HW-65979
UC-10, Chemistry-Separation Processes
for Plutonium and Uranium

THE ZIRFLEX PROCESS
TERMINAL DEVELOPMENT REPORT

By

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September 20, 1960

HANFORD ATOMIC PRODUCTS OPERATION
RICHLAND, WASHINGTON

Work performed under Contract No. AT(45-1)-1350 between the Atomic Energy Commission and General Electric Company

Printed by/for the U. S. Atomic Energy Commission

Printed in USA. Price $1.25. Available from the
Office of Technical Services
Department of Commerce
Washington 25, D. C.

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I. INTRODUCTION

In support of the Atomic Energy Commission's interim reprocessing scheme, Hanford Atomic Products Operation has been conducting research and development studies for the processing of slightly enriched power reactor fuels. Spent nuclear fuels include UO_2, uranium and alloys of U-Mo, U-Al, and U-Zr cores clad in aluminum, stainless steel, or Zircaloy. The Hanford Laboratories Operation is developing chemical decladding and core dissolution flowsheets for these fuels.

In the present report, only the dissolution of the Zircaloy-clad fuel elements is discussed. The term Zircaloy is used to indicate high zirconium alloys such as Zircaloy-2, -3, or 4 which have essentially the same chemical characteristics. Laboratory and pilot plant data are presented for all phases of the decladding and core dissolution steps. Corrosion data and waste neutralization studies are reported. The optimum decladding flowsheet, as determined by pilot studies, and a core dissolution flowsheet are also included.

The Zirflex process is applicable to the reprocessing of fuels from the Dresden and PWR reactors as well as to Hanford's New Production Reactor (NPR) and Plutonium Recycle Test Reactor (PRTR) fuels. Other possible applications are fuels from the Experimental Breeder Reactor I (Arco), NPD-2 (Ontario), and the Carolina, Virginia, Nuclear Power Associates Reactor.

II. SUMMARY

The Zirflex Process employs a boiling aqueous solution of ammonium fluoride and ammonium nitrate to dissolve zirconium or Zircaloy by the following reaction:

$$Zr_{(s)} + 6NH_4F + 0.5NH_4NO_3 \longrightarrow (NH_4)_2ZrF_6 + 5NH_{3(g)} + 1.5\ H_2O$$

$$\Delta H_{100\ C} = -140\ \text{K cal/gm mol}$$

Average unoxidized Zircaloy dissolution rates are from 10 to 15 mils/hr for the optimum charge solution of 5.5 $\underline{M}$ NH_4F - 0.5 $\underline{M}$ NH_4NO_3 at a F/Zr mole ratio of 7. Zircaloy which is oxidized by exposure to high temperature air or water dissolves at rates of three to fivefold less. This is because of the pitting and undercutting attack necessary to penetrate the highly resistant oxide film. Thus, while the time for decladding a typical 30-40 mil unoxidized element is from three to four hours, the removal of an oxidized Zircaloy cladding may require up to twelve hours.

During the Zirflex reaction, hydrogen and ammonia are produced at rates of about 0.1 and 5.0 moles per mole of zirconium dissolved, respectively. The ammonia must be removed from the dissolvent to prevent a decrease in dissolution rate and a lowering of the zirconium solubility. A high boil-up rate with high condenser temperature or a steam sparge without reflux is effective in removing the ammonia. Subsequent air or steam dilution of the off-gases to less than four per cent hydrogen and 16 per cent ammonia in dry air is required to avoid explosive mixtures.

Cores of uranium, uranium-aluminum, and uranium dioxide are not severely attacked by the Zirflex decladding solutions. However, a small amount of core material does dissolve, saturate the dissolvent, and precipitate the excess as UF_4. The solubility of the UF_4 decreases as fluoride is complexed with zirconium and as the solution cools. Hence, the majority of the dissolved uranium is precipitated in the terminal solution. It then is recovered by centrifugation and returned to the dissolver for the subsequent core dissolution. As a result, only the soluble uranium enters the waste; with losses varying from 0.3 to 3.0 grams per liter. Larger losses occur when there is significant oxidation of uranium IV to uranium VI. These losses may be minimized by not air sparging the solution and by centrifuging immediately after cooling.

The Zirflex waste solution is neutralized to a pH of 10 before storage. This requires approximately 0.07 gallon of 50 per cent caustic per gallon of decladding solution. The neutralized waste consists of nearly 20 volume per cent of rapidly settling solids which are easily slurried under turbulent flow conditions. These solids tend to settle out in streamline flow and therefore agitation is required during temporary storage.

Conventional nitric acid core dissolution is generally applicable to Zircaloy-clad uranium and UO_2 elements since the core material is essentially free from zirconium. The addition of aluminum nitrate to the nitric acid dissolvent to an Al/residual F^- mole ratio of approximately three is necessary, however, to inhibit the corrosive action of residual fluoride.

Stainless steel can be used as the material of construction for the Zirflex dissolver equipment because of the dissolvent's comparatively mild corrosive action. A corrosion rate of 11 mils/month was determined using 304L stainless steel exposed to boiling 6 M ammonium fluoride. However, an average corrosion rate of only 4.3 mils/month was encountered in the pilot plant unit during cyclic tests.

III. THEORY AND REVIEW

The reaction of zirconium and Zircaloy with aqueous ammonium fluoride has been well established through laboratory studies.(1)(2) The reaction takes place with the evolution of hydrogen and ammonia gas according to the following equation:

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

The addition of ammonium nitrate to the solution was shown to depress hydrogen evolution and, in the case of Zircaloy, to facilitate the dissolution of tin which is present in the amount of 1.5 per cent. The modified reaction is as follows:

$$Zr_{(s)} + 6\ NH_4F + 0.5\ NH_4NO_3 \longrightarrow (NH_4)_2ZrF_6 + 5\ NH_{3(g)} + 1.5\ H_2O$$

The obvious benefits accruing from the modified reaction led to its intensive study at Hanford.

The Zirflex reaction proceeds with a pseudo first order dependence on "free" fluoride concentration (i.e. fluoride not complexed with zirconium) when the ammonia evolved during the reaction is adequately removed to the off-gases. Laboratory studies by Carroll(3) indicate that the true reaction is more nearly second order with "free" fluoride and one-half order with hydrogen ion. The pseudo first order reaction has been used, however, to satisfactorily describe the engineering behavior of the Zirflex dissolution over the normal operating range. The derivation of first order kinetic equations for the system are given in Appendix I.

The solubility of ammonium hexafluozirconate $\left[(NH_4)_2ZrF_6)\right]$ complex formed during the Zirflex dissolution depends on the free fluoride concentration, ammonium ion concentration, and temperature. Solubility data, reported by Swanson,(2) for optimum dissolvent conditions (ammonia formed during the reaction adequately removed to provide slightly acid solution of pH 6-7) are plotted in Figure 1. Zirconium solubility is shown to decrease with increased free fluoride concentration and lowered temperature. The following solubility expression shows the relative effect of ammonium ion.(4)

$$\text{Zr soluble} = 1.8\ (\underline{M}\ NH_4^+)^{-3}(\underline{M}\ F^-\ \text{free})^{-1}$$

The equation is valid at room temperature under optimum conditions in the range of from 0.3 to 1.3 molar free fluoride. When ammonia evolved during reaction was allowed to build up in the dissolver, a decrease in zirconium solubility proportional to the ammonium hydroxide formed was noted. In a 22 C solution at 0.5 $\underline{M}$ NH_4F, 0.5 $\underline{M}$ $(NH_4)_2ZrF_6$, for a range of from 0.0 to 0.6 $\underline{M}$ NH_4OH, the decrease is represented approximately by the expression:(4)

$$(\Delta\underline{M}\ \text{Zr}) = 0.65\ (\underline{M}\ NH_4OH - 0.05)$$

Although the above expressions are for specific ranges on the solubility curve, qualitatively they are indicative of the over-all ammonia effect.

A passive film of zirconium oxide is encountered on essentially all Zircaloy-clad elements exposed to water or oxygen at high temperatures. The film dissolves quite slowly or not at all in Zirflex solutions. However, it is penetrated in localized areas and subsequent pitting and undercutting occur on the exposed unoxidized Zircaloy. Before penetration there is an induction period which varies from a few minutes to one-half an hour. Its duration depends on the condition of the oxide and the geometry of the

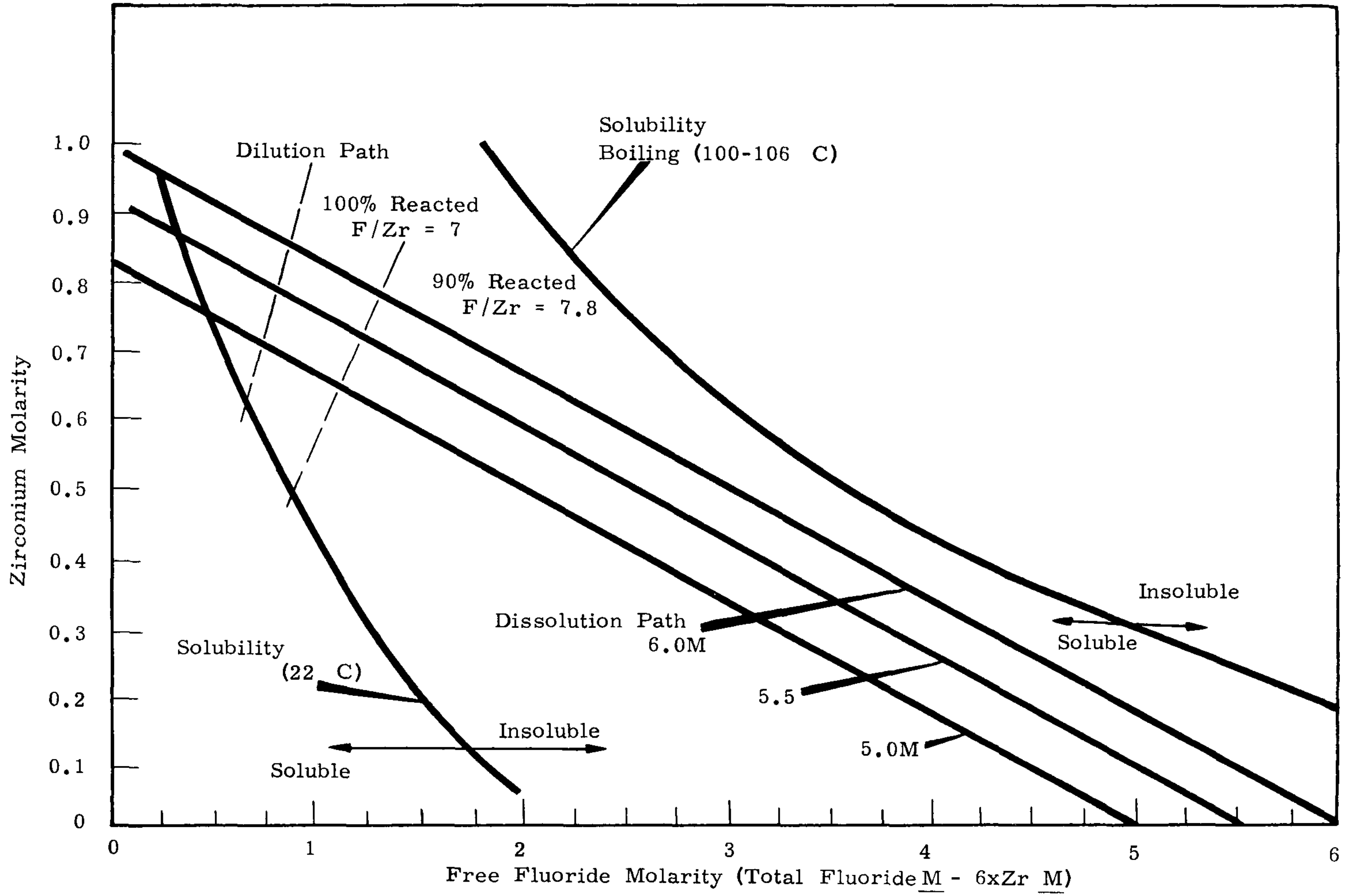


FIGURE 1

Solubility of Zirconium in Ammonium Fluoride Solutions element. Attack occurs first at corners, sharp edges, and surface imperfections. After penetration the reaction proceeds with the regular Zirflex stoichiometry, however the kinetics are completely masked.

IV. DESCRIPTION OF APPARATUS

Preliminary Zirflex studies were made by Cooley(5) with the batch dissolver equipment arranged as shown in Figure 2. A 40-liter, steam-jacketed, stainless-steel vessel was connected through a three-inch ID packed tower to a tubular condenser. Condensate was returned through the tower to the dissolver or was diverted to a separate condensate collector. The off-gases from the condenser passed through a rotameter into a three-inch glass tower containing bubble cap trays for ammonia absorption. Liquid sample ports were provided on the dissolver pot, condensate reflux line, condensate collection vessel, and acid scrub reservoir. Off-gas was sampled from a port just upstream from the absorption tower.

A minimum of instrumentation was used during the preliminary studies. Liquid and gas flows were measured by rotameters and the dissolver vacuum was indicated by Magnehelic gages. To trace the weight change of the metal charge, a stainless steel basket was suspended in the dissolver. The basket hung from a converted, differential pressure transmitter which, in turn, was connected to a pneumatic recorder. Inherent errors in this device due to off-gas buoyancy and density variations did not prevent reasonably accurate records of the dissolution.

Later Zirflex studies by the author utilized a vertical tube recirculating dissolver constructed of Hastelloy F and Nionel (Figure 3). The bottom of a dissolver tube, 7.5-inch ID and 15 feet high, was connected to a 9-inch ID by an 8-foot high steam-jacketed reservoir tube through a 4-inch pipe. The dissolver tube overflow (at the 10.5-foot level) was connected to a disengaging box, approximately 2 feet by 3 feet by 2-1/2 feet high, attached to the top of the reservoir tube. A plate separated the disengaging box into two sections; it contained several orifices for liquid flow measurement and an opening at the top for off-gas passage. Two liquid sample ports were located on the reservoir tube. The reservoir-to-dissolver volume ratio for the unit was 1.5.

