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STORAGE OF RADIOACTIVE SOLUTIONS, EVAPORATION AND
RADIOLYSIS LOSSES FROM TANKS CONTAINING
PLUTONIUM NITRATE SOLUTIONS

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ABSTRACT

The processes leading to mass loss from storage tanks containing radioactive solutions are examined and the methods applied to the estimation of material losses from plutonium nitrate storage tanks, such as those at the Allied General reprocessing plant at Barnwell, South Carolina. The mass loss rate is about 480 g/day from a full tank, of which approximately 98 percent is water.

INTRODUCTION

Knowledge of the losses to be expected from a tank containing radioactive solutions is required for plant design and operations, as well as for the active monitoring of contents of the tank, as required for purposes of nuclear material control. The work described herein was performed as a part of the NRC Material Control and Accounting program at LLL, a portion of which was devoted to the development of process models to be used as a part of active material control systems able to provide fast indication of material losses.^{1,2} Normal process loss of material from storage tanks arises from radiolysis and evaporation of the solution. While both processes are slow, they lead to significant loss of material from the tank if the periods of passive storage are long, such as those contemplated in the plutonium nitrate storage facility at the Allied General Nuclear Services (AGNS) reprocessing facility at Barnwell, SC.

The problem is the estimation of the various streams to allow closing the material balance around the tank. Since the temperature of the solution in the tank is normally maintained well below the boiling point, evaporation losses occur only because there is continuous injection and removal of gases from the tank. The sources of gas are as follows:

1. Radiolysis gas, containing about 60 percent H_2 .
2. Purge air, used to dilute the radiolysis gas to a hydrogen concentration below 4 percent H_2 (lower explosive limit).

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3. Air injected for bubbler-level and density measurement instrumentation.

4. Sparging air, which may be injected into a tank to mix its contents. Radiolysis and evaporation remove water and other volatiles from the solution, leading to mass and density changes. In the following paragraphs, the mass balance equations around the tank will be developed and illustrated by application to tanks containing plutonium nitrate solutions. Since the properties of these solutions are not well known, the estimates obtained will need to be refined using data obtained under actual operating conditions.

TANK GEOMETRY

Due to nuclear criticality problems, the design of storage tanks for solutions containing fissionable materials is restricted to long, small-diameter pipe, thin, flat slab or thin, hollow cylinder geometry. For present purposes thin, hollow cylinder geometry is equivalent to the flat slab and further discussion will assume use of the geometry of the tanks in the Plutonium Nitrate Storage (PNS) facility at Allied-General Nuclear Service (AGNS),³ in Barnwell, SC. These tanks, which are shown in Fig. 1, are also used in Lawrence Livermore Laboratory's test bed design.⁴

Since the radiolysis gas is generated uniformly in the volume of the solution, the purge air inlet and the vent lines must be located at opposite ends of the tank. AGNS does not use sparge air to mix the contents of the tanks in the PNS facility; however, in general the sparge air lines will terminate near the bottom of the tank. The bubbler air lines terminate near the bottom of the tank, except for the air line used to provide reference pressure measurement, which terminates above the maximum level of the solution at the top of the tank.

OVERALL MATERIAL BALANCES

The overall material balances to calculate material loss from the tank should proceed along the lines indicated in Fig. 2. The sparging air (if used) is shown sweeping the entire surface of the tank; however, it is not used in the PNS cell at AGNS or in the test bed. The radiolysis gas is shown split into two parts. This was done to approximate its effect on the average gas velocity and composition in the calculation of evaporation from the surface of the liquid.

FIG. 1. Storage tank penetrations.

FIG. 2. Flow diagram for material balances.

TABLE 1. Stream composition index j.

