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EVALUATION OF AN ENGINEERING DEMONSTRATION OF THE MODIFIED ZIRFLEX AND NEUFLEX PROCESSES FOR THE PREPARATION OF SOLVENT EXTRACTION FEEDS FROM UNIRRADIATED ZIRCONIUM-BASE REACTOR FUELS

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ABSTRACT

In order to recover uranium from zirconium-base reactor fuels by solvent extraction, the metallic fuel and cladding must first be dissolved and a suitable feed solution prepared. Such preparations of solvent extraction feeds were successfully accomplished batchwise using both the Modified Zirflex and Neuflex processes employing an NH_4F-oxidant mixture to dissolve the fuel elements, and HNO_3-$Al(NO_3)_3$ and H_2O additions to adjust the feed. (The HNO_3-$Al(NO_3)_3$ mixture is used to adjust Modified Zirflex feed, and H_2O for the Neuflex feed.)

In the Modified Zirflex process, a dissolvent about 6 M in NH_4F with an excess of NH_4NO_3 is used, along with a continuous addition of H_2O_2 to oxidize uranium to the more-soluble U(VI) valence state. The off-gas, after NH_3 removal, is an H_2-O_2 mixture of small volume, which is diluted with air to a safe concentration. Then nitric acid-aluminum nitrate is added to the dissolution product, yielding a solvent extraction feed from which uranium is recovered by using TBP-Amsco as the extractant.

In the Neuflex process, the dissolvent is NH_4F-H_2O_2, with less than a stoichiometric amount of NH_4NO_3. Without NH_4NO_3, the scrubbed off-gas is principally hydrogen, on the hydrogen-rich side of the flammable range of H_2-O_2 mixtures. Only water is added to this dissolution product, yielding a neutral fluoride feed from which uranium is extractable by use of Dapex reagents.

In both processes the F:Zr charge ratio, initial surface condition, and maximum section thickness of the fuel element were the principal determinants of total dissolution time. The zirconium loading as determined by the free fluoride-zirconium solubility relationship limited the capacity of fuels containing less than 2% U, while the free-fluoride-to-uranium ratio of about 100 required for solution stability was the limiting factor with alloys containing higher percentages of uranium. Hydrogen peroxide concentration was not an important factor in solution stability; the role of ammonia or NH_4OH was not studied.

The feasibility of both processes was demonstrated by a series of batch dissolutions of kilogram quantities of various fuels containing 1 to 8% uranium. Continuous dissolution was demonstrated as was application to TRIGA fuel alloy (8% U--ZrH). Stainless steel type 347 and a low-carbon nickel alloy were suitable materials of construction for the dissolution and the solvent extraction equipment.

Since there were some discrepancies between small-scale and engineering-scale work, especially in the prevention of precipitate formation near the end of the dissolution cycle, it is advised that some further investigation be made prior to attempted scaleup to plant operation.

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1. INTRODUCTION

Investigation of ammonium fluoride-oxidant systems for the dissolution of spent U-Zr-Sn reactor fuels was initiated in an attempt to develop a practical process with lower equipment corrosion rates than the HF dissolution presently used in the Idaho Chemical Processing Plant. Aqueous HF alone will solubilize about 2% U-Zr fuels up to the loading desired, but for the processing of alloys richer in uranium at comparable zirconium solution loadings, an oxidant must be added to convert the uranium to the more soluble hexavalent state. Although the addition of an oxidant solves the problem of uranium solubility it also creates a severe corrosion problem for the processing equipment. On the other hand, the ammonium fluoride systems gave much lower corrosion rates and the addition of H_2O_2 acted to further inhibit corrosion.

Accordingly, the present study, using unirradiated material throughout, was undertaken to investigate these other facets of the concept in both batch and continuous operation:dissolution rates and times, off-gas rates and compositions, the stability of the dissolution product and solvent extraction feed solutions, and quantitative corrosion rates in the

NH_4F-NH_4NO_3-H_2O_2 system. It is, therefore, the purpose of this report to establish the feasibility of these processes while pointing out possible shortcomings and defining areas wherein further investigation is believed advisable.

2. A COMPARISON OF THREE RELATED PROCESSES FOR ZIRCONIUM-BASE FUELS

A family of processes for the NH_4F dissolution of zirconium has evolved in order to meet the requirements for processing various zirconium-containing fuels. Three important examples are the Zirflex decladding[1] process for Zircaloy-clad UO_2 pellet fuels, developed at Hanford, and the Modified Zirflex[2] and Neuflex processes for alloy fuels reported herein. These three processes, inter-related and bearing certain similarities to each other, are compared in Table 1. The aim of Zirflex decladding is

Table 1. Comparison of Three Processes for Zirconium Fuels

	Zirflex Decladding	Modified Zirflex	Neuflex
Uranium species	U(IV), loss	U(VI), product	U(VI), product
Fuel type	Zircaloy-clad UO_2	U-Zr alloy	Zircaloy-clad UO_2, U-Zircaloy alloys
Extractant	None	Tributyl phosphate in Amsco	Dapex, D2HPA-DAAP; TBP for UO_2 core dissolvent
Stabilizer	H_2O	HNO_3-$Al(NO_3)_3$	H_2O
Dissolvent	NH_4F-NH_4NO_3	NH_4F-NH_4NO_3-H_2O_2	NH_4F-H_2O_2
Gaseous products	$5NH_3$, H_2, O_2	$5NH_3$, H_2, O_2	$4NH_3$, $2H_2$, O_2
Off-gas (after scrubbing)	Small volume H_2 + O_2	Small volume H_2 + O_2	Large volume, rich in H_2

the dissolution of zirconium and tin while minimizing UO_2 dissolution. If much uranium is dissolved, it results in uranium loss [U(IV) solubility controlled] because the decladding solution is a waste stream and is not sent through a recovery process. Ammonium nitrate is used as an oxidant for tin dissolution and as a hydrogen depressant; it could be omitted, producing a less corrosive environment, if finely divided elemental tin could be permitted in the decladding waste and hydrogen in the off-gas stream. Hydrogen peroxide could be used for tin oxidation or to reduce corrosion, but it would also oxidize any U(IV) produced so that the uranium loss would be rate controlled rather than solubility controlled.

In both Modified Zirflex and Neuflex (neutral fluoride extraction), total dissolution of Zircaloy-clad U-Zr alloys is accomplished, with the more soluble U(VI) as the ultimate product. Hydrogen peroxide is used as the uranium oxidant, and it will also solubilize the tin. Ammonium nitrate may be added as an additional tin oxidizer and hydrogen depressant. There is only a fine distinction between the Modified Zirflex and Neuflex dissolution procedures, with the principal difference between them being in the solvent extraction system. In Modified Zirflex, residual NH_4NO_3 is not particularly objectionable because the final product is made about 1 M in both HNO_3 and $Al(NO_3)_3$. (Some residual is inevitable if a low-hydrogen off-gas is desired, because an excess of NH_4NO_3 must be used, and, even then, some hydrogen is evolved.) In Neuflex, the presence of residual NH_4NO_3 introduces a foreign ion (NO_3^-) because the water dilution of the product produces a neutral, purely fluoride system. This means that a strict Neuflex dissolution produces a higher hydrogen concentration in the gaseous effluent because less than the stoichiometric amount of NH_4NO_3

is used. By eliminating NH_4NO_3 entirely a much larger volume of scrubbed off-gas results (2 moles of hydrogen per mole of zirconium dissolved), which is on the hydrogen-rich side of the flammable range for H_2-O_2 mixtures.

After dissolution, the concentrated product (about 0.9 M zirconium) is cooled and diluted by the addition of H_2O or HNO_3-$Al(NO_3)_3$ stabilizer solution. In both the Zirflex decladding and Neuflex processes, the volume to which the product must be diluted to produce a stable solution depends on the free fluoride-zirconium solubility relationship, as shown in Fig. 1. The Neuflex product is very similar to the Zirflex decladding waste except that it contains a relatively large amount of U(VI), whereas the latter has a small amount of dissolved U(IV). The solubilities of these species in NH_4F-$(NH_4)_2ZrF_6$ systems are shown in Fig. 2 (a compilation of data by Ferris and by Swanson et al.). Uranium is recovered from the Neuflex product by extraction with Dapex reagents such as a synergistic mixture of di-2-ethylhexyl phosphoric acid and diamyl-amyl phosphonate.[5] The Modified Zirflex product is adjusted to approximately 1 M HNO_3 - 1 M $Al(NO_3)_3$ and extracted with conventional TBP-Amsco. The H^+-Al-Zr-F composition must be chosen for optimum solution stability, salting strength, and corrosion protection (by fluoride ion complexing with aluminum and zirconium ions) in the acid environment. This requirement for complexing becomes the controlling factor as the uranium percentage in the fuel increases. The free F:U ratio must be maintained, and the additional free fluoride thus required must be complexed by aluminum, which has a rather limited solubility in these solutions.

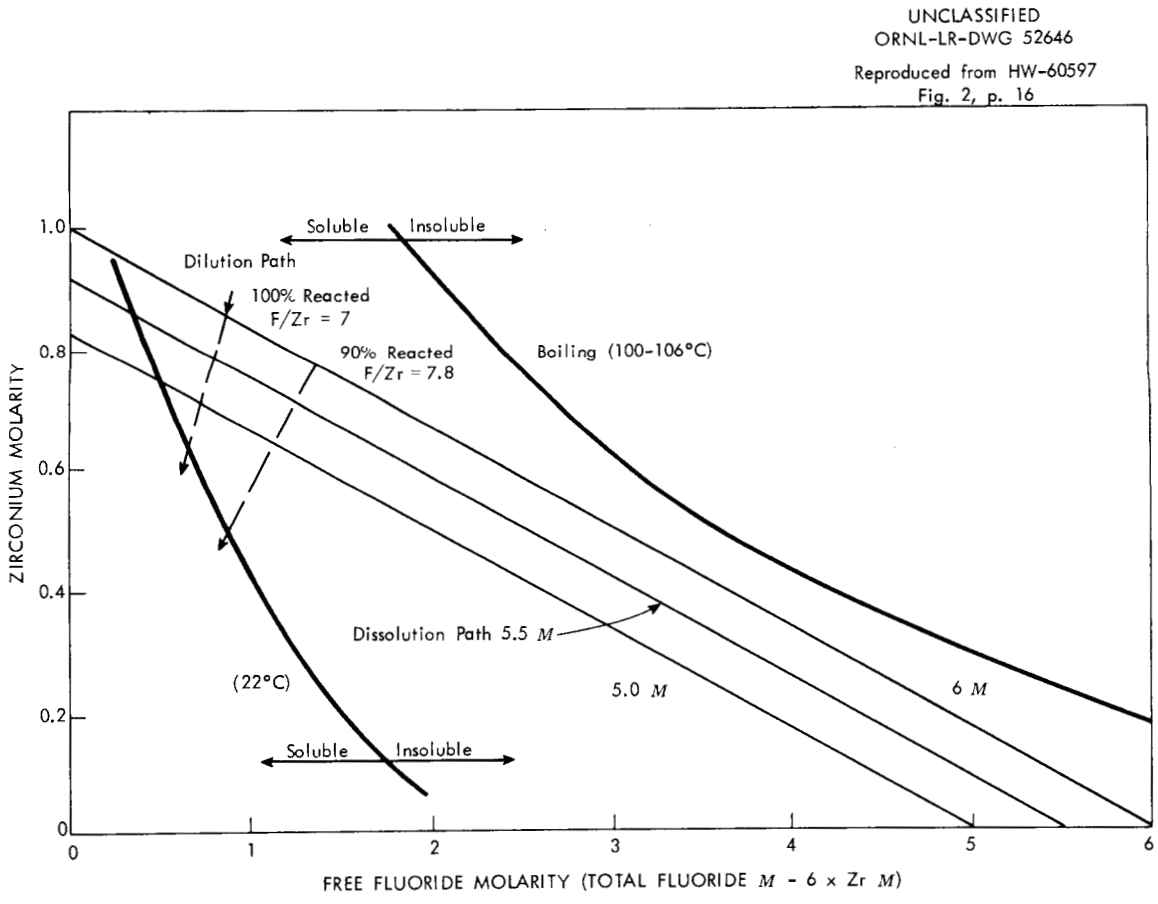

Fig. 1. Solubility of Zirconium in Ammonium Fluoride Solutions.

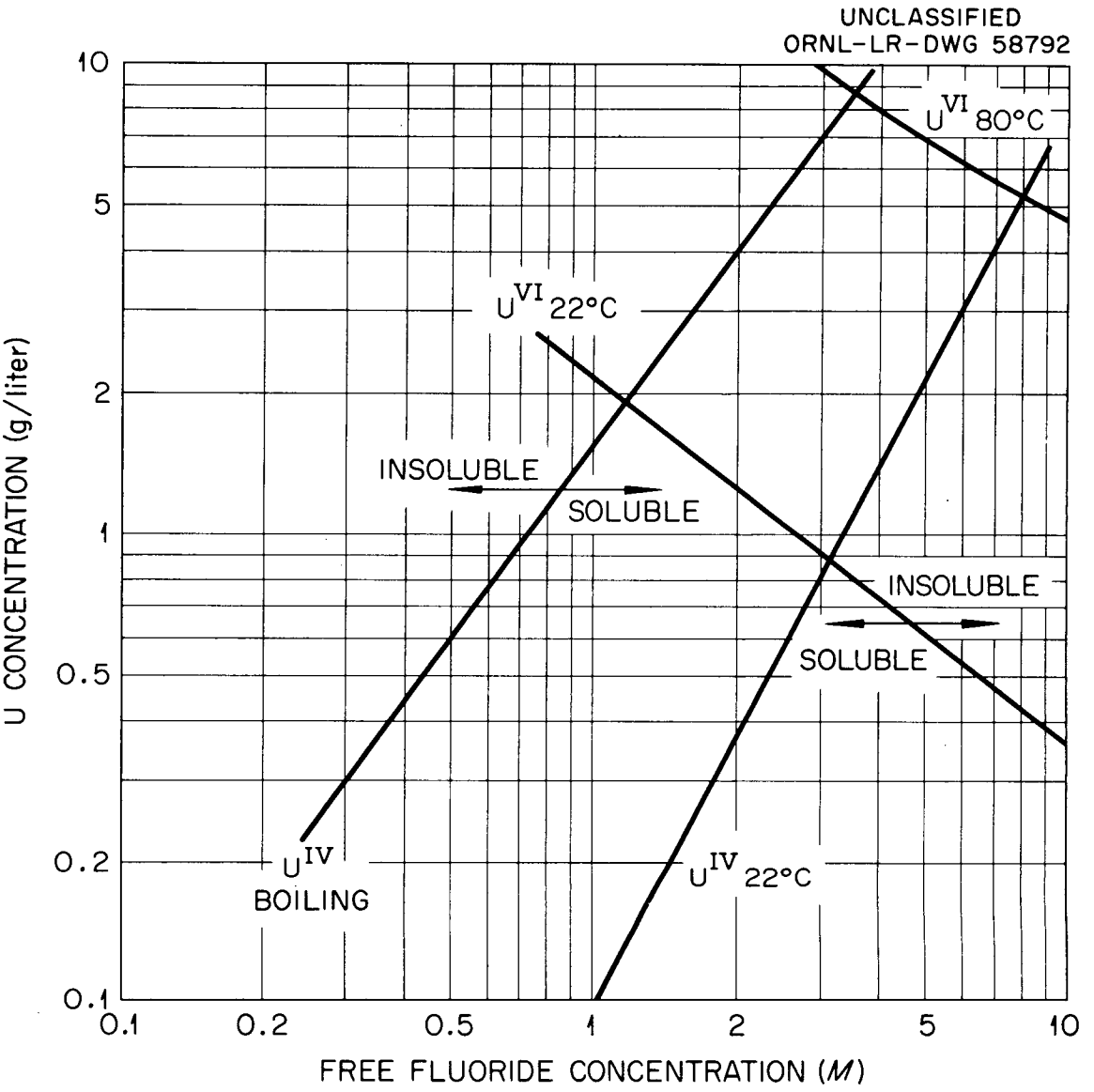

Fig. 2. U(IV) and U(VI) Solubilities as Functions of Free Fluoride Concentration.

The Neuflex dissolution was initially conceived to operate in conjunction with Sulfex (dilute H_2SO_4) decladding. If the zirconium fuels were processed in equipment used also for the Sulfex decladding of stainless steel fuels, common hydrogen metering and disposal facilities could be used, and the effluent hydrogen could serve as a primary means of monitoring reaction progress. There is promise that the same extractant used in Neuflex may also be used to recover uranium losses from Sulfex decladding solutions.[6] With the development of a practical solvent extraction scheme for neutral fluoride solutions, Zirflex decladding wastes could also be processed, thereby eliminating the about 0.3% loss presently reported by Hanford.[3] If such a solvent extraction backup were incorporated and initial decladding losses were no longer an overriding consideration, NH_4F-H_2O_2 could be used for Zirflex decladding, thereby reducing corrosion rates and providing a common dissolvent for all zirconium fuels.

