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RECOVERY AND PURIFICATION OF PLUTONIUM

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ABSTRACT

The various problems of purification and recovery are discussed under the headings of preparation of solution, concentration of plutonium, and purification of plutonium. The methods used in concentration (or recovery) of the plutonium are shown to consist in all cases of one or more of the following procedures: precipitation of hydroxide, oxalate, trifluoride, tetrafluoride, or iodate; ether extraction; and certain carrier methods. A modified purification scheme is described in detail. Data are given dealing with the amounts of material handled and overall recovery efficiency. A resume is made of phases returning material for recovery, type of material returned and impurities present. A flow sheet for the entire recovery and purification scheme is given showing impurity element removal by each step of the process. The colors of various plutonium compounds and solutions as observed on a one-to-ten-gram scale are reported.

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RECOVERY AND PURIFICATION OF PLUTONIUM

INTRODUCTION

In the process of recovery and purification of plutonium, many problems have presented themselves which deal with the separation of small amounts of plutonium from very large amounts of many of the other elements. Since most of the reported work on separations of this type has been done on a milligram scale, and since much of the work of others has dealt mainly with the separation of the last traces of impurities from the plutonium rather than the recovery of small amounts of plutonium from very large amounts of impurities, it was thought that a report of work done on a one-to-ten-gram scale would be of value to others who might encounter these same problems.

Table I gives a summation of the various phases of work returning material to be recovered. It also shows the form in which the plutonium is present, and the types of substances present as impurities with the plutonium.

The work in this laboratory may be divided into three general subheads: preparation of solution, concentration of plutonium (i.e. removal of a major portion of the impurities), and purification of plutonium (i.e. removal of last traces of the impurities). The following discussion will be based on this subdivision.

PREPARATION OF SOLUTION

Examination of Table I shows that the answer to the problems of

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this category lies, in part, in the methods which are available for dissolving plutonium metal, oxide, halides, carbides, oxalate, hydride, and peroxide. Of these compounds all except the oxide and carbide are readily soluble in the common mineral acids, HCl being best suited for the metal and the hydride, HNO_3 for the peroxide and halides, and $HNO_3 + H_2SO_4$ for the oxalate. When it is necessary to render the oxide or the carbide soluble, the most efficient method is a fusion with $K_2S_2O_7$. In this fusion a ratio of $K_2S_2O_7$ to PuO_2 (or carbide) of about 8 to 1 is used. The fused mixture is heated until the molten material turns solid. This gives a fused mass which is much more readily disintegrated by water and HCl than is possible if the heating is stopped while the fusion is still liquid. The fusion mass is greenish while still hot, but on cooling it turns pink. This pink color seems to be characteristic of the plus four state in the presence of sulfate, since it shows up when solutions are fumed with H_2SO_4.

However, the problem of getting plutonium into solution is not as simple as it might seem from the solubility data just stated. It is complicated by the fact that varying amounts of plutonium manage to penetrate so deeply into the refractories used in reduction and remelting that a mere leaching with acids or acid fusions does not extract all of the plutonium from the crucible materials. This necessitates the complete dissolution of the refractories, a procedure which is disadvantageous for two reasons. In the first place many of the refractories resist dissolving to a remarkable extent, requiring long tedious treatment with various acids and with various fusion mixtures. Many of the refractories are dissolved in HF and HNO_3 when other solvents failed. In a few cases however very drastic measures have been required, and it has been found that the $Na_2O_2 + C$ spontaneous fusion

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is very satisfactory for these materials. The second disadvantage of complete solution of the refractories lies in the fact that much greater amounts of impurities are mixed with the plutonium than would be if a leaching process were used. In order to overcome, to a certain extent, this second disadvantage, the unground crucible materials are always leached thoroughly with HCl, HNO_3, and aqua regia and the solutions thus obtained, containing nearly all of the plutonium and only a fraction of the crucible material (provided the crucible is insoluble in the leaching acids), are treated separately. The main portion of the crucible material is then dried, ground to approximately 100 mesh and dissolved completely. This solution contains only a small amount of plutonium, and in general is set aside until other similar solutions have been obtained, at which time it is worked up.

In these cases where the plutonium has had to be separated from metal surfaces, acid washing or $K_2S_2O_7$ fusions (depending on the form of the plutonium) will get the plutonium in solution; the metals are not much affected by these treatments.

