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Results of Research to Evaluate Solid Plutonium Nitrate as a Safe Shipping Form

G. H. Bryan
J. K. Thompson
H. H. Van Tuyl
C. L. Brown
J. L. Ryan

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BATTELLE
PACIFIC NORTHWEST LABORATORIES
Richland, Washington 99352

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INTRODUCTION

Plutonium used in commercial experimental $\text{PuO}_2\text{-UO}_2$ fuels is shipped to fuel fabricators in two forms: $\text{Pu}(\text{NO}_3)_4$ solution and PuO_2 powder. In 1973, the USAEC amended its regulation 10 CFR Part 71 to require that after June 17, 1978 all plutonium in quantities greater than 20 curies be packaged for shipment as a solid (see Appendix 1). After that date the shipment of plutonium nitrate solution will be prohibited.

Depending on the outcome of nuclear reactor performance tests with the experimental mixed oxide fuels, fuel fabricators will decide on a best starting material for the fuel - $\text{Pu}(\text{NO}_3)_4$ solution or dry PuO_2 powder. At first glance, plutonium oxide would seem to be the first choice. It is a stable, fairly easily made powder that would seem to "fill the bill" as an almost ideal shipping form. The oxide, however, is an extremely difficult compound to dissolve in nitric acid alone and the use of hydrofluoric acid is usually necessary. Hydrofluoric acid reacts with stainless steel, thus presenting problems with use of ordinary materials for glove box construction, piping and storage tanks. Purification of the plutonium, which may be necessary after long storage times, is also difficult until the fluoride ion is either complexed or removed. This requires the use of more chemicals which can only add to waste disposal problems. The presence of the fluoride also tends to increase the neutron flux, making shielding more difficult and expensive.

With the above listed difficulties in mind for the use of PuO_2 , a program was funded by the Division of Waste Management and Transportation

to define new chemical forms for the shipment of plutonium as a solid. The criteria for the type of material needed were as follows:

1. Solid
2. Readily soluble in HNO_3
3. Inexpensive to prepare
4. Minimum amount of explosive or flammable gas produced by radiolysis
5. Reasonable storage life without conversion to oxide or some other insoluble form

This material is intended to provide a more convenient form than the oxide for fuel cycle purposes. It would allow the fuel fabrication segment of the fuel cycle to store a solid that could be easily purified before conversion to the oxide without use of specially designed facilities that are able to withstand the use of hydrofluoric acid.

The three compounds chosen for evaluation were $\text{Pu}(\text{NO}_3)_4 \cdot x\text{H}_2\text{O}$, $\text{K}_2\text{Pu}(\text{NO}_3)_6$ and $(\text{NH}_4)_2\text{Pu}(\text{NO}_3)_6$. The nitrates were selected since they would not add an extraneous anion to the process streams. The halides were ruled out since they would not be compatible with stainless steel, and organics were not felt to be sufficiently stable for use.

A systematic study of the radiolytic and thermal stability, solubility, and ease of preparation of each of the three nitrate compounds selected was then accomplished. These results allowed each compound to be evaluated as a potential solid shipping form as a guide to shipping package requirements.

This report presents the results of the chemical development on a laboratory scale. Pilot plant development work on a one-kg scale was begun by Atlantic Richfield-Hanford Company but not completed in FY-1975.^(a) If warranted, a later phase will evaluate pilot facility operations and packaging development for shipment of solid plutonium nitrate.

a. Work performed by R. E. Felt and P. C. Ely, ARHCO. A formal report summarizing the results of this work is to be published at a later date.

SUMMARY AND CONCLUSIONS

The results of the research described in this report indicate that the compound $\text{Pu}(\text{NO}_3)_4 \cdot \text{XH}_2\text{O}$ is a viable material for consideration as a solid shipping form. **It** meets the criteria, as outlined in the introduction, set forth to define a suitable solid form of plutonium.

Several plutonium compounds were considered for study as a shipping form before selecting $\text{Pu}(\text{NO}_3)_4 \cdot \text{XH}_2\text{O}$ as having the most desirable characteristics. **It** is reasonably easy to prepare on a kilogram scale with relatively simple equipment using vacuum evaporation techniques. Plutonium nitrate does begin to thermally decompose at about 100°C; however, proper equipment design and instrumentation can overcome this problem.

Although $\text{Pu}(\text{NO}_3)_4 \cdot \text{XH}_2\text{O}$ does produce some radiolytic gases, such as oxygen and nitrogen, an explosive mixture is not produced as only minor amounts of hydrogen are formed except during extended storage. Excessive pressurization in the shipping mode should not be a problem **if** the transport container is not closed for protracted periods of time. However, some form of thermal insulation would be required to prevent decomposition of the compound and to preclude over-pressurization during a fire.

Plutonium nitrate has been found to be completely soluble in nitric acid even after storage for extended periods of time. After the equivalent of 25 years of storage time of first-cycle reactor-grade plutonium from a radiation damage standpoint, $\text{Pu}(\text{NO}_3)_4 \cdot \text{XH}_2\text{O}$ prepared from 85 wt% ^{238}Pu was found to be completely soluble in 4M HNO_3 . Plutonium nitrate was also found to be soluble in water, but **it** rapidly converted to plutonium polymer.

A possible shipping form other than plutonium oxide has been described in this work. More research is required before the final acceptance of $\text{Pu}(\text{NO}_3)_4 \cdot \text{XH}_2\text{O}$ as an alternate form; however, **it** does appear to meet established criteria.

DISCUSSION

BACKGROUND

At the present time there is considerable debate concerning the relative risk of transporting plutonium in nitrate solution versus the oxide form. Some

of the characteristics of plutonium nitrate solution which might make it less desirable to ship are as follows:

- Nitrate is a liquid, whereas current trends are for shipments of radioactive material in the solid form. It is felt that the potential for release in an uncontrolled manner may be greater for liquids than for solids. In addition, liquid solutions have the potential for producing steam pressurization within the package if sufficient heat is available.

*Plutonium nitrate solution has the potential hazard of pressurization of the container due to the radiolysis of water. The hydrogen and oxygen gas mixture which is evolved eventually could result in significant pressurization or explosion of the containment vessel.

