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RESEARCH AND ECOLOGY
SEMIANNUAL PROGRESS REPORT
JULY THROUGH DECEMBER 1972

CHEMISTRY RESEARCH AND DEVELOPMENT

*William C. Bright
Dana R. Cartwright
Jerry D. Moseley
Edward Vejvoda*

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DOW CHEMICAL U.S.A.
ROCKY FLATS DIVISION
P. O. BOX 888
GOLDEN, COLORADO 80401

U. S. ATOMIC ENERGY COMMISSION
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*Classified section of this report is contained in RFP-2004.

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Corrosion, Gold, Bomb Trailer,
Radioactive Contamination Containers,
Polyvinyl Chloride, HEPA Filters—
Fire Protection,

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RESEARCH AND ECOLOGY SEMIANNUAL PROGRESS REPORT JULY THROUGH DECEMBER 1972

CHEMISTRY RESEARCH AND DEVELOPMENT

*William C. Bright, Dana R. Cartwright, Jerry D. Moseley,
and Edward Vejvoda*

STAFF

NONAQUEOUS CHEMISTRY

J. M. Cleveland and G. H. Bryan

Research in nonaqueous chemistry has been concentrated in two areas, *viz.*, preparation of new plutonium complexes and compounds, and electrodeposition of plutonium. Special attention has been devoted to the preparation of complexes that cannot be prepared in aqueous solution. By use of propane-1,2-diol carbonate as solvent, certain apparently new complexes have been prepared and their identification and characterization is almost complete. These complexes are of considerable theoretical significance to the inorganic chemist.

Electrodeposition work has been hampered by equipment problems, and the experiments conducted to date have been inconclusive. Experiments in this area are resuming, however, and meaningful results should be forthcoming.

PLUTONIUM BEHAVIOR IN THE SOIL/WATER ENVIRONMENT

F. J. Miner, P. A. Glover, and H. W. Miller

Information on the movement of plutonium in the soil is important because other aspects of the environmental behavior of plutonium—its resuspension into the atmosphere, its uptake by plants, its transfer to underground water supplies—all depend primarily on the movement of plutonium through the soil. Information on this movement is available in the literature but it is minimal and often very qualitative. We have undertaken, therefore, a systematic investigation of one area of this movement involving the adsorption of plutonium by soil in a soil/water environment. The objective of this investigation is to measure the adsorption of plutonium under controlled conditions and determine whether there are chemical and physical characteristics of the soil that can be related to the plutonium adsorption. The work that has been done in the past 6 months is summarized in three categories.

SOURCE OF PLUTONIUM

Two forms of plutonium will be used as plutonium sources in the experimental work. The first is PuO_2 to represent "insoluble" plutonium and the second is plutonium in a nitric acid solution to represent "soluble" plutonium. Plutonium oxide to be used as the "insoluble" plutonium source was prepared by hydriding pure plutonium metal, then converting the hydride to oxide, and separating out the material for use with particle diameters falling between 10 and 0.1μ .¹ The oxide was analyzed for impurities by spark source mass spectrometry. The total impurity concentration was 302 parts per million parts plutonium. The impurities with the highest concentrations are U, 73 ppm; W, 54 ppm; C, 40 ppm; Al, 40 ppm. The lattice parameter for the oxide, as determined by x-ray diffraction, is $5.393 \text{ \AA}$. The theoretical value for PuO_2 is $5.396 \pm 0.001 \text{ \AA}$, indicating that the oxide is essentially stoichiometric PuO_2 .

Distribution coefficient measurements require that relatively small amounts of plutonium (nominally 75,000 d/m, equivalent to approximately $0.5 \mu\text{g Pu}$) be added to each soil sample. It is not feasible to weigh out this small amount of oxide for each run so it is planned to add the oxide as a slurry so a volume of approximately 1 ml will contain the required amount of plutonium. Several methods were attempted to prepare a stable slurry. The method that was found best involved adding 200 times the required amount of PuO_2 to water, letting the mixture set for a day, then centrifuging to settle all particles greater than 10μ (the upper limit of particle size to be used in the experiments). The centrifuging was necessary because particles larger than 10μ were formed, apparently by agglomeration or adsorption of the PuO_2 on other particles in the water.

A nitric acid solution of plutonium for use as a source of "soluble" plutonium was prepared by diluting a standard solution already available. After dilution, the solution contained $1.08 \times 10^{-2} \text{ g Pu/l}$. This is equivalent to approximately 75,000 d/m 50λ , the activity desired for the experimental work. The solution was 0.47N in nitric acid.

SOIL: SELECTING, OBTAINING, AND CHARACTERIZING

The percent organic matter in the soils reported previously¹ was based on an analytical method involving the loss of weight on heating to 500°C. This method is not as exact as desired for it could include inorganic as well as organic carbon and in addition, adsorbed water. Since the interpretation of the interaction of plutonium with these soils might be influenced by the kind of carbon-containing material present, more specific analyses were obtained. They are summarized in Table 1.

Table 1. Carbon Content of Soils.

Source	Sampling Location	Organic Matter (%)	Inorganic Carbon ^a (%)
Hanford	Surface	0.3	0.6
	Underlying	0.1	0.0
Rocky Flats, A	Surface	2.4	0.4
Rocky Flats, B	Surface	3.4	0.3
Rocky Flats, C	Surface	0.7	2.4
Los Alamos	Surface	0.7	0.2
Barnwell	Surface	0.7	0.2
West Valley	Surface	2.7	0.0
Oak Ridge	Surface	1.0	0.0
Idaho Falls, A	Surface	1.0	0.0
	Underlying	0.8	17.2
Idaho Falls, B	Surface	0.3	5.2
	Underlying	0.2	7.9

^aTotal carbonate

SOILS: MEASUREMENT OF PLUTONIUM TRANSPORT

The method to be used in measuring the distribution coefficient of plutonium between soil and water involves equilibrating soil with water containing the required amount of plutonium. After equilibration the soil and water are separated by centrifugation and the water removed and analyzed for plutonium. Distribution coefficients are calculated from these results. In separating the soil and water phases, it is desired to remove all of the "insoluble" plutonium, but leave the "soluble" plutonium in solution. In the initial planning for this work, it was decided that the dividing size between "soluble" and "insoluble" plutonium in solution would be particles with a 0.02 μ diameter. This size was based on work done with polonium

and reported in the literature.² Unfortunately, no reason was given for selecting this particular diameter. Subsequent reading in the literature indicates that other diameters have been used: 0.1 μ for separating "soluble" and "insoluble" aluminum hydroxide³ and 0.45 μ for separating "soluble" and "insoluble" material in water samples. Except for the aluminum hydroxide work, no scientifically valid reasons could be found for selecting a particular diameter to use (e.g., 0.45 μ was apparently selected for water samples because it was the size of the pores in the first filters available with exact pore sizes). Therefore, preliminary distribution coefficients were determined, varying centrifugation speeds and times to separate out particles with sizes less than 0.02 μ , less than 0.1 μ , and less than 0.5 μ . The results are summarized in Table 2. The data show the expected increase in "soluble" plutonium in the water phase with the increase in particle size of the material remaining in solution. Since there is apparently no commanding reason requiring the use of one particle size over another, 0.1 μ was selected for subsequent experimental work because the solution contains sufficient activity to give good counting data in a reasonable period of time.

Table 2. Effect of Particle Size on the Activity of Plutonium in the Aqueous Phase.

Particle Size ^a	Pu Source — Pu in HNO ₃	
	Soil ^b	Mean Pu Activity in the Water Phase d/m ml
0.02 μ	SC	86
	RF-C	64
0.1 μ	SC	128
	RF-C	89
0.5 μ	SC	245
	RF-C	175

^aCentrifuge operated so that all particles less than this diameter are precipitated.

^bSC = soil from Barnwell, South Carolina.

RF-C = soil from Rocky Flats near Pond 1.

Experiments are being run to determine how much time is required to attain an equilibrium distribution value of plutonium between the water and soil phases. This information is necessary to determine how long to equilibrate the samples prior to analysis. South Carolina and Rocky Flats soils are being used for these experiments because these soils have quite different physical and chemical characteristics and will hopefully represent the behavior of the rest of the soils. The soil, water, and plutonium are put in centrifuge cones, stoppered, rotated for the required time interval on a Tube Rotator, then centrifuged and a sample aliquant of the water phase removed for plutonium analysis. Four samples are run for each soil at each time interval. The

results are summarized in Table 3. The data indicate that a constant activity value is attained in 180 minutes (3 hours) for the Rocky Flats soil but that after 1440 minutes (24 hours) a constant value has not been attained for the South Carolina soil. This equilibrium work will continue to determine how long is required for the South Carolina soil to attain equilibrium. Then, the equilibrium distribution values will be determined for the remainder of the soils.

Table 3. Effect of Equilibration Time on Plutonium Adsorption.

Equilibration Time Min.	Pu Source — Pu in HNO ₃	
	Mean Pu Activity for Each Soil ^a d/m ml	
	RF-C	SC
10	82	142
60	22	108
180	12	80
300	12	57
420	9	46
960	11	24
1440	—	15

^aSC = soil from Barnwell, South Carolina.

RF-C = soil from Rocky Flats near Pond 1.

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SOLUTION CALORIMETRY

J. D. Navratil and F. L. Oetting

To better understand the capabilities of our LKB reaction calorimeter, and also to become fully aware of its limitations, further measurements of the standard reaction of TRIS [Tris(hydroxymethyl) aminomethane] with 0.1N HCl at 25°C were performed. Our best enthalpy value for the TRIS-HCl reaction, $-7109 \pm 5 \text{ cal} \cdot \text{mol}^{-1}$, is in satisfactory agreement with other reported high precision results.¹⁻⁴

Further enthalpy measurements were performed on the reaction of beryllium in chemical milling solution (750 ml/l H₃PO₄, 31 ml/l H₂SO₄, and 71 g/l CrO₃), as it is necessary to know the heat of this reaction in the design of cooling coils for the production milling process. The final enthalpy value of $-119.8 \pm 6.8 \text{ kcal} \cdot \text{mol}^{-1}$ was determined at 25.0°C. The erratic results, shown by the comparatively high error limit, were attributed to unknown side reactions. The enthalpy of $-107.3 \pm 1.3 \text{ kcal} \cdot \text{mol}^{-1}$ for a used chemical milling solution containing ~5 g/l Be was measured at 25°C and is significantly different than the enthalpy of the fresh solution. The difference between the fresh and used chemical milling solution is also evident in the reaction times ($\Delta t/g$): $5.34 \pm 0.56 \text{ min/g}$ versus $6.06 \pm 0.28 \text{ min/g}$, respectively. Different reaction(s) occurring in the fresh chemical milling solution as opposed to the used solution could account for the different enthalpies obtained. A similar explanation is also attributed to the erratic enthalpy results obtained with the fresh solution. The chemistry of these systems is probably very complex, although results of the chemical analyses of Cr³⁺, Cr⁶⁺, and H⁺ did not differ significantly between the fresh and used solutions. Therefore, no further attempts were made to elucidate the reactions involved. However, the enthalpies obtained are a valuable aid in the design of cooling coils.

The following reactions,

involve pickling uranium and beryllium with concentrated nitric acid and nitric-hydrofluoric acid solutions. The pickling solutions are used to clean the surfaces of these metals. In the pickling process, the NO_x generated is scrubbed, and control of the exothermic reactions by cooling coils is necessary to ensure that the NO_x generated does not exceed the capacity of the scrubbing system. Therefore, the reaction enthalpies were needed, as with the chemical milling solutions, to facilitate proper design of cooling coils. Only the uranium reaction has been measured to date, which gave a preliminary enthalpy value of $-235 \text{ kcal} \cdot \text{mol}^{-1}$ at 25°C.

