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**Mound Laboratory Isotopic
Power Fuels Programs:
January - June 1974**

August 9, 1974

MOUND LABORATORY

Miamisburg, Ohio

operated by

MASTER

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MONSANTO RESEARCH CORPORATION

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for the

U. S. ATOMIC ENERGY COMMISSION

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Foreword

This report presents the technological achievements of Mound Laboratory in its isotopic fuels programs during the past three months. The separate reports compiled here represent the work of the following sections of the Nuclear Operations Department (Director W. T. Cave): Heat Sources (Manager D. P. Kelly), and Technology Applications & Development (Manager R. E. Vallee).

This work is supported by the AEC Division of Space Nuclear Systems.

Summaries of all sections are compiled at the front of this report. Brief introductions to the work are included with each section.

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The design of the punch and die assembly normally used to hot press plutonium oxide fuel spheres was modified to eliminate the use of a recessed spacer, which is presently needed to produce spheres within the Multihundred Watt dimensional specification. Two punch and die assemblies were designed and tested. One design yielded a sphere within dimensional specifications having good equatorial band.

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A technique was developed to obtain the plutonium-240/plutonium-239 ratio using the computer code GAUSS V for spectrum analysis. The complete nondestructive gamma-ray analysis was applied to mixed uranium-plutonium oxide samples.

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Some chemical literature sources suggest that the establishment of the steady state ratio of tetravalent to trivalent plutonium in solutions of hydrogen peroxide may not involve peroxy complexes of tetravalent plutonium.

PRESSING PARAMETERS

Hot-pressing parameters required to fabricate a simulant sphere with the same mass and volume as the PPO (pressed plutonium oxide) MHW (Multi-hundred Watt) fuel sphere were evaluated. One ThO_2 sphere with the same mass as a PPO sphere was pressed using a standard MHW sphere die.

ThO_2 powder of $<150\mu\text{m}$ particle size was sized and screened. The powder was then heated at 600°C for 2-1/2 hr in air. A standard graphite MHW sphere die was charged with 256.0 g of the powder. The die was heated in vacuum to 1850°C , and a force of 19,600 lb was applied to the punches closing the die. After closure, the die was held at 1850°C for 10 min, then cooled in vacuum at an average rate of $14^\circ\text{C}/\text{min}$.

Upon removal of the sphere from the die, two small chips dislodged from a polar section of the sphere. However, the position of these chips did not prevent accurate measurement of the polar diameter. Polar and equatorial diameters were 1.476 and 1.470 in., respectively. The weight of the sphere, including chips, was 252.0 g. The density range of the sphere calculated using the polar and equatorial diameters, respectively, was 90.9-92.1% of theoretical. The sphere as shown in Figure 1 had no visible surface cracks, but had an irregular equatorial band.

An 1100°C heat treatment in air for 1/2 hr did not affect the dimensions, weight, or integrity of the sphere. However, a vacuum heat treatment to 1500°C produced cracks in the sphere. The cracking was probably caused by the very fast heating and cooling rates used. (W. D. Pardieck)

FIGURE 1 - Photograph showing a ThO_2 sphere with the same volume and mass as a PPO MHW fuel sphere. Sphere density was 91.5% of theoretical.

EFFECT OF SINTERING TEMPERATURE

The effect of sintering temperature of the $^{238}\text{PuO}_2$ feed powder on sphere densities and sintering characteristics was evaluated. Three spheres were hot pressed from $^{238}\text{PuO}_2$ feed powder presintered at three different temperatures.

The feed powder was prepared by the hydroxide precipitation method. Granules from 0-297 μm were sintered at 900, 1150, and 1600°C. One sphere was pressed from each of the three sintered batches of feed material.

