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MODIFICATIONS FOR THE STR FUEL RECOVERY PROCESS

O. W. Parrett

December 15, 1960

PHILLIPS
PETROLEUM
COMPANY

ATOMIC ENERGY DIVISION

NATIONAL REACTOR TESTING STATION
US ATOMIC ENERGY COMMISSION

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IDAHO CHEMICAL PROCESSING PLANT

Chemical Development Branch

MODIFICATIONS FOR THE STR FUEL RECOVERY PROCESS

O. W. Parrett

Submitted: December 1, 1960

PHILLIPS PETROLEUM COMPANY
Atomic Energy Division
Idaho Falls, Idaho
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U. S. ATOMIC ENERGY COMMISSION - IDAHO OPERATIONS OFFICE

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IDAHO CHEMICAL PROCESSING PLANT
MODIFICATIONS FOR THE STR FUEL RECOVERY PROCESS

by

O. W. Parrett

A B S T R A C T

In a program directed toward the optimization of the process chemistry of the STR hydrofluoric acid method of reprocessing zirconium-uranium alloy fuels, it has been shown that the process can be modified to dissolve homogeneously, fuels of higher uranium content by either hydrogen peroxide oxidation or dilution of the dissolver solution. Rate of corrosion of Monel was acceptable with both methods of dissolution. Phase and stability studies of the solvent extraction feed and waste solutions indicated that higher concentrations of zirconium and uranium could be used in the process streams. Metastable solutions were obtained when the currently used STR raffinate solutions were evaporated. This operation was not favored for flowsheet use. The batch and continuous dissolution and solvent extraction flowsheets are given embodying the principal results of this study.

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I. SUMMARY

The STR process for enriched uranium-zirconium fuels utilizes hydrofluoric acid for dissolution and aluminum nitrate salting for solvent extraction. The abundant plant scale experience and well-developed technology associated with this process, as well as the large potential usage of this fuel in military and power reactors, have necessitated the optimization of the process chemistry. The objectives of this optimization included developing dissolution flowsheets for fuels of up to three weight percent (overall) uranium, and defining the regions of stability of the extraction feed and stored raffinate systems so that the most economical compositions could be used for these streams.

The batch dissolution studies showed that fuels containing up to two overall weight percent uranium could be homogeneously dissolved by obtaining a dissolver solution so dilute that the uranium tetrafluoride solubility, about two grams of uranium per liter, is not exceeded. Three overall weight percent uranium fuels can be homogeneously dissolved by adding an oxidant for the uranium. The calculated terminal concentrations of two successful oxidants were 1.5M nitric acid and 0.06M hydrogen peroxide. The Monel corrosion rates were about 2 mils per batch when using the nitric acid oxidant, 0.02 to 0.05 mils per batch with hydrogen peroxide, and 0.003 to 0.02 mils per batch with the dilute process.

Samples for phase studies were prepared containing varied concentrations of zirconium, aluminum, fluoride, nitrate, and hydrogen ion, to represent the extraction feed and stored waste solutions. The changes of the solutions at 25°C were observed for 550 days and the solid phases were identified. From these studies, a more concentrated extraction feed composition, 0.8M zirconium with 0.5M aluminum instead of the previously used 0.55M zirconium with 0.75M aluminum nitrate, was found to be practical for a chemical extraction flowsheet. The permanently stored liquid waste could be reduced in volume to 83 percent of that produced by the current flowsheet with an equivalent degree of protection from precipitation.

Additional studies were made of the feasibility of evaporation of the current flowsheet raffinate with the objective of decreasing stored waste volumes. Studies of the effect of wide variations in raffinate solution composition and the temperature of evaporation on the stability of the concentrate product showed that metastable solutions resulted from evaporation.

Based upon considerations of vessel corrosion and flowsheet simplicity, it was concluded that the dilute method of dissolution would be preferred for fuels containing up to two percent uranium, and that the hydrogen peroxide oxidation method of dissolution would be preferred for fuels containing up to three percent uranium. Increased uranium through-put capacity can be obtained by utilizing the more concentrated extraction feed. More concentrated waste storage solutions can be obtained by using solution compositions determined to be stable in these studies. Considering uranium capacity, corrosion, and flowsheet and equipment simplicity, it was found to be more practical to use concentrated extraction feeds rather than to evaporate column raffinate solutions.

Batch and continuous dissolution and solvent extraction flowsheets were written embodying these findings to serve as a basis for optimization of plant production.

II. INTRODUCTION

There are numerous possible ways of treating irradiated Zircaloy-clad, zirconium-uranium or similar fuels, but at present, there is only one proven process which has been operated on a production basis, yielding good uranium recovery and decontamination. This is the STR process at the Idaho Chemical Processing Plant which has been described in some detail during the proceedings of the Second United Nations International Conference on the Peaceful Uses of Atomic Energy.⁽¹⁾ The currently proven STR process involves batch dissolution of the zirconium in hydrofluoric acid, oxidation of tin in the dissolver solution by very dilute nitric acid, adjustment of salting strength and complexing of fluoride ion by the addition of aluminum nitrate, extraction of the uranium with 10 percent tributyl phosphate, solvent recovery, and raffinate storage without further treatment.

Although hydrofluoric acid dissolver product solutions of 2.0M zirconium may be used, the extraction column feed and raffinate were originally, and still are, specified at 0.55M zirconium on the basis of the original column feed stability data.^(1,2,3) This results in a relatively large waste bulk and thus represents an attractive area for economic improvement. In addition, the limited solubility of uranium tetrafluoride in the dissolver product solution would apparently cause incomplete uranium dissolution at normal flowsheet zirconium concentrations with fuels having overall compositions greater than 1.0 to 1.5 weight percent uranium.* The presence of undissolved uranium represents a serious flowsheet and safety limitation in either batch or continuous dissolution.

* In this study, the uranium percentage is defined as the weight of the uranium present in the fuel times 100 and divided by the total weight of the fuel. This total fuel weight includes the cladding, ribs, and the meat of the fuel.

After a careful review of the design data, the plant experience, and the anticipated compositions of future fuel loadings, it was concluded that beneficial process modifications could be made in the following areas:

- (1) obtaining the homogeneous dissolution of up to 3 weight percent uranium fuel compositions,
- (2) increasing the zirconium concentrations to be extracted and stored by determining very completely the relationships between composition, hold-up time and stability, and
- (3) studying the feasibility of concentrating the raffinate and determining if certain early, limited observations on concentrate stability were valid.

With the above information available, flowsheets could be written to utilize a continuous dissolution method and to handle fuels containing up to 3 weight percent uranium. A raffinate could still be produced having less volume than was obtained using the existing STR flowsheets.

III. HOMOGENEOUS DISSOLUTION OF TWO TO THREE PERCENT URANIUM-ZIRCONIUM FUELS

The limited solubility of uranium tetrafluoride in the dissolver system restricts the existing flowsheet to the reprocessing of fuels containing up to 1.5 overall weight percent uranium. However, a homogeneous batch dissolution can be obtained either by adding an oxidant, such as nitric acid, to oxidize sufficient uranium to the more soluble uranium(VI) or by obtaining a dissolver solution so dilute that the uranium tetrafluoride is soluble.⁽⁴⁾ The use of hydrogen peroxide as an oxidant was suggested by preliminary work at ORNL.⁽⁵⁾

A. Experimental Procedure for Oxidation Studies

A series of bench scale dissolutions were performed using fuel coupons containing 2.5 and 3.0 weight percent uranium. In this study, the uranium percentage is defined as the weight of the uranium present in the fuel times 100 and divided by the total weight of the fuel. The fuel specimens consisted of zirconium-uranium alloy as the meat section, which was clad with Zircaloy-2, and bound on the side edges with Zircaloy-2.

These sample coupons were dissolved in a cycle which allowed one hour for cladding dissolution by hydrofluoric acid and 1.5 hours for the dissolution of the meat in mixed hydrofluoric acid and oxidant. An example of this cycle is as follows: In the cladding dissolution step, a 30 gram fuel sample and a Monel coupon were placed in a Teflon dissolver which contained 94 milliliters of water. The solution was allowed to boil (94°C at the local atmospheric pressure of 640 mm of mercury), and then one half of the hydrofluoric acid, 57 milliliters, 14.2M, was added during

the next hour in 10 milliliter aliquots at 10 minute intervals. In the meat dissolution step, the oxidant was mixed with the remaining 60 milliliters of hydrofluoric acid, and this mixture was added during the next 1.5 hours in 7 milliliter aliquots at 10 minute intervals. A one hour digestion period completes the 3.5 hour dissolution cycle. The final volume obtained is about 195 milliliters. Periodic observations were made of the dissolver solutions as to the amount of undissolved fuel, presence or absence of precipitates, and the color of the dissolver solution.

The oxidant concentrations reported were obtained by calculating terminal concentrations assuming no oxidant loss or consumption.

In all the experiments, boric acid was added at the level of 0.5 grams of boron per liter of dissolver solution anticipating the need for a criticality safeguard. Sufficient fluoride was added to react with the boric acid to form a fluoboric acid without reducing the desired fluoride-to-zirconium mole ratio.

Fluoride analyses were performed by means of a pyrohydrolysis technique with a current of moist oxygen in a quartz combustion tube. The liberated hydrofluoric acid was titrated with standard thorium nitrate. Zirconium was determined by amperometric titration of a sulfuric acid solution of the sample with cupferron. Any solid materials observed were analyzed by means of emission spectroscopy to determine if the solids were uranium or zirconium compounds.

