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FURTHER CONSIDERATIONS OF CRITICALITY IN RECUPLEX AND POSSIBLE SHUTDOWN MECHANISM

By

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May 31, 1963

HANFORD ATOMIC PRODUCTS OPERATION
RICHLAND, WASHINGTON

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INTRODUCTION - SUMMARY

Further considerations are given of the Recuplex criticality incident in the 234-5 Building on April 6, 1962. Criticality occurred in a cylindrical vessel about 17½-inches in ID (vessel K-9); the unit became critical when 1400 - 1500 g of Pu in the form of plutonium nitrate solution were inadvertently transferred to the vessel.

The first section of this paper describes the neutron multiplication measurements which were made during the draining of Pu solution from vessel K-9. Subsequent sections include the results of further multigroup diffusion theory calculations which were made, based on the exact chemical analysis of the solution remaining in K-9 at the time of draining. A further effort was made to improve the earlier estimates of critical mass and volume which were calculated for one and two molar plutonium nitrate solutions. Remarks are also given concerning an apparent "shortage of plutonium". An alternate shutdown mechanism is discussed based on mass transfer of Pu from an aqueous phase into an organic phase with subsequent settling of the heavier organic phase (containing concentrated Pu) to the bottom of the vessel.

ESTIMATES OF CRITICALITY

1. Value Derived from In Situ Neutron Multiplication Measurements

Critical Mass Physics personnel set up three complete neutron monitoring channels in the 234-5 Building. The electronics and associated recorders were located in Corridor 912 near the entrance to Corridor 3.

The Robot Monitor positioned the first two counters on the floor behind the SE hood at about 8 feet from vessel K-9 (the criticality vessel) on April 13. These counters were perhaps the only units in the area sensitive enough, and at the same time strategically located,

to obtain any useful information on vessel K-9 while in the subcritical state.

These two units were the constituent elements of channels No. 1 and No. 3 from the safety circuits at the Critical Mass Laboratory. These are low level startup channels for use in the critical experiments with plutonium nitrate solutions. One detector was a fission chamber, and the other a neutron sensitive scintillation crystal (sensitive to both neutrons and gamma rays). The detectors were mounted in paraffin moderators similarly as used in criticality experiments at the Critical Mass Laboratory.

As used in criticality experiments, the fission chamber was normally positioned about one foot from the surface of the vessel; the scintillation detector, being more sensitive, was positioned about 15 to 18 feet from the vessel. Thus, the fission chamber was ~ 7 feet further away while the scintillation counter was actually about 7 to 10 feet closer in comparison to K-9.

During the draining of vessel K-9, it was possible to obtain an estimate of the critical volume from the change in neutron flux, i.e., from the inverse multiplication curve. Since the draining process was not continuous, but somewhat intermittent, it was difficult to obtain an accurate correlation of the observed flux values with solution volume in K-9. Also, there was some question concerning the holdup in the line from K-9 to the receiver vessel.

During the draining process, weight measurements were made of the solution in the receiver vessel. From these measurements, and a correlation in time with the flux measurements, it was possible to associate the proper flux values with solution volume remaining in vessel K-9 (subject to the line holdup uncertainty).

From the neutron flux measurements during the draining process, the critical volume in K-9was estimated to be ~ 44 ± 1 liters. The inverse multiplication curve is shown in Figure 1. This would then be the critical volume for solution of the same composition as existed in vessel K-9 at the time of draining--for a solution containing ~ 35 g Pu/ℓ and ~ 2M nitrate.

For this solution the critical mass in K-9 would be ~ 1.54 Kg Pu -- or the vessel contained ~ 90% of the critical mass (k_{eff} ~ 0.98).

2. Calculated Values of Criticality from Multi-Group Diffusion Theory

The HFN multi-group diffusion code was used to compute the critical radius for a bare sphere of the solution found in K-9. The radius was used to determine the critical buckling of the solution. This buckling was then in turn used to determine the critical height (and volume) of solution in the cylindrical K-9 vessel.

