Laboratory Studies on the Evolution of Iodine-129 During Purex-Uranium Metal Dissolution

L. A. Bray

March 1980

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LABORATORY STUDIES ON THE
EVOLUTION OF IODINE-129
DURING PUREX-URANIUM METAL
DISSOLUTION

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SUMMARY

The path of iodine from the Purex dissolver was determined during fuel dissolution using ^{125}I tracer. Laboratory-scale equipment qualification studies were completed using sections of nonirradiated uranium N-reactor fuel elements. A proof-of-principle dissolution study was completed at the end of FY 79 in the PNL hot cells using wafers of irradiated N-reactor fuel. The findings from these studies include the following:

- The laboratory-scale dissolver/downdraft condenser was designed at a factor of 5×10^{-5} of the Purex flowsheet.
- With no refluxing, 5.6 moles of HNO_3 were required per mole of dissolved uranium. With NO_x recovery in the reflux stream, an average of 3.6 moles of HNO_3 was required. These results formed the basis for adequate modeling of the laboratory Purex downdraft dissolver.
- Approximately 8% of the iodine was found in the final dissolver solution when the ^{125}I tracer was added to the initial dissolver solution prior to the first cut, 6-hr dissolution.
- When the ^{125}I was added continuously during the 6-hr dissolution without any refluxing of the condenser acid back to the dissolver, approximately 16% of the iodine was found in the dissolver solution.
- When irradiated N-reactor fuel was dissolved while ^{125}I tracer was continuously added to the dissolver during the 6-hr test, 11% of the ^{125}I tracer was found in the dissolver solution. After 2 hr of refluxing with air sparging, 6% of the ^{125}I tracer was found in the dissolver solution.
- Analysis of the fission product ^{129}I in the fuel duplicated the tracer study results with 8% and 7% of the iodine remaining in the dissolver solution after 6 and 8 hr, respectively.

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INTRODUCTION

This report presents the results of laboratory studies performed for Rockwell Hanford Operations by the Pacific Northwest Laboratory (PNL), which is operated by Battelle Memorial Institute for the Department of Energy (DOE). The PNL studies concerned the control of ^{129}I during the reprocessing of N-reactor fuel.

The objective of this research was to determine the path of iodine from the Purex dissolver during fuel dissolution. Laboratory qualification studies using sections of metal fuel elements and an iodine tracer were done to determine the behavior of iodine. These were followed during FY 1979 by a proof-of-principle dissolution study in the hot cell using wafers of N-reactor fuel.

BACKGROUND

A program for the control of ^{129}I during zirconium-clad fuel reprocessing at Purex has been outlined by D. W. Jeppson in a letter to H. A. Babad on September 30, 1975. Jeppson stated that laboratory data are needed on the rate of iodine evolution during a typical zirconium-clad coating removal and acid dissolution of uranium. If greater than 1% of the iodine remains in the dissolver after acid dissolution, then methods may be required enhancing evolution. In previous operating periods at the Purex plant, very little data were obtained on ^{129}I releases via the off-gases and condensate. In future operations of the plant, a decontamination factor (DF) of about 1000 is needed in the dissolver off-gas stream (assuming that most of the iodine leaves in the dissolver off-gas) to ensure that the DOE stack release limit of 0.02 pCi/L of released air for ^{129}I is not exceeded. A DF of 4600 is required to comply with the DOE release limit of 60 pCi/L for the process condensate (Jeppson 1976).^(a)

During future fuel reprocessing operations at Purex, routes of ^{129}I from the plant are expected to be the silver reaction collection inventory, coating waste, off-gases, organic wash wastes, process condensate, uranium nitrate products, and high-level wastes. It is desirable to force most of the iodine out of the dissolver solution into the dissolver off-gas stream for collection in an efficient iodine removal system.

(a) Jeppson used an instantaneous limit for determining DF's (total ^{129}I in the feed divided by the total iodine release). Based on an operating period the DF would be ~330, and on a yearly basis the required DF would be ~90 for Table II requirements.

PUREX PLANT EXPERIENCE

C. H. Holm (1951a) found that nitric acid dissolution of Hanford uranium with the sparging action of the gases carried ~80% of the iodine out of the solution. Sparging and carrier precipitation have been investigated for removal of iodine from dissolver solution. About 50% of the iodine was released by sparging.

Holm (1951b) studied the removal of iodine as iodide, iodine, and iodate. He showed that iodine removal increased with increasing temperature. Oxygen, air, and nitrogen affected the iodine removal only slightly, but the flow rate of the gas markedly increased the iodine removal. The presence of uranium metal in the solution caused a more rapid removal of iodine and iodate but a slower removal of iodide. Nitric acid concentration had a definite effect on the rate of iodine evolution for all the oxidation states studied. The uranyl nitrate concentration did not affect iodine removal between 1.5 M and 2.2 M uranium. At a sparging flow rate of 0.4 cm³/min/ml, removal of 65%, 73%, and 65% of the iodine added as iodide, iodine, and iodate, respectively, was achieved after 3 hr.

Many different iodine evolution values have been reported during uranium dissolution at various reprocessing facilities. Aluminum-clad fuel at the Hanford Purex Plant resulted in 95% of the iodine being evolved during air sparging and recycling of the dissolver condensate. The path of iodine from the Hanford Purex dissolver during zirconium-clad fuel reprocessing has not been determined (Schmidt 1957).

PUREX SILVER REACTORS

Early experience at the Savannah River Plant showed that approximately 50% of the iodine is volatilized during dissolution. In normal processing of two batches of uranium, the iodine DF for the silver nitrate reactors was 10 and 6. A DF of 530 was measured during a special neptunium processing campaign. Of the 1600 Ci of ¹³¹I charged, 3 Ci were released during all processing steps. The high retention factor was attributed to 0.005 M mercuric ion present during dissolution (Sheldon 1977).

Iodine at the Hanford Purex Plant is controlled by passing the off-gas from the fuel dissolvers through a bed of unglazed ceramic saddles coated with silver nitrate. Early operating reports indicate that the dissolver silver reactors were removing 99% to 99.9% of the ^{131}I . Reports from 1968 indicate a 90% to 95% ^{131}I removal. Schmidt (1957) reported that "Additional data will be required to determine if silver nitrate reactors can effectively be used to remove iodine during future Purex operations or if studies of alternatives are warranted."

OTHER SUPPRESSION METHODS

Other methods for the suppression of iodine have been suggested: (1) the use of mercury (Hg), (2) the use of MnO_2 and gelatin to release iodine from the dissolver solution to the atmosphere, and (3) precipitation of iodine from dissolution solutions using palladium for long-term storage.

