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Technology-Plutonium

AEC RESEARCH AND DEVELOPMENT REPORT

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THE QUANTITATIVE RECOVERY OF PLUTONIUM FROM LABORATORY RESIDUES

by

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Manufacturing Department

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NUCLEONICS DIVISION OF
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THE QUANTITATIVE RECOVERY
OF PLUTONIUM FROM
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INTRODUCTION

The production and fabrication of plutonium metal involves many carefully controlled steps. As with any large scale industrial operation, plutonium production requires control analysis to insure a uniform product which will meet purity specifications. Discard of sample residues from these analyses cannot be considered because plutonium is a very valuable substance and in addition is extremely toxic to animal life. The residues must either be saved in storage indefinitely or the plutonium must be recovered from the residues.

Saving analytical residues for the reasons cited has posed problems. (These analytical residues are popularly referred to as "wastes", and in the text to follow, the term "waste(s)" will refer to material containing plutonium which results from analyses on plutonium bearing substances carried out in the 234-5 Building at Hanford Works.) Over the first 18 months of operation, the laboratory wastes whose compositions prohibited feedback into process streams were accumulated in 4-liter bottles and held in storage. At the end of that period 43 bottlefuls were on hand as wastes of nine different general impurity compositions. The plutonium content of the wastes exceeded 1100 grams.

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At this point indefinite storage was considered no longer practical. Accidental breakage of the storage containers by personnel error, fire, or act of God would have resulted in extensive high level contamination to the laboratory, which could have unfitted the surroundings for further use. Hazard was also inherent in the criticality implications of build-up of large amounts of fissionable material. Considering the situation economically, over a kilogram of plutonium was being diverted from the purposes of its very costly production and, in addition, laboratory working space (hoods) had to be sacrificed to non-productive waste storage.

The obvious solution to the problems outlined was to recover the plutonium in a form suitable for process feedstock. Several objectives had to be met in order to solve the problem effectively.

Because many different waste compositions existed, it was likely that several different procedures would be required to recover the plutonium from all of the wastes, especially when one considers that new compositions arise and old ones fall as new analytical methods replace old methods. An equipment design which would accommodate a variety of recovery procedures thus became one objective.

In order to solve the storage problem, it was necessary to use separation processes which were efficient enough for plutonium removal that effluent fractions could be economically discarded. Although

recycle of effluents from less efficient plutonium separation processes is possible, the desirability of working with small volumes was considered important enough to seek to avoid processes which might require reworking effluent streams.

The only space available for carrying out the recovery work was in open laboratory hoods so that whatever recovery processes and equipment were developed had to be safe to use in open hoods, handling multiple gram batches of plutonium. Although it was desired to develop an equipment design capable of accommodating a variety of recovery processes, space limitations in the open hoods required the equipment to be simple.

Contamination of personnel with plutonium-bearing materials is an ever present concern in any laboratory handling plutonium and its compounds. To indicate the toxicity of Pu²³⁹ the following recommendation is quoted from the International Commission on Radiological Protection (8, p. 436):

"On the basis of the relative biological effects of plutonium and radium, as observed in animal experiments, it is accepted that:

- a) The maximum permissible amount of Pu²³⁹ fixed in the body is 0.04 microcuries (equivalent to 0.64 micrograms).

For soluble compounds of plutonium in the atmosphere, it is estimated that 10% of the inhaled material is absorbed, with a mean life of 10⁴ days. The maximum permissible concentration in air is, therefore 2×10^{-12} microcuries per cubic centimeter. For insoluble compounds, it is estimated that the mean life in the lung is 200 days. If the irradiation of the lungs by alpha

rays were limited to the biological equivalent of 0.3 roentgens per week, the corresponding concentration of plutonium in air would be 7.5×10^{-12} microcuries per cubic centimeter. In view of the possibility of the transference of some of the insoluble material from the lungs to the skeleton, it is suggested that:

- b) The maximum permissible concentration of Pu²³⁹ in air is 2×10^{-12} microcuries per cubic centimeter for soluble and insoluble compounds.
- c) For Pu²³⁹ in liquid media, assuming that 0.1% of the ingested amount is retained in the skeleton with a mean life of 10^4 days, the maximum permissible concentration is 1.5×10^{-6} microcuries per cubic centimeter."

Usually the quantity of plutonium being manipulated in open hoods will be from 1 to 100 or 200 milligrams. Occasionally, quantities up to 1 gram are handled if very simple manipulations are to be carried out. As our requirement here was to handle multiple gram quantities of plutonium, simplicity of equipment was doubly desirable so as to confine contamination to as few places as possible.

It would thus seem that the objectives for efficient solution of the waste recovery problem could be best met by developing a simple apparatus which would be safe to use in open hood operation and which would have multiple gram capacity for a variety of plutonium separation processes.

HISTORICAL BACKGROUND

Plutonium recovery situations have been met before, but examination will show these situations to be different from the Hanford Works analytical waste recovery program.

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During the early days of the Manhattan Project many research projects had plutonium to purify (4, pp. 3, 11-12). Only milligram amounts were involved, and the plutonium concentrations of the solutions were low. The total volume of solution to be processed could be handled in centrifuge cones and separatory funnels. The workers were interested in recovering the last microgram of product from their residues, and they wanted as high purity as possible. Our analytical waste recovery situation to be outlined differed from this situation in every respect.

Los Alamos Scientific Laboratories had plutonium recovery problems (15, pp. 2-3) (18, p. 170) but one group did all the recovery work for production and research as well as for analytical support. This meant that a large expenditure for facilities and equipment was possible because of the size of the job to be done. The plutonium recovered between April and September, 1945 amounted to 7623 grams; the analytical wastes accounted for only 178 grams of this amount (5, p. 38). Large scale equipment, using either stainless steel, or glass lined tanks, filter presses, and piping to make a closed system, was feasible (18, pp. 214-215). Thus, the recovery equipment was much like a production line itself. The final solution had to be of very high purity because the solution was used directly for metal production.

Recovery of Hanford Works analytical wastes entailed considerations which were different from the cases noted above. Capacity was required

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to recover about 200 grams of plutonium per month from about 30 liters of plutonium solutions in order to process the solutions as they accumulated. A wide range of plutonium concentrations in the solutions was to be met - approximately half the 30 liters contained 5 to 25 grams of plutonium per liter and half contained less than 1 gram of plutonium per liter. The effluents from recovery processes were to contain only small amounts of plutonium so that they could be discarded.

The analytical waste recovery program at Hanford Works was seen then to be a larger scale problem than early investigators of plutonium chemistry faced. At the other extreme, expensive processing facilities were not justified. The analytical waste recovery is seen to fall between production experience and research experience regarding equipment to be used and amount of plutonium to recover. Since the operations were to be carried out in laboratory hoods, limitations were placed on the size and "contamination-proofness" of the equipment.

In deciding what sorts of recovery methods to develop, dry chemical methods were passed over as being too hazardous to the health of personnel for use with open hood operation. This also avoided high temperatures which require extra apparatus. It was felt that not enough data were available to try to set up such separation methods as solvent extraction or ion exchange as a general case for the various waste compositions at hand. Thus recovery by precipitation methods looked most promising and is discussed in the next section.

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EXPERIMENTAL1. Possibility of Recovery by Precipitation

The plutonium to be recovered in this study was associated with a variety of solution compositions, each of which generally resulted from a different analytical determination. Portions of each kind of plutonium solution composition were collected and stored only with other portions of its own kind. This avoided the risk of unduly complicating the recovery problem.

A tabulation of the various solution types which had accumulated up to July 15, 1952, is presented as Table I. The "theoretical plutonium content" is merely the summation of the weights of metal samples taken for the analyses from which the plutonium solutions were collected. The relationship of this figure to the actual plutonium content of the solutions is discussed elsewhere.

The estimation of the amount of any given constituent in a particular type of solution was made assuming the only source of the constituent to be from the reagents used during the course of an analysis and the total amount of plutonium present. This rather rough consideration is the basis of the composition data given in the table except for experimental determination of the composition of Type H solutions, the total acid of Type A and Type G solutions, and the plutonium content of Type D solutions.

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TABLE I

WASTE SOLUTIONS ACCUMULATED
UP TO JULY 15, 1952

<u>Solution Type</u>	<u>Theoretical Pu Content (Grams)</u>	<u>Solution Volume (Liters)</u>	<u>Qualitative Solution Composition</u>
A	725	70	2M in HClO ₄ ; contains 2 l of concentrated H ₂ SO ₄ -Na ₂ Cr ₂ O ₇ cleaning solution.
B	8	28	1M in H ⁺ as Cl ⁻ , SO ₄ ⁼ mixture; contains 25 g Sn and 30 g (NH ₄) ₂ MoO ₄ .
C	190	36	1.5M in H ⁺ as Cl ⁻ , SO ₄ ⁼ mixture; contains 85 g Ce and 1 g Ti.
D	-	100	Contains 400 g HCl, 500 g HOAc, 1400 g NaOAc, 70 g 8-hydroxyquinoline.
E	285	15	2M in HCl; contains 250 g Hg and 100 g Ni.
F	724	24	2M in HCl; contains acetone.
G	760	19	2M in HCl; contains methanol and traces of Ca.
H	273	17	6M in H ⁺ as Cl ⁻ , NO ₃ ⁻ , SO ₄ ⁼ mixture; contains 30 g Na, 5 g Fe, 1 g Ce, 1 g La.
I	195	35	2M in HCl; contains plutonium cupferride and its decomposition products.
J	54	20	1M in HCl; contains 10 g hydroquinone.

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TABLE I (CONT'D)

<u>Solution Type</u>	<u>Theoretical Pu Content (Grams)</u>	<u>Solution Volume (Liters)</u>	<u>Qualitative Solution Composition</u>
K	13	4	A mixture of 3 l Type B, 400 ml Type E, and 200 ml Type G solutions.
L	-	7	Unknown; collected from numerous sources; expected to contain wide range of impurity and to be low in plutonium content.
Totals*	<u>3227</u>	<u>375</u>	

* Credit received for 2379 g returned to process streams up to July 15, 1952. 482 l of effluents from recovery processes containing 2.034 g were discarded during this period.

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Examination of Table I shows that approximately 3/4 of the plutonium to be recovered was present in solution Types A, E, F, and G. The plutonium in these solutions was to be separated from chromium, sodium, nickel, mercury, calcium, chloride, and perchlorate and isolated as a plutonium nitrate solution, the preferred Separations Process feedstock.

Precipitation methods had much to offer the problem as outlined. With a variety of solution compositions to be accommodated, precipitation has the possibility of being made specific for plutonium in each case by choice of precipitant and precipitation conditions. That the range of this choice is wide can be seen from Table II, where solubility data on a variety of plutonium compounds suitable for precipitation is given. Precipitation involves solution chemistry which is preferable to dry chemistry for reasons of health hazard. Precipitation is a batch process, and the operations can be as simple as mixing the plutonium solution and precipitant together, letting the plutonium compound settle out, draining off the supernatant liquid, and dissolving the recovered product cake.

Two compounds listed in Table II, sodium plutonium dioxytriacetate and plutonium (IV) peroxide, are specific for plutonium and are capable of providing one step separation of plutonium from chromium, sodium, nickel, mercury, calcium, chloride, and perchlorate. These two compounds could furnish one step separation of plutonium from Type A, B, C, E, F, G, and H solutions but there are disadvantages to the use of either of

TABLE II

SOME COMPOUNDS SUITABLE FOR PLUTONIUM PRECIPITATION

<u>Compound*</u>	<u>Solubility at 25°C (mg Pu/l)</u>	<u>Solubility Reference</u>	<u>Particular Advantages and/or Disadvantages Offered</u>
$\text{Pu}(\text{IO}_3)_4$	$\underline{2}$ in $1\text{M HNO}_3 + 0.15\text{M IO}_3^-$ $\underline{3}$ in $3\text{M HNO}_3 + 0.15\text{M IO}_3^-$	4, p. 3	<ol style="list-style-type: none"> 1. Solubility is very low even in 3M HNO_3. 2. Filtration characteristics excellent. 3. Not very specific for Pu. 4. Dissolution produces I_2 or I^-.
PuF_3	$\underline{10}$ in $1.5\text{M HCl} + 0.35\text{M HF}$	19, P. 910	<ol style="list-style-type: none"> 1. Filtration characteristics are good. 2. Solubility is somewhat high. 3. Supernatant solution is corrosive to glassware. 4. Dissolution is difficult.
KPuF_5	$\underline{5}$ in $3\text{M HF} + 0.5\text{M KF}$ $\underline{5}$ in $2\text{M HF} + \text{KF/Pu}$ (moles of 4/1)	19, p. 775	<ol style="list-style-type: none"> 1. Solubility is low. 2. Filtration characteristics are good. 3. Supernatant solution is corrosive to glassware. 4. Dissolution is difficult. 5. Introduces K into recovered solution.
$\text{Pu}_2(\text{C}_2\text{O}_4)_3$	$\underline{6}$ in $0.22\text{M H}^+ + 0.14\text{M H}_2\text{C}_2\text{O}_4$ $\underline{20}$ in $0.75\text{M HNO}_3 + 0.25\text{M H}_2\text{C}_2\text{O}_4$	3, p. 71	<ol style="list-style-type: none"> 1. Solubilities are high, especially at higher acidities. 2. Not very specific for Pu.

