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PRODUCTION--DISSOLUTION OF METAL FOILS BY
NITRIC-ACID/SULFURIC-ACID MIXTURES

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ABSTRACT

The first step in processing low-enriched uranium (LEU) targets for production of ^{99}Mo is to dissolve the neutron-irradiated uranium foil coming from the reactor. Appropriate conditions for dissolving the foils were determined by measuring the dissolution rates for uranium foil over a wide range of temperatures and acid concentrations. On the basis of these dissolution rates, the process chemistry, and a model that integrates dissolution rates as a function of temperature and composition, a closed stainless-steel dissolver was designed, built, and tested for dissolving up to 18 g of uranium foil. The results were quite successful, with the uranium foil being dissolved within one hour as desired. To do this, the dissolver temperature must be in the range from 97 to 102°C, and the dissolver solution (cocktail) must have a composition of 3M nitric acid and 2M sulfuric acid. The final dissolver solution is subsequently processed to separate ^{99}Mo from uranium, fission products, and other elements.

INTRODUCTION

Badan Tenaga Atom Nasional (BATAN) is currently producing ^{99}Mo from high-enriched uranium (HEU) UO_2 targets by the Cintichem process. This process was used until 1989 at the Cintichem reactor facilities in Tuxedo, New York. These facilities are no longer operational, and the proprietary rights for the process now belong to the U.S. Department of Energy. BATAN has a license to use the process in its facilities at Serpong, Indonesia. Argonne National Laboratory (ANL) and BATAN are working on a joint R&D project to develop a LEU-metal-foil target and recover ^{99}Mo from the irradiated target by using a modified Cintichem process. Successful completion of the work will enable commercial production of ^{99}Mo (for medical applications) from LEU instead of HEU.

Modifications are necessary to the HEU-Cintichem process in order to use it effectively with the LEU target. Our goal is to keep equipment modifications and process changes to a minimum so that a smooth switch is possible from HEU with UO_2 to LEU with uranium foil. In this paper, we report the results of our work to modify the target dissolution step of the Cintichem process for uranium foil. Experiments were done to determine how the dissolution rate for the irradiated LEU target will change as the temperature and concentrations of nitric and sulfuric acids are varied.

As the modified Cintichem process was developed, three process constraints were applied. First, the dissolution of the target must be rapid since the product ^{99}Mo has a short half-life ($t_{1/2} = 66 \text{ h}$). The design goal was an acceptable combination of the acid composition for the dissolver solution and the dissolver temperature such that the target dissolves within one hour. At the same time the resulting solution must not be so concentrated in nitric acid that it would interfere with subsequent recovery of ^{99}Mo having a yield and purity comparable to that of the HEU product. In any case, other changes may be needed in the process separation steps that follow dissolution of the uranium foil. These changes are discussed elsewhere [1, 2].

Second, the dissolution must be done in a sealed vessel capable of withstanding the pressure generated by the release of gaseous reaction products. A closed dissolver is required so that the volatile radionuclides, produced as the uranium fissioned in the reactor, are contained and subsequently released in a controlled fashion. Some radionuclides, e.g., ^{131}I , may be recovered for further use. Since uranium foil requires three times as much nitric acid per mole of uranium dissolved as UO_2 , three times as much NO will be in the gaseous product. Also, about five times more LEU is needed to produce the same ^{99}Mo yield. Thus, the final pressure in the LEU dissolver will be considerably higher than that in the HEU dissolver.

Third, the LEU dissolver should be similar to the HEU dissolver so that existing dissolution facilities for the Cintichem process can be used with only minor modifications. In the HEU case, the dissolver vessel is used only once. In the LEU case, the dissolver vessel will be reused to cut down on solid wastes.

In this paper, the work on the dissolution of LEU targets is discussed as follows: (1) the chemistry of the process, (2) small-scale dissolver tests, (3) modeling, (4) large-scale dissolver tests, and (5) future directions.

CHEMISTRY

From a knowledge of uranium dissolution reactions, one can determine how high the pressure will become in the closed dissolver vessel and if this pressure might affect the rate of dissolution. This information was used to design a closed dissolver with an appropriate pressure rating. It was also used to develop a model for both open and closed dissolvers.

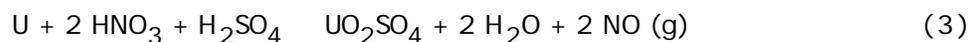
The dissolution of uranium by nitric and sulfuric acids proceeds in the following way:



Then, NO_2 reacts with water (in either the liquid or vapor phase) to form more HNO_3 plus NO ,



The overall reaction is



The presence of H_2SO_4 yields a higher dissolution rate as H_2SO_4 seems to act as a catalyst [3]. As pressure is increased at equilibrium conditions, Eq. 2 indicates that the amount of NO_2 in the

gas space will decrease, and the amount of NO and HNO₃ will increase. Overall, the increased pressure of a closed dissolver should increase the amount of HNO₃ somewhat, with a corresponding decrease in the time for total dissolution.

Some of the NO₂ formed during the initial uranium dissolution (see Eq. 1) will escape to the vapor phase; the rest will react with water to form HNO₃ and NO. Even the NO₂ that escapes to the vapor phase will react with the water vapor to form HNO₃ and NO. Thus, the overall reaction will remain Eq. 3 as long as the concentration of HNO₃ is not too high, typically, 8M or less. At higher HNO₃ concentrations, the reaction given by Eq. 2 shifts to the left, so that more NO₂ remains in the gas phase at equilibrium. At these higher HNO₃ concentrations, the major reaction becomes that given by Eq. 1 [4].

