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AN IMPROVED AQUEOUS PROCESS FOR
ZIRCONIUM ALLOY NUCLEAR REACTOR FUELS
PART III. CONTINUOUS DISSOLUTION IN HYDROFLUORIC ACID
WITH SOLUBLE POISON

B. J. Newby and K. L. Rohde, Editors

RELEASED FOR ANNOUNCEMENT
IN NUCLEAR SCIENCE ABSTRACTS

PHILLIPS
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ATOMIC ENERGY DIVISION

NATIONAL REACTOR TESTING STATION
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A B S T R A C T

The Idaho Chemical Processing Plant Monel-400 batch dissolver was recently converted to semi-continuous operation to provide higher capacity reprocessing facilities. The semi-continuous operation required that about 4 g/l boron be present to make the operation critically safe. Process development studies leading to the higher capacity operation are reported.

Laboratory dissolution studies in a one-inch diameter continuous dissolver using 5M hydrofluoric acid-0.03M nitric acid-4 g/l boron to dissolve 2.2 to 2.5 percent uranium-Zircaloy-2 fuel showed that the dissolver product is suitable for complexing into extraction feed. Operation of a 3.5-inch diameter pilot plant dissolver simulating the ICPP semi-continuous dissolver operation showed only traces of uranium solids formed in the dissolver during operation and that a 16-hour charging-dissolution schedule was possible and adequate to meet production needs.

Uranium solids adhering to dissolver walls were dissolved in 0.1M chromic acid. Uranium-235 is not expected to build-up during dissolver operation because the meat of irradiated fuel has been shown to dissolve faster than its cladding material. Boron was shown to stay in the dissolver product solution at all times even during excessive evaporation and precipitation of uranium or zirconium fluoride.

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I. SUMMARY

The Idaho Chemical Processing Plant (ICPP) Monel batch dissolver for zirconium-clad zirconium-uranium alloy fuels was recently converted to a semi-continuous dissolver to meet the anticipated increased loads for this type of fuel. The conversion necessitated loading the dissolver with more than a minimum critical mass. This was safely accomplished by using about 4 g/l boron as a soluble nuclear poison in the dissolver feed.

Laboratory dissolution studies in a one-inch diameter continuous dissolver using 5M hydrofluoric acid-0.03M nitric acid to dissolve 2.2 to 3 percent uranium-Zircaloy-2 fuel indicate that the presence of 4 g/l boron in the system creates no process problems. The only adverse effect caused by this concentration of boron is that it produces a slightly higher concentration of zirconium-fluoride hydrolysis product in the dissolver and dissolver product. Dissolution results were independent of whether boron was added as boric acid or as fluoboric acid. Similar to dissolutions in the absence of boron, decreasing the operating temperature decreased the quantity of uranium lost to solids held in the dissolver.

A 3.5-inch diameter pilot plant dissolver was constructed to simulate operation in the proposed ICPP semi-continuous Monel dissolver or operation in a 20-inch diameter Carpenter-20 dissolver which was considered as a potential new installation at the ICPP. In runs simulating the Monel dissolver, only trace amounts of uranium solids were produced, and all the fuel was dissolved in a period equivalent to the desired plant time cycle. Successful dissolver operation producing only trace zirconium fluoride hydrolysis products was realized when the dissolver was operated simulating the Carpenter-20 dissolver if the fuel bed inventory and operating temperature were kept low.

Boiling 0.1M chromic acid was found to be satisfactory for removing uranium solids that may deposit on dissolver walls during operation. The meat of irradiated fuel dissolves faster than its cladding; thus eliminating the danger of build-up of uranium-235 in dissolver bottoms. Boron present in zirconium fluoride dissolver product is not volatile and is not carried down with zirconium fluoride or uranium fluoride precipitates.

II. INTRODUCTION

The equipment originally installed at the ICPP⁽¹⁾ for the dissolution of fully enriched, Zircaloy-clad uranium-zirconium alloy fuels was of low capacity and gave inadequate production rates and unnecessarily high processing costs. The installation of equipment for the continuous dissolution of the fuel was shown to be required to achieve both the required production rate and decreased costs⁽²⁾. The preliminary development work for the continuous dissolution process has been reported in the earlier documents in this series^(3, 4). But, a very important change in the development of the process occurred when it was shown that the original batch dissolver installed at ICPP for these fuels could be modified for semi-continuous operation, if a soluble poison could be used in the dissolver reagent^(5,6). Boron, as fluoboric acid, was selected as the soluble poison for this application because of its close chemical compatibility with the process streams.

This report deals with those changes in the dissolution material balance necessitated by the presence of boron in the solutions, with demonstrations of the retention of boron in the dissolver solution under all process conditions, and with extensive corrosion data for Monel-400 (hereafter referred to as Monel), the material of construction of the existing dissolver. In the course of the development work, the construction of a new dissolver was also considered, with both Monel and Carpenter-20 considered as the possible material of construction. Extensive corrosion data for the latter material in the process solution are given, although the existing Monel dissolver was actually used for the plant process.

This document is intended to serve as a record of the extensive development information obtained for this dissolution process. Readers seeking a broader impression are referred to the descriptive report on the zirconium processing capability of ICPP⁽⁷⁾.

III. DISSOLUTION FLOWSHEET DEVELOPMENT

The plant dissolution flowsheet which resulted from the development work reported herein is shown in Figure 1. This plant flowsheet uses batch charging of the fuel with continuous addition of the dissolution reagent to achieve optimum efficiency for the dissolver installed at ICPP. The quantities given represent approximately one day's processing to match the existing solvent extraction capacity of 10 kg per day of uranium. The reagent is prepared from boric acid and hydrofluoric acid with an optional small amount of nitric acid added to oxidize the tin in the Zircaloy cladding. The dissolver environment is essentially a reducing one, with large quantities of hydrogen produced and the uranium in the product present as uranium (IV). This is a compromise condition designed to protect the Monel vessel from excessive corrosion. Prior to solvent extraction the uranium is oxidized to uranyl ion in an adjustment step which is not shown.

