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RESEARCH AND DEVELOPMENT
SEMIANNUAL PROGRESS REPORT FOR
JANUARY THROUGH JUNE 1975

CHEMISTRY RESEARCH AND DEVELOPMENT

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U.S. ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION
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RESEARCH AND DEVELOPMENT
SEMIANNUAL PROGRESS REPORT FOR
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CHEMISTRY RESEARCH AND DEVELOPMENT

Robert H. Karlsson

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Previous progress reports (official use only) in this series are as follows:

<u>Report Number</u>	<u>Time Period Covered</u>
RFP-2360-A	July through December 1974
RFP-2276-A	January through June 1974
RFP-2200-A	July through December 1973
RFP-2102-A	January through June 1973
RFP-2004-A	July through December 1972
RFP-1921-A	January through June 1972
RFP-1837-A	January through December 1971

SUBJECT DESCRIPTORS

Actinides	Measuring Instruments
Air Pollution	Metals
Americium	Molten Salts
Beryllium	Molten Salt Residues
Calculations	Oxalic Acid
Calibration Standards	Particle Size
Calorimeters	Plutonium
Chemical Machining	Plutonium Carbonates
Combustion	Plutonium Dissolution
Computers	Plutonium Peroxide
Computer Codes	Plutonium Processing
Control	Plutonium Recovery
Control Systems	Plutonium Residues
Crucibles	Precipitation
Distribution Coefficients	Purification
Electrorefining	Radiation Detectors
Environment	Radiation Doses
Environmental Analysis	Radiation Monitoring
Evaporation	Radioactive Wastes
Filter Plenums	Radionuclide Migration
Filtration	Radium
Fluidized Bed	Rare Earths
Graphite	Reduction
Hydrofluorination	Separation Processes
Incinerators	Silicon Oxides
Instrumentation and Controls	Soils
Ion Exchange	Statistics
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Lathe Coolants	Vacuum
Lithium Drifted Germanium Detectors	Washing
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*All Development and Development Support (DDS) endeavor numbers refer to FY-1977 Proposed Program for Process Development (DH-09) and Related Work, CD 75-77, February 1, 1975. Production and Production Support programs are identified as PPS.

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*All Development and Development Support (DDS) endeavor numbers refer to FY-1977 Proposed Program for Process Development (DH-09) and Related Work, CD 75-77, February 1, 1975. Production and Production Support programs are identified as PPS.

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*All Development and Development Support (DDS) endeavor numbers refer to FY-1977 Proposed Program for Process Development (DH-09) and Related Work, CD 75-77, February 1, 1975. Production and Production Support programs are identified as PPS.

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A production scale incinerator, utilizing Rocky Flats' fluidized bed process, will be installed and demonstrated for combustion of transuranic solid waste. The unit is being designed for a combustion rate of about 82 kilograms per hour and should be operational in 1977. (DDS-DWMT† Funded)

FLUID BED INCINERATION 35

The pilot-plant incinerator has been operated with plutonium-contaminated liquid and solid waste. The combustion rate obtained with the 0.1-square-metre, cross-sectional area, primary reactor was about 10 litres per hour for liquid waste and about 8.5 kilograms per hour for solid waste. (DDS Endeavor 33*)

†DWMT—Division of Waste Management and Transportation.

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GRAPHITE COMBUSTION 37

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Start-up of a prototype, induction-heated, tilt-pour furnace was completed satisfactorily. The furnace is specially designed for salt extraction and plutonium electrorefining operations on a production duty cycle. (PPS)

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Americium is separated from plutonium metal by extraction into a molten salt. Selection of optimum extraction conditions can result in minimum salt usage. To confirm the selected optimum extraction conditions and to provide feed for a new salt recovery process, a production demonstration run was made. (PPS)

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ANION EXCHANGE COLUMN PLUGGING 41

Anion exchange columns used in plutonium recovery required frequent resin changes because of column plugging. Methods to alleviate the plugging have been investigated. Two methods were implemented. (PPS)

*All Development and Development Support (DDS) endeavor numbers refer to FY-1977 Proposed Program for Process Development (DH-09) and Related Work, CD 75-77, February 1, 1975. Production and Production Support programs are identified as PPS.

RESEARCH AND DEVELOPMENT SEMIANNUAL PROGRESS REPORT FOR
JANUARY THROUGH JUNE 1975

CHEMISTRY RESEARCH AND DEVELOPMENT

Robert H. Karlsson

CHEMICAL RESEARCH

Frend John Miner

EVALUATION OF ION-EXCHANGE RESINS
FOR ACTINIDE SEPARATIONS

James D. Navratil and Gerald M. Dancer

New and conventional ion-exchange resins continued being compared for difficult actinide separations. Previous work compared macroreticular strong base (Dowex® MSA-1 and Amberlite® IRA-900) and weak base (Amberlite IRA 93) anion exchange resins to Dowex 1-X4 (microreticular or gel type) for plutonium-uranium and plutonium-neptunium separations. (See earlier report RFP-2360-A, p.31.) Studies were extended recently to compare these resins for use in plutonium purification. Potential advantages of macroreticular resins over Dowex 1-X4 for plutonium purification include lower resin cost and a faster throughput based on a combination of larger bead size with fast kinetics. During plutonium-uranium separations, faster uranium removal by washing was predicted using pellicular exchangers (inert bead coated with a thin layer of gel ion exchanger). AS Pellionex SAX®, a pellicular strong-base anion exchanger, was tested for plutonium-uranium separation.

The macroreticular resins were compared to Dowex 1-X4 using conventional plutonium purification techniques. The resins were loaded simultaneously with plutonium from a 7M nitric acid (HNO_3) feed solution, washed with 7M HNO_3 , and the plutonium eluted with 0.35M HNO_3 . The effluent streams were then analyzed for plutonium.

Table 1 shows results of the resin comparisons where all four resins were loaded, washed, and eluted identically. The ion column effluent (ICE) results showed increased levels of plutonium using Amberlite IRA-93 and IRA-900 as compared to Dowex 1-X4 and MSA-1.

The level of plutonium in the ICE using Amberlite IRA-93 was not acceptable. All four resins provided wash solutions with plutonium concentrations below discard limits. Plutonium elution efficiency decreased in the following order: Amberlite IRA-93 greater than ($>$) IRA-900 $>$ Dowex 1-X4 $>$ MSA-1.

Dowex MSA-1 was comparable to Dowex 1-X4 for plutonium processing. Amberlite IRA-900 showed excellent plutonium elution behavior, but the

TABLE 1. Results of plutonium processing using different ion-exchange resins

Resin	Plutonium (mg/l)		Elution of Plutonium (%)					
	ICE ^a	Wash ^b	2 ^c	4 ^c	6 ^c	8 ^c	10 ^c	12 ^c
Dowex 1-X4	0.9	2.0	27	53	65	72	78	81
Dowex MSA-1	0.7	0.8	24	48	61	68	73	77
Amberlite IRA-900	1.1	0.3	56	88	96	99	100	100
Amberlite IRA-93	9.8	2.4	72	94	98	99	100	100

- a. Loaded four column volumes of feed containing 4.0 g/l plutonium simultaneously onto each resin at 4 ml/(min · cm²)
b. Washed with four column volumes of 7M nitric acid at 4 ml/(min · cm²)
c. Cumulative column volumes

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FIGURE 1. Plutonium loading and washing curves for Dowex® 1-X4 and Amberlite® IRA-900. Feed contained 4.0 g/l plutonium at a flow rate of 4 ml/(min · cm²).

levels of plutonium in the ICE were higher than Dowex 1-X4. The plutonium breakthrough and washing curves on Dowex 1-X4 and Amberlite IRA-900, shown in Figure 1, illustrate the higher levels of plutonium found in the effluent streams using the latter resin. Examination of other new gel and macroreticular resins for plutonium purification are in progress.

Separation of plutonium and uranium by loading the plutonium (IV) on Dowex 1-X4 was difficult because of the large volume of 7M HNO₃ required to wash the weakly sorbed uranium from the resin (see earlier report RFP-2360-A). Faster uranium removal by washing on macroreticular and pellicular exchangers was tried. The uranium removal

TABLE 2. Uranium removal from ion exchangers by 7M nitric acid washing

7M Nitric Acid Passed (Column Volumes)	Uranium Analysis (g/l)		
	AS Pellionex SAX	Amberlite IRA-93	Dowex 1-X4
5	4.09	4.71	3.76
9	0.002	2.60	2.48
14	<0.002	1.22	1.60
19	<0.002	0.69	1.12

rate from three uranium-saturated anion exchangers by washing with 7M HNO₃ was tested. The results (Table 2) show that uranium removal was fastest with the pellicular exchanger followed by the macroreticular resin. Because of the low capacity of AS Pellionex SAX for anions, however, the pellicular exchangers would probably have only utility in removing small amounts of plutonium (IV) and neptunium (IV) from uranyl (VI).

RECOVERY OF PLUTONIUM AND AMERICIUM FROM MOLTEN-SALT-EXTRACTION WASTE SALTS BY CARBONATE PRECIPITATION

*Paul G. Hagan, Fred John Miner,
and Larry L. Martella*

A molten-salt-extraction (MSE) waste salt is produced as a waste product from a molten-salt, molten-metal process in which americium is extracted from plutonium metal. These waste salts must be processed for the recovery of plutonium and americium in addition to allowing for the discard of the salt matrix.

A new carbonate precipitation process is being proposed for this operation (see RFP-2360-A, p.26). In this process, the waste salts first are dissolved in dilute HCl. The solution is heated and a solution of Na₂CO₃ is added slowly. An americium-plutonium carbonate precipitate is

formed. This is filtered, dissolved, and subsequently processed to separate and recover the plutonium and americium.

Studies have been undertaken to identify and characterize the precipitates and to learn more about the precipitation of other metal ions that may be present as impurities in the waste salts.

Identification and Characterization of the Plutonium-Carbonate Precipitate

Identification and characterization of the carbonate precipitate have been confined thus far to the plutonium species. X-ray diffraction analysis of the plutonium-carbonate precipitate shows the compound is similar isostructurally to $\text{Nd}_2(\text{CO}_3)(\text{OH})_4 \cdot x\text{H}_2\text{O}$. The corresponding plutonium compound, therefore, would be $\text{Pu}_2(\text{CO}_3)(\text{OH})_4 \cdot x\text{H}_2\text{O}$. The structure of the plutonium compound agrees best with the neodymium compound when calculated on the basis of a hexagonal cell. The lattice parameters for the plutonium compound are as follows: $a = 0.846 \pm 0.003\text{nm}$ and $c = 0.716 \pm 0.003\text{nm}$.

The infrared spectrum of the plutonium-carbonate compound produced in the carbonate-precipitate process indicates covalently bonded carbonate groups rather than an ionic carbonate species. There is an indication that both the unidentate and bidentate carbonate groups are present in the carbonate.

Metal Ions Precipitated with the Americium and Plutonium in the Carbonate Precipitation Process

After the plutonium and americium have been recovered from MSE waste salts, the plutonium and americium subsequently must be separated from each other and either recovered by precipitation (americium) or returned to the process stream (plutonium). Since metallic impurities can be present in the MSE waste salts, it is desirable to know whether these impurities will precipitate with the plutonium and americium, thus requiring later separation, or whether the impurities will be removed during the carbonate precipitation.

A series of precipitations was made to determine the behavior of a selected group of metallic ions in the carbonate precipitation. Of the eight ions tested (Fe, Ni, Cr, Al, Zr, Pb, Cu, and Ca), all precipitated quantitatively with the exception of Ca and Cu, which only partially precipitated. The results indicate that these metals, when present as impurities in MSE waste salts, will have to be separated from plutonium and americium by other purification processes.

PLUTONIUM PEROXIDE PRECIPITATION PROCESS

*Paul G. Hagan, Friend John Miner,
and Larry L. Martella*

A basic unit operation in the existing plutonium recovery and purification process at Rocky Flats is the precipitation of plutonium from a nitric acid medium by the addition of hydrogen peroxide (H_2O_2). A non-stoichiometric plutonium peroxide is produced. Two things are accomplished in this operation. First, there is a liquid-to-solid conversion and concentration of the plutonium; secondly, there is a purification of the plutonium from a number of metallic impurities. The peroxide precipitation is followed by a calcination to convert the peroxide to an oxide, which is subsequently fluorinated and reduced to metallic plutonium.

Essentially the same peroxide precipitation process will be used in the new Plutonium Recovery and Waste Treatment Facility being constructed at Rocky Flats. The major differences will be that the precipitation and calcination will be carried out on a batch rather than continuous basis as is now being done, and sulfate, which is now added to help produce an easily filterable peroxide precipitate, will no longer be added (see RFP-1921-A, p.20). These changes in the process require that certain operating parameters be investigated. Results obtained in these investigations are summarized as follows.

Plutonium Peroxide Precipitate Formation

When plutonium feed is first mixed with hydrogen peroxide, either with or without sulfate present, a

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red plutonium peroxy complex is formed. As additional peroxide is added, small particles of an insoluble plutonium peroxide precipitation begins to form within the solution. These particles then agglomerate to form a filterable precipitate.

When sulfate is present during the precipitation, the precipitate particles agglomerate in a somewhat spherical form. In solutions with no sulfate present, the particles agglomerate in a chainlike form.

Particle-size distribution studies showed that in the formation of agglomerates, some small peroxide particles remain unattached. In solutions in which sulfate is present, about 30 percent of the total particles are less than 2.9 μm in diameter. In solutions with sulfate absent, however, only about 4 percent of the particles are less than 2.9 μm in diameter.

In solutions with sulfate present, there is essentially no change in particle size during the precipitation digestion cycle. Particles less than 2.9 μm in diameter remain in the 30 percent range, and particles greater than 58 μm in diameter remain in the 40 percent range.

In contrast, the digestion cycle is important to particle-size growth in solutions with no sulfate present. During digestion, particles less than 2.9 μm in diameter were reduced from 30 to 4 percent. The distribution of particle sizes are summarized in Table 3.