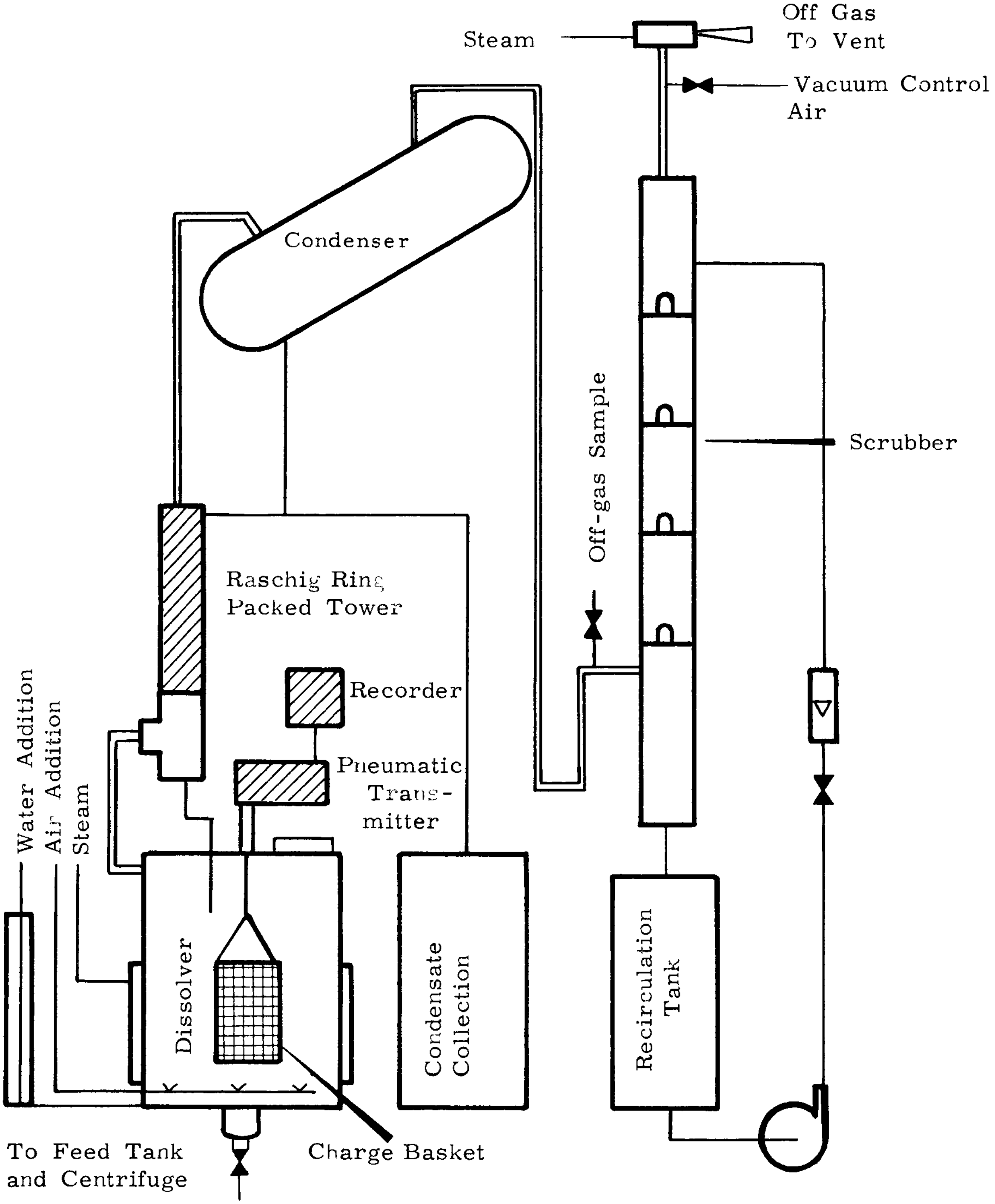


FIGURE 2

Zirflex Batch Pilot Plant Equipment

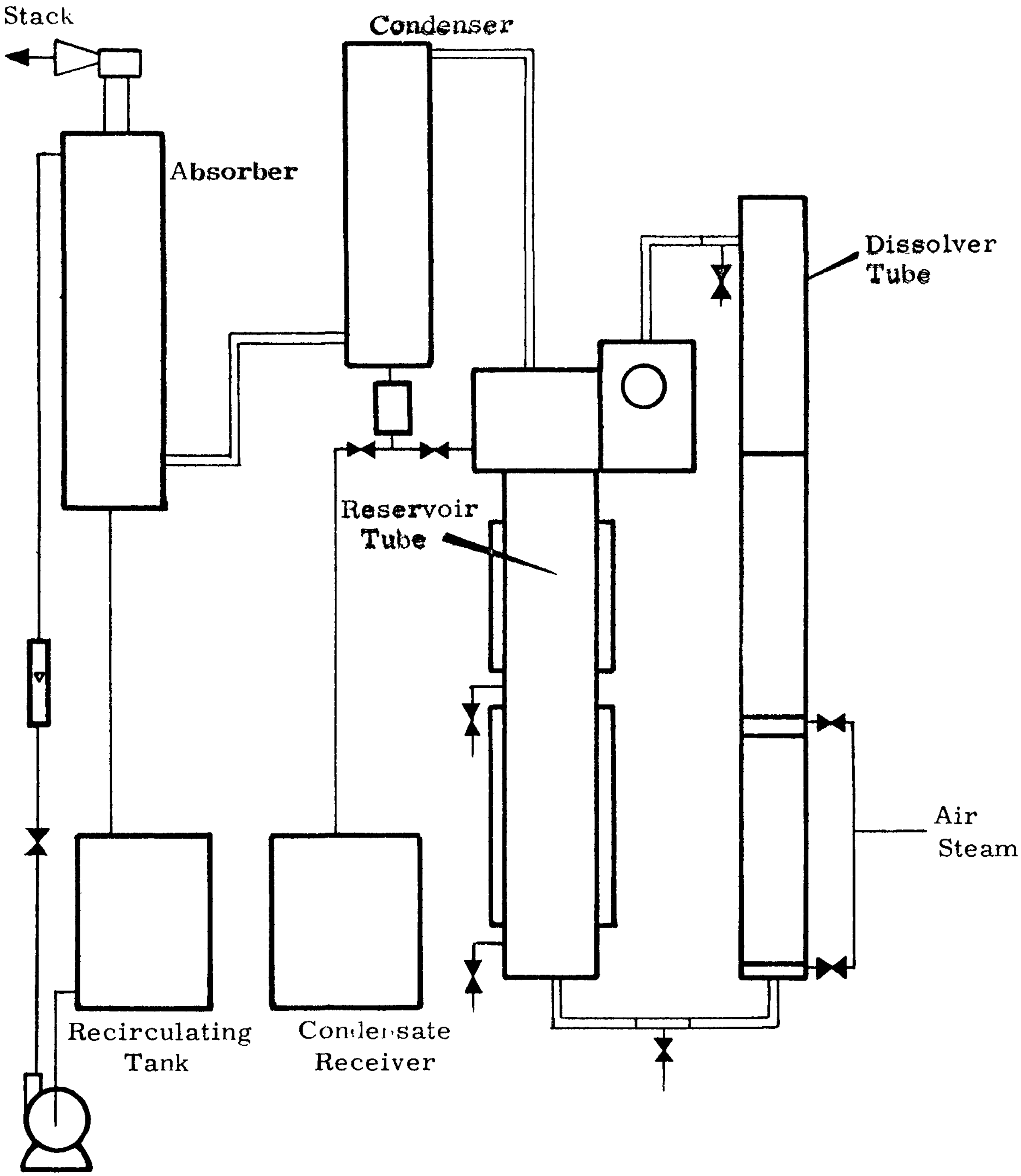


FIGURE 3

Schematic Diagram of Pilot Vertical Tube Dissolver

The Hastelloy F condenser consisted of a 10-foot high 6-inch ID, jacketed tube with a 4 1/4-inch OD cooling finger inside. This condenser and a 10-foot high, 8-inch ID stainless steel scrubbing tower containing one-inch raschig rings were connected in series to the dissolver disengaging box. Condensate was returned through a glass reflux meter to the dissolver or diverted to a stainless steel catch tank. An auxiliary stainless steel tank and pump were connected to the scrubbing tower for recirculation of scrub solution. Off-gas flow through the system was provided by an off-gas jet discharging to a stack.

To dilute off-gases, an air purge was provided on the dissolver; air and steam sparging for agitation and gas lift motivation also was included. Two sparge rings were attached to the dissolver tube, one at the bottom and the other three feet higher. Electrically preheated steam or air was supplied to the rings through Nionel pipe. Air for sparging the reservoir was supplied through a Teflon dip tube. Dilution air was supplied through a bleed line to the top of the dissolver.

Operating variables were measured and recorded by conventional industrial instruments. Dissolvent specific gravity and liquid level were indicated by dip tubes connected to the pneumatic transmitter and recorder units. The same technique was used to measure liquid levels in the reflux meter and disengaging box; where flow rates were determined from the liquid height above an orifice. Pneumatic instruments were also used to record pressure drop across off-gas flow orifices and to control the steam supply to the off-gas jet. Temperatures were measured by thermocouples and recorded on a 12-point recorder. Air and steam for gas lift motivation were metered by a rotameter equipped with a pressure gage on the downstream side. A similar system was used to measure dilution air flow.

V. PROCEDURE

Several operating procedures were used by Cooley(5) in the preliminary Zirflex studies. They differed only in the method of ammonia removal and may be described as follows:

1. Charge Zircaloy metal to the weigh basket and calculated amount of dissolvent to the dissolver.
2. Heat to boiling.
3. Provide adequate ammonia removal from dissolvent by:
    a. distillation with condensate returned to the dissolver from a cool condenser,
    b. distillation with condensate returned through a hot condenser,
    c. distillation with high air dilution of off-gases and condensate returned to dissolver, or
    d. distillation with condensate routed to separate vessel.
4. Add makeup water to maintain liquid level, replacing the ammonia and water removed.
5. Add dilution water just prior to shutdown to prevent precipitation of ammonium hexafluozirconate after cooling.
6. Shut off steam and cool the dissolver.

The dissolution was followed by weighing because of the precipitation problems during the scouting runs. A liquid sample was taken at the end to determine terminal concentrations. Off-gas samples were taken during the runs to verify laboratory data on hydrogen and ammonia in the off-gas.

In the later batch runs made in the tubular dissolver, the same general procedure was followed. Method 3-d (distillation with condensate routed to a separate vessel) was used for ammonia removal. Since charge conditions were well established by earlier work, precipitation was not a major problem and liquid samples were used to follow the dissolution.

Analyses of ammonium, zirconium, and fluoride concentrations and pH were made. The condensate was sampled for ammonia, however off-gas samples were not collected.

When recirculating dissolutions were emphasized in later pilot plant work, the operating procedure was complicated by the mechanics of motivating the dissolvent. The run procedure was as follows:

1. Charge Zircaloy metal and calculated amount of dissolvent to the dissolver.
2. Establish circulation using air supplied to the bottom sparge ring.
3. Heat dissolver to boiling.
4. Adjust boil-off and recirculation rates to desired values.
    a. For air sparge runs, steam jacket pressure and air rate were balanced.
    b. For steam sparge runs, the steam jacket and air sparge were turned off and the steam sparge on. Boil-off rate was equal to steam sparge rate for slightly superheated steam. Either the boil-off or recirculation rate could be set (not both).
5. Maintain liquid level with water addition during the air-sparged runs. (This step unnecessary during steam sparging).
6. Add dilution water just prior to shutdown to prevent zirconium precipitation in the cooled solution.
7. Shut off sparger and heating steam simultaneously (Sparger only for steam sparge run).

The sampling procedure for the recirculating runs was the same as for the batch runs made in the same unit. Although samples were taken from the reservoir tube, the turnover time was sufficiently fast so that they were representative of the dissolver solution.

In addition to sampling, a conductivity probe was used in several of the recirculating runs. The probe was placed in the reservoir where the temperature was essentially constant and dissolvent flow was relatively slow. The end point of the reaction was easily determined by the leveling of the resistance readings recorded on a circular chart. Accurate and continuous reading of dissolvent concentration is required throughout the Zirflex dissolutions. To provide these, laboratory tests have been performed by Hahn(6) with some assistance from the author. The results are given in Appendix 2.

Operation of the gas lift during recirculating dissolutions was similar to that during test runs on a water system. The charges of Zircaloy tubing or rods of Zircaloy-clad uranium dioxide offered no appreciable resistance to flow. Uranium dioxide released from the rods during decladding was evidently fluidized as it was exposed since no pressure drop due to the formation of a packed bed was apparent. Data from test runs on a water system containing no solids and with air for motivation are plotted in Figure 4. These data essentially represent the operation of the recirculating dissolver during a Zirflex dissolution; however, a slightly higher circulation is attained during dissolution because of off-gas evolution.

The recirculation rate with steam motivation was somewhat less than with air. However, adequate flow was attained with the steam sparge, particularly at high submergence. Submergence is defined as the height of liquid in the reservoir above the gas inlet level. It is generally expressed as a percentage of the vertical distance between the gas inlet and the overflow point. The degree of superheat of the steam did not affect the recirculation rate appreciably indicating that most of the superheat was released as soon as the steam contacted dissolvent. Slightly superheated steam was required to provide acceptable dissolvent flow, however. Two pounds per minute, or 30 cubic feet per minute, of steam provided a recirculation rate of eight gallons per minute at 70 per cent submergence and 25 gallons per minute at 80 per cent submergence.

