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CORROSION EVALUATION OF EQUIPMENT USED FOR
REPROCESSING ZIRCONIUM ALLOY NUCLEAR FUELS

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BY

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ABSTRACT

Corrosion rates for Monel-400 and various stainless steels in process solutions were determined in laboratory studies and in plant service. The plant service period included the first reprocessing of zirconium alloy nuclear fuels using boric acid as a soluble poison during dissolution. Corrosion rates for a Monel-400 dissolver using hydrofluoric-fluoboric acid dissolvent and sulfuric and chromic acids for cleanout ranged between two and eight mils per month. Corrosion rates for stainless steel plates containing boron as a fixed poison in the first cycle product evaporator were very low. The low corrosion rates for this and other process equipment indicate that the system can be used for future reprocessing operations.

SUMMARY

Corrosion experience at the Idaho Chemical Processing Plant has demonstrated that the continuous aqueous process for recovery of uranium from zirconium-uranium alloy nuclear fuels does not produce excessive corrosion of the Monel-400 and austenitic stainless steel equipment. These observations were made during the first zirconium alloy fuel processing campaign using boron as a soluble neutron poison in the dissolver. The dissolvent in contact with Monel 400 contained hydrofluoric, nitric, and boric acids. The dissolver product was complexed with aluminum nitrate before contacting stainless steel equipment.

Individual vessels were monitored to study corrosion rates. The dissolver fabricated from Monel-400 had an estimated metal loss of 7.5 mils per month. The first cycle product evaporator, fabricated from Type 304L stainless steel, suffered negligible metal loss from the body of the evaporator. The boron stainless steel grid used for criticality control in the disengaging section had an estimated metal loss of 1.0 mil during 20 months of service which included both aluminum and zirconium processing campaigns. These and other vessels in the system appear to be in serviceable condition and suitable for future processing operations.

Successful operation of a complex processing system such as this requires that careful attention be given to equipment design, specification of materials, and fabrication methods used during construction. Two of the three corrosion problems encountered during the recent processing campaign were the result of improper application of materials, while the third failure appeared to be the result of an improper metal heat treatment.

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CORROSION EVALUATION OF EQUIPMENT USED FOR REPROCESSING ZIRCONIUM ALLOY NUCLEAR FUELS

I. INTRODUCTION

The Idaho Chemical Processing Plant (ICPP) was recently equipped to process Zircaloy-clad zirconium-uranium alloy fuels at a substantially increased rate. The original batch dissolution process, employing hydrofluoric acid alone as the dissolving reagent, was used for several cores [1]. Recently a higher capacity semi-continuous dissolution system was installed [2,3,4], and a significant reprocessing campaign completed in FY 1966 [5]. Because of the higher uranium inventories in the dissolver for the semi-continuous system, boric acid was added to the dissolvent as a soluble nuclear poison [2,6].

Monel-400 was selected as the material of construction for the original batch dissolver, and when the process was modified, both Monel-400 and Carpenter-20 stainless steel were evaluated as materials of construction for a possible new dissolver [6]. As a result of this evaluation, no basis for a change in the material of construction appeared necessary, so the original Monel-400 dissolver was modified to operate in a semi-continuous fashion. This document reports the plant corrosion experience with the new process during the reprocessing campaign of FY 1966 as well as new supporting laboratory data obtained during the campaign. The details of plant operation during this campaign are given elsewhere [7].

A schematic flow diagram for the reprocessing of zirconium alloy fuels at the ICPP is presented in Figure 1 showing the major vessels and their functions. In the process the fuels are dissolved in 6.5M hydrofluoric acid containing boric acid equivalent to four grams of boron per liter. This solution also contained 0.03M nitric acid during the initial dissolution, but this additive was omitted during the remainder of the campaign. The dissolver product solution is complexed with aluminum nitrate solution containing 0.02M chromic acid in a Carpenter-20 stainless steel vessel. The bulk of the solution storage and solvent extraction equipment is constructed of Types 347, 348, 316, 304L, or 304 stainless steel.

The uranium is recovered by extracting it from the complexed dissolver solution with 10 percent tributyl phosphate in kerosene and then stripping with 0.005M nitric acid. The uranium in the stripping solution is concentrated in the first intercycle evaporator. A small amount of fluoride is carried through the solvent extraction system to this evaporator, either by entrainment or by the extraction of hydrofluoric acid and zirconium fluorides, resulting in concern for the condition of this evaporator. The solution leaving the first cycle evaporator is diluted with gross quantities of aluminum nitrate during a second solvent extraction cycle. With this dilution and the very extensive complexing of the fluoride by aluminum, corrosion effects of fluoride containing solutions in the rest of the process are believed to be negligible.

FIGURE 1
FLOW DIAGRAM FOR REPROCESSING ZIRCONIUM ALLOY FUELS AT ICPP.