A more stable and potentially less corrosive waste solution should result from a neutral solvent extraction raffinate. Storage in concrete tanks should be considered (depending upon radioactivity level). Higher temperatures could be tolerated (even boiling, if desired, in stainless steel tanks) without precipitation. Precipitation of aluminum from HNO_3-$Al(NO_3)_3$ waste solutions would produce unwanted solids and might also raise the free fluoride concentration by loss of complexing agent.

Batch operation was chosen for the study of the NH_4F dissolution method because of the opposite effects of free fluoride on dissolution rates and zirconium solubility. Solutions having a high free-fluoride concentration give high dissolution rates but will retain only small amounts of zirconium in stable solution; a low free-fluoride concentration allows

high loadings, but rates are low. A desirable steady-state composition for continuous operation was difficult to choose, especially with the added problem of penetrating the ZrO_2 coating on the surface of oxidized fuel elements. With batch operation, a high free-fluoride concentration and an infinite F:Zr ratio exist upon charging to give fast initiation and high early rates. The dissolution rate gradually falls throughout the dissolution, and at total dissolution the rate is minimum, with the F:Zr ratio in solution equaling the initial charge ratio.

2.1 Experimental Engineering Equipment

The batch-dissolution equipment used in these studies consisted principally of a 6-in.-diam cylindrical dissolver with provisions for heating and continuous H_2O_2 addition, a glass-coil condenser (area = 7 ft^2), a packed scrubber for NH_3 removal, and off-gas metering and sampling facilities (Fig. 3). For continuous operation the dissolver was modified as described in Sec. 3.4.

3. CHARACTERISTICS AND APPLICATIONS OF THE MODIFIED ZIRFLEX PROCESS

Modified Zirflex denotes a process for the recovery of uranium from U-Zr-Sn alloy fuels by batchwise dissolution in NH_4F-NH_4NO_3-H_2O_2 solutions, stabilization with HNO_3-$Al(NO_3)_3$, and TBP extraction.

3.1 Batch Processing Studies: Dissolvents, H_2O_2 Addition Rate, Reaction Products, and Effect on Reaction Times of F:Zr Ratio, Section Thickness, and Initial Surface Condition

Engineering studies demonstrated the feasibility of the Modified Zirflex process for the dissolution of U-Zr-Sn alloy fuels having uranium contents as high as 8%. Batch dissolutions were performed in 6-in.-diam

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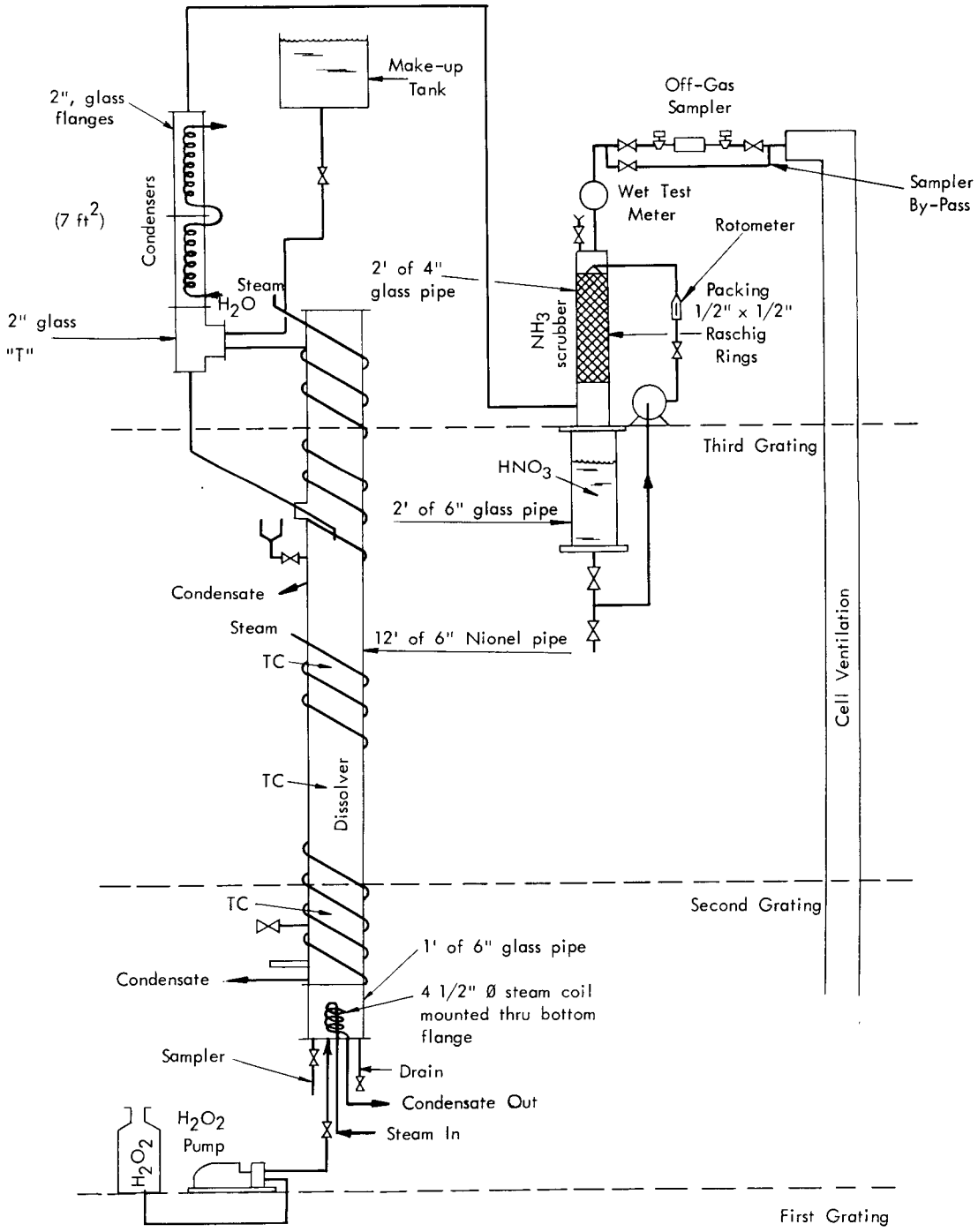

Fig. 3. Schematic of Modified Zirflex Equipment.

equipment, using 6.3 to 6.65 M NH_4F - 0 to 0.7 M NH_4NO_3 and a continuous addition of H_2O_2 to oxidize immediately U(IV) to the more soluble U(VI). [If this additional oxidant were not present U(IV) would precipitate, with fuels containing more than about 2% uranium, before the addition of the HNO_3-$Al(NO_3)_3$ stabilizing solution.] Instantaneous dissolution rates of about 2 to 20 mg cm^{-2} min^{-1} were reported previously[2] for unoxidized material, but since dissolution is initiated by penetration of the oxide film and subsequent undercutting, the surface condition of the material was found to be one of the important determinants of the time required for complete dissolution. Since the free fluoride concentration decreases steadily as dissolution proceeds (free fluoride is defined as total fluoride minus 6 Zr since each mole of zirconium in solution complexes 6 moles of fluoride) and since free fluoride determines the dissolution rate, the final free fluoride concentration as determined by the initial F:Zr charge ratio was the other important determinant of total dissolution time. The addition rate of H_2O_2 was not critical as long as a threshold oxidant concentration was maintained; excess H_2O_2 only diluted the solution somewhat and contributed oxygen to the off-gas.

The gaseous reaction products with an excess of NH_4NO_3 present were 5 moles of NH_3, less than 0.1 mole of hydrogen and traces of oxygen per mole of zirconium dissolved. The NH_3 was removed quantitatively by a dilute HNO_3 scrub. The remaining mixture of hydrogen and oxygen was in the flammable range but was of such a small volume that it could easily be rendered harmless by dilution with air. Reasonably concentrated solvent extraction feeds (about 0.4 M in zirconium, 0.8 M in aluminum and about 1 M in HNO_3) possessing acceptable corrosion rates were made from fuels

containing about 2% uranium. However, as uranium percentages increased, terminal free fluoride concentrations had to be increased to produce stable dissolver solutions. With more free fluoride, more aluminum [as 2 M $Al(NO_3)_3$] had to be added to achieve the required fluoride complexing and more dilute solvent extraction feeds (with respect to zirconium) resulted. During six reflux runs (Table 2) made in the 6-in.-diam equipment, dissolving 1100 to 2275 g batches of unirradiated U-Zr-Sn material containing 1.2 to 8% uranium and 0 to 1.6% tin, the following specific observations were made, substantiating the foregoing generalizations:

1. Dissolvents containing up to 6.6 M NH_4F were used with U-Zr-Sn fuels, and fluorozirconate did not precipitate in the boiling solution.
2. Hydrogen was evolved at rates of < 0.1 to 2.0 moles per mole of zirconium dissolved, depending on the NH_4NO_3 concentration of the dissolvent. Hydrogen was a major component of the off-gas (after NH_3 removal) whatever the initial NH_4NO_3 concentration.
3. The degree of surface oxidation and section thickness were the major determinants of dissolution time.
4. Hydrogen peroxide addition rates of about 10^{-5} mole cm^{-2} min^{-1} were sufficient to prevent U(IV) precipitation when dissolving alloys containing up to 8% uranium.
5. Hydrogen peroxide addition must be continued as long as zirconium is actively dissolving, even if all of the meat alloy has been dissolved in order to prevent the reduction of the previously formed U(VI) in solution.

12. The addition of 1.8 M HNO_3 - 1.8 M $Al(NO_3)_3$ stabilizing solution at room temperature to the dissolution product at about 90°C (below boiling, yet hot enough to prevent fluorozirconate precipitation) produced stable solvent extraction feeds 0.8 to 1.0 M in HNO_3 and $Al(NO_3)_3$.
13. The addition of an excess of H_2O_2 (average rates up to 2.0×10^{-5} mole cm^{-2} min^{-1}) had no deleterious effects on the stability of either the dissolution product or the solvent extraction feed.
14. With low nitrate concentration in the dissolvent the continuous H_2O_2 addition could be controlled by sensing the oxygen concentration in the scrubbed off-gas and varying the H_2O_2 solution pump rate to maintain (~3 ± 2%) O_2 in the off-gas stream.

In the first three runs (CZr-1, -2, and -3) in the engineering-scale equipment three different U-Zr-Sn multiplate prototypes (weighing 1450 to 1850 g) were dissolved in refluxing dissolvent initially 6.5 M NH_4F - 0.33 M NH_4NO_3 - 0.01 M H_2O_2 (Table 2). No elemental tin or UF_4 precipitation was observed when using arbitrary H_2O_2 addition rates of 0.5×10^{-5}, 0.4×10^{-5} and 0.75×10^{-5} mole cm^{-2} min^{-1} while dissolving zirconium-base materials containing 1.24% U-no Sn, 2.73% U-0.26% Sn, and 2.6% U-1.6% Sn, respectively. The time required for dissolution depended on the surface condition of the element: A clean section dissolved completely in 100 min; 90.7% of a partially oxided piece dissolved in 3 hr; a fully oxided element (except for freshly cut ends) was 97.2% dissolved in 4 hr. (These numbers are not directly comparable because of differences in section thicknesses.) In all three runs the H_2O_2 concentrations in the partially loaded dissolvent (sampled at 10-min intervals throughout the run) were of the same order of

magnitude, 0.001 to 0.01 M, with only a factor of about 2 variation during any one run. Hydrogen peroxide addition must be continued until total dissolution of all the zirconium has been accomplished, even if all the U-Zr meat has been dissolved, in order to prevent the reduction of U(VI) by the actively dissolving zirconium. This was shown by interrupting the peroxide flow in run CZr-2; the solution slowly assumed a greenish shade indicating the presence of U(IV) and then cleared [yellow, U(VI)] upon resumption of the peroxide addition.

The number of moles of NH_3 evolved per mole of zirconium dissolved was 4.69 ± 0.15 for the three runs. A value somewhat less than 5 would be predicted for a dissolution following the equation $Zr + 6NH_4 + 1/2NH_4NO_3 \rightarrow (NH_4)_2ZrF_6 + 5NH_3 + 1.5H_2O$, since less than the stoichiometric amount of NH_4NO_3 was present. (Only 4 moles of NH_3 are produced in NH_4F dissolution.) The total scrubbed off-gas (principally hydrogen) volume was inversely proportional to the H_2O_2 addition, indicating that some hydrogen was oxidized to H_2O by the H_2O_2. The number of moles of hydrogen per mole of zirconium dissolved was obtained by assuming the total volume of off-gas to be hydrogen. All three runs were made at approximately the same boil-up rate; no difficulties with foaming were encountered during dissolution, and no solids were deposited on the heated walls of the dissolver above the solution level. Stable solvent extraction feed containing about 0.4 M Zr and 1 g of uranium per liter was prepared by adding enough stabilizer solution [1.8 M HNO_3 - 1.8 M $Al(NO_3)_3$] to yield a product 1 M in both H^+ and Al^{3+}. Since less than a stoichiometric amount of NH_4NO_3 was used in dissolution, Neuflex feeds could have been generated by diluting with an appropriate volume of water rather than the HNO_3-$Al(NO_3)_3$ solution.

Material balances for U-Zr-Sn, assuming that these three metals comprised the entire weight of the elements charged, were 100 ± 5%.

Gas evolution from the dissolution as a function of dissolution time is shown in Figs. 4 and 5. A mixture of NH_3-H_2O and inerts (with respect to HNO_3) flows from the updraft condenser to a scrubber through which a batch of HNO_3 (originally 8 to 10 M) is recirculated. The NH_3 reacts quantitatively, and a measure of the disappearance of H^+ is also a measure of the NH_3 evolved and reacted. This rate of H^+ consumption was monitored by sampling at 10-min intervals. Figure 4 shows the integral and differential NH_3 evolution data obtained by determining H^+ in the HNO_3-NH_4NO_3 scrubber liquid samples. The integral curve is the total NH_3 evolution since the beginning of the run; the differential curve is the average rate in the interval since the preceding sample. The differential NH_3 evolution rate is proportional to the total zirconium dissolution rate (g/min).

The evolution rates of gases not removed by the nitric acid scrubber are shown in Fig. 5. The integral curves were plotted from wet test meter readings, and the differential curves were obtained by dividing the volume increment between points on the integral curves by the time increment. All these curves confirm laboratory data that dissolution rates are initially fast and then tail off as fluoride becomes complexed. The degree of surface oxidation is the principal determinant of the early NH_3 and off-gas evolution rates.

The compositions of off-gas samples from the three runs are shown in Table 3. The sampling bulbs were placed in the off-gas line and the full off-gas stream (of volume indicated) passed through the bulb in the time indicated. The last six samples indicate that the off-gas was principally

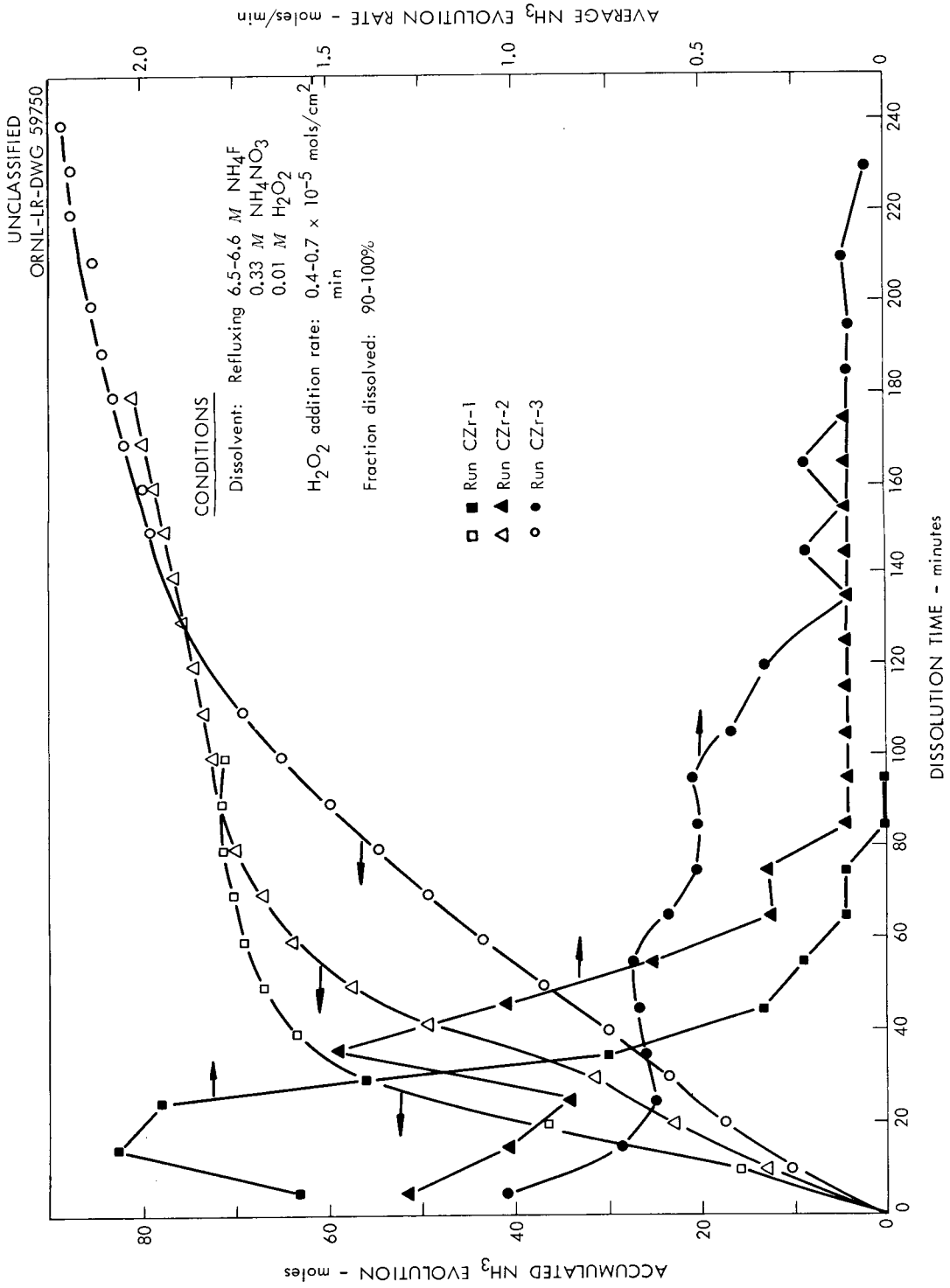

Fig. 4. Modified Zirflex: Ammonia Evolution.

