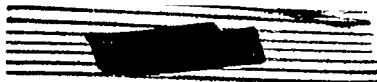


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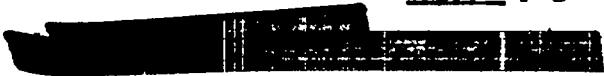
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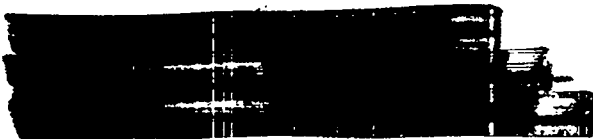


REMOVAL OF IRON FROM PLUTONIUM SOLUTION  
BY BASIC ACETATE PRECIPITATION

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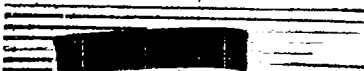


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Technology - Plutonium

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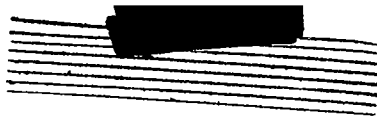
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ABSTRACT

A study has been made of the separation of plutonium from iron by means of a "basic acetate" precipitation. The plutonium was oxidized to  $\text{PuO}_2^{++}$  with  $\text{KMnO}_4$  and the iron precipitated by the addition of ammonium acetate. The following results were obtained:

1. 96 - 98% of the plutonium may be separated from the iron by the acetate method if acetate is  $>1.9 \text{ M}$  and the plutonium is oxidized to the VI state.
2. The carrying of  $\text{PuO}_2^{++}$  by the iron precipitate is primarily a function of acetate concentration.
3. No difference in the carrying of  $\text{PuO}_2^{++}$  by the iron precipitate was noted when Fe was present initially in the concentration range  $.005 \text{ M}--.1 \text{ M}$ .
4.  $\text{UO}_2^{++}$  acts effectively as a holdback carrier for plutonium when plutonium is present in tracer quantities. The effect is negligible for macro concentrations of plutonium.

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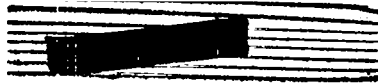
REMOVAL OF IRON FROM PLUTONIUM SOLUTION  
BY BASIC ACETATE PRECIPITATIONI. Introduction:

One of the problems in the recovery and purification of plutonium from plant by-products is the removal of iron. The difficulty lies in the high standards of the iron removal step which requires that the iron waste solution shall not contain more than  $1 \times 10^{-5}$  gpl of plutonium. The usual means of precipitating plutonium and leaving iron in solution are not acceptable because too much plutonium remains behind in the iron waste fraction.

A possible method of precipitating iron without carrying plutonium was suggested in CN 2449 by Beaufait, Stevenson and Rollefson. The process consists of oxidizing plutonium to the VI state and precipitating colloidal ferric hydroxide in the presence of acetate and uranyl ions. It was reported that less than 2% of the plutonium was carried by the iron under these conditions.

The present work was undertaken in an effort to decrease the amount of plutonium carried and to determine the applicability of the process to plant scale operation in recovery work.

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## II. Experimental:

Experiments were performed on a 100 ml scale. The following general procedure was used in all runs:

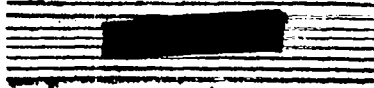
1. Initial Conditions - The plutonium was present as Pu IV at concentrations varying from  $1 \times 10^{-4}$  gpl to 0.2 gpl. The iron was present as Fe III at concentrations ranging from 0.3 gpl to 6.0 gpl. Except for the presence of  $UO_2^{++}$  in some runs, no other metals were present. The initial acidity varied from 0.1  $HNO_3$  to 1.0 N  $HNO_3$ .