II. LABORATORY AND IN-PLANT CORROSION TEST RESULTS

1. DISSOLUTION EQUIPMENT

1.1 Dissolvent Makeup and Storage

The dissolvent makeup tank is a 2500-gallon vessel that is used for preparation and storage of primary dissolvent for zirconium-type fuel elements. The solvent for this type of fuel is prepared by adding 70 percent hydrofluoric acid and sufficient boric acid to water to give a dissolvent containing 7-molar hydrofluoric acid and 4 grams of boron per liter. Initially the dissolvent also contained 0.03-molar nitric acid, but use of this chemical was discontinued after it was found to be unnecessary.

The dissolvent makeup tank is constructed of carbon steel lined with a 3/16-inch-thick proprietary rubber lining -- "Goodyear Plioweld". The tank contains detectors for monitoring the boron content of the dissolvent solution, a cooling coil, and an impeller-type stirrer -- all constructed of Monel-400 alloy.

Inspection of this vessel after one and one half years of service indicates that the lining is flexible and still serviceable. The lining on the lower one-third of the tank has suffered some color change and is now brown rather than black. A loose deposit of rubber particles was found on the tank bottom around the tank outlet. Chemical analysis showed that this deposit contained copper sulfide and traces of elemental sulfur. The sulfur is presumed to have been leached from the rubber lining and the copper to have come from corrosion of the Monel fittings in the vessel.

The detector tubes and the cooling coil showed less than two mils per month of corrosion, and the stirrer impeller was only slightly pitted. All of the Monel-400 alloy fittings remained in serviceable condition.

1.2 Dissolver Vessel

The dissolver vessel is constructed of Monel-400 alloy. The choice of Monel for this vessel resulted from early process scoping studies using bench scale and pilot plant continuous dissolvers [3,4,6]. The second material of choice was Carpenter-20-Cb stainless steel; however, this material suffered significantly greater corrosion attack at welds than did Monel.

1.21 Corrosion Tests Run in the Dissolver During Plant Operation. A 3/4-inch-diameter, Schedule 80, Monel-400 pipe specimen was installed in the dissolver vessel and exposed to process solutions during the entire initial campaign. Examination of this pipe specimen after 1749 hours of service indicated a total loss of 4.5 mils of metal. This is equivalent to a corrosion rate of 1.4 mils per month for the total service exposure. However, only 28 percent of this total exposure was actual dissolution; the remaining exposure time consisted of dissolver decontamination. Assuming the entire 4.5 mils metal loss to have occurred during dissolution, a corrosion rate of 6.6 mils per month is indicated. The specimen was returned to the dissolver and exposed for an additional operating period of 1536 hours. After the pipe specimen had been removed a second time and decontaminated, the metal loss was 16 mils. This is equivalent to a corrosion rate of 7.5 mils per month.

Monel-400 cylinders were installed in the dissolver vessel during the dissolver heel clean-out operation described in Table I. These specimens, which were exposed for a total of 243 hours to hydrofluoric, chromic, and sulfuric acid clean-out solutions alternately, had a corrosion loss of 2.0 mils per month. Microscopic examination showed some denickelization, dendritic attack on some welds, and several pits that were 2.5 mils deep.

TABLE I

REAGENTS USED TO CLEAN MONEL 400 DISSOLVER

Order of Addition to Dissolver	Solution	Concentration	Temperature (°C)	Service (hr)
1	Hydrofluoric Acid	20.0M	75	4.5
2	Hydrofluoric Acid	14.0M	75	12.5
3	Chromic Acid (CrO ₃)	0.1M	60 to 70	11.5
4	Hydrofluoric Acid	7.0M	60 to 70	14.0
5	Chromic Acid	0.05M	60 to 70	36.5
6	Sulfuric Acid	6.0M	92	164.5
Total Hours				243.5

Specimens of material similar to the pipe and the cylinders, designed to monitor the corrosion of the dissolver, have been in the dissolver since it was first used. An estimate of the total cumulative metal loss from the walls of the dissolver indicates that 150 mils remain of the original 188-mil corrosion allowance.

1.22 Laboratory Corrosion Tests. Laboratory test results (Table II) indicated that Monel-400 did not corrode excessively in any of the individual acids listed in Table I except six-molar sulfuric acid in which it had an average corrosion rate of 8.0 mils per month over four consecutive 24-hour periods at 114°C.

