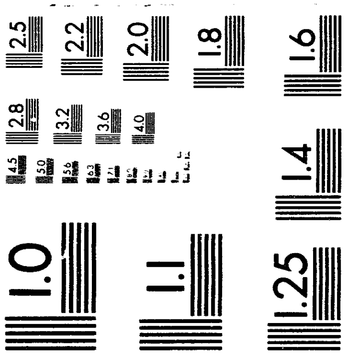
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AUTHOR
[redacted]. H. Van Tuyl

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RECOVERY OF CESIUM FROM PUREX PLANT WASTES BY METAL FERROCYANIDES AND FERRICYANIDES II. FULL LEVEL LABORATORY INVESTIGATIONS

by

H. H. Van Tuyl

Chemical Research
Chemical Research & Development
HANFORD LABORATORIES

February 28, 1957

HANFORD ATOMIC PRODUCTS OPERATION
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I. INTRODUCTION

Laboratory scale experiments with synthetic Purex 1WW and HAW have demonstrated the feasibility of recovering cesium by precipitation with metal ferrocyanides and ferricyanides(1). One method for recovery of cesium involves neutralization of the 1WW to precipitate ferric hydroxide and sodium diuranate, and recovery of cesium from the supernate by precipitation with zinc ferrocyanide. Another method involves precipitation with nickel or ferric ferrocyanide from partially neutralized 1WW, or from HAW. The second method yields a voluminous precipitate with low specific activity and poor radiochemical purity of the cesium, thus necessitating further purification and concentration of cesium before packaging. This can be accomplished by metathesis of the precipitate with sodium hydroxide and precipitation of cesium with zinc ferrocyanide. Other methods for recovering the cesium from metal ferrocyanides have been investigated by other workers(2).

Several of the more attractive cesium recovery flowsheets have been demonstrated with synthetic solutions on the laboratory scale. To demonstrate the feasibility of cesium recovery from plant solutions, the effects of radiation and trace chemicals (such as corrosion products, fission products, and impurities in uranium and process reagents) must be determined. Therefore, the present work was performed with full-level Purex waste solutions, both 1WW and HAW.

II. SUMMARY

1. Comparison of the analyses of two samples of Purex 1WW with Purex flowsheet No. 3 showed that the plant material contained less nitric acid, but more iron, uranium, and sulfate than predicted by the flowsheet. About 0.1 molar aluminum and 0.003 molar phosphate were also found in the plant material. A precipitate, apparently consisting of silica and zirconium phosphate, was found in one sample of 1WW.

2. Neutralization of plant 1WW with sodium hydroxide yielded excessive precipitate volumes. At high pH (9 or over), almost all of the cerium, strontium, and zirconium-niobium were removed by the hydroxide precipitate, but at lower pH, separation was less complete. Over 95 percent of the ruthenium was removed by the hydroxide precipitate at pH 9 or less, but at higher pH, greater amounts of the ruthenium remained in solution.

3. Recovery of cesium from neutralized plant 1WW as cesium zinc ferrocyanide was excellent, being comparable to recovery of cesium tracer from synthetic 1WW. No significant radiation damage to the precipitate was observed, even after it stood for a week or more.

4. Recovery of cesium from plant HAW with ferric or nickel ferrocyanide required a large excess of reagents. No significant differences from tracer experiments were observed.

5. Metathesis of ferric and nickel ferrocyanide precipitates was incomplete with hot 0.5 molar sodium hydroxide or cold 2 molar sodium hydroxide, but was rapid and complete with hot 2 molar sodium hydroxide. No other fission products were detected by gamma spectrometry in the major cesium fractions obtained by metathesis.

III. DISCUSSION AND RESULTS

A. Composition of 1WW

Samples of 1WW were obtained from the Purex plant on June 1 and November 9, 1956. Analyses of these two samples are shown in Table I, along with the flowsheet composition of 1WW. The volume of 1WW per ton of uranium was calculated from the observed concentration of cesium and the theoretical amount of cesium produced in uranium at the listed exposure.