VI. DISCUSSION

The majority of the preliminary Zirflex runs by C. R. Cooley were scouting studies to determine operating procedures, charge ratios, and dilution water requirements for the process. Later runs were made by the author to gather refined data using optimum operating procedures and also to demonstrate the Zirflex process in a recirculating dissolver. Final demonstration runs involved the decladding and dissolution of PRTR 19-rod clusters (uranium dioxide clad in oxidized Zircaloy). The results of pilot plant runs are given in Table I and Table II in Appendix III. Decladding and core dissolution flowsheets are shown in Figures 13 and 14 in Appendix IV.

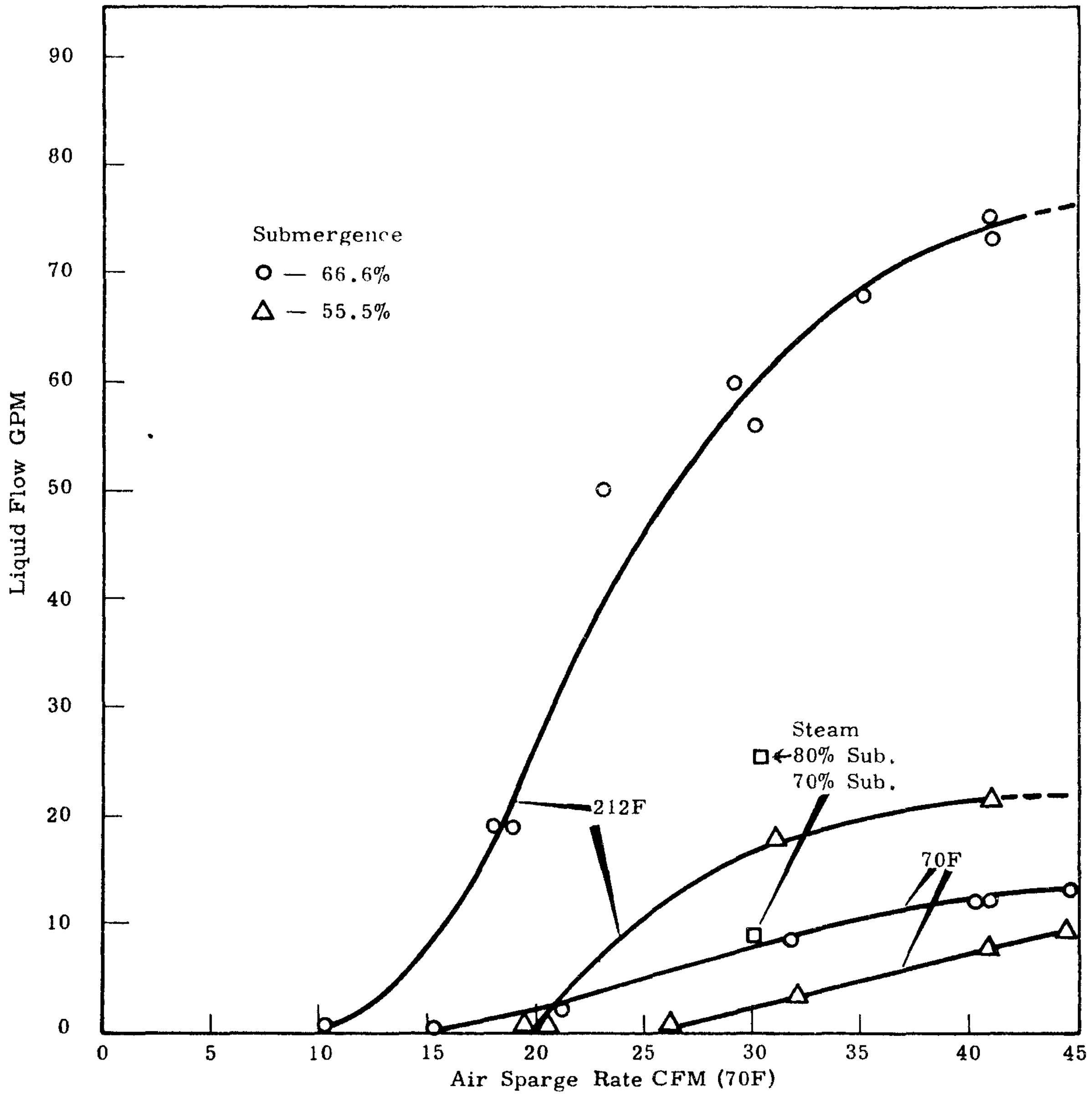


FIGURE 4

Effect of Submergence and Liquid Temperature on Air Lift Performance in a Water System

DISSOLUTION

The dissolution of unoxidized Zircaloy depends primarily on the concentration of "free" fluoride (fluoride not complexed with zirconium) in the solution. In Figure 5, dissolution rates from pilot plant runs and laboratory studies are shown as a function of free fluoride concentration. Dissolution rates under laboratory conditions(2) ranged from 75 mils/hr at 5.5 M free fluoride to 8 mils/hr at 0.8 M fluoride. Under optimum pilot plant conditions, the dissolution rates closely approximate the laboratory results. However, peak rates are lower due to depletion of fluoride by the slow reaction during heat-up. Peak rates for an easily heated batch dissolver charged with 5.5 M free fluoride (run RZA-5) were as high as 65 mils/hr; for a recirculating dissolver (run RZA-11), peak rates were somewhat less (43 mils/hr). Integrated rates in the pilot plant dissolver ranged from 10 to 15 mils/hr on the unoxidized metal. The reporting of dissolution rates as penetration rates is valid in the case of unoxidized Zircaloy because of the exceptionally uniform attack on the metal.

The inadequate removal of ammonia from the dissolvent during Zirflex dissolutions results in a slowing of the reaction rate. Ammonium hydroxide is formed as ammonia accumulates in the dissolvent causing a rise in pH and a lowering of the boiling point. According to Swanson,(2) the dissolution rates are reduced by a factor of four for a pH change of from 5.5 to 8.8. This factor includes the effect of boiling point change, which could vary as much as 10 C.

The combination of a high pH and lowered boiling point affects dissolution rate by lowering the solubility of zirconium complexes in the dissolvent. When the solubility is exceeded, precipitate forms on the reacting surfaces in sufficient quantity to mask the metal from attack. A quantitative measure of the decrease in dissolution rates due to this effect has not been made. In general, it is not desirable to operate under these conditions; the majority of the pilot plant studies were directed toward avoiding them.

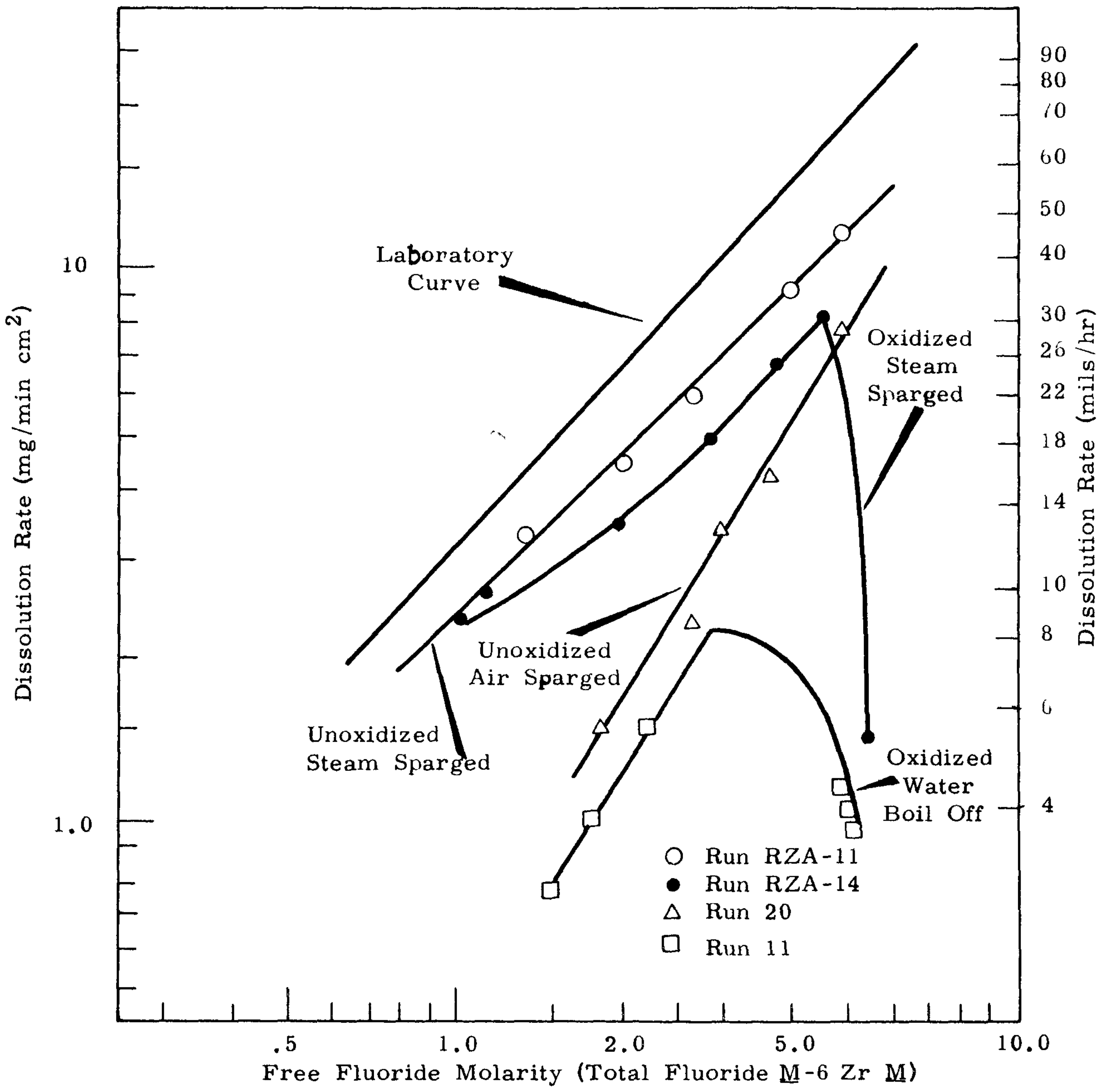


FIGURE 5

Zircaloy Dissolution Rates in Boiling Ammonium Fluoride

The passive zirconium oxide film on Zircaloy-clad fuel elements has a major retarding effect on the dissolution rate in Zirflex dissolvent. It decreases the active surface area and causes a reduction of a factor of three to five in the average dissolution rate below that of unoxidized material; thus, the dissolution time is increased to approximately 12 hours for a heavily oxidized element. The data in Table III illustrate the variation in operating time for the dissolution of oxidized Zircaloy as opposed to a normal three-hour period for 30 mil unoxidized cladding. Dissolvent with an initial concentration of 5.5 $\underline{M}$ NH_4F - 0.5 $\underline{M}$ NH_4NO_3 and a mole charge ratio of seven was used in each run.

The variations in dissolution time give some indication of the tenacity of the oxide film on the cladding. The oxidation occurring under different conditions is shown in Figure 6 to provide a qualitative indication of film condition.

End plugs and other massive Zircaloy were totally dissolved while processing the cladding of PRTR 19-rod clusters in runs RZA-14 and 15. The elements had been oxidized in a steam autoclave for 72 hours at 400 C and 1150 psig. This indicates that once the massive Zircaloy is attacked, the active area increases rapidly and continuously to total dissolution; with cladding, penetration takes place rapidly into the core and then a new surface area must be exposed to continue dissolution. Data from bench scale runs made to illustrate this effect are shown in Table IV. Tubing and massive Zircaloy oxidized by the same method as the PRTR elements were dissolved in 5.5 $\underline{M}$ NH_4F - 0.5 $\underline{M}$ NH_4NO_3 at a F/Zr mole charge ratio of seven. The data show that essentially all of the massive Zircaloy dissolves with the cladding; the same was true in pilot plant runs.

TABLE III

PILOT PLANT DISSOLUTION OF OXIDIZED ZIRCALOY

Run No.	Charge	Temp	Oxidation Medium	Time, Days	Dissolution Time, Hrs	Per Cent Dissolved
11	0.030 in. sheet	400 C	Air	14	6.5	95
38	"	400 C	Air	14	4.0	100
43	"	400 C	Air	14	5.8	93
40	Sealed tubes 0.030 in. walls with UO_2 Cores	400 C	Air	14	10.5	95
41*	"	400 C	Air	14	11.0	99
RZA-14	PRTR Rods 0.033 in. walls with UO_2 Cores	400 C	Steam	3	6.0	100
RZA-15	"	400 C	Steam	3	6.0	100
Beaker Scale Tests	Coupons 0.03 in. thick	360 C	Deionized Water	308	12.0	78
					12.0	85
					12.0	96

* Half of the charge was unoxidized Zircaloy.

