HW-60597

ZIRFLEX PROCESS - INTERIM DEVELOPMENT SUMMARY

INTRODUCTION

The processing of spent fuels from nuclear power and propulsion reactors is planned by Hanford Atomic Products Operation as part of the Atomic Energy Commission's interim reprocessing scheme.

The spent nuclear fuels have cores of UO_2, U, or alloys of U-Mo, U-Al, or U-Zr clad in either stainless steel, aluminum, or Zircaloy. This report discusses only the Zircaloy-clad fuels and the application of the Zirflex Process for dissolution. Zirflex chemical flow sheets are presented as developed by pilot plant operations.

The Zirflex process is applicable to the reprocessing of fuels from the Dresden reactor and the PWR reactor. Other applications of the process are the Plutonium Recycle Test Reactor fuels and the New Production Reactor fuels (HAPO); possible fuels from the Experimental Breeder Reactor (Arco); NPD-2 fuels (Ontario) and fuels from Carolina-Virginia Nuclear Power Associates reactor.

SUMMARY

The Zirflex Process employs a boiling aqueous solution of ammonium fluoride and ammonium nitrate for the selective dissolution of zirconium or Zircaloy cladding from the power reactor fuels. Typical integrated or average dissolution rates of 7-10 mils per hour are obtained on unoxidized Zircaloy. However, zirconium oxidized by exposure to high temperature air or water dissolves by solution penetration and undercutting of the oxide film at rates three- to fivefold less than those obtained on unoxidized fuels. Thus, typical unoxidized cladding may be removed in three to four hours, whereas removal of oxidized claddings may require up to twelve hours.

During the dissolution of zirconium, hydrogen and ammonia are produced at rates of about 0.1 and 5 moles per mole of zirconium dissolved, respectively. Dilution of these gases with steam and/or air is required to avoid explosive concentrations. Also, positive operating steps, such as purge, high boil up, and high condenser temperatures are necessary to remove ammonia and to prevent the adverse effects of ammonia concentrations on either the dissolution rate or the solubility of zirconium. Under proper operating conditions, a concentration of 0.6 M zirconium solution is obtained with a starting charge of 5.5 molar NH_4F and 0.5 molar NH_4NO_3.

Zirflex decladding solutions do not severely attack unirradiated uranium, uranium-aluminum, or uranium dioxide cores. However, a small quantity of core material dissolves to produce both soluble and insoluble uranium. For instance, the solubility of uranium may vary from 0.3 to 3 grams per liter. All other dissolved uranium exists as a UF_4 precipitate. Losses to the cladding waste solution are minimized by nearly saturating the solution with zirconium; i.e., nearly complete complexing of the fluoride by zirconium,

DISCLAIMER

and by cooling the solution to decrease the uranium solubility. The precipitated uranium may be recovered by centrifugation and dissolved in a relatively noncorrosive form by the addition of nitric acid and aluminum nitrate.

Dissolution of the core remaining after the Zirflex decladding step was not studied extensively. However, since such core material is nearly free from zirconium, conventional techniques are applicable if aluminum nitrate is added to inhibit the corrosive action of residual fluoride.

The material to contain the Zirflex process can be stainless steel. For example, an over-all average corrosion rate of 4.3 mils per month was obtained in the pilot unit. A corrosion rate of 11 mils per month was obtained with 304-L stainless steel exposed to boiling six molar ammonium fluoride.

Details of the recommended flowsheet for processing typical power reactor fuels are presented in Figs. 9 and 10.

DISCUSSION

General - Zirconium dissolves in boiling ammonium fluoride solutions by the reaction:

$$Zr_{(s)} + 6\ NH_4F \longrightarrow (NH_4)_2ZrF_6 + 2\ H_{2(g)} + 4\ NH_{3(g)}$$

If ammonium nitrate is added to the system, the evolution of hydrogen is suppressed to below 0.1 mole per mole of Zircaloy dissolved. The dissolution may then be represented by the reaction:

$$Zr_{(s)} + 6\ NH_4F + 0.5\ NH_4NO_3 \longrightarrow (NH_4)_2ZrF_6 + 6\ NH_{3(g)} + 1.5\ H_2O.$$

The dissolution of unoxidized zirconium or Zircaloy is characteristic of a first order reaction with respect to "free" fluoride, i.e., fluoride uncomplexed by zirconium. Derivation of kinetic equations and calculation of the corresponding time cycles for dissolution are shown in the Appendix.

The dissolution proceeds under the best conditions at a rate of about 80 mils per hour (22 $mg/cm^2/min$) with a "free" fluoride concentration of 6 molar. Rates decrease proportionately as the "free" fluoride concentration decreases, as shown in Fig. 1. Marked decreases in dissolution rates also occur if (a) an oxide film is present on the zirconium surfaces, (b) the ammonia by-product of the dissolution reaction is allowed to accumulate in the ammonium fluoride dissolvent, or (c) the solubility of zirconium in the ammonium fluoride solution is exceeded.

Pertinent details are given in the following text on the development work leading to the recommended flowsheets in Figs. 9 and 10.

Zirconium Solubility(1)(2)

The solubility of ammonium hexafluozirconate , $(NH_4)_2ZrF_6$, at room temperature

(22C) and at boiling (100-106 C) is shown in Fig. 2 as a function of the "free" fluoride ion concentration in the presence of NH_4NO_3. The quantity of fluoride not complexed with zirconium is termed "free" fluoride. Zirconium solubility is controlled by the concentration of "free" or unreacted fluoride. Thus, low concentrations of "free" fluoride permit high zirconium concentrations. Hence, waste volumes are reduced if the final solution contains a minimum of "free" fluoride.

The solubility of zirconium abruptly decreases with temperature. Thus, to avoid zirconium precipitation, a water dilution to about 0.6 molar zirconium is normally required.

Ammonium Fluoride Concentrations

The desired concentration of ammonium fluoride for a dissolver charge is determined by balancing all of the desired operating conditions; i.e., dissolution rates, off-gas-rates, zirconium solubility, and the volume of solution required to cover the fuels.

Increasing the NH_4F concentration decreases the dissolution time by increasing the dissolution rates and the associated off-gas rates. However, the maximum concentration of NH_4F that can be used is fixed by the solubility of zirconium in the boiling solution.

In Fig. 2, the zirconium concentration and the "free" fluoride concentration throughout the dissolution are shown by the diagonal lines. These dissolution paths must avoid the vicinity of the bow in the zirconium solubility curve, since an increase in the ammonia concentration at this point causes precipitation of the zirconium. As a result, the surface of the fuel becomes coated with insoluble reaction products, and the dissolution rate is markedly reduced. Precipitation during the dissolution is avoided by starting with NH_4F concentrations of 5.5 molar or below. However, concentrations of near 5.5 molar require a water dilution at the end of the dissolution to prevent precipitation of the zirconium. Concentrations below 4 molar may be concentrated up to 4 molar without a final water dilution.

Solution Volumes

For a set molarity of ammonium fluoride, the volume of dissolver solution is determined by the amount of fluoride required to complete the dissolution. Since six moles of fluoride are complexed with one mole of zirconium, a mole charge ratio, F/Zr, of at least 6 is necessary. In practice, the F/Zr mole ratio must be 6.5 or 7 to expedite complete dissolution. A mole charge ratio of 7 corresponds to 1.67 gallon of 5.5 M NH_4F per pound of zirconium. After water dilution, the coating waste volume is 2.2 gallon per pound of zirconium.

Charge ratios higher than 7 decrease the time required for total dissolution, but offer little advantage, since the residual or excess "free" fluoride lowers the zirconium solubility and increases the uranium solubility. Hence, dilute

solutions would result; waste volumes would be greater; and core losses would be higher.

To keep the zirconium solubility near 0.6 molar, the residual "free" fluoride must be kept below 0.6 molar. This is done by assuring that the F/Zr mole charge ratio is seven or less and by assuring that six moles of fluoride have been complexed with one mole of zirconium. Thus, the volume of solution charged must be based on the expected penetration during the zirconium decladding operation. For example, only a 30 mil surface will dissolve from a 1/4-inch plate if most of the other zirconium present is 30 mils thick. The volume of solution should be charged for the quantity of zirconium within the 30 mils. In general, actual volumes of solution are best predicted by charging for dissolution of 90 percent of an oxidized cladding and 25 percent of the end fittings.

Since end fittings do not completely dissolve in a single batch charge, they accumulate from one batch operation to the next. Approximately four sequential charge and decladding operations are required to completely dissolve the end fittings from the first charge. However, if desired, a single clean-up charge of NH_4F can be used at the end of a Zircaloy-clad-fuel campaign to remove the residual pieces of zirconium.

Actual pilot unit data are shown in Table I with a listing of charge concentrations, actual dissolution times, and final analyses after the water dilution.

Ammonium Nitrate Concentration

The addition of ammonium nitrate eliminates two major objections to the Zirflex process, i.e., gross quantities of hydrogen off-gas and insoluble tin precipitates. The presence of ammonium nitrate reduces the amount of explosive hydrogen evolved in the reaction by the conversion of the nitrate ion into ammonia and water. Ammonium nitrate concentrations of 0.5 and 0.75 molar were adequate to reduce the hydrogen evolution from two to 0.1 mole per mole of zirconium dissolved. A 0.5 molar concentration was as effective as a 0.75 molar concentration. However, the terminal nitrate ion concentration should be kept at a minimum because of its somewhat adverse effect on zirconium and uranium solubility. The average final nitrate ion concentration after the water dilution step in the pilot unit tests was 0.08 molar. The average consumption of nitrate ion was 0.47 mole per mole of zirconium.

Zircaloy-2 cladding contains approximately 1.5 percent tin. Residue, presumably tin compounds, has been reported to be from 0.0 to 1.5 percent of the Zircaloy dissolved (2). Apparently, the presence of the nitrate ion promotes the solubility of the tin, since a factor of 10 reduction in the quantity of residue was experienced with the nitrate ion present.

Trace quantities of residue in the pilot unit operations caused no particular problems. Many of the early runs had considerable quantities of black and black-brown precipitate. However, this precipitation during the dissolution of Zircaloy-2 did not occur in later runs if the removal of ammonia was adequate.

Dissolver Gases

Ammonia and hydrogen are reaction products in the Zirflex process. Concentrations of 15 to 28 percent ammonia in dry air are explosive, but ammonia can be easily absorbed from the off-gases if desired. Hydrogen is explosive above a 4 percent concentration and its safe handling must be considered.