A schematic of the die used to hot press the spheres is shown in Figure 2. Hemispherical cavities were machined in the graphite punch ends so that a spherical compact was formed when the two punches closed. Punch lengths were sized so that graphite spacers came into contact with the die body when the die was closed. Sphere density was determined by the size of the die cavity and weight of the die charge. The dies were charged with 254.00 g of feed material so that spheres of approximately 84% of theoretical density would be produced. The hot pressing parameters, were 1480°C and 2500 lb force to close the die. The temperature was maintained for 10 min after ram movement indicated the die was closed. The die was cooled in a vacuum, requiring about 2 hr.

After being hot pressed, the spheres were given an oxygen-16 treatment at 740°C to remove graphite or carbides and to increase the O/Pu ratio to two. The spheres were weighed and gaged. Then the spheres were given a heat treatment at 1500°C for 1 hr in a vacuum of 1×10^{-5} torr. The spheres were weighed and gaged again. The data obtained are summarized in Tables 1 and 2. Volume and density calculations were based on the polar diameters of the spheres.

As shown in Table 1, a trend relating sphere densities to feed material prefire temperature is not seen. Sphere densities are not affected by the prefire temperature of the feed powder. However, because the dies used to press the spheres were designed to close out, forming spheres of predetermined dimensions and volume, sphere densities would not be expected to vary significantly from the density defined by the volume of the die cavity and the mass of the die charge.

FIGURE 2 - Die used to hot press spheres.

Table 1

CORRELATION OF PREFIRE TEMPERATURE,
SPHERE DIMENSIONS, AND DENSITY

<u>Sphere Identification</u>	<u>Sinter Temperature of Feed (°C)</u>	<u>Polar Diameter (in. at 20°C)</u>	<u>Weight (g)</u>	<u>Density (g/cm³)</u>
SPO-68	900	1.452	253.9	9.67
SPO-67	1150	1.457	251.8	9.49
SPO-70	1600	1.454	253.4	9.61

Table 2

SPHERE DIMENSIONAL CHANGES ON SINTERING 1 HR AT 1500°C

<u>Sphere Identification</u>	<u>Polar Diameter (%)</u>	<u>Volume (%)</u>	<u>Density (%)</u>
SPO-68	-0.14	-0.42	+0.41
SPO-67	-0.34	-1.02	+0.84
SPO-70	-0.07	-0.19	+0.21

Table 2 presents the dimensional changes of the spheres on sintering for 1 hr at 1500°C in a vacuum. All three spheres increased slightly in density. However, a systematic relationship between sphere density increase and feed material prefire temperature is not discernible.

In conclusion, it appears that the overriding control on the resulting sphere density is the size of the die cavity as defined by the closed punches and the mass of the $^{238}\text{PuO}_2$ feed. The marked effect of the feed sinter temperature noted on small cylindrical pellets¹ is not sufficient to overcome the constraints imposed by the size of the die cavity.
(W. D. Pardieck and W. A. Zanolli)

SUBSTOICHIOMETRIC STUDIES

Microstructural changes that occur during reduction, oxidation, and subsequent reheating of $^{238}\text{PuO}_2$ particles and ultimately PPO spheres are being studied.

Three batches of $^{238}\text{PuO}_2$ particles, one aged over a year and the others freshly prepared, are being evaluated. Portions of the different batches were reduced in vacuum at 1900 and 2100°C. The reduced particles were then oxidized in air and the weight gain was followed. The reduced oxides, however, exhibited slow oxidation rates in contrast to work previously done where the oxidation was rapid. The slow oxidation rates do not lend to an accurate determination of the weight gain with the TGA assembly presently available; therefore, the stoichiometries of the reduced oxides cannot be accurately determined. Also, the microstructures of the reduced particles are different from microstructures of reduced particles previously examined. Therefore, effort is being directed toward resolving this anomaly. Whether this anomaly is related to particle size, particle density, material pretreatment, material age, or other factors, has not, as yet, been resolved. (W. D. Pardieck and C. B. Chadwell)

