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BLENDING RAFFINATES FROM  
ZIRCONIUM AND ALUMINUM PROCESSES

**MASTER**

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### IDAHO NUCLEAR CORPORATION

A JOINTLY OWNED SUBSIDIARY OF  
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### ABSTRACT

Laboratory data are given for the corrosion and stability to precipitation of solutions formed when raffinates from the re-processing of aluminum and zirconium alloy nuclear reactor fuels are blended in various proportions.

## SUMMARY

Raffinates from the reprocessing of both aluminum and zirconium alloy nuclear reactor fuels are produced and stored at the Idaho Chemical Processing Plant. The corrosion and stability to precipitation of a series of blends of these raffinates were evaluated to determine which blended compositions were usable and what storage conditions could be permitted. Several compositions containing 20 percent or less, and 90 percent or more zirconium raffinate were stable for one year. Zirconium fluoride hydrolysis products precipitated in the other blends. Both corrosion and solution stability were adversely affected by storage temperatures of 55°C compared to 35°C, and the latter temperature was recommended. At 35°C the corrosion of Types 304L and 347 stainless steel was acceptable for long-term use.

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## I. INTRODUCTION

Nuclear reactor fuel elements containing aluminum or zirconium are reprocessed in separate campaigns at the Idaho Chemical Processing Plant (ICPP). The aluminum-containing fuels are dissolved in nitric acid and the zirconium-containing fuels in hydrofluoric acid. In either case the uranium is recovered by solvent extraction and an aqueous raffinate containing fission products and the metal ions derived from the fuel is produced. The concentrations of the primary constituents in typical samples of these raffinates are shown in Table I.

Table I  
APPROXIMATE COMPOSITION OF RAFFINATES

	Zr	Al	F	$\text{NO}_3^-$	$\text{H}^+$
	<u>M</u>	<u>M</u>	<u>M</u>	<u>M</u>	<u>M</u>
Aluminum Raffinate	--	1.6	--	5.8	1.0
Zirconium Raffinate	0.61	0.64	3.3	1.86	0.84

Both streams contain aluminum nitrate as a major component and it would appear that they might be blended without major adverse chemical consequences. In the course of operations at ICPP this blending occurs inadvertently in one case and may be a desirable, deliberate operation in other cases. With the Waste Calcining Facility in operation on aluminum process raffinates, several of the large, permanent storage tanks have been essentially emptied of aluminum process raffinate. In the current ICPP waste management plans these are being used for the storage of zirconium process raffinates while a process is being developed for the calcination of this second type of raffinate. Since these large storage tanks can never be emptied completely of their former contents without extensive rinsing, some blending of aluminum and zirconium process raffinates is inevitable. Blending may be used deliberately to reduce the total fluoride concentration of the zirconium process raffinate and also to increase the degree of complexing of fluoride by aluminum. This might be advantageous in decreasing corrosive effects due to fluoride and in suppressing the volatility of hydrogen fluoride during calcination of the raffinate. Since precipitation of the hydrolysis products of zirconium fluoride was well known, [1-6] it was necessary to study the stability of the blended solutions to precipitation. Corrosion data were also desirable to determine at what degree of blending a reduction in corrosion rate was obtained. This document reports on these two aspects of the blending process.

## II. STABILITY OF BLENDED RAFFINATES

### 1. EXPERIMENTAL

Zirconium fuel raffinates were prepared by (a) dissolving reactor-grade zirconium in 10M hydrofluoric acid according to the flowsheets found in Tables 8 and 9 of IDO-14522<sup>[1]</sup>; (b) adjusting with nitric acid, hydrofluoric acid, or aluminum nitrate as directed in these flowsheets; (c) analyzing the resulting solutions for zirconium, aluminum, acid, and fluoride concentration; and (e) adding standard aluminum nitrate and/or acid solutions to give the solutions the desired constituent concentrations. Aluminum fuel raffinates were made by adding water, sodium nitrate, mercuric nitrate, and nitric acid in the desired amounts to 2.3M aluminum nitrate solution; the resulting solutions were analyzed for their aluminum concentrations and acidities. The concentrations of the components of each raffinate are given in Table 2. Zirconium Raffinate A represents the first cycle aqueous extraction waste produced in a modified STR flowsheet, in which the fuel is dissolved in 5-10M hydrofluoric acid plus an oxidant; Zirconium Raffinate B represents waste, after jet dilution, produced according to an ICPP plant test STR batch flowsheet; and Zirconium Raffinate C represents waste after heel dissolution produced by the ICPP STR batch flowsheet<sup>[1]</sup>. Maximum and minimum aluminum concentrations in the aluminum nitrate raffinates represent the maximum and minimum values found by analyses of ICPP first cycle wastes remaining after extraction with TBP.

