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BUILDING D PLUTONIUM RECOVERY PROCESSES

WORK DONE BY:	REPORT WRITTEN BY:
Pfc. W. R. Anderson	T/4 D. Duffy
T/4 R. A. Beardsley	T/3 G. B. Fleming
T/4 W. A. Brown	C. S. Garner
T/5 F. H. Coley	T/3 D. L. Wolfe
T/4 D. Duffy	
T/3 W. B. Gibson	
Pvt. D. E. Hirsch	
T/4 B. L. Kelchner	
Pvt. D. Klein	
Pvt. H. W. Long	
Pvt. J. Y. Oldshue	
F. K. Pittman	
Pfc. H. S. T. Rodgers	
T/4 R. Schaffer	
Pvt. W. Seymour III	
T/5 W. G. Thomson	
Pvt. M. T. Walsh	
T/3 D. L. Wolfe	

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Per LMR 6-11-79
By M Ballegas 8-2-96

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ABSTRACT

The standard processes in use in Building D for the recovery of plutonium from the different types of residue are described. The precipitation of plutonium (IV) "peroxide" was generally adopted as an isolation step. Tables are given showing the distribution of plutonium among the various types of residue and the amounts of plutonium per month made available for repurification. A brief discussion is presented of the nature of recovery operations in Building D after the start of plutonium processing at DP site.

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BUILDING D PLUTONIUM RECOVERY PROCESSES [redacted]

INTRODUCTION

The Building D plutonium recovery processes were developed for the purpose of concentrating and partially purifying plutonium-containing residues received from all the plutonium processing and research operations at Los Alamos so as to recover the plutonium in a form suitable for final purification by the Building D plutonium purification process. Hence, the primary task of the recovery processes is the separation of small amounts of plutonium from large amounts of other elements, whereas the purification proper deals with the removal of small amounts of impurities from large quantities of plutonium. The former problem may be amenable to solution by such methods as precipitation of the plutonium with appropriate carriers, extraction of the plutonium into the proper solvent, separation by the use of ion exchangers (such as the Amberlite resins), and concentration by evaporation and crystallization of the major portion of the foreign material under conditions in which negligible amounts of plutonium are adsorbed on the crystals. To date the nature of the recovery operations in Building D has been such that the carrier method has seemed the most straightforward, although solvent extraction methods have been used on special occasion. Final stages of the recovery operations involve precipitation without carriers.

With the termination on September 1, 1945, of all the chemical and metallurgical plutonium production work in Building D the nature of the recovery problems has changed appreciably. When production work is resumed, at DP site, most of the recovery will be undertaken in Operations 2 and 3 at [redacted]

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DP site, leaving for recovery in Building D residues for which processes have as yet not been engineered. This report will deal essentially with the standard recovery processes as they were being used before the Building D shut-down. Mention will be made of the types of residues which will still require recovery in Building D until further processes can be engineered for use at DP site.

The account of the major work of the recovery section which follows does not include any appreciable discussion of the developmental work, which has appeared in various earlier reports, such as the monthly progress reports of the Chemistry-Metallurgy Division, and, in particular, the reports written by F. K. Pittman: "Recovery and Purification of Plutonium" (LA-141, Pittman, 1944) and "Plutonium Recovery Methods" (LA-175, LA-192, Pittman, 1944).

OBJECTIVES OF THE PROCESSES

As indicated in the introduction, the function of the recovery processes is the treating of all plutonium residues in order to put them in a form appropriate for repurification. The following sections indicate some of the factors which were involved in the selection of suitable processes.

Scale of Operations

The scale of operations has varied widely, ranging from recovery of small residues from analytical and assay samples to recovery from tens of gallons of solutions per residue received for recovery. The amount of plutonium in a given residue has varied from less than a milligram to more

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than 200 grams. Accordingly, the size and type of equipment used in the recovery have varied greatly.

In 1944 a divisional policy was adopted concerning control of the amount of plutonium in a given operation or work space, and a "Quantity Control" (or QC) Group was set up to supervise transfers of plutonium (as well as other fissionable material). Safety from neutron chain reactions was the objective. The policy, later modified for certain operations in metallurgy, was to permit not more than 240 grams of plutonium in a given "space-unit" at one time. When the time came for deciding the scale for certain operations (in particular the purification process), the water-tamped critical mass of plutonium in aqueous solution was estimated as about 500 grams. No measurements of plutonium near criticality were available at the time, although estimates for enriched uranium had been checked by actual measurements. Hence, something like half the estimated amount seemed safe under any circumstances which might arise from mistakes or accidents. The recovery processes operated under this policy.

Recovery Product

Partially for the reason of safety from undesired nuclear reactions, the Building D purification process was designed for a nominal 160-g lot per unit on full-scale operation. Because the chemical process was definite and fixed and because the purification equipment was elaborate and of the closed-system type, it was almost essential that a given unit be charged with an amount of plutonium within 10 percent of 160 grams and in a constant chemical form. For this reason the recovery processes endeavored to provide nominal 160-g recovered lots. Because of certain difficulties with taking outs for radio-

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assay this was not always achieved, and recovered lots sometimes had to be "spiked" to bring them up to the nominal 160 grams. In earlier work, prior to purification on the 160-g scale, recovered lots were not definite in amount per lot.

As the purification process underwent chemical changes, particularly on the 8-g scale and earlier, the recovered plutonium was provided in various chemical states. Prior to the full-scale work recovered material was supplied as plutonium (III) chloride solution or as plutonyl nitrate solution. For full-scale processing it was supplied as plutonium (IV) nitrate solution obtained from plutonium "peroxide" (see the section on isolation of plutonium as the "peroxide"). This solution was 1N in nitric acid and contained about 300 grams of plutonium per liter. Purity of the recovered product was not closely controlled nor accurately known, but was probably better than 95 percent with respect to cations. Anions other than nitrate probably varied appreciably since the "peroxide" precipitate is known (CN-3018) to contain very appreciable amounts of many other anions present in the solution from which precipitation is made to take place; in particular sulfate was always present to the extent of approximately 20 percent by weight of the plutonium, and chloride and phosphate were probably present in some recovered lots in significant amounts. It appeared that somewhat more trouble was encountered in the oxidation step of the purification process when recovered lots were used than was the case for lots received from Hanford.

Hold-up and Losses

Roughly 10 percent of the total amount of plutonium at the site has been in process of recovery at a given time. The hold-up time has generally been quite appreciable, sometimes several weeks, for recovery of a given residue containing a moderate or large amount of plutonium. This was true because of the difficult nature of many of the chemical separations and because of health hazards associated with the work, necessitating cumbersome and time-consuming experimental techniques. However, the hold-up was not generally serious in the progress of the laboratory.

It is almost impossible to assess the extent of losses in the recovery processes. In general, it has not been easy to keep accurate records on the amounts of plutonium entering and leaving each of the plutonium processes. There was a tendency, therefore, for each phase to balance its books by attributing differences in receipts and out-going plutonium to the residues turned over for recovery. Accordingly, the accumulated losses of all other chemical and metallurgical operations were partially passed on to the recovery processes. This has been generally recognized and justified as a convenience to book-keeping. Material received for recovery cannot usually be submitted for assay of the plutonium content. In the recovery operations solutions are obtained which are very lean in plutonium and concentrated in various salts. Such solutions are very difficult to radioassay for plutonium, since the salts result in an appreciable error due to self-absorption of the alpha particles in the samples which are alpha-counted.

The processing was carried out in such a way as to make actual losses very unlikely. Essentially all lean supernatants (those of the order of 1 mg of plutonium per liter or less) were stored in large underground tanks. If the assay of such solutions was greatly in error it is likely that more plutonium was put into such waste tanks than was believed from the radioassay results. However, it is not entirely certain that appreciable losses have not occurred.

Health Problem

The hazards arising from the high specific alpha activity of Pu^{239} have been discussed in a report by the Health Group (LA-391, 1945). Because of the very great variety of residues submitted for recovery, the Building D recovery processes have necessarily used open system operations, including evaporations, ignitions and filtrations. Entrained vapors and smoke from ignitions were highly contaminated, and the hoods were not always entirely adequate to handle the load placed upon them. The nature of the equipment used in a given type of recovery operation is described in the sections on the recovery processes themselves. It is sufficient to state here that the recovery rooms and equipment were not designed to handle the large quantities of residues which had to be handled in the last several months of operation prior to the shut-down in Building D. Therefore, the spread of contamination became very serious, and a large portion of the staff was taken off the work because of excessive urine counts. A value of 7.0 counts of plutonium per minute in a 24-hour urine sample was regarded by the Health Group as a count sufficiently high to warrant removing the person from further exposure until the count was reduced below this value. That the exposure of personnel in the recovery processes was appreciable is shown by the fact that nine out of the fifteen workers exceeded the value of 7.0 at one time or another during the processing, the average being 12 counts per minute, and the range 7.5 to 20.9 counts per minute. Counts for personnel who did not exceed the limit ranged from 0.7 to 6.9 counts per minute according to the most recent data available. The urine counts rose very markedly during the rush periods when recovered plutonium was urgently needed for use in making the Trinity and destination pieces.

To reduce exposure to contamination recovery personnel wore overalls, a smock over the coveralls, surgeon's cap, canvas shoe-covers, rubber gloves and one type or another of respirator. The garments were generally changed at least twice a day in a special locker-room adjacent to the recovery quarters, and the shoe-covers and gloves were changed every time the worker left the processing rooms. Early in the work a standard dust respirator with blotting paper filters was worn by each worker. This type of respirator did not furnish adequate protection against the type of contamination encountered. Later several types of commercial positive-pressure respirators were tried, some of which gave fairly good protection, but all of which were uncomfortable to wear for long periods of time. Ultimately a positive-pressure mask was designed and found fairly satisfactory. This mask was made up from a cylinder of thin cellulose acetate, with a hemispherical top of sheet rubber and a bottom of sheet rubber so shaped that the head could be inserted into the mask and the bottom piece would fit snugly around the neck. A head band was used in conjunction with the mask, serving to support an air hose which ran from the top of the head down by the side of the neck and out to a connection on the ceiling in each room. The mask was light weight and permitted good vision. The ceiling hose outlets allowed freedom of movement within a given room. A mask was worn until badly contaminated on the outside (1000 counts per minute) or slightly contaminated on the inside (50 counts per minute) after which it was discarded.