The hydrogen data scattered widely, since the method used to calculate instantaneous rates (suspended basket weights of zirconium) were not accurate. In general, the data indicated the hydrogen evolution was 0.025 to 0.03 moles rather than the 0.1 mole expected per mole of zirconium dissolved.

To assure safe operations, the hydrogen concentration must be kept below the explosive limit by dilution with air. Safe air rates can be based on 0.1 mole of hydrogen per mole of zirconium. For example, if one assumes a hydrogen evolution rate of 0.1 mole per mole of zirconium, a "free" fluoride concentration of 5.5 molar, and an unoxidized zirconium surface of one square foot hydrogen would be evolved at 0.016 standard cubic feet per minute. Thus, an air dilution rate of 0.38 standard cubic feet per minute would be required to limit the hydrogen concentration in the off-gases to 4.0 percent. These air requirements would proportionally change by lowering the fluoride concentrations or by limiting the hydrogen concentration to below 4.0 percent. Initial off-gas concentrations in pilot unit tests averaged 2.8 percent hydrogen under a variety of test conditions. (See data Table I.)

The ammonia evolved during the dissolution of zirconium (5 moles per mole of zirconium dissolved) is highly soluble in the ammonium fluoride dissolvent. Hence, the ammonia concentration in the ammonium fluoride increases; the pH increases; and, as a result, both the dissolution rate and the solubility of zirconium decreases.

Operating conditions of the dissolver system; i.e., boil-up rate, condenser temperature, air purge rate, and the amount of condensate refluxing, affect the partial pressure or solubility of ammonia in the system. Figure 3 shows the calculated molarity of ammonia in the dissolver under fixed, continuous, operating conditions. In general, the ammonia "trap" effect of the dissolver and condenser system is eliminated by: (1) an air flow through the system, (2) a high condenser temperature, and (3) high boil-up rates. In the pilot unit successful techniques included (a) use of very high air sparge rates, (b) high boil-up rates in the dissolver, and routing of the condensate to a separate receiver, and (c) operation with a high condenser temperature and a modest air sparge in the dissolver. As shown by Fig. 4, the latter two techniques were the most successful for prompting high dissolution rates. The typical operating times for comparable runs with equal boil-up rates are shown as follows:

Run No.	Method of Operation	Operating Time, hr	Percent Dissolved	Zircaloy Sheet Thickness, mils
17	Cold Condenser Reflux only	3.5	84	30
10	Cold Condenser air sparge	2.2	85	30
21	Water Boil-off	1.9	100	30
32	Air + high condenser temperature	2.7	100	30

(The Zircaloy was unoxidized, and penetration occurred from both sides of the sheet metal.)

Oxidized Zirconium

The prolonged exposure of Zircaloy to high temperature air or water produces a tenacious oxide film on the metal, as shown by Fig. 5. With moderate exposures, the oxide is a smooth, relatively nonporous black film; further exposure produces a white, less tenacious oxide. Thus, during the operation of all power reactor fuels, some oxide film will be formed.

Zirconium oxide is almost completely resistant to attack by the ammonium fluoride dissolvent of the Zirflex process. Thus, dissolution must occur by pitting and undercutting at points of imperfection in the oxide film. Under such conditions, the active surface area of a fuel is greatly reduced; and, as shown in Figs. 1 and 4, over-all average dissolution rates are a factor of 3-5 below the dissolution rates of unoxidized material. In practice, this raises the four hours normally required to remove a 30 mil unoxidized Zircaloy cladding to near twelve hours for a similar but oxidized cladding.

Reactor oxidized Zircaloy was simulated in pilot unit tests by exposing the Zircaloy to air at 400 C for 14 days. Typical dissolution operating times for oxidized material using 5.5 M NH_4F, 0.5 M NH_4NO_3 with an F/Zr mol ratio of 7 were as follows:

Run No.	Type of Charge	Oxidation (days) in 400 C air	Operating Time, Hr	Percent Dissolved
11	0.030 in. sheet	14	6.5	95
38	0.030 in. sheet	14	4.0	100
40	Sealed Tubes 0.030 Tk w/UO_2 cores	14	10.5	95+
41	Sealed Tubes 0.030 Tk w/UO_2 cores	*	11.0	99
43	0.030 in. sheet	14	5.8	93

*One-half of the charge was unoxidized Zircaloy and the remainder was oxidized for fourteen days.

Additional tests were conducted on three 60-mil Zircaloy 2 coupons that had been oxidized in deionized water at 360 C for 308 days. After twelve hours

In summary, minimum core losses may be obtained by: (a) avoiding the presence of U(VI) in the solution, (b) cooling the terminal solution to room temperature, and (c) obtaining the lowest possible free fluoride concentration by dissolving to reach an F/Zr mole ratio between 6 and 7 in the solution (obtained by nearly complete complexing of the fluoride ion with the zirconium). A loss in soluble uranium (IV) of 0.25 g/l can be expected in a typical diluted decladding solution containing 0.6 molar zirconium. Losses of U(VI) may be as high as 3.0 g/l.

The fraction of the core loss represented by the soluble uranium is a direct function of the ratio of the solution volume to core weight or alternately to the Zr/U ratio, since the quantity of cladding removal solution will be determined by the weight of zirconium charged. A graphical conversion of uranium solubility to uranium core losses is presented in Fig. 7 for three selected zirconium-to-uranium ratios in the fuels. Uranium losses are expected to be in the range of 0.1 to 0.15 percent for U(IV) valence species, and approximately ten times higher if the bulk of the uranium has a valence of VI.

The pilot unit was not equipped to handle plutonium or radioactive materials. However results compiled by J. L. Swanson of Hanford Laboratories Operation, HAPO[2] are presented:

Pu/U Ratio in a U-Pu Alloy x 10^{-4}	Amount in Boiling Solution					Amount in Cooled Solution		
	Solution		U	Pu	Pu/U Ratio x 10^{-4}	U	Pu	Pu/U Ratio x 10^{-4}
	M F^-	M Zr(IV)	g/l	g/l		g/l	g/l	
3	6	-	15.0	4.3	2.9	4.5	1.4	3.1
11	6	-	13.0	6.6	5.1	2.5	1.7	6.8
11	6	0.7	2.5	0.68	2.7	0.2	0.003	0.15
11	6	0.86	1.4	0.23	1.6	0.3	0.015	0.5

The uranium-plutonium alloy was first exposed to the indicated concentrations of boiling Zirflex solutions. As shown, the determined Pu/U ratio in the boiling solution was less than the Pu/U ratio in the metal. Then the solution was diluted to prevent zirconium precipitation and cooled. The plutonium/uranium weight ratios in the cooled solution were much less than those in the alloy. The reduction in the Pu/U ratio occurred after cooling because of an apparent carrying of the plutonium by the precipitated uranium fluoride salt.

Of course, the plutonium losses will depend on the exposure and enrichment of the fuel, the surface area of the core, and the operating conditions. Additional Pu loss data have been given by ORNL in document CF-58-11-91. In general, Pu losses of less than 0.1 percent can be expected.

Uranium Recovery

As previously indicated, the solubility of UF_4 decreases as the concentration of zirconium increases; i.e., greater complexing of fluoride ion. During the decladding of Zircaloy, dissolution of any exposed metallic uranium or sintered UO_2 core material will saturate the solution and form a precipitate of UF_4.

in the Zirflex solution (5.5 M NH_4F, 0.5 M NH_4NO_3 with an F/Zr mole ratio of 7) dissolution was 78, 85, and 96 percent complete.

Other Oxide Treatment

Removal of the Zirconium oxide film has been attempted by various methods. T. A. Gens[3] reported the use of molten ammonium bifluoride (~190 C) for the removal of Zircaloy cladding on reactor fuels. Initial dissolution rates were 19 mg/cm^2/min (68 mils/hr). Almost immediate dissolution of the oxide film was reported; also, tin residue was absent.

In other tests at Hanford, J. L. Swanson used a molten salt (30C) saturated with zirconium and having a composition of NH_4F $(HF)_{2.2}$. After the oxidized pieces were soaked in the salt bath approximately one hour, the oxide film was readily penetrable by aqueous solutions. Neither the molten salt nor the aqueous solutions dissolved the oxide film; but after the salt treatment, the film was very readily "undercut" in the aqueous ammonium fluoride solutions.

Core Losses

Losses of the fuel core material to the Zirflex decladding solution are primarily controlled by the solubility of the core material in the ammonium fluoride dissolvent. In an actual Zirflex decladding step, the exposed uranium continuously dissolves. When the solution is saturated with uranium, further dissolution of the core produces a precipitate of UF_4. Later cooling of the solution further reduces uranium solubility and more UF_4 precipitates. However, the precipitate can be easily recovered by centrifugation, as discussed later.

Figure 6 illustrates the expected uranium core losses and the importance of controlling temperature and zirconium "saturation" (i.e., nearly complete complexing of the fluoride with zirconium). The solubility of U(IV) decreases as the zirconium concentration increases, i.e., more complete complexing of the fluoride by zirconium. Under the same circumstances, the solubility of uranium (VI) increases, i.e., as the "free" fluoride concentration decreases.

Production of uranium (IV) is prevalent during the Zirflex decladding step, while production of uranium (VI) is prevalent during core dissolution with nitric acid. The high solubility characteristic of U(VI) and attendant core losses require very effective flushing between alternate decladding and core dissolution if waste losses are to be low.

Further zirconium dissolution reduces the UF_4 solubility, and additional precipitation may occur. Cooling the solution at the end of the dissolution will cause further precipitation of the uranium.

Centrifugation is a convenient way to isolate the UF_4 precipitate (1 to 3 weight percent of the total uranium) from the solution. A detailed study of the centrifugation step was not made; but a 12-inch centrifuge gave clear solution when operated at 2600 rpm (11 g's) with a feed rate of 200 ml/min and a residence time of 15 minutes.

The precipitated UF_4 cake in the centrifuge was removed in approximately 30 minutes by the addition of cold 1 M HNO_3 and 1 M ANN. Dissolved ANN and HNO_3 with higher temperatures will reduce the dissolution time to about 10 minutes.

In addition to the UF_4 precipitate collected in the centrifuge, a collection of zirconium dioxide flakes, uranium flakes, small fragments of fuel cores, or residue can be expected. All of these particles are easily broken, and most of them will remain in the dissolver unless the solution is severely agitated during transfer. The largest particles noted in the pilot unit were estimated to be 1/4-inch square and up to 10 mils thick.