Table II

COMPOSITIONS OF ALUMINUM AND ZIRCONIUM FUEL RAFFINATES

<u>Raffinate</u>	<u>Zr</u> <u>(M)</u>	<u>Al</u> <u>(M)</u>	<u>F</u> <u>(M)</u>	<u>H<sup>+</sup></u> <u>(M)</u>	<u>NO<sub>3</sub><sup>-</sup></u> <u>(M)</u>	<u>Hg</u> <u>(M)</u>	<u>Na</u> <u>(M)</u>	<u>CrO<sub>3</sub></u> <u>(M)</u>
A	0.76	0.56	3.9	1.3	2.10	--	--	--
B	0.61	0.64	3.3	0.84	1.86	--	--	0.015
C	0.48	0.62	3.0	0.99	1.81	--	--	0.015
D	--	1.75	--	1.0	6.35	0.02	0.1	--
E	--	1.62	--	1.0	5.96	0.02	0.1	--
F	--	1.50	--	1.0	5.60	0.02	0.1	--

Raffinate A was blended with Raffinate D in various proportions; similarly, Raffinate B was blended with Raffinate E, and Raffinate C with Raffinate F. The initial concentrations of the major components in all of these blends are shown in Table III. These blends were stored at 35 and 55°C for 54 weeks in polyethylene bottles. Table III also shows the final compositions of the solutions stored at 35°C after 54 weeks.

Table III

## COMPOSITIONS OF ZIRCONIUM-ALUMINUM RAFFINATE BLENDS

Blend	Initial Composition				Final Equilibrium Composition (After Storage at 35°C for 54 wks)						Solids Contents (After Storage at 55°C for 54 wks)	
	Zr(M)	Al(M)	F(M)	H <sup>+</sup> (M)	Zr(M)	Al(M)	F(M)	H <sup>+</sup> (M)	Solids(g/l)	Packed Volume of Solids (% of total Volume)	Solids (g/l)	Packed Volume of Solids (% of total Volume)
10% A-90% D	0.076	1.63	0.39	1.0	0.078	1.56	0.42	0.98	none	none	12	2
20% A-80% D	0.152	1.51	0.78	1.1	0.150	1.42	0.84	1.14	none	none	23	13
30% A-70% D	0.228	1.39	1.17	1.1	0.223	1.31	1.18	1.09	none	none	--	--
40% A-60% D	0.304	1.27	1.56	1.1	0.309	1.18	1.46	0.99	0.8	0.2	7.6	--
50% A-50% D	0.380	1.16	1.95	1.2	0.390	1.07	2.19	1.16	1.0	< 0.2	18	--
60% A-40% D	0.456	1.04	2.34	1.2	0.462	0.93	2.38	1.01	2.4	0.4	--	--
70% A-30% D	0.532	0.92	2.73	1.2	0.500	0.85	2.59	1.24	22	0	26	6
80% A-20% D	0.608	0.80	3.12	1.2	0.663	0.73	3.28	1.19	0.9	0.4	24	6
90% A-10% D	0.684	0.68	3.51	1.3	0.700	0.55	3.68	1.22	none	none	1	< 0.2
10% B-90% E	0.061	1.52	0.33	0.98	0.071	1.47	0.39	0.91	none	none	11	2
20% B-80% E	0.122	1.42	0.67	0.97	0.123	1.41	0.69	1.02	none	none	19	10
30% B-70% E	0.183	1.33	1.00	0.95	0.189	1.29	1.10	1.05	none	none	24	--
40% B-60% E	0.244	1.23	1.34	0.94	0.244	1.30	1.27	0.94	0.9	0.2	7.6	--
50% B-50% E	0.305	1.13	1.67	0.92	0.307	1.13	1.51	1.07	1.9	0.4	--	--
60% B-40% E	0.366	1.03	2.00	0.90	0.389	1.11	1.94	0.82	1.0	0.2	25	5
70% B-30% E	0.427	0.93	2.34	0.89	0.371	0.92	2.14	0.96	12.8	.2	38	8
80% B-20% E	0.488	0.84	2.67	0.87	0.380	0.84	2.27	0.79	23	3	45	8
90% B-10% E	0.549	0.74	3.01	0.86	0.426	0.76	2.50	1.02	25	3	43	6
10% C-90% F	0.048	1.41	0.30	1.0	0.050	1.36	0.32	0.79	none	none	--	--
20% C-80% F	0.096	1.32	0.59	1.0	0.095	1.26	0.55	1.13	none	none	8.6	9
30% C-70% F	0.144	1.24	0.89	1.0	0.148	1.17	0.88	0.98	0.9	0.1	17	9
40% C-60% F	0.192	1.15	1.18	1.0	---	---	---	---	---	---	--	--
50% C-50% F	0.240	1.06	1.48	1.0	0.230	1.01	1.44	0.96	1.1	0.4	11	--
60% C-40% F	0.288	0.97	1.78	1.0	0.315	0.96	1.74	0.94	0.8	0.1	6.4	2
70% C-30% F	0.336	0.88	2.07	1.0	0.344	0.85	2.04	0.95	1.0	< 0.1	6.5	2
80% C-20% F	0.384	0.80	2.37	1.0	0.384	0.76	2.10	0.96	0.6	< 0.1	9.8	2
90% C-10% F	0.432	0.71	2.66	1.0	0.430	0.67	2.72	0.96	stable	none	0.6	0.4

