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LABORATORY INVESTIGATIONS IN SUPPORT OF
FLUID-BED FLUORIDE VOLATILITY PROCESSES

*Part XVIII. Neutron Counting as an
Analytical Method for Plutonium Fluorides*

by

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Part XVIII. Neutron Counting as an Analytical Method for Plutonium Fluorides

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ABSTRACT

Counting of neutrons generated in plutonium fluorides was investigated as a method of quantitatively determining plutonium hexafluoride (PuF_6) as well as plutonium tetrafluoride (PuF_4) alone or mixed with alumina or sodium fluoride (NaF). The plutonium fluorides were obtained by processing simulated, spent reactor fuels by the fluid-bed fluoride-volatility process. With a water-moderated detector employing four proportional counters filled with 10 atm of helium-3 (^3He), 31.8 counts/(min)(mg PuF_4) are detected, corresponding to about 15% of the neutrons emitted from PuF_4 . This sensitivity allows milligram quantities of plutonium fluorides to be determined rapidly and precisely, the accuracy being limited by the specific neutron activity of the sample. Neutron activity of a plutonium compound, from the (α, n) reaction with fluorine, varies with the alpha activity of the sample, the type of diluent (alumina or NaF), and the size of particles in the mixtures. Neutron counting rates of plutonium dioxide (PuO_2) and uranium tetrafluoride (UF_4) are detectable with the water-moderated detector, although yields of only 0.448 count/(min)(mg PuO_2) and 1.6×10^{-4} count/(min)(mg UF_4) are obtained.

Portable neutron detectors, including several scintillators and a small counter using a ^3He tube, were assembled and tested for use in surveying process equipment. For all the scintillators except one, gamma rays cause interference to an extent that prevents practical shielding. The exception is the scintillator using ^6Li glass for which gamma shielding may be practical if further development of neutron shielding for directional response is effective. Results obtained with two configurations of the ^3He detector in paraffin-cadmium neutron shields indicate that a moderately directional response can be obtained with a portable neutron detector. With a plutonium fluoride source, directional response having a ratio of maximum to minimum counting rate as high as 6.3 can be achieved with a shielded ^3He detector weighing 27 lb.

I. INTRODUCTION

The fluid-bed fluoride-volatility process applied to spent, oxidic reactor fuels uses the volatility of actinide hexafluorides to separate the actinide elements from fission-product elements.¹ The processing method uses fluid-bed reactors to carry out gas-solid reactions whereby the fuel is first oxidized to convert fuel pellets to powder and then fluorinated to form the volatile fluorides. The volatile hexafluorides of uranium, neptunium, and plutonium are distilled from the fluid-bed reactor and are purified in subsequent process steps. It is highly desirable to monitor the movement of plutonium fluorides (PuF_4 and PuF_6) in the various process steps by rapid and precise methods that are compatible with the high beta-gamma activity associated with spent reactor fuel. Chemical methods of analysis, while generally capable of high precision under ideal conditions, are time-consuming and require the withdrawal of samples from process equipment. Instrumental methods of analysis can reduce or eliminate these difficulties and can also be useful in a feedback loop to control certain phases of the process.

The high economic value of plutonium recovered in the process emphasizes the need for complete recovery and, hence, accurate analysis of plutonium-bearing materials. Many instrumental methods of analysis for plutonium are applicable to uranium with little or no modification. This report describes the development of instruments for the counting of neutrons emitted by plutonium fluorides as a result of nuclear reactions of plutonium alpha particles in the fluorine nucleus. Although the specific neutron activity of about $5000 \text{ n}/(\text{sec})(\text{g Pu})$ from plutonium fluorides (with an average energy² of approximately 1.25 MeV) is much smaller than the activity of the low-energy gamma rays and X rays emitted from plutonium, neutrons are much less attenuated than gamma rays in passing through process equipment (which is largely constructed of nickel). Furthermore, the high gamma background from fission products makes selective gamma detection difficult. Neutrons, then, appear most suitable for detecting plutonium fluorides in process equipment for which the wall thickness may not be accurately known.

Instrumental detectors desirable for process or laboratory use are of three functional types:

(1) An easily portable survey instrument that is useful for semi-quantitative in situ plutonium fluoride determinations in fixed sections of equipment. A desirable feature of such a detector would be directional properties, which would prevent interference from large, adjacent sources of plutonium fluorides.

(2) A quantitative detector, with fixed geometry relative to a sample contained in a vessel. If the vessel could be removed from the rest of

the equipment and its attendant background for counting, this detector could supplant chemical methods of analysis.

(3) An in-line instrument that indicates the rate or extent of reactions producing plutonium fluorides and therefore provides a direct means of process control.

A method of detecting neutrons may have application for more than one of the required functions. Since the specifications for the detectors are not completely defined at this time, the approach to detector development has been to determine the characteristics of potentially useful detectors applicable to all known process conditions.

II. NEUTRONS FROM PLUTONIUM FLUORIDES

A. Yield

Plutonium fluorides emit fast neutrons which arise from (α, n) reactions. Although the yield of neutrons from fluorine is relatively low,³ measurable neutron fluxes are produced from either the tetrafluoride or the hexafluoride as a result of the high specific alpha activity of plutonium. Neutrons are produced from the only naturally occurring fluorine isotope by the nuclear reaction

This reaction requires an alpha threshold energy of 2.33 MeV,⁴ which is adequately supplied by plutonium alpha particles.*

Steindler⁵ has calculated the neutron yields for oxides and tetrafluorides of several uranium and plutonium isotopes. His value for plutonium-239 tetrafluoride is 4300 n/(sec)(g Pu). If neutron yield is assumed to be only proportional to the weight fraction of fluorine in the compound of an alpha-emitting isotope, plutonium-239 hexafluoride should yield 6500 n/(sec)(g Pu). Approximately the same relative values of neutron specific activity have been measured for the corresponding uranium fluoride compounds^{6,7} (1.37 instead of 1.50).

B. Energy Spectrum

The average neutron energy from a PuF_4 source has been measured to be 1.25 ± 0.25 MeV.² A peak energy of 0.9 MeV is observed with plutonium that is predominantly ^{239}Pu . Since ^{210}Po alpha particles (5.298 MeV) have energy similar to those for ^{239}Pu (5.147, 5.134, and 5.096 MeV), no large differences would be expected for the neutron spectra generated by the alpha particles of these two nuclei in fluorine. Figure 1 is the neutron-energy spectrum for a ^{210}Po -F source as calculated by Hess.⁸ Tochilin⁹ measured the neutron yield and spectrum of a 1000-g PuF_4 source having an unspecified plutonium isotopic composition. The yield was 7700 n/(sec)(g Pu). The neutron spectrum of this source (PuF_4 -3) and that of another (PuF_4 -2) source of unspecified size and isotopic composition are shown in Fig. 2. The tails in the spectra above the theoretical maximum of 2.8 MeV for the (α, n) reaction are attributed by Tochilin to thermal-neutron fission of the plutonium in the source. The differences in the spectra, especially evident below about 1 MeV, could result from differences in size and shape of the two sources¹⁰ or from differences in isotopic composition. Relatively greater contributions of neutrons from fission

*It can be estimated that the energy of an alpha particle of $E_0 \approx 5.15$ MeV has been reduced to ~ 2.33 MeV after passage through 1 cm of dry, standard air, equivalent to 1.23 mg/cm^2 of air.

and more elastic scattering of neutrons to lower energies can occur as the source is increased in size. Neutron scattering occurs in the source container and in the environment in which the spectrum is recorded. Similar data have been obtained for ^{238}Pu -F sources.¹¹

Fig. 1. Calculated Neutron-energy Spectrum for a Polonium-Fluorine Source⁸

Fig. 2. Neutron-energy Spectra of Two PuF_4 Sources⁹

III. SURVEY OF NEUTRON DETECTORS APPLICABLE TO DETECTION OF PLUTONIUM FLUORIDES

Good reviews of neutron-detecting methods exist,^{12,13} but most of the extensive literature concerning neutron detection is not particularly helpful in selecting a detector as an instrument for quantitative analysis. Even the comparatively few quantitative applications of neutron detection in the unclassified literature^{6,7,14,15} are difficult to evaluate for use in quantitatively detecting plutonium fluorides. The difficulty involves detector sensitivity to neutrons and freedom from background interference, both of which are detector parameters emphasized in this survey. For convenience, the detectors are grouped by the nuclear reaction involved in the detection process. Cross sections of these and a variety of other neutron-induced reactions are compiled in BNL-325.¹⁶

A. Boron-10

Neutrons react with ^{10}B by either of the following reactions:

The relative contribution of these two modes of neutron reaction with ^{10}B depends upon the incident neutron energy.¹² The excited lithium nucleus shown in reaction 2b reaches the ground state by emitting a 0.480-MeV gamma ray. Since the isotopic abundance of ^{10}B in natural boron is approximately 18.8%, detectors using boron frequently contain an enriched ^{10}B content.

1. Thermal-neutron Detection with Boron-10

Reactions 2a and 2b have a combined thermal-neutron (0.025-eV) cross section of 3840 barns, which is inversely proportional to neutron velocity to about 30 keV. About 94% of the reactions produced in ^{10}B by thermal neutrons proceed according to reaction 2b with the accompanying 0.480-MeV gamma ray.

Fowler and Tunnicliffe¹⁷ developed a reliable method for using BF_3 at relatively high pressure in proportional counters. A detector these authors constructed had a 25-in. long x $2\frac{1}{2}$ -in. diam chamber filled to a pressure of 60 cm BF_3 , which was enriched to 96% ^{10}B . They calculated that this detector would be about 60% efficient[†] in detecting thermal neutrons in a small-diameter axial beam. This calculation included a correction for an inactive region of the chamber at the end where the neutron beam entered.

[†]Efficiency was probably defined as the fraction of the neutrons in a beam (parallel to the counter axis) which results in counts.

A similarly filled counter,¹⁸ 12 in. long and 1 in. in diameter, had a reported sensitivity of 4.4 ± 0.4 counts/(neutron)(cm⁻²)[†] for thermal neutrons. This counter was usable in a gamma flux of 230 R/hr from ⁶⁰Co, but lost its proportional plateau altogether when operated with 1150 R/hr from the same gamma source.