1 - HNO_3	4 - H_2	7 - Dry air
2 - $\text{Pu}(\text{NO}_3)_4$	5 - O_2	8 - Total permanent gas
3 - H_2O	6 - N_2	

The total mass flow rate in each of the streams, M_i , is identified using the stream numbers "i", as given in Fig. 2. The flow rate of each of the chemical species in each stream, $M_{i,j}$, is identified using the stream numbers "i" from Fig. 2 and the composition identifiers, J, from Table 1. Thus, $M_{7,4}$ is the flow rate of hydrogen in the radiolysis gas. The total permanent gas is denoted by $J = 8$, i.e.,

$$M_{i,8} = \sum_{J=4}^7 M_{i,j} \quad (1)$$

The calculation also requires a knowledge of the total pressure, P, at the surface of the tank to calculate gas compositions.

For each stream of Fig. 2 the material balance conditions are satisfied, i.e.,

$$\sum_J P_{i,j} = P_i \quad (2)$$

where $P_{i,j}$ is the partial pressure of each component of the gas mixture. The gas compositions are given by:

$$Y_{i,j} = P_{i,j}/P_i \quad (3)$$

It follows from equations (2) and (3) that

$$\sum_j Y_{i,j} = 1 \quad (4)$$

TABLE 2. Nominal parameters for a storage tank assumed to be full.

Surface area:	3290 cm ²
Total plutonium mass:	166 kg
Total solution volume:	664 l
Average cross section for gas flow (when full):	A _c = 223 cm ²
Flow rate for each bubbler line: 1 CFH (70°F)	= 1.17 $\frac{\text{g moles}}{\text{h}}$
Purge air flow rate: 4 CFH (70°F)	= 4.69 $\frac{\text{g moles}}{\text{h}}$
Nominal dew point of instrument air is 20°F; thus	Y _{1,3} = 3.42 × 10 ⁻³
Length for mass transfer calculation X _T	= 16 ft 5 in. = 500 cm

$$M_{i,j} = M_i Y_{i,j} \quad (5)$$

At each node, continuity requires that

$$\sum_i M_{i,j} = 0 \quad (6)$$

The amount and concentration of plutonium solution in the tank (Table 1) determines the radiolysis rate M_7 . The plant operator defines the air flows in streams 2, 3, 4, and 5 (Table 2), as well as the water content of the incoming air $Y_{1,3}$.

The flows and compositions of all the streams can then be estimated as discussed in the following paragraphs.

RADIOLYSIS LOSSES

An estimate of the radiolytic gas-generation rate and of the rates of decomposition for water and nitric acid can be obtained as follows:

The hydrogen gas generation, as obtained from Ref. 5, is:

$$M_{7,4} = G W_t V C_p \quad (7)$$

where

- $M_{7,4}$ = Hydrogen gas generation, g moles/h;
 G = Specific radiolysis rate (G-value) for hydrogen generation, $\frac{\text{g moles}}{\text{watt-hour}}$;
 W_t = Specific power, W/g;
 V = Volume of solution in tank, liters;
 ρ = Density of solution in tank, g/l;
 C = Radioisotope concentration g/g of solution.

The G-value for hydrogen generation is given, for $0 < M < 15$, by:

$$G = 1.203 \times 10^{-4} - 4.259 \times 10^{-5} M + 5.85 \times 10^{-6} M^2 - 2.6 \times 10^{-7} M^3 \quad (8)$$

where M is the nitric acid concentration, g moles/l. The specific power is given by:

$$W_t = \frac{1}{100} \sum_K Z_k W_k \quad (9)$$

where

- W_t = Average specific power of isotopes in solution, W/g of Pu;
 Z_k = Weight percent of each isotope in solution;
 W_k = Specific power generation of isotope-k, W/g (Table 3).

The gas composition can be assumed to be:

	Mole percent	Mole ratios $H_2 = 1$
H_2	6.05	1.0
O_2	39.69	0.51
N_2	<u>0.26</u>	<u>0.004</u>
	100.00	1.514

While the above gas composition is somewhat different from the values given previously,⁵ it is still consistent with literature data and allows for

TABLE 3. Properties of $\text{Pu}(\text{NO}_3)_4$ solution.