The solutions stored at 55°C were not analyzed. During the first month, stability observations were made on the blends five times a week; after that, observations were made once a week. At the end of 54 weeks the blends containing solids were centrifuged in graduated centrifuge tubes to determine the individual volumes of solids; these solids were then slurried and filtered, dried at 105°C, weighed, and examined by X-ray and emission spectrograph. The filtrates were analyzed for zirconium, aluminum, fluoride, and acidity.

## 2. RESULTS

### 2.1 Effect of Temperature

Figure 1 shows the stability<sup>[a]</sup> of all the blends during 54 weeks of storage at 35 and 55°C. All blends stored at 55°C became unstable within 17.5 weeks. At 35°C all blends containing 20 percent by volume or less zirconium raffinate were stable for 54 weeks or more; other blends stable at 35°C included two blends containing 30 percent by volume zirconium raffinate (30% zirconium raffinate A-70% aluminum raffinate D, and 30% zirconium raffinate B-70% aluminum raffinate E) and two blends containing 90 percent by volume zirconium raffinate (90% zirconium raffinate A-10% aluminum raffinate D, and 90% zirconium raffinate C-10% aluminum raffinate F). A few blends showed transient precipitation for several months. This effect had been noted earlier<sup>[1]</sup> and is undoubtedly due to the slow rate of interconversion among the zirconium and aluminum species. At the end of 54 weeks all blends had been unchanged for at least eight weeks; but in these solutions, even this time without apparent change does not guarantee that precipitation will not occur over a still longer period.

Since the stability of these raffinate blends is temperature dependent, it appears the storage tank temperature should not be allowed to increase above 35°C if it is desirable to produce stable blends containing sufficient volumes of both aluminum and zirconium fuel raffinates to make the blending practical.

### 2.2 Effect of Solution Composition

The acidity of all the blends is approximately constant (about 1M). The zirconium, aluminum, fluoride, and nitrate concentrations vary from blend to blend. Past experience<sup>[1]</sup> indicates that the stability of these blends would depend on their zirconium, aluminum, and fluoride concentrations. The stability of blends as a function of aluminum and zirconium concentrations after being stored at 35°C for 54 weeks is shown in Figure 2.

