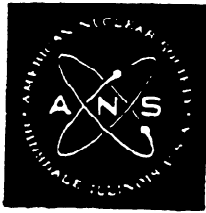L. E. HANSEN AND E. D. CLAYTON, "CRITICALITY OF PLUTONIUM COMPOUNDS IN THE UNDERMODERATED RANGE, H/PU ≤ 20," NUCL. APP. 3:481-487 (1967).

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CRITICALITY OF PLUTONIUM COMPOUNDS IN THE UNDERMODERATED RANGE, H:Pu ≤ 20

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Experimental criticality data do not exist for most plutonium compounds. To obtain guidelines for nuclear criticality safety use, a survey utilizing transport-theory calculations was made to determine the critical masses of bare and water-reflected spheres as a function of density and H:Pu ratio for 12 of these compounds in the undermoderated range (H:Pu ≤ 20). The compounds considered were: PuH_2, PuH_3, PuN, PuC, Pu_2C_3, PuO_2, Pu_2O_3, PuF_3, PuF_4, $PuCl_3$, $Pu(NO_3)_4$, $Pu(C_2O_4)_2$. Also derived were core density exponents which permit critical masses to be predicted for compounds with densities ranging down to one-fifth of their theoretical values. The validity of the calculations was examined by comparing results with the limited criticality data on homogeneous PuO_2 systems in the undermoderated range. Comparisons were also made for Pu metal systems and for three heterogeneous Pu-fueled assemblies.

INTRODUCTION

Lack of experimental data for nuclear criticality control over operations with plutonium and its various compounds frequently requires the use of computed values for guidance. In dealing with these problems often the practice of assuming a homogeneous mixture of plutonium atoms in water is adopted, without regard for the compound in which the plutonium is bound or the variation in compound density from its theoretical value.

For unreflected assemblies the critical mass for a given H:X ratio, where X is the atom density of the fissile material, varies inversely as the square of density, but in the case of a reflected assembly, no single density exponent exists. The density exponent may theoretically have values between 1.0 and 2.0, depending on the relative effectiveness of the core and reflector. The exponent will be constant, however, at a given H:X ratio for a range of densities. In addition to knowledge of critical mass values for the various plutonium compounds as a function of H:Pu ratio, the variation in critical mass with core density for a constant density reflector is of practical interest.

DENSITY EFFECTS ON CRITICAL MASS

Calculations were made to determine the bare and water-reflected spherical critical masses of 12 of the most frequently encountered compounds, in the undermoderated range (H:Pu ≤ 20). The critical masses of plutonium atoms in water were also calculated for undermoderated systems.

Since these compounds are rarely encountered at their theoretical densities, the variation of the critical mass with changes in the concentration of the compounds was also calculated.

For unreflected systems, the critical mass may be expressed[1] as $M_c \propto (\text{density})^{-2}$, and for reflected systems

$$M_c \propto (\text{core density})^{-m} (\text{reflector density})^{-n} \quad , \quad (1)$$

with the provision[1] that $m + n = 2$. If $\rho_{0\ core}$ and $\rho_{0\ refl}$ are the theoretical densities of the core and reflector, and M_{c_0} the critical mass at those densities, the critical mass M_c for other densities may be computed from the equation

$$M_c = M_{c_0} \left(\frac{\rho_{0\ core}}{\rho_{core}} \right)^m \left(\frac{\rho_{0\ refl}}{\rho_{refl}} \right)^n \quad . \quad (2)$$

For the water reflector at full density ($\rho = 1$ g/cm³), the core density exponent m can be easily determined by computing the critical mass at two

concentrations of compound in the core and making use of the equation

$$\ln M_c = -m \ln \rho_{core} + \ln A , \qquad (3)$$

where $A = M_{c_0} (\rho_{0\ core})^m$.

To determine the core density exponent, the spherical critical mass was computed for each compound at core densities ranging from $0.1 \leq \rho/\rho_0 \leq 1.0$, where ρ_0 is the theoretical concentration of the compound at a specific H:Pu ratio. Figure 1 shows the effects of the above variation in concentration on the critical mass of a typical compound, PuN. For the calculation of plutonium density at various H:Pu ratios, water and compound were mixed together by assuming additive volumes (the dry plutonium compound was assumed to exist when there was no water present).[a] The unreflected and fully water-reflected critical masses are shown in Figs. 2, 3, 4, and 5, and are tabulated with their corresponding critical radii compound concentrations in Table I. The core density exponents were found to be constant over the range $0.2 < \rho/\rho_0 \leq 1.0$. At $\rho/\rho_0 = 0.1$, the variation of $\ln M_c$ with $\ln (\rho/\rho_0)$ was no longer linear. If one were to use the given exponents for

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[a]$Pu(C_2O_4)_2$ and $Pu(NO_3)_4$ are unstable compounds and exist only when water of hydration is present.