It is generally recognized that the most vulnerable part of the nuclear fuel cycle for harm to the public from radioactive material is during the transportation mode. Thus, there is considerable emphasis at this time on increasing the safety of this portion of the fuel cycle. If nitrate shipments are to continue, it must be demonstrated that the potential hazards referred to above can be eliminated or reduced to a reasonable level with respect to the hazard associated with transportation of oxide.

If it can be shown that the nitrate solid form and the associated shipping package represent significant improvements in safety of plutonium shipments, this would have a significant impact on public acceptance of the nuclear fuel cycle.

This program investigated the conversion of plutonium nitrate solutions to solid forms in a variety of ways and measurement of the properties of the forms thus produced. Candidate product forms found to be suitable from radiolytic considerations will also be characterized for thermal stability, thermal conductivity, heat capacity, and other parameters which are of interest in both shipping cask design and in transportation safety analysis.

EXPERIMENTAL

Plutonium Composition

The 84.8 wt% ^{238}Pu used in this work was prepared by neutron irradiation of ^{237}Np . The 17.4 wt% ^{238}Pu was prepared by mixing appropriate amounts of nitric acid solutions of the 84.8 wt% ^{238}Pu and 91.3 wt% ^{239}Pu . The results of mass spectrometric isotopic analysis of the final product in each case are shown in Tables 1 and 2. Chemicals were reagent grade and were used without further purification.

Plutonium Compounds

The simple plutonium nitrate salt, $\text{Pu}(\text{NO}_3)_4 \cdot x\text{H}_2\text{O}$, was prepared from an 8M nitric acid solution of plutonium nitrate by vacuum evaporation at 1 torr and ambient temperature. Samples prepared from 17.4 wt% ^{238}Pu and 91.3 wt% ^{239}Pu required from 3-5 days to prepare a solid material. Less than 24 hours was required with the 84.8 wt% ^{238}Pu due to self heating.

TABLE 1. 84.8 wt% ^{238}Pu Isotopic Composition

Pu-238	84.8 ± 0.06 wt%
Pu-239	11.19 ± 0.06 wt%
Pu-240	3.22 ± 0.02 wt%
Pu-241	0.665 ± 0.007 wt%
Pu-242	0.122 ± 0.003 wt%

TABLE 2. 17.4 wt% ^{238}Pu Isotopic Composition

Pu-238	17.4 ± 0.1 wt%
Pu-239	74.9 ± 0.1 wt%
Pu-240	6.946 ± 0.04 wt%
Pu-241	0.635 ± 0.005 wt%
Pu-242	0.079 ± 0.002 wt%

The starting plutonium concentration in all cases was about 230 g/l.

The potassium and ammonium hexanitrate plutonate salts were prepared by the addition of a 10% stoichiometric excess of potassium or ammonium nitrate to plutonium nitrate in 8M nitric acid, followed by vacuum evaporation at ambient temperature. Once again, the 84.8 wt% ^{238}Pu compounds required less than 24 hours to prepare while those samples having lesser amounts of ^{238}Pu required 3-5 days of evaporation before dryness was obtained.

Experimental Procedure

During the course of evaporation the simple plutonium nitrate ($\text{Pu}(\text{NO}_3)_4 \cdot \text{XH}_2\text{O}$) became extremely viscous before becoming a solid, indicating a very high solubility. The potassium and ammonium salts are less soluble and crystallized during the course of evaporation. The uranium salt $\text{KUO}_2(\text{NO}_3)_3$ was prepared for x-ray powder pattern comparison analysis by the mixing of stoichiometric amounts of KNO_3 and $\text{UO}_2(\text{NO}_3)_2$ in nitric acid followed by filtering, washing, and drying.

The rate of radiolytic gas generation was measured using the apparatus shown in Figure 1. A weighed sample of the compound to be tested was placed in the sample container and held in place with a glass wool plug. The sample container was then placed in a stainless steel outer sample container with a cap containing a stainless steel frit to allow the passage of gases. The stainless steel sample container was placed in the gas measurement apparatus and the system purged with helium gas for 30 minutes with pressure pulsing to insure removal of all other gases. This arrangement was found to contain the plutonium compound under study quite well and allowed measurements to be taken in an open hood without contamination of the apparatus.

A 10 mm layer of silicone oil was placed on top of the mercury on each side of the manometer prior to use to retard reaction with any corrosive gases produced during the course of the experiment. All manometer readings were obtained by use of a cathetometer.

Gas samples were taken by evacuating the sample collector and the area between the collector and the measurement apparatus with the gas then being drawn into the collector from the apparatus. Samples were analyzed on a

FIGURE 1. RADIOLYTIC GAS MEASUREMENT APPARATUS

Consolidated Electrodynamics Corporation 21-103 mass spectrometer to determine the composition of gases that had been produced.

The amount of gas generated by the solid per 100 ev (G_T value) was calculated using the ideal gas law, and the dose rate of the material used, as determined by the following equation:

$$\text{Dose Rate} = (\text{Sp. activity } ^{239}\text{Pu}) E_a [\% \text{Pu-239} + 3.7(\% \text{Pu-240}) + 302 (\% \text{Pu-238}) + 60(\% \text{Pu-241})(1 - e^{-0.049Y})]$$

E_a = alpha energy of ^{239}Pu in electron volts

Y = time in years since chemical separation of Am from Pu.

The ^{238}Pu contributes, by far, the largest amount of energy in the case of the 84.8% ^{238}Pu material allowing the energy contributions of the other isotopes to be disregarded.

Thermogravimetric analyses were obtained using an Ainsworth Semimicro Recording Balance. All analyses were made in an air atmosphere to duplicate actual conditions to which the compound might be subjected in the shipping mode. This procedure also converted each compound to PuO_2 , and the final PuO_2 weight was used as the basis for calculation of the original molecular weight of the material in question. A heating rate of $2^\circ\text{C}/\text{min}$ was used in all cases.