The calculated value of 43.3 liters compared favorably with the measured value of 44 ± 1 liters. The two values were brought into final agreement by an adjustment of the radial extrapolation length for the glass vessel (only a slightly adjustment of 0.1-in was required from the value assumed initially). In later calculations, the adjusted radial extrapolation length of 2.69 cm was used.

The measurements and calculations gave a value of the critical volume for solution at 35 g Pu/ℓ. The vessel was never actually critical at this concentration. The concentration during initial criticality, before evaporation and loss of water, would have been less. Adding water to bring the volume up to 46 liters would result in a Pu concentration of ~ 30 g Pu/ℓ.

The critical radii of bare spheres were calculated for $Pu(NO_3)_4$ solutions, starting with the solution composition in K-9 at the time

of draining, and then by adding water to the 39 liter volume. The effect of Pu^{240} was also accounted for in these calculations.

The critical radii of the bare spheres were then used to obtain buckling values as a function of the solution concentration. These values were in turn used to compute the critical solution height as a function of Pu concentration in Vessel K-9, through use of the following relationship:

$$\text{Material Buckling} = \frac{(2.4048)^2}{(R_c + \lambda_r)^2} + \frac{\pi^2}{(h_c + \lambda_t + \lambda_b)^2}$$

with

R_c = 22.07 cm (inside radius of cylindrical vessel)

λ_r = 2.69 cm (radial extrapolation length)

λ_t = 2.2 cm (top extrapolation length)

λ_b = 4.3 cm (bottom extrapolation length)

The thickness of the pyrex glass vessel wall was 0.8 cm; the bottom of the vessel consisted of a steel plate one inch thick. The results of the constant buckling conversions are shown graphically in Figure 2 and tabulated below.

Calculated Critical Volumes and Masses of Pu in Vessel K-9 (Concentration Varied by Adding Water to 39 Liters of Pu Solution at 35 g Pu/ℓ)

Pu Concentration	Critical Buckling (10^{-6} cm^{-2})	Critical Height	Critical Volume	Critical* Mass of Pu
35 g Pu/ℓ	0.017351	28.8 cm	44 ℓ	1.54 Kg
32.5	0.016756	30.2	46.2	1.50
30.3	0.016164	31.8	48.6	1.48
28.4	0.015566	33.6	51.5	1.46
25.8	0.014589	37.3	57.0	1.47
23.1	0.013479	42.9	65.6	1.52
21.0	0.012385	51.3	78.5	1.65

*Total Pu including Pu^{240}.

The minimum mass of about 1460 grams Pu is obtained with a concentration of ~ 27.5 g Pu/ℓ; the volume of the solution is ~ 53 liters. The effective height-to-diameter ratio for this volume is 0.9 (with this H/D ratio the mass would not have been much less even in spherical geometry; the H/D ratio for minimum volume in cylindrical geometry is ~ 0.92).

If one noramlizes the calculations to 43 and 45 liters (measured value 44 ± 1), then minimum masses of ~ 1420 and 1500 g Pu are obtained respectively with volumes of 55 and 53 liters.

SHORTAGE OF PLUTONIUM

Since only 1365 g Pu were in solution (39 liters at ~ 35 g Pu/ℓ), it is apparent that criticality could not have been achieved through the simple process of adding water to the solution remaining in K-9.

Rings left on the glass walls of K-9 indicate criticality to have occurred with 45 - 46 liters of solution.

The concentration needed for criticality at 45 liters is 33.8 g Pu/ℓ (1522 g Pu), and for 46 liters the concentration is 32.7 g Pu/ℓ (1505 g Pu). By adding water to the solution (39 liters) to bring the volume up to 45 liters, the resultant concentration would only be 30.3 g Pu/ℓ, and at 46 liters, 29.7 g Pu/ℓ.