The recovery rooms in Building D were designed with features to reduce loss and contamination hazards. The floors were smooth surfaced and of a relatively resistant material without cracks, with rounded sections at the walls and sloping from the walls to a drain at the center of the floor. The drain terminated in a 10-gallon removable trap from which spilled material and washings could be collected for recovery. The walls of the rooms were covered with a special plastic-coated material (Marlite wall board, Marshall Products Co., Dover, Ohio) so that they could be washed down with a hose. The hoods were equipped with fans giving a high-velocity draft. Steambaths, sinks and hood trays were of welded stainless steel construction, and the sinks and steam-baths had 10-gallon removable traps to catch spilled material. Glass containers and reaction vessels were placed in metal protective cans to reduce breakage and avoid serious loss and contamination in the event of an accident.

Largely as a safety measure in case of fire, an elevator was built at the rear of the recovery laboratory. It passes into an underground fire-proof vault. Residues could be placed on the elevator and lowered into the vault for storage during absence of recovery personnel.

The health problem arising from contamination can be greatly reduced only by the use of closed system equipment, which was not possible under the conditions present in the laboratory. Standardization of the types and amounts of residues submitted for recovery is almost a requirement before all recovery equipment could be of the enclosed type.

RECOVERY FROM PURIFICATION PROCESS RESIDUES

Two general purification processes were used in full-scale processing of plutonium, the "A", or ammonium nitrate, process and the "B",

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or calcium nitrate, process (LA-403, LA-405, 1945). The recovery process was different for each case. Up to 300 liters of residues per day were received from the purification process in Building D, much more than it was originally planned for the recovery processes to handle.

Recovery from the "A" Purification Process Residues

1. Description of the "A" purification process. -- In brief, the "A" process consisted of reduction of the plutonium (IV, VI) nitrates with hydriodic acid (or potassium iodide in some of the early work) in nitric acid solution, followed by precipitation of plutonium (III) oxalate (giving the P-1 residue or first oxalate supernatant); the oxalate was dissolved and oxidized with sodium bromate and nitric acid, followed by precipitation of sodium plutonyl acetate with sodium acetate (giving the P-2 residue or acetate supernatant); the acetate was dissolved in nitric acid nearly saturated with ammonium nitrate, and the plutonyl nitrate extracted into diethyl ether (giving the P-3 residue or the "stripped" solution); the resulting aqueous solution of plutonyl nitrate was reduced with hydriodic acid and the oxalate precipitated for transfer to the dry conversion process (giving the P-4 residue or second oxalate supernatant). Washings from the boiler (P-6 residue) were submitted for recovery together with P-1 and P-4 residues. Table I gives the amount and composition of the residues received from the standard A-8 purification process per nominal 160-gram run.

2. Flowsheet for recovery from "A" purification process residues. -- Flowsheet I indicates the general nature of the recovery process for the "A" purification residues. Some details of the process are described in the numbered sections immediately following.

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TABLE I

STANDARD A-8 PURIFICATION PROCESS RESIDUES (PER NOMINAL 160-g RUN)

P-1, 4, 6

Supernatants and Boiler Wash From Oxalate Precipitations
(Total Volume = 42.6 liters

1.72 M	H^+	69.66 moles
0.0005M	Fe^{++}	0.02
0.0001M	Cr^{+++}	0.004
0.00007M	Ni^{++}	0.003
0.008M	HSO_4	0.34
0.0002M	H_2PO_4	0.008
0.27M	NO_3	11.50
0.16M	I^-	6.82
0.04M	I_3^-	1.70
0.08M	$H_2C_2O_4$	3.40
0.05M	HAc	2.13
1.24M	Cl^-	5.30
0.0002M	Pu^{+++}	0.009

Total Pu = 2120 mg

P-2

Supernatant from Acetate Precipitation
(Total Volume = 12.70 liters)

0.32M	H^+	4.06 moles
3.98M	Na^+	50.50
0.60M	HAc	7.61
0.05M	BrO_3^-	0.635
4.27M	NO_3^-	54.30
0.002M	La^{+++}	0.025
0.0006M	PuO_2	0.008

Total Pu = 1900 mg

P-3

Portion Unextracted by Ether
(Total Volume = 6.67 liters)

0.26M	H^+	1.73 moles
6.66M	NH_4	44.50
0.47M	Na^+	3.14
7.38M	NO_3^-	49.20
0.0002M	BrO_3	0.001
0.003M	HAc	0.020
0.0005M	PuO_2^{++}	0.0033

$SnO_2 \cdot xH_2O \cdot SiO_2 \cdot xH_2O$(0.3g)

Total Pu = 800 mg

P-5*

Acid Bubbler Wash
(Total Volume = 1.70 liters)

0.88M	H^+	1.50 moles
0.88M	NO_3^-	1.50

Total Pu = 1 mg

P-9*

Alkaline Bubbler Wash
(Total Volume = 1.50 liters)

4.50M	Na^+	6.75 moles
0.73M	$SO_3^=$	1.10
0.27M	$SO_4^=$	0.405
0.55M	Br^-	0.825
0.60M	$CO_3^=$	0.90
0.77M	HCO_3^-	1.16

* P-5 and P-9 wash solutions are so low in Pu content that they may be discarded into the waste tanks.

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FLOWSHEET I

BUILDING D PROCESS FOR RECOVERY OF A-8 PURIFICATION PROCESS RESIDUES

(Per nominal 160g run)

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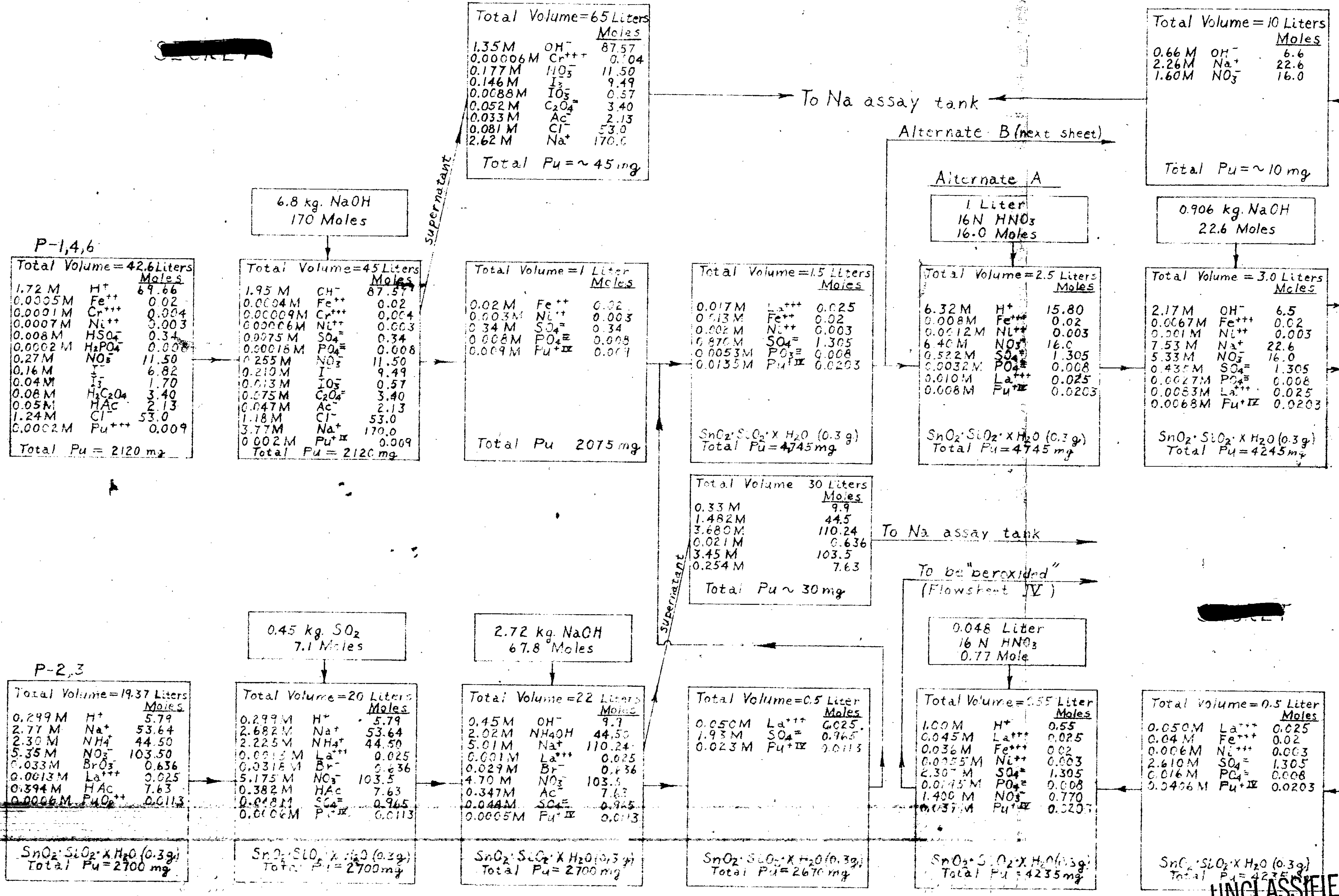