B. Selection of the Fluoride-to-Zirconium Mole Ratio

A batch dissolution time of about 3.5 hours was found in plant operation to give the maximum dissolution rate without creating a serious hydrogen off-gas problem. It was necessary to determine the fluoride-to-zirconium mole ratio which would produce a complete dissolution in this specified time. In Figure 1, the percentage of fuel dissolved in 3.5 hours is plotted against the fluoride-to-zirconium mole ratio. The dissolution reagents are added in increments even in these batch dissolutions, and therefore, the maximum instantaneous fluoride concentrations had to be considered. The maximum instantaneous fluoride concentration was 1.36M for the dissolution using the oxidation method and 0.53M fluoride using the dilution method. From the data in Figure 1, it was evident that a fluoride-to-zirconium mole ratio of between 5.0 and 5.2 is sufficient for complete dissolution using the dilution process. The presence of solid uranium tetrafluoride interfered with the dissolution when inadequate oxidant was used. However, it was thought that the use of about a 5.2 fluoride-to-zirconium mole ratio would produce a complete dissolution with either method.

C. Homogeneous Dissolution Using Nitric Acid as the Oxidant

Zirconium fuels containing three weight percent uranium were dissolved homogeneously when 1.5M nitric acid was used as the oxidant. These dissolutions produced a dissolver solution containing 1.6M zirconium and 8.0M fluoride ion. A small amount of uranium tetrafluoride, too small to isolate and weigh, was produced with 1.0M nitric acid as the oxidant.

Fig. 1 - Dissolution of STR Fuels in Hydrofluoric Acid. The completeness of batch dissolution in 3.5 hours at 94°C and 640 mm pressure is shown as a function of the fluoride-to-zirconium mole ratio. The oxidation method o o o had a maximum instantaneous free fluoride concentration of 1.36M. The dilution method • • • had a maximum instantaneous free fluoride concentration of 0.53M.

Therefore, it was concluded that plant testing may be required to determine exactly the amount of nitric acid needed for a homogeneous dissolution in the plant equipment. The Monel corrosion rates obtained from these scoping studies were found to be 0.07 mils per batch with 1.0M nitric acid oxidation, while corrosion of 2.0 mils per batch was found with 1.5M nitric acid oxidation. The dissolver compositions for these two levels are given in Table 1. The results with these and other nitric acid concentrations studied are given in Appendix 1.

D. Homogeneous Dissolution Using Hydrogen Peroxide as the Oxidant

Homogeneous batch dissolutions of zirconium fuel samples containing 2.5 percent uranium were obtained using hydrogen peroxide as the oxidizing agent. The two-step dissolution procedure was followed, but care was taken to add the oxidizing mixture below the surface of the boiling dissolver solution in order to prevent the premature decomposition of the peroxide when it came in contact with the boiling liquid. Homogeneity was obtained with 0.06M hydrogen peroxide and a small amount of precipitate was found with 0.05M peroxide. See Table 1 and Appendix 1 for the results of these and other hydrogen peroxide oxidations.

The solutions were analyzed for residual peroxide by titrating with potassium permanganate. Manganese(II) is added to speed the reaction and boric acid is added to complex the fluoride which otherwise interferes. The residual peroxide was found to be less than 0.005M.

Corrosion data obtained by means of weight loss showed that 0.06M hydrogen peroxide corroded the Monel coupons about 0.02 to 0.05 mils per batch.

Table 1

HOMOGENEOUS DISSOLUTION OF STR FUEL BY OXIDATION

In all experiments, boric acid was added at the level of 0.5 grams boron per liter of dissolver solution. The dissolution temperature was 94°C at atmospheric pressure of 640 mm of mercury.

Oxidant	Oxidant Conc. M	Dissolver Product			Observed Precipitation	F/Zr Ratio	Monel Corrosion in Liquid Phase mils/batch	Percent Uranium Fuel
		Zr M	F M	U g/l				
HNO ₃	1.5	1.64	8.3	5.0	None	5.1	2.0	3.0
HNO ₃	1.0	1.5	8.0	4.4	Small amt. (1)	4.9	0.07	3.0
H ₂ O ₂	0.06	1.49	9.18	3.72 (6)	None	6.3	0.05	2.4
H ₂ O ₂	0.06	1.60	9.28	3.96 (6)	None	5.7	0.03	2.5
H ₂ O ₂	0.06	1.62	9.0	4.08 (6)	None	5.7	0.02 (3)	2.6
H ₂ O ₂	0.05	1.60	9.18	3.87	Small amt. (1)	5.7	---- (2)	2.5
CrO ₃	0.06	1.5	8.14	3.91	None	5.4	0.1	2.5
CrO ₃	0.03	1.58	8.30	3.81	Small amt. (1)	5.26	---- (2)	2.4
KMnO ₄	0.04	1.4	7.75	3.6	No UF ₄ (4)	5.4	0.2	2.5
KMnO ₄	0.01	1.72	7.89	3.27	Small amt. (5)	4.59	---- (2)	2.1

- (1) The amount of solid was too small to recover.
 (2) Due to the solid formed, a weight gain was experienced.
 (3) This was a welded Monel coupon.
 (4) There was no uranium tetrafluoride, but a large quantity of manganese dioxide did precipitate.
 (5) This contained a small amount of uranium tetrafluoride and no manganese dioxide.
 (6) Uranium(IV) analyses were 1.03, 1.26, 0.86 grams per liter respectively.

E. Homogeneous Dissolution Using Chromic Acid or Potassium Permanganate as the Oxidant

A completely homogeneous dissolution was obtained with 0.06M chromic acid while a small amount of uranium tetrafluoride residue was observed in the dissolver solution obtained with 0.03M chromic acid. However, the corrosion rates experienced with 0.06M chromic acid were much higher than those resulting from the use of hydrogen peroxide as the oxidant, see Table 1.

The dissolution using 0.04M potassium permanganate produced a solid phase that was manganese dioxide with no uranium tetrafluoride present. However, the dissolution using 0.01M potassium permanganate produced a solid phase that was uranium tetrafluoride with no manganese dioxide present. These data indicate that a homogeneous dissolution could be accomplished somewhere within this limited oxidant concentration range.

F. Dilute Process*

The dilute process flowsheet⁽⁶⁾, which utilizes only uranium tetrafluoride solubility for maintaining homogeneity, was studied with respect to uranium solubility, heel buildup, and the corrosion of Monel.

* A dilute process flowsheet is given in Table 14.

A series of bench scale dissolutions were made in which coupons of 1.5 to 2.5 percent uranium alloy were dissolved in a cycle which allowed 4.5 hours for the fuel dissolution with hydrofluoric acid and 1.0 hours for the dissolution of the tin with 0.016M nitric acid. The reagents were added incrementally to the boiling solution. A dilute system is produced which is 1.1M zirconium, 0.42M hydrogen ion, and 4.8M fluoride. This dilute dissolver solution is then adjusted with concentrated reagents to produce the standard feed. In the experiments using 1.5 percent uranium fuel, the hydrofluoric acid was added to the first experiment in the first hour, while in the second experiment, it was added over a two hour period. The dissolver was opened and the solutions were observed at the end of 2.5 hours. The amount of undissolved fuel was approximately the same in both experiments or about 1 gram of the original 20.0 grams. The corrosion and heel buildup data are tabulated in Table 2 for this dilute process. Fuel samples containing 2.2 and 2.5 percent uranium in Zircaloy were studied for uranium solubility. The dissolver solution from 2.2 percent uranium fuel was completely homogeneous. The dissolver solution appeared to be homogeneous at the completion of one of the dissolutions for the 2.5 percent uranium fuel, however, small amounts of precipitate were observed 17 hours later. This process will be adequate for 2 to 2.2 percent fuels, but not for 2.5 percent uranium material. The Monel corrosion was 0.003 to 0.02 mils per batch.

Table 2

HOMOGENEOUS DISSOLUTION OF STR FUEL BY DILUTION

In experiments 42 and 43, boric acid was added at the level of 1.0 gram of boron per liter of dissolver solution. In all the other experiments, boric acid was added at the level of 0.5 grams of boron per liter of dissolver solution. Dissolution temperature was 94°C at an atmospheric pressure of 640 mm mercury.

Experiment Number	Dissolver Product Composition						Observed UF_6 Ppt.	F/Zr	Heel After 3.5 Hours Percent	Monel Corrosion in Liquid Phase mils/batch
	Zr M	F M	U Percent	U Total g/l	U(IV) g/l	U(VI) g/l				
36	1.13	4.93	2.5	2.72	2.16	0.56	Small amt.	5.2	0.4	0.021
37	1.04	5.09	2.5	2.62	2.29	0.33	Small amt. ⁽¹⁾	4.8	2.0	0.003
38	0.96	4.79	2.2	2.33	2.03	0.30	None	4.36	2.4	0.009 ⁽²⁾
42	1.45	6.09	2.1	2.15	1.98	0.17	None	4.75	3.1	0.003 ⁽²⁾
43	1.23	5.34	1.7	1.76	1.63	0.13	None	4.34	2.0	0.004 ⁽²⁾

(1) Precipitation occurred 17 hours after end of dissolution.