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CHEMISTRY INSTRUMENTATION

NEW WASTE PACKAGING FACILITY
SOUTH DRUM COUNTER

*R. A. Deal, L. A. Bidwell, R. N. Chanda,
and J. L. Lawless*

The first of the two proposed drum counters for the waste packaging facility¹ has been constructed, calibrated, and released to production for use. This system, named the South Drum Counter, is being operated in a manner analogous to earlier systems; i.e., gamma rays are used for plutonium analysis and neutron/gamma-ray ratios for diagnostic information. A vertical array of three NaI(Tl) gamma-ray detectors monitors the barrel for plutonium emissions (see Figure 1). The sample barrel is placed on a turntable assembly and rotated during the preset counting interval. A circular array of BF₃ neutron detectors surrounds the barrel.

The system has been calibrated for eight categories of waste with standards supplied by the Rocky Flats' Chemistry Standards Laboratory. These include the following categories with the material status code in parenthesis: graphite (300), dry combustibles (330), wet combustibles (336), insulation (338), drybox gloves (339), Raschig rings (441), resin (430), and CWS or HEPA filters (490).

All raw data were fit with a linear equation of the form:

$$W_{Pu} = \frac{FCe B_2 W_m}{B_1 B_3}$$

where: FC = final gamma-ray counts determined by the settings of two single channel analyzer windows (²³⁹Pu "384" keV complex and an overlapping Compton window),

Figure 1. Schematic View of New Waste Packaging Facility South Drum Counter.

- B_2 = experimentally determined matrix attenuation coefficients,
 W_m = weight of the matrix in kilograms,
 W_{Pu} = weight of plutonium within the barrel in grams,
 $B_1 B_3$ = category dependent constants.

For four of the categories (300, 336, 338, and 339) a quadratic fit of the form,

$$\frac{FCe B_2 W_m}{B_1} = B_3 W_{Pu} + B_4 W_{Pu}^2$$

(where B_4 = category dependent constant) was used to more closely describe the standardization data.

Standardization was performed in a manner similar to previous drum counters where three matrix loadings for each plutonium value and many different plutonium values were used to determine the calibration curves for each category. Most categories were calibrated for the 25 grams to 200 grams range. Exceptions and details of the calibration procedure have been described in internal, unpublished reports.

Constants for drybox gloves differ significantly from those obtained in earlier work as new drybox glove standards have recently been made by the Rocky Flats Chemistry Standards Laboratory. PuO_2 vials were rolled up in each glove so that 80% of the PuO_2 is located in the fingers-to-wrist area rather than spread evenly throughout the entire length of the glove. Such packing was found to better simulate actual production generated waste gloves. The effect of lead absorption of the plutonium gamma-ray radiation is reflected in the value of the gamma per gram factor (B_1) down to 70, compared to 200 obtained with the previous glove standards.

The drum counter is expected to be computer-controlled by January 1, 1973.

EXPERIMENTAL Ge(Li) BARREL COUNTER

H. R. Martin

The waste/scrap counting systems used at Rocky Flats involve passive neutron and gamma-ray measurements. Because of their inherent resolution limitations, there are certain cases where the NaI(Tl) detectors used in the present assay systems cannot distinguish between plutonium gamma

rays and those arising from other sources. Occasionally, waste is generated which cannot be counted, or it yields anomalous neutron or gamma-ray results in the present systems. An experimental Ge(Li) detector counting system has been used to investigate those wastes which exhibit unusual characteristics.

The experimental counting system consists of a turntable rotating at 4 rpm, a 30 cc Ge(Li) detector and its associated electronics, and a multichannel analyzer. In the experiments the source-to-detector distances were varied depending upon how the waste was packaged and on the specific activity of the waste. Absorbers were frequently placed between the sample and the detector to reduce electronic deadtimes. Assays were based on a comparison of the intensities of the 393 and 413 keV ^{239}Pu gamma rays in the sample and in a standard.

A variety of waste materials has been counted using this system. While most of the wastes were different, they usually exhibited some of the same characteristics. These were:

1. Reaction gamma rays produced from ($\alpha, n\gamma$) reactions on low Z elements were observed in almost all samples. Fluorine was the predominant light element observed; but sodium, magnesium, chlorine, potassium, and nitrogen were found in a number of cases. In most cases, the presence of these light elements would influence neutron measurements in present NaI(Tl) assay systems.
2. Varying ^{241}Am concentrations were present in almost all samples. For the very high concentrations, a cadmium absorber was usually placed over the Ge(Li) detector, and some drums were even lead lined. The cadmium and lead were necessary to reduce the intensity of the ^{241}Am gamma radiation. Some interference in the background of the 413 keV ^{239}Pu gamma ray was observed in waste at the higher ^{241}Am concentration.
3. Most waste exhibited significant gamma-ray absorption. This was determined by comparing the intensities of the 129-, 393-, and 413-keV gamma rays from ^{239}Pu and the 208-keV gamma ray from ^{241}Pu . Although a method to determine the accuracy was not available, attempts were made to use configurations where these intensity ratios were comparable in the standard and in the sample.

In addition, the system is being used to assay ^{237}Np waste drums. These drums are allowed to stand for one month, and a qualitative ^{237}Np assay is obtained based on the intensity of the 312-keV gamma ray produced in the decay of the ^{237}Np daughter, ^{233}Pa . At the same time, a check is made to determine whether significant plutonium is present in the waste.

The experimental Ge(Li) counting system has provided a method of estimating the plutonium content of unusual waste materials. The techniques and data analyses from this study will be incorporated in some fashion in the design of the new waste packaging facility north drum counter, which currently is under construction.

the North Drum Counter, is under development for the determination of the NaI(Tl), BF_3 , and Ge(Li) detector configuration and mode of operation. The Ge(Li) development is briefly described in the preceding article of this report by H. R. Martin entitled "Experimental Ge(Li) Barrel Counter."

NEW WASTE PACKAGING FACILITY NORTH DRUM COUNTER

R. A. Deal and R. N. Chanda

The second of the two proposed drum counters for the waste packaging facility is to be used for the detailed analyses of 55-gallon drums which show anomalous results with the South Drum Counter. This second system, named

Exact detector arrangements have not been determined for the North Drum Counter. Experiments are underway with a vertical array of three highly collimated NaI(Tl) detectors located 10 in. from the drum being analyzed. It was found that plutonium localizations in a 55-gallon drum could be pinpointed in a vertical sense to within ± 1 in. by collimating the three NaI(Tl) detectors. A comparison of the response of each detector to a localized source is the method used. Figure 2 shows a typical experimental activity profile using

Figure 2. Activity Profile of Collimated Geometry with a 40 gram PuO_2 Source.

the method. The summation of the counts from all three detectors then yields information on the amount of plutonium present.

Plans call for this study to be continued on actual production barrels. If the results are successful in the actual case, localizations of plutonium as a source of error in barrel assays could be reduced, or even eliminated.

COMPUTER CONTROL FOR SAFEGUARDS INSTRUMENTATION

J. L. Lawless and L. A. Bidwell

HARDWARE DEVELOPMENT

Process residues packaged in one-gallon containers are radiometrically assayed for plutonium content by the Helix Counter and Can Counter II. The Helix Counter was the first of the radiometric systems to be brought under control of a Hewlett Packard 2116-B computer which is located in the process chemistry recovery building near the counting station.¹ Recently, Can Counter II has been interfaced to the computer and brought under its control.

During a counting cycle for either of the counters, the input to the computer comes from two sources. A process operator supplies the sample identifying information, and it is entered into the computer by a mark card reader. The counter scaling units are directly interfaced to the computer and provide the count data. Upon completion of the counting cycle, the calculated plutonium content of the package is printed out on an adjacent teletype. Simultaneously, a paper tape is punched which is submitted to the IBM 360 computer for final printout in material transfer format.

SOFTWARE DEVELOPMENT

The computer programs which control the radiometric counters used in the plutonium chemistry recovery facility are constantly being revised and updated to increase system efficiency. The development work for the Hewlett Packard 2116-B computer is performed on a Hewlett Packard 2116-C computer located in another building.

Buffered input-output has been added to increase the speed of the production computer system. This allows simultaneous printout and input of data, rather than the previous *nonbuffered method* of waiting for completed printout before acquiring new data. The elapsed time interval of

2-3 minutes has been eliminated. As additional systems are brought on-line, the time saved will be significant.

Preliminary research for on-line addition of drum counting systems located in the new waste packaging facility involved the development of a "synthetic" program to test and verify calculations. Nuclear counting systems are artificially attached to the computer; i.e., card reader and scaler data are supplied by a teletype unit. Factors, limits, and count data may then be run on an experimental basis and can be easily modified.

After all software development has been completed and thoroughly tested, the program changes can then be made to the production computer with only minimal interruption of its usage.

SUMMARY

The placement of the two package counters under computer control has resulted in many advantages to process chemistry operations. Personnel now can make immediate decisions on sample disposition, whereas a 24-hour wait was previously required while the data were being calculated by the IBM 360 computer. Material storage problems have been reduced along with criticality implications and personnel radiation exposure.

Present plans now call for the south drum counter in the new waste packaging facility to come under computer control. The target date is January 1, 1973.

REFERENCE

1. M. A. Thompson, "Research and Ecology Semi-Annual Report, Chemistry Research and Development," USAEC RFP-1921-A, August 30, 1972.

REFERENCE REPORT OF ROCKY FLATS WASTE CATEGORIES

J. L. Lawless

An internal unpublished report has been written which describes the 40 types or categories of line-generated waste at Rocky Flats, and gives the frequency distribution of waste samples among the various radiometric counters used for plutonium assay. The report was written to fulfill the need to have a single-source reference document for those concerned with the disposition of radioactive process residues.

Under each category of waste, identified by an MS code, a physical description is given along with the origin, system used for analysis, discard limit, and recovery procedure. The data generated by the radiometric counters have been reduced to extract the following information for each category: the contained plutonium distribution, the net weight distribution, percent occurrence of each category, percent of samples below discard, average plutonium value, average matrix weight, and percent of the total measured plutonium each category represents.

The data were derived from 38,000 analyses performed by the six counters, and generally cover the year up to July 1, 1972. It is planned that this report will be issued in the future on an annual basis.

NUCLEAR MATERIALS SECURITY AND TESTING FACILITY

D. R. Cartwright, R. A. Harlan, and J. R. Loomis

As a means to detect very small amounts ($\leq$ one milligram) of plutonium in 55-gallon waste drums, a previous study¹ has shown activation analysis is feasible with a high neutron flux from a modest nuclear reactor. No other currently available source can achieve the analytical sensitivity and reliability associated with a reactor neutron source in terms of economics, and at the same time compete in terms of versatility for other analytical applications.

During this reporting period, a detailed conceptual design for a one megawatt TRIGA reactor facility was completed and submitted for approval. The design includes two large beam ports for drum interrogation. Other beam ports for neutron radiography, small sample assay, and general research will allow these efforts to take place simultaneously with drum interrogation. Rabbit systems into the core will allow simultaneous use of the reactor to analyze environmental, soil, and health physics samples. Provisions for long term irradiations are also included.

The proposed facility would have a total of 17,900 square feet. Approximately 6,300 square feet will be devoted to experimental projects at the reactor and approximately 7,500 square feet will be devoted to offices, laboratories, and counting rooms. The preliminary environmental assessment indicates the risk with TRIGA reactors is so small that an environmental impact statement is not required.