P-1,4,6

Total Volume = 42.6 Liters

		Moles
1.72 M	H^+	69.66
0.0005 M	Fe^{++}	0.02
0.0001 M	Cr^{+++}	0.004
0.0007 M	Ni^{++}	0.003
0.008 M	HSO_4^-	0.34
0.0002 M	$H_2PO_4^-$	0.008
0.27 M	NO_3^-	11.50
0.16 M	I^-	6.82
0.04 M	I_3^-	1.70
0.08 M	$H_2C_2O_4$	3.40
0.05 M	HAc	2.13
1.24 M	Cl^-	53.0
0.0002 M	Pu^{+++}	0.009

Total Pu = 2120 mg

6.8 kg. NaOH
170 Moles

Total Volume = 45 Liters

		Moles
1.95 M	OH^-	87.57
0.0004 M	Fe^{++}	0.02
0.00009 M	Cr^{+++}	0.004
0.00006 M	Ni^{++}	0.003
0.0075 M	$SO_4^=$	0.34
0.00018 M	$PO_4^{\equiv}$	0.008
0.255 M	NO_3^-	11.50
0.210 M	I^-	9.49
0.013 M	IO_3^-	0.57
0.075 M	$C_2O_4^=$	3.40
0.047 M	Ac^-	2.13
1.18 M	Cl^-	53.0
3.77 M	Na^+	170.0
0.002 M	Pu^{+IV}	0.009

Total Pu = 2120 mg

Supernatant

Total Volume = 65 Liters

		Moles
1.35 M	OH^-	87.57
0.00006 M	Cr^{+++}	0.004
0.177 M	NO_3^-	11.50
0.146 M	I_3^-	9.49
0.0088 M	IO_3^-	0.57
0.052 M	$C_2O_4^=$	3.40
0.033 M	Ac^-	2.13
0.081 M	Cl^-	53.0
2.62 M	Na^+	170.0

Total Pu = ~ 45 mg

To Na assay tank

Total Volume = 1 Liter

		Moles
0.02 M	Fe^{++}	0.02
0.003 M	Ni^{++}	0.003
0.34 M	$SO_4^=$	0.34
0.008 M	$PO_4^{\equiv}$	0.008
0.009 M	Pu^{+IV}	0.009

Total Pu 2075 mg

Total Volume = 1.5 Liters

		Moles
0.017 M	La^{+++}	0.025
0.013 M	Fe^{++}	0.02
0.002 M	Ni^{++}	0.003
0.870 M	$SO_4^=$	1.305
0.0053 M	$PO_4^{\equiv}$	0.008
0.0135 M	Pu^{+IV}	0.0203

$SnO_2 \cdot SiO_2 \cdot X\,H_2O$ (0.3 g)
Total Pu = 4745 mg

Alternate B (next sheet)

Alternate A

1 Liter
16N HNO_3
16.0 Moles

Total Volume = 2.5 Liters

		Moles
6.32 M	H^+	15.80
0.008 M	Fe^{+++}	0.02
0.0012 M	Ni^{++}	0.003
6.40 M	NO_3^-	16.0
0.522 M	$SO_4^=$	1.305
0.0032 M	$PO_4^{\equiv}$	0.008
0.010 M	La^{+++}	0.025
0.008 M	Pu^{+IV}	0.0203

$SnO_2 \cdot SiO_2 \cdot X\,H_2O$ (0.3 g)
Total Pu = 4745 mg

0.906 kg. NaOH
22.6 Moles

Total Volume = 3.0 Liters

		Moles
2.17 M	OH^-	6.5
0.0067 M	Fe^{+++}	0.02
0.001 M	Ni^{++}	0.003
7.53 M	Na^+	22.6
5.33 M	NO_3^-	16.0
0.435 M	$SO_4^=$	1.305
0.0027 M	$PO_4^{\equiv}$	0.008
0.0083 M	La^{+++}	0.025
0.0068 M	Pu^{+IV}	0.0203

$SnO_2 \cdot SiO_2 \cdot X\,H_2O$ (0.3 g)
Total Pu = 4245 mg

Supernatant

Total Volume = 10 Liters

		Moles
0.66 M	OH^-	6.6
2.26 M	Na^+	22.6
1.60 M	NO_3^-	16.0

Total Pu = ~ 10 mg

To Na assay tank

P-2,3

Total Volume = 19.37 Liters

		Moles
0.299 M	H^+	5.79
2.77 M	Na^+	53.64
2.30 M	NH_4^+	44.50
5.35 M	NO_3^-	103.50
0.033 M	BrO_3^-	0.636
0.0013 M	La^{+++}	0.025
0.394 M	HAc	7.63
0.0006 M	PuO_2^{++}	0.0113

$SnO_2 \cdot SiO_2 \cdot X\,H_2O$ (0.3 g)
Total Pu = 2700 mg

0.45 kg. SO_2
7.1 Moles

Total Volume = 20 Liters

		Moles
0.299 M	H^+	5.79
2.682 M	Na^+	53.64
2.225 M	NH_4^+	44.50
0.0013 M	La^{+++}	0.025
0.0318 M	Br^-	0.636
5.175 M	NO_3^-	103.5
0.382 M	HAc	7.63
0.048 M	$SO_4^=$	0.965
0.0006 M	Pu^{+IV}	0.0113

$SnO_2 \cdot SiO_2 \cdot X\,H_2O$ (0.3 g)
Total Pu = 2700 mg

2.72 kg. NaOH
67.8 Moles

Total Volume = 22 Liters

		Moles
0.45 M	OH^-	9.9
2.02 M	NH_4OH	44.50
5.01 M	Na^+	110.24
0.001 M	La^{+++}	0.025
0.029 M	Br^-	0.636
4.70 M	NO_3^-	103.5
0.347 M	Ac^-	7.63
0.044 M	$SO_4^=$	0.965
0.0005 M	Pu^{+IV}	0.0113

$SnO_2 \cdot SiO_2 \cdot X\,H_2O$ (0.3 g)
Total Pu = 2700 mg

Supernatant

Total Volume 30 Liters

	Moles
0.33 M	9.9
1.482 M	44.5
3.680 M	110.24
0.021 M	0.636
3.45 M	103.5
0.254 M	7.63

Total Pu ~ 30 mg

To Na assay tank

Total Volume = 0.5 Liter

		Moles
0.050 M	La^{+++}	0.025
1.93 M	$SO_4^=$	0.965
0.023 M	Pu^{+IV}	0.0113

$SnO_2 \cdot SiO_2 \cdot X\,H_2O$ (0.3 g)
Total Pu = 2670 mg

To be "peroxided"
(Flowsheet IV)

0.048 Liter
16 N HNO_3
0.77 Mole

Total Volume = 0.55 Liter

		Moles
1.00 M	H^+	0.55
0.045 M	La^{+++}	0.025
0.036 M	Fe^{+++}	0.02
0.0055 M	Ni^{++}	0.003
2.37 M	$SO_4^=$	1.305
0.0145 M	$PO_4^{\equiv}$	0.008
1.400 M	NO_3^-	0.770
0.037 M	Pu^{+IV}	0.0203

$SnO_2 \cdot SiO_2 \cdot X\,H_2O$ (0.3 g)
Total Pu = 4235 mg

Total Volume = 0.5 Liter

		Moles
0.050 M	La^{+++}	0.025
0.04 M	Fe^{+++}	0.02
0.006 M	Ni^{+++}	0.003
2.610 M	$SO_4^=$	1.305
0.016 M	$PO_4^{\equiv}$	0.008
0.0406 M	Pu^{+IV}	0.0203

$SnO_2 \cdot SiO_2 \cdot X\,H_2O$ (0.3 g)
Total Pu = 4235 mg

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FLOWSHEET I
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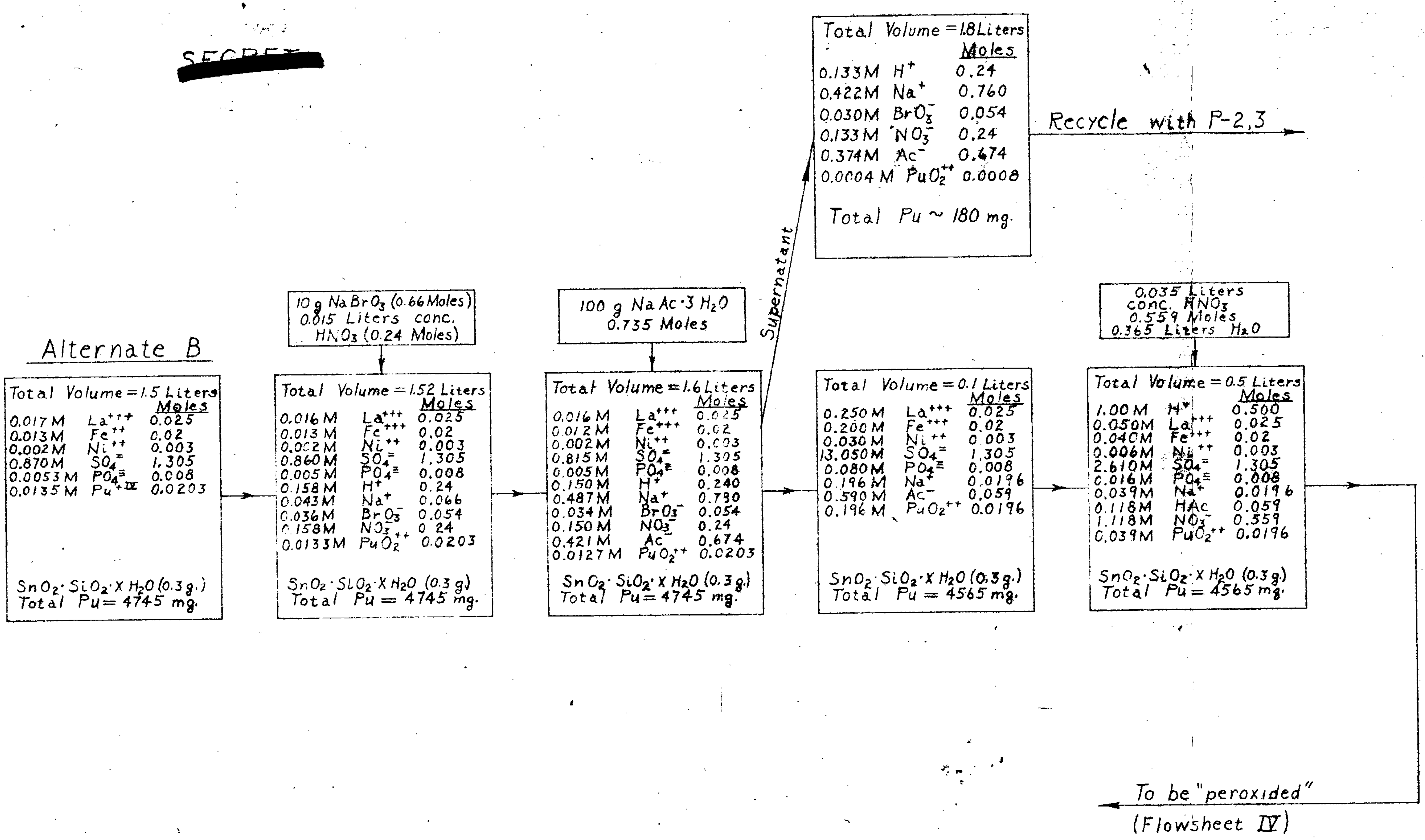

