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Undated

RECOVERY OF URANIUM AND PLUTONIUM FROM REDOX
OFF-STANDARD AQUEOUS WASTE STREAMS

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I. INTRODUCTION AND OBJECTIVES

In the operation of countercurrent extraction columns, as in the Redox process, it is possible, and probable, that from unexpected behaviour of a column, operator error, colloid~~al~~ formation, etc., there will result from time to time excessive losses of uranium and plutonium in the overall process. These losses will naturally ~~accumulate~~ accumulate in the waste streams, particularly in the aqueous waste streams.

If the loss is excessively high, and such lost material can be recovered by some additional method, then if economical and within reason, the recovered materials can be returned to a ISF column for further processing.

The objective of this work has been to develop such a method to recover uranium and plutonium from such off-standard waste streams in a form whereby the uranium and plutonium can be returned to the process line and subsequently purified and separated.

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II. SUMMARY AND CONCLUSIONS

~~The concentration of uranium and plutonium in the waste streams is between 0.1 and 0.2 percent.~~

To recover uranium and plutonium with ~~a~~ 0.1 to 0.2 % net loss from ~~the waste streams~~ concentrated Redox off-standard aqueous waste streams the following procedure is recommended:

1. Heat the solution, in the presence of $\text{Cr}_2\text{O}_7^{=}$, to about 80-85°C. for 10-15 minutes.
2. Add the waste solution to 50% NaOH solution (19.1M) in a reverse strike in a 5:3 ^{VOLUME} ratio (Waste; NaOH).
3. Heat one (1) hour at 90°C. to coagulate $\text{Cr}_2\text{O}_3 \cdot \text{H}_2\text{O}$.
4. Centrifuge and wash precipitate with 0.01 M NaOH solution.

Additional factors which aid in the recovery process are (1) the addition of uranium to greater than 10% in the waste solution, or (2) addition of sufficient persulfate

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ion, and silver catalyst, in an acid solution, with heating, to oxidize Cr(III) to Cr(VI) ^{and, thus,} to prevent interference with plutonium and uranium precipitation. The use of ozone, with silver catalyst, and heat, ^{to oxidize Cr(III) and Pu(IV) to higher valence} prior to precipitation, has been shown to aid materially in the recovery of uranium and plutonium from the non-concentrated waste solution, and it is expected that such treatment likewise would be applicable to the concentrated wastes.

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III. EXPERIMENTAL

The experiments were carried out using simulated waste solutions based on flow-sheets as indicated below. The method of combining reagents is described for any one set of experiments, and solutions were vigorously stirred with either platinum wire or glass stirrers. Centrifugations were performed in laboratory clinical centrifuges and were on a 15 or 50 ml. scale. For material balance considerations the supernate solution obtained, and the dissolved precipitate solutions, were diluted to a known volume in volumetric flasks.

The standard hydroxide- LaF_3 method of analysis for plutonium was used except where so stated.

The simulated waste solutions were made up from data obtained from Redox flow sheets.

The compositions of these solutions are presented in the tables below.

TABLE I.

Composition of pooled waste streams

Basis: ORNL-1 Flow-Sheet (Modified) (HW-13320)

Total Volume of pooled waste streams: 22,175 l./ 1.5 T. U/ Day.

Substance	Kg./22,175 l.	Molar Concentration
$\text{Al}(\text{NO}_3)_3 \cdot 9 \text{H}_2\text{O}$	8,700	1.05
HNO_3	339	0.24
NaNO_3	371	0.23
$\text{Cr}(\text{NO}_3)_3 \cdot 9 \text{H}_2\text{O}$	313	0.035
$\text{Fe}(\text{NO}_3)_3 \cdot 9 \text{H}_2\text{O}$	155	0.017
NH_4HSO_4	88	0.035
$\text{U}(\text{VI})^4$	19(0.6%)*	0.0017
$\text{Pu}(\text{IV})$	0.0024 (0.8%)*	4.5×10^{-7}

* Normal percentage loss to waste.

