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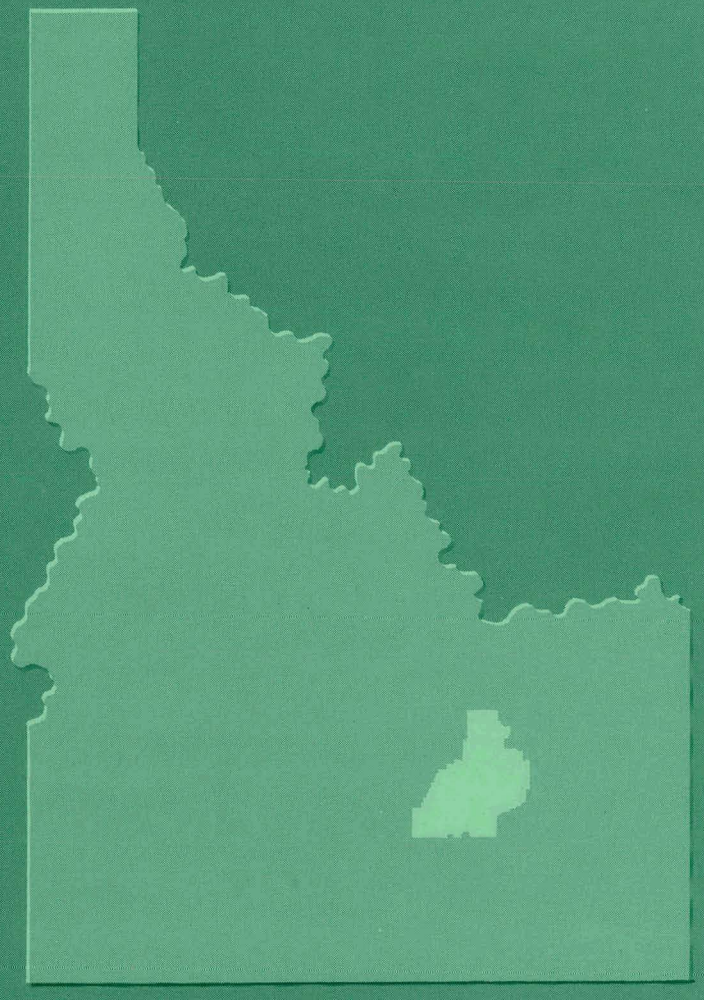
SODIUM FLUOZIRCONATE PRECIPITATION PROCESS FOR ZIRCONIUM FUELS

PART I. LABORATORY DEVELOPMENT

B. J. Newby



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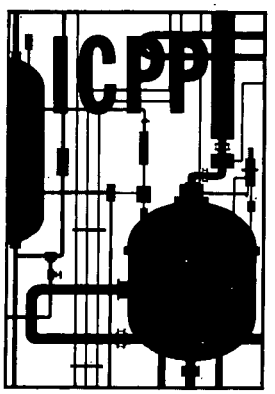

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SODIUM FLUOZIRCONATE PRECIPITATION PROCESS FOR ZIRCONIUM FUELS

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A B S T R A C T

In the reprocessing of zirconium-containing reactor fuels by hydrofluoric acid dissolution, significantly decreased waste volumes and increased column capacities can be obtained by the headend precipitation of the bulk of the fluoride and zirconium. A sparingly soluble complex fluozirconate is formed when the dissolver solution is treated with sodium formate. Precipitation, evaporation, and extraction feed preparation conditions are established for this process. Ninety-five to 99 per cent of the zirconium and fluoride is separated from the uranium with uranium losses of 0.1 per cent or less. Chemical material balances, based on experimental data, have been developed for two flowsheets. In one flowsheet, sufficient nitric acid is added to the combined wash solution and filtrate produced during the precipitation step to destroy the formate ion (which inhibits uranium extraction) and to prevent post-precipitation during the evaporation of these solutions. The other flowsheet calls for addition of sufficient nitric acid to destroy the formate ion, but not enough to prevent post-precipitation during the concentration step. Post-precipitation removes additional zirconium and fluoride, but necessitates an additional solids-separation step.

SODIUM FLUOZIRCONATE PRECIPITATION PROCESS FOR ZIRCONIUM FUELS

PART 1. LABORATORY DEVELOPMENT

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I. SUMMARY

Current Idaho Chemical Processing Plant (ICPP) zirconium fuel processing methods, and several new methods under development, produce large waste volumes. Removing both zirconium and fluoride as a solid from dissolver product solutions results in smaller waste volumes, higher uranium throughputs through extraction equipment, and conversion of a portion of the waste to a solid. Each of these factors is of significance in the design of improved flowsheets for processing fuels at the ICPP. The addition of sodium formate to hydrofluoric acid-zirconium fuel dissolver product solutions removes the zirconium and fluoride almost quantitatively from solutions as a precipitate.

The effective removal of zirconium and fluoride from solution requires two moles of sodium formate per mole of zirconium present. It is rapid at temperatures between 23 and 95°C, and under controlled conditions is independent of the concentration of fluoride in the dissolver solution. Aqueous streams involved in the precipitation are only slightly corrosive to materials of construction commonly used for the chemical processing of uranium. Uranium loss to the precipitate is about 0.1 per cent for a zirconium-uranium fuel containing 2.5 per cent uranium when the uranium is in its highest state of oxidation and the precipitate is washed adequately.

Concentration of the supernatant solution and washes can be accomplished with or without the formation of solids, and the resultant concentrate can be adjusted to give good uranium extraction results when contacted with 10% tributyl phosphate in Amsco. A boildown performed on combined filtrates and wash solutions made 0.4M in nitric acid produces a post-precipitate which removes fluoride from solution. During such an evaporation, corrosion rates of < 0.04 mil per month were found for Carpenter-20 in both the liquid and

vapor phases. Evaporation of combined filtrates and wash solutions made 1.0M in nitric acid to prevent post-precipitation gives corrosion rates of about 3 mils per month. Uranium losses to boildown solids are about 0.03 per cent when the uranium is all oxidized and the solid washed 3 times with 0.1M nitric acid.

Two flowsheets are presented, differing in the type of boildown used. The flowsheet using a boildown resulting in formation of solids removes over 99 per cent of the zirconium, loses approximately 0.1 per cent of the uranium, and produces extraction column feeds equal to 20 per cent of the dissolver solution volume. The flowsheet utilizing solid-free boildown removes about 95 per cent of the zirconium, loses about 0.1 per cent of the uranium, and produces extraction column feed equal to 36 per cent of the dissolver solution volume.

II. INTRODUCTION

Currently, the most successful methods for processing zirconium-uranium alloy reactor fuels involve dissolution with hydrofluoric acid containing an oxidant. The resulting solution is adjusted with aluminum nitrate to permit uranium extraction in stainless steel columns, and the raffinate stored without further treatment. The hydrofluoric acid process or the similar ammonium fluoride process produces large volumes of waste requiring long-term storage. The removal of zirconium and fluoride as a solid from the process solutions would convert the alloy constituents of the waste to a non-corrosive solid, thus allowing concentration of the liquid waste to a small volume for storage or calcination. By removing most of the zirconium and fluoride prior to extraction, the amount of total waste solids can be reduced, because the need for large concentrations of aluminum nitrate to complex the fluoride ion is eliminated. Extraction column feed can also be concentrated to smaller volumes, thereby increasing the uranium throughput of the extraction columns.