To be consistent with the "high water" marks, there is thus an apparent deficiency of Pu of ~ 140 - 160 g; these are the amounts required to raise the concentration to the critical point at either 46 or 45 liters. The quantity of plutonium needed to raise the concentration from the delayed critical state to prompt criticality is small, ~ 15 g Pu, in comparison to other uncertainties.

The lower connecting pipe to the vessel was later found to contain about one liter or strong organic Pu solution, an estimated 130 g Pu. When in the

connecting pipe, this Pu would have had small effect on criticality in K-9. It must, however, have been in solution in the upper portion of the vessel during initial criticality; it is about the amount needed to raise the concentration to the critical point in the range 45-46 liters.

With about one liter of light organic layer (as reflector) on top of the aqueous solution, criticality would have been possible in K-9 with 45 liters of solution at a Pu concentration of ~ 32.7 g/ℓ, or ~ 1470 g Pu.

FURTHER CONSIDERATION OF INITIAL CONDITION FOR CRITICALITY AND POSSIBLE SHUTDOWN MECHANISM

It has been postulated that the reaction went critical with a small amount of light organic phase (~ one liter) on top of the K-9 aqueous.[1] Several paragraphs taken from the report of L. E. Bruns are reproduced below[1] (see appendix for further details).

> "With time, TBP picks up plutonium by diffusion (proven by laboratory data) and also breaks down to DBP, a TBP breakdown product that has a tremendous affinity for plutonium. The TBP-DBP mixture on top in K-9 continually picked up plutonium. When sufficient plutonium was extracted into the organic to increase the organic density above the K-9 aqueous density, the organic went to the bottom, eventually displacing the light aqueous in K-9 to ball valve to pump piping."

> "The black ring in K-9* indicates the TBP-DBP layer; the brown ring was due to aqueous evaporation and liquid equalization in the K-9 outlet piping when the K-9 vacuum was finally turned off. The aqueous did not evaporate to any degree until the organic went to the bottom of K-9 and/or K-9 outlet piping. TBP-DBP has a low vapor pressure, and hence, only some CCl_4 evaporated."

The reaction would then have terminated itself as a consequence of 1) plutonium mass transfer from the aqueous to the TBP-DBP phase (about 100 g Pu); as the density of the organic increased above the K-9 aqueous density, it would have settled to the bottom of the vessel, and also 2) through aqueous evaporation. The mass transfer and subsequent settling would have reduced the concentration to below the critical point irrespective of evaporation.

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[1] Bruns, L. E., Preliminary Report on Interaction of Sample Results Pertaining to Criticality Incident in Recuplex, May 7, 1962.

* Estimated to be at 46 liters.

FINAL COMMENT

Although the above mechanism may seem complex, it is consistent with the critical mass calculations and with plutonium chemistry, and it seems necessary for predicting a critical volume in conformity with the "high water" marks on the glass vessel. Indeed, without the plutonium found in the organic phase in the connecting pipe at the bottom of K-9, criticality does not appear to have been possible at all. The estimated 68 g plutonium found in solids in the vessel was probably not in solution at any time, and therefore, does not effect these conclusions; according to the calculations this amount would have been insufficient to cause criticality even if it were in solution.

ACKNOWLEDGMENT

The author wishes to acknowledge the work of J. D. White who performed the multigroup diffusion calculations with the HFN Code and to Julia J. Woody, who assisted with the buckling conversions. Thanks are also due to L. E. Bruns for informative discussions on the shutdown mechanism which was originally proposed by him.