Washing the Plutonium Peroxide Precipitate

Plutonium peroxide formed in solutions containing sulfate has primarily a hexagonal structure with only a trace of material having a face centered cubic structure. When the precipitate is formed in solutions that do not contain sulfate, the precipitate contains a greater concentration of face centered cubic material. Washing these precipitates with 1, 2, and 3N nitric acid causes no detectable change in their original crystal structures. There is an effect, however, on particle de-agglomeration, plutonium losses to the filtrate, and physical characteristics of the plutonium oxide resulting from calcination.

When plutonium peroxide precipitate, which is formed in solutions that do not contain sulfate, is washed with water, some of the agglomerate structures break down into smaller particles. When this same precipitate is washed with 1, 2, or 3N nitric acid, however, the agglomerates remain essentially unchanged in size. Particle size measurements made of a precipitate washed with water showed an increase from about 9 to 17 percent for particles in the 1.4- to 2.9- μm range. There was an increase from about 26 to 40 percent for particles in the 2.9- to 5.8- μm range. Since particle break-down undoubtedly would affect the filterability of the plutonium peroxide precipitate, precipitates formed without sulfate present should be washed with solutions of dilute nitric acid.

TABLE 3. Distribution of particle sizes

Size (μm)	Percent Distribution with Sulfate Present			Percent Distribution with No Sulfate Present		
	After 2/3 H_2O_2 Added	After Total H_2O_2 Added	After Precipitate Digestion Cycle	After 2/3 H_2O_2 Added	After Total H_2O_2 Added	After Precipitate Digestion Cycle
<2.9	53	26	29	36	30	4
2.9 to 11.6	35	30	25	47	39	6
11.6 to 58.0	11	1	4	14	25	76
58.0 to 145	1	6	4	3	6	14
>145	0	37	38	0	0	0

When plutonium peroxide precipitate formed in sulfate-containing solutions is washed with water or with 1, 2, or 3N nitric acid, there is no detectable change in the size of the agglomerate structures. As concerns the precipitate's filterability, either water or a dilute nitric acid wash is acceptable.

When plutonium peroxide precipitate is washed to remove extraneous occluded ions, some of the plutonium is lost to the wash solution. In an experimental study, precipitates were washed with water and with 1, 2, and 3N nitric acid. The wash solutions were then analyzed for plutonium concentrations. Solutions resulting from the water wash contained about 2×10^{-2} g/l plutonium; solutions from 1N nitric acid contained about 7×10^{-2} g/l plutonium; that from 2N nitric acid contained 8×10^{-2} g/l plutonium; and solutions from 3N nitric acid had about 0.6 g/l plutonium.

Since water washing causes precipitate breakdown, and 3N nitric acid increases plutonium losses to the filtrate, it appears that the precipitate is best washed with solutions of 1N or 2N nitric acid.

Calcination of Plutonium Peroxide Precipitate

When plutonium peroxide is calcined, it is converted to plutonium oxide. The physical characteristics of the oxide are significantly different if the precipitate is formed without sulfate present than it is formed in solutions with sulfate present. This difference is even more noticeable if the precipitate is washed with a nitric acid solution.

Calcined oxides made from sulfate-containing precipitates are olive colored and produce hard, chunky particles when calcined. The oxide particles produced range in size from about 0.1 to 6 mm. Washing the precipitate with water or with 1, 2, or 3N nitric acid prior to calcination does not change these physical characteristics appreciably.

Calcined oxide made from nonsulfate-containing precipitates has physical characteristics that vary according to the type of wash solution used prior to calcination. The oxides formed from precipitates

washed with water are a mixture of olive and black in color with particles that are large, hard, and chunky. The particles range in size from about 0.1 mm to about 8 mm with a crystallite size of about 14.5 nm (145 Å).

Oxides formed from these same precipitates, but washed with nitric acid, are black, shiny, and hard. The range in particle size is smaller than noted above and appears to be a function of the acidity of the washing solution. For instance, precipitates washed in 1N nitric acid prior to calcination have oxide particles that range in size from 0.1 to 1 mm. For a 2N nitric acid wash, the range is from <0.1 to 0.4 mm. And for 3N nitric acid, this range shifts to 0.04 to 0.16 mm in size.

In addition, the crystallite size became smaller as the nitric acid concentration in the wash increased. The average crystallite size for precipitates washed in 1N nitric acid was 8.8 nm (88 Å); in 2N, 6.5 nm (65 Å); and in 3N, 5.3 nm (53 Å).

Additional work is in progress to determine if the temperature and length of calcination has an effect on the physical characteristics of the plutonium oxide produced. Particle size and crystallite size are the physical characteristics of greatest interest since they will have the greatest effect in subsequent processing of the oxide to produce metallic plutonium.

PLUTONIUM AND AMERICIUM BEHAVIOR IN THE SOIL AND WATER ENVIRONMENT

Frend John Miner and Patricia A. Glover

Experimental work relating to plutonium transport in soil has continued. Several additional soils have been obtained, characterized, and their plutonium transport (sorption) determined using a soluble form of plutonium. Methods for producing a stable, aqueous slurry in addition to a solid slurry of plutonium oxide (PuO_2) were evaluated. An initial investigation was made of the plutonium form that exists in the aqueous phase of a soil and water mixture, after equilibration, when PuO_2 is

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used as a source of plutonium. Mathematical relations were determined relating sorption of plutonium (soluble form) to chemical and physical characteristics of the soil.

Measurement of Plutonium Transport

Four additional soils were obtained—three from Arkansas and one from Illinois. Equilibrium sorption is being determined for these soils using a soluble form of plutonium. The results that are currently available, expressed as percent of plutonium sorbed and as distribution coefficients [$K_{d(m)}$], are given in Tables 4 and 5. These data will be combined with that reported previously (RFP-2200-A, p.5) to give a more complete picture of soil behavior in the United States.

TABLE 4. Plutonium Sorbed
(mean % $\pm$ standard deviation)

Soils*	10^{-8} **	10^{-7} **	10^{-6} **
AR-A	99.37 $\pm$ 0.03	99.32 $\pm$ 0.04	99.47 $\pm$ 0.08
AR-B	94.23 $\pm$ 0.23	97.82 $\pm$ 0.24	---
AR-C	98.95 $\pm$ 0.05	99.20 $\pm$ 0.05	99.49 $\pm$ 0.02
IL	97.96 $\pm$ 0.10	99.13 $\pm$ 0.10	---

*AR = Arkansas; IL = Illinois

**Initial plutonium concentration in moles

TABLE 5. Distribution Coefficients
[mean $K_{d(m)}$ $\pm$ standard deviation]

Soils*	10^{-8} **	10^{-7} **	10^{-6} **
AR-A	714 $\pm$ 36	660 $\pm$ 33	756 $\pm$ 45
AR-B	80 $\pm$ 3	228 $\pm$ 9	---
AR-C	430 $\pm$ 23	573 $\pm$ 44	874 $\pm$ 30
IL	227 $\pm$ 10	633 $\pm$ 95	---

*AR = Arkansas; IL = Illinois

**Initial plutonium concentration in moles

Because of the likelihood of plutonium occurring in an insoluble form in a natural soil and water system, initial plans included measuring sorption using finely divided PuO_2 (<10 nm) as the source of plutonium (see RFP-2004-A). A slurry was proposed for use in adding the PuO_2 to the soil since the quantity of PuO_2 required (approximately 1 μg) would be too small to adequately weigh and transfer.

Three aqueous PuO_2 slurry systems were studied—water, water containing a surfactant (Triton X-100), and 0.005M HNO_3 . Previous attempts at preparing PuO_2 -water slurries resulted in non-homogeneous mixtures. It was believed that this non-homogeneity was related to a wide range in particle size caused by either the PuO_2 particle agglomerating or by sorption of PuO_2 on other particles present in the water. To minimize this problem, aqueous slurries were prepared, allowed to stand for a period of time to let the large particles settle out, then filtered through a 0.25- μm Millipore® filter. The filtered solutions were then tested for stability by taking a series of samples for plutonium analysis. These samples were collected on three separate days over a period of a month and a half.

The analyses indicated statistically significant variations in the water and water-plus-surfactant slurries. These variations were noted in mean plutonium concentrations obtained on the three different days and also between the individual analyses on any given day. This is not the case with the nitric acid slurry; however, even though the nitric acid slurry was relatively stable and homogeneous, its plutonium concentration was low. An unacceptably large volume of this slurry would be required to obtain the plutonium concentration necessary for the experimental work. Because of the problems of non-homogeneity and unacceptably low plutonium content, plans for using an aqueous slurry as a means for quantitatively transferring PuO_2 were abandoned.

A study is now underway on the use of a solid PuO_2 "slurry" using soil, rather than water, as the diluent. A weighed quantity of PuO_2 was thoroughly mixed with a soil. Homogeneity of the mixture was tested by leaching five aliquants of the soil successively with HNO_3 , HCl , and HF , then analyzing the resulting leach solutions for

plutonium. The results were close, which indicated that the slurry was relatively homogeneous. A second leach of the same aliquants gave comparable results.

There are difficulties, however, associated with the use of PuO_2 as a source of plutonium in sorption equilibrium work. The difficulties are related to the separation of plutonium that is sorbed by the soil from that which remains in solution. This separation is accomplished by centrifugation. (see RFP-2004-A). The density of PuO_2 is 11.7 g/cm^3 while that of soil particles is about 2.5. To centrifuge, using conditions that would remove soil particles, would, at least theoretically, also remove PuO_2 remaining in the aqueous phase. Any plutonium that did remain in the aqueous phase after centrifugation would most likely be some "soluble" form resulting from the "solubility" of PuO_2 . The meaning of sorption results calculated from these data would, at best, be unclear. Because of this, sorption equilibrium work with PuO_2 was delayed until information could be obtained about the plutonium species that exist in the aqueous phase when PuO_2 is used as the plutonium source. In the meantime, work with PuO_2 as a plutonium source was transferred to soil column elution studies. In those studies, the above noted problems associated with separation do not occur.

An exploratory sorption-equilibration run was made, using PuO_2 , to get an idea of how much plutonium would remain in the aqueous phase. A second reason was to investigate the form that the plutonium had in the aqueous phase if indeed any plutonium was there. After equilibration, the solid and aqueous phases were separated using conditions that would settle all soil particles greater than $0.1 \mu\text{m}$ in diameter. The aqueous phase was then analyzed for plutonium concentration. In addition, nuclear track and electron microscope techniques were used in analyzing the aqueous phase for the physical form and size of the plutonium species it contained.

The initial, total plutonium activity from PuO_2 in the soil was 810,000 disintegrations per minute (dpm) or approximately 10^{-6} moles. The activity in four aliquants of the aqueous phase after

equilibration was 2.25, 1.75, <1 , and 1.25 dpm/ml in a total of approximately 30 ml. These results indicate that there was some plutonium in the aqueous phase, but that most of the plutonium was either sorbed by the soil or centrifuged down with it.

Samples of the aqueous phase were evaporated on polycarbonate films for the nuclear track experiments. One film was exposed to a total radiation of $1.43 \times 10^{13} \text{ neutrons/mm}^2$ and the other to $4.3 \times 10^{13} \text{ neutrons/mm}^2$ in a TRIGA-type reactor. The track patterns of the two were compared.

On the film exposed to the lowest total radiation, it was possible to identify both particulate and "dispersed" plutonium. The maximum size of the particulate plutonium was $0.1 \mu\text{m}$. On the film exposed to the higher radiation, there was an increase in the particulate rather than the "dispersed" form of plutonium. The latter would be expected if the plutonium were present as a soluble species. The increase in the particulate plutonium indicates that the "dispersed" plutonium could actually be small particles. The minimum particle size detected with higher radiation was $0.04 \mu\text{m}$.

One of the films was analyzed by electron microscopy. The results indicated that 95 percent of the particles had a diameter less than $0.05 \mu\text{m}$. The remaining 5 percent had a mean diameter of $0.17 \mu\text{m}$. These results confirm data from the nuclear track work that the plutonium is present as particles rather than "dispersed" plutonium.

It is possible that the particulates observed resulted, in part at least, from drying out of a solution containing polymers. This possibility can be tested by a nuclear track experiment in which the aqueous drops containing the plutonium are converted to a gel rather than being evaporated to a solid on the film.

Mathematical Relationship Between Sorption and the Chemical and Physical Characteristics of the Soil

An objective of this program has been to determine if any chemical or physical characteristics of the

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soils are more important than others in influencing the sorption of plutonium. To determine this, those characteristics that could reasonably be expected to influence plutonium sorption were measured. These characteristics and plutonium sorption data were then evaluated by regression analysis to determine if there were any significant relationships between them.

Initial regression analyses were made using sorption data, expressed as percent of plutonium sorbed or distribution coefficients, as the dependent variables; chemical and physical characteristics of the soils [CEC (cation exchange capacity), pH, and percent sand, for example] were considered independent variables. No statistically significant relationships were found from these data. (See RFP-2276-A, p.2.)

Principal-component analyses were then used to group those initial, independent variables shown to be related mathematically. What resulted were new, independent variables representing certain qualities of the soils. An example was ion exchange capabilities, which included weighted percentages of the CEC, percent clay, and percent sand values for each soil. Another example was soil acidity, which included weighted percentages of the pH, percent organic carbon, and percent inorganic carbon. Using stepwise regression, statistically significant correlations were found between these new, independent variables and plutonium sorption as expressed by percent plutonium sorbed and distribution coefficients. The coefficients of variation (R^2) associated with these correlations were rather low, however, indicating that either additional cause-effect relationships or variables likely exist that have not been identified (see RFP-2276-A, p.2). Additional soils will need to be investigated.

In determining whether there were significant relationships between sorption and soil characteristics, percent plutonium sorbed and distribution coefficients were used as dependent variables. This was done so that resulting equations would contain units conventionally used to express sorption of material by soil; however, the experimentally measured plutonium concentrations from which percent plutonium sorbed and distribution coefficients values were calculated were disintegra-

tions per minute per millilitre (dpm/ml). Mathematical manipulations were involved in converting the disintegration (or count) data into percent plutonium sorbed or distribution coefficients values. It is possible that this conversion could transform the initial sorption data in such a way that relationships between sorption and independent variables would be minimized or perhaps lost in subsequent regression calculations. To check this possibility, regression calculations were carried out using the original count data as the dependent variable and factors such as CEC, pH, and percent sand as independent variables. Statistically significant relationships were found. This was not the case, as noted above, when sorption was expressed as percent plutonium sorbed or distribution coefficients. The relationships found using the count data are given in Table 6.