Smith (1968) at Savannah River has described a series of tests conducted to determine the suppression effect of various mercury concentrations on ^{131}I evolution during Purex operation. Without mercury, 50% of the iodine is evolved. When 0.04 M Hg^{2+} was added to the dissolver, approximately 1% of the iodine was released during dissolution. Some iodine remained in the organic tributyl phosphate (TBP) extractant where it was slowly released by caustic scrubbing. The uranyl nitrate dissolver solution is then transferred to a clarification tank and a solution of 1% gelatin is added before centrifugation; most of the iodine is released during gelatin precipitation. For special materials, MnO_2 instead of gelatin is used; MnO_2 is generated by first adding manganous nitrate and then slowly adding potassium permanganate. In this way most of the iodine is released to the atmosphere. During solvent extraction, the remaining iodine extracts with the solvent and remains until removed by caustic scrubbing.

Mailen and Horner (1977) have suggested that iodine be removed from the dissolver solution by the addition of hydroxylamine ($\text{NH}_2\text{OH}\cdot\text{HNO}_3$) to cause precipitation of insoluble PdI_2 , which is suitable for long-term storage.

ORGANIC IODINE COMPOUNDS

Several researchers have observed organic radioiodine compounds in the off-gas from a nuclear fuel separations plant.

Perkins' (Haller and Perkins 1967) studies of the gaseous stack effluents from the Hanford nuclear fuel separations plant indicated that a large fraction of the ^{131}I was in organic forms. The ratio of the organic to inorganic radioiodine released in the Purex plant's gaseous effluent was determined after Perkins compared samples of the radioiodine which was concentrated by bubbling the gas directly into a liquid nitrogen-cooled trap. During a 20-day period the ratio of organic to inorganic radioiodine varied from 0.12 to 1.47.

E. Tachikawa and others (Numakura, Saeki, and Tachikawa 1973) found that organic iodides were formed by the reaction of carrier-free ^{131}I in nitric acid solutions, and that their yield was dependent on the concentration of nitric acid. In the actual reprocessing of the irradiated fuel on a large scale, 10 M HNO_3 is used. The amount of organic iodide was found to be in the range of 1% to 4% of the total iodine found at dissolving temperatures which are from 90° to 115°C. It markedly diminished as the dissolving temperature was decreased, and it was only 0.2% at 70°C. The addition of various iodine compounds into the concentrated nitric acid also changed the amount of iodine and the percent of organic iodine found in the sodium hydroxide trap. There was also a noticeable effect when other acids were used. When concentrated HCl rather than HNO_3 was used as a dissolving agent, methyl iodide amounted to less than 0.1% (Tachikawa 1971). From this paper, no suggestion was made concerning the source of the carbon for the formation mechanisms of the organic iodides.

Eggleton and Atkins (1964) identified methyl iodide as the principal iodine compound formed when amounts of carrier-free ^{131}I were released in the gas phase by the oxidation of Na^{131}I and neutron-irradiated uranium metal or by the heating of irradiated UO_2 in mixtures containing CO_2 .

Tachikawa (Saeki, Numakura, and Tachikawa 1974) and others further examined CO_2 and discounted it as a source of carbon. The results obtained with various carbon compounds indicated that an important carbon source is high-molecular-weight organic compounds which are mostly contained in HNO_3 as an impurity. Furthermore, the information contained by the purification of HNO_3 and by replacing the flushing gas, He , by O_2 revealed that the organic iodides are formed by radical reactions of the organic species that result from fragmentation of organic compounds with ^{131}I .

ROCKWELL HANFORD STUDIES

D. M. Strachan, in letters to D. C. Lini in March and April of 1976 and in June of 1977, reported that he completed tracer-level experiments to determine the pathways of radioiodine in the Purex operations. Problems were encountered during the investigation due to the small quantities of iodine and the large sampling volumes. Solutions were spiked with ^{131}I before and after dissolution of Zircaloy cladding and again after uranium dissolution. It was determined that:

- At the Zircaloy-uranium interface, 40% to 50% of the iodine present vaporized.
- During uranium dissolution, 90% to 95% of the remaining iodine volatilized.
- Organic iodides volatilized in proportion to the boiling point with methyl iodide (CH_3I) completely volatilized.

Poor iodine material balance was observed during dissolution of a wafer of N-reactor fuel. Most of the tracer work has been completed in the project to identify the pathways of ^{129}I in Purex. Tracer work shows that less than 90% of the iodine is volatilized during dissolution of uranium metal.

EXPERIMENTAL PROCEDURES

The path of iodine from the laboratory scale Purex dissolver was determined during fuel dissolution. The amount of iodine was measured in the off-gas and nitric acid feed. Laboratory qualification studies using sections of unirradiated fuel elements and ^{125}I tracer were done to determine the behavior of iodine during uranium dissolution. The initial results formed the basis for additional laboratory-scale studies and a proof-of-principle dissolution study using irradiated N-reactor fuel. The laboratory-scale program provides a technical basis for determining the adequacy of the iodine control system during future Purex plant operation.

During the initial program review, the following major points were outlined:

- The laboratory chemical flows will be based on a factor of 2×10^4 of the Purex flowsheet (Jeppson 1976).
- The design of the laboratory-scale downdraft condenser based on the acid required for uranium dissolution will be accepted as adequate modeling. With no reflux, approximately 5.5 moles of HNO_3 are required per mole of uranium. However, with NO_2 recovery in the reflux stream, plant experience shows that 3 to 4 moles of HNO_3 per mole of uranium are required.
- Initial laboratory and hot-cell studies will focus on the nitric acid dissolution of uranium.
- Since all acid used in dissolution is recycled HNO_3 , the potential exists for organics, such as TBP or its degradation products, to be present in the recycled acid in significant quantities. This is expected to have a pronounced effect on both the amount and species of iodine that evolve. The effect of recycled acid will not be included in the initial tracer study.

LABORATORY-SCALE DOWNDRAFT CONDENSER-DISSOLVER

A laboratory-scale downdraft condenser fabricated for previous Purex studies and a dissolver were modified for the initial investigation. Figure 1 illustrates this equipment which includes the off-gas sampling traps and support equipment.

N-REACTOR FUEL FOR TRACER STUDIES

Approximately 2000 g of uranium metal (unannealed) was initially obtained for this study. Before the dissolution was started, the zirconium-clad half-circles of metal were conditioned by contact with hot HNO_3 for 15 to 30 min. The acid leachant removed the uranium oxide film and the organic oils present from handling and cutting the half-circles. Figure 2 shows the uranium metal (including the zirconium cladding freed from the uranium metal) before and after dissolution. After completion of test 3, it was noted that the dissolver penetration was greater on the cut ends of the fuel than on the curved surfaces. Since dissolution rates may vary with the physical properties of the metal, annealed metal was obtained for the remaining tests.