X-ray analyses were performed on a General Electric SRD-5 x-ray diffractometer. Analyses were performed on samples of all compounds, as well as any intermediates found during thermogravimetric analysis. Patterns were obtained only for those materials which were prepared from 91.3% ^{239}Pu . All others were found to be amorphous.

The pilot-plant scale work to produce kilogram quantities of $\text{Pu}(\text{NO}_3)_4 \cdot \text{XH}_2\text{O}$ was accomplished using 4 liters of plutonium nitrate solution that was initially 5M in nitric acid and contained 920 grams of plutonium. The isotopic composition and impurities are shown in Tables 3 and 4.

TABLE 3. Isotopic Composition of Plutonium Nitrate Feed

<u>Isotope</u>	<u>wt% Abundance</u>
^{238}Pu	0.062
^{239}Pu	89.667
^{240}Pu	8.907
^{241}Pu	1.159
^{242}Pu	0.205

TABLE 4. Plutonium Nitrate Feed Impurities

<u>Element</u>	<u>PPM</u>	<u>Element</u>	<u>PPM</u>
Ag	<8	Mg	100
Al	250	Mn	25
As	<100	Mo	<10
B	<2	Na	400
Ba	<100	Nb	<8
Be	<2	Ni	<50
Bi	<5	P	250
Ca	140	Pb	<10
Cd	<2	Si	<40
Co	1	Sn	<15
Cr	125	Ta	<40
Cu	<20	Ti	400
Fe	270	V	<50
Ga	<4	W	<10
K	2000	Zn	<20
Li	<10	Zr	200

The evaporation vessel in which all large-scale operations were performed is shown in Figure 2. The Equipment Schematic for the pilot-plant scale work was as shown in Figure 3.

Results

A. Radiolytic Gas Generation

The G_T values (molecules per 100 ev) have been calculated as a function of accumulated radiation dose for each of the three compounds under consideration - $\text{Pu}(\text{NO}_3)_4 \cdot \text{XH}_2\text{O}$, $\text{K}_2\text{Pu}(\text{NO}_3)_6$, and $(\text{NH}_4)_2\text{Pu}(\text{NO}_3)_6$ - as shown in Figure 4. The high G_T values found in the case of $(\text{NH}_4)_2\text{Pu}(\text{NO}_3)_6$ were not completely unexpected as the NH_4^+ ion is rather sensitive to radiation damage producing gaseous products!) The G_T values of $\text{Pu}(\text{NO}_3)_4 \cdot \text{XH}_2\text{O}$ and $\text{K}_2\text{Pu}(\text{NO}_3)_6$ were found to be similar (each decreasing with accumulated dose and approaching a value of about 0.025 above about 10^{18} Mev/g Pu).

Each of the compounds was prepared with 84.8 wt% ^{238}Pu to accelerate the acquisition of data. The simple plutonium nitrate, $\text{Pu}(\text{NO}_3)_4 \cdot \text{XH}_2\text{O}$, was also prepared using 17.4 wt% ^{238}Pu as TGA results indicated the 84.8 wt% material did not have the proper molecular weight and may have degraded to some intermediate (see TGA section for further explanation). Therefore, the numbers used for Figure 4 were found using the 17.4 wt% ^{238}Pu material which also more closely simulated actual reactor grade ^{238}Pu content.

Given the G_T values, the rate of radiolytic gas generation with a specified amount of $\text{Pu}(\text{NO}_3)_4 \cdot \text{XH}_2\text{O}$ is $g_{\text{Pu}} \left(\frac{\text{sp. activity}}{6.02 \times 10^{23}} \right) E_{\alpha} G_T / 100 = 1.67$

$$g_{\text{Pu}} G_T \left[(\% \text{Pu-239}) + 3.7 (\% \text{Pu-240}) + 302 (\% \text{Pu-238}) + 60 (\% \text{Pu-241}) \right. \\ \left. (1 - e^{-0.049Y}) \right] \text{ moles gas per day}$$

$$\text{and } G_T = G_{(\text{H}_2)} + G_{(\text{O}_2)} + G_{(\text{N}_2)} + \dots$$

The rate of pressurization in a given container will be:

$$\frac{dp}{dt} = 2.01 \times 10^{-4} \left(\frac{K}{V-W/2.90} \text{ g/cm}^3 \right) g_{\text{Pu}} G_T \left[(\% \text{Pu-239}) + 3.7 \right. \\ \left. (\% \text{Pu-240}) + 302 (\% \text{Pu-238}) + 60 (\% \text{Pu-241}) (1 - e^{-0.049Y}) \right]$$

FIGURE 2 EVAPORATION VESSEL

FIGURE 3. EQUIPMENT SCHEMATIC

FIGURE 4. G_T VALUE VS ACCUMULATED DOSE

where K = degrees Kelvin

t = time in days

V = container volume in ml

W = weight of $\text{Pu}(\text{NO}_3)_4 \cdot \text{XH}_2\text{O}$ of density 2.90 g/cm^3 (ref. 6)

Y = time in years since chemical separation of Am from Pu

E = alpha energy in electron volts

g_{Pu} = grams plutonium

p = pressure in psi.

Figure 5 gives the total accumulated gas production as a function of total accumulated radiation dose for $\text{Pu}(\text{NO}_3)_4 \cdot \text{XH}_2\text{O}$. In this plot, the origin represents the point at which the $\text{Pu}(\text{NO}_3)_4 \cdot \text{XH}_2\text{O}$ was prepared. By determining from this plot the difference between the accumulated gas production at the time (and accumulated dose) a container is sealed and some later time (and accumulated dose), the total gas production in the container is obtained. From this and the container void volume the pressure is easily calculated.

Hydrogen is not a major constituent (see Table 5) in any of the three cases studied and should not present an explosive hazard. Upon long term storage the relative amount of radiolytic hydrogen does increase in the case of $\text{Pu}(\text{NO}_3)_4 \cdot \text{XH}_2\text{O}$, but when viewed from the standpoint of total gas produced by the solid, it remains at a low level.