MEASUREMENT OF THE IRIIDIUM TEMPERATURE FOR MHF-47 UNDER VARIOUS HEAT TRANSFER CONDITIONS

The temperature excursions that can be expected in an iridium clad MHW fuel sphere under various heat transfer conditions have been of interest for some time. After welding of the iridium PICS (post impact containment sphere) about the fuel sphere, the fuel is typically stored in special heat sinked air, in helium-filled storage cans, or in water-cooled chill blocks which contact the iridium only in the lower hemisphere. During helium leak checking of the iridium sphere, the iridium has, to date, been heat sinked via cooling contacts in both lower and upper hemispheres. Some debate has occurred about the necessity of heat sinking the upper hemisphere of the iridium shell during helium leak checking. The present work provides temperature data that can be used as a basis for leak check fixture and chill block design.

The sphere used for this work was MHF-47 and contained fuel sphere PPS-107 which had a thermal power of 101.9 W. MHF-47 had been previously rejected for use in the MHW Q-1 HSA assembly partially because a weld was not leak tight but this had no bearing upon its applicability for this work.

The temperature measurements were made in the original helium leak test fixture that was installed for measuring the leak rates of iridium-clad fuel spheres.

A sketch of the fixture is shown in Figure 3-A and 3-B, including the three thermocouples placed in the fixture for temperature measuring purposes. Thermocouple (TC 1) passed through the top of the fixture, and its length was such that the junction made good physical contact with the iridium clad when the top skirt of the fixture rested against the three stop screws (Figure 3-A) mounted in the wall of the fixture base. The purpose of the stop screws was to prevent the water-cooled contact cone in the fixture top from contacting the iridium and thus conducting heat from it. The thermocouple bead contacted the iridium within about 0.3 cm of the uppermost point of the iridium sphere as it sat in the fixture. The burst disk was oriented at about 30° to the horizontal and was thus not in the temperature measuring area as it was felt that making good physical contact with the thermocouple bead in the burst disk area would be too difficult in the box line. Thermocouple (TC 3) measured the temperature of the skirt portion of the fixture top.

(A)

(B)

FIGURE 3 - Arrangement used for making temperature measurements.

The fixture was closed as shown in Figure 3-A and evacuation was started. Contact of TC head No. 1 with the iridium was checked by a test circuit consisting of a battery, small bulb, and electrical leads connecting one side of TC No. 1 and the base of the fixture. Checking of the circuit continuity required about 2 min. Just prior to being placed in the fixture, the sphere was stored in chilled water and it was placed in the fixture with manipulators immediately after the last trace of water had evaporated from the iridium surface.

The first temperature measurement obtainable with TC No. 1 was $\approx 110^{\circ}\text{C}$. The fixture was evacuated by a small roughing pump in the Veeco helium leak tester and the pressure at the pump dropped to $\approx 10^{-2}$ torr within about 2 min.

Figure 4 shows the approximate heating curve for the iridium (Curve A) immediately under the bead of TC No. 1. Experimental problems prevented the acquisition of some early heating data. Under the stated heat transfer conditions, the top of the iridium sphere achieved an equilibrium temperature $\approx 500^{\circ}\text{C}$ in about 25 min. At the end of about 40 min, the fixture was vented with air and the top was immediately removed. The top of the iridium sphere in the vicinity where TC No. 1 contacted the iridium was a dull red color and immediately cooled due to convective gas cooling after the fixture was opened. At the end of this measurement, TC No. 3 indicated that the skirt was at $\approx 33^{\circ}\text{C}$. No discoloration was visible on the iridium clad.

After about 2 min, the top was replaced on the fixture with the bottom of the skirt on the stop screws, and the fixture was evacuated to 10^{-2} torr. The first reading obtained with TC No. 1 was 393°C and after 4 min had stabilized at $\approx 515^{\circ}\text{C}$, essentially agreeing with the equilibrium temperature shown in Figure 4. This temperature is representative of that obtained for the fuel sphere in vacuum and under conditions where the hot top of the sphere radiates to a relatively low emissivity surface.