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TABLE II (CONT'D)

<u>Compound*</u>	<u>Solubility at 25°C (mg Pu/l)</u>	<u>Solubility Reference</u>	<u>Particular Advantages and/or Disadvantages Offered</u>
Pu(O ₂ O ₄) ₂	<u>11</u> in 0.5M HNO ₃ + 0.05M H ₂ C ₂ O ₄	14, p. 8	1. Solubilities are high, especially at higher acidities. 2. Not very specific for Pu.
	<u>15</u> in 2.0M HNO ₃ + 0.05M H ₂ C ₂ O ₄		
PuPO ₄	<u>20</u> in 0.1M HCl + 0.8M H ₃ PO ₄	14, p. 6	1. Solubilities are high, especially at higher acidities. 2. Not very specific for Pu.
	<u>210</u> in 0.5M HCl + 0.8M H ₃ PO ₄		
Pu(HPO ₄) ₂	<u>18</u> in 0.1M H ₂ SO ₄ + 0.8M H ₃ PO ₄	3, p. 79	1. Solubilities are high, especially at higher acidities. 2. Not very specific for Pu.
	<u>81</u> in 0.5M H ₂ SO ₄ + 0.8M H ₃ PO ₄		
K ₄ Pu(SO ₄) ₄	<u>21</u> in 0.33M K ₂ SO ₄ + 12% CH ₃ OH (vol)	19, p. 725	1. Filtration characteristics are good. 2. Dissolution is very easily accomplished. 3. Solubility is somewhat high. 4. Introduces K into recovered solution.
NaPuO ₂ (C ₂ H ₃ O ₂) ₃	<u>70</u> in 5.7M NaNO ₃ , 0.2M NaC ₂ H ₃ O ₂ + 0.6M HC ₂ H ₃ O ₂	7, p. 23	1. Very specific for Pu and U 2. Filtration characteristics are good. 3. Solubility is high 4. Introduces Na into recovered solution. 5. Requires oxidation to Pu (VI) before precipitation.
	<u>280</u> in 2.1M NaNO ₃ , 0.2M NaC ₂ H ₃ O ₂ + 0.6M HC ₂ H ₃ O ₂		

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TABLE II (CONT'D)

<u>Compound*</u>	<u>Solubility at 25°C (mg Pu/l)</u>	<u>Solubility Reference</u>	<u>Particular Advantages and/or Disadvantages Offered</u>
Pu (IV) Hydroxide	<u>0.02</u> at pH 5.4 <u>1</u> in 1-10M NaOH or NH ₄ OH	9, p. 13	<ol style="list-style-type: none"> 1. Solubility is very low. 2. Introduces no unwanted ions into final solution - anion is the operator's choice. 3. Dissolution is very easily accomplished. 4. Not very specific for Pu - note, however, that Pu is not amphoteric and does not form ammono complexes. 5. Filtration characteristics are poor.
Pu (IV) Peroxide	<u>20</u> after 24 hours in 1M HNO ₃ at 0°C with 10% excess H ₂ O ₂ <u>50</u> after 1 hour in 1M HNO ₃ at 20°C with 10% excess H ₂ O ₂	3, p. 33	<ol style="list-style-type: none"> 1. Very specific for Pu. 2. Introduces no unwanted ions into final solution. 3. Solubility is high. 4. Requires control over rate of dissolution.
Barium Plutonate	<u>10</u> in 0.1M Ba(OH) ₂	13, p. 8	<ol style="list-style-type: none"> 1. Introduces Ba into recovered solution. 2. Not very specific for Pu. 3. Requires oxidation to Pu(VI) before precipitation.
Pu Trichloracetate	<u>100</u> in 1M (CCl ₃)COOH	2, p. 2	<ol style="list-style-type: none"> 1. Salt is soluble in some immiscible organic solvents. 2. Solubility is high - may be lower at other conditions.

* Formula does not include or exclude substances such as water of crystallization.

these compounds. The most troublesome factor is their high solubilities. In the case of sodium plutonium dioxytriacetate the introduction of sodium and acetate is undesirable. The possibility of reworking the plutonium-rich filtrates exists, but this is in turn a complicating factor and is undesirable.

If the requirement for a one-step separation is relaxed in the case of Type E solutions and separation of the trace of calcium is neglected in Type G solutions, the recovery of Type A, E, F, and G solutions could conveniently proceed by way of a hydroxide cycle. Chromium (III) hydroxide is the only material in Type A solutions which would precipitate along with plutonium (IV) hydroxide if the solutions were made basic. Chromium is amphoteric and could be redissolved by using an excess of strong base. Type E solutions, after preliminary treatment with hydrogen sulfide to remove mercury, would result in precipitates of plutonium (IV) hydroxide and nickel (II) hydroxide upon being made basic. If ammonium hydroxide were used and added to excess, the nickel (II) hydroxide would redissolve as an ammonia complex. Type F and G solutions do not contain any impurities which are insoluble in basic solution except a trace of calcium in Type F.

The condition of using a hydroxide cycle with excess strong base is also seen to meet the recovery requirement of Type B solution where all impurities except tin are soluble. Tin is amphoteric and would redissolve under the conditions.

Application of a hydroxide cycle to Type D solutions would eliminate a large part of the storage requirement by concentrating the plutonium 8-hydroxyquinolate into a much smaller volume than 100 liters. Upon making Type D solutions basic, the complex would precipitate and the cake could subsequently be redissolved in a small volume of nitric acid.

In summary, a hydroxide cycle used with the various conditions mentioned is seen to be applicable, at least "on paper" to recovery of 75% of the plutonium which was accumulated by July 15, 1952. The storage space occupied by the recoverable 75% of the plutonium amounted to 70% of the total storage space requirement. As for the plutonium remaining in the solution types not discussed, it was felt that the general nature of precipitation as a separation means would allow other precipitation applications to be worked out for those cases, and that whatever equipment was devised for carrying out hydroxide cycles would find ready usage for making those other precipitation separations.

Equipment requirements for a hydroxide recovery scheme were expected to be simple. A system was visualized which consisted of a tube having a bulb in it with a porous glass disc sealed across the tube at the bottom of the bulb. Using vacuum transfer, solutions could be drawn into the bulb through the fritted disc. After precipitation had occurred within the bulb, reversing the vacuum would transfer the supernatant liquid back out through the fritted disc while the precipitated plutonium

compound would be retained within the bulb. Experience with vacuum transfer of plutonium solutions indicated that this method of transferring plutonium solutions into the system would be safe against contamination hazards for open hood operation of the system.

Small units were designed around this basic idea and were fabricated in the project glass shop. By running samples of the plutonium solutions through the proposed cycles in these small units, information concerning the applicability of both the recovery scheme and the equipment was obtained.

2. Critical Mass Considerations

Any system which operates with large amounts of fissionable materials must be considered on the basis of criticality implications. The amount of plutonium which had to be stored during the waste recovery program exceeded the critical mass, as determined by F. E. Krusei (11, pp. 1-85), for some sets of conditions which could have resulted had no thought been given to non-critical arrangement of the stored plutonium solutions.

Krusei's extensive studies investigated how the critical mass of plutonium in aqueous solutions varies with extraneous materials content of the solution, plutonium concentration, isotopic composition of the plutonium, temperature, water tamping, dimensions and geometric shape of the containing vessel, and the material and construction of the vessel.

As concerns geometric shape of a system containing plutonium, neutron losses from an aqueous solution are minimized by holding small

surface to volume ratios provided the volume is above a minimum size. If the volume is below a minimum size, the system cannot be made critical regardless of the plutonium content (in solution) because of neutron leakage. These values as given by Krusei are: (11, p. 58)

"A maximum safe tamped cylindrical diameter of 6 inches is indicated. The maximum safe thickness of 2.8 inches is found for an infinite tamped slab. The maximum safe volume of a moderated fuel solution is 5.8 liters, containable in an 8.8 inch diameter thin steel sphere."

"Tamping" is the term applied to the result of surrounding a neutron source with a material which will reflect some of the escaping neutrons back into the source. If water is the tamper, an effectively infinite tamper results from a layer 12 inches thick (11, p. 19).

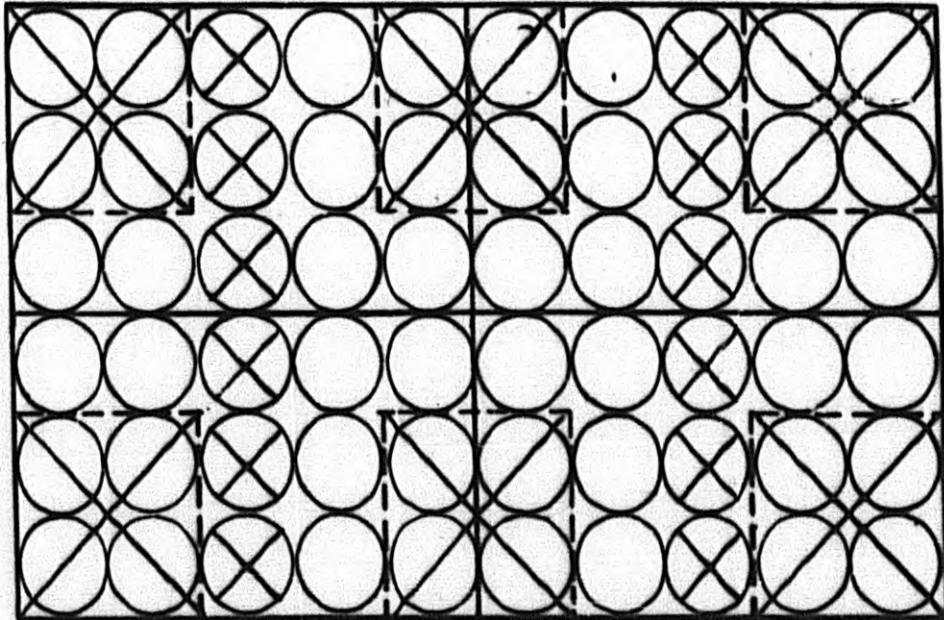
From this there was clearly no possibility in being able to add enough plutonium in solution to the 5 liter reactor which was used for this study or to any one 4 liter bottle to make a critical system. The situation to guard against was that neutron interaction between sub-critical bottlefuls of plutonium solution did not result in a critically assembled system. In order to guard against such possibilities a storage pattern was worked out which would accommodate up to 2800 grams of plutonium in 60 four-liter Pyrex bottles. This storage arrangement is diagramed in the accompanying Figure 1. Figure 2 is a photograph of a quarter of the storage area. Approval of the storage arrangement by the

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DIAGRAM OF SPECIFIED STORAGE ARRGT.



- A. AREAS BOUND OFF BY DOTTED LINES TO CONTAIN A MAXIMUM OF 400 G Pu, THE DISTRIBUTION OF Pu WITHIN EACH AREA NOT NECESSARILY BEING UNIFORM.
- B. EACH BOTTLE MARKED WITH AN "X" SIGN TO CONTAIN 25 G Pu OR LESS.
- C. EACH BOTTLE NOT INCLUDED BY "A" OR "B" TO CONTAIN 5 G Pu OR LESS.

FIGURE 1

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SOLUTIONS IN A PART OF THE STORAGE SECTION

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Figure 2

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critical mass experts of Hanford Works (10, pp. 1-2) was contingent on several conditions. Possibility that the storage hoods might be flooded with water had to be excluded because of the moderating and tamping effect a layer of water would have. Even tanks of water in rooms directly above or below the storage area were advised against. Calculations were based on an 8 inch slab thickness (the height of the bottles) so care had to be taken not to increase slab thickness in the storage area. This would, of course, decrease the surface to volume ratio and thus make conditions towards criticality more favorable. As an added precaution, cadmium sheeting 0.020 inch thick was to be inserted between each rank and file of bottles to serve as thermal neutron absorbers.

The position of the reactor with respect to the storage area was in a plane 1 foot above and parallel to the plane of the storage area and 3 1/2 feet from the nearest 400 gram location. The maximum batch processed in the reactor is 300 grams of plutonium. Although the reactor is under the maximum safe volume of 5.8 liters, and as such, cannot within itself be made critical by a plutonium solution, the 300 gram limit is imposed to avoid any possibility of disaster in case of inadvertent double batching of two recovered solutions followed by neutron interaction with other stored solutions or with itself upon dilution to 25 liters for preparing process feedstock.

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3. The Reactor

The reaction system for carrying out recovery work was designed to be the simplest possible construction which would accommodate the processing requirements. A minimum number of operating parts was used because of the hazardous nature of plutonium. The equipment consists of a reaction flask, a reactor spray trap, a condenser, a distillate receiver, a filtrate receiver, and appropriate connections for vacuum control. A schematic diagram is given in Figure 3. Figure 4 is a photograph of the equipment as set up in a hood.

The reaction flask was made ^{by} sealing a Pyrex Buchner funnel with a 90 mm. coarse fritted disc to the bottom of a five liter flask. The neck of the flask is a standard taper, ground glass, female joint to which the reactor spray trap is fitted. A detailed drawing of the reaction flask is given in Figure 5.