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3. Precipitation of "hydroxides" from P-1, 4, 6. -- Residues P-1, P-4, and P-6, containing plutonium (III) were combined and transferred by centrifugal pump or steam jet into a 100-liter rubber-lined steel barrel fitted with a lucite top. Solid sodium hydroxide was added slowly with constant mechanical stirring (proper holes provided in lucite cover), an excess being used to dissolve any iodine present. Considerable steam was released during the neutralization, resulting in a contamination hazard. The "hydroxide" precipitate was allowed to settle and cool for 4 to 5 hours. The supernatant and finally the slurry were siphoned into a 13-inch Büchner funnel equipped with a Whatman No. 2 or similar filter paper reinforced with a heavy paper. Suction filtration was used, the filtrate being caught in a 50-liter bottle. The iron and lanthanum impurities precipitated as hydroxides and evidently acted as carriers for the plutonium (III), so that good recovery was obtained in spite of the considerably greater solubility of plutonium (III) hydroxide relative to that of the very insoluble plutonium (IV) hydroxide. (Moreover, Pu(III) has a strong tendency to be oxidized to Pu(IV) in alkaline medium.) Attempts to use performed carriers, such as aluminum hydroxide, to ensure more complete removal of plutonium resulted in inconsistent carrying, generally no better than without the use of added carriers.

4. Precipitation of "hydroxides" from P-2, 3. -- Residues P-2 and P-3, containing plutonium (VI), were combined and the plutonium reduced by the passage of sulfur dioxide through the solution for 15-20 minutes. It was not satisfactory to combine P-1, P-2, P-3, P-4 and P-6, reduce with sulfur dioxide, because of the formation of iodine. Moreover, a saving of time was achieved by avoiding the unnecessary reduction treatment for the oxalate supernatants

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which supplied the bulk of the residues. As before, the "hydroxides" were precipitated by slow addition of solid sodium hydroxide and filtered. The filtrates from the treatment of P-1, 2, 3, 4, 6 were radioassayed and found to contain about 1 mg of plutonium per liter. These filtrates, totalling about 100 liters from each 160-g purification run, were piped out to 1000-gallon tanks to be temporarily stored until DP site can recover the remaining plutonium by use of a preformed aluminum hydroxide carrier (apparatus for such recovery has been installed at DP site). There were two alternate methods developed for handling the "hydroxide" precipitates combined from P-1, 2, 3, 4, 6. Simple dissolution in an acid was not possible because a considerable portion of the "hydroxides" would not dissolve, probably because of the formation of compounds containing sulfate, phosphate and silicate.

5. Refluxing "hydroxides" with concentrated nitric acid. -- The combined "hydroxides" were transferred to a 6-liter reflux flask and refluxed with an excess (about 1 liter) of 16N nitric acid for 16 to 20 hours. Even after this long reflux treatment a considerable residue remained. Spectrographic analyses by Group CM-9 showed the residue to consist mainly of silicon and sodium. This residue, containing an appreciable amount of plutonium, was generally fused with potassium pyrosulfate (see section on pyrosulfate fusions). The solution was filtered and the filtrate treated with sodium hydroxide to precipitate plutonium (IV) hydroxide (as a concentration step). The hydroxide was dissolved in nitric acid for precipitation later as plutonium "peroxide". This procedure is the alternate A method indicated on Flowsheet I.

6. Oxidation of the "hydroxides" and precipitation of sodium plutonyl acetate. -- An alternative method (alternate B, Flowsheet I) was to treat the

[redacted]

"hydroxide" precipitate with 1.8 moles of sodium bromate per mole of plutonium and 9.2 moles nitric acid per mole of plutonium for 4-6 hours at 85°C (plutonium concentration 0.2 molar). All the "hydroxide" dissolved generally (any residue was saved for fusion). The solution was treated with enough sodium acetate to make the solution 4 molar in sodium ion, precipitating the sodium plutonyl acetate, which was centrifuged or filtered and twice washed with an acetate, acetic acid wash. Dissolution of the acetate in 16N nitric acid gave a solution ready for precipitation of plutonium "peroxide". Filtrates were recycled with the P-2, 3 solutions. This method was the more generally used one because it was faster and the dissolution of the "hydroxide" was usually complete.

Recovery from the "B" Purification Process Residues

1. Description of the "B" purification process. -- The "B" process differed from the "A" process in that calcium nitrate was substituted for the ammonium nitrate as a salting-out agent in the ether extraction. The resulting extraction was so efficient that the first oxalate and the acetate steps were not needed. The process involved oxidation of the plutonium with sodium bromate in nitric acid, ether extraction of the plutonyl nitrate with calcium nitrate salting-out agent, followed by reduction with hydriodic acid and precipitation of plutonium (III) oxalate. Table II gives the composition, amounts and designations of the residues involved per 160-g run for the standard B-2 purification process. This process was faster than the "A" process and gave less plutonium in the residues, although recovery was made somewhat more difficult by the fact that calcium hydroxide would precipitate if sodium hydroxide were used in the "hydroxide" precipitation step.

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TABLE II

Standard B-2 Purification Process Residues (Per Nominal 160-g Run)

P-1

Portion Unextracted by Ether
(Total Volume = 7.50 liters)

0.27 M	H^+	2.06 moles
2.72	Ca^{++}	21.00
0.06	Na^+	0.45
0.003	Fe^{+++}	0.022
0.0004	Ni^{++}	0.003
0.003	La^{+++}	0.022
0.0009	$H_2PO_4^-$	0.007
0.0002	$Cr_2O_7^{=}$	0.0015
5.77	NO_3	43.30
0.03	BrO_3	0.225
0.04	$CaSO_4$	0.30
0.00009	PuO_2^{++}	0.0006

$SiO_2 \circ xH_2O, SnO_2 \circ xH_2O$ (0.3g)

Total Pu = 160 mg

P-2*

Wash Solution from Ether Extraction Apparatus
(Total Volume = 11.50 liters)

Traces of H^+, NO_3^-, Ca^{++}, PuO_2^{++}

P-3

Supernatant from Oxalate Precipitation

(Total Volume = 29.40 liters)

2.00 M	H^+	58.80 moles
0.0001	Cr^{+++}	0.0029
0.10	I^-	2.94
0.003	I_3^-	0.088
1.87	NO_3	55.00
0.07	$H_2C_2O_4$	2.06
0.0002	Pu^{+++}	0.0056

Total Pu = 1340 mg

P-*

Alkaline Bubbler Wash
(Total Volume = 1.50 liters)

4.50 M	Na^+	6.75 moles
0.92	$SO_3^{=}$	1.38
2.34	OH^-	3.51
0.08	$SO_4^{=}$	0.12
0.16	Br^-	0.24

P-*

Acid Bubbler Wash
(Total Volume = 1.70 liters)

0.88 M	H^+	1.50 moles
0.88	NO_3	1.50

Total Pu ≅ 1 mg

* The acid bubbler wash alkaline bubbler wash and wash of the extraction apparatus are so low in Pu content that they may be discarded into the waste tanks.

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2. Flowsheet for recovery from "B" purification process residues. -- Flowsheet II gives the general procedure for the recovery of the B-2 process residues.

3. Precipitation of "hydroxides" from P-1. -- The P-1 residue, containing plutonium (VI) and large amounts of calcium nitrate, was treated with 30% hydrogen peroxide (DuPont's Albone) in 25-liter battery jars to reduce the plutonium. About 500 ml of hydrogen peroxide was added with stirring to the P-1 residue from a 160-g run, and the mixture was allowed to stand about 20 minutes. "Hydroxides" were precipitated by the addition of 15N ammonium hydroxide, and the mixture filtered and handle as for recovery from the "A" process. The filtrate was placed in 250-gallon trailer tanks for transporting to a 50,000-gallon waste tank reserved for solutions containing large amounts of calcium or nagnesium. (This tank is located at DP site.)

4. Precipitation of "hydroxides" from P-3. -- The process was the same as indicated earlier for the "A" process. The "hydroxides" from P-1 and P-3 were combined and handled by the refluxing or oxidation technique. Isolation of the plutonium was achieved by "peroxide" precipitation.

Recovery from Purification Process Miscellaneous Residues

Other residues from the purification process included various special washes, purified oxalate left in the transfer containers and process failures. The former were generally so low in plutonium that they could be stored in the DP waste tanks. The oxalate was dissolved in concentrated hydrochloric acid, treated with nitric acid to oxidize the plutonium to the tetravalent state, then plutonium (IV) hydroxide precipitated. Failures from the purification process were treated according to the causes resulting in the failure.