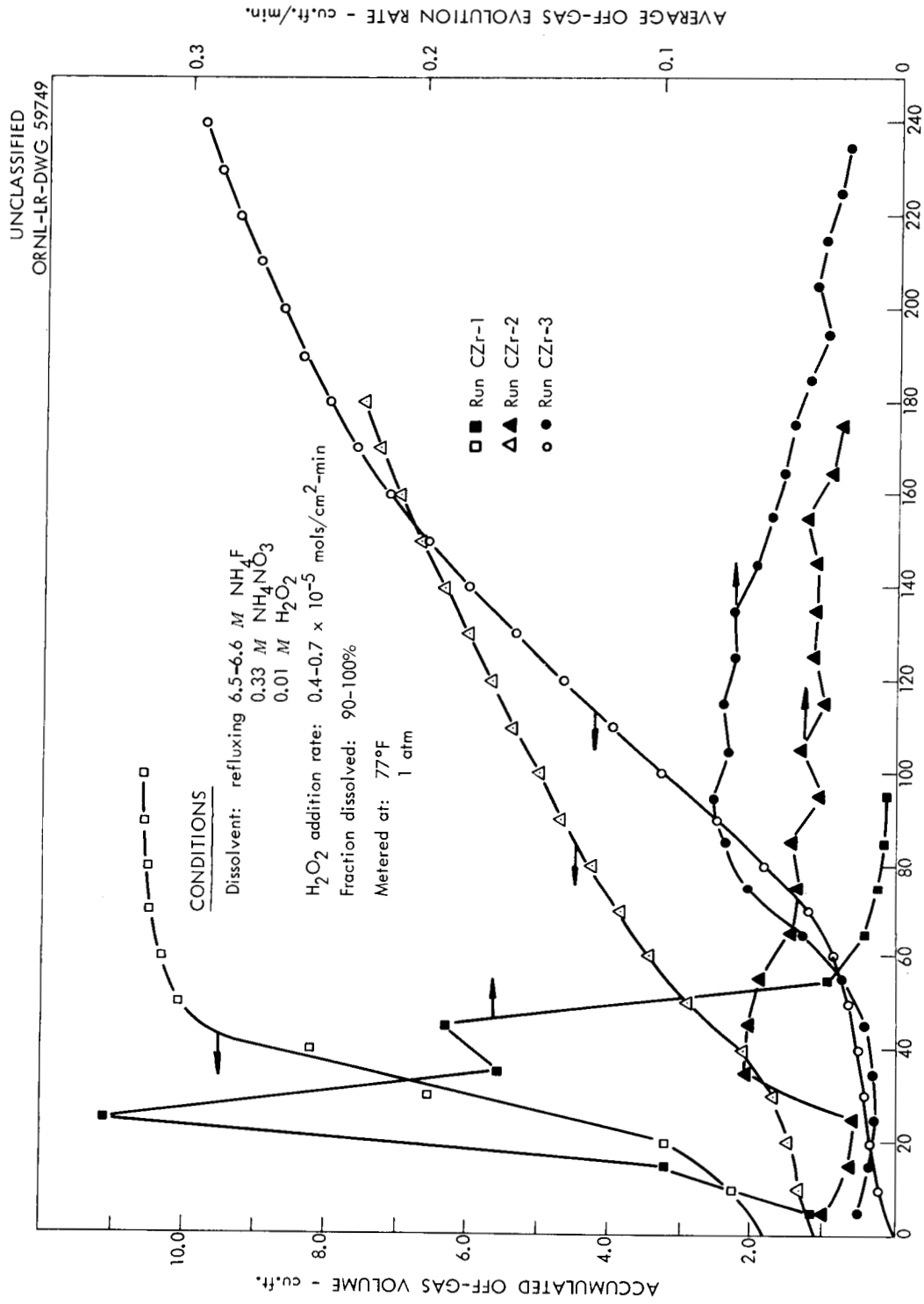

Fig. 5. Modified Zirflex: Off-Gas Evolution.

Table 3. Modified Zirflex Off-Gas Samples

Run No.	Sample No.	Sample Bulb Purged With:	Vol. Sent Thru Bulb (cu ft)	Period on Stream (min)	Composition		
					H_2 (%)	O_2 (%)	N_2 (%)
CZr-1	1	Air	8.2	0-55	72.1	5.4	20.1
CZr-2	1	Argon	1.3	0-10	20.4	15.0	51.6
	2	Argon	0.8	10-40	68.2	1.7	0.7
	3	Argon	1.7	40-75	72.7	0.4	0.4
	4	Argon	2.1	75-124	59.5	0.7	0.3
CZr-3	1	Argon	1.6	23-84	84.1	ND[a]	ND
	2	Argon	2.4	84-117	98.4	ND	ND
	3	Argon	3.2	117-169	100	ND	ND

[a]Not detected.

hydrogen. Although sample CZr-1, which should have been valid, shows appreciable quantities of nitrogen and oxygen, it appears very coincidental that these should be in the same ratio as found in air. Air probably contaminated sample 1 of run CZr-2 since much of the first 1.3 ft^3 through the system was air purged from the upper portion of the dissolver.

Run CZr-4 was made using dissolvent initially 6.65 M in NH_4F, 0.67 M in NH_4NO_3, and 0.01 M in H_2O_2. The unoxidized PWR-1 prototype weighing 1738 g was 98.2% dissolved (portions of the thicker, inert Zircaloy-2 side plates remained) in 4 hr of refluxing. Although 140% of the NO_3^- required to oxidize the hydrogen to NH_3 was present, the off-gas after HNO_3 scrubbing (total volume for complete run, 0.94 ft^3 at 1 atm and 78°F) contained 27

to 42% hydrogen. Ammonia evolution was 4.86 moles per mole of zirconium dissolved. The off-gas was sampled by flowing the entire stream through the sampler for the period indicated. Off-gas data are shown in Table 4. The N_2/O_2 ratio of about 4 in sample 2 suggests air contamination, but the ratio of 2.7 in sample 1 indicates that more oxygen was evolved early in the dissolution when the NH_4NO_3 concentration was higher; the H_2O_2 addition rate was constant.

Table 4. Off-Gas Data for Run CZr-4

Sample No.	Volume Passed (ft^3)	% of Dissolution Time	Composition (%)		
			H_2	O_2	N_2
1	0.32	9-25	42	14	38
2	0.12	25-52	27	14	54

A boil-up of 0.07 cc cm^{-2} min^{-1} (based on initial fuel surface) was sustained by external heat; this was more than doubled (Fig. 6) at the peak dissolution rate by heat of reaction; no stable foam was observed. The condensate (boil-up) rate and NH_4OH concentration in the condensate behaved as would be predicted for unoxided fuel with high boil-up and NH_4OH initially, tailing off. Ammonia and scrubber off-gas evolution behaved similarly.

Run CZr-5 was made in the engineering-scale equipment using dissolvent initially 6.53 M in NH_4F, 0.00 M in NH_4NO_3, and 0.01 M in H_2O_2, with an H_2O_2 addition rate of 0.5×10^{-5} mole cm^{-2} min^{-1}. This is, by the definition given, a Neuflex dissolution, but the data are repeated here since a Modified Zirflex solvent extraction feed was produced by adding HNO_3-$Al(NO_3)_3$.

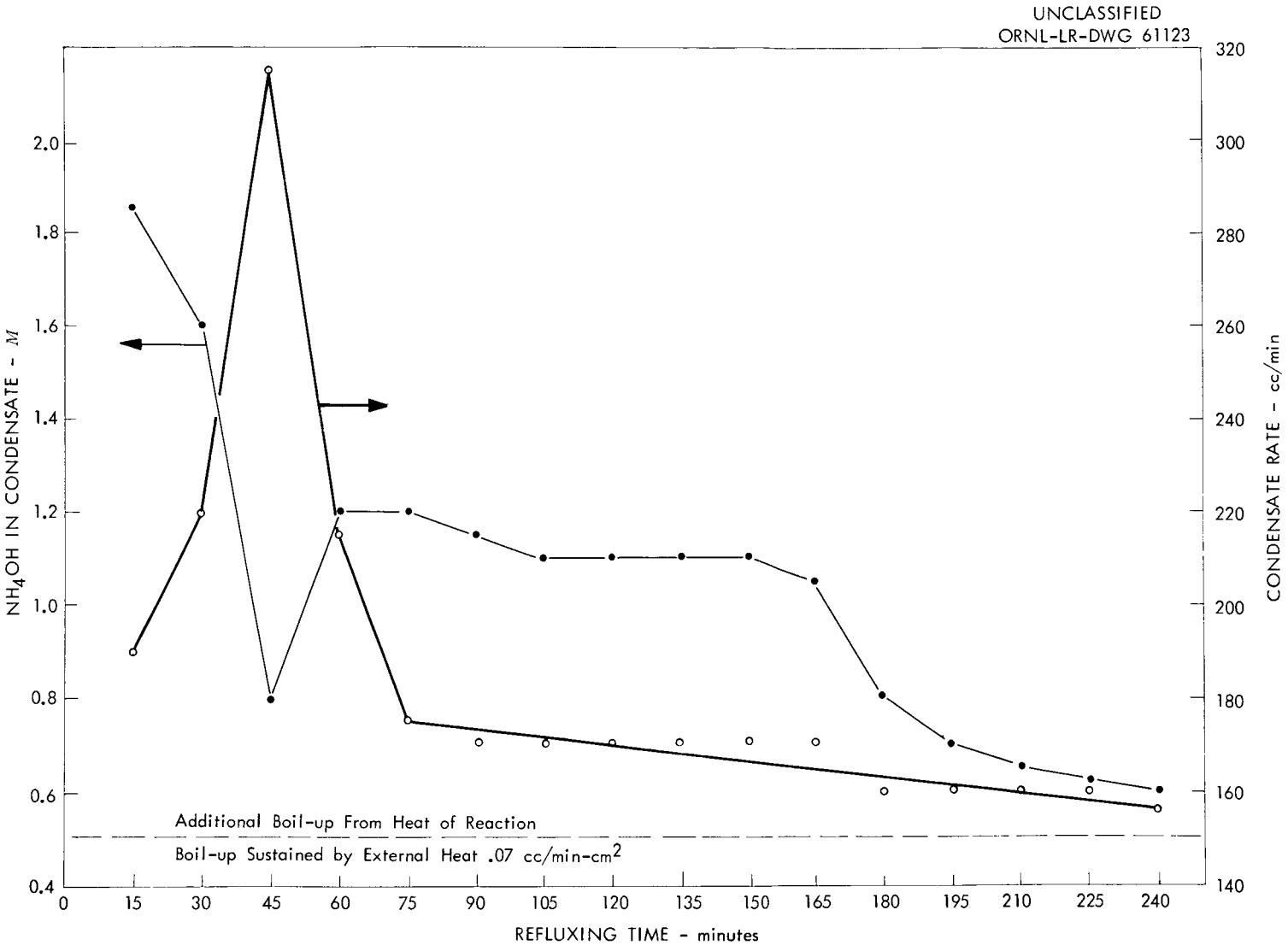

Fig. 6. Condensate Rate and NH_4OH Concentration as Functions of Refluxing Time.

The 1.103 kg of unoxidized 8% U-Zr alloy plate (0.122 in. thick) was completely dissolved in 2 hr of refluxing. About 4 g of a green precipitate was collected which contained 56% U, 25% F and 3% Zr. It is assumed that this is the same material involved in the coat formation reported by Gens (ORNL-2905) since the free fluoride (total F-6Zr) to uranium ratio was only 51. The amounts of gaseous reaction products evolved agreed very well with the assumed stoichiometry of the dissolution reaction with 2.0 moles of hydrogen and 4.2 moles of NH_3 observed per mole of zirconium dissolved. Four samples of the scrubbed off-gas taken at intervals throughout the run showed $H_2 \geq 93\%$ with $H_2 + H_2O \cong 99\%$ and $O_2 \leq 0.15\%$. The average boil-up rate (obtained by measuring the reflux to the dissolver) was 0.15 ml min^{-1} cm^{-2} of the initial fuel surface. The addition of stabilizer [1.8 M HNO_3 - 1.8 M $Al(NO_3)_3$] at room temperature when the dissolution product had cooled to about 90°C produced a stable solvent extraction feed containing 0.35 M Zr, 2.78 g U per liter, 2.7 M F, 1 M HNO_3, and 1 M $Al(NO_3)_3$. Material balances for zirconium, uranium, and fluoride accounted for 93.5 to 95.5% of the total amount of each element charged.

Run CZr-6 (Table 2) was the dissolution of a TRIGA "meat" slug (8% U-ZrH, about 1.4 in. in diameter x 14 in. long, see Sec. 3.3). The large diameter (about 1.4 in.) of the slug resulted in a low area-to-mass ratio and a long dissolution time. This necessitated high H_2O_2 addition and boil-up rates, on an area basis, in order to give streams of the desired magnitude. The H_2O_2 volumetric rate was still low (2 to 6 cc/min) so that considerable gassing (indicating H_2O_2 decomposition) was observed at the inlet to the dissolver. Although the NH_3 evolution rate was believed reliable, no scrubbed off-gas data were reported because a leak developed in the metering system downstream from the ammonia scrubber.

Apparently hydrogen will be a major component of the scrubbed off-gas regardless of the NH_4NO_3 concentration, but if either Modified Zirflex or Neuflex is used in conjunction with Sulfex the equipment for the handling of large volumes of hydrogen-containing off-gas already will have been provided for. Since hydrogen evolution is inevitable, the use of about 6.5 M NH_4F - H_2O_2 as a dissolvent should be considered; both tin and uranium are oxidized by the H_2O_2 and zirconium is dissolved by the NH_4F producing 4 moles of NH_3 and 2 moles of hydrogen per mole of zirconium dissolved. The greater hydrogen evolution will provide an additional means of monitoring the progress of the dissolution. Another obvious advantage is the elimination of NO_3^- during the dissolution step, which should lower corrosion rates in the dissolver. The lowering of NH_4^+ concentration in the product solution should also have a beneficial effect on zirconium solubility.

3.2 Solution Stability: The Delicate Balance Between Fluoride, Zirconium, Aluminum and Acid Concentrations in the Solvent Extraction Feed

A brief study of the stability of solvent extraction feeds made by HNO_3-$Al(NO_3)_3$ stabilization of NH_4F dissolution products was undertaken not as a definitive study but to show a useful range of stable solutions and to show that with respect to stability Modified Zirflex feeds (NH_4F) are comparable to the STR feed (HF) studied extensively at ICPP.[4]

The dissolution product from run CZr-4 was stabilized with 13 different combinations of HNO_3-$Al(NO_3)_3$ to produce solutions for corrosion and stability tests. Two levels of HNO_3 (0.75 and 1.5 M) and three levels of $Al(NO_3)_3$ (0.6, 0.8, and 1.0 M) were evaluated with variable zirconium concentrations from 0.36 to 0.58 M at a constant F:Zr ratio of 6.8. Table 5

Table 5. Compositions, Relative Complexing, and Stability of Solutions

Solution No.	HNO_3 (M)	Al (M)	Zr (M)	F (M)	C 4Zr + Al	C/F	F-C	Remarks About the One-Year Stability
1	0.75	0.6	0.58	3.9	2.91	0.74	0.99	Large amount of crystals
2	0.75	0.6	0.49	3.3	2.56	0.77	0.74	Small amount of crystals
3	0.75	0.6	0.40	2.7	2.20	0.81	0.50	OK
4	0.75	0.8	0.49	3.3	2.76	0.83	0.54	Few crystals
5	0.75	0.8	0.40	2.7	2.40	0.88	0.30	OK
6	0.75	1.0	0.40	2.7	2.60	0.96	0.10	OK
7	0.75	1.0	0.36	2.4	2.44	1.00	0.0	OK
8	1.5	0.6	0.54	3.6	2.74	0.75	0.86	Large amount of crystals
9	1.5	0.6	0.45	3.0	2.39	0.79	0.61	Few crystals
10	1.5	0.6	0.36	2.4	2.04	0.84	0.36	OK
11	1.5	0.8	0.45	3.0	2.59	0.85	0.41	OK
12	1.5	0.8	0.36	2.4	2.24	0.92	0.16	OK
13	1.5	1.0	0.36	2.4	2.44	1.00	0.0	OK

shows approximate compositions, relative complexing and long-term stability for these solutions. No precipitates formed in any of the solutions in the first 24 hr, but after 16 days a coarse, white crystalline precipitate was observed in solutions 1 and 8; these contained the highest zirconium concentrations and the lowest aluminum concentrations evaluated. All the other compositions were stable after 16 days at room temperature. After a few months crystals were observed in solution 2, and after a year some

crystals were observed also in solutions 4 and 9. Long-term stability correlated with the quantity F-C listed in Table 5. This number is related to free fluoride and is calculated by subtracting the complexing (arbitrarily defined as 4Zr + Al) from the total fluoride. The acid level appears to have had no noticeable effect on stability in the particular solutions studied.