If approved, the facility would analyze essentially all Rocky Flats' waste and provide definitive proof as to whether or not irretrievable waste does indeed meet the

irretrievable definition. Existence of the facility will permit substantial cost and time savings in certain routine assays of air, water, soil, and urine samples. It would also provide, for the first time, an adequate neutron radiography capability at Rocky Flats.

REFERENCE

1. M. A. Thompson, "Research and Ecology Annual Report, Chemistry Research and Development," USAEC RFP-1837-A, April 14, 1972.

SAFEGUARDS PERSONNEL MONITOR

J. L. Martinez and G. J. Cunningham

The safeguards personnel monitor described previously¹ was installed in a Rocky Flats' production area guard post to gain experience with personnel traffic flow and to test the instrument's reliability under actual operating conditions. It was found that about 30 persons per minute could pass through the monitor, thereby causing delays of personnel at shift-change time. The acceptance of the monitor was unfavorable because of these delays.

The monitor, as originally installed, required that a person step on a switchmat, pass through the detectors, and then step off the switchmat for a monitoring cycle to be complete. While a person was on the switchmat, the instantaneous count of the detectors was being compared to the background count observed by the detectors just prior to the engagement of the switchmat. If the two counts were statistically different, an alarm would sound at the instant the switchmat was disengaged. A study of the electronic circuitry revealed another approach for comparing the two counts which did not require disengagement of the switchmat. After the necessary changes were made in the circuitry, the monitor was found to accept people as fast as they physically could pass through without any loss in sensitivity.

Six months' operation have revealed the monitor to be reliable in performance with no major malfunctions. Because of the increased personnel throughput, only single systems are planned for the guard posts at the production areas. The first permanent installation is now being made by an outside contractor at the guard post to the chemical recovery facility.

REFERENCE

1. M. A. Thompson "Research and Ecology Annual Report, Chemistry Research and Development," USAEC RFP-1837-A, April 4, 1972.

PLUTONIUM BUTTON VERIFICATION COUNTER

R. A. Deal, R. N. Chanda, and L. A. Bidwell

At Rocky Flats plutonium buttons are stored in sealed tin cans. To verify that the contents have not been replaced with other material, such as uranium or lead, a radiometric counting system is used. The original system equipped with a Ge(Li) gamma-ray detector¹ has been replaced with a system which is more simple to operate, yet furnishes adequate verification data.

The new system uses a 2-in. diameter by 1-in. thick NaI(Tl) crystal for the detection of the 384 keV gamma rays from ²³⁹Pu, and four symmetrically placed BF₃ neutron detectors for additional verification information (see Figures 3 and 4). The system is mounted on a movable cart so the entire system can be readily moved. This is in contrast to the earlier system which was placed in an underground pit

Figure 3. The Plutonium Button Verification Counter.

and required that material be carried from storage vaults for counting.

The portable system has sufficient shielding so that operation inside a storage vault has been found to be quite satisfactory, and the system has now operated trouble-free for six months.

REFERENCE

1. M. A. Thompson, "Research and Ecology Semi-Annual Progress Report, Chemistry Research and Development," USAEC RFP-1921-A, August 30, 1972.

REACTION GAMMA-RAY STUDY

H. R. Martin

Reaction neutrons and gamma rays arise from alpha particle bombardment of certain light elements in combination with plutonium and other alpha emitters. These gamma rays have distinct and characteristic energies and can be used for identification and analysis of light elements in alpha emitting materials. Reaction gamma-ray spectra have now been accumulated and analyzed from a variety of plutonium compounds, mixtures, and alloys. The application of these

Figure 4. Detector Layout of the Button Verification Counter.

spectra in explaining anomalous neutron and gamma ray counts caused from light element interferences has been demonstrated in waste/scrap material.

Gamma-ray spectra have been obtained with Ge(Li) detectors for 14 light elements from ${}^3\text{Li}$ to ${}^{19}\text{K}$. Gauss $5^{1,2,3}$ spectrum analyses were performed and computer plots have been generated for these data. Typical spectra obtained from B, Na, and Al compounds mixed with plutonium dioxide are shown in Figures 5-7. Reaction gamma rays in the figures are denoted by the product nuclei. Spectra were also obtained with 2 in. by 2 in. NaI(Tl) detectors for the more prolific reaction gamma-ray emitters. No significant interferences were observed from any of the mixtures in the plutonium "384" keV gamma-ray region. In addition, neutron ratios were obtained between several plutonium dioxide light element mixtures.

These reaction rates can vary considerably depending on a variety of factors, including particle size, chemical form, elemental distribution in the sample, and the isotopic composition of the sample. Therefore, absolute emission rates were not determined.

Instead, efforts were directed toward obtaining gamma-ray energies, elemental assignments, and "useful" ratios of neutron emission rates on a qualitative or semi-qualitative basis.

In most waste/scrap materials examined, reaction gamma rays have been observed and with the aid of the spectra obtained in this study, a logical explanation for the origin of the reaction gammas and neutrons has been provided. For example, the absence of reaction gamma rays may allow neutron assay of heavy or lead-lined waste. The data have proved useful in understanding potential pitfalls of present assay systems and in designing new systems.

REFERENCES

1. R. G. Helmer, R. L. Heath, M. Putnam, and D. H. Gipson, *Nucl. Inst. Method*, 57 (1967), 46.
2. M. H. Putnam, Private Communications. Phillips Petroleum Co., 1968.
3. M. H. Putnam, Private Communications, 1972.

Figure 5. Ge(Li) Spectrum of B Compound Mixed with PuO_2 .

Figure 6. Ge(Li) Spectrum of Na Compound Mixed with PuO₂.Figure 7. Ge(Li) Spectrum of Al Compound Mixed with PuO₂.

DATA PROCESSING

H. R. Martin, G. L. Kaes, and J. W. Krogh

High resolution gamma-ray spectra obtained from solid-state detectors are generated in several Chemistry Instrumentation programs. The data are currently obtained as output on punched paper tape. Because of the complexity and large number of spectra, computer processing of the data is essential.

Computer programs have been obtained, tested, and are in use for analyzing the spectra data. These programs convert data from paper tape to magnetic tape, yield spectrum plots,¹ and provide Gauss 5^{2,3} energy and intensity analyses. The following capabilities are provided:

1. Data storage is on magnetic tape rather than punched paper tape.
2. Computer plots are easily obtainable, which aids in further data analysis and these are readily converted to figures for publication.
3. Accurate spectral analyses providing gamma-ray energies and intensities are obtained.

The programs are continually being updated to provide new capabilities, or to compensate for differences caused by new equipment.

REFERENCES

1. G. L. Kaes, Private Communication, Dow Chemical Co., 1972
2. R. G. Helmer, R. L. Health, M. Putnam, and D. H. Gipson, *Nucl. Inst. Method*, 57 (1967), 46.
3. M. H. Putnam, Private Communication, Phillips Petroleum Co., 1968.

GLOVEBOX SURVEY INSTRUMENTATION

R. A. Harlan

A study of the feasibility of surveying gloveboxes with special radiometric instrumentation was performed to improve safeguards and accountability, to assist in determining normal operating losses (NOL), and for criticality considerations.

A shield was developed for a 1 in. by 1 in. NaI(Tl) detector which was connected to a portable rate meter. The shield features a conical entrant aperture in a lead cylinder which fits over the detector probe. This aperture is covered with 0.41 in. of iron, which removes 99.99% of any 60 keV ²⁴¹Am gamma rays, while removing only 50% of the higher energy gamma rays from plutonium. Therefore, the iron shield makes the detector response relatively independent of the age of the plutonium.

The aperture in the lead allows gamma rays originating within 41° of the detector centerline to enter the detector. This collimation makes the meter fairly directional while maintaining very approximate independence of source distribution. For a given amount of plutonium the response is the same within a factor of two if the plutonium is a point source, a line source, or an extended area source. With the shield, the meter reads 8,000 c/m gram of plutonium when the source-to-detector distance is 1.5 in. This reading corresponds to 0.039 gram Pu/cm² and is independent of source-to-detector distance for a uniform area source as long as the source is larger than the area defined by the collimator.

The instrument has been very satisfactory for glovebox survey work at Rocky Flats, and generally has been accurate to within a factor of two when plutonium identified by the meter has actually been recovered. Routine surveys are being instituted by four production groups as a result of this work.

²³⁹Np TRACER DETERMINATION

H. R. Martin and R. A. Nixon

The ²³⁷Np radiochemical procedure used by the Rocky Flats Analytical Laboratories involves chemical separation of neptunium. The chemical yield is determined by NaI(Tl) x-ray counting of a ²³⁹Np tracer. The principal difficulty with this method is the inconsistent separation of the ²³⁷Np daughter, ²³³Pa. The short-lived ²³³Pa causes gamma-ray interferences in the assay of the ²³⁹Np tracer.

A procedure based on a Ge(Li) gamma-ray count for assay of the ²³⁹Np has been developed. The tracer determination is now based on comparison of the intensities of the 228 and 278 keV ²³⁹Np gamma rays in the sample and in a standard. The procedure was checked by comparing a spectrum, where the ²³³Pa 312 keV gamma ray was 1.4 times more intense than the 278 keV gamma ray, with an identical "pure" ²³⁹Np spectrum containing insignificant ²³³Pa. The intensities of the 228 and 278 keV gamma rays

varied less than 1.5% between the two spectra. This indicates insignificant ^{233}Pa interference at this concentration, which is similar to the concentration levels usually encountered by the Analytical Laboratories.

OXYGEN DEMAND SYSTEM FOR SEWAGE TREATING PLANT

C. M. Johnson and C. E. Hausburg

Last year one of the four aerators at the sewage treating plant was placed on a demand mode of operation.¹ For this one aerator, a polarographic probe, manufactured by Beckman Instruments, senses the dissolved oxygen content of the aerator effluent, and by suitable instrumentation the on-off cycle of the aerator motor is controlled.

After a year of successful operation for the one aerator, the remaining three aerators are to be placed on the demand mode of operation. The new control system has been designed, and installation is planned for the near future.

REFERENCE

1. M. A. Thompson, "Research and Ecology Annual Report, Chemistry Research and Development," USAEC RFP-1837-A, April 14, 1972.

STACK EMISSIONS MONITORS

C. M. Johnson

To effectively control the amount of pollution that stationary emitters produce, it is necessary to know the amount and source of each pollutant. A program has been initiated to locate the amount and source of any pollutant originating at Rocky Flats.

There are 106 numbered structures on the plant site, and the majority of these buildings have the possibility of adding pollutants to the atmosphere. However, only a small number of these buildings could emit pollutants in significant quantities. Therefore, a survey of all the buildings was conducted to determine the prime candidates for initial surveillance.

The first building selected for instrumentation was the steam generating plant, which was known to emit NO_x ,

SO_2 , and particulates. Commercially available NO_x and SO_2 analyzers were installed on one boiler stack and made operational. A particulates analyzer has also been obtained and is awaiting installation. From the preliminary results it appears that the emission of these three substances will be well within state regulations.

The second building selected for instrumentation had a problem with a visible plume of NO_x coming from a stack. The NO_x originated from an acid spray process for metal cleaning contained within the building. The intent of the instrumentation was to eliminate the presence of the NO_x plume when the acid spray process was being used.