### 2.3 Characteristics of Unstable Blends

The compositions of the synthetic raffinate solutions at the time they were prepared and after 54 weeks at 35°C are shown in Table III. The

---

[a] In this work a stable solution was defined as one that contained no precipitate detectable to the unaided eye. A solution containing any detectable precipitate was classified as unstable. Many of the solutions labeled here as "unstable" might be tolerable in process equipment. Prior to rejection or use of these solutions having borderline properties, more detailed evaluation should be made. Data on the weight and volume of precipitate given later in this report will aid in this evaluation.

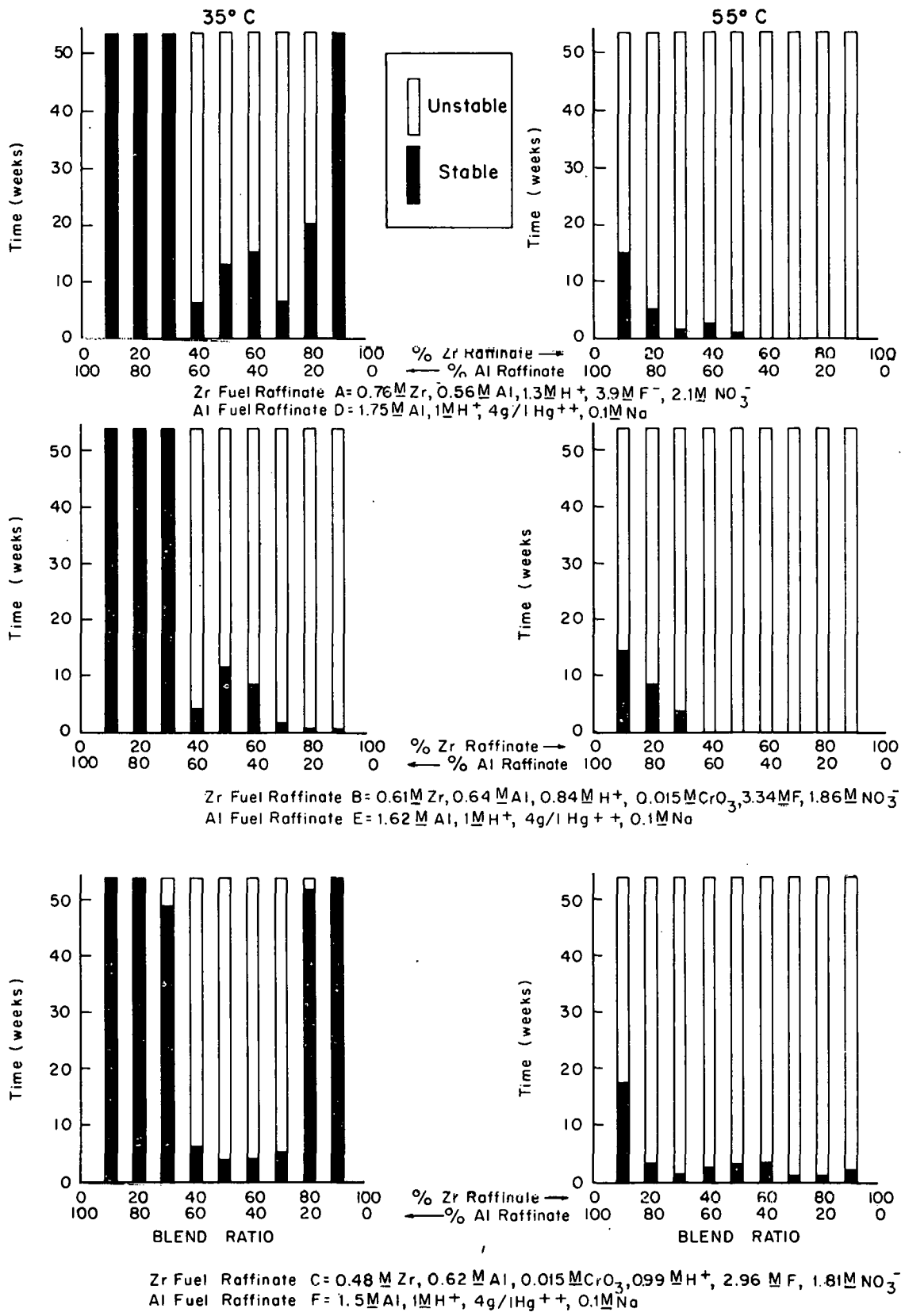


Fig. 1 Stability of Aluminum-Zirconium Raffinate Blends as a Function of Time and Temperature