TABLE ~~IX~~ ^{II}

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Composition of concentrated pooled waste streams

Basis: Flow-sheet HDC-1333

Volume of concentrated pooled waste streams: 17,900 l. (after JD)/ 2.5 short T. U/day

Substance	Kg./17800 l.	Molar Concentration
$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	13,360	2.0
NaNO_3	1,090	0.67
HNO_3	255	0.23
$\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$	156	0.028
$\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	76	0.011
$\text{Fe}(\text{NH}_4\text{SO}_4)_3$	151	0.021
$\text{Fe}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	67	0.011
$\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	35.4	0.004
$\text{Pu}(\text{VI})$	0.0056 (0.885 loss)	1.3×10^{-6}

(U- 38 lbs.- 0.76% loss)

IV. RESULTS

NORMAL POOLED WASTE

Initial studies were made on simulated pooled wastes (SPW) of the composition given in Table I, except the uranium concentration was increased ten fold and the plutonium was omitted.

The problem has been to separate uranium and plutonium from aluminum and chromium in both the normal and concentrated pooled wastes. The presence of small amounts of these ions would not be detrimental to column operation, but large amounts of either ion would bulk ^{up} the precipitate ^{up} to such a volume as to make centrifuging difficult. It has been shown (HW-13667) that $\text{Cr}(\text{III})$ interferes with the recovery of uranium and plutonium from solutions of similar composition. Qualitative tests indicated that all of the ~~chromium~~ ^{50%} $\text{Cr}(\text{III})$ in a SPW-1 solution was not being precipitated by the addition of/caustic. Hence, it was decided to use ammonium persulfate to oxidize the $\text{Cr}(\text{III})$ to $\text{Cr}(\text{VI})$ ^{to eliminate its interference} and quantitatively determine the amount of uranium carried down with the final precipitate. Iron was left in the solution to act as a scavenger when the solution was made basic. Table III gives the results of these experiments.

Table III

When $\text{Cr}(\text{III})$ and $\text{Fe}(\text{III})$ are precipitated together they tend to form a colloidal

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URANIUM RECOVERY AND CHROMIUM DISTRIBUTION IN THE COURSE OF

SODIUM DIURANATE PRECIPITATION FROM SPW-1

Exp't No.	SPW-1 (ml)	50% NaOH (ml)	Pretreatment	Precipitation Conditions	% Uranium		% (Cr(III) / Cr(VI))	
					Precipitate	Supernate	Precipitate	Supernate
1C	25	15	None	0.5 g (NH ₄) ₂ S ₂ O ₈ added to mixed solutions. Stirred 1/2 hr. Centrifuged 1 hr.	85.1	14.8	(9)	(54)
12	10	10	0.5 g (NH ₄) ₂ S ₂ O ₈ at 80°C. for 10 min.	Stirred 1/2 hr. Centrifuged 2 1/2 hrs.	96.4	Trace	(18.5)	(67.1)
22	10	10	0.5 g (NH ₄) ₂ S ₂ O ₈ and 0.05 M Ag ⁺ at 80°C. for 10 min.	Stirred 1/2 hr. Centrifuged 2 hrs.	(134)	Trace	-	100
18	10	10	Ca. 2% ozone and 0.05 M Ag ⁺ at 80°C. for 6 hrs.	Stirred 1/2 hr. Centrifuged 3 hrs.	(144)	Trace	13.5	96.5
20	10	10	100 mg NH ₂ OH·HCl and 3.5 mg La ⁺⁺⁺ at room temperature for 15 min.	Stirred 1/2 hr. Centrifuged 2 hrs.	17.1	82.9	56.3	54.7

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suspension which is not readily filtered from the solution. This possibly has been the cause of previous failures to recover uranium and plutonium from ~~waste~~ solutions containing ~~these two ions~~ ^{chromium and iron}. From the data in Table III it is apparent that oxidation of the Cr(III) to Cr(VI) materially aids in the recovery of uranium. Analytical difficulties in analyzing these solutions has not permitted accurate analyses to be obtained, but from the trends indicated it is believed that the uranium is completely precipitated when the Cr is oxidized. The presence of Cr in the precipitate in certain cases may be partially attributed to incomplete washing of the ~~Cr~~ from the solid precipitate.