Tests were conducted to determine the amount of NO_x that could be allowed before a visible plume was detected. It appeared that a concentration of 10 ppm would preclude plume formation under most conditions; however, concentrations of 100 ppm could be tolerated without plume formation if wind and temperature conditions were just right. A recorder was installed at the acid spray station within the building so that an operator could keep close control of the NO_x concentration in the stack.

All other pollutant sources will be studied on a priority basis, with the most serious sources receiving first consideration. Other emissions from certain buildings identified for future analyses are total hydrocarbons, CH_4 , CCl_4 , CO , and trichloroethylene. Instrumentation has been ordered to perform these analyses.

AMBIENT AIR MONITORS

C. M. Johnson, D. E. Hausburg, and J. L. Lawless

The continued concern over air pollution, and the resultant state and federal regulations, makes it increasingly important that each pollution emitter knows the extent of his contribution to the general problem. A program has been initiated that will furnish the necessary information concerning Rocky Flats. There are presently two parts to the program: a mobile ambient air facility, and a stationary sampling and measuring facility.

The mobile facility is a van-type vehicle which will contain instrumentation to sample and analyze all pollutants covered in the proposed regulations for 1975. The plans for this vehicle are complete (see Figure 8), and the vehicle is on procurement. The facility is expected to be operational July 1, 1973.

Figure 8. Layout of the Mobile Ambient Air Monitoring Vehicle.

The stationary sampling and analyzing system is an interim action to give Rocky Flats personnel experience in ambient air measurement and data analyses. This system has revealed two problem areas that will affect the operation of the mobile facility. The first problem area concerns the lack of on-site meteorological data, and the second involves the amount of data that will be generated by the mobile facility.

The stationary system consists of three instruments: an SO₂ analyzer, a total hydrocarbon analyzer, and a total oxidants analyzer. They presently are located in a combined process-office building located on the southeast part of the plant. The sample points are on the roof of the building, and the system has been operational for 3 months.

The need for a meteorological study was revealed by observations that periods of high instrument readings at the plant site coincided with periods of high pollution in Denver, which is located some 20 miles to the southeast of Rocky Flats. The mean altitude of Denver is 5,200 feet,

while it is 6,000 feet at the plant. When the mixing layer for Denver is 1,000 to 1,400 feet above ground level, it would place the plant in the top 200 to 600 feet of the inversion layer. Higher concentrations of pollutants in the top of the inversion layer could account for higher than normal readings at the plant site.

During periods of high winds, higher than normal SO₂ readings have been observed. Irregular peak recording may indicate plume dispersion from the Rocky Flats' steam plant, or the SO₂ could be coming from Boulder located 10 miles to the north. A meteorological study would help clarify these two phenomena.

The data generated by these three instruments require a considerable amount of time to digest. When the mobile facility is made operational, the amount of data will soon be unmanageable. Equipment is now being acquired to put the data in forms that will be compatible with a computer.

PROCESS CHEMISTRY

RECOVERY AND PURIFICATION OF PLUTONIUM BY A VOLATILE FLUORIDE PROCESS

R. L. Standifer, R. O. Wing, and J. R. Sheets

The development of a volatile fluoride process for the recovery and purification of plutonium has progressed from gram-scale laboratory experiments to the design and installation of a production-scale prototype system.^{1,2} The prototype unit was designed to convert impure plutonium oxide (PuO_2) and plutonium tetrafluoride (PuF_4) to purified PuF_6 , at a throughput capacity of 12 kg/day plutonium. Preliminary runs using PuO_2 feed have just been started, and it is anticipated that several weeks will be required to shake down the system before full-scale processing runs can begin. The current schedule calls for extended periods of around-the-clock operation from April to July 1973. During this period the process will be evaluated comparing it with current processing methods in the following areas: (1) product quality, (2) safety,

(3) reliability, (4) radiation exposure, (5) operating and maintenance costs, (6) quantities of plutonium-bearing residues generated which require reprocessing, and (7) quantities of plutonium-contaminated waste generated.

A simplified layout of the prototype system is shown in Figure 9. The major equipment items (numbered items in Figure 9) are as follows:

- 1 Primary fluid bed reactor—converts PuO_2 or PuF_4 to PuF_6 .
- 2-4 Sodium fluoride traps—remove trace amounts of PuF_6 from waste gas streams.
- 5 Residue collection vessel—non-volatile impurities are pneumatically conveyed to this vessel from primary reactor.
- 6-9 Cold traps— PuF_6 formed in primary reactor is condensed and collected.

Figure 9. Equipment Layout of Volatile Fluoride System, Room 146A, Building 771. (Note: see text for explanation of numbers.)

- 10-12 Recycle compressor, interstage cooler and after-cooler—recirculates fluorine.
- 13 Feed transfer vessel— PuO_2 feed is pneumatically conveyed to primary reactor.
- 14 Thermal decomposition reactor— PuF_6 collected in cold traps during primary reactor operation is subsequently passed through a heated PuF_4 bed where it decomposes to PuF_4 .
- 15 Product separator—removes solids from off-gas stream from thermal decomposition reactor.
- 16 Product transfer vessel—product PuF_4 is collected and pneumatically transferred 100 feet to reduction area.
- 17-25 Charcoal traps—dispose of fluorine in waste gas streams.
- 26 Vacuum pump—used for purging and leak-testing equipment.
- 27-31 Water scrubbers—saturate exhaust air from glove-boxes with water vapor to hydrolyze PuF_6 and react F_2 in the event of equipment failure.

Following is a brief description of the operating sequence for the system:

A cyclic flow of inert gas is established from the compressor discharge (10), through the heated primary reactor (1), through a chilled cold trap (6), and returned to the compressor suction (10). Impure PuO_2 or PuF_4 is transferred into the primary reactor and fluorine is introduced with the recycling inert gas. As the fluorine reacts with the feed material, the contained plutonium is converted to gaseous PuF_6 and passes out of the reactor, leaving most of the impurities behind. The gas stream discharged from the primary reactor, containing approximately 1% PuF_6 in F_2 , is passed through a chilled cold trap (6) where the PuF_6 is condensed and collected. The unreacted F_2 is returned to the compressor (10). When the plutonium is depleted from the primary reactor, the fluorine is removed and the residue is transferred pneumatically to the residue collector (5) before recharging the primary reactor with feed (1).

In a subsequent operation the cold trap containing PuF_6 (collected during the primary reactor operation) is warmed and the PuF_6 vaporized by passing nitrogen through the trap (8). This stream, containing N_2 and PuF_6 , passes through a heated fluidized bed of PuF_4 particles in the thermal decomposition reactor (14), causing most of the

PuF_6 to decompose to solid PuF_4 . The effluent gas from the thermal decomposition reactor passes through a second chilled cold traps (9) to remove the remaining PuF_6 and then passes through the disposal traps. As PuF_4 is formed in the thermal decomposition reactor (14) it passes to the product transfer vessel (16) and is transferred, batch-wise, to the reduction area. Two sets of cold traps were provided (6, 7, 8, 9) to permit simultaneous operation of both the primary reactor (1) and the thermal decomposition reactor (14).

The off-gas streams from both process steps are combined and pass through heated traps containing pelletized sodium fluoride (2,3) to remove trace amounts of PuF_6 and then through charcoal traps (17-22) where F_2 is converted to carbon tetrafluoride (CF_4).

REFERENCES

1. R. L. Standifer, "A Fluidized Bed Fluoride Volatility Pilot Plant for Plutonium Purification," *Chemical Engineering Symposium Series*, Vol. 66, 105 (1970).
2. M. A. Thompson et al., "Chemistry Research and Development Semi-Annual Progress Report," January-June, 1972, USAEC Report RFP-1921-A, August 30, 1972.

PRECIPITATION OF PLUTONIUM PEROXIDE

P. G. Hagan, P. A. Glover, and F. J. Miner

Precipitation of plutonium from a nitric acid medium by the addition of hydrogen peroxide (H_2O_2) to form a non-stoichiometric plutonium peroxide is a basic unit operation in the plutonium recovery and purification process at Rocky Flats. The operation accomplishes two objectives: a liquid-to-solid conversion and concentration; and a purification from several impurity elements, notably americium.

The initial step of this unit operation is adjustment of the plutonium-nitric acid solution to a HNO_3 concentration of approximately 3.9M to 4.0M and a sulfate ion concentration of approximately 0.04M. The precipitation and subsequent filtration is presently accomplished using a H_2O_2 addition pot and a cascade of digestion pots, followed by a continuous rotary drum filter. The wet but solid product is scraped from the wheel in lots of approximately 2000 grams and subsequently transferred to a continuous rotary tube dryer where it is converted to a purified plutonium dioxide (PuO_2) form.

The flow sheet for the New Plutonium Recovery Facility (NPRF) calls for essentially the same chemistry of precipitation, except that no sulfate ion will be added in the initial batching operation. The objective here is to reduce equipment corrosion in subsequent operations. In addition, the equipment design criteria calls for batch rather than semi-continuous operation. An evaluation of certain equipment and operating parameters was therefore required.

PRECIPITATION OF PLUTONIUM PEROXIDE FROM 20 g/l PLUTONIUM SOLUTIONS

In prior studies on the batch precipitation process¹ information was obtained on the precipitation of plutonium from solutions with a nominal concentration in the 40 g/liter plutonium range. This concentration range was used because it is the one in which the present plutonium recovery facility normally operates. In the New Plutonium Recovery Facility (NPRF), however, there is the possibility that at times the plutonium feed stream could be in the 20 g/liter range. Information was needed on how well plutonium precipitates from solutions at this lower concentration.

Two precipitations were made from plutonium solutions in the 20 g/liter range. In both cases, the precipitate appeared to form in a manner similar to that of precipitates made from plutonium solutions in the 40 g/liter range. The precipitates were easily filtered and after being washed were fairly crumbly. The only differences noted was that the relative filtration times for the 20 g/liter precipitates were slightly longer than for the 40 g/liter solutions, and the quantitative yields were not quite as good. For example, from the 20 g/liter solutions, the precipitates required approximately 10 minutes to filter and the filtrates contained about 1 g/liter plutonium, constituting a total loss of plutonium to the filtrate of about 7%. For comparison, a previous study in which the same volumes of 42 g/l plutonium solutions were used, approximately 5 minutes were needed to filter through the same filtration equipment and the plutonium loss to the filtrate was only about 2%.

The experiments showed that plutonium peroxide can be precipitated from a 20 g/liter solution. The filtration time and filtrate loss are both higher than from a 40 g/liter solution, but certainly acceptable. And it is a reasonable expectation that both the filtration time and the filtrate loss could be improved by optimizing the precipitating conditions for the 20 g/liter solutions.

REACTIVITY OF PLUTONIUM PEROXIDE PRECIPITATE

In the current semicontinuous plutonium peroxide precipitation process, sulfate is added to improve the filterability of the precipitate. In the subsequent processing of the plutonium peroxide, the sulfate ion and its decomposition products have a corrosive effect on the equipment, causing problems in equipment maintenance as well as increasing the impurity level in the final metal product.

In the batch plutonium peroxide precipitation process, sulfate is not required. Information was needed on how this sulfate-free plutonium peroxide reacts in the processing steps following precipitation. It has been postulated that when plutonium peroxide containing sulfate decomposed during calcination and fluorination, fracturing of the crystal structure occurred, making the resulting material more reactive and therefore more easily fluorinated. The absence of sulfate from batch-produced peroxide might be unreactive and thus unacceptable. To investigate this possibility, two batches of plutonium peroxide containing 12 g of plutonium were precipitated, calcined in a laboratory muffle furnace at 400°, fluorinated using fluorine, and then reduced. The metal yields were 92% and 94%, respectively. A control sample of plutonium oxide produced using sulfate in the precipitation process showed a metal yield of 92%. Based on these two runs, the absence of sulfate in the precipitation process does not appear to affect the reactivity of the material.

