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MUC-GTS-37

DATE 2-23-43

SUBJECT Wet Flouride Separation Method

TO C. M. Cooper

FROM J. E. Willard

COPY NO. [redacted]

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FINAL DETERMINATION
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BY A E Barber DATE 2-4-82

JE Savely 3-19-03
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Metallurgical Laboratory

MUC-GTS No. 6

February 23, 1943

Mr. C. M. Cooper Metallurgical

J. E. Willard Metallurgical

INV. 9-47

In accordance with my memo to you of February 9th we have been conducting tests on the corrosion, metal coating, and lanthanum fluoride dissolving problems connected with the wet fluoride separation method. Our conclusions to date are summarized below.

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1. Possibility of dissolving LaF_3 in Zirconium solutions and concentrating the 94 by an oxidation-reduction cycle

It has been demonstrated that large quantities of fluoride can be readily dissolved in acid solutions of zirconium at room temperature. It has also been shown, by microexperiments that plutonous fluoride is readily soluble in such solutions.

Quantitative oxidation of tracer amounts of plutonium in zirconium solutions of lanthanum fluoride may be obtained with peroxydisulfate and silver (30 minutes at room temperature) or with dichromate (4 hrs. at 98°). The lanthanum can be quantitatively precipitated away from the oxidized plutonium in such solutions and it is believed that the plutonium can then be satisfactorily reduced (with SO_2) and recovered by precipitation with a tenth, or less, of the original amount of fluoride. The individual steps in this cycle are discussed in more detail below.

<u>A. Dissolving LaF_3 in zirconium solution.</u> A solution 3 N in HNO_3 and containing 50 mg. Zr per ml. (approximately 15% in $ZrO(NO_3)_2 \cdot 2H_2O$) was found satisfactory to readily dissolve LaF_3 precipitates. If the zirconium concentration is too high or the acidity too low some of the zirconium may precipitate on subsequent addition of HF. Forty ml. of this solution (2 g of Zr) readily dissolves, at room temperature, a LaF_3 precipitate containing 1 gm. of lanthanum which has been washed with 0.5 N HF. It may be possible to use less of the solution. With the quantities given, the weight ratio $\frac{Zr}{La} = 2$ and the molar ratio $\frac{F}{Zr} = 1.0 -- 1.5$.

<u>B. Oxidation of 94 in the Zirconium Solution by Dichromate.</u> The rate of oxidation of 94 in the solution formed by dissolving the LaF_3 with zirconium is slower than the oxidation in the absence of zirconium and fluoride under otherwise identical conditions. High temperatures are necessary for rapid oxidation. At these elevated temperatures high acidities are necessary to prevent the conversion of zirconium to a fluoride - insoluble form which, if formed, produces an undesirably large bulk of precipitate. The high acidities in turn lower the rate of oxidation, so that the determination of the optimum conditions with respect to time, corrosion, temperature, zirconium precipitation and 94 oxidation involves the correlation of a number of interrelated variables.

Conditions under which we have found 94 can be quantitatively oxidized and separated from lanthanum by means of HF without precipitation of the

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zirconium are the following:

Total final volume for 1 gm La: 200 ml.
HNO_3 concentration : 4 N (~ 25%)
$K_2Cr_2O_7$ concentration : 0.1 N (~ 0.5%)
Temperature : 98°
Time of heating : 4 hours

It is possible that less drastic conditions might be found.

C. Oxidation of 94 in the zirconium solution by Peroxydisulfate and Silver. Peroxydisulfate catalyzed by silver appears to be a much more satisfactory oxidant than dichromate, since the oxidation goes more rapidly at room temperature.

Satisfactory conditions are the following:

Total final volume for 1 gm La : 200 ml.
HNO_3 concentration : 1 N
Ag^+ concentration : 1 mg/ml (~ 0.15% $AgNO_3$)
$S_2O_8^{=}$ concentration : 0.1 M (~ 2.5% $Na_2S_2O_8$ or $K_2S_2O_8$)
Temperature : 25°, (Room temperature)
Time : 0.5 hour

It is probable that the silver and peroxydisulfate concentrations can be reduced, though this may increase the time necessary. It is also possible that the volume can be reduced. When $AgNO_3$ is added to the $ZrO(NO_3)_2$ solution a white precipitate (presumably AgCl) is formed; this does not, however, interfere with the oxidation process. Three brands of zirconyl nitrate gave a positive test for chloride with silver ion.

D. Separation of Lanthanum from the Oxidized 94. By making the oxidized solutions 1 N in HF, the lanthanum can be precipitated leaving the 94 quantitatively in solution.

E. Recovery of 94 from the Solutions. As the next step the proposed procedure calls for the reduction of the 94 and its coprecipitation with LaF_3, which because of the presence of HF will be a "preformed" precipitate. This step has not been studied in detail, but preliminary experiments indicate that with either oxidant the 94 can be readily reduced with excess SO_2 and carried by a preformed LaF_3 precipitate with a reduction of the amount of lanthanum carrier by at least a factor of 10.

2. Effect of steel corrosion on the recovery of 94 by the wet fluoride method

The following conclusions are indicated by the tests which have been completed.

1. The presence of corroding steel in the oxidized solution (Wet B flow sheet conditions) leads to reduction of tracer amounts of 94 even in the presence of nearly the original concentration of unreduced dichromate at room temperature. The amount of reduction increases with increasing amount of corrosion.