Ozone also was used ^{TD} as an oxidizing ^e agent for Cr(III) to Cr(VI) and ^{TD} would also oxidize any lower valent Pu to Pu(VI). The presence of Pu in the hexavalent state is believed to be beneficial in the carrying of Pu on sodium diuranate. Experiment 18 which was run in parallel with a plutonium experiment indicates that here again removal of the Cr interference by oxidization permits complete recovery of the uranium. The use of hydroxylamine hydrochloride has been reported (KAPL 193) to aid in the recovery of plutonium from waste streams. However, uranium was not of interest in that work. To determine the effects of $\text{NH}_2\text{OH}\cdot\text{HCl}$ on uranium recovery Experiment 20 was carried out. From the data in Table III it is apparent that the presence of $\text{NH}_2\text{OH}\cdot\text{HCl}$ adversely affects the recovery of ^{uranium} ~~plutonium~~. This adverse affect is attributed to the formation of a ^{soluble} ~~uranium complex which is soluble~~. The presence of unoxidized Cr(III) in the solution has ^{also} contributed to the low ^{uranium recovery} ~~value~~ in recovery value, but the value is much lower than other experiments where $\text{NH}_2\text{OH}\cdot\text{HCl}$ was not present.

Using the same solution, SPW-1, a series of experiments ^{were carried out} with Pu(IV) being added to the solution to give a Pu concentration of about 0.8 g/l., i.e., 7.5 times the the flow-sheet loss, or a 6% Pu loss. In a few cases the plutonium concentration was increased to higher concentrations to determine if good recovery could be effected if a major loss occurred during processing. The data from these experiments are presented in Table IV.

Berkeley analyses of the precipitates from the ozone ^{and persulfate} experiments indicated the presence

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BY 7/19/52 TVPLUTONIUM RECOVERY ~~FROM~~ SODIUM DIURANATE PRECIPITATION FROM SPW-1

Ten ml SPW-1 used in each experiment.

Exp't No.	Plutonium Spike % Loss	Pretreatment	50% NaOH (ml)	Precipitation Conditions	% Plutonium			% Net Loss
					Precipitate	Supernate	Total	
8	6	None	7	Stirred 1/2 hr. Centri- fuged 1/2 hr.	65.2	36.7	102	2.2
9	6	None	10	Stirred 1/2 hr. Centri- fuged 1/2 hr.	70.1	17.2	87.3	1.0
10	6	None	10	0.7 g (NH ₄) ₂ S ₂ O ₈ added to mixed solutions. Stirred 1/2 hr. Centri- fuged 2 1/2 hrs. Precipitate in supernate on standing 24 hrs.	76.4	25.6	102	1.5
11	6	0.05 M Cr ₂ O ₇ ⁼ at 80°C. for 10 min. then 0.5 g (NH ₄) ₂ S ₂ O ₈ added.	10	Stirred 1/2 hr. at 90°C. Centrifuged 2 1/2 hrs. Precipitate in supernate on standing 24 hrs.	79.4	15.4	94.8	0.9
14	6	0.5 g (NH ₄) ₂ S ₂ O ₈ and 0.05 M Ag ⁺ at 80°C. for 10 min. in acid solution.	10	Stirred 1/2 hr. Centri- fuged 3 hrs.	94.5	5.3	99.8	0.32
21	15	Same as (14).	10	Stirred 1/2 hr. Centrifuged 2 hrs.	90.9	4.2	95.1	0.63
23	100	0.4 g (NH ₄) ₂ S ₂ O ₈ and 0.05 M Ag ⁺ at 80°C. for 10 min. in acid solution.	5	Same as (21) .	99.1	0.89	99.99	0.89
24	7 (Pu(VI))	Same as (23)	5	Same as (21) .	95.7	4.2	99.9	0.42

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TABLE IV (concluded)

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Exp't No.	Plutonium Spike % Loss	Pretreatment	50% NaOH (ml)	Precipitation Conditions	% Plutonium		Total	Loss
					Precipitate	Supernate		
13	6	Ca. 2% ozone and 0.05 M Ag ⁺ at 80°C. for 6 hrs. in acid solution.	10	Stirred 1/2 hr. Centrifuged 3 hrs.	95.1	3.9	99.0	0.023
17	15	Same as (13).	10	Same as (13).	97.9	0.8	98.7	0.12
15	6	50 mg NH ₄ OH.HCl and 1 mg La ⁺⁺⁺ at room temperature for 15 min.	10	Stirred 1/2 hr. Centrifuged 3 hrs.	91.9	6.1	98.0	0.37