From a theoretical consideration of multiple-layer detectors, Lowde¹⁹ designed and constructed a very small and efficient ion chamber using 1.2-mg/cm² thick layers of ¹⁰B. This detector used 12 such boron layers on one side of thin aluminum backing plates arranged in pairs, with the boron layers facing away from each other, to form negative electrodes. Thin copper positive electrodes and pairs of the boron-coated plates were interleaved at 1-mm intervals. Argon at 5 atm was sufficient to maximize the counting rate with 70 V on the electrodes. Although this detector was only 24% efficient for thermal neutrons, compared to a predicted 46%, it had the same calculated efficiency as a BF₃ detector of the same size filled to 3 atm. Lowde calculated a theoretical efficiency of 95% for a detector of this construction containing 19 plates coated with 3-micron layers of ¹⁰B.

Sun et al.²⁰ constructed several scintillators for thermal-neutron detection from a boron polyester plastic containing about 20% natural boron and silver-activated zinc sulfide. A design nearly optimum with respect to efficiency was a 5-cm diam, 1.2-mm thick disc which contained one part of the polyester and two parts of ZnS(Ag) by weight. In a neutron flux of 24 n/(sec)(cm²) and 0.1 mR/hr of gamma rays from a moderated polonium-beryllium source, the efficiency of thermal-neutron detection was 33%. When the discriminator was adjusted so that the gamma contribution was less than 1% of that due to neutrons, the efficiency of thermal-neutron detection dropped to 21%.

2. Fast-neutron Detection with Boron-10

The cross section of reactions 2a and 2b is only 0.2 barn for neutrons of 1-MeV energy. Reaction 2b (and the 0.480-MeV gamma ray arising from the excited lithium nuclei) occurs in about 30 and 50% of the (α ,n) reactions for 1.8 and 2.5 MeV neutrons, respectively.¹² Because of the low cross section of ¹⁰B for fast neutrons, such neutrons are in practice often moderated to lower energies by a suitable material in the detector assembly.

Hanson and McKibben²¹ developed a "long counter," which is nearly uniform in its response to neutrons over a wide energy range. This proportional counter consisted of an 8-in. long, and 1-in. diam tube, filled to a pressure of 25 cm with BF₃ enriched to 80% in ¹⁰B. Surrounding the

[†]I.e., 4.4 ± 0.4 counts per unit flux.

tube was an 8-in. diam cylinder of paraffin. The measured sensitivity was only 1 count/ 10^5 n from a radium-beryllium source 1 m from a face of the counter. About 15% of the counting rate was from scattered neutrons, even though precautions were taken to prevent scatter contributions. A shielded version of this counter, using a layer of B_2O_3 and over it a second paraffin cylinder approximately equal in thickness to that of the first one, increased the sensitivity to higher-energy neutrons and reduced the scatter contribution by a factor of three. Energy uniformity was restored by the use of eight 1-in. holes in the front face of the inner paraffin cylinder, which increased the low-energy response. A precision long counter²² with an annular cut in place of the eight holes produced similar energy response, and for different counters of the same design counts agreed within 1% when radioactive neutron sources were measured under carefully controlled conditions.

A detector²³ using 12 commercially available $^{10}BF_3$ proportional counters embedded in an 18-in. cube of paraffin, in approximately 4π geometry, was tested. It was demonstrated to have an efficiency of about 10% for neutrons generated within a centrally located, 1-in. diam tube, having energies of 0.1 to about 2.5 MeV. The proportional counters were equally spaced in rings of 6- and 8-in. diameter around the neutron source. A diminishing efficiency for added rings of counters was observed; the relative efficiency of the inner six counters was twice that of the outer six counters.

Bollinger *et al.*²⁴ examined a number of cerium-activated glass scintillators that were loaded with either boron or lithium as oxides. One of the best of these contained 355 mg/cm³ of natural boron. For a 5-cm thickness using ^{10}B , the calculated detection efficiency for 1-MeV neutrons is 1.46%. One difficulty of these detectors is thorium impurity in the cerium, which caused 0.7 background count/(sec)(cm³) of detecting material. This can be reduced to 0.05 by reducing the thorium content of the cerium to 19 ppm.

B. Helium-3

Helium-3 reacts with neutrons according to the reaction

1. Thermal-neutron Detection with Helium-3

The thermal-neutron cross section of this reaction is 5400 barns. Mills *et al.*²⁵ tested several proportional 1-in. diam counters of various lengths containing ^3He at pressures up to 150 psi. One counter with an active length of 6 in. was compared with a BF_3 counter of similar size filled to a pressure of 65 cm (12.57 psi). At ^3He pressures above about 50 psi, this counter was about five times as

efficient in counting moderated polonium-beryllium neutrons as was the BF_3 counter. Increasing the pressure of ^3He resulted in little increase in efficiency since the counter absorbed practically all the thermal neutrons entering it at the lower ^3He pressure. Some low-energy pulses were observed from ^3He recoils and gamma rays. It was concluded that the best gamma discrimination could be obtained by using fast delay-line clipping of the pulses.

Extensive work on noble-gas scintillators has been reported by Northrop *et al.*²⁶ These investigators found that a gas mixture containing about 90% helium in xenon gives a light output which is 20% greater than pure xenon and is maximum for any such binary mixture when detecting alpha particles. The light output from scintillators of this type is mainly ultraviolet. Thus it is necessary to use a wavelength shifter or an ultraviolet-sensitive photomultiplier tube. Since the light output of these devices is quite sensitive to contaminants in the gas mixture, the scintillator is often cooled or supplied with fresh or continuously purified gas. Although, as pointed out by Huddleston,²⁷ a ^3He scintillator should have excellent gamma discrimination because of the very fast light decay, this type of counter does not appear attractive for routine use.

2. Fast-neutron Detection with Helium-3

At a neutron energy of 1 MeV, the (n,p) cross section of ^3He is 0.8 barn.

Mills *et al.*²⁵ compared the relative efficiencies of the previously described 6-in. long ^3He and BF_3 proportional counters for fast neutrons when using a polonium-beryllium source of 10^6 n/sec. With fast neutrons, the improvement of using ^3He rather than BF_3 in proportional counters was greater than that for thermal neutrons, about to the extent expected from the cross sections involved. The relative efficiency of the ^3He counter increased linearly with ^3He pressure to 150 psi; at this pressure, the ^3He counter was about 20 times as efficient for fast-neutron detection as was the 65-cm BF_3 counter.

Batchelor *et al.*²⁸ built a proportional counter for use as a neutron spectrometer using ^3He , krypton, and CO_2 at pressures of 27, 164, and 1.8 cm Hg, respectively. This counter was $9\frac{3}{8}$ in. long and $2\frac{1}{8}$ in. in diameter and had a sensitive volume of 279.5 cc. A ^3H impurity in the ^3He resulted in 1.5×10^5 counts/sec of low-energy background. These counts prevented resolution of 60-keV neutrons and contributed a continuous background into the MeV region. This situation was improved by additional purification of the ^3He by condensation of ^3H at 2.4°K.²⁹ Low-energy background was estimated to have been reduced to 800 counts/sec, which was calculated to correspond to four parts of ^3H in 10^{10} parts of ^3He . The improved detector

used ^3He , krypton, and CH_4 at pressures of 103, 340, and 0.5 cm of Hg, respectively, in the previously tested chamber. These gases required 4000 V, instead of the previously used 2600 V, to obtain the same multiplication of about 10.

C. Lithium-6

Production of charged particles by bombardment of ^6Li with neutrons involves the reaction

Naturally occurring lithium contains about 7.5% ^6Li . Reaction 4 has not often been used in conjunction with ion chambers for the detection of neutrons, since a suitable gas containing lithium has not been found¹³ and lithium-lined chambers apparently offer little advantage over those containing boron. The most frequent use of ^6Li in neutron detection has been with single crystals of lithium iodide containing up to about 0.1 m/o of a suitable metal halide as a scintillation activator.

1. Thermal-neutron Detection with Lithium-6

The cross section of reaction 4 for thermal neutrons is 945 barns. The advantage of detectors using a neutron-detecting material in the condensed phase, coupled with a relatively large cross section, is illustrated by the calculated efficiency of about 70% for thermal neutrons in a 1-cm-thick LiI crystal containing natural lithium. Such dense materials can also be so efficient in detecting gamma rays that serious interference results.

Nicholson and Snelling³⁰ reported lithium iodide to be as efficient in detecting gamma rays as an equal weight of sodium iodide. These authors compared the scintillation characteristics of tin-, europium-, and samarium-activated crystals of LiI and found the europium-activated detector to be superior in light output and stability over a period of time. The light-decay times (time required for light intensity to fall to $1/e$ of the maximum) were found to be 0.8 μsec for tin-activated, 1.4 μsec for europium-activated, and 0.25 μsec for samarium-activated crystals. Despite the large Q (4.78 MeV) of reaction 4, Nicholson and Snelling found that direct interference from gamma rays occurs above energies of 3.5 MeV.

When two or more low-energy gamma rays react in a detector within the resolving time of the associated electronic circuits, the combined light output may be as great as that from a thermal neutron. This type of background interference is called gamma pileup. The resolving time of the electronics is limited by phosphor light-decay time, since

reduction of the electronic resolving time significantly below this time seriously attenuates the output-pulse height. Accordingly, Nicholson and Snelling³⁰ tested the gamma interference to thermal-neutron detection in a 2-cm-long, and 2-cm diam natural LiI(Sn) crystal with an amplifier differentiation time of 0.8 μ sec. In this arrangement, 20 mR/hr of 2- to 3-MeV gamma rays produced a pileup count that required about 10 counts/sec from neutrons for reliable operation. The gamma pileup would be greater for the generally more desirable europium-activated crystal and for larger crystals. Crystals using either tin or samarium activation are unstable under neutron irradiation.

2. Fast-neutron Detection with Lithium-6

At a neutron energy of 1 MeV, the cross section of reaction 4 is 0.3 barn, and the calculated efficiency of a 1-cm thick ^6LiI crystal is about 0.5%.

Murray³¹ has extensively studied the scintillation response of LiI(Eu) to fast neutrons up to an energy of 14 MeV. His investigation was largely concerned with the development of a neutron spectrometer, and neutron-detection efficiency was only of secondary importance. He used various crystals from 2 to 10 mm thick containing 0.01-0.1 m/o europium. All crystals contained lithium enriched to 96% in ^6Li . His results indicate that the background problem is not minor. Slow neutrons (scattered by surrounding apparatus and especially by a Lucite light pipe used to connect the crystal to the photomultiplier), as well as gamma rays, contribute to the background.