Fig. 1 Semi-continuous dissolution flowsheet for zirconium alloy fuels

1. Laboratory Development Studies

Two arrangements of equipment were used for laboratory dissolution studies. A portion of the studies were made in a one-inch-diameter continuous laboratory dissolver constructed of Monel. A detailed description of the equipment and procedures is given in Part I of this series of reports⁽³⁾. The dissolution section of the dissolver was 16 inches high, and the rate of fuel addition was regulated to maintain within the dissolver undissolved fuel having a surface area of approximately 320 square centimeters at all times, which was generally a depth of 6 inches of fuel. During the usual method of dissolver operation, reagent was pumped into the bottom of the dissolver and dissolver product overflowed from the dissolver 16 inches above the feed inlet (upflow dissolution). For upflow forced recirculation operation, dissolver product was removed from the dissolver at a rate of 300 ml/min by a positive displacement pump, through a line one inch below the dissolver outlet and was pumped back into the bottom of the dissolver. In downflow forced recirculation operation, the dissolver solution was removed from the bottom of the dissolver and was pumped back into the dissolver through a line four inches above the dissolver outlet. With both recirculation systems, fresh acid reagent was pumped into the dissolver through the recirculation line, and dissolver product solution left the dissolver through the same line that served as the dissolver outlet during upflow dissolution.

The second dissolver was a natural recirculating, Carpenter-20, continuous dissolver. This dissolver was similar to the Monel dissolver with the exception that operating temperature and recirculating rates were controlled by a combination of applying heat to the dissolver body and removing heat from the recirculating line. During recirculation operation, temperatures within the dissolver varied by about 3°C. These temperatures were measured at the point in the dissolver where solution entered the recirculation line (17 inches from the bottom of the dissolver), at a point in the dissolver nine inches from its bottom, and at a point in the recirculation line two inches below its cooling portion.

Of all the fuels tentatively scheduled to be processed at the ICPP, only one is three weight percent uranium, and all other fuels will contain less than 2.2 weight percent uranium. Therefore, Zircaloy-2 fuel containing from 2.2 to 3 percent uranium was used in all studies. A ratio of dissolvent feed rate to fuel surface area of 0.04 cm/min (a feed rate of about 11 ml/min) was always used. The length of a dissolution run depended upon how quickly dissolution equilibrium was attained. It was assumed that the dissolver was at equilibrium when three consecutive specific gravity measurements of dissolver product, taken at half-hour intervals, were identical within the uncertainty of the measurement. In general, equilibrium was reached within three hours; and the total run time was about 6.5 hours. For determination of the material balance, uranium adhering to dissolver walls was removed by boiling with 20 percent sodium hydroxide in the presence of metallic zinc.

2. Addition of Fluoboric Acid

Dissolution runs were performed under various conditions in which the dissolvent boron concentration was varied from 0 to 6 g/l. Table I A summarizes the results obtained from dissolution experiments using an operating temperature of about 90°C, a dissolvent approximately 4M in free fluoride (total fluoride concentration minus four times the boron concentration), a boron concentration in the dissolvent from 0 to 6 g/l, and an upflow dissolver. As shown in Table I A, variation of boron concentration from 0 to 6 g/l has little effect on the system. Table II shows boron material balances for all runs that used a hydrofluoric acid-0.03M nitric acid-boron dissolver feed. Based on the 95 percent confidence level 101 ± 3 percent of the boron added to the dissolver feed was found as a soluble component of the dissolver product. In studying all the runs of Table I, it is evident that dissolutions involving 4 to 6 g/l boron produced dissolver products containing a higher average solid content than those using 2 g/l or less boron; the dissolver products containing high boron (4 to 6 g/l) were also slightly more unstable. Dissolver product solutions produced from runs using 4 to 6 g/l boron contained solids in the concentration range 0.08 to 0.28 g/l compared to a solid content of 0.02 to 0.14 g/l when the boron content was 2 g/l or less. The solids in the high boron dissolver product (4 to 6 g/l) contained zirconium-fluoride hydrolysis products, whereas, at the low boron concentrations, the solids were primarily undissolved tin.

3. Hydrofluoric Acid Concentration

Results from a run using 6.0M hydrofluoric acid-0.03M nitric acid-0.55M boric acid to dissolve 2.2 percent uranium-Zircaloy-2 fuel at an operating temperature of 90°C in an upflow dissolver were compared to those of a run using 7.0M hydrofluoric acid-0.03M nitric acid-0.55M boric acid (see Table I B). The run using 7.0M hydrofluoric acid had a higher dissolution rate, resulting in dissolver product having a zirconium concentration sufficiently higher to produce a fluoride-to-zirconium mole ratio equal to that in the dissolver product from the 6.0M hydrofluoric acid dissolution. The 6.0M hydrofluoric acid dissolution produced a dissolver product that was more stable than that produced in the other run. Other dissolution results seemed to be independent of whether the dissolvent was 6.0 or 7.0M hydrofluoric acid.

4. Boron Source Material

Two dissolutions were performed using 5.2M hydrofluoric acid-0.03M nitric acid-0.38M boric acid at 60 and 90°C respectively in upflow dissolvers, and two dissolutions were carried out using 3.72M hydrofluoric acid-0.03M nitric acid-0.37M fluoboric acid at the two different temperatures. The dissolution was independent of whether boron was added as boric or fluoboric acid (Table I C). Similar to dissolutions in the absence of boron, decreasing the operating temperature decreased the quantity of uranium lost to solids held in the dissolver⁽³⁾. Other dissolution phenomena did not appear to be temperature dependent.

Table I
DISSOLUTION OF ZIRCALOY-TYPE FUEL IN HYDROFLUORIC ACID CONTAINING BORON

Conditions: Up-flow dissolver, feed to fuel surface area rate 0.04 cm/min.