Stepwise regression analyses were also carried out using count data as the dependent variable and new, independent variables generated by principal-component analyses. The new, independent variables were identified as Z_1 , Z_2 , and Z_3 and consisted of a combination of independent variables as noted earlier. The relationships found by the regression analyses are summarized in Table 7. Z_1 , the only new, independent variable that appears in the relationships in Table 7 has the form

$$Z_1 = 0.56 (\text{CEC}) + 0.54 (\% \text{ clay}) - 0.53 (\% \text{ sand}).$$

TABLE 6. Stepwise regression analysis

Independent Variables: Nine variables such as CEC, pH, and % clay
Dependent Variables: Count data

Initial Plutonium Concentration (Moles)	Relationship
10^{-8}	dpm/ml = $14.880 - 0.3025 (\% \text{ clay})$
10^{-7}	dpm/ml = $125.154 - 5.904 (\% \text{ clay}) + 6.965 (\text{CEC})$
10^{-6}	dpm/ml = $-249.68 + 34.85 (\% \text{ sand}) + 233.41 (\text{CEC}) - 122.38 (\% \text{ clay})$

TABLE 7. Stepwise regression analysis

Independent Variables: Z_1, Z_2, Z_3
Dependent Variables: Count data

Initial Plutonium Concentration (Moles)	Relationship
10^{-8}	dpm/ml = $6.192 - 2.220 (Z_1)$
10^{-7}	dpm/ml = $52.257 - 15.356 (Z_1)$
10^{-6}	dpm/ml = $1097 - 361.05 (Z_1)$

The components of Z_1 are the same characteristics of the soil that were found most important from the regression analyses using the original independent variables (Table 6). Results from two different treatments of the data indicate, then, that it is these soil characteristics that are most significant in the sorption (movement) of plutonium in the soil. Work evaluating these characteristics will continue.

COMPUTERIZED MODEL OF ION EXCHANGE COLUMN PERFORMANCE

*James D. Navratil and Larry L. Kirkby**

Anion exchange techniques are used at Rocky Flats for the purification and concentration of plutonium in various aqueous process streams. Development of a mathematical model that will enable the predication of column performance during the anion exchange purification of plutonium was desired. Such a model should allow optimization of column operations, improvement in separations, minimization of aqueous waste, and a prediction of column operation in the new plutonium recovery facility.

The computer program is written in the Fortran programming language and is designed for use in an

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IBM-370/158 computer. The program is an adaptation of a code written by Cooper and James** for processing plutonium with Dowex® 1-X4 resins. Using empirical rate expressions, the program calculates breakthrough curves and column concentration profiles for the sorption process. Quantitative verification of the adapted computerized model has been completed experimentally, and results indicated satisfactory predication of column breakthrough during the loading (sorption) step (see RFP-2276-A, p.13).

Current work has involved modification of the computer program to incorporate column washing, elution logic, and better empirical models for the sorption step. In addition, it was desirable to incorporate provisions for changing the flow rate during the course of a run and to develop plotting capabilities in the program to aid in better presentation of column breakthrough curves.

Program modifications have been made and preliminary verification of the washing and elution models completed. Experimental lab-scale and production-scale ion exchange column data have been obtained for the loading, washing, and eluting steps in the plutonium purification process. The experimental data were in good agreement with predicted data.

SPENT LATHE-COOLANT OIL STUDIES

James D. Navratil

A research program was completed to determine the nature of plutonium in lathe-coolant oil and to develop methods for removing plutonium and for recycling the oil. The plutonium-contaminated lathe-coolant oil, with its carbon tetrachloride diluent, is generated in plutonium machining areas. Previous studies (RFP-2360-A, p.33) showed that the spent oil, carbon tetrachloride mixtures contained both particulate plutonium and water or oil-soluble plutonium species. The particulate

**R. S. Cooper and D. B. James. Theoretical Studies of Ion Exchange with Slow Particle Diffusion. LA-3046. Los Alamos Scientific Laboratory, New Mexico. 1964.

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plutonium was removed by filtration; the non-filterable plutonium was removed by adsorption on various drying agents. Preliminary tests showed the lathe-coolant mixture could be separated by distillation of the carbon tetrachloride to yield recyclable products.

Attempts to identify the plutonium species in the used lathe-coolant mixture were concluded. X-ray diffraction studies showed that the particulate material, which had a concentration of approximately one milligram plutonium per litre, was removed by filtration through a 0.8-micrometre filter. The material was plutonium oxide. Nonfilterable plutonium remaining in the oil (approximately 0.5 milligram plutonium per litre) was presumed present as hydrated chloro species since the mixture usually contained about 1 millimolar (mM) water and about 5 mM chloride.

Another potential ligand for plutonium in the oil is the anti-oxidant (2, 6-di-tertiary-butyl-4-methylphenol) present in the oil. Experiments with plutonium metal coupons stored in batches of synthetic oil carbon tetrachloride mixtures containing various amounts of anti-oxidant showed increasing levels of nonfilterable plutonium with increasing concentrations of anti-oxidant. Attempts to characterize the actual plutonium species in the oil mixture by separation-mass spectroscopy techniques failed.

Previous studies showed that increased water content of the carbon tetrachloride and oil gave increased corrosion of plutonium metal. Dry-air distillation appeared to yield products with low water content, but precautions against absorption of water from the atmosphere above the products were necessary. Residual water in the reclaimed products could be removed by further dry-air distillation or adsorption on calcium sulfate. If necessary, soluble plutonium species could also be removed by adsorption on calcium sulfate or charcoal, but its removal was not necessary to provide recyclable oil.

A tentative flow sheet for recycling the oil and carbon tetrachloride was developed and tested on a laboratory scale. The flow sheet consists of (1) dry-air distillation of the carbon tetrachloride

from the mixture, (2) filtration of the oil bottoms, (3) analysis of both recovered components, (4) further drying of components if necessary and the addition of anti-oxidant to the oil, and (5) testing of the products before reuse by conventional (weight loss) plutonium metal corrosion tests.

Demonstration of the flow sheet on a larger scale is needed. If such a demonstration occurs, data will be used to evaluate the economic feasibility of the process to recycle oil and carbon tetrachloride for machining operations.

CHEMICAL TECHNOLOGY

Edward D. Erickson

CHEMICAL MILLING BERYLLIUM THIN FILM

Robert L. Riegel

Beryllium foil, made for X-ray windows, has been produced for several years as two mils [0.05 millimetre (mm)] in thickness and one inch [2.54 centimetres (cm)] in diameter. No problems were encountered in providing windows that met all requirements. Recently, efforts to produce thinner one-mil (0.025 mm) windows two inches (5 cm) square and larger have failed because of pin holes.

Development work has now produced one-mil (0.025 mm) beryllium foil, without pin holes, in 2- by 5-inch (5- by 13-cm) sections. The new technique involves lapping beryllium blanks after rolling and prior to chemical milling in a solution developed at Lawrence Livermore Laboratory (LLL) and described in Table 8. Lapping removes about three mils (0.075 mm) per surface and eliminates surface imperfections and roughness that are not corrected by chemical milling. The chemical-milling solution reduces the thickness uniformly and, with flat blemish-free starting material, produces one-mil beryllium foil that is free of pin holes.

TABLE 8. Lawrence Livermore Laboratory solution used to produce thin beryllium foil

50 parts lactic acid
40 parts phosphoric acid
10 parts sulfuric acid
10 parts water

Research is continuing to produce stronger foil and to produce starting material with smaller grain size.

AMERICIUM RECOVERY FROM RARE-EARTH RESIDUES

Stephen G. Proctor

A precipitation process has been used to recover americium from gross quantities of rare-earth elements in americium, rare-earth residues. These residues were generated by design agency projects and contained gross quantities of lanthanum and yttrium (30 to 50 percent). The method of americium recovery consisted of precipitating the insoluble rare-earth fluorides (LaF_3 and YF_3) with hydrofluoric acid (HF). This was done while maintaining the americium in solution by oxidation to the hexavalent state. Two batches of residues were processed with this technique, and 22.5 grams (g) of americium were recovered for a 78 percent recovery rate.

The oxide residues initially were dissolved in 7M nitric acid (HNO_3) with heat being added to achieve complete dissolution. After dissolution was complete, the acidity was reduced to 0.1M (H^+) by slowly adding 8M ammonium hydroxide (NH_4OH). After the acidity adjustment, the solution was heated to 80 °C and made 0.2M in ammonium persulfate and 0.002M in argentic oxide. The solution temperature (80 °C) was maintained for 40 minutes to achieve maximum oxidation of the americium from Am(III) to AmO_2^{++} .

The solution was next made 0.2M in HF to precipitate the rare earths and was then allowed to digest for five minutes prior to filtration. The insoluble rare-earth fluorides were removed from solution by filtration. The americium was then precipitated as americium oxalate by adding a 0.1M excess of oxalic acid. The americium oxalate was separated by filtration, washed with water, and calcined at 600 °C for four hours to convert the americium oxalate to AmO_2 . This procedure was repeated on the first batch to obtain AmO_2 of acceptable purity. The second batch of residues required four successive fluoride strikes before AmO_2 of acceptable purity was obtained. Prior to purification, the first batch of residue weighed 20.0 g with an americium assay of 53 wt %; the second batch weighed 55.4 g with a 32 wt % americium assay.

Analytical results from the two batches of purified AmO_2 showed the lanthanum and yttrium impurities were reduced to 0.4 percent from initial concentrations of 30 to 50 percent. A typical impurity analysis is shown in Table 9. The americium content in the first batch of AmO_2 was 0.84 g Am/g AmO_2 and the americium content in the second batch was 0.85 g Am/g AmO_2 . The americium recovery for the first batch was 95 percent; americium recovery on the second batch was

TABLE 9. Typical impurity analysis of recovered americium oxide

Element	Concentration (ppm*)
Aluminium	250
Calcium	100
Iron	80
Lanthanum	3500
Lead	450
Plutonium	5000
Silicon	500
Yttrium	5000

*ppm - μg of impurity per g of AmO_2

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TABLE 10. Americium recovery

Batch No.	Input			Output		
	Total Weight (g)	Americium Weight (g)	g Americium/ g Oxide	Total Weight (g)	Americium Weight (g)	g Americium/ g Americium Oxide
1	20.0	10.6	0.53	12.0	10.1	0.84
2	55.4	18.1	0.32	14.6	12.4	0.85

69 percent. The rare-earth fluoride residue was analyzed and found to contain 6.2 g americium in 63.2 g residues (0.098 g Am/g residues). An americium recovery summary is shown in Table 10.

Recovery rates were within the range anticipated. Americium recovery for the first batch was excellent at 95 percent. The second batch recovery (69 percent) was good considering four successive fluoride strikes were required to achieve AmO₂ of acceptable purity. Small americium losses are expected during the fluoride strike because trivalent AmF₃ is insoluble and will carry down with the rare-earth fluorides during precipitation. Small amounts of Am(III) are expected in the oxidized solution because of disproportionation of the americyl (AmO₂⁺⁺) ion.

The fluoride residue resulting from the many fluoride strikes was discarded. The low concentration of americium (9 percent) and the high rare-earth concentration (approximately 80 percent) make the americium recovery undesirable because of economic and radiation factors.

REMOVAL OF URANIUM-232 DAUGHTERS FROM URANIUM-233 BY DOUBLE CARRIER PRECIPITATION

Donald L. Baaso

Previous work has shown the feasibility of removing the daughters of uranium-232 (²³²U) from uranium-233 (²³³U) by a double carrier precipitation

technique (see RFP-2360-A, p.16). This technique uses normal thorium and barium as carriers for precipitating thorium-228 tetrafluoride (²²⁸ThF₄)

TABLE 11. Thorium-228 and radium-224 precipitation conditions for ten tests

Test No.	Carrier Concentration*	Uranium-233 (g)	Precipitate Temperature (°C)
15	4 g/l thorium	one	88 ± 2 Single carrier
16	4 g/l each of thorium and barium	↓	Double precipitation
17	1 g/l each of thorium and barium		
18	1 g/l each of thorium and barium		
20	3 g/l each of thorium and barium		
21	1 g/l each of thorium and barium		25 ± 2
24	1 g/l each of thorium and barium		88 ± 2
25	2 g/l each of thorium and barium		↓
26	3 g/l each of thorium and barium		
27	4 g/l each of thorium and barium		

*All tests were performed with a double carrier in a single precipitation unless otherwise noted.

and radium-224 sulfate ($^{224}\text{RaSO}_4$) from a uranyl-233 nitrate solution at pH 1. Additional tests have been performed in which the carrier concentrations were varied from one to four grams per litre (g/l) of each carrier, and double precipitations were performed with one gram per litre of each carrier. Each double carrier precipitation contained equal amounts of the thorium and barium carriers. The tests were performed using one gram of ^{233}U for each test. After precipitation, the samples were digested for one hour at either $88 \pm 2^\circ\text{C}$ or $25 \pm 2^\circ\text{C}$. Table 11 is a summary of the precipitation conditions of each test.

After digesting the precipitates, the samples were filtered on Whatman 42 paper. Results were determined by measuring both the total gamma and the

2.61 million electron volts (MeV) gamma activities of the precipitated solutions. The total gamma activity was measured with an ionization chamber; the 2.61 MeV gamma from thallium-208 (^{208}Tl) was measured by a lithium drifted germanium detector coupled with a pulse height analyzer.

The effect of increasing the normal thorium and barium carriers from 1 to 4 g/l was to increase the decontamination of ^{228}Th and ^{224}Ra by a factor of five. This was determined by the decrease of gamma activity from ^{208}Tl . The double precipitation with one g/l carriers at $88 \pm 2^\circ\text{C}$ gave an additional decontamination factor that was five times better than the best single precipitation test. This reduced the 2.61 MeV gamma to less than 0.1 percent of its steady state level after two to three days.