The pulse-height spectrum for a source of monoenergetic fast neutrons reacting in LiI(Eu) is broad and flat compared to a narrow Gaussian curve obtained for slow neutrons. Murray attributes this spectrum broadening to the variable partition of energy between the alpha and triton from fast neutrons and to the relative scintillation efficiency (light output per unit particle energy expended in the crystal) of these particles. The scintillation efficiency of the triton in LiI at room temperature is about half that of the alpha. Significantly narrower, nearly Gaussian, peaks for fast neutrons were obtained when the crystal was cooled to -140 to -196°C.

One spectrum Murray obtained³¹ was that for neutrons above about 1 MeV from a 1-Ci polonium-beryllium source. With the LiI(Eu) crystal cooled to -196°C, and using a 20-channel analyzer, he obtained data for 49 energy intervals in 5 hr. The long counting time presumably was used to reduce the standard deviation of counting below the uncertainty caused by other sources of error. A background correction amounted to

about 60% of the counts recorded at 1.5 MeV. A large part of this background was generated from reactions other than ${}^6\text{Li}(n,\alpha){}^3\text{H}$. These reactions, ${}^6\text{Li}(n,dn){}^4\text{He}$, ${}^6\text{Li}(n,p){}^6\text{He}$, and ${}^6\text{Li}$ recoils, arise from the polonium-beryllium neutrons in the energy range of 7-11 MeV. Also at 1.5 MeV, the scattered neutron correction to a ${}^{235}\text{U}$ fission spectrum was only 15%. Both these spectra satisfactorily agree with data previously reported in the literature. A more recent investigation³² of the polonium-beryllium spectrum with an uncooled ${}^6\text{LiI}(\text{Eu})$ crystal and perhaps a less careful background correction results in a spectrum that is less well resolved and contains more data scatter than the one due to Murray. The effect of cooling the crystal is most pronounced for monoenergetic neutrons since broadening of the spectrum yields a large fractional increase of effective "window" needed for efficient detection. When the neutron-energy distribution is already "broad," such as the plutonium-fluorine spectra, the additional spread in apparent energy caused by an uncooled crystal appears only as a relatively small increase in the "window." Thus, crystal cooling does not appear important for limiting background in the detection of neutrons from plutonium fluoride.

D. Fission Reactions

A method of neutron detection is based on neutron-induced fission of any of several heavy elements. Since each of the two fission fragments have an average energy of about 80 MeV, an effective means is available for limiting the gamma background problem associated with neutron detection. In the application of this method, ion chambers filled with gaseous forms of fissionable elements are usually avoided because of corrosion difficulties and negative-ion formation. Thin layers of the fissionable material on the inner surfaces of the chambers are used in conjunction with a gas having suitable properties for use in either an ion chamber or a scintillation detector.

Alpha activity of fissionable elements must be considered in the detector design. Spacing of the fissionable layers close to each other or the detector walls and a sufficiently low gas pressure allow alpha particles to expend most of their energy in the detector walls. Highly charged fission fragments, by contrast, lose most of their energy at the beginning of their range and can be efficiently detected³³ at a discriminator setting that eliminates pulses from single alpha particles. Pileup of alpha pulses, however, limits the maximum amount of fissionable material that can be used in a detector. The reasonably low specific alpha activity of ${}^{235}\text{U}$ permits the use of a few grams of this material in fission detectors. The presence of ${}^{234}\text{U}$ and ${}^{236}\text{U}$ in enriched ${}^{235}\text{U}$ produces³⁴ an alpha-emission rate of about 2.4×10^3 per sec/mg of contained ${}^{235}\text{U}$. Only a few milligrams of fissionable materials with a specific alpha activity as great as that of 2.3×10^6 alphas/(sec)(mg) for ${}^{239}\text{Pu}$ can be used in fission detectors. For the materials

most commonly employed in fission detectors, spontaneous fission needs to be considered as a source of background only at very low neutron counting rates.

1. Thermal-neutron Detection with Fission Reactions

Thermal neutrons can produce fission in ^{233}U , ^{235}U , and ^{239}Pu . Thermal-neutron cross sections for such reactions are 532, 582, and 738 barns, respectively.

Baer and Bayard³⁵ constructed a 2-in. diam, 10-in. long fission chamber, containing four concentric cylinders coated on adjacent surfaces with U_3O_8 . The electrodeposited layers, enriched to more than 90% in ^{235}U , had an area of 1020 cm^2 and a thickness of 2 mg/cm^2 . Cylinder spacing was 0.15 in., and 1 atm of argon containing 1% nitrogen was used inside the fission chamber. This detector, used with an amplifier having a time constant of $0.75\text{ }\mu\text{sec}$, had a sensitivity of $0.7\text{ count}/(\text{neutron})(\text{cm}^{-2})$ and an alpha background of 5 counts/sec . At a discrimination level to produce the above sensitivity, no gamma pileup was observed from exposure to $3.3 \times 10^4\text{ R/hr}$ of gamma rays estimated to have an average energy of 2 MeV. With a gamma level of $1.1 \times 10^5\text{ R/hr}$, additional background was noted. This effect was counteracted by increasing the discriminator setting, so that the total background rate was reduced to that previously observed, essentially the background from alphas, and the loss of neutron sensitivity was 11%. This detector could operate at 80°C with only a slight reduction in pulse height.

2. Fast-neutron Detection with Fission Reactions

Fission cross sections for ^{233}U , ^{235}U , and ^{239}Pu for neutrons having energies of 1 MeV are 1.90, 1.27, and 1.85 barns, respectively. Neutrons with sufficient energy can produce fission in materials that are not thermally fissile. Several of these nuclei¹³ (and their neutron-induced fission threshold in MeV), ^{232}Th (1.3), ^{231}Pa (0.6), ^{234}U (0.4), ^{236}U (0.8), ^{238}U (1.2), and ^{237}Np (0.4), are potentially applicable to the detection of neutrons from plutonium fluoride. However, except that their use would eliminate thermal-neutron background, detectors with fission thresholds appear to be less useful than detectors using the three first-mentioned materials.

E. Proton Recoil

A method of neutron detection based on elastic recoil of protons differs from those so far discussed in that a Q value is not associated with the process. Thus pulse-height discrimination is not as effective in dealing with low-energy gamma background in proton-recoil detectors as it is in

the other types. Recoiling protons acquire all of the neutron kinetic energy in a head-on collision. Glancing collisions of monoenergetic neutrons with protons theoretically produce a spectrum that is uniformly distributed in energy from zero to that of the incident neutrons. The spectrum actually observed is distorted by multiple collisions of a single neutron in the detecting material and by various wall effects.³⁶ Low-energy protons are difficult to detect, and those produced from thermal neutrons do not have sufficient energy to be detected.

1. Thermal-neutron Detection by Proton Recoil

The preceding discussion of proton-recoil kinematics indicates that methods of detection employing proton recoil are not possible for detecting thermal neutrons. Generally, hydrocarbons are not suitable materials for detection of neutrons below about 100 keV, but by the use of hydrogen, and with considerable attention to detail, successful detection of neutrons having energies as low as 10 keV is possible.³⁷

2. Fast-neutron Detection by Proton Recoil

At a neutron energy of 1 MeV, the total cross section for hydrogen is about 4.2 barns. Total cross section is the sum of values associated with each of the processes (such as elastic scatter, inelastic scatter, and neutron-capture reactions) that remove neutrons of a given energy from a neutron beam. In hydrogen, the total cross section at 1 MeV is almost entirely due to elastic scattering.

A proportional counter lined with 1/8 in. of polyethylene and filled with argon and CO₂ was used for detecting fast neutrons at distances as great as several hundred yards from an unmoderated reactor operating at 1-1200 W.³⁸ Between 0.03 and 20 MeV, the efficiency of this detector was nearly proportional to neutron energy. At 1 MeV, the efficiency was 0.05%. No quantitative gamma-discrimination characteristics were given for this detector. A similarly lined counter,³⁹ containing an organic filling gas, was used as a nearly tissue-equivalent dosimeter. The gamma sensitivity of this dosimeter was such that 2 and 20 R/hr produced a reading equal to that for a fast-neutron dose of 0.4 and 80 mrad/hr, respectively.

Hornyak⁴⁰ developed a small molded scintillator, which has served as a prototype for several fast-neutron proton-recoil detectors. His optimum detector design consisted of a 1-in. diam, and 5/8-in. thick button, containing 1.5 g of ZnS dispersed in 10 g of Lucite mounting powder, mounted on the face of a photomultiplier tube. For monoenergetic neutrons of 0.5 MeV, the detection efficiency was 0.28%. At the same time, detection efficiency was about 0.02 and 0.0001% for gamma rays of 2.9 and 1.2 MeV, respectively. A similar 2-in. diam, 1 1/4-in. thick detector,⁴¹

containing 4 g of ZnS and 70 g of Lucite, was useful to about 10 fast neutrons/(sec)(cm²) and was unaffected by ⁶⁰Co gamma rays up to 4 R/hr. Emmerich⁴² improved the neutron-detection efficiency of the Hornyak button detector about fourfold by embedding Lucite strips in the scintillator to increase light transmission.

Organic scintillators frequently have light-decay characteristics that can be resolved into two components: a fast component and a slow component, with decay constants of a few nsec and several hundred nsec, respectively.⁴³ For protons, the intensity of the slow component is about twice the intensity for electron excitation, while the intensity of the fast component is the same in each case. Pulse-shape discrimination therefore is possible and has been successfully employed as a means of rejecting gamma-ray pulses in organic scintillators used for neutron detection.

A scintillator using the method of pulse-shape discrimination⁴⁴ was made that consisted of a commercial liquid scintillator (NE 213) in a 6-cm long, 6-cm diam glass container. This detector had an efficiency of 5 and 12% for neutrons of 1 and 3 MeV, respectively, and 0.03% for ⁶⁰Co gamma rays. Surrounding the main scintillator was about 1 cm of a plastic phosphor (NE 102) in which the incident charged particles were absorbed in the production of pulses similar to those for gamma rays. Thus neutrons and charged particle or gamma rays were discriminated against by pulse-shape analysis in this composite scintillator, which was viewed with a single photomultiplier.