In addition to stability with respect to crystalline U-Zr-F-Al precipitates, there is also the problem, both in dissolvent and feed solutions, of flocculent precipitates composed primarily of hydrated zirconium oxides. Although increasing the boil-up rate (or steam sparging) and the removal of overhead condensate appears to help to alleviate the problem, the role of NH_3 (or NH_4OH) in the formation of such precipitates is not clear. If the NH_3 reacts at the metal surface immediately upon its formation, it would be impossible to prevent the reaction from occurring. On the other hand, it would be easy to keep NH_4OH from the overhead from returning to the dissolvent by collecting it and returning an equal volume of H_2O to maintain the batch volume balance. These precipitates usually give the solution a cloudy appearance and drop out only on long standing. They carry little or no uranium and are dissolved in HNO_3-$Al(NO_3)_3$, but excess amounts might be objectionable in water-stabilized Zirflex decladding or Neuflex solutions.

3.3 Application of the Modified Zirflex Process to a TRIGA Prototype (Core 8% U-ZrH) after Aluminum Decladding and Graphite Disintegration by Fuming Acid

Run CZr-6 included the decladding, graphite cylinder disintegration and dissolution of the 8% U-ZrH meat slug of a prototype TRIGA element

(normal uranium, 1.476-in.-diam x 28.5-in. long) in the 6-in.-diam dissolver. (Laboratory development data for TRIGA are presented in ORNL-3065 and ORNL-2905, by T. A. Gens.) The dissolution of the 0.030-in.-thick aluminum cladding, and 0.050-in. Al-Sm poison discs was accomplished in less than 1/2 hr at reflux (Fig. 7) in an excess of 2 M NaOH - 1.8 M $NaNO_3$ (the large volume of dissolvent was required to cover the element). The soluble uranium loss was 0.015%, with about an equal amount carried by a gelatinous precipitate [presumed to be $Fe(OH)_3$].

After thorough washing and drying of the dissolver and contents, 1.0 liter of 90 vol % nitric acid - 10 vol % H_2SO_4 (fuming) was admitted to the dissolver for disintegration of the two about 1.4-in.-diam x 4-in.-long graphite slugs. Corrosion rates of various materials of construction in this mixture are presented in Table 6. After 2 hr of exposure at room temperature the graphite was 2/3 (by weight) disintegrated, with equal attack on both pieces. It is possible that a longer exposure time, higher temperature, or agitation might have accomplished a greater degree of disintegration. Due to the configuration of the system the U-ZrH slug was not subjected to the acid mixture; however, Gens (ORNL-3065) reports < 0.01% weight loss during graphite disintegration. The aluminum heel (end pieces, about 68.5 g) showed a 1/4% weight loss during the mixed-acid contact.

After thorough washing and graphite removal, the "meat" slug (2274 g of 8% U-ZrH, about 1.4-in.-diam x 14-in. long, initial area = 412 cm^2) was dissolved in 27.5 liters of refluxing dissolvent initially 6.3 M in NH_4F, 0.6 M in NH_4NO_3, and 0.01 M in H_2O_2, with an average continuous H_2O_2 addition rate of 1.6×10^{-5} mole cm^{-2} min^{-1}. Dissolution was 99-3/4%

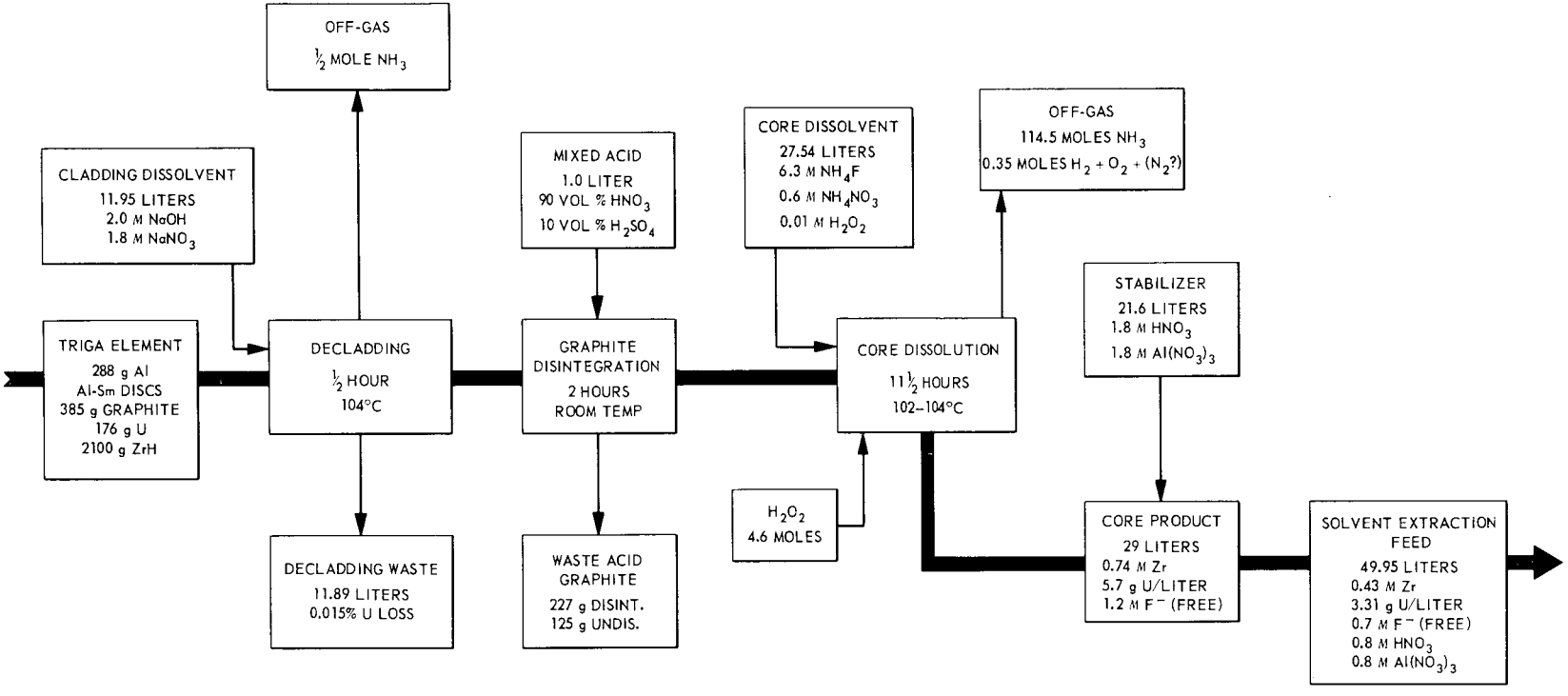

Fig. 7. Aqueous Processing of TRIGA Fuel.

Table 6. Corrosion of 90 vol % 21 N HNO_3 - 10 vol % 40 N H_2SO_4 at 50°C[a]

Material	Position of Specimen	Corrosion rate (mils/month) 24 hr	168 hr	336 hr	504 hr	672 hr
Nichrome V (unwelded)	V	0.14				
	I	0.19				
	S	0.20				
Carpenter 20SCb (welded)	V	2.60				
	I	0.18				
	S	0.23				
Type 347 SS (welded)	V	4.1				
	I	0.06				
	S	0.07				
Type 304 L SS (welded)	V	3.1				
	I	0.03				
	S	0.11				
INOR-8 (unwelded)	V		0.17-0.18	0.15-0.16	0.16-0.17	0.16-0.17
	S		0.25-0.26	0.15-0.17	0.12-0.13	0.10-0.11
CD4MCu (wraught, unwelded)	V		1.74			
	S		0.02			
CD4MCu (cast, unwelded)	V		1.41			
	S		0.03			
LCNA (welded)	V		0.57-0.57	0.90-0.90	(Grain boundary attack	
	I		0.03-0.03	0.03-0.03	(noted	
	S		0.06-0.06	0.06-0.06		
LCNA (welded)	V	(Vapor space flushed in dry air)	0.09-0.10	0.30-0.30	0.42-0.45	0.48-0.52 (Diminished grain boundary attack)
	S		0.04-0.05	0.05-0.06	0.06-0.06	0.06-0.06
Type 309SCb SS (welded)	V		1.65-1.93	2.80-2.89	(Grain boundary attack	
	I		0.03-0.17	0.03-0.10	(noted	
	S		0.02-0.03	0.04-0.03		

[a]Data by L. Rice.

complete in 11-1/2 hr; the average boil-up rate was 0.4 ml cm^{-2} min^{-1}, and the reflux to the dissolver contained 0.6 to 0.1 M NH_4OH. Ammonia evolution was 5.3 moles per mole of zirconium found in the dissolvent. After dissolution 21.6 liters of 1.8 M HNO_3 - 1.8 M $Al(NO_3)_3$ stabilizing solution was added (dissolution product about 90°C) producing 49.95 liters of solvent extraction feed 0.78 M in HNO_3 and $Al(NO_3)_3$, containing 3.27 M F, 0.43 M Zr, and 3.31 g of uranium per liter. Material balances for U, Zr, and F were 93.8, 94.4 and 94.3%, respectively. The species in the off-gas NH_3, H_2, O_2 and N_2 were confirmed, but the amount of scrubbed off-gas (principally H_2, with O_2, and N_2 initially, Fig. 7) is not reliable (low) due to a malfunction in the metering system downstream from the HNO_3 scrubber.

It is believed that any future effort on the reprocessing of TRIGA fuel should include an investigation of the feasibility of a mechanical preparation of elements prior to dissolution, which would remove the aluminum end fittings, the graphite slugs and the Al-Sm poison discs from the dissolution cycle. This could be accomplished by cutting the 0.030-in.-thick aluminum tube near each end of the U-ZrH slug. If the U-ZrH slug could then be removed from its tubular aluminum cladding, the aqueous processing would be reduced to a Modified Zirflex dissolution; even if it could not, a much simpler two-step process would result, retaining the obvious advantages of avoiding (1) the use of mixed fuming HNO_3-H_2SO_4, (2) exhaustive washings, (3) the removal of aluminum and graphite heels from the dissolver, and (4) the uncertainties of samarium chemistry.

3.4 Continuous Dissolution of Zircaloy-2: Higher Reaction Rates and Throughputs

In order to compete with HF dissolution processes it was desired to

demonstrate the highest dissolution rates possible with Modified Zirflex while maintaining reasonable loadings. An adaptation to continuous operation was the obvious route to higher throughputs in comparable equipment. In order to define the area of favorable operating conditions, the relationship between the reaction rate and the dissolvent feed rate to specimen surface area (F/S) ratio was investigated by dissolving multiplate Zircaloy-2 assemblies in the 6-in.-diam dissolver.

The reaction rate increased as the F/S ratio increased, but the increase was not linear so that although the amount dissolved (total throughput) increased with increasing F/S, the dissolvent loading decreased, leaving a rather narrow range of operation giving practical dissolution rates and loadings high enough to avoid excessive waste volumes. A reasonable approximation of steady-state operation was shown in all three runs. Apparently a small beneficial effect was observed when the NH_4OH-containing overhead condensate was withdrawn and an equal volume of water was returned to the dissolver.

The data for three runs in engineering-scale equipment are reported in Table 7; the reaction rate R (mg cm^{-2} min^{-1}), feed rate F (cm^3/min), and specimen surface area S (cm^2) are listed along with various solution compositions. These three are correlated in Fig. 8 as reaction rate vs F/S. Figure 9 shows the instantansoue zirconium concentration in the dissolver at 5-min intervals over the period of steady-state operation for the three runs. The curved line in Fig. 8 is the relationship between reaction rate and F/S established by previous work in 2-in.-diam equipment (see Appendix B) with total reflux of NH_4OH-containing overheads. This shows reaction rate increasing with F/S but at an ever decreasing rate. This means that

Table 7. Continuous Modified Zirflex Runs in 6-in.-diameter Equipment

Run No.	Dissolvent				Specimen Area (cm^2)	Diss. Time (min)	△ Wt (g)	Reaction Rate (mg $cm^{-2}min^{-1}$)	F/S (cm/min)
	Feed Rate (cm^3/min)	NH_4F (M)	NH_4NO_3 (M)	H_2O_2 (M)					
1	330	6.6	0.61	0.1	4046	55	1245	5.60	0.0816
2	307	6.7	1.0	0.1	4160	50	1191	5.73	0.0738
3	288	6.6	1.0	0.1	4700	60	1271	4.5	0.0613

Run No.	Diss. Load. (g Zly-2/liter)	Prod.[a] Free F^- (M)	Stabilizer			Solvent Extraction Feed[b]			Material Balance	
			Vol (liters)	HNO_3 (M)	$Al(NO_3)_3$ (M)	Vol (liters)	Zr (M)	Total F^- (M)	Zr (%)	F (%)
1	68.63	2.1	15.0	1.8	1.8	30.4	0.36	3.3	90	101
2	77.64	1.6	12.8	1.8	1.8	25.5	0.44		85[c]	
3	73.4	1.9	14.0	1.8	1.8	29.5	0.42	3.5	92	90

[a]Average values calculated from $L = \frac{R}{F/S}$. See Fig. 9 for instantaneous experimental values.

[b]Also contained about 1 M HNO_3 and about 1 M $Al(NO_3)_3$.

[c]A portion of the dissolution product was lost before stabilization.

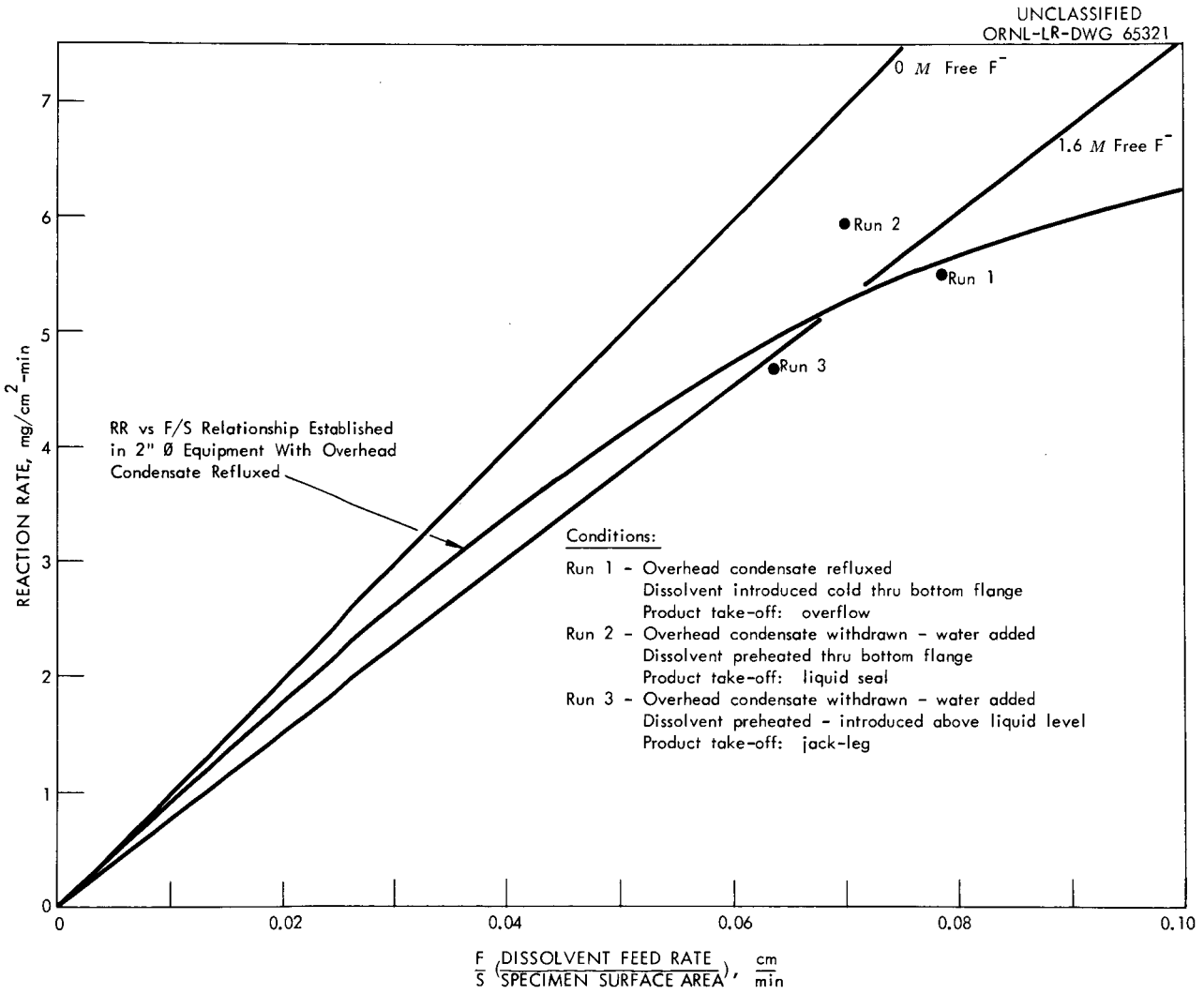

Fig. 8. Continuous Modified Zirflex: Correlation of Reaction Rate, Dissolvent Feed Rate and Specimen Surface Area.