Run #	Dissolver	% U in Fuel (with Zircaloy-2)	Operating Temperature °C	Dissolver Acid Flow Direction	Effect of Boron Concentration		% of U Lost to Solids Held in Dissolver	% of U in Fur. that Could Have Been Dissolved	Dissolver Product Analyses					
					Dissolution Rate mg/(cm ²)(min)	Wt. of Solids Left in Dissolver (g)			Zr (M)	H ⁺ (M)	F to Zr Mole ratio	B (g/l)	B (M)	Solids (g/l)
125 & 130 Average	4.8M HF-0.02M HNO ₃	3.0	90		1.7	3.7	2.8	2.4	1.17	0.5	4.6	0.6	-	0.14
131	5.2M HF-0.02M HNO ₃ -0.22M H ₂ BO ₃	3.0	90		1.4	4.3	3.4	2.4	1.10	0.5	4.8	0.5	0.20	0.05
138	5.2M HF-0.02M HNO ₃ -0.38M H ₂ BO ₃	2.2	90		1.3	5.1	0.8	2.2	1.00	0.7	5.3	0.4	0.39	0.19
141	6.0M HF-0.02M HNO ₃ -0.55M H ₂ BO ₃	2.2	90		1.3	5	2.2	2.3	1.03	0.8	5.7	0.6	0.55	0.08
B														
Effect of Hydrofluoric Acid Concentration														
140	7.0M HF-0.02M HNO ₃ -0.55M H ₂ BO ₃	2.2	90		1.9	5.1	5.6	2.1	1.24	0.9	5.7	0.8	0.58	0.15
141	6.0M HF-0.02M HNO ₃ -0.55M H ₂ BO ₃	2.2	90		1.3	7.7	2.2	2.3	1.03	0.8	5.7	0.6	0.55	0.08
C														
Effect of Boron Source Material and Operating Temperature														
135	3.72M HF-0.02M HNO ₃ -0.37M H ₂ BO ₃	2.2	90		1.1	3.8	1	2.2	1.01	0.8	5.2	-	0.39	0.23
136	3.72M HF-0.02M HNO ₃ -0.37M H ₂ BO ₃	2.2	60		1.6	4.7	0.11	2.2	1.11	0.5	4.9	0.5	0.39	0.25
138	5.2M HF-0.02M HNO ₃ -0.38M H ₂ BO ₃	2.2	90		1.3	6.1	0.84	2.3	1.00	0.7	5.3	0.4	0.39	0.19
137	5.2M HF-0.02M HNO ₃ -0.38M H ₂ BO ₃	2.2	60		1.5	5.3	0.10	2.3	1.07	0.5	5.0	0.3	0.39	0.13
D														
Effect of Mode of Operation														
133	4.4M HF-0.02M HNO ₃ -0.20M H ₂ BO ₃	2.2	60	Forced down- flow recirculation	1.7	5.1	0.008	2.3	1.14	0.4	4.6	0.3	0.19	0.05
134	4.4M HF-0.02M HNO ₃ -0.20M H ₂ BO ₃	2.2	90	Forced upflow recirculation	1.4	4.4	0.47	2.1	1.14	0.6	4.6	0.6	0.20	0.06
139	4.4M HF-0.02M HNO ₃ -0.20M H ₂ BO ₃	2.2	60	Forced upflow recirculation	1.7	5.5	0.014	2.2	1.17	0.5	4.9	0.3	0.21	0.02
137	5.2M HF-0.02M HNO ₃ -0.38M H ₂ BO ₃	2.2	60	Upflow	1.5	5.3	0.10	2.3	1.07	0.5	5.0	0.3	0.39	0.13
144	5.2M HF-0.02M HNO ₃ -0.37M H ₂ BO ₃	2.4	60	Natural upflow recirculation	1.2	1.4	0.04	2.4	1.00	0.5	5.4	0.3	0.41	0.15
145	5.2M HF-0.02M HNO ₃ -0.37M H ₂ BO ₃	2.5	60	Natural upflow recirculation	1.3	0.89	0.20	2.7	1.02	0.6	5.0	0.2	0.38	0.15

Table II

BORON MATERIAL BALANCES DURING DISSOLUTION

Run #	Boron Concentration in Dissolver Feed g/l	Volume Shrinkage During Dissolution %	Boron Concentration in Dissolver Product g/l	Boron Material Balance
131	2.38	0.8	2.33	97
132	2.30	8.4	2.48	100
133	2.00	2.4	2.05	100
134	2.00	1.2	2.21	109
135	4.10	7.0	4.32	98
136	4.25	2.2	4.29	99
137	4.05	6.2	4.10	95
138	3.95	1.0	4.22	106
139	2.17	0.6	2.26	104
140	5.76	4.5	6.27	104
141	5.66	1.1	5.96	104
143	4.2	1.6	4.3	100
144	4.2	3.0	4.4	102
145	4.3	1.8	4.1	95

5. Mode of Operation

Recirculation dissolvers should offer an advantage over the upflow dissolvers because they can utilize the same low feed-to-fuel-surface area ratio while allowing the solution within the dissolver to be in rapid motion, thus giving solids less chance to adhere to dissolver walls and build up in the bottom of the dissolver. Table I D summarizes the results obtained from various recirculation dissolution systems; an upflow dissolution made under optimum conditions is also included for comparison purposes. The most marked phenomena indicated is that the natural recirculation dissolver runs allowed much less solids to build up than did forced recirculation and upflow dissolvers. This was probably due to the fact that the solution within the natural recirculation

dissolver was in more rapid motion than in the other dissolvers, thus allowing effective slurring of undissolved solids out of the dissolver. A recirculation dissolution (Run 134) made at a temperature (90°C) which results in about one percent of the uranium being lost to solids held within the dissolver in non-recirculation dissolver (Runs 135 and 138) lost less than 0.5 percent of the uranium to the dissolver. Thus, motion within the dissolver and/or prevention of the fuel from being in contact with concentrated hydrofluoric acid appears to result in reduced uranium losses to the dissolver. A study of Table I also shows that uranium losses to the dissolver decrease as the uranium content of the fuel which is in excess of that which can be dissolved and retained in solution is decreased (eg, compare Runs 126, 130, and 131 with Runs 135 and 138).

6. Volatility of Boron from Dissolver Solutions

Studies were performed to determine the volatility of boron under conditions which might result in the evaporation of solution from the plant dissolver. Four 100 ml aliquots of dissolver solution (1.05M zirconium, 5.8M fluoride, 0.8M acid, 0.6 g/l tin, 2.2 g/l uranium, and 6.08 g/l boron) were evaporated to 78 percent of their original volume, four aliquots were boiled down to 56 percent of their original volume, and four aliquots were boiled down to 35 percent of their original volume (to dryness). Each concentrated aliquot (residue) was then dissolved in hydrofluoric acid-hydrogen peroxide, diluted back to its original volume, and the boron content of the resulting solution determined.

The average boron concentration on the four samples that had been concentrated to 78 percent of their original volume, then dissolved, and diluted back to the original volume was 6.09 ± 0.16 g/l; on those that had been evaporated to 56 percent of their volume it was 6.10 ± 0.15 g/l; and on those that had been boiled to dryness (35 percent of the original volume) it was 6.02 ± 0.10 g/l. Each value represented eight determinations. These results demonstrate that boron was not volatile even when the dissolver product was boiled to dryness.

7. Carrying of Boron on Precipitates

Special batch dissolutions were made to simulate a dissolver malfunction which would cause precipitation within the dissolver. For a flowsheet containing 4 g/l boron, about one percent of the total boron was found in a precipitate of more than five grams of uranium tetrafluoride in 300 ml of dissolver product solution from a 15 percent uranium fuel. Large amounts of zirconium precipitate resulting from over-dissolution of the zirconium also contained only about one percent of the total boron. These results indicate that the boron does not precipitate or carry on the precipitate significantly when gross precipitation of uranium or zirconium fluoride occurs.