F. Evaluation of Neutron Detectors for Analysis of Plutonium Fluorides

Relative detection efficiencies of neutron detectors for use with plutonium fluorides are not apparent from descriptions of performance in the literature. Direct comparison of materials for detecting neutrons (Table I) shows the calculated efficiencies of several detecting materials in configurations based on the reviewed detectors. Detecting materials are chosen for detectors whose sizes (including the photomultiplier tube for scintillators) are similar, except where limitations in useful size are known. Calculated efficiencies are shown for neutrons of 1 MeV, for neutrons having a polonium-fluorine spectrum (by using an average cross section as indicated in Table I), and for neutrons moderated from a polonium-fluorine spectrum as outlined below.

Relative efficiencies for moderated neutrons are based on the assumption that moderation increases the detection efficiency in proportion to the ratio of thermal cross section (measured at 0.025 eV) to the average cross section over the polonium-fluorine spectrum for each detecting material. These ratios of cross sections are 11,000, 7110, 2620, and 437 for ¹⁰B, ³He, ⁶Li, and ²³⁵U, respectively. These ratios are normalized to

an improvement in detection efficiency of 100 for a $^{10}\text{BF}_3$ detector when moderating with 2 in. of paraffin, as Stephens and Aceto³⁸ have shown to be attainable with a polonium-mock-fission source. Moderated detection efficiencies are 100, 65, 24, and 4 times as great as those for bare detectors using ^{10}B , ^3He , ^6Li , and ^{235}U , respectively.

TABLE I. Calculated Efficiencies of Neutron-detecting Materials for 1-MeV Neutrons and Over Polonium-Fluorine Neutron Spectrum

Detector	Atom Density, N, atoms/cm ³ x 10 ⁻¹⁹	Thickness, d, cm	Cross Section, cm ² x 10 ⁻²⁴		Efficiency for Given Neutron Spectra, % ^(b)			
			σ ₁ MeV	σ _{av} ^(a)	1 MeV	Po-F ^(c)	Po-F Moderated ^(d)	
Ion Chamber Proportional Counters								
Material	Amount							
¹⁰ BF ₃	1 atm	2.69	20	0.2	0.35	0.010	0.014	1.4
¹⁰ B layers	0.5 mg/cm ² with 1-mm spacing	30.1	20	0.2	0.35	0.085	0.147	14.7
³ He	150 psi	27.4	20	0.8	0.76	0.304	0.290	18.8
⁶ Li layer	1.25 mg/cm ² with 1-mm spacing ^(e)	126	20	0.3	0.36	0.524	0.625	14.9
²³⁵ U ₃ O ₈ layer	2 mg/cm ² with 0.15-in. spacing	2.05	20	1.27	1.33	0.038	0.037	0.147
Scintillators								
¹⁰ B glass	255 mg/cm ³	2130	5	0.2	0.35	1.46	2.546	100
¹⁰ B plastic-ZnS	-	1360	0.12	0.2	0.35	0.028	0.040	4.0
⁶ Li ^(e)	-	135	5	0.3	0.36	0.140	0.167	3.98
Anthracene ^(e)	-	4230	5	4.2	4.8	99.998	100	-
Lucite-ZnS	-	4950	1.59	4.2	4.8	31.47	-	-

$$^{(a)} \sigma_{av} = \bar{\sigma} / \bar{N}, \text{ where } \bar{\sigma} = \sum_{i=1}^{28} \frac{N_i \sigma_i}{28} \text{ and } \bar{N} = \sum_{i=1}^{28} \frac{N_i}{28}$$

with N_i from UCRL-3839 for a calculated polonium-fluorine neutron spectrum and σ_i from BNL-325 for the detecting atom at an average energy for the 0.1-MeV interval, i .

^(b) Efficiency is expressed as $1 - e^{-N\sigma d}$, where N , σ , and d are the number of reactive atoms per cm³, reaction cross section, and thickness of detector material in the direction of a beam of neutrons, respectively.

^(c) Average efficiency over 0 to 2.8-MeV neutron spectrum of the polonium-fluorine type.

^(d) Normalized to an improvement of 100 with 2 in. of paraffin surrounding a BF_3 detector.³⁸ Relative improvement of a detector with moderator is based on the ratio of thermal cross section to average cross section over polonium-fluorine spectrum. (See the text for a detailed discussion.)

^(e) Hypothetical detector.

High-pressure ^3He proportional detectors are useful in the present application because they exhibit high neutron-detection efficiency and because gamma sensitivity should be low. For small quantities of plutonium fluorides, several such detectors can be conveniently used simultaneously. Glass scintillators loaded with B_2O_3 , or scintillators using proton recoil, are also capable of high sensitivity to plutonium fluorides because high density of the detecting species is possible. The latter feature is desirable for portable detectors. However, gamma interference from plutonium or fission products appears to be a serious problem with these scintillators.

IV. EXPERIMENTAL PROCEDURE

The properties of several scintillators and a small, high-pressure ^3He proportional detector were investigated for use in a portable instrument to detect plutonium fluoride deposits in process lines and equipment by neutron counting. Quantitative neutron counting rates of plutonium fluorides and other materials of interest in a fluoride-volatility processing of spent reactor fuels were determined in fixed geometry with another type of detector. The quantitative determinations were made with two configurations of large, high-pressure ^3He proportional counters in a geometry of nearly 4π with respect to the samples. Gamma response of all neutron detectors was determined with a ^{60}Co source of 200 mR/hr measured at 2 in.

Electronic equipment of standard design with vacuum tubes was used for most of the scintillator investigations. This equipment included photo-multiplier tubes, A-70 Argonne preamplifiers, an A-100 Tullamore linear amplifier, and a PHA-2 Tullamore high-voltage supply. An RCL Model 20611, 256-channel analyzer was used to rapidly determine pulse-height spectra of all scintillators except the lithium glass.

Spectra of the latter scintillator and the proportional detectors were scanned using an ND-100 Nuclear Data, 256-channel analyzer. Transistorized electronics of an Argonne design⁴⁵ and a 412B Fluke high-voltage supply were used for the proportional ^3He tubes, as shown schematically in Fig. 3. Counting intervals were timed by counting pulses derived from the 60-cycle power line.

Fig. 3. Block Diagram of System for Helium-3 Detectors

A. Portable Detectors

1. Scintillators

Properties of scintillators using proton recoil or other nuclear reactions for detecting neutrons were examined in a laboratory containing

over 100 g of plutonium, largely as PuF_4 , which produced substantial neutron and gamma background. Gamma interference so obscured the response of a 0.3602-g source of PuF_4 that 2 in. of lead was used to shield all scintillators, except a lithium glass scintillator (for which a larger PuF_4 source was employed), from room background.

Proton-recoil response to fast neutrons was determined with two sizes of Pilot B scintillators (one of which was $1\frac{5}{8}$ in. in diameter and $3\frac{3}{4}$ in. long and the other $1\frac{1}{2}$ in. in diameter and 12 in. long) and with a Hornyak button.⁴⁰ The latter detector, containing 2.10 g of RCA-33-Z-20C silver-activated zinc sulfide thoroughly mixed with 14.1 g of Buehler Transoptic metallurgical mounting powder, was pressed into a $1\frac{1}{4}$ -in.-diam, $5\frac{5}{8}$ -in.-thick button, polished with Linde B alumina on the flat ends. These scintillators were mounted on a 6342 photomultiplier tube with Dow Corning C-20057 light-coupling compound and were protected from ambient light by several layers of aluminum foil.

Light transmission through several molded buttons was tested. These buttons contained Pilot B for its scintillating properties and also materials in which exoergic reactions with neutrons can occur. Since scintillation of Pilot B was unimpaired after it was filled to a powder and remolded, this powder was mixed with Li_2CO_3 , H_3BO_3 , or ^{10}B powders and pressed into $1\frac{1}{4}$ -in.-diam buttons. One gram of either compound or an amount of ^{10}B was mixed with 5 g of powdered scintillator. Transmission of light through the buttons was determined qualitatively by measuring with the photomultiplier tube scintillations of alpha particles impinging on the face of the button opposite the photomultiplier tube.

Gamma rays with an energy of 480 keV from the instantaneous decay⁴⁶ ($t_{1/2} = 7.7 \times 10^{-14}$ sec) of ^7Li produced in its excited state by neutron reactions in ^{10}B were briefly examined as a basis for neutron detection. These gamma rays were observed with a 2- by 2-in. $\text{NaI}(\text{Tl})$ scintillator mounted on a 6292 photomultiplier tube. A 266-mg/cm² layer of powdered ^{10}B next to the scintillator was used as an efficient converter for production of the gamma rays. The ^{10}B (about 70 thermal-neutron half-thicknesses) was evenly distributed in a polyvinyl pouch taped to the scintillator. Interference of gamma rays from plutonium in the PuF_4 source necessitated the use of 2 in. of lead between the source and the detector.

A cadmium-shielded lithium-6 glass scintillator was tested for angular response. A $3\frac{3}{8}$ -in.-diam, $1\frac{1}{8}$ -in.-thick cylinder of NE 905 scintillator, containing 17% Li_2O with a ^6Li enrichment of 96% was coupled to a 6199 photomultiplier tube with a $1\frac{3}{4}$ -in. light pipe. A 2-in.-diam Masonite cylinder was drilled to accept the scintillator, and it provided $1\frac{1}{2}$ in. of neutron moderation along the detector axis. This moderator thickness produced maximum counting rates for this detector geometry. A cylindrical shield, consisting of a 0.024-in. layer of cadmium inside a $1\frac{1}{4}$ -in. layer of

either Masonite or paraffin, surrounded the detector and extended from the front of the axial moderator to the preamplifier mounted on the opposite end of the photomultiplier tube. The only gamma shielding used was that provided by the detector components already mentioned.

After preliminary testing of the scintillator with 48.34 g of PuF_4 , the detector geometry was modified to that shown in Fig. 4 by recessing the scintillator and moderator 4 in. into the shield to narrow the neutron-acceptance angle. This modification lowered axial neutron sensitivity to an extent that required the use of an additional $5/8$ in. of paraffin for an axial moderator. Angular response was determined by rotating the detector in a horizontal plane about the glass scintillator.

