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SIMULATION OF THE ZIRFLEX PROCESS WITH AN ANALOG COMPUTER

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SIMULATION OF THE ZIRFLEX PROCESS WITH AN
ANALOG COMPUTER

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INTRODUCTION

The Zirflex process was studied extensively at Hanford in the development of technology for the interim reprocessing of power reactor fuels. The process involves the dissolution of Zircaloy in aqueous ammonium fluoride-ammonium nitrate solution. It is of particular interest at Hanford because of the impending fuel recovery from Zircaloy clad PRTR and NPR elements. Development data on the process are summarized in a terminal report⁽¹⁾ which includes references to various contributors and to earlier Zirflex reports.

The chemical kinetics of the Zirflex reaction were not fully defined at the end of the original studies. However, a pseudo first order reaction with "free" fluoride (fluoride not complexed with zirconium) was deemed to describe the kinetics adequately for engineering calculations. Observations in the laboratory indicating approximately second order dependence on "free" fluoride and one half order dependence on hydrogen ion led to further studies in this area. The results provided a more accurate kinetic equation. Direct mathematical solution of the model defining the system was not possible but an analog computer solution was effected.

In this report the refined kinetic equation and the analog computer solution are discussed. In addition the results of thirty computer simulated dissolutions are presented and the data are used to illustrate the effects of the process variables on the Zirflex dissolution time cycle. The data from a selected few of the runs are directly applicable to the reprocessing of PRTR fuel elements in Redox.

SUMMARY

The Zirflex reaction kinetics are dependent on "free" fluoride ion to the 2.017 power and on hydrogen ion to the 0.457 power according to laboratory data secured after completion of the original research and development studies. The direct integration of the kinetic equation was prevented by the complex interdependence of the chemical variables. However an analog computer circuit was evolved which was used to solve the defining equations simultaneously. The circuitry is discussed in the report because of its applicability to future studies and its novel aspects.

The results of computer simulated dissolutions of PRTR elements are in the form of continuous graphs of the major chemical variables and the dissolution rate versus dissolution time. A comparison of two simulated dissolutions with actual pilot plant runs shows an agreement within 20 percent in dissolution time at 5.5 M NH_4F initial concentration and within 10 percent at 4 M NH_4F . The dissolution time decreased with large boil-up rates, high initial fluoride concentrations and high F/Zr mole charge ratios but increased for oxidized fuel cladding dissolutions.

The data from the computer runs verified the results of the earlier laboratory and pilot plant work. However, a much clearer view of the process is presented with the continuous graphs of the variables prepared from the computer data. In addition data not available from the pilot plant studies but applicable to Redox reprocessing of PRTR fuels are presented.

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DISCUSSION

The Zirflex process was studied extensively on the laboratory and pilot plant scale for application to power reactor fuel reprocessing. The early work⁽¹⁾ culminated in the recommendation of a flowsheet using a 5.5 M NH_4F -0.5 M NH_4NO_3 aqueous dissolvent with a F/Zr mole charge ratio of 7 to carry out the reaction:

Further laboratory studies were made to clarify the kinetics of the process. The earlier studies had shown that a rate equation involving a pseudo first order reaction with "free" fluoride (fluoride not complexed with zirconium) was adequate for engineering calculations. However, a substantial effect of ammonia build-up or hydrogen ion decrease on dissolution rate was apparent and led to further experiments by J. L. Carroll. The rate equation resulting from statistical resolution of the laboratory data follows:

$$(2) \frac{d C_{\text{Zr}}}{d \theta} = A_0 k_1 C_{\text{F}}^{-2.02} C_{\text{H}^+}^{0.46}$$

where

C_{Zr} = concentration of zirconium, M

C_{F} = concentration of free fluoride, M

C_{H^+} = concentration of hydrogen ion, M

A_0 = initial area of cladding per unit volume of solution, ft^2/liter

k_1 = kinetic rate constant, $\text{liter}^{2.4742}/\text{ft}^2\text{-min-g mol}^{1.4742}$