FIGURE 1: Laboratory-Scale Purex Downdraft Condenser/Dissolver

Before Dissolution

After Partial Dissolution

FIGURE 2: Unirradiated N-Reactor Fuel Element Test Segments

Heat-treated uranium metal for tests 5 through 8 was prepared by Glenn Burnett of UNC Nuclear Industries, Inc., Hanford. Twenty half-circles of zirconium-clad, heat-treated uranium were cut from an inner X09 fuel element with an enrichment of 0.947% ^{235}U .

IRRADIATED N-REACTOR FUEL

An inner (1.45 in. OD), irradiated N-reactor fuel pin was obtained through the cooperation of J. P. Schmidt, manager of Fuel Engineering at UNC Nuclear Industries, Inc. The Post Irradiation Testing Facility at the Hanford Engineering Development Laboratory sectioned the fuel element, and twenty 1/2-inch semi-circles were sent to the PNL 325-A hot cells for testing. The history of the fuel pin is given below:

- in reactor --- 13 July 1977
- out of reactor --- 15 May 1978
- 6th fuel pin from the downstream end
- 2000 MWd/tonne burnup
- 0.947% ^{235}U
- 1.45 in. OD

REMOVAL OF ZIRCONIUM CLADDING

The zirconium cladding was dissolved off the uranium metal fuel surface by use of the Zirflex method. Approximately 500 g of fuel were placed in a 1.2 L Teflon lined stainless steel beaker with 500 ml of solution containing 5.6 M NH_4F and 0.5 M NH_4NO_3 . The solution was heated for 6 hr at 80 to 90°C. Water was added to maintain the volume. The off-gas was scrubbed through a 0.5 M NaOH bubbler trap connected to a large funnel. The funnel acted as a cover for the heated beaker, and the fumes were contained in the caustic trap. After completion of zirconium dissolution, the uranium metal was washed with HNO_3 and H_2O .

PUREX NITRIC ACID

Recycled acid from the Purex plant was sampled to determine the carbon content. The sample was taken from a process tank containing acid estimated to be five to six years old and recently (1979) diluted with process water. The original concentration of nitric acid should have been approximately 10 M HNO_3 . The analysis by the 222-S Laboratory at Rockwell Hanford Operations of the acid sent for this study was as follows:

- 5.34 M in H^+
- 5.34 M in NO_3^-
- $<1.5 \times 10^{-4}$ M in oxides as NO_2^-
- 0.055 g/L in total organic carbon
- <1.68 pCi/ml in ^{129}I

When received, it was determined that the bright yellow color in the acid was due to the sample containing 5.4 g U/L.

PHYSICAL MEASUREMENTS

The hydrogen ion concentration in the dissolver solution was determined by titrating of an aliquot with standard NaOH after adding 17% potassium oxalate (adjusted to a pH of 5.55) to complex the uranium. Caustic solutions were titrated using standardized nitric acid. A Beckman Research Model pH Meter was used to determine the end point. Uranium concentration in the dissolver solution was determined using a Cary 14-H spectrophotometer.

IODINE COUNTING TECHNIQUES

Iodine-125 with a half life of 60 days was supplied by New England Nuclear. The tracer was obtained in dilute sodium hydroxide solution and was added to stock feeds containing inactive iodine. Counting was performed by a RIDL 400 channel analyzer, model 24-2, which has a NaI 3-inch. crystal detector. The iodine concentration in the caustic gas trap was determined by counting an aliquot of the caustic solution for ^{125}I . The I_2 and organic iodides in the dissolver solution were coextracted with toluene before counting to eliminate

the radiochemical interference of the dissolved uranium. In an attempt to determine the percent of the organic iodide in the dissolver solution, the uranium solution was adjusted with 0.2 M hydroxylamine nitrate ($\text{NH}_2\text{OH}\cdot\text{HNO}_3$) prior to extraction with toluene. The results were not conclusive, and additional work is required to perfect this analysis.

Five samples containing ^{129}I and spiked ^{125}I were counted by D. A. Dodd and C. P. McLaughlin of the Chemical Sciences Group at Rockwell Hanford Operations using a Hyper pure germanium well detector. The samples were obtained after dissolution of irradiated N-reactor fuel in the 325-A High-Level Radiochemical Cells.

RESULTS AND DISCUSSION

Three series of tests were conducted on iodine control: (1) laboratory-scale equipment qualification studies, (2) iodine distribution studies using tracer techniques, and (3) an iodine distribution study using irradiated N-reactor fuel. A summary of the results of the tracer and hot-cell studies are shown in Table 1. All of the studies are discussed in more detail in the following subsections.

LABORATORY EQUIPMENT QUALIFICATION STUDIES

Test 1

In the first test the dissolver, condenser, reagent addition, and air sparging systems were demonstrated. No uranium metal was added. The use of sand and a hot plate provided excellent heating of the dissolver. The iodine off-gas system consisted of two 100-ml traps containing 10 M HNO_3 and 0.4 M $\text{Hg}(\text{NO}_3)_2$, and a caustic trap containing 100 ml of 2 M NaOH .

Test 2

The objective of the second test was to determine the moles of nitric acid consumed per mole of uranium dissolved and to determine the effectiveness of the analytical iodine trapping system. N-reactor fuel contains approximately 14 grams of iodine per tonne of metal. This test was modified by adding a 200-fold excess of iodine to the initial dissolver acid. The excess iodine (0.0067 M I/L of final dissolver solution) was added to identify potential problems throughout the dissolver and downdraft system during dissolution of the uranium metal.