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B. 25-12 stainless steel (present with a ratio of surface area to solution volume of about three times that which will be encountered in the tanks at site X) shows little or no corrosion and no reduction of 94 in 23 hours at room temperature. At 63° C for 19 hours the same sample showed 5% or less reduction of the 94 which was present.

C. 18-8 stainless steel (cut from the centrifuge in the cyclotron lab) showed 12% reduction of 94 in 23 hours at room temperature with only partial reduction of the dichromate. At 63° C this steel appeared to completely reduce the dichromate in 19 hours or less and 85% of the 94 was reduced. In contrast to the 18-8 steel from the centrifuge 18-8 tube steel from the heating coils showed only 1% reduction of 94 in 60 hours at room temperature although at 100° C complete reduction of the dichromate and 85% reduction of the 94 occured in ½ of an hour.

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The tests which have thus far been made have utilized tracer amounts of 94^{238}. The weight of metal lost by corrosion in some of these tests is many times more than equivalent to the amount of 94 present. Tests are now being made to determine the effect of 94 concentration on the percentage of 94 reduced. It is hoped that a correlation may be made between amount of corrosion and amount of 94 reduced.

Some of the data which lead to the conclusions given above are tabulated below. All of the tests have been made using the concentrations of reagents specified in the Wet B process flow sheet and using 10 cc. of solution. All experiments were done in lusteroid except those marked* which were done in platinum dishes with the metal supported on a piece of non-conducting fluo-carbon resin (** not so supported). A ratio of metal surface area to volume three times as great or more than that proposed for the tanks at site X was used in all cases.

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Mr. C. M. Cooper

Metallurgical Laboratory

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February 23, 1943

Tests on the reduction of oxidized plutonium in $K_2Cr_2O_7$-HNO_3-HF-$UO_2(NO_3)_2 \cdot 6H_2O$ solutions as a result of standing in contact with steel

Sample	Temperature °C	Wt. loss of steel	Time of standing of oxidized solution + HF with the steel	% reduction of 94
Control (no steel present)	25°		3.5 Hr.	0
"	"		10	0
"	"		23	0
25-12 steel	"		3.5	0
"	"		10	0
"	"	.0002 g	23	0
"	63°	.0045	19	5**
"	"	.0045	19	0*
18-8 steel (from centrifuge)	25°		3.5	1
"	"		10	3.5
"	"	.0064	23	12
"	63°	.032	19	85*
18-8, Mo steel	25°		3.5	0
"	"		10	0
"	"	.0002	23	0
18-8 steel (tube steel from heating coils)	"	.0018	60	1.0*
"	"	.0011	60	0.9*
"	"	.0011	60	1.3*
"	"	.0016	60	1.1*
"	100°	.016	0.75	85*

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3. Effect of proposed coating metals on the recovery of 94 by the wet fluoride method

Tests made on the separation of 94 by the wet fluoride method from solutions which contain the proposed coating metals (53% Sn, 46% Cu, 1% Ni; 67% Sn, 32% Cu, 1% Ni; 99% Sn, 0.7% Ni, 0.1% Al; 97% Pb, 3% Sn; 100% Al) indicate that probably less than 10% loss of 94 will result from the presence of any of these metals or their ions during the chemical procedure. In drawing conclusions from a rapid series of tests of this nature it is impossible to state the results with greater precision than this 10% range. These tests were made using 94^{238} tracer and were carried out in lusteroid tubes with no steel present; it seems improbable that either the use of higher concentrations of 94 or the presence of steel would alter these conclusions.

Determinations of the distribution of fission activity made at the same time as the 94 determinations indicate that it is not greatly altered by the presence of the metals except in the case where aluminum is present. (The aluminum apparently interferes with the precipitation of $BaSO_4$ from the oxidized solution in consequence of which some of the 44 hr. La daughter of the barium appears in the product precipitate.)

Table 1 shows the results of three series of experiments on the five metals and alloys which were tested. Table 2 shows the c/m carried by the insoluble metastanic acid which was formed, in experiment 3, from those coatings which contain tin. For comparison the c/m (due to U) in control tests where no 94 was present are given. From these data it is clear that the possibility that a few per cent of the 94 is carried by the metastanic acid cannot be ruled out.

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TABLE 1

	94 YIELD Exp.#1	94 Yield Exp.#2	94 Yield Exp.#3	Soft γ in product precipitate Exp. 1 and 2	in product precipitate Exp. 1 and 2
53% Sn, 46% Cu, 1% Ni	84	120	90	1.2; 3.0	1.7; 2.1
67% Sn, 32% Cu, 1% Ni	92	100	94	1.5; 3.3	2.0; 2.3
99.3% Zn, 0.7% Ni, 0.1% Al	83	99	93	1.1; 1.6	1.9; 2.0
97% Pb, 3% Sn	108	98	100	2.3; 2.8	2.4; 2.0
100% Al	106	98	102	9.7; 8.6	2.5; 2.3

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TABLE 2

	94 Yield Exp. #1	94 Yield Exp. #2
Metastanic acid ppt. separated from oxidized solution containing 1200 c/m of 94.	108 c/m	108 c/m
Metastanic acid ppt. separated from identical uranyl solution which contained no 94.	75	58

c/c to Mr. W. Q. Smith
Mr. G. T. Seaborg

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