(2) Welded Monel coupons.

G. Uranium Tetrafluoride Solubility

In the original flowsheet work⁽²⁾, it was shown that no more than 1.7 grams per liter of uranium as uranium tetrafluoride is soluble in a system obtained from the dissolution of simulated fuel when the fluoride-to-zirconium ratio was between 4.5 and 5.5 moles per mole. In the recent work in which actual fuel dissolutions were made, about 2.0 grams per liter of uranium as uranium tetrafluoride was found to be soluble in essentially the same dissolver system. See Table 2 and Appendix 2.

H. Uranium(IV) and Uranium(VI) Distribution

The data of Tables 1 and 2 show the uranium(IV) and uranium(VI) concentrations from the processing of 2.0 and 2.5 percent uranium fuels by both the oxidation and the dilution methods.

These uranium analyses were obtained by adding a 2.0N acid-deficient salting solution composed of 2.8M aluminum nitrate and 0.025M tetrapropyl ammonium nitrate. This salted system is then contacted with hexone which extracts only the uranium(VI). The quantity of extracted uranium(VI) is determined by colorimetric analysis. The uranium(IV) remaining in the original sample is oxidized to uranium(VI) with ammonium persulfate. This oxidized uranium is then extracted in the same manner.

These distribution data show that a homogeneous dissolution can be obtained from 2.0 to 2.5 percent uranium fuel as long as the uranium(IV) concentration does not exceed 2.0 grams per liter of dissolver solution. With 0.06M hydrogen peroxide, about 1.0 gram of uranium(IV) per liter of dissolver solution is produced in processing 2.5 percent uranium fuels, see Table 1, Footnote 6, and therefore, there is little danger of exceeding the uranium(IV) solubility limit. However, with the dilute process, essentially all of the uranium is present as uranium(IV) and therefore, there is danger of exceeding the solubility limit when this method is applied to the processing of greater than 2.0 percent uranium fuels. A more complete table of uranium(IV) and uranium(VI) concentration levels is given in Appendix 2.

I. Monel Corrosion

In order to obtain approximately the same Monel surface-to-volume ratio in the laboratory as is experienced in the existing plant batch dissolver, the dissolutions were performed in a Teflon dissolver in the presence of a Monel coupon. Each Monel coupon was initially cleaned with a five percent hydrofluoric acid solution. After dissolution, the coupons were washed with water, dried under a heat lamp for one hour, cooled and weighed.

In some cases when the Monel was coated with the uranium tetrafluoride precipitate, it was impossible to obtain a weight loss due to the tenacious adherence of the precipitate, and as a result, no corrosion data were reported. In most cases the coupons had not been mechanically treated, however, some welded coupons were tested and these are noted in the tables. More detailed corrosion studies are being undertaken.

J. Instantaneous Oxidant Levels

Providing the presence of an oxidant does not corrode the dissolver at a prohibitive rate, oxidation during dissolution could be applied to a continuous dissolution process. Also, by assuming that there were no effective residual oxidant, an estimate of the level of oxidant needed in a continuous dissolution can be obtained from these batch dissolution studies.

Based upon the above assumption, the data obtained from the batch dissolution studies showed that approximately 0.01M hydrogen peroxide would be needed for a completely homogeneous continuous dissolution of 3.0 percent uranium fuels. The nitric acid level was obtained in the same way and was found to be 0.3M.

K. Conclusions

By adding an oxidizing agent during the dissolution to insure homogeneity, the STR process can be modified to handle fuels containing up to 3.0 overall weight percent uranium. Also, a homogeneous dissolution of between 2.0 and 2.2 percent by weight uranium fuels can be obtained by producing a dissolver solution so dilute that the uranium tetrafluoride is soluble.

The calculated terminal concentrations of oxidants for batch dissolutions were determined. These are between 1.0 and 1.5M in nitric acid, 0.05 and 0.06M in hydrogen peroxide, 0.03 and 0.06M chromic acid, and 0.01 and 0.04M in potassium permanganate.

The limit of solubility of uranium tetrafluoride in this system was found to be about 2.0 grams per liter.

The corrosion of Monel was determined by weight loss. These corrosion rates were found to be 0.1 to 2.0 mils per batch for the nitric acid oxidant, 0.02 to 0.05 mils per batch for the hydrogen peroxide process, and 0.003 to 0.02 mils per batch for the dilute process.

IV. THE STABILITY OF THE EXTRACTION COLUMN FEED

One method of improving the original STR process flowsheet is to obtain a more concentrated and yet stable extraction feed. This modification would in turn increase the uranium capacity of a given extraction system and reduce the waste volume.

Original stability data^(1,2,3) were obtained from extraction feeds which were aged for a four-day period. The extreme boundaries of the stability regions of the system were not clearly defined by this short-term data and no data were available for a system that had aged for a period of greater than four days.

In previous studies^(5,6) with raffinate solutions that were produced from hydrofluoric acid dissolutions, it was found that increasing the hydrogen ion concentration enhanced the short-term, ten-day stability and it was indicated that a reduction in the aluminum concentration could improve the long-term, 150-day stability.

The purpose of this current study was (1) to utilize the above information and determine the effect of variation in the composition of the system upon the stability of the extraction process feeds, (2) to define more completely the boundaries of the stability regions as affected by aging, and (3) to determine the position of the existing flowsheet in these stable regions.

A. Experimental

The initial compositions of a series of extraction process feed solutions are shown in Table 3. These feeds were obtained from hydrofluoric acid dissolutions of reactor-grade zirconium and these dissolver solutions adjusted to the composition desired. The initial aluminum nitrate concentrations were held constant at three levels: 1.0M, 0.75M, and 0.5M. The initial fluoride ion concentration was varied from 3.2M to 6.2M and the hydrogen ion concentration varied correspondingly from 0.5M to 3.5M in each level of aluminum nitrate. The zirconium concentration was initially constant at 0.75M and 0.8M. These samples were allowed to reach equilibrium at room temperature. Periodic samples of the supernatant liquid were taken for analysis of the zirconium concentration. Emission spectroscopy analyses of the solids showed them to be compounds of aluminum and zirconium, however, x-ray diffraction patterns obtained from these solids disclosed that the crystalline compounds present were the zirconium tetrafluoride trihydrate, and another, as yet, unclassified zirconium compound which is thought to be zirconium hydroxy trifluoride monohydrate. (7)

Table 3
STR FEED STABILITY STUDIES

STR feed solutions of the compositions shown were prepared from dissolver solution and allowed to stand for up to 550 days.

Sample No	Initial Composition (moles/l)					Final Equilibrium Composition (M)		
	Zr	F	Al	H ⁺	NO ₃	Zr	F	Al
11	0.75	3.75	0.75	1.05	2.55	0.603	3.4	0.75
12	0.75	4.00	0.75	1.30	2.55	0.514	3.15	0.75
13	0.75	4.25	0.75	1.55	2.55	0.453	3.4	0.75
14	0.75	4.50	0.75	1.80	2.55	0.462	3.5	0.70
15	0.75	4.75	0.75	2.05	2.55	0.488	3.5	0.52
16	0.75	5.00	0.75	2.30	2.55	0.513	3.2	0.39
17	0.75	5.25	0.75	2.55	2.55	0.544	2.9	0.25
18	0.8	3.2	0.75	0.51	2.56	0.476	2.55	0.74
19	0.8	3.7	2.75	1.01	2.56	0.595	3.20	0.75
20	0.8	4.2	0.75	1.51	2.56	0.467	3.34	0.73
21	0.8	4.7	0.75	2.01	2.56	0.473	3.19	0.46
22	0.8	5.2	0.75	2.51	2.56	0.526	3.16	0.19
23	0.8	5.7	0.75	3.01	2.56	0.779	4.76	0.18
24	0.8	6.2	0.75	3.51	2.56	0.79	5.13	0.12
25	0.8	3.2	0.5	0.51	1.81	0.60	3.07	0.471
26	0.8	4.2	0.5	1.51	1.81	0.666	4.17	0.472
27	0.8	5.2	0.5	2.51	1.81	0.777	4.02	0.182
28	0.8	6.2	0.5	3.51	1.01	0.785	5.85	0.130
29	0.8	3.2	1.0	0.51	3.31	0.433	2.52	1.04
30	0.8	4.2	1.0	1.51	3.31	0.408	3.14	0.99
31	0.8	5.2	1.0	2.51	3.31	0.319	2.34	0.53
32	0.8	6.2	1.0	3.51	3.81	0.550	3.31	0.15
78	0.75	3.2	0.75	0.51	2.56	0.478	2.47	0.74
79	0.75	3.7	0.75	1.01	2.56	0.600	3.22	0.76
80	0.75	4.2	0.75	1.51	2.56	0.470	3.26	0.72
81	0.75	4.7	0.75	2.01	2.56	0.468	3.26	0.42
82	0.75	5.2	0.75	2.51	2.56	0.550	3.51	0.20
83	0.75	5.7	0.75	3.01	2.56	0.715	4.62	0.20
84	0.75	6.2	0.75	3.51	2.56	0.722	5.22	0.12

In seven sets of samples, numbers 11 through 17, material balances were made for fluoride, aluminum, and zirconium between the initial solutions and the final solutions plus precipitates. The material balance for the zirconium was found to be 101 ± 3 percent; for the aluminum, the material balance was found to be 97 ± 12 percent; and for the fluoride, the material balance was found to be 84 ± 8 percent. Further investigations indicate that the low fluoride material balance results from the solid analyses and is not an error inherent in the solution fluoride analyses. See Appendix 3 for calculations verifying this conclusion.

