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CHEMICAL RESEARCH—PRODUCTION AND
EXTRACTION OF 94

Report for Period April 16–April 30, 1943

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Metallurgical Project

A. H. Compton, Project Director

* * *

CHEMICAL RESEARCH -- PRODUCTION AND EXTRACTION OF 94

J. Franck, Division Director; G. T. Seaborg, Section Chief
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* * *

REPORT FOR PERIOD APRIL 16 - APRIL 30, 1943

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I. ABSTRACT

J. E. Willard

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Wet fluoride method for the extraction and decontamination of plutonium.
Aluminum will probably be used to coat the uranium billets in the operating piles. It has been found that the presence of this aluminum (1.2% of the U by wt.) in the extraction solutions inhibits the precipitation of LaF_3 and lowers its carrying power for Pu. As a result the Al coating must be removed from the U before the metal is dissolved for the extraction process or the process must be modified to accomodate the aluminum. The effect is observed even in the presence of a large excess of fluoride ion over aluminum ion.

Zirconium nitrate is now used to dissolve the LaF_3 precipitates which carry the PuF_4 in the wet fluoride process. When an oxidation-reduction decontamination cycle is carried out in the solution so obtained some of the zirconium precipitates with the LaF_3 by-product precipitate and a smaller amount comes down with the product precipitate. A single gravimetric determination has shown that 0.58% of the Zr comes down with the product precipitate - indicating that any radioactive zirconium which was present at the start of the cycle would be decreased by a factor of 170 in the product precipitate.

Adsorption methods for extraction and decontamination of plutonium.
Further investigations of the properties of silica gel as an extracting agent show that adsorbed Pu is quantitatively eluted from the gel in as little as one minute time of contact with either 1 N or 6 N HNO_3 . The moisture content of certain samples of the gel as received and ground for use has been found to be 4%.

Further investigations of the properties of heat-treated zirconium phosphate as an adsorbent for Pu indicate that: (1) the temperature of treatment (in the range of 400° - 800°) does not appreciably affect the characteristics of the adsorbent; (2) the rate of adsorption of Pu from uranyl solutions is rather low although the percentage adsorbed at equilibrium is equivalent to that with silica gel; (3) adsorption of Pu in the absence of uranyl ion, at pH = 0 to pH = 2.5 is nearly 100% complete in one minute at solution to solid ratios where it would be only 40-50% complete in the presence of 10% $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$; (4) when adsorption occurs in the absence of uranyl ion quantitative elution with HNO_3 or $\text{HNO}_3 + \text{H}_3\text{PO}_4$ is not obtained in batch tests; (5) heat-treated zirconium phosphate which has been heated to dryness with excess phosphoric acid shows similar adsorption characteristics to that which has not had the excess phosphoric acid treatment.

Bismuth phosphate method for extraction and decontamination of plutonium.
The oxidation conditions previously prescribed for the bismuth phosphate process have been found to introduce corrosion hazards. It has now been found possible to oxidize quantitatively in 2 N HNO_3 at 75°C (as contrasted to 6 N HNO_3 at 95°C). This is done with the use of 0.002 M Ce^{+4} and 0.02 M $\text{K}_2\text{Cr}_2\text{O}_7$. The presence of the small amount of Ce^{+4} allows the original solution to be diluted to 2 N HNO_3 without precipitation of BiPO_4 .

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Volatility methods for the extraction and decontamination of plutonium. A series of four successive distillations of a sample of bombarded UF_6 separated it from over 99% of the gamma fission activity and 99% of the Pu which was initially associated with it. There is apparently a volatile fission product constituent which distills with the UF_6 and which is present to a very small extent after bombardment.

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ABSTRACT (cont'd.)

In a continuously operated extraction unit for a UF_6 pile there will be a certain equilibrium distribution of each fission species between the pile, the concentration still, and the disposal system. Mathematical expressions for this distribution in terms of the decay constant of the species and the fractional bleeding rates from the pile and the still are given. The equilibrium heat evolution in the still of a 5×10^5 KW UF_6 - heavy water pile should be enough to distill all of the UF_6 nearly three times in a day.

A revised dry fluoride process for the extraction of Pu from the U metal of a chain reacting pile is suggested. It involves converting the metal to a mixture of fluoride and oxide with HF and steam at 500° - 700° C followed by fluorination at 500° C. The plutonium may readily be condensed at a higher temperature than that at which the UF_6 condenses. Bismuth may be used as carrier for the Pu. This type of extraction would involve less corrosion hazard and a lesser problem of temperature control than was present in the dry fluoride method originally proposed.

General problems in the chemistry of plutonium. The importance of testing all extraction and decontamination procedures at concentrations of both fission products and plutonium such as will occur at Site "W" is stressed again. The preparation of a solution containing a mixture of inactive forms of 16 of the fission species is described.