The uranium flakes are produced by a film formed on the surface of metallic uranium during the decladding step. Some of this black film (approximately 4 mils thick) dislodges from the metallic uranium surface and settles to the bottom of the dissolver. (The uranium flakes were readily soluble in cold 30 percent nitric acid -- within 10 minutes. The flakes in the pilot unit tests were estimated to be 0.1 g/sq cm of exposed surface.)

The quantity of zirconium dioxide flakes can be predicted from the film thickness, as shown indirectly by Fig. 5.

Slight traces of other residue were usually found in the centrifuge bowl, both before and after the addition of aluminum nitrate and nitric acid. Such residue could have been precipitates of stannic acid and stannic oxide, as reported by ORNL[7], or the precipitates of residual zirconium or aluminum fluorides. However, the residue caused no particular problem.

The behavior and isolation of plutonium in the centrifuge is not known at this time. In order to assume complete recovery of the uranium and plutonium, "slurry" of the centrifuge contents back to the dissolver for the core dissolution step or "slurry" to the oxidizing or digesting tank is proposed. Here all of the material, other than zirconium oxide flakes, should dissolve. Then the flakes can be removed during the feed centrifugation and later washed and "slurried" from the centrifuge to waste storage.

Entrainment

Entrainment is of particular importance in the Zirflex process, since entrained zirconium solution contacts refluxing ammonium hydroxide and precipitates as an adherent zirconium-hydroxide sludge. Plugging of the off-gas system may result. The pilot unit with a 3-inch tower of 1-inch stainless steel raschig rings was operated at a calculated vapor velocity of 4 feet per second without any serious buildup of zirconium precipitates; traces of the precipitate on the walls of the glass tower was easily removed by the nitric acid reflux during the uranium dissolution step.

The method of entry of the condensate into the dissolver is perhaps more important in the refluxing dissolver system. Early pilot unit tests allowed the condensate to run down the side of the dissolver. As a result, large white mounds of zirconium hydroxide adhered to the dissolver walls around the condensate entry. Further trouble was avoided by installing a line to discharge condensate directly onto the boiling surface.

Foaming

Foaming has been reported by L. M. Ferris[7] and J. L. Swanson as appreciable during the reaction. There was no evidence of severe foaming in the pilot plant dissolver when operated with a liquid to zirconium surface ratio of 0.17. The dissolver had at least 0.17 cu ft of freeboard per square foot of zirconium surface in contact with dissolver solution.

Solution Conductivity

Preliminary conductivity tests were successful in indicating the progress of the reaction during the decladding step. A standard 1000-cycle conductivity bridge by Industrial Instruments was used to indicate values from a shiny platinum electrode cell with a cell constant of 9.8. A 0.2 mfd capacitance was used to give more distinct readings on the null indicator eye. Operating range was from 35 to 55 ohms.

Conductivity Measurements at Boiling (ohms)

Run No.	Start	Final
28	40	50
29	40	55
30	35	53
31	35	55

Core Dissolution

Sintered uranium dioxide is the core component in the Dresden and PWR Zircaloy clad fuels. After the Zirflex decladding step, conventional nitric acid can be used for the dissolution of the UO_2 core. However, aluminum nitrate must be added to inhibit the corrosive action of the residual fluoride on the dissolver vessel.

The dissolution rates of sintered UO_2 were three to four times more rapid than those of metallic uranium in 10 molar nitric acid concentrations. As dissolution continued, the rates decreased to equal or below that of metallic uranium. Satisfactory dissolution of the UO_2 was obtained as long as the acid concentration was above 1 molar.

Corrosion

The Zirflex process is particularly attractive, since ordinary stainless steel equipment is applicable for the decladding and core dissolution step. Coupons of types 304-L, 347, and 316 gave a corrosion rate of 4.3 mils per month in the pilot plant dissolver (based on 55-hour decladding and 55-hour HNO_3 core dissolution). Other corrosion data were in this same range.

Corrosion in 6 M NH_4F 0.5 M NH_4NO_3

(24-48 hours at boiling in Teflon or stainless steel containers)

Material	Mil/mo
304-L	11.4
309 Scb	9.6
Carpenter 20	5.6
Hastelloy F	3.3
Ni-o-nel	4.4
Incaloy 804	5.9
Hanes 25	5.5
304-L	38*
Hastelloy F	18*

* Heat transfer surface

The corrosion of mild steel by neutralized wastes was nil at 40 C if the pH was 8.5 or above. Higher temperatures have not been tested.

Some residual fluoride in the nitric acid core dissolution step could cause corrosion problems. However, addition of aluminum to at least a 1:1 mole ratio of aluminum to fluoride complexes fluoride and prevents excessive corrosion, as

shown by the following data.

CORROSION OF 304-L

10 M HNO_3, 0.02 M UNH, 0.08 M HF	
Al/F Mole Ratio	Mils/Mo
6.25	1.97
3.12	2.82
1.00	13.7

Equipment

The pilot unit was arranged as shown in Fig. 8. A 40-liter steam-jacketed stainless steel vessel was connected through a 3-inch ID glass tower of 1-inch raschig rings to a tubular condenser. Condensate returned through the tower to the dissolver, or was delivered to a separate condensate collector. The off-gases from the condenser passed through a rotameter into a bubble cap glass tower for absorbing ammonia.

To follow dissolution, an ordinary pneumatic differential pressure transmitter was used to indicate the weight of a wire basket suspended inside of the dissolver. The weight of the basket provided the force ordinarily developed by the differential pressure on the diaphragm. The diaphragm of the transmitter was removed to eliminate the effect of dissolver vacuum on the readings. A pneumatic recorder provided a recorded trace of the dissolution of the material in the basket.

The buoyant effect of the gases on the indicated weight certainly caused some magnitude of error, which is difficult to predict. The dissolution rates calculated from the pilot unit data are probably lower than actual because the buoyant effect becomes progressively less significant as the rate of reaction decreases. However, the weighing device was very useful, since liquid samples during the reaction would precipitate and plug sample lines. A specific gravity of 1.09 (cold) did not change appreciably during the dissolution.

Liquid sample ports were provided on the dissolver, condensate reflux line, condensate collector, and the acid reservoir. Samples were taken at the off-gas flow just before entry to the scrubbing tower.

Operating procedure

A customary procedure for dissolver operation was used in the decladding tests. The metal and calculated amount of solution were charged to the dissolver. The solution was then heated to boiling and maintained at boiling throughout the run. At the end of the dissolution, water was added to replace that lost to the off-gas system and to dilute the solution to a soluble zirconium concentration at room temperature. During boil-off operations, water was continuously added to maintain a constant liquid level.

Initially, vapors were condensed and routed directly to the dissolver. After difficulty in obtaining complete dissolution, air was sparged through the dissolver and off-gas system. Later, the condensate from the condenser was routed to a separate receiver or the condenser temperature was operated high enough to adjust the vapor pressures of ammonia for optimum removal.

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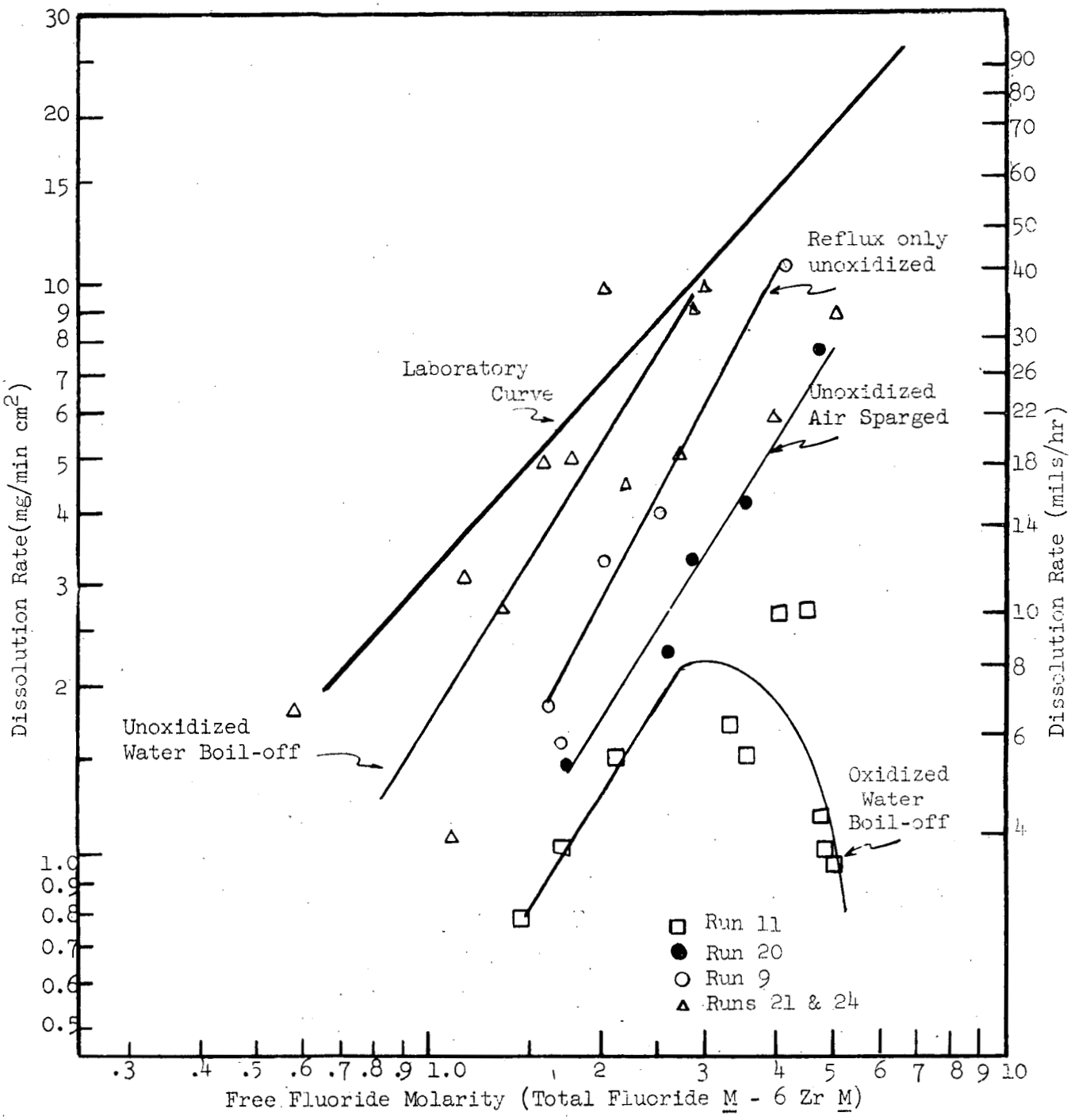