B. Approach to Equilibrium

In Figures 2 through 6, the concentrations of zirconium in solution are shown at any given time period up to 200 days. The data points connected by the solid lines indicate those samples that did not precipitate aluminum compounds, while the points connected by the broken lines indicate those samples that did precipitate aluminum compounds. In Figure 2, the samples were stored at 0°C for 89 days and then allowed to equilibrate at room temperature. In the other experimental runs, Figures 3 through 6, the samples were allowed to reach equilibrium only at room temperature.

In several cases, the zirconium precipitation appeared to be reversible with aging at constant temperature. This was especially evident in samples 23 and 24 of Figure 3, samples 27 and 28 of Figure 4, and samples 32 of Figure 5. In these samples, the slow competing

Fig. 2 - STR Extraction Feed Stability-- 0.75M aluminum nitrate, 0°C and 25°C

Fig. 3 - STR Extraction Feed Stability--0.75M aluminum nitrate, 25°C

Fig. 4 - STR Extraction Feed Stability--0.5M aluminum nitrate, 25°C

Fig. 5 - STR Extraction Feed Stability--1.00M aluminum nitrate, 25°C

Fig. 6 - STR Extraction Feed Stability--0.75M aluminum nitrate, 25°C

precipitation of aluminum fluoride apparently altered the aqueous phase composition before the zirconium precipitation was complete. In the samples that produced no aluminum precipitation, there were indications of a similar reversal, suggesting very slow changes in the solution or solid species of zirconium.

In most cases, equilibrium appears to have been reached by the 180th day, however, later analyses were made in order to insure that this was true, especially in the samples which did not precipitate aluminum compounds and therefore, were of primary interest. The equilibrium curves presented in Appendix 4 and the long-term stability data utilize these later analyses.

C. The Effect of Composition Variation Upon Long-Term Stability

The final equilibrium compositions for these samples are tabulated in Table 3. From these data, it was found that in a system in which a dissolver solution was adjusted with hydrofluoric acid and aluminum nitrate, the hydrogen ion concentration must not exceed 1.5M if the aluminum is to be soluble. This is true at 0.5M, 0.75M, or 1.0M aluminum nitrate. At all these levels, precipitation of aluminum compounds occurred when the hydrogen ion concentration exceeded 1.5M, whereas at lower hydrogen ion concentrations, only the zirconium compounds precipitated.

Other conclusions can also be made at each of the three levels of aluminum concentrations that were studied:

- (1) At the 0.75M aluminum nitrate concentration, the highest zirconium concentration in solution was about 0.6M in a system composed of 3.2M fluoride, 1.05M hydrogen, and 2.56M nitrate; see samples 11, 19, and 79 in Table 1.
- (2) At the 1.00M aluminum nitrate concentration level, the highest zirconium concentration in solution was about 0.4M in a system composed of 2.5M fluoride, 0.51M hydrogen, and 3.31M nitrate; see sample 29 in Table 1. Sample 30 also retained this amount of aluminum in a solution with a slightly different composition.
- (3) At the 0.5M aluminum nitrate concentration level, the highest zirconium concentration in solution was about 0.67M in a system composed of 4.17M fluoride, 1.51M hydrogen, and 1.81M nitrate; see sample 26 of Table 1. Sample 25 also retained this amount of aluminum in a solution with a slightly different composition.

D. Long-Term Stability Regions at 0.75M Aluminum Nitrate

1. Solid Phase Identification

Figure 7 is a graph of zirconium and fluoride concentrations which show the initial and final equilibrium compositions of the system at 0.75M aluminum nitrate.

FIGURE 7
SOLID PHASES OF ZIRCONIUM
EXPERIENCED IN STR EXTRACTION FEEDS
(0.75 M ALUMINUM NITRATE - 25° C)

LEGEND

- ⊗ = FAIRLY PURE ZIRCONIUM TETRAFLUORIDE TRIHYDRATE - SAMPLES 79, 80, & 20
- ⊙ = ZIRCONIUM TETRAFLUORIDE TRIHYDRATE PLUS AS MUCH AS ONE THIRD BY WEIGHT OF AN UNIDENTIFIED AMORPHOUS MATERIAL - SAMPLES 12, 13, AND 19.
- ⊖ = ZIRCONIUM HYDROXY TRIFLUORIDE MONOHYDRATE - SAMPLES 18 AND 78.
- = INITIAL COMPOSITION

Samples numbered 13, 80, and 20 could be considered to be equivalent since their initial compositions were approximately the same: 4.2M fluoride, 0.75M and 0.8M zirconium, and 1.5M hydrogen ion. Samples numbered 11, 19, and 79 are also of approximately the same composition: 3.75M fluoride, 1.0M hydrogen ion, and 0.75M and 0.8M zirconium. Samples numbered 18 and 78 contained even less hydrogen ion, 0.75M, and fluoride, 3.2M, and about the same zirconium concentration, 0.75M and 0.8M. Sample number 12 was not duplicated. Its composition was 1.3M hydrogen ion concentration and 4.0M fluoride. The compositions of the final solutions also were arranged into orderly groups.

The solids produced in these systems were identified by their x-ray diffraction patterns and were found to be of three varieties. The solids from 20, 79, and 80 were moderately pure zirconium tetrafluoride trihydrate. These are designated by the letter "X" in Figure 7. The solids from experiments 13, 12, and 19 also contained zirconium tetrafluoride trihydrate, but they also contained amorphous material, possibly as much as one third by weight. These samples are given in order of their purity, that is, sample number 19 contains the most amorphous material. This group is designated by the letter "Y" in Figure 7. Samples 18 and 78 were identified as a hydrolyzed species which was thought to be zirconium hydroxy trifluoride monohydrate⁽⁷⁾ and are designated by the letter "Z" in Figure 7. The solids obtained from sample number 11 were insufficient in quantity for x-ray analysis.

If a line is drawn to connect the initial and final compositions as designated in Figure 7, the slope of that line will represent the fluoride-to-zirconium mole ratio of the solid produced when the solution changed from the initial to the final composition. No volume change was assumed in the calculation. Therefore, the fluoride-to-zirconium mole ratio obtained by the slope of this line should be identical to that mole ratio given by the x-ray identification of the solids. Therefore, a slope of four should be obtained from samples numbered 20, 79, and 80. A slope of somewhat less than four should be obtained for samples numbered 12, 13, and 19 since they contained some amorphous zirconium-containing material. And a slope of three should be obtained for samples numbered 18 and 78. However, this was not the case. The slopes were found to range from 2.0 to 3.9 without a recognizable pattern. See Table 4.

One explanation might be deduced from the equilibrium curves in which the zirconium concentration is plotted against time. In several cases, there is zirconium precipitation in the early stages which is redissolved in the latter stages, see Figure 6, sample numbered 79. This is in agreement with other data which show that the solubility of these hydrolytic species in dilute nitric acid increases with time.⁽⁸⁾ Therefore, it is feasible that precipitation and redissolution could occur. This redissolution could be accomplished by replacing a hydroxyl radical with a fluoride ion which appears to occur in systems in which the fluoride-to-zirconium mole ratio is two and the acidity is low.⁽⁹⁾

2. The Effect of Temperature on Stability

A series of concentrated extraction feeds, 0.75M in zirconium, was prepared from actual STR fuel dissolution, and allowed to reach equilibrium at 25°C. After about four weeks, a cake of crystalline precipitate appeared which was found to be zirconium tetrafluoride

Table 4

FLUORIDE-TO-ZIRCONIUM MOLE RATIOS OF THE SOLID PHASES

<u>Sample Number</u>	<u>F/Zr Mole Ratio by the Slope Method</u>	<u>F/Zr Mole Ratio by Solid Identification</u>
13	3.4	4
20	2.6	4
80	3.6	4
11	2.9	---
19	2.3	4
79	3.4	4
12	3.9	4
18	2.0	3
78	2.4	3

trihydrate. An analysis of the supernatant liquid showed that the solution had reached equilibrium at about the 0.57M zirconium level. Two extraction feed samples containing precipitate solids were placed in a 50°C water bath. A portion of the precipitate dissolved very rapidly and all of it was dissolved in about 24 hours. Analyses of the supernatant liquid showed that these solutions had returned to their original composition, 0.75M in zirconium.

From this experiment and the more extensive data of Figure 2, it was concluded that the zirconium tetrafluoride trihydrate had a positive and advantageously high temperature coefficient of solubility. The values experienced ranged up to + 0.08M zirconium per 10°C temperature rise.

If operational difficulties are caused by precipitation, these solids could presumably be redissolved by appropriate temperature increases.

It is also noteworthy that all the stability studies were made at temperatures around 25°C, while the average temperatures that would be experienced in plant operation would be approximately 10 degrees higher. Therefore, the stability regions should represent the more conservative values.

3. Long-Term Stability Regions (200 Days)

The standard deviation obtained from control data of the fluoride analyses were such that several more analyses were needed to establish the long-term stability regions with a degree of confidence appropriate to the importance of the data.

