate areas where a recycle loop has been detected. These recycle loops indicate a series of equations that must be solved simultaneously instead of algebraically.

Table G.1: Structural Array for Determining the Bulk Rate of Dissolution of PuO_2.

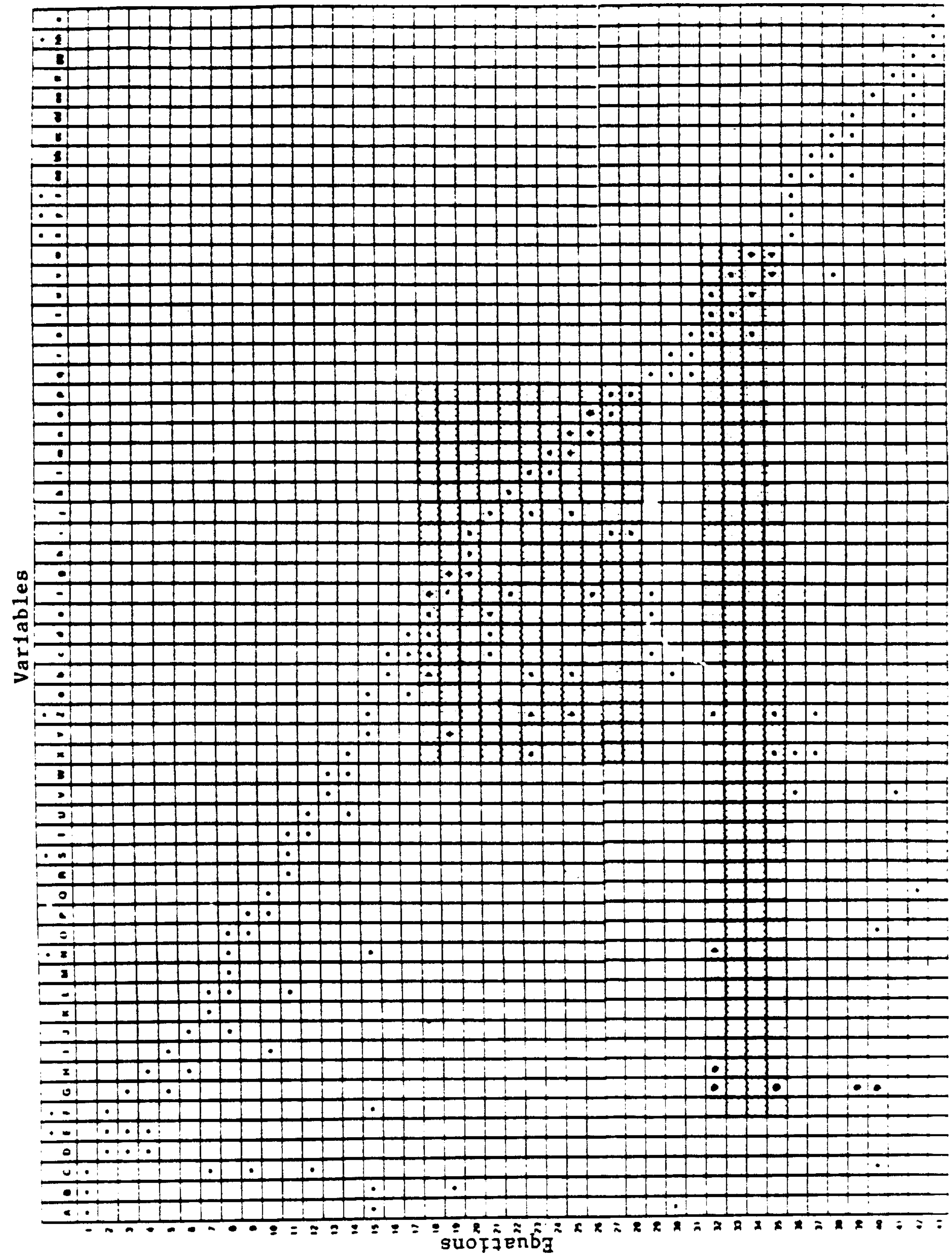

Table G.2: Listing of the Equations for the Structural Array (Part 1)

(1) $V = (\frac{\pi}{4})D_o^2 L$ (G.1)
(2) $d_p = CMD\exp(3\,[ln\sigma_g]^2)$ (G.2)
(3) $d_s = CMD\exp([ln\sigma_g]^2)$ (G.3)
(4) $d_v = CMD\exp(1.5\,[ln\sigma_g]^2)$ (G.4)
(5) $SAP = \pi d_s^2$ (G.5)
(6) $VOLP = (\frac{\pi}{6})d_v^3$ (G.6)
(7) $\tau = \frac{V}{VFRL}$ (G.7)
(8) $N_{PuO_2} = \frac{\tau F_{PuO_2}}{\rho_S VOLP}$ (G.8)
(9) $PD_{PuO_2} = N_{PuO_2}/V$ (G.9)
(10) $S = (SAP)(PD_{PuO_2})$ (G.10)
(11) $TVOL = \frac{FRF\tau}{\rho_{ash}}$ (G.11)
(12) $\phi_S = TVOL/V$ (G.12)
(13) $\mu_L = \mu_{Lo}\exp(\frac{B}{RT})$ (G.13)
(14) $\frac{\mu_M}{\mu_L} = 1 + \frac{1.56\phi_S}{0.52-\phi_S}$ (G.14)
(15) $u_c = K(d_p/D_1)(D_1/D_o)^2\sqrt{2gL\frac{\rho_S-\rho_L}{\rho_L}}$ (G.15)
(16) $A_c = (\frac{\pi}{4})d_c^2$ (G.16)

Table G.3: Listing of the Equations for the Structural Array (Part 2)

(17) $G_A = A_c u_c$ (G.17)
(18) $\frac{G_A}{\epsilon A_c} = 1.2\frac{G_A+L'}{A_c} + 0.35\sqrt{gD_c}$ (G.18)
(19) $x_1 = L - D_1$ (G.19)
(20) $aa = x_1/x_2$ (G.20)
(21) $V_N = \frac{G_A+L'}{A_c}$ (G.21)
(22) $\frac{dH_h}{dx} = 1 - \epsilon$ (G.22)
(23) $N_{Re} = \frac{D_c V_N \rho_L}{\mu_M}$ (G.23)
(24) $f = 0.0014 + 0.125N_{Re}^{-0.32}$ (G.24)
(25) $\frac{dH_s}{dx} = (\frac{4f}{D_c})(\frac{V_N^2}{2g_c})\rho_L$ (G.25)
(26) $\frac{dH_f}{dx} = (1-\epsilon)\frac{dH_s}{dx}$ (G.26)
(27) $\frac{dH}{dx} = \frac{dH_h}{dx} + \frac{dH_f}{dx}$ (G.27)
(28) $\frac{dH}{dx} = aa$ (G.28)
(29) $V_L = \frac{L'}{A_c(1-\epsilon)}$ (G.29)
(30) $V_L D_c^2 = V_o(D_o^2 - D_c^2)$ (G.30)
(31) $V_{L,AVE.} = \frac{V_o+V_L}{2}$ (G.31)

Table G.4: Listing of the Equations for the Structural Array (Part 3)

(32) $C_d(\frac{\pi}{8})\rho_L d_s^3(V_{L,Ave.} - V_p)^2 + (\frac{\pi}{6})d_v^3\rho_L g - (\frac{\pi}{6})d_v^3\rho_S g = 0$ (G.32)

(33) $C_d = \Phi(N_{Re,p})$ (G.33)

(34) $V_{Rel.} = V_{L,Ave.} - V_p$ (G.34)

(35) $N_{Re,p} = \Phi(d_s, \rho_L, V_{Rel.}, \mu_M)$ (G.35)

(36) $D = \Phi(M_{HNO_3}, T, \mu_M, V_{HF}, V_{HNO_3})$ (G.36)

(37) $N_{Sc} = \Phi(\mu_M, D, \rho_L)$ (G.37)

(38) $N_{Sh} = \Phi(N_{Re,p}, N_{Sc})$ (G.38)

(39) $N_{Sh} = \frac{k_m d_s}{D}$ (G.39)

(40) $a = \frac{\pi(N_{PuO_2})d_s^2}{V}$ (G.40)

(41) $k_r = k_{ro}exp(\frac{-E}{RT})$ (G.41)

(42) $\frac{1}{k_{oa}} = \frac{1}{k_r S} + \frac{1}{k_m a}$ (G.42)

(43) $r_{PuO_2} = k_{oa}[HF]_B$ (G.43)

Table G.5: Listing of the Variables for the Structural Array

A - D_o
B - L
C - V
D - CMD
E - σ_g
F - d_p
G - d_s
H - d_v
I - SAP
J - $VOLP$
K - $VFRL$
L - τ
M - F_{PuO_2}
N - ρ_S
O - N_{PuO_2}

P-PD_{PuO_2}
Q -S
R-FRF
S-ρ_{ash}
T-$TVOL$
U-ϕ_s
V-T
W-μ_L
X-μM
Y-D_1
Z-ρ_L
a-u_c
b-D_c
c-A_c
d-G_A

e-L'
f-ϵ
g-x_1
h-x_2
i-aa
j-V_N
k-$\frac{dH_h}{dx}$
l-N_{Re}
m-f
n-$\frac{dH_s}{dx}$
o-$\frac{dH_f}{dx}$
p-$\frac{dH}{dx}$
q-V_L
r-V_o
s-$V_{L,Ave.}$
t-C_d

u-V_p
v-$N_{Re,p}$
w-$V_{Rel.}$
x-M_{HNO_3}
y-V_{HF}
z-V_{HNO_3}
aa-D
bb-N_{Sc}
cc-N_{Sh}
dd-k_m
ee-a
ff-k_r
gg-k_{oa}
hh-$[HF]_B$
ii-r_{PuO_2}