Provision for heating the contents of the reactor was made by placing a heating mantle around the reaction flask. Since a mantle of appropriate design and size was not available as a stock commercial item, a special mantle was designed and made to order. The special Glas-Col heating mantle is included in Figure 5. This design employs two circuits in the bottom mantle so that independent adjustment of the power input to different portions of the mantle is possible. Volumes of solution as low as 500 milliliters can be boiled without forming crusts of crystallized salts on the reactor walls above the liquid level. The heating

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SCHEMATIC SKETCH OF EQUIPMENT SETUP

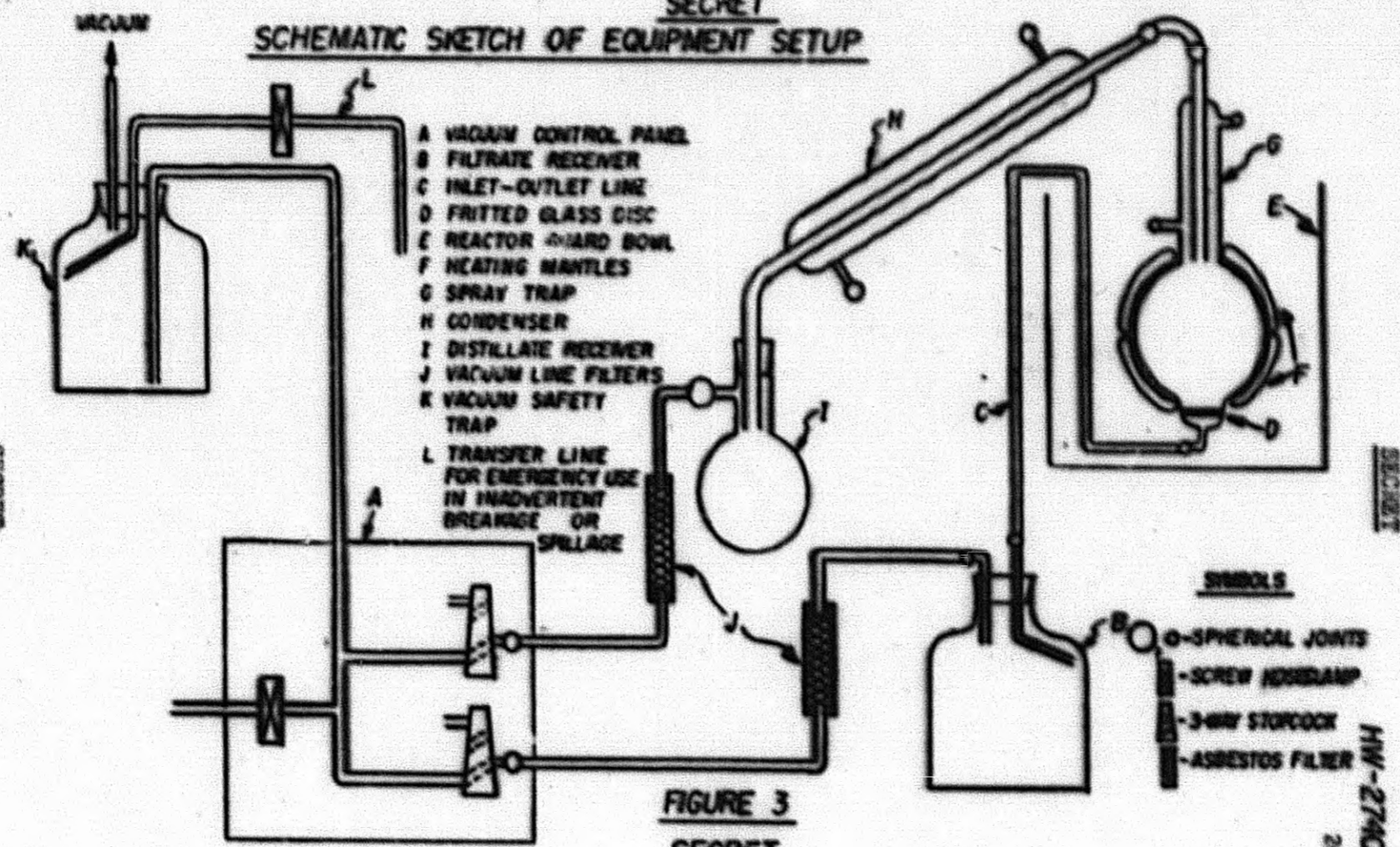


FIGURE 3
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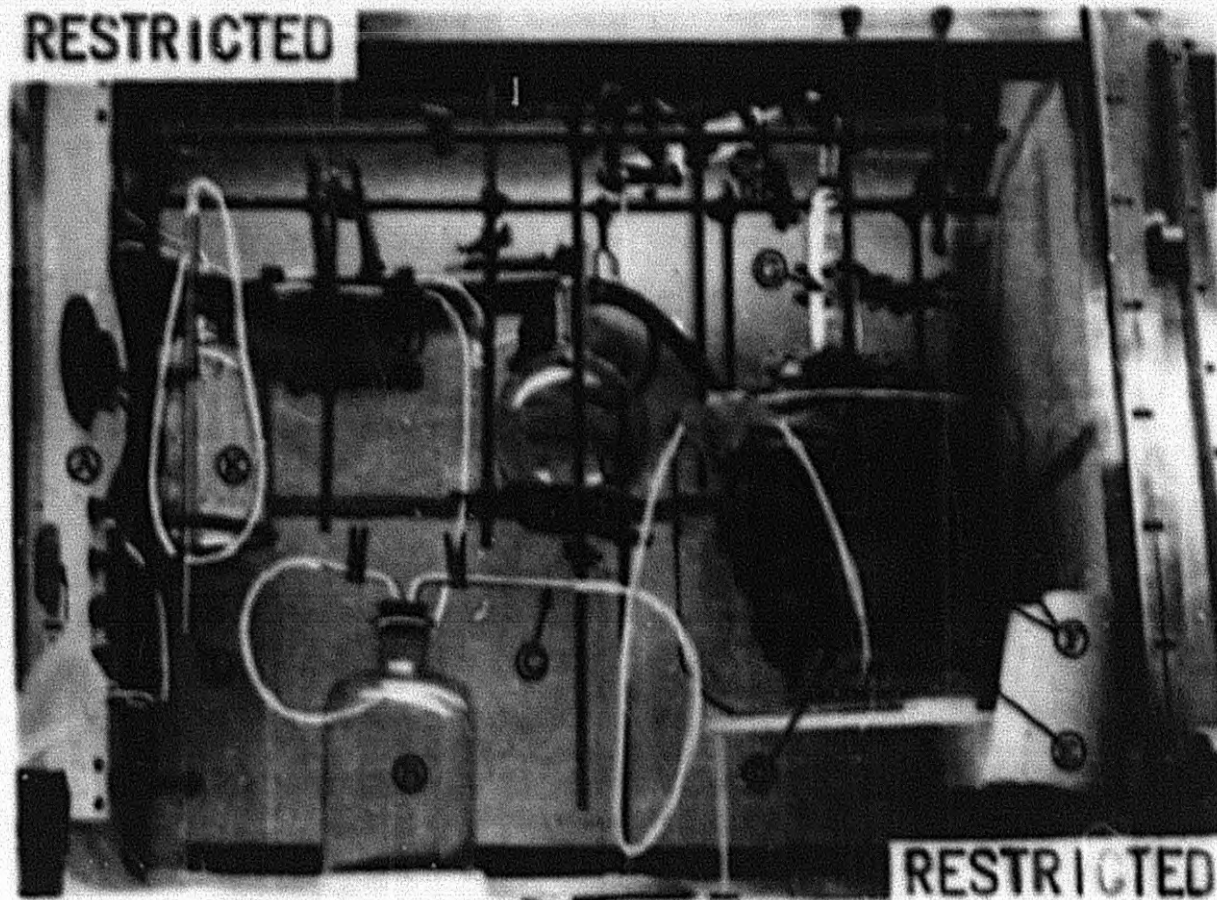
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EQUIPMENT SETUP IN A HOOD

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Figure 4

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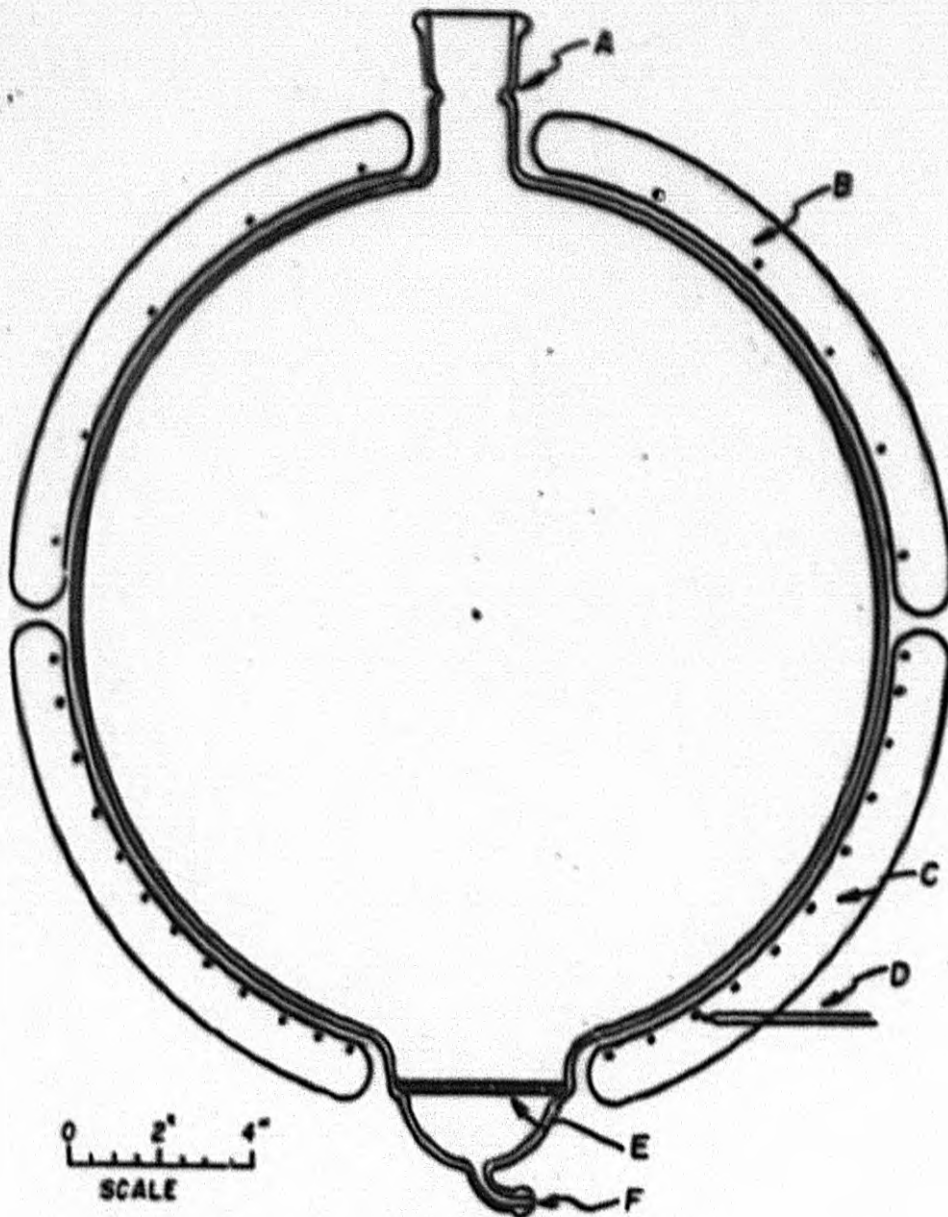
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REACTION FLASK



A-PYREX GLASS BULB, 5 LITER WITH $\frac{3}{8}$ 45/50 NECK

B-UPPER HEATING MANTLE - ONE 300 WATT CIRCUIT

C-LOWER HEATING MANTLE - TWO 300 WATT CIRCUITS

D-IRON-CONSTANTAN THERMOCOUPLE

F-SPHERICAL JOINT

E-FRITTED PYREX
GLASS DISC, 90
MM DIAMER

12/5 BALL

FIGURE 5

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system can be utilized for boiling under total reflux as for digestion of difficulty soluble solids, for distillation steps as for eliminating excess acid, and for metathesizing chloride solutions to nitrate solutions. Sometimes it is merely desired to warm a solution to aid an oxidation. Electrical heating by means of mantles was found to meet these needs without extensive auxiliary apparatus.

The reaction flask is placed in a guard bowl consisting of a 12 gallon carboy with the top removed. This protects the flask from inadvertent breakage. It would also serve to contain the flask contents should the flask break.

Solutions are added to and removed from the reaction flask by vacuum transfer. Stirring is accomplished by applying a vacuum to the top of the flask and allowing air to enter the bottom through the frit.

A contaminated mist is associated with the air leaving the reaction flask during stirring. Since it is desirable to keep the plutonium in the reaction flask, it must be removed from the air stream. This is done by passing the air through the reactor spray trap, which is fitted to the reaction flask by a standard taper male joint. A detailed drawing of the spray trap is given in Figure 6. It includes provision for directing the air through nozzles against the several bulb walls, which action effectively removes the plutonium from the effluent air. Drip holes at the base of the nozzles allow liquid to flow back into the reaction flask. Visible

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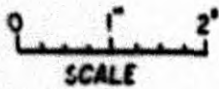
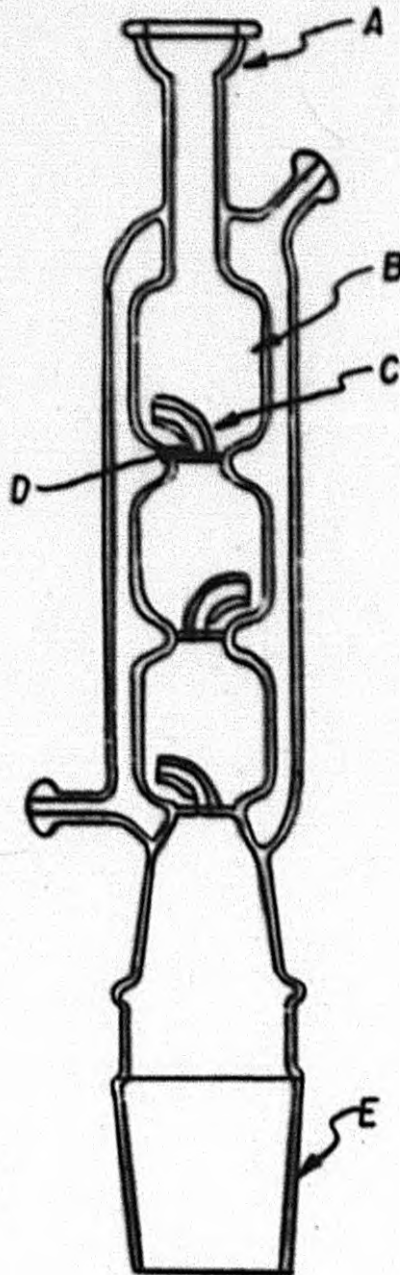
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REACTOR SPRAY TRAP



- A SPHERICAL JOINT 28/12 SOCKET
- B SPRAY BULB
- C NOZZLE
- D DRIP HOLE
- E INNER JOINT 8 45/50

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FIGURE 6

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amounts of liquid are present in the spray trap only when the contents of the flask are heated.