The nitric acid concentration is lower than flowsheet, while the concentration of all of the other constituents is higher than expected (except for cesium in the 200 MWD/T sample). The nitric acid analyses were performed by titrating a small portion of the 1WW with standard base, and were checked roughly by measuring the volume of 50 percent sodium hydroxide required to neutralize five ml of 1WW, thus demonstrating conclusively that the acid concentration is below flowsheet.

TABLE I

COMPOSITION OF PUREX 1WW

Constituent	Purex Flowsheet #3	Sample 6/1/56	Sample 11/9/56
Exposure, MWD/T	600	200	750
Volume, Gal./Ton U	150	~ 150	100
HNO_3, M	7.6	4.0	5.6
Fe^{+3}, M	0.1	0.20	0.32
UNH, M	< 0.02	0.036	0.031
Al^{+3}, M	0	0.13	0.056
SO_4^{-2}, M	0.2	0.50	0.39
PO_4^{-3}, M	0	0.003	--
Cs^+, M	7×10^{-4}	$\sim 2 \times 10^{-4}$	1.2×10^{-3}

Iron comes from ferrous sulfamate, corrosion of stainless steel, and impurities in uranium and process reagents. Spectrographic analysis of the 750 MWD/T 1WW showed nickel and chromium at about 0.01 molar. This indicates that corrosion of stainless steel accounts for one-third to one-half of the total iron. The amount of iron introduced as an impurity in uranium should be negligible, since 100 parts of iron per million parts of uranium corresponds to only 0.03 molar iron in 1WW when concentrated to 150 gallons per ton of uranium.

The high uranium concentration on the 200 MWD/T material must be caused by high uranium losses in the plant. For the 750 MWD/T material, the loss is not excessive since the volume of waste in this case is substantially less than flowsheet.

Aluminum is presumably introduced by incomplete washing of the slugs after coating removal, and can probably be reduced to a negligible level by more careful and thorough washing.

The only known sources of sulfate and phosphate are ferrous sulfamate, and decomposition of tributyl phosphate, respectively. Cesium, of course, is introduced only as a fission product.

The 750 MWD/T sample contained particulate matter as received, with the centrifuged volume of the precipitate being about one percent of the total volume. Spectrographic analysis of the unwashed precipitate revealed zirconium, phosphorous, and silicon in addition to the expected components of 1WW. This indicates that the precipitate consists of silica and zirconium phosphate. About half of the plutonium and two-thirds of the zirconium-niobium were found by radiochemical analysis of the precipitate.

B. Neutralization of 1WW

Before cesium can be recovered effectively from Purex 1WW with zinc ferrocyanide, the iron and uranium must be removed. This can be accomplished by precipitation with sodium or ammonium hydroxide. Ideally, the precipitate should be small in volume and contain none of the cesium, but all of the iron, uranium, plutonium, and fission products other than cesium. This would permit precipitation of cesium from the supernate with zinc ferrocyanide to obtain a product of high radiochemical purity, with only a small loss of cesium. The precipitate could be stored in a small volume, packaged for use as a gross fission product source, or used as the feed material for recovery of uranium, plutonium, or fission products other than cesium. The allowable deviation from ideal conditions has not been firmly established, but was tentatively set at five percent loss of cesium to the precipitate, and five percent loss of other constituents to the solution.

Experiments on the neutralization of 750 MWD/T with 50 percent sodium hydroxide to different pH values are summarized in Table II. The volume of precipitate is quite large, amounting to 50 percent or more of the original 1WW volume when the iron, aluminum, and uranium are precipitated together. Washing the precipitate with one volume of water reduces the precipitate volume to about 35 percent of the original 1WW volume. The cesium is apparently distributed uniformly throughout the supernate and precipitate, being lost from solution only by mechanical entrainment in the precipitate. More thorough washing of the precipitate, or reduction of the precipitate volume by filtration or by slow precipitation from hot solution with gaseous ammonia should provide acceptable cesium recovery in the solution. The zirconium-niobium and cerium loss to solution is not excessive even at pH 4, and seems to be negligible at or about pH 9. The high loss of zirconium-niobium at pH 12 is anomalous,

TABLE II

NEUTRALIZATION OF 1WW

Conditions: Five ml of 750 MWD/T 1WW neutralized with 50 percent sodium hydroxide and centrifuged for 15 minutes.