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of 9.7, 1.1, and 9.2% Pu(IV) in experiments 21, 23, and 17 respectively. In an ~~attempt~~^{alkaline} attempt to recover the remainder of the plutonium from certain of the supernates 40 mg. of ferric nitrate nonahydrate were added to precipitate ferric hydroxide. Analyses of the resultant precipitates indicated ~~it~~ carrying of but 19.7, 29.4, 26.4, and 47.5 % of the plutonium remaining in the supernate after the basic precipitation step of experiments 11, 13, 14, and 15 respectively. The data from experiments 23 and ~~24~~ 24 indicate that a ^{2:1 ratio} ~~ratio~~ of waste to ^{50%} caustic is sufficient to precipitate the requisite materials for carrying of the uranium and plutonium. 5.3

CONCENTRATED POOLED WASTE

Upon the basis that Redox aqueous wastes would be concentrated before neutralization, and subsequent disposal, simulated concentrated pooled wastes (CPW) of the composition given in Table II were made up, ^{less} ~~lower~~ uranium, chromium and plutonium. These latter ions were added as desired to give various concentrations as stated below.

DETERMINATION OF OPTIMUM CAUSTIC VOLUME

A number of experiments were carried out to determine the amount of 50% NaOH required to neutralize a given volume of concentrated pooled waste, CPW (normal composition, less plutonium) to greater than pH 10 (above pH 10 aluminum remains in solution either as the AlO_2^- ion or AlO_3^- ion). It was desired to precipitate the uranium as ~~the~~ diuranate, with a minimum contamination of aluminum, so as to give an adequate concentration of uranium when the precipitate was dissolved in nitric acid in preparation of a ISF feed. Any ions which would be expected to precipitate with the uranium, such as iron, chromium, and traces of aluminum, should cause no trouble in the operation of a Redox column. However, the Cr(III), as shown above, might be expected to interfere with the recovery of uranium by forming a colloidal suspension with the hydrated ferric oxide which would result when the solution was made basic.

The experiments were carried out by reacting the reagents in a reverse strike in order to prevent localized precipitation of aluminum hydroxide which can be difficult

to redissolve, even in the presence of a large excess of caustic. The volume of 50% NaOH required to maintain the Al(III) in solution was determined by adding 5 ml portions of CPW to varying volumes of caustic. These data are presented in Table V.

Table V

VOLUME PRECIPITATE VERSUS VOLUME 50% NaOH

Volume 50% NaOH, ml	2.25	2.50	2.75	3.00	4.00
Volume Ppt., ml	0.58	0.25	0.27	0.24	0.25

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The 50% by volume addition of caustic found adequate to solubilize the Al(III) may be compared with a stoichiometric requirement of 43% assuming conversion to AlO_2^- and of 65% assuming $AlO_3^=$. In the following work a 60% by volume addition of 50% NaOH was used in all cases to provide an excess of caustic, including that required to precipitate sodium diuranate.

STUDY OF REVERSE STRIKE AND SIMULTANEOUS ADDITION METHODS

A series of CPW solutions, with a normal chromium concentration, and ~~containing~~ an uranium concentrations equivalent to 0, 5, 10, 20, and 50% loss to waste, were prepared. Aliquots of each solution were added in a reverse strike to a volume of 50% NaOH equal to 60% of the CPW volume. Equal aliquots of the same solutions were mixed simultaneously* with the same volume of 50% NaOH. The resultant slurries were

* When two reagents are added simultaneously to a reaction vessel containing a heel from the preceding centrifugate, the reaction takes place immediately upon simultaneous delivery. A precipitate forms which leaves the sphere of reaction, thus permitting further droplets to react as they are added. This method is called simultaneous addition and has the advantage of preventing local excesses of either of the two reagents.

digested for less than one minute and then centrifuged for 20 minutes. The reactions were carried out at the temperature of reaction. The volume of precipitate per volume of CPW was measured at the various concentrations of uranium. The results, given in Table VI, show that the method of reaction, i.e., by reverse strike or simultaneous addition, has very little effect on the nature of the precipitate with respect to packing. Since a reverse strike is simpler to perform in the laboratory this method

has been used in subsequent experiments.

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Table VI.