• Nominal isotopic composition^a:

Isotope	Specific power ^b w/g	AGNS design wt%
^{238}Pu	567.16	2.5
^{239}Pu	1.9293	50.0
^{240}Pu	7.098	25.0
^{241}Pu	3.390	15.0
^{242}Pu	0.1146	7.5
^{241}Am	--	--

Average specific power 17.44 w/kg of Pu; average atomic weight 239.80

• Nominal composition (25°C):

250 g/l of Pu or 0.02159 mole fraction of $\text{Pu}(\text{NO}_3)_4$

3.0 MHNO_3 or 0.06214 mole fraction HNO_3

• Nominal temperature:

60°C

• Nominal density, estimated using AGNS density correlation^c:

1.47 g/l at 20°C

1.44 g/l at 60°C

^aSee reference 3.

^bSee reference 12.

^cSee reference 5.

making a material balance on the tank. This portion of the model will probably need to be modified once actual plant operating data are obtained.

The total radiolysis gas evolved is:

$$M_7 = 1.514 M_{7,4} \frac{q \text{ moles}}{h} \quad (10)$$

The estimation of water and nitric acid decomposition rates requires a knowledge of the stoichiometry of the decomposition reactions. While the reaction path is not known, the reactions shown by equations (11) and (12) pro-

vide gaseous decomposition products consistent with the assumed gas composition given above:

The changes in composition of the solution can be obtained from the following equations.

The rate of HNO_3 loss from solution by radiolysis is:

$$M_{7,1}^l = 0.008 M_{7,4} \frac{\text{g moles}}{\text{h}} \quad (13)$$

The rate of water loss from solution by radiolysis is:

$$M_{7,3}^l = M_{7,4} - 0.004 M_{7,4} \approx 0.996 M_{7,4} \frac{\text{g moles}}{\text{h}} \quad (14)$$

EVAPORATION MODELS

In the calculation of the amounts of material evaporated from the solution into a gas stream, the following must be considered:

1. The equilibrium vapor pressure of water and nitric acid over the solution.
2. The initial composition (water content) of the gas stream.
3. The mass transfer between the solution and the gas stream, which is governed by the hydrodynamics of the problem.

Items 1 and 3 above will be discussed in more detail below.

EQUILIBRIUM VAPOR PRESSURES

The available data on vapor liquid equilibrium in the nitric acid-water-plutonium nitrate system were reviewed in an attempt to obtain a general correlation covering the range of conditions encountered in nuclear reprocessing.⁶ Unfortunately, the complex chemistry of the system and the poor quality of the data⁷⁻¹⁰ precluded such correlation. However, enough information was obtained to develop a set of estimates useful for an initial approximation to

the evaporation rates. The vapor pressures estimates were obtained by a combination of techniques,⁶ as follows:

	Vapor pressures, Torr		
	Water	Nitric acid	Total pressure
Low estimate	129	0.13	129
Most likely	129	0.39	129
High estimate	129	0.91	130

The above estimates apply to the solution composition given in Table 3 and an operating temperature of 60°C. Clearly, this is an area deserving additional experimental and theoretical work; however, the nature of the system (containing plutonium and low relative volatility) makes obtaining reliable data a difficult problem.

MASS TRANSFER CONSIDERATIONS

In the tank we have two entirely different situations, as follows:

• Evaporation of the solution into a well-dispersed gas stream. -- The gas stream can be bubbles of radiolytic gas (M_7), bubbles of air in the bubbler dip tube supply (M_5), or sparging air (M_5). Since there is a large interfacial area involved, we can assume that by the time the bubbles reach the surface, thermodynamic equilibrium has been achieved. The gas compositions for streams 9 and 10 are given by:

$$y_{9,1} = y_{10,1} = \frac{P_1}{P} \quad (15)$$

$$y_{9,3} = y_{10,3} = \frac{P_3}{P} \quad (16)$$

$$y_{9,8} = y_{10,8} = 1 - \frac{P_1 + P_3}{P} \quad (17)$$

• Mass transfer at the surface of the solution. -- A detailed model of the problem would describe the laminar flow circulation patterns in the space above the liquid and the effect on mass transfer of the injection of material across the entire surface of the tank by the radiolysis gas.