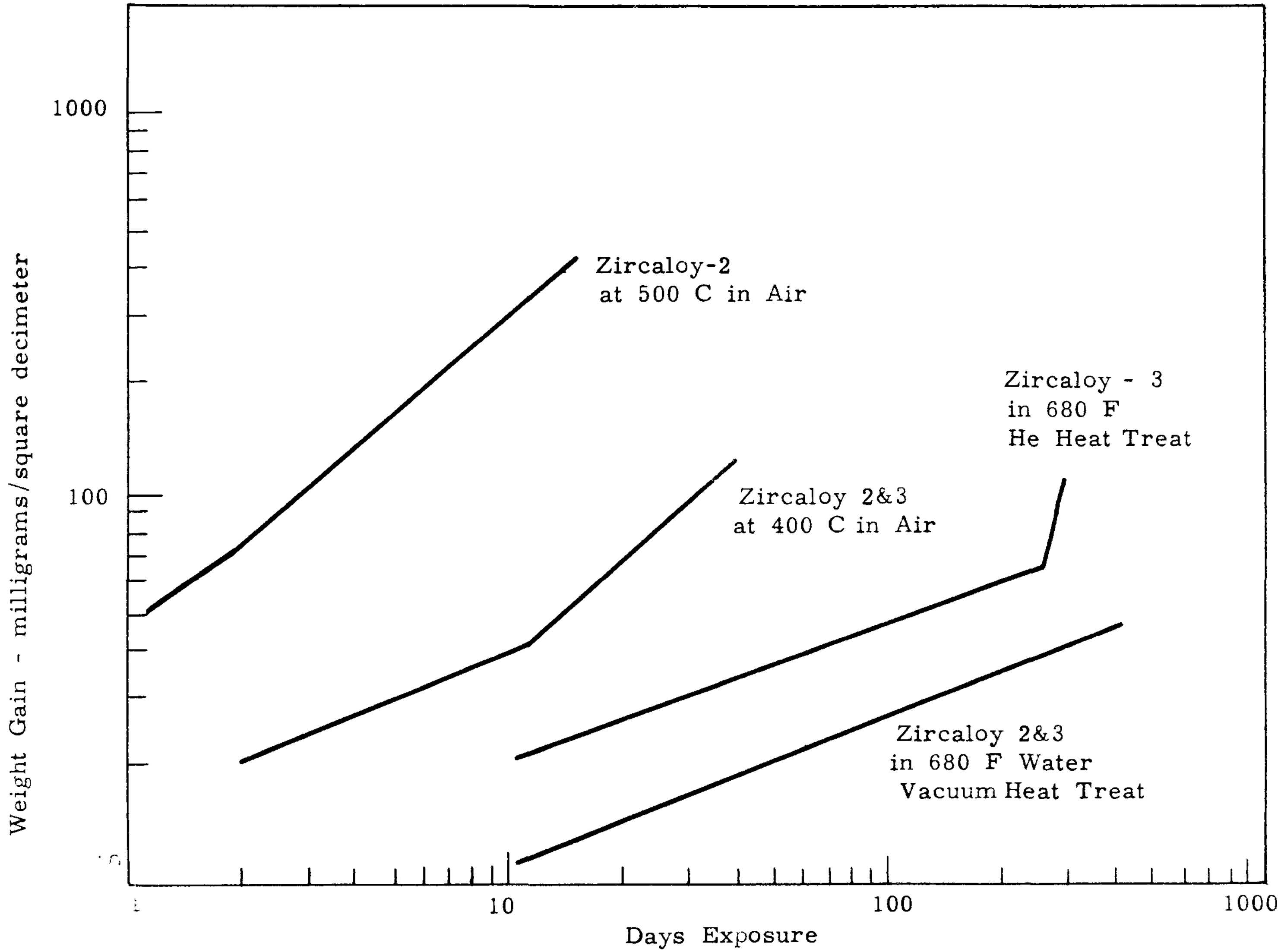


FIGURE 6

Oxidation of Zircaloy

TABLE IV

SIMULTANEOUS LABORATORY SCALE DISSOLUTION OF OXIDIZED ZIRCALOY CLADDING AND MASSIVES

	Zircaloy Tubing			Massive Zircaloy			
	Geometry (Inches)	Weight Charged	(Grams) Final	Geometry (Inches)	Weight Charged	(Grams) Final	Dissolution Time, Hrs
1.	33 mil, 0.75 OD, 5.625 L tubing	43.6	0	0.485 D-0.506 L End plugs (2)	19.6	0.07	4.75
2.	33 mil, 0.75 OD, 5.648 L tubing	43.7	0.1	0.486 D-0.501 L End plugs (2)	19.9	0.7	4.58
3.	35 mil, 0.75 OD, 7 L tubing	55.5	1.2	0.827 x 0.957 x 0.226 plate	19.0	3.3	3.25
4.	35 mil, 0.75 OD, 7 L tubing	57.7	3.4	0.827 x 0.957 x 0.226 plate	19.4	0.5	4.00

* The remainder of the plates from Experiment 3 (oxide removed) were dissolved with the oxidized Zircaloy in Experiment 4.

The heat of reaction for the Zirflex dissolution was estimated during batch run RZA-6 in the tubular dissolver reservoir. A closely controlled heat balance was effected throughout the reaction. The net heat output attributed to the reaction was approximately 140 K cal/gm mol zirconium indicating a comparatively exothermic reaction. The heat balance data verified an earlier estimate (ΔH_{25C} = -178 K cal/gm mol zirconium) from a theoretical calculation by Fisher.(7)

SOLUTION CONCENTRATION AND VOLUME

The solution concentrations and volumes used in Zirflex decladding depend on several variables which may be balanced to provide an optimum flowsheet for a given set of conditions. Considerations include the dissolution time cycle, maximum allowable off-gas rates, solubility of ammonium fluozirconate, core losses to the dissolvent, and solution volume necessary to cover the elements. The variables which may be balanced to provide the optimum flowsheet are the fluoride/zirconium mole charge ratio and the charge concentrations of ammonium fluoride and ammonium nitrate. The paths at near-optimum flowsheet conditions for Non-Production Fuel dissolutions of 5.5 $\underline{M}$ NH_4F, 0.5 $\underline{M}$ NH_4NO_3 and a fluoride/zirconium mole charge ratio of seven are shown in Figure 1 with solubility curves for Zircaloy.

The minimum fluoride/zirconium mole charge ratio for complete dissolution of the Zircaloy cladding is six, since each mole of zirconium dissolved complexes six moles of fluoride. However, to achieve practical dissolution rates near the end of the reaction, a mole charge ratio of at least 6.5 to 7 was required. The use of a charge ratio higher than seven increased dissolution rates. Unfortunately, it also raised the dilution water requirements necessary to maintain the solubility of ammonium fluozirconate complex in the cooled dissolvent. Because core losses to the dissolvent are directly dependent on uranium solubility, and hence on total solution volume, a fluoride/zirconium ratio of greater than seven is not desirable. Nevertheless, higher charge ratios may be used in special dissolutions tailored for specific fuels.

The charge concentration of ammonium fluoride in the dissolvent is established as high as possible since the dissolution rates increase with fluoride concentration. It is limited by the solubility of ammonium fluozirconate, however, as is shown in Figure 1. The dissolution path must be below the bow in the solubility curve in order to avoid precipitation. Since ammonia buildup in the dissolver would lower the solubility curve, a concentration of 5.5 M fluoride was selected as optimum. The starting ammonium fluoride concentration is not limited by the high off-gas rates associated with high dissolution rates since methods of handling the off-gas have been concurrently developed.

The ammonium nitrate charge concentration was established from laboratory data by Swanson(2) and confirmed in the pilot plant. It was determined that a 0.5 M ammonium nitrate concentration was adequate to limit hydrogen evolution to less than 0.1 mole/mole of zirconium dissolved and minimize tin residues in the dissolvent. Raising the concentration above 0.5 M had little effect on either the hydrogen evolution or tin dissolution; however, it definitely had a bad effect on solubility because of the extra ammonium ion in the solution. If the charge concentration of ammonium fluoride is changed, the ammonium nitrate concentration may be changed proportionally without reducing its effectiveness. In general, a nitrate/zirconium mole charge ratio of 0.67 is adequate. Consumption of ammonium nitrate in pilot plant runs was approximately 0.47 moles/mole of zirconium dissolved, leaving a terminal nitrate concentration in the dissolvent of 0.08 M.

With solution concentration and charge ratio fixed, the total volume of dissolvent required for a given dissolution depends on the amount of Zircaloy that is to be dissolved. In the calculation of volume the condition of the cladding and massive Zircaloy pieces involved must be considered. For unoxidized Zircaloy, the volume of solution charged must be based on the expected penetration during decladding. Massive Zircaloy, such as end plugs and hangers, would lose only 30 mils during the decladding of a 30 mil clad rod. For oxidized Zircaloy-clad elements, which almost exclusively will be encountered in power reactor fuel decladdings, the volume must be based on the total weight of Zircaloy charged since almost complete dissolution of the massive zirconium is attained.

Final volumes must be such that when the solution is cooled to room temperature the solubility of ammonium fluozirconate is not exceeded. For a normal run at the optimum flowsheet conditions, the final concentration of zirconium and free fluoride should be about 0.6 $\underline{M}$ each. This is accomplished by diluting the terminal solution to 131 per cent of the original volume. No precipitation problems were apparent in the pilot plant unit using this dilution, even with the rather unpredictable dissolutions of oxidized elements. However, dilutions of up to 150 to 200 per cent may be justified in an operating plant in certain cases; for example, where excess ammonium fluoride is charged to insure element dissolution when cladding weight is uncertain. The volume of solution during dissolution at optimum charge conditions is approximately 1.67 gallons/pound of zirconium. After dilution to 131 per cent, the coating waste is 2.2 gallons/pound of zirconium.

OFF-GASES

The hydrogen and ammonia gases evolved during the Zirflex dissolution are potentially explosive in air. For this reason, hydrogen must be held to less than four per cent in the off-gas; an ammonia concentration of from 15 - 28 per cent in dry air must be avoided.(8) Air dilution, the most straight-forward method of controlling off-gas concentrations, has been used successfully in pilot plant operations. As an alternative, inert gas dilution may be used when the off-gas capacity is limited.

The volume of hydrogen in the off-gas depends only on the Zircaloy dissolution rate. Pilot plant data indicate that hydrogen is evolved at approximately 0.025 to 0.03 moles/mole of Zircaloy dissolved when the mole charge ratio of ammonium nitrate to Zircaloy is 0.67 or greater. Laboratory measurements(2) show that hydrogen is less than 0.1 mile/mole of Zircaloy dissolved; this figure may be used to calculate conservative dilution air requirements. The peak rate of hydrogen evolution from one square foot of unoxidized Zircaloy surface in 5.5 $\underline{M}$ NH_4F - 0.5 $\underline{M}$ NH_4NO_3

would be 0.016 standard cubic feet/minute. Dilution air at 0.38 standard cubic feet/minute would be required to limit the hydrogen to four per cent in the off-gas.

The amount of ammonia in the off-gas is dependent not only on the dissolution rate of Zircaloy, but also in the method used to release it from the Zirflex solution. Maximum removal of the highly solvent ammonia from the dissolvent is desirable due to its detrimental effect on dissolution rate and zirconium solubility. Several distillation methods were attempted to accomplish this removal.

The boiling off of water and ammonia vapor with the condenser reflux returning to the dissolver pot was proven feasible for a batch dissolver with adequate heat transfer surface. Figure 7 shows the ammonia removal rate versus dissolvent ammonia concentration with boil-up and air rates as parameters. The curves indicate that high boil-up rates or high condenser temperatures are necessary to keep ammonia concentration in the dissolvent at a low level. Therefore, the logical alternatives in the case of inadequate heat transfer surface are to (a) operate with a hot condenser and allow the ammonia water mixture to escape to the stack or (b) condense the vapor and remove it to a separate vessel. In either event, make-up water must be added to the dissolvent.

The use of an air sparge in a batch or recirculating dissolver had little effect on ammonia removal. In operation it performed similar to the steam distillation of an organic solution. That is, it provided a partial pressure on the system which reduced the boiling temperature of the dissolvent. The heating requirements for ammonia removal with an air sparge were essentially the same as for the water and ammonia boil off.

The best method of removing ammonia from dissolvent in the pilot plant recirculating tubular dissolver was a steam sparge. Steam was used both as a heating medium and a motivating force for circulation. The dissolver solution was first heated to boiling by a steam jacket with recirculation by air sparge. Then, the steam sparge was turned on and the jacket steam and air sparge off. Two pounds per minute of steam (100 psig throttled