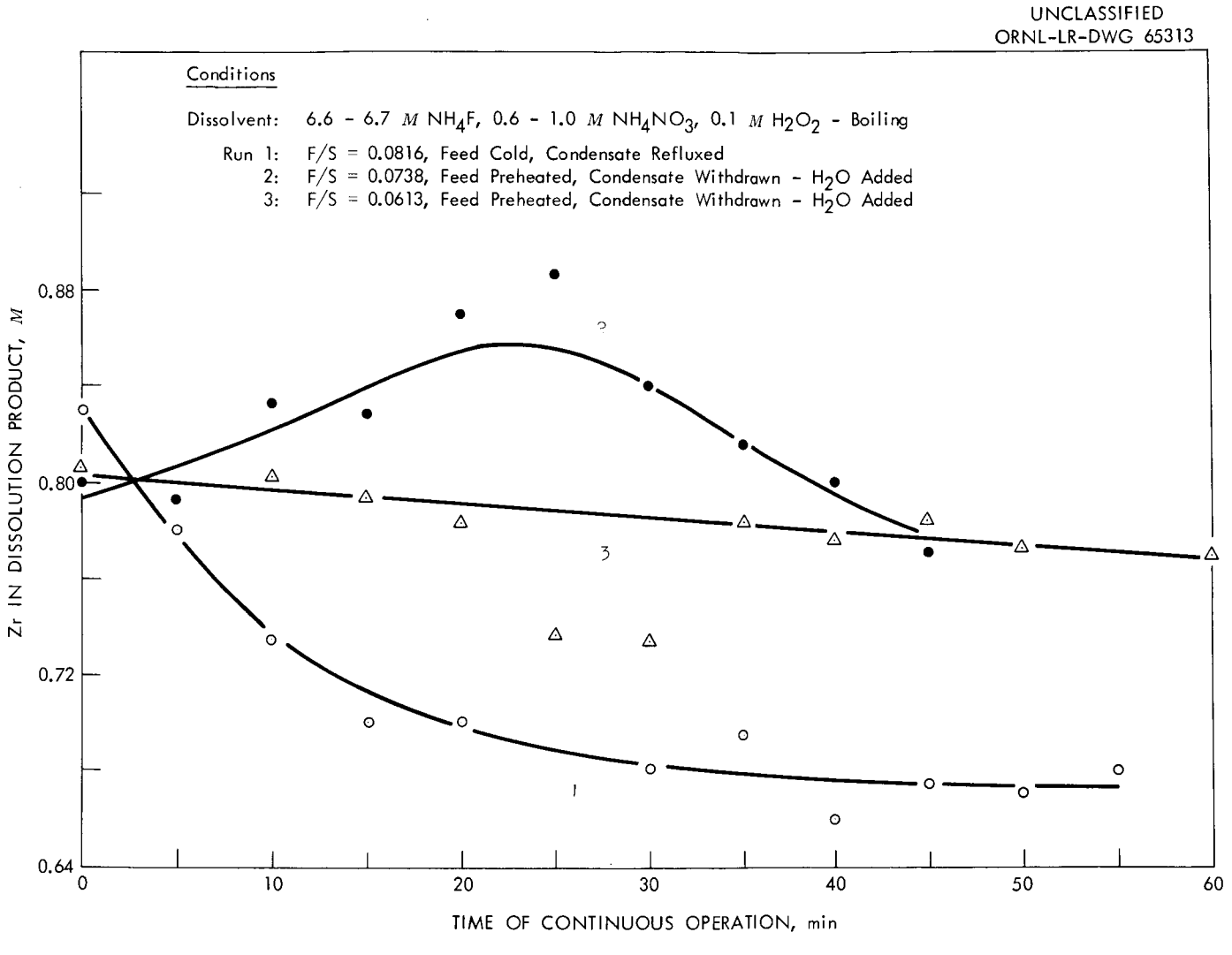

Fig. 9. Continuous Modified Zirflex: Steady State Zirconium Concentration in Dissolver Solution.

although total throughput increases, solution loading ($L = \frac{R}{F/S}$) decreases, with attendant increase in chemical costs and waste volumes. The straight lines are lines of constant loading and free F^- concentration. The three runs in the 6-in.-diam equipment (indicated on Fig. 8) probably fit the curve within experimental error; however, some differences should be pointed out. Run 1 was made at total reflux (with rectification) while in runs 2 and 3 the overhead condensate was withdrawn and water was returned at the same rate. Runs 2 and 3 indicate that higher rates and loadings might be obtained operating at a higher F/S with condensate withdrawal. Run 2 was exceptional in that it gave a higher reaction rate than run 1 (made at higher F/S) and a higher loading than run 3 (made at lower F/S). The superiority of run 2 is probably explained by the hump in the curve of dissolver solution zirconium molarity vs time (Fig. 9). Runs 1 and 3 show relatively steady-state operation, while run 2, which should have produced a horizontal line between runs 1 and 3, is displaced upward and is more erratic.

All three runs were made by first producing by batch dissolution a dissolver charge of the volume and composition estimated as the steady-state condition in continuous dissolution. These compositions are shown as time zero in Fig. 9 and were relatively accurate except in run 1, where a steady reduction in zirconium molarity characterized the approach to steady state. This resulted in a low observed dissolution rate since for the first portion of the run dissolution was occurring in a free F^- concentration less than that calculated for the true steady-state condition. After completion of the batch dissolution the element was charged (totally immersed) and feed was begun; the dissolver effluent flowed into a batch

of stabilizer (Table 6) whose volume was 0.8 that of the expected dissolver effluent. The reaction rates reported were calculated from the element weight-loss, initial surface area and time of immersion. The elements (multiplate, Zircaloy-2, 0.068-in. thick) were attacked about 0.015-in. so that the error introduced by assuming constant area throughout a run should be less than that caused by the change in element surface roughness.

The equipment for the three runs differed significantly only in the method of product withdrawal. In run 1 a simple overflow was used, with cold dissolvent fed at the bottom; the simple overflow method, with the absence of a liquid seal, allowed NH_3 to contact the stabilized product, and a flocculent white precipitate was formed. In run 2 a jack-leg entering the dissolver adjacent to the reaction zone was used as the overflow device providing a liquid seal, with preheated dissolvent entering the bottom, but operation was hydraulically unstable due to intermittent blowing of the shallow seal. In run 3 satisfactory operation was achieved by using a jack-leg entering the sidewall of the dissolver near the bottom flange and feeding preheated dissolvent above the liquid level. The feeding of dissolvent from above should provide for some attack of the ZrO_2-coated elements stacked in the dissolver before they are immersed in the dissolvent.

4. THE NEUFLEX PROCESS: A NEUTRAL FLUORIDE EXTRACTION FEED SIMILAR TO ZIRFLEX DECLADDING WASTE

The Neuflex process is similar to the Modified Zirflex process except that it eliminates the excess NH_4NO_3 from the dissolvent and employs water rather than the HNO_3-$Al(NO_3)_3$ mixture as an additive to the dissolution product to produce a more stable solvent extraction feed. The result is a neutral fluoride system containing neither H^+ nor NO_3^-, in which the

zirconium loading attainable is determined by the free-fluoride-zirconium solubility relationship and not by the degree of complexing (aluminum addition) required. Higher terminal free fluoride concentrations can be used which result in shorter dissolution times. Conventional TBP extraction of uranium is not applicable to such solutions, but Dapex reagents (D2HPA and DAAP) were effective in uranium recovery.

Four runs in engineering equipment (Table 8) demonstrated the feasibility of the Neuflex process for the dissolution of U-Zr-Sn alloy fuels having uranium contents as high as 8%. A typical chemical flowsheet for 2% U-Zr fuel is presented in Fig. 10.

Batch dissolutions were performed in 6-in.-diam equipment using 6.5 M NH_4F with a continuous addition of H_2O_2 to oxidize immediately U(IV) to the more soluble U(VI). If such an oxidant were not present U(IV) would precipitate from fuels containing more than about 2% uranium, before dilution of the metastable dissolution product solution. Instantaneous dissolution rates varied from 2 to 20 mg/cm^2 min as in the Modified Zirflex process with the free fluoride concentration determining the dissolution rate. The solution F^-:Zr ratio decreases steadily as dissolution proceeded, with each mole of zirconium in solution complexing 6 moles of fluoride. To minimize the dissolution period, and ensure solubility stability, it is important to maintain a terminal free-fluoride-to-uranium ratio of 50 to 100. For each terminal free-fluoride-to-uranium ratio selected, there must be suitable dilution with water to keep the zirconium in solution. The net effect is a final uranium loading dependent upon the amount of diluent water required to form a solution stable with respect to zirconium.

Table 8. Data for Neuflex Runs

Run No.	Dissolvent[a] Vol (liters)	NH_4F (M)	NH_4NO_3 (M)	U-Zr-Sn Fuel Plate Type	Wt (g)	Diss. (%)	Area (cm^2)	Thickness (in.)	Diss. Time (hr)	H_2O_2[e] Add Rate $\left(\frac{\text{mole}}{cm^2\text{-min}}\right)$ x 10^{-5}	moles H_2 / mole Zr	moles NH_3 / mole Zr	Boil-up Rate $\left(\frac{\text{ml}}{cm^2\text{-min}}\right)$	NH_4OH in Reflux (M)
4	18.9	6.65	0.67	PWR seed	1738	98.2	2150	0.081	4	0.4	0.06	4.86	0.08	1.85-0.6
5	13.35	6.53	0.00	8% U-Zr	1103	100	1077	0.122	2	0.5	2.0	4.2	0.15	0.6-0.1
7	6.42	6.53	0.15	8% U-Zr	517	99	519	0.122	3	1.2		5.17	0.23	0.4-0.1
8	7.0	6.53	0.15	8% U-Zr	515	100	517	0.122	2-1/4	2.0	1.32	4.6	0.24	0.3-0.05
9	6.75	6.53	0.00	PWR seed	590	>99	862	0.081	4-2/3	1.1	1.89	4.06	0.17	0.43-0.0

Run No.	Scrubbed Off-Gas Vol[b] (ft^3)	O_2 (%)	H_2 (%)	H_2O (%)	Add H_2O Vol (liters)	Solvent Extraction Feed Vol (liters)	Zr (g/liter)	U (g/liter)	F (M)	Free F/U	Material Balances Zr (%)	U (%)	F (%)
4	0.94				4.0	11.16	51.0	1.2	3.75	80	96.4[d]		93.7
5	18.2	< 0.15	93-98	0.5-6	17.0[f]	30.3	31.9	2.8	2.7	51	95.2	95.4	93.7
7		3.3	95	0.2	5.7	12.35	33.3	2.9	3.19	82	86.5	86.6	94.3
8	5.77	0.5-5.1	88-97	0.8-2.5	7.3	14.315	32.3	2.65	3.04	82	97.6	92.1	95.2
9	10.2	0.2-1.3	94-97	1-5	4.19	11.09	51.3	1.03	3.87	115[c]	100.6[d]		97.5

[a] Also contained 0.01 M H_2O_2.

[b] Metered at 25°C and 1 atm.

[c] F/Zr more important here for low U fuel = 6.88.

[d] Combined weight balance given since U and Zr percentages not known accurately.

[e] As 3-10% solution.

[f] 1.8 M HNO_3 - 1.8 M $Al(NO_3)$.

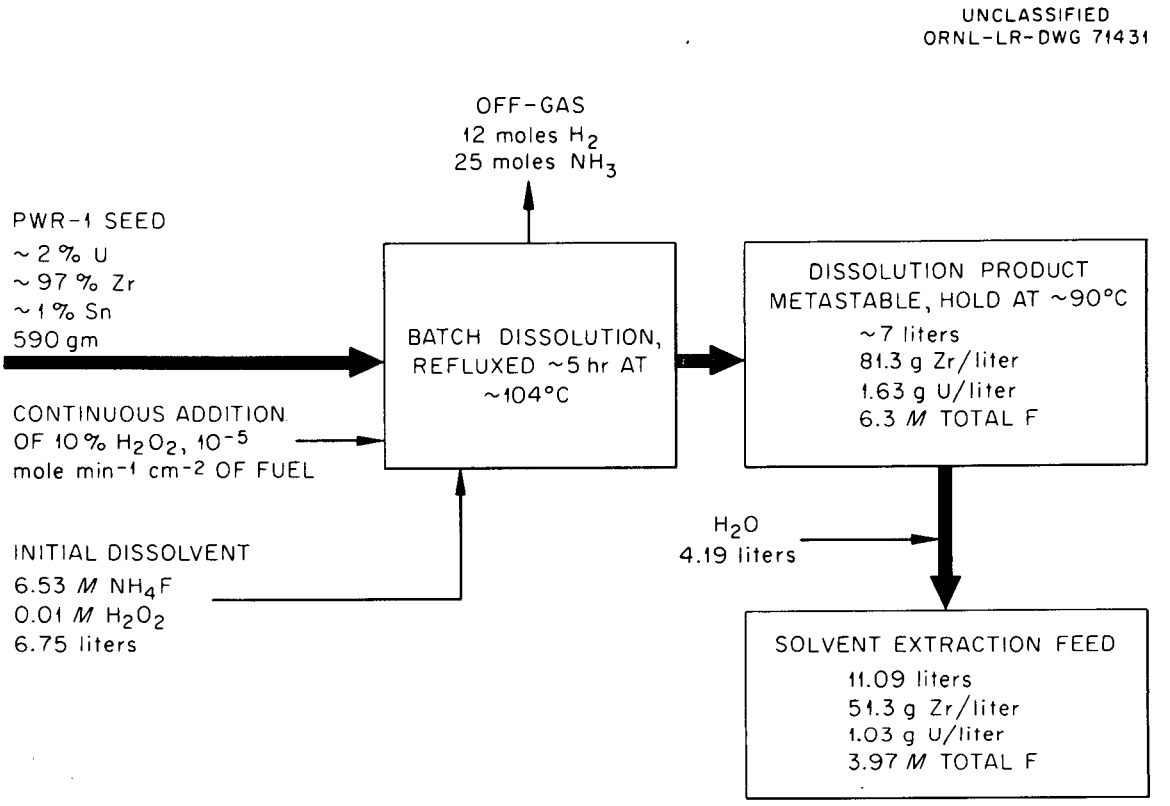

Fig. 10. The Neuflex Process: Flowsheet for Run 9.

Gaseous products evolved during Neuflex dissolution consisted of 4 moles of NH_3, 2 moles of hydrogen and traces of oxygen per mole of zirconium dissolved (no NH_4NO_3 in dissolvent). The NH_3 was removed quantitatively by scrubbing with dilute HNO_3 in a packed tower. The remaining mixture of hydrogen and oxygen was hydrogen-rich, generally above the limit of flammability for H_2-O_2 mixtures. The greater, stoichiometric evolution of hydrogen provided a convenient method of following dissolution progress and suggested that monitoring of the oxygen concentration in the hydrogen-rich scrubbed off-gas might be used to control the continuous H_2O_2 addition throughout the dissolution cycle.

Run CZr-5 was made in the engineering-scale equipment using dissolvent initially 6.53 M in NH_4F, 0.01 M in NH_4NO_3, and 0.01 M in H_2O_2 and an H_2O_2 addition rate of 0.5×10^{-5} mole cm^{-2} min^{-1} (Table 8). The 1.103 kg of unoxidized 8% U-Zr plate (0.122 in. thick) was completely dissolved in 2 hr of refluxing. At the end of the run about 4 g of a green precipitate which contained 56% U, 25% F and 3% Zr was removed from the bottom of the dissolver. It is assumed that this is the same material involved in the coat formation reported by Gens (ORNL-2905), since the free-fluoride-to-uranium ratio in the solution was only 51. The amounts of gaseous reaction products evolved agreed very well with the assumed stoichiometry of the dissolution reaction, with 2.0 moles of hydrogen and 4.2 moles of NH_3 observed per mole of zirconium dissolved. Four samples of the scrubbed off-gas taken at intervals throughout the run show $H_2 \geqq 93\%$ with $H_2 + H_2O \cong 99\%$ and $O_2 \leqq 0.15\%$. The average boil-up rate (obtained by measuring the reflux to the dissolver) was 0.15 ml min^{-1} cm^{-2} of initial fuel surface. The addition of stabilizer [1.8 M HNO_3 - 1.8 M $Al(NO_3)_3$] at room temperature

when the dissolution product had cooled to about 90°C produced a stable solvent extraction feed containing 0.35 M Zr, 2.78 g of uranium per liter, 2.7 M F^-, 1 M HNO_3 and 1 M $Al(NO_3)_3$. Material balances for zirconium, uranium and fluoride accounted for 93.5 to 95.5% of the total amount of each element charged.