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FLOWSHEET II

BUILDING D PROCESS FOR RECOVERY OF B-2 PURIFICATION PROCESS RESIDUES

(Per nominal 160-g run)

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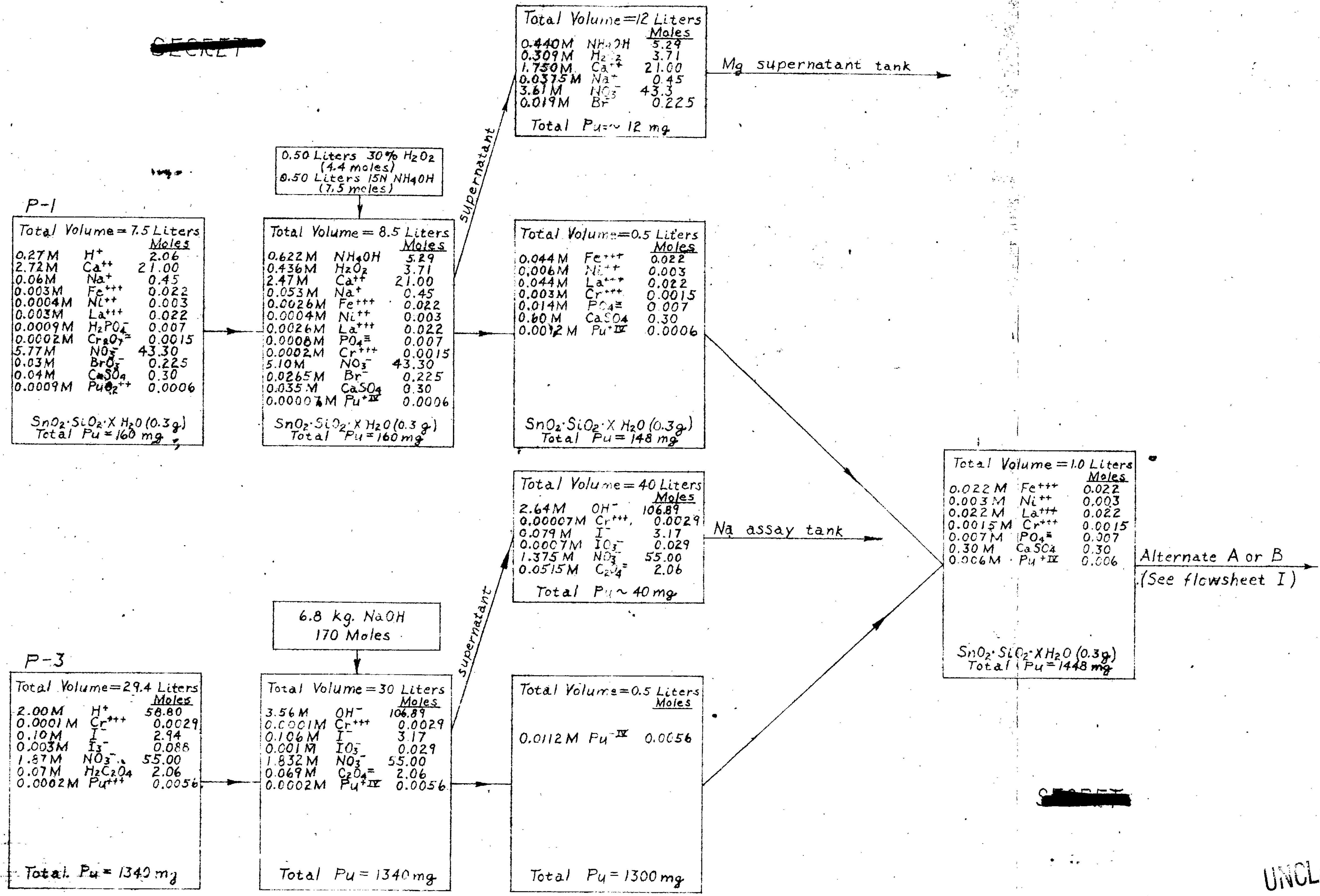

P-1

Total Volume = 7.5 Liters

		Moles
0.27 M	H^+	2.06
2.72 M	Ca^{++}	21.00
0.06 M	Na^+	0.45
0.003 M	Fe^{+++}	0.022
0.0004 M	Ni^{++}	0.003
0.003 M	La^{+++}	0.022
0.0009 M	$H_2PO_4^-$	0.007
0.0002 M	$Cr_2O_7^=$	0.0015
5.77 M	NO_3^-	43.30
0.03 M	BrO_3^-	0.225
0.04 M	$CaSO_4$	0.30
0.0009 M	PuO_2^{++}	0.0006

$SnO_2 \cdot SiO_2 \cdot X H_2O$ (0.3 g)
Total Pu = 160 mg

0.50 Liters 30% H_2O_2
(4.4 moles)
0.50 Liters 15N NH_4OH
(7.5 moles)

Total Volume = 8.5 Liters

		Moles
0.622 M	NH_4OH	5.29
0.436 M	H_2O_2	3.71
2.47 M	Ca^{++}	21.00
0.053 M	Na^+	0.45
0.0026 M	Fe^{+++}	0.022
0.0004 M	Ni^{++}	0.003
0.0026 M	La^{+++}	0.022
0.0008 M	$PO_4^{\equiv}$	0.007
0.0002 M	Cr^{+++}	0.0015
5.10 M	NO_3^-	43.30
0.0265 M	Br^-	0.225
0.035 M	$CaSO_4$	0.30
0.00007 M	Pu^{+IV}	0.0006

$SnO_2 \cdot SiO_2 \cdot X H_2O$ (0.3 g)
Total Pu = 160 mg

Total Volume = 12 Liters

		Moles
0.440 M	NH_4OH	5.29
0.309 M	H_2O_2	3.71
1.750 M	Ca^{++}	21.00
0.0375 M	Na^+	0.45
3.61 M	NO_3^-	43.3
0.019 M	Br^-	0.225

Total Pu = ~ 12 mg

Total Volume = 0.5 Liters

		Moles
0.044 M	Fe^{+++}	0.022
0.006 M	Ni^{++}	0.003
0.044 M	La^{+++}	0.022
0.003 M	Cr^{+++}	0.0015
0.014 M	$PO_4^{\equiv}$	0.007
0.60 M	$CaSO_4$	0.30
0.0012 M	Pu^{+IV}	0.0006

$SnO_2 \cdot SiO_2 \cdot X H_2O$ (0.3 g)
Total Pu = 148 mg

Total Volume = 40 Liters

		Moles
2.64 M	OH^-	106.89
0.00007 M	Cr^{+++},	0.0029
0.079 M	I^-	3.17
0.0007 M	IO_3^-	0.029
1.375 M	NO_3^-	55.00
0.0515 M	$C_2O_4^=$	2.06

Total Pu ~ 40 mg

Total Volume = 1.0 Liters

		Moles
0.022 M	Fe^{+++}	0.022
0.003 M	Ni^{++}	0.003
0.022 M	La^{+++}	0.022
0.0015 M	Cr^{+++}	0.0015
0.007 M	$PO_4^{\equiv}$	0.007
0.30 M	$CaSO_4$	0.30
0.006 M	Pu^{+IV}	0.006

$SnO_2 \cdot SiO_2 \cdot X H_2O$ (0.3 g)
Total Pu = 1448 mg

P-3

Total Volume = 29.4 Liters

		Moles
2.00 M	H^+	58.80
0.0001 M	Cr^{+++}	0.0029
0.10 M	I^-	2.94
0.003 M	I_3^-	0.088
1.87 M	NO_3^-	55.00
0.07 M	$H_2C_2O_4$	2.06
0.0002 M	Pu^{+++}	0.0056

Total Pu = 1340 mg

6.8 kg. NaOH
170 Moles

Total Volume = 30 Liters

		Moles
3.56 M	OH^-	106.89
0.0001 M	Cr^{+++}	0.0029
0.106 M	I^-	3.17
0.001 M	IO_3^-	0.029
1.832 M	NO_3^-	55.00
0.069 M	$C_2O_4^=$	2.06
0.0002 M	Pu^{+IV}	0.0056

Total Pu = 1340 mg

Total Volume = 0.5 Liters

		Moles
0.0112 M	Pu^{+IV}	0.0056

Total Pu = 1300 mg

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Recovery from Reduction Liners and Slag and from Remelt Crucibles

The dry conversion process supplied the reduction process with plutonium tetrafluoride (LA-440, 1945). The fluoride was mixed with metallic calcium and iodine and fired in a magnesium oxide liner inside an iron bomb. After the metal button was removed, the remaining slag (chiefly calcium fluoride and calcium iodide) and liner, containing about 2% of the amount of plutonium charged into the bomb, were turned over to the recovery process. For reduction on the nominal 320-g scale a liner weighing about 1.8 kg was used, giving a ratio of liner weight to plutonium to be recovered of about 300 to 1.

Following the reduction, the metal was pickled, then remelted in vacuum in various types of crucibles. Fortunately for the recovery, most of the experimentation with remelt crucibles made of different materials was performed on a small scale. Full-scale processing made use of essentially only magnesium oxide crucibles which were handled like the liners from the reduction process. Magnesium oxide casting crucibles were also processed with the reduction liners. Adhering metal and oxide were separated and handled like metal.

Since dissolution of the entire liner or crucible was a slow process, some effort was made to leach out the plutonium. Leaching with hydrochloric acid, partial dissolution of the magnesium and fusion with potassium pyrosulfate were all only partly successful. Grinding the liners (100-mesh) and fusion with a sodium peroxide-carbon mixture was fast and thorough, but this method caused high contamination of the rooms and was dangerous. Ultimately, it was regarded that complete dissolution with an acid was the best answer to the problem.