At the 0.75M aluminum nitrate concentration level, there were nine samples that did not precipitate aluminum compounds. Using these nine samples, a region of stability could be established, however, the limit of error associated with the fluoride analyses was $\pm 0.4M$ and since it was so large, it obscured this stability region. Triplicate analyses of the fluoride component in the nine sample solutions reduced this limit of error to $\pm 0.15M$ at the 95 percent confidence level.

This region of stability is shown on Figure 8. The limits of error associated with both the fluoride analyses and the zirconium analyses are shown. The boundary of the stability regions was drawn by using an average of each of the three groups of data. Since in each group the data are equivalent, the experimental error should be at a minimum. Sample number 12 was not included in establishing the boundary because it was not duplicated.

The existing flowsheet has a raffinate composition that appears to lie in a doubtful area of the stability region, see Figure 8. Therefore, firm conclusions cannot be made as to the long-term stability of this 0.55M zirconium and 3.2M fluoride system. However, this raffinate is diluted by jet transfers before it is permanently stored. The long-term stability of solutions with this more dilute composition is discussed in a following section.

4. The Effect of Aging Upon the Regions of Stability for the 0.75M Aluminum Nitrate Level

The effect of aging upon the location of the stability region is shown in Figure 9. The initial and equilibrium solutions were analyzed for aluminum, zirconium, fluoride, and hydrogen ion, whereas, the metastable solutions were analyzed only for zirconium. Therefore, the corresponding fluoride values used in this figure had to be estimated. These estimated fluoride concentrations were obtained by connecting the points representing the initial and final fluoride concentrations with a straight line. The intermediate stages of fluoride concentration were then located on this line according to their analyzed zirconium concentrations.

The compositions of the two experiments shown in Figure 9 were the same except for the initial zirconium concentration. One set of samples was initially 0.8M in zirconium and the other set of samples was 0.75M in zirconium initially. However, even with these different starting levels, the final concentrations obtained were approximately the same. Compare samples 78 and 18, 19 and 79, and 20 and 80. Observations of samples 19 and 79 indicate that conditions were not favorable for the formation of hydrolytic species. In fact, in sample number 19, there were no solids formed after 24 days of aging.

FIGURE 8

REGIONS OF LONG-TERM STABILITY
(UP TO 550 DAYS)
(0.75 M ALUMINUM NITRATE - 25°C)

LEGEND

THE COMPOSITION OF THE STR RAFFINATE PRODUCED BY THE EXISTING PROCESS IS DESIGNATED BY ⊕

Fig. 9 - STR Extraction Feed Stability--The effect of aging at 25°C upon solution stability--The solutions were initially 0.8M or 0.75M in zirconium and 0.75M in aluminum. The zirconium and fluoride concentrations are shown at zero days ., 24 days +, 59 days x, 105 days Δ, and 551 days o.

E. Four-Day Stability Data

From the data presented in Figure 9, it was evident that there was some short-term stability advantage to be had in a system composed initially of 3.7M fluoride, 1.0M hydrogen ion and 0.75M aluminum nitrate. Six additional samples were prepared which covered the composition range from 3.2 to 4.2M fluoride and the corresponding hydrogen ion. The zirconium was initially 0.7 and 0.8M at 0.75M aluminum nitrate. The samples were observed at 25°C for the presence of solids. Figure 10 shows that precipitation occurred at 4.0M fluoride with 0.7M zirconium and at 4.2M fluoride with 0.8M zirconium. However, there were no solids formed at 3.2, 3.7 and 3.8 M fluoride. Therefore, it was concluded that about 3.8M fluoride is about the maximum that can be utilized without the formation of solids.

F. The Effect of Composition Variation Upon Stability at 0.5M Aluminum Nitrate

1. Short-Term Stability Regions

The data in Figure 11 show how the zirconium concentration in solution changes with aging time. The 0.5M aluminum nitrate concentration level appears to offer maximum short-term stability throughout the entire range of fluoride and hydrogen ion concentrations studied. Solutions containing 0.8M zirconium were stable after aging 24 days. From these data, there is no indication as to which is the most beneficial concen-

Fig. 10 - Four-Day Stability Data for STR Extraction Feeds--The aluminum nitrate concentration was 0.75M; the temperature was 25°C. The composition of precipitate-free solutions is designated by O, precipitate containing by X.

Fig. 11 - Stability Data for Stored Wastes--The aluminum nitrate concentration was 0.5M. The temperature was 25°C. The initial compositions of the stability study samples are designated by +, the composition after 24 days by ., and the equilibrium composition, aged 434 days, by $\odot$.

tration of fluoride and hydrogen ion, however, it was found that at fluoride concentrations above 4.2M, aluminum compounds are eventually precipitated. Several additional solutions were prepared having compositions similar to samples numbered 25 and 26, see Table 5. These additional samples were observed for several days for the appearance of solids. The hydrogen ion concentrations of these samples varied from 1.1 to 1.5M while the aluminum nitrate concentrations varied from 0.49 to 0.69M. The results of these observations are shown in Figures 12, 13, and 14. After nine days aging there were only three samples, numbers 55, 58, and 60, which were free of solids. However, after aging for 123

Table 5

THE INITIAL COMPOSITIONS OF EXTRACTION FEEDS
WITH 0.49M TO 0.69M ALUMINUM NITRATE

<u>Sample Number</u>	<u>Zirconium M</u>	<u>Aluminum M</u>	<u>Fluoride M</u>	<u>Hydrogen M</u>	<u>Nitrate M</u>
50	0.745	0.69	3.6	1.1	2.1
51	0.747	0.67	4.2	1.2	2.1
52	0.748	0.68	3.7	1.2	2.1
53	0.748	0.61	4.0	1.1	1.6
54	0.716	0.62	3.6	1.2	1.6
55	0.740	0.63	4.2	1.3	1.6
56	0.721	0.62	3.8	1.4	1.6
57	0.747	0.49	4.1	1.2	1.4
58	0.743	0.49	4.2	1.3	1.4
59	0.75	0.49	4.2	1.3	1.4
60	0.75	0.49	4.4	1.4	1.4
61	0.75	0.49	4.4	1.5	1.4

days, there were nine samples which were free of solids and these are numbered 50, 53, 54, 55, 57, 58, 59, 60, and 61. This indicated that the solids in six samples were redissolved. There is no conclusive reason why the solids in some of the samples were redissolved while in other samples of similar compositions, the solids were not formed or were not redissolved.

2. Long-Term Stability of Waste Solutions

The waste streams from the extraction cycle are diluted somewhat as a result of jet transfer. The resulting composition of the waste accumulated⁽¹¹⁾ in the storage tanks is 0.47M zirconium, 0.65M aluminum nitrate, 2.87M fluoride, and 1.06M hydrogen ion. The composition of these wastes are shown in Figure 11 along with the long-term stability regions at 0.5M aluminum nitrate. From these data, it was concluded that there should be no solid material in the permanent storage vessels and that a more concentrated waste could be utilized.

G. Conclusions

From this study, it was concluded that waste solutions containing 0.5 to 0.6M zirconium and 0.75M aluminum nitrate were stable for 200 days. The use of these more concentrated solutions would result in a reduction in permanent waste storage volumes.

Fig. 12 - Four-Day Stability Data for STR Extraction Feeds at 25°C-- The aluminum nitrate concentration varied between 0.49 and 0.69M. The composition of precipitate-free solutions is designated by O, precipitate containing by X.

Fig. 13 - Nine-Day Stability Data for STR Extraction Feeds at 25°C-- The aluminum nitrate concentration varied between 0.49 and 0.69M. The composition of precipitate-free solutions is designated by O, precipitate containing by X.

Also, if a short-term stability system can be utilized in conjunction with some immediate waste treatment, such as calcination, than a more concentrated extraction feed can be used, which increases the uranium capacity and further reduces the waste volume to be calcined.

V. CONCENTRATION OF THE STR RAFFINATE

Another method of improving the present flowsheet might be to reduce the raffinate volumes by evaporation. A study was made of the effects of the concentration of fluoride, aluminum, hydrogen ion, and the temperature of evaporation upon the stability of the concentrated raffinate. It was thought that the most desirable feed composition might

be utilized and then the raffinate concentrated for storage by some method such as evaporation.

A. Experimental Procedure

A series of synthetic raffinates were prepared from a dissolver solution of an actual STR fuel coupon. The initial concentrations of each component and the method of evaporation were varied according to the statistical design which is presented in Table 6. Zirconium concentration levels were established by taking samples periodically during the evaporation. These samples were observed daily for the presence of solids and in this manner, the effect of aging upon the stability of these solutions was determined. The aging effects are also shown in Table 6.

Fig. 14 - 123-Day Stability Data for STR Extraction Feeds at 25°C--The initial aluminum nitrate concentration ranged between 0.49 and 0.69M--The composition of precipitate-free solutions is designated by O, precipitate containing by X.

B. Results

This investigation has shown that the current STR process raffinate solutions can be evaporated from 0.55M to 0.85M zirconium to produce metastable solutions. These solutions, after standing for 35 days, had precipitated solid phases of zirconium tetrafluoride trihydrate and other salts, returning to stable solutions having about the original, 0.55M in zirconium, composition. The ultimate stable concentration was not significantly influenced by the addition of nitric acid up to 2.0M or by varying the fluoride-to-zirconium mole ratio from 4.5 to 6.0 moles per mole. The stability of the solutions was not significantly

influenced by the mode of evaporation, that is, by air distillation at 45°C or by boil-down at 100°C. There were indications that a more concentrated stable flowsheet might be obtained by lowering the aluminum nitrate concentration.