FIGURE I - ZIRCALOY DISSOLUTION RATES IN BOILING AMMONIUM FLUORIDE

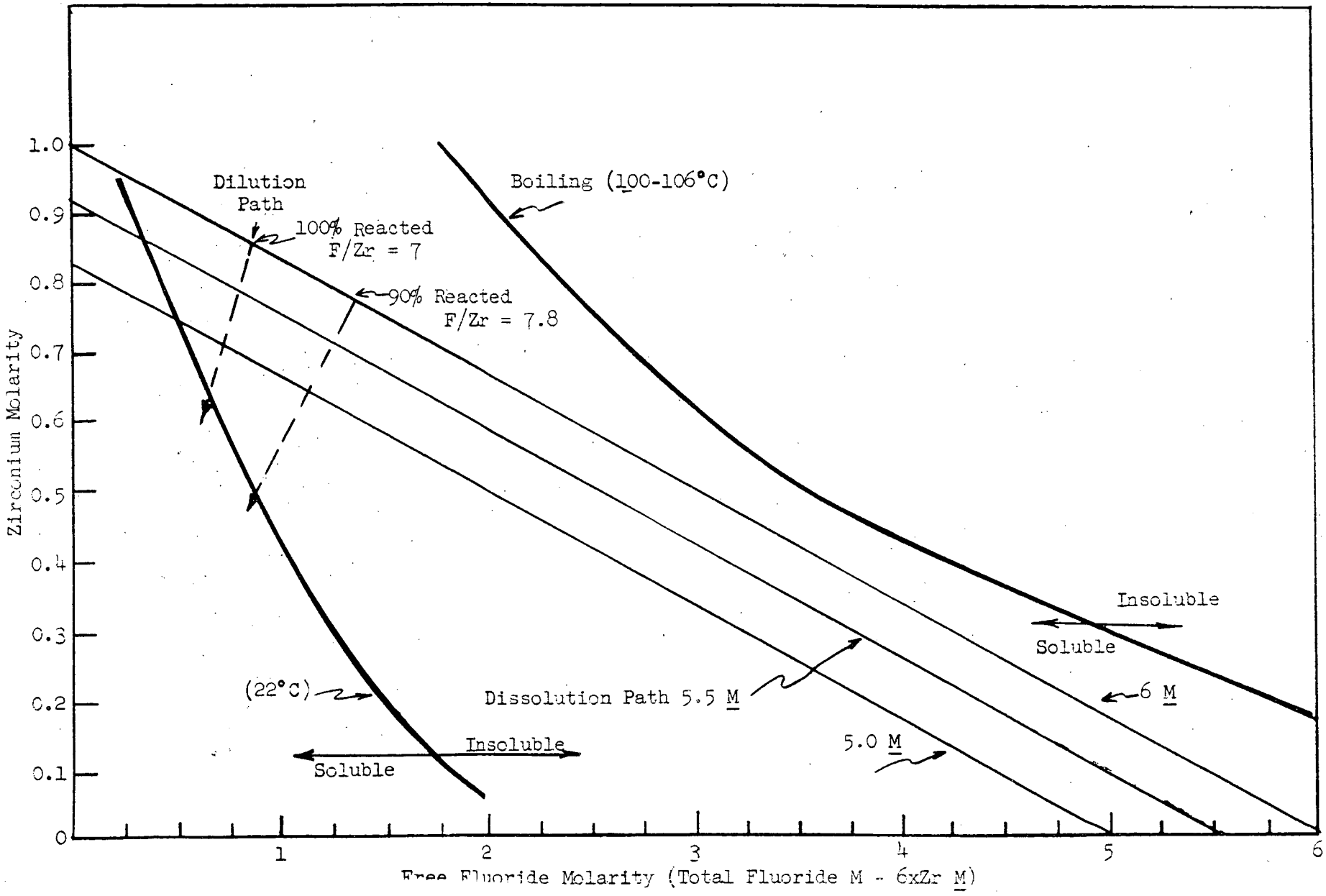
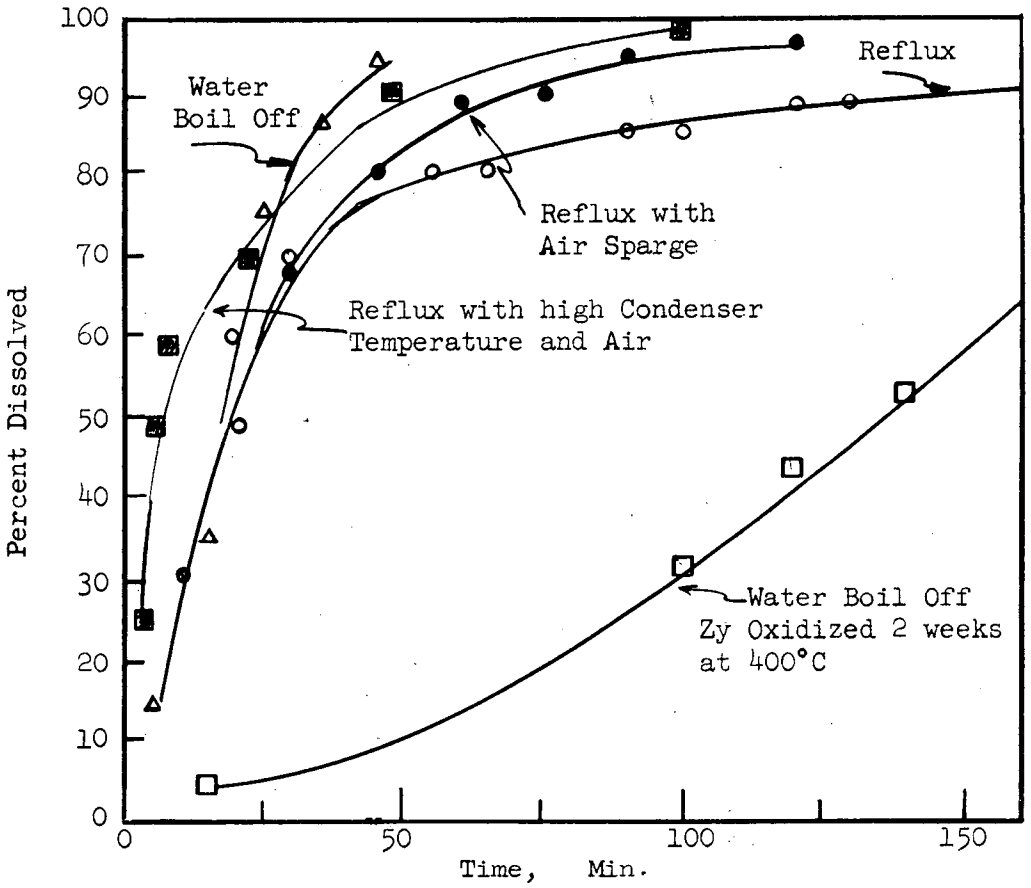


FIGURE 2 - SOLUBILITY OF ZIRCONIUM IN AMMONIUM FLUORIDE SOLUTIONS



■ - 32 - Reflux with Air and High Condenser Temperature
○ - 9 - No Air Sparge
□ 11 - Oxidized-Water Boil Off
△ 24 - Water Boil Off
● 20 - Air Sparged