Fig. 2.   Unreflected spherical critical mass for homogeneous Pu compound-water mixtures (computed using DTF transport-theory code). (Note suppressed zero on ordinate.)

Fig. 3.   Unreflected spherical critical mass for homogeneous Pu compound-water mixtures (computed using DTF transport-theory code).

densities with $\rho/\rho_0 < 0.2$ the predicted critical masses would be less than those computed directly at those densities by means of the DTF transport-theory code (see next section). A similar departure from linearity is also evident from material presented by Paxton[2]. The calculated values of the core density exponents and the theoretical densities of the compounds are given in Table II. The difference in not considering
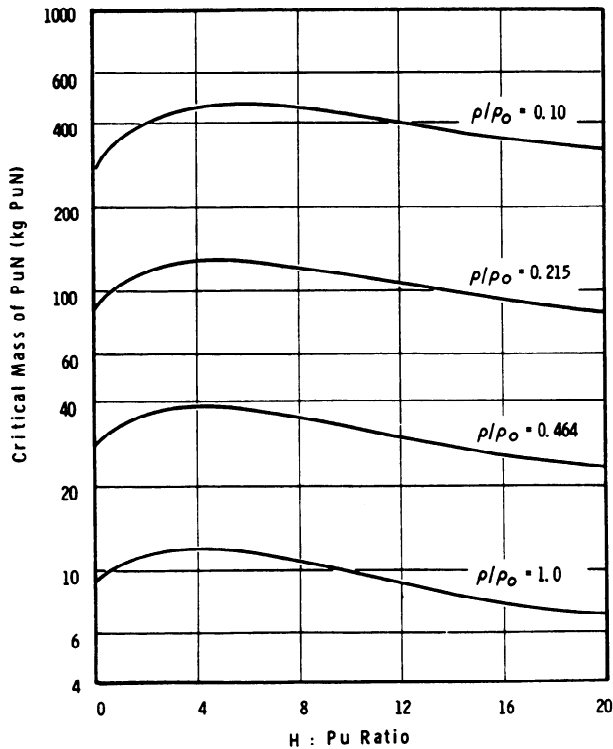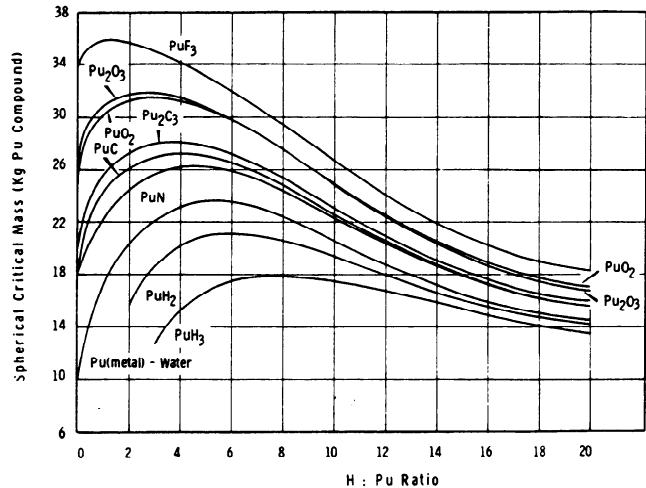

Fig. 1.   Water-reflected critical mass of PuN at various ratios of ρ/ρ_0. (Note suppressed zero on ordinate.)