The addition of sodium formate to zirconium-hydrofluoric acid process solutions removes greater than 97 per cent of the zirconium and fluoride as a precipitate. Uranium loss is of the order of 0.1 per cent provided uranium is in the hexavalent state. Furthermore, the volume of filtrate and wash solutions can be reduced by evaporation to as little as 20 per cent of the volume of the original dissolver solution. After removal of solids, uranium can be extracted from the resulting filtrate with 10 per cent TBP in Amsco.

This report is intended to provide sufficient information for the selection of favorable conditions for removing zirconium and fluoride from dissolver solutions by precipitation with sodium formate. In addition, favorable conditions for boiling down the resulting filtrates and wash solutions with or without solids formation, and for extracting uranium from the resulting media with 10 per cent TBP in Amsco, are included. Hydrofluoric acid dissolver solutions corresponding to the ICPP STR process were used because considerable information pertaining to the dissolution of zirconium-

uranium alloy fuel in hydrofluoric acid is available. However, much of the data presented in this report can be applied to any hydrofluoric acid-zirconium fluoride process. Two different flowsheets together with a brief supporting description are given in the main body of the report. The information used to prepare these flowsheets was obtained from experiments described in the Appendix of this report. These experiments involved a study of the precipitation of zirconium and fluoride using sodium formate concentration, reaction time, temperature, flocculating agents, and dissolver solution composition as variables. The Appendix also contains a description of boildown and extraction studies, wash solution studies, and corrosion studies under precipitation and boildown conditions.

III. SODIUM FORMATE FLOWSHEETS

From the information obtained in the studies described in the Appendix, two tentative flowsheets were prepared. One flowsheet uses conditions which result in the elimination of solids during boildown; the other flowsheet requires two filtrations, the second being necessary to remove solids formed during boildown.

The washed precipitates obtained from the reaction of sodium formate with solutions of zirconium and fluoride contained about 1.5 moles of sodium and 5 moles of fluoride for each mole of zirconium present. It was concluded that the precipitates contained no organic radical since carbon could not be detected. It was not possible to analyze for oxygen in the presence of the fluoride; therefore, there is no direct measure of the degree of hydrolysis. The X-ray pattern for the major crystalline species present was similar to the pattern given by β Na_2ZrF_6; however, there are many possible sodium fluozirconates, and patterns were available for only Na_2ZrF_6 and $NaZrF_5$. Thus, these precipitates could be a sodium fluozirconate or a hydrolysis product.

In preparing flowsheets, the following reaction was assumed to take place when sodium formate was added to dissolver product solution:

$$2\ ZrF_4 + 2HF + 3NaCOOH \longrightarrow 2HCOOH + Na_3Zr_2F_{10}(COOH)$$

$$\uparrow\ \downarrow\ H_2O$$

$$Na_3Zr_2(OH)F_{10} + HCOOH$$

The insolubility of the hydrolysis product would drive the hydrolysis reaction to completion. Similar hydrolysis reactions involving sodium formate are mentioned by Blumenthal[1].

Boildown and extraction experiments showed that uranium could not be extracted from boiled-down solutions with 10 per cent TBP in Amsco when formate ion was present. When evaporations were done in the presence of nitric acid (sodium nitrate could not be substituted for nitric acid), uranium was easily extracted. Nitric acid reacts with the formate ion to form carbon dioxide, water, and oxides of nitrogen[2, 3, 4]. The use of nitric acid in the boildown also

permits concentration of the solution to smaller volumes without solids formation.

A. Flowsheet Utilizing Two Solid-Liquid Separations

A flowsheet for a headend sodium formate precipitation involving a boildown with solids formation is shown in Figure 1; more detailed stream concentrations are shown in Table 1. The precipitation is made at 60°C using 3.2M sodium formate as the precipitant. Stream volumes could possibly be reduced if slightly more concentrated sodium formate were used. The slurry should be agitated at the precipitation temperature for about 10 minutes before cooling. If filters are used, filtrations should be made with fine-porosity filters (about 5 microns). The precipitate is washed with 4 volumes of 0.1M sodium nitrate, each equal to one-half the volume of dissolver solution used. Filtrate and wash solutions are combined and sufficient nitric acid is added to destroy the formate ion but not to dissolve residue formed during the evaporation. The combined filtrate and wash solutions are boiled down to a volume equal to 20 per cent of the volume of dissolver solution used. Solids are removed by filtration or centrifugation and the residue washed with 3 volumes of 0.1M nitric acid each equal to 20 per cent of the volume of the boiled-down slurry. Filtrate and wash solution are kept separate; the wash solution is blended with the evaporator feed while the filtrate is fed to the extraction columns after aluminum nitrate and nitric acid have been added to provide salting strength and stability.

This chemical material balance flowsheet yields an extraction feed containing only a small amount of aluminum and essentially no zirconium or fluoride. Unwelded coupons of SS 316 (extra low carbon), Hastelloy F, and Carpenter-20, located in vapor and liquid phases, gave corrosion rates of less than 2.2 mils per month under flowsheet precipitation and boildown conditions (see Appendix, sections B-6 and C-3).

B. Flowsheet Utilizing One Solid-Liquid Separation

A flowsheet for the precipitation of zirconium and fluoride with sodium formate followed by a boildown free from solids formation is shown