APPENDIX H

DERIVATION OF AN EQUATION TO RELATE THE AMOUNT OF FLUORIDE CONSUMED TO THE AMOUNT OF SILICA DISSOLVED

To determine the concentration of fluoride in the dissolver, an estimate must be made of how much fluoride reacts with the silica in the ash. This estimate can be done with an equation which has been derived from a mass balance equation for silica. Consider a mass balance for SiO_2 written around one dissolver at steady-state conditions. The terms for the mass balance equation can be written as follows:

$$Input\ of\ SiO_2 = F_{SiO_2} \tag{H.1}$$

$$Output\ of\ SiO_2 = F_{SiO_2}(1 - X_{SiO_2}) \tag{H.2}$$

$$Consumption\ of\ SiO_2 = (-r_{SiO_2})S'_{SiO_2}V \tag{H.3}$$

where:

S'_{SiO_2} - surface area of silica per unit volume of dissolver fluid

By the law of conservation of mass

$$\text{Input} = \text{Output} + \text{Consumption} \tag{H.4}$$

Combine equations (H.1)-(H.4) and rearrange to obtain

$$F_{SiO_2}X_{SiO_2} = (-r_{SiO_2})S'_{SiO_2}V \tag{H.5}$$

From Blumberg[24], the rate law for the dissolution of silica by HF is written as follows:

$$-r_{SiO_2} = k'_o \exp(\frac{-E'}{RT})[HF]_B \tag{H.6}$$

Therefore, by assuming that HF reacts only with the SiO_2 in the ash, one obtains by combining (H.5) and (H.6)

$$F_{SiO_2}X_{SiO_2} = k'_o \exp(\frac{-E'}{RT})S'_{SiO_2}V[HF]_B \tag{H.7}$$

Assume a constant density system so that

$$[HF]_B = [HF]_o(1 - X_{HF}) \tag{H.8}$$

Also let

$$k' = k'_o \exp(\frac{-E'}{RT}) \tag{H.9}$$

Combine (H.7), (H.8), and (H.9) to obtain

$$F_{SiO_2}X_{SiO_2} = k'[HF]_o(1 - X_{HF})S'_{SiO_2}V \tag{H.10}$$

with

$$[HF]_o = F_{HF}/VFRL \tag{H.11}$$

where

$VFRL$ - volumetric flow rate of liquid being pumped to a dissolver stage, length^3/time

From stoichiometric considerations:

$$\text{Number of g-moles } HF \text{ consumed} = \frac{(Z \text{ g-moles } SiO_2)(4 \text{ g-moles } HF)}{\text{g-moles } SiO_2} \tag{H.12}$$

Let

$$Z = F_{SiO_2}X_{SiO_2} \tag{H.13}$$

then

$$\text{Number of g-moles } HF \text{ consumed} = 4F_{SiO_2}X_{SiO_2} \tag{H.14}$$

therefore

$$X_{HF} = \frac{\text{g-moles } HF \text{ consumed}}{\text{g-moles } HF \text{ fed to dissolver}} = \frac{4F_{SiO_2}X_{SiO_2}}{F_{HF}} \tag{H.15}$$

Combine (H.10) and (H.15) and rearrange to obtain

$$X_{SiO_2} = \frac{k'[HF]_o S'_{SiO_2} V F_{HF}}{F_{SiO_2}F_{HF} + 4k'[HF]_o S'_{SiO_2} V F_{SiO_2}} \tag{H.16}$$

APPENDIX I

DISSOLVER FEED AND EFFLUENT STREAM MAKEUP

Figure I.1 shows the components of the influent and effluent streams around a typical dissolver stage. The diagram is divided up into three sets of components. The first set is components 1-30. These are the components that are found in the feed stream of each dissolver. This same numbering system is used for the leaving liquid effluent stream as well. The second stream is the sparge air. It will be assumed that only molecular nitrogen (listed as component 31) and oxygen (component 32) make up this stream. Last is the off-gas stream with component numbers 33-36. The components in the off-gas stream consist of the sparge air plus any by-product gas of a chemical reaction in the dissolver such as SiF_4.

Use is made of this numbering system in the computer model of the dissolvers. In the model, there is a two-dimensional array named F. This array will be used to store the molar flow rate of each component under the guidelines given above and according to Figure I.1. This array has also been set up to indicate in which stream in a cascade dissolver system a certain component can be found. As an example, $F_{2,1}$ indicates the molar flow rate of calcium oxide (CaO) into the first dissolver. This number can be found in location (2,1) of the array F. Likewise, $F_{35,2}$ is the molar flow rate of silicon tetrafluoride (SiF_4) out of the second dissolver. Its location in the array F is (35,2).

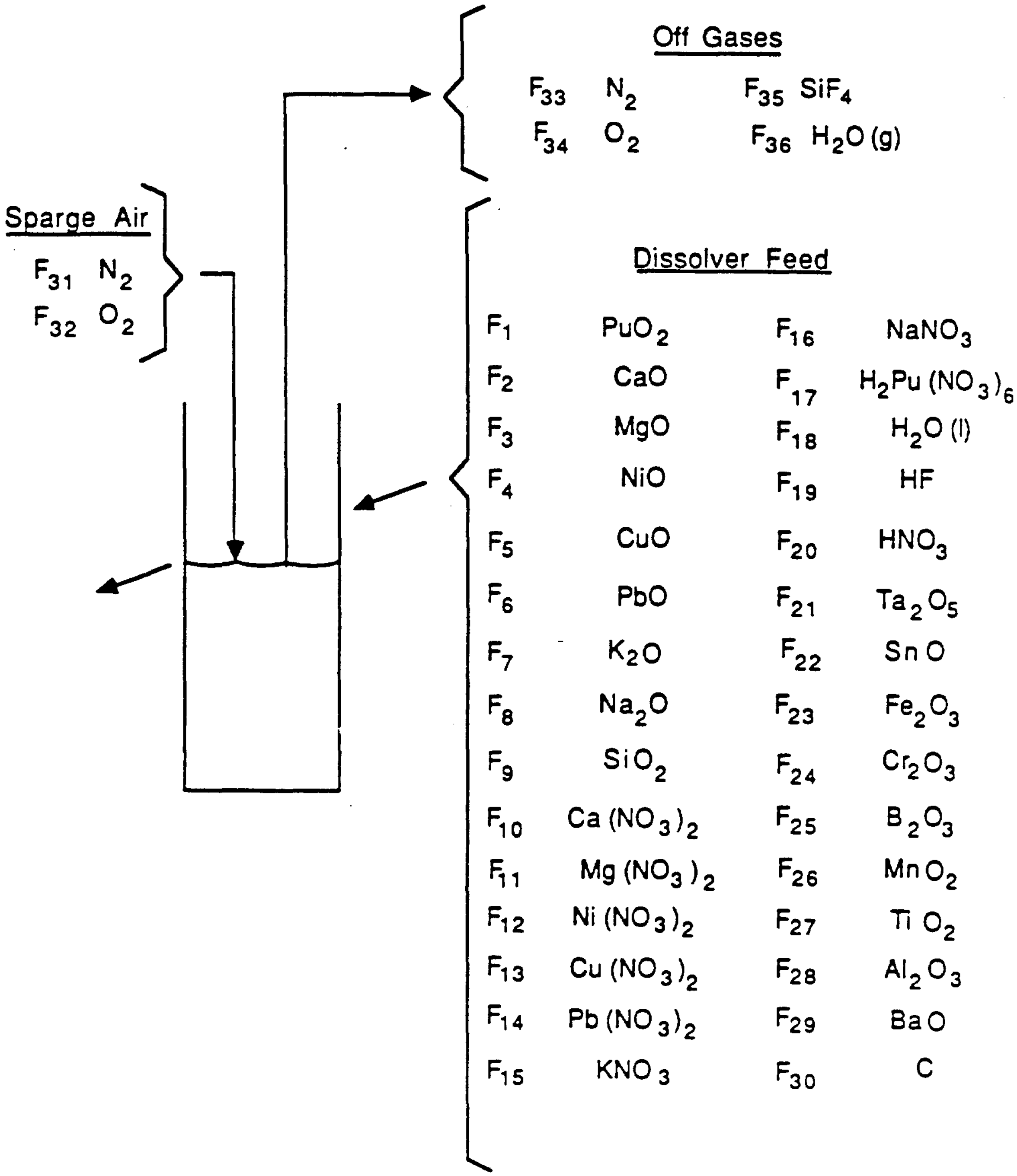

Figure I.1: Schematic Showing the Components in the Dissolver Feed and Effluent Streams

APPENDIX J

A DESCRIPTION OF THE HEAT CAPACITY EQUATIONS

The heat capacity equation at constant pressure, C_p, is written for most of the components in one of the following forms:

$$C_{p,j} = a_j + b_j T + c_j T^{-2} \tag{J.1}$$

$$C_{p,j} = a_j + b_j T + d_j T^2 + e_j T^3 \tag{J.2}$$

where

$C_{p,j}$ - heat capacity at constant pressure of component j, energy/(g-mole-degree)

a_j, b_j, c_j, d_j, e_j - empirical constants for the heat capacity equations

Values of $C_{p,j}$ for the components in this modeling operation were found in the literature[35,49,50,51,52,53].