FIGURE 4. EFFECT OF OPERATING CONDITIONS ON DISSOLUTION RATE

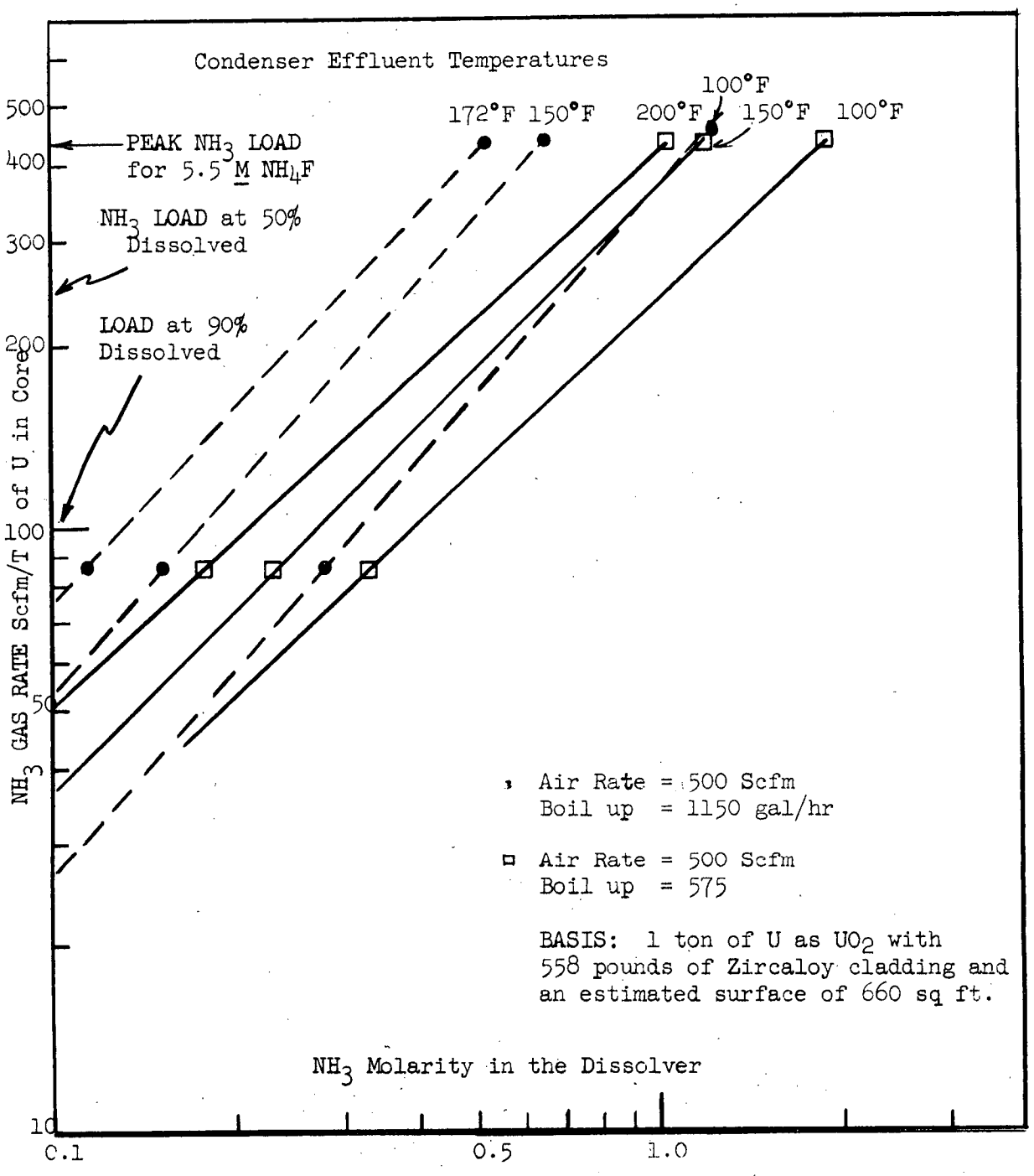


FIGURE 3. EFFECT OF AIR RATE, BOIL UP RATE AND CONDENSER TEMPERATURE ON NH_3 CONCENTRATION IN THE DISSOLVER

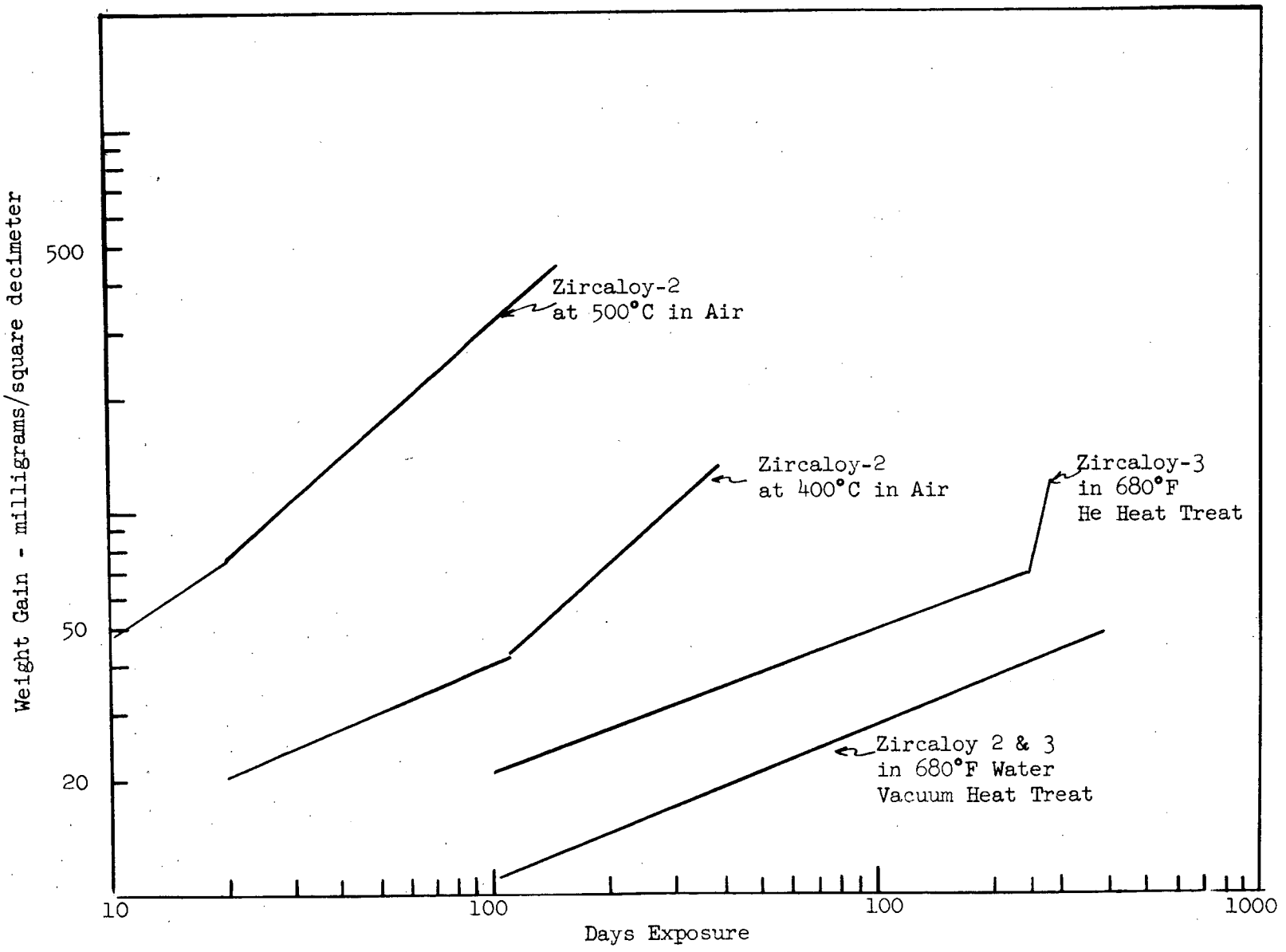


FIGURE 5 - OXIDATION OF ZIRCALOY

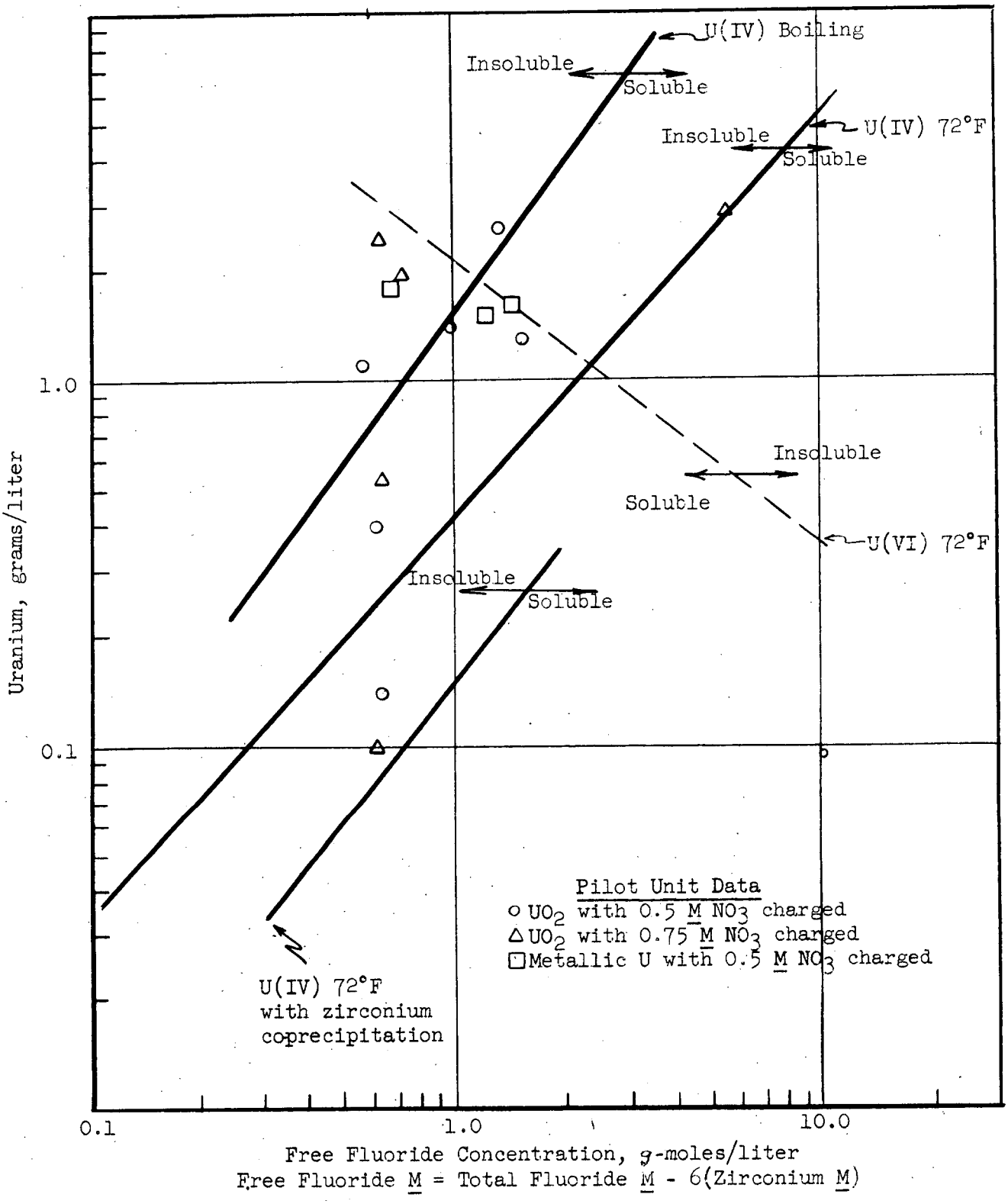


FIGURE 6 - SOLUBILITY OF URANIUM IN ZIRFLEX SOLUTIONS

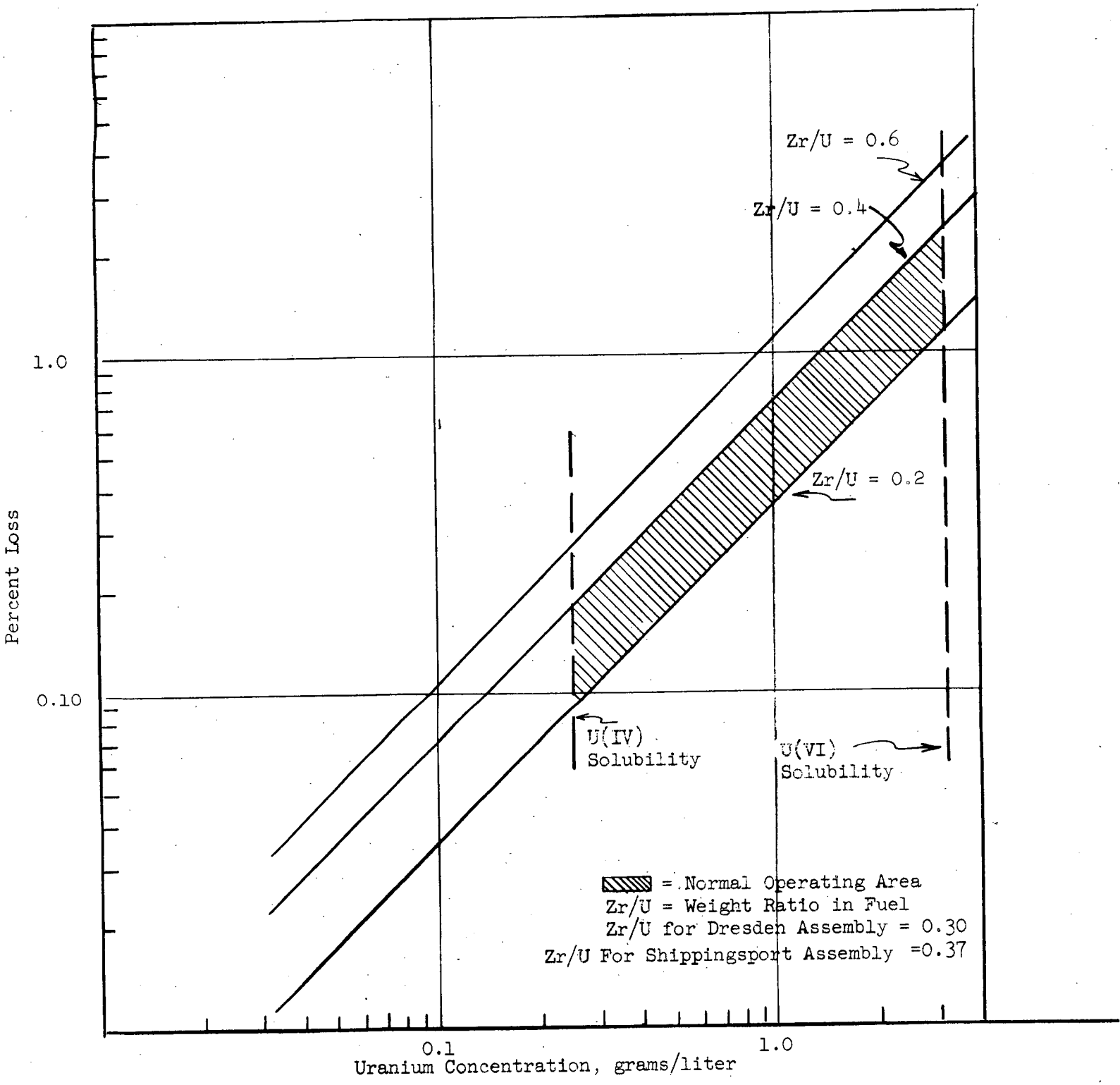


FIGURE 7 - PERCENT LOSS OF URANIUM IN ZIRFLEX SOLUTIONS

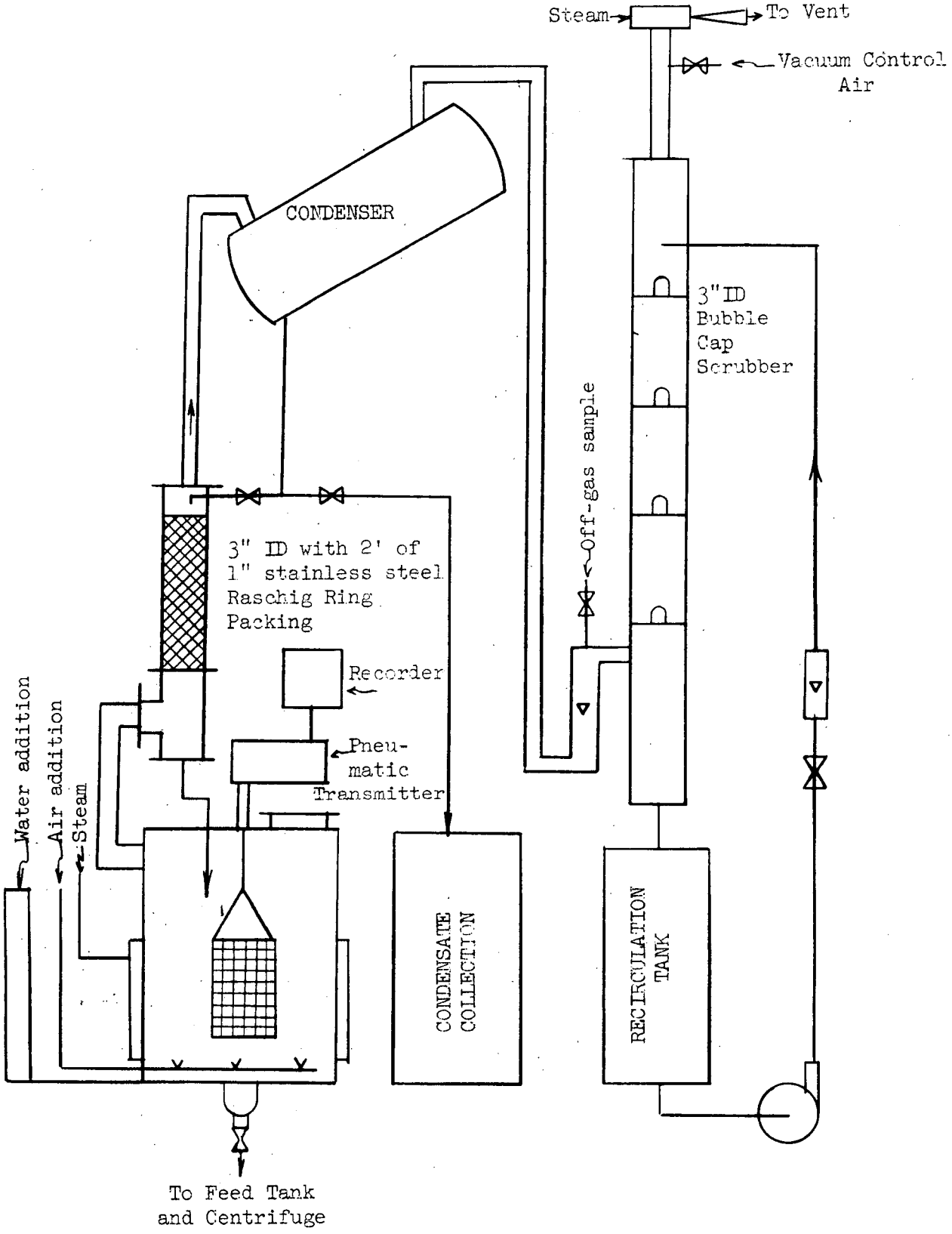


FIGURE 8 - ZIRFLEX PILOT PLANT EQUIPMENT

ZIRFLEX FLOWSHEET BASIS FOR FIGURES 9 and 10

1. A mole of Zircaloy is 100 percent zirconium. (Zircaloy 2 is 98.5 percent zirconium.)

2. Seven moles of ammonium fluoride is required per mole of Zircaloy.

3. Five moles of ammonia is evolved per mole of Zircaloy.

4. One-tenth mole of hydrogen is evolved per mole of Zircaloy.

5. No Zircaloy is present in dissolver at charging. Approximately 558 pounds of Zircaloy is removed during the decladding step. Approximately 172 pounds of Zircaloy is left in the dissolver as undissolved tube sheets and end fittings.

6. Estimated surface area of the Zircaloy is 650 square feet per ton of uranium.

7. Peak gas rates assume a starting dissolution rate of 66 mils/hour with unoxidized Zircaloy. Peak rates for oxidized Zircaloy are approximately 10 to 15 percent of rates for unoxidized Zircaloy.

8. Uranium solubility in Zircaloy waste solution is approximately 1.6 grams per liter at boiling and 0.25 grams per liter at 22 C.

9. Air rates are based on a 2 percent hydrogen concentration during peak off-gas evolution.

10. Condenser temperature and boil up is based on the partial pressures and rates necessary to permit adequate ammonia removal during peak operating conditions.

11. Criticality or dissolver geometry has not been considered.

12. Nitric acid consumption for the dissolution of one mole of UO_2 is approximately 2.2 moles per mole of uranium dissolved.