Experiments numbered 1, 2, and 3 in Table 6 show that a raffinate containing 0.85M zirconium and 0.56M aluminum would be stable for a four-day period, at either of the two levels of fluoride or hydrogen concentration studied. This metastability might be utilized to obtain a 35 percent volume reduction.

Table 6

THE STABILITY OF EVAPORATED STR RAFFINATE

The Effects of Fluoride, Aluminum,
and Hydrogen Ion Concentrations, and Evaporation Temperature

A series of synthetic raffinates (0.5M zirconium) prepared according to a statistical design were evaporated batchwise. Samples taken periodically during the evaporation were observed daily until equilibrium was reached.

Experiment Number	Experimental Design				The Zirconium Concentration (M) of the Raffinates that were Stable After Standing at 25°C for											
	Initial Compositions			Evaporation Temperature °C												
	F	Al	H													
	M	M	M		1 day	2 day	3 day	4 day	5 day	6 day	7 day	10 day	15 day	30 day	100 day	
1	2.57	0.37	1.02	45	0.90	0.84	0.84	0.84	----	----	0.78	0.78	0.66	0.66	0.56	
2	3.30	0.37	1.02	100	0.85	0.85	0.85	0.85	0.85	0.85	0.85	0.60	0.60	0.59	0.59	
3	2.57	0.37	1.47	100	0.85	0.85	0.85	0.85	0.85	0.85	0.80	0.80	0.80	0.80	0.54	
4	3.3	0.37	1.47	45	0.85	0.85	0.78	0.78	0.78	0.78	0.78	0.78	0.78	0.70	0.55	
5	2.57	0.73	1.02	100	0.60	0.60	0.60	0.60	0.60	0.60	0.60	0.60	0.55	0.55	0.55	
6	3.30	0.73	1.02	45	0.85	0.85	0.78	0.78	0.78	0.78	0.78	0.78	0.78	0.65	0.45	
7	2.57	0.73	1.47	45	----	----	----	0.73	0.73	0.73	0.73	0.73	0.73	0.65	0.54	
8	3.30	0.73	1.47	100	----	----	----	0.76	0.76	0.76	0.76	0.76	0.76	0.76	0.47	

The effect of each of the four variables was determined using the Yates method of data analysis and these results are given in Table 7. During the metastable stage, less than 35 days, the greatest effect was due to the nitric acid concentration. This can readily be seen in Figure 15 in which the zirconium concentration of the stable solutions is compared to the hydrogen ion concentration. The stability of the solutions can be improved by increasing the hydrogen ion concentration from 1.39M to 2.0M if the composition of the solution appears to lie near the limits of the stable regions as outlined by early work.⁽¹¹⁾ They are not improved if the composition lies near the center of the stable region.

After the system had reached equilibrium, 100 days standing time, the greatest effect was attributed to the aluminum concentration. However, when the variance ratio test was applied to the data, none of the effects were significant at the 0.1 confidence level.

C. Conclusions

It is apparent that it is more advantageous to utilize a more concentrated raffinate than a dilute raffinate which is later evaporated prior to storage. This is particularly true if some waste treatment such as calcination is to be used.

Table 7

DESIGN AND INTERPRETATION OF CONCENTRATED RAFFINATE EXPERIMENTS

The Significance Level of the Effect of Fluoride,
Aluminum and Hydrogen Ion Concentrations, and Evaporation Temperature

Variable	Base Levels	Unit Change	After 4 Days		After 14 Days		After 30 Days		After 100 Days	
			Effect	Sig. Level	Effect	Sig. Level	Effect	Sig. Level	Effect	Sig. Level
Hydrogen	1.69M	$\pm 0.3M$	+0.0125	Insig.	+0.120	0.15	+0.115	0.13	-0.01	Insig.
Aluminum	0.75M	$\pm 0.25M$	-0.11	0.12	+0.02	Insig.	-0.035	Insig.	-0.06	0.11
Fluoride	4.0 M	$\pm 0.5 M$	+0.0375	Insig.	+0.02	Insig.	+0.02	Insig.	-0.035	Insig.
Temperature	72.5°C	$\pm 27.5^\circ C$	-0.0175	Insig.	-0.060	Insig.	+0.01	Insig.	+0.015	Insig.

VI. MODIFIED STR FLOWSHEETS

Given in the following

tables are several flowsheets which utilize the data and recommendations from the preceeding sections. The objectives of these flowsheets are: (1) to provide dissolution conditions for up to 3 percent uranium-zirconium fuels, (2) to utilize the most concentrated extraction feed practical in order to limit raffinate volumes and obtain maximum uranium through-put for a given column, (3) to reduce the volume of the stored waste, and (4) to reduce the aluminum content of the extraction column feed to give a raffinate which will ultimately produce less solid bulk for long-term storage. However, these flowsheet objectives are limited. The extraction feed concentration for the batch-type flowsheet is limited to about 0.7M zirconium at the 0.75M aluminum level or about 0.75M zirconium at the 0.5M aluminum level by the short-term, 4-day stability, at 25°C. By taking advantage of the high temperature coefficient of solubility, this concentration can be increased to 0.8M zirconium since the ambient operating temperature of the plant is about ten degrees higher than that temperature at which the stability data were obtained. The composition of the liquid waste is limited to about 0.6M

Fig. 15 - The Effect of Nitric Acid on the Stability of Concentrated Hydrofluoric Acid Process (STR) Raffinate at 25°C.

in zirconium at the 0.66M aluminum nitrate level by long-term, 500-day stability. The reduction in aluminum nitrate concentration is limited to about 0.55M aluminum nitrate for 0.7M zirconium by extraction column design.

A. STR Batch Flowsheets

1. Flowsheets Using Existing Equipment

The current flowsheet can be modified without changing the existing plant equipment to obtain a 17 percent reduction in permanent waste storage volumes. In the current flowsheet, 0.55M zirconium is the composition used in extraction feeds which are further diluted by heel dilutions and jet transfers to give a stored waste containing 0.47M zirconium. The Plant Test flowsheet utilizes a more concentrated extraction feed, 0.667M zirconium, which in turn can give a stable and more concentrated stored waste that is 0.6M in zirconium. This flowsheet has recently been used successfully in plant production. The current flowsheet and Plant Test flowsheet are given in Table 8.

2. Advanced STR Batch Flowsheets

A flowsheet can be written with all of the possible modifications proposed in preceeding sections. In order to realize the full advantage of the increased uranium through-put capacity offered by these flowsheets, portions of the existing ICPP solvent extraction equipment would have to be modified. The advantages in waste bulk resulting from the reduced

Table 8

CURRENT STR BATCH FLOWSHEET

	Dissolution Charge	Dissolver Reagent		Dissolver Solution	Diss. Wash	Coarse Feed Adj.	Coarse Feed	Fine Feed	IAR	Waste After Jet Dilution	Waste After Heel Dissolution
		Clad Removal	Meat. Diss.								
Liter/Batch		460	20.1	610	75	1022	1764	1073	1073	2037	2112
U g/l	1.9 kg			3.07			1.08	1.03	1x10 ⁻⁴		
Zr, M	93.0 kg			1.65			0.578	0.55	0.55	0.50	0.48
Al, M						1.36	0.788	0.75	0.75	0.68	0.66
Sn, M	1.4 kg			0.019			0.0067	0.0063	0.0063	0.0057	0.0055
Cr, M						0.030	0.018	0.017	0.017	0.015	0.015
H ⁺ , M		10	1.0	0.84		1.60	1.22	1.16	1.16	1.06	1.02
F, M		10		7.44		1.60	3.53	3.36	3.36	3.06	2.96
NO ₃ M			1.0	0.016		4.09	2.42	2.31	2.31	2.08	2.00
H ₂ O l	160				Pure						

PLANT TEST STR BATCH FLOWSHEET

Liter/Batch		460	20.1	618	75	711	1450	1529	1529	1669	1744
U g/l	1.9 kg			3.07			1.31	1.24	1x10 ⁻⁴		
Zr, M	93.0 kg			1.65			0.70	0.667	0.667	0.611	0.585
Al, M						1.61	0.788	0.75	0.75	0.684	0.66
Sn, M	1.4 kg			0.019			0.0081	0.0077	0.0077	0.0071	0.0067
Cr, M						0.036	0.018	0.017	0.017	0.015	0.015
H ⁺ , M		10	1.0	0.84		1.31	1.00	0.952	0.952	0.865	0.87
F, M		10		7.44		1.31	3.80	3.62	3.62	3.29	3.25
NO ₃ M			1.0	0.016		4.83	2.37	2.26	2.26	2.06	2.00
H ₂ O l	160				Pure						

molarity of aluminum can be obtained at any flowsheet rate. The recommended extraction feed contains 0.55M aluminum nitrate and therefore has a lower salting strength than that which is required in the existing flowsheet for use with ten percent tributyl phosphate (TBP) in Amsco. However, by increasing the TBP concentration from 10 to 12.5 volume percent, adequate extraction can be obtained.