If a form of $C_{p,j}$ as given by equations (J.1) or (J.2) was not readily available, an estimated value of $C_{p,j}$ is used. This value was calculated using Kopp's rule as described by Felder and Rousseau[51].

Tables J.1–J.3 give a listing of the heat capacity coefficients of each compound in the dissolver system for equations (J.1) and (J.2). If Kopp's rule was used to estimate the heat capacity, this fact is mentioned in the tables. Also, listed in Table J.4 and J.5 is the heat of formation for each component at 25 Degrees Celsius[35,50,52,53]. In the case of the hexanitrato complex of plutonium (IV), ($H_2Pu(NO_3)_6$), a heat of formation for this component had to be estimated since no heat data was available in the literature. The value used was the heat formation of thorium nitrate ($Th(NO_3)_4$)[54]. This heat of formation was chosen for two reasons. The first is because in this instance, thorium has the same valence number (+4) as does the plutonium in the computer model. The second reason is that in the past[55,56], thorium dissolution models have been used as a basis for modeling plutonium dissolution.

Table J.1: Heat Capacity Data for the Equation $C_{p,j} = a_j + b_jT + c_jT^{-2}$ (Part 1)

Component	a_j	$b_j * 10^3$	$c_j * 10^5$	Ref. No.
PuO_2	22.18	0.208	-4.935	[50]
CaO	10.	4.84	-1.08	[35]
MgO	10.86	1.197	-2.08	[35]
NiO	11.3	2.15	0.	[35]
CuO	10.87	3.576	-1.506	[35]
PbO	10.33	3.18	0.	[35]
K_2O	15.9	6.4	0.	[49]
Na_2O	16.52	0.	0.	[53]
SiO_2	10.87	8.712	-2.412	[35]
$Ca(NO_3)_2$	29.37	36.8	-4.13	[51]
$Mg(NO_3)_2$	10.68	71.2	1.79	[51]
$Ni(NO_3)_2$	43.0	(estimated using Kopp's rule)		
$Cu(NO_3)_2$	43.0	(estimated using Kopp's rule)		
$Pb(NO_3)_2$	43.0	(estimated using Kopp's rule)		
KNO_3	6.42	53.0	0.	[35]
$NaNO_3$	4.56	58.0	0.	[35]
$H_2Pu(NO_3)_6$	121.22	(estimated using Kopp's rule)		
$H_2O(l)$	18.021	0.	0.	[52]
HF	12.35	0.	0.	[53]
HNO_3	26.2911	0.	0.	[52]
Ta_2O_5	32.3	0.	0.	[53]

Table J.2: Heat Capacity Data for the Equation $C_{p,j} = a_j + b_jT + e_jT^{-2}$ (Part 2)

Component	a_j	$b_j * 10^3$	$e_j * 10^5$	Ref. No.
SnO	9.55	3.5	0.	[51]
Fe_2O_3	24.72	16.04	-4.234	[35]
Cr_2O_3	28.53	2.2	-3.74	[51]
B_2O_3	8.73	25.4	-1.31	[51]
MnO_2	16.6	2.44	-3.88	[51]
TiO_2	11.81	7.54	-0.419	[35]
Al_2O_3	27.49	2.82	-8.38	[51]
BaO	11.79	1.88	-0.88	[51]
C	2.673	2.617	-1.169	[35]
SiF_4	21.95	2.66	-4.72	[51]

Note: The value of $C_{p,j}$ in the heat capacity equation has the units of calories/(g-mole-Deg. C). The value of T is in units of Kelvin except for the heat capacity of SiF_4. The value of T in this case is in units of degrees Celsius.

Table J.3: Heat Capacity Data For the Equation $C_{p,j} = a_j + b_jT + d_jT^2 + e_jT^3$

Component	a_j	$b_j * 10^3$	$d_j * 10^6$	$e_j * 10^{10}$	Ref.
N_2	6.93129	0.52558	1.36785	-6.86198	[52]
O_2	6.95519	2.76774	-1.45222	3.13342	[52]
$H_2O(g)$	7.99727	1.64439	1.81743	-8.58763	[52]

Note: The value of $C_{p,j}$ in the heat capacity equation has the units of calories/(g-mole-Deg. C.). The value of T is in the units of degrees Celsius.

Table J.4: Heat of Formation at 25 Degrees Celsius for the Compounds in the Cascade Dissolver System (Part 1)

Component	Heat of Formation, kcal/g-mole	Ref. No.
PuO_2	-252.35	[50]
CaO	-151.7	[35]
MgO	-143.84	[35]
NiO	-58.4	[35]
CuO	-38.5	[35]
PbO	-52.39	[52]
K_2O	-86.2	[35]
Na_2O	-99.45	[35]
SiO_2	-203.35	[35]
$Ca(NO_3)_2$	-224.05	[35]
$Mg(NO_3)_2$	-188.77	[35]
$Ni(NO_3)_2$	-101.5	[35]
$Cu(NO_3)_2$	-73.1	[35]
$Pb(NO_3)_2$	-106.88	[35]
KNO_3	-118.08	[35]
$NaNO_3$	-111.71	[35]
$H_2Pu(NO_3)_6$	-344.5	(See Text in Appendix J)
$H_2O(l)$	-68.3174	[35]
HF	-71.65	[53]
HNO_3	-41.40	[52]

Table J.5: Heat of Formation at 25 Degrees Celsius for the Compounds in the Cascade Dissolver System (Part 2)

Component	Heat of Formation, kcal/g-mole	Ref. No.
Ta_2O_5	-486.0	[35]
SnO	-67.7	[35]
Fe_2O_3	-198.5	[35]
Cr_2O_3	-268.8	[35]
B_2O_3	-302.	[35]
MnO_2	-124.58	[35]
TiO_2	-225.	[35]
Al_2O_3	-399.09	[35]
BaO	-133.0	[35]
C	0.	[35]
N_2	0.	[35]
O_2	0.	[35]
SiF_4	-370.	[35]
$H_2O(g)$	-57.7979	[35]