The mechanism by which the gases (see Table 5) are formed during the radiolysis of each compound is not fully understood. Products usually associated with the alpha-radiolysis of nitrate solutions have been studied(2,3) to some extent, and have been found to usually contain nitrites, hydrogen peroxide, hydrogen, and oxygen. Several papers have been published on the decomposition of inorganic nitrates; (4,5,6,7,8) however, they deal with salts that were irradiated with gamma or x-rays and so do not necessarily correspond to experimental results found during this research.

The studies that have been made on the radiation-induced decomposition of inorganic nitrates show a very complex nature. Different nitrates show varying degrees of stability when exposed to ionizing radiation leading to numerous explanations for the different yields (G-values) that are observed.

FIGURE 5 TOTAL MOLES OF GAS PRODUCED AS A FUNCTION OF ACCUMULATED DOSE
 $[\text{Pu}(\text{NO}_3)_4 \cdot x\text{H}_2\text{O}]$

TABLE 5. Composition of Radiolytic Gases in Mole Percent Evolved From $\text{Pu}(\text{NO}_3)_4 \cdot x\text{H}_2\text{O}$, $(\text{NH}_4)_2\text{Pu}(\text{NO}_3)_6$, and $\text{K}_2\text{Pu}(\text{NO}_3)_6$ as a Function of Accumulated Alpha Dose*

	1×10^{17} Mev			9×10^{17} Mev			20×10^{17} Mev		
	$\text{Pu}(\text{NO}_3)_4 \cdot x\text{H}_2\text{O}$	$\text{K}_2\text{Pu}(\text{NO}_3)_6$	$(\text{NH}_4)_2\text{Pu}(\text{NO}_3)_6$	$\text{Pu}(\text{NO}_3)_4 \cdot x\text{H}_2\text{O}$	$\text{K}_2\text{Pu}(\text{NO}_3)_6$	$(\text{NH}_4)_2\text{Pu}(\text{NO}_3)_6$	$\text{Pu}(\text{NO}_3)_4 \cdot x\text{H}_2\text{O}$	$\text{K}_2\text{Pu}(\text{NO}_3)_6$	$(\text{NH}_4)_2\text{Pu}(\text{NO}_3)_6$
O_2	57	24	0.2	71	23	0.2	49	18	0.2
N_2	18	6	55	13	20	61	27	49	56
H_2	1.4	0	0.5	2.4	0.3	0.5	6	0	0.7
NO_x	15	56	23	4	39	2.7	7	18	32
N_2O	0	14	20	6	11	8	4	8	8
CO_2	7	0	0	4	7	0	7	7	1
CO	0	0	2	0	0	3	0	0	2

*Typical reactor grade plutonium might undergo a dose of about 1.3×10^{17} Mev/g per month whereas the dose from the material used to compile this table was 1.6×10^{18} Mev/g per month for $\text{Pu}(\text{NO}_3)_4 \cdot x\text{H}_2\text{O}$ and 7.8×10^{18} Mev/g per month for $(\text{NH}_4)_2\text{Pu}(\text{NO}_3)_6$ and $\text{K}_2\text{Pu}(\text{NO}_3)_6$.

The inorganic nitrates appear to decompose when subjected to ionizing radiation in the following manner:

The variation in yield found when using different cations has been attributed to field strength exerted by the cation on the nitrate ion.⁽⁹⁾ Henning, Lees, and Matheson⁽¹⁰⁾ found large differences in yields during radiation decomposition of NaNO_3 and KNO_3 . They felt bonding energy differences were insufficient to account for these differences and proposed that the variation in "free space" might be a possible explanation. "Free space" was defined as the average volume per ion pair minus the average volume of cation and anion as calculated from standard ionic radii. Cunningham and Heal⁽⁵⁾ made an extensive study of the radiolysis of several nitrates and their yields (G-values) plotted as a smooth function of free space.

The salts with the smallest free space also had the largest temperature coefficient which supported the free space thesis. The order of decreasing G values was as follows:

There is an anomaly in this work; however, inasmuch as CsNO_3 has subsequently been found to have a higher G-value than KNO_3 but a smaller free space.⁽⁶⁾

An ambient temperature study of inorganic nitrate decomposition by Chen and Johnson⁽⁷⁾ has led to a proposed mechanism that would seem to agree with experimental data. It is as follows:

The back reaction was found to occur in all the nitrates studied and decompositions appeared to approach a steady state. The first derivative of the NO_2^- yield vs. dose curve (dx/dT where $x = \text{NO}_2^-$ concentration and T is proportional to dose) or slope indicates CsNO_3 approaches a steady state more rapidly than does KNO_3 or NaNO_3 . This information indicates that the back

reaction for CsNO_3 is much greater than it is for KNO_3 which is a more loosely packed lattice or NaNO_3 which is a more tightly packed lattice. Free space, therefore, would appear to have no substantial effect on the kinetics of the reaction.

Logan and Moore⁽¹¹⁾ have indicated that G values are affected by the relative ease of transferring energy to lattice vibrational modes and the density of vibrational states, as well as their average energies. The amount of electronic coupling to lattice vibrations will have some relationship to the polarizability of the cation and to the free space in the lattice and these parameters are also responsible for a particular crystal structure.

Factors such as reactions between radiation induced reaction products, lattice damage from the radiation, stability of primary products and impurities may also be expected to play some role - major or minor - in the radiation decomposition of any given inorganic nitrate. Variations on any or all of these factors may change the yields (G values) to an appreciable extent.

The ammonium salt is somewhat different inasmuch as the cation itself may be decomposed and is sensitive to the effects of heat and radiation. The radiolytic decomposition of ammonium nitrate at high dose rates has been reported to be comparable to thermal decomposition. Ammonium nitrate volatilizes reversibly at moderate temperatures and irreversibly at higher temperatures. At still higher temperatures, the N_2O decomposes into nitrogen and oxygen. (1)

Very little oxygen was found in the gaseous products of $(\text{NH}_4)_2\text{Pu}(\text{NO}_3)_6$; however, a large amount of nitrogen was noted. The high nitrogen, low oxygen, and relatively high NO_x content of the gas along with the relatively high G values for this salt indicates a low radiation stability for the ammonium ion. The hydrogen atoms from the ammonium ion presumably end up as water with the nitrate ions furnishing necessary oxygen. Although the total gas evolution from $\text{Pu}(\text{NO}_3)_4 \cdot x\text{H}_2\text{O}$ and $\text{K}_2\text{Pu}(\text{NO}_3)_6$ are similar, the former produces a larger amount of oxygen and a smaller amount of nitrogen oxides than the latter. This variation can probably be attributed to lattice vibrations, cation polarizability, and the other effects discussed previously. Radiolytic

release of H_2 from the water of hydration of $Pu(NO_3)_4 \cdot xH_2O$ apparently does not become significant until high accumulated radiation dose. To make a measurement of the contribution of any one factor would be extremely difficult and probably cannot be done except on a theoretical basis.