PLUTONIUM(VI) IN THE PLUTONIUM PEROXIDE PRECIPITATION PROCESS

In both the present plutonium recovery facility and the flow sheet for the New Plutonium Recovery Facility, plutonium feed solutions are concentrated by boiling prior to precipitation as plutonium peroxide. In the course of this concentration, a portion of the plutonium is oxidized to Pu(VI). Because Pu(VI) does not form any insoluble complexes with the peroxide ion, its disposition in the peroxide precipitation process has always been somewhat in question. It has been speculated that in the first stages of the precipitation process, the Pu(VI) is reduced to Pu(IV) by hydrogen peroxide. However, the plutonium feed solutions contain metallic impurities and Leary has shown that such impurities greatly reduce the reductant properties of hydrogen peroxide in relation to Pu(VI).² A study was undertaken, therefore, to determine if Pu(VI) in the presence and/or absence of metallic impurities in a nitrate feed solution is reduced to Pu(IV) and subsequently precipitated with hydrogen peroxide, or if its rate of reduction is affected to the point where plutonium as Pu(VI) will be lost to the filtrate.

Runs were made with Pu(VI) present with and without impurities; and with Pu(IV) only, with and without impurities. The results are summarized in Table 4. From the amount of plutonium in the filtrate, it does not appear that Pu(VI) is lost to the filtrate. It is probable that in the course of the precipitation, the Pu(VI) present is reduced to Pu(IV) and subsequently precipitated. The filtrates were analyzed spectrophotometrically immediately after filtration and no Pu(VI) peak was observed. Although the literature has indicated that the reduction of Pu(VI) to Pu(IV) is so slow that it causes an increase in the filtrate loss^{3,4} under the conditions at which these precipitations were made, this is not the case.

Table 4. Effect of Pu(VI) and Impurity Concentration on Plutonium Lost to the Filtrate.

Pu — 52.3 g/l HNO ₃ during precipitation — 4.35M				
Initial Pu(VI) Concn. (%)	Impurities*	No. Runs	Pu Conc. in Filtrate (g/l)	
			Mean	SD
34	No	8	0.19	0.16
34	Yes	6	0.042	0.006
0	No	8	0.74	0.47
0	Yes	10	0.24	0.36

*When present, the individual metal ion impurities and their concentrations in the HNO₃-plutonium solution are as follows: Fe, 0.31 g/l; Cr, 0.04 g/l; Ni, 0.06 g/l; Cu, 0.03 g/l; Pb, 0.02 g/liter. These are typical stream averages as experienced in the existing process plant.

The data in Table 4 indicate that the filtrate loss is less with Pu(VI) present than when it is absent. And this difference is statistically significant. However, only a minimal number of runs were made and more data should be obtained to increase the confidence in the observation.

REFERENCES

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CONTINUOUS LIQUID LEVEL MEASUREMENT IN PROCESS TANKAGE

G. D. Lehmkuhl

Continuous liquid level measurements in aqueous process tankage are necessary for process operation and for nuclear materials accountability. Sight gages are presently used in the Rocky Flats aqueous plutonium recovery operations. These sight gages are prone to leaking at the glass-metal seal and are not applicable where remote tank level measurements are required. Therefore, various continuous liquid level measuring devices are being studied in an effort to find suitable substitutes for the sight gages.

A report was written on "Time Domain Reflectometry for Liquid Level Measurement" and published in August 1972.¹ Work is continuing to ascertain the reliability of other methods of continuous liquid level measurement and to compare the merits of the various systems.

REFERENCE

1. G. D. Lehmkuhl, "Time Domain Reflectometry for Liquid Level Measurement," USAEC Report RFP-1902, August 21, 1972.

OXIDE REMOVAL FROM CALCIUM CHLORIDE-CALCIUM FLUORIDE-CALCIUM OXIDE SYSTEM

G. D. Lehmkuhl, J. Vasquez, and J. C. Brown

Plutonium dioxide can be reduced with calcium in a molten salt flux.^{1,2} The resultant plutonium collects in the bottom of the reduction vessel while the calcium oxide reaction product is taken up by the CaCl₂-26 mol% CaF₂ cover salt. Since it is desirable to reduce waste generation, it would be advantageous to recycle the salt. To do this the calcium oxide must be removed from the salt or must be converted to calcium, calcium chloride, or calcium fluoride which can be reused.

Experiments indicate that the calcium oxide in a calcium chloride-calcium fluoride-calcium oxide system can be chlorinated to reduce the oxide content. The calcium oxide in 2600 grams of molten salt was reduced from 5% to 0.5% in 180 minutes with hydrochloric acid gas bubbling through the melt at 1 liter/minute (STP).

Electrowinning of calcium from the calcium oxide in the above system has also been tried. The calcium oxide is

electrolyzed preferentially but side reactions cause the salt and metal products to be impure. The electrolysis experiments have been performed in equipment with a poorly inerted atmosphere and with electrodes and crucibles of iron and graphite. The product purity should improve with proper component selection and better control of the atmosphere in the cell:

REFERENCES

1. W. Z. Wade and T. Wolf, "The Production of Plutonium Metal by Direct Reduction of the Oxide," USAEC Report UCRL-50403.
2. Argonne National Laboratory, Chemical Engineering Division Annual Report, USAEC Report ANL-7575, April 1969, p 28ff.

CRITICALITY DRAIN PERFORMANCE STUDY

*G. D. Lehmkuhl, R. L. Smith, D. E. Auten
and J. R. Wolf*

Critical mass incidents (i.e., accidental uncontrolled fission reactions) are prevented from occurring by controlling the quantity of fissionable material in a particular location and by controlling the geometry of the containment vessel. The quantity of fissionable material allowed as well as its container geometry is based on a number of considerations, among them the neutron reflection properties of the immediate environment. Water and similar hydrogenous media reflect neutrons into a potentially fissionable mass, thereby lowering the amount of fissionable material required to achieve a critical mass. Relatively large volumes of solutions of fissionable materials may be maintained in small diameter, properly spaced cylinders, flat slab tanks, or in Raschig ring-filled tanks so that the neutron population per unit volume is lower than that required for a self-sustaining fission reaction. Gloveboxes used to contain more than a few grams of plutonium are normally required to have a means of controlling the level of water or solution of fissionable material that might accidentally accumulate. The accidental accumulation might be due to such events as a process solution line break, a cooling water line break, or a window rupture during a time when the room water sprinklers are activated.

The most frequently used method of control at the Rocky Flats Division is provision of a raised drain outlet in the glovebox floor (Figure 10). To ensure containment of the radioactive materials, the boxes are kept at approximately 1 inch of water vacuum (relative to room ambient pressure).

Figure 10. Criticality Drain Performance Test Box.

The drain has a liquid seal to prevent movement of air through the drain. When the liquid level in a box reaches the height of the drain outlet opening, the liquid will begin to flow out of the box through the drain. The rate of liquid flow, out of the criticality drain, is related to the height of liquid in the box above the drain outlet opening. This height is called the liquid head. Higher flow rates require larger liquid heads. To provide a safe operation from a nuclear safety standpoint, the liquid level in a glovebox must not rise above a given maximum level. Therefore, it is necessary to know the liquid heads required to produce various liquid drain outlet flow rates from the glovebox. The maximum permissible liquid level, the maximum liquid leak flow rate into the glovebox, and the liquid head-drain outlet flow rate relation can then be used to design the proper criticality drain for the glovebox.

A study was made to determine the aqueous liquid head necessary to sustain various liquid flow rates in criticality drains. Glovebox criticality drains were simulated in a glovebox model including bottom and side drains: one each for 1-, 2-, and 3-in.-diameter pipes. The 1-in. side and bottom drains, the 2-in. side drain, and the 3-in. side drain require considerably higher liquid heads than the other three drains. For example, a 2-in. side drain requires a 1.7-in. head to flow 12 gpm, whereas a 2-in. bottom drain requires only a 0.7-in. head (Figure 11). A formal report on these flow studies will be issued.

These test data will be used in design of future gloveboxes and for evaluation of present glovebox criticality drains. Probably leak rates into process gloveboxes will be determined and used with these test data to predict possible liquid levels in the gloveboxes.

Figure 11. Comparison of Drains Without Pot or Cover.

CHEMICAL TECHNOLOGY

FABRICATION OF PLUTONIUM-242 METAL TARGET FOIL FOR LAWRENCE LIVERMORE LABORATORY

W. V. Conner *et al.*

In cooperation with the Materials Technology Research and Ecology Group, a plutonium-metal target foil was fabricated for the Lawrence Livermore Laboratory (LLL). The final dimensions of the foil were 2.750 ± 0.010 in. by 3.930 ± 0.010 in. and 0.0062 ± 0.0005 -in. thick. The finished foil weight was 17.0659 grams. The plutonium alloy (Pu-1 wt% Al) used for the fabrication was in the form of a 1-in. diameter by 0.180-in.-thick disk which had been cast previously¹ for the Los Alamos Scientific Laboratory (LASL). The ^{242}Pu content of the plutonium involved in the fabrication was 98 wt%.

The 1-in.-diameter disk was rolled to the required 0.006-in. thickness. A blank was cut from the rolled sheet and was clamped between two precision machined aluminum plates. The clamped blank was annealed at 300°C for 10 minutes to ensure a flat foil configuration. The annealed blank was

trimmed to match the precision machined aluminum plates which provided for an accurate determination of foil dimensions. The fabricated foil was placed into an aluminum foil (0.006-in. thick) envelope and the open end of the envelope was welded closed. The encapsulation was accomplished without contaminating the external surfaces of the aluminum envelope.

REFERENCE

1. W. V. Conner, S. G. Proctor, and D. L. Baaso, "Fabrication of Plutonium-242 Metal Disks," USAEC RFP-1835, June 1972.

STEAM OXIDATION OF PLUTONIUM METAL

S. G. Proctor

Routine practices at Rocky Flats dictate the conversion of plutonium chips and turnings to a stable oxide form within a short time of their generation. The conversion to an

oxide is accomplished by burning the chips in an air atmosphere. This burning technique has a tendency to form small quantities of high fire oxide which is difficult to dissolve.

Previous research at Hanford¹ has shown the feasibility of using a steam oxidation technique to convert plutonium metal to a low fired oxide which exhibited favorable dissolution characteristics. A laboratory scale unit has been fabricated to evaluate steam oxidation systems for converting plutonium chips and turnings to a stable processable oxide. The oxidation unit was constructed with two heating zones capable of attaining temperatures of 600°C. The steam was preheated to 250°C in the first zone and was then heated from 250°C to 600°C in the second zone. The plutonium metal was introduced into the second zone. Preliminary runs have been carried out using second zone temperatures of 250°, 400°, and 600°C. X-Ray diffraction analyses on the pyrohydrolyzed oxides showed complete conversion to PuO₂. Oxidation parameters and chemical reactivity of the resultant oxide will be evaluated for scale up possibilities.