APPENDIX K

CASCADE DISSOLVER SYSTEM COMPUTER PROGRAM AND DATA

The computer program that was written to model the dissolver system is in this section. The first part of this section is the computer program itself complete with comment statements describing the program in detail. The next section contains a sample data set that was read into the program for a single stage cascade dissolver. Last is the output data from the computer program for this input data set.

```
C
C                              ERIC BROWN
C                 CASCADE DISSOLVER MODELING COMPUTER PROGRAM
C                     GEORGIA INSTITUTE OF TECHNOLOGY
C
C  THE PURPOSE OF THIS PROGRAM IS TO SIMULATE AN N STAGE CASCADE DISSOLVER
C  SYSTEM.  THIS PROGRAM IS DESIGNED TO PREDICT THE FRACTIONAL AMOUNT OF
C  PLUTONIUM OXIDE THAT CAN BE DISSOLVED IN A NITRIC ACID SOLUTION.  THE
C  PLUTONIUM OXIDE COMES FROM INCINERATOR ASH WITH FLUORIDE BEING USED AS A
C  CATALYST FOR THE DISSOLUTION. THE PROGRAM IS SET UP SO THAT THE MATERIAL
C  BALANCE FOR ALL SPECIES IS WRITTEN AROUND THE FIRST DISSOLVER.  NEXT, AN
C  ENERGY BALANCE IS WRITTEN AROUND THE DISSOLVER TO PREDICT THE AMOUNT OF
C  HEAT THAT IS REQUIRED FOR THE DISSOLUTION (ASSUMING THAT THERE ARE NO HEAT
C  LOSSES TO THE ENVIROMENT). ONCE THIS IS DONE, THE PROGRAM IS SET UP SO THAT
C  THE SIMULATION CAN BE PERFORMED OVER AND OVER AGAIN FOR EACH SUBSEQUENT
C  STAGE OF THE DISSOLVER SYSTEM WITH THE EFFLUENT STREAM FROM THE ITH STAGE
C  BEING THE FEED STREAM TO THE (I+1)TH STAGE.  A DESCRIPTION OF THE EQUATIONS
C  AND THE VARIABLES USED IN THIS MODELING CAN BE FOUND IN THE THESIS
C  "INCINERATOR ASH DISSOLUTION MODEL FOR THE SYSTEM:  PLUTONIUM NITRIC ACID
C  AND HYDROFLUORIC ACID" BY ERIC BROWN.
C
      REAL LP,K,NREP,NSC,KM,NSH,KR,KOA,L,NPUPAR,NSIPAR,KP,MW
      REAL MWNO3(9)
      INTEGER C
      DIMENSION F(36,10),AI(36),BI(36),CI(36),AG(36),BG(36),CG(36),
     CDG(36),EG(36),DELHF(36),DP(10),T(10),MW(36),FRF(10),PVSTAR(10),
     C FNEW(10,10)
C
C   UNITS FOR THE DATA STATEMENT VARIABLES AND OTHER INPUT DATA TERMS
C   G - ACCELERATION OF GRAVITY, 32.2 FEET/SECOND**2
C   L - DEPTH OF CONTENTS IN THE DISSOLVER, FEET
C   RHOS - DENSITY OF THE PLUTONIUM OXIDE, POUNDS/FEET**3
C   K - A CONSTANT FOR USE IN THE SPARGE AIR VELOCITY EQUATION
C   D1- DISTANCE BETWEEN THE BOTTOM OF THE AIR SPARGE LINE AND THE
C       BOTTOM OF THE DISSOLVER, FEET
C   DC - DIAMETER OF THE DRAFT TUBE, FEET
C   X2 - DISTANCE BETWEEN THE TOP OF THE DRAFT TUBE AND THE BOTTOM OF THE
C        AIR SPARGE LINE, FEET
C   DO - OUTER DIAMETER OF THE DISSOLVER, FEET
C   YY - MOLECULAR WEIGHT OF SOLVENT, GRAMS/GRAM-MOLE
C   V1, V2 - MOLECULAR VOLUMES OF THE SOLUTE AND SOLVENT, CC/GRAM-MOLE
C            SOLVENT - NITRIC ACID, SOLUTE - UNDISSOCIATED HF
C   C - NUMBER OF COMPONENTS
C   P - ATMOSPHERIC PRESSURE INSIDE THE DISSOLVER, MM MERCURY
C   RHOASH - DENSITY OF THE INCINERATOR ASH, GRAMS/CUBIC CENTIMETER
C   TREF - REFERENCE TEMPERATURE FOR THE ENERGY BALANCES, 298 DEGREES KELVIN.
C   F - AN ARRAY TO HOLD ALL MATERIAL BALANCE NUMBERS
C
      DATA G,L,RHOS,K,D1,DC,X2,DO,YY,V1,C,V2,P,
     CRHOASH,TREF/32.2,2.41666,140.4,38.173, 0.083333,
     C0.25,2.6667,0.5,63.02,19.598,33,52.3031,760.0,0.22,298.16 /
      DATA MWNO3/487.,164.,148.3,182.7,189.5,331.19,202.2,170.,
     C 348.5/

C     OPEN (7, STATUS='OLD', FILE='INPUT1.DAT')
C      OPEN (8, STATUS='OLD', FILE='OUTPUT1.DAT')
```

```
C
C FOR THE PURPOSES OF THIS PROGRAM, A CONSTANT DENSITY FOR THE NITRIC
C ACID SOLUTION WILL BE ASSUMED.  THIS VALUE WILL BE BASED UPON THE
C SPECIFIC GRAVITY OF ACID FOR A 46 WEIGHT % HNO3-H2O (9 M) SOLUTION NEAR
C THE OPERATING TEMPERATURE OF THE DISSOLVER AS FOUND IN PERRYS CHEMICAL
C ENGINEERS HANDBOOK.
C
      RHOL=75.222
      V=(3.14159/4.)*DO*DO*L
C
C  READ THE INPUT DATA AS FOLLOWS:  MOLAR FLOW RATE OF CALCIUM FLUORIDE IN
C  GRAM-MOLES/HOUR, MOLAR FLOW RATE OF NITRIC ACID IN GRAM-MOLES/HOUR, NUMBER
C  OF DISSOLVER STAGES, TEMPERATURE OF THE INPUT STREAM TO THE FIRST DISSOLVER
C  IN DEGREES KELVIN, A MULTIPLICATION FACTOR FOR THE RATE OF DISSOLUTION
C  OF PLUTONIUM OXIDE AS COMPARED TO THE RATE OF DISSOLUTION OF ALL OTHER
C  SPECIES IN THE INCINERATOR ASH WHERE
C
C                 R(PuO2)* FACTOR = R(ALL OTHER SPECIES)
C
C  AVERAGE PARTICLE DIAMETER IN FEET, GEOMETRIC STANDARD DEVIATION OF THE
C  ASH FEED, VOLUMETRIC FLOW RATE OF DISSOLVER FLUID IN LITERS/HOUR, MASS
C  FLOW RATE OF THE INCINERATOR ASH FEED IN GRAMS/HOUR, RELATIVE HUMIDITY
C  OF THE OFF-GASES IN PERCENT, AND A MULTIPLICATION FACTOR FOR INCREASING
C  THE AMOUNT OF SPARGE AIR TO THE DISSOLVER(S).
C
      READ (*,*) CAF2,HNO3,N,T(1),FACTOR,DP(1),SIGMA,VFRL,FRF(1),RH,FKE
      DO 1 LL=1,C
C
C  READ THE MOLAR FLOW RATES OF ALL SPECIES IN THE INCINERATOR ASH.
C
      READ (*,*) F(LL,1)
    1 CONTINUE
C
C  READ THE MOLAR FLOW RATE OF Dy2O3
C
      READ (*,*) FNEW(1,1)
C
C  READ IN THE HEAT CAPACITY DATA AND THE HEAT OF FORMATION FOR ALL SPECIES.
C  THESE COEFFICIENTS ARE IN SUCH UNITS SO THAT THE HEAT CAPACITY IS IN UNITS
C  OF CALORIES/(GRAM-MOLE*DEGREE CELSIUS).  ALSO, THE HEAT OF FORMATION IS IN
C  UNITS OF KILOCALORIES/GRAM-MOLE.
C
      DO 2 LL=1,30
      READ (*,*) AI(LL),BI(LL),CI(LL),DELHF(LL)
    2 CONTINUE
      DO 3 LL=31,36
      READ (*,*) AG(LL),BG(LL),CG(LL),DG(LL),EG(LL),DELHF(LL)
    3 CONTINUE
C
C  READ IN THE MOLECULAR WEIGHTS OF ALL FORMS THAT ARE ASSUMED TO BE IN
C  A SOLID FORM IN THE INCINERATOR ASH FEED.
C
      DO 4 LL=1,17
      READ (*,*) MW(LL)
    4 CONTINUE
      DO 5 LL=21,30
      READ (*,*) MW(LL)
    5 CONTINUE
      DO 6 LL=1,N
      LLP1=LL+1
```

```
C
C  READ IN THE TEMPERATURE OF EACH DISSOLVER STAGE IN DEGREES KELVIN AND
C  THE CORRESPONDING VAPOR PRESSURE OF WATER AT THAT TEMPERATURE
C  IN MM. MERCURY.
C
      READ (*,*) T(LLP1), PVSTAR(LLP1)
    6 CONTINUE
      F(20,1)=HNO3-2.*CAF2
      F(19,1)=2.*CAF2
      F(10,1)=CAF2
      NP1=N+1
      DO 99 I=1,N
      IP1=I+1
C
C  THESE NEXT SERIES OF EQUATIONS ARE USED TO ESTIMATE THE EXPOSED SURFACE