FIGURE 2. Thallium-208 gamma activity after precipitation of thorium-228 and radium-224

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FIGURE 3. Total gamma activity from Uranium-233 and daughters after precipitation of thorium and radium

An elevated precipitation, digestion, and filtration temperature was found to increase the precipitation efficiency. A double precipitation at $25 \pm 2^\circ \text{C}$ with one g/l carrier returned the gamma activity to 2 percent of its steady state level in 18 days compared to approximately 30 days for a similar precipitation done at $88^\circ \pm 2^\circ \text{C}$. The data from these tests are represented in Figure 2. These data compare favorably with reported ion exchange separation results.*

Measurement of the total gamma activity gave similar but higher relative readings. This is most likely due to the ^{233}U gamma being included in the readings. The total gamma activity was reduced to approximately 2 percent and remained below

5 percent of its steady state level for 30 to 35 days when the double precipitation method was used. When only thorium was precipitated, about 28 days were required to reduce the total gamma activity to 5.5 percent of its steady state level. These data are represented in Figure 3.

Figure 2 shows the advantage of the double carrier in which only the thorium is precipitated. The gamma activity is significantly lower during the first 25 to 30 days.

GAMMA SCINTILLATION SYSTEM FOR AMERICIUM PROCESS MONITORING

Stephen G. Proctor

A gamma scintillation counting system (GSCS) for monitoring americium during aqueous processing

*R. H. Rainey. Laboratory Development of a Pressurized Cation Exchange Process for Removing the Daughters of ^{232}U from ^{233}U . ORNL 4731. Oak Ridge National Laboratory, Tennessee, December 1972.

has been developed. The GSCS has been used for monitoring americium during the processing of approximately 25 kilograms (kg) of plutonium-amerium co-reduction residues. The GSCS utilizes the 60 kilo electron volts (keV) gamma radiation resulting from the radiolytic decay of americium-241. Gamma radiation is detected by coupling a thallium-activated sodium iodide (NaI) crystal with a photomultiplier tube. The resulting signal pulse is then amplified and counted. The GSCS has demonstrated a capability for detecting and differentiating americium concentrations in solutions varying from 10^{-6} to 0.1 grams per litre (g/l). Americium in the process solution was monitored continuously using an in-line, flow-through detector cell. Instantaneous detection of americium concentration changes in the process are therefore possible.

The GSCS consisted of the following equipment:

1. Tennelec High Voltage Supply, Model AEC-5000,
2. Ortec Amplifier, Model 440A,
3. Tennelec Singel Changel Analyzer, Model TC440,
4. Tennelec Dual Counter/Timer, Model TC555P.

The detector consisted of a 12.5-mm (0.5-in.) diameter photomultiplier tube (Amperex XP-1110) coupled to a Harshaw 12.5-mm (0.5-in.) diameter by 12.5-mm (0.5-in.) long, thallium-activated sodium iodide crystal. The in-line, flow-through detector through which the americium solution passed for monitoring consisted of a 76-mm (3-in.) diameter by 12.5-mm (0.5-in.) thick polyvinyl chloride (PVC) cell surrounded by a 12.5-mm (0.5-in.) lead shield.

The GSCS was initially used without any means for moderating the americium-241 gamma radiation. Tests revealed that operation of the detection system without any absorber to moderate the radiation resulted in high count rates at low americium concentrations (50,000 counts = 1×10^{-3} g/l americium). When the americium concentration reached 1×10^{-2} g/l, the phototube became flooded and produced erroneously low count rates. After installing a 1.6-mm (0.063-in.)

cadmium absorber to lessen the count rate, the count rate dropped to 10,000 counts for a 1.0 g/l americium solution. This indicated over-absorption of the 60 keV americium-241 gamma radiation.

A successful compromise was made with a 0.8-mm (0.031-in.) cadmium absorber that yielded a 30 counts per second count rate for americium concentrations of 10^{-6} g/l and 100,000 counts per second count rate for 0.3 g/l americium concentration. A complete listing of the count rates for various concentrations of americium are shown in Table 12. All count rates are based on counting only the 60 keV gamma energy of americium-241. A plot of the data yields a curve from which the americium concentration is obtained for a given count rate (Figure 4). A complete gamma pulse height analysis of the americium process material was made, and the results are shown in Figure 5.

The effect of plutonium in the process stream was found to have no effect on the readings observed using the GSCS. Plutonium concentrations as high as 5 g/l were passed through the flow-through detector, in the presence of 10^{-2} g/l americium, with no observable change in count rate being noted.

TABLE 12. Gamma-scintillation-counting-system count rates versus americium-241 concentration

Americium Concentration (grams per litre)*	Count Rates (counts per second)
10^{-6}	30
10^{-5}	100 to 400
10^{-4}	400 to 1200
10^{-3}	1200 to 7000
10^{-2}	7000 to 10,000
10^{-1}	10,000 to 100,000

*All americium analyses were accomplished by radiometric methods.

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FIGURE 4. Gamma scintillation counting system (GSCS) count rate versus americium concentration

FIGURE 5. Gamma energy profile of americium process material

The gamma scintillation counting system has been used to monitor the processing of 1600 litres of americium feed resulting from 25 kg of reduction residues. By relying entirely upon the GSCS for control of the americium during processing, less than 1 percent of the total americium input was

lost in waste solutions. The small losses experienced were normal operating losses and were expected.

AMERICIUM PURIFICATION FOR CHEMICAL OPERATIONS

Stephen G. Proctor

Two batches of impure americium oxide (AmO_2) were purified using precipitation techniques. Both batches contained large quantities of lead and potassium and were below purity standards set by the Isotopes Pool at Oak Ridge National Laboratory (ORNL). The purification technique used was a combination of oxalate-chloride precipitation procedures designed to remove the unwanted impurities.

The impure AmO_2 was initially dissolved in 7M nitric acid (HNO_3) followed by chloride precipitation of the lead impurity. The insoluble lead chloride (PbCl_2) was then removed from solution by filtration and was discarded. The filtrate was processed using an oxalate precipitation technique to recover americium. Solution acidity was first reduced to 0.3M with the slow addition of 8M ammonium hydroxide (NH_4OH). Sufficient oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$) was next added to the solution to precipitate the americium and leave the filtrate 0.1M in oxalic acid. Following an eight-hour digestion period, the insoluble americium oxalate [$\text{Am}_2(\text{C}_2\text{O}_4)_3$] was filtered, washed with water, and calcined at 600 °C for four hours to convert the $\text{Am}_2(\text{C}_2\text{O}_4)_3$ to AmO_2 .

Both batches were processed using the above procedure. The major impurities in both batches were potassium and lead. In the first batch of AmO_2 , the americium assay was improved from 77 to 88 percent with 99.9 percent americium recovery. The americium assay on the second batch was increased from 38.5 to 85.5 percent with 93 percent americium recovery. The material balance for both batches is shown in Table 13.

Following purification, both batches of AmO_2 were of acceptable purity and were subsequently shipped to the Isotopes Pool at ORNL. A total of

TABLE 13. Americium material balance

BATCH 1						
	Americium Oxide (g)	Americium (g)	Americium (g/g)	Potassium (wt %)	Lead (wt %)	Recovery (%)
Before Purification	40.66	31.3	0.77	10.0	2.0	—
After Purification	35.80	31.5	0.88	0.005	0.3	99.9
BATCH 2						
Before Purification	96.01	35.70	0.371	1.0	40.0	—
After Purification	38.90	33.28	0.855	0.005	0.5	93.1

136.67 grams of AmO_2 was purified using the combination precipitation procedure. The americium recovery efficiency was 96.7 percent.

RECOVERY OF PLUTONIUM FROM LECO CRUCIBLE RESIDUES

Kay K. Kunert

Leco crucibles are contaminated by the Analytical Laboratory during analysis of carbon in plutonium metal. No method has been developed for recovering plutonium from these crucibles; consequently, there are currently 136 drums of Leco crucible residues containing 75 kilograms (kg) of plutonium in storage.

The Leco crucibles currently being used are made from high-fired aluminum silicate ($\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$). Approximately 0.5 gram of plutonium metal, along with one gram of iron accelerator, are used for each analysis. These two materials are placed in a crucible and are fired to 2000 °C. This results in a hard, glassy residue composed of ferric oxide (Fe_2O_3), plutonium dioxide (PuO_2), silicon dioxide (SiO_2), and magnetic iron oxide (Fe_3O_4).

Before being packaged for storage, the Leco crucibles are broken into pieces of various sizes by

the Analytical Laboratory. The first attempt at processing Leco crucible residues was made using the crucible residues as they were received.

An initial nitric acid leach of the broken crucible pieces was tried but with little success. For subsequent tests, the crucible pieces were ground with a mortar and pestle before further processing was attempted.

The high content of magnetic iron oxide in the crucible residues renders the plutonium-bearing portion of the residue magnetic. A test was conducted to determine if this property could be used to separate the plutonium from the bulk of the crucible. A magnet was passed through some of the ground crucible residue several times until the bulk of plutonium-bearing material had been removed. The magnet removed 83 percent of the plutonium and left a mixture of solids containing 3×10^{-3} grams plutonium per gram of mixture. This is below the discard limit.

A second test was conducted to determine if the particle size of the ground material had an effect on the magnetic separation. A 980-gram batch of ground crucible residue was screened into three different portions: >1.19 mm (14 mesh), 0.42 to 1.19 mm (14 to 35 mesh), and <0.42 mm (35 mesh). The plutonium-bearing portion of the residue was separated from each fraction using a magnet. Table 14 shows the size distribution of

TABLE 14. Results of magnetic separation of plutonium from ground Leco crucibles

Mesh Size of Fraction	Portion of Total Batch Contained in Fraction (%)	Total Plutonium Contained in Fraction (%)	Plutonium in Fraction Removed with Magnet (%)
Retained on 14-mesh	33	39	99
Pass 14, Retained on 35-mesh	31	43	86
Pass 35-mesh	36	18	82

the ground residue, the plutonium in each size fraction, and the percentage of plutonium removed from each fraction by the magnet. A total of 34.6 grams of plutonium was removed from the residue leaving the crucible with 5.14×10^{-3} grams of plutonium per gram of crucible. As shown in Table 14, the best separation was achieved on the >14-mesh portion retained on a 14-mesh screen. Ninety-nine percent of the plutonium contained in this fraction was removed.

Several different methods have been investigated for recovering plutonium from the plutonium-bearing portion of the crucible residue. Leaching of the residue in 12M nitric acid (HNO_3) with various concentrations of hydrofluoric acid (HF) resulted in 6 percent of the plutonium being dissolved at 0.1M HF to 53 percent of the plutonium being dissolved at 1.0M HF. Pretreatment of the plutonium residue with a 10M sodium hydroxide (NaOH) leach before the 12M HNO_3 , 0.1M HF leach improved the plutonium dissolution. The results indicated dissolution of 28 to 53 percent of the plutonium with the percentage of dissolution increasing with the decrease in particle size. Pretreatment of the residue with a sodium carbonate (Na_2CO_3) fusion increased the plutonium dissolution in the 12M HNO_3 , 0.1M HF leach to 87 percent.

Additional work on Leco crucibles will be done to substantiate the data obtained thus far and to evaluate other possible ways of improving dissolution of the plutonium.

PREPARATION OF THORIUM METAL

Donald L. Baaso and William V. Conner

A 100-gram (g) batch of high-purity thorium oxide was received from Oak Ridge National Laboratory (ORNL) for conversion to metal. The thorium had been purified in the calutrons at Oak Ridge to remove all thorium daughter products. The metal was to be fabricated into targets for a particle accelerator experiment. The experiment required high-purity thorium—free from other radionuclides. A literature survey indicated that thorium metal could be prepared by reducing thorium tetrafluoride (ThF_4) with calcium metal in the presence of zinc. The zinc forms an alloy with thorium metal. This lowers the melting point to prevent freezing of the metal before coalescence occurs. Thorium metal melts at 1750°C , and a 6 wt % zinc alloy was reported to melt at approximately 1200°C .^{*} Large-scale thorium reductions are made with 6 wt % zinc as zinc chloride (ZnCl_2). The zinc is subsequently removed from the alloy by vacuum distillation.^{**}

Several small-scale test reductions were performed using normal thorium with charges ranging from 35 to 100 g of thorium. Since these tests were made using small quantities of thorium, an iodine (I_2) booster was used to supply additional heat to the system. Iodine ratios of 1 to 1.3 moles of I_2

^{*}*The Metal Thorium*. Harley A. Wilhelm, Ed. Proceedings of the Conference on Thorium. American Society for Metals, Cleveland, Ohio. October 11, 1956.

^{**}F. L. Cuthbert. *Thorium Production Technology*. Addison-Wesley Publishing Company, Inc. 1958.

per mole of thorium were used for these tests. The ThF_4 was prepared by reacting thorium oxide (ThO_2) with hydrofluoric acid (HF) gas at 600 °C. The zinc content of the test charges was varied from 6 to 12 wt %. The zinc location in the charge had a marked effect on the reduction yields. Placement of the zinc in the main charge caused the charge to boil because of the high vapor pressure of zinc. This produced low yields because a portion of the charge was lost from the crucible and insufficient zinc remained to alloy with the thorium, which caused premature freezing of the metal. Placement of the zinc in the bottom of the crucible reduced boiling and gave better yields.

Purified ThO_2 was converted to ThF_4 with HF at 600 °C. The charge containing the purified thorium was prepared using a 30-percent excess of calcium, 1.2 moles of I_2 per mole of thorium, and 9 wt % zinc. The reduction produced a Th-Zn alloy that was porous and brittle. Because of the porosity, the alloy could not be separated cleanly from the slag, and the metal yield could not be determined. The slag could not be removed by pickling because the alloy hydrolyzes rapidly in aqueous solution; therefore, a rough separation was made from the slag, and final purification was performed at ORNL using vacuum distillation techniques. The purified thorium metal was fabricated into targets at the target preparation center at ORNL and these targets are currently in use.*

It has been reported that the quality of metal from small-scale thorium reductions can be improved if the zinc content of the charge exceeds 50 wt %;** however, the increased zinc content resulted in low (50 percent) metal yields. The low yields were most likely caused by boiling of the zinc, which might be controlled by placing the zinc in the bottom of the crucible. The tight delivery schedule for this project limited the amount of development work that could be performed before the actual reduction. Any future work on small-scale thorium reduction will include an evaluation of higher zinc

contents with the zinc at the bottom of the crucible.