Next in series in the reaction system is a condenser which is used for condensation of materials boiled out of the reactor, such as acids, volatile organic materials, and iodine. These are caught in the distillate receiver, a flask of three liters capacity.

The vacuum system is attached to the reaction system such that a vacuum can be applied to the top of the flask while venting the bottom to atmosphere, as during stirring; one can apply a vacuum to the bottom of the flask venting the top as is done during filtration. A fine control is included in the vacuum system to regulate flow rates. Asbestos filters isolate the vacuum train from the reaction system.

Entry into the reaction system for addition of plutonium solutions, reagent solutions, and washes is very simple and in such a manner as not to contaminate outside surfaces of the equipment. It is very important that contamination of exposed surfaces, particularly on parts which must be handled, be controlled for reasons of health hazard to personnel as indicated previously.

From Figure 3 it is seen that proper positioning of the vacuum control panel stopcocks will vent the filtrate receiver to the atmosphere and draw a vacuum on the upper side of the glass fritted disc. The pressure differential which is maintained between the reactor and the atmosphere is adjustable by a hoseclamp operated vent on the vacuum

manifold at the control panel. This of course controls the rate of flow of air (or liquid) into the reactor.

To charge a plutonium solution into the system, one makes the vacuum control settings just indicated, disconnects the inlet-outlet line from the filtrate receiver at the spherical joint, temporarily connects a disposable tip to the inlet-outlet line, and immerses the disposable tip into the plutonium solution to be transferred. After the desired volume of solution has been transferred by vacuum through the glass fritted disc into the reactor, withdrawal of the tip from the waste solution allows air to sweep the inlet-outlet line and the void below the glass fritted disc free of liquid. A small volume of rinse added to the reactor in a like manner completes a quantitative transfer of waste solution into the reactor during which contamination of the exposed surfaces of the system have been confined to the end of a spherical joint.

The precipitant is added to the reactor in the same manner as the plutonium solution. After addition of a solution of the precipitant to the reactor, air is continually drawn through the bottom of the fritted disc, agitating the mixture to uniformity. The reactor is essentially a closed system at this point with respect to activity - the spray traps prevent loss in the air stream and the active solids are retained by the glass fritted disc. The mother liquor is filtered off by connecting the inlet-outlet line to the filtrate receiver, venting the space above the reactor contents to the atmosphere and drawing vacuum in

the filtrate receiver by manipulation of the vacuum panel stopcocks. The filtrate is active only to the slight extent of the solubility of the precipitated plutonium compound. Washing of the precipitated cake is accomplished as necessary by transferring wash liquid into the reactor, stirring, and removing the wash liquid into the filtrate receiver, all during which activity is confined to the reactor.

The plutonium precipitate is dissolved by an appropriate solvent which is added to the reaction flask in the manner previously described. The active solution resulting from dissolution of the precipitated plutonium compound presents little contamination problem upon removal from the system. As soon as the inlet-outlet line has emptied of excess recovered solution, it should be disconnected from the filtrate receiver and cleaned, lest the traces of recovered solution wetting the inside of the line evaporate to dryness and flake off particles of the plutonium compound into the air at a later time. A small volume of fresh solvent taken into the reactor, agitated, and removed to the main portion of recovered solution accomplishes the cleaning.

The rather simple reaction equipment design is seen then to be capable of making the necessary solution transfers for processing in such a manner as to avoid extensive contamination of exposed surfaces of the equipment. Provision for mixing of the reactor contents after precipitation and during washing and dissolution of product cakes and provision for separation of product solids from effluent liquids is furnished. These are provided for without auxiliary equipment by having the vacuum transfer feature do double duty to provide air agitation for mixing and by having the glass

fritted disc be an integral part of the precipitation vessel. No access ports, or mechanical parts such as stirring rods, propellers, or magnetic stirring devices, are required for mixing. No auxiliary equipment is needed for separation of the product cake from the effluent.

While all of the essential functions have been provided for in this simple apparatus design, it is a compromise on other features which could be termed "convenient" for the purpose of the analytical waste recovery program. One example of this lies in the fact that the contents of the reactor cannot be sampled without first removing the contents from the reactor. This does not result in particular inconvenience in ordinary cases because of the possibility of calculating the composition of the reactor contents. Analytical results are obtained for all solutions before adding them to the reactor and account is kept of all rinses and reagent solutions added to the system and all effluent solutions removed from the system. Thus, information such as plutonium concentration or acidity of the reactor contents can be calculated at any time.

No provision is made for the possibility that the glass fritted disc may at some time become plugged while a solution is in the reactor except that the system can be opened at the standard taper joint between the spray traps and the 5-liter bulb. Opening of the system and removal of the active solution would be a hazardous undertaking but this is unlikely to be necessary if a thorough knowledge of the characteristic composition and reactions of each solution type is obtained beforehand

from analytical data and from small scale experiments in the 1/50 size reaction units to be subsequently described.

No means to rapidly remove heat from a reaction mixture is available in the present equipment design. Thus, any reactions which tend to go out of bounds if not cooled should not be run in this system.

Small scale reaction equipment was designed and built for use in evaluating proposed recovery schemes. The design was small so that large amounts of plutonium need not be involved in testing out ideas, yet large enough so that most of the proposed features of the full scale apparatus could be duplicated. The ratio between both the fritted disc areas and the reaction flasks of the two reactors is 1/50. A drawing showing the construction of a 1/50 size reactor is given as Figure 7. The reactors are used in a 1/50 size reaction unit such as is photographed for Figure 8. The unit is seen to consist of:

- A. A glass tube which is the point of entry into the system;
- B. A glass fritted disc of approximately 1 square centimeter area;
- C. A 100 milliliter bulb capable of being heated by means of an electric heating mantle;
- D. A condenser;
- E and E¹. Vacuum filter flasks so connected to stopcocks by tubing that either flask can be vented to atmosphere while evacuating the other, or that both can be vented to atmosphere at once. 1/50

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1/50 SIZE REACTOR

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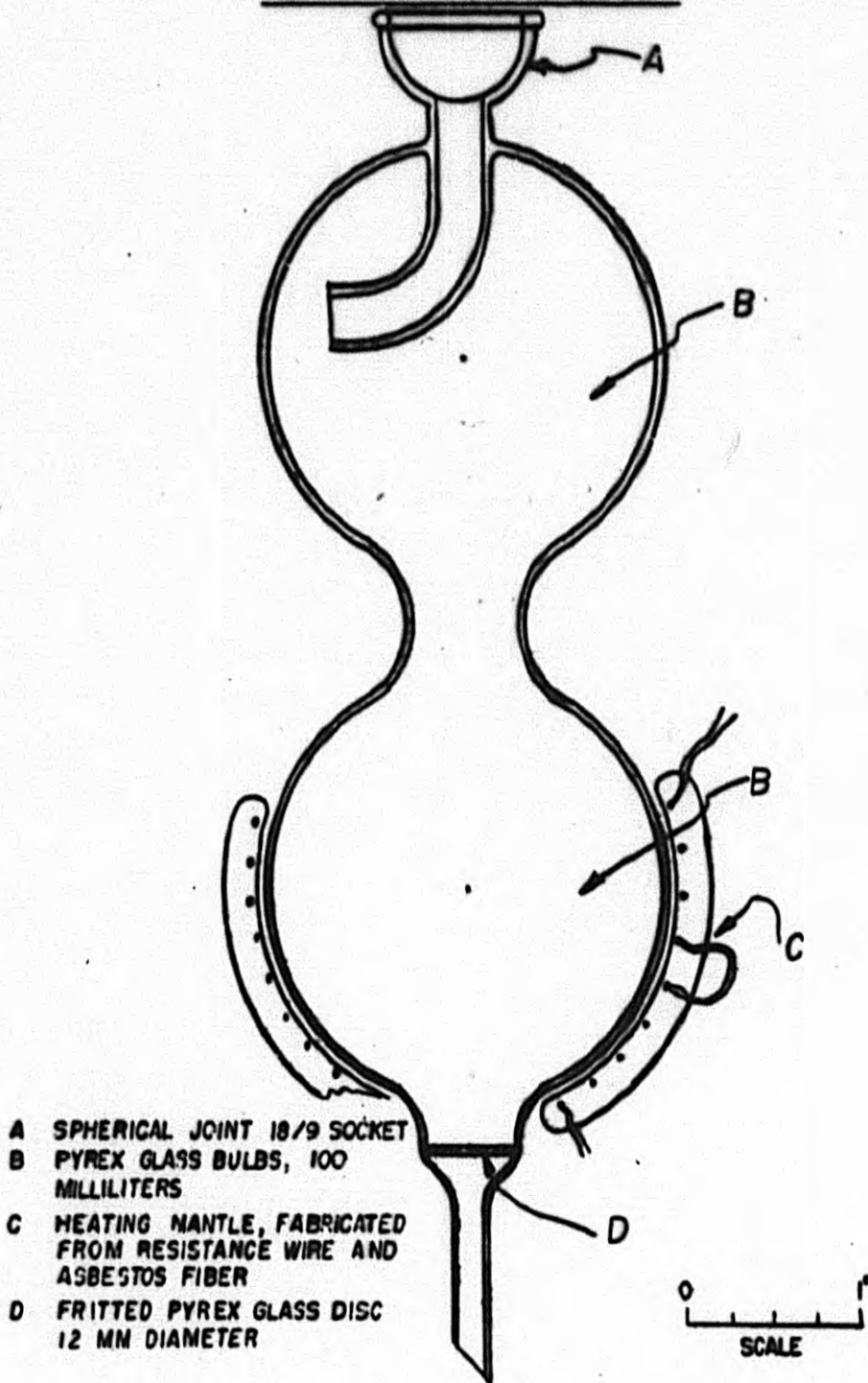


FIGURE 7

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1/50 SIZE REACTION UNIT

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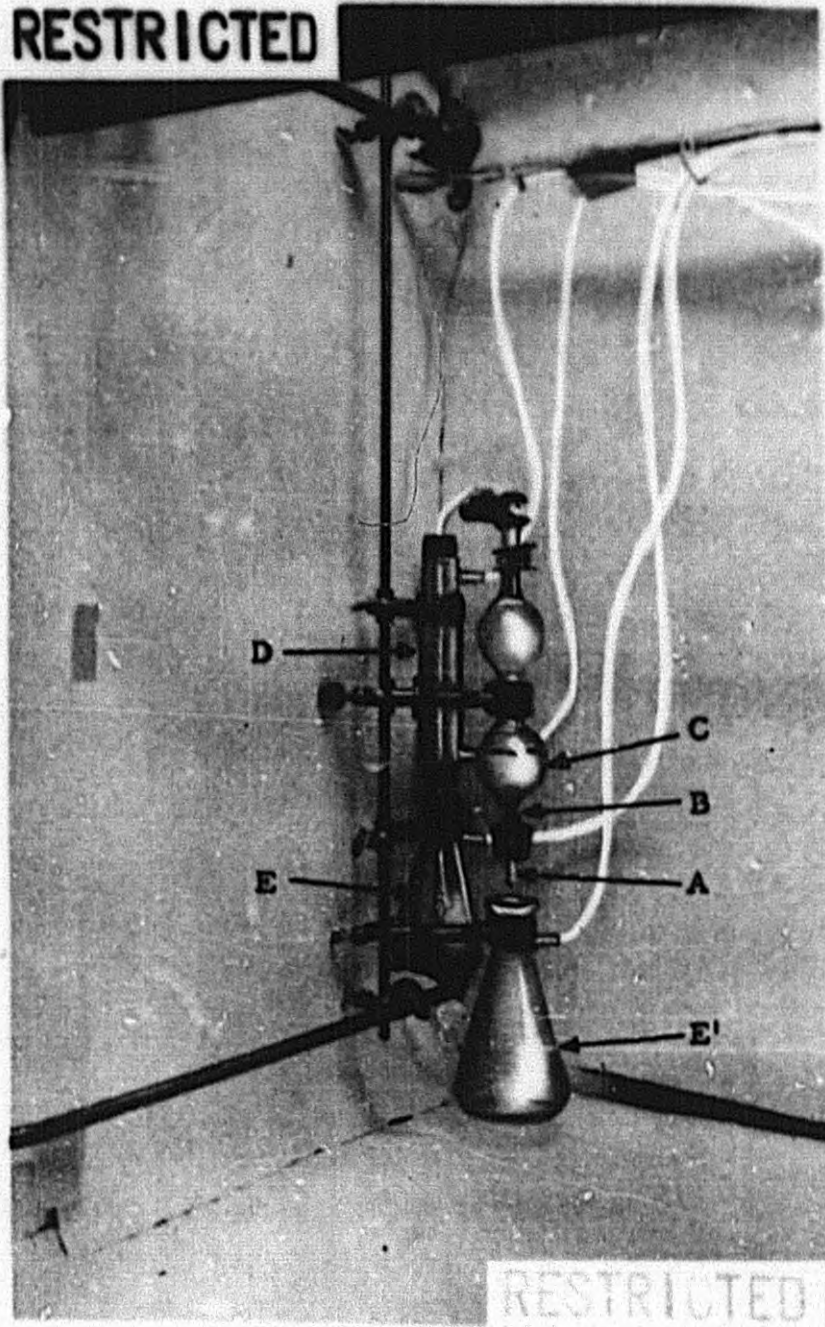


Figure 8

4. Analytical Methods

This investigation required determination of plutonium at many points to furnish such data as the plutonium content of the starting material, the plutonium content of the effluent waste streams, and the plutonium in the recovered product. Two general methods are available for plutonium assay. One depends upon the radioactive decay rate of plutonium and is called a radioassay. The second method depends on the quantitative oxidation of Pu (III) to Pu (IV) by a standard solution of an oxidizing agent, such as Ce (IV). This method is known as a chemical assay for plutonium.