The fixture was again vented with air, and the fuel sphere was allowed to cool via convective heat transfer to the box atmosphere for approximately 2 min. The fixture was again closed as in Figure 3-A, and evacuated, and temperature measurements of TC No. 1 were started. The results

FIGURE 4 - Heating curve for MHF-47 obtained with H_2O cooling in fixture base and top.

are shown as Curve B, Figure 4. For this measurement the fuel sphere had a considerably higher starting heat content than the initial run A. Therefore, the iridium temperature at $t=0$ was considerably higher than for run A, but the final equilibrium temperature was essentially identical for runs A and B. The skirt temperature (TC No. 3) was still $\approx 33^\circ\text{C}$.

The fixture was vented with air, the top was removed, and the fuel sphere was returned to the water storage tank. The stop screws were removed, a vacuum leak in the fixture was repaired, and thermocouple TC No. 1 was bent so that the bead would no longer contact the iridium when the fuel sphere was placed in the fixture. Thermocouple TC No. 2 now made contact with the top of the iridium sphere when the fixture was closed with the stop screws removed.

The sphere was removed from water storage and placed in the fixture as was done previously. The arrangement was now that shown in Figure 3-B. Pressure in the fixture was limited to 6×10^{-2} torr because of some vacuum leaks about the thermocouple insulator inserts in the top of the fixture. The temperature of the iridium at the top of the sphere as a function of time is shown under these conditions as Curve C in Figure 4. This series of measurements clearly showed the effect of having water-cooled heat sinks contacting the iridium in the upper portion of a fuel sphere. Heat transfer in the fuel and in the iridium clad is not sufficient to prevent large temperature gradients in the fuel sphere if only one hemisphere is in contact with a water-cooled heat sink. The gradients are particularly large when the sphere is located in a reasonably good vacuum.

Other measurements included determining the iridium temperature on the top of the sphere when it is sitting in a conical, water-cooled heat sink in air. This temperature, measured by physically holding a thermocouple bead on the iridium at point A, Figure 5, while the sphere sat in the bottom of the fixture, was $\approx 320^\circ\text{C}$. This arrangement closely approximated that of spheres sitting in chill blocks in the box line. Contact temperature measurements made at points B and C, Figure 5, gave temperatures of $\approx 112^\circ\text{C}$ and $\approx 37^\circ\text{C}$, respectively. Because of the difficulty in maintaining good thermal contact between the thermocouple bead and the measured surface, these latter values may have errors as large as $\pm 5^\circ\text{C}$, but the results should still be useful for fixture design purposes.

(V. J. Tennery, P. L. Blue, R. C. McWilliams, and C. P. Johnston)

FIGURE 5 - Contact temperature measurement points.

PPO SPHERE DIE MODIFICATION

The diametrical dimensional specifications for Multihundred Watt (MHW) pressed plutonium oxide (PPO) fuel spheres is 1.465 ± 0.015 in. A punch and die assembly having a closed cavity of 1.450 in. diameter with 0.008 in. thick knife edges was developed using the single-action vacuum hot press. There was no problem meeting the dimensional specifications with this punch and die assembly and the press. However, this punch and die assembly used with the double-action press, yielded average equatorial and polar diameters of 1.461 and 1.433 in., respectively. Thus, the polar diameters were not within specifications. Therefore, a recessed spacer which expands the pole-pole diameter of the punch and die assembly by 0.015 in. is presently used to produce spheres within specification.

To eliminate the use of the recessed spacer, a new punch and die assembly was designed and tested. This design incorporated an expanded closed cavity diameter of 1.464 in. as defined by the closed punches, which were designed to close with a gap of 0.145 in. The inside diameter of the die body was 1.465 in. To reduce the equatorial band, the thickness of knife edges on the punches were reduced by 50% to 0.004 in. The polar and equatorial diameters of a sphere (PPS-33) pressed from this die, using normal conditions, were 1.461 in. and 1.467 in., respectively. Both the polar and the equatorial diameters were well within specification limits. However, the thinner knife edges broke, resulting in an irregular equatorial band approximately 0.220 in. wide.