AMERICIUM PROCESS DEVELOPMENT

Stephen G. Proctor

A process has been developed for the recovery and purification of americium found in molten salt and metal reduction residues. Since the bulk of the americium at Rocky Flats is contained in molten salt extraction (MSE) residues, a process was sought to accommodate this material. Lesser amounts of americium are contained in metal reduction (MR) residues, which also figured in the process development.

The process that was developed utilizes the complexing ability of citric acid with americium. The same steps are used as described on page 21 of this report in a section entitled "Plutonium and Americium Recovery from Reduction Residues." By washing an americium-loaded cation column with buffered citric acid (pH 3.5), the americium was selectively eluted from the resin. The eluted americium was then precipitated with oxalic acid, and the resulting americium oxalate [$\text{Am}_2(\text{C}_2\text{O}_4)_3$] was calcined to an americium oxide (AmO_2) product of acceptable purity.

Americium feed solutions used in the process development originated from two separate sources. Metal reduction residues were processed and produced solutions high in plutonium and americium. Anion exchange treatment of these solutions yielded anion effluents that were high in americium content and were used as a feed source. Similar anion effluents were obtained from the processing of MSE residues. These solutions also resulted from the plutonium-americium separation by anion exchange and were used as a second feed source. Both types of americium feed solutions were processed in the same manner regardless of their origin.

The developed process has been demonstrated as an effective method for recovering and purifying

*E. H. Kobisk. Oak Ridge National Laboratory, Tennessee. Private communication.

**F. H. Spedding, H. A. Wilhelm, W. H. Keller, J. E. Iliff, and C. Neher. Production of Thorium Metal by the Metallothermic Reduction of ThF_4 . USAEC Report CT-2950. Iowa State College, Ames, Iowa. 1945.

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americium from molten salt extraction residues and metal reduction residues. A major portion of the impurities are eliminated during the initial cation exchange (80 to 85 percent removal). The oxalic acid wash effectively removed the remaining plutonium and iron (99 percent) without any americium losses. The citric acid elution of the americium effectively separated the americium from the remaining impurities (Mg, Ca, K, and Na) without loss of americium. The buffered citric acid eluting agent was easily adjusted for the correct pH range by adding ammonium citrate. Weighing errors in the citric acid-ammonium citrate makeup may be as high as 10 percent without seriously affecting the correct pH range of the eluting agent. The recovery of americium as AmO_2 of acceptable purity averaged 96 percent with individual batch recoveries running from 93 to 96 percent.

CATION EXCHANGE PROCESS EVALUATION FOR 30 MOLE PERCENT MAGNESIUM CHLORIDE MOLTEN SALT RESIDUES

Stephen G. Proctor and Kay K. Kunert

A new salt composition has been formulated by J. B. Knighton and co-workers for improved extraction of americium from plutonium metal. The new salt will reduce tenfold the quantity of spent salt generated; consequently, plutonium and americium concentrations in the spent salt will be increased.

The new composition is 30 mole percent magnesium chloride (MgCl_2), 35 mole percent potassium chloride (KCl), and 35 mole percent sodium chloride (NaCl). Compared to the molten salt residue currently being used, the new salt decreases the KCl and NaCl equally and increases the MgCl_2 concentration from 6 to 30 mole percent.

An investigation was undertaken to determine what effect the salt composition would have on the cation exchange process, which is used to recover

plutonium and americium from the present molten salt residue.

The process used to evaluate the new molten salt residue was the same as that currently used by Chemical Operations to process the 6 mole percent MgCl_2 molten salt residue. The spent salt initially was dissolved in 0.5M hydrochloric acid (HCl) to give a solution concentration of 100 grams molten salt per litre of solution. After dissolution (30 minutes at 90 °C), the solution was filtered to remove any insoluble heel. The filtrate was then passed through a 100-mm (4-in.) diameter by 600-mm (24-in.) high column of Dowex® 50-X8 cation resin at a flow rate of 18 litres per hour. After the cation resin was loaded to capacity, it was water washed (1.5 column volumes) to remove the chloride impurity. The plutonium and americium were then eluted with 7M nitric acid (HNO_3). Approximately three column volumes of 7M HNO_3 were required to remove all of the plutonium and americium. The plutonium was then separated from the americium by a routine anion exchange technique.

Results of the process demonstration runs show the new molten salt is compatible with the existing cation exchange process. Table 15 shows the cation feed composition.

The insoluble heel from the salt dissolution averaged 0.6 gram per 100 grams of molten salt for the four

TABLE 15. Cation feed composition

Element	Concentration (g/l)
Plutonium	18.5
Americium	1.9
Magnesium	6.1
Potassium	12.0
Sodium	6.9
Chlorine	57.2
Hydrogen	0.5M

batches of dissolved salts. The heel composition was 30 wt % plutonium oxide (PuO_2) and 28 wt % americium oxide (AmO_2).

The cation effluent and wash solutions were analyzed for plutonium content [1.1×10^{-3} grams per litre (g/l)] and americium content (4.2×10^{-6} g/l). These solutions were well below the discard limits for both actinides and subsequently were discarded to Waste Treatment. The cation elution was analyzed, and the results are shown in Table 16.

The cation eluate was then passed over a column of Dowex® 1-X4 anion resin to separate the plutonium from the americium. The hexanitrate complex of plutonium quantitatively loaded onto the anion resin with the americium passing through in the effluent. The plutonium subsequently was eluted with 0.35M HNO_3 and was returned to the process stream. Americium was recovered by a separate process. The anion effluent analysis showed a plutonium concentration of 5×10^{-3} g/l and an americium concentration of 1.08 g/l.

Each cation exchange run made with the new salt composition proceeded without incident. The results of each run were comparable to results obtained using the old 6 mole percent molten salt residue. The only difference noted was the cation resin capacity for the new salt. The cation resin capacity for the 30 mole percent MgCl_2 molten salt was 200 g/l; the capacity of 6 mole percent MgCl_2 molten salt was 400 g/l of resin. The 30

mole percent MgCl_2 molten salt, however, contains 10 times the plutonium and americium found in 6 mole percent MgCl_2 molten salts. This amounts to a fivefold increase in the americium and plutonium throughput in the process.

In summary, the 30 mole percent MgCl_2 molten salts can be processed effectively using the cation process presently used for processing the 6 mole percent MgCl_2 molten salt residues.

PLUTONIUM AND AMERICIUM RECOVERY FROM REDUCTION RESIDUES

Stephen G. Proctor and Kay K. Kunert

Metal reduction (MR) residues were generated at Rocky Flats as part of design agency special projects. These residues were comprised of plutonium, americium, calcium, magnesium, and iron. The plutonium and americium concentrations were 8×10^{-3} grams (g) plutonium/g residue and 3×10^{-3} g americium/g residue. These concentrations dictated that recovery efforts be made for both actinides. The method of recovery consisted of initially dissolving the MR residues in nitric acid (HNO_3). This was followed by plutonium adsorption on anion exchange resin; americium recovery was accomplished by a cation exchange process. The combination ion-exchange procedure was used to recover 200 g of plutonium and 76 g of americium from 25 kilograms of MR residues. A 99 percent recovery was realized for plutonium and 96 percent recovery for americium.

The MR residues initially were dissolved in concentrated nitric acid (HNO_3) by boiling for four hours. After dissolution was complete, the resulting solution was filtered to remove any insoluble heel. The filtrate was made 0.05M in sodium nitrite to ensure that the plutonium was in the tetravalent state. The filtrate was then made 7M in HNO_3 in preparation for anion exchange treatment. The adjusted solution subsequently was passed through a 75-mm (3-in.) diameter by 735-mm (30-in.) high column of XE-270 Amberlite® anion resin where the hexanitrate complex of plutonium adsorbed. The noncomplexed americium passed through in

TABLE 16. Cation eluate composition

Element	Concentration (g/l)
Plutonium	11.20
Americium	1.15
Magnesium	0.4
Potassium	2.5
Sodium	1.4
Chlorine	<0.5

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the effluent. The residual americium was washed from the resin with one column volume (CV) of 7M HNO_3 . Elution of the plutonium was achieved by passing 2 to 3 CV of 0.35M HNO_3 through the anion resin bed. The plutonium eluate was then sampled and returned to the process stream. The americium-bearing effluent was next adjusted for cation exchange adsorption.

The acidity of the anion effluent was reduced to 0.4M (H^+) by dilution with water and neutralization with 10M sodium hydroxide (NaOH). The adjusted anion effluent (cation feed) was next loaded on a column of Dowex® 50-X8 (H^+ form) cation resin where the americium quantitatively adsorbed and the bulk of the impurities passed through in the effluent. When the cation resin had been loaded to capacity (determined by an in-line gamma scintillation counter), the plutonium and iron impurities were removed by a 0.1M oxalic acid wash (2 to 3 CV).

The americium was eluted selectively from the cation resin using buffered citric acid (pH 3.5). The americium was then precipitated from the citrate eluate using a routine oxalate precipitation technique. The insoluble americium oxalate was calcined to convert it to americium oxide (AmO_2), which was sampled and stored.

Dissolution of the MR residue was accomplished with only a 50-g discardable heel remaining after dissolution of the entire 25 kilograms (kg) of MR residues. A typical MR residue-dissolution composition is shown in Table 17.

TABLE 17. Residue dissolution composition

Element	Concentration (g/l)
Plutonium	2.1
Americium	0.88
Magnesium	44.6
Calcium	8.9
Iron	1.1

The nitric acid solution from dissolution of the residues was passed over the anion resin where 99.7 percent of the plutonium was adsorbed. All of the americium, magnesium, calcium, and iron passed through with the effluent. A typical anion effluent analysis is shown in Table 18.

The plutonium eluate had an average plutonium concentration of 6.4 grams per litre and showed a 99 percent plutonium recovery. These solutions were returned to the process stream.

From the anion effluents, 99.9 percent of the americium was adsorbed onto the cation resin with only 15 to 20 percent of the magnesium, calcium, and iron adsorbing. The cation effluents averaged only 8.2×10^{-4} g Am per litre of effluent. These solutions were discarded to Waste Treatment. Any adsorbed plutonium and iron were removed

TABLE 18. Anion effluent analysis

Element	Concentration (g/l)
Plutonium	0.026
Americium	0.40
Magnesium	14.9
Calcium	1.6
Iron	0.5

TABLE 19. Americium citrate eluate analysis

Element	Concentration (g/l)
Plutonium	2.1×10^{-4}
Americium	1.25
Magnesium	0.042
Calcium	0.005
Iron	0.0003

TABLE 20. Americium oxide analysis

Element	Concentration (g/l)	Decontamination Factor
Americium	0.855	—
Plutonium	0.000800	50
Magnesium	0.000010	10 ⁶
Calcium	0.000800	5000
Iron	0.000010	10 ⁵

effectively with the oxalic acid wash (99 percent removal). The americium then was selectively eluted with the citric acid, which resulted in the eluate composition shown in Table 19.

Americium oxide from oxalate precipitation of the citrate eluate gave the analysis shown in Table 20. Also shown is the decontamination factor (DF) achieved from the total process. The americium recovery was 96.7 percent for the entire process.

In summary, a total of 25 kg of MR residues have been processed with 99 percent of the plutonium being recovered and returned to the process stream and 96.7 percent of the americium being recovered as AmO₂ of acceptable purity. The process involved three phases of operation: (1) dissolution of MR residues, (2) anion exchange separation of plutonium, and (3) cation exchange recovery and purification of the americium. All three phases worked well with only minimal difficulties being encountered in the MR residue dissolution step.

CHEMISTRY INSTRUMENTATION

D. Ray Cartwright

RADIOMETRIC COUNTERS FOR NEW PLUTONIUM PROCESSING FACILITY

James L. Lawless

Several radiometric systems have been designed for the new plutonium processing facility under con-

struction at Rocky Flats. All of this equipment was purchased under the government furnished classification (GFE). Most of the equipment has been received, tested, and put into storage awaiting contractor installation. The systems include four can counters, molten salt furnace detectors, sodium fluoride trap monitors, an incinerator ash monitor, part decontamination monitors, a grit blasting gamma probe, and americium ion column breakthrough detectors.

Gamma-ray shields required for the can counters, molten salt detectors, and sodium fluoride trap monitors are being fabricated at Rocky Flats and will be ready on demand for contractor installation.

HELIX COUNTER IMPROVEMENTS

*James L. Lawless, Ronald A. Harlan,
and Richard N. Chanda*

The Helix Counter* measures the plutonium content of four-litre packages of process residues. A package placed in the counter has its gamma radiation recorded while being scanned by a detector for 100 seconds. Secondly, an external plutonium-239 radiation source is inserted directly across from the detector and the package is again scanned. The reduction in radiation intensity from the external source is used to measure the package's gamma-absorbing characteristics.

The previous external source was fabricated using 200 grams of plutonium oxide. The gamma-ray flux was insufficient to penetrate highly dense materials and yield statistically precise counts in 100 seconds. It was apparent that a stronger source was desirable. Adding more plutonium to the existing source was not practical because of source self-absorption effects.

The isotope, barium-133, emits gamma rays with nearly the same energies as plutonium, but it has a higher specific activity. The amount of barium

*J. L. Lawless and R. N. Chanda. "A Plutonium Waste Counter." *Trans. Am. Nucl. Soc.* 13:748. (1970).

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required to increase the radiation field by a factor of 10 was calculated to be 10 milligrams. Such a barium source was ordered and adapted for Helix Counter operation.

The Helix Counter response to known standards, utilizing the new barium source, revealed improvements in precision by a factor of 2.5. The computer programs were modified to accept the new source, and that source is now in routine use. Initial results using measurement control standards showed no bias; however, it is known that one category, to be discussed below, is biased because standards cannot duplicate metal lumps in the scrap.