8. Dissolver Cleanout

Studies were made to investigate the removal from Monel surfaces of uranium-containing solids which adhere to dissolver surfaces during continuous dissolution of zirconium alloy fuel with hydrofluoric acid. This study was undertaken to find a reagent that could be used to "clean-out" a continuous Monel dissolver of solids adhering to the Monel surfaces. A reagent was desired that would effectively remove uranium solids from Monel surfaces yet be relatively non-corrosive to Monel.

Reagents known to dissolve uranium compounds or form soluble uranium complexes were studied. Some of the work was done using Monel coupons having approximately 3.3 square inches of surface area that had been coated with uranium solids during continuous dissolution of uranium-Zircaloy-2 fuel pieces; in other experiments, sections of about 2.5 square inches were cut from 1/2-inch (inside diameter) continuous dissolvers that had become coated with uranium solids during operation. To better utilize the Monel samples that were coated with uranium solids, the same piece was sometimes used to test the effectiveness of a number of treatments. The quantity of uranium solid that was deposited on a given surface area varied widely, which tended to complicate interpretation of the results. The coated sample (along with a welded Monel corrosion coupon in many experiments) was suspended in a given volume of the reagent to be tested, the solution was stirred, and small aliquots of solution were removed periodically to indicate how rapidly the uranium was removed. Some treatments consisted of removing uranium by flaking it off surfaces; in such treatment, the amount of uranium flaked off during a predetermined time interval was ascertained. Sometimes uranium was removed by dissolution and flaking-off in the same treatment. Experiments performed at the boiling point of the reagent were done under conditions of total reflux, and experiments involving hydrofluoric acid were done in plastic equipment. In experiments in which a coated piece was subjected to only one treatment, the remaining uranium was removed later to determine the percentage of total uranium that had been removed by the treatment.

The uranium removal experiments are summarized in detail in the Appendix. The Appendix shows reagents used, conditions under which uranium removal was carried out, previous treatment given to the adhering uranium, exposure times for maximum effect, quantity (and percent where possible) of uranium removed, and approximate Monel corrosion rates encountered during many of the treatments. Of all the reagents tested, boiling 0.1M chromic acid was by far the most effective in removing uranium solids. For example, 200 ml of boiling 0.1M chromic acid removed 3.4 g of uranium (all of the uranium) from 2.5 square inches of surface area in 2 hours. In addition, the measured corrosion rate on a welded Monel coupon in this system was only about 2.5 mils per month. In addition to its "clean-out" properties and low corrosion rate, this reagent is compatible with the solvent extraction process at the ICPP.

IV. PILOT PLANT DEVELOPMENT STUDIES

The mode of operation of the ICPP semi-continuous dissolver for zirconium fuel is to charge fuel once each day and feed dissolvent into the dissolver the remainder of the day with the dissolver product overflowing to the complexing vessel continuously. Dissolver holdup time is one to two hours. As dissolution proceeds, the fuel charge slips down into the dissolvent until all the fuel charge is dissolved. An alternate continuous dissolution plan was to install a 20-inch diameter Carpenter-20 dissolver capable of dissolving either aluminum or zirconium fuels.

A scale model dissolver of the planned ICPP Monel dissolver was fabricated of Monel having a 3.5-inch diameter outer shell and 1.0-inch diameter removable basket. The fuel surface-to-volume ratio of this dissolver closely matches the Monel plant dissolver with the basket in place and conforms to operation in the Carpenter-20 dissolver without the basket. The 3.5-inch dissolver was designed for upflow operation, and temperature was controlled by a water bath. Fuel was added every 30 to 60 minutes through a valve lock to simulate the plant conditions, and the whole apparatus kept purged with nitrogen gas. Fuel used was typical fuel plate scrap material, solution depth inside the dissolver was approximately 12 inches, and the operating volume was 1800 ml. The dissolvent for runs using boron was 5.0M hydrofluoric acid-0.03M nitric acid-0.2M fluoboric acid.

A total of 16 runs were made in the 3.5-inch dissolver, five without the basket and 11 with the basket in place, at varying temperatures, through-put rates, fuel bed sizes, and uranium compositions. Boron was present in the reagent in 10 of the runs. The overall objectives of these runs were to determine optimum operating conditions, to find any undesirable operating conditions, to determine if boron remains soluble under all possible operating conditions, and to test the effect of reduced temperature operation on uranium solubility. The results of these runs are summarized in Table III. Holdup times in the dissolver were varied from one to four hours and run durations were from 6 to 38 hours. Product solution was analyzed for acid, zirconium, uranium, boron (when used), fluoride, specific gravity, and undissolved solids. Solids found in the dissolver after a run were also observed and analyzed. Samples were taken several times throughout each run and a composite sample was taken at the end of each run.

The dissolver product, with the exception of that from one run (E-17) was suitable material for complexing into extraction feed. In that one run, it was unstable due to high zirconium concentration but could have been suitable for extraction feed after special analysis and adjustment. In several of the runs, a zirconium precipitate was found in the dissolver on the surface of the fuel. This material, $\text{Zr}(\text{OH})\text{F}_3$, is formed at low fluoride-to-zirconium ratios and high temperatures.³ All runs in which this white solid was found were without the basket in place and were run at high ratios of dissolving metal surface areas to dissolver volume and with high holdup times. Conditions were found where $\text{Zr}(\text{OH})\text{F}_3$ could be reduced to a trace when operating without a