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II. Wet Fluoride Process Extraction and Decontamination of Uranium

R. A. James, W. J. Knox, and T. P. Koh

A. The effect of aluminum on the wet fluoride extraction cycle. The most recent plans for coating uranium metal to be used in the pile call for an aluminum coating which corresponds to 1.2% by weight of the uranium. This coating is to be dissolved with the uranium in HNO_3 containing the catalyst Hg (0.025% of the uranium) and the resulting solution will contain Al^{+3} and Hg^{+2} . These facts necessitated a retesting of the wet fluoride process in the presence of these ions to determine the possible effects on the oxidation and reduction of Pu and the carrying power of LaF_3 . It has been found that concentrations of Al which will prevail in plant operation inhibit the precipitation of LaF_3 and lower its carrying power for Pu to such an extent that the Al coating must be removed from the U before the metal is dissolved for the extraction process, or the extraction process must be modified. This effect of Al is observed even in the presence of a large excess of fluoride ion over aluminum ion. Experiments which have been carried out in this connection are described below.

Two complete extraction cycles were carried out on two 10 g. samples of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. The reagents and concentrations used were those recommended in the wet process B flow sheet (R. S. Apple 1-12-43) except that NaAsO_2 instead of H_2O_2 was used as a reducing agent and Al^{+3} was present. At an aluminum concentration of 3.6% by weight of the uranium the Pu recovery was 0.15%; with 1.8% of Al, Pu recovery was 45-50%. In neither of these runs was Pu lost in the by-product precipitate and in both cases reduction was complete. Thus the presence of Al^{+3} has no effect on oxidation or reduction. In other words the effect of Al^{+3} is on the completeness of precipitation and/or carrying power of LaF_3 . The precipitates were of normal size by visual estimation. They were also shown to be partially, if not entirely, LaF_3 , rather than AlF_3 , by dissolving the precipitate in H_2SO_4 , heating to fumes, and precipitating the hydroxide which failed to dissolve completely in excess NaOH .

In precipitating a given amount of La^{+3} from solutions containing Al^{+3} the size of the precipitate was noticeably decreased with increasing Al^{+3} concentrations, so an experiment was performed to test this effect more quantitatively and also to determine the amount, if any, of AlF_3 precipitating. A number of 10 cc. solutions of varying concentrations of Al^{+3} were made 0.56 N in HNO_3 and 1 N in HF . Five mg of La^{+3} were added and the solutions were allowed to stand one hour. The precipitates were centrifuged and visually compared to 5 mg. of La^{+3} precipitated with HF in the absence of Al^{+3} . Then the precipitates were washed in 3 N HNO_3 to dissolve any AlF_3 present, centrifuged, and the size estimated again. The results are given in Table 1. They show that with increasing Al^{+3} concentrations the amount of precipitated LaF_3 is decreased and the amount of precipitated AlF_3 is increased.

Figure 1 shows the extent to which the carrying power of LaF_3 for Pu falls off with increasing Al^{+3} concentrations. The results also show that the carrying power of LaF_3 in the presence of Al is further decreased in the presence of other ions such as are introduced by the oxidizing and reducing agents used in the process.

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FIGURE 1

Carrying Power of LaF_3 at Various Al^{+3} Concentrations

Composition of Solutions:

I. 10% $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$
 0.6 N HNO_3
 1.0 N HF
 0.15 mg La^{+3}/cc

II. Same as I with addition of:

.06 N H_2SO_4
 2.0 mg $\text{K}_2\text{Cr}_2\text{O}_7/\text{cc}$
 3.7 mg NaAsO_2/cc

It was suggested that the inhibition of the precipitation of LaF_3 under these conditions might possibly be due to the adsorption of Al^{+3} ions by particles of LaF_3 , thus creating a colloidal suspension which could not be centrifuged. To test this La^{+3} was precipitated as the fluoride in the presence and in the absence of Al^{+3} , the precipitates centrifuged out, and the supernatant solutions compared in a beam of light. The Tyndall effect was definitely greater in the case where Al^{+3} was present.

TABLE 1

Precipitation of LaF_3 and AlF_3 from Solutions with Various Al^{+3} Concentrations

$\text{HNO}_3 = .56 \text{ M}$ $\text{HF} = 1 \text{ M}$ $\text{La}^{+3} = 0.5 \text{ mg/cc}$

Al ³⁺ mg/cc	Mole Ratios			Size of pre- cipitate	Size of ppt. after 3 N HNO_3 wash
	F ⁻ /Al ³⁺	F ⁻ /La ³⁺	La ³⁺ /Al ³⁺		
0	∞	33	∞	1	1
0.2	165	"	5	1	1
0.4	82.5	"	2.5	1	0.5
0.8	29.7	"	0.9	0.5	0.1
1.6	16.5	"	0.5	0.2	0
3.2	6.6	"	0.2	1	0
6.4	3.3	"	0.1	2*	0

* precipitate observed before La added.