2. Oxidation Step - 0.52 M  $KMnO_4$  (standardized) was added to the initial solution to a final concentration of .05 M  $KMnO_4$ . At least two hours were allowed for oxidation of Pu IV to Pu VI at room temperature. The oxidation state of the plutonium was checked by spectrophotometric analysis after oxidation.

3. Precipitation Step -  $Fe(OH)_3^*$  was precipitated by the addition of  $NH_4OH$  or  $NH_4$  acetate. The procedure is given in the tables. In those cases where  $NH_4Ac$  was used, a calculated amount was added to bring the pH to the desired value and the solution was then heated at  $75^\circ C$  for 30 - 120 minutes until precipitation was complete.

\*For simplicity  $Fe(OH)_3$  is used to designate hydrous ferric oxide, colloidal ferric hydroxide or basic ferric acetate.





4. Filtration and Dissolution of the Fe (OH)<sub>3</sub>- MnO<sub>2</sub> Precipitate - After precipitation and digestion, the slurry, consisting chiefly of Fe (OH)<sub>3</sub> and MnO<sub>2</sub>, was collected on No. 42 filter paper and washed with 100 ml of .1% NH<sub>4</sub>OH. The filtrate and wash solutions were analyzed for both plutonium and iron. The filter cake was leached with a 1 N HNO<sub>3</sub>, 0.2 N H<sub>2</sub>SO<sub>4</sub> solution and then dissolved completely in a H<sub>2</sub>O<sub>2</sub> -HNO<sub>3</sub> solution.

The leach solution was analyzed spectrophotometrically for the plutonium oxidation state if the plutonium concentration was sufficiently high (> .02 gpl Pu VI) and then combined with the dissolving solution. The plutonium and iron concentrations were determined in the combined solution.

Effect of Acetate Concentration on the Carrying of PuO<sub>2</sub><sup>++</sup> by Ferric Hydroxide

Table I summarizes the dependence of PuO<sub>2</sub><sup>++</sup> carrying by ferric hydroxide on acetate concentration. Experiments 1 and 4 were done in triplicate, the other experiments in duplicate. The arithmetical mean and the average deviation of the arithmetical mean are given in the "Precipitate" column. The results show that as the acetate concentration is increased, the carrying of PuO<sub>2</sub><sup>++</sup> diminishes until a minimum value of 2.1% is reached at a 6 M NH<sub>4</sub>Ac concentration. The solubility of the iron precipitate increases with increasing acetate concentration.





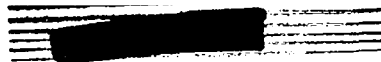


Table I

EFFECT OF ACETATE CONCENTRATION ON THE  
CARRYING OF PuO<sub>2</sub><sup>++</sup> BY FERRIC HYDROXIDE

Initial Conditions . . . . Pu IV      0.2 gpl  
                                  Fe III      3.0 gpl (Expt's 1-3)  
    5.6 gpl (Expt's 4-6)  
                                  HNO<sub>3</sub>      0.1 N

Oxidation . . . . . 0.05 M KMnO<sub>4</sub>, room temperature, 2 hours

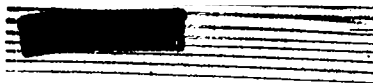
Precipitation . . . . . NH<sub>4</sub>Ac added as indicated in table, a  
    calculated amount of NH<sub>4</sub>OH or HNO<sub>3</sub> added to make pH 5.3.  
    Solution heated for 1 - 2 hours at 75°C after acetate addition.

Experiment No.	NH <sub>4</sub> Ac Conc. M.	Percent of Fe and Pu in Precipitate <sup>(1)</sup>		Oxidation State of Plutonium carried by Precipitate <sup>(2)</sup>
		Fe - %	Pu - %	
1	0	99.8 (±0.0)	99.9 (±0.0)	Pu VI
2	0.014	100.0 (±0.1)	99.7 (±0.1)	Pu VI
3	0.14	100.0 (±0.2)	79.4 (±0.4)	Pu VI
4	1.86	99.2 (±0.1)	3.5 (±0.6)	---
5	4.0	94.3 (±0.2)	4.0 (±1.0)	---
6	6.0	95.0 (±0.1)	2.1 (±0.2)	---

(1) The percents listed in this and all subsequent tables are the percent of the initial plutonium or iron carried by the precipitate.