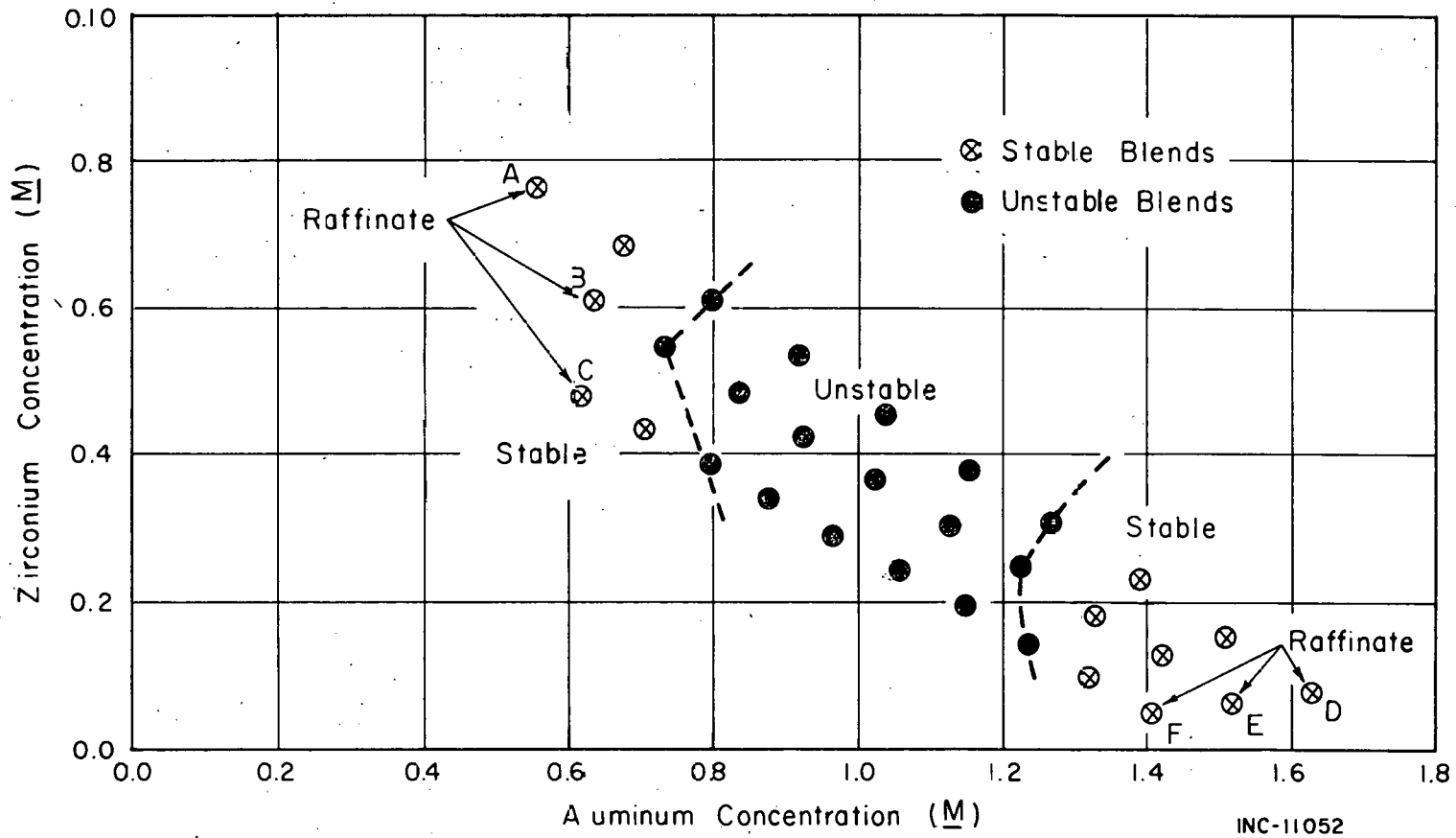


Fig. 2 Stability of Aluminum-Zirconium Raffinate Blends at 35°C as a Function of Aluminum and Zirconium Concentration (54 weeks stability test)