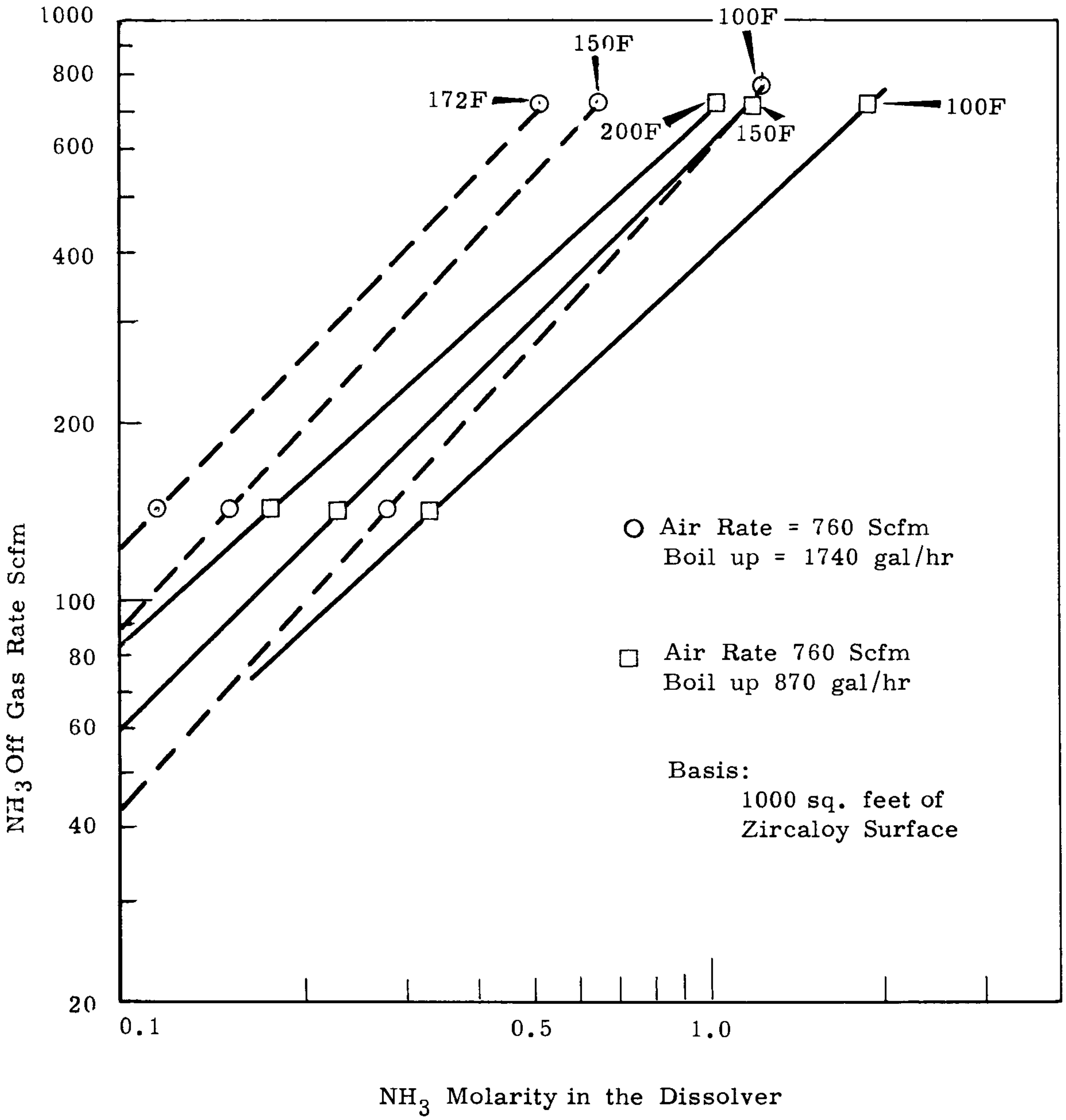


FIGURE 7

Effect of Air Rate, Boil Up Rate and Condenser Temperature on NH_3 Concentration in the Dissolver to 4 psig) were sufficient to provide dissolvent circulation and to hold the solution at boiling. The boil-up rate was equal to the steam input rate and the dissolvent volume thus remained constant. Ammonia removal was equivalent to water boil-off, indicating that the steam stripping action was quite efficient. The steam sparge method is generally applicable to batch dissolvers as well, although no pilot plant tests were made to illustrate this.

Air dilution for ammonia may be determined from kinetic data for the reaction combined with boil-off calculations using equilibrium data on the relative volatility of ammonia and water over the Zirflex dissolvent. A vapor-liquid equlibrium diagram for the Zirflex system, contributed by Carroll,(3) is presented in Figure 8. Table II gives the maximum ammonia off-gas rates and other operating data for the runs made in the tubular dissolver. In general, air dilution is not required unless the vapors are condensed since ammonia is only 10 to 15 per cent of the total boil-off volume.

CORE LOSSES

Uranium losses to the Zirflex decladding solution depend primarily on the fuel core solubility. This, in turn, is governed by the uranium valence state and terminal free fluoride concentration. The solubility of uranium IV and uranium VI as a function of free fluoride is illustrated in Figure 9.(2) It is apparent that uranium IV solubility decreases with decreasing free fluoride concentration while uranium VI solubility increases. In addition, the solubility of uranium IV decreases even further when the solution is cooled.

Initially, the uranium in the decladding solution is almost exclusively quatrevalent. This is due to the charge valence state (UO_2 or uranium metal) and to the reducing properties of the Zirflex reaction. If the solution is allowed to stand after dissolution, the uranium IV tends to oxidize to uranium VI which is considerably more soluble. The rate of oxidation may be estimated from the graph in Figure 10,(9) which shows the oxidation rate-constant plotted versus pH with free fluoride concentrations as

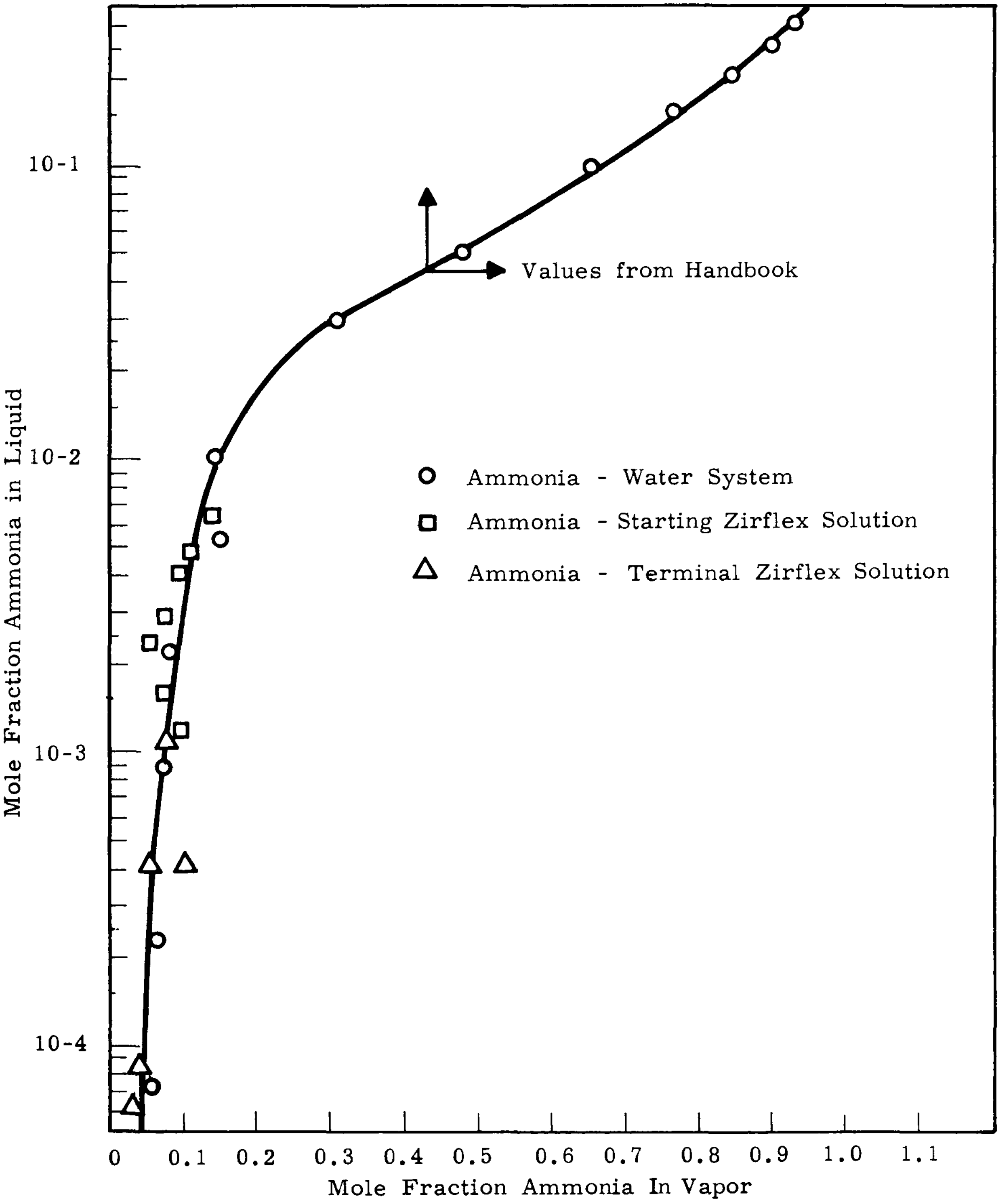
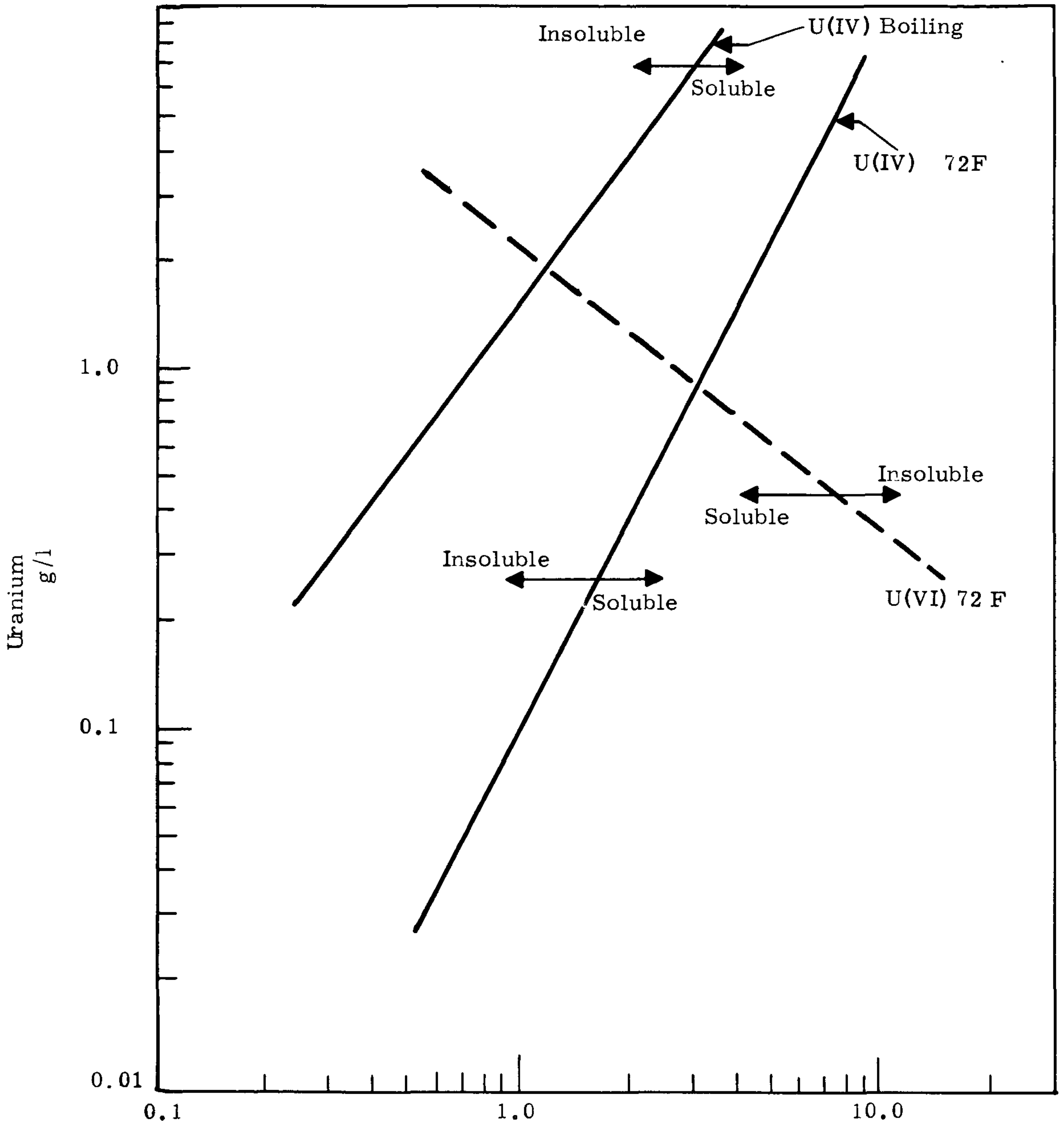


FIGURE 8

Liquid Vapor Equilibrium for Ammonia in Zirflex Solution



Free Fluoride Concentration, g-moles/liter
Free Fluoride M = Total Fluoride M - 6 (Zirconium M)

FIGURE 9

Solubility of Uranium in Zirflex Solutions

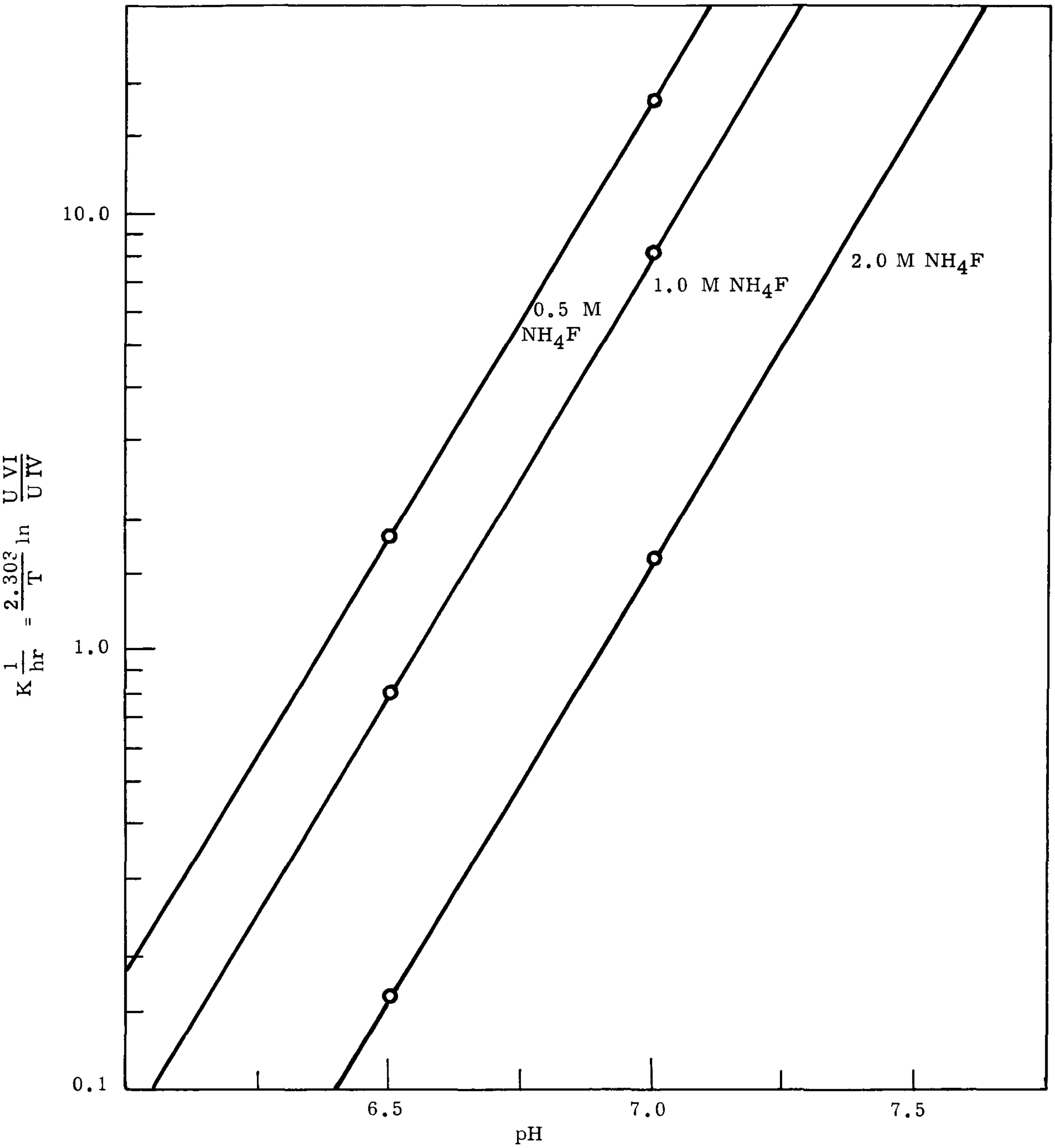


FIGURE 10

Maximum Oxidation Rate of Uranium IV to Uranium VI in Zirflex Decladding Waste parameters. More than enough uranium IV is available for oxidation from UF_4 precipitated during the dissolution to exceed uranium VI solubility.