The principal plutonium isotope produced in the Hanford piles is Pu-239 with a half life of 24,340 years, which decays by alpha emission to U-235. The daughter is an alpha emitter of half life 8.9×10^8 years. The fact that the plutonium which we wish to determine has a long half life which is still much shorter than its alpha active daughter allows measurement of the activity of plutonium solutions to be a simple measure of the plutonium concentration of those solutions. The data required to make the determination are the specific activity (the number of disintegrations per minute which are associated with one gram of plutonium) and the number of disintegrations per minute per unit volume which occur in the solution being assayed. The specific activity, d/m/g, of plutonium cannot be uniquely calculated from the half life of Pu-239 because of

other plutonium isotopes. The specific activity of such mixtures depends upon the relative amounts of the isotopes present which in turn varies with the total neutron irradiation received by the uranium in the pile.

The second most abundant isotope produced is Pu-240, an alpha emitter of 6,000 years half life. As total neutron irradiation increases, so does the ratio Pu-240/Pu-239. Thus it can be seen that the longer a batch of uranium is irradiated in a pile, the higher will be the specific activity of the plutonium finally isolated from the uranium. It is not feasible to determine the isotopic composition of each sample of plutonium produced, so radio assay results are calculated from unit volume disintegration rates as if all the plutonium present were Pu-239. An appropriate "isotopic correction factor" is then applied to the result to give the true plutonium concentration. The source of the isotopic correction factor will follow discussion of plutonium determination by chemical assay.

The chemical assay for plutonium depends on the quantitative oxidation of Pu (III) to Pu (IV) by Ce (IV) in 3 N H₂SO₄ solution. To change the plutonium in the sample from its equilibrium distribution of Pu (III), Pu (IV), and Pu (VI) to Pu (III), excess Ti (III) is added. Using Ce (IV) for the oxidant and titrating with potentiometric detection of equivalence points, a rapid change of emf is noted first at the completion of oxidation of the excess Ti (III) to Ti (IV) and again at

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the completion of oxidation of Pu (III) to Pu (IV). Substances, such as iron, which react with Ce (IV) under these conditions interfere. Independent determinations of the interferences must be made and the appropriate corrections applied. Iron is the only interference which is corrected for. A radioassay is used if additional interferences are present. Samples which are not sulfate solutions must be fumed with sulfuric acid to give a sulfate medium. Ordinarily a 1 milliliter Gilmont type buret is used to deliver a 0.05 N Ce (IV) solution to an aliquot of the sample containing 7-8 milligrams of plutonium.

It is seen that having a choice between making a radioassay or a chemical assay is valuable in recovery work. Solutions whose compositions prohibit a chemical assay are determined radiometrically. For relatively pure solutions, the chemical assay can give the true plutonium concentration directly.

The chemical assay does not depend upon the isotopic composition of the sample - all isotopes of a given element are chemically identical. This fact furnishes an experimental method for relating conditions of pile operation to the specific activity of the plutonium which is produced. Samples of a batch of plutonium can be determined by radioassay, assuming all plutonium to be Pu-239 having a specific activity of 1.37×10^{11} d/m/g. Determination of the actual plutonium concentration by chemical assay is also made. The ratio CA/RA is then the isotope

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correction factor for converting results of a radioassay into a true plutonium concentration for that particular batch of plutonium. After accumulation of data for isotope correction factors at various conditions of production in the pile, a factor can be chosen for a particular batch of plutonium on the basis of the pile conditions at which the batch of plutonium was produced.

5. Type A Solutions: a. Sodium Hydroxide Precipitant

Type A solutions were known to contain plutonium at an average concentration of 10 g/l along with varying amounts of sulfate, dichromate, chromium (III), sodium, and traces of organic matter in 2M perchloric acid. Table I shows that 725 g of plutonium were contained in 70 l of solution. The 70 l was stored in fractions of about 4 l each. The compositions of the fractions varied markedly from the average, evidenced by the presence of a solid in some fractions. This solid was considered to be $\text{Pu}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ because of its typical red color and the known presence of sulfate in the solution.

The chemical nature of the impurities is such that precipitation with strong base is specific for the plutonium in the solution, present predominantly as plutonium (IV); chromium (III) exhibits amphoteric properties, and the other salts present are soluble in water. A trial separation was made using a 1/50 size reaction unit in the following manner.

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Nineteen and four-tenths ml. of Type A solution was introduced into a 1/50 size unit, making the transfer quantitative by water rinsing. Addition of 6.0 ml of 10M NaOH caused a flocculent green precipitate to form which is characteristic of plutonium (IV) hydroxide. After stirring the mixture for about 10 minutes, the supernatant liquid was removed by filtration. The precipitate was then washed several times with water to remove adhering salts, dissolved in 3.0 ml of concentrated HNO₃, and the plutonium removed from the unit as a solution. This solution was analyzed spectrochemically for impurities. Four 1/50 scale runs were made varying the conditions of the separation. Table III contains the data from two of the runs.

TABLE III
RECOVERY FROM TYPE A SOLUTIONS
 Plutonium (IV) Hydroxide Precipitation, 1/50 Scale Runs

	<u>Run 1</u>	<u>Run 2</u>
Pu in run, g:	0.400	0.352
Pu lost in filtrate and washes, g:	1.3×10^{-5}	1.4×10^{-5}
Disc porosity of 1/50 scale unit:	Medium	Coarse
Wash conditions:		
1st wash	10 ml. H ₂ O	25 ml. H ₂ O
2nd wash	25 ml. H ₂ O	10 ml. H ₂ O
3rd wash	10 ml. H ₂ O	---
Filtration rates, ml/min:		
mother liquor	0.38	0.38
1st wash	0.17	0.17
2nd wash	0.42	0.22
3rd wash	0.33	---
Product purity, impurity in parts/million parts Pu:		
Ca	200	40
Cr	10,000	10,000
Hg	400	400
Na	10,000	10,000
Ni	100	20

The data given in Table III shows that the separation of the impurities was accomplished with very little loss of plutonium. Increasing the amount of plutonium per run and the average filtration rate by a factor of 50 indicates that the full scale equipment should be able to separate at least 20 g of plutonium as the hydroxide per batch with a filtration rate of from 8.5 to 21 ml/min. It was also noted that a coarse porosity disc will perform the separation as well as a medium porosity disc. Two water washes were found to be satisfactory.

Four hundred thirty-three grams of plutonium had been recovered from Type A solutions by sodium hydroxide precipitation up to July 15, 1952. Recovery runs numbered 20. The processing was essentially as described in the preceding paragraphs for the 1/50 scale runs. Precipitation was made using enough caustic to give 1 M excess NaOH in the supernatant liquid. Two water washes each of 30 ml H₂O/g Pu were given the cake before dissolution in concentrated HNO₃, which was added in an amount of 8 ml HNO₃/g Pu. Presentation of processing data on a typical full scale recovery run using sodium hydroxide as the precipitant are given in Table VI.

During the course of full scale recovery work with hydroxide precipitation of Type A solutions, it was found that with up to 28 g of plutonium precipitated as plutonium (IV) hydroxide filtration rates of about 10 ml/min. obtain, but with larger batches (30 to 35 g) the filtration rate falls off rapidly to less than 1 ml/min. Thus, the practical batch

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size for hydroxide cycles in the reaction equipment is limited to 28 g of plutonium.

The recovered solutions consisting of the plutonium hydroxide dissolved in concentrated nitric acid were composited as recovery proceeded until 140 g had been collected. A considerable amount of silicic acid was found to settle out of the composited solutions after about 3 weeks, although no silicon compounds are used in the analysis from which Type A solutions are collected. A possible source of the silica may be the result of the reaction of the 10 M caustic used for precipitation on the fritted disc of the reactor. This seems unlikely since the amount of silica observed was quite large and the time of contact of the frit with 10 M caustic is but 2 or 3 minutes for each 28 g recovery batch. Reaction of caustic with the frit should cause formation of sodium silicate, a soluble material one would expect to be removed with the filtrate.

Another explanation is that the silicic acid results from the action of perchloric acid on the soft glass in the apparatus in which the control determination giving rise to Type A solutions is made. The silicic acid particles in the accumulated plutonium solutions being small enough to remain suspended, pass the fritted disc pores when the solution is charged into the reactor later to be adsorbed by the hydroxide precipitate rather than reacting with caustic to give soluble sodium silicate. Dissolution of the hydroxide cake with acid would release the

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particles which later coagulate in the concentrated nitric acid solution.

In time the material settles out as a jelly, and it is necessary to separate this material from the recovered solution. The separation is accomplished by increasing the particle size of the silica until it can be filtered off. The reaction equipment is used to advantage here. After 150 g or so of plutonium have accumulated as a combined recovered solution and before the silicic acid has coagulated appreciably, the solution is charged into the reactor and boiled for about 2 hours. Partial dehydration of the silicic acid occurs in the strongly acid solution so that withdrawal of the solution from the reactor leaves a pad of silica in the reactor on the fritted disc. Solution which is adsorbed by the pad is removed to the main portion by a few dilute nitric acid rinses, after which the pad of silica is easily peptized by 6 M sodium hydroxide to be removed through the fritted disc as a milky suspension.

5. Type A solutions: b. Iodic Acid Precipitant

It has been observed that the separation of plutonium from Type A solutions by hydroxide precipitation is satisfactory but is limited to 28 g batches. Thus, it was desired to investigate the usefulness of iodate precipitation. Although plutonium nitrate is the preferable form for solutions to be returned to process streams, a point is available in the Separations Process at Hanford where sulfate solutions containing

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chromium can be tolerated. The strict requirements on solutions returned to the process stream at this point are that ions corrosive to stainless steel be absent and that the plutonium can be precipitated as the fluoride. In terms of Type A solutions this means that the perchlorate ion is the main objectionable feature.

Work was carried out to formulate a precipitation cycle in acid solution using iodate as the precipitant. It was indicated from the work of Fries (6, pp. 14-16) that this salt, in contrast to plutonium hydroxide, is quite filterable. Another expected advantage was complete avoidance of silicic acid coagulation. Of the contaminants, only chromium would remain with the plutonium.

Two of three 1/50 scale runs using iodate precipitation will be described. In the first run, 35.0 ml of Type A solution was introduced into a 1/50 size reaction unit with a coarse porosity disc, making the transfer quantitative by water rinsing. Addition of 5.0 ml of 1.5 M HIO_3 gave the finely divided pink precipitate of $\text{Pu}(\text{IO}_3)_4$. After stirring the mass to uniformity, removal of the supernatant liquid was completed by filtration, which was very rapid. Thirty-eight ml more of Type A solution was added to the 1/50 size unit containing the previous cake, rinsed in with water, and precipitated with 5.0 ml of 1.5 M HIO_3 . Filtration this time was also rapid, so 43.0 ml more of Type A solution was added to the unit, precipitated, and filtration completed. At this point the solid in the 100 ml bulb occupied about 1/3 of the space.

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The cake was washed once with 50 ml of 0.1 M HIO_3 rather than with water because of lower solubility of the cake in the HIO_3 .

Dissolution was accomplished by reducing the iodate to iodide with sulfur dioxide, plutonium (III) sulfate being formed in the process. To do this the $\text{Pu}(\text{IO}_3)_4$ was slurried in 50 ml of 1 M HNO_3 and treated at room temperature with 42 g of sulfur dioxide. It took 5 hours to complete the reaction. By then boiling the solution, the nitric acid present oxidized the iodide to iodine, which was evolved from the solution and trapped in caustic in the distillate receiver. Plutonium(III) sulfate is converted to plutonium(IV) sulfate on boiling the solution. This differed from the work of Fries, who separated the plutonium from the iodide by precipitating plutonium(III) hydroxide.

Several things were unsatisfactory about the run described. During the course of the filtrations it was noted that a small amount of the $\text{Pu}(\text{IO}_3)_4$ solid passed through the pores of the coarse frit into the filtrate. Dissolution by passing sulfur dioxide through the cold dilute acid slurry of the cake was slow. This was due in part to the formation of iodine as an intermediate product during the reduction which caused the reaction mixture to become a rigid, unreactive mass so that most of the gas bubbled through without reacting. When the solution was heated, much difficulty was experienced because of the condensation of solid iodine in the cooler sections of the apparatus. This in turn created an unsafe condition due to possible plugging of the system during the heating.