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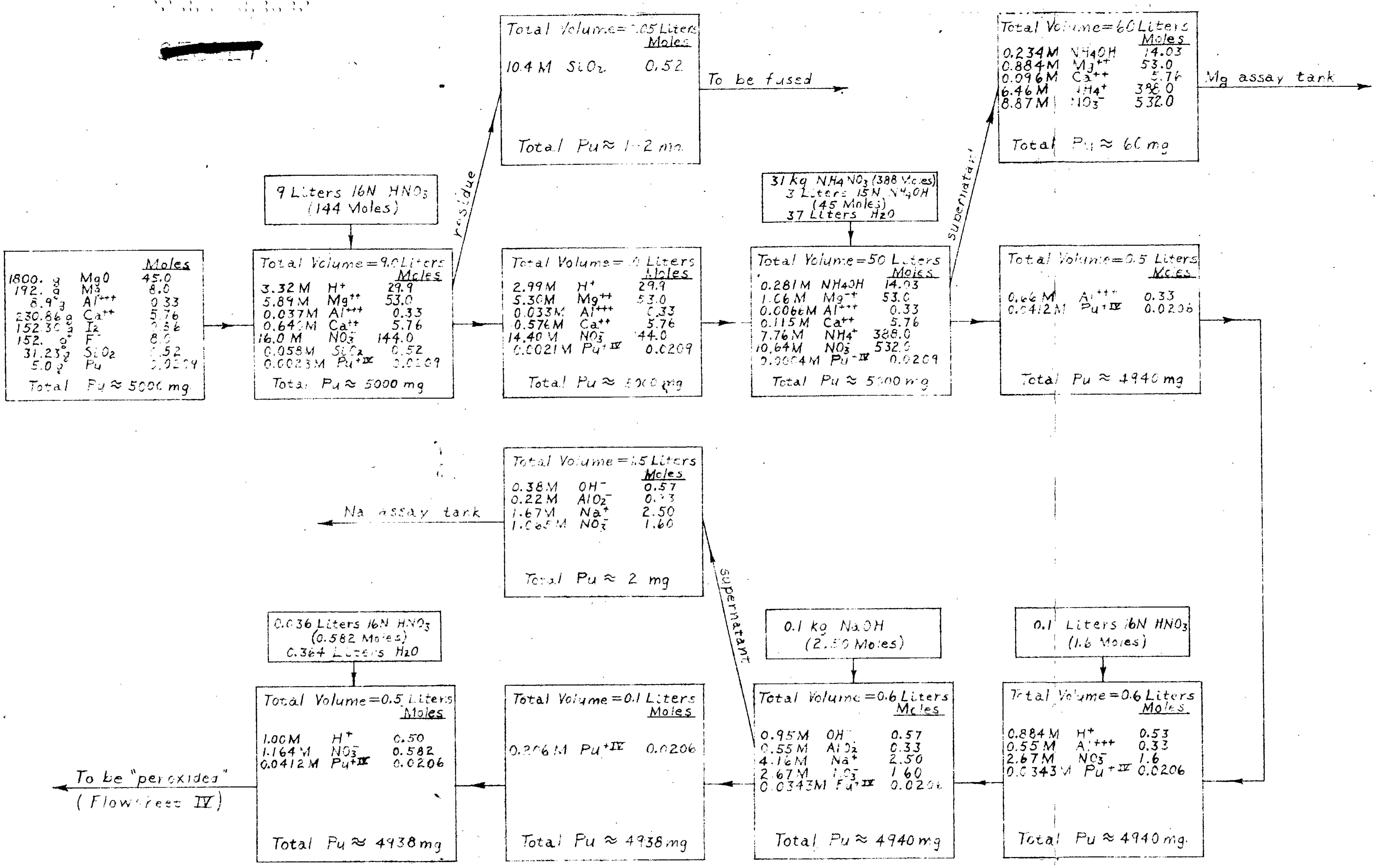
BUILDING D PROCESS FOR RECOVERY OF MgO LINERS & CRUCIBLES AND SLAG

(Per nominal 320g run)



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3. Precipitation of hydroxides from dissolved liners. -- In order to keep the magnesium in solution, the plutonium (IV) hydroxide was precipitated at a pH of 5 to 6. Magnesium hydroxide does not precipitate at this pH, and the small amounts of iron and aluminum impurities form hydroxides which serve as carriers for the plutonium. The solution was maintained at a pH of 5 to 6 by increasing the ammonium ion concentration to six to eight times that of the magnesium ion concentration, and using ammonium hydroxide as the precipitant.

The precipitation of plutonium (IV) hydroxide was done in two 30-liter battery jars. A concentrated solution of ammonium nitrate was made by dissolving 31 kg of the solid reagent in about 30 liters of water. The solution of the magnesium oxide liner was decanted into the ammonium nitrate solution and any undissolved pieces of magnesium oxide were left in the flask to be refluxed with the next liner.

The solution in the battery jar was diluted by approximately 45 liters, and the hydroxides precipitated by adding about 3 liters of 15N ammonium hydroxide to a pH of 5-6(as indicated by universal test paper). The precipitate was allowed to settle a few hours and the solution siphoned off through a filter paper. The hydroxide was washed three times with about 10 liters of water to remove the magnesium. The slurry was dissolved with 16N nitric acid and re-precipitated with solid sodium hydroxide in excess to remove the aluminum as sodium aluminate. This reduced the volume of the precipitate about one-third and made it easier to establish the proper conditions for the "peroxide" step. The re-precipitated hydroxides were filtered through the same paper as was used to filter the ammonium hydroxide supernatant. The precipitate could then be dissolved in nitric acid and "peroxided" directly.

The filtrate from the ammonium hydroxide precipitation contained a

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large amount of magnesium and was transferred by trailer tank to the DP waste tank reserved for solutions containing large quantities of calcium or magnesium. This filtrate contained 1 to 2 mg of plutonium per liter. The filtrate from the sodium hydroxide precipitation was transferred to the 50,000-gallon sodium supernatant tank at DP site for storage.

Recovery from Metal Turnings, Scrap, Skulls and Alloys

All metal or alloy samples from metallurgy were dissolved and "peroxided" directly. The sample was leached with concentrated hydrochloric acid in a 6-liter flask fitted with an efficient condenser to cut down contamination. Enough hydrochloric acid was added to dissolve the metal and give a solution of plutonium (III) chloride, 1M in hydrochloric acid, at the volume desired for the "peroxide" precipitation. The solution was filtered to remove any undissolved oxide coating on the metal or other residue, and the volume adjusted so that the plutonium concentration was 5 to 25 grams per liter. This filtrate was then "peroxided" directly. The oxide and other residues were ignited and fused with potassium pyrosulfate. Some of the experimental alloys created special recovery problems.

Recovery from Pickling and Plating Residues

Four principal types of residue were obtained from the pickling and plating processes used in certain metallurgical operations:

(1) Solutions of plutonium in concentrated nitric acid.

(2) Etching solutions of ammonium acid sulfate.

(3) Suspensions of plutonium in aqueous trisodium phosphate.

(4) Solutions of orthophosphic acid plus ethylene glycol.

The first two types of solution were "hydroxided" directly with

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ammonium hydroxide or sodium hydroxide, and presented no problem. The third type of residue, consisting of a suspension in trisodium phosphate, could be filtered. Since the suspension contained but little plutonium, the filtrate was stored.

The fourth type of residue, of phosphoric acid and ethylene glycol, has presented quite a problem for recovery and a great deal of work has been done on it. It was found that direct hydroxide precipitation of the mixture would not work, since too much plutonium was held up in the supernatant due to complexing of the plutonium. Removal of the glycol was attempted by distillation under atmospheric pressure using a 50% phosphoric acid-50% glycol blank. There was too much charring of the glycol to make this method practical. Vacuum distillation resulted in a residue of black syrupy liquid and a block of solid carbon. In an attempt to reduce the dehydrating effect of the phosphoric acid, the solution was neutralized and the distillation was continued to dryness. The residue was mostly monosodium phosphate and disodium phosphate. Nitric acid was added and any remaining carbon thereby removed. The salts were diluted and the solution "hydroxided" and allowed to settle for some time before centrifuging. The basic supernatant contained about 3 mg of plutonium per liter. This has been the most satisfactory method devised, but it is still too difficult for a good standard procedure. Care had to be taken, for there was some tendency for violent bumping if the temperature was not controlled. Attempts were made to convert the glycol to a more volatile compound by the separate use of phosphorus pentachloride, phosphorus trichloride, phosphorus tribromide and hydriodic acid, but all these failed. Extraction with unsymmetrical trifluoroacetylacetone (T.F.A.) was also unsuccessful under the conditions tried.

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Recovery from Analytical Residues

A great variety of residues was received from the analytical operations, including oxides, carbides, oxalates, cupferrides, and solutions of chlorides, nitrates, sulfates, and phosphates.

The acid insoluble materials, such as oxides and carbides, were fused with potassium pyrosulfate. The plutonium in the solutions was precipitated as plutonium (IV) hydroxide. In cases where organic materials were present, it was found desirable to destroy them before the hydroxide precipitation, since plutonium may be held in solution by organic substances, possibly due to the formation of complexes. To decompose the organic material, the solution was evaporated down and fumed with nitric and sulfuric acids until the organic material was destroyed. The solution was then diluted and the plutonium (IV) hydroxide precipitated with ammonium hydroxide or sodium hydroxide. Readily volatile materials, such as acetone and hexane, were driven off by gentle heating on a steam bath.

Recovery from Miscellaneous Residues

Occasionally the recovery processes received appreciable amounts of such materials as alundum, oil used in cutting, silicone and cerium sulfide crucibles, none of which normally contained much plutonium.

The alundum, in the form of holders from the remelt phase sometimes had small splatters of metal or oxide. They were leached and washed thoroughly with hydrochloric acid and water since there was no evidence of penetration of plutonium into the interior. The plutonium (III) chloride solution was treated in the usual manner.