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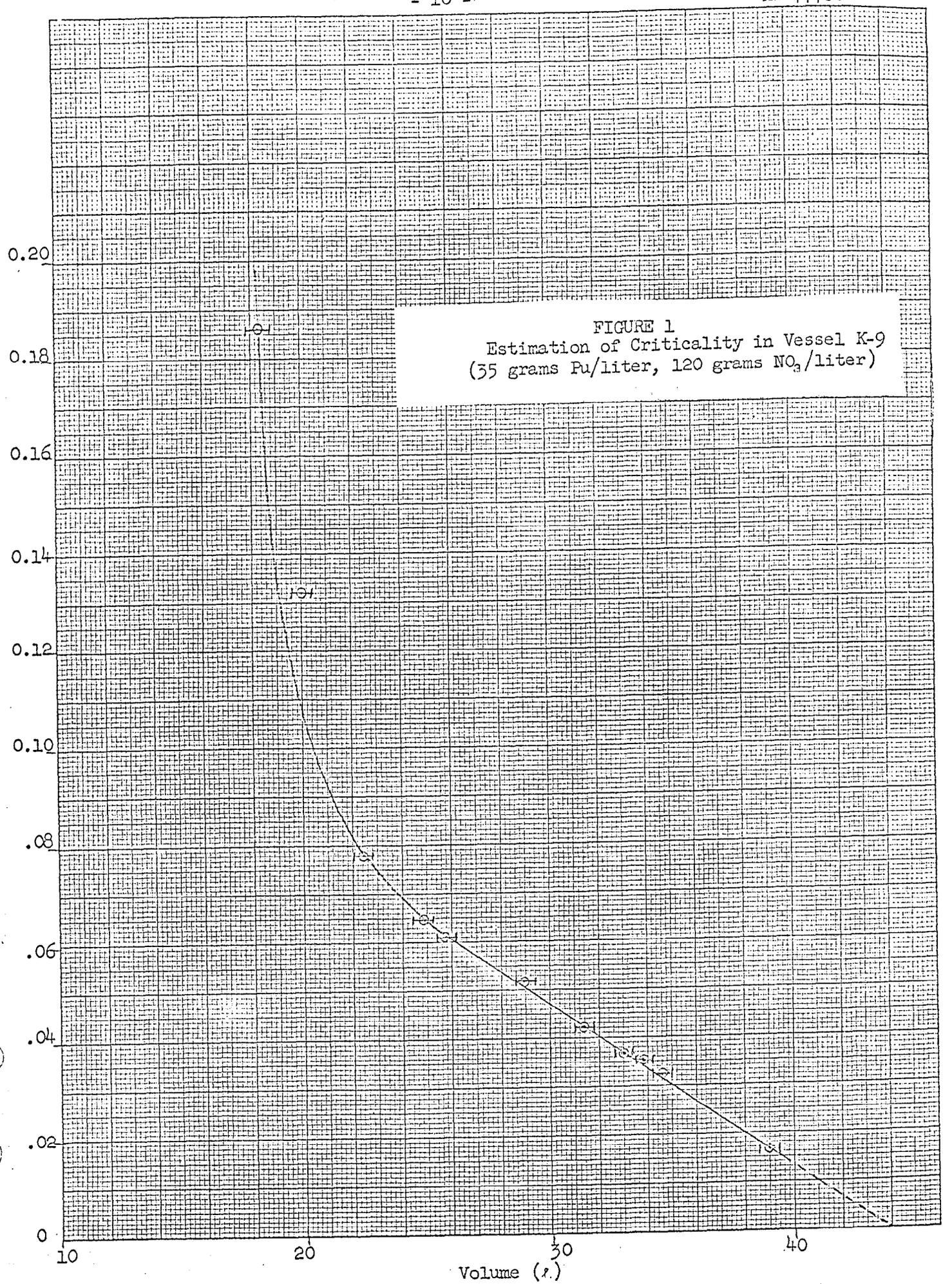

FIGURE 1
Estimation of Criticality in Vessel K-9
(35 grams Pu/liter, 120 grams NO_3/liter)