θ = time in minutes

With the solution of equation 2 as an objective the chemistry of the Zirflex reaction was reduced to mathematical terms. The interdependence of the variables is shown in the following equations for a constant liquid volume in the dissolver.

$$(3) \frac{d C_{\text{NH}_3}}{d \theta} = 5 \frac{d C_{\text{Zr}}}{d \theta} - A_0 B (K_2 C_{\text{NH}_3})$$

$$(4) C_{\text{H}^+} = \frac{C_{\text{NH}_4^+}}{C_{\text{NH}_3}} (4.0 \times 10^{-10})$$

$$(5) C_{\text{NH}_4^+} = C_{\text{NH}_4^0} - 4 C_{\text{Zr}}$$

$$(6) C_{\text{F}^-} = C_{\text{F}_0} - 6 C_{\text{Zr}}$$

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where

C_{NH_3} = concentration of ammonia M

$C_{\text{NH}_4}^+$ = concentration of ammonium ion M

B = boil-up rate g mols/min ft² of initial Zircaloy

$(K_2 C_{\text{NH}_3})$ = mole fraction of ammonia in the vapor determined from a liquid vapor equilibrium diagram

$K_2 = K_3 V_M$ = equilibrium constant times the molar volume

Subscript 0 = initial conditions

In equation 3 the concentration of ammonia in the dissolvent is shown to increase due to the zirconium dissolution but to decrease with the boil-off. The boil-off is replaced by incremental water addition or steam sparge to maintain a constant volume, justifying the use of concentration terms in the kinetic equations. The factor $(K_2 C_{\text{NH}_3})$ indicates that the mole fraction of ammonia in the vapor is dependent on the ammonia concentration in the dissolvent with the K_2 representing a function that is not readily reducible to a single formulation from the liquid vapor equilibrium diagram. The equilibrium diagram was determined by J. L. Carroll for the earlier work and is presented here in Figure 1.

The concentration of hydrogen ion is expressed as a function of dissolved ammonia and ammonium ion in equation 4. The equation was derived by treating the dissolved ammonia as a weak base in a buffered solution and using established ionization constants. The derivation is given in Appendix I.

Equations 5 and 6 equate the concentration of ammonium ion and "free" fluoride ion to the concentration of zirconium and the starting conditions. This completes the relating of the variable concentrations to the concentration of zirconium and reduced the rate equation to a function of only two variables.

The complex chemistry of the process prevented a direct integration of the rate equation (Equation 2). However, a simultaneous solution of the equations was accomplished on an analog computer. Circuitry for the computer simulation was worked out by Taylor⁽³⁾ and is shown in Figure 2. An EASE analog computer was used in the study which provided an estimated accuracy for the circuit of approximately ± 10 percent.

According to Taylor the analog circuit is of interest principally because of the method used to generate the non-integral powers of the variables C_{F^-} and C_{H^+} . This was accomplished through the use of log diode fixed function generators. When this type of function generator is used as the input impedance of an operational amplifier the output of the amplifier is proportional to the logarithm of the input signal. When used as a feedback impedance the output of the amplifier is proportional to the antilogarithm of the input signal. With these two types of circuits in correct sequence the output consists of the product of the input signals each raised to the appropriate power.

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FIGURE 1

Liquid Vapor Equilibrium for Ammonia in Zirflex Solution

FIGURE 2
Analog Circuit for Zirflex Kinetics

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The results of the computer runs were recorded on continuous graphs of the variables versus time. Curves of the concentration of H^+ , Zr, NH_3 , NH_4^+ and F^- were obtained as was a continuous trace of the dissolution rate in mils/hr. Thirty Zirflex dissolutions were simulated in all at the run conditions recorded in Table I.