When air was bubbled through a dissolving-uranium-foil solution in an open system to enhance mixing, the rate of dissolution dropped sharply [5]. This drop in dissolution rate apparently occurs because some of the NO₂ is able to escape with the air. This loss reduces the formation of HNO₃ by Eq. 2, and, thus, lowers the rate of uranium dissolution. If all the NO₂ were immediately removed, the reaction would follow Eq. 1, and the HNO₃ concentration would drop three times as fast as indicated by Eq. 3 per unit of uranium dissolved. In a closed system, no NO₂ will be lost so that the overall reaction will be close to that given by Eq. 3. The double arrow of Eq. 2 indicates an equilibrium reaction. Thus, there will always be some NO₂ present. The presence of gaseous NO₂ is easily detected, as its brown fumes are visible at low concentrations, 75 to 100 ppm.

Any oxygen in the system will react with NO to form NO₂ as follows:



This reaction is essentially irreversible at typical uranium dissolution conditions [4]. The NO₂ so formed will produce more HNO₃, following the reaction given by Eq. 2. Thus, for each mole of O₂ initially present, the final number of moles of NO will be reduced by two moles as long as there is excess NO relative to the O₂.

Some nitrous acid is always found along with nitric acid in solution, especially in dilute solutions, because of the reaction



However, the concentration of nitrous acid is not high since it is unstable in the presence of stronger acids and decomposes to HNO₃, NO, and H₂O [4].

SMALL-SCALE DISSOLVER TESTS

Numerous small-scale dissolver tests were done where depleted uranium metal foil was dissolved in a solution containing both nitric acid and sulfuric acid. The foils were about 5-mil (0.13-mm) thick, the same thickness as the LEU target. In these experiments, known masses (30 to 700 mg) of uranium foil were dissolved using 3 mL of acid in a glass apparatus. Unless noted otherwise, the glass apparatus was a 15-mL centrifuge tube covered with a watch glass at a constant temperature. This is considered to be an open system because excess gas escapes past the watch glass and does not pressurize the system. There was no way to control whether the

initial gas (usually air) or the reaction-product gases escaped from the gas space over the dissolver liquid. The end of the dissolution was taken as that time when no more gas bubbles were evolved. The rate of dissolution, in units of $\text{mg}/(\text{min}\cdot\text{cm}^2)$, was calculated from the mass and surface area of the foil along with the time for complete dissolution. These experiments were used (1) to specify the temperature of dissolution, (2) to specify the composition of the dissolver cocktail, and (3) to calculate the pressure increase in the dissolution of a full-size target.

In some cases a special glass system was used with a gas-tight closure to measure the pressure and composition of the gases released by dissolution. This special glass dissolver had a volume of 200 mL. Only a small portion of the apparatus containing the dissolver solution and the uranium foil was immersed in the constant temperature bath. A major portion of the apparatus (190 mL of the 200 mL volume) was at room temperature. The pressure changes were recorded by a Baratron gauge. The composition of the gaseous products was determined by a mass spectrometer.

Dissolution Rates at Constant Process Conditions at ANL

In ANL tests of dissolution rates at constant process conditions, the mass of uranium foil was small relative to the volume of solution, so that the concentration of the nitric and sulfuric acids did not change much over the course of the dissolution. A constant temperature was maintained by keeping the dissolution tube in a constant-temperature bath. The acid concentrations associated with these tests are those of nitric and sulfuric acid at the start of each test.

Concentration Effect

A series of experiments was done in which the concentrations of HNO_3 and H_2SO_4 were varied in the dissolver solution. In these tests, 30 mg samples of depleted uranium metal with a surface density of $203 \text{ mg}/\text{cm}^2$ were dissolved in six different solutions containing nitric acid concentrations of 0.75, 1.5, and 3M and sulfuric acid concentrations of 1 and 2M . The uranium concentration in the final solution was about 0.04M . The temperature during the dissolution was maintained at $92 \pm 2^\circ\text{C}$. The measured dissolution rates, shown in Figure 1, indicate that the dissolution rate is directly proportional to the nitric acid concentration at a fixed concentration of sulfuric acid. A similar proportionality is evident for variations in sulfuric acid concentration when the nitric acid concentration is fixed.

In these tests, the dissolution proceeded smoothly, with a steady evolution of gases from the foil surface after a delay of about a minute. The presence of an oxide coating on the surface of the uranium foil appeared to be causing the delay. The gas space acquired a brown color due to the release of NO_2 . The color vanished slowly, but not completely, with time. This effect was either due to the escape of NO_2 from the gas space or the reactions indicated by Eqs. 2 and 5.

Based on these tests, the initial dissolver solution (cocktail) must contain at least 3M HNO_3 and 2M H_2SO_4 if the dissolution is to be done at 92°C . At these conditions, the rate of dissolution is $3.8 \text{ mg}/(\text{min}\cdot\text{cm}^2)$ so that a 5-mil (1.3-mm) thick foil dissolves in 27 min. For other solution compositions shown in Figure 1, the foil dissolves more slowly so that the time for complete dissolution exceeds one hour. In practical dissolutions, the final solution will have a uranium concentration close to 1.0M . For these cases, the dissolution rate declines steadily as the dissolution proceeds because the concentrations of both nitric and sulfuric acid decrease, as indicated by Eq. 3. This means that large samples with the same thickness as small samples will take more time to dissolve in the same volume of the dissolver solution. This is

discussed further in the sections below on modeling and dissolution rates under varying process conditions.