C  AREA OF THE PLUTONIUM OXIDE AND THE SILICON OXIDE IN THE DISSOLVER.
C
      CMD=DP(I)/EXP(3.*ALOG(SIGMA)*ALOG(SIGMA))
      DS=CMD*EXP(ALOG(SIGMA)*ALOG(SIGMA))
      DV=CMD*EXP(1.5*ALOG(SIGMA)*ALOG(SIGMA))
      BETA=DV/DS
      SAP=3.14159*DS*DS
      VOLP=(1./6.)*3.14159*DV*DV*DV
      TAU=V*28.317/VFRL
      NPUPAR=TAU*F(1,I)*271./(454.*RHOS*VOLP)
      PDPUO2=NPUPAR/V
      S=SAP*PDPUO2
      TVOL=FRF(I)*TAU/(RHOASH*28317.)
      PHIS=TVOL/V
C
C  HERE, THE VISCOSITY OF THE DISSOLVER FLUID IS CALCULATED.  THIS VISCOSITY
C  IS THAT WHICH WOULD BE EXPECTED FOR A SOLUTION WITH SUSPENDED SOLIDS.
C
      UL=1.4924E-02*EXP(1692.2528/T(IP1))
      UM=UL*(1.+1.56*PHIS/(0.52-PHIS))
C
C  CALCULATE THE AMOUNT OF SPARGE AIR THAT IS REQUIRED TO SUSPEND THE SOLIDS.
C
      SUM1=2.*G*L*((RHOS-RHOL)/RHOL)
      UC=K*(DP(I)/D1)*(D1/DO)*(D1/DO)*SQRT(SUM1)
      GA=3600.*(3.14159/4.)*DC*DC*UC
      X1=L-D1
      AA=X1/X2
      AC=(3.1415/4.)*DC*DC
C
C  CALL THE SUBROUTINE AIRLIF TO CALCULATE THE LIQUID VELOCITY OF THE FLUID
C  FLOWING UP THE DRAFT TUBE.
C
 21   LP=AIRLIF(UC,AC,DC,AA,UM,G,RHOL,EPS,KODE)
C
C  IF THE CALCULATED GAS VELOCITY IS INSUFFICIENT TO CAUSE FLUID MOVEMENT,
C  THEN THE GAS VELOCITY IS INCREASED BY AN ARBITRARY FACTOR AS FOLLOWS:
C
C                     GA(OLD)*FKE = GA(NEW)
C
      IF (KODE .EQ. 1) THEN
         GA=GA*FKE
         UC=UC*FKE
         KODE=0
         GO TO 21
```

```
      END IF
C
C  FOR THE MASS TRANSFER CALCULATIONS, AN AVERAGE VELOCITY, VLAVE, IS USED
C  WHERE VLAVE IS THE AVERAGE VELOCITY OF THE FLUID IN THE DRAFT TUBE AND
C  THAT IN THE ANNULUS SPACE.
C
      VL=LP/((1.-EPS)*AC)
      VO=VL*DC*DC/(DO*DO-DC*DC)
      VLAVE=(VO+VL)/2.
C
C  THESE NEXT SERIES OF STATEMENTS CALCULATE THE REYNOLDS NUMBER FOR A
C  PARTICLE OF SIZE DP WHICH IS THE AVERAGE PARTICLE SIZE IN THE DISSOLVER.
C
      CALL VELNEW(RHOL,DS,DV,VLAVE,G,RHOS,UM,NREP)
      IF (NREP .LT. 500.) THEN
         UMS=UM/3600.
         CALL VELLOW(RHOL,VLAVE,DS,DV,RHOS,G,NREP,UMS)
      END IF
C
C  ESTIMATE THE DIFFUSIVITY OF A FLUORIDE MOLECULE DIFFUSING THROUGH NITRIC
C  ACID.
C
      D=DIFF(YY,T(IP1),V1,V2,UM)
      D=D*3600./(30.48*30.48)
C
C  CALCULATE THE MASS TRANSFER AND THE REACTION RATE RESISTANCE TERMS FOR
C  THE OVERALL REACTION RATE CONSTANT.
C
      NSC=UM/(RHOL*D)
      NSH=2.+0.6*(NSC**0.3333)*SQRT(NREP)
      KM=D*NSH/DS
      A=NPUPAR*3.14159*DS*DS/V
      KR=24004.172*EXP((-1.)*6293.8748/T(IP1))
      Z=1./(KM*A)+1./(KR*S)
      KOA=1./Z
      H2OGEN=0.
      ACID=0.
C
C  BASED UPON THE MIXED REACTOR ASSUMPTION, CALCULATE THE AMOUNT OF FREE
C  FLUORIDE AVAILABLE FOR USE AS A CATALYST TO DISSOLVE THE
C  PLUTONIUM OXIDE.
C
      NSIPAR=F(9,I)*TAU*60./(454.*140.1*VOLP)
      PDSIO2=NSIPAR/V
      SSIO2=PDSIO2*SAP
      CHFO=F(19,I)/VFRL
      SUM2=EXP((-1.)*9.*1000./(1.987*T(IP1)))
      KP=SUM2*0.120*30.48*30.48*3600./(28.+32.)
      SUM3=KP*CHFO*V*SSIO2
      XSIO2=SUM3*F(19,I)/(F(19,I)*F(9,I)+4.*F(9,I)*SUM3)
      XHF=4.*F(9,I)*XSIO2/F(19,I)
      FSIF4=F(9,I)*XSIO2
      F(9,IP1)=F(9,I)-F(9,I)*XSIO2
      F(19,IP1)=F(19,I)-F(19,I)*XHF
      F(35,IP1)=F(9,I)*XSIO2
      H2OGEN=H2OGEN+2.*F(9,I)*XSIO2
      CHF=F(19,IP1)/VFRL
C
C  CALCULATE THE RATE OF DISSOLUTION OF PLUTONIUM OXIDE AND ESTIMATE THE
C  RATE OF DISSOLUTION OF ALL OTHER SPECIES IN THE INCINERATOR ASH.
```

```
C
      R=KOA*CHF*28.31598
      RATE=FACTOR*R
C
C  CALCULATE THE AMOUNTS OF NITROGEN AND OXYGEN IN THE SPARGE AIR.
C
      F(32,I)=GA*454.*(1./359.)*(T(IP1)/273.)*0.21
      F(31,I)=F(32,I)*3.7619
C
C  CARRY OUT MASS BALANCES ON ALL SPECIES IN THE DISSOLVER SYSTEM.
C  THESE NEXT STATEMENTS ARE THE STOICHIOMETRIC RELATIONSHIP FOR
C  THE DISSOLUTION OF PLUTONIUM OXIDE.
C
      F(1,IP1)=F(1,I)-R*V
      CONS=F(1,I)-F(1,IP1)
      IF (F(1,IP1) .LT. 0.) CALL CHECK(F(1,IP1),F(1,I),CONS)
      ACID=ACID+6.*CONS
      H2OGEN=H2OGEN+2.*CONS
      F(17,IP1)=CONS+F(17,I)
C
C  MASS BALANCES FOR CALCIUM OXIDE DISSOLUTION
C
      F(2,IP1)=F(2,I)-RATE*V
      CONS=F(2,I)-F(2,IP1)
      IF (F(2,IP1) .LT. 0.) CALL CHECK (F(2,IP1), F(2,I), CONS)
      ACID=ACID+2.*CONS
      H2OGEN=H2OGEN+CONS
      F(10,IP1)=CONS+F(10,I)
C
C  MASS BALANCES FOR MAGNESIUM OXIDE DISSOLUTION
C
      F(3,IP1)=F(3,I)-RATE*V
      CONS=F(3,I)-F(3,IP1)
      IF (F(3,IP1) .LT. 0.) CALL CHECK (F(3,IP1),F(3,I), CONS)
      ACID =ACID+CONS*2.
      H2OGEN=H2OGEN+CONS
      F(11,IP1)=CONS+F(11,I)
C
C  MASS BALANCES FOR NICKEL OXIDE DISSOLUTION
C
      F(4,IP1)=F(4,I)-RATE*V
      CONS=F(4,I)-F(4,IP1)
      IF (F(4,IP1) .LT. 0.) CALL CHECK(F(4,IP1), F(4,I), CONS)
      ACID=ACID+CONS*2.
      H2OGEN=H2OGEN+CONS
      F(12,IP1)=CONS+F(12,I)
C
C  MASS BALANCES FOR COPPER OXIDE DISSOLUTION
C
      F(5,IP1)=F(5,I)-RATE*V
      CONS=F(5,I)-F(5,IP1)
      IF (F(5,IP1) .LT. 0.) CALL CHECK(F(5,IP1), F(5,I) , CONS)
      ACID=ACID+CONS*2.
      H2OGEN=H2OGEN+CONS
      F(13,IP1)=CONS+F(13,I)
C
C  MASS BALANCES FOR LEAD OXIDE DISSOLUTION
C
      F(6,IP1)=F(6,I)-RATE*V
      CONS=F(6,I)-F(6,IP1)
```

```
      IF (F(6,IP1) .LT. 0.) CALL CHECK(F(6,IP1), F(6,I),CONS)
      ACID=ACID+CONS*2.
      H2OGEN=H2OGEN+CONS
      F(14,IP1)=CONS+F(14,I)
C
C  MASS BALANCES FOR POTASSIUM OXIDE DISSOLUTION
C
      F(7,IP1)=F(7,I)-RATE*V
      CONS=F(7,I)-F(7,IP1)
      IF (F(7,IP1) .LT. 0.) CALL CHECK( F(7,IP1), F(7,I), CONS)
      H2OGEN=H2OGEN+CONS-2.*CONS
      ACID=ACID+CONS*2.
      F(15,IP1)=2*CONS+F(15,I)
C
C  MASS BALANCES FOR SODIUM OXIDE DISSOLUTION
C
      F(8,IP1)=F(8,I)-RATE*V
      CONS=F(8,I)-F(8,IP1)
      IF (F(8,IP1) .LT. 0.) CALL CHECK (F(8,IP1), F(8,I),CONS)
      H2OGEN=H2OGEN+CONS-2.*CONS
      ACID=ACID+CONS*2.
      F(16,IP1)=2.*CONS+F(16,I)
      F(20,IP1)=F(20,I)-ACID
      F(33,IP1)=F(31,I)
      F(34,IP1)=F(32,I)


C
C  MASS BALANCES FOR DYSPROSIUM OXIDE DISSOLUTION
C
      FNEW(1,IP1)=FNEW(1,I)-RATE*V
      CONS=FNEW(1,I)-FNEW(1,IP1)
      IF(FNEW(1,IP1).LT.0.)CALL CHECK(FNEW(1,IP1),FNEW(1,I),CONS)
      H2OGEN=H2OGEN+3.*CONS
      ACID=ACID+CONS*6.
      FNEW(1,IP1)=FNEW(1,I)-CONS
      XDYSP = (FNEW(1,I)-FNEW(1,IP1))/FNEW(1,I)