VOLUME PRECIPITATE VERSUS % U LOSS IN CPW

% U Loss in CPW	$V_{\text{ppt}} / V_{\text{CPW}}$	
	Reverse Strike	Simultaneous Addition
0	0.048	0.048
5	0.064	0.064
10	0.079	0.091
20	0.134	0.126
50	0.230	0.244

COMPACTION OF PRECIPITATE ON CENTRIFUGATION

A study was made of the rate of packing of a diuranate precipitate with time of centrifugation. A CPW solution with a uranium concentration equivalent to 1% loss, and normal chromium content, was reacted in a reverse strike with 50% NaOH. The slurry was stirred vigorously during the reaction and allowed to digest for one minute. The centrifugation was carried out stepwise. The volume of precipitate per volume of CPW was measured as a function of centrifugation time. The results are tabulated in Table VII.

Table VII.

TIME OF CENTRIFUGATION vs. $V_{\text{ppt.}} / V_{\text{CPW}}$

Time (min)	$V_{\text{ppt.}} / V_{\text{CPW}}$
2	0.078
5	0.062
15	0.056
20	0.052
25	0.050
30	0.048
35	0.046
40	0.044

The precipitate packs rapidly at first but slows down to a small packing increment after 15 minutes. A more or less constant ~~in~~ value is obtained after 30 minutes. To avoid prolonged centrifugation times 10 minutes, or ^{to Account For} 80% of the maximum packing obtained in 30 minutes, has been used in subsequent experiments.

PER CENT NET URANIUM LOSS

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To avoid repetition normal conditions for subsequent experiments will be to :

- (1) The volume of 50% NaOH used will be equal to 60% of the CPW volume.
- (2) The CPW will be added to the 50% NaOH in a reverse strike.
- (3) Agitation will be maintained for one-half to one minute after completion of the addition of CPW.
- (4) After addition, the slurry will be digested for from one to two minutes, including the agitation time in (3).
- (5) The reaction will be carried out at the temperature of reaction.
- (6) The slurry will be centrifuged for ten minutes at full speed, about 700 G's, in a clinical centrifuge.

As a result of the work described above on normal pooled wastes wherein the chromium was shown to interfere with the recovery of uranium a series of experiments were carried out to find what range of concentration of chromium could be tolerated and still maintain less than 0.1 to 0.2 % net loss of uranium in a caustic precipitation process. /Solutions were prepared containing varying amounts of Cr(III) up to a maximum of 0.067 M. The total chromium in the solutions ~~was~~ maintained at 0.067 M by adding $\text{Cr}_2\text{O}_7^{2-}$ as necessary. The uranium concentrations in these solutions was likewise varied. The compositions of these solutions is given in Table VIII. The % net loss was determined as follows:

$$\% \text{ net loss} = \frac{\text{U in centrifugate}}{\text{U total in CPW}} \times \% \text{ U loss in CPW}$$

TABLE VIII
PER CENT NET LOSS OF URANIUM
TO CENTRIFUGATE

% U loss in CPW	Molarity Cr(III)	% Net U Loss to Centrifugate				
		0.0	0.01	0.02	0.04	0.067
1		0.041	0.086	0.146	0.168	0.246 (0.250)
5		0.037	0.052	0.052 (1.44)	0.094	0.105
10		0.031	0.037	0.041	0.045	0.104 (0.164)
25		0.016	0.029	0.036	0.037	0.037 (0.064)

Inspection of Table VIII shows increasing % net uranium loss with increasing Cr(III) concentration and decreasing % net uranium loss with increasing uranium concentration in CPW. The results in parenthesis are the results of a duplicate set of experiments to verify the unusually low losses ~~are~~ found in the first case. In effect ~~chromium~~ uranium in increasing concentrations apparently overcomes the colloidal effect of

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hydrated chromium oxide, which obviously is a factor in keeping the uranium in the supernate at lower uranium concentrations. At maximum Cr(III) concentration (0.067 M) the net loss would be less than 0.25% regardless of the uranium concentration.

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In view of possible changes in flow-sheet characteristics ~~etc.~~ etc., it was decided to dilute the CPW to determine if any appreciable change in the recovery would occur. Accordingly, a series of solutions were diluted two fold and the % net uranium loss determined. The results are tabulated in Table IX.

Table IX.
PER CENT NET LOSS OF URANIUM ON
TWO FOLD DILUTION OF CPW

% U loss in CPW	Cr(III)(M)	% Net Uranium Loss	
		without dilution	with two fold dilution
0.5	0.0	0.041	0.090
0.5	0.005	0.086	0.190
0.5	0.0336	0.250	0.195
12.5	0.005	0.029	0.045

Comparison of the data indicates that dilution definitely increases the % net uranium loss by a factor of about two at low Cr(III) concentrations.