When the plutonium is already in solution, there are three treatments that may be necessary before this solution is in a condition satisfactory for use of chemical procedures of concentration. If the volume of the solution is so large that the plutonium concentration is of the same order of magnitude as the solubilities of the compounds to be precipitated, it must be evaporated. If the plutonium is in the hexavalent state, it must be reduced before the chemistry used in concentration can be successful. This reduction is best done by passing SO_2 into the acid solution until the blue color of the trivalent plutonium becomes evident.

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The solution is then boiled to remove the excess SO_2, and HNO_3 is added to reoxidize the trivalent plutonium to tetravalent plutonium. In this reoxidation, care must be taken that the HNO_3 does not cause a large portion of the plutonium to become hexavalent. It is probable, but not as yet proved, that the addition of small amounts of H_2SO_4 before reoxidation will prevent this. If organic matter is present, it must be removed before chemical concentration can be accomplished. The volatile organic material is removed by evaporation, and the non-volatile organic material is removed by oxidation with HNO_3 and H_2SO_4.

THE CHEMICAL CONCENTRATION OF PLUTONIUM

The three prerequisites of a good concentration method are:

1. The major portion of the impurity must be removed in one operation.

2. The amount of plutonium removed with the impurity must be small. 3. If the operation depends upon a precipitation procedure, it should, if possible, cause the plutonium to be precipitated away from the impurity rather than the impurity to be precipitated away from the plutonium. All of the methods described here exhibit the first two characteristics, and nearly all exhibit the third.

The exact procedure which is to be used for the separation of the plutonium from other elements will naturally depend largely upon what contaminating materials are present, and to what extent. Thus, if a metal button is returned for recovery, almost no pre-purification procedures are needed. If, on the other hand, the sample for recovery consists of dry box sweepings, several separate concentration steps are required. However, in all cases, the procedure for the concentration of plutonium will consist of one or more of the following processes.

Hydroxide precipitation

The first process after the preparation of the solution always involves the precipitation of plutonium hydroxide. This serves not only to separate many impurity elements from the plutonium, but also to give a compound which when dissolved in acid leaves a solution of approximately known acidity and plutonium concentration. For this precipitation, either NaOH or NH_4OH may be used, and the choice of reagents depends upon the type of impurities present in the solution. Thus, when Be, Al, and other amphoterics are present, an excess NaOH is used to precipitate the plutonium hydroxide, leaving the impurities in solution. If Mg or other alkaline earths, alkalies, or elements which form ammonio complexes are present, NH_4OH is used. In the case of alkaline earths NH_4OH is added until the pH of the solution is between 5 and 6 as shown by indicator paper. This gives a basicity sufficient to precipitate the plutonium hydroxide, but not to precipitate the alkaline earth hydroxides. In those cases where elements which form ammonio complexes are present, the NH_4OH is added in excess. Many times the elements of all three classes (amphoteric, complex formers, and alkaline earths) are present in the solution, and suitable combinations of reagents and conditions are used. Whenever both NaOH and NH_4OH are to be used in a series of operations, NaOH is always used first, followed by NH_4OH at a pH 5 to 6, and finally followed by NH_4OH in excess. The precipitate from each operation is washed thoroughly and dissolved in acid before the succeeding precipitation. By using these processes, a major portion of all the elements present is removed with the exception of Ce, La, Zr, Th, Ti, Fe, Si, Ta, and Pt (of these Si and Ta are removed more or less in the preparation of the

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solution since both of these elements precipitate insoluble oxides from acid solutions; Pt is removed by means of acid H_2S in the rare cases when it is present in solution).

Oxalate Method

The solution containing the tetravalent plutonium nitrate is heated to convert all uranium to the hexavalent state. To this is added enough solid KI to give three mols of iodide per mol of plutonium, and the solution allowed to stand for thirty minutes with occasional stirring. After this enough 1M $H_2C_2O_4$ solution is added to give 1.5 mols of oxalate ion per mol of plutonium and to make the final solution 0.2 M in excess oxalic acid. The volume is then adjusted until the plutonium concentration, based on total amount present, is 0.2 M. This mixture is allowed to stand for 30 to 60 minutes, after which the green oxalate precipitate is centrifuged and washed with water until the supernatant is free of I_3^- color. The precipitate is fumed with HNO_3 and H_2SO_4 to completely decompose the oxalate, and the red sulfate thus formed is dissolved in water and HCl. Plutonium hydroxide is precipitated from this solution with NH_4OH, and the precipitate is washed free of sulfate.