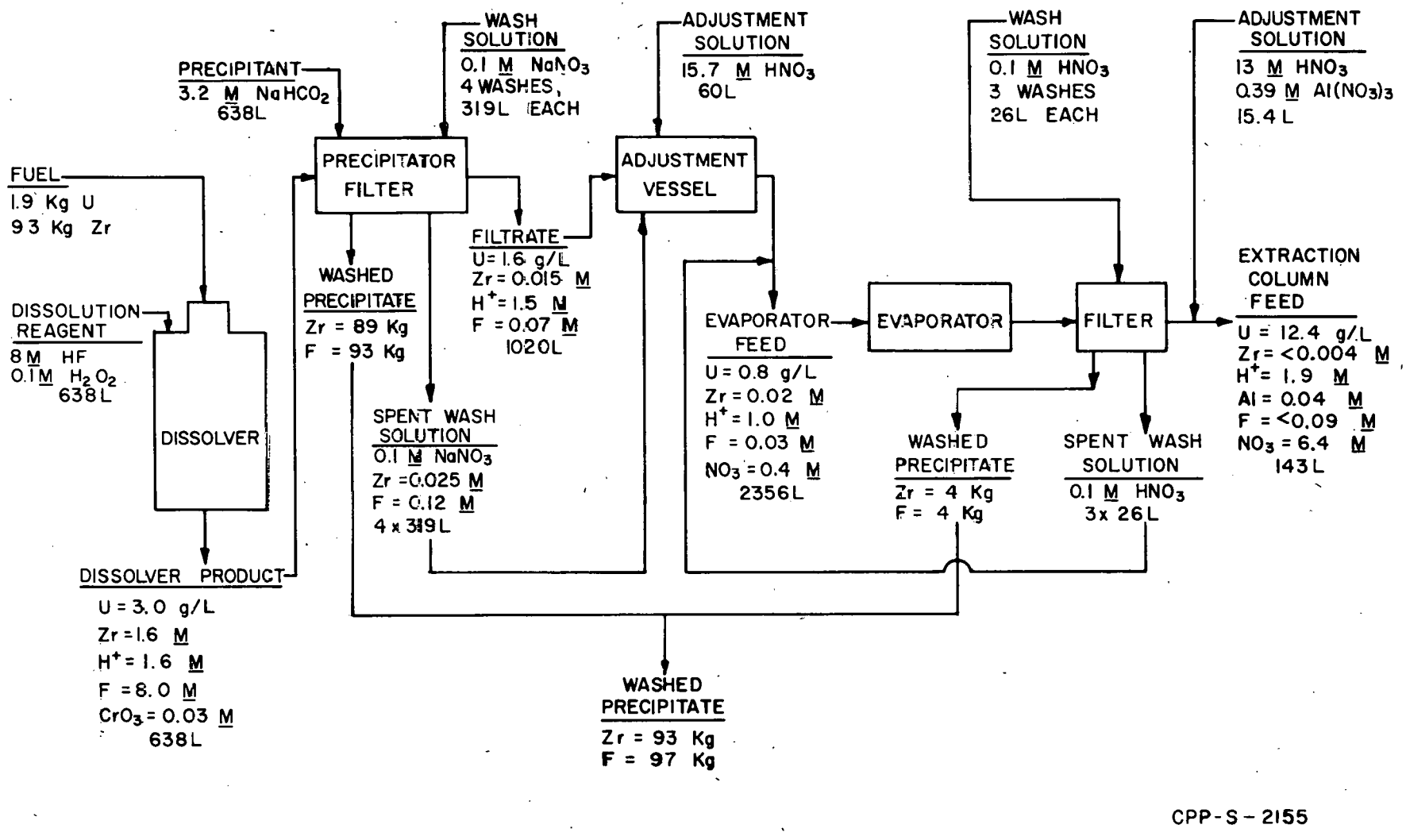

Fig. 1. Flowsheet for Sodium Formate Headend Precipitation Using Two Solid-Liquid Separations

Table 1

Material Balance for Sodium Formate Headend Precipitation Using Two Solid-Liquid Separations

	Fuel	Dissolution Reagent	Dissolver Product	Precipitant	Supernate	Precipitate	Precipitate Wash Soln.	Evaporator Feed Adjustment Solution	Adjusted Evaporetor Feed	Unwashed Evaporation Solids	Off-Gas Produced During Evap.	Evaporator Product	Wash Soln of Evap. Solids (Blended With Adjusted Evap. Feed) before use	Wash Soln of Evap. Solids (Blended With Adjusted Evap. Feed) after use	Extraction Column Feed Adjustment Solution	Extraction Column Feed
Flow, l/batch		638	638	638	1020	256	1276	60	2434	--		128	78	78	15.4	143
U g/l	1.9 Kg		3.0		1.6	1.9 g			0.8	0.6 g		13.8		1.6		12.4
Zr M	93 Kg		1.6		0.015	980 moles			0.02	47 moles		< 0.005		0.05		< 0.004
Sn M	1.4 Kg		0.02		0.01				0.004			0.08				0.07
H^+ M		8.0	1.6		1.5			15.7	1.0			0.6	0.1	0.1	13.0	1.9
F^- M		8.0	8.0		0.07	4900 moles			0.03	235 moles		< 0.1		0.25		< 0.09
H_2O_2 M		0.1	< 0.005		< 0.003				< 0.001			< 0.02				< 0.02
CrO_3 M			0.03*		0.02				0.009			0.15				0.13
Na M				3.2	0.5	1470 moles	0.1		0.27	85 moles		4.3				3.8
HCO_2^- M				3.2	2.0				0.87							
NO_3^- M							0.1	15.7	0.40			5.6	0.1	0.1	14.2	6.4
Al M															0.39	0.04
CO_2											2040 moles					
Oxides of Nitrogen											225 moles					
OH						490 moles				24 moles						

* Chromic Acid was added to dissolver product.

in Figure 2; more detailed information is shown in Table 2. The precipitation is identical to that of the flowsheet described in Table 1, with the exception that, after addition of all the precipitant, flocculating agent is added and the resulting slurry stirred at precipitation temperature. After filtration, the precipitate is washed on the filter with four portions of 0.1M nitric acid, each wash being equal in volume to one-half of the volume of dissolver solution used. Filtrate and wash solutions are combined and sufficient nitric acid added to destroy the formate ion and to prevent post-precipitation during evaporation. The combined filtrate and wash solutions are boiled down to a volume equal to 20 per cent of the volume of dissolver solution used; while this solution is still at an elevated temperature, a volume of 2.26M aluminum nitrate is added equal to 80 per cent of the volume of the boiled-down solution. Addition of aluminum nitrate stabilizes the solution and adds salting strength. This flowsheet eliminates a second separation step at the expense of higher corrosion during boildown, larger extraction column feed volumes, and higher concentrations of zirconium, fluoride, and aluminum in the extraction column feed. Unwelded coupons of SS 316 (ELC), Hastelloy F, and Carpenter-20, located in both the vapor and liquid phases, showed corrosion rates of less than 2.2 mils/mo under flowsheet precipitation conditions and less than 4.2 mils/mo under boildown conditions (see Appendix, sections B-6 and C-3).

IV. CONCLUSIONS

Precipitates formed by the addition of sodium formate to zirconium-hydrofluoric acid dissolver solutions can remove greater than 99 per cent of the zirconium and fluoride as solid waste, allowing concentration of the liquid waste to small volumes for storage. Solution volumes are reduced by as much as 80 per cent. Waste storage costs for the raffinates from hydrofluoric acid zirconium fuel reprocessing methods, that exist or have been proposed for use at the Idaho Chemical Processing Plant, vary from 20 to 42 per cent of the total processing costs as the production is increased from 2 to 10 Kg of uranium per day[5]. Thus, a significant reduction of processing cost is