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Suspension in solution of the LaF_3 or slow formation of the precipitate was also indicated by another experiment in which a preformed precipitate of LaF_3 was made in the presence of Al^{+3} . The precipitate which came down after one hour was smaller in volume than usual and carried only 2% of the Pu. On standing overnight another precipitate came down carrying 11% of the Pu.

The effect of Al^{+3} in preventing precipitation of Pu with LaF_3 has been shown to be serious enough to necessitate either removal of the coating before dissolving the uranium or modification of the extraction procedure. These experiments indicate a definite inhibition of the precipitation of LaF_3 and a lowering of the carrying power of the LaF_3 which precipitates.

B. Distribution of Zirconium in the Zirconium Cycle of the Wet Fluoride

Method. Present plans call for dissolving the LaF_3 and PuF_4 from the extraction cycle of the wet fluoride process in zirconium nitrate solution. The subsequent oxidation-reduction cycle in zirconium nitrate solution is herein termed a "zirconium cycle". As discussed in CN-601 when LaF_3 is precipitated by adding excess HF to a solution containing relatively high concentrations (several mg/ml) of lanthanum and zirconium, the precipitate contains appreciable amounts of zirconium. When the precipitation is made by adding lanthanum to a solution containing zirconium and excess HF, the ("preformed") precipitate contains considerably less but still definite amounts of zirconium. Since the decontamination of plutonium with respect to radioactive zirconium in a single zirconium cycle would be limited by the fraction of this element which coprecipitated with the preformed LaF_3 containing the $\text{Pu}^{(x)}$, an experiment was performed to determine quantitatively the distribution of zirconium in such a cycle.

500 mg. La was precipitated as the fluoride and treated by a zirconium cycle, oxidizing with persulfate and silver, under the conditions recommended in CN-601, adding HF to precipitate LaF_3 (by-product), and reducing overnight with SO_2 equivalent to four times the $\text{S}_2\text{O}_8^{--}$. A second LaF_3 precipitate was then produced by adding La according to wet process B directions and the precipitate washed twice with 20 cc of 0.5 N HF. The lanthanum was reduced by a factor of 10 in the cycle. The first and second LaF_3 precipitates were dissolved by means of fuming H_2SO_4 . The zirconium content of each precipitate and of the original zirconium dissolving solution was determined gravimetrically by precipitation of zirconium phosphate from 3 N H_2SO_4 and ignition to ZrP_2O_7 . The results are given in Table 2.

TABLE 2

Precipitation of Zirconium with LaF_3 in Wet Fluoride Decontamination Cycle

Fraction	Wt. of Zr.	% of total
Dissolving solution	905 mg.	100
By-product precipitate (from oxidized solution)	145 mg.	16
Product precipitate (preformed precipitate from reduced solution)	5.2 mg.	0.58

Since 0.58% of the inactive zirconium followed the product thru the cycle, and since the radioactive zirconium is presumably present in the same chemical form as the inactive zirconium and hence distributes itself in the same manner, it is evident that the decontamination factor for the cycle with respect to zirconium is $1/0.0058 = 170$. This result is based on a single experiment and is to be considered simply as a qualitative indication of the degree of decontamination with respect to zirconium that can be obtained in one cycle. The exact value of the decontamination factor may be rather sensitive to the conditions under which the preformed precipitate is formed. The amount of zirconium carried with this precipitate might be reduced by precipitating from more dilute zirconium solutions, using less lanthanum, and possibly by increasing the HF concentration or altering the acidity.

III. Adsorption Methods for Extraction and Decontamination of Plutonium

R. H. Beaton, V. R. Cooper, B. A. Fries, T. La Chapelle,
R. A. Stoughton, I. Sheft, E. H. Turk

A. Rate of elution of plutonium from silica gel with 1 N HNO₃ and 6 N HNO₃. Tests previously reported (CN-522) indicate that plutonium is quantitatively eluted from silica gel by 1 N or 6 N HNO₃ in five minutes. These tests have been repeated and similar tests made with one minute, two minute and ten minute times of contact between the eluting acid and the gel containing adsorbed plutonium.

Samples were prepared for the elution tests by presoaking lg. portions of the gel with 10% UO₂(NO₃)₂·6H₂O for three hours, shaking with 10% UO₂(NO₃)₂·6H₂O containing Pu²³⁹ in tracer amounts, and eluting with 10 cc. of acid. 83% of the Pu was adsorbed in each case. Calculations were made on the assumption that the holdup liquid from the presoaking, and from the adsorption was not chemically bound and was all homogeneously mixed with the next solution placed with the gel. Mechanical shaking was used during the two hour adsorption periods and manual shaking during the short elution periods. The tests were made with 60-100 mesh Hyporsil silica gel.

In all cases (1 min., 2 min., 5 min., and 10 min.,) 98% or more of the Pu was eluted with either 1 N or 6 N HNO₃. The results are tabulated below.