The first ten runs (Figures 9 through 18) were made for unoxidized elements at flow sheet conditions of $5.5 \text{ M } NH_4F - 0.5 \text{ M } NH_4NO_3$ with a F/Zr mole charge ratio of 7. These were the conditions selected as optimum for power reactor fuel reprocessing in the earlier pilot plant studies. A boil-up range of 0.5 to 4.0 g mols/min ft^2 was investigated, although in pilot plant experiments successful dissolutions were not attained at boil-up rates less than 1.0 g mol/min ft^2 because of ammonium fluozirconate $((NH_4)_2 ZrF_6)$ precipitation. The upper limit was set at 4.0 g mol/min ft^2 because off gas handling equipment size for production plants becomes excessive above this rate.

Two alternate flow sheets, also for unoxidized elements, were investigated in the next ten runs. Five were run at $3 \text{ M } NH_4F - 0.273 \text{ M } NH_4NO_3$ (Figures 19 through 23), and five at $4 \text{ M } NH_4F - 0.363 \text{ M } NH_4NO_3$ (Figures 24 through 28). The F/Zr mole charge ratio and the boil-up range examined were the same as for the first ten simulations. Boil-up rate of 0.5 g mol/min ft^2 is an operable value however, for these lower fluoride conditions because of slower ammonia buildup in the dissolvent.

The final ten runs were made to simulate probable dissolving conditions for the reprocessing of PRTR fuels in a multipurpose dissolver. The dissolver was not designed specifically for these elements and therefore an excess of solution is required to cover the fuel. A flowsheet of $4 \text{ M } NH_4F - 0.363 \text{ M } NH_4NO_3$ with a F/Zr mole charge ratio of 21 was selected to minimize excess fluoride while providing a reasonable dissolution rate. Five runs were made for the case of unoxidized fuel elements (Figures 29 through 33) to compare with the results of the non-production fuels flowsheet. Five others (Figures 34 through 38) were made to simulate the dissolution of oxidized cladding. A boil-up range of 1.0 to 4.0 g mol/min ft^2 was investigated.

The simulated decladding of oxidized elements was of necessity an approximation since the dissolution occurs by pitting and undercutting the insoluble oxide film. The kinetic rate constant for unoxidized zircaloy was reduced by a factor of three to approximate this effect based on data from the pilot plant decladding of oxidized PRTR rods. The five runs provide a good estimate of the time cycle for the decladding of irradiated PRTR fuel elements.

The computer simulated dissolutions differed slightly from the corresponding pilot plant dissolutions due to difficulty in control of operating conditions in the pilot unit. The boil-up rate in the pilot unit runs was initially higher than the average because of the high rate of dissolution and the exothermic reaction. This caused a volume decrease in the dissolver and hence increased dissolution rate due to concentration of the dissolvent. The effect was offset somewhat since the reaction was started in cold dissolvent in the pilot runs while with the computer the reaction was considered to start at boiling. The latter effect was small, however, because the pilot unit heat up period was short and the reaction is slow at low temperatures.

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TABLE 1
Computer Run Conditions

<u>Figure</u>	<u>Run No.</u>	<u>Concentration</u> <u>NH₄F - NH₄NO₃</u>	<u>Boil-Up Rate</u> <u>g mol/ft²min</u>	<u>Area</u> <u>ft²/liter</u>	<u>Cladding</u> <u>Condition</u>	<u>Time</u> <u>Minutes</u>
9	1	5.5M - 0.5M	0.5	0.152	Unoxidized	450
10	2	" "	0.75	"	"	350
11	3	" "	1.0	"	"	290
12	4	" "	1.25	"	"	250
13	5	" "	1.50	"	"	225
14	6	" "	1.75	"	"	205
15	7	" "	2.0	"	"	195
16	8	" "	2.5	"	"	175
17	9	" "	3.0	"	"	145
18	10	" "	4.0	"	"	125
19	11	3.0M - 0.272M	0.5	0.080	"	810
20	12	" "	1.0	"	"	525
21	13	" "	1.5	"	"	425
22	14	" "	2.5	"	"	345
23	15	" "	4.0	"	"	280
24	16	4.0M - 0.363M	0.5	0.110	"	595
25	17	" "	1.0	"	"	375
26	18	" "	1.5	"	"	325
27	19	" "	2.5	"	"	260
28	20	" "	4.0	"	"	200
29	21	" "	1.0	0.03203	"	240
30	22	" "	2.0	"	"	165
31	23	" "	2.5	"	"	145
32	24	" "	3.0	"	"	130
33	25	" "	4.0	"	"	105
34	26	" "	1.0	"	Oxidized	375
35	27	" "	2.0	"	"	235
36	28	" "	2.5	"	"	210
37	29	" "	3.0	"	"	190
38	30	" "	4.0	"	"	165