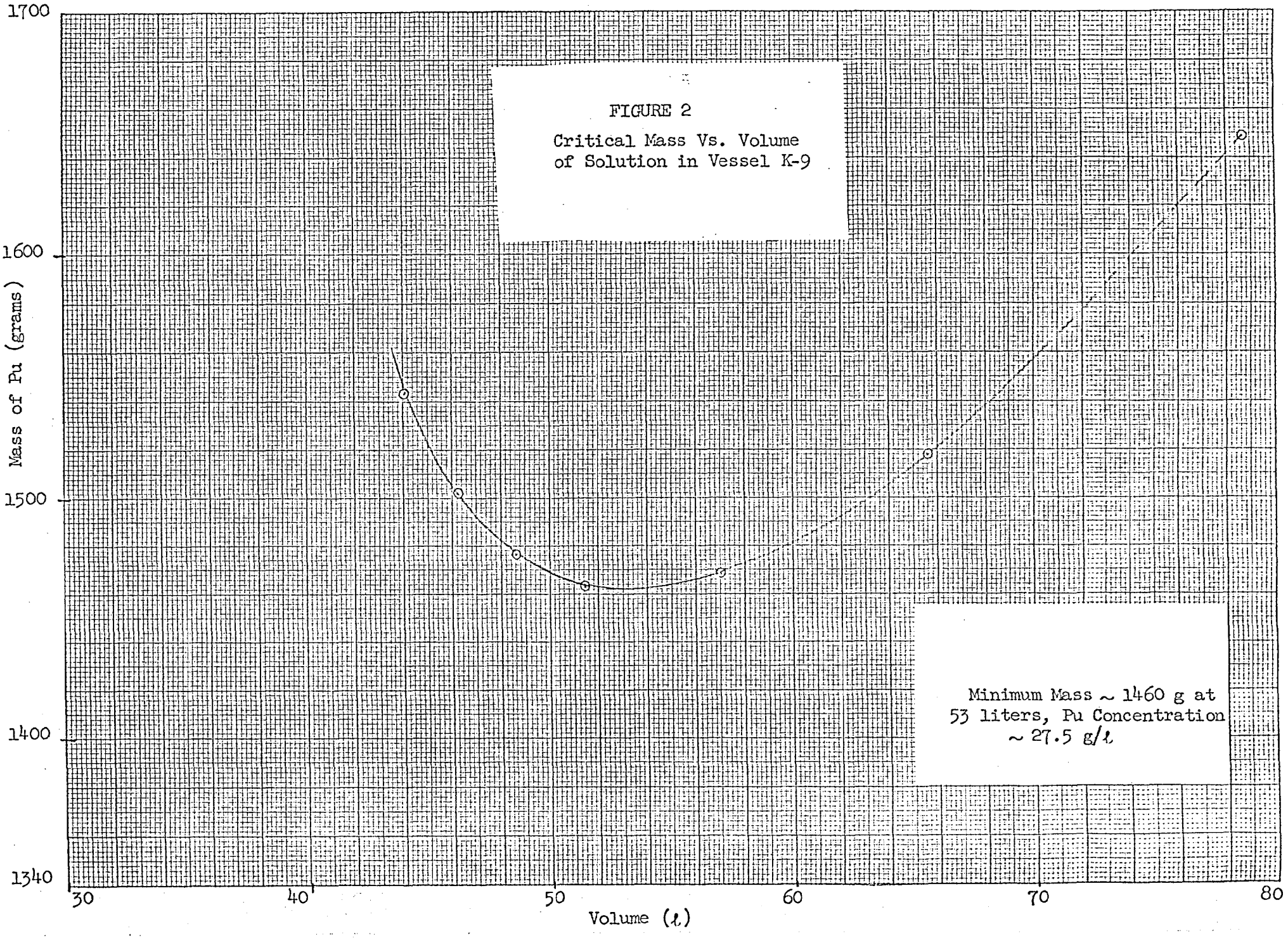
FIGURE 2
Critical Mass Vs. Volume
of Solution in Vessel K-9
Minimum Mass ~ 1460 g at
53 liters, Pu Concentration
~ 27.5 g/ℓ
Mass of Pu (grams)
1700
1600
1500
1400
1340
30
40
50
60
70
80
Volume (ℓ)

APPENDIX

PRELIMINARY REPORT
INTERPRETATION OF SAMPLE RESULTS
PERTAINING TO CRITICALITY INCIDENT IN RECUPLEX

REVISION 2

May 7, 1962

Further sample results and other new evidence have led to some revised conclusions and some additional conclusions. Since more sampling, more sample results, and more evidence will be forthcoming, continued revisions will be made (if significantly different than the previous revision) until a final report is written. Revision 2 takes precedence over Revision 1.