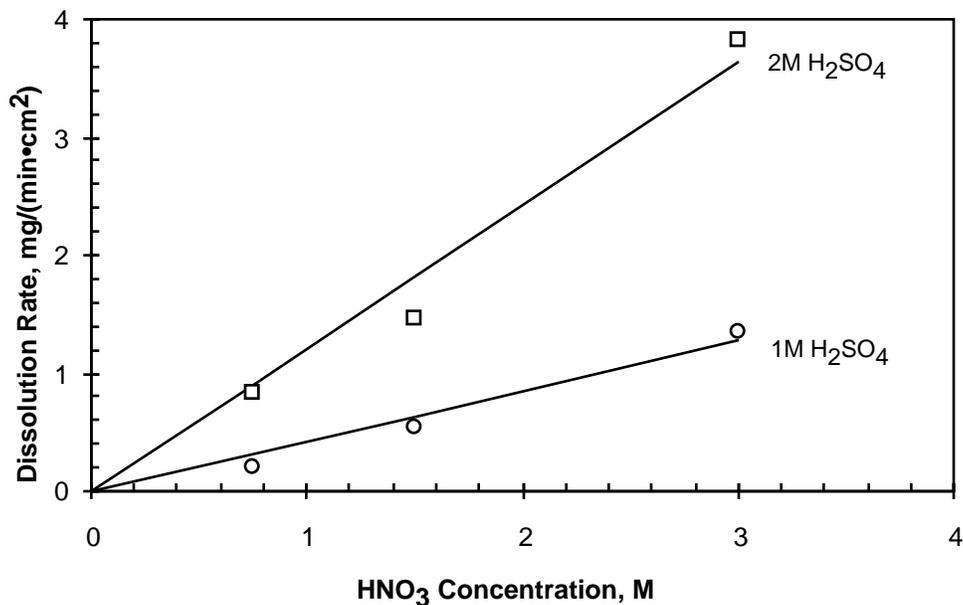


Figure 1. Effect of Nitric and Sulfuric Acid Concentrations on the Dissolution Rate of Uranium Metal Foil at 92°C

Dissolution Rates under Varying Process Conditions at ANL

In ANL tests of dissolution rates under varying process conditions, the mass of uranium foil was large enough relative to the volume of solution that the concentration of the nitric and sulfuric acids changed significantly over the course of the dissolution. These tests are closer to actual production conditions for irradiated targets. A constant temperature was maintained during dissolution. The time to dissolve the foil gives an overall (average) dissolution rate appropriate for the varying process conditions of the test. Because these data are not at constant process conditions, they were not a part of the data correlation given in the modeling section below. However, some of these results were used to check the model, which integrates uranium-foil dissolution over varying process conditions.

Increasing Uranium Mass

In the processing of LEU targets, it is essential to prepare concentrated uranium solutions, preferably about 1M or greater. This cuts down on the volume of liquid to be processed and reduces the amount of waste generated. In a series of tests, progressively larger masses of depleted uranium, starting at 230 mg and ending at 700 mg, were dissolved so that the final uranium concentration increased from 0.3M to 1M. (Note that, since the surface density of these foils was 173 mg/cm² in all cases, the total dissolution time would have been the same if the acid concentration in the dissolver solution had not changed.) The dissolutions were done at 90°C, using 3 mL of solution consisting of 3M nitric acid and 2M sulfuric acid. As shown in Figure 2, the total dissolution time increases as the final uranium concentration increases. Extrapolating to zero uranium concentration gives a total dissolution time of 25 min, very close to the 27 min mentioned above for constant process conditions. As one prepares

more concentrated uranium solutions, the total dissolution time becomes longer. For example, the preparation of a 1M solution will take about 100 min. Based on this result as well as the modeling below, the time to dissolve 1M of uranium will take longer than the 60 min desired. However, as reported below, the uranium-foil dissolutions in the stainless-steel dissolver went faster than expected and showed dissolution times significantly less than 60 min.

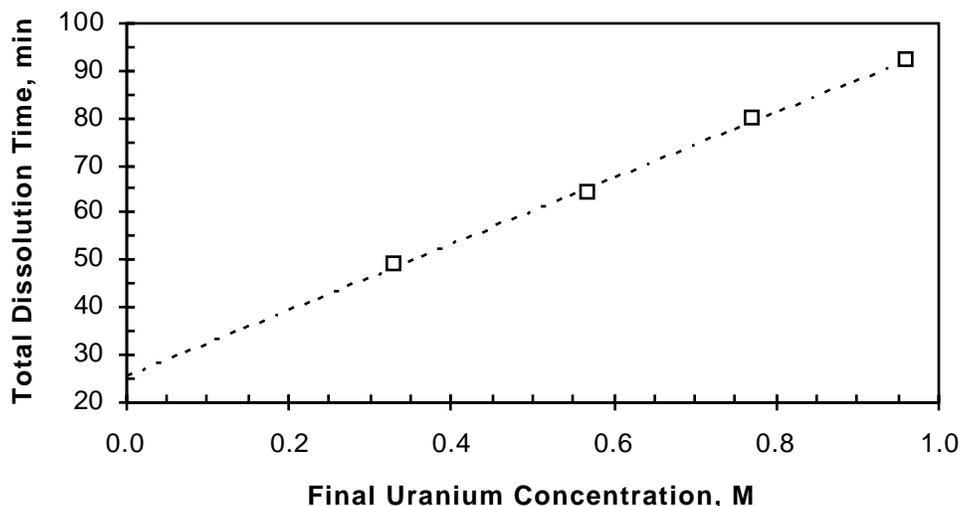


Figure 2. Effect of Final Uranium Concentration on the Time to Dissolve 5-mil-thick Uranium Foil Using a Solution of 3M Nitric Acid and 2M Sulfuric Acid at 90°C

The final dissolver solution was a greenish yellow, possibly due to the presence of blue nitrous acid mixed with yellow UO_2^{2+} solution. As expected, boiling the solution destroyed the nitrous acid, and thus the green color, yielding a straw yellow solution. The presence of nitrite ions and dissolved NO_x gases in the dissolved solution may adversely affect the yield and purity of the ^{99}Mo product because of unwanted redox reactions involving nitrite. Work is needed to determine the tolerance level for nitrite in the Cintichem process.