Fig. 4. Water-reflected spherical critical mass of homogeneous Pu compound-water mixtures (computed using DTF transport-theory code). (Note suppressed zero on ordinate.)
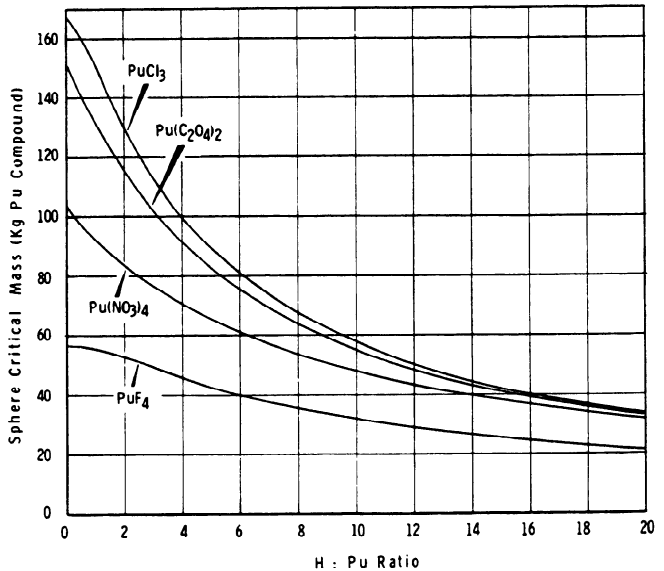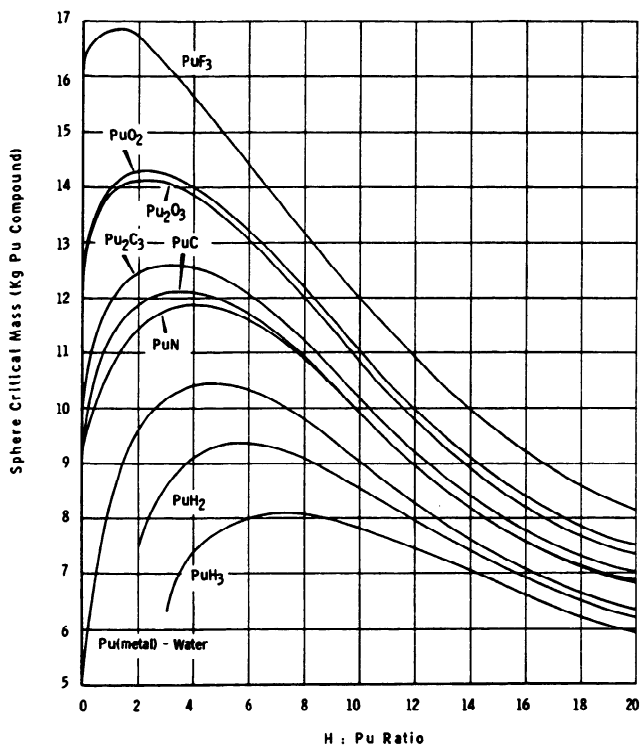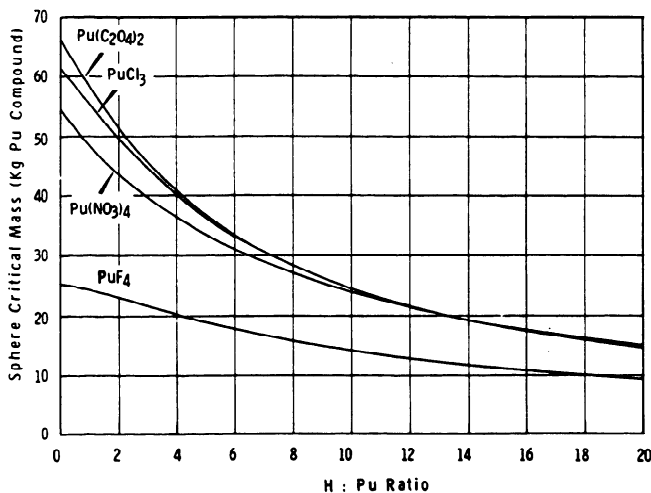

Fig. 5. Water-reflected spherical critical mass of homogeneous Pu compound-water mixtures (computed using DTF transport-theory code).

deviation of compound density from theoretical values becomes apparent when the computed critical masses are compared. Critical masses of PuO_2-water mixtures based on measured densities