SAMPLE RESULTS AND OTHER EVIDENCE

K-9 Tank

Pu X-Ray	35.1 g/ℓ
X-Ray	34.9 g/ℓ
X-Ray	34.4 g/ℓ
Sp. Gr.	1.118
HNO_3	1.04 M
Total Fe	0.052 M
H^+	1.5 M
Na^+	0.018 M
NO_3^-	1.96 M
$SO_4^=$	0.11 M
Al^{+++}	0.52 M
NH_4^+	0.013 M
F^-	0.024 M
Cl^-	0.04 M

Solution in Piping Below K-9

Above Valve 431 and Between Valve 431 and ¼ Turn Ball Valve:

Pu	196 g/ℓ (organic)
	(Volume of Solution ~ 1 ℓ; total Pu ~ 100 - 130 g)
Ba^{140}	2.3 x 10^8 fissions/ℓ
Zr-Nb	4.6 x 10^9 fissions/ℓ
Ru^{103}	3.8 x 10^9 fissions/ℓ

Suction Side of K-9 Pump:

Pu	186 g/ℓ (organic)
Ba^{140}	2.0 x 10^8 fissions/ℓ
Zr-Nb	4.9 x 10^9 fissions/ℓ
Ru^{103}	3.7 x 10^9 fissions/ℓ

At K-9 Pump

Pu	145 g/ℓ (few drops organic found)

Fission Products:

*Ru^{103} 2.20 x 10^{16} fissions/ℓ

*Zr^{95} 2 x 10^{16} fissions/ℓ

*Ba^{140} 1.6 x 10^{16} fissions/ℓ

*Back calculation to 11:00 AM.

Fission Products Found: Mo^{99}, Ce^{143}, Te-I^{132}, Nd^{147}, Ru^{103}, Zr-Nb^{95}, Ba-La.

Distribution Coefficients:

K-9 solution versus 15% TBP in CCl_4 (equal volume) E o/a = 0.22.

K-9 solution versus 25% DBBP in CCl_4 (equal volume) E o/a = 5.0.

Pu Valence:

All Pu^{IV}

Spectrographic:

Al and Fe, strong	1%
Cu and S, moderate	0.01 - 1%
Mg and Mn, trace to moderate	0.001 - 0.1%
Others, interference	

K-1 TANK			Total Pu
Aqueous Phase:	0.391 g/ℓ	Volume = 107 ℓ	42.0 g
Organic Phase:	2.68 g/ℓ*	Volume = 110 ℓ	295.0 g
			337.0 g

(Fe = 0.042 M in aqueous phase.)

* 300 Area Pu = 2.4 g/ℓ.

K-2 TANK

Aqueous Phase:	0.022 g/ℓ	Volume = 83 ℓ	1.9 g
Organic Phase:	2.4 g/ℓ*	Volume = 192 ℓ	460.0 g
			461.9 g

*Average of 8 results.

L-2 TANK — Total Pu

Aqueous only: 0.043 g/ℓ Volume = 450 ℓ — 19.4 g

(Fe = 0.004 M)

L-3 TANK

Aqueous only: 0.472 g/ℓ Volume = 850 ℓ — 402.0 g

(Fe = 0.007 M)

L-8 TANK

Aqueous only: 0.027 g/ℓ Volume = 565 ℓ — 15.2 g

(Fe = 0.017 M)

SE SUMP

Sump Top: Aqueous Pu 1.2 g/ℓ
Fe 1.15 M

Organic Pu 120 g/ℓ

Sump Middle:

Aqueous Pu 0.73 g/ℓ
Fe 1.15 M

Organic Pu 120 g/ℓ

Sump Bottom:

Organic Pu 55 g/ℓ

NOTE: Indication of small amounts of fresh fission products.