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TABLE 3

Elution of Pu Adsorbed on Silica Gel

Time of elution	% of adsorbed Pu eluted	
	1 N HNO ₃	6 N HNO ₃
1 min.	99	96
2 min.	98	98
5 min.	99	100
10 min.	94	98
15 min.	100	-

B. Moisture content of silica gel. Silica gels such as those being tested as adsorbents in this work are able to adsorb up to about 45% of their own weight in moisture from air at high humidity. For this reason it is necessary to either dry the gel or know the water content before preparing weighed samples for adsorption tests. Tests which have been made of the water content by weighing a 40-60 mesh sample of the gel before and after heating in an oven at 175° for overnight indicate that for Hyporsil silica gel it may be as low as 4% even after grinding, screening and storing (in a stoppered bottle) for several weeks. A similar value (4.3%) was obtained by heating a 60-100 mesh sample of the gel at 250° for several days.

C. Heat treated zirconium phosphate as an adsorbent for plutonium. In (CN-522) it was reported that a material prepared by precipitating zirconium phosphate from 9 N HCl solution, drying the gel and heating to 400° C showed a high equilibrium value for the adsorption of tracer amounts of Pu from uranyl nitrate solutions and appeared to have mechanical properties which would make it suitable for use in a column. Further tests suggest that a variation in the temperature to which the zirconium compound is heated from 400° to 800° does not alter its adsorption characteristics. They also show that adsorption is more complete in the absence of uranyl ion than when it is present and that the equilibrium value for the Pu desorbed by HNO₃ is lower when the adsorption has taken place in the absence of uranyl ion than when uranyl is present. 010 010

1. Effect of temperature of preparation on adsorption characteristics of zirconium phosphate. One half gram samples of zirconium phosphate which had been prepared by precipitation from 9 N HCl, drying and heating were shaken for two hours with 10 cc portions of 10% UO₂(NO₃)₂·6H₂O 60-days after a two month neutron bombardment of the uranyl salt. The results obtained for adsorption and elution of Pu and of beta fission products by samples of the zirconium compound which had had different heating and soaking treatments are given in Table 4. They indicate that the adsorption capacity of the zirconium phosphate preparation is not greatly altered by rather great changes in its heat pretreatment.

TABLE 4

Adsorption and Elution of Plutonium Using Heat-Treated
Zirconium Phosphate as Adsorbent

Preparation of zirconium phosphate	Adsorption		Elution with 5 cc. 6 N HNO ₃		Subsequent elution with 5 cc. 8 N HNO ₃	
	% Pu	% β F. P.	% Pu	% β F. P.	% 94	% β F. P.
Heated to 400° C for 4 hr.	87	19	31	14	15	4
Heated to 800° C for 15 hr.	83	12	56	8	12	2
Heated to 800° C for 15 hr. and pre-soaked in water for 4 hrs.	78	16	46	8	12	2

(All %'s given are %'s of material present in the original 10% uranyl nitrate solution.)

2. Rate of adsorption of Pu from uranyl solution by zirconium phosphate.

Zirconium phosphate which had been prepared by precipitation from 9 N HCl, washing with dilute HCl, drying, heating at 600° C for 5 hours, screening to 40-60 mesh and presoaking with water for 18 hours was used to test the rate of adsorption of Pu²³⁸ from 10% UO₂(NO₃)₂·6H₂O solutions in batch tests. 0.3 g. of the zirconium phosphate was shaken with 10 cc. of Pu²³⁸ solution. The results, given in Table 5 indicate that the rate of attainment of equilibrium is not rapid.

TABLE 5

Rate of Adsorption of Pu from Uranyl Nitrate Solution
by Heat Treated Zirconium Phosphate

Time for Adsorption (min.)	% of Pu Adsorbed
12	37
32	54
128	73
18.5 hr.	88

3. Adsorption of plutonium from uranyl free solutions by heat treated zirconium phosphate. After the plutonium has been separated from the uranium and part of the fission activity of the pile further decontamination from fission activity will be necessary. Since the adsorption and elution characteristics of plutonium on a given adsorbent may be greatly different in the uranyl-free solutions of the decontamination steps than in the initial extraction step the heat treated zirconium phosphate has been tested in such solutions. The results show that under

conditions where one obtains 40-50% adsorption of Pu in thirty minutes in the presence of uranyl nitrate the adsorption is nearly 100% complete in one minute in the absence of uranyl ion at pH of 2 to 0. When adsorption occurs in the absence of uranyl ion, however, quantitative elution with HNO_3 is not obtained in batch tests. Table 6 gives the results of a series of elution tests made with different solutions and at different temperatures. These tests were all made with a volume of 10 cc. of eluant solution to 0.3 g. of the zirconium phosphate which had previously adsorbed 100% of the Pu^{238} in two hours from 10 cc. of an HNO_3 solution of pH 2.4 (no uranyl present). The zirconium compound had been heated to 600° for 5 hours in preparing it and had been screened to 60-100 mesh. The elution time in all of the experiments was 20 minutes. Constant shaking on a rotor was employed in the 25°C experiments and frequent stirring in the 93° tests. A certain amount of disintegration of the adsorbent occurred in these tests, especially in the 3 N solutions where 3 N H_3PO_4 was used.