TABLE 1: Summary of Results and Test Conditions

	TEST NUMBER	TEST CONDITIONS	INITIAL DISSOLVER FEED					ADDITION DURING TEST			FINAL RESULTS - DISSOLVER SOLUTION						
			1.6 M ANN, ml	10 M HNO ₃ , ml	KIO ₃ , mg l	TRACER 125I	METAL, g	10 M HNO ₃ , ml	KIO ₃ , mg l	TRACER 125I	VOLUME, ml	HNO ₃ , M	MOLE RATIO, H/U	U DISSOLVED, %	% I IN SOLUTION 6 HRS	% I IN SOLUTION REFLUXING	IODINE MATERIAL BALANCE, %
TRACER STUDIES	3	URANIUM NOT HEAT-TREATED; TRACER ADDED INITIALLY; 6 HR TEST	108	240	7.4	YES	429.3	430	--	--	765	4.5	3.38	54.4	7.8	3.8 (8 HRS)	92.6
	5	HEAT-TREATED; TRACER ADDED DURING TEST; CLADDING ON; 6 HR TEST	108	240	--	--	435.5	430	7.4	YES	751	5.3	3.3	53.8	33	--	99.7
	6	HEAT-TREATED; TRACER ADDED DURING TEST; CLADDING OFF; LOWER HNO ₃ ; 6 HR TEST	108	240	--	--	492.6	230	3.7	YES	562	1.65	3.46	55.5	29.2	--	99.0
	7	HEAT-TREATED; TRACER ADDED DURING TEST; CLADDING OFF; USED "PUREX ACID"; 6 HR TEST	108	240	--	--	417.9	230	3.7	YES	532	1.49	4.3	58.2	32.7	--	90.4
	8	HEAT-TREATED; TRACER ADDED DURING TEST; CLADDING OFF; NO REFLUX; 6 HR TEST	108	340	--	--	495.0	230	3.7	YES	445	0.97	5.56	47.4	16	--	112.8
HOT CELL STUDY		N-REACTOR FUEL; TRACER ADDED DURING TEST; CLADDING OFF 7/9 OF FUEL; 6 HR TEST WITH 2 HRS REFLUX WITH AIR	108	240	--	--	423.1	230	--	YES	535	--	--	68.8	10.7 8 (BASED ON 125I)	5.4 (2 HRS) 7 (2 HRS) (BASED ON 129I)	104.8 (AVE)

The test plan was as follows:

1. The downdraft water-cooled condenser containing glass beads was conditioned by adding 76 ml of H_2O through the top.
2. The uranium metal was cleaned using 8 M HNO_3 + H_2O . The oil film and uranium oxide surfaces were removed. The initial weight of the fuel was 435.6 g of uranium and 9.4 g of Zircaloy cladding.
3. The uranium metal was placed on a stainless steel grid two inches from the bottom of the dissolver.
4. The sweep air across the surface of the dissolver solution was turned on and maintained at $426\text{ cm}^3/\text{min}$.
5. To initiate the test, 135 ml of 1.6 M aluminum nitrate (ANN) and 300 ml of 10.4 M HNO_3 were added to the dissolver, and the sand bath was heated with the hot plate.
6. The air sparge through the bottom of the dissolver was maintained at $170\text{ cm}^3/\text{min}$.
7. Approximately 150 min into the run, 550 ml of 10.4 M HNO_3 was added at 4 ml/min through a side-port in the dissolver.
8. The off-gas from the dissolver downdraft condenser system was sparged through two 100-ml bottles containing 10 M HNO_3 and 0.4 M $Hg(NO_3)_2$, and a third sparge bottle containing 2 M NaOH. No sparge bottles were attached to the air sweep inlet (as shown in Figure 1).

The test was terminated after 7 hr. The dissolver solution was not removed from the dissolver for an additional 112 hr. No uranium metal was thought to be undissolved. However, when the solution was removed from the dissolver, 136.5 g of uranium metal (31.3%) was found undissolved. Approximately 1.26 moles of uranium metal had been dissolved. A sample of the final 1049 ml of dissolver solution was analyzed for H^+ concentration. The initial acid was also analyzed for H^+ concentration and was found to be 12.14 M instead of 10.4 M as was called for in the procedure. The initial solution contained 10.31 moles of acid, and the final dissolver solution contained 5.17 moles of HNO_3 . The dissolution of uranium metal using the laboratory downdraft condenser required 4.1 moles of HNO_3 per mole of uranium metal.

During test 2, the sweep air was pulled through the three gas sparge bottles by the vacuum system. The caustic trap (2 M NaOH) was determined to be inadequate to contain the NO_x but was kept in the system during the test. A pink mercury iodine precipitate was observed inside the dry, fritted gas tube of the first bottle during the run and only partially dissolved in 10 M HNO_3 -Hg before being sampled.

The most significant observation during test 2 was the needle-like iodine crystals formed on the glass beads in the condenser and on the cool arm sticking out of the top of the dissolver at the air sweep inlet. The entire dissolver and off-gas glassware had been covered with ceramic insulation with the exception of the side arm and the water condenser. When the side arm was covered during the run, the iodine redissolved. Figure 3 shows the upper portion of the H_2O condenser. The initial I_2 was observed on the upper bead surface but moved down about one inch during the 7 hr run. Some of the crystals broke free of the mass and slowly worked their way to the bottom of the condenser. Some of the I_2 redissolved and dropped back into the dissolver pot.

FIGURE 3: Iodine Observed in Downdraft Condenser--Test 2

Test 2A

The objectives of Test 2A were to: (1) repeat the Test 2 run plan, (2) reduce the iodine 50-fold from 1.5 to 0.028 g of KIO_3 , and (3) increase the aqueous reflux condensate flow by increasing the temperature of the sand bath hot plate.

As in Test 2, black iodine crystals were observed in the top of the condenser during the first 50 min of Test 2A, but the crystals readily dissolved at the completion of the first hour as the condenser began to reflux. The sparge traps were constructed using coarse, fritted glass tube. The back pressure resulting from the fine frits and the increase in dissolver temperature (to force a higher reflux) resulted in a very high foam level in the dissolver which eventually spilled over into the $\text{Hg}(\text{NO}_3)_2$ and HNO_3 trap. In addition, the sweep air flow rate became erratic, and NO_x periodically vented out of the air sweep inlet. The experiment was terminated before additional results were obtained.

Test 2B

The objectives of Test 2B were to: (1) reduce the total dissolver solution volume from 1000 ml in the previous tests to 800 ml, (2) replace the iodine traps using Hg-HNO_3 with caustic traps, and (3) guard against iodine escape from the air sweep inlet by using a caustic trap bubbler at the air inlet. To accomplish these objectives Test 2 was modified as follows:

1. First, 50 ml of H_2O was added to the dissolver through the tower to wet the glass beads.
2. Next, 428.7 g of uranium metal and 2.4 g of Zircaloy were placed in the dissolver.
3. Then, 100 ml of 10 M NaOH was placed in the first two sparge traps and 2 M NaOH in a third trap.
4. Two traps were placed on the sweep air inlet; 200 ml of 2 M NaOH were put in the first trap, and the second trap remained empty.
5. In order 0.028 g of KIO_3 , 135 ml of 1.6 M ANN, and 300 ml of 10.3 M HNO_3 were added to the dissolver.

6. Air was maintained at $426 \text{ cm}^3/\text{min}$ and sparged at $170 \text{ cm}^3/\text{min}$ in the dissolver.
7. Approximately 150 min into the run, 350 ml of 10.3 M HNO_3 was added at 4 ml/min .
8. The experiment was terminated after 6 hr.