and theoretical densities are presented in Fig. 6. The measured density for the PuO_2 at an H:Pu ratio of zero was, in this case[3], 5.6 g/cm^3. The corresponding theoretical and experimental concentrations, as well as an additional computed concentration curve that could be inferred from the dry-measured PuO_2 density, are shown in Fig. 7 as a function of H:Pu ratio. Since different samples of PuO_2 may well have significantly different densities, and hence critical masses, Fig. 6 serves only as an example of typical data encountered. The difference between the measured and computed curve starting with 5.6
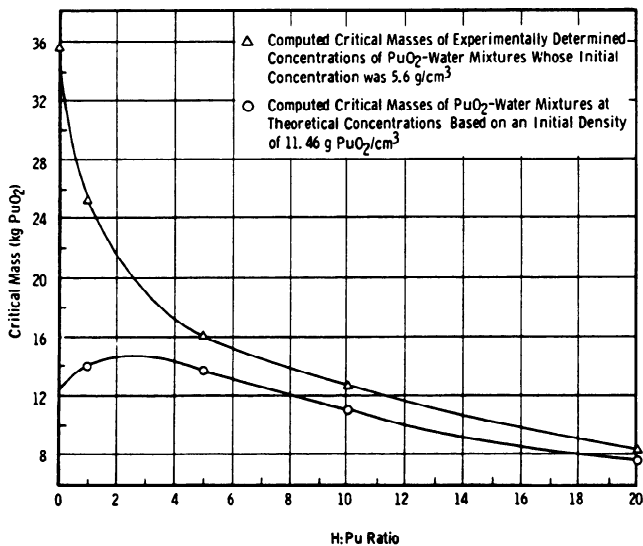

Fig. 6. Water-reflected spherical critical mass for experimental and theoretical concentrations of homogeneous PuO_2-water mixtures. (Note suppressed zero on ordinate.)
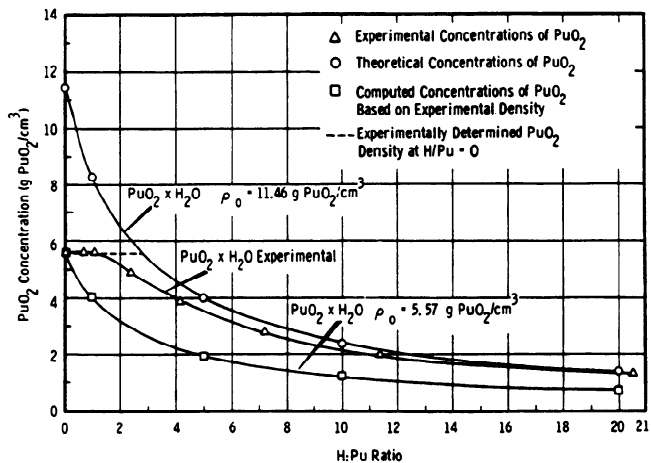

Fig. 7. Experimental and theoretical concentrations of homogeneous PuO_2-water mixtures.