Expt. No.	Final pH	Volume of Ppt., ml	Wash	Final Vol. of Ppt., ml	Percent in Supernate*				
					Cs	Zr-Nb	Ru	Ce	Sr
1	4	2.5	2 ml water	1.7	80	1	1	5	50
2	9	2.5	2 ml water	1.7	85	< 0.2	2	0.09	3
3	12	2	None	2	70	2	7	< 0.03	--
4	13	2	None	2	70	0.1	17	< 0.03	0.05
5**	5	2	None	2	50	< 0.1	1	< 0.03	--

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* Based on original 1WW as 100.

** Supernate from experiment 4 acidified to pH 5 to precipitate aluminum.

probably being caused by poor phase separation or dirty equipment. Strontium behaves qualitatively like zirconium-niobium and cerium, but the loss to solution is much higher. However, strontium is removed from solution adequately at pH 9 or over. A completely different behavior was observed with ruthenium. Satisfactory ruthenium removal was observed at pH 4 and 9, but loss of ruthenium to solution increased with increasing pH above this range.

The optimum pH for hydroxide precipitation appears to be about 9 since higher pH values result in excessive ruthenium loss, and lower pH values result in excessive strontium loss. Also, at pH 9 aluminum will precipitate along with the other hydroxides, thus avoiding any possible aluminum interference with cesium recovery.

C. Recovery of Cesium from Neutralized 1WW

Tracer level experiments have demonstrated recovery of 95 percent or more of the cesium from synthetic neutralized 1WW (1WW-NS) by precipitation with zinc ferrocyanide. For concentrations of cesium below 4 x 10^{-4} molar, an excess of reagents is required over the stoichiometric amounts for precipitation of $Cs_2ZnFe(CN)_6$, while for higher cesium concentrations, the stoichiometric amount of reagents is sufficient. Tentative requirements for the cesium precipitation step have been established as 95 percent cesium recovery from the supernate, with the use of a twofold or smaller excess of zinc ferrocyanide (to retain high specific activity in the precipitate). Thus, overall cesium recovery will be 90 percent or over (five percent loss to the hydroxide precipitate, and five percent loss to the ferrocyanide supernate), and the specific activity of cesium in the precipitate will be high enough to permit packaging of the precipitate directly, or after simple chemical operations for purification and conversion to a more radiation stable form.

The first five experiments in Table III were performed to determine the effects

TABLE III

RECOVERY OF CESIUM FROM NEUTRALIZED 1WW

Conditions: Five ml of 200 MWD/T 1WW for first five experiments, 750 MWD/T 1WW for last three experiments. Neutralized with 50 percent sodium hydroxide to pH in second column, centrifuged 15 minutes, supernatant removed from precipitate, and adjusted to pH shown in third column. Centrifuged 15 minutes to remove aluminum hydroxide when present. Zinc and ferrocyanide added as indicated, and stirred. Centrifuged 15 minutes and analyzed. Resampled for analysis after standing the times indicated in the last three columns.

Expt. No.	Hydroxide Pptn. pH	Ferrocyanide Pptn. pH	Molar Concentration x 10^4			Cesium Recovery, Percent[a]			
			Cesium	Zinc	Ferrocyanide	1 hr.	1 d	2 d	7 d
1	10.7	1.2	1.4	3	3	46	54	57	
2	10.2	2.0	1.0	3	3	96			87
3	10.8	4.2	1.3	3	3	95	94	93	
4	10.4	6.3	1.0	3	3	91			88
5	10.7	7.5	1.0	3	3	90			86
6	4	4	8.0	7.7	7.7	99	99	98	98 9
7	12	2	8.5	7.7	7.7	90			87[c]
8	9[d]	9	7.5	3.6	3.6	70 80[e] 90[f] 92[g] 85[h] 90[i]			