      CDYS = (FNEW(1,I)-FNEW(1,IP1))*2.*162.5/VFRL

C
C  ESTIMATE THE QUANTITY OF WATER VAPOR BEING EVAPORATED FROM THE DISSOLVER.
C  DUE TO THE FACT THAT THE ASSUMPTION IS BEING MADE THAT THE VOLUMETRIC
C  FLOW RATE OF LIQUID PASSING THROUGH THE SYSTEM IS CONSTANT, A CONSERVATIVE
C  ESTIMATE IS BEING MADE OF THE RELATIVE HUMIDITY OF THE WATER VAPOR IN THE
C  OFF-GASES ( < 5% RH).
C
      PV=RH*PVSTAR(IP1)/100.
      H=PV*18./((P-PV)*29.)
      F(36,IP1)=H*(F(33,IP1)*28.+F(34,IP1)*32.)/18.
      F(18,IP1)=F(18,I)+H2OGEN-F(36,IP1)
      IF (F(18,IP1) .LT. 0.) THEN
         F(18,IP1)=0.
         F(36,IP1)=F(18,I)+H2OGEN
      END IF
C
C  ACCOUNT FOR ALL OF THE INERT SPECIES IN THE DISSOLVER SYSTEM.
C
      DO 166 J=21,30
      F(J,IP1)=F(J,I)
  166 CONTINUE
C
```

```
C  THIS NEXT SECTION IS THE ENERGY BALANCE SECTION OF THE COMPUTER PROGRAM.
C  THE UNITS OF EACH VARIABLE IS IN CALORIES/HOUR.
C
      HINFL=ENSGAS(T(I),TREF,I,F,AI,BI,CI,AG,BG,CG,DG,EG,DELHF,1,30)
      HGASIN=ENSGAS(298.16,TREF,I,F,AI,BI,CI,AG,BG,CG,DG,EG,DELHF,31,32)
      HEFFL=ENSGAS(T(IP1),TREF,IP1,F,AI,BI,CI,AG,BG,CG,DG,EG,DELHF,1,30)
      HGASOT=ENTOUT(T(IP1),TREF,IP1,F,AG,BG,CG,DG,EG,DELHF)
C
C  CALCULATE THE AMOUNT OF HEAT BEING ADDED TO THE DISSOLVER IN BTU/HOUR.
C
      Q=(HGASOT+HEFFL-(HGASIN+HINFL))*(9.486E-04/0.23901)
C
C  CALCULATE THE NEW AVERAGE PARTICLE SIZE BASED UPON THE DISSOLUTION OF
C  PLUTONIUM OXIDE BY THE SHRINKING SPHERE MODEL.
C
      XPUO2=(F(1,I)-F(1,IP1))/F(1,I)
      DP(IP1)=(DP(I)*DP(I)*DP(I)*(1.-XPUO2))**0.33333
      XPUOA=(F(1,1)-F(1,IP1))/F(1,1)
      XHFOA=(F(19,1)-F(19,IP1))/F(19,1)
      CPU=(239.0*F(17,IP1))/VFRL
      FRF(IP1)=0.
C
C  CALCULATE A NEW FLOW RATE OF FEED INTO THE (I+1)TH DISSOLVER.
C
      SUMNO3=0.0

      DO 210 J=2,8
      SUMNO3=SUMNO3*(F(J,I)-F(J,IP1))*MWNO3(J)

 210  CONTINUE
      SUMNO3=SUMNO3+(FNEW(1,I)-FNEW(1,IP1))*MWNO3(9)

      DENSITY = 75.222/62.4
      CMASS = (SUMNO3)/VFRL
      XMASS=CMASS/(CMASS+DENSITY)

      DO 10 J=1,17
      FRF(IP1)=MW(J)*F(J,IP1)+FRF(IP1)

   10 CONTINUE

      DO 11 J=21,30
      FRF(IP1)=MW(J)*F(J,IP1)+FRF(IP1)
      SUMMASS=SUMMASS+FRF(IP1)
   11 CONTINUE
C
C  PREPARE TO PRINT THE OUTPUT DATA.
C
      WRITE (*,100) I
      WRITE (*,200) DP(I)
      WRITE (*,300) DP(IP1)
      WRITE (*,350) T(IP1)-273.16
      WRITE (*,400) GA
      WRITE (*,500) Q
      WRITE (*,550) RH
      WRITE (*,600) XPUO2
      WRITE (*,700) XPUOA
      WRITE (*,710) XDYSP
      WRITE (*,800) XHF
      WRITE (*,890) XMASS
```

```
      WRITE (*,900) XHFOA
      WRITE (*,950) CHF
      WRITE (*,1000) F(35,IP1)
      WRITE (*,1100) CPU
      WRITE (*,1110) CDYS
      WRITE (*,1200)
      WRITE (*,1300) F(1,IP1)
      WRITE (*,1310) FNEW(1,IP1)
      WRITE (*,1400) F(2,IP1)
      WRITE (*,1500) F(3,IP1)
      WRITE (*,1600) F(4,IP1)
      WRITE (*,1700) F(5,IP1)
      WRITE (*,1800) F(6,IP1)
      WRITE (*,1900) F(7,IP1)
      WRITE (*,2000) F(8,IP1)
      WRITE (*,2100) F(9,IP1)
      WRITE (*,2110) FSIF4
      WRITE (*,2200) F(10,IP1)
      WRITE (*,2300) F(11,IP1)
      WRITE (*,2400) F(12,IP1)
      WRITE (*,2410) F(13,IP1)
      WRITE (*,2420) F(14,IP1)
      WRITE (*,2500) F(15,IP1)
      WRITE (*,2600) F(16,IP1)
      WRITE (*,2700) F(17,IP1)
      WRITE (*,2710) (FNEW(1,1)-FNEW(1,IP1))
      WRITE (*,2800) F(18,IP1)
      WRITE (*,2900) F(19,IP1)
      WRITE (*,3000) F(20,IP1)
      WRITE (*,3100) F(21,IP1)
      WRITE (*,3200) F(22,IP1)
      WRITE (*,3300) F(23,IP1)
      WRITE (*,3400) F(24,IP1)
      WRITE (*,3500) F(25,IP1)
      WRITE (*,3600) F(26,IP1)
      WRITE (*,3700) F(27,IP1)
      WRITE (*,3800) F(28,IP1)
      WRITE (*,3900) F(29,IP1)
      WRITE (*,4000) F(30,IP1)
      WRITE (*,4100) F(33,IP1)
      WRITE (*,4200) F(34,IP1)
      WRITE (*,4300) F(36,IP1)
  99  CONTINUE
      STOP
C
C  FORMAT STATEMENTS
C
  100 FORMAT (' ',T20,'SUMMARY OF DATA AROUND DISSOLVER NO.',1X,I2,/,/)
  200 FORMAT (' ',T6,'AVERAGE PARTICLE DIAMETER IN FEED STREAM (FT.)',2
     CX,'=',1X,E12.5,/)
  300 FORMAT (' ',T9,'"',8X,'"',8X,'"',4X,'LEAVING DISSOLVER (FT.)',2X,
     C'=',1X,E12.5,/)
  350 FORMAT (' ',T6,'OPERATING TEMPERATURE OF DISSOLVER (DEGREES CELSIU
     CS) =',1X,F5.1)
  400 FORMAT (' ',T6,'FLOW RATE OF SPARGE AIR (CU. FT./HR) =',3X,F7.2)
  500 FORMAT (' ',T6,'RATE OF HEAT INPUT TO DISSOLVER (BTU/HR.) =',1X,F
     C7.1)
  550 FORMAT (' ',T6,'RELATIVE HUMIDITY OF AIR ABOVE DISSOLVER (%) =',1
     CX,F5.1,/)
  600 FORMAT (' ',T6,'FRACTION OF PUO2 CONSUMED IN DISSOLVER =',1X,F7.5
```

```
     C)
  700 FORMAT (' ',T6,'OVERALL FRACTION OF PUO2 DISSOLVED =',1X,F7.5,/)

  710 FORMAT (' ',T6,'OVERALL FRACTION OF DY2O3 DISSOLVED =',1X,F7.5,/)
  800 FORMAT (' ',T6,'FRACTION OF HF CONSUMED IN DISSOLVER =',1X,F7.5)

  890 FORMAT (' ',T6,'FRACTION OF NV SOLIDS DISSOLVED =',1X,F7.5)
  900 FORMAT (' ',T6,'OVERALL FRACTION OF HF CONSUMED =',1X,F7.5)
  950 FORMAT (' ',T6,'CONCENTRATION OF HF(G-MOLES/LITER) =',1X,F6.4,/)
 1000 FORMAT (' ',T6,'FLOW RATE OF SIF4 GAS (G-MOLES/HR.) =',1X,F7.4,/)
 1100 FORMAT (' ',T6,'CONCENTRATION OF PLUTONIUM LEAVING DISSOLVER (GRAM
     CS/LITER) =',1X,F5.3,/,/)

 1110 FORMAT (' ',T6,'CONCENTRATION OF DYSPROSIUM LEAVING DISSOLVER (GRAM
     CS/LITER) =',1X,F5.3,/,/)
 1200 FORMAT (' ',T33,'MOLAR FLOW RATE',/,T11,'SPECIES',15X,'OUT OF DISS
     COLVER',/,T36,'(G-MOLES/HR.)',/)
 1300 FORMAT (' ',T13,'PuO2',17X,E13.6,/)

 1310 FORMAT (' ',T13,'Dy2O3',17X,E13.6,/)
 1400 FORMAT (' ',T13,'CaO',18X,E13.6,/)
 1500 FORMAT (' ',T13,'MgO',18X,E13.6,/)
 1600 FORMAT (' ',T13,'NiO',18X,E13.6,/)
 1700 FORMAT (' ',T13,'CuO',18X,E13.6,/)
 1800 FORMAT (' ',T13,'PbO',18X,E13.6,/)
 1900 FORMAT (' ',T13,'K2O',18X,E13.6,/)
 2000 FORMAT (' ',T13,'Na2O',17X,E13.6,/)
 2100 FORMAT (' ',T13,'SiO2',17X,E13.6,/)
 2200 FORMAT (' ',T13,'Ca(NO3)2',13X,E13.6,/)
 2110 FORMAT (' ',T13,'SiF4',17X,E13.6,/)
 2300 FORMAT (' ',T13,'Mg(NO3)2',13X,E13.6,/)
 2400 FORMAT (' ',T13,'Ni(NO3)2',13X,E13.6,/)
 2410 FORMAT (' ',T13,'Cu(NO3)2',13X,E13.6,/)
 2420 FORMAT (' ',T13,'Pb(NO3)2',13X,E13.6,/)
 2500 FORMAT (' ',T13,'KNO3',17X,E13.6,/)