Because of the continuous reaction of exposed uranium or uranium dioxide cores with the decladding solution and the low solubility of uranium IV at the terminal conditions, uranium fluoride is precipitated during decladding. This precipitate is recovered along with UO_2 or uranium fines by centrifugation. In the pilot plant, if a cooling and settling period were allowed in the dissolver, only a small percentage of the precipitate and fines were carried into the centrifuge. The particles that did reach the centrifuge were completely removed from the solution by a force of 85 g's with a residence time of approximately three minutes. The resulting centrifugate was easily returned to the dissolver as a slurry for processing with the core.

Since the uranium losses are solubility, or concentration controlled, the percentage losses are a function of the total decladding solution volume and, hence, the ratio of zirconium to uranium in the fuel elements. At large zirconium-to-uranium ratios, the decladding solution volume required per pound of uranium is high, resulting in a high percentage uranium loss. The effect of the ratio on percentage losses is shown in Figure 11; here, the loss in grams/liter is plotted versus per cent loss with zirconium-to-uranium ratio as a parameter. The expected loss range for typical power fuels is crosshatched on the graph.

Uranium losses to the decladding solutions were measured during pilot unit dissolutions of cladding from simulated and reject fuel elements. The results are shown in Table V, along with data from bench scale runs by Carroll.(3) The losses during the preliminary studies varied randomly with Zircaloy surface condition (oxidized or unoxidized) and operating conditions. However, during later pilot unit and bench scale studies, the losses were shown to be a function of Zircaloy surface condition and dissolver sparge medium. An increase in uranium losses during the dissolution of oxidized Zircaloy-clad fuel elements was observed. It was attributed to the longer dissolution cycle for oxidized elements, combined with the early

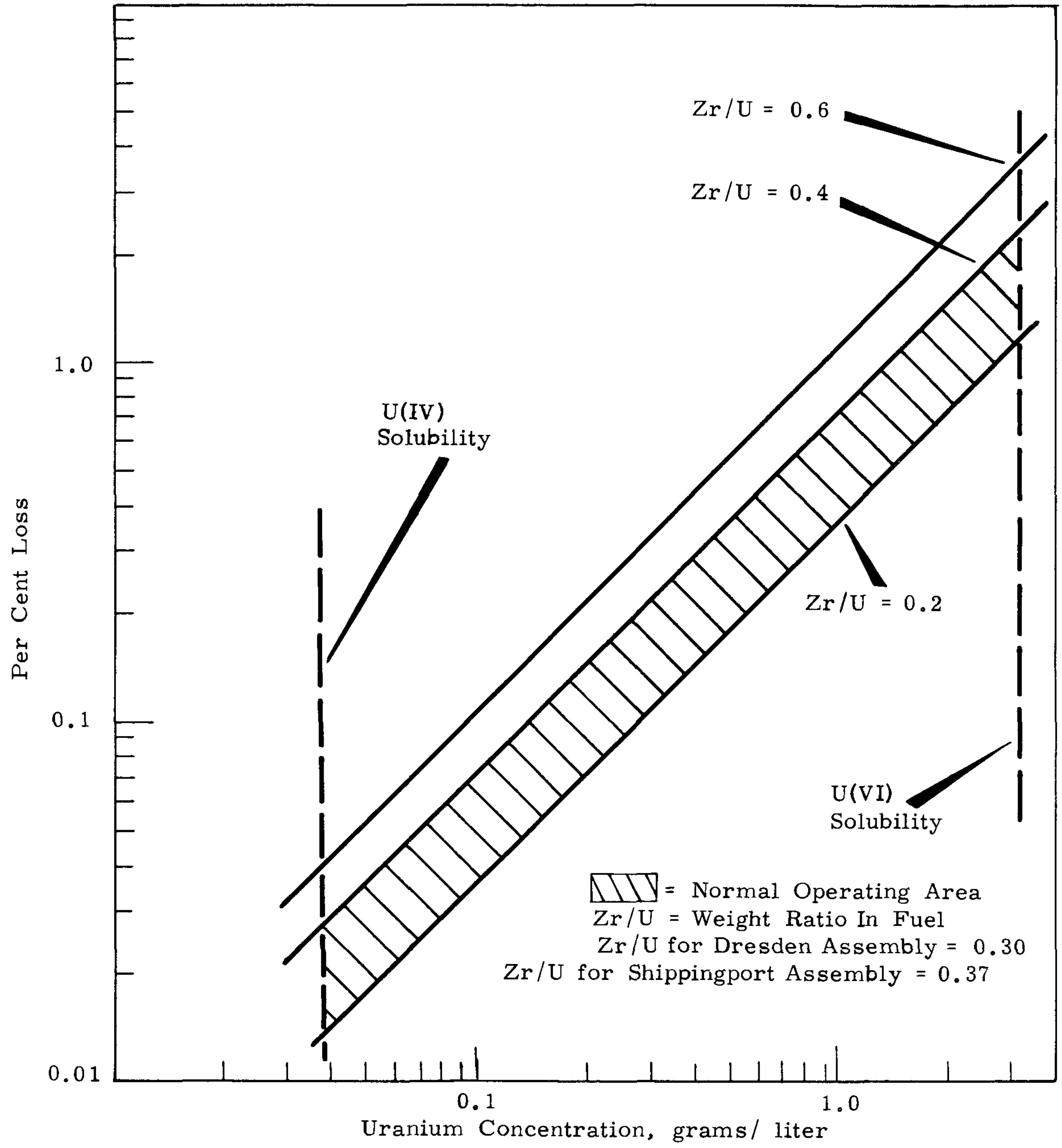


FIGURE 11

Per Cent Loss of Uranium in Zirflex Solutions

TABLE V

SOLUBLE URANIUM LOSSES - ZIRFLEX PILOT UNIT STUDIES

Run No	Cladding Surface Condition	Sparge Medium	Core Material	Cooling Period hrs	Zr/U Weight Ratio	Average Uranium g/l	Per Cent Loss
Preliminary Studies							
33	unoxidized	--	sintered UO_2	--	0.16	0.14	0.04
34	unoxidized	--	sintered UO_2	--	0.17	0.54	0.17
35	unoxidized	--	sintered UO_2	--	0.17	1.9	0.57
36	unoxidized	--	sintered UO_2	--	--	2.9	0.63
37	oxidized	--	sintered UO_2	--	0.17	2.4	--
38	oxidized	--	sintered UO_2	--	0.17	0.10	0.03
39	unoxidized	--	swaged UO_2	--	0.15	1.3	0.37
40	oxidized	--	sintered UO_2	--	0.21	2.6	1.3
41	oxidized	--	sintered UO_2	--	0.29	1.4	0.82
42	oxidized	air	sintered UO_2	--	0.17	0.4	0.13
43	oxidized	air	sintered UO_2	--	0.17	1.1	0.37
44	oxidized	air	sintered UO_2	--	0.16	1.8	0.50
45	unoxidized	air	2.25% U-Al	--	--	0.0036	0.25
46	unoxidized	--	2.25% U-Al	--	--	0.07	2.9
47	unoxidized	--	0.9% U-Al	--	--	0.06	9.4
48	unoxidized	air	uranium	--	0.034	0.91	0.09
49	unoxidized	air	uranium	--	0.046	1.50	0.08
Flowsheet Demonstrations							
RZA-12	unoxidized	steam	swaged UO_2	2	0.23	0.04	0.02
RZA-13	unoxidized	steam	swaged UO_2	2	0.23	0.07	0.03
RZA-14	oxidized	steam	swaged UO_2	24	0.23	0.7	0.30
RZA-15	oxidized	air	swaged UO_2	24	0.23	2.0	0.85
Bench Scale Studies							
ULA	oxidized	steam	swaged UO_2	24	0.23	0.64	0.27
ULB	oxidized	air	swaged UO_2	24	0.23	0.96	0.41
ULC	unoxidized	air	swaged UO_2	24	0.23	0.84	0.36
ULD	unoxidized	steam	swaged UO_2	24	0.23	0.38	0.16

exposure of the core characterized by pitting attack. In addition, an increase in losses of greater than a factor of two was observed when an air sparge rather than a steam sparge was used for dissolvent motivation. This was ascribed to the increased oxidation of uranium IV to uranium VI by the air.

Losses during the later studies ranged from 0.07 grams per liter for the steam-sparged decladding of unoxidized elements to 2.0 grams per liter for the air-sparged decladding of oxidized elements. In general, uranium losses of approximately 0.8 gram per liter, corresponding to 0.3 per cent waste loss, are anticipated for the steam-sparged decladding of oxidized power reactor fuels.

Plutonium losses to the decladding solution were studied only on a laboratory scale, since the pilot plant was not equipped nor properly located for this purpose. Laboratory data by Swanson(2) are reported here to provide an indication of the losses that may be expected.

TABLE VI

URANIUM AND PLUTONIUM CONCENTRATIONS IN SIMULATED DECLADDING SOLUTIONS

Ratio in a U - Pu Alloy	In Boiling Solution					In Cooled Solution		
Pu/U $\times 10^{-4}$	$\underline{M}$ F^-	$\underline{M}$ ZrIV	U g/l	Pu mg/l	Pu/U $\times 10^{-4}$	U g/l	Pu mg/l	Pu/U $\times 10^{-4}$
3	6	0	15	4.3	2.9	4.5	1.4	3.1
11	6	0	13	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

Uranium-plutonium alloys were exposed to boiling Zirflex solutions of the indicated concentrations. For the experiments employing alloy with a plutonium-to-uranium ratio of 11×10^{-4} (1000 grams plutonium/ton uranium), in each case the Pu/U ratio in the solutions was less than that in the alloy. The decrease in Pu/U ratio was greater after dilution and cooling. Plutonium concentrations in solutions prepared by the action of zirconium-ammonium fluoride solutions on plutonium-aluminum alloy did not decrease significantly on cooling. This implied that the marked decrease observed in the solutions saturated with uranium IV is due to the carrying of plutonium on the uranium fluoride salt which precipitates on cooling.

From these data, it is apparent that the percent plutonium loss to the decladding solution will be equal to or less than the percent uranium loss, with some dependence on the amount of UF_4 precipitated at the end of the dissolution. Thus, the uranium loss data reported earlier provide an indication of the upper limit for plutonium losses to the decladding solution.

WASTE NEUTRALIZATION

Zirflex decladding waste is to be neutralized to a pH of 10 with 50 per cent caustic prior to its transfer to storage. This treatment results in the precipitation of zirconium oxide or hydroxide, which must be transferred to the waste storage tanks as a slurry.

Amos(10) performed development studies on Zirflex decladding waste treatment. He indicated that 0.035 gallons of 50 per cent caustic per gallon of decladding solution were required to complete the precipitation of solids and raise the pH to nine, while double that amount was needed to raise the pH to 10. The solids were observed to slurry well during turbulent flow (Reynolds number greater than 2500) but to settle out in streamline flow (Reynolds number less than 2000). Thus, agitation was required during temporary storage. Transfer lines were easily flushed with water under turbulent flow conditions.

The specific gravity of the neutralized waste was 1.06 as a slurry and 1.03 for the supernate, as opposed to 1.05 for the unneutralized decladding solution. The viscosity of the neutralized waste slurry measured with a Brookfield Viscometer was 1.4 centipoises at 20 C.

CORE DISSOLUTION

The core materials associated with Zircaloy-clad fuels at Hanford consist of swaged UO_2 and uranium metal. Following the Zirflex decladding, these fuels may be dissolved by the conventional nitric acid dissolution. However, aluminum nitrate must be added to inhibit the corrosive action of residual fluoride on the dissolver vessel.

The dissolution rates of core materials depend upon their physical condition (solids or chips and fines) and the nitric acid molarity. Pilot plant(11)(12) and laboratory(13) data are available for UO_2 and uranium dissolutions. In general, pilot plant core dissolutions during total cycle feed preparations have been completed in less than five hours. A starting nitric acid concentration of 6 $\underline{M}$, a nitric acid-to-uranium mole ratio of five, and an aluminum nitrate-to-fluoride mole ratio of three were used. However, the core dissolutions may be tailored to almost any condition by using the data cited. A typical core dissolution flowsheet is given in Figure 13.