Runs CZr-7 and 8 were made in the engineering-scale equipment dissolving 8% U-Zr plate (0.122-in. thick) in refluxing dissolvent initially 6.53 M NH_4F - 0.15 M NH_4NO_3 - 0.01 M H_2O_2 with a continuous H_2O_2 addition at an average rate of 1 to 2 x 10^{-5} mole cm^{-2} min^{-1}. In these runs and CZr-9 the H_2O_2 was introduced into the bulk of the boiling dissolvent through a water-cooled nozzle. This eliminated the gassing which had been observed at the H_2O_2 inlet. At the end of run CZr-7 about 2.5 g of an apparently crystalline, green precipitate was collected which contained 60% U, 23% F and 6.4% Zr. Near the end of the run this material formed on the surface of the U-Zr alloy and then dropped to the bottom of the dissolver; it is assumed to be the same material involved in the coat formation report by Gens (ORNL-2905). After dilution of the dissolution product and standing for 24 hr, a fine, white precipitate settled; this material (1.7224 g) contained 3.6% U (probably imparted by fines of the green material above) which represented a uranium loss of 0.15%. This solid (assumed to be a hydrated oxide of zirconium) was removed by centrifugation and should present no problem unless uranium loss (through adsorption on the solid) is significant. These materials had been produced in previous dissolutions but were not collected from the solvent extraction feeds because both dissolved upon the addition of the 1.8 M HNO_3 - 1.8 M $Al(NO_3)_3$ stabilizing solution. In run CZr-8, 9% more fluoride was charged (calculated terminal

free-F:U ratio = 81 compared with 60 for run CZr-7), and total dissolution was achieved in a shorter time (other conditions comparable) with only a trace of the green precipitate observed. Although different amounts of F^- were charged, equal terminal free-F:U ratios of 82 were calculated from analytical results; however, a lower free F^- would have been calculated in run CZr-7 had the zirconium balance been normal (about 95%) rather than the 86.5% reported. Probably a calculated free-F:U ratio of 90 to 100 should be used to ensure rapid dissolution and prevent coat and precipitate formation.

Run CZr-9 was made by dissolving PWR seed plate (about 2% U-Zr-Sn) in 6.53 M NH_4F - 0.01 M H_2O_2. The amount of F^- charged was calculated to yield a terminal F:Zr ratio of about 6.8; this is about the lowest ratio which will yield a reasonable dissolution time. In this run about 2.6 g of a green-black precipitate was formed although the free-F:U ratio was = 115. Here a higher F:U ratio resulted from a much lower free F^- concentration since the uranium was lower by a factor of 4. This suggests that not only must a free-F:U ratio of 90 to 100 be maintained (controlling for high uranium fuels) but also that the free F^- molarity of the dissolvent must not drop below about 1 M (limiting for low uranium fuels) if total dissolution without precipitation is to be accomplished.

A significant finding from the point of view of plant operation was the observation of the behavior of the O_2 concentration in the HNO_3-scrubbed off-gas when dissolving with low nitrate concentration. The concentration of this component is plotted as a function of refluxing time for runs CZr-8 and 9 in Fig. 11. Since the oxygen concentration in the system was reduced initially to less than 0.1% by nitrogen purging, the initial peak

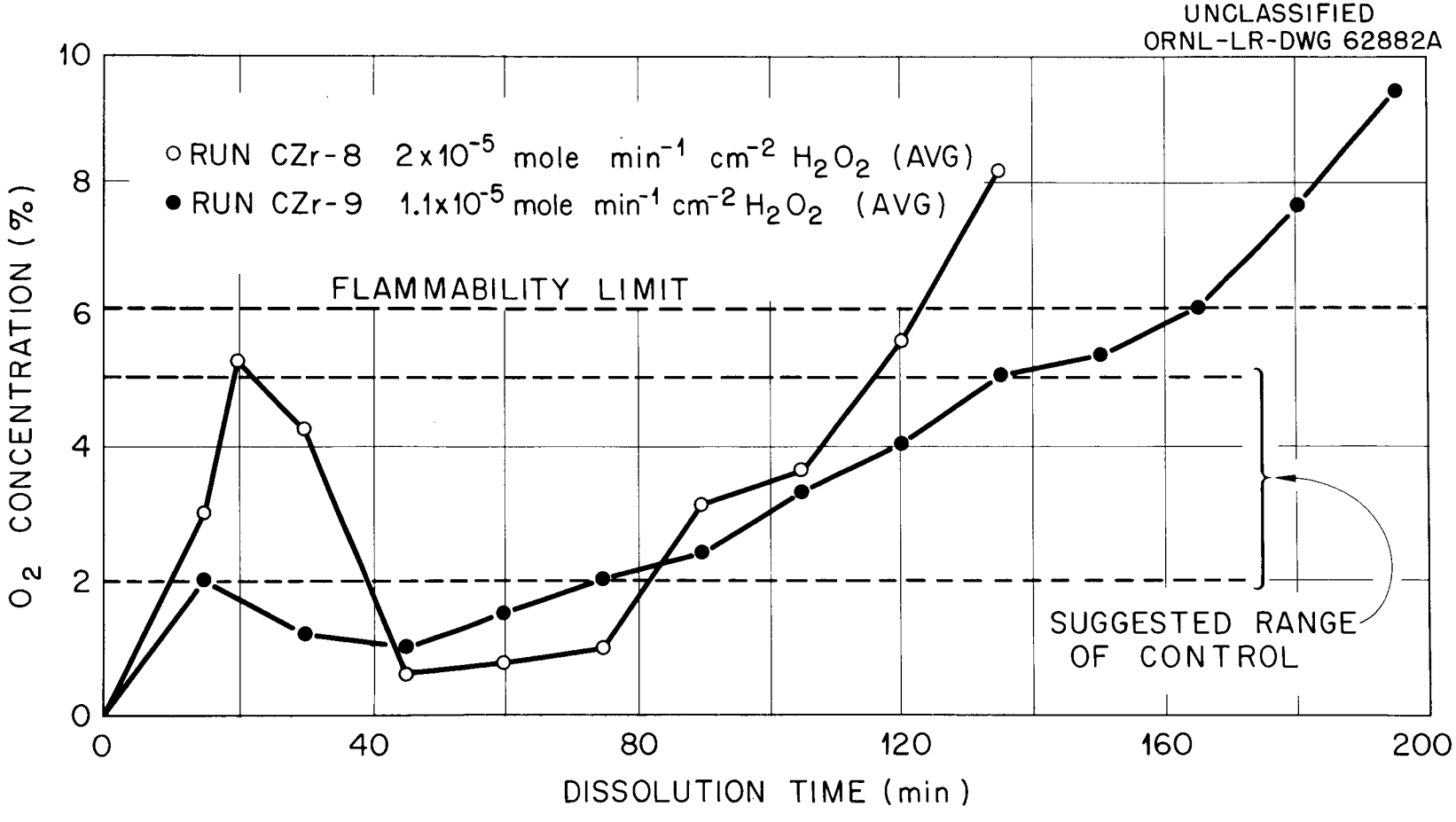

Fig. 11. Oxygen Concentration in Scrubbed Off-Gas as a Function of Refluxing Time.

probably is attributable to the decomposition of the 0.01 M H_2O_2 in the dissolvent and was more pronounced in run CZr-8 where the dissolvent contained 0.15 M NH_4NO_3 which depressed hydrogen evolution during the early portion of the run. The concentration remained low during the period of rapid dissolution and then rose steadily as decomposition became the major mode of H_2O_2 destruction. This suggests that the continuous H_2O_2 addition rate could be controlled to maintain the oxygen concentration in the off-gas at about $3 \pm 2\%$. The presence of more than 1% oxygen in the off-gas indicated an H_2O_2 addition rate high enough to maintain uranium as U(VI) in the dissolvent. While a reasonable excess of H_2O_2 is not detrimental to dissolution, limiting the oxygen in the off-gas to less than 5% avoids the flammable range for H_2-O_2 mixtures. (The lower limit for oxygen in hydrogen is 6%.)

From this cursory investigation it was concluded that this process of NH_4F-H_2O_2 dissolution followed by H_2O stabilization and special-reagent solvent extraction shows sufficient promise and versatility to warrant further investigation to the point of fully characterizing the process with respect to dissolution rates, off-gas and process control, corrosion rates (both in dissolution and waste storage), solution stability, solvent extraction, and ultimate waste disposal.

5. STAINLESS STEELS AND NICKEL ALLOYS SUITABLE FOR DISSOLUTION AND EXTRACTION EQUIPMENT

Corrosion tests at 50°C were made with candidate materials and proposed solvent extraction feed solutions containing various amounts of acid and aluminum ions added to the dissolver solution. All solutions were prepared by adding appropriate amounts of HNO_3-$Al(NO_3)_3$ to portions of the

dissolution product of run CZr-4 made in the 6-in.-diam dissolver. Four alloys were tested for 336 hr in these solutions, and the results are shown in Table 9. From the tabulated corrosion rates the following general statements can be made: (1) in similar solutions doubling the acid concentration more than doubled the corrosion rate of all materials, and (2) little, if any, additional inhibition was observed by the addition of more than 0.80 M Al^{3+} to similar solutions. The specimens of type 304L stainless steel experienced grain-boundary attack along with some etching in localized areas, while the appearance of the type 347 stainless steel specimens was like that produced by a light pickle. The specimens of low-carbon nickel alloy (LCNA) appeared to have been etched locally, while the Carpenter 20SCb specimens suffered some intergranular attack in the heat-affected zone of the welds, especially in the high-acid solutions.

Corrosion tests with types 304L and 347 stainless steel were continued to 700 hr in two proposed solvent extraction feed solutions at 50°C to determine whether the observed cumulative corrosion rates continued to decrease with increased exposure time. A continued decrease was noted (Table 9). From a plot of weight loss versus time, it was observed that after about 320 hr in test, the corrosion of type 304L stainless steel proceeded at a linear rate of about 0.1 to 0.2 mil/month, regardless of test solution or specimen position. This also appeared to be the case with type 347 stainless steel except that the rate was about 0.11 mil/month. It should be pointed out that these tests were conducted in the same solutions for the entire test period and therefore the observed corrosion rates could represent a loss of a given constituent from the solutions by the corrosion reaction. The specimens of type 304L stainless steel experienced

Table 9. Corrosion Rates[a] of Proposed Materials of Construction in Modified Zirflex Solvent Extraction Feed Solutions at 50°C

Solution Composition (M)				Test Period	LCNA[b] Corrosion Rate (mil/month)			347 Stainless Steel Corrosion Rate (mil/month)			Carpenter 20SCb Corrosion Rate (mil/month)			304L Stainless Steel Corrosion Rate (mil/month)		
HNO_3	Al	Zr	F	(hr)	V	I	S	V	I	S	V	I	S	V	I	S
0.75	0.6	0.49	3.33	168	0.08	0.12	0.20	0.09	0.19	0.22	0.10	0.27	0.28	0.10	0.67	1.26
				336	0.08	0.10	0.15	0.07	0.13	0.16	0.10	0.25	0.26	0.07	0.43	0.74
				504				0.06	0.10	0.13				0.09	0.31	0.50
				700				0.07	0.09	0.10				0.09	0.24	0.38
0.75	0.6	0.40	2.72	168	0.03	0.09	0.15	0.06	0.11	0.18	0.03	0.15	0.23	0.06	0.19	0.49
				336	0.04	0.08	0.11	0.06	0.07	0.12	0.05	0.13	0.21	0.05	0.12	0.30
0.75	0.8	0.49	3.33	168	0.04	0.09	0.10	0.05	0.10	0.19	0.04	0.17	0.20	0.04	0.10	0.24
				336	0.05	0.09	0.10	0.05	0.06	0.10	0.05	0.15	0.18	0.04	0.06	0.13
0.75	0.8	0.40	2.72	168	0.05	0.08	0.09	0.02	0.10	0.12	0.05	0.15	0.16	0.03	0.08	0.11
				336	0.03	0.07	0.09	0.02	0.05	0.07	0.04	0.12	0.15	0.03	0.05	0.06
0.75	1.0	0.40	2.72	168	0.04	0.06	0.12	0.04	0.07	0.11	0.05	0.11	0.12	0.04	0.06	0.07
				336	0.03	0.05	0.09	0.03	0.04	0.05	0.05	0.09	0.09	0.03	0.03	0.02
0.75	1.0	0.36	2.44	168	0.03	0.05	0.04	0.03	0.06	0.08	0.04	0.08	0.11	0.05	0.04	0.06
				336	0.02	0.04	0.04	0.03	0.04	0.06	0.04	0.05	0.08	0.03	0.03	0.03
1.5	0.6	0.45	3.04	168	0.17	0.25	0.35	0.17	0.24	0.36	0.25	0.39	0.46	0.19	0.83	2.12
				336	0.18	0.22	0.25	0.17	0.23	0.26	0.21	0.27	0.31	0.14	0.55	1.27
1.5	0.6	0.36	2.44	168	0.13	0.16	0.22	0.12	0.18	0.36	-	0.27	0.55	0.14	0.21	1.21
				336	0.11	0.13	0.17	0.11	0.15	0.24	0.02	0.20	0.56	0.11	0.15	0.82
				504				0.12	0.13	0.19				0.11	0.14	0.61
				700				0.12	0.13	0.19				0.11	0.12	0.49
1.5	0.8	0.45	3.04	168	0.20	0.16	0.19	0.15	0.20	0.32	0.19	0.31	0.49	0.14	0.17	0.21
				336	0.17	0.14	0.15	0.15	0.17	0.22	0.18	0.28	0.46	0.14	0.14	0.19
1.5	0.8	0.36	2.44	168	0.08	0.10	0.15	0.05	0.13	0.22	0.09	0.16	0.31	0.09	0.13	0.15
				336	0.08	0.09	0.12	0.07	0.11	0.14	0.09	0.14	0.27	0.09	0.11	0.13
1.5	1.0	0.36	2.44	168	0.05	0.11	0.15	0.07	0.13	0.23	0.07	0.16	0.25	0.06	0.09	0.15
				336	0.05	0.10	0.12	0.06	0.10	0.15	0.08	0.14	0.22	0.07	0.08	0.11

[a] The cumulative time in test was used to calculate all corrosion rates.

[b] A low-carbon nickel alloy.

grain-boundary attack along with etching in localized areas, whereas the type 347 stainless steel specimens were attacked preferentially only in the heat-affected zone near welds.

Either type 347 stainless steel or the LCNA could be used to contain any of the test solutions. The solution containing 0.75 M HNO_3, 1.0 M Al^{3+}, 0.36 M Zr^{4+} and 2.44 M F^- was the least aggressive of any solution tested, regardless of material.

Table 10 shows the corrosion of four candidate materials (welded specimens) suspended in the 6-in.-diam dissolver during the dissolutions described in Secs. 3 and 4. After about 40 hr of exposure during dissolver operation the vapor phase rates for all four materials had leveled out between 0.3 and 0.6 mil/month. The solution rates were more erratic, but the maximum average rate was 1.2 mil/month except for Hastelloy F, which had rates of 1.8 and 2.5 mil/month. Here the higher rate was decreasing and the lower rate was increasing with exposure time; possibly both specimens were approaching a steady rate slightly above 2 mil/month. Apparently any of the alloys tested would be satisfactory for the fabrication of Modified Zirflex-Neuflex processing equipment.

6. CONCLUSIONS AND RECOMMENDATIONS

The feasibility of dissolving 1-8% U-Zr in NH_4F-NH_4NO_3-H_2O_2 systems was shown in engineering-scale equipment processing up to 2 kg batches of prototype fuel.

Solutions consisting of NH_4F (5.4 to 6.6 M), NH_4NO_3 (0 to 0.7 M), and H_2O_2 (initially 0.01 M) dissolved 1/8-in.-thick sections of U-Zr-Sn alloy in 4 hr or less with a continuous addition of H_2O_2 at about 10^{-5} mole per minute per square centimeter of initial fuel surface. The H_2O_2 addition

Table 10. Corrosion of Specimens in 6-in.-diam Dissolver

Alloy	Location	Corrosion Rate (mil/month) 14 hr 4 cycles[a]	28 hr 6 cycles	39-1/2 hr 9 cycles
309SCb	Vapor	0.269	0.397	0.422
		0.497	0.448	0.469
	Liquid	1.027	0.697	0.499
		0.453	1.094	0.819
304L SS	Vapor	0.466	0.550	0.536
		0.507	0.547	0.605
	Liquid	0.875	1.247	1.292
		0.966	1.094	1.041
Hastelloy F	Vapor	0.014	0.300	0.314
		0.036	0.336	0.354
	Liquid	0.922	1.297	1.789
		4.855	2.755	2.518
LCNA	Vapor	0.237	0.265	0.287
		0.118	0.193	0.359
	Liquid	0.381	0.738	1.559
		0.433	0.652	0.687

[a]A cycle consisted of essentially complete dissolution of U-Zr-Sn simulated fuels in NH_4F-NH_4NO_3-H_2O_2 at reflux, with free fluoride depleted from about 6.5 M to about 1 M, followed by about 5 min of exposure to the product solution after the addition of about an equal volume of a solution consisting of 1.8 M HNO_3 and 1.8 M $Al(NO_3)_3$.

rate was not critical so long as an excess was maintained. The dissolution of 8% U-ZrH fuel-moderator for the TRIGA reactor was not noticeably different from that of 8% U-Zr alloy.