 2600 FORMAT (' ',T13,'NaNO3',16X,E13.6,/)
 2700 FORMAT (' ',T13,'H2Pu(NO3)6',11X,E13.6,/)

 2710 FORMAT (' ',T13,'Dy(NO3)3',11X,E13.6,/)
 2800 FORMAT (' ',T13,'H2O(l)',15X,E13.6,/)
 2900 FORMAT (' ',T13,'HF',19X,E13.6,/)
 3000 FORMAT (' ',T13,'HNO3',17X,E13.6,/)
 3100 FORMAT (' ',T13,'Ta2O5',16X,E13.6,/)
 3200 FORMAT (' ',T13,'SnO',18X,E13.6,/)
 3300 FORMAT (' ',T13,'Fe2O3',16X,E13.6,/)
 3400 FORMAT (' ',T13,'Cr2O3',16X,E13.6,/)
 3500 FORMAT (' ',T13,'B2O3',17X,E13.6,/)
 3600 FORMAT (' ',T13,'MnO2',17X,E13.6,/)
 3700 FORMAT (' ',T13,'TiO2',17X,E13.6,/)
 3800 FORMAT (' ',T13,'Al2O3',16X,E13.6,/)
 3900 FORMAT (' ',T13,'BaO',18X,E13.6,/)
 4000 FORMAT (' ',T13,'C',20X,E13.6,/)
 4100 FORMAT (' ',T13,'N2',19X,E13.6,/)
 4200 FORMAT (' ',T13,'O2',19X,E13.6,/)
 4300 FORMAT (' ',T13,'H2O(g)',15X,E13.6,/)
      END
C
C
C
      FUNCTION AIRLIF(UC,AC,DC,A,UM,G,RHOL,EPS,KODE)
```

```
C
C IN THIS SUBROUTINE, A SIMULATION IS BEING MADE OF THE AIR LIFT SECTION
C OF THE DRAFT TUBE.  THE PURPOSE OF THIS SECTION IS TO FIGURE OUT THE
C LIQUID VELOCITY THAT OCCURS IN THE DRAFT TUBE AS THE SPARGE AIR IS
C BEING PUMPED INTO THE DISSOLVER.
C
      KODE=0
      UMP=UM/3600.
      SUM1=1.2*UC+0.35*SQRT(G*DC)
      X1L=0.0
      FX1L=PREGRA(X1L,SUM1,UMP,DC,UC,A,RHOL,EPS)
      X1R=X1L
      KOUNT=0
  51  X1R=X1R+1.0
      KOUNT=KOUNT+1
      FX1R=PREGRA(X1R,SUM1,UMP,DC,UC,A,RHOL,EPS)
      IF (KOUNT .GT. 100) THEN
         KODE=1
         GO TO 91
      END IF
      IF ((FX1R*FX1L)  .GT. 0.) GO TO 51
      X2OLD=10000.
   17 X2=(X1L*FX1R-X1R*FX1L)/(FX1R-FX1L)
      FX2=PREGRA(X2,SUM1,UMP,DC,UC,A,RHOL,EPS)
      IF (ABS((X2-X2OLD)/X2) .GT. 0.0001) THEN
         IF ((FX2*FX1L) .GT. 0.0) THEN
            X1L=X2
            FX1L=FX2
         ELSE
            X1R=X2
            FX1R=FX2
         END IF
         X2OLD=X2
         GO TO 17
      END IF
      AIRLIF=X2*AC
 91   RETURN
      END
C
C
C
      FUNCTION PREGRA(X,SUM1,UMP,DC,UC,A,RHOL,EPS)
C
C PREGRA IS THE NAME OF THE PRESSURE DROP EQUATIONS THAT IS USED IN AN
C ITERATIVE MANNER TO SOLVE FOR THE PROPER LIQUID VELOCITY.
C
      REAL NRE
      SUM2=SUM1+1.2*X
      EPS=UC/SUM2
      VN=UC+X
      DHHDX=1.-EPS
      NRE=DC*VN*RHOL/UMP
      F=0.0014+0.125/(NRE**0.32)
      DHSDX=1.60191E-02*4.*F*VN*VN*RHOL/(DC*2.*32.174)
      DHFDX=(1.-EPS)*DHSDX
      DHDX=DHHDX+DHFDX
      PREGRA=DHDX-A
      RETURN
      END
C
```

```
C
      SUBROUTINE  VELNEW(RHOL,DS,DV,VLAVE,G,RHOP,UM,NREP)
C
C IN THIS SUBROUTINE, THE PARTICLE REYNOLDS NUMBER WILL BE CALCULATED.
C THIS WILL BE DONE WITH THE ASSUMPTION THAT THE DRAG COEFFICIENT IS
C EQUAL TO 0.44, MEANING THAT THE PARTICLE IS IN THE TURBULENT REGION.
C
      REAL NREP
      SUM1=3.1415*(1.0/6.0)*DV*DV*DV*RHOL*G
      SUM2=3.1415*(1.0/6.0)*DV*DV*DV*RHOP*G
      SUM3=SUM2-SUM1
      SUM4=SUM3/(0.44*3.1415*(1./8.)*RHOL*DS*DS)
      SUM5=SQRT(SUM4)
      VP=VLAVE-SUM5
      VREL=VLAVE-VP
      NREP=3600.*DS*VREL*RHOL/UM
      RETURN
      END
C
C
      SUBROUTINE VELLOW(RHOL,VLAVE,DS,DV,RHOP,G,NREP,UM)
C
C IF THE PARTICLE REYNOLDS NUMBER IS IN THE LAMINAR OR TRANSISION REGIONS,
C A TRIAL-AND-ERROR SOLUTION IS REQUIRED.  THIS SOLUTION WILL CONSIST OF
C SOLVING FOR THE PARTICLE REYNOLDS NUMBER.
C
      REAL NREP
      SUM1=3.1415*(1.0/6.0)*DV*DV*DV*RHOL*G
      SUM2=3.1415*(1.0/6.0)*DV*DV*DV*RHOP*G
      X1L=0.0001
      CD=DRAGC(X1L,UM,DS,RHOL,VP,VLAVE)
      FX1L=CD*(3.1415/8.0)*RHOL*DS*DS*(VLAVE-VP)*(VLAVE-VP)
     C+SUM1-SUM2
      X1R=X1L
   14 X1R=X1R+50.0
      CD=DRAGC(X1R,UM,DS,RHOL,VP,VLAVE)
      FX1R=CD*(3.1415/8.0)*RHOL*DS*DS*(VLAVE-VP)*(VLAVE-VP)
     C+SUM1-SUM2
      IF (X1R .GT. 500.0) THEN
         WRITE (*,1000)
 1000    FORMAT (' ',T4,' WARNING: NREP > 500.  ',/)
         STOP
      END IF
      IF ((FX1R*FX1L) .GT. 0.0) GO TO 14
      X2OLD=10000.0
   11 X2=(X1L*FX1R-X1R*FX1L)/(FX1R-FX1L)
      CD=DRAGC(X2,UM,DS,RHOL,VP,VLAVE)
      FX2=CD*(3.1415/8.0)*RHOL*DS*DS*(VLAVE-VP)*(VLAVE-VP)
     C+SUM1-SUM2
      IF (ABS((X2-X2OLD)/X2) .GT. 0.0001) THEN
         IF ((FX2*FX1L) .GT. 0.0)  THEN
            X1L=X2
            FX1L=FX2
         ELSE
            X1R=X2
            FX1R=FX2
         END IF
         X2OLD=X2
         GO TO 11
      END IF
```

```
      NREP=X2
      RETURN
      END
C
C
      FUNCTION DRAGC(X,UM,DS,RHOL,VP,VLAVE)
C
C DRAGC IS THE SUBROUTINE THAT WILL CALCULATE THE DRAG COEFFICIENT FROM
C THE CORRECT EQUATION.  THE EQUATION CHOSEN WILL DEPEND ON WHETHER THE
C FLOW AROUND THE PARTICLE IS LAMINAR OR IN THE TRANSITION REGION.
C
      IF (X .LT. 0.2) THEN
         DRAGC=24.0/X
      ELSE
         DRAGC=(24.0/X)*(1.+((X**0.666667)/6.0))
      END IF
      REL=X*UM/(DS*RHOL)
      VP=VLAVE-REL
      RETURN
      END
C
C
      FUNCTION DIFF(YY,T,V1,V2,UM)
C
C HERE, WE ARE CALCULATING THE VALUE OF THE DIFFUSION COEFFICIENT FOR THE
C MASS TRANSFER CALCULATIONS.
C
      VC=UM/2.42
      IF ((V2/V1) .LE. 1.5) THEN
         DIFF=10.0E-8*SQRT(YY)*T/(VC*V1**0.33333*V2**0.33333)
      ELSE
         DIFF=8.5E-8*SQRT(YY)*T/(VC*V1**0.33333*V2**0.33333)
      END IF
      RETURN
      END
C
C
      FUNCTION ENSGAS(T,TREF,J,F,AI,BI,CI,AG,BG,CG,DG,EG,DELHF,L,M)
C
C ENSGAS WILL CARRY OUT A CALCULATION OF THE ENTHALPY OF THE INLET STREAMS
C TO THE DISSOLVERS.  THIS WILL BE DONE FOR BOTH THE INLET FEED STREAM AND
C THE SPARGE AIR.  THE ENTHALPY OF THE EFFLUENT LEAVING THE DISSOLVER WILL
C BE CALCULATED AS WELL.
C
      DIMENSION F(36,10),AI(36),BI(36),CI(36),AG(36),BG(36),CG(36),
     CDG(36),EG(36),DELHF(36)
      SUM1=0.
      DO 27 I=L,M
      IF (I .LE. 30) THEN
         SUM1=SUM1+HEATS(T,TREF,F(I,J),AI(I),BI(I),CI(I),DELHF(I))
      ELSE
         SUM1=SUM1+HEATG(T,TREF,F(I,J),AG(I),BG(I),CG(I),DG(I),EG(I),
     C        DELHF(I))
      END IF
   27 CONTINUE
      ENSGAS=SUM1
      RETURN
      END
C
C
```

```
      FUNCTION ENTOUT(T,TREF,J,F,AG,BG,CG,DG,EG,DELHF)
C
C ENTOUT WILL CALCULATE THE ENTHALPY OF THE OFF-GASES LEAVING THE DISSOLVER.
C
      DIMENSION F(36,10),AG(36),BG(36),CG(36),DG(36),EG(36),DELHF(36)
      SUM2=0.
      DO 391 I=31,36
      IF (I .NE. 35) THEN