After dissolving 714 mg of uranium as outlined above, the composition of the final solution was measured. From the concentrations of nitrate, sulfate, and free H^+ , which were measured with an uncertainty of $\pm 5\%$, the final composition was determined to be 1M UO_2SO_4 , 1.7M HNO_3 , and 1M H_2SO_4 . The total H^+ concentration was 3.7M. The LEU target solution from plant tests in the stainless-steel dissolver will be similar to this composition. The experiments done by [1, 2] show that such solutions can be processed by the Cintichem process to recover ^{99}Mo with high yield and required purity.

Temperature Effect

The effect of temperature and solution composition on dissolution rate was studied in the range from 60 to 90°C in 10°C increments. Because the mass of uranium foil ranged from 120 to 145 mg, the final UO_2^{2+} concentrations ranged from 0.17 to 0.20 M. Following Eq 3, the sulfuric acid was decreased by 0.17 to 0.20M and the nitric acid was decreased by 0.34 to

0.40M. Thus, the changes in solution concentration were significant, and the rate of dissolution was the overall rate for these conditions. However, since the final uranium concentration was about the same, the overall dissolution rates can be plotted as a function of temperature to derive the activation energy for the dissolution rate of uranium foil. From the curves shown in Figure 3, the activation energy is 44 ± 2 kJ/mol for the two sets of data. If the dissolution rates are extrapolated to 100°C, they are 50% greater than at 90°C. Thus, increasing dissolver temperature is another way to reduce the dissolution time.

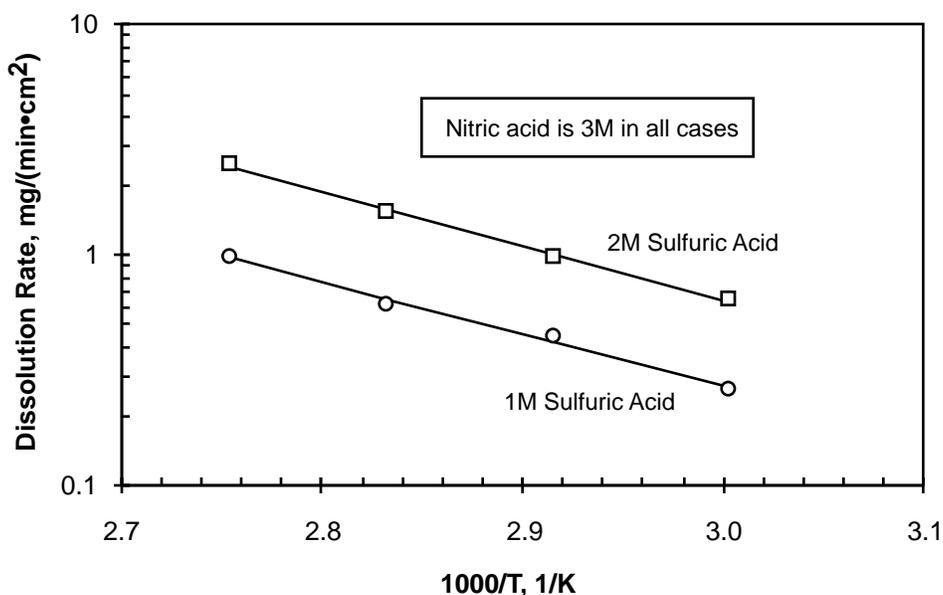


Figure 3. Effect of Temperature on the Overall Dissolution Rate of Uranium Foil at Two Solution Compositions

Dissolution in a Closed Glass System

In the closed glass system, uranium foils from 150 to 650 mg were dissolved at 90°C by using 3 mL of dissolver solution consisting of 3M nitric acid and 2M sulfuric acid. The corresponding uranium concentrations increased from 0.2M to 0.9M. Pressure changes were measured as a function of time, and the gas compositions were determined from samples collected at the end of each test. A key finding was that no hydrogen evolved during the dissolution reaction. Therefore, explosive mixtures of hydrogen and oxygen will not be created by the dissolution of uranium foil.

In this system, the rate of dissolution was affected by the initial pressure. At 1 atm of air (743 torr), 157 mg of uranium dissolved in 40 min; at 0.5 atm of air (375 torr), the same amount of uranium took three times longer to dissolve. (Note that three different units of pressure are used in the paper, torr, atmosphere, and psi. This is a natural consequence of the units used in the pressure measuring apparatus: Baratron gauge, mercury barometer, and Bourdon tube.) The final uranium concentration was 0.22M. The pressure variation during the dissolution of 157 mg uranium is shown in Figure 4. The reduction in pressure is likely the result of the consumption of oxygen (dissolved oxygen as well as gas-space oxygen) following Eq. 4.

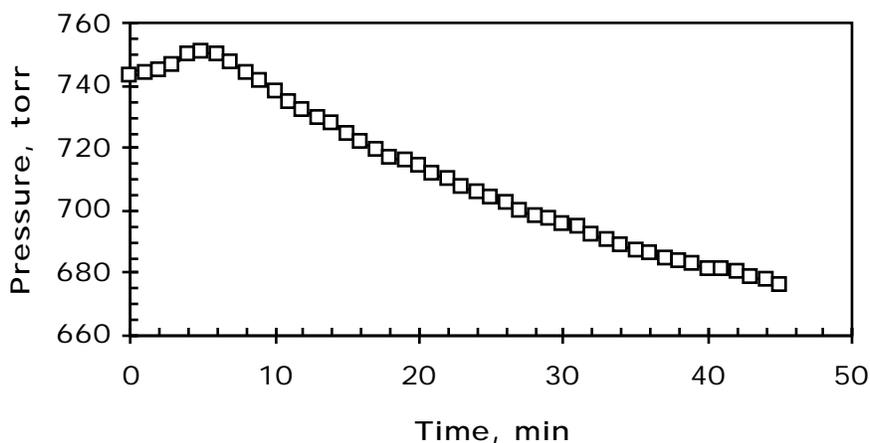


Figure 4. Variation of Pressure with Time during Dissolution of Uranium Foil at 90°C in a Closed System with a Solution of 3M Nitric Acid and 2M Sulfuric Acid