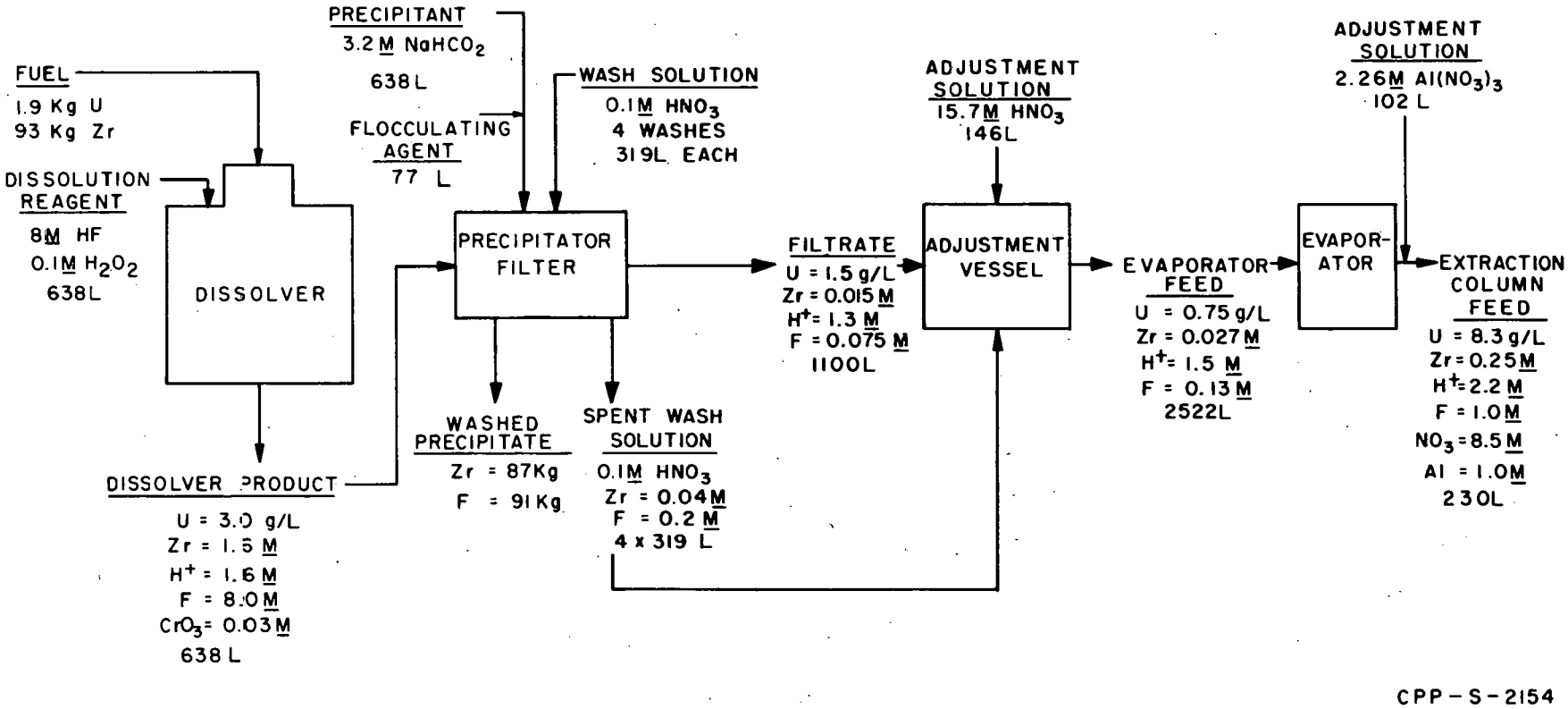

Fig. 2. Flowsheet for Sodium Formate Headend Precipitation Using One Solid-Liquid Separation

Table 2

Material Balance for Sodium Formate Headend Precipitation Using One Solid-Liquid Separation

	Fuel	Dissolution Reagent	Dissolver Product	Precipitant	Flocculating 0.1% Reagent*	Supernate	Precipitate	Precipitate Wash Soln.	Evaporator Feed Adjustment Solution	Adjusted Evaporator Feed	Evaporator Product	Off-Gas Produced During Evap.	Extraction Column Feed Adjustment Solution	Extraction Column Feed
Flow, l/batch		638	638	638	77	1100	253	1276	146	2522	128		102	230
U g/l 1.9 Kg			3.0			1.5	1.9 g			0.75	14.8			8.3
Zr M 93 Kg			1.6			0.015	955 moles			0.027	0.45			0.25
Sn M 1.4 Kg			0.02			0.01				0.004	0.08			0.04
H^+ M		8.0	1.6			1.3		0.1	15.7	1.5	4.0			2.2
F^- M		8.0	8.0			0.075	4775 moles			0.13	1.8			1.0
H_2O_2 M		0.1	< 0.005			< 0.003				< 0.001	< 0.02			< 0.01
CrO_3 M			0.03**			0.02				0.009	0.15			0.08
Na M				3.2		0.55	1432 moles			0.24	5.6			3.1
HCO_2^- M				3.2		1.9				0.81				
NO_3^- M								0.1	15.7	0.96	9.9		6.8	8.5
Al M													2.26	1.0
CO_2												2042 moles		
Oxides of Nitrogen												1154 moles		
OH							477 moles							

* This can be 0.1% by weight General Mills' Galactasol CAM, Dow's Separan NP-10, Stein Hall's Jaguar, or Cyanamid's Aercfloc 550 Reagent.

** Chromic acid was added to dissolver product.

possible by using the sodium formate precipitation process in combination with one of these reprocessing methods.

Since the sodium formate precipitation reaction is complete within 5 minutes after precipitant addition, it may also be conveniently adapted to continuous zirconium fuel dissolutions.

All streams involved in the flowsheet of Figure 1 are non-corrosive to materials of construction commonly used in the atomic energy industry. Thus, the materials that must be used to fabricate a precipitator, solid-liquid separation devices, evaporator, and adjustment vessels are readily available. An 80 per cent volume reduction can be realized prior to uranium extraction. This flowsheet produces an extraction column feed that contains negligible fluoride concentrations and appears to be quite stable. Such a stream should be non-corrosive to stainless steel extraction columns. The raffinate from the extraction column is low in aluminum and contains essentially no zirconium or fluoride; thus, the solids content of the material to be stored is low.

The flowsheet of Figure 2 eliminates a second solid-liquid separation step. However, the construction materials used to fabricate the evaporator used in the boildown may be a problem, since unwelded coupons gave corrosion rates varying from 2.8 to 4.2 mils/mo when subjected to boildown conditions. This chemical material balance provides for a 64 per cent volume reduction prior to extraction. The flowsheet uses an extraction column feed with a higher aluminum-to-fluoride mole ratio than the process being currently used at the ICPP or in the flowsheets proposed by Parrett[6] for future hydrofluoric acid dissolutions; thus, the stream should be non-corrosive to stainless steel extraction columns. The extraction column feed appeared to be stable at room temperature. The density of the extraction column raffinate is higher than in the other sodium formate flowsheet.

Fluoride and zirconium recovery should not be affected by variation in dissolver solution fluoride concentration, provided the fluoride-to-zirconium mole ratio is 5 or less; good recoveries at higher mole

ratios would require sodium formate-to-zirconium mole ratios greater than 2 to 1. Sodium formate solutions of 6M might be used as a precipitant, which would decrease many of the process stream volumes considerably.

Uranium losses to the precipitates from the sodium formate process are comparable to the usual over-all process losses, but are somewhat high for a single step of an enriched uranium process. Effective removal from solids requires that the uranium be in its highest state of oxidation; chromic acid is a convenient oxidizing agent. At the end of four washes with a wide variety of 0.1M wash solutions, each wash having one-half the volume of the dissolver product solution, the uranium loss to the sodium precipitate decreases to about 0.1 per cent and approaches the limit of effectiveness. Washing solids (formed during boildown) 3 times with a volume of dilute nitric acid equal to one-fifth the volume of boiled-down slurry results in a uranium loss of 0.03 per cent and approaches the limit of effectiveness.

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VI. APPENDIX

A. Experimental Methods and Materials

1. Zirconium Alloy Fuel Solutions

The zirconium dissolver product stock solution was prepared by dissolving zirconium alloy fuel pieces in sufficient hydrofluoric acid to produce a 5-to-1 mole ratio of fluoride to zirconium. Hydrogen peroxide was added to oxidize the uranium and to prevent precipitation of uranium tetrafluoride. The fuel pieces consisted of zirconium-uranium alloy meat sections clad with Zircaloy-2. These samples averaged about 3.0 weight per cent uranium. The stock solution was 1.6M zirconium, 8.0M fluoride, 1.6M acid, and contained 3.7 grams of uranium per liter. To determine how the fluoride-to-zirconium mole ratio of the dissolver solutions affected the sodium formate precipitation, solutions having a mole ratio greater than 5 were prepared. These increased mole ratios were obtained by addition of concentrated hydrofluoric acid.

2. Equipment and Procedure

Precipitations and boildowns were made in polypropylene equipment using either a mechanically driven Teflon stirrer or a magnetic stirrer with a Teflon stirring bar. Precipitations made at 60°C or at lower temperatures were carried out in tall beakers without attempting to prevent loss due to evaporation; those made at a temperature above 60°C were carried out under total reflux. Except for experiments in which zirconium recovery was studied as a function of stirring time and sodium formate concentration, slurries resulting from precipitant addition (with or without the presence of flocculating agents) were allowed to stir at the precipitation temperature for one-half hour. The slurry was then cooled to room temperature and vacuum filtered through a fine-(4-5.5 microns) porosity sintered glass filter.

