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PRECIPITATION OF PLUTONIUM AND URANIUM
FROM OFF-STANDARD AQUEOUS WASTES

The present concept for reworking off-standard aqueous wastes, around which Redox Production Plant No. 1 is designed, consists of routing economically recoverable concentrated metal wastes back to IS column on an "as is" basis. No precipitation step is followed for separating the recoverable metals from the concentrated salt solution before preparing a rework feed. This document describes an alternate rework method in which uranium and plutonium are coprecipitated from off-standard wastes prior to IS feed preparation. The information contained herein is intended for record purposes and possible consideration in Plant No. 2 chemistry. The basic chemical data were procured by the Chemical Research Section.

I. SUMMARY

Studies of the precipitation method were made by the Chemical Research Section and reported in their monthly reports for September and October, HW-14743 and HW-15074 respectively.

The reported data indicate that both uranium and plutonium can be precipitated by controlled neutralization of off-standard aqueous wastes with less than 0.2% net loss (based on feed metal); when the original waste solution contains 1% net loss equivalent of uranium, and 10% net loss equivalent of plutonium. The trends of the data suggest that waste stream plutonium losses in excess of 10% should be recovered by the precipitation technique to within the 0.2% net loss bracket by increasing the accompanying uranium content in the waste stream to more than the 1% net loss equivalent.

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The resultant daily volume of neutralized concentrated Redox waste solution (2.5 ton basis) would require ca. 20 hours of centrifugation to separate the precipitates. This estimate is based on residence time studies made by the Chemical Research Section in a clinical type centrifuge, and does not allow for any scale-up factors incurred by going to plant sized equipment. Centrifugation studies simulating plant scale in 321 Building equipment are not planned for the present.

A minimum of two additional equipment pieces would have to be installed in the waste treatment section of Plant No. 1 in order to accommodate the precipitation method of rework handling. These would include an additional waste neutralizer in order to effect proper precipitation and centrifugation of an off-standard waste without holding up the main waste stream, and one (or more) 40-inch solid bowl centrifuges. Dissolution of the precipitate for IS feed preparation could be accomplished in the existing rework adjustment tank TK-167.

A process flowsheet for the precipitation method of reworking off-standard aqueous Redox wastes is shown in Figure I. Precipitation data are given in Table I.

II. DISCUSSION

A. Precipitation Technique and Metal Recovery - Chemical Research Section data indicate that uranium and plutonium may be precipitated successfully (0.2% net loss) from a waste solution comparable to that given in HDC-1333 (Production Plant No. 1 Material Balance Flowsheet) with ANH at 2.0 M. The waste solution as received from the salt waste concentrator is agitated, preferably at room temperature, with 50% NaOH in a 5 : 3 volume ratio (waste: caustic). After precipitation the slurry is heated to 90°C. for 1 hour in order to coagulate $\text{Cr}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ which interferes with plutonium carry when allowed to remain in the colloidal form. The slurry is then centrifuged for separation of the precipitated metals. Data from several Chemical Research Section studies are given in Table I. It will be noted that the majority of the tests were conducted on waste solutions containing net loss equivalents of 1% and 10% of uranium and plutonium respectively. The data indicate (Tests No. 32, 35, 37 and 54) that improved plutonium recovery may be expected when the uranium content of the waste is increased above 1% net loss.

B. Centrifugation Cycle - The daily volume of a neutralized waste solution comparable to that given in HDC-1333, adjusted to 2.0 M ANH, will be about 7,500 gallons. Assuming a 45 gallon average bowl slurry capacity and a 7 minute hold up, based on clinical type centrifuge tests, the centrifugation cycle would consume ca. 20 hours for separation alone. If the waste solution contains 0.4 M uranium (equivalent to 7.5% net loss), the total cake volume will be about 450 gallons. Assuming 30 gallons as an average cake size, and 15 min. for washing the centrifuge bowl, the washing

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cycles will require 3-4 hours in addition to the 20 hours used for centrifuging. The techniques required for successful centrifugation in a solid bowl would have to be explored further in plant scale equipment in order to determine any scale-up factors involved.

C. Equipment Requirements - Additional equipment required in order to adapt Production Plant No. 1 waste treatment facilities to this alternate method of waste rework would include one or more 40-inch centrifuges (a deep bowl may be required, depending on scale-up factors), and a precipitation vessel. The precipitator is advocated since it appears desirable to cool the concentrated wastes before adding the caustic solution. Further, since the precipitation step requires digestion at 90°C. for 1 hour when the uranium content is low, this treatment should be done in a separate vessel in order to maintain continuity of plant operation. The precipitator should be equipped for heating and cooling, agitation, chemical addition, and sampling in addition to the standard control instrumentation. Dissolution of the centrifuge cake could be accomplished in the rework adjustment tank (No. 107) which now exists in the design scope.

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TABLE I

RECOVERY OF PLUTONIUM AND URANIUM BY PRECIPITATION FROM OFF-STANDARD AQUEOUS
REDOX WASTES - DATA FROM HW-15074

Test No.	M Cr ³⁺	M Cr ₂ O ₇ ²⁻	% U	% Pu	% Pu Recovered	% Pu Supernate	Material Balance %	Net Loss %	Remarks
39	0.011	0.028	1	9.6	71.1	24.6	95.7	2.4	No heat before or after precipitation.
31	0.02	0.023	1	9.6	60.7	35.8	96.5	2.5	Same as above.
35	0.02	0.023	10	9.6	93.3	4.5	97.8	0.4	Same as above.
32	0.02	0.023	25	9.6	99.3	0.9	100.2	0.08	Same as above.
33	0.02	0.023	1	9.6	61.4	37.1	98.5	2.6	Heated before precipitation.
37	0.02	0.023	10	9.6	96.1	2.0	98.1	0.2	Same as above.
48	0.011	0.028	1	9.8	99.6	1.3	100.9	0.12	Heated before and after precipitation.
55	0.011	0.028	1	9.8	98.3	1.1	99.4	0.11	Same as above.
53	0.02	0.023	1	9.8	95.6	2.2	97.8	0.21	Same as above.
54	0.02	0.023	5	9.8	95.5	0.7	96.2	0.07	Same as above.
49	0.011	0.028	1	9.8	99.7	2.8	102.5	0.27	Heated after precipitation.
47	0.067	---	1	0	<u>% U Recovered</u> 77.9	<u>% U Supernate</u> 19.5	97.4	0.2	Same as above.
51	0.067	---	1	0	83.1	14.6	97.7	0.15	Same as above.

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Constituente	1	2	3	4	5	6	7
Al(NO ₃) ₃ ·9H ₂ O	2.0	---	1.25	---	1.34	---	---
NaNO ₃	0.67	---	0.8	---	0.86	---	---
HNO ₃	0.23	---	---	---	---	15	---
Na ₂ Cr ₂ O ₇ ·2H ₂ O	0.028	---	0.018	---	0.02	---	---
Cr(NO ₃) ₃ ·9H ₂ O	0.011	---	0.007	0.1	---	---	0.1
Fe ₂ (SO ₄) ₃ (NH ₄) ₂ SO ₄ ·24H ₂ O	0.011	---	0.007	0.1	---	---	0.1
Fe(NO ₃) ₃ ·9H ₂ O	0.011	---	0.007	0.1	---	---	0.1
(NH ₄) ₂ SO ₄	0.021	---	---	---	---	---	---
NaOH	---	19	6.7	---	7.2	---	---
UHM	0.04	---	0.025	0.375	---	---	0.325
Volume (Gal.)	4700	2800	7500	500	7000	78	578