B. Thermal Stability

Each of the compounds under study - $Pu(NO_3)_4 \cdot xH_2O$, $K_2Pu(NO_3)_6$, and $(NH_4)_2Pu(NO_3)_6$ - was subjected to thermogravimetric analysis. This procedure was carried out in order to determine intermediates that may have formed and to convert the compounds to oxide for molecular weight determinations. All runs were made in air to duplicate actual conditions the compounds might be subjected to as a shipping form.

TGA curves for each compound are shown in Figures 6, 7, and 8. The compound used in each case was freshly made using ^{239}Pu so as to preclude excessive radiation damage. The curve found for $Pu(NO_3)_4 \cdot 3H_2O$ (Figure 6) is much the same as that determined by Drummond and Welch⁽¹³⁾ for $Pu(NO_3)_4 \cdot 5H_2O$. From molecular weight calculations the intermediate has been postulated to be $PuO_2(NO_3)_2$. Spectrophotometric analysis on freshly dissolved solid also indicated the presence of PuO_2^{2+} ; however, the intermediate formed was not identified by x-ray analysis due to its instability.

The simple plutonium nitrate salt suffers from the standpoint of the low temperature required for decomposition. Present shipping cask designs may not be adequate to ship large quantities without thermal degradation from self-heating.

The TGA curve for $K_2Pu(NO_3)_6$ (Figure 7) indicates a low temperature loss of water. Because of the low temperature at which the water is lost, the water may not be a part of the crystal structure, but rather may be sorbed. This compound also produces a somewhat unstable intermediate, probably of the formula $K_2PuO_2(NO_3)_4$, before decomposition to KNO_3 and PuO_2 . The end point of this TGA is not specific; however, due to slow formation of K_2O and evaporation of KNO_3 . The intermediate formed is stable enough to allow the obtaining of an x-ray powder pattern and is apparently not a mixture of KNO_3 and $KPu(NO_3)_3$ as will be described in greater detail under the x-ray analysis section.

FIGURE 6 THERMOGRAVIMETRIC CURVE FOR PLUTONIUM NITRATE

FIGURE 7. THERMOGRAVIMETRIC CURVE FOR POTASSIUM HEXANITRATOPLUTONATE

FIGURE 8. THERMOGRAVIMETRIC CURVE FOR AMMONIUM
HEXANITRATOPLUTONATE

Thermogravimetric analysis of the ammonium salt, $(\text{NH}_4)_2\text{Pu}(\text{NO}_3)_6$, indicated no intermediates were formed (see Figure 8). Copious amounts of gas were evolved during the course of the analyses.

C. X-ray Analysis

All x-ray patterns of ^{238}Pu salts indicated they were amorphous; presumably from radiolytic breakdown of the crystal structure. Therefore, each of the three salts under study was made from ^{239}Pu to obtain patterns for identification and classification (see Figure 9). The intermediate in the thermal degradation of $\text{Pu}(\text{NO}_3)_4 \cdot \text{XH}_2\text{O}$ (as indicated by TGA) is unstable and powder pattern identification was not achievable; however, the intermediate found with $\text{K}_2\text{Pu}(\text{NO}_3)_6$ is sufficiently stable to produce an x-ray pattern as indicated in Figure 9.

Positive identification of the intermediate formed by heating of $\text{K}_2\text{Pu}(\text{NO}_3)_6$ has not been achieved. TGA indicates it may be $\text{K}_2\text{PuO}_2(\text{NO}_3)_4$ by molecular weight considerations. X-ray patterns of the intermediate and the well known uranium salt $\text{KUO}_2(\text{NO}_3)_3$ do not compare indicating that it is probably not a mixture of $\text{KPuO}_2(\text{NO}_3)_3$ and KNO_3 . The uranium double salt $\text{KNO}_3 \cdot \text{KUO}_2(\text{NO}_3)_3$ is known,⁽¹⁴⁾ and it seems likely that the intermediate observed here is similar.

The x-ray powder pattern (see Figure 9) obtained for $\text{Pu}(\text{NO}_3)_4 \cdot 3\text{H}_2\text{O}$ is not the same as that found by Staritzky⁽¹⁵⁾ for $\text{Pu}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$. The pentahydrate was found to be orthorhombic and isomorphous with the corresponding nitrates of thorium and cerium. It also has 8 formula units per cell, has a density of 2.90 grams per cc, and is hygroscopic.

No known x-ray powder patterns are available for $(\text{NH}_4)_2\text{Pu}(\text{NO}_3)_6$ and $\text{K}_2\text{Pu}(\text{NO}_3)_6$. Complete analyses of the x-ray patterns in each case was not possible; however, further investigation could conceivably give added insight as to the difference in radiolytic decomposition behavior.

D. Effect of Radiation on Solubility

The solubility of each of the three compounds prepared was determined using 84.8% ^{238}Pu to accelerate experimental test results. The compound $\text{Pu}(\text{NO}_3)_4 \cdot \text{XH}_2\text{O}$ was stored in a dessicator for 171 days and still found to

FIGURE 9. X-RAY POWDER DIFFRACTION PATTERNS

be soluble in 4M HNO_3 at 28° with 4 hours of agitation. This is equivalent to 25 or more years of radiation damage from reactor grade plutonium. The compound $\text{K}_2\text{Pu}(\text{NO}_3)_6$ was stored for the reactor grade plutonium radiation equivalent of about five years and $(\text{NH}_4)_2\text{Pu}(\text{NO}_3)_6$ for the equivalent of about three years, and both were rapidly soluble in 4M HNO_3 at 25°C.