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With previous experience at hand, another run was made using a 1/50 size reaction unit having a medium porosity frit. For dissolution the $\text{Pu}(\text{IO}_3)_4$ -1 M HNO_3 slurry was heated to boiling before sulfur dioxide was admitted to the system. Dissolution required a total of 20 minutes and 8 g of gas (stoichiometric amount was 4 g) compared to 5 hours and 42 g of gas when the experiment was run in the cold. The iodine was evolved as it was formed during the reduction so that after dissolution was complete, only traces of iodide and iodine remained in the solution. No hazard due to clogging of the system with solid iodine was possible because the "cooler" parts of the system had been preheated by the condensing hot vapors of the boiling slurry and no deposits of iodine formed. The medium frit retained all solids.

Data from the two runs described are given in Table IV.

TABLE IV
RECOVERY FROM TYPE A SOLUTIONS
Plutonium (IV) Iodate Precipitation, 1/50 Scale Runs

	Run 1	Run 2
Pu in run, g:	1.29	1.29
Pu lost in filtrates and washes, g:	(solids leaked thru filter)	1.8×10^{-4}
Disc porosity of 1/50 scale unit:	Coarse	Medium
Filtration rates, ml/min:		
1st charge	0.2	(Not measured
2nd charge	0.43	(but not noticeably
3rd charge	0.2	(different from
1st wash	0.17	(Run 1

The amounts of plutonium and the filtration rates given in Table IV indicate that 65 grams of plutonium should be easily processed in one

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batch in the larger reactor. Plutonium losses in the filtrate are low enough to be acceptable if a medium porosity frit is used.

Full scale recovery of Type A solutions by iodate runs have been carried out under the conditions described for Run 2 of the 1/50 scale experiments cited in Table IV. Limitation on the capacity of the reaction equipment for recovery by iodate precipitation is not the filtration step -- the first full scale run was carried up to 153.2 g of plutonium in the cake where the filtration rate was still high. Filtration rate data on this run are given in Table V. No explanation is known for the rather erratic behavior exhibited by the filtration rate.

TABLE V
RATES OF FILTRATION OF PLUTONIUM(IV) IODATE

<u>Pu in Pu(I₃)₄ Cake (g)</u>	<u>Average Filtration Rate (ml/min)</u>	<u>Filtrate Collected (ml)</u>	<u>Pu Assay of Filtrate (g/l)</u>
15.20	35.0	5000	0.003
28.68	41.0	4000	0.001
50.52	29.2	3500	0.002
88.40	24.2	4000	0.001
121.66	11.1	4000	0.001
132.40	54.1	7500	0.001
153.20	30.0	4000	0.005

After the Pu(I₃)₄ cake of the first full scale run was completely dissolved, the SO₂ addition was stopped. The solution was allowed to cool to room temperature, air being passed through the solution during the cooling period. Some of the 153.2 g of plutonium crystallized as the

sulfate in the reactor because of the solubility limit of plutonium(IV) sulfate and the fact that the working volume of the reactor is 4 l maximum. At present, no difficulty arises due to crystallization because the batches are kept down to 100 g in plutonium content.

Phosphate was inadvertently present in one particular 4 l portion of Type A solution. This caused the contents of the bottle to form a semi-solid gel. Advantage was taken of the characteristic variation of solubility of plutonium phosphates with acidity by adding concentrated HNO_3 to the precipitated phosphates until all were in solution. This occurred when the solution was approximately 8 M in HNO_3 . Upon reduction of the acidity to 3 M by dilution with water, no solids precipitated out. The fact that plutonium is soluble to only 0.003 g Pu/l in a solution of 3 M HNO_3 containing 0.15 M excess iodate provided a basis for recovery of this material. Processing the solutions in this condition using an iodate precipitation effected successful elimination of phosphate and perchlorate. Due to the chemistry of plutonium phosphates, a hydroxide recovery of this material would have been impossible.

Up to July, 15, 1952, Type A solutions having a theoretical total plutonium content of 584 g had been recovered and returned to process streams. Hydroxide cycles had been used to recover 433 g with the balance being recovered by an iodate cycle. Processing data for the iodate run and a typical hydroxide run are given in Table VI.

TABLE VIRECOVERY FROM TYPE A SOLUTIONS

Plutonium (IV) Hydroxide and Plutonium (IV) Iodate Precipitation
Compared, Full Scale Runs

	<u>NaOH Run</u>	<u>HIO₃ Run</u>
Pu in run, g:	25.82	153.20
Pu lost in filtrate and washes, g:	0.001	0.062
Average filtration rate, ml/min:	11.7	32.1
Recovery rate, g Pu/hr operation:	3	6
Product purity, impurity in parts/million parts Pu:		
Ca	40	Not determined
Cr	10,000	"
Hg	400	"
Na	20,000	"
Ni	40	"

The impurity data of the hydroxide runs are taken from a spectrochemical analysis of a 143 g plutonium composite consisting of the run cited along with 6 similar runs. Thirty-one elements are read from the spectrogram so that the presence of gross amounts of unexpected impurities will be evident. Most of the elements which are present in very low concentrations and therefore are of no interest have been omitted. Impurity analytical results were not obtained on the product of the iodate run because of the presence of the large amount of chromium. The recovery rates given in Table VI show that the iodate procedure is more rapid than the hydroxide procedure.

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The product recovered from the hydroxide runs is in nitrate solution and is relatively free of chromium. Iodate runs yield a product in sulfate solution which contains any chromium originally present in Type A solutions. Effluent losses per unit of plutonium recovered are 10 times as high for iodate runs as for hydroxide runs. By economic considerations, effluent losses do not become alarming until concentrations of about 10^{-2} g Pu/l of effluent are reached. As the iodate losses are well below this value, there is little preference between the two methods on the basis of plutonium losses, and the choice must be made on the basis of other factors. The situation is one of spending a specified time to recover plutonium at a relatively high degree of purity or of requiring only half the specified time to merely render the plutonium solution compatible with the plant process purification facilities. The choice is obvious - a 5 liter glass vessel cannot successfully compete with plant process equipment once the plant equipment is able to take over. Thus, for the particular situation which exists here, the more impure but more easily prepared product is most economic.

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Differences between the data of Table III and the NaOH run of Table VI are minor. Although the total plutonium lost in the filtrate of the full scale run is double that anticipated from the 1/50 scale run, this is good agreement considering the large scale up factor. The filtration rate is approximately 80 per cent that predicted by the average rate of 1/50 scale runs. The reported spectrochemical results are accurate to within a factor of two, so the impurity results compare favorably between the 1/50 and full scale runs when the precision of the reported values is kept in mind.

Differences between the data of Table IV and the HIO_3 run of Table VI are somewhat large in the cases of filtration rates and plutonium lost to effluents. However these differences are not unreasonable for this type of comparison.

Dissolution of the $\text{Pu}(\text{IO}_3)_4$ cake from full scale runs shows some peculiar behavior of iodine not observed to occur during 1/50 scale dissolutions. Part of the reason may be due to concentration effects

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existing in the reactor spray traps and distillation condenser. The diameter of the openings in the reactor spray traps is nearly the same as that for the outlet from the upper bulb of the 1/50 size reactors. The restricted portions of the full size condenser are of approximately the same diameter as the condenser on the 1/50 size unit. Thus, with 100 times as much material passing one system as another, concentration differences between the two systems will be marked.

Iodine evolution during dissolution in the 1/50 scale units is in the form of the characteristic violet vapor which condenses to a solid in the condenser or passes as a vapor into the caustic scrubber, depending on temperature of the condenser. In any case the H_2O-HNO_3 vapors condense to liquid and run down the condenser into the caustic scrubber, washing the condenser free of any solid iodine which forms. It is noted that the solid iodine which may form in the condenser is not very soluble in the dilute HNO_3 which condenses.

Iodine evolution during dissolution in the full scale apparatus is in the form of a very dark brown vapor, which easily condenses to a dark brown liquid much resembling liquid bromine in appearance. The proper heat balance in the condenser, obtained by adjustment of the flow of water, will cause the brown liquid to run out of the condenser in a small stream into the caustic solution where it rapidly fades to yellow and finally becomes colorless. Removal of too much heat from the condensing system causes very heavy deposits of solid iodine to form throughout the

condenser. The dilute HNO_3 continues to condense and runs from the condenser as a faint yellow stream but does not remove iodine as fast as it deposits. The only way the dissolution can continue for more than a few minutes without plugging the condenser with iodine is to restrict the flow of condenser water so that the temperature rises and the brown liquid again condenses out. Under these conditions the deposits of solid iodine are soon removed by the brown liquid. The temperature of the condenser must be about 40°C or warmer in order to prevent formation of solid iodine.

Simple tests showed that the solubility of iodine in dilute HNO_3 between room temperature and 100°C is much too low for the brown liquid which is observed to be merely a solution of iodine in dilute HNO_3 . The fact that one prepares aqueous solutions of iodine by forming the soluble I_3^- complex with iodide furnishes a clue to explaining the behavior mentioned. Evidently some of the iodine is reduced to iodide by excess SO_2 , either in the vapor phase in the spray traps or in the liquid slurry. Condensation of vapors containing both iodine and iodide would result in the formation of the I_3^- complex so that all condensed substances enter a single liquid phase. As a drop in temperature below 40°C yields solid iodine, the system must be near the limit of solubility of the "soluble" I_3^- complex.

It is fortunate that the iodine can be handled as a liquid because of the ease with which the liquid clears itself from the condenser

compared to the problem of keeping the condenser clear of solid deposits.

6. Type B Solutions: a. Sodium Hydroxide Precipitant

Type B solutions are seen from Table I to contain plutonium at an average concentration of 0.3 g/l in a solution 1M in hydrogen ions. Sulfate, molybdate, chloride, tin, and ammonium ion are also present. A total of 8 g of plutonium was dissolved in 28 l of solution. As in the case of Type A solutions, precipitation of plutonium hydroxide offers a ready means of plutonium recovery. Tin is amphoteric, and all other contaminants remain soluble in basic solution.

Due to the low plutonium concentration in the solutions, it was felt that precipitation of the plutonium as the solutions stood in the bottles would afford convenient preliminary operation. Here, in contrast to solutions of 10 g Pu/l, the volume of precipitate was a small part of the volume of the supernatant liquid. Letting the precipitate settle by gravity and decanting off the supernatant liquid is a feasible means of separation of solid from liquid in such circumstances.

A volume of 200 microliters of Type B solution was added to a 2 ml centrifuge cone and made basic with 25 microliters of 10M NaOH. After

thorough mixing, the plutonium hydroxide was allowed to settle out by gravity for 16 hours. A radioassay of the supernatant liquid in the centrifuge cone indicated 0.001 g Pu/l to be present. On the basis of this experiment, each bottleful of Type B solution was made basic with excess NaOH, stirred with a motor driven glass stirring rod, and allowed to stand overnight. After decanting the supernatant liquids by vacuum transfer, all cakes were transferred as slurries into one bottle where the solids were washed twice with 1 liter portions of distilled water. Decantation was again used to separate solids from liquid. Finally, the solids were dissolved in concentrated nitric acid.

On this series of operations, the plutonium in the original bottles totaled 7.897 g, and that found in the recovered solution was 7.804 g. No spectrochemical determination of purity was made. The recovered solution was merely composited with other recovered solutions, and a single impurity determination was finally made on the composite.

7. Type C Solutions: Iodic Acid Precipitant

Table I shows Type C solutions to contain 5 g Pu/l as an average approximate concentration. A total of 36 l collected had a plutonium content of 190 g. The contaminants are chloride, sulfate, cerium, and titanium in acid solution. In this case it was decided to remove the chloride by aniodate cycle as described for Type A solutions and return the recovered solution, containing sulfate, cerium, titanium, and

plutonium, to process streams at the point referred to under "Type A Solutions: Iodic Acid Precipitant".

With the experience of processing Type A solutions by iodate cycles at hand, the only experimental work undertaken prior to full scale processing of Type C solutions was to test the activity of the supernatant liquid over a small scale precipitation made in a centrifuge cone. This was found to correspond to 0.0002 g Pu/l at 0.082M excess iodate. Full scale processing of Type C solutions was carried out by the identical procedure described for "Type A Solutions: Iodic Acid Precipitant". Spectrochemical analysis to determine the purity of recovered solutions was not attempted due to the gross amount of cerium known to be present. Data on filtration rates and plutonium lost to filtrates and washes is similar to that of Table VI, HIO_3 Run. Type A solutions and Type C solutions are usually recovered together as part of the same HIO_3 recovery cycle because of the similarity of handling. By July 15, 1952, a total of 148 g of plutonium had been recovered from Type C solutions.

8. Type D Solutions: Ammonium Hydroxide - Nitric Acid - Iodic Acid Treatment.

The Type D solutions listed in Table I were found by experimental determination to contain approximately 20 g of plutonium in 100 l of solution. For convenience in accounting for the plutonium, the 20 g of

plutonium is included in the theoretical plutonium content figures of Table I for Type E and Type F solutions. Contaminants are listed as hydrochloric acid, acetic acid, sodium acetate, and 8-hydroxyquinoline. The plutonium was known to be complexed with 8-hydroxyquinoline. Such a system made basic yields the plutonium complex as a voluminous brown solid, while all other constituents remain soluble. This fact was utilized to effect volume reduction from 100 l of solution to approximately 3 l of solution while separating all contaminants except some undesirable organic material. Details of the experimental development follow.