When more uranium (664 mg) was dissolved at atmospheric pressure (737 torr), the pressure changes were different. In the first 7 min, there was a small increase to 755 torr followed by a small decrease to 738 torr. Then the pressure climbed steadily to 1026 torr (5.1 psig) at the end of dissolution in 78 min. The concentration of uranium in the final solution was 0.93M. Based on the pressure rise in this test, the final pressure in the stainless-steel dissolver with 18.1 g of uranium foil at 102°C was estimated to be 155 psig. The actual pressure (see below) was 245 psig. The difference in these two pressures can be explained by the relatively large amount of O₂ in the glass system relative to the amount of uranium dissolved. For this system, the oxygen reacted with NO to form NO₂ (see Eq. 4) and, hence, nitric acid (see Eq. 2) so that the pressure was reduced significantly.

Dissolution Rates at BATAN

At BATAN small-scale tests of the dissolution rate for uranium foil were conducted at both constant and varying process conditions. A constant temperature was maintained by keeping the glass dissolver tube in a constant-temperature bath. The BATAN results are reported in Table 1 along with selected ANL results. A key responsibility of the BATAN work is to compare the dissolution rates for small samples of unirradiated, depleted uranium foil with irradiated LEU metal foil under the same conditions. At this point, the irradiated foil tests have not been done because of problems with the irradiated LEU target [6].

Table 1. Results of Test Tube Dissolution Experiments

Test	Temp., °C	Amt of U Foil Dissolved, mg	Foil Area (one side), cm ²	Initial Conc, <u>M</u>		Total Dissolution Time, min		Notes
				HNO ₃	H ₂ SO ₄	Exp.	Model	
ANL	92	714	3.82	3.0	2.0	98	110	a
"	90	664	3.27	"	"	78	110	b
"	"	156.5	0.77	"	"	40 ± 1	29	c
BATAN	"	77.2	0.346	"	"	30.5	27	
"	"	63.9	0.285	"	"	30.7	26	
"	92	24.9	0.12	1.5	1.0	180	262	d
"	"	21.2	0.12	2.25	0.5	360	243	e

^aOnly 2.9 mL of the initial 3.0 mL of solution was left at the end of the dissolution.

^bThis test was done around 14.7 psia with an atmosphere of air in the large gas space over the liquid.

^cThis result represents three tests that were done around 14.7 psia with atmospheres of air, oxygen, and helium, respectively, in the large gas space over the liquid.

^dStarted with 49.0 mg of U foil, ended with 24.1 mg.

^eStarted with 24.1 mg of U foil, ended with 2.9 mg.

MODELING

To estimate the rate of dissolution for uranium foil as a function of the temperature and the concentration of HNO₃ and H₂SO₄, the above data on dissolution rates at constant process conditions were combined with earlier data [5]. These earlier rate-of-dissolution data were extrapolated to 92°C for the various pairs of acid concentrations. Then, the rate of uranium dissolution at 92°C (R_{U92}) was obtained by a least-squares fit of the data using an equation of the form

$$R_{U92} = a_{n1} \cdot x + a_{s1} \cdot y + a_{n2} \cdot x^2 + a_{s2} \cdot y^2 + a_{22} \cdot x^2y^2 + a_{s3} \cdot y^3 + a_{33} \cdot x^3y^3 \quad (6)$$

where the a's are coefficients that were adjusted by using the least-squares fit, x is the molar concentration of HNO₃, and y is the molar concentration of H₂SO₄. For this least-squares fit, the coefficients were constrained to be zero or positive so that R_{U92} is always positive. This gave a_{22} of 0.0253, a_{33} of 0.01554, a_{n1} of 0.0262, a_{n2} of 0.0389, a_{s1} of 0.0984, a_{s2} of 0.0679, and a_{s3} of 0.01473. The correlation given by Eq. 6 yielded the contour plot in Figure 5, which shows how the uranium dissolution rates vary in the expected range of operation. For a typical reaction path, indicated by the dashed arrow going from point A to point B, the initial dissolution rate will be much higher than the final dissolution rate. The direction of this path for a given initial concentration of HNO₃ and H₂SO₄ follows from the overall reaction given by Eq. 3.