Fig. 4

Cross Section of Modified Directional Detector Using Lithium-6 Glass

2. Directional Helium-3 Proportional Detectors

Angular response of a 1-in. diam, 2-in. long proportional detector containing 10 atm of ^3He was determined in each of two cadmium shields. The ^3He tube, operated proportionally with a potential of 1775 V, and its moderator were placed eccentrically in the shields, as shown in Fig. 5. This detector design provides a compromise between maximum forward and minimum reverse response to neutrons. The quantity of moderator used with the large detector was sufficient to obtain nearly a maximum counting rate of a source. The amount of moderator used with the small detector was necessarily less than that required to obtain a maximum counting rate. The shields used 0.062-in. thick cadmium with paraffin for the small detector and water for the large one. Shielding was not used on the cylindrical ends of these detectors since they were tested for angular response only in a plane passing

Fig. 5. Two Directional Neutron Detectors Using Cadmium-moderator Shields

through the center of the detector, perpendicular to the detector axis. These detectors were each 6 in. high, exclusive of the preamplifier, with diameters of $6\frac{3}{8}$ and $11\frac{1}{4}$ in. They weighed 9.3 and 27 lb, respectively.

The contribution to the total response of scattered neutrons entering the unshielded ends of the detectors was limited by measuring angular response with the detectors at least 18 in. from the nearest extraneous moderator (e.g., the concrete floor), a separation twice the greatest detector-source separation used. An indication of the influence of an extraneous moderator near the detector was determined with the small detector placed 6 in. from a concrete block wall.

B. Quantitative Determination with Water-moderated Helium-3 Detectors

Proportional detectors, 1 in. in diameter by 12 in. long and containing 10 atm of ^3He , were suspended around a sample holder in a 55-gal drum filled with water to moderate neutrons from a sample placed in the sample holder. The 5-in. diam, 12-in. long sample holder had a 7-in.-diam extension at the top to accommodate valve assemblies of laboratory vessels. The three or four ^3He tubes used were spaced equally around the sample holder, flush with its bottom, and about 2 in. from its side, as shown in Fig. 6. Although the separation between the source and the proportional detectors was greater than that for maximum counting rate, adequate sensitivity was achieved for laboratory samples. Closer spacing of the ^3He tubes and the sample holder was prevented by the 7-in.-diam extension on the sample holder and the preamplifier mounted on each ^3He tube.

Fig. 6. Diagram of Helium-3 Neutron Detector

Signals from each preamplifier were fed to a transistorized mixer and then to the amplifier (as shown in Fig. 3). All determinations with the ^3He detectors were made with a minimum discriminator setting since no interference from a 200-mR/hr (2-in.) source of ^{60}Co was observed in the sample holder. The discriminator setting appeared to have no effect on noise, which was observed occasionally. With few exceptions, notable in background counting, counting rates were determined from an accumulation of at least 10,000 counts.

Initially, counting was performed with three of the four ^3He tubes received, since the fourth tube was defective. A potential of 1175 V was

supplied to each of the three tubes by a common power supply. Neutrons from samples of PuF_4 and one sample of PuF_6 were successfully counted in a laboratory containing large amounts of plutonium fluorides, which produced a variable neutron background of about 4000 counts/min.

Determination of counting rates with four ^3He tubes required an increase of the applied potential to 1225 V to permit operation on the

Fig. 7. Voltage Plateaus of 1-in. diam by 12-in. long 10-atm Helium-3 Proportional Counters

plateau of all ^3He tubes, as shown in Fig. 7. Increasing the operating potential from 1210 to 1260 V increased the counting rate of a sample by only 0.7%. Samples of PuF_4 , PuF_4 on alumina, PuF_4 from the decomposition of PuF_6 on NaF, pellets of 5 w/o PuO_2 in UO_2 , and UF_4 were counted using the four ^3He tubes. Background during these determinations, obtained in a laboratory containing only small amounts of plutonium fluorides which were not moved during counting sessions, was nearly uniform at about 23 counts/min.

A modified procedure involving double counting of each sample and background was used, with the detector employing four ^3He tubes. Thus, noise occurring for brief periods was less likely to be unnoticed. Duplicate counting of samples also served to check the accuracy of visual positioning of samples on the detector axis. The second determination of sample counting rate was made after rotating the sample 135° around the detector axis from the position of the first determination. In this way, for example, a high counting rate obtained with the sample not on the detector axis, but near a ^3He tube during the first determination, was compensated for by a low counting rate after the rotation with the sample still not on axis and between two ^3He tubes.

V. RESULTS AND DISCUSSIONS

A. Portable Detectors

1. Hornyak Button Scintillator

Pulse-height spectra obtained with the Hornyak button are similar for operating potentials of 900, 1000, and 1100 V. Since lower counting rates at the lower potentials require more time for comparable statistics, only spectra obtained at an operating potential of 1100 V are shown. Figure 8 shows spectra for 0.3602 g of PuF_4 at two distances from the scintillator, for two gamma sources, and for background. The ratio of net counting rate obtained with the PuF_4 source at a distance of 4 in. to the counting rate at a distance of 12 in. ranges from about 11 to 6, with increasing energy, and agrees moderately well with the value of 9 expected from the inverse-square law. Channel numbers were not calibrated for neutron energy, since monoenergetic neutron sources were not available.

The similarity of the shapes of the spectra of PuF_4 and those of the gamma sources prevents the use of pulse-height techniques to discriminate against the gamma response. This similarity further suggests that the response of PuF_4 may be due almost entirely to gamma rays from plutonium in the source. This possibility is verified by spectra (Fig. 9)

Fig. 8. Gross Counting Rates from PuF_4 and Other Sources Using Hornyak Detector. (Photomultiplier potential of 1100 V.)

Fig. 9. Effect of Lead Shield on Net Counting Rate from PuF_4 Using Hornyak Detector. (Photomultiplier potential of 1100 V.)

which show the effect obtained by placing 0.134 in. of lead between the source and the detector. A reduction of two orders of magnitude in the counting rate by such shielding clearly indicated the seriousness of gamma interference. A further deficiency of this detector is the low neutron-detection efficiency, which cannot be significantly improved by increasing its thickness; ZnS(Ag) is not transparent to the light it emits.

2. Pilot B Scintillator

A $1\frac{5}{8}$ -in.-diam, $3/4$ -in.-thick Pilot B scintillator yields a low counting rate for PuF_4 , not appreciably different from background.

Fig. 10. Gross Counting Rates from PuF_4 , Cobalt-60, and Background Using a 1.5-in. diam, 12-in. long Pilot B Scintillator. (Photomultiplier potential of 1100 V.)

Figure 10 shows pulse-height spectra for 0.3602 g of PuF_4 , for ^{60}Co , and for background obtained with a 1.5-in.-diam, 12-in.-long Pilot B scintillator, with a potential of 1100 V on the photomultiplier tube. Although some differences are apparent in the shapes of these spectra, pulse-height discrimination against gamma response also is not possible with this scintillator.

Gamma interference from the PuF_4 source is indicated in Fig. 11, which shows the effect upon the PuF_4 spectrum of successive increments of 0.134-in. thick lead shields between the source and the scintillator. The large reduction in response with the use of a single thickness of lead is due almost entirely to gamma attenuation, whereas the succeeding nearly equal logarithmic decrements may be due primarily to neutron losses. Neutron losses in the lead occur by absorp-

tion and by scattering, either to a lower energy or through an angle sufficiently large to prevent interception of the neutron by the scintillator. The changes in slope of the linear portion of the spectra with successive shielding qualitatively illustrate such gamma and neutron attenuation in the lead. Gamma attenuation, relatively greater at low energies than at high energies, is indicated by a decrease in slope with a single lead thickness. Neutrons scattered to an average lower energy by the lead emphasize low-energy response, which appears, with the gamma response lessened, as an increase in slope with additional lead shielding.

Fig. 11. Net Counting Rate through Lead from a 0.3602-g PuF_4 Source, 2 in. from a 1.5-in. diam, 12-in. long Pilot B Scintillator. (Photomultiplier potential of 1100 V.)

4.5 counts/min for distances between the source and the scintillator similar to the distances between each source and the Hornyak button. The ratios of gamma-to-neutron counting rates thus obtained are 264 and 266 for the Hornyak button and the Pilot B scintillator, respectively. Although gamma interference is comparable in both scintillators, the Pilot B scintillator is not limited in thickness and neutron-detection efficiency, as is the Hornyak button.

At the operating potentials used, the 6342 photomultiplier tube without a scintillator is sensitive to gamma rays. With the ^{60}Co source 3 in. from the photocathode, integral counting rates obtained are 350,000, 60,000, 380, and 100 counts/min for operating potentials of 1100, 1000, 900, and 800 V, respectively. None of these photomultiplier gamma counts appear in a channel greater than number 128 when the electronic gain is identical to that used for the spectra shown.

Gamma interference to neutron detection with Pilot B can be limited by pulse-height discrimination if the neutron response is confined

The response to both PuF_4 neutrons and ^{60}Co gamma rays of the Pilot B scintillator, which is much larger than the Hornyak button, is greater than the corresponding response of the Hornyak button. The gamma interference in these scintillators can be quantitatively compared from data presented in Figs. 8-11. Electronic gain, operating potential, and sources are the same for these detectors, but, since distances between the sources and the scintillators are different, inverse-square approximations are necessary.

Comparison of these scintillators at channel 150 avoids inclusion of the gamma response of the photomultiplier tube, as indicated below. Net counting rates for ^{60}Co gamma rays and neutrons (i.e., scintillator response to PuF_4 through 0.134 in. of lead), respectively, are: 211 and 0.8 counts/min for the Hornyak button and 133 and 18 counts/min for the Pilot B scintillator. The latter two counting rates were calculated to correspond to 1197 and

to a peak. The spectrum produced by proton-recoil scintillations in Pilot B alone does not allow significant discrimination by this method since gamma response is of similar shape to neutron response. The desired response may be obtained by incorporation of a reactive material, which exhibits a large release of energy upon reaction with neutrons, into a composite scintillator with Pilot B.

Composite scintillators containing 5 g of Pilot B and 1 g of either Li_2CO_3 or H_3BO_3 are transparent to alpha-particle scintillations. These scintillators (with natural element loadings) are efficient enough to capture about 63 and 15% of incident thermal neutrons or to capture 99.4 and 89.4% of incident thermal neutrons with similar amounts of compounds fully enriched in ^6Li and ^{10}B , respectively. A composite of 5 g of Pilot B and as little as 50 mg of powdered boron containing 87.3% ^{10}B , which is sufficient to capture 72% of incident thermal neutrons, is not transparent to the same scintillations. Further testing of such composites, prevented at the time of the preliminary testing by malfunction of electronic equipment, does not appear warranted since a subsequently investigated lithium glass scintillator appears more promising of successful development.