A volume of 200 microliters of Type D solution was added to a 2 ml centrifuge cone and made basic with concentrated NH_4OH to a pH of more than 10. The characteristic brown precipitate of plutonium 8-hydroxyquinolate was allowed to settle overnight before radioassaying the supernatant liquid. The concentration of the plutonium remaining in solution after settling was 0.0004 g/l. After removing the supernatant liquid, the solid was dissolved in 100 microliters of concentrated HNO_3 to give a dark brown solution. To destroy the organic complex, the solution was heated to boiling in the centrifuge cone and allowed to reflux gently. Gradually the bright green color of plutonium ion in concentrated HNO_3 solution appeared, indicating destruction of the organic complex.

On the basis of these observations and other experiments, the 4 l fractions of Type D solution were made basic by adding NH_4OH directly

to the bottles. Solids settled out and were separated from the supernatant liquid as described for Type B solutions. The small cake in each bottle was then dissolved in 100 ml of concentrated HNO_3 and composited. The original bottles were rinsed with small portions of HNO_3 and the rinses were added to the composite. Having concentrated the plutonium of Type D solution into a workable volume of approximately 3 l, the solution was then added to the reactor and digested at boiling temperature for several hours until the color was bright green.

At this point a small sample of the material was evaporated to dryness in a porcelain dish on a hotplate and then heated in a muffle furnace. As the sample became dry during evaporation the appearance became black and tarry. The characteristic appearance would have been brown crusts if no organic matter were present. Raising the temperature of the sample in the furnace actually caused some loss of sample due to vigorous combustion. Thus, destruction of organic matter in the solution was found to be incomplete.

Further treatment was in the form of an iodate cycle. This involved precipitation in acid solution where the organic matter was expected to remain soluble. It was also expected that the finely divided crystalline $\text{Pu}(\text{IO}_3)_4$ precipitate would not carry the organic matter. A 1/50 scale run was made to test these possibilities.

A 25.0 ml portion of the digested solution was diluted to 50 ml with distilled H_2O and then neutralized to 3M H^+ using 6M NaOH . The 3M

acid solution was then added to a 1/50 size reaction unit and processed as previously described for iodate cycles. Some experimental data on the iodate precipitation are given below.

TABLE VIIRECOVERY FROM TYPE D SOLUTIONS

Plutonium 8-Hydroxyquinolate Precipitation and Nitric Acid Digestion
Preceding Plutonium (IV) Iodate Precipitation, 1/50 Scale Run

Pu in run, g:	0.218
Pu lost in filtrate and washes, g:	1.1×10^{-4}
Disc porosity of 1/50 scale unit:	Medium
Product purity, impurity in parts/million parts Pu:	
Ca:	2,000
Cr	100
Na	5,000
Ni	40

The fact that the product remaining dissolved in the effluent from the iodate precipitation is 1×10^{-3} g Pu/l (filtrate and wash volume was 110 ml) shows that the HNO_3 digestion did release the plutonium from the organic complex quantitatively so that all of the plutonium was available to react with iodate. Another ignition test of the solution after the iodate cycle indicated that no organic matter was present. Thus, hydroxide precipitation, HNO_3 digestion, and iodate precipitation are shown to complement one another very well for the recovery of Type D solutions.

No data uniquely applicable to the full scale iodate cycle following HNO_3 digestion are available because the digested solution was combined with other solutions for the iodate processing and therefore lost its identity.

9. Type E Solutions: Ammonium Hydroxide Precipitant.

Type E solutions contained plutonium at an average concentration of 19 g/l with variable amounts of nickel and mercury in 2M hydrochloric acid. Much of the mercury was precipitated as mercurous chloride, but some was in solution as a soluble chloride complex. From Table I it can be seen that 285 g of plutonium were to be processed from 15 l of solution.

The plutonium was present predominantly as plutonium (IV) so that no oxidation or reduction treatment would be necessary to precipitate plutonium (IV) hydroxide. Nickel forms a soluble complex with excess NH_4OH and so could be separated in a hydroxide cycle precipitation. The mercury of Type E solutions would unfortunately give insoluble $\text{Hg}(\text{NH}_2)\text{Cl}$ on treatment with NH_4OH .

The characteristics of the sulfides of the cations present suggests a simple preliminary separation of mercury from the acid solution as HgS . The sulfides of nickel and plutonium are soluble in acid solution. Attractive features of this preliminary separation are that HgS is a

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very insoluble precipitate which settles rapidly to a small volume. Thus, the supernatant liquid containing the plutonium and washes of the residue can be removed by decantation.

One of two 1/50 size runs was conducted as follows. Twenty-one and three tenths ml of Type E solution was taken into a 100 ml Erlenmeyer flask and reduced so that addition of H_2S would not result in the formation of free sulfur. The reduction was accomplished by passing SO_2 through the cold acid solution until the blue color of plutonium (III) ion appeared.

Hydrogen sulfide was passed through the solution until a sample of the supernatant liquid gave no further precipitate with H_2S treatment. Thus the mercury was shown to be completely precipitated. After a 30 minute settling period, the supernatant liquid was transferred into a 1/50 size reaction unit with a coarse porosity frit. Two 1N HCl washes of the residue were added to the solution in the 1/50 size unit.

The hydroxide cycle is best carried out with plutonium (IV) which forms a more insoluble hydroxide than plutonium (III). Oxidation of plutonium (III) to plutonium (IV) was accomplished by gently warming the solution after adding 1.0 ml of concentrated HNO_3 . Heating was stopped as soon as the blue color of plutonium (III) gave way to the orange-brown of plutonium (IV). Six ml of concentrated NH_4OH were added

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as a precipitant and the mixture thoroughly stirred by air agitation. The filtrate, and to a lesser extent the first wash consisting of 1M NH_4OH , showed the blue color of $\text{Ni}(\text{NH}_3)_4^{++}$. The second wash was with pure water. Spectrochemical analysis of the recovered solution, made by dissolving the cake in 3.0 ml of concentrated HNO_3 , completed the run. The details of the experiment appear in Table VIII.

The data in Table VIII indicate essentially the same filtration rates and plutonium losses in the filtrate as for the hydroxide cycles of Table III. Mercury is seen to be very effectively removed from the solution.

TABLE VIII

RECOVERY FROM TYPE E SOLUTIONS

Mercuric Sulfide Precipitation Preceding Plutonium (IV)
Hydroxide Precipitation, 1/50 Scale Run

Pu in run, g:	0.328
Pu lost in filtrate and washes, g:	2.8×10^{-5}
Disc porosity of 1/50 size unit:	Coarse
Wash conditions:	
1st wash	10 ml 1M NH_4OH
2nd wash	10 ml H_2O
Filtration rates, ml/min:	
Mother liquor	0.14
1st wash	0.25
2nd wash	0.30
Product purity, impurity in parts/million parts Pu:	
Ca	100
Cr	200
Hg	400
Na	250
Ni	2,000

When the full scale recovery processing was done on Type E solutions, the sulfide precipitations were carried out by passing the gases (SO_2 and H_2S) directly into the solutions in 4-liter bottles. The plutonium bearing supernatant liquid was decanted from the HgS through the filtration setup shown in Figure 9. This is merely a vacuum transfer line containing a filter made from a Pyrex glass Buchner funnel having a 90 millimeter diameter fritted disc.

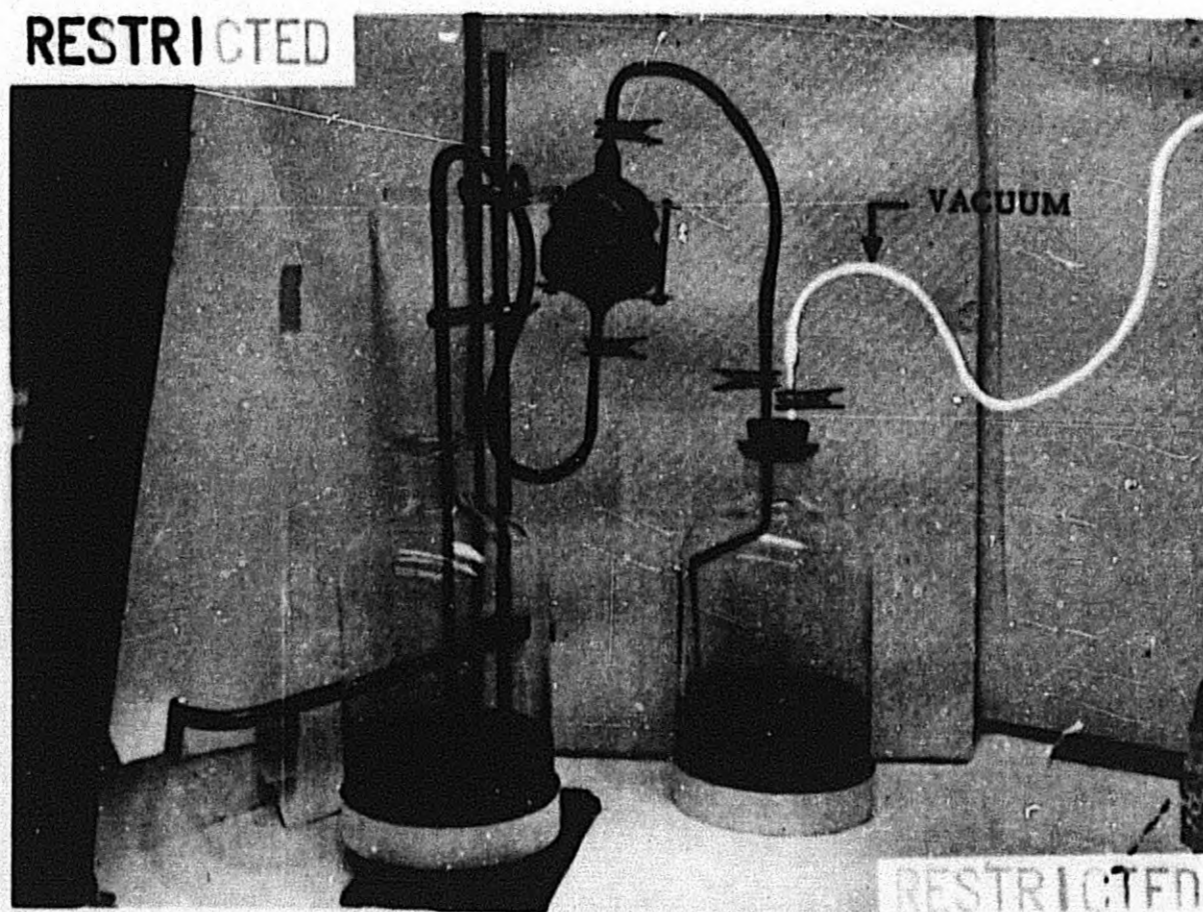
The entire collection of Type E solutions was recovered by July 15, 1952. Five precipitations with H_2S were made in 4-liter bottles to separate mercury. The mercury-free solutions were then processed in ten hydroxide runs to complete the recovery. After oxidation of plutonium (III) to plutonium(IV) the conditions of the hydroxide runs were the same as outlined for full scale hydroxide runs with Type A solutions except that NH_4OH was used as the precipitant in place of NaOH , and the first wash was with 1 M NH_4OH rather than H_2O . The processing details on a typical hydroxide run using NH_4OH are given in Table IX.

In Table IX the impurity results are from a composite solution of similar hydroxide runs containing 150 g of plutonium rather than on only the run cited. Comparing the data of Table IX to Table VI data for the NaOH run, we find about the same figures except for impurity results. This is of course primarily due to the two types of solutions containing different impurities initially; however, excess NH_4OH seems to separate

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nickel from plutonium more effectively than excess NaOH separates chromium from plutonium. Another point of interest is that the preliminary separation of mercury does not affect the estimated recovery rate because the preliminary separation does not require use of the reactor. The preliminary separation and the hydroxide cycles can progress simultaneously.

TABLE IX

RECOVERY FROM TYPE E SOLUTIONS

Mercuric Sulfide Precipitation Preceding Plutonium(III) Hydroxide Precipitation, Full Scale Run.

Pu in run, g:	28.03
Pu lost in filtrate and washes, g:	0.003
Average filtration rate, ml/min:	9.2
Recovery rate, g Pu/hr operation:	3
Product purity, impurity in parts/million parts	Pu:
	Ca 40
	Cr 200
	Hg 400
	Na 500
	Ni 2,000

10. Type F Solutions: Metathesis of Chloride to Nitrate.

Type F solutions had accumulated to the extent of 724 g of plutonium in 24 l so the average concentration was 30 g Pu/l. (See Table I). These solutions were objectionable as Separations Process stream feedstocks only in that they contained chloride ion which is corrosive to stainless

steel process equipment. The presence of acetone in the solutions is not pertinent to the consideration. Thus, replacement of the anion with nitrate would effect a very simple satisfactory recovery of the solutions.

A method for this replacement is to evaporate the acid solution and fume just to dryness several times, each time taking up the residue with HNO_3 . Conversion of chloride to nitrate in acid solution is straight forward because of the reaction between chloride and nitrate to give gaseous products. Conversion without going to dryness was considered desirable as this would eliminate any possibility of overheating, which might yield difficulty soluble solids.

Preliminary experience in converting chloride solutions to nitrate solutions was obtained by working with non-radioactive material. In these runs, concentrated HNO_3 was added to a given volume of HCl in a distilling flask connected to a condenser and the flask contents heated to boiling. During distillation the volume in the flask was never allowed to become smaller than the original volume of chloride solution, concentrated HNO_3 being used to maintain the amount of liquid. As distillation progressed portions of distillate were tested qualitatively for chloride with AgNO_3 until the test was negative. At that point the material in the distilling flask was also tested and found chloride free. Over the range of concentrations from 4 M HCl to 12 M HCl , it was found that a total of 2 volumes of concentrated HNO_3 were always required to convert 1 volume of chloride solution, regardless of whether the HNO_3

was added in many small increments, fewer large increments, or even all at once before distillation had begun. The most efficient conversion of a given amount of chloride solution is done by reducing the volume of the solution to be converted to the smallest practical amount before beginning the conversion.