Each of the compounds under study was also prepared from ^{239}Pu and stored in a dessicator. The samples were all found to be completely and readily soluble in 4M HNO_3 at 25°C after 1.5 years of storage. No further solubility tests were carried out on these compounds; however, complete solubility for several years would be expected.

E. Pilot-Plant Work

The first large-scale production of $\text{Pu}(\text{NO}_3)_4 \cdot x\text{H}_2\text{O}$ was made using 920 grams of plutonium. The resultant solid was a large, dark-green mass that was taken as a single piece from the evaporation vessel. The solid was noted to be hygroscopic when left for extended periods of time exposed to glove box atmosphere.

The evaporation of the plutonium nitrate solution to one liter was accomplished at 180 torr during the first run. The final evaporation to dryness with use of a vacuum pump varied from 9 torr to 2 torr. Several days were required to complete the evaporation as the process was not continuous, and a few minor modifications to the equipment were required. The solution was never allowed to exceed 80°C during the final stages of the evaporation to insure the $\text{Pu}(\text{NO}_3)_4 \cdot x\text{H}_2\text{O}$ was not converted to an insoluble form. Some foaming was noted during the evaporation as the solution became more viscous.

Analytical results of the first run plutonium nitrate solid indicated an excessive amount of water, probably due to insufficient evaporation time. A portion of this material was then dried for 48 hours at 1 torr and ambient temperature. The material was then found to contain 41% plutonium by weight as determined by chemical analysis. Calcination to an oxide determined its molecular weight to be about 577 gm/mole indicating 6 waters of hydration.

The solid was found to be completely soluble in 4M HNO_3 . It was also found to be soluble in water but rapidly converted to plutonium polymer.

It is concluded that the plutonium compound, $\text{Pu}(\text{NO}_3)_4 \cdot x\text{H}_2\text{O}$, selected also has several other advantages that have not been enumerated in this report. It requires less equipment to prepare than does PuO_2 , making the overall preparative procedure quite simple. The oxide may also be easily made from the nitrate if desired. The preparation of mixed oxides could be readily achieved by a precipitation step to insure uniform mixing rather than by mechanical mixing of the oxides. Also, as plutonium nitrate is a nitric acid soluble compound, purification just prior to formation of the oxide is easily accomplished if, for example, long storage times before use of the plutonium were necessary and undesirable amounts of americium from ^{241}Pu decay were present.

A possible problem that could arise due to the variable weight of plutonium nitrate could be in plutonium accountability. However, if the plutonium content of the solution prior to evaporation to the solid is known, the amount to be shipped is known. The receiver may then easily check the plutonium content by conversion of a weighed amount to the oxide or by dissolution of the solid in nitric acid for analysis.

Further development of solid plutonium nitrate, $\text{Pu}(\text{NO}_3)_4 \cdot x\text{H}_2\text{O}$, would seem desirable in order to allow some flexibility in the shipment of plutonium. Plutonium nitrate may well be the solid form that could supply that flexibility.

BASIS FOR FUTURE SHIPPING PACKAGE DESIGN

Information on several key parameters needed for the design of a shipping package for solid plutonium nitrate is summarized in this section. The purpose of this summary is to provide insight and a starting point for this future development work. Most of the information is based on the chemistry development work described in the previous section. The criticality safety and shielding information was calculated. The information is sufficiently complete to show that an acceptable shipping package for solid plutonium nitrate can be developed.

Plutonium Isotopic Composition

Packaging design features that involve radiation safety, thermal safety, and criticality safety must be based on a conservative estimate of the plutonium isotopic composition expected to be shipped during the life of the package. For shielding requirements, the plutonium composition selected must consider the highest dose rate credible. For thermal assessment, the plutonium composition selected must consider the highest heat output credible. For criticality safety design features, the composition selected must consider the highest value of the effective multiplication constant that is credible.

Basic compositions recommended for consideration in shielding and thermal safety assessments are presented in Table 6. These estimates were prepared by M. G. Zimmerman and E. T. Merrill, BNW.

TABLE 6. Estimated Composition of Recycle Plutonium

Isotope	Isotopic Composition, wt%					
	Plutonium From Uranium Cycles		Plutonium From Plutonium Recycles			
	1st Uranium Cycle	Equilibrium Uranium Cycle	1st Pu Recycle	2nd Pu Recycle	3rd Pu Recycle	4th Pu Recycle
^{236}Pu	Neg.	0.06 (ppm)	0.06 (ppm)	0.06 (ppm)	0.06 (ppm)	0.06 (ppm)
^{238}Pu	1	2	3	4	5	7
^{239}Pu	70	57	44	38	32	20
^{240}Pu	17	24	28	30	27	27
^{241}Pu	10	12	16	15	16	16
^{242}Pu	2	5	9	13	20	30

For criticality safety assessments, the recommended plutonium composition is 80 wt% ^{239}Pu , 10 wt% ^{240}Pu , and 10 wt% ^{241}Pu . This composition is slightly more reactive (from the criticality safety viewpoint) than any plutonium composition expected to be shipped. The important considerations are minimum ^{240}Pu content and maximum ^{241}Pu content. The effect of ^{240}Pu is to increase critical mass, while the effect of ^{241}Pu is to lower critical mass. When the decision is made regarding the use of recycle plutonium as a fuel, perhaps a less restrictive base-isotopic-composition can be established.

Thermal Decay Energy

Heat generation within the solid $\text{Pu}(\text{NO}_3)_4$ will depend primarily on the ^{238}Pu content and somewhat less on the balance between ^{241}Pu and ^{241}Am . The sensitivity of thermal output for recycle plutonium can be estimated from Table 7. These estimates are based on the physical decay heat constants summarized in Table 8.