THE EFFECT OF Fe(III) ON % NET URANIUM LOSS

The role of Fe(III) concentration in uranium recovery, or % net uranium loss, was investigated with respect to % U loss, Cr(III) concentration, and different source materials for Fe(III) ions. One set of experiments was carried out with solutions of the expected composition given in Table I, ~~expected composition~~ Another set was carried out with the Fe(III) source being entirely from $\text{Fe}(\text{NO}_3)_3 \cdot 9 \text{H}_2\text{O}$ (FNN). The Third set of experiments used solutions with the Fe(III) source being $\text{Fe}_2(\text{SO}_4)_3 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot \text{H}_2\text{O}$ (FeAS). The results of these experiments are tabulated in Table X.

TABLE X.
EFFECT OF Fe(III) ON % NET
URANIUM LOSS

% U loss	Cr(III) (M)	% Net Loss		
		Normal Fe(III)	FNN (0.031 M)	FeAS (0.016 M)
1	0.0	0.041	0.041	0.037
10	0.0	0.031	0.023	0.031
1	0.01	0.086	0.041	0.067
10	0.01	0.037	0.036	0.031
1	0.067	0.25	0.24	0.22
10	0.067	0.10	0.22	0.15

These data appear to agree within experimental data, hence it is concluded that the source of the Fe(III) has little, if any effect, on the % net loss of uranium, whereas, the Cr(III) concentration again shows its deleterious effect on the recovery of uranium. As a result of these experiments a set of experiments was carried out with varying concentrations of Fe(III) with the source of the Fe(III) being FNN. These results are tabulated in Table XI.

TABLE XI.

EFFECT OF Fe(III) CONCENTRATION ON
% NET URANIUM LOSS

% U Loss	Cr(III) (M)	FNN (0.00 M)	% Net Loss			
			0.01 M	0.032 M	0.10 M	
1.0	0.0	0.027	0.029	0.041	0.027	
10	0.0	0.021	0.018	0.023	0.013	
25	0.0	0.016	-	-	-	
1	0.01	0.090	0.448*	0.041	0.052	
10	0.01	0.041	0.037	0.036	0.018	
1	0.067	0.287	0.313*	0.243	0.037	
10	0.067	0.231	0.042	0.220	0.156	
25	0.067	0.052	0.064	0.101	0.052	

* The high results are believed to be due to cross-contamination.

With the exceptions (*) none of the results vary drastically from those obtained under normal conditions. Any variation which does occur is in the direction of a lower % net uranium loss.

VOLUME OF PRECIPITATE/ VOLUME CPW

During the course of the experiments above the volume ratios of precipitate to CPW were recorded. Table XII gives these ratios corresponding to the concentrations of Table VIII.

TABLE XII
VOLUME RATIOS OF PRECIPITATE TO CPW

% U Loss	Cr(III) (M)	Volume of precipitate / Volume of CPW				
		0.0	0.01	0.02	0.04	0.067
0	0	0.040			0.026	
1	0.056	0.048	0.042	0.030	0.026	
5	0.080	0.076	0.070	0.060	0.058	
10	0.110	0.114	0.118	0.122	0.112	
25	0.180	0.180	0.180	0.180	0.180	

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Determination of Hold-Up Time

In all the experiments carried out, the volume ratios (ppt/PW) were recorded after "normal condition".

Table VIII gives the ratios corresponding to the concentration of Table IV.

TABLE VIII

V-ppt/ V-PW vs. % loss to (PW and Cr(III) concentration

% U loss	Volume ppt/ volume PW					
	Cr(III)(M)	0.00	0.01	0.02	0.04	0.067
0.0			0.040		0.026	
1.0		0.056	0.048	0.042	0.030	0.026
5.0		0.080	0.076	0.070	0.060	0.058
10.0		0.110	0.114	0.118	0.122	0.112
25.0		0.180	0.180	0.180	0.180	0.180

Table IX relates the volume ratios corresponding to the concentrations given in Table VII.

TABLE IX

Volume ppt/ volume PW vs. % loss to ~~PW~~, Cr(III) conc., and Fe(III) conc.