Table III
SUMMARY OF COLD PILOT PLANT ZIRCONIUM-URANIUM FUEL DISSOLUTION
IN 3-1/2-INCH MONEL-400 DISSOLVER

Conditions: Dissolver: 5.0M HF, 0.03M HNO ₃ ; Runs E-10 through E-19a contained 0.2M HBF ₄															
Run No.	Basket Used	Run Duration (hr)	Dissolver Holdup (hr)	Feed Rate (ml/hr)	Metal Rate (g/hr)	Initial Fuel Charge (g)	Uranium in Alloy (wt%)	Temperature (°C)	Precipitate in Dissolver	Approximate Product Composition					
										Zr (M)	H ⁺ (N)	U (g/l)	F (M)	B (g/l)	Specific Gravity
E-10	Yes	6	1	1900	190	188	2.0	85	Trace U	1.12	0.97	1.88	6.10	2.41	1.170
E-11	Yes	14	2	920	98	103	2.0	85	Trace U	0.99	1.12	1.68	5.31	2.32	1.162
E-12	Yes	34	4	510	64	123	2.0	83	Trace U	1.09	0.69	1.70	5.52	2.48	1.166
E-13	No	7	1	1900	192	1617	2.0	87	Small Zr	1.18	0.69	2.02	5.52	3.32	1.179
E-14	No	7	2	1230	85	0	2.0	83	Small Zr	1.04	0.82	2.36	5.01	2.44	1.158
E-15	No	26	3	630	83 ^[a]	1612	2.0	88	Large Zr	0.98	0.52	1.25	4.60	-	1.160
E-16	No	17	4	480	62	100	2.0	55 to 60	Trace Zr	1.11	0.98	2.21	5.50	2.52	1.171
E-17	No	27	4	480	6	1600	2.0	60	Very high Zr	[b]	0.23	1.73	[b]	[b]	1.202
E-18	Yes	12	1	1700	206	205	2.0	60	Trace U	1.05	1.04	1.83	5.52	2.3	1.159
E-19a	Yes	13.5	1	1800	185 ^[a]	314	2.0	60	Trace U	1.09	0.82	2.30	5.59	2.45	1.168
E-19b	Yes	18	1	1750	206 ^[a]	183	2.0	60 to 75	Trace U	1.10	0.68	2.09	5.18	0	1.160
E-19c	Yes	15	1	1750	200 ^[a]	200	2.0	60 to 75	Trace U ^[c]	1.07	0.67	2.16	5.03	0	1.154
E-19d	Yes	17.5	1	1850	191 ^[a]	273	2.3	64	Trace U	1.07	0.83	2.32	4.78	0	1.156
E-19e	Yes	17.5	1	1775	194 ^[a]	450	2.1	55 to 60	Trace U	1.13	0.69	2.13	4.79	0	1.163
E-19f	Yes	17	1	1775	195 ^[a]	450	2.4	50 to 75	Trace U	1.12	0.96	2.49	5.33	0	1.155
E-19g	Yes	17	1	1775	195 ^[a]	435	2.2	57	Trace U ^[d]	1.18	0.90	2.33	5.45	0	1.164

[a] No fuel was charged for last two hours of run.

[b] Samples were unstable and these analyses were cancelled.

[c] A cleanout after run 19c with aluminum nitrate yielded 0.46 g of uranium.

[d] A cleanout after run 19g with aluminum nitrate yielded 1.25 g of uranium.

basket, with low fuel bed inventory, and at reduced operating temperature.

The last six runs of this series produced only 1.76 g of uranium solids out of more than 450 grams dissolved or less than 0.4 percent of the total uranium. This does not represent a loss of uranium, since a dissolver wash at the end of a specific period of dissolver operation will dissolve this solid. Suspended solids in the dissolver product were approximately 0.1 g/l and were principally tin which dissolves in the complexing step. An exception to this was found on two runs (E-15 and E-17). In these runs, there were several grams per liter of solids in the dissolver product, these solids being $Zr(OH)F_3$. This difficulty was associated with the high initial metal charge and long hold-up time in the dissolver, each of which could lead to excessive depletion of fluoride in the dissolver. In the last five runs where fuel addition was stopped for the last two hours of each run to simulate clean-out of the fuel bed, no undissolved fuel was found in the dissolver. In the other runs, various amounts of undissolved metal were found, depending on the size of the fuel bed that was being maintained. Boron was found to pass through the system without depletion from the solution. In the last four runs, uranium solubilities equivalent to fuel compositions of two weight percent and as high as 2.4 percent were demonstrated for conditions of low temperature, low fuel bed, and low holdup times.

V. DISSOLUTION RATES OF IRRADIATED MATERIAL

Although unirradiated fuel meat material did not accumulate in the laboratory and pilot plant continuous dissolver in these tests, the same could not be inferred a priori about irradiated fuel. If the meat of the fuel were to dissolve at a slower rate than the cladding, uranium rich alloy would accumulate in the dissolver, creating a nuclear safety problem. Therefore, it was necessary to prove that the meat of irradiated fuel dissolves at a faster rate than the cladding for safe dissolver operation.

Two-inch by two-inch samples were cut from a greater than 50 percent burned up uranium-Zircaloy-2 fuel plate. The meat was exposed on all edges. These samples were dissolved in 5.2M hydrofluoric acid-0.03M nitric acid-0.37M boric acid at 95°C. Aliquots were taken during dissolution after two minutes, three minutes, and every two minutes thereafter to fifteen minutes. Each sample was analyzed for zirconium, uranium, and cesium. Duplicate dissolutions were made for both irradiated and unirradiated fuel.

The expression

$$I = \frac{R_c}{R_m} = \frac{A_m}{A_c} \left[\frac{(Zr)_i W_u}{(U)_i} - W_{Zr} \right]^*$$

was used to determine the relative rates of dissolution where:

- I = relative rate,
- R_c = rate of dissolution for cladding material,
- R_m = rate of meat,
- A_m = area of meat exposed,
- A_c = area of cladding,
- (Zr)_i = zirconium concentration in solution at time t_i,
- (U)_i = uranium concentration at t_i,
- W_u = weight fraction uranium in meat,
- W_{Zr} = weight fraction zirconium in meat.

The ratio of rate of meat dissolution to rate of cladding dissolution was about 2 for the unirradiated fuel and about 20 for the irradiated fuel. Thus, the meat material will dissolve essentially as rapidly as it is exposed by the dissolution of the cladding, particularly for irradiated fuel, and will not accumulate in a continuous dissolver.

* Derived and calculated by Floyd Spraktes, Operations Evaluation.

Approximate absolute dissolution rates calculated from relative dissolution rate data are shown in Table IV.

Table IV

DISSOLUTION RATES OF URANIUM-ZIRCALOY-2 FUEL
IN HYDROFLUORIC ACID SOLUTIONS

Conditions: Operating temperature = 95°C, dissolvent = 5.2M HF-0.03M
HNO₃-0.37M H₃BO₃, insignificant amount of Zr dissolved.

<u>Fuel Condition</u>	<u>Dissolution Rate of Cladding [mg/(cm²)(min)]</u>	<u>Dissolution Rate of meat [mg/(cm²)(min)]</u>
Unirradiated	80	160
Irradiated	25	500

VI. CORROSION EVALUATION

Preliminary corrosion studies for Monel and stainless steel Type Carpenter-20 (Cb), (hereafter referred to as C-20) were given in the first report of this series⁽³⁾. It was tentatively concluded then that both Monel and C-20 were suitable for service in the hydrofluoric acid flowsheet even under mild oxidizing conditions. Some concern was expressed for the reliability of the welds on the C-20 structure when complete annealing was impossible, as it might be on a dissolver. Monel was of special interest for this flowsheet because an existing plant dissolver of that material was available and could potentially be adapted for continuous dissolution. C-20 appeared as reasonable material for a more "universal" dissolver which might be used for fluoride, sulfate, or nitrate reagents. To furnish a firmer basis for the evaluation of the two materials, corrosion test loops of Monel and C-20 were prepared, and dissolver product solution was circulated through these for periods of 4121 and 1803 hours for Monel and C-20, respectively. Observations on the general corrosion and evidences of localized attack on the components of these loops are given here and form a firm basis for the evaluation of these materials in this service.

