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DATE: November 10, 1952

SUBJECT: Corrosion of Stainless Steels by HNO_3 - HF - $\text{Al}(\text{NO}_3)_3$ Mixtures
During Evaporation of Plutonium Product Streams

TO: F. L. Steahly

FROM: T. A. Arehart, T. C. Runion

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TO: F. L. Steahly

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November 10, 1952

FROM: T. A. Arehart, T. C. Runion

SUBJECT: Corrosion of Stainless Steels by HNO_3 -HF-Al(NO_3)₃ Mixtures
During Evaporation of Plutonium Product Streams

1.0 Introduction

Corrosion studies on various stainless steels were carried out using aluminum ion as a fluoride complexing agent to minimize corrosive attack on the evaporator metal.

It would be desirable to utilize dilute solutions of HF for the partitioning of plutonium from uranium in Purex-type flowsheets for the following reasons:

- (1) Because of the strong plutonium fluoride complex formed, excellent separation of plutonium from uranium may be obtained in a relatively short column.
- (2) It is possible to concentrate the very dilute plutonium-fluoride streams by evaporation to a greater extent than is permissible with most reducing agents (e.g., ferrous sulfamate).
- (3) Since dilute HF in water is used for the separation, excess HNO_3 is removed from the solvent, facilitating subsequent uranium stripping.
- (4) Additional beta and gamma decontamination for uranium is obtained in this step. (This is important in the metal recovery process in which uranium recovery is the primary objective.)

However, the successful use of HF for Pu partitioning is contingent on:

- (1) Maintaining an acceptably low rate of corrosion in the partitioning column, and during volume reduction of the Pu product.
- (2) Recovering fluoride-free HNO_3 for recycle to the process.

2.0 Summary

The rate of corrosion of stainless steels during the evaporation of HF- HNO_3 mixtures is quite high even in the presence of excess Al. With two moles of aluminum ion per mole of fluoride ion, the corrosion rate of stainless steel types 329 and 309-Cb was approximately 30 to 40 mils per year. Corrosion rates of other types of stainless steel (304, 316, 347) were three to four times higher.

In addition, 25 to 50% of the fluoride ion was distilled with the nitric acid. Because separation of HF and HNO_3 in conventional distillation equipment is very difficult, the recovered HNO_3 would be unfit for recycling in any plutonium recovery process and would have to be discarded.

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2.0 Summary (Continued)

It is believed that the above factors will prohibit the use of fluoride ion as a plutonium partitioning agent in the Purex Process. However, because of the extreme dilution of the plutonium in the metal recovery process at ORNL, and because of the short term nature of the project, the use of HF will be permissible in the TBP metal recovery process at ORNL.

Laboratory corrosion tests using type 347 stainless steel resulted in lower corrosion rates, 4 to 17 mils per year. However, it was suspected that fluoride loss occurred during these tests (ORNL-947, The Effect of Fluoride on the Corrosion of Stainless Steel in the Presence of Excess Al^{+++} Ion, A. R. Olsen).

3.0 Experimental

In order to approach process conditions, an existing "falling-film" evaporator was modified to process 300 cc of solution per minute. Since the evaporator pumping arrangement was such that a volume reduction of 100-1 could not be achieved, the constituents of the feed to the evaporator were doubled, and only a 50-1 volume reduction factor was actually demonstrated.

The evaporator components (see UNOP-14) are as follows: a 10' x 1.5" I.D. falling-film section; a 14" x 6" I.D. control pot evaporator; feed preheater; vapor head; entrainment trap; condenser; cooler; feed and concentrate pumps; catch tank and feed tank.

Samples of the various types of stainless steel as indicated in Table II were suspended in the vapor head and in the liquid phase of the control pot evaporator.

The evaporator was operated continuously for 144 hours (six days) for each run. By recombining the condensate and concentrate, and pumping back into the feed tank, the original feed was reused continuously for the duration of the run. Periodic analyses were made and necessary adjustments were made to maintain the concentration of the feed constituents at a constant level.

The three 144 hour runs had the following feed conditions:

Run #1	Run #2	Run #3
3.0M HNO_3	3.0M HNO_3	3.0M HNO_3
0.27 mg/ml Al^{+++}	0.27 Mg/ml Al^{+++}	0.54 mg/ml Al^{+++}
0.00 mg/ml HF	0.20 mg/ml HF	0.20 mg/ml HF
0.01 mg/ml U	0.01 mg/ml U	0.01 mg/ml U

Run #1 was made as a control run to determine the degree of corrosion occurring in the strong nitric acid system with no F^- present. However, analyses indicated the presence of approximately 80 ppm of Cl^- as impurities which probably accelerated the corrosion rate.