Oils from the cutting processes were rarely received. Aliquots of

[redacted]

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the oil, fumed to destroy all organic material, were assayed and found to contain little plutonium. Assays showed the filtered oil itself to have insignificant amounts of dissolved plutonium. Therefore, the oil was diluted with hexane and filtered, and the paper was ignited and fused with potassium pyrosulfate.

The silicone after filtration also showed no plutonium in recoverable amounts. Hence, it was diluted with benzene and filtered, the paper ignited and fused with potassium pyrosulfate.

Cerium sulfide crucibles often had appreciable amounts of plutonium on the surface and dispersed throughout the interior. The best method of recovery was to dissolve the entire crucible in hydrochloric acid and "peroxide" the solution in the standard manner. This was done separately from other solutions to be "peroxided" because the presence of the cerium in the supernatant makes recovery of plutonium from the supernatant difficult. Overheated lots of tetrafluoride (or oxide-oxyfluoride-tetrafluoride mixture) from the dry conversion process were handled by fusion with potassium pyrosulfate.

Potassium Pyrosulfate Fusions

When it was necessary to render the oxide, fluorides or carbides of plutonium soluble, the best method was to fuse them with potassium pyrosulfate or potassium acid sulfate. In this fusion a ratio of pyrosulfate to plutonium of about eight to one was used. The fusion mixture was heated in a 500-ml platinum dish until the molten material turned solid. This gave a fused mass which was readily disintegrated by digestion in water and hydrochloric or nitric acids. From this solution, plutonium (IV) hydroxide was precipitated with sodium hydroxide or ammonium hydroxide, the hydroxide dissolved in nitric acid and a

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"peroxide" precipitation carried out. Sometimes it was necessary to "oxalate" and "acetate" the dissolved hydroxide first.

All types of rags, paper, Kleenex, etc., were ignited or wet-ashed before fusing. Concentrated sulfuric acid was highly satisfactory as a wet-ashing agent, and caused less contamination and loss than direct ignition. After the material was completely ignited, it was fused in the same manner as described for the oxide. This was a tedious process and required an excellent hood to carry off contaminated vapors and smoke; it was one of the most hazardous of the recovery operations.

Another method not involving fusion was experimented with for treating oxide. Prolonged refluxing of oxide with hydriodic acid would often put the oxide in solution. Following this treatment, the plutonium could be precipitated as a hydroxide. This procedure was not satisfactory, however. It took too long and would not work unless relatively pure oxide was used, and the amount of plutonium in the hydroxide supernatant was too high.

Isolation of Plutonium as the "Peroxide"

The methods outlined in the previous sections did not give a good separation of plutonium from rare earths (cerium from the use of cerium sulfide crucibles in certain metallurgical operations being particularly troublesome) nor from large amounts of uranium, thorium, zirconium and iron. Studies were carried out to determine whether the precipitation of plutonium as the "peroxide" would result in good separation, making unnecessary the oxalate and acetate steps sometimes used. A complete description of this work is being reported separately by W. A. Brown.

In general, conditions for the "peroxiding" followed in Building D resembled those used at Hanford (CN-2021). Flowsheet IV gives the method as it was used at Los Alamos.

The concentration of plutonium was adjusted to 0.035-0.3M, nitric acid to 1.0M and sulfuric acid to 0.1M, and enough 30% hydrogen peroxide was added to be equivalent to the plutonium present plus an excess equivalent to 10% of the total volume. The hydrogen peroxide was added dropwise with constant stirring at 12 to 20°C. The mixture was then cooled to 4°C to reduce effervescence and permit better settling of the precipitate. At one time about nine hours was allowed for the settling, but the time was later reduced to two hours. Various types of equipment were used for the precipitation, none of which were very good. Asbestos was used with a 6-inch Büchner funnel for the filtration, since the "peroxide" did not filter well when paper filters were used. Top draw-off of the supernatant was planned, but it was found generally quicker to employ filtration as indicated. The asbestos with the "peroxide" precipitate was treated with 16N nitric acid (2 ml acid per gram of plutonium) filtered, and the resulting nitric acid solution of plutonium (IV) nitrate evaporated down on a steambath to a thick syrup in 600-ml Pyrex beakers in copper jackets. After approximately 160 grams of plutonium was accumulated in syrup form, the syrup was diluted with 1N nitric acid to about 300 g of plutonium per liter in a graduated transfer bottle supplied by the purification process. The solution was stirred well, then a 0.5-ml sample removed with an automatic pipet for radioassay. The total volume of the solution was estimated from the graduations on the transfer bottle. The assay served to find out if the concentration and amount of plutonium was satisfactory for transfer to the purification process. The actual transfer was made by placing the transfer bottle with its outer lucite protecting case in a boron can, and requesting quantity control to approve the transfer.

FLOWSHEET IV

BUILDING D PROCESS FOR ISOLATION OF PLUTONIUM BY "PEROXIDE" METHOD

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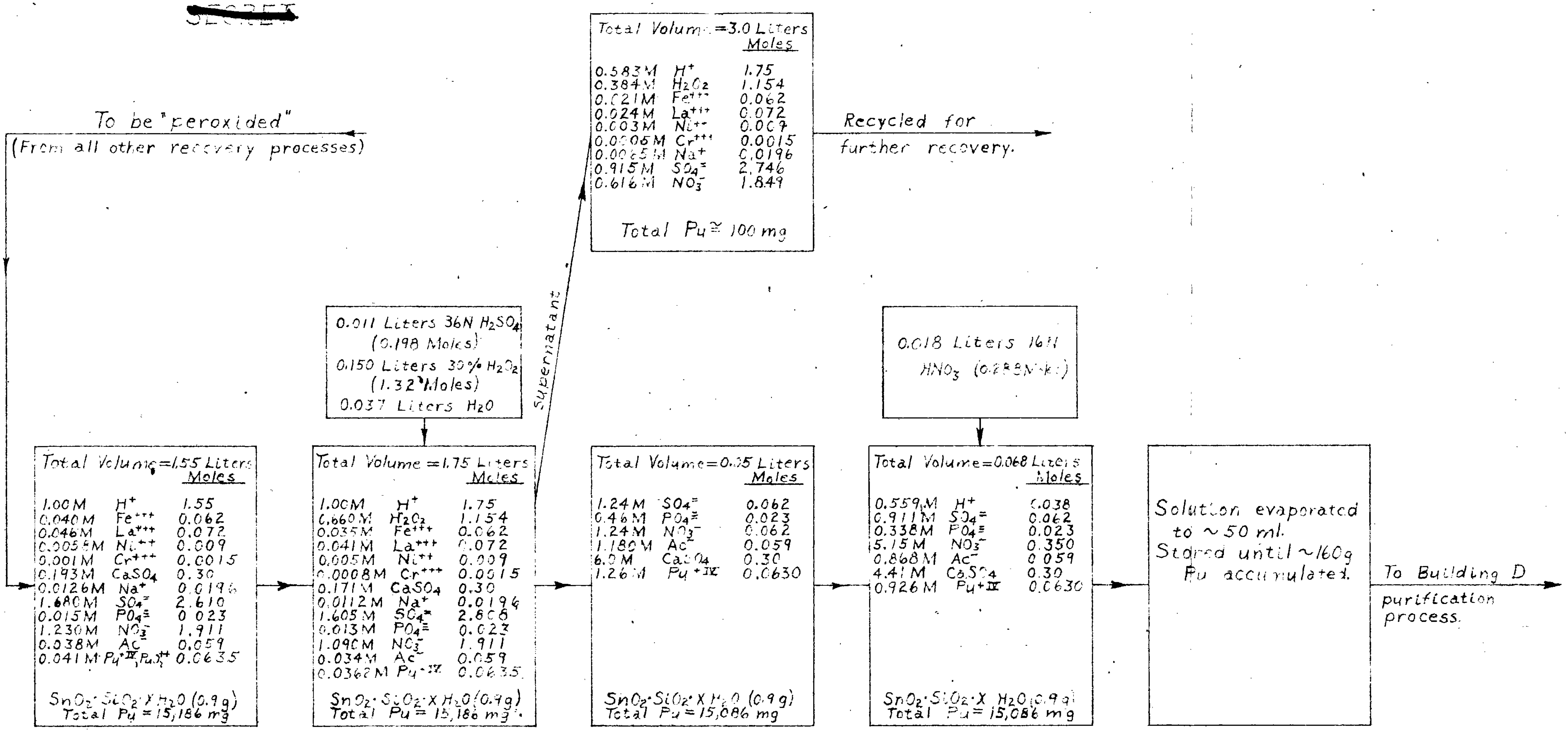

Total Volume = 1.55 Liters

		Moles
1.00 M	H^+	1.55
0.040 M	Fe^{+++}	0.062
0.046 M	La^{+++}	0.072
0.0055 M	Ni^{++}	0.009
0.001 M	Cr^{+++}	0.0015
0.193 M	$CaSO_4$	0.30
0.0126 M	Na^+	0.0196
1.680 M	$SO_4^=$	2.610
0.015 M	$PO_4^{\equiv}$	0.023
1.230 M	NO_3^-	1.911
0.038 M	Ac^-	0.059
0.041 M	Pu^{+IV}, PuO_2^{++}	0.0635

$SnO_2 \cdot SiO_2 \cdot XH_2O$ (0.9 g)
Total Pu = 15,186 mg

0.011 Liters 36N H_2SO_4
(0.198 Moles)
0.150 Liters 30% H_2O_2
(1.32 Moles)
0.037 Liters H_2O

Total Volume = 1.75 Liters

		Moles
1.00 M	H^+	1.75
0.660 M	H_2O_2	1.154
0.035 M	Fe^{+++}	0.062
0.041 M	La^{+++}	0.072
0.005 M	Ni^{++}	0.009
0.0008 M	Cr^{+++}	0.0015
0.171 M	$CaSO_4$	0.30
0.0112 M	Na^+	0.0196
1.605 M	$SO_4^=$	2.808
0.013 M	$PO_4^{\equiv}$	0.023
1.090 M	NO_3^-	1.911
0.034 M	Ac^-	0.059
0.0362 M	Pu^{+IV}	0.0635