A second similar design was tested. The only difference in this design and the previous one was that the knife edges were increased back to the normal 0.008 in. and the gap between punches as closeout was increased to 0.187 in. Unfortunately, the 0.015 in. recessed spacer was used during the first pressing with this design. The polar and equatorial diameters of the resulting sphere (PPS-57) were 1.471 in. and 1.462 in., respectively. The second pressing with this die design and without the spacer resulted in a sphere (PPS-71) with polar and equatorial diameters equal to 1.455 and 1.469 in., respectively. These diameters are well within specification. The knife edges of the punches were intact and yielded a sphere with a uniform equatorial band of about 0.175 in. wide.

Additional pressings will be made with this die to determine whether it will consistently produce spheres within specification. (W. D. Pardieck and J. L. McFadden)

PLUTONIUM ISOTOPICS MEASUREMENT BY GAMMA-RAY SPECTROSCOPY

The development of the nondestructive analysis of plutonium isotopics and americium-241 content in bulk nuclear material is continuing. Accomplishments for this report period include the development of a technique to obtain the plutonium-240/plutonium-239 ratio using the computer code GAUSS V² for spectrum analysis. The complete nondestructive gamma-ray analysis was applied to mixed uranium-plutonium oxide samples. Results of these measurements are compared to those obtained by chemical methods.

The technique developed to determine the atom ratios plutonium-238/plutonium-239, plutonium-241/plutonium-239, and americium-241/plutonium-239 have been described previously.³ To summarize briefly, gamma-rays from the decay of the plutonium isotopes 238, 240, 241 and americium-241 have been chosen for analysis which are within 10 keV of a gamma-ray from plutonium-239. This was done so that corrections to the intensities of the gamma rays in the recorded spectra due to self-absorption in the source, absorption of the gamma rays by the packaging material, and changes in the gamma-ray detection efficiency in the detector could be neglected. The samples are rotated as they are counted to increase the size of the sample seen by the detector and to average any inhomogeneities. However, the isotopic composition of the plutonium material is assumed to be homogeneous even though the sample shape and distribution of the plutonium in the sample are not.

Figure 6 shows a typical spectrum obtained from a 9-g metal sample of high fissile plutonium. The major plutonium-239 peaks are labeled as well as the gamma rays from the other isotopes which are used in the analysis. Table 3 lists the gamma rays used for the analysis and identifies each by its half-life and branching intensity.⁴ The desired atomic ratio is obtained from the equation

$$\frac{N_i}{N_{239}} = K_i \frac{I_i}{I_{239,j}}$$

where N_i is the isotope of interest, I_i is the intensity of the gamma ray associated with the decay of N_i , and $I_{239,j}$ is the intensity of the associated gamma ray from the decay of plutonium-239. K_i is the conversion factor obtained by combining the appropriate decay constants and branching intensities. The right hand side of this equation is listed

FIGURE 6 - Typical spectrum obtained from a 9-g metal sample of high fissile plutonium.

Table 3

LIST OF GAMMA-RAYS AND BRANCHING INTENSITIES
OF ISOTOPES OF INTEREST

(Gunnink and Morrow)

<u>Isotope</u>	<u>$T_{\frac{1}{2}}$ (days)</u>	<u>Energy (keV)</u>	<u>Branching Intensity</u>
^{238}Pu	3.2×10^4	152.77	1.01×10^{-5}
^{239}Pu	8.908×10^6	141.64	3.11×10^{-7}
		144.19	2.84×10^{-6}
		146.05	1.13×10^{-6}
		203.52	5.63×10^{-6}
		637.97	2.50×10^{-8}
		640.15	7.95×10^{-8}
		658.99	9.50×10^{-8}
		717.76	2.67×10^{-8}
^{240}Pu	2.41×10^6	642.30	1.45×10^{-7}
^{241}Pu	2.070×10^8	148.60	7.74×10^{-2}
^{237}U	6.75	207.97	2.080×10^{-1}
^{241}Am	1.582×10^5	146.55	4.58×10^{-6}
		207.98	7.60×10^{-6}
		662.37	3.46×10^{-6}
		721.92	1.58×10^{-6}

in Column 3 of Table 4 for obtaining the part-per-million ratios of the desired isotopes relative to plutonium-239.