TABLE 6

Elution of Adsorbed Pu from Heat-Treated Zirconium Phosphate

Eluant used	Temperature of elution ($^\circ\text{C}$)	% 94 eluted
6 N HNO_3	93	19
6 N HNO_3 + 1 mgm. Zr^{+3}	93	19
8 N HNO_3	93	24
3 N HNO_3 + 3 M H_3PO_4	93	53
3 M H_3PO_4	25	25
1 M H_3PO_4	25	3
1 M H_3PO_4 + 6 N HNO_3	25	18
3 M H_3PO_4 + 3 N HNO_3	25	40

Further elution tests have been made with a zirconium phosphate prepared by heating at 600° for 5 hours, wetting with H_3PO_4 and heating at 600° until no further fumes were given off and the solid seemed dry (18 hours or so). The results, given in Table 7, for two consecutive elutions of 94^{238} by 10 cc. of 8 N HNO_3 per 0.3 g. of adsorbent show that the adsorbed Pu is not quantitatively desorbed in this system and suggest that the adsorbed Pu is in equilibrium with the solution (i.e. not a case of partial irreversible adsorption).

TABLE 7

Elution of Pu^{238} from Phosphate-Treated, Heat-Treated Zirconium Phosphate by 8 N HNO_3

% desorption	
1st HNO_3	2nd HNO_3
14.3	15.3
15.4	15.8
18.1	17.8
16.5	14.4

D. Elution of adsorbed plutonium from titanium adsorbents A series of titanium compounds prepared in the Separation Processes section of the Technical Division were tested as adsorbents for Pu and fission products with results reported in CN-556. More recently the ability of HNO_3 to elute Pu^{238} from some of these materials has been tested with the results given in Table 8. Both the adsorption and elution in these tests were done with 1 g. of adsorbent to 10 cc. of added solution. The times of contact with the eluting solutions were: 25 minutes for samples 70A975, and 70B975; 45 minutes for samples 70C975, and 71A600; 1 hour for each acid wash of samples 75A950, and 75B950.

TABLE 8

Adsorption and Elution of Pu Using Titanium Adsorbents

Code of Adsorbent	Nature of Adsorbent	% Pu Adsorbed	% Desorption with 6 N HNO ₃	
70A975*	Titanium phosphate	87	13	
70B975*	Titanium phosphate	82	9	
70C975*	Titanium phosphate	87	3	
71A600*	Titanium oxide	80	43	
			1st HNO ₃ wash	2nd HNO ₃ wash
75A950**	Titanium phosphate	93	0	1.0
		94	1.0	1.0
75B950**	Titanium phosphate	96	0	0
		95	0.4	0.4

* presoaked 2 hours with H₂O

** presoaked 17.5 hours with 10% UO₂(NO₃)₂·6H₂O solution

IV. Bismuth Phosphate Method for Extraction and Decontamination of Plutonium

D. R. Miller

A. Oxidation of plutonium in the phosphate method with dichromate and cerium (Ce⁺⁴). In report CN-601 it was mentioned that the use of Ce⁺⁴ in conjunction with Cr₂O₇⁻⁻⁻ to oxidize plutonium in 2-3 N HNO₃ solutions of BiPO₄ showed promise of being rapid and complete at temperatures at least as low as 75° C. Such a method, which should minimize the corrosion of stainless steel which occurred with the previous procedure, has now been developed further and found to be a satisfactory laboratory method. In 2 N HNO₃, with 0.02 M K₂Cr₂O₇ and 0.002 M Ce⁺⁴, 99% of the Pu is oxidized in 2 hours at 75° C.

In Table 9 are listed some results showing that Ce⁺⁴ alone exerts a considerable oxidation effect, but that the rate of oxidation can be increased by adding Cr₂O₇⁻⁻⁻. The experiments recorded in the table were done with solutions containing the normal amount of Bi⁺³ and H₃PO₄ which would be present in decontamination cycles with the bismuth phosphate method.

TABLE 9

Oxidation of Pu by Ce^{+4} and by Ce^{+4} and $K_2Cr_2O_7$
(0.002 M Ce^{+4} , Time = $\frac{1}{2}$ hour)

$K_2Cr_2O_7$ Conc.	HNO_3 Conc.	Temp.	% Pu Oxidized
0	4 N	95° C	93.1
0	2 N	70-80° C	77.3
0.01 M	2 N	70-80° C	95.7
0.02 M	2 N	73° C	96.8
0.03 M	2 N	73° C	97.1

The procedure as finally developed is carried out with the following laboratory proportions. 25 mg. Bi^{+3} , precipitated as $BiPO_4$, is dissolved in 1 cc. 10 N HNO_3 . 1.4 mg. of Ce^{+4} is added as a solution of $(NH_4)_2 Ce(NO_3)_6$, the solution is made 0.02 M in $Cr_2O_7^{--}$ after dilution to 5 cc. with H_2O , and is heated at 75° C. 99% oxidation of Pu is attained after heating for 2 hours, as illustrated in Table 10.