Tables 8, 9, and 10 show the batch flowsheets for the existing STR, modified STR, and modified Zirflex process⁽¹²⁾, respectively. A tabulation of the main characteristics is shown in Table 11. Three percent by weight uranium fuels can be processed with the modified STR and the modified Zirflex flowsheets, whereas, a limit of 1 percent uranium or less was inherent in the existing STR flowsheet. The solubility problem imposed with increasing uranium content is solved in both flowsheets by oxidation of sufficient uranium to the more soluble uranium(VI) with hydrogen peroxide. A calculated terminal concentration of 0.06M peroxide is used in the modified Zirflex process. The dissolver product produced in the Zirflex process must be kept at 50°C to maintain stability, whereas, the dissolver product produced with the modified STR process is stable at 25°C. The raffinate volume produced from the dissolution of one 96 kilogram fuel charge with the modified STR flowsheet amounts to 1342 liters as compared to the existing STR process' 1853 liters, which is a 25 percent volume reduction. The modified Zirflex process produces twice the volume, 4000 liters, as does the existing flowsheet. This increased raffinate volume and the additional aluminum concentration used in the Zirflex process, 1.0M, would produce almost twice the bulk of solid waste if these raffinates were subjected to calcination. See Table 11 for a comparison of the moles of zirconia and alumina produced per kilogram of uranium processed.

B. Tentative Continuous Dissolution Flowsheets

In Tables 12, 13, and 14, three continuous dissolution flowsheets are given which use 0.01M hydrogen peroxide, 0.3M nitric acid, and 0.1M aluminum nitrate to illustrate three different oxidizing agents that could be used to obtain a homogeneous dissolution of up to 3 percent uranium fuels. The levels of the oxidants selected here are extrapolated from data obtained during batch dissolution studies and they therefore constitute only suggested initial levels for further continuous dissolution studies. The aluminum nitrate value was selected on the basis of the nitric acid experience.

In Table 15, a continuous dissolution flowsheet is given which uses the dilute method to obtain homogeneous dissolution. Due to the limited uranium tetrafluoride solubility, this flowsheet is restricted to the processing of zirconium fuels that contain up to 2 weight percent uranium.

The extraction feed used in all of these flowsheets is 0.8M in zirconium and 0.55M in aluminum nitrate. This probably is the most concentrated composition which is practical with respect to stability and extraction salting strength. The 1.3M hydrogen ion level was obtained by adding nitric acid in the coarse feed adjustment since this level was thought to be the most advantageous for the short-term and long-term stability at this level of aluminum nitrate.

C. Conclusions

The potential advantages of these flowsheets as compared to the currently-used flowsheets (see Table 8) are (1) the STR hydrofluoric acid process can be adapted to handle up to 3 per cent uranium fuels, (2) the uranium through-put of a given extraction system can be increased by as much as 20 per cent by using the more concentrated extraction feed, and (3) the more concentrated stored waste can be obtained without the corrosion and stability problems associated with evaporation.

VII. ACKNOWLEDGEMENT

Members of the Idaho Chemical Processing Plant Analytical Section contributed materially to the success of this investigation by careful analysis of the many samples in the stability studies.

Table 9

MODIFIED STR BATCH FLOWSHEET
0.55M Aluminum Nitrate Salting

	Diss. Charge	Dissolver Cladding Removal	Reagent Meat Diss.	Dissolver Solution	Diss. Wash	Coarse Feed Adj.	Coarse Feed	Fine Feed	IAF	IAX
Liters/Batch		255	255	510	75	661(3)	1275(3)	1342(3)	1342	839
U g/l	1.9 kg			3.72					1.42	
Zr, M	93.0 kg			2.00			0.80	0.76	0.76	
Al, M						1.116	0.58	0.55	0.55	
Sn, M	1.4 kg			0.02			0.008	0.0076	0.0076	
H ⁺ , M		10(1)	10(1)	1.94		1.14	1.37	1.3	1.3	
F, M		10(1)	10(1)	10.0		0.534	4.29	4.07	4.07	
H ₂ O ₂ M			0.12(1)	<0.005						
NO ₃ M						3.953	2.05	1.95	1.95	
H ₂ O M					Pure					
B g/l		2.0(2)		1.0			0.4	0.38	0.38	
TBP %										12.5

- (1) The dissolution reagents, hydrofluoric and hydrogen peroxide are added in the following manner: approximately one-half of the hydrofluoric acid is added in the first hour, the remaining acid plus the hydrogen peroxide is added during the next 1.5 hours; a one-hour digestion completes the 3.5 hours dissolution cycle.
- (2) Boron is added (as boric acid) as a criticality safeguard.
- (3) The dissolver product, coarse feed, and fine feed are transferred by means of steam jetting which results in about a five percent dilution for each transfer.

Table 10

MODIFIED ZIRFLEX PROCESS⁽¹²⁾ BATCH FLOWSHEET

1.0M Aluminum Nitrate Salting

	Fuel	Diss. Reagent	Diss. Product	Coarse Feed Adj.	IAF
Flow 1/batch		1500	1500	2500	4000
U g/l	1.9 kg		1.27		0.475
Zr, M	93.0 kg		0.68		0.25
Al, M				1.6	1.0
H ⁺ , M				1.6	1.0
NO ₃ , M		0.3		6.4	4.0
F, M		5.4	5.4		2.03
H ₂ O ₂ , M		0.13 ⁽¹⁾			
Sn, M	1.4 kg		0.008		0.003
NH ₄ ⁺ , M		5.7 ⁽²⁾	2.7		1.00

- (1) Hydrogen peroxide at the 0.13M level is added continuously during dissolution to oxidize the uranium.
- (2) All the ammonium fluoride is added at the beginning of dissolution.

Table 11

COMPARISON OF THE THREE PROPOSED BATCH FLOWSHEETS

Existing STR, Modified STR and Zirflex⁽¹²⁾

	Existing STR	Modified STR	Modified Zirflex
Uranium in Fuel, Percent	1 or less	3 or less	3 or less
Dissolution Reagent	10 HF	10 HF	5.4 NH ₄ F 0.3 NH ₄ NO ₃
Oxidation of Uranium in Dissolver	0.016M HNO ₃	0.06M H ₂ O ₂	0.13M H ₂ O ₂
IAF Volume, Liters	1853	1342	4000
Molec of ZrO ₂ + Al ₂ O ₃ /kg U	900	750	1590

Table 12

CONTINUOUS STR FLOWSHEET NUMBER 1

This flowsheet features 0.01M hydrogen peroxide for uranium oxidation during dissolution and 0.55M aluminum nitrate salting strength. (Arbitrary rates).

	<u>Fuel Charge</u>	<u>Diss. Reagent</u>	<u>Diss. Product</u>	<u>Coarse Feed Adj.</u>	<u>IAF</u>	<u>IAX</u>
Flow Rate Liters/Hour		510	510	765	1275	797
U g/l	1.9 kg		3.73		1.49	
Zr, M	93.0 kg		2.0		0.80	
Al, M				0.917	0.55	
Sn, M	1.4 kg		0.023		0.009	
H ⁺ , M		10.0	1.94	0.873	1.3	
F, M		10.0	10.0	0.375	4.23	
H ₂ O ₂ M		0.01	0.005			
NO ₃ M				3.249	1.95	
B g/l		1.0	1.0		0.40	
TBP %						12.5

Table 13

CONTINUOUS STR FLOWSHEET NUMBER 2

This flowsheet features 0.3M nitric acid for uranium oxidation during dissolution and 0.55M aluminum nitrate for optimum stability and extraction salting strength. (Arbitrary rates).

	<u>Fuel Charge</u>	<u>Diss. Reagent</u>	<u>Diss. Product</u>	<u>Coarse Feed Adj.</u>	<u>IAF</u>	<u>IAX</u>
Flow Rate Liters/Hour		510	510	765	1275	797
U g/l	1.9 kg		3.73		1.49	
Zr, M	93.0 kg		2.0		0.80	
Al, M				0.917	0.55	
Sn, M	1.4 kg		0.023		0.009	
H ⁺ , M		10.3	2.24	0.673	1.3	
F, M		10.0	10.0	0.174	4.10	
NO ₃ M		0.3	0.3	3.25	1.95	
B g/l		1.0	1.0		0.4	
TBP %						12.5

Table 14

CONTINUOUS STR FLOWSHEET NUMBER 3

This flowsheet features 0.1M aluminum nitrate for uranium oxidation during dissolution and 0.55M aluminum nitrate for optimum stability and extraction salting strength. (Arbitrary rates).

	<u>Fuel</u> <u>Charge</u>	<u>Diss.</u> <u>Reagent</u>	<u>Diss.</u> <u>Product</u>	<u>Coarse</u> <u>Feed</u> <u>Adj.</u>	<u>IAF</u>	<u>IAX</u>
Flow Rate		510	510	765	1275	797
Liters/Hour						
U g/l	1.9 kg		3.73		1.49	
Zr, M	93.0 kg		2.0		0.80	
Al, M		0.10	0.10	0.85	0.55	
Sn, M	1.4 kg		0.023		0.009	
H ⁺ , M		10.0	1.94	0.873	1.30	
F, M		10.0	10.0	0.375	4.23	
NO ₃ M		0.30	0.30	3.155	1.95	
B g/l		1.0	1.0		0.40	
TBP %						12.5

Table 15

CONTINUOUS STR FLOWSHEET NUMBER 4

This flowsheet features homogeneous dissolution by the dilute method, which maintains the uranium tetrafluoride concentration below its solubility limit. Concentrated reagents are added to obtain 0.55M aluminum nitrate for optimum stability and extraction salting strength. (Arbitrary rates).