REFERENCE

1. R. C. Smith "Plutonium: Steam Oxidation and Oxide Dissolution," USAEC HW-66431, August 12, 1960.

AMERICIUM RECOVERY AND PURIFICATION

S. G. Proctor

A Special Order was received from the Lawrence Radiation Laboratory (LLL) for the recovery and purification of americium-241. The americium was contained in a mixture of aluminum metal and americium oxide which had been generated by pellet fabricating processes at LLL. The material received consisted of 139.5 grams of Al-AmO₂ powder mixture and 64.6 grams of Al-AmO₂ pellets with a total americium content of 59.2 grams. The specifications on the recovered product oxide (AmO₂) were: (1) the ²⁴¹Am assay of the oxide would be greater than 84.8 wt% americium-241, (2) the aluminum content in the recovered AmO₂ would be less than 1000 ppm, and (3) the individual rare earth elements would be reduced to less than 500 ppm each.

The method of separating the americium from the aluminum consisted of a caustic dissolution of the aluminum leaving the AmO₂ behind as an easily filterable solid. The rare earths were removed from the americium by a fluoride precipitation of the rare earths. The americium was oxidized to the hexavalent state to prevent its coprecipitation with the rare earths. The nonrare earth elements were separated from the americium by precipitating the americium as an oxalate thereby leaving the soluble impurities in the filtrate.

The analytical results on the purified AmO₂ product showed only 920 ppm of the total detectable impurities. The rare earths contributed only 50 ppm to this total, and the aluminum contributed only 20 ppm. The major impurity was calcium at a concentration of 500 ppm. The total weight of the purified AmO₂ was 65.2 g with an americium content of 57.0 g based on a calorimetric assay of 0.875 g Am/g AmO₂. The recovery of americium as purified AmO₂ was 96.3 percent.

AMERICIUM RECOVERY PROCESS-RESIN DEGRADATION

S. G. Proctor

In the ion exchange process used at Rocky Flats to recover and purify americium-241, a Dowex 50 cationic resin column (chloride form) is used to concentrate the americium product and to remove any residual traces of ammonium thiocyanate. The americium is eluted from this column with 7M HCl and passed through a Dowex 1-X4 anion column for final plutonium removal. The americium is precipitated from the column effluent as an oxalate which is subsequently calcined to the final americium oxide product.

Americium loading difficulties have been experienced with the Dowex 50 cationic column. The cation resin was often left loaded with americium for periods of 7 to 10 days while awaiting additional americium for loading. This practice was followed to regulate the batch size for the final oxalate precipitation step. After an extended period (approximately 6 months) of operation, americium loading problems developed.

A check of the process feed to the chloride cation columns failed to detect any deviation from the correct process parameters. When the used resin was replaced with fresh

resin, the process feed loaded quite well with the effluent conforming to the process discard limits. Samples of the used resin were then taken for x-ray diffraction and microscopy analyses.

A photomicrograph (Figure 12) of the used resin showed gross amounts of material clinging to the resin beads which were also badly discolored. Repeated washings of the resin beads with 7M HNO_3 produced beads relatively free of foreign material but still badly discolored. The foreign particulate matter was identified as $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$ while the wash solution contained significant amounts of sulfate ion. The surface of the washed beads appeared to be blistered as shown in Figure 13. A photomicrograph (Figure 14) shows no such characterization for fresh resin. The source of sulfate ion in the residue and in the wash solution was concluded to have come from the resin sulfonic acid exchange group. The intense americium radiation in close contact with the resin beads disrupted the bonds of the exchange groups from the polymer lattice of the resin. The exchange group was then left free to combine with impurities in the process stream. The intense radiation eventually destroyed enough resin loading sites to render the resin useless for americium processing. Since the full consequences of resin degradation are not completely understood at this time, it was recommended that the practice of leaving the americium loaded on the cation resin be discontinued.

Figure 12. Used Chloride Form Cation Exchange Resin From Americium-241 Recovery Process.

Figure 13. Used Chloride Form Cation Exchange Resin After Washing with 7M HNO_3 .

Figure 14. Fresh Chloride Form Cation Exchange Resin.

PLUTONIUM RECOVERY FROM DICESIUM PLUTONIUM HEXACHLORIDE SALT

T. B. Patterson and D. R. Van Hooser

A few years ago several batches of dicesium plutonium hexachloride (Cs_2PuCl_6) salt were prepared for evaluation as a primary analytical standard. Low NGS (2.30 wt% ^{240}Pu) which is considered a national resource material was used for the salt preparation. The recovery of 740 g of plutonium as an oxide from 2249 g of aged Cs_2PuCl_6 has been accomplished.

The salt was dissolved in a minimum of nitric acid and the plutonium was precipitated as an oxalate by the addition of oxalic acid. The oxalate precipitate was calcined to an oxide for storage as a national resource material.

SECONDARY PLUTONIUM RECOVERY DEVELOPMENT

W. G. Eggerman, S. G. Proctor, and D. A. Burton

Experimental and theoretical approaches are being explored and developed for reducing the concentration of plutonium in process waste streams generated initially by plutonium recovery processing. Mathematical models incorporating the usual processing parameters for anion exchange and solvent extraction are also being developed.

ANION EXCHANGE STUDIES

The first candidate considered for secondary plutonium recovery was ion column effluent (ICE) which was 7.2M HNO_3 with a plutonium concentration varying from 1 to 5 mg/l. The salt content of ICE will run as high as 90 g/l.

Laboratory studies were carried out to determine the optimum level to concentrate the ICE to reduce the volume and increase the plutonium concentration. Volume reductions ranging from 4:1 to 8:1 were carried out using a still fitted with a fractional distillation column. A volume reduction of 5:1 was considered optimum for this phase of the recovery operation. The plutonium concentration of the collected distillates was 8×10^{-8} g/l.

A precipitate was formed in the still bottoms and was easily removed by filtration. The precipitate was discarded as the major constituent was hydrated SiO_2 and was free of plutonium.

Plutonium recovery evaluations on the concentrated still bottoms were carried out using anion exchange technology. The ICE was concentrated to 4:1 by distillation, adjusted to 7.8M HNO_3 and passed through an ion exchange column packed with Dowex 1-X4 (50-100 mesh) nitrate form resin. A twenty-fold reduction in plutonium concentration in the concentrated ICE was realized. Final plutonium concentrations were in the 10^{-4} range.

A search for the optimum operating conditions for Dowex 1-X4 (80 mesh) resin with low plutonium solutions was also initiated. The distribution coefficients (K_D) were determined using dilute plutonium solutions in contact with a static resin bed and extended contact periods to reach equilibrium. The distribution coefficients calculated from the experimental data are reported in Table 5. The equilibration times are somewhat misleading in that 99% of the equilibrium value was attained within 10 minutes. Elution studies showed that 40-50 column volumes of 0.35M HNO_3 were required to remove enough plutonium to permit reuse of the resin. Elution in a dynamic system with the aid of a reducing agent would probably improve the elution rate.

Table 5. Distribution Coefficients for Dowex 1-X4 Resin.

Plutonium Solution (g/l)	K_D Value ^a	Equilibration Time (hr)
0.1	2000	24
0.01	2250	20
0.001	2000	20

$$^a K_D = \frac{\text{g Pu/g resin}}{\text{g Pu in effluent/g of solution}}$$

The effect of using more resin than necessary to load all the plutonium present was also evaluated. Resin quantities equivalent to a two-fold excess, five-fold excess, and a ten-fold excess were studied. The plutonium content in solution was reduced four-fold using a ten-fold excess of resin and two-fold using a five-fold excess of resin. No appreciable change was observed using a two-fold excess of resin. Using excess resin in a static system does not reduce the plutonium concentration enough to justify its use.

SOLVENT EXTRACTION

Preliminary experiments have been conducted to study the applicability of solvent extraction systems for secondary plutonium recovery. A synthetically prepared plutonium (2.0×10^{-3} g/l) 7M HNO₃ solution was extracted with 0.1M tri-*n*-octylphosphine oxide (TOPO) in cyclohexane. The plutonium solution was contacted twice with an equal volume of organic. The plutonium concentration in the aqueous phase was reduced from 2.0×10^{-3} g/l to 2.3×10^{-6} g/l for the first contact and to 6.7×10^{-8} g/l for the second contact. An extraction coefficient of 868 was determined which agrees favorably with literature values. This preliminary data suggests that solvent extraction may be an effective method for removing plutonium from process waste solutions.

5. The aluminum foil did not stick to either type of button.
6. The PVC plastic bag is severely discolored, weakened, and its integrity as an initial contamination barrier becomes marginal with continued storage.

PLUTONIUM STORAGE STUDIES

R. E. Giebel

Experimental studies have continued to establish practical guide lines for packaging and storing plutonium materials. Alpha and delta plutonium buttons (1500-2200 g each) were being packaged three different ways and were stored for periods of 2 weeks to 8 months. The buttons were packaged in air and in contact with aluminum foil, PVC plastic, or a metal can. Each button was buffed free of corrosion product and was weighed before packaging. The button was again buffed and weighed at the time of observation. The weight loss was used to measure the quantity of corrosion product formed. The integrity of the PVC plastic bag and sticking tendency of the aluminum foil surrounding the metal button were also evaluated.

The following observations have been made based upon 4-months of storage:

1. The major portion of the corrosion product forms within the first 2 weeks after being buffed.
2. For the packaging methods studied, the method of packaging did not influence the quantity of corrosion products formed.
3. Corrosion was very minimal for delta buttons.
4. Two to four grams of corrosion products were formed on alpha buttons.

ELECTROPLATING SUPPORT

T. A. Blatter and K. R. Souply

ELECTROPLATING OF TOOLS FOR CORROSION PROTECTION

Electroplating of common tools used in the plutonium recovery area and exposed to nitric acid fumes is under evaluation for corrosion protection purposes. Protecting the tools from corrosion will increase their longevity, reduce the potential of iron contamination in the plutonium stream, and reduce the quantity of contaminated scrap metal waste.

The tools are plated with a base of gold (0.002-in.) followed by an over plate of chromium (0.00025-in.). The plated tools are then subjected to a vacuum heat treatment for 2 hours at 600°C. For corrosion testing purposes, the plated tools are exposed to nitric acid fumes coming from a nitric acid (50 vol%) solution heated to 60°C. An as-received wrench will start to corrode after 2 or 3 hours of acid fume exposure whereas a plated wrench will withstand 256 hours of exposure. Gold-chromium plated tools have been placed in plutonium processing gloveboxes for corrosion evaluations.

GOLD PLATING STAINLESS STEEL GAS BOTTLES

An electroplating technique was developed for plating 0.001-in. of gold onto the inside of a stainless steel cylindrical (1-in. diameter by 6-in. long) gas sampling bottle. The plating was made more difficult by having only a 0.25-in.-diameter opening into the inside of the bottle. A unique fixture fabricated from Micarta® (see Figure 15) was used to shield the outer surface of the bottle. A hollow

Figure 15. Fixture Configuration with Sample Bottle.

gold anode was inserted into the bottle through the 0.25-in. hole. The gold plating solution was pumped through the hollow anode into the bottle and out through a hole in the fixture. Electrical contact was made with the bottle by means of a titanium screw in the upper portion of the fixture. The plated bottles are being used by the Mass Spectroscopy Laboratory.

The bottle surface was vapor degreased using trichloroethylene followed by anodic cleaning with an alkaline cleaner (60°C) at 6V for 1 minute. A stainless steel rod was inserted into the bottle to serve as the anode during

the anodic cleaning cycle. After a water rinse, the inside surface was subjected to an acid dip (50 vol% HCl) followed by a water rinse. A Wood's nickel strike was applied using a nickel anode rod at a current density of 100 A/ft² for 1 minute. The plating fixture with sample bottle was assembled for gold plating so as to circulate the gold plating solution through the hollow gold anode rod. The gold plating was accomplished at a current density of 5 A/ft² for 72 minutes using an AuroVel UP-24 gold bath operated at 70°C. The hollow gold anode rod was electroformed by plating onto a hollow brass tube and then dissolving away the brass with nitric acid.