The intensities of the peaks for the plutonium-238, -241 determination are obtained by using a FOCAL program which simply draws a straight line background under the peaks of interest. The peak intensities for the 658 keV and 662 keV peaks used for the americium-241/plutonium-239 determinations were made using the ratio of the peak heights and choosing point B in Figure 6 as the background. The results of using these measurement techniques on 15 9-g metal samples showed the following biases when the gamma-ray determined results were compared to destructive analysis results: plutonium-238/plutonium-239, -5%; plutonium-241/plutonium-239, +2%; americium-241/plutonium-239, -3%.

The nondestructive analysis was expanded to include the plutonium-240/plutonium-239 ratio. This determination was facilitated by compiling the program GAUSS V² on the IBM-360 computer. This program performs a nonlinear least squares fit of a Gaussian function to the peaks of interest and computes the area of the peak.

Table 4

GAMMA RAYS AND CONVERSION FACTORS USED FOR ISOTOPIC DETERMINATIONS

<u>Isotopic Ratio</u>	<u>Gamma-rays Used</u>	<u>Conversion Factors to Express Ratio in ppm</u>
$^{238}\text{Pu}/^{239}\text{Pu}$	153 keV/144 keV	$1010.3 \frac{I_{153}}{I_{144}}$
$^{240}\text{Pu}/^{239}\text{Pu}$	642 keV/640 keV	$153600 \frac{I_{642}}{I_{640}}$
$^{241}\text{Pu}/^{239}\text{Pu}$	208 keV/203 keV	$623.7 \left\{ \frac{I_{208}}{I_{203}} - .0373 \frac{I_{662}}{I_{659}} \right\}$
	148 keV/144 keV	$852.7 \frac{I_{148}}{I_{144}}$
$^{241}\text{Am}/^{239}\text{Pu}$	662 keV/659 keV	$487.5 \frac{I_{662}}{I_{659}}$
	722 keV/717 keV	$156.3 \frac{I_{722}}{I_{717}}$

The program was also applied to the peaks at 660 keV used for the americium-241/plutonium-239 isotopic ratio. The samples analyzed for application of this technique was applied to 34 nominal 1-g plutonium metal, plutonium oxide, and mixed plutonium and uranium oxides on which complete destructive analysis was also performed. The average percent difference between the nondestructive analysis (NDA) and the destructive analysis (DA) for the various ratios using the destructive analysis results as a reference are: plutonium-238/plutonium-239, $(-4.9 \pm 20.8)\%$; plutonium-240/plutonium-239, $(-1.5 \pm 6.2)\%$; plutonium-241/plutonium-239, $(6.6 \pm 8.1)\%$; and americium-241/plutonium-239, $(-5.5 \pm 4.7)\%$. Statistically, no differences were observed between the americium-241/plutonium-239 determinations as measured using the ratio of peak heights and the ratio of the areas of the peaks as determined using Gauss V.

The technique was also applied to three 9-g samples associated with the Plutonium Metals Exchange Program. A complete comparison of the NDA and DA results are shown in Table 5. The results are in good agreement for all determinations with the possible exception of the plutonium-240/plutonium-239 ratio for sample MO-0973-2. However, the spectrum for this sample was accumulated for only 7 hr, compared to 16 hr for the other two spectra, and the total counts for the peaks at 640 keV were less than 600 counts/channel. Better agreement may be obtainable with better counting statistics.

Isotopic determinations for plutonium-238, -241 and americium-241 were also calculated for about 100 samples selected at random from contractor inventories as part of the Audit Verification Program sponsored by the Albuquerque Operations Office of the U. S. Atomic Energy Commission.