An alternate treatment of the precipitated oxalate may be used if no further concentration processes are necessary. The solid oxalate is treated with enough 1M $NaBrO_3$ solution to give 1.8 mols of bromate per mol of plutonium, and enough 16N HNO_3 to give 9.2 mols of H^+ per mol of plutonium. The volume of the solution is then adjusted so that the plutonium concentration in the final solution will be 0.2 M, and the mixture is heated for 4 to 6 hours at 85°C. This method of dissolution of the oxalate yields a solution of the hexavalent nitrate of plutonium.

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The oxalate procedure separates uranium (if not present in large amounts) some alkaline earths, (Zr, Th), Ti, Fe, Be, Cr, and the alkalies. It has no value as a method for separating Ce and La. The precipitation is always used as the last step prior to purification, and in many cases it is used previously to clean up solutions.

Trifluoride Method

A solution of the tetravalent plutonium nitrate in 1M HNO_3 is reduced by passing SO_2 into the ice-cold solution for about 20 to 30 minutes. (Reduction may also be made by means of KI as described in the previous section.) Twenty-seven normal HF is added to this blue solution until the amount added is three mols per mol of plutonium and enough excess to make the solution 1 to 2 M in HF. The mixture is allowed to stand for 30 minutes and the purple trifluoride is centrifuged, washed, and fumed with HNO_3 and H_2SO_4 to remove all fluoride. The sulfate thus formed is dissolved in water; the hydroxide is precipitated with NH_4OH and washed free of sulfate.

This method accomplishes the separation of uranium to about the same extent as the oxalate. It has the advantages that the plutonium fluoride is less soluble than the oxalate, and if large amounts of uranium are present the separation is still successful. It has the disadvantages that Th and Zr are not separated from the plutonium, that the precipitate is more difficult to dissolve, and that handling of large amounts of HF solutions involves certain difficulties.

Tetrafluoride Method

A solution containing the tetravalent nitrate of plutonium in 1M HNO_3 is heated to oxidize all uranium to the hexavalent state, and solid KNO_3 is added until there are two mols of K^+ per mol of plutonium and

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the solution is 3 molar in excess. Twenty-seven normal HF is then added to give six mols of HF per mol of plutonium and to make the solution 1 to 2 molar in excess. After 30 minutes the grey potassium plutonium fluoride is centrifuged, washed, and fumed with H_2SO_4 to remove HF, and the sulfate thus formed is dissolved in water. From this solution the hydroxide is precipitated and washed free of sulfate.

This method has the same disadvantages and advantages as the trifluoride method, and may be used interchangeably with it. It is probably the best method for separating large amounts of uranium from plutonium. Since this does not require reduction of the plutonium it is somewhat faster. However, the trifluoride is a neater, more clean-cut reaction.

Iodate Method

Precipitation of $Pu(IO_3)_4$ from a solution which is 2 M in HNO_3 with a 0.2 molar excess of KIO_3 or HIO_3 serves to separate the plutonium from uranium in the hexavalent state. It is not nearly as satisfactory as the previously described methods for uranium separation. However, it does show promise as a method for separating cerium, which resists most other separations when present in large amounts. The iodate of trivalent cerium is soluble and should remain in solution when the plutonium is precipitated. The preliminary attempts at this separation have indicated that it will be useful, but the data are too incomplete at this time to state definitely that the method is successful. The most satisfactory method of solution of the iodate depends upon the use of HCl and SO_2. This reduces the iodate to iodide and the plutonium to the

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trivalent state. The completion of the reduction is noted by the fact that all the I_2 liberated from the iodate by SO_2 is redissolved and the solution turns blue due to trivalent plutonium. The plutonium is precipitated from this solution as $Pu(OH)_3$ by means of NH_4OH. It is not possible to reoxidize the plutonium to the tetravalent state before precipitation of the hydroxide because the iodide which is present prevents oxidation of the trivalent state.

Other methods for separation of cerium

All other methods which are used for the separation of cerium from plutonium involve an oxidation of the plutonium to the hexavalent state. This oxidation is achieved by means of $NaBrO_3$ in HNO_3 solution. Since hexavalent plutonium does not precipitate as a fluoride, the cerium can be precipitated from the oxidized solution by the addition of HF. By repeating this process, fairly complete separation can be brought about. The procedure has the disadvantage that the impurities are precipitated rather than the plutonium. A second treatment of the oxidized solution consists of ether extraction of the plutonium. This is perhaps the most efficient method of separation of plutonium from cerium, but it is also more time-consuming. If only small amounts of cerium are present, no special precautions need be taken since the regular purification scheme will effect its removal.