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3.0 Experimental (Continued)

Conditions for Run #3 were found to be the most effective and stainless steel types 329 and 309 were the least attacked. The former corroded at the rate of ~ 30 mils/year in both the liquid and vapor phase and the latter at a rate of ~ 30 mils/year in the liquid phase and ~ 45 mils/year in the vapor phase. There was no evidence of excessive localized corrosion on any of the weld test corrosion strips.

From these results, it is estimated that an evaporator fabricated from 309 stainless steel with a $\frac{1}{4}$ " corrosion allowance would endure for a minimum of five years under the conditions of Run #3. From the standpoint of economy, it is probably advisable to replace the stainless steel evaporators every five years rather than to install an evaporator made of more costly materials which may have a life of perhaps 20 years.

TABLE I

Run Conditions

Run No.	Al ⁺⁺⁺ mg/ml	F ⁻ mg/ml	HNO ₃ M	U mg/ml	Volume Reduction Ratio	Al ⁺⁺⁺ mg/ml	HF mg/ml	HNO ₃ M	U mg/ml	Cond. HF mg/ml
1	0.27	0	3.011	0.01	50/1	12.5	0	10	0.5	0
2	0.27	0.19	3.011	0.01	50/1	15	6.4	9.5	0.5	0.08
3	0.54	0.18	3.0	0.01	50/1	25	6.8	8.8	0.5	0.05

With a feed rate of 300 ml/min and a condensate rate of 294 ml/min., approximately 59% of the HF remained complexed in Run #2, while in Run #3, 73% remained complexed.

Corrosion data for various types of stainless steel are compiled in Table II:

Sample Location	S/S Types	Run No. 1 mils/year	Run No. 2 mils/year	S/S Types	Run No. 3 mils/year
Vapor	309-Y	49**	46.5	--	--
"	309-Y	4**	14.7	--	--
"	*309-4-C	63**	32.2	309-CB-1	37
"	*309-4-D	74**	26.8	309-CB-2	55
"	--	--	--	329-9	32
"	*304-2-C	20**	65.5	304-A-4	32
"	*304-2-D	30**	73.8	304-B-4	136
"	316-X	43**	49.3	316-6-CS-ELC	87
"	316-Y	61**	--	316-7-CS-ELC	96
"	347-C	52**	47.5	--	--
"	347-D	50**	47.8	--	--
"	*347-6-C	57**	126.2	347-1-CS	117
"	*347-6-D	55**	128.6	347-2-CS	85

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3.0 Experimental (Continued)

Sample Location	S/S Types	Run No. 1 mils/year	Run No. 2 mils/year	S/S Types	Run No. 3 mils/year
Liquid	309-A	9.2	145	--	--
"	309-B	12.7	133	--	--
"	*309-5-A	8.0	105	309-CB-3	29
"	*309-5-B	13.2	101	309-CB-6	30
"	--	--	---	329-10	28
"	--	--	---	329-11	33
"	*304-3-A	14.9	130	304-C-4	102
"	*304-3-B	15.5	139	304-D-4	90
"	316-A	17.8	194	316-8-CS-ELC	67
"	316-B	20.1	219	316-9-CS-ELC	52
"	347-A	17.8	137	--	--
"	347-B	20.6	137	--	--
"	*347-2-A	21.3	129	347-3-CS	58
"	*347-2-B	19.5	125	347-4-CS	47

Legend: CS - Sensitized
CB - Columbium Stabilized
ELC - Extra low carbon

Note: All other numbers and letters for identification purposes only.

* Welded Samples

** Demineralized water containing 80 ppm Cl was inadvertently used in the feed make-up of Run #1. It is estimated that this increased the corrosion rate in the vapor phase by a factor of 10.

A study of the data shows that stainless steel types 329 and 309 have the most effective resistance to attack by HF. However, even in Run #3, in which the mole ratio of Al^{+++} to F^- was 2/1, the corrosion rate was six to ten times the rate normally considered permissible.

The use of even higher Al concentrations would probably decrease the rates of corrosion, but would limit the amount of volume reduction possible. Other fluoride complexing agents such as thorium and lanthanum were considered but were not thought sufficiently promising to carry out full-scale tests.

It is planned to investigate briefly the use of Si for removal of F^- as SiF_4 prior to evaporation. If the laboratory results show merit, larger scale Unit Operation tests will be carried out.

TAA;TCR:mh

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		CHECKED BY T.A.A.	DATE 11/1/50
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