A yellow color in the first caustic trap indicated that the iodine was being captured. Reducing the volume of total dissolver solution did not reduce the foam level. The sweep air flow rate continued to be erratic. The caustic trap on the air inlet did prevent the escape of NO_x and I^- during high foam conditions. The parameters of test 2B are listed below:

Initial HNO_3	650 ml of 9.89 M H^+ (6.429 moles)
Final HNO_3	895 ml of 3.97 M H^+ (3.586 moles)
HNO_3 used	2.84 moles
Initial weight of metal	428.7 g
Final weight after 6 hr	236 g
Uranium dissolved	192.7 g (45%), 0.81 moles
Mole ratio (moles H^+ /mole U)	3.51

IODINE DISTRIBUTION STUDIES USING ^{125}I TRACER TECHNIQUES

Test 3

The objective of the first tracer study was to determine the iodine distribution in the laboratory-scale Purex dissolver and downdraft condenser. Iodine as KIO_3 and tracer ^{125}I were added to the nitric acid dissolver solution before the test began. Approximately 74% of the iodine was captured in the caustic off-gas scrub solution during the first hour of uranium metal dissolution. An additional 10% was released to the caustic scrub during the next 5 hr of dissolution. Approximately 8% of the iodine was found in the dissolver solution after 6 hr of dissolution. Refluxing of the dissolver solution (no metal present) under normal dissolving conditions (Test 4) for an additional 10 hr released an additional 4% of the iodine. Approximately 54% of the uranium metal dissolved in 6 hr, and the mole ratio of acid consumed to metal dissolved was 3.4. An iodine material balance of 93% was achieved for the tracer experiment.

The equipment for the tracer experiment was modified as shown in Figure 1. The frit in the caustic bubbler was replaced with extra coarse glass to reduce the back pressure experienced in the previous runs. A sample port was added to the first trap. An ice bath was added to remove condensate that had been collecting on the rotometer ball. The run plan for Test 3 was modified as follows:

1. Water was added to the top of the condenser to wet the beads and to fill the condensate return tube.
2. The uranium metal was cleaned using HNO_3 and H_2O , and then was dried and weighed.
3. The uranium metal was placed on a stainless steel grid two inches from the bottom of the dissolver.
4. The air sweep across the surface of the dissolver solution was maintained at $426 \text{ cm}^3/\text{min}$.
5. For this experiment, 108 ml of 1.6 M ANN and 240 ml of 10.16 M HNO_3 were added to the dissolver solution.
6. Then 7.4 mg of iodine as KIO_3 and 5 ml of ^{125}I tracer were added to the dissolver solution.
7. The air sparge through the bottom of the dissolver was maintained at $170 \text{ cm}^3/\text{min}$.
8. Approximately 150 min into run, 430 ml of 10.16 M HNO_3 were added at $2.7 \text{ ml}/\text{min}$.
9. The run was completed in 6 hr. The dissolver solution was cooled to 25°C within 30 min, and all solutions were sampled.

For Test 3, N-reactor fuel that was not heat treated was used, the cladding was not removed, and the tracer was added to the dissolver before the test was started. The parameters and results of Test 3 are listed below. A breakdown of the sample analyses is given in Table 2.

Starting Dissolver Feed	108 ml of 1.6 M HNO_3 ; 240 ml of 9.89 M HNO_3 ; 0.5 ml of 25 g KIO_3/L (7.4 mg I); 5 ml of ^{125}I tracer
Acid addition	430 ml of 9.89 M HNO_3
Initial HNO_3	670 ml of 10.16 M H^+ + 765 ml of 4.51 M H^+ (3.5 moles)
Final HNO_3	
HNO_3 used	3.3 moles
Initial weight of metal	429.3 g (not heat-treated, zirconium clad)
Final weight of metal	195.7 g
Uranium dissolved	233.6 g (54%) (0.98 moles)
Mole ratio (moles H^+ /mole U)	3.4
Iodine in dissolver solution after 6 hr	7.8%
Iodine added	7.4 mg I/233.6 g U dissolved = 31.7 g I/tonne U
Iodine material balance	92.6%

Test 4

Two weeks after completion of Test 3, the dissolved uranium solution was reanalyzed for ^{125}I . The 750 ml of solution containing 4.5 M H^+ and 1.28 M U(VI) had not lost iodine to the atmosphere during storage. The solution was placed in the dissolver vessel and heated to 95° to 105°C as in Test 3 (no uranium metal present). The caustic trap was sampled each hour to determine the loss of iodine to the sparge and sweep air. After 8 hr of refluxing, 45% of the remaining iodine (4% of the initial Test 3) was released to the caustic trap. The results are shown in Table 3.

Test 5

Test 3 was completed by adding all of the ^{125}I tracer to the dissolver solution before the experiment was initiated. However, in reality, the iodine from spent N-reactor fuel is released as a function of uranium dissolution. Therefore, Test 5 was designed to simulate iodine release with uranium

TABLE 2: Summary of Uranium Metal Dissolution -- Test 3

Sample	Time, min.	Test Volume, ml	% of Initial Iodine	H ⁺ or (OH ⁻) Concentration	
				Initial	Final
First Caustic Trap					
1	60	135	73.5	(10)	
2	120	140	80.1		
3	180	145	80.1		
4	240	150	82.8		
5	300	155	<u>83.0</u>		
6	360	161	84.1	(10)	1.91
Second Caustic Trap	360	100	0.44	(10)	(10)
Condensate Return ^(a)	360	5	0.28	--	8.77
Air Inlet Trap	360	200	0	(10)	(10)
Dissolver Solution	360	765	7.8	8.9	4.51
Initial Dissolver Solution Spike		5			
Total recovery			<u>92.6</u>		

(a) Contained 4 ml of acid; 1 ml of acid was assumed to be still on the beads.

TABLE 3: Loss of Iodine from a Dissolver Solution with Refluxing and Air Sparging as a Function of Time

Sample	Time, min.	% of Iodine in Dissolver Solution Found in Caustic Trap
First Caustic Trap		
1	60	0.4 ^(a)
2	115	8.7
3	188	20.9
4	240	27.9
5	310	34.4
6	410	39.6
7	480	45.5 (~4% of initial Test 3 iodine)
Second Caustic Trap	480	0.01
Condensate Return, 5 ml	480	1.0 (H ⁺ , 0.17)

dissolution by adding the ^{125}I tracer with the HNO_3 addition continuously throughout the 6 hr run. In addition, there was an interest in obtaining uranium metal dissolution data as a function of time during Test 5. Because of the uneven pitting of the metal surface during dissolution, heat-treated metal was used for Test 5 and all subsequent tests. Approximately 33% of the iodine remained in the dissolver solution after 6 hr compared to 8% when the tracer was added to the initial dissolver solution. The mole ratio of acid consumed to metal dissolved was 3.3, with 54% of the uranium dissolved. Uranium and acid concentration in the dissolver solution were determined as a function of time. The parameters and results of Test 5 are listed below. A more detailed breakdown of the results is given in Table 4.