3. Analytical Methods

Most of the solids were dissolved for analytical purposes by heating in dilute nitric acid. However, a few of the solids required prolonged heating with various combinations of boric, hydrofluoric, nitric, sulfuric, or hydrochloric acids to dissolve them.

The methods that were used to analyze solutions or solids for zirconium, fluoride, nitrate, uranium, and acid are reported in "The Manual of Analytical Methods of the Control Laboratory at the Idaho Chemical Processing Plant", IDO-14316, edited by M. J. Shepherd, Jr., and J. E. Rein.

Total carbon and hydrogen were analyzed by direct combustion. Flame photometry was used for all sodium analyses.

B. Precipitation of Zirconium and Fluoride with Sodium Formate

1. Effect of Sodium Formate Concentration

The effect of sodium formate concentration on the recovery of zirconium after stirring for one hour at room temperature and at elevated temperature under total reflux is shown in Figure 3. A solution of 3.2M sodium formate was used as the precipitant. In addition, the effect of sodium formate-to-zirconium mole ratio in the range 1.5 to 2.0 was determined at 60°C using a one-half hour stirring time. Zirconium recovery over this range gradually increased from 89.6 per cent at the lower ratio to 97.4 per cent at the upper ratio. These results indicate that a sodium formate-to-zirconium mole ratio of two is adequate for good zirconium removal from solution.

The addition of precipitant as a solution more concentrated than 3.2M would have the desirable effect of decreasing stream volumes. Therefore, precipitations were made using 8.0M sodium formate as the precipitant; however, greater volumes of wash solution were necessary to remove uranium from precipitates formed with 8.0M than with 3.2M sodium formate under identical conditions. Increased wash solution volumes negated the volume decreases realized by the use of 8.0M sodium formate solutions. In addition, slurries formed by the use of 8.0M

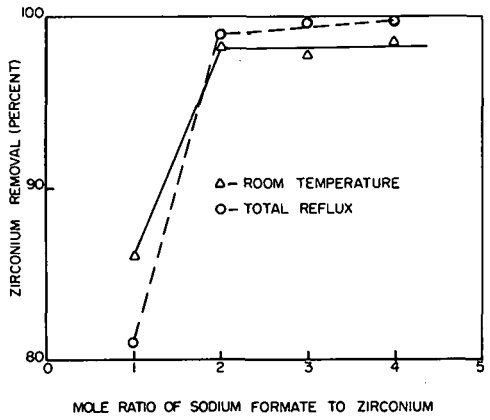

Fig. 3. Effect of Sodium Formate Concentration on Zirconium Recovery

Precipitate was from a solution containing 1.6M Zr, 8.0M F, 1.6M H^+, and 3.7 g/l U. 3.2M sodium formate used as the precipitant. Reaction time was 1 hour.

precipitant were too thick for handling in process equipment. The use of a precipitant concentration between 3.2 and 8M may be feasible; however, no laboratory data were obtained in this concentration range.

2. Effect of Reaction Time

At appropriate time intervals during the reaction between 3.2M sodium formate and uranium-Zircaloy dissolver solution, aliquots of slurry were removed, filtered, and the filtrate analyzed for zirconium. The sodium formate-to-zirconium mole ratio in these experiments was 2 to 1, and two temperatures, room temperature and boiling temperature with total reflux, were used. The precipitation reaction was rapid, as shown in Figure 4; it was complete within 5 minutes over the temperature range studied and was nearly complete in 2 minutes.

3. Wash Solution Studies

Water and 0.1M solutions of 7 different reagents were tested for their ability to remove uranium from precipitates formed by the sodium formate precipitation. Precipitates were formed at 60°C from untreated stock dissolver solutions, from stock dissolver solutions boiled about 10 minutes with 30 per cent hydrogen peroxide added immediately before precipitation, and from solutions made 0.03M in chromic acid prior to precipitation. Others were prepared at room temperature or at refluxing temperatures from untreated solutions. Approximately 8.5 g of residue was washed with four 12.5-ml aliquots of wash solution. Wash solutions tested in addition to water were nitric acid, hydrofluoric acid, formic acid, sodium formate, sodium nitrate, sodium fluoride, ammonium nitrate, ammonium fluoride, and aluminum nitrate. Table 3 summarizes the uranium removal and precipitate dissolution data pertinent to

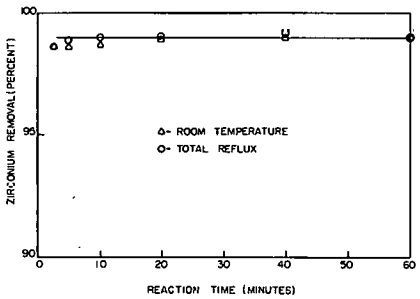

Fig. 4. Effect of Reaction Time on Zirconium Recovery

Precipitate was from a solution containing 1.6M Zr, 8.0M F, 1.6M H^+, and 3.7 g/l U. 3.2M sodium formate used as the precipitant. Sodium formate-to-zirconium mole ratio was 2 to 1.

Table 3

Effect of Various Wash Solutions
on Uranium Removal and Precipitate Solubility

Conditions: Precipitation made from 25 ml of dissolver soln.; 8.5 g of ppt. (weight on a dry basis) was washed 4 times with 12.5 ml of wash soln.

Wash Soln.	Treatment of Dissolver Soln. Prior to Precipitation	Precipitation Temperature °C	Per Cent of Total Uranium Remaining in Washed Precipitate	Zirconium Conc. in the used Wash Solution (M)
Water	none	room temp.	16	-----
Water	soln. made 0.03M in CrO_3	60°C	0.17	0.036
0.1M HNO_3	none	room temp.	20	-----
0.1M HNO_3	none	60°C	8.9	0.036
0.1M HNO_3	none	refluxing temp.	5.3	0.071
0.1M HNO_3	boiled with 1-1/2 ml of H_2O_2	60°C	0.10	0.035
0.1M HNO_3	soln. made 0.03M in CrO_3	60°C	0.16	0.045
0.1M $NaNO_3$	none	room temp.	18	-----
0.1M $NaNO_3$	boiled with 1-1/2 ml of H_2O_2	60°C	0.24	0.021
0.1M $NaNO_3$	soln. made 0.03M in CrO_3	60°C	0.16	0.023
0.1M $NaHCO_2$	none	room temp.	18	-----
0.1M $NaHCO_2$	soln. made 0.03M in CrO_3	60°C	0.24	0.021
0.1M NaF	none	room temp.	18	-----
0.1M NaF	soln. made 0.03M in CrO_3	60°C	0.25	0.029
0.1M $Al(NO_3)_3$	none	room temp.	16	-----
0.1M $Al(NO_3)_3$	soln. made 0.03M in CrO_3	60°C	0.12	0.030
0.1M HCO_2H	none	room temp.	18	-----
0.1M HCO_2H	soln. made 0.03M in CrO_3	60°C	0.19	0.048
0.1M HF	none	room temp.	20	-----
0.1M HF	soln. made 0.03M in CrO_3	60°C	0.18	0.058

each system. About 20 per cent of the uranium originally in the dissolver solution was held tightly by residues formed at room temperature from untreated solutions and could not be washed off with any of the wash solutions. The slow addition of sodium formate solution to dissolver solutions at elevated temperatures with stirring decreased the amount of uranium lost to the solid. When this technique was preceded by oxidizing all of the uranium in solution to the hexavalent state, uranium losses were decreased to less than 0.3 per cent.