13. Zirflex contaminants (Zr, F and NH_4 ions) are based on a 50-gallon liquid heel per ton of uranium.

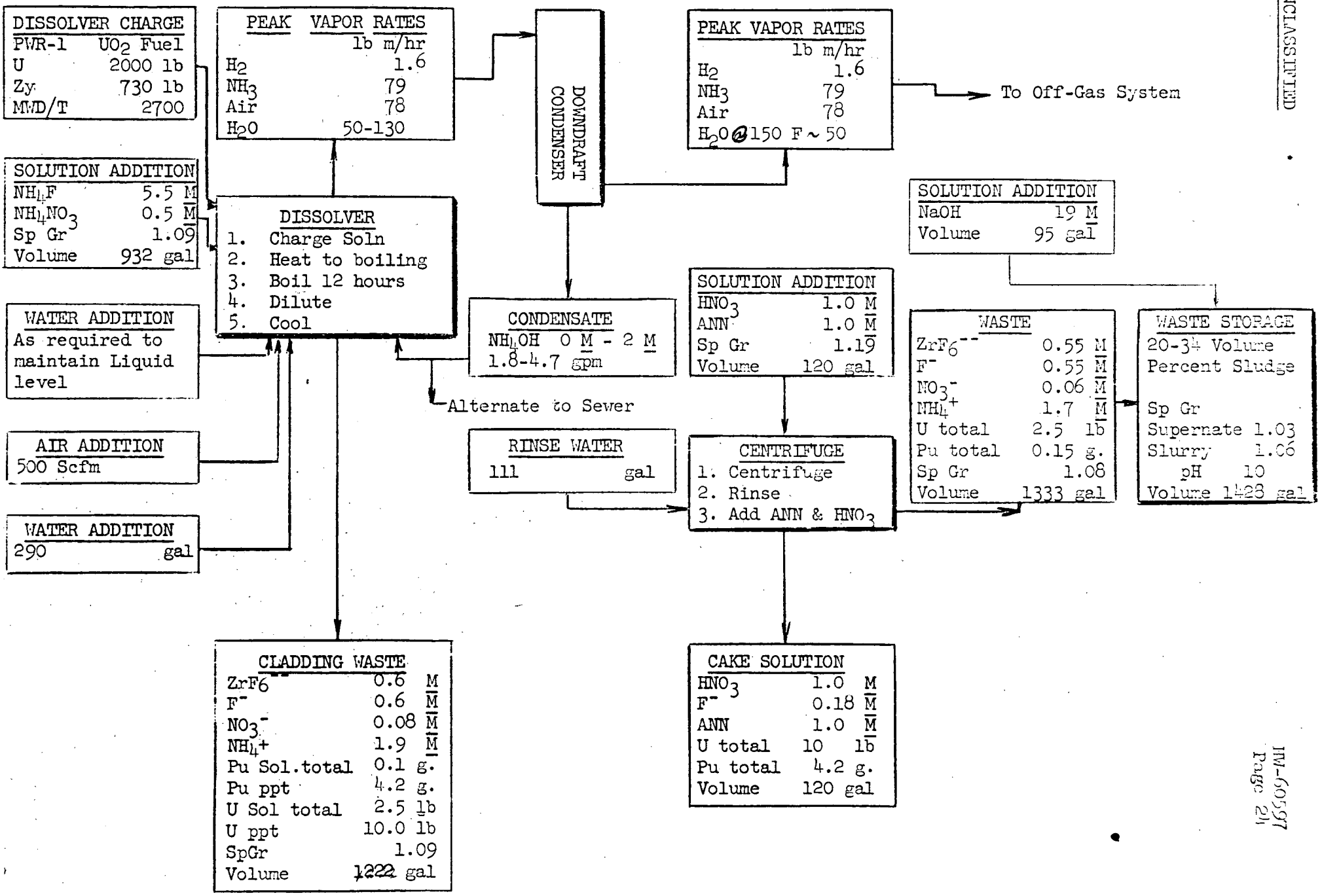
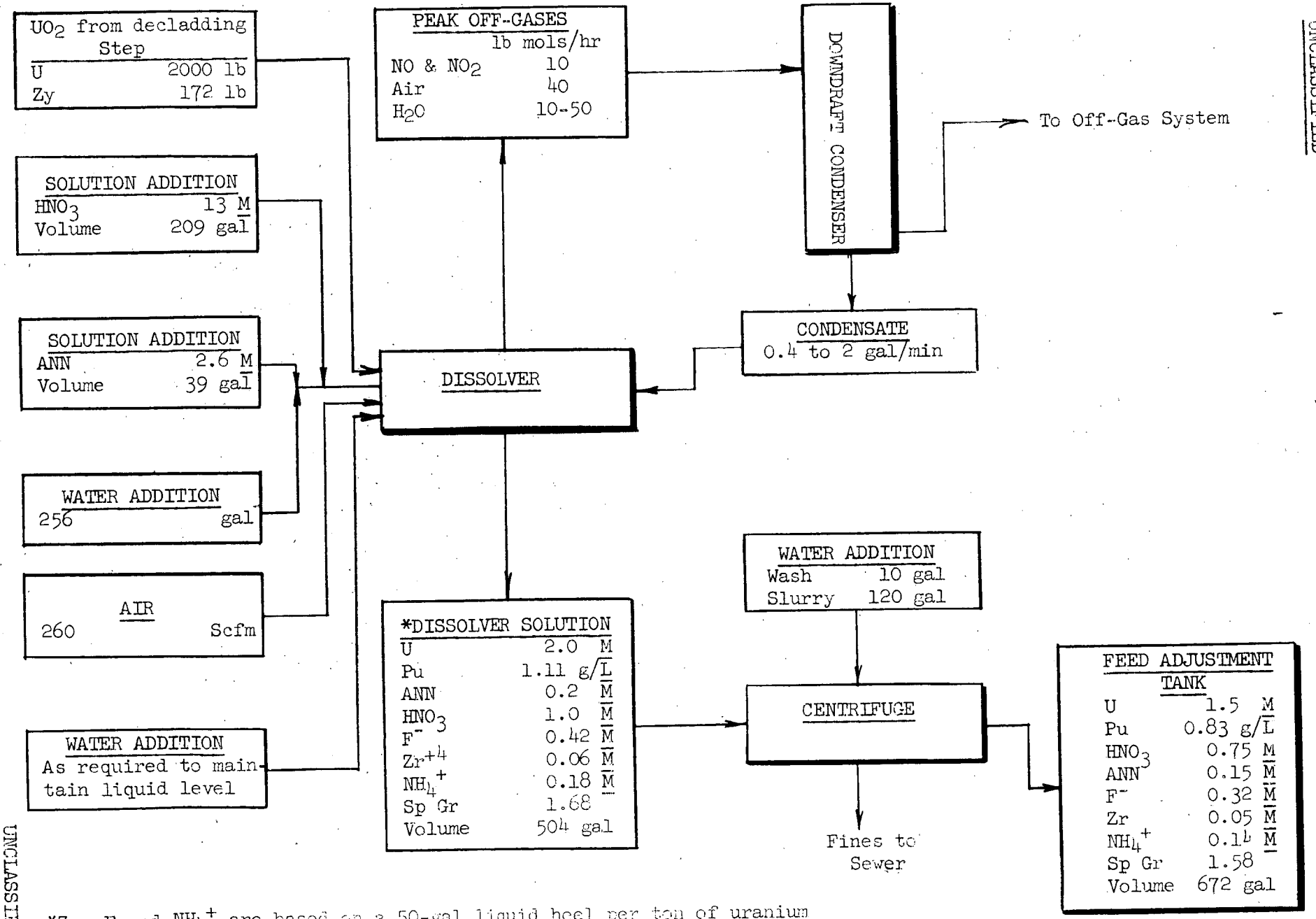


FIGURE 9 - ZIRFLEX CLADDING REMOVAL - PWR-1 FUEL

FIGURE 10 - PWR-I CORE DISSOLUTION



*Zr, F and NH_4^+ are based on a 50-gal liquid heel per ton of uranium

TABLE I - KIRCALOY DISSOLUTION

KINFLEX PILOT UNIT TESTS

	CHARGE CONDITIONS						OPERATING CONDITIONS								RESULTS												
																			Off-Gas Hydrogen Analysis (% in Air)					Final Solution Analysis		
Run No.	Fluoride Molarity	Nitrate Molarity	Mole Ratio	Surface Area of Kircaloy	Amount of Kircaloy	Approx. Max. Sheet Thickness	Oxidation in Air 400° C	Operating Time	Reflux Only	Water Boil-off	Avg Air Leakage Rate	Air Sparge Rate	Peak Total Gas Rate	Pot Temp. °C	Reflux Condensate Temp °C	Percent Dissolved	Moles NH_3 Evolved per Mole Zy Dissolved	Moles NO_3^- Consumed per Mole Zy Dissolved	Rate Constant	1	2	3	4	pH	Zr g/l	NO_3 g/l
	Gr	C_{max}^-	F/Zr	in.^{2}	lb	in.	da	hrs																			
1	6.0	0.5	7.0	198	1.32	.13	0	3.8	I	-	2.5	-	-	-	-	94	-	-	-	-	-	-	-	-	56.3	-
2	6.0	0.5	7.0	586	2.88	.03	0	4.1	I	-	0.3	-	7.2	96-98	28	99.6	-	-	13.1 -3.96	2.6	0.6	0.4	0.1	-	77.3	-
3	4.0	0.5	7.0	568	2.12	.06	0	3.5	-	-	-	6.8	12.7	90-92	55	100.0	-	0.53	7.14	-	-	-	-	-	45.3	13.0
4	8.0	0.5	7.0	700	3.71	.125	0	2.0	I	-	-	-	10.3	100-101	30	21.0	-	-	-	-	-	-	-	-	-	-
7	6.0	0.5	10.0	575	2.32	.03	0	1.6	I	-	<0.2	-	8.5	94	-	99.9	4.0	0.57	13.75	15.6	3.1	3.8	-		59.1	12.3
8	6.0	0.5	8.5	648	2.87	.03	0	3.7	I	-	<0.2	-	2.3	94-98	30	100.0	-	-	15.75	0.2	2.5	-	-	7.3	61.3	-
9	6.0	0.5	7.0	568	3.10	.03	0	3.7	I	-	-	-	4.9	94-96	37	99.9	-	-	14.7 -2.36	0.7	0.9	-	-	4.7	-	-
10	5.5	0.5	7.0	565	3.15	.03	7	2.2	-	-	-	3.2	7.4	92-98	30	55.0	4.5	0.46	3.33	1.0	0.4	0.5	-	-	32.0	6.1
11	5.5	0.5	7.0	552	3.08	.03	14	6.5	-	4.1	<0.2	-	7.7	101	30	95.0	4.1	0.49	4.1	1.7	1.1	-	-	5.6	53.2	6.2
12	6.0	0.5	7.0	563	3.08	.03	3	6.4	I	-	<0.2	-	6.7	98-100	30	84.0	-	-	3.38	2.1	-	-	-	7.4	58.3	9.0
17	4.6	0.5	7.0	568	2.82	.13	0	3.5	I	-	-	-	7.9	-	30	84.0	4.7	0.61	18.0	2.4	-	-	-	-	34.1	15.4
18	6.0	0.5	7.0	628	2.79	.19	0	3.0	-	-	-	3.2	5.4	9.6	50	99.0	-	0.68	31.9 -4.23	-	-	-	-	-	34.1	2.0
19	6.0	0.5	7.0	606	2.03	.06	0	4.5	I	-	<0.2	-	17.2	96-98	35	83.0	4.1	0.64	14.5	1.0	5.0	-	-	7.1	37.6	10.8
20	5.5	0.5	7.0	719	2.72	.03	0	4.0	-	-	-	2.1	7.4	94-98	68	100.0	5.0	0.46	10.3	0.6	-	-	-	-	50.1	6.6
21	5.5	0.5	7.0	621	2.46	.03	0	1.9	-	4.3	<0.2	-	7.9	100	30	100.0	4.6	0.40	13.0	0.9	-	-	-	5.5	32.4	3.8
22	5.5	0.5	6.5	742	2.61	.03	0	5.3	-	3.4	0.5	-	7.7	100	32	100.0	3.9	0.41	6.57	2.2	1.1	-	-	5.5	56.9	8.1
23	5.5	0.5	7.0	713	2.57	.03	3	3.5	-	3.1	<0.5	-	5.6	99	30	100.0	4.5	0.40	5.27	6.1	5.8	-	-	5.0	65.0	5.8
24	5.5	0.5	7.0	694	2.59	.03	0	2.1	-	3.0	0.3	-	6.5	98	35	100.0	4.7	0.47	12.6	2.6	2.4	-	-	5.1	-	7.0
25	4.5	0.4	7.0	715	2.72	.03	0	4.2	-	-	-	Yes	7.7	90	-	100.0	-	0.46	4.66	-	-	-	-	4.9	55.9	7.0
26	5.0	0.5	7.0	660	2.54	.03	14	11.0	-	-	-	3.8	4.5	-	-	90.0	4.4	0.36	1.39	0.42	0.68	-	-	5.2	44.4	10.1
27	4.5	0.5	7.0	682	2.53	.03	21	15.5	-	7.0	<0.3	-	4.4	94	40	89.2	-	0.40	1.59	1.0	-	-	-	-	33.6	5.8
28	5.0	0.5	7.0	414	2.48	.03	0	2.2	-	-	-	3.6	-	92	30	98.8	-	-	9.18	-	-	-	-	7.0	59.4	6.7
29	5.0	0.5	7.0	330	2.38	.03	0	4.3	-	-	-	6.7	9.4	92	70	100.0	5.1	0.42	15.5	-	-	-	-	4.3	50.5	7.5
30	5.0	0.5	7.0	488	2.54	.03	0	4.0	-	-	-	2.5	6.1	94	70	100.0	4.6	0.43	7.77	-	-	-	-	5.0	50.1	8.0
31	5.0	0.5	7.0	570	2.36	.03	0	4.9	-	-	-	2.1	4.0	90	70	100.0	-	-	-	-	-	-	-	-	-	-
32	5.5	0.5	7.0	370	2.83	.06	0	2.7	-	2.78	-	1.89	17.9	100	65	100.0	3.0*	0.46	20.6	-	-	-	-	6.1	46.5	9.54
33	5.5	0.5	7.0	-	2.70	.03	0	2.0	-	Yes	-	-	-	-	-	100.0	4.8	0.42		4.9	2.9	-	-	5.5	58.0	7.4
34	5.5	0.75	7.0	776	2.71	.03	0	2.7	-	4.3	0.4	-	6.1	-	-	100.0	2.2	0.28		3.4	1.7	-	-	2.9	58.5	15.3
35	5.5	0.75	7.0	782	2.71	.03	0	4.0	-	4.4	0.4	-	8.3	94-98	45	100.0	5.0	0.40		1.2	1.6	-	-	4.1	54.4	19.4
36	5.5	0.75	-	-	0.0	-	0	6.2	-	Yes	-	-	-	98	30	-	-	-		-	-	-	-	6.2	-	-
37	5.5	0.75	7.0	617	2.74	.03	7	5.2	-	4.0	0.3	-	9.1	96-98	35	-	4.7	-		1.4	0.8	1.6	-	5.2	57.2	18.0
38	5.5	0.75	7.0	-	2.74	.03	14	4.0	-	Yes	<0.2	-	-	-	-	100	4.6	0.70		4.2	3.6	2.1	-	6.4	60.1	10.1
39	5.5	0.5	7.0	-	2.50	.03	0	2.1	-	8.4	<0.4	-	-	98	35	100	4.4	0.36		4.9	0.9	-	-	5.1	60.2	11.2
40	5.5	0.5	7.0	307	2.16	.03**	14	10.5	-	3.4	0.7	-	2.6	98-100	30	95*	4.1	0.49		1.8	1.6	-	-	-	39.0	6.4
41	5.5	0.5	7.0	409	2.33	.03**	28	11.0	-	7.1	0.5	-	8.8	98-100	-	99	4.5	0.48		0.6	-	-	-	4.4	51.9	5.0
42	5.5	0.5	7.0	772	2.71	.03	14	3.7	-			-	1.6	4.0	100-104	-	38.9	5.4	-	3.0	-	-	-	5.2	51.7	6.6
43	5.5	0.5	7.0	637	2.74	.03	14	5.8	-			-	1.0	4.7	100-102	-	93	4.7	-	4.1	-	-	-	5.1	50.3	-
44	5.5	0.5	7.0	680	2.67	.03	14	5.0	-			-	1.8	-	100	50	92.3		-	2.73	-	-	-	4.8	52.0	-
45	5.5	0.5	7.0	670		.03	0	3.9	-	-	-	-	6.0				100	4.1	0.46	-	-	-	-	4.7	56.3	6.0
46	5.5	0.5	-	-		.03	0	4.0	-	-	-	-					100	-		-	-	-	-		0.6	
47	5.5	0.5	7.0	-		.03	0	9.3	-	-	-	-					100	-		-	-	-	-			3.8
48	5.5	0.5	7.0	371		.03	0	5.0	-	-	-	-	11.4				100	3.8	0.47	-	-	-	-		45.5	9.1
49	5.5	0.5	7.0	412		.03	0	8.0	-	-	-	-	10.2				100	-		-	-	-	-		57.2	