Table 5

COMPARISON OF RESULTS FROM NONDESTRUCTIVE
ANALYSIS AND DESTRUCTIVE ANALYSIS

Sample	$^{238}\text{Pu}/^{239}\text{Pu}$ (ppm)		$^{240}\text{Pu}/^{239}\text{Pu}$ (ppm)		$^{241}\text{Pu}/^{239}\text{Pu}$ (ppm)		$^{241}\text{Am}/^{239}\text{Pu}$ (ppm)	
	NDA	DA	NDA	DA	NDA	DA	NDA	DA
MO-0973-1	131 $\pm$ 35	126 $\pm$ 2	57720 $\pm$ 4020	63200 $\pm$ 2530	4245 $\pm$ 120	4130 $\pm$ 400	460 $\pm$ 40	493 $\pm$ 6
MO-0973-2	188 $\pm$ 60	179 $\pm$ 2	52790 $\pm$ 6500	62450 $\pm$ 2500	4910 $\pm$ 300	4740 $\pm$ 470	605 $\pm$ 40	630 $\pm$ 12
MO-0973-3	198 $\pm$ 40	183 $\pm$ 2	62870 $\pm$ 4500	62690 $\pm$ 2500	4900 $\pm$ 160	4750 $\pm$ 470	586 $\pm$ 30	627 $\pm$ 12

Errors are $\pm$ 2 sigma

These ratios, together with the stream average values for the plutonium-240/plutonium-239 ratios supplied by the contractors, were used in conjunction with the calorimetrically determined heat output to give the total plutonium content of the samples. Sample weights varied from 100 g to several kg of plutonium having chemical compositions of metal, oxide, pulverized crucibles, green cake, fluorides, and ash wastes. The gamma-ray analysis for the plutonium-240/plutonium-239 determination was not yet developed sufficiently to include in the analysis of these samples for the audit program.

The goals of future work will focus on eliminating the biases present between the NDA and DA results. Special emphasis will be placed on accumulating spectra to have sufficient statistics in the peaks of interest. Standard Reference Material 946, 947, and 948 plutonium have been purchased from the National Bureau of Standards. Spectra will be accumulated for these samples with these goals in mind. Additionally the analysis of these samples will extend the nondestructive gamma-ray capabilities to lower fissile content material. (F. X. Haas and J. Y. Jarvis)

REACTION OF PLUTONIUM WITH HYDROGEN PEROXIDE

In a recent discourse,⁵ the observation was made that it may someday be possible to explain the observed ratios of Pu(IV)/Pu(III) in hydrogen peroxide-plutonium solutions by assuming that hydrogen peroxide is in false equilibrium with one or more of its decomposition products such as the perhydroxyl radical HO₂. The proposed model applied only to steady state conditions in plutonium solutions in which there is at least a small excess of hydrogen peroxide and is based upon a mathematical technique applicable to equilibrium (not steady state) circumstances. In solutions containing less than the stoichiometric amount of hydrogen peroxide, ratios which differ from the steady state ratios have been observed. This may be explained in terms of the model. Hydrogen peroxide in aqueous solution may react with plutonium in a manner leading to decomposition:

and may also decompose of its own accord in aqueous solution:

The rate of disappearance of H₂O₂ may be taken as at least the sum of the rates of Equations 1 and 2. But when less than the stoichiometric amount of H₂O₂ is added to a plutonium solution, there is insufficient peroxide to allow Equation 1 to reach steady state, so that the peroxide may be completely removed before the steady state ratio predicted by Equation 1 can be achieved. Hence, some other ratio than the steady state ratio may be expected in solutions containing insufficient peroxide to allow establishment of steady state via Equation 1. Even with exactly the stoichiometric quantity of H₂O₂, steady state via Equation 1 may not be achieved since some peroxide may be lost via Equation 2 before such steady state is reached. Moreover, hydrogen peroxide may be removed from the solution in a manner which is even faster than the sum of removals via Equations 1 and 2. For example, the reactive perhydroxyl radical, or other reactive intermediates, may allow removal of H₂O₂ at an accelerated rate:

The model proposed in Reference 5 predicted a Pu(IV)/Pu(III) ratio which did not agree with the observed ratio. This error could derive from uncertainties surrounding present knowledge of hydrogen peroxide and its reactions and also from neglect of reactions such as Equation (3) above which lower the H_2O_2 concentration in peroxide solutions. It could also derive from the tendency of plutonium(IV) to form complexes with H_2O_2 , so that the observed ratio Pu(IV)/Pu(III) is shifted to higher values by virtue of the complexes which H_2O_2 and Pu(IV) may form. Additionally, the extension of a mathematical method for examining equilibrium solution conditions into nonequilibrium (steady state) circumstances is at best questionable. It is curious that Pu(IV) and hydrogen peroxide are universally recognized as forming complexes, yet when the reaction of H_2O_2 and Pu(IV) is discussed, it is usually the ionic forms of plutonium, and not the complexes, which are pictured as the reactant species.^{6,7} It may be that the steady state ratio Pu(IV)/Pu(III) is obtained through decomposition of the brown peroxy complex. But this complex is formed in aqueous solution by an equilibrium reaction⁶

$$K \sim (9)(10^6) = \frac{[\text{complex}][\text{H}^+]^3}{[\text{Pu}^{4+}]^2[\text{H}_2\text{O}_2]} \quad (4)$$

such that the complex concentration should be affected by the concentration of H_2O_2 . But if the complex concentration is affected by the concentration of H_2O_2 , and if the rate of complex decomposition determines the steady state Pu(IV)/Pu(III) ratio, then the ratio Pu(IV)/Pu(III) should also be affected by the H_2O_2 concentration since the total quantity of plutonium in solution in most experiments is a fixed constant. But this ratio is not affected by the H_2O_2 concentration, so it would appear that the brown peroxy complex may not be involved in the establishment of the Pu(IV)/Pu(III) ratio.⁷ In this connection, it is very desirable to define symbols exactly, although clear definitions are not always apparent from early work. For example, it seems likely that "Pu(III)" when used in "Pu(IV)/Pu(III) ratio" means ionic Pu^{3+} , but does "Pu(IV)" mean ionic Pu^{4+} , or total Pu(IV) as in the sum of ionic Pu^{4+} and the tetravalent plutonium in the peroxy complex, i.e., $(\text{Pu}^{4+} + 2[\text{peroxy complex}])$ (since the brown peroxy complex contains two tetravalent plutonium atoms)? Perhaps, as Connick⁸ has pointed out, true steady state does not involve peroxy complexes and occurs at low peroxide concentrations. Balakrishnan et al. have proposed a method for assaying the relative amounts of trivalent plutonium and hydrogen peroxide in solution together.⁹ This method uses information from two titrations only. These two pieces of data are sufficient for assaying the two unknowns in the solution. These authors do not mention Pu(IV) peroxy complexes. If present, such complexes should at least be mentioned to allay reader curiosity, since the plutonium in any such complexes is capable of being reduced, and the peroxy part of such complexes is capable of being both oxidized and reduced in a manner which might interfere with the Pu^{3+} and H_2O_2 determinations. Hence, some chemical literature resources suggest that the tetravalent/trivalent plutonium ratio in H_2O_2 solutions involves principally ionic species, and not peroxide complexes of these ionic species. Ghosh Mazumdar and Vaidyanathan¹⁰ have suggested that the brown Pu(IV) peroxy complex may decompose to yield Pu(III) in a manner which is rate controlling in solutions containing a significant portion of the brown

complex. This may occur at early stages in the $\text{H}_2\text{O}_2 - \text{Pu}^{4+}$ reaction, but, as Connick has pointed out,⁸ does not necessarily dictate the solution conditions at steady state which may involve other, perhaps more important reactions than those of the brown peroxy-Pu(IV) complex. The model⁵ of the H_2O_2 -plutonium reaction has been criticized in Reference 11.
(G. L. Silver)

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