TABLE 10

Oxidation of Pu vs. Time of Heating
(0.02 M Ce^{+4} , 0.02 M $Cr_2O_7^{--}$, 2 N HNO_3 , at 70-72° C)

Time of Heating	$\frac{1}{4}$ hr.	$\frac{3}{4}$ hr.	1 hr.	2 hours
% of Pu Oxidized	86.0	90.4	95.9	99.0

Analyses to determine the per cent oxidation were made by diluting the oxidized solution to 1 N in HNO_3 with 0.3 M H_2PO_4 , to precipitate $BiPO_4$ and ceric phosphate. The supernatant, containing the oxidized Pu, was reduced with SO_2 , and LaF_3 precipitated and counted. The precipitate of $BiPO_4$ and ceric phosphate, containing the reduced Pu, was dissolved in 10 N HNO_3 and H_2O_2 , and the $BiPO_4$ reprecipitated by diluting to 1 N HNO_3 . The $BiPO_4$ was dissolved in HCl, and LaF_3 precipitated and counted.

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Ceric phosphate precipitates during the oxidation procedure outlined above and thus presumably removes sufficient PO_4^{--} from solution to prevent precipitation of $BiPO_4$ which otherwise would occur after dilution of the original 10 N HNO_3 to 2 N HNO_3 . The phosphate concentration in the oxidizing solution is about 0.02 M, and the Ce^{+4} therefore removes only about 10% of the phosphate from solution. However, the precipitation of $BiPO_4$ from a solution containing 0.002 M Ce^{+4} has never been observed (heating at 75° C for 3 hours), while $BiPO_4$ will

precipitate from a solution of 2 N HNO_3 , in the absence of Ce^{+4} , at 75°C in less than $\frac{1}{2}$ hour.

An orange, crystalline precipitate, probably bismuthyl dichromate, separates during the oxidation together with the ceric phosphate, but does not inhibit the oxidation. The BiPO_4 - ceric phosphate precipitate obtained after oxidation by dilution to 1 N HNO_3 and adding H_3PO_4 was filtered on a medium porosity sintered glass filter with no difficulty.

V. Volatility Methods for the Extraction and Decontamination of Plutonium

H. S. Brown, E. G. Bohlmann, and O. F. Hill

A. The distillation of bombarded UF_6 . In order to obtain further information about the possible separation of fission activity from the UF_6 in a continuously operating UF_6 pile by distillation processes the experiments below have been carried out.

A tube containing 210 grams of UF_6 was bombarded at the St. Louis cyclotron for about 50,000 μah . It was allowed to stand for fifty days and then the UF_6 was distilled in the following manner. The tube was placed in a chamber maintained at 70°C to liquify the UF_6 . A furnace was then placed around it and the UF_6 was slowly volatilized. The vapors were passed into a condenser cooled with boiling methyl alcohol (b.p. 64.7°C) thus condensing the vapors to the liquid state. The liquid drops fell into a collection vessel maintained at $65^\circ\text{--}70^\circ \text{C}$. The gamma activity of the UF_6 was measured before and after the distillation. The residue from the initial tube was dissolved in water and analyzed for Pu. The distillate was volatilized again in exactly the same manner and the gamma activity again measured. This was repeated two more times until a total of four distillations had been made. Table II shows the percentage of gamma activity distilled over in each case and the percentage of the total initial gamma activity to which it corresponds. Likewise the percentage of Pu which distilled in each case is given.

Table II

Separation of Fission Activity from UF_6 by Distillation

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Distillation	% gamma activity which distilled	% original gamma activity present in UF_6	% 94 which distilled	% original 94 present in UF_6
1	3.1	3.1	5.1	5.1
2	35	1.1	60	3.1
3	86	.95	22	.7
4	78	.74	-	-

It can be seen that there is apparently a volatile fission product constituent that distills with the UF_6 and which is present to a very small extent 50-days after bombardment. As can be seen from the above tables it amounts to less than .74% of the total gamma activity as measured through several grams of lead. Of the fission products which form volatile fluorides these data fairly well exclude the possibility of yttrium, zirconium, and columbium distilling over, all of which are present to a considerably greater percentage in a sample of this age. On this basis the activity distilling is probably bromine, molybdenum, 43, rhodium, antimony, tellurium, or iodine.

The rather large percentage of Pu distilling after the first distillation indicates the possibility of there being a small amount of a higher 94 fluoride present in the bombarded UF_6 . This effect has been observed before, and the theoretical implications have been discussed in previous reports.