blends were initially synthesized from standard solutions of known concentration and the compositions of the various blends calculated from the proportions of standard solutions used in their preparation; these values rather than analytical values for each solution are given as the initial compositions in Table III. On the other hand, laboratory analytical results are shown in Table III for the compositions of the solutions after being held at 35°C for 54 weeks. The solids content of the solutions at 54 weeks is also shown in Table III. Emission spectrographic analysis of these solids showed that zirconium was always a major constituent and aluminum a minor. X-ray showed that those solids originating in blends containing 50 percent or less zirconium raffinate were amorphous. Solids formed in blends containing 70 percent or more of zirconium raffinate gave the X-ray pattern associated with the first hydrolysis product of zirconium tetrafluoride. [7] This is thought to have the chemical formula  $Zr(OH)F_3 \cdot H_2O$ . It is thought that both the crystalline and amorphous solids were zirconium hydrolysis products although contamination by aluminum salts was possible.

Solids appearing in blends containing 50 percent or less zirconium raffinate were gelatinous and colloidal; centrifuging these blends at speeds up to 8000 RPM would not clear them up, and the solids passed through 5 micron filters. Solids separating from blends containing 70 percent or higher zirconium raffinate were granular; the solids would settle out without centrifugation, and could be rapidly separated from solution with a 14 micron filter. Blends containing 60 percent zirconium waste contained a large amount of both the granular and colloidal-gelatinous solids. Table III shows the volume of solids (where sufficient amount of solids would settle under centrifugal forces to give such a value) and weight of solids (dried at 105°C) present in blends stored at 35 and 55°C for 54 weeks.

### III. CORROSION IN BLENDED RAFFINATES

#### 1. EXPERIMENTAL

Bench scale corrosion studies were conducted in several of the aluminum and zirconium raffinates and blends whose compositions are given in Table III. The compositions of alloys used as corrosion specimens are listed in Table IV.

Table IV  
COMPOSITION OF STEELS IN CORROSION COUPONS

<u>Steels</u>	<u>C</u>	<u>Ni</u>	<u>Cr</u>	<u>Mn</u>	<u>Cb</u>	<u>Ta</u>
Type 304L	0.03	9.25	20.0	1.15	--	--
Type 347	0.07	10.1	19.5	1.85	0.67	< 0.10



The coupons were prepared by welding together narrow strips of like alloys using the tungsten inert gas welding process. American Welding Society classification ER 308 bare electrodes were used to join strips of Type 304L ss and ER 347 electrodes for Type 347 ss. The welded pairs were sheared, and then machined to uniform size and 125 RMS surface finish. For corrosion measurements, these coupons were placed in polyethylene bottles that were partially filled with raffinate solution. Using polyethylene strings, two coupons were suspended totally in the vapor space, two at the interface, and two were totally submerged. A solution volume-to-coupon area ratio of 150 ml/in<sup>2</sup> was maintained during this study. The test procedure consisted of (a) weighing each test coupon prior to placing it in the test environment, (b) exposing the coupons at 35 or 55°C for two-, six-, and twelve-month terms, (c) weighing each test coupon, and (d) examining each coupon at a magnification of 20X and 430X.

## 2. RESULTS

The experimental data from the pairs of coupons that were exposed in the three positions in the various test vessels are summarized in Tables V, VI, and VII. The initial solution concentrations and the concentrations after exposure are given in Table III. A comparison of these two values indicates that typically there was little change in composition for the twelve-month exposure period. Corrosion rates in the range 0.1 - 30 x 10<sup>-3</sup> mpm were experienced. These are equivalent to rates measured earlier on coupons in ICPP storage tanks.[8] The lower values in this range are entirely acceptable for stainless steels in this service.

### 2.1 Comparison of Types 304L and 347 Stainless Steel

Table V shows data for Types 304L and 347 ss in a blended raffinate containing three molar total fluoride at 35°C. The two alloys gave equivalent good performance in this test with definite indication that the vapor phase was more corrosive than the liquid.