ENVIRONMENTAL RESEARCH

DEVELOPMENT OF BOMB REMOVAL TRAILER

W. E. Domning and S. G. Thomas

Because of the increasing frequency of bomb threats, devices are needed for the safe removal and disposal of explosives from threatened facilities.

The use of vermiculite as a means for mitigating the effects of an explosion has been reported.¹ Tests at the Los Alamos Scientific Laboratory and by the Sandia Corporation have demonstrated the effectiveness of this material. For possible need at Rocky Flats, a bomb trailer and smaller transporter have been designed based on the use of

vermiculite as a blast suppressant. The completed units are shown in Figure 16.

The trailer unit consists of 6-foot square steel box with a 53-in. steel tank in the center of the structure forming the bomb-holding cavity. The space between the two structures is filled with vermiculite. The inside of the bomb-holding cavity contains truck tires which serve as shrapnel catchers. After an explosive device is loaded into the trailer, the cavity is filled with vermiculite and additional bags of vermiculite are piled on top of the trailer. The smaller drum-like vehicle shown in Figure 16 is a transporter to be used in transporting a device from a building to the trailer. Both units have been tested and will withstand various quantities and types of explosives postulated as potential bomb threats.

Figure 16. Bomb Trailer.

It is estimated that the explosion of 25 sticks of 40 percent dynamite would not destroy the trailer. The smaller bomb cart should contain the blast effect of four sticks of dynamite.

With trained bomb disposal experts, these vehicles comprise an effective method of dealing with potential bomb threats.

REFERENCE

1. Patent application 239,762. Rocky Flats Division, Dow Chemical U.S.A.

GLOVEBOX MATERIALS

*J. W. Lindsay, R. L. Hauser, J. F. McLachlan,
and W. H. Reid*

GLOVEBOX GASKETS

Rocky Flats glovebox gaskets are presently made of neoprene. Frequent and costly replacement of gaskets is required in the plutonium recovery glovebox lines (Building 771). The problems stem from the inherent permanent-set characteristic of neoprene and its lack of resistance to degradation by the nitric and hydrofluoric acid vapors in the line atmosphere.

Samples of a new chlorinated polyethylene rubber (CPE), produced by Dow's Louisiana Division, have been procured and tested. Tensile bars of neoprene and CPE were cut from one-eighth-in. sheet. Tests were performed to determine the effects of:

1. Acid (exposure to vapors above 13N HNO₃-1N HF solution)
2. Aging (accelerated aging at 150°F, 100% relative humidity)
3. Radiation (exposure to 1.04×10^8 Rads of gamma radiation)

Table 6 shows the results of mechanical tests performed on the tensile bars before and after exposure.

In resistance to acid exposure, CPE is distinctly better than neoprene. Changes in the two materials in the aging test are not significantly different. Flexibility is not greatly

Table 6. Comparative Exposure Tests of Neoprene and Chlorinated Polyethylene.

Exposure	Days	Ultimate Elongation (%)		Tensile Strength (psi)		Modulus (psi)	
		Neoprene	CPE	Neoprene	CPE	Neoprene	CPE
None		195	207	1015	2863	354	1143
Acid	7	70	135	358	2166	256	1121
	14	50	130	358	2243	256	1038
	21	55	130	269	1769	185	935
	28	60	115	293	1782	179	871
	35	55	120	205	1692	153	833
Aging	7	180	150	1012	2897	346	1257
	14	195	170	1089	3025	371	1282
	21	145	180	910	3000	397	1230
	28	170	160	1038	2974	397	1192
Radiation		78	35	924	2666		

affected. CPE appears to be somewhat inferior to neoprene in radiation resistance. The exposure test, however, is equivalent to many years of normal glovebox exposure.

The tests performed indicate that CPE may be well suited for use in glovebox gasketing. In fabrication trials, the Kirkhill Rubber Company has demonstrated the capability to fabricate gaskets of CPE which meet Rocky Flats use criteria. A number of gaskets have been obtained and in-use tests are being arranged.

GLOVEBOX BAGS

Large quantities of plasticized polyvinyl chloride (PVC), in the form of bags, are used at Rocky Flats for removal of materials from plutonium-containing gloveboxes. After use, most of the bags are incinerated for waste volume reduction and as a first stage in recovery of plutonium. Combustion of PVC releases hydrogen chloride which corrodes the incinerator and must be removed by caustic scrubbing from the off-gases. One solution to this problem is the incinerator development project described in a later section of this report. Another approach is to find a substitute for PVC film which does not evolve corrosive gases when it is burned.

In cooperation with the Hauser Laboratories, Boulder, Colorado (under Dow subcontract), a variety of sheet and film materials have been evaluated for possible use in glovebox bags. Mechanical properties, chemical resistance, and flammability properties were evaluated. Costs were also estimated. Along with PVC, coated polyesters, urethanes, polyolefins, ethylene vinyl acetate, polyimide, and Nylon-12 were tested. Prototype bags of each material were fabricated and evaluated.

No film examined possessed all the desirable properties of PVC. The film which most closely approached PVC in chemical resistance, flexibility, weldability, strength, tear resistance, puncture resistance, and price was ethylene vinyl acetate (EVA). This film is not as elastic, flexible, puncture proof, or fire resistant as PVC. Desirable features, however, are sufficiently attractive to justify further evaluation.

Twenty-four EVA bags made from extruded and blown tubing have been obtained. The bottom seal is heat welded. The Hauser Laboratory has fabricated and installed in the bags polyurethane O-rings for glove port attachment. These bags are completely free of halogen-containing materials. A use-test, along with further laboratory evaluation is being arranged.

REVERSE OSMOSIS FOR AQUEOUS WASTE PROCESSING

C. E. Plock

WATER RECYCLE

There are, on the average, two million gallons of cooling tower blow-down waters and seven million gallons of sanitation plant effluent discharged from Rocky Flats each month. Blow-down waters from the major cooling towers and the sanitary effluent were sampled in 55-gallon drums and processed by reverse osmosis, as described in a previous report; except, that 95 percent of the water was recovered instead of 50 to 75 percent. The larger recovery was accomplished by recirculating the concentrate stream from the reverse osmosis unit to the feed as shown in Figure 17.

Figure 17. Recirculating System.

Table 7 shows the drinking water standard as recommended by the United States Public Health Service (USPHS), followed by the concentration range of these impurities in the product waters, the average concentration of the impurities, and the rejection rate of these impurities by the reverse osmosis unit. These data are for 18 drums of cooling tower blow-down water and five drums of sanitary effluent.

Generally, the rejection rates shown in Table 7 are not as good as reported previously. This was expected because a larger percentage of the water was recovered in these tests.

Table 7. Reverse Osmosis Product Water Data.

Substances	Max. Std. Conc. (USPHS)	Product Waters					
		Cooling Towers			Sanitary Effluent		
		Conc. Range	Avg. Conc.	Rejection Rate (%)	Conc. Range	Avg. Conc.	Rejection Rate (%)
Alkyl Benzene Sulfonate (ABS)	0.5	<0.02 – 0.16	0.04	NA	0.04 – 0.11	0.07	NA
Arsenic (As)	0.001	0.002 – 0.02	0.006	84	0.003 – 0.01	0.006	80
Barium (Ba)	1.0	0.0005 – 0.007	0.0018	91	0.0007 – 0.004	0.0023	93
Beryllium (Be)	None	<0.0001 – 0.0004	0.0001	82	<0.0001 – 0.0002	0.0001	91
Boron (B)	(5.0)	0.004 – 0.030	0.010	49	0.006 – 0.030	0.015	34
Cadmium (Cd)	0.01	0.0023 – 0.010	0.0062	79	0.005 – 0.010	0.007	89
Calcium (Ca)	(200)	0.4 – 4.5	1.04	96	0.3 – 1.1	0.7	98
Chloride (Cl)	250	3.2 – 84	33	74	24 – 66	43	65
Chromium (Cr ⁶⁺)	0.05	<0.05	<0.05	NA	<0.05	<0.05	NA
Copper (Cu)	1.0	0.002 – 0.03	0.01	84	0.006 – 0.009	0.045	90
Carbon Chloroform Extract (CCE)	0.2	0.3 – 3.2	1.3	NA	0.4 – 2.6	1.2	NA
Cyanide (CN)	0.01	ANALYTICAL RESULTS INCONCLUSIVE					
Fluoride (F)	0.6 – 1.7	<0.10 – 0.20	0.14	NA	<0.10 – 0.20	0.1	NA
Iron (Fe)	0.3	0.003 – 0.70	0.054	88	0.007 – 0.03	0.015	99
Lead (Pb)	0.05	<0.0001 – 0.007	0.0011	91	0.0008 – 0.003	0.0013	98
Magnesium (Mg)	(150)	<0.05 – 0.90	0.36	94	2.5 – 6.9	4.7	81
Manganese (Mn)	0.05	0.0003 – 0.003	0.0014	93	0.001 – 0.009	0.004	86
Mercury (Hg)	(0.05)	<0.0005 – 0.004	0.0013	84	0.0006 – 0.002	0.0013	76
Nitrate (NO ₃)	45	0.17 – 6.0	1.7	81	1.4 – 3.7	2.2	76
Phenols	0.001	ANALYTICAL RESULTS INCONCLUSIVE					
Phosphate (PO ₄)	(0.2)	0.03 – 2.1	0.50	96	<0.1 – 2.9	1.3	94
Selenium (Se)	0.01	<0.01	<0.01	NA	<0.01	<0.01	NA
Silver (Ag)	0.05	<0.0001 – 0.002	0.0005	74	0.0001 – 0.002	0.0014	95
Sulfate (SO ₄)	250	<1 – 5.6	1.6	99	<1 – 3	1	99
Thorium (Th)	None	<0.0005 – 0.004	0.0014	83	0.0006 – 0.002	0.0011	80
Total Dissolved Solids (TDS)	500	20 – 191	95	87	56 – 137	82	82
Uranium (U)	(5.0)	0.02 – 0.10	0.06	82	0.03 – 0.10	0.06	80
Zinc (Zn)	5.0	<0.002 – 0.020	0.007	90	0.003 – 0.010	0.006	95

NOTES: The concentrations are reported in mg/l. The substances whose values in the USPHS column are shown in parentheses are not required by the USPHS, but are recommended by the Canadian Water Resources Commission. Substances which could be of concern to Rocky Flats are also shown, and in the USPHS column, the word "none" appears for these substances.
NA = not available.

PLUTONIUM SCAVENGING

Although aqueous waste streams from plutonium recovery operations in Building 771 meet established discard levels before being processed in the Building 774 waste treatment facility, it is desirable to further reduce the plutonium level in these wastes. Reverse osmosis is being investigated as a possible means for improving plutonium recovery efficiency and for reducing the total amount of waste that must be shipped and stored as radioactive waste.

In a preliminary test of reverse osmosis for plutonium scavenging, a synthetic plutonium solution was prepared and processed. The feed solution contained 746 ng (nanograms) of plutonium in 140 liters. The 126 liters of product water contained only 19 ng of plutonium but the overall material balance was very poor. Only 75 ng were found in the concentrate and flush solutions while about 450 ng were found in the reverse osmosis (RO) unit prefilters. Approximately 200 ng were found on the RO unit membranes when they were later disassembled and assayed.