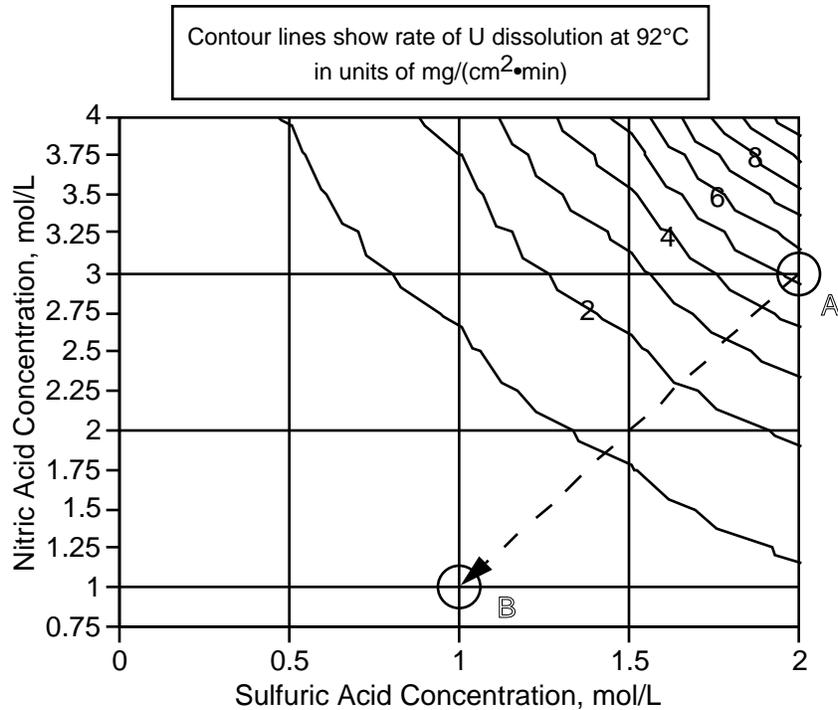


Figure 5. Effect of the Concentration of Nitric Acid and Sulfuric Acid on the Dissolution Rate of Uranium Foil

In extrapolating the data to 92°C, all solution compositions tested were found to have the same activation energy, as mentioned earlier. To obtain the best activation energy for all the data, a least-squares fit was done using an equation of the form

$$R_U = R_{U92} \cdot e^{\frac{E_d}{R} \cdot \frac{t - 92}{365.2 \cdot (t + 273.2)}} \quad (7)$$

where E_d is the activation energy associated with dissolution rate in cal/mol, R is the gas constant of 1.987 cal/(mol·K), R_U is the rate of uranium foil dissolution in mg/(min·cm²) at temperature t in °C, and R_{U92} is the rate of uranium foil dissolution in mg/(min·cm²) at 92°C. The results gave an E_d value of 10,300 cal/mol (43 kJ/mol). The experimental conditions used in this correlation include: temperature from 25 to 95°C, HNO₃ concentration from 0.75 to 16M, and H₂SO₄ concentration from 0 to 2M.

Employing the correlation given by Eq. 7 and the overall reaction given by Eq. 3, and knowing how the temperature varies with time during the dissolution of the uranium foil, we developed a dissolver model which calculates the time that it will take for a given mass of uranium foil to dissolve. The dissolver model integrates the calculated dissolution rate for uranium with time, keeping track of the changes in the concentrations of HNO₃ and H₂SO₄ as the uranium dissolves. The model assumes that the heat of reaction for the dissolving uranium can be neglected. If the dissolver system is closed, as is the case for the stainless-steel dissolver used in our large-scale tests, the model calculates how the dissolver pressure will vary with time.

The dissolver model was applied to several of the small-scale dissolver tests discussed above. In these tests, the acid solution was not mixed except by the gas bubbles coming off the surface of the dissolving uranium foil. Given the nature of these experiments, there seems to be reasonable agreement between the experimental and model values for the total dissolution time listed in Table 1. The differences between the experimental and model values are the greatest for the two tests with the lowest dissolution rates (the highest dissolution times). The low rate was expected because the initial acid concentrations were much lower than those used for the other five tests. Factors that contribute to these differences are (1) the poorer mixing at low dissolution rates, (2) the small number of low dissolution rates in the data used to develop the correlation, and (3) an increased relative error in the correlation at low dissolution rates.

The dissolver model was also applied to the large-scale dissolver tests presented next. The results of applying the dissolver model to these tests are given there.

LARGE-SCALE DISSOLVER TESTS

With regard to the large-scale dissolver tests, two stainless-steel dissolvers, one for ANL and one for BATAN, were designed, built, and tested hydrostatically. The two units were then calibrated for temperature. Finally, several large-scale dissolver tests were done with depleted uranium metal foil. The foils were about 5-mil (0.13-mm) thick, the same thickness as the LEU target. Based on the small-scale dissolver tests, the initial dissolver solution was set at 3M nitric acid and 2M sulfuric acid and the steady-state dissolver temperature at 102°C.

Equipment Design

A special 304-stainless-steel dissolver was designed to process up to 18 g of 5-mil (0.13-mm) uranium foil. Desired design features included the following: (1) the dissolver fits in existing Cintichem heating equipment, (2) the dissolver is light weight so that it can be handled by the manipulators in a shielded-cell facility, (3) the wall is thin so that the solution inside can be heated relatively easily, (4) any seals work for both vacuum and pressurized operation, (5) the 5-mil (0.13-mm) uranium foil slides easily into the dissolver as one piece, which has a length of 4 in. (101.6 mm) and a width of 3 in. (76.2 mm) [note that the width is bent around so that the foil has a diameter of 1 in. (25.4 mm)], and (6) all parts are easy to assemble and disassemble in a shielded-cell facility. Starting with the basic Cintichem concept [7, 8], a dissolver was designed that was 18-in. (457-mm) long with an outside diameter of 1.25 in. (31.8 mm) and a wall thickness of 35 mil (0.89 mm). This design allows for a maximum operating pressure of 700 psig, about twice the pressure expected when 80 mL of solution is used to dissolve 18 g of uranium foil, following Eq. 3. A flange at the open end of the dissolver allows the uranium foil to be inserted easily. The flange has two Viton O-rings so that it will seal during both pressurized and vacuum operations. The current Cintichem tee, which attaches to the open end of the dissolver, can still be used. It now attaches to the removable flange. This tee allows the user to evacuate the dissolver, add solution, vent or recover pressurized gases in the dissolver, remove solution, and rinse the dissolver. A photograph of the disassembled dissolver is shown in Figure 6.