Starting dissolver feed	108 ml of 1.6 <u>M</u> ANN; 240 ml of 10.86 <u>M</u> HNO_3 .
Acid addition	430 ml of 10.86 <u>M</u> HNO_3 ; 5 ml of ^{125}I tracer; 0.5 ml of 25 g KIO_3/L (7.4 mg I); addition rate = 1.24 ml/min.
Initial HNO_3	670 ml of 10.86 <u>M</u> HNO_3 (7.28 moles)
Final HNO_3	751 ml of 5.3 <u>M</u> HNO_3 + 5 ml of 6.4 <u>M</u> HNO_3 (4.0 moles)
HNO_3 Used	3.27 moles
Initial weight of metal	435.3 g (4 pieces, zirconium clad on two faces)
Final weight of metal	201.2 g
Uranium dissolved.	234.3 g (54%) (0.984 moles)
Mole ratio (moles H^+ /mole U)	3.3
Iodine in dissolver solution after 6 hr	31.7 + 1.3% (33%)
Iodine material balance	99.7%
Iodine added	7.4 mg I/234.3 g U dissolved (31.6 g I/tonne)
Surface area of metal	6.688 in^2 to 5.089 in^2 after dissolution

TABLE 4: Summary of Uranium Metal Dissolution -- Test 5

	Sampling Time, hr						
	1	2	3	4	5	6	Final
Dissolver Solution							
% Iodine	88.3	42.8(?)	34.9	36.0	32.5	30.95	31.66
H ⁺ , <u>M</u>	7.2	6.2	6.4	5.9	5.6	5.5	5.3
U, g/L	49.0	146.0	198.0	224.0	284.0	326.0	328.0
Volume, ml	488.1	540.7	593.2	645.8	698.4	751.0	751.0
First Caustic Trap							
% Iodine	13.3	17.3	59.6	58.0	59.5	61.7	66.5
OH ⁻ , <u>M</u>	8.6	7.4	5.5	4.2	3.2	2.1	2.0
Volume, ml	135	139	144	148	153	157.5	157.5
Second Caustic Trap							
% Iodine	--	--	--	--	--	--	0.23
OH ⁻ , <u>M</u>	--	--	--	--	--	--	8.0
Volume, ml	100	100	100	100	100	100	104
Backup Trap							
% Iodine	--	--	--	--	--	--	0
OH ⁻ , <u>M</u>	--	--	--	--	--	--	9.3
Volume, ml	100	100	100	100	100	100	96
U-Tube							
% Iodine	0.96	2.6	1.9	1.3	1.2	1.4	1.3
H ⁺ , <u>M</u>	7.6	7.4	6.5	6.4	6.2	6.4	3.2
Volume, ml	5	5	5	5	5	5	20 ^(a)
% Iodine ^(b) Recovered	102.6	62.7	101.7	95.2	93.2	94.1	99.7

(a) Washed downdraft column and U tube to remove all iodine and HNO₃.

(b) % of available iodine with time.

Test 6

Test 6 was completed to determine the effect of a lower acid concentration on the release of iodine. In addition, the cladding was removed from the uranium to more nearly represent flowsheet conditions. Iodine tracer and HNO_3 acid were added continuously throughout the test; other conditions were similar to Test 5. Approximately 30% of the iodine remained in the dissolver solution after 6 hr. The final dissolver solution contained 2 M uranium and 1.65 M H^+ . The acid consumed was 3.5 moles per mole of dissolved uranium. The 0.95% enriched, heat-treated, N-reactor uranium metal was weighed and measured before and after dissolution. The final material balance was 99%. The test parameters and results for Test 6 are listed below. A more detailed breakdown of the results is given in Table 5.

Starting dissolver feed	108 ml of 1.6 <u>M</u> ANN; 240 ml of 10.52 <u>M</u> HNO_3
Acid addition	230 ml of 10.52 <u>M</u> HNO_3 ; 5 ml of ^{125}I tracer; addition rate = 0.695 ml/min.
Initial HNO_3	470 ml of 10.52 <u>M</u> H^+ (4.94 moles)
Final HNO_3	562 ml of 1.65 <u>M</u> H^+ + 31 ml of 1.65 <u>M</u> H^+ (0.98 moles)
HNO_3 used	3.97 moles
Initial weight of metal	942.6 g (5 pieces, no zirconium clad)
Final weight of metal	219.3 g
Uranium dissolved	273.3 g (55.5%) (1.148 moles)
Mole ratio (moles H^+ /mole U)	3.46
Iodine in dissolver solution after 6 hr	24.1% + 5.8% (29.9%)
Iodine added	3.7 mg I/273.3 g U dissolved = 13.5 g I/tonne U
Iodine material balance	99%

TABLE 5: Summary of Uranium Metal Dissolution -- Test 6

	Sampling Time, hr						
	1	2	3	4	5	6	Final
Dissolver Solution							
% Iodine	85.9	39.5	37.2	32.8	31.0	28.3	24.1
H ⁺ , M	8.2	5.7	3.6	2.6	2.6	1.7	1.65
U, g/L	38	198	332	414	452	496	512
Volume, ml	356.7	384	419	455	526	562	562
First Caustic Trap							
% Iodine	21.9	50.2	49.9	55.1	53.5	53.1	45.0
OH ⁻ or (H ⁺), M	8.3	5.1	2.4	0.67	(0.06)	(0.15)	(0.89)
Volume, ml	153	157	160	163	167	170	147 ^(a)
Second Caustic Trap							
% Iodine	--	--	--	--	--	--	25.0
OH ⁻ , M	--	--	--	--	--	--	5.5
Volume, ml	100	--	--	--	--	--	127 ^(a)
Backup Trap							
% Iodine	--	--	--	--	--	--	0
OH ⁻ , M	--	--	--	--	--	--	9.2
Volume, ml	--	--	--	--	--	--	97
Uranium Tube							
% Iodine	1.0	2.9	2.4	7.0	2.3	3.5	5.8 ^(b)
H ⁺ , M	1.3	7.75	6.2	6.0	5.0	3.3	1.65
Volume, ml	5	5	5	5	5	5	31
% Iodine ^(c) Recovered							
	108.7	92.5	89.5	94.9	86.8	84.9	99.9

(a) Spilled Bubbler #1 into #2 during cooling of dissolver solution.