TABLE I

Critical Parameters of Unreflected and Fully Water-Reflected Spheres

Compound	H/Pu	Grams of Compound per cm³	Reflected Critical Radius (cm)	Reflected Critical Mass of Compound (kg)	Unreflected Critical Radius (cm)	Unreflected Critical Mass of Compound (kg)
Pu(metal)	0	19.60	4.00	5.24	4.90	9.65
Pu(metal)	1	11.27	5.60	8.31	7.15	17.27
Pu(metal)	5	4.18	8.42	10.45	11.05	23.63
Pu(metal)	10	2.34	9.73	9.01	12.80	20.51
Pu(metal)	20	1.24	10.69	6.36	14.05	14.44
PuO₂	0	11.46	6.33	12.20	7.99	24.50
PuO₂	1	8.30	7.39	14.02	9.55	30.23
PuO₂	5	3.95	9.38	13.64	12.28	30.62
PuO₂	10	2.38	10.33	11.02	13.56	24.91
PuO₂	20	1.33	11.04	7.49	14.50	16.97
PuN	0	14.25	5.37	9.23	6.72	18.10
PuN	1	9.92	6.36	10.71	8.13	22.31
PuN	5	4.11	8.82	11.81	11.52	26.31
PuN	10	2.38	9.98	9.89	13.08	22.28
PuN	20	1.29	10.84	6.86	14.22	15.50
PuC	0	13.60	5.42	9.07	6.80	17.93
PuC	1	9.14	6.66	11.30	8.61	24.40
PuC	5	3.95	8.97	11.97	11.79	27.14
PuC	10	2.31	10.07	9.90	13.25	22.54
PuC	20	1.26	10.88	6.82	14.31	15.53
PuH₂	2	10.40	5.56	7.49	7.11	15.64
PuH₂	3	7.49	6.49	8.58	8.41	18.66
PuH₂	5	4.80	7.74	9.33	10.13	20.90
PuH₂	10	2.53	9.30	8.53	12.24	19.43
PuH₂	20	1.30	10.44	6.20	13.74	14.12
PuH₃	3	9.61	5.39	6.32	6.81	12.69
PuH₃	5	5.60	6.92	7.78	8.92	16.67
PuH₃	10	2.74	8.79	7.81	11.49	17.44
PuH₃	15	1.82	9.65	6.84	12.65	15.41
PuH₃	20	1.36	10.15	5.94	13.32	13.43
Pu₂C₃	0	12.70	5.72	9.96	7.18	19.72
Pu₂C₃	1	8.79	6.88	11.99	8.87	25.67
Pu₂C₃	5	3.94	9.09	12.37	11.90	27.82
Pu₂C₃	10	2.33	10.14	10.18	13.31	23.04
Pu₂C₃	20	1.28	10.92	7.01	14.35	15.86
Pu₂O₃	0	11.47	6.31	12.05	8.04	24.95
Pu₂O₃	1	8.24	7.39	13.91	9.64	30.88
Pu₂O₃	5	3.87	9.41	13.49	12.39	30.79
Pu₂O₃	10	2.33	10.36	10.84	13.64	24.75
Pu₂O₃	20	1.30	11.06	7.33	14.55	16.69
PuCl₃	0	5.70	13.72	61.59	19.13	167.05
PuCl₃	1	4.96	13.90	55.84	19.40	151.72
PuCl₃	5	3.27	13.81	36.07	18.68	89.28
PuCl₃	10	2.29	13.66	24.48	18.19	57.80
PuCl₃	20	1.43	13.44	14.57	17.66	33.12
PuF₃	0	9.32	7.43	16.00	9.42	32.59
PuF₃	1	7.26	8.21	16.84	10.57	35.88
PuF₃	5	3.85	9.76	15.01	12.71	33.11
PuF₃	10	2.43	10.56	11.97	13.79	26.66
PuF₃	20	1.40	11.16	8.12	14.59	18.18
PuF₄	0	7.00	9.52	25.29	12.43	56.29
PuF₄	1	5.83	10.00	24.42	13.15	55.56
PuF₄	5	3.50	10.88	18.87	14.27	42.60
PuF₄	10	2.33	11.32	14.15	14.83	31.84
PuF₄	20	1.40	11.61	9.16	15.23	20.69
Pu(C₂O₄)₂	0	4.50	15.25	66.87	20.05	152.00
Pu(C₂O₄)₂	1	4.10	15.03	58.38	19.72	131.84
Pu(C₂O₄)₂	5	3.03	14.27	36.82	18.67	82.41
Pu(C₂O₄)₂	10	2.28	13.70	24.54	17.92	54.92
Pu(C₂O₄)₂	20	1.52	13.11	14.38	17.16	32.24
Pu(NO₃)₄	0	6.20	12.84	54.94	15.88	103.96
Pu(NO₃)₄	1	5.56	12.78	48.62	15.83	92.39
Pu(NO₃)₄	5	3.94	12.65	33.38	15.83	65.49
Pu(NO₃)₄	10	2.89	12.53	23.79	15.83	48.02
Pu(NO₃)₄	20	1.88	12.36	14.91	15.80	31.10