### 2.2 Effect of Total Fluoride Concentration

The data in both Tables VI and VII are arranged in decreasing order of total fluoride concentration in the test solution. The correlation between total fluoride and corrosion rate is clear at both 55°C (Table VI) and at 35°C (Table VII). It is assumed in these solutions that the active corrodent is either the small concentration of uncomplexed fluoride ion or hydrofluoric acid, the latter being active in the vapor phase. In these test solutions, with zirconium and aluminum present, the concentrations of uncomplexed fluoride ion and hydrofluoric acid are not directly proportional to the total fluoride concentration and therefore simple, direct relationships between total fluoride and corrosion rate would not be anticipated. However, the general trend suggests a qualitative correlation.

Table V  
CORROSION OF TWO STAINLESS STEELS IN  
RAFFINATE FROM ZIRCONIUM PROCESS AT 35°C  
(Solution C)

<u>Alloy</u>	<u>Test Environment</u>	<u>Cumulative Corrosion Rate (10<sup>-3</sup> MPM)</u>			<u>Micro Examination</u>
		<u>2 Mo.</u>	<u>6 Mo.</u>	<u>12 Mo.</u>	
SS Type 304L	Vapor	2	4	4	Uniform Etch
	Interface	3	2	2	Resistant Below Liquid
	Liquid	1	1	1	Resistant
SS Type 347	Vapor	1	5	4	Feeble Etch Machining Present
	Interface	1	3	2	Resistant Below Liquid
	Liquid	1	1	2	Resistant

Table VI  
CORROSION OF STAINLESS STEEL TYPE 304L IN  
RAFFINATES FROM ZIRCONIUM AND ALUMINUM PROCESSES AT 55°C

<u>Test Solutions</u>	<u>Test Environment</u>	<u>Cumulative Corrosion Rate (10<sup>-3</sup> MPM)</u>			<u>Micro-Examination</u>
		<u>2 Mo.</u>	<u>6 Mo.</u>	<u>12 Mo.</u>	
Solution C (2.96 MF)	Vapor	30	29	27	Heavy Weld Etch Light Wrought Etch Weld Anodic
	Interface	20	23	23	Uniform Etch
	Liquid	8	19	25	Uniform Etch
10% A-90% D (0.39 MF)	Vapor	0.4	2.1	3	Resistant
	Interface	0.5	1.8	2	Resistant
	Liquid	0.4	1.3	1	Resistant

Table VII  
CORROSION OF STAINLESS STEEL TYPE 304L IN BLENDED RAFFINATES  
FROM ZIRCONIUM AND ALUMINUM PROCESSES AT 35°C

Test Solutions in Order of Decreasing Fluoride Concentration	Test Environment	Cumulative Corrosion Rate ( $10^{-3}$ MPM)			Micro- Examination
		2 Mo.	6 Mo.	12 Mo.	
		90% "A" - 10% "D" (3.51 MF)	Vapor	9.3	
	Interface	4.3	7.8	7.0	Knife-line
	Liquid	4.0	6.8	7.0	Weld Etch with Machining Gone
Solution "C" (2.96 MF)	Vapor	2.0	4.0	4.0	Uniform Etch
	Interface	3.0	2.0	2.0	Resistant Below Liquid
	Liquid	1.0	1.0	1.0	Resistant
90% "C" - 10% "F" (2.66 MF)	Vapor	1.0	3.8	3.5	Uniform Etch
	Interface	1.3	1.7	1.0	Resistant
	Liquid	1.0	0.8	1.0	Resistant
80% "B" - 20% "E" (2.67 MF)	Vapor	< 0.1	1.4	2.0	Feeble Etch
	Interface	< 0.1	0.5	< 0.1	Feeble Etch
	Liquid	< 0.1	0.8	1.0	Resistant
60% "A" - 40% "D" (2.34 MF)	Vapor	< 0.1	2.7	3.0	Etch Edges
	Interface	< 0.1	2.2	2.0	Feebly Laminated Edges
	Liquid	< 0.1	1.2	1.0	Feebly Laminated Edges
10% "A" - 90% "D" (0.39 MF)	Vapor	0.1	< 0.1	0.4	Resistant
	Interface	0.4	< 0.1	0.4	Resistant
	Liquid	0.1	< 0.1	0.2	Resistant
10% "B" - 90% "F" (0.33 MF)	Vapor	0.2	0.1	< 0.1	Resistant
	Liquid	0.2	0.1	< 0.1	Resistant
	Interface	0.1	< 0.1	< 0.1	Resistant
Solution "D" (0.00 MF)	Vapor	0.8	0.2	< 0.1	Resistant
	Liquid	0.2	< 0.1	< 0.1	Resistant
	Interface	0.3	0.1	< 0.1	Resistant