OTHER EVIDENCE

1. Ball valve between K-9 and the SE sump was found closed and not leaking.
2. A leak point between H-3 and J-2 has been found.
3. H-2 column drained, indicating either an organic leak to the floor or to the receiver tank, H-10.

INTERPRETATIONS*

1. The incident occurred in the K-9 tank.

2. The aqueous solution that existed in K-9 is estimated as follows:

   1 ℓ FS solution (by NH_4^+ analysis)

   2 ℓ salt solution (by Al^{+++} analysis)

   35 ℓ product solution (analysis similar to H-3 column product being processed at time of and before incident)

   38 ℓ Total Aqueous

3. At the same time H-3 product solution leaked to the sumps, organic leaked to the SE hood floor. Before reaching the aqueous in the sump, the CCl_4 evaporated, leaving a greater than 80% TBP solution floating on top of the aqueous. If the organic came from the H-2 column, initially the plutonium concentration in the high percent TBP organic would be low.

4. Aqueous was first transferred to K-9 until the light organic layer was approached. Then a combination of aqueous and light organic went to K-9 (the solution that came from the bottom of the K-9 tank should be checked for organic).

5. The reaction went critical and a small amount of light organic phase existed on top of the K-9 aqueous.

6. With time, TBP picks up plutonium by diffusion (proved by laboratory data) and also breaks down to DBP, a TBP breakdown product that has a tremendous affinity for plutonium. The TBP-DBP mixture on top in K-9 continually picked up plutonium. When sufficient plutonium was extracted into the organic to increase the organic density above the K-9 aqueous density, the organic went to the bottom, eventually displacing the light aqueous in the K-9 to ball valve pump piping.

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*Calculations and explanations of the above interpretations will appear in the final report.

7. The black ring in K-9* indicates the TBP-DBP layer; the brown ring was due to aqueous evaporation and liquid equalization in the K-9 outlet piping when the K-9 vacuum was finally turned off. The aqueous did not evaporate to any degree until the organic went to the bottom of K-9 and/or K-9 outlet piping. TBP-DBP has a low vapor pressure, and hence, only some CCl_4 evaporated.
8. The reaction went sub-critical by plutonium mass transfer from the aqueous to the TBP-DBP phase and by aqueous evaporation after the organic phase went to the bottom of K-9.
9. The same thing that happened to the organic in K-9 happened on the SE floor. In the sump, the ratio of organic to aqueous was high, while in K-9 it was low. In the sump, almost all of the plutonium was extracted from the aqueous to the organic.
10. The TBP (or DBBP) percent in any of the Recuplex tanks rarely exceeds 30 percent. All organic systems in Recuplex usually have an aqueous cap. Even a very thin aqueous cap (K-2 situation for sample) will prevent CCl_4 evaporation. The floor, when relatively free of aqueous, presents a large surface area, hence, rapid evaporation of CCl_4 takes place with the high air flow through the hood.
11. The equilibrium saturation point for 25% TBP (or 25% DBP) is about 85 g/ℓ plutonium, for 80% TBP, about 260 g/ℓ plutonium.
12. It is postulated that the K-2 aqueous cap was small based on the recheck K-2 analyses, 2.4 g/ℓ. If sump material came up with organic from I-2, enough mixing should have taken place to substantially increase the plutonium content in the DBBP organic.
13. A leak was discovered between the H-3 column and the J-2 tank. This would have given a constant supply of H-3 product to the floor via black iron

*Estimated to be at 46 liters.

supports. A sample of the crud at the leak point indicated 37 percent plutonium by weight. It is concluded that this was plutonium nitrate.

L. E. Bruns
Finished Products
Chemical Technology
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