The safeguard calorimeter (see RFP-2360-A, p.4) built at Rocky Flats was used to check results from an independent laboratory prior to the instrument's use in verifying calibrations of Rocky Flats counters. The calorimeters from the two laboratories were in good agreement. The Rocky Flats calorimetry values are considered to be the standard values. The first scrap stream residue category studied was sand, slag, and crucible (residue category MDC 392). Results from the first six samples indicated that the Helix Counter with the new source and with the present correction function may have a small positive bias for this category. More data are being collected before refining constants in the function. Work is in progress to gather more calorimetry data on MDC 392, on other residues, and to refine the counter calibrations.

COMPUTER DEVELOPMENT

James L. Lawless

A continuing effort to improve the operation of the radiometric counters in the plutonium recovery facility at Rocky Flats has resulted in several computer program changes. New discard limits, effective February 1975, reflect a change in the economics of residue or scrap recovery. Further processing information was provided by identifying the process line from which the material originated. Computer messages then inform the operator as to the disposition of the material. Drybox gloves, for

example, are identified as wet or dry, and an appropriate handling procedure is given. Further tightening of control on input data has been provided by programming the computer to accept only specific tare weights; thus, unusual containers for which the system is not calibrated will cause a diagnostic message, and counting will be prohibited.

Necessary equipment has been purchased to permit the Hewlett-Packard computer in the plutonium recovery building to transmit its data through a pair of wires to the IBM 360 computer in the central computing facility. When implemented, this capability will allow for updating nuclear materials control accountability records and the history file several times daily at the discretion of the user. The present procedure has a 24-hour turnaround time.

LITHIUM DRIFTED GERMANIUM DETECTOR ANALYSIS OF ELECTROREFINING SALTS

Richard N. Chanda

As a by-product of electrorefining plutonium metal, salt residues are generated that contain varying amounts of plutonium. Traditionally, these salts have been assigned plutonium values based upon a weight difference; that is, the plutonium in the salt is the difference between plutonium metal weighed into the process and the plutonium weighed out. Such a procedure may indeed be accurate over a large number of samples, but for any given sample the error in plutonium content could be quite large because of mechanical hold-up (or release) in the system.

Sixty-eight electrorefining salt samples were assayed with the lithium drifted germanium detector [Ge(Li)] North Drum Counter, and plutonium values were compared with by-difference assignments. As expected, large, individual sample errors were found. For 32 salt samples that assayed ≥ 10 g using the Ge(Li) system, the average difference per sample was 72 percent. Totals for the same 32 samples and the entire 68 samples, however, differed by only 3.3 and 5 percent

respectively, which is well within the limit of error of the Ge(Li) system calibration. A precise determination of the difference between the two methods must await a better calibration of the Ge(Li) system using NDA (Non-Destructive Analysis) standards. These standards are currently being prepared.

Regardless of the absolute difference, salts of this type will be Ge(Li) assayed when the Ge(Li), discussed below, becomes operational.

LITHIUM DRIFTED GERMANIUM DETECTOR PACKAGE COUNTER

Richard N. Chanda and James L. Lawless

A lithium drifted germanium detector [Ge(Li)] equipped counting system is under construction for the assay of four-litre and smaller packages of plutonium-contaminated waste and scrap residues. The hardware construction is nearly complete. This hardware consists of a lead detector shield, detector support, and a turntable and scanning mechanism, all of which will be installed on a four-wheel cart.

Upon receipt of the computer-based multichannel (discussed under the next subject heading), the system will be set up and evaluation will begin. Several modes of operation will be evaluated: (1) segmented scan with transmission source, (2) no scan with matrix correction based upon net weight, and (3) the differential attenuation method now being used in the North Drum Counter. Measurement control standards, in addition to calorimetric residues, will be utilized in the evaluation.

GAMMA-RAY SPECTRA ANALYSES FOR LITHIUM DRIFTED GERMANIUM DETECTOR COUNTERS

James L. Lawless and Richard N. Chanda

A computer-based multichannel analyzer has been purchased for integration with the North Drum

Counter, which is equipped with a lithium drifted germanium [Ge(Li)] detector, and the Ge(Li) Package Counter presently under construction. The new system, to be used by production personnel, will provide rapid analyses of waste and scrap materials and will report data.

The system has the capability of acquiring and analyzing gamma-ray spectra by identifying gamma-ray peaks, determining their energies, and comparing them to known radionuclide libraries. The system then prints a record of the radionuclides found and their concentration.

The system hardware consists of a PDP-11/05 16K Computer, Canberra Model 8100 (4096 Channel) Multichannel Analyzer, a 1.2-million-word disc, a Digital-Cassette System, and a Dec Writer. The system software utilizes the "Class" Interpretative Language for user-written programs to control disc access and multichannel analyzer control. Spectrum stripping and peak identification routines are written in Assembly Language. The system is relatively fast, requiring only a few minutes to analyze a 4096 channel spectrum.

A software package will be written by the Chemistry Instrumentation Group to tailor the system to the specific Rocky Flats problem of analyzing the concentration of uranium, plutonium, and americium in waste drums.

THE MAY THROUGH JUNE 1975 INVENTORY VERIFICATION AND CALIBRATION EXPERIMENT

Ronald A. Harlan and Charles D. Zeis

The Rocky Flats Plant and U.S. Energy Research and Development Administration are cooperating in an experiment with two purposes: (1) verification of plutonium content in five types of contaminated waste and scrap stored in drums for further processing, and (2) refining the calibration

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of Helix and Can Counters for certain materials for which accurately synthesized standards are difficult or impossible to make. The current experiment is larger in scope and goals than earlier verification experiments that led to the development in January, 1975 of a new calibration function (see RFP-2360-A, p.2) for the Helix Counter.

Waste categories represented in the experiment are virgin ash; leached ash heels; graphite scarfings; sand, slag, and crucible; and leached sand, slag, and crucible heels.

Over 110 samples are being calorimetered—some at Rocky Flats and some at an independent laboratory. Results will be compared to inventory values and to recounts of the samples under current counter-operating parameters. The samples must be repackaged and the heels materials must be calcined before shipment.

This effort is being performed by Chemical Operations personnel; planning and data reduction will be performed by Chemistry Instrumentation and the Statistical Laboratory.

WASTE CATEGORY REPORT

James L. Lawless

This is the fourth in a series of reports that documents historical data obtained from radio-metric counters used to determine the plutonium content of waste and scrap containers. This report, which covers the first quarter of calendar year 1975, reduces the data obtained from 8,280 samples.

The report includes the following information for each counting system:

1. Total number of containers counted for each category of waste and scrap
2. Total number of containers counted for all categories

3. Percent occurrence of each category
4. Percentage of containers, in each category, below discard limits
5. Average plutonium content per container of each category
6. Average net weight per container for each category
7. Total number of containers for each category presented as plutonium distribution and net weight distribution.

PROCESS CHEMISTRY CALORIMETER

George P. Minges

The design and fabrication of a 0.75-litre, twin isothermal calorimeter has been completed (Figure 6). The unit will be used by the Process Chemistry Research and Development Group to assay special radioactive materials.

The 0.75-litre calorimeter incorporates the knowledge of materials and techniques gained in building the safeguards 4-litre calorimeter described earlier

FIGURE 6. The 0.75-litre, twin isothermal calorimeter

19496-4

(see RFP-2360-A, p.4). One additional feature of the 0.75-litre calorimeter is a pneumatic load and unload system. When loading or unloading, the sample container becomes the piston, and the calorimeter becomes the cylinder of a low-pressure pneumatic lift. This system will allow an operator to load and unload the calorimeter without reaching into the instrument. The system will be evaluated on this calorimeter for possible use on future calorimeters installed in dryboxes.

Performance testing, calibration, and evaluation of the unit will now begin, and beneficial use of the calorimeter is expected in early July 1975.

MONILLE: A LOW-LEVEL RADIOMETRIC EFFLUENT MONITOR

Ronald A. Harlan

The first of three planned monitors for low level effluents (MONILLE) was installed at Rocky Flats preaeration facility. A brief description of the monitor was reported earlier (see RFP-2360-A, p.8). MONILLE will continuously check the sanitary sewage upstream from the sewage plant for inadvertent release of radioactive material. MONILLE was designed for plutonium and americium, but will

also exhibit excellent sensitivity for small fractions of permissible concentrations for nearly all gamma-ray emitting radionuclides.

The low-energy detector for MONILLE was tested on prepared solutions of ^{239}Pu and ^{241}Am . Results are shown in Table 21 where the minimum detectable amounts (sensitivities) are given for a 300-second count at a confidence level of 99.8 percent. Note that MONILLE's sensitivity for ^{239}Pu is equal to maximum permissible concentration (MPC) for release to an uncontrolled population, and its sensitivity to ^{241}Am is about $\frac{1}{26}$ of the MPC.

Table 22 compares MONILLE's sensitivity with two other low-level monitors.*† Data for the three monitors were adjusted by the square root of the counting time to enable direct comparison of sensitivities. The ratios in Table 22 are chosen such that MONILLE results are in the denominator. A ratio of 1.0 indicates equivalent performance, and larger ratios indicate the factor by which MONILLE is more sensitive.

*J. L. Cate and T. L. Hoeger. A Radioisotope Monitoring System for Sewage Effluents. UCRL-73299-Rev. 1. Lawrence Livermore Laboratory, Livermore, California. 1972.

†C. J. Umbarger. "Demonstration of the SAFE Effluent Monitor at K-25." Nuclear Analysis Research and Development Progress Report. LA-4994-PR. Page 12. Los Alamos Scientific Laboratory, Los Alamos, New Mexico. 1972.

TABLE 21. MONILLE sensitivities for ^{239}Pu and ^{241}Am

Nuclide	Sensitivity at 99.8% Confidence Level ($\mu\text{Ci/ml}$)		Count Rate (cpm/MPC _w) ^a	
	10 to 100 keV window	10 to 25 keV window	10 to 100 keV window	10 to 25 keV window
^{239}Pu	2.1×10^{-6}	1.7×10^{-6}	4.4	3.9
^{241}Am	6.5×10^{-8}	1.2×10^{-7}	172.8	57
Background	NA ^b	NA ^b	16.8 ^c	8.33 ^c

a. Counts per minute per maximum permissible concentration in water

b. NA = Not applicable

c. Counts per minute only

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TABLE 22. Comparison of MONILLE with other systems adjusted for analysis time

Isotope	Ratio of Sensitivity Values ^a	
	LLL ^b MONILLE	SAFE ^c MONILLE
²³⁹ Pu	1.8	1.0
²⁴¹ Am	1.2	2.0

- a. Ratio of sensitivity equal to 1 means equal performance. Ratios greater than 1 mean MONILLE is more sensitive.
- b. J. L. Cate and T. L. Hoeger. A Radioisotope Monitoring System for Sewage Effluent. UCRL-73299-Rev. 1. Lawrence Livermore Laboratory, Livermore, California. 1972.
- c. C. J. Umbarger. Demonstration of the SAFE Effluent-Monitor at K-25. Nuclear Analysis Research and Development Progress Report. LA-4994-PR, p.12. Los Alamos Scientific Laboratory, Los Alamos, New Mexico. 1972.

STACK MONITORING OF POWER-PLANT COMBUSTION GASES

L. Harry Faber and Charles M. Johnson

The new boiler at the power plant has been connected to the Envirostation® Monitoring system. This completes the sampling network for all boiler stacks for oxides of nitrogen (NO_x) and sulfur dioxide (SO₂).

The dual recorder for presenting NO_x and SO₂ data from the Envirostation® is mounted on a boiler control panel located in the control room. As the data are difficult to interpret, a data acquisition system is being proposed that will gather complete stack data from each stack exhaust, present real-time information of the condition of each stack, and compile necessary periodic reports.

CLASSIFIED-WASTE INCINERATOR SMOKE MONITOR

L. Harry Faber and Charles M. Johnson

An instrument system has been installed on the classified-waste incinerator to provide a continuous

measurement of smoke emissions. This system assists operators of the incinerator to keep smoke density below the State of Colorado Regulations of 20 percent opacity and to provide a permanent record of emission levels.

The instrument system incorporates a smoke-opacity monitor, a readout and alarm unit, and an air-purge unit manufactured by Lear Siegler Company of Englewood, Colorado.

The electro-optical units of the smoke monitor can be seen mounted on both sides of the incinerator stack (Figure 7). The air purge for protection of the optics is mounted between the units. If the air purges fails, safety shutters mounted between the optics and the stack ports will close, thus protecting the instruments from any stack-gas contamination.

The electrical cabinet's location enables the incinerator operator to observe the meter while feeding the incinerator. As a result, the operator can anticipate the amount of waste material to be fed into the fire, thus controlling smoke emission.

FIGURE 7. Classified-waste incinerator stack monitor

19495-6

MOBILE AMBIENT-AIR MONITORING SYSTEM

Charles M. Johnson and L. Harry Faber

Concern over air pollution and resultant state and federal regulations make it increasingly important to know Rocky Flats' contribution of pollutants, if any, to the atmosphere. There are over 100 identifiable buildings at Rocky Flats and over 1000 roof penetrations that can be sources of pollutants; consequently, it is almost impossible to instrument every potential pollution emitter. Only the major roof penetrations or stacks are planned for such instrumentation.

An alternative approach to the problem was taken about three years ago when plans were made to acquire a mobile van. This van was to contain sufficient instrumentation to monitor air pollutants. The mobile van would enable Rocky Flats to determine the extent and the direction pollutants were coming from off-site. It would also permit a determination as to whether Rocky Flats was contributing to the particular pollution episode. An additional benefit to be derived because of the plant's location with respect to Denver would be the possibility of the van serving as an early warning system for the Denver area during an air-pollution alert.