B. General problems in the extraction of plutonium from a UF_6 pile.
In a continuously operated extraction unit for a UF_6 pile there would almost certainly be a concentration still. Liquid UF_6 would be bled from the pile circulation system into the still, where it would be volatilized, condensed and fed back into the pile. The question arises as to the amount of heat evolved by the fission products present in the concentration still at equilibrium. This of course will depend very strongly on the fractional bleeding rate (CN-454) from the pile into the still, and on the fractional bleeding rate from the still to the external extraction system, whatever it might be. The fractional bleeding rate for the pile is defined as the fractional of the total amount of UF_6 bled from the pile per day. The fractional bleeding rate for the concentration still is defined as the fraction of the total amount of UF_6 in the still that is bled from the still per day into the extraction unit.

For fission products that do not volatilize we have the following expressions for the fraction of their total activity in the pile, in the still, and in the disposal storage outside of the pile at equilibrium.

fraction of total activity in pile

$$F_0 = \frac{\lambda}{f_0 + \lambda}$$

fraction of total activity in concentration still

$$F_1 = \frac{\lambda}{f_0 + \lambda} \cdot \frac{f_0}{f_1 + \lambda}$$

fraction of total activity disposed of outside

$$F_2 = \frac{f_0}{f_0 + \lambda} \cdot \frac{f_1}{f_1 + \lambda}$$

where λ = decay constant expressed in reciprocal days

f_0 = fractional bleeding rate from the pile

f_1 = fractional bleeding rate from the concentration still

For fission products that volatilize with UF_6 we have:

fraction of total activity in pile

$$F_0 = \frac{\lambda + f_v - f_0}{\lambda + f_v}$$

fraction of total activity in concentration still

$$F_1 = \frac{f_0}{\lambda + f_v}$$

Where f_v = fractional distillation rate from concentration still. Assuming that no attempt is made to cut out the volatile constituents, none of these products will be in disposal outside.

From the above equations one can calculate the activity in the various locations due to any fission product, given the branching ratio for the formation of the product and the various fractional bleeding rates. We have applied such a calculation to the case of $f_0 = 1$, $f_1 = 1$, and $f_v = 10$, (which are quite reasonable fractional bleeding rate values) and have calculated the equilibrium heat evolution in the concentration still. The results of the calculations follow.

TABLE 12

Heat Produced by Np and Fission Products in Concentration Still of UF_6 Pile

Substance	Heat output (percent of pile power)	Heat output for 500,000 KW pile
Neptunium	0.078%	390 KW
Non-volatile fission products	0.040%	202 KW
Volatile fission products	<u>0.023%</u>	<u>114 KW</u>
TOTAL	0.141%	706 KW

This result can be compared to the heat of evaporation of liquid UF_6 which may be taken to be 6.9 K. cal. per mole. 1 KW will evaporate 1.14 tons of UF_6 per day, or 706 KW (as we have above) will evaporate about 800 tons of UF_6 per day. Preliminary engineering investigations have indicated that a 500,000 KW UF_6 heavy water pile would contain in the neighborhood of 284 tons of UF_6 . (See CE-545). A fractional bleeding rate value of 2, as assumed above means that 284 tons of UF_6 would be fed each day into the still. However, we have enough heat evolution in the still to vaporize 800 tons per day. Consequently at equilibrium operation of such a pile coupled with such a concentration still it would not be necessary to supply any heat to the still. Obviously a considerable amount of reflux or distillate feedback would be necessary to remove the heat evolved. This large heat evolution of the fission products and element 93 will quite likely make possible the use of a much higher fractional bleeding rate than the one assumed above, and thus further cut down the activity present in the pile. Investigations on this point are continuing.

C. Revised dry fluoride extraction process for the separation of plutonium. In the dry fluoride process for extraction of Pu from the U of the pile as originally worked out, there were several rather serious difficulties, from an engineering point of view, that caused further consideration for such a process on a large scale to be minimized. The steps used in the old process were as follows:

- (1) Convert the U metal to a mixture of the fluoride and oxide by treatment with HF and steam at a temperature between 500° and 700° C.
- (2) Reduce any higher oxide present to UO₂ by using hydrogen at 500° C to 700° C.
- (3) Convert the UO₂ to UF₄ using HF at 500° C.
- (4) Volatilize the uranium away by treatment with fluorine at 250° C.
- (5) Volatilize the plutonium away by treatment with fluorine at 500° C.

In the process the uranium is freed from 99% of the original fission activity, and the plutonium is obtained likewise with less than 1% of the original activity.

One of the most serious objections to the process was the temperature control in step (4). Due to the fact that the range of temperature between the point where uranium volatilizes completely and plutonium starts to volatilize is only about 35° C, excellent temperature control would be necessary. As the non-volatile fission activity accumulates in the reactor during each run, liberating considerable quantities of heat, the maintenance of the desired temperature in step (4) becomes extremely difficult.