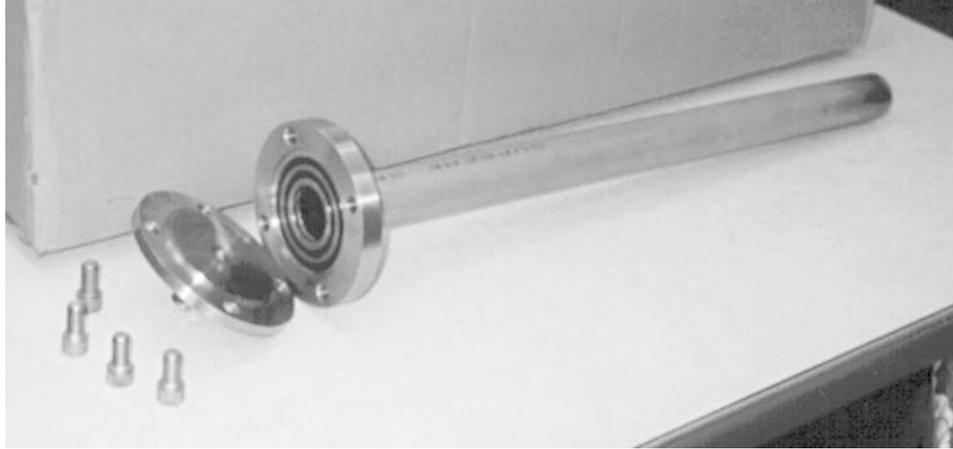


Figure 6. Flanged Dissolver for Uranium Foil

Because the Cintichem-style tee on the removable flange is small, it cannot accommodate a bimetal thermometer. Thus, before a dissolver is used in a specific Cintichem heating system, a calibration must be performed for the steady-state dissolver temperature as a function of the controller set point. To do this thermal calibration, a special removable-flange-and-tee system was developed that puts a bimetal thermometer 4 in. (102 mm) into the dissolver cavity and allows the dissolver pressure to be measured at the same time. This system was used to calibrate the dissolver with 80 mL of water. This calibration was used to set the heater controller to the desired steady-state temperature in subsequent tests with the flanged dissolver. The flanged dissolvers at ANL and BATAN were both calibrated in this way.

A part of the total dissolution time is devoted to the heatup and cooldown of the dissolver. Thus, when the thermal calibration was carried out to determine the steady-state dissolver temperature, the rates of heatup and cooldown for the dissolver were also measured and correlated.

Test Results

As shown in Table 2, six dissolver tests were completed with the new dissolver, one at ANL, five at BATAN. In all the tests the nominal thickness of the uranium foil was 5 mil (0.13 mm), the steady-state temperature was $102 \pm 2^\circ\text{C}$, the initial composition of the 80-mL dissolver solution was 3M HNO_3 and $2\text{M H}_2\text{SO}_4$, and the dissolver orientation was either horizontal or at a 45° angle to the horizon with the dissolver flange at the upper end. The variation of pressure with time during five of the six tests is shown in Figure 7. A plot of the final dissolver pressure for various amounts of uranium foil, given in Figure 8, shows that the final pressure is proportional to the amount of foil.

Table 2. Results of Stainless-Steel Dissolver Experiments

Test Location	Dissolver Orientation	5-mil U foil, g	Pressure, psig		Time, min			Start Cooling
			Max.	Final	At Max. Press.	Press. About Flat ^a	Press. Flat ^b	
BATAN	Horizontal	0.17	30	21	25	20	55	65
BATAN	45°	3.04	50	50	21	20	24	46
BATAN	45°	5.29	75	78	19	19	26	42
BATAN	45°	9.98	200	140	16	30	44	54
ANL	Horizontal	12.89	250	180	8	16	106	180
BATAN	Horizontal	18.14	390	245	10	26	44	170

^aPressure was within 10 psi of the final pressure.

^bPressure did not change after this time.

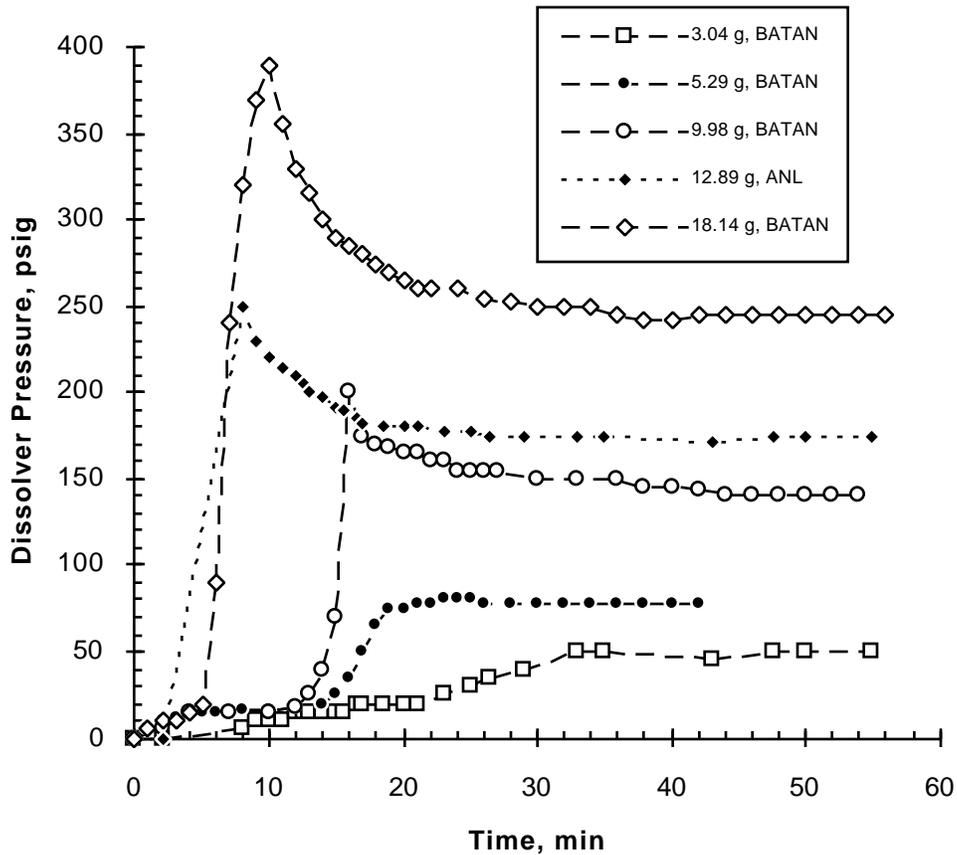


Figure 7. Variation of Pressure with Time during Dissolution of Uranium Foil in the Stainless-Steel Dissolver