Carrier Procedures

All supernatants from precipitation of hydroxides were stored until about 380 liters were on hand. Assay of these solutions showed a much higher plutonium content than would be accounted for by the solubility of $Pu(OH)_4$ in basic solutions. The probable explanation of this is the fact

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that tetravalent plutonium in dilute HNO_3 converts to the extent of about 50 to 60 per cent to hexavalent state. This is either a straight oxidation or a disproportionation of the tetravalent to the hexavalent and the trivalent states. Regardless of mechanism, the presence of the hexavalent plutonium in solutions from which the hydroxide is to be precipitated would cause undue loss in the supernatant since the hexavalent hydroxide is quite soluble. Since there was considerable amount of plutonium tied up in these solutions an effort was made to recover this.

These supernatants were obtained from hydroxide precipitations using both NaOH and NH_4OH, and when they were mixed, precipitates formed due to the nature of the elements in the basic solution. Thus magnesium, in solution in the NH_4OH supernatant, was precipitated by the more basic NaOH supernatant, and beryllium, in solution in the NaOH supernatant, was precipitated by the less basic NH_4OH supernatant. This precipitation of hydroxides from the supernatant solutions acted as a carrier, and most of the plutonium was found to be in the precipitate. However, the concentration of the plutonium in this precipitate is so low as to make the usual precipitation methods untenable. For this reason LaF_3 carrier methods were used. A solution of the tetravalent plutonium nitrate in 1M HNO_3 was treated with SO_2 until the solution was saturated. Lanthanum was added in the form of $La(NO_3)_3 \cdot 6H_2O$, and enough HF to precipitate the LaF_3 and to make the solution 1 to 2 molar in excess. The LaF_3 was centrifuged, washed, fumed with H_2SO_4, and the La was separated from the plutonium by one of the methods previously described. The basic supernatants after this treatment still contained enough plutonium to warrant its recovery, hence further carrier procedures are being used at the present time. Ferric nitrate

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is added to the solution and the ferric hydroxide thus formed is allowed to settle through the solution. Results of this experiment are not known yet.

PURIFICATION

After one or more of the concentration procedures just described have given a product which is 80 to 100 per cent plutonium, the processes of purification are carried out. The procedure used for this purification is based, with modifications, on those described in a previous report1). However, since there are certain major changes in procedure, the new method will be described in some detail. As has been previously stated, the final procedure of concentration is an oxalate precipitation in nearly all cases, and this is dissolved and oxidized according to the method described under oxalate procedure. The solution thus oxidized is treated with solid sodium acetate until the precipitation of the sodium plutonyl acetate is complete, and an excess of one third has been added. The pink $NaPuO_2Ac_3$ is centrifuged and washed twice with acetate wash solution (5M Na^+ 0.2M Ac^-, 0.35M HAc). The washed acetate is dissolved in the smallest amount of 16N HNO_3 that will give a clear solution, and the volume of this solution is reduced by evaporation until $NaNO_3$ begins to crystallize. This solution - about 1 to 2 cc per gram of plutonium - is then extracted with di-ethyl ether in a modified Soxhlet extractor having a design similar to that described in (1), but being of greater capacity. The hexavalent nitrate obtained from the ether extraction is diluted somewhat and treated with enough 7N HI to give 9 mols of I^- per mol of plutonium. This mixture is allowed to stand 30 to 60 minutes, and 1 molar oxalic acid is added in sufficient amounts to

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1) Mastick, Pittman, and Wahl, LAMS-72

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give 1.5 mols of oxalate per mol of plutonium, and to make the final solution 0.2 M in excess. The volume of the solution is then adjusted so that the plutonium concentration (total) is 0.2 M. This mixture is allowed to stand for an hour or so, and the green oxalate washed free of I_3^-. This slurry is turned over to the "dry" chemist for conversion into compounds suitable for metallurgical reduction.

During the purification processes, various solid residues are obtained. These are always removed from the solution before the succeeding procedure is carried out.