Our recent work indicates that it is not necessary to use a separation based on temperature of volatilization in the dry fluoride extraction process. It would appear that the uranium and the plutonium can be separated by utilizing the fact that plutonium condenses with BiF₅ at a temperature that allows the uranium to pass on, (CN-556). Thus all steps could be made to take place at temperatures between 500° C and 700° C.

Due to the low temperature needed in step (4), it was quite important that steps (1) and (3) give complete conversion to UF₄. In the modified process, where the fluorination takes place at 500° C, this is not necessary, as almost any uranium compound will be converted to UF₆ at that temperature. Thus steps (2) and (3) can be eliminated. In view of these facts, the modified dry fluoride process would then be as follows:

- (1) Convert U-metal to a mixture of fluoride and oxide with an HF-steam mixture at 500°-700° C
- (2) Fluorinate the mixture at 500° C

A small amount of bismuth would be placed in the reactor initially with the uranium. The Pu would condense with the bismuth. This condensate could then be put through a dry decontamination cycle such as has been described in previous reports.

The elimination of step (2) in the old process should reduce corrosion problems to a considerable extent. Hydrogen tends to reduce the protective metal fluoride coatings in reaction vessels. The metal thus formed in turn scales off leaving a fresh metal surface for reaction with fluorine. We have observed in the laboratory that if the use of hydrogen is eliminated, corrosion problems are much less serious.

VI. General Problems in the Chemistry of Plutonium

N. R. Davidson

A. Preparation of a concentrated solution of fission product elements (inactive isotopes). Calculation by Kohman, and by Connick, Prestwood, and Wahl (CN-522) indicate that the fission products produced at Site W will be present at such concentrations that they may precipitate during the plutonium extraction processes at points where they are not carried when present in tracer quantities. It is therefore necessary to test each process in the presence of the calculated Site "W" concentrations of inactive isotopes of fission product elements. Such tests should determine the effect of these elements on plutonium recovery, decontamination, and the important mechanical properties of the precipitates (with respect to filtration, etc.). Tests of this type have already been carried out on the acetate process by the Berkeley group.

It should be noted that such tests may be misleading if they are done with "macroscopic" quantities of fission species but only tracer quantities of plutonium since, at Site "W", the plutonium will be present in "macroscopic" amounts at concentrations greater than that of any one fission product. More conclusive experiments must therefore be performed on a microchemical scale with both plutonium and fission products at Site "W" concentrations. Valuable preliminary information may however be obtained with experiments involving only tracer concentrations of plutonium.

We have therefore prepared a relatively concentrated "master" solution of fission products in the correct proportions. (Element 43 was unavailable. Columbium was not added since it was not expected to remain in solution in the "master" solution. It must be added separately as columbate.)

Assuming a plutonium yield of 250 grams per metric ton of uranium, one may calculate from Kohman's results the data given in Table 13.

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TABLE 13

"W" Quantities of Fission Product Elements in Micrograms
per Gram of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$
(assuming production of 250 g. Pu per ton of U):

Element	Sr	Y	Zr	Cb	Mo	"43"	Ru	Rh	Pd	Sb	Te	I	Cs	Ba	La	Ce	Pr	Nd
Micrograms fission product per gram $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	4.8	7.2	10.8	2.4	3.6	4.8	7.2	3.6	3.6	.06	.12	.6	12	3.6	4.8	23	4.8	10.8

The master solution is so adjusted that .05 cc. added to one gram of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ will give the quantities listed in Table 13. The concentration of fission species in the master solution is approximately a hundred times that which would be encountered in a 20% $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solution from Site "W".

The solution (in 5 N HNO_3) has a light brown color (Pd, Ru, Rh principally) and the components seem to be combatible, since no precipitation had occurred several days after preparation.

As far as possible, the components were added as the nitrates. Cesium, palladium, ruthenium and rhodium were available only as chlorides. It is unlikely that this small amount of chloride will cause any trouble. Ruthenium chloride was first refluxed with 70% nitric acid to attempt to adjust it to the valence state it will assume in the solution step. Some of the ruthenium appears to reflux in this treatment and some of it precipitates out of the boiling acid. The precipitate was filtered out before adding the ruthenium in solution to the master solution. The apparent slight volatility of Ru under these conditions is being further investigated to determine whether any of this element will be evolved with the off gases from the process of dissolving the uranium metal of the pile in nitric acid.

Cerium was added in the trivalent state, molybdenum as ammonium molybdate, tellurium from a potassium tellurite solution, and iodine as iodic acid. Probably most of the iodine will distill out in the metal dissolving of the actual plant process, but some could conceivably remain as iodate. Praseodymium was used to represent both praseodymium and neodymium.

Probably the columbium present in the pile metal will be converted to the pentavalent state during the solution step and some of it may then slowly precipitate as the oxide. It is difficult to obtain columbium in solution in such a way as to simulate its behavior in an actual plant extraction process. This may perhaps best be done by making tests with a uranium-columbium alloy which has undergone neutron bombardment. When such an alloy is not available the columbium may be added to the extraction solution as an alkaline columbate solution.

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