NOTE: *Hot Scrubber apparently did not absorb all of the NH_3
**Sealed 1/2-inch diameter tubes with UO_2 cores
***50% unoxidized and 50% oxidized 14 days

Runs 1 through 32 contained Zy only
Runs 33 through 44 contained Zy and UO_2
Runs 45 through 47 contained Zy and Al-U alloy
Runs 48 and 49 contained Zy and U

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TABLE II. URANIUM LOSSES - ZIRFLEX PILOT UNIT TESTS

	CHARGE CONDITIONS					RESULTS			
Run No.	Fluoride Molarity	Nitrate Molarity	Fluoride-to Zircaloy Mole Ratio	Average Uranium g/l Before Centrifugation	Average Uranium g/l After Centrifugation	Zr/U Weight Ratio	Percent Loss to Solution After Centrifugation	Percent of Total Uranium as UF_4 Precipitate in Centrifuge	Core Material
33	5.5	0.5	7	0.14	Not Cent.	0.16	0.04	-	Sintered UO_2
34	5.5	0.75	7	0.47	0.54	0.17	0.17	0.06	"
35	5.5	0.75	7	0.25	1.9	0.17	0.57	-	"
36	5.5	0.75	-	12.5	2.9	-	0.63	0.15	"
37	5.5	0.75	7	2.4	Not Cent.	0.17	-	-	"
38	5.5	0.75	7	0.11	0.10	0.17	0.03	0.01	"
39	5.5	0.5	7	4.3	1.3	0.15	0.37	-	Swaged UO_2
40	5.5	0.5	7	2.8	2.6	0.21	1.3	0.10	Sintered UO_2
41	5.5	0.5	7	2.2	1.4	0.29	0.82	0.21	"
42	5.5	0.5	7	0.4	0.4	0.17	0.13	0.02	"
43	5.5	0.5	7	1.2	1.1	0.17	0.37		"
44	5.5	0.5	7	1.1	1.8	0.16	0.50	-	"
45	5.5	0.5	7	0.0036	-	-	0.25	-	***
46	5.5	0.5	7	0.07	-	-	2.9	-	***
47	5.5	0.5	7	0.06	-	-	9.4*		****
48	5.5	0.5	7	1.6	0.91	0.034	0.09	-	Metallic U
49	5.5	0.5	7	1.5	-	0.046	0.08	0.03**	Metallic U

NOTE: *Dissolver contamination may have contributed to the high loss
**Approximately 1% remained in dissolver as flakes
***U-Al alloy 2.25% U
****U-Al alloy 0.9% U

APPENDIX

ZIRCONIUM DISSOLUTION RATE EQUATIONS

A. Nomenclature

Zr	= gram moles of metallic zirconium
Θ	= time from start, minutes
V	= volume of solution, liters
C_F	= molarity of solute, unreacted fluoride
C_{Zr}	= molarity of solute, zirconium
F/Z_r	= total fluoride to zirconium mole ratio in batch
K	= reaction constant, liters/in^2-min
A	= surface area of zirconium, square inches

B. Derivation

1) Since the dissolution of zirconium is first order in "free" (unreacted) fluoride, the rate of dissolution may be expressed as:

$$-dZr/Ad\Theta = K\,C_F$$

2) Known relationships of the system are:

$$Zr = Zr_o - V\,C_{Zr}$$

$$C_F = C_{Fo} - 6\,C_{Zr}$$

$$C_F = C_{Fo} - \frac{6(Zr_o - Zr)}{V}$$

4) or,

$$\frac{-VdZr}{KAd\Theta} = VC_{Fo} - 6\,Zr_o + 6\,Zr$$

5) Rearranging,

$$\int_{Zr_o}^{Zr} \frac{-dZr}{VC_{Fo} - 6\,Zr_o + 6\,Zr} \int_{6}^{\Theta} \frac{KA\,d\Theta}{V}$$

6) Integrating,

$$-1/6 \ln \frac{VC_{Fo} - 6\ Zr_o + 6\ Zr}{VC_{Fo}} = \frac{KA\theta}{V}$$

7)

$$\ln \frac{C_{Fo}}{C_{Fo} - 6\ C_{Zr}} = \frac{6\ KA\theta}{V}$$

8) or substituting

$$\ln \frac{C_{Fo}}{C_F} = \frac{6\ KA\theta}{V}$$

C. Time Cycle Calculations

1) Basis:

a) One-pound Zr tube of 30 mil thickness, (4.97 g-moles)

b) A = 143 in^2 (only outside surface exposed to solution)

c) Initial solution batch of 5.5 M NH_4F and 0.5 M NH_4NO_3

d) Seven moles of fluoride charged per mole of Zirconium

e) Reaction constant of 23 x 10^{-5} liters/in^2-min, maximum possible (Note: 14 x 10^{-5} was the average K value for unoxidized pilot unit runs and 3.3 x 10^{-5} was the average for oxidized fuels.)

2) Volume of charge solution, V = (g-moles Zr)(F/Zr)(1/C_{Fo})

or V = (4.97 g-m Zr)(7 g-m F/ g-m Zr)(1/5.5 g-m F) = 6.3 liters or (1.66 gal)

3. For 100 % dissolution, end concentration, $C_F = C_{Fo}$ - (6)(moles Zr)/V or C_F = 5.5-(6)(4.97)/6.3 = 0.77 M

4. Hence, from Equation No 8 above

θ = V/6 KA ln C_{Fo}/C_F = $\left[6.3/(6)(23x10^{-5})(143)\right]$ ln 5.5/0.77

and θ = 63 min or approximately 1 hour

5) Theoretical dissolution times can be calculated in a similar manner for other conditions. Since surface area changes with the degree of total dissolution, actual values are 2 to 5 hours longer.

Conditions					Theoretical Time
C_{Fo} M	F/Z_r moles/mole	V Liters	K Liters/in^2-min	A	θ Hours
5.5	7	6.3	23×10^{-5}(max)	143	1.0
5.5	7	6.3	14×10^{-5}(avg)	143	1.7
5.5	7	6.3	3.3×10^{-5}(oxidized)	143	7.0
3.0	7	11.6	23×10^{-5}(max)	143	1.9
3.0	7	11.6	14×10^{-5}(avg)	143	3.1
3.0	7	11.6	3.3×10^{-5}(oxidized)	143	13.3

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