TABLE II

CORROSION OF WELDED MONEL 400 IN ACID MEDIA
(mils per month)

Period	7M HF at 65°C	20M HF at 65°C	0.05M CrO ₃ at 65°C	0.1M CrO ₃ at 65°C	6M H ₂ SO ₄ at 114°C
1	0.06	0.02	0.01	0.06	8.9
2	0.01	0.03	0.01	0.02	7.6
3	0.03	0.07	0.02	0.01	7.4
4	0.07	0.07	Wt Gain	0.00	7.8

Cyclic tests (Table III) run over four consecutive 24-hour periods revealed that the corrosion of Monel-400 is appreciably increased in chromic acid when preceded by a period in 20-molar hydrofluoric acid. The corrosion of Monel exposed in the sequence chromic acid, seven-molar hydrofluoric acid and chromic acid showed a tendency to increase on the second exposure to chromic acid. In general, those cycles not involving sulfuric acid gave entirely acceptable corrosion rates.

TABLE III

CORROSION OF WELDED MONEL 400 IN
ACID MEDIA DURING CYCLIC CORROSION TESTS (MPM)

Test	Period	<u>7M HF</u> at 65°C	<u>20M HF</u> at 65°C	<u>0.05M CrO₃</u> at 65°C	<u>0.01M CrO₃</u> at 65°C	<u>6M H₂SO₄</u> at 114°C
1	1	0.05				
	2		0.02			
	3	0.04				
	4		0.14			
2	1	0.04				
	2				0.06	
	3	0.03				
	4				0.11	
3	1	0.06				
	2					7.3
	3	0.05				
	4					6.6
4	1	0.06				
	2				Wt. Gain	
	3		0.04			
	4				0.28	
5	1	0.11				
	2					5.3
	3		0.05			
	4					6.6
6	1	0.09				
	2				0.09	
	3					15
	4	0.07				
7	1	0.12				
	2				0.14	
	3		0.09			
	4			0.25		
8	1		0.14			
	2			0.34		
	3					7.7
	4			0.10		
9	1	0.10				
	2				0.29	
	3					8.4
	4				0.09	

1.3 Corrosion During Fuel Charging

During fuel charging the dissolver is partially filled with a dilute boric acid solution which cushions the fall of the heavy fuel elements. During dissolution this "charging water" is stored in a separate vessel and is reused for many cycles during a campaign. To investigate the possible corrosion of Monel by this solution, accelerated corrosion studies were made. A 48-hour laboratory test of Monel-400 alloy in boiling 0.14-molar boric acid (1.5 grams per liter boron) solution simulating the charging water showed an average corrosion rate of 0.09 mil per month and a maximum corrosion rate of 0.11 mil per month. Extension of this test to 92 hours showed an average corrosion rate of 0.06 mil per month with a maximum corrosion rate of 0.08 mil per month.

2. FIRST CYCLE PRODUCT EVAPORATOR

2.1 Plant Experience

The first cycle product evaporator vessel is constructed of Type 304L stainless steel with Type 304 stainless steel plates containing boron suspended in the large-diameter disengaging section of the vessel for criticality control. Since fluoride was detectable in the evaporator concentrate and the boron-containing stainless steel is somewhat sensitive to corrosion, special surveillance was given to this vessel. Aluminum was present with the fluoride in the concentrate and it was assumed that physical carry-over of aqueous phase from the IA (extraction) and IB (scrubbing) columns was at least partially responsible for the presence of fluoride in the evaporator.

Stainless steel corrosion coupons (Type 304 containing 1.5-percent boron and ordinary Type 304L) placed in the disengaging section of the evaporator were examined after 14,568 hours of exposure. This total period included decontamination and evaporation of product from both aluminum and zirconium alloy fuels. The former solutions were fluoride free. Based on the results of this examination, the boron-containing stainless steel plates in the disengaging section of this evaporator had lost an estimated 1.0 mil of metal from each exposed surface. The type 304L stainless steel of the vessel walls lost an estimated 0.02 mil.

Analysis of the evaporator product indicated the presence of boron. Assuming that this boron was totally from corrosion of the plates containing boron in the evaporator disengaging section, a corrosion rate of about 0.2 mil per month was calculated [8].

2.2 Laboratory Tests

A series of corrosion tests were conducted in the laboratory to determine the effect of fluoride carryover from the extraction section on the stainless steel plates containing boron in the first cycle product evaporator disengaging

section. Results of these tests, presented in Table IV, indicate that the solutions containing no fluoride or containing 0.1M fluoride along with aluminum (3 moles of aluminum per mole of fluoride) do not result in excessive corrosion. On the other hand, significant corrosion is indicated for solutions containing 0.1 molar uncomplexed fluoride.