1. Equipment

A test loop was constructed of the screwed fittings and pipe listed in Table V. These were assembled in such a manner that the loop could be disassembled and the components cleaned and weighed like corrosion coupons. At one phase of the development, a square dissolver was being considered and therefore a fitting of square cross section was fabricated by welding flat plates into a box nipple. Later a perforated

Table V
CORROSION IN ZIRCONIUM DISSOLVER PRODUCT
SOLUTION AT 100°C

		<u>Carpenter-20 (Cb)</u>			<u>Monel-400</u>					
<u>Exposure Period</u>										
Period (hrs)		363	672	768	683	400	718	640	912	768
Total (hrs)		363	1035	1803	683	1083	1801	2441	3353	4121
<u>Purge Gas</u>		H ₂	N ₂	N ₂	H ₂	H ₂	N ₂	N ₂	N ₂	N ₂
Corrosion Rates for Each Period-MPM										
<u>Specimens</u>	<u>Service</u>									
1½" Tee	Vapor	0.8	0.4	0.1	0.2	0.3	0.4	2	2	3
1½" Nipple	Vapor	0.3	0.3	0.5	0.3	0.7	2	3	2	3
1½" Couple	Vapor	0.8	0.5	0.9	0.4	0.4	1	2	2	4
1½" Nipple	Vapor-liquid	0.4	0.3	0.5	1	0.7	2	3	2	4
1½" Couple	Liquid	0.8	0.4	0.9	0.7	0.9	1	3	3	5
Box Nipple	Liquid	0.4	0.3 ^(a)	0.6	0.7	0.8	1	2	2 ^(a)	1
1½" Couple	Liquid	0.9	0.6	1	0.5	0.7	1	3	3	5
Pipe	Vapor	0.2	-	0.2	0.2	0.1	0.8	0.3	0.3	0.6
Perforated tube	Vapor-liquid	No specimen				No specimen				0.9

(a) In both cases the box nipple failed at an improper weld, and was replaced for the next period.

tube basket was suggested for the plant dissolver, and a corrosion specimen of similar construction was inserted in the Monel test loop for one period. The test solution was circulated through each loop by a gas lift which used either hydrogen or nitrogen for motivation. This gas also served as a purge gas for the system. Each loop was heated with electric tape, and valves were provided at several locations for taking solution samples for control purposes. The temperature of the recirculating solution was monitored and used to control the power to the heating tape. Temperatures of the liquid were about 100°C and those of the vapor were about 94°C.

2. Test Solution

The test solutions were portions of the dissolver product solutions produced in the process development experiments described in Section II of this report. These varied significantly in composition from one exposure period to the next as shown in Tables VI and VII. These variations followed the trends in the process development, for example the addition of boric acid, or the variations in the composition of the process solutions as various effects were studied. In general, the compositions remained close to those typical of the reference flow-sheet.

Table VI

COMPOSITION OF ZIRCONIUM DISSOLVER PRODUCT
SOLUTIONS-CARPENTER-20 LOOP.

Exposure Period			1	2	3	(Typical)
Component						
F ⁻	<u>M</u>	(Average)	5.7	6.1	6.0	6.0
Zr	<u>M</u>	"	0.96	1.0	0.87	0.95
H ⁺	<u>M</u>	"	1.1	1.2	0.95	1.1
NO ₃ ⁻	<u>M</u>	"	0.024	0.03	0.025	0.026
B	g/l	"	2.4	2.4	4.6	3.1
U	g/l	"	0.93	0.85	2.1	1.3
Sn	g/l	"	0.42	0.20	0.23	0.27
Cr	g/l	(Maximum)	0.98	1.9	0.95	1.3
Ni	g/l	"	1.3	2.3	0.2	1.2
Mo	g/l	"	< 0.05	0.1	0.1	0.07

3. Performance of Monel-400

The loops were disassembled after each of the exposure periods shown in Table V. Uniform corrosion rates for the individual periods were calculated from the weight changes experienced by the components. At the end of the final exposure period, the various fittings were sectioned to permit microscopic examination of the interior portions, especially in the vicinity of the welds. Over the 4121-hour test period the corrosion rates for the Monel components ranged between 0.2 and 5 MPM. The rates in general appeared to increase with total exposure time, although this observation is confounded by the higher acidity and greater fluoride concentration of some of the solutions used in the latter portion of the test. The results of the microscopic examination are given in Table VIII. There were seven instances of accelerated attack detected on the Monel specimens. The majority of these involved attack at the end grain, an area which can be protected in many vessels by proper design. Denickelization was evidenced by the appearance of the metal surfaces and the analysis of the solutions for nickel and copper. The box nipple failed after 3353 hours of service at a crack in the welding which resulted apparently from momentary loss of purge gas during welding. This was the only failure in the components of the test loop.

During the short term dissolution runs described in Section II-1 (Table I), the corrosion rates on welded Monel ranged between 0.4 and 1.2 MPM. It was generally concluded that while the measured uniform corrosion rates on Monel might be higher than desirable in some cases (depending on the details of the composition of the solution and how the vessel was used), the small evidence of selective localized attack at the weld areas was sufficiently encouraging for the continued use of the existing vessel.

Table VII
COMPOSITION OF ZIRCONIUM DISSOLVER PRODUCT
SOLUTIONS-MONEL-400 LOOP

Exposure Period			1	2	3	4	5	6	(Typical)
Component									
F ⁻	M	(Average)	5.3	5.2	6.3	8.0	8.4	5.9	6.6
Er	M	"	1.2	1.2	1.4	1.1	1.4	0.94	1.2
H ⁺	M	"	0.57	0.44	0.53	1.2	1.4	0.80	0.82
NO ₃ ⁻	M	"	10 ⁻⁴	0.071	0.032	0.032	0.035	0.026	0.04
B	g/l	"	0	0	0	3.4	3.7	4.1	1.8
U	g/l	"	2.0	2.0	2.5	1.2	1.1	1.9	1.8
Sn	g/l	"	0.81	(a)	(a)	(a)	0.40	0.21	0.5
Ni	g/l	(Maximum)	3.1	5.5	15	25	17	16	13 ^(a)
Cu	g/l	"	< 0.5	< 0.5	1.57	0.13	0.1	< 0.1	0.8 ^(b)

(a) Not sought in analysis.

(b) Typical value for weight ratio of Ni/Cu in solution was 16.