The mobile, ambient-air monitoring facility has been placed into operation. It is contained in an 8.25-metre Travco Van (Figure 8). The aluminum platform on top supports a meteorological tower, a high-volume air sampler, and two sample intakes. The analysis instrumentation includes a Beckman Model 6800 Air Quality Chromatograph that measures carbon monoxide, methane, and total hydrocarbons (Figure 9); a Beckman Model 952 Chemiluminescent Analyzer for nitrogen oxide and nitrogen dioxide; a Beckman Model 950 Chemiluminescent Ozone Analyzer; and a Beckman Model 906A Sulfur Dioxide Analyzer. The latter three instruments are on a common panel that includes a Monitor Labs Model 8500 standardization unit and a status panel. Meteorological parameters are determined by a Weather Measure Corp. wind speed and direction indicator and by a Beckman humidity and temperature indicator.

A view of the instrumentation panel is shown in Figure 10.

All necessary utilities such as compressed air and hydrogen are supplied by equipment located in the van. Power for the equipment can be supplied by a temporary hookup to power lines or by connection to a 20-kW generator (Figure 11).

FIGURE 8. Mobile ambient air monitoring facility

19494-2

FIGURE 9. Air quality chromatograph in the van

19494-11

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FIGURE 10. Instrument panel in the van

19494-8

FIGURE 11. The 20kW generator that powers equipment in the van

19494-1

PORTABLE BREATHING-AIR QUALITY MONITOR

L. Harry Faber

Certain conditions at Rocky Flats require personnel to work in supplied air suits. Under some circumstances, breathing air is furnished by portable breathing-quality air compressors. As a matter of good safety practices for the protection of personnel, the air being used should be monitored constantly for purity. There are also Occupational Safety and Health Administration (OSHA) regulations in existence that are concerned with breathing air quality.* Instruments and controls have been assembled into a unit called "Sentry" for continuous in-line monitoring of breathing air (Figure 12). A feature of the Sentry is portability to permit ease of location at the sites of the various portable breathing-air compressors.

The Sentry analyzes the oxygen by a paramagnetic cell and the carbon monoxide by an electrochemical cell. Both analyzers are provided with appropriate alarms. The Sentry is connected in-line with a reinforced plastic hose between the breathing-air compressor outlet and the supplied-air distribution cart. The air flows through the Sentry, makes a loop through the piping in the cabinet, and is sampled and analyzed. The air enters and exits the piping through special quick-disconnect couplings that have been dedicated to the breathing-air system only. The couplings cannot be interconnected to any other type of air supply.

There will be uninterrupted flow of air through the Sentry providing the analyses are within the limits of the set points of the analyzers' relay meters. When the limits are exceeded or when power fails, a solenoid valve in the main air line will close, thus stopping the air flow. A horn and light will activate at that time. This directs personnel attending the supplied-air operation to take predetermined emergency measures.

Two of the Sentry systems have been constructed at this time.

*Federal Register. Occupational Safety and Health Administration, Vol. 36, No. 105, Part II, Paragraph 1910.134. May 20, 1971.

18317-2

FIGURE 12. Portable breathing-air quality Sentry

BREATHING-AIR COMPRESSOR SITE SELECTION

L. Harry Faber and Charles M. Johnson

A study has been made for the presence of carbon monoxide (CO) in outside air at a building location selected for a new breathing-air compressor system. Because of the proximity of the proposed air intake to a parking lot and a roadway, it was necessary to determine whether the air intake location would have unacceptable levels of CO. According to Occupational Safety and Health Administration (OSHA) regulations, any amount of CO over 20

ppm is unacceptable for air supplied as respiratory protection.*

A monitoring system was designed to simultaneously analyze and record CO (at levels of 0 to 100 ppm), wind direction, wind speed, and ambient temperature. The direction of the ambient air movement was critical to ascertain whether any CO would come from the local traffic patterns, special equipment, or the Metro-Denver air system.

Instruments used for the study were an ECOLYZER®, which is an electro-chemical type sensor for CO analyses, and an MRI Mechanical Weather Station. Both instruments had associated recorders. The weather station was placed on the roof of the building; the sample inlet for the CO analyzer was placed on the exterior of the building wall at the proposed compressor inlet area.

The monitoring equipment was operated for a period of three months during which time five instances of CO levels greater than 20 ppm were recorded. All were attributed to air pollution coming from Denver. Many low-level CO spikes were observed that came from automobile exhausts during plant shift changes.

As a result of the study, it was concluded that the location chosen for the breathing-air compressor intake was acceptable, and that the influence from the Metro-Denver area could not be avoided no matter where the intake was placed. Precautionary measures should be taken, however, to prevent automobiles, with motors idling, from parking in the immediate vicinity of the intake.

CONTROL INSTRUMENTATION FOR THE EXPERIMENTAL LIQUID-WASTE RECYCLE PLANT

David E. Hausburg

Investigation of the reverse osmosis process to permit recycling liquid-waste effluents at Rocky

*Federal Register. Occupational Safety and Health Administration, Vol. 36, No. 105, Part II, Paragraph 1910.134. May 20, 1971.

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19479-4

FIGURE 13. Allen-Bradley programmable logic controller

Flats has continued. This investigation is the responsibility of other Research and Ecology groups; however, control instrumentation for the process is the responsibility of the Chemistry Instrumentation group.

It was reported previously (RFP-2360-A, p.12) that an electrodialyzer unit would be investigated

for concentrating the brine produced by a hollow-fiber, reverse osmosis unit. That approach was later discarded. Being considered now is a spiral-wound, reverse osmosis unit to process the brine from a hollow-fiber unit.

Preliminary tests showed that the hollow-fiber unit requires continuous control whereas the spiral-wound unit, at least for the pilot plant experimental installation, requires batch control. To perform these control functions, an Allen-Bradley programmable logic controller (PLC) was installed (see Figure 13) and has successfully controlled the two reverse osmosis units. The present PLC system has a 4K memory, which is expandable to 8K, and uses 52 input/output terminals with expansion capabilities up to 512 terminals.

Evaluation of the PLC will continue. The ultimate objective is control of the future, permanent, liquid-waste recycle facility. It is believed that the PLC offers the best features of both the hard-wired system and the computer-control system.

COOLING-TOWER WATER ANALYSIS INSTRUMENTATION

David E. Hausburg

Rocky Flats' aqueous effluent restrictions in the near future will require recycling of all plant wastewater. Excessive or unnecessary wasting of cooling-tower water to the proposed, wastewater recycle facility would increase the recycle load. To conserve water and electrical power, automatic blowdown of the cooling-tower water and the permitting of higher levels of total dissolved solids are now in effect. In addition, pH control of the water is required to prevent deterioration of cooling-tower structures.

Previous attempts to use instrumentation in cooling-tower water generally have been unsuccessful because silt suspended in the water has caused a high incidence of sensor failure with a related, high maintenance need. A recently developed, electrodeless, total-dissolved-solids

analyzer (Figure 14) by Balsbaugh Company has been installed in a cooling tower sump pit and has been evaluated. The electrodeless analyzer uses two toroidal transformers encased in epoxy as a sensor, and the analyzer has been found to be unaffected by silt coating.

In addition to the total-dissolved-solids analyzer, a pH analyzer with an antimony-type sensor has been installed in the sump pit. The purpose of this installation is to evaluate the instrument's reliability.

FIGURE 14. Cooling tower instrumentation panel
19386-1

At present, automatic blowdown of the cooling-tower water is controlled by a seven-day timer. After the reliability of the total-dissolved-solids analyzer has been proven, automatic blowdown will be on a demand rather than timed basis.

PILOT PLANT DEPARTMENT

Donald L. Ziegler

FLUIDIZED BED INCINERATION OF RADIOACTIVE WASTE

Donald L. Ziegler

A project has been initiated to provide a demonstration plant for combustion of radioactive waste using the Rocky Flats fluidized bed incineration process. The demonstration plant is being designed for a capacity of 82 kilogram per hour. The primary objectives of this project are to demonstrate the adaptability of the fluid bed process for combustion of a wide variety of waste materials and to prove scale-up information developed on the pilot plant equipment.

The demonstration plant will be installed in an existing building (Bldg. 776) at the Rocky Flats plant. A heat and material balance for the process has been completed, and engineering design has been initiated. Design is expected to be about 30 percent complete by July 1, 1975. Engineering should be essentially complete and construction work is to be started about October 1975. Some materials and supplies are being purchased during FY '75; delivery of purchased equipment and fabrication of process vessels are expected to be complete by October 1976. The plant should be installed and preliminary testing should be initiated about February 1977. Testing with low specific activity (LSA) waste should begin in June or July 1977.

The process used in the demonstration plant will depart from that of the pilot plant in several areas.

FIGURE 15. Flow diagram for fluid bed incinerator

A high-temperature, heat-transfer fluid, for example, will be used to extract heat from the fluidized bed afterburner. This has the effect of reducing the required size of the afterburner and associated off-gas cleaning equipment. A water-cooled heat exchanger will be used to reduce the off-gas temperature to about 50 °C (122 °F). On the pilot unit, air was blended with flue gas to lower the temperature prior to high efficiency particulate air (HEPA) filtration. A blower will be used instead of an air-jet ejector to provide process vacuum.

A schematic flow diagram of a demonstration plant is presented in Figure 15.

A minicomputer will be installed for data acquisition and process computations for the incinerator. This unit will be interfaced directly with the process equipment; the calculated information will be displayed on a CRT unit and will be used for process control. It is not intended at this time to use direct computer control of the process.

FIGURE 15. continued

FLUID BED INCINERATION

Andrew J. Johnson

The pilot plant incinerator has been put into operation for the combustion of both liquid and solid waste. Liquid waste has consisted of contaminated paint thinner (used) and associated solvents along with obsolete or surplus laboratory hydrocarbon-type chemicals. Solids were general, low-specific-activity waste, mostly paper and

plastic film materials. Minor modifications have been made as dictated by operational problems.

Liquid-Waste Incineration

The pilot plant fluid bed incinerator (see RFP-2360-A, p.28) was used for week-long, continuous operation runs to determine optimum conditions for liquid-waste burning. Liquid wastes are stored in specially constructed drums that can be

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connected, when desired, into the feed system. From the drum, the liquid is pumped into 30-litre pencil tanks mounted outside of the incinerator area. Either of the two tanks can be selected for feed into the incinerator by switches on the control panel. A nitrogen pad is used during all liquid transfers to prevent the accumulation of explosive vapor mixtures in the vessels.

A fluidized bed of chromic oxide oxidation catalyst is used in the primary reactor for burning non-halogenated hydrocarbons. Liquids are metered into the bed by a pulse-type pump; the rate is adjusted to give an afterburner bed temperature of 600 to 625 °C (1100 to 1150 °F) during operation. A mixed fluidizing gas of air and nitrogen is used, and the ratio is adjusted to provide the desired operating temperature in the primary reactor. The exit gases flow into the catalytic afterburner where they mix with additional air and are totally burned. After passage through a cyclone, the off-gas is filtered through sintered metal filters. The off-gas is then blended with canyon ventilation air to lower the temperature prior to HEPA filtration.

The feed rate is governed by average heat content of the liquid waste. A rate of about 10 litres per hour or 2.6 gal/hr has been maintained for some waste, with the average around 8 litres per hour during a week's run. On a test run with kerosene, the heat capacity was found to be 2.5×10^5 kilojoule per hour (kJ/hr) or 2.4×10^5 btu/hr for the total system. Some of this heat is removed by circulating cooling water in coils wrapped around the catalytic afterburner; the remaining heat of combustion is removed by the sensible heat of the off-gas stream. The addition of canyon ventilation air to the incinerator off-gas, before HEPA filtration, finally cools the plenum air to less than 42 °C (110 °F).

Solid-Waste Incineration

Solid-waste processing equipment has operated well after initial adjustments and minor modifications. Drum lift, drum box entry, and waste shredders perform well; the agitator on the screw-feed hopper has undergone design changes and now should prevent bridging and should fill the screw conveyor adequately. Waste bags were found to

contain considerable metal, but this was expected. A large sorting box provides space to inspect the waste-bag contents before shredding and to remove most of the metal objects. The metal that goes through the shredder has posed no problem for the feed screw. At the conclusion of one test run in which 153 kilograms (337 pounds) of waste was burned, the final primary bed contained 1.2 to 1.5 kilograms (2.6 to 3.3 pounds) of tramp metal.

Solid-waste incineration differs from liquid-waste burning in that sodium carbonate is used in the primary bed instead of a catalyst. This is to neutralize the acid gases given off, which chiefly originates from halogen-containing plastics. The fly ash, sodium carbonate, and sodium chloride from the primary bed is removed by a cyclone from the flue gas before entry into the catalytic afterburner. Some difficulty was encountered with this dust because of its packing characteristics in the cyclone drain. A minor correction in the drain should alleviate this difficulty.

The dust discharge box operates well in keeping fine cyclone and filter dust contained during transfers. Vacuum-controlled transfer lines in this box and the primary bed box permit the afterburner bed and the primary bed to be dumped into the boxes and also to be reloaded from the boxes. The same lines are used also for replenishing the beds during operation.

Test runs have been made at a feed rate of 8.5 kilogram per hour (18.7 pounds per hour) while maintaining a temperature of 550 °C (1020 °F) in the primary and 600 °C (1110 °F) in the afterburner. Two different mesh sizes of catalyst have been used in the afterburner; a 16 to 32 mesh (Tyler) size was selected as preferable. The sintered metal filters performed well and have kept the second-stage HEPA filters clean.

Off-Gas Analysis

Three in-line analyzers sample the system off-gases for contained hydrochloric acid, hydrocarbons, and carbon monoxide. A sample of gas from the primary cyclone is bubbled through a water solution, and the chloride is measured with a specific

ion electrode. Total hydrocarbons and carbon monoxide are measured in exit gases from the afterburner. Unburned hydrocarbons and carbon monoxide in the exit gas have been below 210 ppm after operational conditions are attained. Hydrochloric acid content of the system's exit gas has been held below 20 milligrams per cubic metre; this is the lower detection limit of the analyzer.

Construction

Construction on dust-containment boxes and major process equipment is essentially complete. Service piping, platforms, instrumentation, and electrical requirements are approximately 70 percent complete.