TABLE II
Core Density Exponents for Plutonium Compounds in Water

Compound	H/Pu	Theoretical Compound Concentration ρ_0 (g/cm³)	Core Density Exponent (m)
Pu(Metal)	0	19.60	1.441
Pu(Metal)	1	11.27	1.466
Pu(Metal)	5	4.18	1.525
Pu(Metal)	10	2.34	1.560
Pu(Metal)	20	1.24	1.594
PuO₂	0	11.46[a]	1.486
PuO₂	1	8.30	1.504
PuO₂	5	3.95	1.567
PuO₂	10	2.38	1.599
PuO₂	20	1.33	1.625
PuN	0	14.25[a]	1.454
PuN	1	9.92	1.478
PuN	5	4.11	1.552
PuN	10	2.38	1.592
PuN	20	1.29	1.622
PuC	0	13.60[a]	1.453
PuC	1	9.14	1.476
PuC	5	3.95	1.548
PuC	10	2.31	1.603
PuC	20	1.26	1.671
PuH₂	2	10.40[a]	1.455
PuH₂	3	7.49	1.478
PuH₂	5	4.80	1.517
PuH₂	10	2.53	1.554
PuH₂	20	1.30	1.612
PuH₃	3	9.61[a]	1.465
PuH₃	5	5.60	1.504
PuH₃	10	2.74	1.563
PuH₃	15	1.82	1.589
PuH₃	20	1.36	1.605
Pu₂C₃	0	12.70[a]	1.466
Pu₂C₃	1	8.79	1.486
Pu₂C₃	5	3.94	1.553
Pu₂C₃	10	2.33	1.591
Pu₂C₃	20	1.28	1.621
Pu₂O₃	0	11.47[a]	1.484
Pu₂O₃	1	8.24	1.493
Pu₂O₃	5	3.87	1.558
Pu₂O₃	10	2.33	1.595
Pu₂O₃	20	1.30	1.625
PuCl₃	0	5.70[b]	1.623
PuCl₃	1	4.96	1.622
PuCl₃	5	3.27	1.659
PuCl₃	10	2.29	1.677
PuCl₃	20	1.43	1.692
PuF₃	0	9.32[b]	1.525
PuF₃	1	7.26	1.535
PuF₃	5	3.85	1.587
PuF₃	10	2.43	1.613
PuF₃	20	1.40	1.633
PuF₄	0	7.00[b]	1.558
PuF₄	1	5.83	1.567
PuF₄	5	3.50	1.605
PuF₄	10	2.33	1.622
PuF₄	20	1.40	1.641
Pu(C₂O₄)₂	0	4.50[d]	1.674
Pu(C₂O₄)₂	1	4.10	1.675
Pu(C₂O₄)₂	5	3.03	1.676
Pu(C₂O₄)₂	10	2.28	1.676
Pu(C₂O₄)₂	20	1.52	1.660
Pu(NO₃)₄	0	6.20[c]	1.697
Pu(NO₃)₄	1	5.56	1.699
Pu(NO₃)₄	5	3.94	1.693
Pu(NO₃)₄	10	2.89	1.688
Pu(NO₃)₄	20	1.88	1.681

[a] Joseph J. Katz and Glenn T. Seaborg, *Chemistry of the Actinide Elements*, Wiley, New York (1957).
[b] R. K. Steunenberg and R. C. Vogel, "Fluoride and Other Halide Volatility Processes," *Reactor Handbook, Fuel Reprocessing, Second Edition*, Vol. II, pp. 254-268, eds. S. M. Stoller and R. B. Richards, Interscience Publishers, Inc., New York (1961).
[c] Density computed by a least-squares fit of experimental data on Pu(NO₃)₄ solutions with excess nitrate.
[d] Density computed by assuming the maximum density of Pu(C₂O₄)₂·6H₂O to be 3 g/cm³ and that the water can be replaced by an equal volume of Pu(C₂O₄)₂.

g/cm³ at an H:Pu ratio of zero is due to voids in the compound not properly taken care of in the calculations.

To illustrate the use of the density scaling laws in conjunction with the density exponents computed, let us assume the material of interest is that reported above at an H:Pu ratio of zero. From Table II, the density exponent m of PuO₂ at an H:Pu ratio of zero is 1.486, and the theoretical concentration ρ_0 is 11.46-g PuO₂/cm³. From Table I, the fully water-reflected critical mass M_{c_0} of PuO₂ at an H:Pu ratio of zero and a density of 11.46 g PuO₂/cm³ is 12.20-kg PuO₂. The fully water-reflected critical mass M_c of the compound whose density ρ_{core} is 5.57-g PuO₂/cm³, can be computed using Eq. (2). The critical mass is then given by

$$M_c = 12.20\left(\frac{11.46}{5.57}\right)^{1.486}\left(\frac{1.0}{1.0}\right)^{0.514} ,$$

or $M_c = 35.6$-kg PuO₂. This procedure could likewise be followed at any specified H:Pu ratio.

Figure 8 shows the core density exponents for homogeneous mixtures of Pu atoms in water at H:Pu ratios ranging from zero to 3665, $k^\infty \approx 1.0$. The density exponents were also computed for various water-reflector thicknesses (see Fig. 9). The results show that reflector thicknesses of 15 to 20 cm correspond to effectively infinite reflectors. This agrees with the 6- to 8-in. water thicknesses which are generally accepted as being effectively infinite water reflectors. These data were computed primarily to obtain assurance that the computed density exponents are self-consistent.
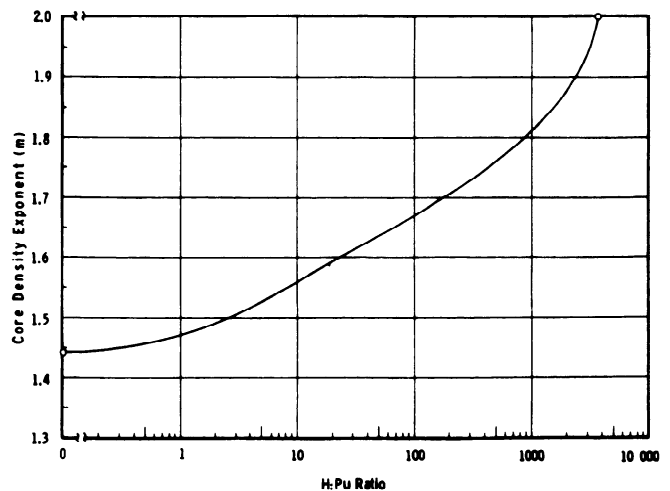