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The data from the computer runs agreed with the corresponding pilot plant dissolutions within 20 percent in spite of the difficulty with control of pilot unit operating conditions. This is shown in Figures 3 and 4 where pilot runs R2A-13 ($5.5 \text{ M NH}_4\text{F}$) and R2A-3 ($4 \text{ M NH}_4\text{F}$) are compared to equivalent computer runs. In Figure 3 the concentration of zirconium in the pilot run reaches its peak about 20 percent faster than the computer curve due to the high fluoride concentration caused by initially high boil-up rate. In Figure 4 the curves are much closer and although the pilot run was terminated early extrapolation shows that the dissolution time cycle agrees within 10 percent. The second comparison was closer because the pilot unit run conditions were more easily controlled at the lower dissolution rates encountered at lower fluoride concentrations.

The influence of the major process variables on the dissolution time is illustrated with data from the computer simulations. The effects of changing boil-up rate, initial fluoride concentration and F/Zr mole charge ratio are presented and a comparison of dissolution times for oxidized and unoxidized cladding is shown. The results can be used to facilitate the selection of a flowsheet for a given application.

The variation in time cycle with boil-up rate is shown in Figure 5 which is a plot of the data from the first twenty runs on the simulation of the non-production fuels flowsheet. The curves illustrate the effect for three different initial fluoride concentrations. The dissolution time shortens rapidly as the boil-up rate increases but the rate of change is slower at the high boil-up rates.

In Figure 6 the influence of initial fluoride concentration on dissolution time is shown. It includes the variation of hydrogen ion concentration which is intimately related to the fluoride. The dissolution time would vary approximately as the inverse of the square of the fluoride concentration at a constant pH. However, hydrogen ion enters the reaction as shown in Equation 2 and slows the rate of increase of dissolution time with decreasing fluoride concentration. The overall effect is slower dissolution with decreased initial fluoride concentration.

The effect of increasing the excess fluoride concentration (i.e., using a larger F/Zr mole charge ratio) was to shorten the dissolution time as would be expected from the law of mass action. This is clearly illustrated in Figure 7 with curves of boil-up rate versus dissolution time for 5.5 M and $4 \text{ M NH}_4\text{F}$ initial concentrations at a F/Zr mole charge ratio of 7 and $4 \text{ M NH}_4\text{F}$ at a F/Zr ratio of 21. The curves show that the dissolution time is considerably shorter with the F/Zr ratio at 21 than at 7 for $4 \text{ M NH}_4\text{F}$ initial concentrations. It is also shorter than for the $5.5 \text{ M NH}_4\text{F}$ with a F/Zr ratio of 7. The same results were observed in the pilot plant runs but the larger F/Zr mole charge ratios are to be avoided unless dictated by geometry considerations because core losses and waste storage problems are multiplied as the excess fluoride is increased.