% U loss	Cr(III)(M)	Volume ppt/ volume PW					
		0.00	0.01	0.032	0.10	FeAS (0.016)	
0.00	0.00	0.00	--	--	--	--	
1.0	0.00	0.014	0.024	0.050	0.116	0.050	
10.0	0.00	0.116	0.102	0.102	0.140	0.096	
25.0	0.00	0.200	--	--	--	--	
1.0	0.00	0.008	0.012	0.044	0.123	0.036	
10.0	0.01	0.094	0.098	0.100	0.124	0.100	
1.0	0.067	0.006	0.010	0.018	0.084	0.012	
10.0	0.067	0.080	0.084	0.096	0.118	0.100	
25.0	0.067	0.166	0.162	0.160	0.196	--	

Table X relates the volume ratios corresponding to the concentrations when for a the CPW is diluted 1/2. Two fold dilution of CPW.

TABLE X

Volume ppt/ volume CPW vs. % loss to CPW, Cr(III) Concentration at 1/2 dilution

% U loss	Cr(III)(M)	Volume ppt/ volume CPW
0.00	0.005	0.024
0.5	0.00	0.028
0.5	0.005	0.022
0.5	0.0336	0.008
12.5	0.005	0.136

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Generally it may be said that ~~xx~~ the ratio of precipitate to CPW ~~decreases with~~ increasing Cr(III) concentration and increases with increasing Fe(III) concentration. With a two fold dilution of the CPW solution the precipitate to CPW volume ratio is decreased, but does ^{Not} do so by an expected factor of two. This might be expected on the basis that a larger volume of precipitate would pack more tightly because of the increased weight of the precipitate throughout its depth than for a smaller volume of precipitate with less "head". With increasing % U loss the ratio of precipitate volume to CPW volume approaches a nearly constant value. This is illustrated in Figure I.

DETERMINATION OF FLOW RATES AND RESIDENCE TIME IN A BOWL CENTRIFUGE

For the lower concentrations of % uranium loss, the curve in Figure I approximates a straight line of slope 0.0074 crossing the ordinate axis at 0.040. The equation of this straight line is represented by the equation

$$\frac{\text{Volume of precipitate}}{\text{Volume of CPW}} = 0.074(\% \text{ U loss to CPW}) - 0.040 \quad (1)$$

It must be remembered that the packing changes with the time of centrifugation and that the above equation is valid only for a ten minute centrifugation in a clinical centrifuge at full speed (approximately 700 G's)

From the above equation, and assuming an average slurry volume of 45 gallons, For a 60 gallon bowl centrifuge(to lip), HW-10475, which holds 30 gallons of precipitate when loaded, it may be assumed that the average slurry volume in the centrifuge during the loading operation is 45 gallons. The unloading time of the centrifuge is assumed to be approximately 15 minutes. The volume of CPW normalized to 2.0 M aluminum nitrate, HDC-1333, based on 2.5 short tons of uranium throughput per day is about 4700 gallons. This corresponds to a slurry volume of about 7500 gallons per day. By applying this data to the above equation calculations were made of flow rates and residence times. ^{as follows} The flow rate can be represented by the relationship

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and from the straight line equation (1) , we obtain

$$\text{Volume of precipitate} = 34.8 (\% \text{ U loss to CPW}) - 188 \quad (4)$$

Total time to pass slurry through the centrifuge/ day =

$$24 - \text{total time to empty centrifuge/day (in hours).} \quad (5)$$

The residence time may be calculated from the following relationship

$$\text{Residence time} = \frac{45 \text{ gal/ centrifuge} \times 60 \text{ min/hr}}{\text{flow rate (gal/hr)}} \quad (6)$$

the
For ~~the same~~ range of 0-10% ~~U~~ uranium losses, the volume of precipitate, unloading time per day, flow rate, and residence time are tabulated in Table XV.