CONCLUSIONS AND DISCUSSION

Although none of the procedures described in this paper can be termed as completely quantitative, a continuous recycling of all residues and supernatants can be said to achieve quantitativeness to a large degree. For example during the past eight months about 250 individual samples have been turned in for recovery. These totaled 117, 936 mg, or an average of approximately 450 mg per sample. Of this amount 109,639 mg of essentially pure plutonyl nitrate and plutonium oxalate have been turned over to the "dry" chemists. About one gram is in the various supernatants and residues which will be worked up over a period of time. The apparent loss of 7.3 grams is most probably due to errors in estimations of amounts turned in for recovery, since no assays are made on any of the incoming materials, whereas all outgoing samples are assayed either by weight or by radioactive means.

Outline I may be considered to be a composite of all recovery and purification work done in this laboratory. Naturally, the entire procedure

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is not followed for each individual recovery problem, but only those portions which are necessary to remove the particular elements present. It is only in case all possible impurities are present at one time that the complete scheme is followed.

COLORS OF SOLUTIONS AND PRECIPITATES

Since the colors of the various precipitates and solutions have been reported by different people as being entirely different, and since our work has dealt with large amounts of quite pure compounds, a report is made of colors of precipitates and solutions. Table II gives the colors as observed in this laboratory.

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TABLE I - MATERIAL RETURNED FOR RECOVERY

Phase of work returning material	Form in which Pu is present	Form of Impurity
METALLURGY		
Bomb Reduction	Oxide, slag, metal	MgO, CaO, BeO, Al_2O_3, Ce_2S_3, UN, Ca, Pt, Cu, Ni, Co, Zn, Fe, Halogens
Electrolytic Reduction	Oxide, metal, trichloride	$BaCl_2$, KCl, NaCl, C, Zn, Ni, Cr, W, glass, organic
Remelt	Oxide, metal	Ce_2S_3, ZrN, C, BeO, Ni, BaS, MgO, CaO, UN, ThN, ZrC, TiC, ThS_2, Ta, Si, Mo, Ti
Physical Expts.	Oxide, metal	Fe, quartz, glass, organic, abrasive
Hydride Expts.	Oxide, metal, hydride	BeO
Special Reduction	Oxide, metal, carbide	UN, UO_2, ZrN, ThO_2, TiN, ThN, Ce_2S_3, ThS_2, CaO, BeO, TaC, Ta, Mo, W, Si, C, WC
Electrolytic polishing	Solutions (tri- & tetravalent)	H_3PO_4, organic
X-ray	Oxide, metal, trihalide	None
Dry Box Sweepings	Oxide, metal, halides	Kleenex, rags, wood, TaO_2, Cr, BeO, MgO, Fe, Fe_2O_3, Ta, Cu, ZrO_2, ZrN, Ce_2S_3, brush hair

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TABLE I - MATERIAL RETURNED FOR RECOVERY (CONTINUED)

Phase of work returning material	Form in which Pu is present	Form of Impurity
CHEMISTRY		
"Wet" chemistry	Solutions (tri-, tetra-, hexa-valent)	Organic, $CrO_4^=$
"Dry" chemistry	Oxide, metal, trihalide	Pt alloy, U, La, Ce
Assay	Solutions (tri-, tetra-, hexa-valent)	Any element shown above
Analysis	Oxide, metal, peroxide, oxalate, gallate, cupferride	U, Mo, W, organic, C
Apparatus wash	Trihalides	None
Dry Box Sweepings	Trihalides, oxide	Brush hair
PHYSICS	Metal, oxide	None
PROJECT X	Tetra-nitrate and peroxide	Zr, La

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TABLE II - COLOR OF PRECIPITATES AND SOLUTIONS

Name of Compound	Formula*	Color
Pu^{IV} hydroxide	$Pu(OH)_4$	Dark green
Pu^{III} hydroxide	$Pu(OH)_3$	Light Blue
Pu^{VI} hydroxide	$PuO_2(OH)_2$ (?)	Brown
Sodium Pu^{VI} acetate	$NaPuO_2Ac_3$	Pink
Pu^{III} fluoride	PuF_3	Purple
Potassium Pu^{IV} fluoride	K_2PuF_6	Grey
Pu^{III} oxalate	$Pu_2(C_2O_4)_3$	Brilliant green
Pu^{IV} iodate	$Pu(IO_3)_4$	Light pink
Pu^{IV} sulfate	$Pu(SO_4)_2$ (?)	Pink
Pu^{III} chloride solution		Blue
Pu^{IV} chloride solution		Brown
Pu^{IV} nitrate in conc. HNO_3		Green
Pu^{IV} nitrate in dil. HNO_3		Brown
Pu^{VI} solutions in H_2O or ether		Brown

*Water of hydration is not included or excluded by the formula.