$SnO_2 \cdot SiO_2 \cdot XH_2O$ (0.9 g)
Total Pu = 15,186 mg

Total Volume = 3.0 Liters

		Moles
0.583 M	H^+	1.75
0.384 M	H_2O_2	1.154
0.021 M	Fe^{+++}	0.062
0.024 M	La^{+++}	0.072
0.003 M	Ni^{++}	0.009
0.0006 M	Cr^{+++}	0.0015
0.0065 M	Na^+	0.0196
0.915 M	$SO_4^=$	2.746
0.616 M	NO_3^-	1.849

Total Pu ≅ 100 mg

Total Volume = 0.05 Liters

		Moles
1.24 M	$SO_4^=$	0.062
0.46 M	$PO_4^{\equiv}$	0.023
1.24 M	NO_3^-	0.062
1.180 M	Ac^-	0.059
6.0 M	$CaSO_4$	0.30
1.26 M	Pu^{+IV}	0.0630

$SnO_2 \cdot SiO_2 \cdot XH_2O$ (0.9 g)
Total Pu = 15,086 mg

0.018 Liters 16N
HNO_3 (0.288 Moles)

Total Volume = 0.068 Liters

		Moles
0.559 M	H^+	0.038
0.911 M	$SO_4^=$	0.062
0.338 M	$PO_4^{\equiv}$	0.023
5.15 M	NO_3^-	0.350
0.868 M	Ac^-	0.059
4.41 M	$CaSO_4$	0.30
0.926 M	Pu^{+IV}	0.0630

$SnO_2 \cdot SiO_2 \cdot XH_2O$ (0.9 g)
Total Pu = 15,086 mg

Solution evaporated to ~50 ml.
Stored until ~160 g Pu accumulated.

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The "peroxide" isolation had the disadvantage that the plutonium had to be fairly pure in order to obtain a good "peroxide" precipitate, and that the peroxide supernatants contained 10-500 mg of plutonium per liter, necessitating recovery from them to relatively complicated procedures. Moreover, the spray from the "peroxiding" operation as carried out in Building D was a major source of contamination.

Isolation of Plutonium as the Oxalate.

In cases where the plutonium residue contained impurities such as uranium (if not present in large amounts), zirconium, thorium, titanium, iron, beryllium, or chromium, a precipitation of plutonium (III) oxalate was a fair preliminary separation method. The solution containing plutonium (IV) nitrate was heated to convert any uranium to the hexavalent state. Enough solid potassium iodide was added to give three moles of iodide to each mole of plutonium. After allowing the solution to stand a few minutes, enough solid oxalic acid was added to give one and one-half moles of oxalic acid per mole of plutonium and to make the final solution 0.2M in oxalic acid. The plutonium concentration should be about 0.2M. This solution was allowed to stand for about one hour, after which the plutonium (III) oxalate was centrifuged out and washed with water until the supernatant was free of triiodide color.

This oxalate precipitate was then oxidized by the use of sodium bromate and nitric acid, as indicated earlier. This yielded a solution of plutonyl nitrate which was "acetated", dissolved, and "peroxided", as a convenient means of getting the solution into a form satisfactory for transfer to the purification process.

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Recovery from Supernatants from Hydroxide, "Peroxide" and Oxalate Precipitations

During the course of recovery operations, supernatant solutions from hydroxide, "peroxide" and oxalate precipitations were continually obtained. They were not sufficiently dilute to be discarded and further treatment was necessary.

Recovery from Hydroxide Supernatants

The solutions resulting from the precipitation of plutonium (IV) hydroxide with either ammonium hydroxide or sodium hydroxide were found to contain 1 to 5 mg of plutonium per liter, an amount too great to be discarded. The concentration of plutonium in these solutions can be lowered to a value of approximating 0.1 mg of plutonium per liter by treatment with aluminum nitrate to give a preformed aluminum hydroxide carrier. The pH of these supernatant solutions was adjusted to eight and a solution of aluminum nitrate (0.5 g aluminum per liter of treated solution) added. The aluminum hydroxide thus formed was allowed to settle, the solution filtered by suction, and the filtrate, containing about 0.1 mg of plutonium per liter, transferred to the DP storage tanks. The aluminum hydroxide precipitate, carrying plutonium, was dissolved in acid and reprecipitated with an excess of sodium hydroxide to keep the aluminum in solution. The hydroxide precipitate was then either "oxalated" or "peroxided", depending upon impurities present.

Recovery from "Peroxide" Supernatants

The "peroxide" supernatants contained 10 to 500 mg of plutonium per liter. The method of recovery from these supernatants used in Building D was

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as follows; the excess hydrogen peroxide was decomposed by heating on a steam bath. Excess sodium hydroxide was added to precipitate the plutonium (IV) hydroxide. This hydroxide was dissolved in nitric acid and an oxalate precipitation step, followed by an acetate step, was used further to purify the plutonium. This method was tedious and not satisfactory in all cases. Therefore, a new method must be developed for handling such residues from DP site. Two procedures which may have promise involve an ion exchange reaction and a solvent extraction.

Recovery from Oxalate Supernatants

The supernatant solutions from the oxalate precipitation were found to precipitate out plutonium (III) oxalate upon standing. Thus, the first step in working up the mixture was to filter it with suction. The oxalate residue may be oxidized, "acetated" and "peroxided" as previously discussed.

The filtrate was treated with an excess of sodium hydroxide and the hydroxide precipitate filtered off. Since the oxalate supernatants contained all the impurities removed in the oxalate precipitation step, a very copious precipitate containing a large number of elements was obtained. In fact, the amount of precipitate was so great, compared with the amount of plutonium present, that a good recovery procedure has not as yet been devised for this problem. The hydroxide precipitate was, therefore, dissolved in nitric or hydrochloric acid and stored as "acid wash". At present the "acid wash" consists of about 250 liters of solution containing 50 to 70 g of plutonium.

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Results of the Recovery Processes in Building D

Table III indicates the approximate amount of plutonium recovered each month during operation in Building D.

Table III

Plutonium Recovered in Building D for Repurification

1944		1945	
Month	Grams Pu Recovered	Month	Grams Pu Recovered
March	0.1	January	135
April	0.6	February	45
May	5.5	March	226
June	14	April	1250
July	17	May	810
August	22	June	1980
September	18	July	1440
October	60	August	750
November	52	Total recovered, March, 1944, through August, 1945: 6958 grams Pu.	
December	132		

The amount refers to plutonium transferred to the purification process for repurification, rather than amount turned in for recovery according to estimated receipts. The nominal 160-g purification runs became standard procedure in April, 1945.

Table IV shows the distribution of plutonium among the various

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types of residue turned in for recovery.

Table IV

Types of Residues Submitted for Recovery

(April-September, 1945)

Type of Residue	Amount of Pu grams	% of Total Pu in Residues
Purification supernatants (including failures)	3297	43
Reduction liners, slag and remelt crucibles	684	9
Metal, alloy, skulls, scrap	3334	44
Pickling and plating residues	130	2
Analytical and misc. residues	178	2
Total:	7623	100%

The discrepancy between amount recovered and amount turned in is partially due to an unknown amount of plutonium in residues not yet recovered, and partially to incorrect estimates of the amount of plutonium in residues submitted for recovery.

The processes described in this report were the standard ones used for the majority of the recoveries. However, there were many special methods which were developed for a given residue and which were used only once or twice.

Recovery Problems after the Start of DP Site

Operations 2 and 3 at DP site have been planned to take over many of the processes which were in use in Building D recovery work. As far as

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possible, the DP site recovery operations have been engineered with closed system equipment. Thus, the dissolution of reduction liners and slag and of remelt crucibles and the dissolution of the hydroxide precipitates will be brought about at DP site in glass-lined steel vessels. Each vessel is equipped with a dry-box through which the materials are introduced into the system in magnesium capsules. After refluxing, the solution is transferred to stainless steel hydroxide pots by means of suction through an enclosed asbestos filter. The solution is precipitated twice with ammonium hydroxide and once with sodium hydroxide, as described in a previous section. All supernatants are sucked off and are sent through the filter before disposal. The final dissolved hydroxide then is transferred to the peroxide pots which are completely enclosed in a dry-box. After the plutonium is "peroxided", washed, and dissolved, it is transferred to the stainless steel bomb used for transfer to the purification process and evaporated down to a thick syrup. It is believed these precautions will be reflected in reduced contamination.

It is appropriate to list the residues which will still be handled in Building D following the start-up of DP site, and until additional recovery processes can be engineered and installed at DP site. Table V gives this information. In addition, accidents may lead to residues requiring handling in Building D. Also, there will be residues from research operations in Building D.

It is proposed to recover all plutonium in Building D recovery to the stage of a crude hydroxide and to turn such hydroxide over to DP site for further handling, including repurification.

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Table V

Residues from DP Site requiring Recovery in Building D

Residue	DP Operation No.	Remarks
Sample of solution	2	More conveniently handled in D
Asbestos filter cake	3	May require fusion
Peroxide supernatants	3	After recycling through operation 2
Assay samples	3	More conveniently handled in D
Assay cuts	4	More conveniently handled in D
Kleenex	5	Requires fusion
Dry-box sweepings	5	Requires fusion
Acetone	6	May be possible to discard
Bomb pickling solutions	6	Hydrochloric acid; handle at DP later
Casting skulls	7	Oxide requires fusion;
Alundum crucibles (accidental contam.)	7	Requires acid leaching
Filings and cutting dust	7	Requires fusion
Hydrochloric acid rinse	7	Handle at DP later
Flash trimmings	8	Requires fusion; handle at DP later
Abrasive papers	8	Requires fusion; handle at DP later
[redacted] Phosphoric acid-ethylene glycol	9	
Trisodium phosphate	9	
Acetone, benzene rinses	9	May be possible to discard

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