The initiation of dissolution depended on the degree of oxidation of the metal surface. A clean surface reacted immediately, and the total dissolution time after initiation depended on the section thickness and the F:Zr charge ratio. Attack is uniform and this creates a foreseeable problem in the total dissolution of thick unfueled sections of fuel assemblies. This material does not dissolve as rapidly as fuel alloy and will remain after the free fluoride concentration of the dissolvent has been depleted in dissolving the thinner, more reactive fuel sections.

The rate of dissolution at any time depends on the instantaneous free fluoride concentration. Higher F:Zr charge ratios result in higher instantaneous free fluoride, higher rates and shorter dissolution times, but also produce higher terminal free fluoride concentrations. Zirconium solubility is inversely proportional to free fluoride concentration; so, loading must be sacrificed to achieve high rates. In dissolving low uranium alloy ($\leq$ 3% uranium) the F:Zr charge ratio is the governing factor; this may be set as low as compatible with the time allowable for dissolution (about 7 is probably the practical minimum). As the uranium content of the fuel increases, another factor, the free fluoride to uranium ratio, becomes important if stable solutions are to be produced. This ratio, upon completion of dissolution, must be about 100, and, with fuels containing > 3% uranium, this necessitates a F:Zr ratio of greater than 7 and thus the free F:U ratio becomes controlling. This ratio, calculated as (total F-6Zr)/U, is very dependent on analytical determinations. Scatter in the free F:U

ratios added to the difficulty of studying the solution stability of an already complicated system.

Since there were some discrepancies between small-scale and engineering-scale work, especially in the prevention of precipitate formation near the end of the dissolution cycle, it is advised that some further investigation be made prior to attempted scale-up of the batch process to plant operation.

The off-gas from the NH_4F-excess NH_4NO_3 dissolution is 5 moles of NH_3/mole Zr dissolved with small amounts of hydrogen, oxygen, and nitrogen. With no NH_4NO_3 present the reaction produces 4 moles of NH_3 and 2 moles of hydrogen with traces of oxygen. Scrubbing of the former mixture produced a flammable mixture of H_2-O_2, but its relative volume was quite small so that dilution with air to a safe concentration should be straightforward. With no NH_4NO_3, the scrubbed off-gas is on the hydrogen-rich side of the flammable range of H_2-O_2 mixtures.

Metastable solutions approaching 1 M zirconium are produced at the end of dissolution, but these must be diluted before cooling in order to avoid precipitation. Dilution with 1.8 M $Al(NO_3)_3$ - 1.8 M HNO_3 stabilizer solution produced stable feeds suitable for conventional TBP extraction; solutions diluted with H_2O yielded neutral fluoride systems amenable to uranium separation with Dapex reagents. The role of NH_4OH in these near neutral systems should be investigated further since some of the solutions were cloudy and would with time settle a fine white precipitate.

Experiments with continuous dissolution of multiplate Zircaloy-2 assemblies with NH_4F-NH_4NO_3-H_2O_2 showed that dissolution rates above approximately 6 mg cm^{-2} min^{-1} would not be achieved while maintaining dissolvent loadings of about 0.8 M zirconium. The differential in dissolution rate

between zircaloy and fuel alloy mentioned above should be even more important in continuous dissolution than in batch dissolution. As the fuel alloy disappears leaving the structural zircaloy, the area will change making it impossible to maintain the desired loading at a fixed dissolvent flow rate. Also the overall dimensions of these "skeletons" will be very near the original dimensions thus making introduction of additional fuel into the dissolver difficult if not impossible.

Common construction materials such as several stainless steels (types 347, 309SCb, and Carpenter 20SCb) and LCNA (a low-carbon nickel alloy similar to Ni-O-Nel) were suitable construction materials for both dissolution and solvent extraction equipment.

7. REFERENCES

1. J. L. Swanson, "The Zirflex Process," P/2429, Proc. 2nd Internatl. Conf. Peaceful Uses Atomic Energy, Geneva, 1958, Vol. 17, UN, New York, p. 155.
2. T. A. Gens, Modified Zirflex Process for Dissolution of 1-10% U-Zr Alloy Fuels in Aqueous NH_4F-NH_4NO_3-H_2O_2: Laboratory Development, ORNL-2905 (Mar. 4, 1960).
3. P. W. Smith, The Zirflex Process: Terminal Development Report, HW-65969 (Aug. 20, 1960).
4. J. R. Bower, Jr., Idaho Chemical Processing Plant Technical Progress Report, October through December 1959, IDO-14512 (June 20, 1960) and other quarterly reports.
5. Chemical Technology Division Annual Progress Report for Period Ending June 30, 1962, ORNL-3314, pp. 10-15.
6. D. E. Horner, C. F. Coleman, Recovery of Uranium and Plutonium from Sulfuric Acid Decladding Solutions, ORNL-2830 (November 1959).

8. APPENDIX

A. BATCH STUDIES IN SMALL EQUIPMENT PRELIMINARY TO LARGE-SCALE OPERATION

In preparation for runs in the engineering-scale dissolution equipment 23 laboratory runs were made in the 1-in.-diam recirculating batch dissolver shown in Fig. A.1. Dissolvents used were 5.4 to 6.8 M NH_4F with H_2O_2 (as 3 and 4.5% solutions), added at rates of 3×10^{-6} to 2.5×10^{-5} mole min^{-1} g^{-1} of U-Zr-Sn charged. In all runs the solution darkened, indicating the presence of elemental tin, but cleared as oxidation progressed. At no time was precipitation of UF_4 observed. Based on the laboratory runs, the following conclusions concerning operation of the engineering-scale equipment were reached:

1. The dissolvent should contain 6 to 6.5 M NH_4F, 0.3 to 0.5 M NH_4NO_3, and about 0.01 M H_2O_2.
2. A continuous addition of H_2O_2 at about 0.5×10^{-5} mole min^{-1} cm^{-2} of U-Zr-Sn charged should be maintained throughout dissolution.
3. A single stabilizing solution containing approximately equal amounts of HNO_3 and $Al(NO_3)_3$ (1.7 to 2 M) can be added to the dissolution product to produce a stable solvent extraction feed.
4. The temperature of the dissolution product should be about 90°C when the stabilizing solution (room temperature) is added.
5. The presence of H_2O_2 is not a major factor in feed stability.

Initially it was feared that aluminum might precipitate if a HNO_3 - $Al(NO_3)_3$ solution were added to the neutral dissolver solution. In early tests (runs 1 and 3, Table A.1) the dissolver solution was acidified by using 15.8 M HNO_3 before the HNO_3 - $Al(NO_3)_3$ mixture was added. In both

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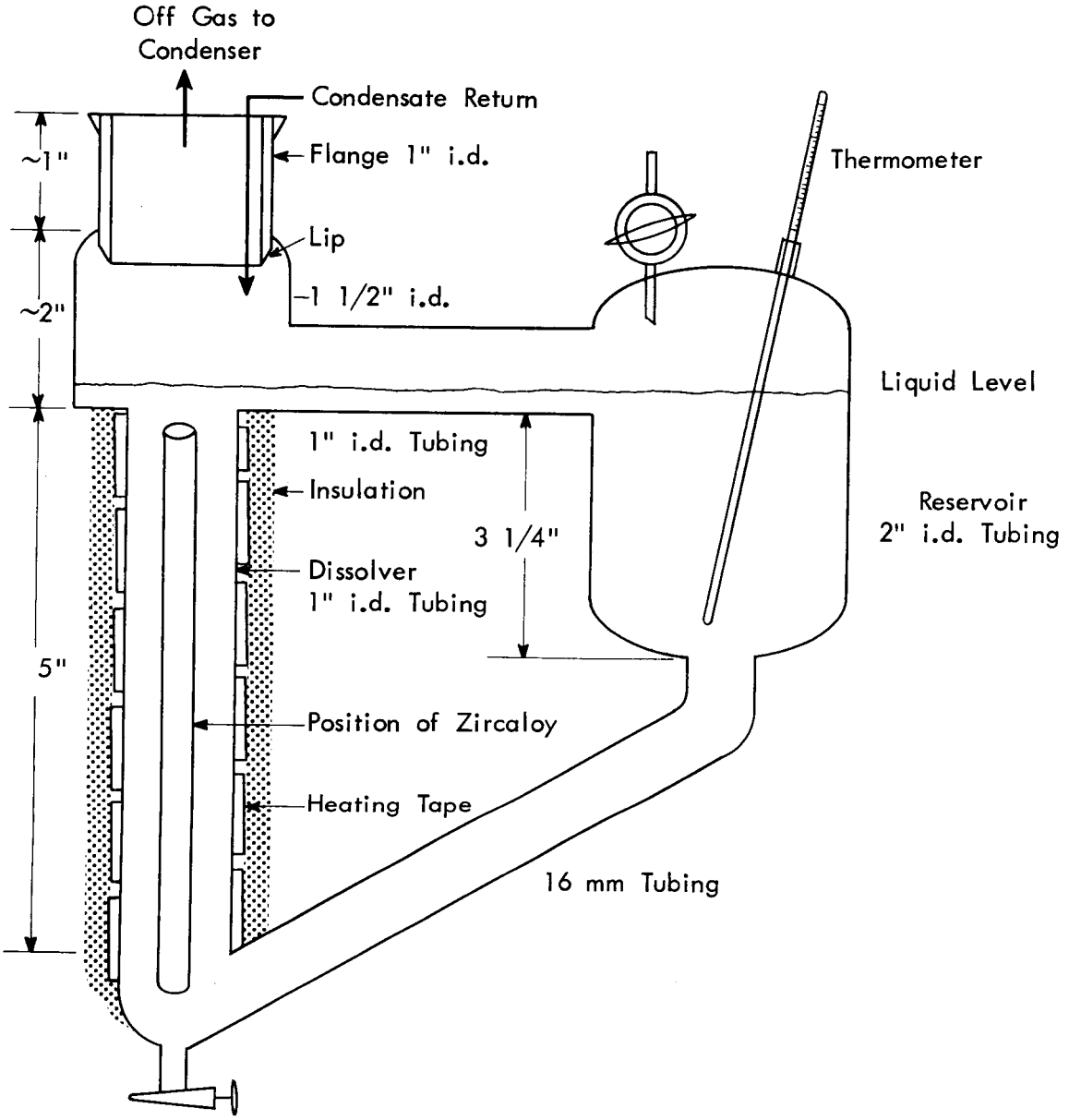

Fig. A.1. Zirflex Recirculating Batch Dissolver.

Table A.1. U-Zr-Sn Dissolution in NH_4-NH_4NO_3-H_2O_2 in 1-in. Recirculating Batch Dissolver

Run No.	Dissolvent				U-Zr-Sn Fuel Specimens					Addition Rate, H_2O_2 (moles/cm^2-min)	Diss. Time (min)	Stabilizer		
	Vol (cc)	NH_4F (M)	NH_4NO_3 (M)	H_2O_2 (M)	Type	Wt (g)	Diss. (%)	Area (cm^2)	Thick. (in.)			Vol (cc)	HNO_3 (M)	$Al(NO_3)$ (M)
MZr-1	315	5.4	0.45		U-Zr	23.736	93.9	~ 56	0.08	1×10^{-5}	128	265[a]	1.5	2.4
MZr-2	315	5.4	0.45		U-Zr	23.718	98.4	~ 56	0.08	0.4×10^{-5}	131	305	2.1	2.1
MZr-3	315	5.4	0.45		U-Zr	23.896	98.2	~ 56	0.08	0.5×10^{-5}	120	307[c]	2.6	2.1
MZr-4	315	5.4	0.45		U-Zr	23.910	98.0	~ 56	0.08	0.4×10^{-5}	120	305	2.1	2.1
MZr-5	315	5.4	0.45		U-Zr	24.06	96.8	~ 56	0.08	0.3×10^{-5}	138	305	2.1	2.1
MZr-6	315	5.4	0.45		U-Zr	24.72	85.9	~ 56	0.08	[d]	206	305	2.1	2.1
MZr-7	270	6.05	0.33	0.01	U-Zr-Sn	22.846	99.9			~ 1×10^{-5}	124	330	1.8	1.8
MZr-8	292	6.05	0.33	0.01	PWR-1 seed	24.703	98.9	~ 35	0.08	0.33×10^{-5}	180	357	1.8	1.8
MZr-9	270	6.05	0.33	0.01	PWR-1 seed	23.798	99.4	~ 35	0.08	0.36×10^{-5}	240	330	1.8	1.8
MZr-10	270	6.36	0.50	0.01	PWR-1 seed	24.206	98.5	~ 35	0.08	0.56×10^{-5}	240	350	1.8	1.8
MZr-11	220	6.6	0.32	0.01	TRIGA	17.158	100	~ 12	~ 0.2	0.6×10^{-5}	150	260	1.8	1.8
MZr-12	280	6.6	0.32	0.01	TRIGA	27.512	94.1	~ 15	~ 0.3	0.6×10^{-5}	210	330	1.8	1.8
MZr-13	260	6.54	0	0.01	PWR-1 seed	23.973	95.1	~ 40	0.08	0.4×10^{-5}	240	350	1.8	1.8
MZr-14	290	6.5	0	0.01	TRIGA	27.063	94.6	~ 40		0.5×10^{-5}	195	360	1.8	1.8
MZr-15	285	6.65	0.67	0.01	PWR-1 seed	26.764	96.3	~ 40	0.08	0.5×10^{-5}	180	350	1.8	1.8
MZr-16	316	6.79	0	0.01	8% U-Zr	27.136	100	~ 30	0.12	0.6×10^{-5}	222	277[i]	0	0
MZr-17	254	6.53	0	0.01	8% U-Zr	20.999	100	23	0.12	1.3×10^{-5}	114[k]	155	1.8	1.8
												200	0	0
MZr-18	241	6.53	0	0.01	8% U-Zr	20.323	100	23	0.12	1.1×10^{-5}	120	145	0	0
												108	0	0
MZr-19	245	6.58	0	0.01	TRIGA	20.938	100	14	0.5	1.1×10^{-5}	225	96	1.8	1.8
												150	1.8	1.8
MZr-20	243	6.58	0	0.01	8% U-Zr	20.796	100	23	0.12	0.9×10^{-5}	144	87	0	0
												94	0	0
MZr-21	248	6.58	0	0.01	8% U-Zr	20.803	100	23	0.12	2.5×10^{-5}	216	200	0	0
MZr-22	242	6.58	0	0.01	8% U-Zr	18.178	100	20	0.12	2.0×10^{-5}	84	267	0	0
MZr-23	287	6.58	0	0.01	PWR-1 seed	25.380	100	46	0.08	0.8×10^{-5}	252	160	0	0

Table A.1. Continued

Run No.	Solvent Extraction Feed: Vol (cc)	Zr (M)	U (g/liter)	F (M)	H^+ (M)	Al (M)	Free F^- (M)	F^-/U	Material Balances: Zr (%)	U (%)	F (%)	Remarks
MZr-1	628	0.39	0.32	2.58	0.91	1.01	0.3	[b]	101[e]		95.6	Gel in SX feed
MZr-2	630	0.40	0.43	2.54	0.98	1.02	0.3		100[e]		94.1	Stable SX feed
MZr-3	628	0.40[h]	0.4	2.7	1.0	1.0	0.3					Gel in SX feed
MZr-4	630	0.40	0.4	2.7	1.0	1.0	0.3					Stable SX feed
MZr-5	630	0.40	0.4	2.7	1.0	1.0	0.3					Stable SX feed
MZr-6	570	0.40	0.4	3.0	1.1	1.1	0.6					Stable SX feed
MZr-7	593	0.40	0.96	2.66	1.0	1.0	0.3		99.9	94.9	96.6	Stable SX feed
MZr-8	663	0.39	0.86	2.65	1.0	1.0	0.3		98.5[e]		99.5	Stable SX feed
MZr-9	595	0.41	0.99	2.65	1.0	1.0	0.3		98.3[e]		96.5	Stable SX feed
MZr-10	630	0.39	1.44	2.7	1.0	1.0	0.3		98.4[e]		101	Stable SX feed
MZr-11	473	0.37	2.6	2.94	1.0	1.0	0.75	68	101[g]	90[g]	95.8	Stable SX feed
MZr-12	602	0.42	2.47[f]	2.93	1.0	1.0	0.41	40	97.8	71.5	95.4	Green ppt in SX feed
MZr-13	627	0.36	0.94	2.24	1.0	1.0	0.1		95.2[e]		82.7	Gel in SX feed
MZr-14	660	0.38	2.72	2.69	1.0	1.0	0.42	37	97.7	87.6	95.0	Stable SX feed
MZr-15	645	0.42	0.95	2.83	1.0	1.0	0.33		99.0[e]		96.3	Stable SX feed
MZr-16	608	0.39	2.12	3.10	0	0	0.77	86[j]	86.5	59.4	87.9	Green and white ppts
MZr-17	266	0.37	2.92	2.98	1.0	1.0	0.75	61	95.2	94.8	97.5	Stable solution
	323	0.32	2.53	2.54	0	0	0.63	59				Stable solution
MZr-18	263	0.38	3.01	2.85	0	0	0.56	44	97.9	97.9	94.9	Stable solution
	226	0.44	3.54	3.28	0	0	0.62	42				Stable solution
MZr-19	216	0.46	3.44	3.53	0.8	0.8	0.78	54	94.5	88.8	91.9	Stable solution
	265	0.37	2.76	2.66	1.0	1.0	0.46	40				Stable solution
MZr-20	208	0.46	3.12	3.81	0	0	1.05	80	92.1[l]	85.5	100	Some precipitation
	215	0.45	3.6	3.76	0	0	1.05	70				Stable solution
MZr-21	440	0.45	3.58	3.65	0	0	0.97	65	93.8	94.7	98.4	Small amt. green ppt
MZr-22	500	0.37	2.81	3.13	0	0	0.93	79	99.9[e]	96.6	98.1	Stable solution
MZr-23	456	0.58	1.71	4.13	0	0	0.64		99.9[e]		99.5	Stable solution

[a] Added 15 ml 15.8 M HNO_3 to dissolver prior to draining into stabilizer.