Experimental work was continued in a 1/50 size reaction unit, having a coarse porosity fritted disc, using Type F solutions. A 200 ml portion of Type F solution was added in several increments to the 1/50 size unit, concentrating as necessary by distillation between increments. Finally all had been added and concentrated to a volume of 15 ml. The plutonium concentration at this point was approximately 400 g/l. A 35 ml portion of concentrated HNO_3 was added to the system and the mixture heated gently until finally it was boiling smoothly. After volume reduction of the solution back to 15 ml, a few drops of the last fraction of distillate were tested with AgNO_3 and found chloride-free. The recovered solution was also found to be chloride-free upon testing, after cooling and removing it from the 1/50 size unit. Spectrochemical analytical data was gotten on a portion of the solution. Details on the run appear in Table I.

The impurity content of the recovered solution is not excessive. This is to be expected since the only reagents contacting the samples are HCl , acetone, and HNO_3 .

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TABLE I

RECOVERY FROM TYPE F SOLUTIONS

Metathesis of Chloride to Nitrate, 1/50 Scale Run

Pu in run, g:	3.618
Pu lost in distillate, g:	0.0025
Product purity, impurity in parts/million parts	
Pu:	
Ca	50
Cr	20
Hg	400
Na	1,000
Ni	500

A full scale recovery run of 300 g of plutonium was carried out on the basis of the 1/50 scale experience and all aspects of the run were as expected. Conversion to nitrate was made after concentrating the chloride solutions containing the 300 g of plutonium to a composite volume of 1½ l.

By July 15, 1952 a total of 581 g of plutonium had been recovered from Type F solutions and returned to process streams. Data on a typical run are given in Table II.

TABLE II

RECOVERY FROM TYPE F SOLUTIONS

Metathesis of Chloride to Nitrate, Full Scale Run

Pu in run, g:	223.50
Pu lost in distillate, g:	0.012
Recovery rate, g Pu/hr. operation:	10
Product purity, impurity in parts/million parts	
Pu:	
Ca	50
Cr	40
Hg	400
Na	500
Ni	500

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It is observed that the concentration of plutonium in the distillate from the large scale recovery is less than was found in the distillate from the 1/50 scale run (See Tables I and II). The total distillate volume for the 1/50 scale run was about 220 ml containing nearly 0.01 g Pu/l. The distillate volume from the full scale run was about 11 liters containing 0.001 g Pu/l. This difference is due to the fact that mechanically entrained spray is more efficiently trapped by the full scale spray trap than by the single bulb of the 1/50 size reactor.

Whenever this simple conversion by metathesis will effect recovery of a solution, advantages are to be gained by using it rather than a precipitation method. The expenditure of time and effort per unit of plutonium recovered is lower than for precipitation methods because of reduced handling - the larger batch size means that the reactor need be unloaded but once per 300 g, and it can be loaded in as few times as it takes to get enough waste volume to represent 300 g of plutonium - and the fact that the processing requires little attention between loadings or unloadings. Along with time savings comes less exposure to the hazardous operation of plutonium handling, which is an important safety consideration.

The batch size for distillation is limited only by criticality restrictions discussed elsewhere provided that no interferences are present to cause crystallization of salts from the solution being converted.

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In the presence of such interferences, the solubilities of whatever species are present in the solution and the volume of the solution will determine the plutonium batch size.

11. Type G Solutions: Metathesis of Chloride to Nitrate.

Type G solutions represent another system in which the only objectionable feature is presence of chloride. (See Table I) The traces of calcium can be tolerated and methanol does not interfere with the process. Table I shows 19 l of solution had collected containing 760 g of plutonium at an average concentration of 40 g/l. The solutions were processed as indicated for Type F solutions. The recovered solutions contained 5000 ppm of calcium but otherwise yielded processing data similar to that of Table XI. A total of 496 g of plutonium had been recovered and returned to process streams by July 15, 1952.

12. Type H Solutions: Metathesis of Chloride to Nitrate.

Table I lists Type H solutions as containing 273 g of plutonium in 17 l of 6M acid solution along with sodium, iron, cerium, and lanthanum. Anions in the solution were chloride, nitrate, and sulfate. These solutions were also processed by metathesis of chloride to nitrate. The material was processed in three separate batches because the distribution of plutonium and sulfate among the 4 l portions in which the solutions were collected was such that some of the solutions could not be concentrated

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to more than 40 g of Pu/l without crystallization of $\text{Pu}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$. All of the 273 g of plutonium had been returned to process streams by July 15, 1952.

11. Type I, J, K, and L Solutions:

No discussion of Type I, J, K, and L solutions will be presented. Due to time limitations no full scale recovery work had been done on these solutions by July 15, 1952.

DISCUSSION OF RESULTS

The problem as previously presented was seen to be the recovery of plutonium from a variety of analytical residues in multiple gram batches, with the restriction on the process that virtually no loss of product could be tolerated. The physiological effects and nuclear properties of plutonium imposed restrictions on the equipment to be used. The health hazard of plutonium handling necessitated an equipment setup which could be easily kept free of plutonium on its outer surfaces. A careful space arrangement of the stored residues, processing equipment, and recovered product had to be maintained so as to prevent critically assembled systems of plutonium solutions.

It was decided that precipitation methods were best suited for plutonium recovery from the wide variety of analytical residues on hand.

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Many plutonium compounds were known to be insoluble enough to use for plutonium recovery, and equipment requirements for precipitation processes were compatible with the space and health hazard requirements of the problem. In particular plutonium (IV) hydroxide and plutonium (IV) iodate were successfully utilized in precipitation methods as compounds for plutonium recovery. Both compounds give only slight plutonium loss in the waste filtrates. The plutonium (IV) hydroxide is rather difficult to filter compared to the iodate, but is very easily dissolved. The plutonium (IV) iodate is easily filtered in the reaction equipment in amounts up to 150 grams of plutonium but dissolution of the iodate is much harder to accomplish than for the hydroxide. Neither compound offers specific recovery of plutonium from many of the cations of the periodic system. Each recovery situation has to be considered individually as to whether an iodate precipitation cycle or a hydroxide precipitation cycle will give the best plutonium recovery for that situation.

The reaction equipment was designed to meet heating requirements as well as the ordinary requirements for precipitation methods such as solution transfer, stirring, filtration, and dissolution. Capability of heating the reaction flask allowed very rapid recovery of plutonium by nitric acid metathesis in the simplest system containing chloride as the only objectionable feature. The advantage of heating was also invaluable for wet digestion of systems containing organic matter.

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Designing the reaction flask to have a fritted glass bottom and to utilize vacuum transfer of solutions yielded provision for solution transfer, stirring, and filtration without any auxiliary apparatus. The 5 liter flask in which reactions take place is below the minimum size for the possibility of being made critical with plutonium solutions as discussed under "Critical Mass Consideration". The reaction equipment successfully meets the requirements of this problem, shown by the fact that 2375 grams of plutonium were recovered and returned to process streams by July 15, 1952, with only small plutonium loss to waste effluents and no air contamination in the processing room to levels requiring respiratory equipment (assault masks).

A small 1/50 scale reaction unit proved to serve an important function in setting up the recovery procedures. The initial experimentation which enters into defining the recovery procedure for a specific type of plutonium solution is carried out with small amounts of material. To start immediately working with large amounts of material could have very serious contamination consequences in case of an accident resulting from ignorance. Another risk would be that any failure in the experimental processing could be economically costly due to the value of the plutonium in a large batch. Definition of a recovery procedure results from following through the three step scale up to be described.

At the first step a procedure selected for investigation is run on a milligram scale in centrifuge cones. Micro techniques are particularly

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valuable at this stage. Runs can be made rapidly, especially when plutonium is determined by radioassay, and contamination is easily controlled. Interferences which become evident by spoiling a run involve little enough plutonium that the whole run can be discarded to burial facilities. Usually the information sought at this stage includes the reagent concentrations to give the least plutonium loss during the separation and assurance that one hasn't overlooked an important factor which disqualifies the procedure which was chosen for development.

After preliminary work on the smallest scale, the information gained is applied to runs using 0.1 to 1 gram of plutonium in a 1/50 size reaction unit. The proper 1/50 size reactor is used, according to whether a fine, medium, or coarse porosity fritted disc is under consideration for a given application. This level of scale-up is a convenient point at which to find whether a fine, medium, or coarse porosity fritted disc best fits the requirements of a precipitation procedure and to roughly indicate the likely recovery rate of the full scale equipment.

Another value of experimentation in the 1/50 size reaction unit with 0.1 to 1 gram of plutonium is the opportunity to observe any reactions which tend to be vigorous. Obviously, an energetic reaction is likely to be more safely and efficiently carried out in 100 gram batches on the basis of observations on 1 gram batches than on the basis of observation of milligram scale runs.

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A specific example of benefit yielded by the scale-up approach to recovery procedure definition occurred in work on dissolution of plutonium (IV) iodate. Experiencing on a 1 gram scale the difficulties described undoubtedly spared the author much anxiety, discouragement, and hazard which would have accompanied a 50 or 100 gram recovery run conducted in the manner of the first 1 gram run described.

Recovered solutions from 0.1 to 1 gram runs have use as samples for spectrochemical analysis for impurities, the amount of material from milligram runs being too small to conveniently serve this purpose. With an impurity analysis available, the capability of the separation conditions to remove unwanted cations can be judged.

When conditions are established by which the proposed procedure is considered feasible for full scale recovery, full scale recovery actually proceeds as the final step in the scale-up. After any necessary modifications are incorporated the recovery procedure can be used routinely by laboratory personnel.

A strict accountability must accompany handling of all fissionable materials to meet the bookkeeping requirements of the Atomic Energy Commission. For waste recovery, this amounts to performing the requisite manipulations very carefully so that no material is unaccountably discarded. A material balance on all processing is maintained by securing various analytical data during collection of the residues and the course of the recovery.

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Initial data are available from the recorded weight of metal samples taken for determination of a particular constituent, an account being kept of which samples are collected in particular waste bottles. Summation of the sample weights gives the amount of plutonium expected to be contained in a particular bottle. Such summations have been referred to as "theoretical plutonium contents" because they do not allow for the fact that some loss of material is likely to occur during the course of analytical determinations and that the samples weighed out are not 100% plutonium.

The total of the theoretical plutonium contents of all solutions which had been recovered and returned to Separations Process streams by July 15, 1952, was 2375 grams. Credit received for return of plutonium to process streams from these recoveries was 2379 grams. In addition, 482 liters of effluent solutions from recovery processing containing 2.034 grams of plutonium were known to have been discarded during the period under consideration.

The theoretical plutonium content of the solutions recovered should actually be more than the credit received for return of the plutonium to process streams, assuming the two figures to be true values, because of the impurity in the samples weighed out. Any losses of plutonium during analysis would also make the figure for credit received smaller than the figure for theoretical content. It is obvious that the figures

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cited for theoretical content and credit received are not "true values", for credit received is the larger.

The figure for the theoretical content could be lower than the true theoretical content only if weighings were negatively biased or if some samples which were weighed out were not recorded. The case of summation of thousands of sample weights being taken by many different individuals on a number of balances in various locations over a 3 year period is likely to be only slightly positively or negatively biased. The book-keeping system precludes sample weights not being recorded.

In some cases there was known to be lack of agreement on the plutonium contents of particular shipments of recovered material returned to Separations Process streams when the estimates were based on analytical results from different control laboratories. These differences were not always resolved because the shipment of material would be mixed with production streams after sampling and could not be resampled. In view of this fact and the relatively few shipments made, it seems likely that the apparent extremely good agreement in the overall material balance figures is caused from the figure for the plutonium content of some of the shipments back to process streams being positively biased from the true value.

The quality of the recovered product varied primarily with the kind of impurity associated with the analytical residue as collected.

This information influenced the choice of the recovery procedure required to yield a solution compatible with Separations Process stainless steel equipment and Process separation reactions. Thus, Type F solutions which contained only plutonium, hydrochloric acid, and acetone, yielded a much more pure recovered solution than did the iodate recovered Type A solutions which initially contained plutonium, perchloric acid, sulfuric acid, and sodium dichromate. The goal in each case was the same, namely make the residues compatible with production streams. Nothing precludes choice of recovery procedures capable of giving high purity recovered products if this is easily accomplished while meeting the stated goal.

In other applications of this recovery scheme and reaction equipment it may be desired to produce high purity products. In such cases where plutonium purification is the goal, other precipitations highly specific for plutonium are available and would fit the purpose.

SUMMARY

A scheme for making quantitative recoveries of plutonium from analytical residues by using precipitation and metathesis reactions has been worked out and is presented. Precipitation of plutonium (IV) hydroxide, plutonium (IV) iodate, plutonium 8-hydroxyquinolate, partial destruction of organic matter with nitric acid, and metathesis of chloride solutions to nitrate solutions are used singly and in combinations for the recovery procedures.

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Pyrex glass laboratory scale equipment for performing reactions with up to 300 grams of plutonium was designed and is described. This equipment features a fritted glass disc as an integral part of the reaction flask for use in filtration, vacuum transfer of all solutions, and air sparge stirring.

Using the recovery scheme presented and the equipment described, the losses on recovery of a total of 2375 grams of plutonium from 8 different types of analytical residues amounted to 2.034 grams or 0.09%.

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