CORROSION

The relatively mild corrosive effects of the Zirflex solution on conventional materials of construction make the process particularly attractive for use at Hanford. Stainless steel is sufficiently resistant to be used in the decladding and core dissolution steps. Coupons of type 304L, 347 and 316 stainless steel corroded at a rate of 4.3 mils/month in the pilot plant dissolver, based on a 55-hour decladding and core dissolution.(5) Other corrosion data reported by Maness(14) were in the same range.

TABLE VII

CORROSION IN BOILING 6 M NH_4F, 0.5 M NH_4NO_3

Material	Mils/Mo	Material	Mils/Mo
304-L	11.4 38*	Incaloy 804	5.9
309 SCb	9.6	Haynes 25	5.5
Carpenter 20	5.6	Ni-O-Nel	4.4
Hastelloy F	3.3 18*		

* Heat transfer surface (bulk metal temperature 140 C).

Corrosivity is reduced in the presence of dissolving zirconium due to ammonia evolution with a resulting increase in pH. The corrosion of mild steel by neutralized wastes was slight (0.01 mil/month) when the pH was 8.5 or above.

Potentially high corrosion of the dissolver vessel due to residual fluoride during nitric acid core dissolution is essentially eliminated by the addition of aluminum nitrate to the dissolvent. As shown in Table VIII, an aluminum-to-fluoride mole ratio of one complexes the fluoride sufficiently to prevent excessive corrosion. Higher aluminum-to-fluoride mole ratios may be used without detrimental effects on dissolver operation. An Al/F ratio of three was used in the pilot plant runs.

TABLE VIII

CORROSION OF 304-L IN 10 M HNO_3, 0.02 M UNH, 0.08 M HF SOLUTION

Al/F Mole Ratio	Mils/Mo
6.25	1.97
3.12	2.82
1.00	13.70

VII. ACKNOWLEDGEMENT

To present a unified report on the Zirflex process, considerable research and development data prepared by several Hanford personnel were included. The author is pleased to recognize this assistance and has referenced the work of individual contributors. Two components of the Hanford Laboratories Operation deserve particular recognition. The services of the Analytical Laboratories were most valuable and necessary test materials were contributed by the Ceramic Fuels Development Operation.

APPENDIX I

ZIRCONIUM DISSOLUTION RATE EQUATIONS(5)

A. Nomenclature

Zr = gram moles of metallic zirconium.

θ = time from start in minutes.

V = volume of solution in 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 constants in liters/in^2-min.

A = surface area of zirconium in 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 system relationships are:

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

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

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

3. or,

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

4. Rearranging the relationship yields:

   $$\int_{Zr_o}^{Zr} \frac{-dZr}{VC_{Fo} - 6\,Zr_o + 6\,Zr} = \int_o^{\theta} \frac{KA\,d\theta}{V}\ .$$

5. By integrating, this equation becomes:

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

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

7. Finally, by substituting the final equation becomes:

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

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

2. Volume of charge solution: $V = (\text{g-moles Zr}) (F/Zr) (1/C_{Fo})$, or $V = (4.97 \text{ g-m Zr}) (7 \text{ g-mF}/ \text{ g-mZr}) (1/5.5 \text{ g-m F}) = 6.3$ liters, or (1.66 gal).

3. For 100 per cent 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 7 above:

   $\theta = V/6\ KA \ln C_{Fo}/C_F = 6.3/(6)(23 \times 10^{-5}) (143) \ln 5.5/0.77$ and $\theta = 63$ min, or approximately 1 hour.

5. Theoretical dissolution times can be calculated in a similar manner for other conditions.

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

APPENDIX II

ZIRFLEX SOLUTION CONDUCTIVITY TESTS

Laboratory tests were conducted by Hahn(6) to determine the feasibility of using a conductivity probe to trace reaction progress throughout a Zirflex dissolution. As a basis for the tests, a dissolution path starting at 5.5 M ammonium fluoride - 0.5 M ammonium nitrate with a fluoride-to-zirconium mole charge ratio of seven was used. Solutions for points along the path were prepared by dissolving weighed Zircaloy coupons in the starting solution. This provided the desired free fluoride and zirconium concentrations. In addition, non-zirconium bearing solutions were prepared for the same points on the dissolution path so that the effect of dissolved zirconium on the conductivity could be measured.

The results of the tests showed that the change in conductance with concentration was overshadowed by the change with temperature (temperature coefficient of conductance = 0.003 mho/cm °C). In addition the conductivity curves at 100 C plotted in Figure 12 show a marked influence of zirconium concentration indicating that the data are good only for the specified dissolution path. Conductivity traces for other dissolution paths may be determined and used with comparative accuracy as long as charge conditions are controlled, temperature corrections are made and constant dissolver volume is maintained. The principal value of a conductivity probe, however, will continue to be in the determination of the Zirflex reaction end point by the leveling of resistance readings.

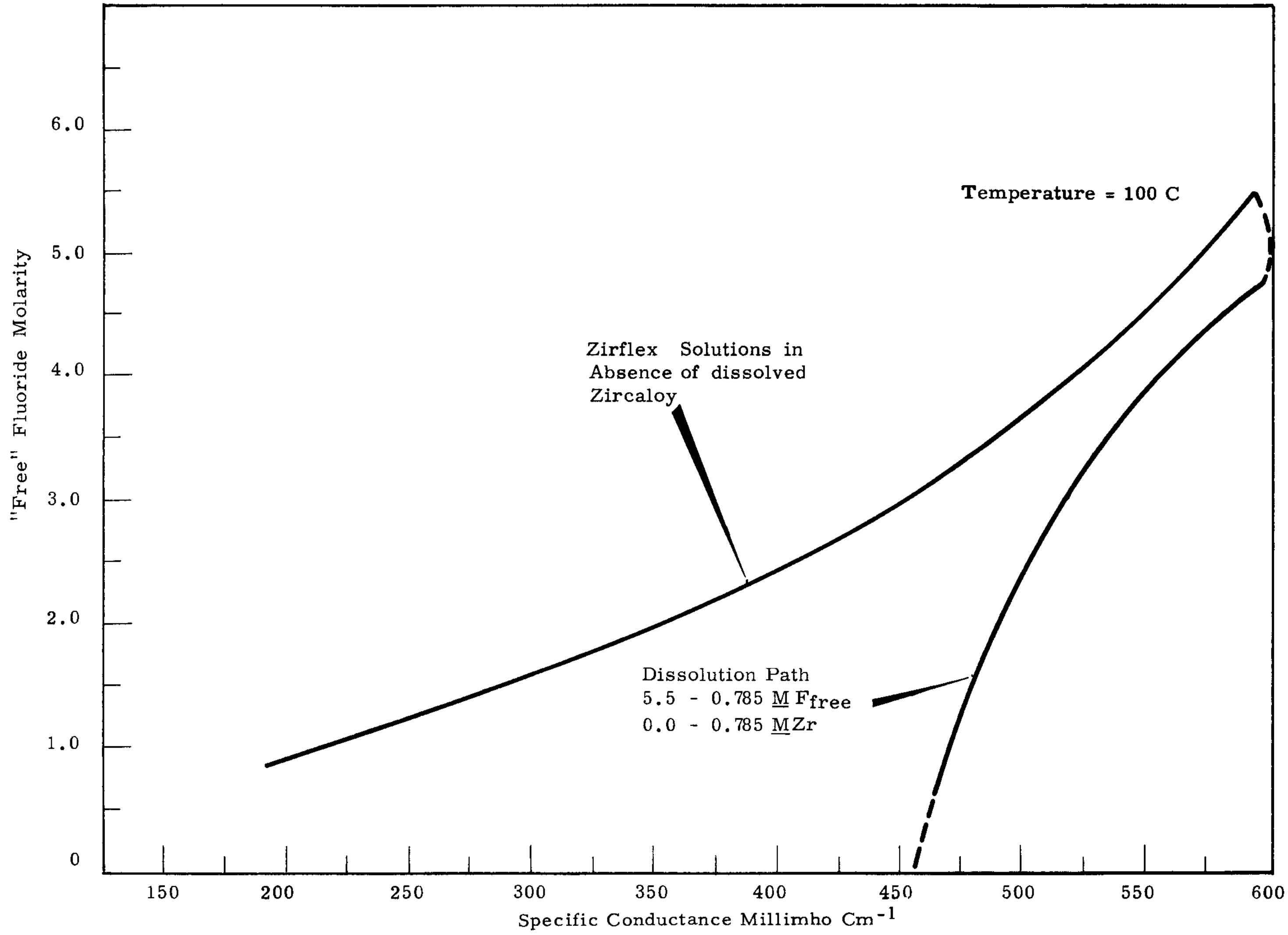


FIGURE 12

The Effect of Dissolved Zircaloy on the Specific Conductance of Zirflex Solutions

APPENDIX III

TABLE I

Preliminary Zircaloy Dissolutions

Cylındrical Tank Pilot Unit Dıssolver

Run No	CHARGE CONDITIONS						OPERATING CONDITIONS									RESULTS										
	Fluoride Molarity	Nitrate Molarity	Mole Ratio	Surface Area of Zircaloy	Amount of Zircaloy	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 $K\times10^5$	Off Gas Hydrogen Analysis (% in Air)				Final Solution Analysis		
	C_f	C_{NO_3}	F/Zr	in.^{2}	lb	in.	da	hrs		$\frac{Gal\times10^{-3}}{hr\ in^2 Zy}$	$\frac{Scfm\times10^{-3}}{in^2 Zy}$	$\frac{Scfm\times10^{-3}}{in^2 Zy}$	$\frac{Scfm\times10^{-3}}{in^2 Zy}$						$\frac{Liters}{in^2(Zy)min}$	1	2	3	4	pH	Zr g/L	NO_3^- g/L
1	6 0	0 5	7 0	198	3 32	13	0	3 8	X	-	2 5	-				94	-	-	-	-	-	-	-		56 3	-
2	6 0	0 5	7 0	586	2 88	03	0	4 1	X	-	0 3		7 2	96-98	28	99 6		-	13 1 3 96	2 6	0 6	0 4	0 1		77 8	
3	4 0	0 5	7 0	568	2 12	06	0	3 5	-		-	8 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	X			-	10 3	100-101	30	21 0	-	-		-		-	-			
7	6 0	0 5	10 0	575	2 32	03	0	1 6	X	-	<0 2	-	8 5	94		99 9	4 0	0 57	13 75	15 6	3 1	3 8			9 1	12 3
8	6 0	0 5	8 5	6 8	2 87	03	0	3 7	X		<0 2		2 3	94 98	30	100 0			15 75	0 2	2 5		-	7 3	61 3	
9	0	0 5	7 0	568	3 10	03	0	3 7	X		-		4 9	94 96	37	99 9	-		14 7 -2 34	0 7	0 9	-	-	4 7		-
10	5 5	0 5	7 0	5 5	3 15	03	7	2 2	-			3 2	7 4	92 98	30	85 0	4 5	0 46	3 33	1 0	0 4	0 5			32 0	6 1
11	5 5	5	7 0	562	3 08	03	14	6 5		4 1	<0 2	-	7 7	1 1	30	95 0	4 1	0 49	4	1 7	1 1		-	5 6	3 2	6 2
12	6 0	0 5	7 0	5 3	3 08	03	3	6 4	X	-	<0 2		6 7	98-100	30	84 0		-	3 38	2 1	-	-	-	7 4	58 3	9
17	5 6	0 5	7 0	568	2 82	13	0	3 5	X	-			7 9		30	84 0	4 7	0 41	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 48	31 9 4 23						34 1	2 0
19	4 0	0 5	7 0	406	2 03	06	0	4 5	X		<0 2		17 2	96-98	35	83 0	4 1	0 64	14 5	4 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	1 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	6 9	8 1
23	5 5	0 5	7 0	713	2 57	03	3	3 5		3 1	<0 5		6 6	99	30	100	4 5	0 40	5 27	6 1	6 8	-		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	14 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 4
27	4 5	0	7 0	682	2 53	03	21	1 5		7 0	<0 3	-	4 4	94	50	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	60	98 8	-	-	6 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 6
30	5 0	0 5	7	488	2 54	03	0	4 0			-	2 5	6 1	94	70	100 0	4 6	0 43	7 77		-			5 0	60 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	85	100 0	3 0*	0 46	20 6	-			-	6 1	46 5	6 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 48		3 4	1 7		-	4 9	58 5	15 0
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 50		1 2	1 6	-	-	4 1	64 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 8	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	40 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**	***	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		88 9	5 4	-	3 0	-		-	-	5 2	51 7	6 6
43	5 5	0 5	7 0	37	2 74	03	14	5 8	-		-	3 0	4 7	100-102		93	4 7		4 1	-	-			5 1	50 3	
44	5	0 5	7 0	690	2 67	03	14	5 0	-		-	1 8	-	100	50	92 3		-	2 73	-	-			4 8	62 0	
45	5 5	0 5	7 0	670		03	0	3 9		-	-	6 0				100	4 1	0 46		-	-			4 7	56 9	6 0
46	5 5	0 5				03	0	4 0		-	-					100	-		-	-	-				0 0	
7	5 5	0 5	7 0			03	0	9 3	-	-						100						-				3 8
8	5 5	0 5	7 0	371		03	0	5 0				11 4				100	3 8	0 47	-	-					4 5	9 1
49	5 5	0 5	7 0	412		03	0	8 0			-	10 2				100			-		-				57 2	

OTE: *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 ontained Zy and UO_2
Runs 45 through 47 contained Zy and Al-U alloy
Runs 48 and 49 contained Zy and U