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a Based on cesium content of hydroxide supernate as 100.
b Stirred, re-centrifuged, and analyzed after sampling for analysis at seven days.
c Analyzed at 23 days.
d Made 0.2 molar in ammonium hydroxide after neutralization with sodium hydroxide.
e Adjust to pH 8, add ferrocyanide to 1.5 x 10-3 molar
f Adjust to pH 1
g Adjust to pH 8
h Add ammonium acetate buffer to 0.1 molar
i Add ferrocyanide to 2 x 10^{-3} molar total

of pH and standing time on cesium recovery. Since the cesium concentration was low with the 200 MWD/T waste, a rather large excess of zinc and ferrocyanide were added. The values for cesium recovery after one hour at pH 1, 2, and 4 agree reasonably well with tracer experiments, but the experiments at higher pH resulted in lower cesium recovery than expected. A possible explanation of this is the presence of carbonate in some or all of the experiments. At low pH, carbonic acid would be expected, while at high pH the concentration of bicarbonate and carbonate ions becomes greater by dissociation of carbonic acid. Since the low cesium recovery observed by adding sodium carbonate in tracer experiments at pH 6 is probably caused by bicarbonate or carbonate ions, the low cesium recovery at high pH can be qualitatively explained. There are several possible explanations of the slight decrease in cesium recovery with standing. Two possible causes are radiation decomposition of the precipitate, and oxidation of ferrocyanide to ferricyanide.

In experiment 6 of Table III, excellent cesium recovery was obtained with slightly less than a twofold excess of reagents, and the slight decrease in cesium recovery on standing demonstrates that radiation decomposition of the precipitate is not excessive. Experiment 7 is similar to experiment 6, but aluminum was not removed from solution before cesium precipitation. The low recovery may be caused by formation of some aluminum ferrocyanide, which does not carry cesium. In experiment 8, the initial low recovery at pH 8, and the high recovery at pH 8 after acidification to pH 1, strongly indicates that carbonate was present initially, and was decomposed by acidification. The amounts of zinc and ferrocyanide added were inadvertently slightly less than stoichiometric to the cesium, thus limiting cesium recovery to a maximum of about 95 percent, even if all of the reagents precipitated as the cesium compound. The maximum observed recovery of 92 percent is excellent under these conditions, and agrees well with tracer experiments. In addition, the 0.3 molar ammonium ion present in these experiments does not affect cesium recovery significantly.

These data, especially experiments 6 and 8, demonstrate that cesium can be separated adequately from full-level Purex 1WW, provided the proper conditions are employed.

The precipitates from experiments 2, 4, and 5 of Table III were washed with one ml of water, and the washes and precipitates were analyzed for the major fission products, as shown in Table IV. The precipitates contained only cesium and ruthenium in large amounts, and these are not removed appreciably by the water wash. The only apparent value of washing the precipitate with water is to remove inert constituents such as sodium nitrate. The beta activity of the precipitates is about 92 percent cesium, 6 percent ruthenium - rhodium, 0.5 to 1 percent each cerium-praesodymium, and zirconium-niobium, and 0.2 percent strontium. The gamma activity of the precipitate is about 91 percent cesium. This radiochemical purity appears to be sufficiently high for most applications, even though more extraneous gamma activity is present than might be desired for some applications. Chemical treatment of the precipitate to obtain a more radiation stable form for packaging should provide adequate additional purification of the cesium from other fission products.

TABLE IV

RADIOCHEMICAL ANALYSES OF CESIUM ZINC FERROCYANIDE PRECIPITATES

Conditions: Precipitates from experiments 2, 4, and 5 of Table III were stirred for five minutes with one ml of water, and centrifuged for five min. The water wash was analyzed by gamma spectrometry, and the precipitate was analyzed by standard radiochemical methods.

Ferrocyanide	Activity in Wash, Percent*				Activity in Precipitate, Percent*			
Pptn. pH	Cs	Zr-Nb	Ru	Ce	Zr-Nb	Ru	Ce	Sr
2.0	0.6	0.01	0.15	0.006	0.5	1.5	0.2	0.01
6.3	0.4	0.003	0.05	0.002	0.007	0.9	0.04	0.01
7.5	1.8	0.004	0.03	0.002	0.1	0.6	0.01	0.01

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* Based on original 1WW as 100 percent

D. Recovery of Cesium from HAW

The recovery of cesium from HAW by precipitation of ferric and nickel ferrocyanides was investigated as shown in Table V. To obtain cesium recovery of over 90 percent, a large excess of reagent is required in each case. With ferric ferrocyanide, a nine-fold excess over stoichiometric $CsFeFe(CN)_6$ is required, while with nickel ferrocyanide, a six-fold excess over $Cs_2Ni_3[Fe(CN)_6]_2$ is required. The recovery observed with nickel ferrocyanide at low concentrations may be due to precipitation of the iron present in the HAW as ferrocyanide, since nickel ferrocyanide is soluble under these conditions. The possible effects of adding ammonium ion under similar conditions were not investigated (earlier tracer experiments(1) showed that ammonium ion improved cesium recovery with nickel ferrocyanide). In each of the experiments listed in Table V, cesium recovery was slightly higher in full level experiments than with tracer work. No reason for this slight increase in recovery is apparent.