Dissolution time was lengthened considerably and somewhat unpredictably in the pilot plant runs by a zirconium oxide coating which is to be encountered on essentially all Zircaloy clad reactor fuel elements. The effect is illustrated with

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FIGURE 3

Comparison of Pilot Plant and Computer Data for a 5.5 M NH_4F -0.5 M NH_4NO_3 Dissolution

FIGURE 4

Comparison of Pilot Plant and Computer Data For a 4 M NH_4F -0.363 M NH_4NO_3 Dissolution

FIGURE 5
The Effect of Boil-up Rate on Dissolution Time

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FIGURE 6

The Effect of Initial Fluoride Concentration on Dissolution Time

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FIGURE 7

The Effect of F/Zr Mole Charge Ratio on Dissolution Time

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computer data in Figure 8. A plot of boil-up rate versus dissolution time for the dissolution of oxidized and unoxidized Zircaloy in 4 M NH_4F at a F/Zr mole charge ratio of 21 is presented. The curves show the increased dissolution time for the oxidized case. Unfortunately the absolute value of the time cycle predicted from the curve for the oxidized cladding would not necessarily cover a broad range of oxide quality. The computer runs were made using an empirical rate constant obtained from the dissolution of PRTR elements which had been oxidized in an autoclave at 400°C and 1150 psi for 72 hours. The data should apply fairly well to most oxidized claddings however, unless an exceptional layer of oxide is encountered.

The prediction of fuel cycle times from computer calculations should facilitate the impending reprocessing of NPR and PRTR fuels. Although the fuels will be oxide coated and the decladding of oxidized elements is somewhat unpredictable, a good approximation of the dissolution time can be made by the method employed here. In particular the advantages of a given set of run conditions may be determined by comparison with other simulated runs to provide a reasonable guide in flowsheet selection.

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FIGURE 8

The Effect of Oxide Coating on Dissolution Time

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APPENDIX I

Derivation of Equation 4

The ammonia water system is thought to be represented by the following set of equilibria: (4)

The ratio of NH_3 to NH_4OH is essentially constant for the first equation when the concentrations are small ($\text{NH}_3/\text{NH}_4\text{OH} = B$). The value of B at 25°C and at low concentrations is 0.885. (5)

The ionization constants may be written as follows:

$$(c) K_b(\text{true}) = \frac{(\text{NH}_4^+)(\text{OH}^-)}{(\text{NH}_4\text{OH})}$$

$$(d) K_b(\text{apparent}) = \frac{(\text{NH}_4^+)(\text{OH}^-)}{(\text{NH}_4\text{OH}) + (\text{NH}_3)} = \frac{(\text{NH}_4^+)(\text{OH}^-)}{(\text{NH}_4\text{OH})(1+B)}$$

The constant K_b (apparent) is cited in the literature as the ionization constant for ammonia in water and it is generally written:

$$(e) K_b = \frac{(\text{NH}_4^+)(\text{OH}^-)}{(\text{NH}_4\text{OH})}$$

where the term NH_4OH represents the total ammonia present both as NH_4OH and NH_3 .

The relationship between hydrogen ion concentration, dissolved ammonia and ammonium ion was established by modifying equation (e) as follows:

$$(f) \frac{1}{K_b} = \frac{\text{NH}_4\text{OH}}{(\text{NH}_4^+)(\text{OH}^-)}$$

$$(g) \text{OH}^- = K_w/\text{H}^+$$

$$(h) \frac{1}{K_b} = \frac{(\text{NH}_4\text{OH})(\text{H}^+)}{(\text{NH}_4^+)(K_w)}$$

$$(i) \text{H}^+ = \frac{(\text{NH}_4^+)}{(\text{NH}_4\text{OH})} \frac{K_w}{K_b}$$

The ratio $\frac{K_w}{K_b}$ is 4.0×10^{-10} at 100°C as evaluated by J. L. Carroll from laboratory tests on the Zirflex process. The ratio calculated from data in the International Critical Tables was 3.7×10^{-8} at 100°C , approximately a factor of 100 higher. This data was for dilute solutions however and was not readily applicable to the Zirflex solution because of its high ionic concentration. After completion of the computer runs a recheck of laboratory data showed that the $\frac{K_w}{K_b}$ could be as high as 5.5×10^{-10} and it is felt that this ratio would provide the most accurate computer simulations of the Zirflex process.

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FIGURE 9

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FIGURE 12

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Reaction Time (minutes)

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