For present purposes, the flow will be taken as a one-dimensional laminar in a flat plate geometry. The mass transfer will be approximated using the Pohlhausen solution to the problem, as summarized by Sherwood, et al.¹¹ (which does not include the injection of material into the boundary layer). The average value of mass transfer for each chemical species over the entire plate of length X_T in the downstream direction is given by:

$$M_{13,j} = k_j A (C_{IN,j} - C_{11,j}) \quad (18)$$

where

$C_{IN,j}$ = Equilibrium concentration of component j at interface, g moles/cm³, where $C_{IN,j} = C_{9,j} = C_{10,j}$ for nitric acid (j = 1) and water (j = 3);

$C_{11,j}$ = Initial concentration of component j, g moles/cm³;

k_j = Mass transfer coefficient of component j, cm/s;

A = Surface area of tank (see Table 2).

The concentrations are obtained from:

$$C_{ij} = y_{ij} / V_M \quad (19)$$

where V_M is the average molar volume. If it is assumed that ideal gas law applies, at 60°C and 760 Torr, then:

$$V_M = 2.735 \times 10^4 \text{ cm}^3/\text{g mole.}$$

The mass transfer coefficient is obtained from:

$$\frac{(k_j)_{av} X_T}{D_j} = 0.664 (Re_{X_T})^{1/2} (Sc_j)^{1/3} \quad (20)$$

where

$$Re_{X_T} = \frac{\bar{U} X_T}{\nu} \quad (21)$$

$$Sc_j = \frac{\nu}{D_j} \quad (22)$$

and

D_j = Diffusion coefficient of component j into gas mixture, cm^2/s
(Table 4);

ν = Kinematic viscosity, μ/ρ , cm^2/s ;

Sc = Schmidt number, dimensionless;

Re_{XT} = Reynolds number, dimensionless;

X_T = Length of plate, cm ;

$\bar{U}$ = Average initial gas velocity, cm/s .

Clearly, the flow patterns and evaporation rates will change as the tank is being filled. The above calculation assumes that the interface is in thermodynamic equilibrium with the solution.

TABLE 4. Approximate values of molecular transport parameters at 60°C .

-
- Kinematic viscosity of dry air:

$$\nu = 0.19 \text{ cm}^2/\text{s}$$

- Binary diffusion coefficients, obtained using the correlation of Fuller, Schettler, and Giddings (as quoted by Sherwood, et al.^a):

D_j in cm^2/s at one atmosphere pressure

$$K_{\text{H}_2\text{O}-\text{N}_2} = 0.32$$

$$D_{\text{O}_2-\text{N}_2} = 0.25$$

$$D_{\text{H}_2-\text{N}_2} = 0.95$$

$$D_{\text{HNO}_3-\text{N}_2} = 0.19$$

For the purpose of this calculation N_2 was considered to be the equivalent of air.

^aSee reference 10.

CHANGES IN THE CONCENTRATION AND DENSITY OF THE SOLUTION

The amounts of nitric acid and water lost from the solution by radiolysis was obtained previously using equations (13) and (14). The rate of nitric acid and water evaporation can be obtained using an overall material balance for nitric acid. Equation (23) gives this rate for nitric acid and equation (24) for water.

$$M_{12,1}^L = M_{12,1} + 0.008 M_{7,4} \quad (23)$$

$$M_{12,3}^L = M_{12,3} - M_{1,3} + 0.996 M_{7,4} \quad (24)$$

The changes in solution composition (and density) take place very slowly and can be neglected, except when the total amount of material lost by radiolysis and evaporation exceeds about two percent of the solution. For a full tank, such as used at AGNS or in our test bed design, this amount of evaporation would require periods of static storage longer than about 40 days.