Table VIII
RESULTS OF EXAMINATION OF MONEL-400 AND CARPENTER-20 (Cb) FITTINGS

Specimen	Type Alloy	Service	Temp. Service °C	Observed Accelerated Corrosion						
				Uniform Attack	Maximum Film Mile Deep	Worm Holes ^(b)	Half-Line	Weld Decay	End Grain	Stress Crack ^(c)
1½" T	C-20	Vapor	94		< 5			x	x	
	Monel	"	94	100%	20	x			x	
Nipple	C-20	"	94		0		x	x	x	
	Monel	"	94	100%	5	x				
Couple	C-20	"	94		10-15		x			x
	Monel	"	94	100%	5			x		
Nipple	C-20	Liquid-vapor	100		10		x	x	x	
	Monel	"	100	30%	5	x				
Couple	C-20	Liquid	100		15 ^(a)					x
	Monel	"	100	100%	40			x		
Box	C-20	"	100		10			x		
Nipple	Monel	"	100	100%	< 5			x		
Couple	C-20	Liquid	100		5					x
	Monel	"	100	100%	< 5					
Perforated tube	Monel	Liquid	100	100%	< 5					

(a) Evidence suggests that pit was caused by undercutting of the weld deposit due to insufficient purge gas.

(b) Accelerated end grain attack which proceeds parallel to the axis of rolling.

(c) In unmachined portion of forging.

The existing plant vessel had been in service earlier for 1078 hours on a batch dissolution cycle. Over this period the corrosion rate had been 5.8 MPM; this value compares favorably with that obtained in these tests.

4. Performance of Carpenter-20

The C-20 loop was disassembled for detailed examination after 1803 hours. The uniform corrosion rates were below one MPM on all components for all exposure periods. As shown in Table VIII, there were 13 instances of selective attack noted on the C-20 fittings, most of these associated with the welds. The box nipple of C-20 also failed. In this case the failure occurred at a thin weld where the base metal was improperly aligned. It is generally concluded that C-20 could be used in this service, but that particular attention to annealing of all welds would be required. Because of the sensitivity of the weld areas, it is recommended that prior to use in fluoride systems a detailed study be made of the effect of welding and post-weld treatment on selective corrosion attack, and that fabrication techniques be adjusted to insure the best possible welds.

VII. CONCLUSIONS

To convert the ICPP Monel batch dissolver to a semi-continuous operation, it was necessary that greater than 3.8 g/l boron be present in the dissolver to make the operation critically safe. Laboratory dissolution studies in a one-inch diameter continuous dissolver using 5M hydrofluoric acid-0.03M nitric acid to dissolve 2.2-3.0 percent uranium-Zircaloy-2 fuel indicate that 4 g/l boron in the system poses no serious problems. The only adverse effect caused by this concentration of boron is that it produces a slightly higher zirconium-fluoride hydrolysis product content in the dissolver and the dissolver product. Based on dissolution studies in a scale model dissolver operated similarly to the ICPP dissolver, these hydrolysis products along with tin and small amounts of uranium solids can be washed out of the dissolver at the end of a specified period of dissolver operation (16 hours); the tin and uranium solids and possibly the zirconium fluoride hydrolysis products can be dissolved in a successive adjustment step. Also based on pilot plant data, the 16-hour dissolution period planned for the ICPP semi-continuous dissolver is sufficient to dissolve all of the fuel load planned for that dissolution period. Any uranium solids adhering tightly to dissolver walls can be removed by boiling the dissolver with 0.1M chromic acid for about two hours. Boron will remain in solution even during dissolver malfunctions in which there are evaporation losses from the dissolver or formation of gross amounts of precipitate within the dissolver. Since the meat of irradiated fuel dissolves faster than its cladding, uranium-235 will not collect in the dissolver during operation.

A recirculation dissolver showed promise in reducing the plating of sparingly soluble uranium tetrafluoride within the dissolver. Such a design should be considered for future installations.