         SUM2=SUM2+HEATG(T,TREF,F(I,J),AG(I),BG(I),CG(I),DG(I),EG(I),
     C        DELHF(I))
      ELSE
         SUM2=SUM2+HEATS(T,TREF,F(I,J),AG(I),BG(I),EG(I),DELHF(I))
      END IF
  391 CONTINUE
      ENTOUT=SUM2
      RETURN
      END
C
C
      FUNCTION HEATS(T,TREF,Q1,A1,B1,C1,C)
C
C THE ONLY PURPOSE OF HEATS AND HEATG IS TO PROVIDE THE INTEGRATED FORM
C OF THE ENTHALPY EQUATION FOR THE HEAT INPUT CALCULATION.
C
      SUM5=A1*(T-TREF)
      SUM6=(B1/2.)*(T*T-TREF*TREF)
      SUM7=C1*((1./T)-(1./TREF))
      SUM8=C*1000.
      HEATS=(SUM5+SUM6-SUM7+SUM8)*Q1
      RETURN
      END
C
C
      FUNCTION HEATG(T,TREF,Q2,A2,B2,C2,D2,E2,E)
      TC=T-273.16
      TRC=TREF-273.16
      SUM3=A2*(TC-TRC)
      SUM4=(B2/2.)*(TC*TC-TRC*TRC)
      SUM5=(C2/3.)*(TC*TC*TC-TRC*TRC*TRC)
      SUM6=(D2/4.)*(TC*TC*TC*TC-TRC*TRC*TRC*TRC)
      SUM7=E2*((1./TC)-(1./TREF))
      SUM8=E*1000.
      HEATG=(SUM3+SUM4+SUM5+SUM6-SUM7+SUM8)*Q2
      RETURN
      END
C
C
      SUBROUTINE CHECK(A,B,C)
C
C THIS SUBROUTINE WILL ENSURE THAT WE DO NOT ATTEMPT TO DISSOLVE MORE
C OF A PRODUCT THAT HAS ALREADY DISSOLVED.
C
      C=B
      A=0.
      RETURN
      END
```

```
1.992,180.,1,295.16,21.,0.001586,2.56,20.,583.2,5.,3.
0.06
0.3382
0.03507
0.
0.
0.003
0.
0.
7.6254
0.
0.
0.
0.
0.
0.
0.
0.
743.
0.
180.
0.0
0.0002925
0.03109
0.01223
0.
0.
0.06904
0.1075
0.003822
4.533
0.
0.
0.
0.060
22.18,     2.080E-04,    -4.935E05,    -252.35
10.,       4.84E-03,       -108000.,   -151.70
10.86,     1.197E-03,      -208000.,   -143.84
11.3,      0.00215,            0.,      -58.4
10.87,     0.003576,       -150600.,    -38.5
10.33,     0.00318,            0.,      -52.39
15.9,      6.4E-03,            0.,      -86.2
16.52,     0.,                 0.,      -99.45
10.87,     0.008712,       -241200.,   -203.35
29.37,     36.8E-03,       -4.13E05,   -224.05
10.68,     71.2E-03,        1.79E05,   -188.77
43.,          0.,              0.,     -101.5
43.,          0.,              0.,     -73.1
43.,          0.,              0.,     -106.88
6.42,       0.0530,            0.,     -118.08
4.56,       0.0580,            0.,     -111.71
121.22,        0.,             0.,     -344.5
18.021,        0.,             0.,     -68.3174
12.35,         0.,             0.,     -71.65
26.2911,       0.,             0.,     -41.4
32.3,          0.,             0.,     -486.0
9.55,          3.5E-03,        0.,     -67.7
24.72,         0.01604,      -423400.,  -198.5
28.53,      2.2E-03,        -3.74E05,  -268.8
8.73,       25.4E-03,       -1.31E05,  -302.0
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16.6,       2.44E-03,       -3.88E05,  -124.58
11.81,      0.00754,        -41900.,   -225.
27.49,      2.82E-03,       -8.38E05,  -399.09
11.79,      1.880E-03,      -0.88E05,  -133.
2.673,      2.617E-03,      -1.169E05,  0.
6.93129,  5.25583E-04,  1.36785E-06,  -6.86198E-10,  0.,   0.
6.95519,  2.76774E-03, -1.45222E-06,   3.13342E-10,  0.,   0.
6.93129,  5.25583E-04,  1.36785E-06,  -6.86198E-10,  0.,   0.
6.95519,  2.76774E-03, -1.45222E-06,   3.13342E-10,  0.,   0.
21.95,    2.66E-03,        0.,       0.,       4.72E05,  -370.
7.99727,  1.64439E-03,  1.81743E-06,  -8.58763E-10,  0.,  -57.7979
271.
56.1
40.312
74.71
79.546
223.19
94.204
61.978
60.086
164.07
148.306
182.704
187.54
331.84
101.1
84.9868
612.982
441.896
134.69
159.65
151.992
69.622
86.938
79.9
101.963
153.74
12.01
359.66, 449.8
359.66, 449.8
359.66, 449.8
359.66, 449.8
0.
```

```
                    SUMMARY OF DATA AROUND DISSOLVER NO.  1

AVERAGE PARTICLE DIAMETER IN FEED STREAM (FT.)  =  0.15860E-02

   "        "        "    LEAVING DISSOLVER (FT.)  =  0.15589E-02

OPERATING TEMPERATURE OF DISSOLVER (DEGREES CELSIUS) =  86.5
FLOW RATE OF SPARGE AIR (CU. FT./HR) =      41.41
RATE OF HEAT INPUT TO DISSOLVER (BTU/HR.) =  4796.8
RELATIVE HUMIDITY OF AIR ABOVE DISSOLVER (%) =    5.0

FRACTION OF PUO2 CONSUMED IN DISSOLVER = 0.05062
OVERALL FRACTION OF PUO2 DISSOLVED = 0.05062

OVERALL FRACTION OF DY2O3 DISSOLVED = 1.00000

FRACTION OF HF CONSUMED IN DISSOLVER = 0.11434
FRACTION OF NV SOLIDS DISSOLVED = 0.46446
OVERALL FRACTION OF HF CONSUMED = 0.11434
CONCENTRATION OF HF(G-MOLES/LITER) = 0.1764

FLOW RATE OF SIF4 GAS (G-MOLES/HR.) =  0.1139

CONCENTRATION OF PLUTONIUM LEAVING DISSOLVER (GRAMS/LITER) = 0.036


CONCENTRATION OF DYSPROSIUM LEAVING DISSOLVER (GRAS/LITER) = 0.975

                             MOLAR FLOW RATE
     SPECIES                 OUT OF DISSOLVER
                               (G-MOLES/HR.)

       PuO2                    0.569627E-01

       Dy2O3                    0.000000E+00

       CaO                     0.274416E+00

       MgO                     0.000000E+00

       NiO                     0.000000E+00

       CuO                     0.000000E+00

       PbO                     0.000000E+00

       K2O                     0.000000E+00

       Na2O                    0.000000E+00

       SiO2                    0.751152E+01

       SiF4                    0.113883E+00

       Ca(NO3)2                0.205578E+01

       Mg(NO3)2                0.350700E-01
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Ni(NO3)2               0.000000E+00

Cu(NO3)2               0.000000E+00

Pb(NO3)2               0.300000E-02

KNO3                   0.000000E+00

NaNO3                  0.000000E+00

H2Pu(NO3)6             0.303735E-02

Dy(NO3)3             0.600000E-01

H2O(l)                 0.741423E+03

HF                     0.352847E+01

HNO3                   0.175794E+03

Ta2O5                  0.000000E+00

SnO                    0.292500E-03

Fe2O3                  0.310900E-01

Cr2O3                  0.122300E-01

B2O3                   0.000000E+00

MnO2                   0.000000E+00

TiO2                   0.690400E-01

Al2O3                  0.107500E+00

BaO                    0.382200E-02

C                      0.453300E+01

N2                     0.545073E+02

O2                     0.144893E+02

H2O(g)                 0.209241E+01
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