A few similar experiments were performed with 300 MWD/T HAW containing abnormally high amounts of uranium, corresponding to a three percent loss of uranium in the HA column. Cesium recovery was only 95 percent with 0.004 molar ferric ferrocyanide, and 99 percent with 0.003 molar nickel ferrocyanide, as compared with over 99 percent in each case at normal uranium concentrations. With nickel ferricyanide at 0.004 molar, cesium recovery was slightly over 99 percent, which is comparable to recovery at normal uranium concentrations in tracer level experiments. The precipitates from these experiments all contained about five percent of the zirconium-niobium, one percent of the cerium, and less than two percent of the ruthenium, in addition to the cesium.

TABLE V

CESIUM RECOVERY FROM HAW

Conditions: Five ml of 600 MWD/T Purex HAW were made 0.1 molar in urea. Ferrocyanide was added as shown, and the indicated metal ion was added in stoichiometric amounts to form the compounds $Fe_4[Fe(CN)_6]_3$ or $Ni_2Fe(CN)_6$. The slurry was stirred, centrifuged for five minutes and analyzed. After standing for the times indicated in the last two columns, the supernate was resampled for cesium analysis. The initial cesium concentration was 8×10^{-5} molar.

Ferrocyanide Concentration, M	Cesium Recovery, Percent			
	Metal Ion	5 min.	5 hrs.	14 days
0.004	Ferric	99.4	99.6	98
0.0015	Ferric	98	98	92
0.00075	Ferric	86	94	76
0.0002	Ferric	67	70	--
0.0001	Ferric	52	56	--
0.0025	Nickel	99.7	99.2	99
0.0010	Nickel	98	98	98
0.0005	Nickel	99	99	98
0.0002	Nickel	70	70	--
0.0001	Nickel	61	63	--

E. Metathesis of Precipitates

The ferrocyanide precipitates formed from high uranium content HAW were washed with water and treated with sodium hydroxide, as shown in Table VI. The volume of precipitate decreased by a factor of 3 to 5 after metathesis to the hydroxide. In each experiment the volume of water or sodium hydroxide added was equal to the volume of the original precipitate. Since the solutions were analyzed by gamma spectrometry only, positive data were not obtained for all fission products in many of the experiments.

With both ferric and nickel ferrocyanides, a wash with one precipitate volume of water removed much of the ruthenium, half of the cerium, ten percent of the zirconium-niobium, and about 0.5 percent of the cesium, based on the total of

TABLE VI

METATHESIS OF FERROCYANIDE PRECIPITATES

Conditions: Precipitates were formed from 300 MWD/T HAW with a high uranium content (corresponding to three percent waste loss) by adding either ferric or nickel nitrate, and potassium ferrocyanide to 0.005 molar each. The precipitates were washed with an equal volume of water, and contacted for 15 minutes with successive portions of sodium hydroxide, each equal in volume to the original volume of precipitate. The supernate after centrifugation was analyzed by gamma spectrometry.