Fig. 8.   Core density exponents for fully water-reflected Pu (metal)-water spheres derived from Eq. (3). (Note suppressed zeros.)
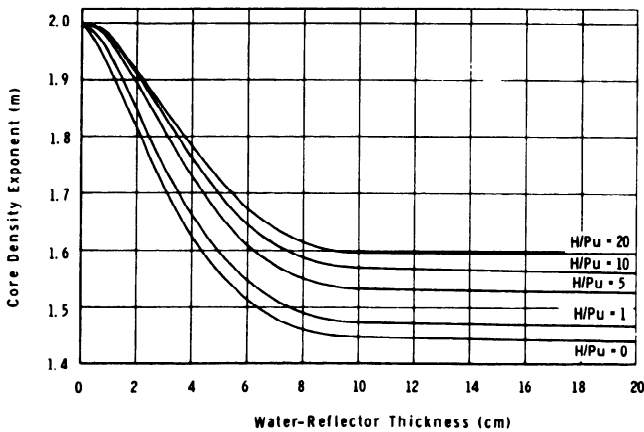
Fig. 9. Core density exponents for Pu (metal)-water systems vs water-reflector thickness derived from Eq. 3. (Note suppressed zero on ordinate.)

COMPUTATIONAL METHOD

The spherical critical radii were computed by means of the DTF multigroup, multiregion transport-theory code using an S_4 approximation in the solution of the transport equation[4]. The anisotropic scattering was defined through the first Legendre moment of the scattering kernel. Multigroup constants (18 energy groups) used in the DTF code were obtained from the GAMTEC-II computer code[5]. The fast-group constants (E > 0.683 eV) were averaged using a 64-group slowing down spectrum calculated using the B_1 approximation to the Boltzmann equation with the source defined by the [239]Pu fission spectrum. One thermal group was used, the group constants for which were averaged over a Wigner-Wilkins spectrum.

VALIDITY OF CALCULATIONS

It should be borne in mind that there is a lack of general experimental verification of the computed critical masses and density exponents derived therefrom. The results of critical experiments performed at the Pacific Northwest Laboratory may be used to partially confirm the computational method and plutonium cross sections used. Critical masses of homogeneous PuO_2-polystyrene assemblies with an H:Pu ratio of 15, both bare and Plexiglas-reflected, were reported by Richey et al.[6]. For the bare PuO_2-polystyrene assembly, 2.2 wt% [240]Pu, the critical radius in spherical geometry was derived from experiments to be 18.58 ± 0.22 cm. The calculated critical radius, using the DTF code with multigroup constants obtained from the GAMTEC-II code, was 18.31 cm. For the Plexiglas-reflected sphere, the experimentally derived critical radius was 13.54 ± 0.22 cm, which also compares favorably with the computed value of 13.46 cm. The critical height of a bare parallelepiped whose base was a square 30.68 cm on a side was measured to be 32.84 ± 0.52 cm. The value computed using the DTF code was 33.95 cm.

Critical data from recent experiments on heterogeneous rectangular parallelepipeds composed of alternate layers of Plexiglas and PuO_2-polystyrene (H:Pu = 15), provide data at three additional H:Pu ratios: 22, 35, and 39. These H:Pu ratios were obtained by varying the thickness of Plexiglas and fuel-bearing cubes. Measured and calculated critical dimensions are compared below. For these more complex heterogeneous slab reactors, the computed critical heights (and masses) are within 10% of the measured values.

	H:Pu (Average Over Core)	Measured Critical Mass (kg Pu)	Length (cm)	Width (cm)	Measured Critical Height (cm)	Computed Critical Height (cm)
Alternate layers of 3-in.-thick fuel blocks and 1-in. Plexiglas	22	26.4	31.0	31.8	33.4	33.8
Alternate layers of 2-in.-thick fuel blocks and 2-in. Plexiglas	35	25.0	31.1	41.4	35.6	38.8
Alternate layers of 1-in.-thick fuel blocks and 1½-in. Plexiglas	39	24.3	36.0	50.6	28.2	27.2

To compute the critical height of the parallel-epipeds, since DTF is a one-dimensional code, a buckling correction was used to account for the leakage in the transverse directions. The fuel and Plexiglas regions of the heterogeneous assemblies were handled discretely.