TABLE 7. Estimated Decay Heat For Some Compositions of Plutonium For Various Times After Separation

<u>Composition</u>	<u>Decay Heat (watts/kg Pu) For Various Times</u>		
	<u>At Separation</u>	<u>1 Year</u>	<u>5 Years</u>
Uranium First Cycle	8.5	9.4	11.0
Uranium Equilibrium Cycle	14.6	15.5	17.3
First Plutonium Recycle	20.4	21.7	24.0

TABLE 8. Thermal Decay Heat For Relevant Isotopes

<u>Decay Mechanism</u>	<u>$T_{1/2}$</u>	<u>Next Ignored</u>	<u>$T_{1/2}$</u>	<u>Decay Heat (watts/g)</u>
$^{238}\text{Pu} \xrightarrow{\alpha} ^{234}\text{U}$	86.4	$^{234}\text{U} \xrightarrow{\alpha} ^{230}\text{Th}$	247000	0.570
$^{239}\text{Pu} \xrightarrow{\alpha} ^{235}\text{U}$	24390	$^{235}\text{U} \xrightarrow{\alpha} ^{231}\text{Th}$	7.1×10^8	0.00188
$^{240}\text{Pu} \xrightarrow{\alpha} ^{236}\text{U}$	6580	$^{236}\text{U} \xrightarrow{\alpha} ^{232}\text{Th}$	2.4×10^7	0.00696
$^{241}\text{Pu} \xrightarrow[\sim 0.0023\%]{\alpha, \beta} ^{237}\text{Np}$	13.2, 0.0185	$^{237}\text{Np} \xrightarrow{\alpha} ^{233}\text{Pa}$	2.2×10^6	$\sim 160.$
$^{241}\text{Pu} \xrightarrow[\sim 100\%]{\beta, \alpha} ^{237}\text{Np}$	13.2, 458	$^{237}\text{Np} \xrightarrow{\alpha} ^{233}\text{Pa}$	2.2×10^6	0.00335, 0.106
$^{242}\text{Pu} \xrightarrow{\alpha} ^{238}\text{U}$	3.8×10^5	$^{238}\text{U} \xrightarrow{\alpha} ^{234}\text{Th}$	4.5×10^9	0.00011

Radiolytic Gas Evolution

The composition of radiolytic gases tabulated as function of accumulated a-dose are given in Table 5. These compositions correspond to about 1 month, 7 month, and 15 month doses during storage respectively for typical reactor

grade plutonium. In addition, gas evolution data (G_T values) are shown in Figure 4 as a function of accumulated α -dose up to 40×10^{17} MeV/g Pu which would correspond to 2 1/2 years of storage for reactor grade plutonium. Based on these experimental data, a preliminary appraisal of flammability and pressurization considerations is given below.

Flammability. The lower limit for H_2 -air mixtures being an explosive hazard is approximately 4 mole% H_2 in air. The hydrogen evolution for the first two accumulated doses (1×10^{17} MeV/g Pu and 9×10^{17} MeV/g Pu) is below 2.5 mole% H_2 , so the evolved gases should pose no problem as an explosive hazard. The hydrogen evolution for an accumulated dose of 20×10^{17} MeV/g Pu (corresponding to ~ 15 months storage for reactor grade plutonium) is 6 mole% H_2 which could pose an explosive hazard if only the radiolytic gas were present. However, the radiolytic gases are only a fraction of the total gas present above the material, assuming a reasonable void space in the container. As long as the mixture is less than 2/3 radiolytic gases, the H_2 concentration will be below the explosive limit threshold. If one is concerned about flammability for long storage times, the material could be "aged" in a circulating atmosphere before closing the container. Consequently, for storage times of up to at least three years, there should be no explosive hazard due to the H_2 gas generation. This should be particularly true if the radiolytic gases are: 1) contained within a pressure vessel closed in air under ambient conditions; 2) vented to the atmosphere (H_2 will preferentially escape); or 3) contained in a pressure vessel that has been flushed with N_2 or a noble gas, since in each instance the mole% of H_2 will be even lower than in just the radiolytic gases.

Pressurization. Pressurization of the container of solid $Pu(NO_3)_4 \cdot xH_2O$ is a possible problem due to radiolytic gas evolution and material decomposition at elevated temperatures. The pressurization due to radiolytic gas evolution depends upon the integrated G_T curve (see Figure 5) and the void volume of the container. Assuming temperatures below the threshold for material decomposition, then:

$$P(t_2) = \frac{P(t_1) K(t_2)}{K(t_1)} + \frac{R K(t_2) g_{Pu} (M_{(AD_2)} - M_{(AD_1)})}{V - W/2.90 \text{ g/cm}^3}$$

where:

t_1 = the time since preparation of the solid nitrate at which the container is sealed,

t_2 = some later time since preparation at which the pressure is to be determined,

AD_1 and AD_2 = the accumulated radiation doses in $\text{Pu}(\text{NO}_3)_4 \cdot \text{XH}_2\text{O}$ at t_1 and t_2 respectively as determined by the expression: $AD_i = 1.01 \times 10^{15} \text{ Mev/day} \left(t_i \right) \left[(\% \text{ Pu} - 239) + 3.7(\% \text{ Pu} - 240) + 302(\% \text{ Pu} - 238) + 60(\% \text{ Pu} - 241) (1 - e^{-0.049Y}) \right]$ where Y is as defined on page 14,

$M_{(AD_1)}$ and $M_{(AD_2)}$ = values of moles of gas/ g_{Pu} determined from Fig. 5 for accumulated doses AD_1 and AD_2 respectively,

R = the gas constant in appropriate units,

$P(t_1)$ and $P(t_2)$ = pressures at times t_1 and t_2 respectively, and

K , g_{Pu} , V and W are defined on page 14.

At elevated temperatures two possible modes of thermal decomposition of $\text{Pu}(\text{NO}_3)_4 \cdot \text{XH}_2\text{O}$ are as follows:

Thus, pressurization must be given adequate consideration as a safety problem under such adverse conditions.

Shielding

Dose rates were estimated for 2 kg, 10 kg, and 25 kg Pu as $\text{Pu}(\text{NO}_3)_4 \cdot 2\text{H}_2\text{O}$ with a density of 2.0 g/cm^3 in spherical geometry with 1/4" stainless steel cladding assuming one-year since separation. Results are presented in Table 9 for shielding calculations. The dihydrate form of plutonium nitrate is considered to be conservative for dose rate and shielding calculations relative to the pentahydrate form.