3. Sodium Iodide(Tl) Scintillator with a Boron-10 Converter

Figure 12 shows spectra obtained with the NaI(Tl) scintillator for (1) 0.3602 g of PuF_4 $4\frac{3}{4}$ in. from the ^{10}B converter without moderator,

(2) 0.3602 g of PuF_4 with $1\frac{7}{8}$ in. of paraffin for maximum response, and (3) background. Gamma rays with an energy of 480 keV are observed. These gamma rays are emitted promptly after neutron capture in ^{10}B from the decay of ^7Li from its first excited state (see Eq. 2b). Severe interference from background neutrons is seen under the 480-keV peak, and the response of 380-keV gamma rays from plutonium through the source shield of 2 in. of lead is apparent at the low-energy side of the neutron peak. Integral counting rates obtained with an auxiliary single-channel analyzer for channels 60-80, as indicated on the multichannel spectra, more clearly reveal the difficulty caused by background. Integral

Fig. 12. Gross Counting Rates of PuF_4 and Background Using a 2-in. by 2-in. NaI(Tl) Crystal to Observe 480-keV Gamma Rays from (n, α) Reactions in Boron-10. (Photomultiplier potential of 600 V.)

counting rates are 412 and 360 counts/min for the moderated source and background, respectively. The background rate, however, decreases to

about 320 counts/min with a person near the detector (i.e., between it and the nearest interfering source of about 100 g of PuF_4 15 ft from the detector). Such a change in background is nearly as great as the difference between the counting rate of the source and the background counting rate. The quantity of gamma shielding necessary for laboratory use of this scintillator makes its further development for portable use unattractive.

The effect of the thicknesses of the source gamma shield and moderator on the response of a similar scintillator using a ^{10}B converter was calculated by Kearns and Peddicord⁴⁷ as an AMU-ANL Summer Engineering Practice School problem. Using a multigroup-age-diffusion computer code for a detector geometry centered on a source of PuF_4 with a bismuth gamma shield and paraffin moderator, they found that the ratio of neutron-to-gamma response increases indefinitely as the shield thickness is increased. Maximum neutron response occurs with about 4 cm of paraffin, less being required as the shield thickness is increased; but for a selected shield thickness, maximum neutron-to-gamma response is obtained with a range of paraffin thicknesses of about 5-8 cm.

4. Lithium Glass Scintillator

Angular response of the lithium glass scintillator with its modified neutron shield (see Fig. 4) is shown in Fig. 13 for a 48.34-g

Fig. 13. Angular Response of a Lithium-6 Glass Scintillator Directional Neutron Detector to 48.34 g of PuF_4 . (Source-scintillation separation of 6-3/4 in.)

source of PuF_4 6 3/4 in. from the scintillator. The inadequate shielding used produces a directional response which is the opposite of that desired: radial response is greater than axial response. Spectral response of this small scintillator to PuF_4 , ^{60}Co , and background is shown in Fig. 14. Although the neutron peak is nearly obscured by 200 mR/hr of ^{60}Co gamma rays, better resolution of the neutron peak and lessened gamma response can be expected if a relatively small amount of shielding is added to attenuate gamma rays. Perhaps directional neutron detection can be developed for this scintillator; however, further development of

this detector does not seem promising now, especially in view of the results obtained for ^3He detectors described below.

5. Helium-3 Proportional Detector

Angular responses of the two cadmium-shielded ^3He detectors are shown in Fig. 15. The directional response of the large detector is not

greatly enhanced by increasing the thickness of cadmium in the shield; the observed differences in response appear to be due to small errors in relocating the detector in its original position after altering the cadmium thickness. Maximum and minimum counting rates of both detectors occur at the designed detection angles of 0 and 180°, respectively. Shielding ratios (i.e., maximum to minimum angular counting rates) of 4.85 and 14.9 for the small and large detectors, each with the ^3He tube 9 in. from the source at a detection angle of 0°, exaggerate the relative effectiveness of the large detector. Rotation of the detectors to obtain angular response and the greater eccentricity of the large detector geometry are responsible for this exaggeration. Corrected shielding ratios, calculated with the inverse-square law for the geometry changes occurring with detector rotation, are 3.4 for the small detector and 6.3 for the large detector. The main advantage of the large detector is that at detection angles less than 60-90°, the angular response increases more rapidly than it does for the small detector.

Fig. 14. Differential Counting Rates of a Lithium-6 Glass Scintillator Directional Neutron Detector to PuF_4 , Cobalt-60, and Background. (Photomultiplier potential of 485 V.)

Fig. 15. Angular Responses of Two Shielded Detectors Using a 2-in. long, 1-in. diam, 10-atm Helium-3 Proportional Counter with a 48.34-g PuF_4 Source at Two Distances.

The effect of an extraneous moderator near the small detector on its angular response is shown in Fig. 16, obtained with this detector

Fig. 16. Effect of an Extraneous Moderator on Angular Response of 6-3/8-in. diam, Shielded Helium-3 Detector Using 48.34 g of PuF_4

6 in. from a concrete block wall and with the line connecting the centers of the source and the detector parallel to the wall. The increased scatter of neutrons from the source by the wall increases the counting rates previously obtained by 15-30% for all angles when the detector is rotated towards the wall. For rotation away from the wall, counting rates increase only near detection angles of 0 and 180°, at which angles they approach the increases of 15 and 30% obtained with detector rotation towards the wall at the same angles.

Gamma response of the ^3He tube used in these detectors is so slight that it has not been possible to measure it accurately. No statistically significant response is obtained, even with the 200-mR/hr (measured at 2 in.) ^{60}Co gamma source placed on the center of the ^3He tube.

B. Quantitative Detectors

Approximately 10 and 15% of the neutrons emitted by PuF_4 are detected with three and four ^3He tubes, respectively, in the water-moderated geometry previously described. These efficiencies are based on Steindler's⁵ value of 4300 n/(sec)(g Pu) and on specific counting rates of 20,800 and 31,800 counts/(min)(g PuF_4) (see parts 2 and 3 of this section) for these detectors.

Precision and stability of the detector using four ^3He tubes are adequate for quantitative determinations. The relative standard error for 11 determinations on different days of a single sample of PuF_4 on alumina is 0.26%. This reproducibility is comparable to that of a similar instrument.¹⁴

Variables of detector operation that limit or were thought to limit the precision obtained with any sample are discussed below. Following these are results obtained with each detector configuration for several types of fluoride-volatility laboratory samples and a discussion of sample variables that can reduce the precision obtainable with one of these types of samples.

1. Variables in Detector Operation

The effect of sample position, water level, sample container, background, detector resolving time, and sample variables on sample counting rate is for the detector using three ^3He tubes, unless otherwise noted.

a. Sample Position. Changes in counting rate with position in the sample holder of a compact neutron source containing 0.3602 g of PuF_4 are shown in Figs. 17 and 18, which indicate axial and circumferential sensitivity of the detector, respectively. Circumferential sensitivity should be more nearly uniform with four or more ^3He tubes in the detector. Although the axial sensitivity appears to be rather sharply peaked, it is uniform within $\pm 5\%$ along the detector axis for nearly 5 in. at the peak. Axial sensitivity obtained with four ^3He tubes is similar to that shown in Fig. 17, but shows less scatter because of the more nearly uniform background in the location in which it was determined. At the sample level of maximum axial sensitivity, circumferential variation is about $\pm 8\%$.

Fig. 17. Axial Sensitivity of a Water-moderated Helium-3 Neutron Detector. (Three Helium-3 tubes.)

Fig. 18. Circumferential Sensitivity of a Water-moderated Helium-3 Neutron Detector with the Source at the Circumference of, and at Several Levels above, the Bottom of the Sample Holder. (Three Helium-3 tubes.)

More uniform axial response appears difficult to achieve without a loss of detector efficiency. Neither staggering nor slanting the positions of the ^3He tubes appreciably changes the axial response. The uniformity of detector sensitivity is adequate for most samples, which usually occupy less than an inch along the detector axis.

b. Water Level. A decrease in the amount of water in the detector decreases the sample counting rate and increases the background counting rate. These effects for the detector using four ^3He tubes are shown, with statistical standard errors, in Figs. 19 and 20, respectively. A decrease of 0.4% in sample counting rate and an increase of less than 7% in background counting rate are indicated for each liter of water removed from the detector. The average evaporation rate of water from the detector is about 700 ml/day. Thus, changes in counting rates from these effects are important only during the long counting intervals necessary to precisely determine samples containing less than 1 mg of PuF_4 .

Fig. 19. Effect of Water Level on Sample Counting Rate in a Water-moderated Neutron Detector. (Four Helium-3 tubes.)