APPENDIX III

TABLE II

Final Zircaloy Dissolutions
Tubular Pilot Unit Dissolver

Run No.	Charge Conditions						Operating Conditions						Results			
	NH_4F M	NH_4NO_3 M	F/Zr Mole Charge Ratio	Zircaloy Surface Area ft^2	Weight of Zircaloy lbs.	Oxidized In Autoclave 400°C 1150 psig hr	Condensate Rate lb mol/ft^2 hr	Circulation Rate GPM	Sparge Rate lb mol hr	Sparge Medium	Temperature °F	Maximum Ammonia Removal lb mol/hr ft^2	Reaction Rate Integrated mil/hr	Reaction Rate Maximum mil/hr	Order Of Reaction	Reaction Rate Constant liters/in min
RZA-1	5.5	0.5	7	44.0	35.1	0	--	34.3	4.2-5.5	Air	212-220	--	--	28	--	--
RZA-2	4.0	0.364	7	36.6	29.6	0	0.297	19.8	--	Air	218 Avg	0.0318	20	--	--	--
RZA-3	4.0	0.364	7	36.6	29.3	0	0.355	66.0	2.0-2.5	Air	204-210	0.0485	15	28.6	--	--
RZA-4	6.0	0.65	7	35.9	28.6	0	0.215	Batch	--	--	203-212	0.0335	>15	64	--	--
RZA-5	5.5	0.5	7	8.6	11.8	0	0.528	Batch	--	--	212-217	0.0788	>15	66	1.5	16×10^{-5}
RZA-6	4.8		7	29.3	23.3	0	0.153	Batch	--	--	202-206	0.0262	12	22.7	2	--
RZA-7	6.0	0.65	7	43.2	34.4	0	0.246	11.9	3.0-5.5	Air	212-216	0.0252	--	18	--	--
RZA-8	5.5	0.5	7	43.0	34.5	0	0.211	15.8	1.0-5.9	Air	208-218	0.0327	>15	35	1.5	8×10^{-5}
RZA-9	5.5	0.5	7	37.5	29.1	0	0.132	15.8	5.9-8.7	Air	184-216	0.0128	9	19	--	--
RZA-10	5.5	0.5	7	37.3	29.9	0	0.251	9.2	8.7	Steam	210-212	0.0392	>15	41.2	1	15×10^{-5}
RZA-11	5.5	0.5	7	36.3	28.7	0	0.277	7.9	8.7	Steam	210-212	0.0327	27	42.9	1	18×10^{-5}
RZA-12	5.5	0.5	7	42.5	28.5	0	0.218	8.5	7.7	Steam	210-212	0.0237	27	43.3	1	22.5×10^{-5}
RZA-13	5.5	0.5	7	36.4	37.8	72	0.215	17.1	7.8	Steam	210-212	0.0314	20	43.0	1	16.5×10^{-5}
RZA-14	5.5	0.5	7	37.0	41.2	72	0.207	26.4	7.7	Steam	210-211	0.0235	6	--	--	--
RZA-15	5.5	0.5	7	33.0	33.5	72	0.222	19.8	1.3-2.5	Air	207-211	0.0219	6.5	--	--	--

Note: Runs RZA-1 - RZA-11 55 mil Zircaloy Tubing Only.
Runs RZA-12 - RZA-15 33 mil Zircaloy clad swaged UO_2.

APPENDIX IV

ZIRFLEX FLOWSHEETS

Flowsheet Basis for Figure 13

1. Cladding is 100 per cent zirconium. (Zircaloy is 98.5 per cent zirconium).
2. A fluoride-to-zirconium mole charge ratio of seven is used.
3. Five moles of ammonia are evolved per mole of Zircaloy dissolved.
4. One-tenth mole of hydrogen is evolved per mole of Zircaloy dissolved.
5. Peak ammonia rate to off-gas is based on the maximum rate observed in the pilot plant.
6. Peak hydrogen evolution rate is estimated at one-half maximum rate during dissolution of unoxidized Zircaloy.
7. Essentially complete dissolution of Zircaloy is attained.

Flowsheet Basis for Figure 14

1. Nitric acid consumption is three moles per mole of UO_2.
2. Nitric acid charge ratio is 3.5 moles per mole of UO_2.
3. Residual contaminants in the dissolver are based on a 20-gallon heel.
4. Aluminum-to-fluoride mole charge ratio is three.
5. Maximum off-gas rates are based on the estimated maximum dissolution rate from pilot unit runs.

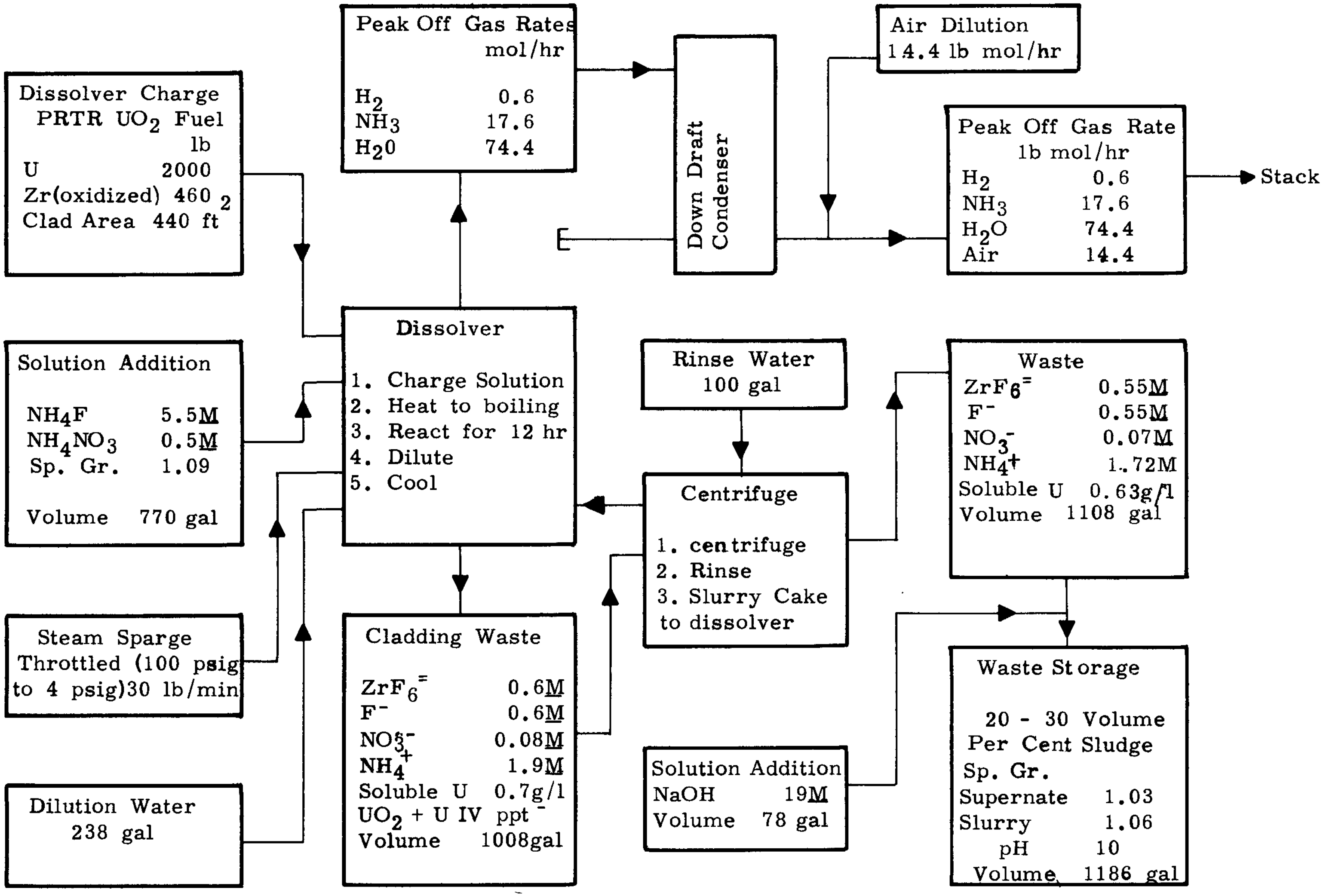
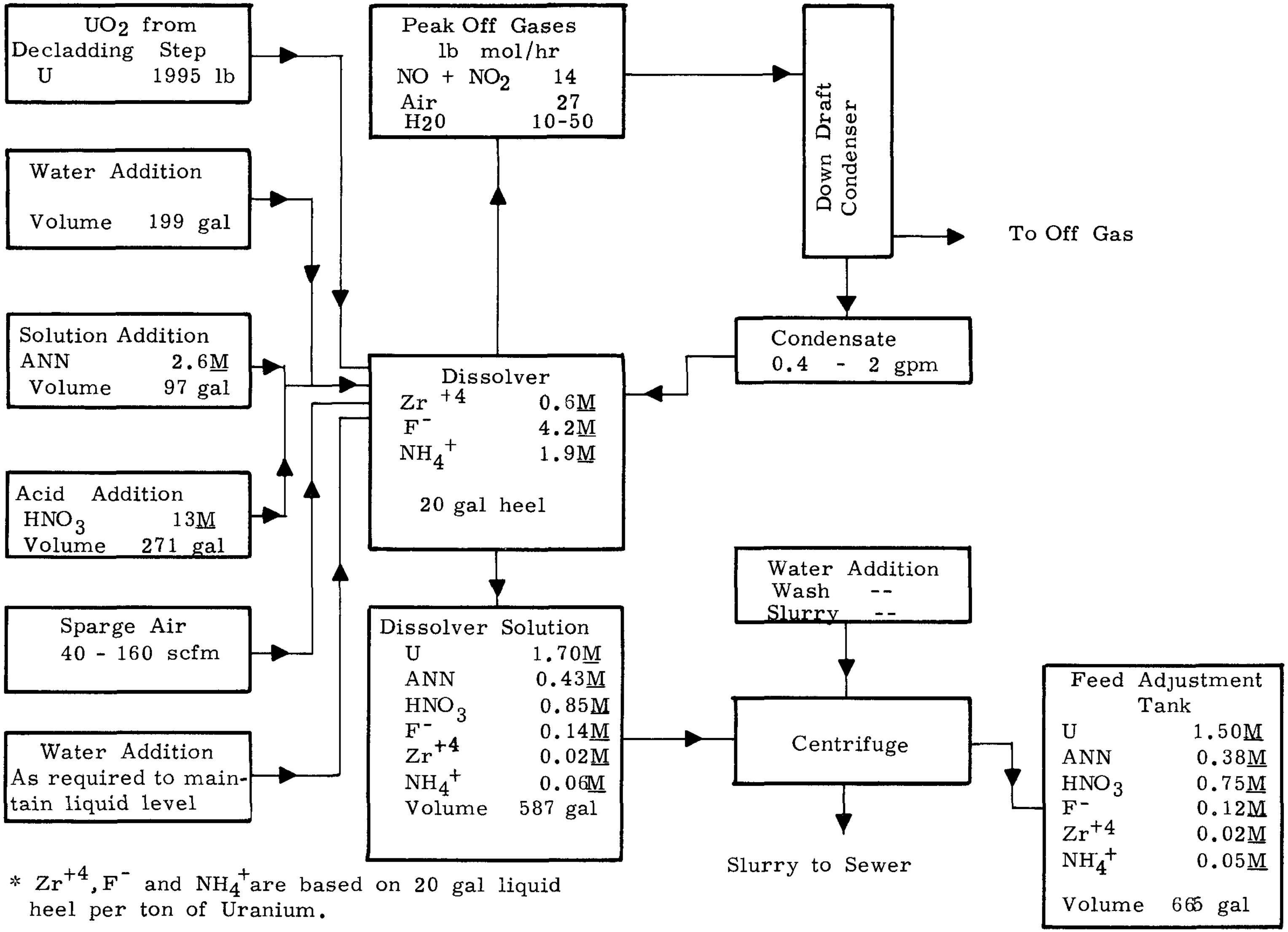


FIGURE 13

Zirflex Recirculating Decladding of Oxidized PRTR Elements



* Zr^{+4}, F^- and NH_4^+ are based on 20 gal liquid heel per ton of Uranium.

FIGURE 14

Recirculating Core Dissolution of PRTR Elements

REFERENCES

1. Swanson, J. L. *Dejacketing of Zircaloy Clad Fuel with Ammonium Fluoride Solution*, HW-49633. April, 1957. (CONFIDENTIAL).
2. Swanson, J. L. *The Zirflex Process*, Second International Conference on the Peaceful Uses of Atomic Energy, Geneva, Paper No. 2429. 1958.
3. Carroll, J. L. Hanford Laboratories Operation. Unpublished.
4. Bupp, L. P. *Monthly Report, December, 1959, Chemical Research and Development Operation*, HW-63303 C, C-14. January, 1960. (SECRET).
5. Platt, A. M. and C. R. Cooley. *The Zirflex Process Interim Development Summary*, HW-60597. June, 1959.
6. Hahn, K. J. Hanford Laboratories Operation. Unpublished.
7. Fisher, F. D. Hanford Laboratories Operation. Unpublished.
8. Coward, J. F. and G. W. Jones. *Limits of Flammability of Gases and Vapors*, Bureau of Mines Bulletin 503. 1952.
9. Swanson, J. L. Hanford Laboratories Operation. Unpublished.
10. Amos, L. C. *Physical Properties of Neutralized Zirflex Waste*, HW-60614. June, 1959.
11. Smith, P. W. *The Pilot Plant Operation of a Vertical Tube, Recirculating Dissolver for the Dissolution of Uranium Dioxide in Nitric Acid*, HW-64416. March, 1960.
12. Blaine, H. T. *Dissolution of Nonproduction Fuel Cores*, HW-66320 RD. August, 1960.
13. Bressee, J. C. *Unit Operations Section - Monthly Progress Report*, ORNL-CF-59-1-74. January, 1959.
14. Maness, R. F. *Power Reactor Fuels Reprocessing Progress Report on Corrosion Studies*, HW-61662. August, 1959.

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