TABLE 9. Estimated Dose Rates For Recycle Plutonium

	Distance (ft.)	Dose Rate (mrem/hr)					
		2 kg Pu		10 kg Pu		25 kg Pu	
		Neutron	Gamma	Neutron	Gamma	Neutron	Gamma
1st Uranium Cycle	Surface	160.	135.	260.	190.	730.	270.
	3.0	1.3	1.2	5.8	3.0	15.	3.5
	6.0	0.3	0.3	1.5	0.7	3.7	0.9
	10.0	0.1	0.1	0.6	0.3	1.3	0.3
Equilibrium Uranium Cycle	Surface	260.	222.	420.	310.	120.	440.
	3.0	2.1	1.9	9.4	4.9	24.	5.8
	6.0	0.5	0.5	2.4	1.2	6.0	1.5
	10.0	0.2	0.2	0.9	0.4	2.2	0.5
1st Plutonium Recycle	Surface	430.	365.	680.	520.	1900.	720.
	3.0	3.5	3.2	15.	8.0	39.	9.6
	6.0	0.8	0.8	4.0	2.0	9.9	2.4
	10.0	0.3	0.3	1.5	0.7	3.5	0.8

Criticality Safety

The criticality safety aspects of shipping solid plutonium nitrate were investigated. It is concluded that a package loading equal to, or higher than, current plutonium packaging designs can be achieved safely.

Minimum critical masses and critical cylindrical radii calculated for $\text{Pu}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$ and compositions of greater water contents with a plutonium isotopic composition of 80 wt% ^{239}Pu , 10 wt% ^{240}Pu , and 10 wt% ^{241}Pu , are presented in Tables 10 and 11. The tables also include critical parameters for PuO_2 in water for comparison.

The relationship between plutonium density and H/Pu atom ratio used in the calculations is given in Figure 10. Two calculational methods were used in order to obtain reasonably accurate critical values. For the well-moderated systems, cross sections from the BW Master Library in 18 energy groups from the GAMTEC II⁽¹⁶⁾ code were used in the one-dimensional diffusion theory code HFN⁽¹⁷⁾. For the undermoderated and dry systems, 16-group Hansen-Roach cross sections were used in the KENO III⁽¹⁸⁾ Monte Carlo Code.

TABLE 10. Calculated Spherical Critical Masses For $\text{Pu}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$ and PuO_2 in Water
(80 wt% ^{239}Pu ; 10 wt% ^{240}Pu ; 10 wt% ^{241}Pu)

Concentration (g Pu/l)	Spherical Critical Mass (kg Pu)			
	$\text{Pu}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$		PuO_2	
	Bare	Full Water Reflection	Bare	Full Water Reflection
10	6.24	5.17	5.96	4.93
20	1.29	0.856	1.26	0.832
30	1.21	0.733	1.18	0.709
50	1.48	0.826	1.41	0.795
70	1.89	1.01	1.77	0.951
100	2.61	1.36	2.40	1.25
300	8.89	3.95	6.97	3.30
1,000	37.2	16.8	21.3	9.20
1,201 ^(a)	45.3	20.6	-	-
3,000	-	-	30.9	14.1
10,107 ^(b)	-	-	24.2	12.2

a. Theoretical density of $\text{Pu}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$

b. Theoretical density of PuO_2

TABLE 11. Calculated Minimum Critical Radii For $\text{Pu}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$ and PuO_2 in Water

(80 wt% ^{239}Pu ; 10 wt% ^{240}Pu ; 10 wt% ^{241}Pu)

Concentration (g Pu/l)	Minimum Critical Cylinder Radius (mm)			
	$\text{Pu}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$		PuO_2	
	Bare	Full Water Reflection	Bare	Full Water Reflection
10	400	367	394	361
20	186	153	184	151
30	158	124	156	123
50	142	106	140	105
70	137	101	134	98
100	136	98	132	95
300	140	98	130	91
1,000	155	109	125	84.5
1,201 ^(a)	154	108	-	-
3,000	-	-	100	64.5
10,107 ^(b)	-	-	60	39.5

a. Theoretical density of $\text{Pu}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$

b. Theoretical density of PuO_2

FIGURE 10. PLUTONIUM DENSITY AS A FUNCTION OF H/Pu ATOM RATIO

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APPENDIX 1

Amendment to 10 CFR Part 71, "Packaging and Transportation of Radioactive Material"

20.623-2 Regulations-Nuclear Regulatory Commission 52 3-28-75

[¶ 14,833j]

†Sec. 71.41. Previously constructed packages for irradiated solid nuclear fuel.--Notwithstanding any other provisions of this Subpart, a package, the use of which has been authorized by the Commission for the transport of irradiated solid nuclear fuel on or after September 23, 1961, and which has been completely constructed prior to January 1, 1967, shall be deemed to comply with the package standards of this subpart for that purpose.

[¶ 14,833k]

Sec. 71.42. Special requirements for plutonium shipments after June 17, 1978.--(a) Notwithstanding the exemption in 71.9, plutonium in excess of twenty (20) curies per package shall be shipped as a solid.

(b) Plutonium in excess of twenty (20) curies per package shall be packaged in a separate inner container placed within outer packaging that meets the requirements of Subpart C for packaging of material in normal form. The separate inner container shall not release plutonium when the entire package is subjected to the normal and accident test conditions specified in Appendices A and B. Solid plutonium in the following forms is exempt from the requirements of this paragraph.

- (1) Reactor fuel elements;
- (2) Metal or metal alloy; or
- (3) Other plutonium bearing solids that the Commission determines should be exempt from the requirements of this section.

(c) Authority in licenses issued pursuant to this part for delivery of plutonium to a carrier for transport under conditions which do not meet the limitations of paragraphs (a) and (b) of this section shall expire on June 17, 1978.

[Sec. 71.42 as added June 17, 1974, effective July 17, 1974 (39 F. R. 20960); amended effective March 3, 1975 (40 F. R. 8792).]

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