Fig. 20. Effect of Water Level on Background Counting Rate in a Water-moderated Neutron Detector. (Four Helium-3 tubes.)

c. Sample Container. Cylinders of 5/16-in. thick iron and 5/8-in. thick aluminum around a sample appear to decrease the counting rates by about 2.5 and 1.3%, respectively, when determined with 1% counting statistics (10,000 counts). The apparent decrease is most likely due solely to random changes in background at a location having a variable background of about 4000 counts/min. A secondary container of 0.1-in. thick polyethylene does not produce a detectable change in the counting rate of a sample (in 1-oz polyethylene or glass bottles and a polyvinyl bag), when determined with four ^3He tubes in a uniform background. The effect of sample container upon the neutron counting rate of fluoride samples is not significant.

d. Background. Gamma rays from the ^{60}Co source are not detectable, even in a low neutron-background location. With a neutron source of 10 g of PuF_4 about 22 ft from the detector and four ^3He tubes in the detector, the observed background of approximately 23 counts/min is increased by 27 counts/min. Neutron background in a laboratory containing about 100 g of plutonium fluorides is approximately 4000 counts/min when the detector is used with only three ^3He tubes. Variations of 10% in such background are not unusual in an active laboratory due to sources and moderators being moved.

e. Detector Resolving Time. A pulse-height spectrum obtained with 48.34 g of PuF_4 is shown in Fig. 21. The spectrum above

Fig. 21. Spectrum of a 48.34-g Source of PuF_4 Obtained with a Water-moderated Helium-3 Neutron Detector. (Three Helium-3 tubes.)

channel 105 is relatively less intense compared to the rest of the spectrum when smaller sources are observed. This effect is due to the coincidence of two or more neutron pulses taking place in the ^3He tubes within the resolving time of the detector. A knowledge of the resolving time is necessary to quantitatively determine samples for which counts are lost by these coincidences. Resolving times of 7.35 and 7.24 μsec for detectors using three and four ^3He tubes, respectively, are calculated from the counting rates of two sources and the formula⁴⁸

$$T = \frac{R_1 + R_2 - R_t - R_b}{R_t^2 - R_1^2 - R_2^2},$$

in which R_1 , R_2 , R_t , and R_b are counting rates of source 1, source 2, combined sources, and background, respectively. The higher voltage used with four ^3He tubes apparently decreases the time of ion collection sufficiently to compensate for the increased efficiency of the added ^3He tube, thus producing nearly the

same resolving time as for three ^3He tubes. Coincidence-corrected counting rates, R^* , are then calculated from the observed counting rates, the resolving time previously determined, and the formula⁴⁸

$$R^* = \frac{R}{1 - TR}.$$

Coincidence corrections greater than 30% of the observed counting rate are required for the largest amount of PuF_4 determined (134.5 g of PuF_4).

f. Sample Variables. Several sample variables other than the amount of plutonium fluorides present can influence the generation of neutrons within a sample. These variables are: plutonium specific alpha activity; concentration and specific alpha activity of other alpha emitters (especially ^{241}Am) relative to plutonium; type, particle size, and fluorine content of diluent; and uniformity of sample mixing and plutonium fluoride particle size if a diluent is present. Unfortunately, these variables cannot be sufficiently separated and controlled to determine the quantitative effect of individual sample variables on sample counting rate. The qualitative effects of the sample variables that have been observed are discussed in Section 3 below with the results obtained for typical fluoride-volatility samples.

2. Detector Using Three Helium-3 Tubes

Maximum neutron counting rates (i.e., at the detector axial position that produces the maximum counting rate) for several compact samples of PuF_4 are shown in Table II. The specific counting rate for each sample is also indicated, but this value cannot be correlated with the alpha activity of plutonium in the sample because isotopic analysis and volatility history of the samples are not completely known. Since the PuF_4 of the three smallest samples is from a common source, the large but reasonably constant background prevents precise determination of the sample containing 12.4 mg of PuF_4 .

TABLE II. Maximum Axial and Specific Counting Rates for Neutrons from Compact PuF_4 Sources in a Water-moderated Detector Using Three Helium-3 Proportional Counters

Weight of PuF_4 Source, g	Observed Counting Rate, R, counts/min	Coincidence-corrected Counting Rate, ^a R*, counts/min	Net Counting Rate, ^b counts/min	Specific Counting Rate, counts/(min)(g PuF_4)
0.3602	10,200	10,200	7,420	20,600
0.0124	3,060	3,060	299	24,100
0.3289	9,600	9,600	6,840	20,800
48.34	918,000	1,030,000	1,030,000	21,300
11.26	197,600	203,000	200,000	17,700
134.48	2,050,000	2,750,000	2,750,000	20,400
			Average	20,800

^a $R^* = R/(1 - TR)$, where T is the detector resolving time, 1.23×10^{-7} min.

^bBackground: first (three sources): 2765 counts/min; second (three samples): 2757 counts/min.

The maximum counting rate of a sample of PuF_6 , prepared by fluorination of 134.48 g of PuF_4 and condensed in a 2.5-in. diam, 4-in. long vessel, is 2,649,000 counts/min after correction for both coincidence and background. The specific counting rate of 20.4 counts/(min)(mg PuF_4) for the sample that was fluorinated can be converted to a specific counting

rate for PuF_6 by assuming a ratio of 1.37 for PuF_6 to PuF_4 neutron activity, the same ratio observed^{6,7} for the neutron counting rates of UF_6 and UF_4 . This calculated specific counting rate for PuF_6 and the observed sample counting rate indicated the presence of 94.6 g of PuF_6 . This result agrees quite well, within the limitations of the methods, with 100.9 g of PuF_6 subsequently determined by weighing. Neutrons generated by nonvolatile americium in the PuF_4 but not in the PuF_6 result in one limitation of this method. The calculated specific neutron activity of PuF_6 is too high, making the estimate of the amount of PuF_6 low by an unknown amount.

3. Detector Using Four Helium-3 Tubes

Specific neutron counting rates of samples of plutonium-bearing materials, representative of those encountered in fluoride-volatility processes, are indicated in Tables III and IV and in Fig. 22. The counting rates of these materials (5 w/o PuO_2 - UO_2 pellets, PuF_4 -NaF, and alumina- PuF_4) are discussed separately below.

Appreciable amounts of uranium fluorides are contained in many fluoride samples which are analyzed for plutonium. The interference to plutonium fluoride determination by neutrons from uranium fluorides is negligible, as expected from a consideration of the relative specific alpha activities. Specific neutron counting rates of 31.8 counts/(min)(mg) and 1.6×10^{-4} counts/(min)(mg) obtained for samples of PuF_4 and UF_4 , respectively, are in the ratio of 1.98×10^5 , which may be compared with the ratio of 1.85×10^5 for alpha activities for ^{239}Pu and ^{238}U .

TABLE III. Neutron Counting Rates of 5 w/o PuO_2 - UO_2 , Type II Pellets

Sample Weight, g	Weight of PuO_2 , mg ^a	Net Neutron Counting Rate, counts/min	Specific Neutron Counting Rate, ^b counts/(min)(mg PuO_2)
11.57	577	258.8	0.449
11.41	570	247.7	0.435
11.58	579	266.9	0.462
11.69	584	253.8	0.435
11.57	578	257.8	0.446
11.62	581	266.2	0.459
11.58	578	253.4	0.438
11.56	578	266.5	0.453
11.76	588	265.8	0.452

^aBased on nominal 5% PuO_2 . Three pellets contained 5.06, 4.88, and 4.76 w/o PuO_2 , as determined by alpha counting.

^bAverage value of all samples is 0.448 counts/(min)(mg PuO_2) with a relative standard error of 1.4%.

- TABLE IV. Neutron Counting Rates of PuF_4 - NaF Samples

Sample Weight, g	Pu, w/o	PuF_4 , mg	Neutron Counting Rate, counts/min	Specific Neutron Counting Rate, counts/(min)(mg PuF_4)	Specific Plutonium Alpha Activity, dis/(min)(mg PuF_4) $\times 10^{-8}$
3.2	0.37	16	532.4	34	1.74
20.3	0.029	7.7	290.2	38	4.4
899.2	1.78	20,800	639,000 ^a	30.6	1.67
12.8	0.512	86.4	2,925	33.9	1.67
990.7	0.319	4,170	136,600 ^a	37.1	1.67
15.72	0.17	35	1,160	33	1.67
13.58	0.136	24.4	799.7	32.8	1.67
17.65	0.132	30.7	958.5	31.2	1.67
16.04	0.126	26.7	928.5	34.8	1.67
6.82	0.125	11.2	400.4	35.7	1.67
866.3	0.110	966	37,950	39.3	1.67
175.31	0.068	160	5,899	38	-
1288.2 ^b	0.032	540	20,920	39	1.67
892.6 ^b	0.032	380	15,410	41	1.67
870.5 ^b	0.0062	71	1,977	28	1.67
895.0	0.0060	71	1,242	18	-
881.7	0.0048	54	1,052	20	-
862.0	0.0032	36	920.5	26	1.67
1166.7	0.0027	42	1,078	26	1.67
856.0	0.0022	22	561.5	25	1.67
942.4	0.0011	14	449.4	32	-
864.6	0.00098	11	289.9	26	1.67

^aCoincidence-corrected rate.^bOne analysis with sample in two containers. Fig. 22. Specific Neutron Counting Rates of Alumina- PuF_4 Samples

a. 5 w/o PuO_2 - UO_2 Pellets. Counting rates of nine 5 w/o PuO_2 - UO_2 pellets, a material representing used nuclear fuel elements and typical of the charge to fluoride-volatility fluid-bed reactors, are listed in Table III.

The average specific neutron counting rate of these pellets is 0.448 count/(min)(mg PuO₂) with a standard error of 1.4%, based on the nominal plutonium concentration (5 w/o). Analysis of the same type of pellet by an alpha-counting technique yields 4.90 w/o PuO₂ with a relative standard error of 6.5% for three determinations. For analysis of these pellets, the precision of neutron counting appears greater than that of alpha counting. The low analysis obtained for the nominal 5 w/o PuO₂ pellets by alpha counting may indicate incomplete recovery of plutonium during sample dissolution.

b. NaF-PuF₄. Counting rates of PuF₄ deposited on NaF are shown in Table IV. The specific counting rate of samples containing more than 0.006 w/o plutonium is 35.6 counts/(min)(mg PuF₄) with a standard error of 5.9%. In this concentration range, the average specific counting rate for the smaller samples, less than 20 g, is 34.1 counts/(min)(mg PuF₄) (S.E. of 3.5%); for the remaining, larger samples, it is 37.4 counts/(min)(mg PuF₄) (S.E. of 5.9%). The difference in specific counting rates of the larger and smaller samples is greater than the 10% indicated by the above counting rates since the larger samples extend significantly beyond the position of maximum axial sensitivity of the detector. The average detection sensitivity for the larger samples is estimated to be nearly 5% less than that for the smaller samples, and the difference between small and large samples is thus nearly 15%. Qualitatively, the only known difference between the two groups of samples, other than size, is the fact that different operators prepared each group of samples. Sample preparation, which includes grinding of the NaF pellets on which PuF₄ is deposited, may entirely account for the observed difference in counting rate of these two groups of samples.

Samples of NaF containing less than 0.006 w/o plutonium produce specific counting rates both smaller and more variable than samples having greater plutonium concentrations. A probable cause of such results is contamination of the sample during sample preparation for alpha counting.