			Activity in Solution, Percent*							
			Ferric Ferrocyanide				Nickel Ferrocyanide			
Expt. No.	Reagent	Temp., °C	Cs	Zr-Nb	Ru	Ce	Cs	Zr-Nb	Ru	Ce
1a	Water	25	<0.6	0.8	0.8	0.5	<0.7	0.9	1.1	1.0
1b	0.5 M NaOH	90	0.08	0.008	0.02	0.05	0.1	0.01	<0.01	<0.00
1c	0.5 M NaOH	90	44	<0.6	<3	<0.4	4	<0.04	<0.2	<0.1
2a	Water	25	<0.5	0.6	1.2	0.4	<0.2	0.3	0.8	0.2
2b	2 M NaOH	25	15	<0.2	<1.0	<0.15	8	<0.08	<0.4	<0.06
2c	2 M NaOH	25	31	<0.4	<2.1	<0.3				
2d	2 M NaOH	25	15	<0.2	<1.0	<0.15				
3a	Water	25	<0.5	0.5	1.3	0.4				
3b	2 M NaOH**	25	45	<0.6	<3	<0.4				
3c	2 M NaOH**	25	14	<0.2	<0.9	<0.13				
4a	Water	90					0.3	0.6	0.7	0.8
4b	2 M NaOH	90					61	<0.6	<3	<0.5
4c	2 M NaOH	90					27	<0.3	<1.4	<0.2
4d	2 M NaOH	90					7.5	0.1	0.4	<0.06
4e	2 M NaOH	90					2.6	0.3	0.3	0.01
5a	Water	90	1.1	0.2	0.8	1.3	0.2	0.09	0.2	0.3
5b	2 M NaOH	90	65	<0.8	<4	<0.6	84	<0.9	<5	<0.6
5c	2 M NaOH	25	10	<0.1	<0.6	<0.09	11.3	<0.1	<0.6	<0.09
5d	2 M NaOH	90	4	0.03	0.4	<0.04	2.4	0.04	<0.1	<0.02
5e	2 M NaOH	90	0.8	0.09	0.15	0.02	0.7	0.02	0.06	<0.005

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* Percent of total nuclide in original HAW. Cesium values do not total 100 percent because of cesium loss to supernate (about 20 percent loss with ferric ferrocyanide, and 2 percent loss with nickel ferrocyanide), and because of cesium occlusion in the precipitate after metathesis.

** Contacted one hour with continuous, vigorous stirring.

each nuclide in the precipitate as 100 percent. Of course, after contacting the precipitate, the wash solution became about one molar in acid since the ferrocyanide precipitation was made from a solution about 2 molar in nitric acid, and the solution was partly occluded in the precipitate. Therefore, this wash not only removed much of the ruthenium and cerium activity, but also reduced the amount of sodium hydroxide required for neutralizing the precipitate.

The first contacting of each precipitate with an equal volume of hot 0.5 molar sodium hydroxide served only to neutralize the excess acid. The second contacting of ferric ferrocyanide with hot 0.5 molar sodium hydroxide yielded over half of the remaining cesium in solution. This indicates almost complete metathesis since a rather large amount of the dissolved cesium is retained by occlusion in the precipitate. Only slight metathesis of nickel ferrocyanide precipitates was obtained under these conditions.

With 2 molar sodium hydroxide at room temperature, the results were similar to the second contacting with hot 0.5 molar sodium hydroxide, but ferric ferrocyanide was less rapidly metathesized. Rapid and apparently complete metathesis of both ferric and nickel ferrocyanide precipitates was obtained with hot sodium hydroxide at concentrations of 2 molar or over. Complete metathesis in a single contacting was strongly indicated since the ratio of cesium in solution to cesium in the precipitate remained about constant for all four contactings with caustic. In no case was an appreciable amount of any other fission product removed during the metathesis.

HH Van Tuyl:rd

IV. REFERENCES

(1) H. H. Van Tuyl, Recovery of Cesium from Purex Plant Wastes by Metal Ferrocyanides and Ferricyanides, I. Tracer Scale Laboratory Investigations, HW-48829, February 28, 1957, Confidential.

(2) J. L. Hepworth and R. L. Moore, Cesium Packaging Studies; Conversion of Cesium Zinc Ferrocyanide to a Stable Product, HW-48832, February 28, 1957, Confidential.

V. ABSTRACT

The composition of two samples of plant 1WW are compared with the nominal flowsheet composition. The precipitate volumes and fission product distribution obtained by neutralizing one of these samples with sodium hydroxide are presented. The recovery of cesium from neutralized 1WW with zinc ferrocyanide, and recovery from HAW with ferric and nickel ferrocyanides is discussed. The metathesis of ferric and nickel ferrocyanide precipitates with sodium hydroxide is described. The excellent cesium recovery obtained from these full level 1WW and HAW solutions confirmed tracer level results which were previously reported.

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