(b) Washed downdraft condenser and column uranium tube to remove all I and HNO₃.

(c) % of available iodine with time.

TABLE 6: Physical Measurements of 0.95% Enriched
Inner N-Reactor Fuel -- Before and After
Dissolution Test 6

		Measurement Before and After Dissolution					
Fuel Piece	Dimensions, ^(a) in.					Weight ^(b) , g	
	A	B	C	D	E		
1	1.2 ^(c)	0.515	0.755	0.346	0.591	96.0	
	1.055	0.585	0.573	0.244	0.435	46.3	
2	1.2	0.515	0.729	0.352	0.591	103.2	
	1.072	0.585	0.610	0.255	0.450	43.0	
3	1.2	0.515	0.778	0.346	0.591	98.7	
	1.089	0.585	0.581	0.262	0.450	42.3	
4	1.2	0.515	0.727	0.344	0.591	95.0	
	1.086	0.585	0.561	0.264	0.466	45.4	
5	1.2	0.515	0.764	0.354	0.591	99.4	
	1.071	0.585	0.578	0.243	0.437	42.3	

- (a) The dimensions (A, B, C, D, and E) that were measured are indicated below.
- (b) Initial weight of five pieces of metal = 492.6 g; the final weight after 6 hr of dissolution = 219.3 g.
- (c) The top number is the "before" measurement, and the bottom number is the "after" measurement.

Test 7

Recycled acid from the Purex plant may contain organic acids that could increase the formation of organic iodine compounds when recycled back to the dissolver. In an attempt to address this problem, a sample of Purex recycled acid was analyzed by the Rockwell Hanford Operations analytical laboratory (see Experimental section). The acid was then adjusted to 10 M HNO_3 (468 ml of Purex acid + 532 ml of 15.7 M HNO_3) and was used in Test 7. No major differences were noted between Test 6 and Test 7. Approximately 33% of the iodine was found in the final dissolver solution. A change in procedure in heating the dissolver with glycol (an initial temperature of 97°C instead of the sand bath at 25°C) increased the uranium metal dissolution rate in the first hour. In addition, the cooling H_2O in the downdraft water jacket was not turned on during the first 2 hr resulting in a premature neutralization of the first caustic trap, a release of iodine into the second trap, and an overall increase in HNO_3 consumption.

The HNO_3 consumed during Test 7 was 4.2 moles of H^+ per mole of uranium metal dissolved. The 0.95% ^{235}U metal, heat-treated, N-reactor uranium was weighed before and after dissolution. Iodine results were obtained for the dissolver, the first and second traps, and the uranium return tube each hour during dissolution. The final iodine material balance was 90.5%. The parameters and results of Test 7 are listed below. A more detailed breakdown of the results is given in Table 7.

Starting dissolver feed	108 ml of 1.6 <u>M</u> ANN; 240 ml of Purex Acid
Acid addition	230 ml of Purex Acid; 5 ml of ^{125}I tracer; 0.24 ml of 25 kg KIO_3/L (3.7 mg I); addition rate = 0.62 ml/min.
Initial HNO_3	470 ml of 10.86 <u>M</u> H^+ (5.10 moles)
Final HNO_3	532 ml of 1.49 <u>M</u> H^+ + 6 ml of 10.28 <u>M</u> H^+ (0.85 moles)
HNO_3 used	4.25 moles
Initial weight of metal	417.9 g (6 pieces, zirconium removed)
Final weight of metal	174.5 g
Uranium dissolved	243.4 g (58.2%)(1.02 moles)
Mole ratio (moles H^+ /mole U)	4.2
Iodine in dissolver solution after 6 hr	24.8% + 7.9% = 32.7%
Iodine added	3.7 mg I/243.4 g U dissolved = 15.2 g I/tonne
Iodine material balance	90.4%

TABLE 7: Summary of Uranium Metal Dissolution -- Test 7

	Sampling Time, hr					
	1	2	3	4	5	6.25
Dissolver Solution						
% Iodine	54.3	36.4	25.6	20.2	17.4	24.8
H ⁺ , M	4.6	2.89	1.96	1.6	1.3	1.49
U, g/L	238	310	370	440	440	450
Volume, ml	375	410	440	470	500	532
First Caustic Trap						
% Iodine	61.1	62.7	60.6	56.3	41.1	33.7
OH ⁻ or (H ⁺), M	2.67	0.17	0.12	0.07	(0.38)	(0.77)
Volume, ml	115	130	132	134	136	136
Second Caustic Trap						
% Iodine	0.4	6.1	10.5	13.5	13.2	23.1
OH ⁻ or (H ⁺), M	9.26	9.14	8.0	6.9	5.39	4.99
Volume, ml	100	100	101	102	103	103
Backup Trap						
% Iodine	--	--	--	--	--	0.84 ^(a)
OH ⁻ , M	--	--	--	--	--	--
Volume, ml	--	--	--	--	--	192
Uranium Tube						
% Iodine	7.0	12.5	10.3	7.8	6.3	7.0
H ⁺ , M	11.95	12.35	11.05	10.38	10.28	--
Volume, ml	6	6	6	6	6	33 ^(b)
% Iodine Recovered ^(c)	123	118	107	97.8	78	90.4

(a) Plugging in the second trap caused a gas backup during run.

(b) Washed downdraft condenser and column uranium tube to remove all I and HNO₃.

(c) % of available iodine with time.

Test 8

Test 8 was designed to determine the iodine remaining in the dissolver solution after 6 hr of dissolution without recycling the acid condensate (~ 0.01 g I/L of ~ 10 M HNO_3). Previous tests (5 through 8) showed that $\sim 32\%$ of the iodine remained in the dissolver solution, including 5% that was found in the acid held up in the return leg of the dissolver from the reflux condenser. Therefore, the test glassware was modified by cutting the glass tube return to the dissolver. Additional acid was added to the dissolver throughout the 6-hr uranium dissolution to compensate for the loss of the reflux acid.

Approximately 16% of the iodine remained in the dissolver solution after 6 hr of dissolution. Eliminating the recycled acidic condensate reduced the iodine found in the final dissolver solution by 50%. The final dissolver solution contained 2.1 M U and 0.97 M H^+ . The acid consumed was 5.56 moles of H^+ per mole of uranium dissolved. Approximately 47% of the metal dissolved. The final iodine material balance was 112.8%. The dissolver solution was refluxed at 100°C with air sparging for an additional 6 hr without a significant reduction in iodine. After 6 hr of metal dissolution and 6 hr of refluxing, 12.5% of the iodine remained in the dissolver solution. The parameters and results of Test 8 are listed below. A more detailed breakdown of the results is given in Table 8.