The water-reflected spherical critical mass of ^{239}Pu, 19.6 g/cm^3, derived from experiments at Los Alamos[7,8], is given as $\approx$ 5.6 kg. The computed value for this example is 5.24 kg, which agrees to within 7%. The bare critical mass was reported to be 10.0 kg, which compares quite favorably with the computed value of 9.65 kg.

The experimental data available indicate for the moderation ratios of interest, that the spherical critical masses of plutonium systems may be computed to an accuracy of about 10%, and it is difficult to see how the calculations could be off by such an extent that the critical masses for any of the water-reflected compounds would differ by as much as 20% from measurements of the systems defined.

Core density exponents for plutonium atoms in water as computed by W. R. Stratton with DTK and reported by Paxton may be compared[5] with values given in Fig. 7. Stratton's values for plutonium, obtained using the Hansen-Roach cross-section set, fall within about ± 3% of those given here. For a variation of five in density (i.e., ρ/ρ_0 = 0.2), with this uncertainty in exponent, the difference in critical mass would be 10% or less. This assumes that the same critical mass at theoretical density is used to make both predictions. The Hansen-Roach cross-section set, however, has been shown to yield results inferior to those obtained using cross sections derived from the GAMTEC-II code[9].

CONCLUSIONS

By making use of the computed critical masses and core density exponents, the critical masses for the given compounds may be predicted for any concentration down to 0.2 of the theoretical concentration at a specified H:Pu ratio. The use of these data, in conjunction with density relationships, provides a simple method of obtaining estimates of the spherical critical mass of some of the most frequently encountered plutonium compounds, i.e., plutonium in combination with elements of atomic number Z $\leq$ 17. Although the available data indicate the calculations are conservative for spherical systems, the results should be used with caution until additional confirming experimental data are available. However, the results can provide guidance for nuclear criticality control.

REFERENCES

1. C. M. NICHOLLS, E. R. WOODCOCK, and A. H. GILLIESON, "Criticality," *Nuclear Science and Technology 1, Chemical Processing of Reactor Fuels*, p. 394, Academic Press, Inc., New York (1961).

2. H. C. PAXTON, "Criticality Control in Operations With Fissile Material," LA-3366, Los Alamos Scientific Laboratory, January 1966.

3. E. D. CLAYTON, "Nuclear Safety in Chemical and Metallurgical Processing of Plutonium," *Criticality Control in Chemical and Metallurgical Plant*, p. 372, Karlsruhe Symposium, European Nuclear Energy Agency (1961).

4. G. B. CARLSON, W. J. WORLTON, G. GUBER, and M. SHAPIRO, "DTF Users Manual," UNC Phys/Math 3321, Vol I, United Nuclear Corporation (1963).

5. L. L. CARTER, C. R. RICHEY, and C. E. HUGHEY, "GAMTEC-II: A Code for Generating Consistent Multi-Group Constants Utilized in Diffusion and Transport Theory Calculations," BNWL-35, Battelle Northwest Laboratory (March 1965).

6. C. R. RICHEY, J. D. WHITE, E. D. CLAYTON, and R. C. LLOYD, "Criticality of Homogeneous Plutonium Oxide-Plastic Compacts at H:Pu = 15," *Nucl. Sci. Eng.*, **23**, 150 (October 1965).

7. G. A. JARVIS, G. A. LINENBERGER, J. D. ORNDOFF, and H. C. PAXTON, "Two Plutonium Metal Critical Assemblies," *Nucl. Sci. Eng.*, **8**, 525 (1960).

8. H. C. PAXTON, J. T. THOMAS, A. D. CALLIHAN, and E. B. JOHNSON, "Critical Dimensions of Systems Containing ^{235}U, ^{239}Pu, and ^{233}U," Technical Note No. TID-7028, Div. of Tech. Info. Exten., USAEC (June 1964).

9. C. R. RICHEY, "Theoretical Analyses of Homogeneous Plutonium Critical Experiments," *Trans. Am. Nucl. Soc.*, **8**, 515 (October 1966). Submitted March 1967 for publication in *Nucl. Sci. Eng.*