Table 3 points out that the water and acid washes dissolved more of the precipitate than did the washes containing sodium, but were not much more effective for uranium removal. Water, the aluminum nitrate wash, and the acid washes contained residue immediately after contact with the precipitate, while the washes containing sodium were stable for at least a day; only a trace of residue was found in the sodium washes after a week.

Studies were also performed to determine the smallest volume of wash solution necessary for effective uranium removal from the precipitates. These experiments were done both with and without the addition of flocculating agent (6 ml of 0.1 per cent, General Mills' Galactasol CAM). Precipitates were formed at 60°C using 50 ml of dissolver solution (0.03M in chromic acid) and 50 ml of 3.2M sodium formate solution. Wash solutions studied were 0.1M solutions of nitric acid, formic acid, sodium formate, and sodium nitrate. The results of successive washings using nitric acid without a flocculating agent as the wash solution are plotted as an equilibrium curve in Figure 5. In the calculation of the operating line, the total weight of precipitate was corrected for the weight of the individual samples removed for analysis. The amount of uranium remaining in the precipitate after one wash was 2.4 per cent. At the end of four washes, the amount remaining had decreased to about 0.2 per cent, and washing had approached the limit of effectiveness. Curves obtained with the other wash solutions were very similar. Both of the sodium washes resulted in about a 2 per cent

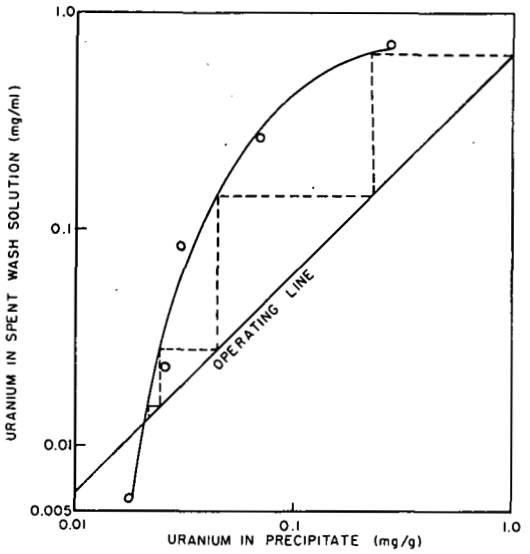

Fig. 5. Uranium Equilibrium Curve for Precipitate Washing

Precipitate: 16 g prepared from 50 ml of STR solution containing 0.03M CrO_3 and 3.7 g/l uranium.

Washes: 25 ml each using 0.1M HNO_3 at 20°C.

Precipitate Treatment: Filtered and dried at 105°C for analysis.

zirconium loss to the wash solutions; the acid washes resulted in a zirconium loss two to three times higher.

4. Effect of Temperature and Flocculating Agents

Laboratory experiments were performed to investigate the effect of precipitation temperature and quantity of flocculating agent on the physical characteristics of the precipitate and the stability of the filtrate. The temperature range investigated was from room temperature to reflux temperature. Flocculating agents studied were potato starch, General Mills' Galactasol CAM, Dow's Separan NP-10, Stein Hall's Jaguar, and Cyanamid's Aerofloc 550 Reagent.

The precipitates formed below 60°C had to be formed by adding the sodium formate precipitant rapidly to prevent the formation of thick immobile slurries. The addition of flocculating agents to this system did not prevent post-precipitation in the filtrates and wash solution.

The precipitates formed at or above 60°C were granular and fast settling, and the physical appearance of the precipitate was independent of the rate of precipitant addition. The addition of 40 mg/liter of slurry of all the flocculating agents (with the exception of potato starch) produced a filtrate free from residue and decreased the solubility of the precipitate in the wash solutions.

The precipitates formed at reflux temperature were granular and fast settling, the filtrates were free of residue, and the precipitates were relatively insoluble in the wash solutions. Flocculating agents

had no apparent beneficial effects.

5. Fluoride and Zirconium Concentrations in Dissolver Solution

Since the fluoride-to-zirconium mole ratio of dissolver solutions may vary, experiments were performed to determine whether an increase in this ratio would reduce zirconium and fluoride removal. Removal was decreased from about 97 to 91 per cent as the fluoride-to-zirconium mole ratio was increased from 5 to 6 (see Table 4). Increasing the fluoride-to-zirconium mole ratio also resulted in a precipitate with higher fluoride-to-zirconium and sodium-to-zirconium mole ratios, even though the sodium formate concentration was constant.

6. Corrosion

Tests were performed to determine the corrosion resistance at 60°C of unwelded coupons of SS 316 (extra low carbon), Carpenter-20, Monel, and Hastelloy F, in the following systems:
(1) slurries produced by the reaction of zirconium dissolver solutions (0.03M in chromic acid) with sodium formate (both with and without flocculating agents), and (2) zirconium dissolver solutions which were 0.03M in chromic acid. These media are expected to bracket all conditions occurring during precipitation. The expected corrosion rates for precipitation-vessel materials should be between the corrosion rate in the slurry to which all precipitant had been added and the corrosion rate in the solution prior to precipitant addition. Sodium formate was added in this corrosion experiment as an 8-molar solution at the rate of 2 moles per mole of zirconium. The flocculating agent used was Stein Hall's Jaguar at a concentration of 6 ml of 0.1 per cent Jaguar for every 50 ml of dissolver solution. Tests lasted 48 hours, and coupons of each material were suspended within, at the surface, and above the slurry. Monel was tested in a nitrogen atmosphere. Table 5 shows that all of these materials except Monel could be considered for the construction of a precipitation vessel.

C. Boildown and Extraction Studies

1. Boildown with Solid Formation, Followed by Extraction

The volume of solution resulting from sodium formate

Table 4

Effect of Fluoride-to-Zirconium Mole Ratio

on Sodium Formate Precipitation

Conditions: Two moles of sodium formate added per mole of zirconium present; precipitation temperature = 60°C; dissolver solution composition originally was 1.6M Zr, 0.03M Cr^{+6}, 3.7 g/l U, 8.0M F and 1.6M H^{+}; F varied by HF addition; precipitate washed 4 times with a volume of 0.1M $NaNO_3$ equal to 1/2 the dissolver solution volume.

F-to-Zr Mole Ratio of Dissolver Solution	Precipitate Composition		% Zr loss to Filtrate	% F loss to Filtrate
	F-to-Zr Mole Ratio	Na-to-Zr Mole Ratio		
5.0	5.0	1.5	2.7	< 3.0
5.5	5.2	2.1	5.4	5.8
6.0	5.7	2.4	6.9	9.0

Table 5

Corrosion During the Precipitation of Zirconium and Fluoride with Sodium Formate

Conditions: Temperature = 60°C; 2 moles of sodium formate added per mole of Zr; dissolver solution composition - 1.6M Zr, 1.6M H^+, 8M F, 0.03M CrO_3, 3.7 g/l U; flocculating agent - 6 ml of 0.1% Stein Hall's Jaguar per 50 ml of dissolver solution; length of test - 48 hours.