### 2.3 Effect of Temperature

Comparing the results for identical solutions between Tables VI and VII indicates a significant effect of the temperature on the corrosion rate in this system. This led to the recommendation that for solutions containing > 0.5 molar fluoride the temperature of the storage tanks should not be allowed to rise above 35°C.

### 2.4 Variation in the Corrosion Rate with Exposure Time

Any evidence of the acceleration of the corrosion rate with time of exposure is important in this particular system since a large extrapolation of the data with respect to time is required. A survey of all of the data of Tables V, VI, and VII indicates that in many cases there was a significant increase in the observed corrosion rate between two and six months exposure. Where significant corrosion rates ( $1 \times 10^{-3}$  MPM or greater) were observed, there was no evidence of an increase in corrosion rate between the observations made at six and at 12 months. This is extremely encouraging for the first several years storage of raffinate in large stainless steel tanks. For information on the condition of the tanks after the first several years corrosion coupons are placed in the actual storage tanks when they are filled, and are removed remotely for examination at appropriate time intervals. [8]

### 2.5 Localized Attack

While the general corrosion rates based on weight loss which are presented in Tables V-VII are very encouraging, evidence of certain types of localized corrosion attack would indicate the possibility of failure far earlier than indicated by the weight loss data. On one of the two specimens of Type 304L stainless steel exposed in the vapors from solution C for 12 months at 55°C there were definite evidences of stress corrosion cracking. These cracks were seen at 430X adjacent to the metal-punched coupon identification numbers. Neither the duplicate coupon in the same environment nor any other coupon in the study showed this phenomenon. It is therefore concluded that this particular environment, the vapors from solution C at 55°C, was about the threshold for this type of corrosive attack. In addition, grain boundary attack was observed in the wrought areas at the weld-wrought interface on all coupons which were exposed for 12 months in solution C or its vapors at 55°C. More and deeper grain boundary attack was found on the Type 304L stainless steel coupons which were exposed in the vapors than those exposed in solution. Grain boundary attack was not observed on similarly exposed coupons in the vapor or liquid of solution C at 35°C. This selective attack by the vapor phase is probably associated with the evaporation of hydrofluoric acid from the solution and its condensation on the coupon in the vapor space where the fluoride, even though low in concentration, is completely uncomplexed by metallic ions until corrosion occurs. These observations of localized attack at 55°C confirmed the conclusion based on the weight loss data that storage of these raffinates at 35°C was significantly safer than storage at 55°C.

#### IV. CONCLUSIONS

##### 1. REGARDING STABILITY TO PRECIPITATION

It is possible to make blends of zirconium and aluminum process raffinates which are stable to precipitation for greater than one year, however, blends made from only certain proportions of the two raffinates have this long-term stability. At 35°C incubation temperature, several blends containing 20 percent by volume or less zirconium raffinate and 90 percent or more zirconium raffinate, both with aluminum raffinate, were stable for 54 weeks. At an incubation temperature of 55°C the range of stable compositions was even more limited. Where precipitation did occur, the precipitates varied widely in nature and amount, and the time before the first appearance of precipitate also varied with the composition of the solution and the temperature. The detailed data given in this document should be consulted before reaching a judgement as to the utility of any particular blended solution.

##### 2. REGARDING CORROSION

Types 304L and 347 stainless steel gave essentially identical performance in these tests, and either could be considered candidate materials for the construction of new tanks for storage service of this type of solution. The corrosion which did occur appeared to be directly related to the total fluoride concentration of the test solutions and was significantly higher at 55° than at 35°C. Although all of the corrosion rates measured by weight loss were very small, and equivalent to the rates observed from long-term exposure of specimens in actual storage tanks, the evidences of localized attack experienced at 55°C suggested that an upper limit of 35°C be placed on the storage solution in actual service.

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