GRAPHITE COMBUSTION

*Alton R. Teter, Larry L. Martella,
and Carl J. Smith*

Contaminated waste-graphite is generated at Rocky Flats from plutonium processing operations. It is necessary to burn the graphite to obtain plutonium dioxide and other inert materials for further recovery processes. Preliminary tests, using a small-scale rotary incinerator, revealed approximately 40 percent of the graphite remained unburned at operating temperatures as high as 1000 °C (1832 °F) and with a retention time of one and one-half hours.

Plutonium oxide formed at a temperature above 1000 °C (1832 °F) becomes increasingly difficult to dissolve. A small-scale, stack-kiln type of unit was constructed to evaluate burning scrap graphite. Preliminary tests were made with noncontaminated graphite.

Design and Operation

A stack-kiln type incinerator (Figure 16) was fabricated for burning the graphite. This incinerator incorporates a resistance furnace to ignite the graphite. The operating temperature is measured by thermocouples located near the top and bottom

FIGURE 16. Graphite incinerator

of the graphite bed. After the graphite attains a temperature of 980 °C (1796 °F), the resistance furnace is lowered from the bed. The combustion rate is controlled by adjusting the air flow. A heat-exchanger jacket is installed in place of the furnace to rapidly remove heat and to increase the burning rate without increasing the burning temperature. The fine graphite passes slowly through a 254-millimetre [(mm) (10-in.)] layer of alumina balls to complete burning. The ash produced falls by gravity through the grate to the holding chamber.

TABLE 23. Burning investigations completed with graphite incinerator*

	Combustion Air (m ³ /hr)	Bed Temperature (°C)		Burning Rate (kg/m ² · hr ⁻¹)
		Bottom	Top	
Furnace in place, not operating	2.26	980	710	11.0
Furnace lowered	2.04	973	707	15.0
Heat exchanger used	2.69	988	716	18.5
Heat exchanger used, two burning beds				
Top bed	3.11	965	—	34.8**
Bottom bed	2.55	930	—	

*Each result is an average of four runs

**Applies to the combined beds

The incinerator uses a stationary burning bed of 6 to 13 mm (0.25 to 0.5 in.) graphite. Tests indicated that the burning bed must be maintained at a minimum height of 100 mm (4 in.) to produce a uniform burning rate. Table 23 lists results for the various burning studies conducted. Based on the reactor's cross-sectional area, the studies demonstrated that the graphite's burning rate was 11 kg/m² · hr⁻¹ (2.32 lb/ft² · hr⁻¹) with the furnace left in place (not operating). When the furnace was lowered, the burning rate was increased by 37 percent. Employing the heat-exchanger jacket, in place of the furnace, with an air flow of 0.04719 m³/s (100 ft³/min), the rate was increased by 68.5 percent.

A second air-metering system was installed to burn two layers of graphite at a temperature below 1000 °C (1832 °F). This was accomplished by fabricating a stainless steel tube containing a series of air holes and installing it 100 mm (4 in.) above the base of the combustion chamber. The graphite is fed into the layers from the top of the stack. Tests using the heat exchanger proved that the burning rates could be doubled with the initiation of this method.

PROCESS CHEMISTRY

Edward D. Erickson

TILT-POUR FURNACE

*James B. Knighton, Robert G. Auge,
James W. Berry, and Richard C. Franchini*

The induction-heated, tilt-pour furnace described in a previous semiannual report (RFP-2360-A) has undergone startup. This furnace is a prototype of furnaces to be installed in the new Chemical Processing Building (Building 371), and it is especially designed for production operations in molten-salt extraction and plutonium electrorefining. Extensive molten-salt extraction tests have been made in the furnace, and the furnace met the design requirements of two batches per eight-hour shift. Preparations are being made to start plutonium electrorefining experiments in July 1975. For this purpose, a tungsten crucible has been installed that will serve as the cathode in the electrorefining process.

MOLTEN SALT EXTRACTION

*James B. Knighton, Robert G. Auge,
and James W. Berry*

Americium is separated from plutonium metal by extraction into a molten salt. The selection of optimum extraction conditions was described in the previous semiannual report (RFP-2360-A). With optimum extraction conditions, the amount of salt is decreased by an order of magnitude. To obtain this decrease, the magnesium chloride (MgCl_2) content of the salt is increased from 5.7 to 30 mole percent MgCl_2 .

Since the last semiannual report, recovery processes have been developed for the 30 mole percent MgCl_2 salt. A production demonstration was made to confirm the selected, optimum extraction conditions and to provide feed for the new, salt-recovery processes. Collection of extraction data ended after 27 plutonium buttons were processed. Use of the new salt has continued since the production demonstration ended.

Results of the production demonstration and subsequent production use of the new (30 mole percent MgCl_2) salt are summarized:

1. The desired 90 percent americium removal was obtained.
2. Because of a higher than usual americium content in the plutonium metal feed, an americium removal of greater than 90 percent was required to lower the americium content to the specified level of 200 ppm. This increased removal was obtained by a slight increase in the salt-to-metal weight ratio used in the extraction.
3. Because of the smaller amount of salt, operation of the process is simplified. The salt and metal are removed easily from the crucible. The crucibles take less physical abuse during production breakout, and radiation exposure to the operators is decreased because less hand-in-glove time is required.

Advantages expected from use of the 30 mole MgCl_2 salt are:

1. The americium and plutonium contents in the extraction salt is increased by an order of magnitude.
2. The amount of salt fed to the extraction is decreased by an order of magnitude, which in turn decreases the amount of salt fed to subsequent aqueous salt recovery process. The amount of salt also decreases the amount of process waste ultimately sent off-site to long-term storage.

PROCESS ENGINEERING

Edward D. Erickson

AMERICIUM RECOVERY FROM MOLTEN-SALT RESIDUES

Clyde C. Perry

The process for separating americium from plutonium-recovery waste streams was developed by Ryan and Pringle* in 1960. No basic changes were made in this americium recovery scheme until 1974. At that time, Proctor's work** resulted in hydroxide precipitation for chloride removal being replaced by a cation exchange process. A second major change was initiated in May 1975 when the tedious, ion-exchange purification steps were replaced with a double oxalate-precipitation process.

In 1969, a molten-salt extraction process was developed to separate americium from molten plutonium.† These molten-salt residues became the only significant feed material for the americium recovery process. The residues do not contain any significant rare earth elements or aluminum.

*V. A. Ryan and J. W. Pringle. Preparation of Pure Americium. RFP-120. The Dow Chemical Company, Rocky Flats Division, Golden, Colorado. January 8, 1960.

**S. G. Proctor. Cation Exchange Process for Molten Salt Residues. RFP-2347. Dow Chemical U.S.A., Rocky Flats Division, Golden, Colorado. March 10, 1975.

†J. L. Long and C. C. Perry. "The Molten Salt Extraction of Americium from Plutonium Metal." *Symposium on Reprocessing of Nuclear Fuels* 15:385-402. The Metallurgical Society of AIME. August 1969.

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The double oxalate-purification process has eliminated unnecessary process operations that were designed to separate impurities. An example of these impurities is rare earth elements that are no longer present.

Americium-rich, anion-column, nitric acid wash solutions from the molten-salt recovery process are used as feed for americium recovery and purification. A simplified process scheme was put into operation in May 1975. The process consists of the following operations:

1. Evaporation of anion column wash solutions.
2. Acid normality adjustment (water dilution) to 0.5M H^+ .
3. Oxalate precipitation.
4. Calcination of the oxalate precipitate at 600 °C.
5. Dissolution of the oxalate precipitate in 12M HNO_3 .
6. Acid normality adjustment (water dilution) to 0.5M H^+ .
7. Oxalate precipitation.
8. Calcination at 600 °C.

The entire process is carried through in a nitrate system that reduces corrosion to the glove box and equipment.

A final plutonium decontamination is accomplished without adding a reductant to the precipitator feed. Approximately two-thirds of the residual plutonium found in the first oxalate precipitate is discarded in the second oxalate filtrate. This results from high solubility of the quadrivalent plutonium oxalate. An optional process step that can be used to separate lead is adding chloride salts to the dissolution acid. If the feed solutions contain certain rare-earth elements or aluminum, extensive ion-exchange process steps will be required to recover the americium.

A process demonstration of the double oxalate process was completed in May. Ninety-seven grams of americium as americium oxide was recovered

from 674 litres of feed solution containing 117.84 grams of americium. The purity of the americium product was 98.14 weight percent as americium oxide. Total americium losses to filtrate and distillate streams were 5.78 percent. Assuming that six grams of americium collected in floor wash solutions was recovered, the overall efficiency was 88.03 percent. In addition to product from the demonstration run, 295 grams of americium oxide was produced in May. Complete analysis of this material is not yet available. As a result of the higher efficiency of the new process, approximately two kilograms of americium ultimately will be recovered from the existing backlog of americium-bearing residues. These residues would have been lost to waste streams by use of the old process.

VOLUMETRIC FLOWMETER FOR VACUUM TRANSFER OF SOLUTIONS

*Charles R. Forrey, Thomas C. Johnson,
and Robert L. Smith*

An instrument was developed to provide flow information on vacuum filtration systems. This instrument measures and automatically samples the solution flowing in the system (Figure 17). The volumetric flow-measuring system consists of a four-litre, calibrated vessel with high- and low-level sensing probes. Other components are a control system that operates two three-way valves and an event counter.

The vessel or tank initially has vacuum applied at the top opening; the bottom drain is closed. Solution flows from the filter into the glass tank and is disengaged from the accompanying gases and vapors. When the level in the tank reaches the high-level probe, the control system receives a signal. The system then changes the position of both three-way valves and records an event on the counter. When the valves change position, the tank is vented and vacuum is applied to the drain line. The tank empties in about 10 seconds. When the level drops below the low-level probe, the control system again changes the three-way valves and the cycle is complete.

FIGURE 17. Volumetric flowmeter for vacuum transfer of solutions

Liquid-volume calculation is made by multiplying the volume of the tank by the number of times the tank is emptied. This system shuts off vacuum to the filter during the 10 seconds the tank is emptying; but this does not upset the type of filter used in plutonium recovery operations.

To provide stream-concentration information on the liquid part of the stream, an automatic sampler was installed on the tank drain. Each time the tank is filled, the Isolox® sampler withdraws a three-millilitre sample from the contents. These samples are collected in a bottle from which a small sample is taken periodically for analysis. Using the volumetric-flow information and the concentration, material accountability of the stream can be made.

FUME SCRUBBER OPERATION IMPROVEMENTS

Charles R. Forrey

Plutonium from a wide variety of residues is recovered by dissolution in a hot, nitric acid

(HNO_3), hydrofluoric acid (HF) solution. The corrosive vapors generated are pulled through a caustic fume scrubber by a large Hoffman blower. The blower is cast iron and originally had a Heresite®* coating on the inner surfaces. The fume scrubber is a packed tower with 2N potassium hydroxide (KOH) at 25 °C flowing countercurrent to the corrosive vapors.

Investigation of several blowers that had failed because of holes in the housing revealed the coating had either or both eroded and corroded away, thus exposing the cast iron to the vapors. During upset conditions, nitric acid would condense in the blower and corrode the housing. In a full scale test, it was determined that an uncoated blower failed in 15 days. Since the type of blower required is made in cast iron only, it was apparent that a different coating material was required.

A Ceilcoat Flakeline 242 coating was selected because of its resistance to both HNO_3 and KOH. A heavy coating was applied to the blower housing, and the blower was placed in service. At the same time, the temperature of KOH in the fume scrubber was reduced by a refrigeration unit to 6 °C to lower the dew point of the scrubbed air. After 10 months of continuous operations, the blower was shut down for inspection. No failures in the coating were detected visually, and no condensation was detected in the entire 10-month period. The blower will be returned to service and should continue to operate without problems for an equivalent period of time. Sample taps will be installed at the box exhaust, before and after the caustic scrubber, and after the Hoffman blower to characterize the vapors and to determine the fume scrubber's efficiency.

ANION EXCHANGE COLUMN PLUGGING

James D. Navratil and Robert Southworth

Anion exchange is a unit operation used at Rocky Flats for purification of plutonium nitrate

*Trademark of Heresite Chemical Co., Manitowoc, Wisconsin 54221

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solutions. This process consists of sorption of plutonium onto a static bed of Dowex® 1-X4* 0.30- to 0.15-mm (50 to 100 mesh) resin from a 7N nitric acid (HNO_3) solution followed by desorption with a 0.35N HNO_3 solution.

This process is troubled periodically by plugging of the resin bed with an accompanying reduction of solution throughput rate. In one such instance in the past, plugging was caused by precipitation of silica dioxide (SiO_2) arising from excess aluminum nitrate $\text{Al}(\text{NO}_3)_3$ being added during feed preparation.

Plugging has recently been caused by incomplete filtration of feed solutions despite filtration through a polypropylene-felt roughing filter, two 3-micrometre (μm) cartridge filters, and a final 1- μm cartridge filter. Particulate concentrations in the feed solutions have ranged as high as 0.8 gram per litre (g/l). Although the particulate material proved to be primarily SiO_2 , the material is believed to have originated from inadequate filtration of feed solutions rather than from precipitation.

Three measures were taken to alleviate the plugging problem. First, the resin beds were flushed with a

0.1N HF, 0.35N HNO_3 solution. This dissolved the silica particles and increased flow through the column; however, this was only temporary, and particulate matter in the feed again plugged the column. It was necessary to repeat the flushing treatment at one-week intervals.

The second measure taken to alleviate the plugging problem involved the addition of 1 milligram per litre (mg/l) of Separan® NP-10* to the feed solution prior to filtration. Separan is a polyacrylamide flocculating agent. It flocculated the particulate matter such that the particulate matter was less than 0.1 g/l, instead of 0.8 g/l, after passing through the filters.

The third measure taken to alleviate plugging was to replace the 0.15- to 0.3-mm (50 to 100 mesh) resin with larger 0.84- to 0.30-mm (20 to 50 mesh) resin. This will make it less likely that particulate material will become entrapped in the column.

These measures have resulted in reducing the particulate load to the resin bed in addition to facilitating the movement of the particles through the bed once the particulates get there. The overall result is that the throughput of the column has returned to normal.

*Product of the Dow Chemical Company, Midland, Michigan

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