Construction Material (unwelded)	Corrosion in Slurry Containing Flocculating Agent (mils/mo)			Corrosion in Slurry Without Flocculating Agent (mils/mo)			Corrosion in Dissolver Soln. which is 0.03M chromic acid (mils/mo)		
	liquid	interface	vapor	liquid	interface	vapor	liquid	interface	vapor
SS 316 (ELC)	0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	0.79	2.1	1.6
Monel	2.5	0.99	0.18	9.1	4.3	0.42	25*	5.8*	< 0.03
Hastelloy F	0.03	0.04	0.02	0.07	0.08	0.07	0.52	0.63	0.32
Carpenter-20	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	0.53	0.33	0.24

*Pitted

precipitation from dissolver solution followed by evaporation of the filtrates and washes can be reduced to 20 per cent of the original dissolver solution volume without the formation of a thick slurry.

a) Boildown Studies

A few studies were performed to determine how boildown was affected by precipitation temperatures, flocculating agents, oxidants, and boildown techniques. Twenty-five milliliters of 3.2M sodium formate solution was added at 60°C or boiling temperature to 25 ml of dissolver solution which was either 0.03 or 0.06M in chromic acid or had been treated with hydrogen peroxide. The precipitations carried out at boiling in the presence of a flocculating agent contained 40 mg of Jaguar per liter of slurry; those carried out at 60°C with a flocculating agent contained 60 mg per liter. The precipitates were filtered and washed 4 times with 12.5 ml of 0.1M sodium nitrate, and the wash solution and filtrate were combined. The resulting solution was boiled down to either 4 or 10 ml, and the resulting slurry filtered and washed again. The 5 ml of solution used to wash the solid from the 4 ml of slurry was combined with the filtrate for analysis; that used to wash the solid from the 10 ml of slurry was kept separate from its filtrate and the two analyzed separately. In experiments involving hydrogen peroxide, the oxidant was added continually during boildown and also used in the 0.1M sodium nitrate wash solutions.

A summary of the uranium removed from precipitates, the fluoride and zirconium removed from filtrates, the solids produced during boildown, as well as other information obtained during these boildown experiments, is shown on Table 6. Chromic acid was much more efficient than hydrogen peroxide in keeping uranium in the hexavalent state; no difference could be discerned between the efficiency of the two chromic acid concentrations used. None of the other variables studied had any appreciable effect on the boildown.

b) Wash Solution Studies

Studies were performed to determine the smallest volume

Table 6

Boildown Characteristics of Filtrates and 0.1M Sodium Nitrate Wash Solutions Produced During Sodium Formate Precipitation

Conditions: Precipitate was formed by adding 25 ml of 3.2M sodium formate solution to 25 ml of dissolver solution; 8.5 gm of sodium formate precipitate was washed four times with 12.5 ml of 0.1M sodium nitrate.

Boildown Techniques	Oxidant Conc. in Dissolver Solution	Precipitation Temperature	Analysis of Process Streams before Boildown: % of total U lost to ppt	Filtrate Zr (M)	Filtrate H^+ (M)	Wash Soln. Zr (M)	Analysis of Process Streams after Boildown: Solids wt in g	Solids % of total U lost to solid	Filtrate Zr (M)	Filtrate F (M)	Filtrate H^+ (M)	Wash Soln. Zr (M)	Filtrate and Wash Soln. Zr (M)	Filtrate and Wash Soln. F (M)	Filtrate and Wash Soln. H^+ (M)	% Zr Removed
A, D	H_2O_2 used(C)	60°C	0.9	0.010	0.94	0.027	0.45	> 2	0.002	< 0.15	0.03	~0.008				99.8
A, F	H_2O_2 used(C)	60°C	1.8	0.015	1.04	0.020	0.45	> 2	0.004	< 0.15	0.5	< 0.01				> 99.7
B, D	H_2O_2 used(C)	boiling	0.6	0.025	0.97	0.025	0.34	1.3					0.004	< 0.08	0.11	99.9
B, E	H_2O_2 used(C)	boiling	0.3	0.023	1.13	0.014	0.33	0.97					< 0.004	< 0.16	0.08N[b]	> 99.9
A, D	0.06M CrO_3	boiling	0.4	0.023	1.0	0.026	0.23	0.07	0.005	< 0.11	1.6	0.007				99.8
A, E	0.06M CrO_3	boiling	0.4	0.018	0.95	0.020	0.24	0.2	0.005	< 0.11	1.5	< 0.01				> 99.7
A, F	0.03M CrO_3	60°C	0.2	0.012	1.15	0.021	0.19	0.008	0.004	< 0.11	0.6	0.015				99.7
B, D	0.06M CrO_3	60°C	0.3	0.014	1.04	0.021	0.35	0.05					0.007	< 0.08	0.74	99.8
B, E	0.03M CrO_3	boiling	0.3	0.022	0.93	0.021	0.23	0.03					0.11	< 0.11	1.3	99.7

A) 52 ml of 0.1M $NaNO_3$ and 25 ml of filtrate was boiled down to 10 ml, the resulting residue was filtered and washed 4 times with 1.5 ml of 0.1M $NaNO_3$; the latter wash solution and filtrate were kept separate.

B) 52 ml of 0.1M $NaNO_3$ and 25 ml of filtrate was boiled down to 4 ml, the resulting residue was filtered and washed 4 times with 1.5 ml of 0.1M $NaNO_3$; the latter wash solution and filtrate were combined.

C) 25 ml of dissolver solution was boiled 10 minutes with 1-1/2 ml of 30 per cent H_2O_2 prior to sodium formate precipitation; 2 ml of 30 per cent H_2O_2 was added a little at a time during the boildown; 0.1M $NaNO_3$ wash solutions were made 2.8M in H_2O_2 before using.

D) No flocculating agent present.

E) Precipitation carried out in the presence of 40 mg of Jaguar per liter of slurry.

F) Precipitation carried out in the presence of 60 mg of Jaguar per liter of slurry.

of 0.1M nitric acid or sodium nitrate necessary for effective uranium removal from the solids which separated out during boildown. The solids for the washing experiments were formed by adding, at 60°C, 50 ml of 3.2M sodium formate to an equal volume of dissolver solution, 0.03M in chromic acid. The resulting slurry was stirred for one-half hour, the precipitate filtered and washed with four 25-ml aliquots of 0.1M sodium nitrate. Four and six-tenths milliliters of 15.7M nitric acid was added to the combined filtrate and wash solution, and the resulting solution was boiled down to 10 ml and filtered. The 0.7 g of residue separating out during evaporation was washed various times with fresh 2-ml aliquots of wash solution. The results of uranium analysis of the liquid and solid phases were plotted as equilibrium curves similar to that shown in Figure 5. At the end of three washes, the uranium lost to the solids decreased to about 0.03 and 0.1 per cent when 0.1M nitric acid and sodium nitrate were used, respectively, and the washing approached the limit of effectiveness as shown by equilibrium curves. A zirconium loss of 0.1 and 0.4 per cent to the wash solution (due to the solubility of the solid) occurred when the solids were washed 3 times with 2 ml of 0.1M sodium nitrate or nitric acid, respectively. One-tenth molar nitric acid is the more effective wash for removing uranium from the solids. Since the used wash solution can be kept separate from the filtrate and added to successive combined filtrates and wash solutions prior to boildown, the somewhat greater solubility of residue in nitric acid is not of great importance.

c) Solution Adjustment Prior to Extraction

Several studies were performed to determine the amount of nitric acid in the boildown which would lead to low fluoride and zirconium supernate concentrations and also to uranium distribution coefficients greater than 10 when the filtrate was contacted with 10 per cent TBP in Amsco. In these experiments, the preparation of the solid containing zirconium and fluoride and the washing of the resulting precipitate was identical to that described for the wash solution studies of part VI-B-3. The wash solutions and filtrates were combined, various amounts of 15.7M nitric acid were added, the

resulting solution boiled down to a volume equal to 20 per cent of the dissolver solution volume, and the slurry filtered. Some of these filtrates were extracted with no further treatment. In some cases, nitric acid and aluminum nitrate or aluminum nitrate alone were added prior to TBP extraction.