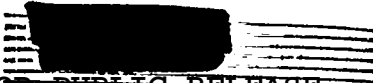
(2) Oxidation states were determined in the leach solutions.



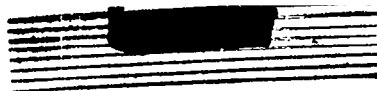


Effect of Iron Concentration on the Carrying of PuO<sub>2</sub><sup>++</sup> by Ferric Hydroxide

In the plant byproducts from which Pu might be recovered, the plutonium concentration will be fairly constant, 0.1 to 0.2 gpl. The iron concentrations, however, will vary considerably (1 gpl to 25 gpl). It is, therefore, desirable to know the extent to which the initial iron concentration affects the carrying of PuO<sub>2</sub><sup>++</sup>. Table II shows that in the iron concentration range .279 gpl (.005 M) to 5.59 gpl (.1 M), no significant difference is noted in the carrying of PuO<sub>2</sub><sup>++</sup>.

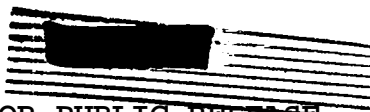






Effect of  $UO_2^{++}$  on the Carrying of  $PuO_2^{++}$  by  $Fe(OH)_3$

In CN-2449, the authors describe the precipitation of colloidal ferric hydroxide with ammonium acetate in the presence of  $PuO_2^{++}$  and  $UO_2^{++}$ . Only 2% of the plutonium was carried by the precipitate. Their data suggest that  $UO_2^{++}$  might serve as a holdback for  $PuO_2^{++}$ . The experiments tabulated in Table III were done in an effort to duplicate the results of CN-2449 and determine the holdback effect of  $UO_2^{++}$  for tracer and macro concentrations of plutonium. It will be noted that for tracer concentrations of plutonium (Experiments 1 and 2),  $UO_2^{++}$  has a marked effect on the carrying of  $PuO_2^{++}$ . For macro concentrations of plutonium, however, the holdback effect of  $UO_2^{++}$  is insignificant. Experiments 1 and 2 were done in duplicate; experiments 3 and 4 in triplicate.





### III. Discussion:

Although the basic acetate precipitation of iron affords a gross separation of iron from plutonium, it has the following disadvantages:

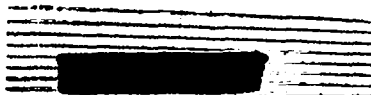
1. A minimum of three precipitations and two dissolvings would be required to achieve filtrates containing  $<10^{-5}$  gpl Pu.
2. The precipitate is difficult to filter. It filters at about one quarter the rate of a corresponding concentration of ferric hydroxide precipitate.

The use of oxidizing agents other than  $\text{KMnO}_4$  has been suggested as a possible means of improving the plutonium-iron separation. It is believed that such a study would be fruitless because of the following factors:

1. Table I shows that it is actually Pu VI which is carried. No evidence of lower oxidation states was observed in the leach solutions.
2.  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  (.075 M) with  $\text{Ag}^+$  catalyst (.004 M) was used as an oxidizing agent in some preliminary experiments but gave poorer results than .05 M  $\text{KMnO}_4$ .
3. Beaufait, Stevenson and Rollefson report in CN-2449 that  $\text{KMnO}_4$  is superior to  $\text{Na}_2\text{Cr}_2\text{O}_7$  as an oxidizing agent in the acetate process and recommend the use of  $\text{KMnO}_4$ .



In view of the above disadvantages, it does not seem likely that a practical application of the acetate process can be developed as part of a recovery flowsheet.



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