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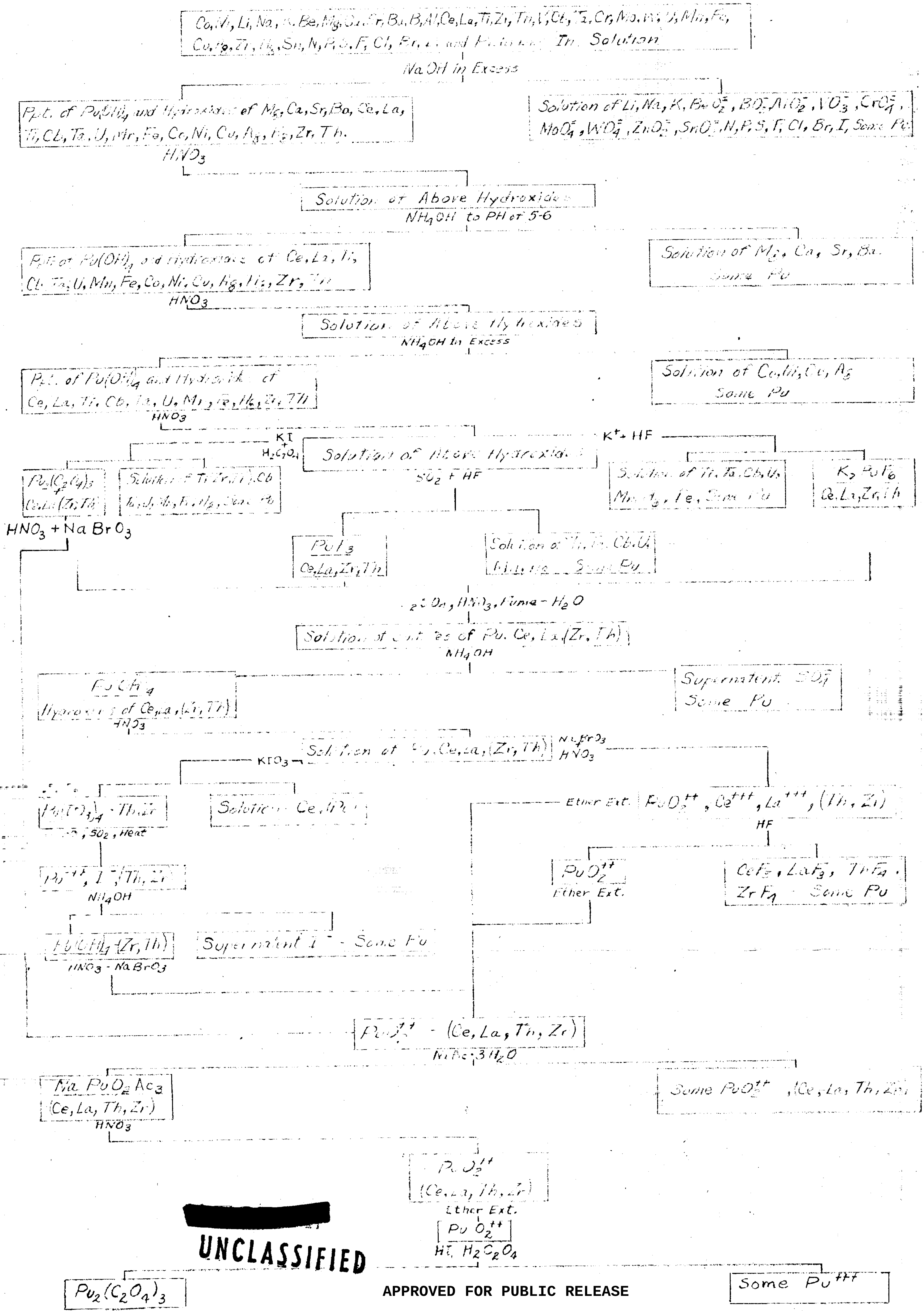
OUTLINE I

FLOW SHEET FOR RECOVERY AND PURIFICATION OF PLUTONIUM



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