As shown in Table 7, the addition of 72 millimoles of nitric acid to 100 ml of wash solution plus 80 ml of filtrate prior to boildown results in a solution that, when evaporated to the appropriate volume and filtered, yields a filtrate containing almost no zirconium and fluoride ions and from which uranium can be effectively extracted with TBP. However, addition of varying amounts of aluminum nitrate or aluminum nitrate and nitric acid is required to stabilize the solution. The effect of these additions is shown in Table 7; 4.5 millimoles of aluminum nitrate or 0.45 millimole of aluminum nitrate and 16 millimoles of nitric acid stabilizes the solution and provides good extraction characteristics. The combination of aluminum nitrate and nitric acid is preferable, since it adds less non-volatile material to the system.

2. Boildown Without Solid Formation, Followed by Extraction

During the boildown experiments described in Table 7, it was observed that the allowable concentration factor before the onset of solids formation increased with increasing nitric acid addition. Accordingly, some experiments were done to study boildown conditions leading to stable evaporator products from which no solids formed. Precipitation conditions were as summarized in Table 7; 11.4 ml of 15.7M nitric acid was added to the supernate before boildown. Varying amounts of aluminum nitrate were also added, either before or after concentration.

The smallest stable concentrate volumes occurred when the addition of aluminum nitrate was made after evaporation and when a flocculating agent (Jaguar) was used during the precipitation. In experiments using 0.1M nitric acid as wash solution, slightly smaller stabilized volumes could be obtained than when 0.1M sodium nitrate was used under the same conditions. Optimum results were obtained for an evaporator

Table 7

Boildown and Extraction Characteristics of Filtrates Produced During Sodium Formate Precipitation Followed by a 0.1M Nitric Acid or Sodium Nitrate Wash

Conditions: Precipitate was formed by adding 50 ml of 3.2M sodium formate solution to 50 ml of dissolver solution (0.03M in chromic acid) with stirring for 1/2 hour at 60°C; 16 gm of sodium formate precipitate was washed 4 times with 25 ml of 0.1M $NaNO_3$; HNO_3 was added to the combined 80 ml of filtrate and 100 ml of wash solution and the resulting solution boiled down to 10 ml.

Wash Soln. Used	Mls of 15.7M HNO_3 added prior to boildown	Reagents added to 10 ml of boildown product	Analysis of Boildown Product After Reagent Addition				48-hour stability of boildown product	Extraction of boildown product with 10% TBP in Amsco		
			Zr (M)	H^+ (M)	F^- (M)	Na^+ (M)		U in Aqueous (g/l)	U in Organic (g/l)	E $\frac{o}{a}$
HNO_3	2.8	none	0.023	0.76	--	--	unstable	2.97	12.21	4.1
HNO_3	4.1	none	0.021	0.46	--	--	unstable	1.01	12.55	12.4
		0.2 ml of 2.26M $Al(NO_3)_3$	0.007	0.62	< 0.10	2.7	unstable	4.14	10.84	2.6
HNO_3	5.5	none	0.20	0.63	--	--	unstable	0.66	11.97	18
HNO_3	6.8	none	0.17	1.10	--	--	unstable	0.49	12.28	25
HNO_3	8.1	none	0.16	1.81	--	--	unstable	0.42	9.50	23
HNO_3	10.5	none	0.23	4.3	--	--	unstable	1.68	13.97	8.3
$NaNO_3$	4.6	none	0.021	0.46	--	--	unstable	1.01	12.55	12.4
		0.2 ml of 2.26M $Al(NO_3)_3$	0.005	0.69	< 0.10	3.2	stable	4.24	10.40	2.5
		0.05 ml of 2.26M $Al(NO_3)_3$	-----	----	--	--	unstable	----	-----	----
		1 ml of 2.26M $Al(NO_3)_3$	< 0.005	0.81	< 0.10	--	unstable	2.03	11.69	5.8
		2 ml of 2.26M $Al(NO_3)_3$	-----	0.56	--	--	stable	0.92	9.27	10
		3 ml of 2.26M $Al(NO_3)_3$	-----	0.38	--	--	stable	0.22	10.16	46
		4 ml of 2.26M $Al(NO_3)_3$	-----	0.29	--	--	stable	0.20	8.75	44
		0.2 ml of 2.26M $Al(NO)_3$ 1 ml 15.7M HNO_3	-----	0.77	--	--	stable	0.33	11.71	35
		0.2 ml of 2.26M $Al(NO_3)_3$ 2 ml 15.7M HNO_3	-----	1.36	--	--	stable	0.34	10.84	32

feed composed of the following: 80 ml of filtrate containing a flocculating agent; 100 ml of 0.1M nitric acid washes; and 11.4 ml of 15.7M nitric acid. After concentration of such a solution to 10 ml, the addition of 8 ml of 2.26M aluminum nitrate before cooling produces an extraction feed of the following composition: 0.25M Zr, 1.0M F, 2.2M H^+, 3.1M Na^+, 1.0M Al^{+3}, and 8 g/l U. Such a solution is stable for at least two weeks, and a uranium extraction coefficient of 27 was achieved when it was contacted with an equal volume of 10 per cent TBP in Amsco. This method of boildown avoids any solids formation during the evaporation step, but results in a greater extraction volume and higher concentrations of aluminum, fluoride, and zirconium in the extraction feed.

3. Corrosion

The corrosion resistance of unwelded coupons of SS 316 (extra low carbon), Carpenter-20, and Hastelloy F was tested during concentration. Evaporations were approximately 48 hours in duration, and coupons were immersed within the media and suspended above the media. In one series of boildowns, 13.8 ml of 15.7M nitric acid was added to 240 ml of filtrate plus 300 ml of 0.1M sodium nitrate (prepared as described in Table 7, using three times the volumes), and the resulting solution boiled down to 48 ml. In the other series, 34.2 ml of 15.7M nitric acid was added to 258 ml of filtrate containing 18 ml of 0.1 per cent Jaguar plus 300 ml of 0.1M nitric acid wash solution, and the resulting solution boiled down to 48 ml. Coupons tested in the former evaporations showed no discernible corrosion; those tested in the latter system (immersed within the media) showed corrosion rates varying from 2.8 to 4.2 mils per month (see Table 8).

Table 8

Corrosion During the Boildown of Filtrates and Wash Solutions Formed from the Precipitation of Zirconium and Fluoride with Sodium Formate

Construction Material (unwelded)	Boildown Description	Length of Boildown (hrs)	Corrosion mils/mo	
			Liquid	Vapor
Stainless Steel 316(ELC)	A	53	< 0.04	< 0.04
Stainless Steel 316(ELC)	B	48.5	4.2	0.53
Hastelloy F	A	48	< 0.04	< 0.04
Hastelloy F	B	48.5	3.5	0.43
Carpenter-20	A	44	< 0.04	< 0.04
Carpenter-20	B	48.5	2.8	0.76

A. 240 ml of filtrate (prepared by adding 150 ml of 3.2M sodium formate at 60°C to 150 ml of dissolver solution - 0.03M in CrO_3) plus 300 ml of 0.1M $NaNO_3$ used to wash the precipitate plus 13.8 ml of 15.7M HNO_3 boiled down to 48 ml.

B. 258 ml of filtrate (prepared by adding 150 ml of 3.2M sodium formate at 60°C to 150 ml of dissolver solution (0.03M in CrO_3) in the presence of 18 ml of 0.1 per cent Jaguar) plus 300 ml of 0.1M HNO_3 used to wash the precipitate plus 34.2 ml of 15.7M HNO_3 boiled down to 48 ml.

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