TABLE IV

VAPOR PHASE CORROSION OF TYPE 304L
STAINLESS STEEL CONTAINING 1.5 PERCENT BORON

<u>Test Solution Composition:</u>		<u>Solution 1</u>	<u>Solution 2</u>	<u>Solution 3</u>
U	<u>M</u>	0.84	0.84	0.84
NO ₃	<u>M</u>	3.78	3.78	4.68
H	<u>M</u>	2.1	2.2	2.2
F	<u>M</u>	----	0.1	0.1
Al	<u>M</u>	----	----	0.3

Corrosion Rates (MPM)

Following Individual Exposure Periods

24 hours @ 85 C	----	0.8 ^[a]	0.2 ^[a]
23 hours @ b.p.	0.16	8.6 ^[a]	0.11
90 hours @ b.p.	0.30	8.6	0.32

[a] Results of a single determination -- other results represent the average of two determinations.

3. STORAGE TANKS

Aqueous wastes containing fluoride from processing zirconium alloy fuel elements may be stored in existing Type 304L or 348 stainless steel waste tanks provided the temperature does not exceed 35°C^[8]. Results of laboratory tests with blends of synthetic raffinates from zirconium and aluminum fuel at 35 and 55°C showed the most severe corrosion attack (0.03 mils per month) on coupons suspended in the vapor phase at 55°C. Stress corrosion cracking and grain boundary attack were found on Type 304L stainless steel in the experiments at 55°C. In exposures at 35°C, the maximum corrosion attack experienced was 0.004 mil per month. Corrosion in the raffinate from the regular zirconium process flow sheet was only slightly greater than corrosion in the blends.

III. ADVERSE EXPERIENCE WITH MATERIALS OF CONSTRUCTION

Several problems occurred during the processing run caused by the presence of materials incompatible with fluoride. In some cases the effect of complexed fluoride on the materials of construction was underestimated. A Carpenter-20-Cb stainless steel jet used in fluoride solution failed due to corrosive attack in a weld area. This jet, which had been installed in the as-welded condition, was replaced with a similar jet which was fully annealed after welding. The vitreous enamel lining (Albyline) in an electromagnetic flowmeter, exposed to complexed dissolver product solution, failed as did a titanium evaporator component. Because of the equipment arrangement, the titanium tube bundle of the evaporator was exposed to the process solution although the evaporator was not being used. It remains highly desirable to use this installed evaporator containing the titanium tube bundle to concentrate the IB, scrub column, raffinate in future runs. Therefore, an extensive study of the maximum fluoride concentration tolerable by titanium in this environment is underway and will be reported separately.

IV. CONCLUSIONS

Major equipment used in this reprocessing campaign appeared to have incurred only very modest corrosion attack. The Monel 400 dissolver experienced an estimated 7.5-mils per month (maximum) metal loss during dissolution operations. At this rate, the vessel, built with a corrosion allowance of 188 mils, will have an adequate life for all foreseeable process use. Corrosion of the stainless steel body and the poisoned plates in the disengaging head of the first intercycle evaporator was measurable but not excessive even though some fluoride was present. Laboratory corrosion measurements made during development studies indicated that Types 347, 348, 316, 304L and 304 stainless steel vessels in the extraction and waste storage systems, which are operated at 35°C or less, will not undergo any significant corrosion. It is presently indicated that all of the process equipment is suitable for use in future processing operations.

The three equipment failures occurring during this initial zirconium alloy nuclear fuel reprocessing campaign are recognized as having resulted from the use of materials incompatible with the processing solutions, or (in one case) improper annealing of the material. Such difficulties can be prevented by improved design specifications and closer materials control during fabrication and installation of equipment.

V. REFERENCES

1. J. R. Bower, "ICPP Operational Schedule, Performance and Problems", in Phillips Petroleum Company, Chemical Processing Technology Quarterly Progress Report April - June 1960, IDO-14534 (December 1960) pp 13-16.
2. J. R. Bower, Zirconium Processing Capability of the Idaho Chemical Processing Plant, IDO-14645 (October 1964).
3. K. L. Rohde et al, An Improved Aqueous Process for Zirconium Alloy Nuclear Reactor Fuels Part I. Preliminary Laboratory Studies, IDO-14594 (October 1962).
4. B. J. Newby, An Improved Aqueous Process for Zirconium Alloy Nuclear Reactor Fuels Part II. Continuous Dissolution with 5M Hydrofluoric Acid, IDO-14619 (September 1963).
5. J. R. Bower (ed.), Chemical and Process Development Branch Annual Report Fiscal Year 1966, IDO-14680 (October 1966).
6. B. J. Newby and K. L. Rohde (eds.), An Improved Aqueous Process for Zirconium Alloy Nuclear Reactor Fuels Part III. Continuous Dissolution in Hydrofluoric Acid with Soluble Poison, IDO-14674 (June 1966).
7. G. F. Offutt et al, First Zirconium Alloyed Fuel Reprocessing Campaign Using Soluble Nuclear Poisons, IN-1091 (to be issued).
8. B. J. Newby and T. L. Hoffman, Blending Raffinates from Zirconium and Aluminum Processes, IN-1114 (September 1967).