The neutron counting rate obtained for the NaF sample with a specific alpha activity greater than twice that of the other samples is lower than would be expected. It is not apparent why the specific neutron counting rate of this sample is similar to that of other samples rather than being proportionally greater in relation to its greater specific alpha activity.

c. Alumina-PuF₄. In laboratory investigations of plutonium recovery from spent nuclear fuels by fluoride-volatility processing, simulated fuels are fluorinated from a fluid bed of alumina. The extent and rate of plutonium removal from the alumina (as plutonium hexafluoride) is conveniently determined by analysis of alumina samples progressively taken from the fluid bed during a fluorination experiment. The application of neutron counting to the quantitative determination of nonvolatile PuF₄

remaining in fluid-bed alumina samples is complicated by (1) neutron generation by americium, (2) possible alumina matrix changes which occur during fluorination, and (3) the difficulty of obtaining reproducible analyses for plutonium in alumina samples. Neutron counting rates of alumina-PuF₄ samples obtained successively during a single fluid-bed experiment vary as a continuous function of the plutonium concentration in the alumina. Plutonium concentration was determined by X ray or by alpha-counting techniques.

Specific neutron counting rates of alumina-PuF₄ samples obtained from six typical laboratory runs are shown in Fig. 22 as a function of plutonium concentration of the samples. As plutonium concentration decreases, the specific neutron counting rate increases, increasing most rapidly near a plutonium concentration of 0.01 w/o plutonium in the alumina. This increase in specific neutron counting rate of alumina samples during an experiment can be attributed to a progressively greater contribution of nonvolatile americium fluoride to the total neutron generation. However, physical and chemical changes in the matrix in which neutron generation takes place are also believed to influence neutron generation. Differences observed in neutron counting rates for samples from individual runs were found to correspond to known matrix differences. The scatter of data at least partly reflects the difficulty of sampling and analyzing these samples.

Neutron counting rates for samples of uniform weight from a single experiment can be extrapolated to find a residual counting rate, produced by neutrons from americium alpha particles in fluorinated alumina containing no plutonium. Such an extrapolation for one experiment (run Pu-6) indicates that plutonium charged to the alumina would have contained less than 100 ppm of americium. However, alpha counting rates for americium and plutonium in the charged material (PuF₄ in this case) show about 1400 ppm americium associated with the plutonium. From americium alpha counting rates of samples taken near the end of this experiment (run Pu-6), a value of 260-480 ppm americium in the charged plutonium was calculated, suggesting that 65-80% of the charged americium was removed from the alumina bed during volatilization of plutonium.

Apparently americium is elutriated from the fluidized alumina during an experiment. Evidence is the high specific neutron counting rate of a filter sample from run Pu-14 (Fig. 22), which suggests that americium is deposited on filters in the gas stream above the fluid bed.

The estimate of americium in the PuF₄ charged to run Pu-6, obtained by neutron counting, may have been low because of physical and chemical changes occurring in the alumina matrix during fluorination. The PuF₄ charged in this experiment produces 31.8 counts/(min)(mg PuF₄), whereas the alumina samples with the largest plutonium concentrations yield only 15-20 counts/(min)(mg PuF₄). Therefore a significant part of the alpha energy capable of producing neutrons in PuF₄ is probably dissipated in the alumina. Thus, changes in alumina particle size and fluorine concentration may alter the partition of alpha energy in the alumina-PuF₄ matrix. The

effect of such matrix changes is illustrated by ancillary experiments in which samples with high plutonium concentration from run Pu-6 were ground or immersed in a fluorinated oil-Halocarbon 208-4 ($\text{CF}_2\text{-CClF}_n$). The specific neutron counting rate of one sample decreased from 18.1 to 6.48 counts/(min)(mg PuF_4) upon grinding of the nominal 48-100 mesh alumina. In contrast, addition of Halocarbon oil increased the neutron counting rate of the ground sample to 16.7 counts/(min)(mg PuF_4), and in another sample, without grinding, from 19.1 to 34.3 counts/(min)(mg PuF_4). Both the amount of fines and the fluorine concentration of alumina from fluid beds are known to increase with continued fluorination during plutonium removal, but no further quantitative work has been done to elucidate the opposing effects of these variables on neutron counting rates. Another matrix effect, which could account entirely for the low estimate (from neutron count data) of the amount of americium charged, is the removal of americium particles from intimate association with PuF_4 as the latter is removed from alumina during fluorination. Thus, americium alpha particles, encountering proportionately fewer fluorine nuclei as PuF_4 is removed from the matrix, produce fewer neutrons in being slowed predominantly by aluminum and oxygen nuclei.

The low specific counting rates shown in Fig. 22 for samples from runs Purse-18 and Purse-19 at the higher plutonium concentrations appear consistent with the assumed matrix effects and the fact that these experiments were performed with 90% 48-100 mesh alumina and 10% fines (-100 mesh alumina), whereas 48-100 mesh alumina was used exclusively in the other runs.

Specific neutron counting rates for runs Pu-14 and Pu-15 are higher than those obtained for the other experiments, run Pu-15 having the highest rate. These counting rates show an increase that approximates the counting rates expected for the additional americium present in the alumina in these runs. The alumina charged to the fluid bed of run Pu-14, which contained residual americium from about 15 g of plutonium from previous experiments, was reused as the alumina for run Pu-15. Both runs (Pu-14 and Pu-15) were charged with about 25 g of plutonium from the $\text{PuO}_2\text{-UO}_2$ pellets used for all runs represented in Fig. 22 except Pu-6 and Pu-13. The isotopic composition and specific alpha activity of the plutonium charged as PuF_4 in runs Pu-6 and Pu-13 are slightly different from those of the other experiments.

The scatter in specific neutron counting rates of alumina samples from a single fluorination run is largely attributed to difficulty in obtaining reproducible analyses for the plutonium. For example, neutron counting data based on each of two analyses by alpha counting for two samples with originally low specific neutron counting rates are indicated in Fig. 22. The results of duplicate alpha analyses are 6.5 and 23% greater in plutonium concentration than the corresponding original analyses. Such analytical variations are probably due to segregation of PuF_4 and alumina particles during sampling handling.

VI. SUMMARY

Determination of the quantity of plutonium fluoride (PuF_4 and PuF_6) by neutron counting methods was investigated for analytical use in fluoride-volatility processes. In these processes, uranium and plutonium are recovered from spent nuclear fuels. Because of the high specific alpha activity of plutonium, significant neutron fluxes are generated in plutonium fluorides by (α, n) reactions. Neutron counting rates were determined with several hand-portable instruments for potential use in surveys of process equipment and also with a large water-moderated detector for quantitative determinations of plutonium in routine samples. Selection of specific neutron detectors for these uses was aided by a literature survey (included in this report) of methods of neutron detection.

Neutron detectors investigated for portable use are: scintillators using proton recoil (Hornyak button, Pilot B), NaI(Tl) with ^{10}B converter, and lithium-6 glass, and a small proportional detector filled to 10 atm with ^3He . Gamma-ray interference occurs in all the scintillators to the extent that shielding appears impractical except possibly for the ^6Li glass. In contrast, ^3He detectors are insensitive to plutonium gamma rays and may be useful in gamma fluxes accompanying moderate amounts of fission products.

The use of neutron shields to lessen background neutron counts from plutonium fluoride sources not being measured was investigated by determining the directional sensitivity to plutonium fluorides of portable detectors. Paraffin-cadmium shields were tested with the lithium-6 glass scintillator and with the ^3He proportional detector in two configurations. Inadequate shielding employed with the scintillator produced greater sensitivity through the shield than in the desired direction. Results with the ^3He detectors show that moderate directional sensitivity can be obtained. Values of 3.4 and 6.3 were obtained for the ratios of maximum to minimum counting rates of a sample of PuF_4 with shielded ^3He detectors weighing 9.3 and 27 lb, respectively.

Quantities of plutonium fluorides as small as a few milligrams can be accurately determined with multiple, high-pressure ^3He detectors with the sample surrounded by a moderator. About 10 and 15% of the neutrons emitted by PuF_4 are counted with either three or four ^3He tubes in such a detector, and the detector with four ^3He tubes produces 31.8 counts/(min)(mg PuF_4). Precision obtainable with a detector of this type is better than 1%, although accuracy of plutonium fluoride determinations is further limited by variables affecting the specific neutron emission rate of the sample.

The specific neutron emission rate of a sample is determined by its specific alpha activity; an increase in neutron activity is particularly evident with increased ^{241}Am concentration. Process diluents decrease neutron activity of a sample by dissipating alpha energy; the decrease depends upon both the fluoride concentration of the diluent and the sample particle size. The effects of these variables have been studied in greater detail with alumina as the diluent than with NaF as the diluent. Quantitative effects of such diluents on neutron emission rate of PuF_4 have not yet been determined. However, neutron counting appears useful as an analytical method for fluoride-volatility processes, even with diluted samples of plutonium fluorides. Specific neutron counting rates of alumina- PuF_4 samples vary smoothly with increased processing time.

APPENDIX

Neutron Counting of Sodium Fluoride Pellets

Recently, an extremely useful correlation between the neutron counting rates of NaF pellets and plutonium concentration from 0.001 to 26 w/o plutonium was determined.* This correlation is shown on a log-log plot of plutonium concentration and neutron counting rate in Fig. 23. Material balances and possibly fluorination rates will be calculated for fluid-bed

operations from this type of calibration.

Fig. 23. Plot of NaF Pellet Neutron and Plutonium Analysis Data

These NaF samples were counted in plastic bottles that contained about 0.5-1.0 kg of 1/8-in. diam, 1/8-in. long NaF pellets, containing plutonium from a common batch introduced into the pellets as PuF_6 . The samples occupied approximately 3-6 in. of the height of the containers. Several operators counted the pellets and prepared them for plutonium analysis by grinding them.

The effect of particle size of the NaF samples on the neutron counting rates is apparently minor

compared with that observed for alumina samples (Fig. 22). The original data for NaF pellets included results from six samples having a low plutonium concentration and showing considerable scatter compared to the other samples. Since other sources of error were eliminated, these six samples were recounted after being ground for sampling. In addition, five samples having a low plutonium concentration, but showing a good correlation with the remaining samples, were recounted after being ground for sampling to serve as standards. The ground standard samples produced specific counting rates 1.07 times that determined for the same material as pellets. The counting rates for the six powdered samples assumed to be in error were corrected by the factor obtained from the standards. This procedure gave a good correlation with counting rates for the NaF pellets, as shown in Fig. 23.

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