The cause of the plutonium precipitation was probably the high pH. Reverse osmosis feed solutions should be at a pH of three or higher to prevent damage to the membranes. At that pH, however, plutonium precipitates. In future scavenging attempts the plutonium will be chelated before being processed by reverse osmosis. It will then be possible to optimize pH of the feed solution for reverse osmosis processing (5.5–6.0 pH).

REFERENCE

1. M. A. Thompson, et al., Research and Ecology Semi-Annual Report, Chemistry Research and Development, USAEC, RFP-1921-A, August 30, 1972.

FLUID BED INCINERATION

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Much plutonium contaminated combustible waste at Rocky Flats is burned to facilitate recovery of plutonium or to reduce the volume of waste which must be shipped for storage. Polyvinyl chloride sheet material is found in most waste. The burning of PVC releases hydrogen chloride which corrodes the incinerator and which must be scrubbed from the off-gas before release. In addition, high temperature incineration produces a very insoluble form of plutonium oxide, making recovery operations difficult.

Development is continuing¹ on an incineration system in which the waste is decomposed and the hydrogen chloride is neutralized in a fluidized bed of granular sodium carbonate maintained at 500°C to 550°C. Because combustion at these temperatures is not complete, a catalytic after-burner is being tested which completes oxidation of the off-gases at 500°C to 600°C as compared to 1,000°C to 1,200°C for an open flame after-burner.

The low incineration and after-burner temperatures should facilitate plutonium recovery and eliminate the need for maintaining refractory lined equipment. In addition, if hydrogen chloride neutralization is sufficiently complete, off-gas scrubbing will not be necessary and incinerator corrosion will be greatly reduced.

INCINERATOR FEED PREPARATION

All the incineration tests to date have been performed with pelletized waste material. Pellets are formed by passing the waste through a heated die where the plastic or rubber becomes partially molten and holds the remaining materials together in coherent strands. A pilot scale, 6-in. diameter hydraulically driven ram-type of extruder, has been fabricated and tested. This unit is capable of processing about 10 pounds of waste per hour.

For the extruder to function well, a reasonable mixture of plastic with the other materials must be maintained. Shredding of the waste would provide a suitable mixture for the extruder. In addition, it may prove to be possible to feed shredded waste directly to the incinerator. Shredding tests of typical waste materials were made using four different types of shredders. The materials run in these shredders are listed in Table 8.

Table 8. Waste Used in Shredding Tests.

Shredded as Mixture:

55-lb polyvinyl chloride bags
25-lb polyethylene bags and bottles
20-lb paper wiping towels

Shredded Individually:

17.5-lb scrap graphite
4 each polyethylene bottles (one gallon)
20 each Cuno FulFlo filters
50 feet Tygon tubing (5/8-in o.d.)
6 each HEPA filters (8 by 8 by 5 7/8)
5 each rolls PVC tape (two-inch)
10 each PVC O-ring bags
1 bag surgéon's gloves (~5 gallon volume)
30 each leaded gloves (30 mil)

The first three materials constitute the vast bulk of plutonium-contaminated combustible wastes which must be disposed of and the proportions are those typically observed. The materials shredded individually are occasionally found in waste and were included for completeness. Of the shredders tested, the Shred-Pax unit (American Ecology Corporation) was found to be the most acceptable for Rocky Flats-type waste materials. It is a small low speed cutter unit which could be installed in a glovebox for operation. It can be inspected for nuclear safety (buildup of plutonium residues) without disassembly and it has an over-torque device to prevent damage by tramp metal which could be introduced with the waste materials.

A rubber chopper did a superior shredding job but was eliminated from consideration mainly because it was not protected from damage by tramp metal. One hammer mill

was rejected because it did not do a satisfactory shredding job with the size of packages which will be fed to the machine. The second hammer mill did a satisfactory job with all the waste materials tested. It was rejected mainly because it was quite large and would require disassembly for nuclear safety inspection.

INCINERATOR DESIGN AND OPERATION

A 2.5-in.-diameter quartz system was used to demonstrate the feasibility of the fluid bed incinerator concept with *in situ* neutralization of hydrogen chloride.² This system incorporated, in series with the fluidized sodium carbonate incinerator bed, a static bed of Na_2CO_3 to improve HCl removal, the catalyst bed, and aqueous scrubbers to remove residual HCl.

Table 9 presents data, averaged from a number of runs, showing the chloride balance with and without Na_2CO_3 added to the waste before pelletizing.

Table 9. Percent Chloride Retained.

	Total Recovery	Lower Bed	Upper Bed	Catalyst Bed	Scrubbers	Lost
Non- Na_2CO_3 Pellets	91.1	78.4	11.6	No data	1.0	8.9
Na_2CO_3 Pellets	95.1	89.2	3.0	2.2	1.1	4.9

Tests were run in this small reactor to determine the effect of oxygen concentration in the fluidizing gas on the amount of ash generated. Ash is the residue remaining after water leaching of the contents of the fluidized bed. Data, averaged from several runs, are presented in Table 10.

A 4.5-in.-diameter quartz reactor has been set up for intermediate-scale incineration tests and to permit the secondary bed of sodium carbonate to be fluidized. Many operating features of the pilot-scale incinerator which is now being fabricated will be studied with this system. Several runs have been made on this reactor but analysis is not yet

Table 10. Percent Ash Retained.

Oxygen Conc. (%)	Ash (wt%)
0 (argon)	9.5
8.1 (in argon)	5.3
21.0 (air)	3.9

complete. The complete test system is shown schematically in Figure 18.

INCINERATOR AFTER-BURNER CATALYSTS

Since the Na_2CO_3 beds are not 100% effective in removing the HCl from the flue gas, an acceptable oxidation catalyst must remain active after being exposed to the residual HCl. A Pyrex tube was set up to allow contacting a number of possible catalysts heated to 500°C with an HCl-moist air mixture. The catalysts were exposed to the HCl-containing atmosphere for 2 hours. A methane-air mixture was then passed over each catalyst at various temperatures and the oxidation efficiencies were calculated. Table 11 lists the results of these tests. The various catalysts require different temperatures to achieve essentially 100% oxidation efficiency. The Harshaw chromic oxide-on-alumina catalyst (CR-0211T) and the copper oxide-on-alumina catalyst (Grace No. 908) both demonstrated essentially 100% efficiency by 400°C. However, the copper oxide catalyst was degraded by the HCl environment. The chromic oxide-on-alumina catalyst is the best catalyst found to date for use in the after-burner.

REFERENCES

1. M. A. Thompson, et al., Research and Ecology Semi-Annual Report, Chemistry Research and Development, USAEC RFP-1921-A, August 30, 1972, p. 36.
2. Ibid.

Table 11. Catalyst Oxidation Temperature Requirements.

Temp. (°C)	Percent Oxidation Efficiency					
	Shell 105X	Linde Zeolon 200H	Harshaw ZR-0304T	Harshaw CR-0211T	Linde 13X Series	Grace No. 908
200	0	0.89	0	0	0	0
300	0	6.14	0	13.5	0	0
400	6.72	4.8	33.59	99.95	0	99.3
500	66.67	59.96	99.99	99.99	99.99	99.88
600	97.24	99.96	99.99	99.99	99.45	99.89
700	—	99.91	—	—	—	—

Figure 18. Fluid Bed Incineration System—4.5 Inch Diameter.

EFFICIENCY OF MIST ELIMINATORS

W. E. Domning and J. A. Vigil

All HEPA filters installed in plenums at Rocky Flats are being protected from the degrading effects of fire-heated air by a water evaporative heat exchanger. The length of plenum required for heat exchange will be shorter than that required to allow fall-out of water spray. Therefore, a mist eliminator is needed to keep the filter face dry.

This study was designed to compare the effectiveness of two types of mist eliminators under various air flow rates at a water flow of 21 gpm. Test air speeds were varied from 63- to 635-feet per minute. The method for evaluating the efficiency of the eliminator consisted of placing 140, 4-in. diameter open produce cans on the floor of the test plenum

downstream from the demister. The water collected in each can was weighed after a running time of one to 1.25 hours. The amount of water sprayed into the heat exchange area was measured by a water meter. Since the cans did not cover the entire floor area downstream of the mist eliminator frame, a correction was made when efficiencies were computed. The efficiency of the chamber even without the mist eliminator would be rather high because most of the water would fall to the floor. Therefore, the high efficiencies reported in Figure 19 include the effect of gravity with the chamber.

Curves "A" and "B" are for tightly-packed fine wire mesh eliminators from two manufacturers and show maximum efficiency at 175 feet per minute with very good performance up to about 350 feet per minute. The fact that curves A

Figure 19. Efficiency as a Function of Velocity.

and B are fairly close for mist eliminators of similar constructions indicate the precision of the method of measurement. Curve "C" represents results for a coarse wire mesh. The efficiency was essentially constant over the velocity range tested. The reason for the difference in performance of eliminators of different construction is not known. It has been determined however, that the inexpensive coarse mesh mist eliminator is sufficient to prevent filter damage as evidenced by the fact that the pressure drop across a bank of HEPA filters located 6-feet downstream from the mist eliminator did not increase during the test.

HYDROFLUORINATION OF PLUTONIUM-BEARING WASTES

W. E. Domning

The use of a rotating tube hydrofluorination reactor to remove silica (SiO_2) from incinerator ash and HEPA filter media had been planned for the proposed Rocky Flats plutonium recovery building (Building 371). A previous report¹ described a particle suspension problem which could plug the off-gas system of this reactor.

When plutonium is to be recovered from incinerator ash by dissolution, other, more easily dissolved oxides such as SiO_2 are dissolved first. Since these other oxides use up the acid values in preference to plutonium, multiple contacts are necessary to obtain high plutonium recoveries.

Several methods for removing SiO_2 from incinerator ash are compared in Table 12. The hydrofluorination technique used by the Los Alamos Scientific Laboratory appears to be as efficient as the $\text{HCl-SnCl}_2\text{-HF}$ and uses wet-cake hydrofluorination which minimizes particle suspension. A process equipment change to the Building 371 flowsheet has been proposed to incorporate this process. To obtain additional operating data on this proposed process, a pilot unit is being-designed for process demonstration in Building 771. Completion is expected in the summer of 1973.

REFERENCE

1. M. A. Thompson, et al., Research and Ecology Semi-Annual Report, Chemistry Research and Development, USAEC RFP-1921-A, August 30, 1972.

Table 12. Incinerator Ash Process Comparison.

Incinerator Ash Process Comparison							
$\text{HNO}_3 - \text{HF}^a$		$\text{HCl} - \text{SnCl}_2 - \text{HF}^a$		Los Alamos		Fluorine ^a	
Percent Pu Removed	Leached Heel $\times 10^3$ Conc.	Percent Pu Removed	Leached Heel $\times 10^3$ Conc.	Percent Pu Removed	Heel Conc. $\times 10^3$	Percent Pu Removed	Heel Conc. $\times 10^3$
59.2	33.2	98.4	1.02	98.5	1.8	97.7	0.54
76.6	15.6	98.2	0.97	96.3	2.6	87.5	9.1
76.0	17.0	97.8	1.26	97.8	0.78	67.7	1.1
73.9	17.5	99.0	0.60			94.4	1.1
		95.5	1.73			97.4	0.28
		97.6	0.92				
		97.2	0.83				
		94.1	2.21				
Average:							
71.42	20.8	97.23	1.19	97.53	1.73	88.94	

^aData from D. L. Ziegler, et al., "Evaluation of Methods to Recover Plutonium From Incinerator Ash," USAEC, RFP-1723, August, 1971.