NUMERICAL EXAMPLE

The quality of the data available for radiolysis and liquid vapor equilibria, as well as the relative importance of this aspect of the problem to the NRC program, does not justify a careful parameter study.

The amounts of solution lost by radiolysis and evaporation from a full tank, such as described in Tables 2 and 3, were calculated for the three estimates of equilibrium vapor pressures given above.

The results can be summarized as follows:

	Vapor pressure estimate		
	Low	Most likely	High
Radiolysis gas, g/day	57	57	57
Nitric acid loss, g/day	2.6	5.2	10.5
Water loss, g/day	473	473	473
Total mass loss, g/day	476	478	483

About half of the loss is due to evaporation across the surface of the tank, and will change as the level in the tank and corresponding hydrodynamics of the gas flow change. An upper limit can be obtained by assuming that the exit gas is in thermodynamic equilibrium with the liquid; the corresponding values are:

	Vapor pressure estimate		
	Low	Most	High
	<u>likely</u>		
Nitric acid loss, g/day	3.9	9.1	19.5
Water loss, g/day	772.0	772.0	772.0
Total mass loss, g/day	776.0	781.0	792.0

The mass of water and nitric acid evaporated is low compared to the total mass of material in the tanks, and is of interest only when long periods of storage or online nuclear material control systems are contemplated.

REFERENCES

1. D. R. Dunn, "Dynamic Models, Estimation, and Detection Concepts for Safeguarding $\text{Pu}(\text{NO}_3)_4$ in Storage Tanks," *Inst. of Nucl. Mat. Mgmt. Journal*, Vol. VI, No. III, 509 (1977).
2. J. V. Candy, D. R. Dunn and R. B. Rozsa, "On-Line Safeguards Design and an Application of Estimation/Detection," (1st ESARDA Symposium, Brussels, Belgium, April 1979).
3. Barnwell Nuclear Fuel Plant, FSAR, Figures 4.5-2A, 5.10-2 and Table 4.3-2.
4. I. J. Sacks, *Safeguards Material Control and Accounting at Licensed Processing Facilities*, Quarterly Report, July-September 1977, Lawrence Livermore Laboratory, Livermore, CA, NUREG/CR-0663; UCRL-52703 (December 1978).
5. A. Maimoni, *Density and Radiolytic Decomposition of Plutonium Nitrate Solutions*, Lawrence Livermore Laboratory, Livermore, CA, UCRL-52727 (October 1979).
6. A. Maimoni, *Vapor-Liquid Equilibria, Nitric Acid-Water and Plutonium Nitrate-Nitric Acid-Water Solutions*, Lawrence Livermore Laboratory, Livermore, CA, (to be published).
7. *Purex Technical Manual*, General Electric Hanford Atomic Products Operation, Richland, WA, HW-3100 (Del.), (March 25, 1955).
8. R. A. Pugh, *Notes Pertaining to Recuplex Product Evaporation*, General Electric Hanford Works, Richland, WA, HW-32100 (April 1954).
9. S. M. Stoller, and R. B. Richard, *Reactor Handbook*, Figure 11.3, Vol. II, (Interscience, New York, New York 1961).
10. J. L. Swanson, "Properties of Concentrated Plutonium Nitrate Solutions," (February 1976) work done at Battelle Pacific Northwest Laboratories under contract to Allied-General Nuclear Services and reported by J. L. Swanson and J. H. Gray (Am. Nucl. Soc., Savannah, GA., March 1978).
11. T. K. Sherwood, R. L. Pigford and C. R. Wilke, *Mass Transfer*, (McGraw-Hill 1975).
12. American National Standards Institute, Inc., *ANSI Standard N15.22* (1975).

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