TABLE XV.
CENTRIFUGATION TIME STUDY

% U loss	volume-ppt	t to unload/day	t to fill/day	flow rate	residence time
0.00	188 gal	1.57 hrs	22.43 hrs	334 gal/hr	8.1 min
1.0	222.8	1.86	22.14	338	8.0
2.0	257.6	2.15	21.85	343	7.9
3.0	292.4	2.44	21.56	348	7.8
4.0	327.2	2.73	21.27	352.5	7.7
5.0	362	3.02	20.98	357.5	7.65
6.0	396.8	3.31	20.69	362.5	7.55
7.0	431.6	3.60	20.40	367.5	7.35
8.0	466.4	3.89	20.11	372.5	7.25
9.0	501.2	4.18	19.82	378	7.15
10.0	536.0	4.47	19.53	384	7.00

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No. 330-10

10X10 PER INCH

.130
.170
.160
.150
.140
.130
.120
.110
.100
.090
.080
.070
.060
.050
.040

FIGURE I

-17*

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PER CENT NET PLUTONIUM LOSS

To study the behaviour of plutonium in a CPW solution a series of experiments similar to a portion of those above were carried out with the plutonium being spiked into the CPW solution to give various concentrations of plutonium. Five milliliters of the ~~subsequently~~ spiked CPW solution were added to three milliliters of 50% NaOH in a reverse strike in the same manner as was done above ~~with~~ in the uranium studies. The resultant slurry was stirred for ten minutes and then centrifuged for ten minutes in a laboratory clinical centrifuge. The supernate was removed and diluted to 25 ml while the precipitate was dissolved in a minimum of nitric acid and diluted to five ml. These solutions were then analyzed by the normal hydroxide-lanthanum fluoride method of analysis.

Since the above work on normal pooled wastes with both uranium and plutonium, and in the case of the concentrated wastes with uranium only being present, has shown the adverse effect of Cr(III) ions steps were taken to try and eliminate this difficulty in this set of experiments. Preheating the CPW solution, in the presence of $\text{Cr}_2\text{O}_7^{2-}$, to oxidize the Pu(IV) to Pu(VI) did not appear to be sufficient treatment. Oxidation ~~of~~ of the Cr(III) and Pu(IV) with ammonium persulfate, silver catalyst, and heat prior to neutralization was found to aid materially in the recovery of plutonium. In this case if the uranium concentration was of the order of 1% the results obtained were not sufficient. Increasing the uranium concentration to 10% was found to give much better carrying of the plutonium.

As a result of these experiments not being completely satisfactory in all cases at low concentrations of uranium it was decided to utilize the fact that hydrated chromium oxide will coagulate on heating, and thus should be able to be centrifuged out of a solution. If the colloidal suspension of the hydrated oxide was holding plutonium in the supernate then such a coagulation treatment should bring down the plutonium into the precipitate. It was found that heating the CPW solution prior to the precipitation step, in the presence of $\text{Cr}_2\text{O}_7^{2-}$, and then heating to 90°C . again after neutralization to pH 10,

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that the precipitate became quite flocculent and readily ~~was~~ removed from the solution on centrifuging. In all cases better than 90% of the plutonium was recovered. Time studies indicated that a maximum of one (1) hour's heating was sufficient to coagulate the hydrous chromium oxide. In certain cases the supernate, after dilution, was cloudy or discolored, but on setting 18-24 hours a precipitate settled out. Analyses of the precipitates, or of the finally clear supernate, indicated that ~~approximately~~ from 2-16% of the original activity was carried in this precipitate. It is believed that this precipitate ~~is~~ largely is hydrous ferric oxide.

A few experiments were performed wherein the Fe(III) was omitted. From the data obtained it appears that the hydrous ferric oxide is instrumental in carrying ^{at least} a portion of the plutonium from the CPW solution.

TABLE XVI

The data obtained from the above experiments is tabulated in Table XVI. From this data it appears that recovery of plutonium and uranium with less than 0.2% net loss can be accomplished with either (a) heating the CPW solution before and after neutralization to restrict colloidal suspensoid formation, or (b) oxidation of Cr(III) to Cr(VI), and oxidation of Pu(IV) to Pu(VI) where possible, or (c) adding sufficient uranium (10-25 %) or other scavenging agent to carry the plutonium, with or without oxidation of the chromium and plutonium to higher valence states.

If the pooled wastes are to be concentrated it is expected that the plutonium will be oxidized to the higher valence state by any dichromate present. Since the wastes will be neutralized in any event, heating the solution after neutralization and prior to centrifugation, appears to be the most practical and economic means of recovering high losses in plutonium and uranium.

TABLE XVI

RECOVERY OF PLUTONIUM FROM CONCENTRATED POOLED WASTES

(copy from pp. 19-21 in HW-~~104~~ 17054, Monthly report for OCT. 49)
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