[b] F/U listed only when limiting.

[c] Added 10 ml 15.8 M HNO_3 as in (a).

[d] Added 3 ml 3% H_2O_2 batchwise after 150 min of dissolution.

[e] Total metals; exact % U not known initially.

[f] Also a small amount of green ppt.

[g] Assuming TRIGA contains 91% Zr, 8% U.

[h] Zr and U in runs 3-6 calculated from specimen weight and solution volume

[i] H_2O.

[j] In supernate.

[k] After dissolution, the product was split and each half stabilized as indicated.

[l] Some precipitation occurred before sampling.

these runs with prior acidification (in run 1 excess H_2O_2 was present; in run 3 the solution was refluxed 1 hr to decompose excess H_2O_2) a substantial amount of a stable gel was formed upon standing for a few hours. In all other runs a clear, stable solution was produced initially. Run 2 was made with an hour of reflux after dissolution in order to decompose H_2O_2, and the dissolver product was added to the HNO_3 - $Al(NO_3)_3$ solution. A stable solution resulted, proving that the earlier method rather than the composition [0.4 M Zr, 1 M HNO_3, 1 M $Al(NO_3)_3$] had given rise to the instability. In run 4 after 1-1/2 additional hours of refluxing a portion of the dissolution product was withdrawn and cooled to 70°C; upon addition of HNO_3 - $Al(NO_3)_3$, a stable solution resulted. When HNO_3 - $Al(NO_3)_3$ solution was added to the refluxing dissolver solution a cloudy solution resulted, with a small amount of solids precipitating immediately. In run 5, stabilizing solution was added (dissolution product about 75°C) immediately after H_2O_2 addition and after 1 hr of reflux; clear solutions resulted in both instances. Run 6 was made with no H_2O_2 present except for 3 cc of 3% H_2O_2 added batchwise after dissolution was essentially complete (2-1/2 hr of refluxing). This showed that the 0.45 M NH_4NO_3 was sufficient to oxidize the small amounts of tin present.

In runs MZr-7 through 10, U-Zr-Sn material containing higher percentages of uranium and tin were dissolved. With all H_2O_2 addition rates tried, the solutions darkened initially and cleared as dissolution and H_2O_2 addition proceeded. It was not determined whether H_2O_2 could be added fast enough to maintain clear solutions. It is possible that the rate of loss of H_2O_2 through thermal decomposition is high enough to prevent the build-up of an H_2O_2 concentration high enough to oxidize the tin as fast as it is

released from the dissolving alloy. In all runs where analytical results were obtained, the material balances for total metals (uranium, zirconium, and tin) were within 1.7%.

Runs MZr-11 and 12 made with 7% U-ZrH alloy showed that dissolution could be accomplished to free fluoride to uranium (F:U) ratios of less than 70, with a probable lower limit of about 40. Run 13 showed that dissolution rates were comparable witn no NO_3^- present; more foaming was evident due to the increased hydrogen evolution. Run 14 showed that the same H_2O_2 addition rate would oxidize uranium when present in higher percentages. Run 16 showed very little difference between 8% U-Zr and 8% U-ZrH. Slightly higher dissolution rates were observed with less foaming in run 15 due to a smaller volume of hydrogen evolved.

Runs MZr-17, 18 and 19 were made to learn the effect on dissolution of a different strength (6%) and method (to the reservoir) of H_2O_2 addition. The volumetric rate was maintained (same as with 3% solution) resulting in an approximate doubling of the molar rate. No change in dissolution rate was observed, but the solutions turned yellow earlier, indicating a lower U(IV) concentration in the middle stages of dissolution. All three of the H_2O stabilized solutions were stable; the most highly loaded one contained 0.444 M Zr, 3.28 M F, and 3.54 g of U per liter. The HNO_3 - $Al(NO_3)_3$ stabilized portion of MZr-17 was a stable solution. Neither solution in MZr-19 [both HNO_3 - $Al(NO_3)_3$ stabilized] was stable for 30 days; the first portion [0.8 M HNO_3 - $Al(NO_3)_3$] contained white crystals, while the second [1.0 M HNO_3 - $Al(NO_3)_3$] contained a suspended gelatinous precipitate.

Four runs, MZr-20, 21, 22, and 23, were made in order to study solution stability and to function as pilot runs for the larger equipment. Run MZr-20 was made with a calculated free F:U = 50; a small amount of green precipitate formed near the end of the run. Crystals formed in the more concentrated solvent extraction feed after about 36 hr (before sampling), while the more dilute solution stood for about 30 days at room temperature before a small amount of crystals appeared. A small amount of precipitate again formed in the dissolution step of MZr-21 (calculated F:U = 55); however, a highly loaded, stable (no crystals after 36 days) SX feed was produced. Run MZr-22 at a calculated F:U ratio of 81 produced no green precipitate; although the SX feed shown in Table A.1 (volume = 500 ml) was stable (no crystals after 30 days), crystals formed in less than 24 hr when it was first diluted to a volume of only 475 ml. An additional 25 ml of water dissolved the crystals and produced a stable solution. Run MZr-23 was made under the same calculated terminal conditions (F:Zr ratio = 6.8) as run CZr-9 in the engineering-scale equipment, but no green precipitate formed in the small scale dissolver. The U-Zr-Sn material dissolved in the small run contained 1.6 times as much uranium as that used in the large scale run, resulting in a much lower free-F:U ratio (88 compared with 115 for the cell run) but a higher free F (F:Zr = 7.16 compared to 6.88) since less zirconium was present for F^- complexing. [The initial fluoride charge was calculated: F^- = 6.8 (total weight of U-Zr-Sn/91.22)]. This observation strengthens the hypothesis that some minimum free fluoride concentration (about 1 M in the dissolution product) must be maintained as well as free-F:U $\geqq$ 90 in order to prevent uranium precipitation during dissolution.

B. CONTINUOUS OPERATION IN SMALL EQUIPMENT

Twenty-three runs in a 2-in.-diam dissolver were made in order to determine the effect on reaction rate of F/S (feed rate/surface area) ratio, oxidant concentration, and boil-up rate in continuous dissolution. It was found that reaction rate increased with F/S, but the relationship was nonlinear (Fig. B.1) so that lower loadings (calculated from the relationship $L = \frac{R}{F/S}$) resulted at conditions which gave higher dissolution rates. Oxidant concentrations of 1.0 M NH_4NO_3 and/or 0.1 M H_2O_2 in the dissolvent gave comparable results, while rates obtained with 1.5 M NH_4NO_3 were quite erratic (Table B.1). The higher boil-up rate produced higher reaction rates (Fig. B.1).

The first rate determinations were made under static conditions, using short exposure times and dissolvents which represented continuous dissolution with three levels of loading and hence three free F^- concentrations. These results (Table B.2) were higher than those found under flowing conditions, probably due to the shorter exposure, which dissolved only a more reactive surface layer of the Zircaloy-2 specimens.

The runs reported in Table B.1 were made under reflux conditions, with dissolvent feeding into and overflowing a 2-in. Pyrex dissolver heated through its stainless steel bottom flange. A strip of Zircaloy-2 the same length and width as the specimen (about 0.9 x 9.5 x 0.068 in.) was dissolved under controlled conditions of feed rate and heat input until a steady-state operation had been achieved; the strip was removed and the weighed specimen was inserted simultaneously, and the run was continued without disturbing dissolver operation. Reproducible steady-state conditions were achieved as can be seen by comparing runs made under similar conditions

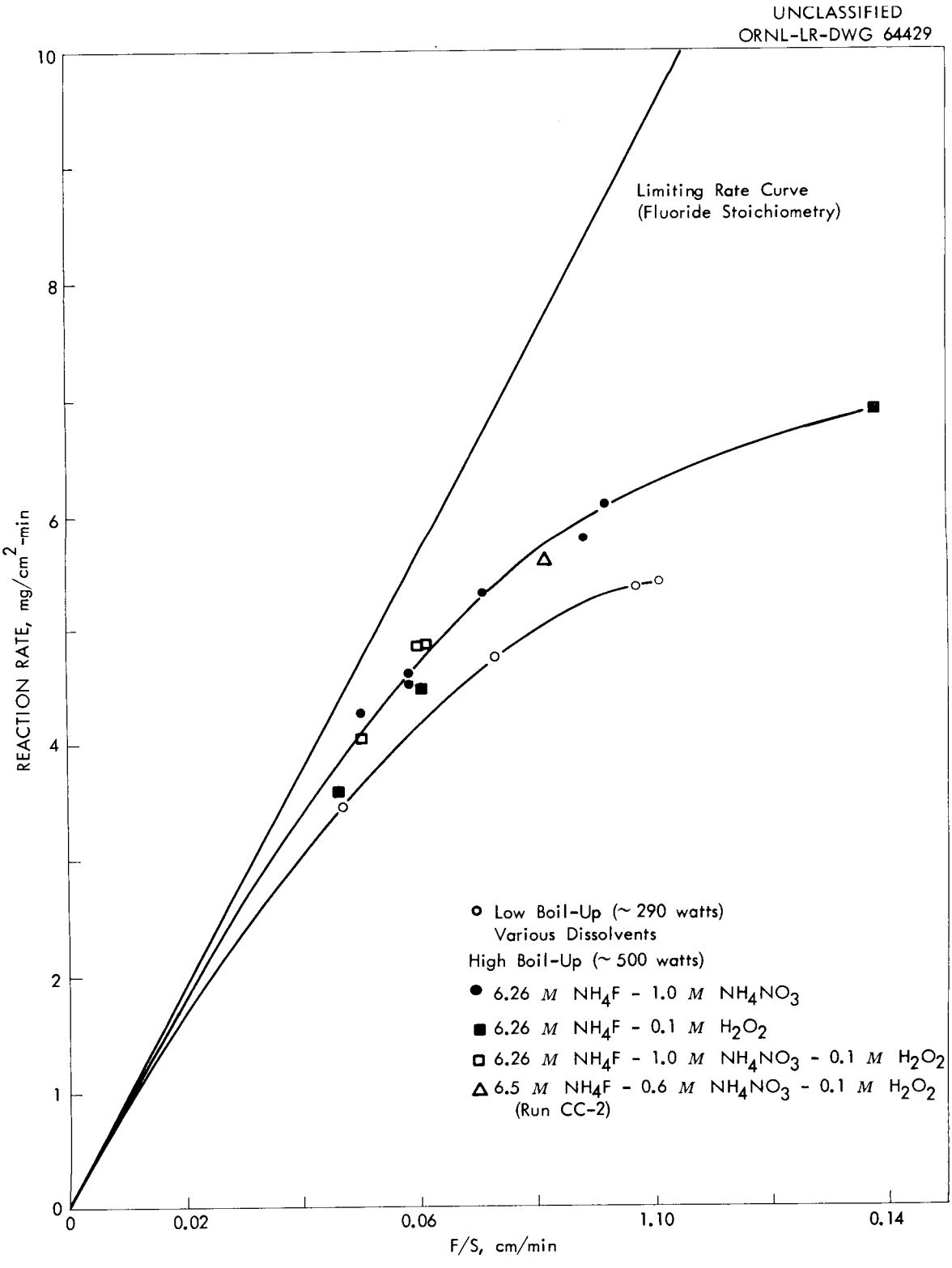

Fig. B.1. Reaction Rate as a Function of Feed Rate/Specimen Area Ratio.

Table B.1. Dissolution Rates in Continuous Processing

Run No.	Dissolvent NH_4F (M)	Dissolvent NH_4NO_3 (M)	Dissolvent H_2O_2 (M)	Feed Rate (cm^3/min)	Surface (cm^2)	F/S	Weight Loss (g)	Dissol. Time (min)	Reaction Rate (mg/cm^2-min)	Loading Zircaloy-2 (g/liter)	Loading Zr (M)	SX Feed Zr (M)
1[a]	6.5		0.01	12.0	124	0.097	22.177	33.3	5.37	55.4	0.60	0.34
2	6.0	0.6		12.2	121	0.101	21.453	32.7	5.42	53.7	0.58	0.33
3	6.0	0.6		6.0	128	0.047	14.723	33.3	3.45	73.4	0.79	0.44
4	6.26	1.0		6.33	127	0.050	17.134	31.6	4.27	85.7	0.92	0.52
5	6.26	1.0		9.43	133	0.071	22.468	31.8	5.31	74.8	0.80	0.45
6	6.26	1.0		9.26	126	0.073	19.405	32.4	4.75	64.6	0.69	0.39
7	6.26	1.0		6.65	115	0.058	15.830	30.1	4.58	79.2	0.85	0.48
8[b]	6.26	1.0		6.61	115	0.058	15.575	30.3	4.48	77.9	0.84	0.47
9	6.26	1.0		11.66	127	0.092	19.864	25.7	6.08	66.2	0.71	0.40
10	6.26	1.0		11.59	131	0.088	19.713	25.9	5.79	65.8	0.71	0.40
11	6.26		0.1	7.13	120	0.060	14.979	28.1	4.46	74.9	0.81	0.45
12	6.26		0.1	5.45	119	0.046	15.657	36.7	3.58	78.3	0.84	0.47
13	6.26		0.1	16.40	119	0.138	25.197	30.5	6.94	50.3	0.54	0.31
14	6.26	1.5		7.15	234	0.030	29.781	28.0	4.54	149[c]	1.60	0.89
15	6.26	1.5		7.02	119	0.059	23.945	28.5	7.07	120[c]	1.29	0.72
16	6.26	1.0	0.1	7.19	119	0.060	16.020	27.8	4.84	80.1	0.86	0.48
17	6.26	1.0	0.1	7.30	119	0.061	15.828	27.4	4.85	79.1	0.85	0.48
18	6.26	1.0	0.1	5.99	121	0.050	16.406	33.4	4.06	82.0	0.88	0.49
19	6.26	1.5	0.17	9.72	119	0.082	8.048	30.9	2.19	26.8	0.29	0.16
20	6.26	1.5	0.1	9.19	122	0.075	8.530	32.6	2.14	28.4	0.31	0.17
21	6.26	1.5	0.04	9.58	121	0.079	8.615	31.3	2.27	28.7	0.31	0.18
22	6.26	1.5		9.06	119	0.076	12.312	33.1	3.13	41.1	0.44	0.25
23	6.26	1.5		9.43	119	0.079	23.149	31.8	6.12	77.3	0.83	0.47

[a] Runs 1-3, and 6 were made with a heat input of about 280 w; all others were made at about 500 w.

[b] Rerun of 7 using same specimen.

[c] Steady-state conditions did not prevail because loadings are considerably above those allowed by F^- stoichiometry.

Table B.2. Instantaneous Dissolution Rates Under Static Conditions

Dissolvent		Weight Loss	Specimen Area	Exposure Time	Reaction Rate
Zr (M)	Free F^- (M)	(g)	(cm^2)	(min)	(mg cm^{-2} min^{-1})
0.75	2	0.0560	6.48	1.0	8.64
0.75	2	0.1172	6.41	2.0	9.14
0.83	1.5	0.1142	6.48	2.5	7.05
0.83	1.5	0.1119	6.39	2.5	7.00
0.92	1.0	0.1307	6.15	3.0	7.08
0.92	1.0	0.1143	6.21	3.0	6.14

such as 7 and 8, and 16 and 17 (Table B.1). Reaction rates were calculated from weight loss, exposure time, and initial area, which did not change appreciably during a run (about 10 mils uniform attack). Loading was calculated from $L = \frac{R}{F/S}$. The column in Fig. B.1 headed solvent extraction feed indicates the zirconium concentration which would result from adding 0.8 volume of stabilizer [1.8 M HNO_3 - 1.8 M $Al(NO_3)_3$] per volume of dissolver effluent.

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