Starting dissolver feed	108 ml of 1.6 M ANN; 340 ml of 10.38 M HNO_3
Acid addition	230 ml of 10.38 M HNO_3 ; 5 ml of ^{125}I tracer; 0.25 ml of 25 g KIO_3/L (3.7 mg I); addition rate was not constant during run.
Initial HNO_3	570 ml of 10.38 M H^+ (5.92 moles)
Final HNO_3	445 ml of 0.97 M H^+ (0.43 moles)
HNO_3 used	5.49 moles
Initial weight of metal	260.2 g
Uranium dissolved	234.8 g (47.4%) (0.986 moles)
Mole ratio (moles H^+ /mole U)	5.56
Iodine in dissolver solution after 6 hr	16.2% (after 6 hr of refluxing = 12.5%)
Iodine added	3.7 mg I/234.8 g U dissolved = 15.8 g I/tonne
Iodine material balance	112.8%

TABLE 8: Summary of Uranium Metal Dissolution -- Test 8

	Sampling Time, hr					
	1	2	3	4	5	6
Dissolver Solution						
% Iodine	8.8	14.8	19.5	16.4	15.7	16.2
H ⁺ , M	6.15	3.12	1.94	1.08	0.94	0.97
U, g/L	104	238	384	455	480	505
Volume, ml	461	426	419	420	428	445
First Caustic Trap						
% Iodine	3.3	15.8	20.3	35.9	37.3	38.0
OH ⁻ , M	5.27	1.97	0.41	0.18	0.19	0.18
Volume, ml	105	110	115	120	125	128
Second Caustic Trap						
% Iodine	1.5	7.1(?)	0.2	3.0	4.5	6.1
OH ⁻ , M	9.52	9.55	9.24	8.10	8.03	7.20
Volume, ml	100	100	100	100	100	100
Backup Trap						
% Iodine	--	--	--	--	--	0.5
OH ⁻ , M	10	--	--	--	--	10
Volume, ml	125	125	125	125	125	125
Condensate Recovered During ΔT (Total)						
% Iodine	1.3 (1.3)	9.4 (10.7)	15.9 (25.6)	10.4 (37.0)	7.9 (44.9)	7.1 (52.0)
H ⁺ , M	11.72 (11.72)	10.11 (10.48)	10.52 (10.50)	9.33 (10.26)	9.22 (10.12)	8.80 (10.00)
Volume, ml	20.6 (20.6)	69.0 (89.6)	40.5 (130.1)	32.0 (162.1)	25.9 (188.0)	20.0 (208.0)
% Iodine Recovered ^(a)	14.9	48.4	66.6	92.3	102.4	112.8

(a) % of available iodine with time.

IODINE DISTRIBUTION STUDY USING IRRADIATED N-REACTOR FUEL

A proof-of-principle dissolution study was attempted using irradiated N-reactor fuel and a previously tested laboratory-scale downdraft condenser and dissolver that was in the 325-A High Level Radiochemistry facility, 325 Building, 300 Area. The fuel was received as 80-g half-circles of uranium metal with cladding on the curved inner and outer surfaces. The zirconium cladding was dissolved with $\text{NH}_4\text{F}-\text{NH}_4\text{NO}_3$ and nine half-circles of metal (423 g) were suspended in the lower portion of the dissolver from a stainless steel screen basket and wire. The dissolution procedure was similar to the previous tracer tests. Nitric acid containing ^{125}I tracer was added continuously during the 6-hr test; this was followed by 2 hr of refluxing with air sparging. The objective of the test was to compare the iodine tracer studies using unirradiated and irradiated fuel with iodine found as a fission product (^{129}I) in the irradiated fuel.

Approximately 11% and 6% of the initial ^{129}I tracer was found in the dissolver solution after 6 and 8 hr, respectively. An iodine material balance of 105% was achieved for the irradiated fuel experiment. Fission product ^{129}I results for the irradiated fuel test duplicated the tracer study with 8% and 7% of the iodine remaining in the dissolver solution after 6 and 8 hr, respectively. Approximately 1,012 pCi of ^{129}I were found per g of N-reactor fuel dissolved. The tracer and fission product iodine results do not agree with unirradiated uranium metal dissolution tests, which showed approximately 30% of the iodine remaining in the dissolver solution after 6 hr of dissolution. The parameters and results of the irradiated fuel dissolution test are listed below. A breakdown of the iodine analysis is given in Table 9.

Starting dissolver feed	108 ml of 1.6 M ANN; 240 ml of 10 M HNO_3
Acid addition	230 ml of 10 M HNO_3 ; 5 ml of ^{125}I tracer
Initial weight of metal	423.1 g (9 pieces, zirconium removed from 7)
Final weight of metal	132.1 g
Uranium dissolved	291.0 g (69%)(1.22 moles)

TABLE 9: The Results of the Iodine Analyses for the N-Reactor Fuel
Dissolution Test

Sample and Time Sample Taken	Amount of Iodine Found			
	325 Laboratory	222-S Laboratory		
	$^{125}\text{I}, \%$	$^{125}\text{I}, \%$	$^{129}\text{I}, \%$	$^{129}\text{I}, \text{pCi/g}$
Dissolver solution, 6 hr	12.0	9.4	8	81.8
Dissolver solution, 8 hr	4.9	6.0	7	72.6
Caustic gas trap, 8 hr	98.7	99.9	93	939.2
Iodine material balance, 8 hr	103.6	105.9	100	1011.8

CONCLUSIONS

Laboratory and hot-cell studies indicate that the Purex plant cannot meet the goal of less than 1% of the iodine remaining in the dissolver solution after acid dissolution of uranium metal N-reactor fuel. Methods are needed for enhancing iodine evolution.

The laboratory-scale dissolver/downdraft condenser was successfully tested for use in the Purex plant simulation studies. Approximately 8% of the iodine remained in the dissolver solution after 6 hr of uranium metal dissolution. Four additional ^{125}I tracer studies were completed prior to the proof-of-principle dissolution study using irradiated N-reactor fuel. These studies were modified to permit the cold iodine (KIO_3) and ^{125}I tracer to be added to the dissolver solution as a function of time, simulating the release of iodine with uranium metal dissolution. Approximately 30% of the iodine remained in solution after 6 hr of dissolution.

When irradiated N-reactor fuel was dissolved, ^{125}I tracer was again added to the dissolver solution as a function of time. The tracer ^{125}I and the fission product ^{129}I results showed that 11% to 8% of the iodine remained in the dissolver solution after 6 hr of dissolution. After 2 hr of air sparging, 6% of the ^{125}I and 7% of the fission product ^{129}I remained in solution.

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