VIII. LITERATURE CITED

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APPENDIX
REMOVAL OF URANIUM FROM MONEL-400 SURFACES

Treatment #	Reagent	Treatment Description	Approx. Surface Area of Monel-400 Coated with U (sq")	Previous Treatment on U Coating	U Removed By Dissolution or Flaking off (mg)	% of Total U Removed	Corrosion Rate (mils/yr)
1	H ₂ O	Stirred in 400 ml for 4 hrs at 24°C Stirred in 400 ml for 1 hr at 24°C	2.5 2.5	None 4 hrs treatment 1 and 4 hrs treatment 2a)	4 3	- -	- -
2 a)	1M HF	Stirred in 400 ml for 4 hrs at 24°C	2.5	4 hrs treatment 1	5	-	-
b)	5M HF	Stirred in 400 ml for 4 hrs at 24°C	2.5	4 hrs treatment 3a)	13	-	-
c)	20M HF	Stirred in 400 ml for 4 hrs at 24°C	2.5	4 hrs treatment 3d)	6	-	-
3 a ₁)	0.1M Al(NO ₃) ₃	Stirred in 400 ml for 4 hrs at 24°C	2.5	None	10	-	-
a ₂)	0.1M Al(NO ₃) ₃	Stirred in 400 ml for 1 hr at 24°C	2.5	4 hrs treatment 3e ₁) and 4 hrs treatment 2b)	18	-	-
a ₃)	20M HF-0.1M Al(NO ₃) ₃	Boiled in 200 ml for 1 hr Boiled in 200 ml of 20M HF for 4 hrs; then boiled in 200 ml of 0.1M Al(NO ₃) ₃ for 1 hr	3.3 3.3	None	39 56	36 93	63 2.7
b)	20M HF-0.3M Al(NO ₃) ₃	Boiled in 200 ml of 20M HF for 4 hrs; then boiled in 200 ml of 0.3M Al(NO ₃) ₃ for 1 hr	3.3	None	142	57	35
c)	0.5M Al(NO ₃) ₃	Stirred in 400 ml for 4 hrs at 24°C Stirred in 400 ml for 1 hr at 24°C	2.5 2.5	None 4 hrs treatment 3c) and 4 hrs treatment 4	3 32	- -	- -
d ₁)	2.2M Al(NO ₃) ₃	Stirred in 400 ml for 4 hrs at 24°C Stirred in 200 ml for 4 hrs at 24°C	2.5 2.5	None	8 135	- 15	- 3.0
		Stirred in 400 ml for 1 hr at 24°C	3.3	None	170	75	3.5
d ₂)	20M HF-2.2M Al(NO ₃) ₃	Boiled in 200 ml of 20M HF for 4 hrs; then stirred in 200 ml 2.2M Al(NO ₃) ₃ for 4 hrs	3.3	None	41 86	- 93	- 1.7
4	Dilute Flowsheet dissolver product	Stirred in 400 ml for 4 hrs at 24°C	2.5	Treatment 3c)	3	-	-
5 a)	0.1M HNO ₃	Boiled in 200 ml for 1 hr	3.3	None	156	57	218
b ₁)	0.3M HNO ₃	Boiled in 200 ml for 1 hr	3.3	None	503	81	528
b ₂)	20M HF-0.3M HNO ₃	Boiled in 200 ml of HF for 4 hrs; then boiled in 200 ml of HNO ₃ for 1 hr	3.3	None	259	82	464
b ₃)	4.8M HF-0.3M HNO ₃	Boiled in 200 ml of 4.8M HF-0.3M HNO ₃ for 1 hr	3.3	None	6,4	4	439
c)	0.5M HNO ₃	Boiled in 200 ml of HNO ₃ for 1 hr	3.3	None	136	100	520
d ₁)	1M HNO ₃	Stirred in 400 ml for 4 hrs at 24°C	2.5	5 hrs treatment 3e ₁) and 4 hrs treatment 2b)	104	-	-
d ₂)	1M HNO ₃ -0.2M H ₃ BO ₃	Stirred in 400 ml for 4 hrs at 24°C	2.5	5 hrs treatment 3c) and 4 hrs treatment 4	92	-	-
6 a ₁)	5M NH ₄ OH-0.1M H ₂ O ₂	Stirred in 400 ml of 5M NH ₄ OH-0.1M H ₂ O ₂ for 15 min at 24°C	2.5	5 hrs treatment 3d ₁) and 4 hrs treatment 2c)	2.8	-	-
a ₂)	5M NH ₄ OH-0.1M H ₂ O ₂	Boiled in 200 ml of 5M NH ₄ OH-0.1M H ₂ O ₂ (initially) for 2 hrs; 30% H ₂ O ₂ added at periodic intervals	2.5	5 hrs treatment 3d ₁), 4 hrs treatment with 2c), 15 min treatment with 6e ₁), 1 hr treatment with 6b), and 1 hrs with 6c)	1.8	-	-
a ₃)	5M NH ₄ OH-0.1M H ₂ O ₂	Stirred in 200 ml of 5M NH ₄ OH-0.1M H ₂ O ₂ (initially) for 1 hr at 24°C; 30% H ₂ O ₂ added at periodic intervals	0.5	None	3	-	-
b)	0.5M NH ₄ OH-0.01M H ₂ O ₂	Stirred in 400 ml of 0.5M NH ₄ OH-0.01M H ₂ O ₂ for 1 hr at 24°C	2.5	5 hrs treatment 3d ₁), 4 hrs treatment with 2c), 15 min treatment with 6e ₁)	0.3	-	-
c)	5M NH ₄ OH-0.01M H ₂ O ₂	Stirred in 400 ml of 5M NH ₄ OH-0.01M H ₂ O ₂ for 1 hr at 24°C	2.5	5 hrs treatment 3d ₁), 4 hrs treatment with 2c), 15 min treatment with 6e ₁), and 1 hr with 6b)	1	-	-
7	20M HF-0.5M H ₂ O ₂	Boiled in 200 ml of 20M HF for 4 hrs; then boiled in 200 ml of 0.5M H ₂ O ₂ for 1 hr	3.3	None	157	58	1.6
8 a)	0.5M NaOH-0.1M Na ₂ O ₂	Stirred in 200 ml of 0.5M NaOH-0.1M Na ₂ O ₂ for 1 hr at 24°C	2.5	5 hrs treatment 1, 4 hrs treatment with 2a), and 4 hrs with 5a ₁)	14	-	-
b)	2M NaOH-0.1M Na ₂ O ₂	Stirred in 200 ml of 2M NaOH-0.1M Na ₂ O ₂ for 1 hr at 24°C	2.5	5 hrs treatment 3c), 4 hrs treatment 4, and 4 hrs with 5d ₂)	41	-	-
		Stirred in 200 ml of 2M NaOH-0.1M Na ₂ O ₂ for 4 hrs at 24°C	3.3	None	90	-	-
		Stirred in 200 ml of 2M NaOH for 1 hr at 24°C; solution was made 0.1M Na ₂ O ₂ by adding 1/3 of the necessary solid Na ₂ O ₂ every 20 min.	2.5	None	279	91	0.1
c)	2M NaOH-0.2M Na ₂ O ₂	Stirred in 200 ml of 2M NaOH-0.1M Na ₂ O ₂ for 2 hrs at 24°C; solution made 2M NaOH-0.2M Na ₂ O ₂ and stirred for 2 hrs more	2.5	None	41	-	-
d)	2M NaOH-0.3M Na ₂ O ₂	Stirred in 200 ml of 2M NaOH-0.3M Na ₂ O ₂ for 1 hr at 24°C	2.5	None	234	24	0.2
e)	2M NaOH-0.4M Na ₂ O ₂	Stirred in 200 ml of 2M NaOH for 4 hrs at 60°C; solution was made 0.4M Na ₂ O ₂ by adding 1/4 of the necessary solid Na ₂ O ₂ every 1 hr	3.3	None	56	-	-
f)	5M NaOH-0.1M Na ₂ O ₂	Stirred in 200 ml of 5M NaOH-0.1M Na ₂ O ₂ for 1 hr at 24°C	2.5	None	231	92	0.4
9 a ₁)	4% (NH ₄) ₂ C ₂ O ₄	Stirred in 200 ml for 4 hrs at 24°C	2.5	5 hrs treatment 3a ₁), 4 hrs treatment with 2b), and 4 hrs with 5d ₁)	43	-	-
a ₂)	4% (NH ₄) ₂ C ₂ O ₄	Boiled in 200 ml for 4 hrs	3.3	None	22	-	-
			2.5	None	134	100	0.4
					1,604	31	< 0.1
10	1.8M Na ₂ CO ₃ -0.1M Na ₂ O ₂	Stirred in 200 ml of 1.8M Na ₂ CO ₃ -0.1M Na ₂ O ₂ for 1 hr	2.5	None	40	-	-
11	20% NaOH-metallic Zn	Boiled in 200 ml of 20% NaOH-metallic Zn for 1 hr Boiled in 200 ml of 20% NaOH-metallic Zn for 2 hrs	3.3 2.5	None	154 356	99 39	< 0.1 0.3
12	0.1M CrO ₃	Boiled in 200 ml for 1 hr Boiled in 200 ml for 2 hrs	3.3 2.5	None	322 3,356	100 100	2.3 2.6

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