	<u>Fuel</u> <u>Charge</u>	<u>Diss.</u> <u>Reagent</u>	<u>Diss.</u> <u>Product</u>	<u>Coarse</u> <u>Feed</u> <u>Adj.</u>	<u>IAF</u>	<u>IAX</u>
Flow Rate		927	927	348	1275	797
Liters/Hour						
U g/l	1.9 kg		2.05			
Zr, M	93.0 kg		1.10		0.80	
Al, M				2.02	0.55	
Sn, M	1.4 kg		0.013			
H ⁺ , M		4.84	0.374	3.77	1.3	
F, M		4.81	4.81	2.667	4.23	
NO ₃ M		0.027(1)	0.027	7.16	1.95	
B g/l		1.0	1.0		0.4	
TBP %						12.5

(1) Nitric acid is used for oxidation of the tin.

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IX. APPENDICES

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Appendix 1

HOMOGENEOUS DISSOLUTION OF STR-TYPE FUEL
AT 94°C AND ATMOSPHERIC PRESSURE OF 640 mm MERCURY

Experiment Number	Weight of Fuel Coupon grams	Final Volume ml	Oxidant Level M	Uranium		Zr M	H ⁺ M	F M	NO ₃ M	F/Zr Mole Ratio	Observed Solids	Fuel Dissolved in 3.5 Hrs Percent	Monel Corrosion: mils/batch
				g/l	Wt. % of Fuel								
By Oxidation with Nitric Acid													
16	----	----	1.50	5.0	3.0	1.64	0.04	8.3	0.65	5.1	None	100.0	2.0
17	31.3	195	0.62	5.67	3.0	1.66	1.02	6.96	0.51	4.2	Yes ⁽¹⁾	96.8	0.05
18	30.7	197	0.85	4.83	3.0	1.67	1.05	7.4	0.61	4.4	Yes ⁽¹⁾	97.8	0.06
19	34.1	217	0.85	4.71	3.0	1.62	1.09	7.9	0.50	4.9	Yes ⁽¹⁾	95.6	0.07
20	32.7	225	1.00	4.35	3.0	1.46	1.83	8.1	0.69	5.5	Yes ⁽¹⁾	100.0	0.07
21	30.2	202	1.00	4.77	3.0	1.46	1.14	7.1	0.68	4.9	Yes ⁽¹⁾	97.8	0.07
By Oxidation with Hydrogen Peroxide													
22	35.5	185	0.75	5.02	2.66	1.96	1.99	10.2	----	5.2	None	100.0	----
23	30.12	200	0.25	3.81	2.53	1.5	1.8	7.99	----	5.3	None	100.0	0.27
24	30.1	195	0.25	3.96	2.57	1.51	1.83	8.25	----	5.14	None	100.0	0.19
29	30.13	185	0.125	4.38	2.69	1.56	1.97	9.18	----	5.9	None	100.0	0.13
30	30.14	195	0.0625	3.72	2.41	1.49	1.94	9.18	----	6.3	None	100.0	0.05
31	30.05	190	0.031	2.67	1.68	1.61	1.90	8.33	----	5.2	Yes ⁽¹⁾	99.0	0.001
33	30.05	190	0.049	3.87	2.45	1.60	1.85	9.18	----	5.7	Yes ⁽¹⁾	99.0	----
34	30.31	188	0.0625	3.96	2.46	1.60	1.84	9.16	----	5.7	None	100.0	0.03
35	30.2	192	0.0625	4.08	2.6	1.62	1.25	9.0	----	5.7	None	100.0	0.02
By Oxidation with Chromic Acid													
28	30.14	195	0.06	3.91	2.53	1.52	1.53	8.14	----	5.4	None	100.0	0.1
39	30.06	210	0.02	2.97	2.1	1.38	1.32	7.28	----	5.3	Yes ⁽¹⁾	100.0	----
40	30.0	192	0.03	3.81	2.44	1.6	1.79	8.3	----	5.3	Yes ⁽¹⁾	100.0	----
By Oxidation with Potassium Permanganate													
25	30.11	205	0.04	3.60	2.45	1.43	----	7.75	----	5.4	Yes ⁽²⁾	100.0	0.02
41	30.9	215	0.01	----	----	----	----	----	----	---	Yes ⁽³⁾	-----	----
By Dilution													
26	15.16	205	None	1.02	1.38	0.72	0.47	3.7	----	5.2	None	99.6	0.02
27	15.17	185	None	1.20	1.46	0.81	0.46	3.87	----	4.8	None	98.0	0.003
36	20.2	183	None	2.70	2.45	1.13	0.72	4.93	----	4.36	Yes ⁽¹⁾	97.6	0.009
37	20.98	195	None	2.67	2.32	1.04	0.70	5.09	----	4.98	Yes ⁽⁴⁾	98.9	0.007
30	21.58	208	None	2.31	2.23	0.962	0.62	4.79	----	4.98	None	98.3	0.005
42	22.63	218	None	2.15	2.07	1.45	0.98	6.09	----	4.75	None	96.2	0.003
43	19.94	188	None	1.76	1.67	1.23	0.78	5.34	----	4.34	None	97.8	0.004

(1) Quantities too small to separate and weigh.

(2) No Uranium precipitated, but large quantity of MnO₂.

(3) No MnO₂, but small amount of UF₄.

(4) Small amount of precipitate 17 hours later.

Appendix 2

URANIUM(IV) AND URANIUM(VI) DISTRIBUTION

<u>Sample Number</u>	<u>Oxidant</u>	<u>Observed UF₆ Bpt.</u>	<u>Total Uranium g/l</u>	<u>U(VI) g/l</u>	<u>U(IV) g/l</u>
21	1.0M HNO ₃	Yes	5.18	2.82	2.36
28	0.06M CrO ₃	No	4.39	3.91	0.48
30	0.06M H ₂ O ₂	No	4.03	3.12	0.91
34	0.06M H ₂ O ₂	No	3.97	3.09	0.88
35	0.06M H ₂ O ₂	No	3.94	3.03	0.91
36	None	Yes	2.82	0.85	1.97
37	None	Yes	2.76	0.67	2.09
39	0.02M CrO ₃	Yes	3.0	1.24	1.76
38	None	No	2.33	0.30	2.03
42	None	No	2.15	0.17	1.98
43	None	No	1.76	0.13	1.63

Appendix 3

VERIFICATION OF THE FLUORIDE CONCENTRATION OF THE LIQUID PHASE OF THE STABILITY SAMPLES

In seven sets of samples, numbers 11 through 17, material balances were made for fluoride, aluminum, and zirconium between the initial solutions and final solutions plus the precipitates. The material balance for the zirconium was found to be 101 percent with a standard deviation of ± 3 percent; for the aluminum, the material balance was found to be 97 ± 12 percent; and for the fluoride, the material balance was found to be 84 ± 8 percent. This material balance suggested a significant bias in the solution or solid fluoride analyses. To determine what level of confidence could be placed in the final solution fluoride concentration values, they were compared by four different methods:

- (1) The analytical fluoride value with no bias correction.
- (2) The analytical fluoride value plus the assumed correction.
- (3) The ion balance, the difference between total analyzed cations and anions not including fluoride.
- (4) The analyzed zirconium analyses multiplied by 3 or 4 assuming zirconium hydroxide trifluoride or zirconium tetrafluoride.

The second and fourth methods are based on the original fluoride analysis, whereas, the other two methods are not. These calculated values for fluoride are listed in the following table. The comparison shows that the bias is not an error inherent in the solution fluoride analysis and must have occurred in the solid analysis measurements.

FINAL FLUORIDE CONCENTRATIONS BY VARIOUS METHODS

Sample Number	Analytical Value F,M	Method Used			
		Analytical Value Plus Material Balance Bias F,M	Zirconium Analyses		Ion Balance F,M
			Assuming F/Zr=4 F,M	Assuming F/Zr=3 F,M	
11	3.2	3.8	3.16	3.29	3.16
12	3.4	4.0	3.06	3.29	3.06
13	3.4	4.0	3.05	3.35	3.07
14	3.5	4.2	3.14	3.43	3.20
15	3.5	4.2	3.06	3.31	3.01
16	3.2	3.8	2.96	3.2	2.98
17	2.9	3.5	2.91	3.12	2.93

App. 4 - Long-Term Stability Curves - 1.5M Acid--The initial compositions of the solutions were 0.75M aluminum nitrate, 1.5M hydrogen ion, 4.2M fluoride, and 0.75 or 0.8M zirconium. The final fluoride concentrations were about 3.3-3.4M. The temperatures were 0°C - - - and 25°C——.

App. 4 - Long-Term Stability Curves - 1.0M Acid--The initial compositions of the solutions were 0.75M aluminum nitrate, 1.0M hydrogen ion, 3.7M fluoride, and 0.75 or 0.8M zirconium. The final fluoride concentrations were about 3.2-3.4M. The temperatures were 0°C - - - and 25°C——.

App. 4 - Long-Term Stability Curves - 0.5M Acid - 25°C--The initial compositions of the solutions were 0.75M aluminum nitrate, 0.5M hydrogen ion, 3.2M fluoride, and 0.75 or 0.8M zirconium. The final fluoride concentrations were about 2.5M.

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