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DATE 2-25-44 [redacted]

SUBJECT Metathesis of Potassium Plutonium Fluoride with K_2CO_3

To I. Perlman

FROM B. A. Fries

[redacted]

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1. Perlman
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4/25/44

I. Perlman — Research

B. A. Fries — Research

[redacted]

Metathesis of Potassium Plutonium Fluoride with K_2CO_3

(Supplementary Report On Prob. Assignment No. 213-440C)

Introduction:

The potassium plutonium fluoride received from W. R. Cooper for subsequent Pu purification has heretofore been fumed with H_2SO_4 in order to put it into solution. This procedure has several disadvantages. First, from the health standpoint, the method is dangerous owing to spraying of the H_2SO_4. Second, Pu sulfate has a relatively low solubility and the presence of sulfate during the succeeding operations has caused some difficulty.

The Pu received from Batch 107 (Cooper) was metathesized with 10 M KOH at 95°. Although this metathesis was essentially 100% complete, large amounts of silica were present. This silica interfered with the subsequent peroxide precipitation.

Since K_2CO_3 is being successfully employed in the metathesis of the 30 gm La-1 gm Pu fluorides received from Room D without evidence of any considerable quantity of silica, an attempt was made to metathesize potassium plutonium fluoride with K_2CO_3.

Experiment:

Before metathesizing any Pu fluoride, several micro-scale experiments were performed in order to determine the solubility of Pu in several of the solutions employed.

In the first experiments the solubility of Pu in ~~[illegible]~~ K_2CO_3 solution was determined. In these experiments Pu chloride was added to K_2CO_3 solution so that no fluorine ion was present. The following results were obtained under the following conditions:

[redacted]

Table 1

Solubility of Pu in K_2CO_3 Solution

Expt.	K_2CO_3 M	Pu gm/l	Solubility mg/l	Remarks
1	0.4	0.7	3250	Light green ppt.
2	4.0	2.6	2,600*	No ppt. - all Pu added in solution

*Since all the Pu remained in solution, this figure represents a minimum solubility.

Perlman [redacted] 4-3-44

The carbonate precipitated in 0.4 % K_2CO_3 was light green in color, and had a solubility of 325 mg/l. Cunningham and Werner have described a carbonate ppt'n of solubility of 72 mg/liter in 1 % K_2CO_3 which was white.

The [illegible] solution was also determined. This is the solution from which $Pu(III)_4$ is precipitated by mixing KI to the K_2CO_3 solution. In this experiment, Pu chloride was added to a solution 2% in K_2CO_3 [illegible]. The solubility in this solution was 22 mg/liter.

The main [illegible] was next attempted with a 5 mg sample of Pu. The Pu used was relatively pure, being even precipitated as the iodate, then fluoride, then converted to the nitrate. The Pu was precipitated with KF in the presence of 0.5 % K_2CO_3. A fine, crystalline, grayish-white precipitate was obtained. To this was added 20 cc of 5% K_2CO_3 (about 25 cc/g which represents the minimum amount of K_2CO_3 needed to dissolve PuF_3). On adding the K_2CO_3 the precipitate turned to a bright green. The solution was then heated at 90° for 30 minutes. After the first several minutes the bright green precipitate turned a yellowish brown and as the heating continued, became more tan. After 30 minutes, the tube was centrifuged. The supernatant was a bright green color. The precipitate consisted of 2 zones; a lower, large, brown precipitate; and an upper, small, light green precipitate.

Another 130 cc of 4% K_2CO_3 was added and the above treatment repeated, this time the supernatant was colorless and no change was observed in the precipitate. A third 130 cc portion of 4% K_2CO_3 was added and the same treatment repeated with the same results. At this point, the precipitate was dissolved with HNO_3 to give a light amber colored solution with a small amount of residue. The precipitate was a carbonate since CO_2 was evolved as long as solid was present.

The Pu extracted by the K_2CO_3 treatments were as follows:

1.	1st K_2CO_3 treatment	1.7 mg
2.	2nd " "	0.05 mg
3.	3rd " "	0.03 mg
4.	HNO_3 solution of residue	3.2 mg

Conclusions:

It is obvious that these results indicate very unsatisfactory results. The solubility of Pu in the first K_2CO_3 extraction was quite high, 13 gm/liter, but the other K_2CO_3 extractions failed to take out Pu. The color of the residue - dark brown - was quite unusual. However, a small part of the residue was light green.

It also seems difficult to explain these poor results on the basis of impurities in the original Pu.

From the results of this experiment, it would not seem advisable to attempt to metathesize Pu fluoride with K_2CO_3.

DeF/dee

[redacted]
Bernard S. Fries