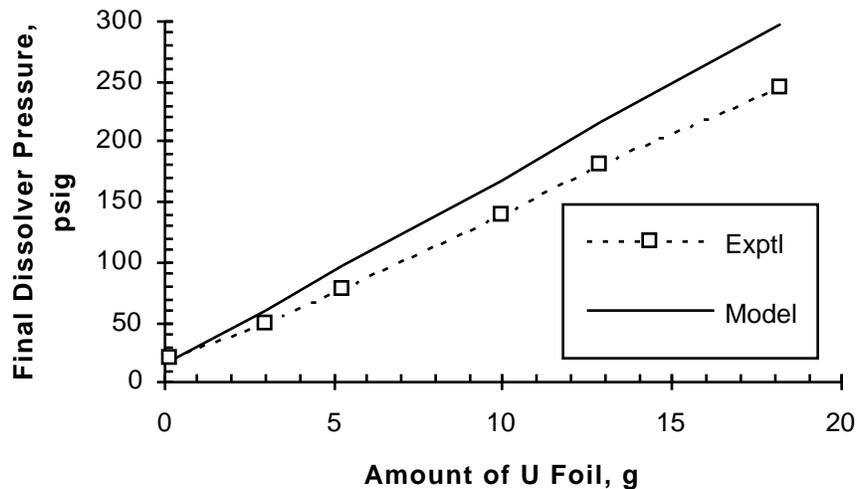


Figure 8. Variation of Final Dissolver Pressure with Amount of Uranium Foil

The dissolver model predicted that pressure would rise steadily with time until a final maximum pressure was reached when all the uranium foil was dissolved. The experimental results show that, for five or more grams of uranium foil, the dissolution went through maximum pressure before all the foil was dissolved. One explanation is that the high pressure is a result of NO_2 generated from the reaction given by Eq. 1. If this happened, the HNO_3 concentration in the solution would fall below that used in the model, and the total dissolution time would be greater than given by the model. Just the opposite was the case: the model predicted that four cases would have uranium foil left in the amounts of 0.26, 1.29, 2.52, and 0.67 g for initial uranium masses (see Table 2) of 3.04, 5.29, 9.98, and 18.14 g, respectively.

A second explanation for the initial high pressure is that the heat of uranium dissolution caused rapid self-sustaining heatup of the solution in the dissolver. To test this, the time for each foil to dissolve completely was estimated as the average of the time when the pressure is about flat (within 10 psi of the final pressure) and the time when the pressure is flat (the final pressure). The model was then modified so that rapid heating could be included during the time leading up to the peak pressure. The rate of rapid heating was increased until, according to the model, the foil would dissolve at the estimated average time. In most cases, the model then showed a peak pressure that was at, or above, the observed peak pressure. For the ANL test, where the two times being averaged were so different (16 and 106 min), such a peak pressure did not occur until the time for complete dissolution was required to be very close to the shorter time. For the foils in Table 2 with masses of 0.17, 3.04, 5.29, 9.98, 12.89, and 18.14 g, the peak model temperatures associated with the peak measured pressures were 121, 144, 148, 172, 174, and 211°C, respectively. The corresponding complete-dissolution times from the model were 38, 33, 23, 37, 16, and 35 min. Thus, it appears that all dissolutions occurred in 16 to 38 min and the heat of uranium dissolution was very important in supplying the temperatures needed to obtain these short dissolution times.

For each experimental curve in Figure 7, the point where the pressure starts to rise rapidly is taken as the point where self-heating starts. The 12.89- and 18.14-g cases became self-heating about 5 min after heating started. The heating of the 5.29- and 9.98-g cases became self-sustaining about 15 min after heating started. The 3.04-g case (and the 0.17-g case, not shown) did not have a period of rapid pressure rise. That these last two cases did not

have a period of rapid pressure rise is attributed to the small amount of foil relative to the solution present. Of the other four cases, the first two had the dissolver in a horizontal position, the other two had the dissolver at a 45° angle. In the horizontal position, the 4-in. (102-mm) long foil cylinder was in the bottom of the dissolver, while the 80 mL of solution was spread out along the 18 in. (457 mm) of dissolver length. Thus, only the 20 mL of solution around the foil needed to be heated to a temperature where the reaction becomes self-sustaining. Note that the hot air heating the dissolver strikes the bottom (closed end) of the dissolver first. In the angled position, the foil cylinder and all 80 mL of solution were in the bottom of the dissolver. Thus, the longer time before rapid heating started in the angled cases is attributed to the longer time needed to heat 80 mL of solution to a temperature where rapid self-heating occurs.

As shown in Figure 8, the model predicted that the final dissolver pressure would be proportional to the amount of foil dissolved. However, this pressure was somewhat (about 25%) higher than the actual pressure. This suggests that some of the NO and NO₂ gases may be dissolved in the solution. The solubility of these gases was not included in the current model.

FUTURE DIRECTIONS

Future work includes (1) improving the model for the dissolution process, (2) determining the best orientation for the dissolver, (3) optimizing the dissolver for the amount of LEU to be charged to a production dissolver, and (4) identifying the best materials of construction for a production dissolver. The model needs to include the heat of uranium dissolution as well as other factors, such as the amount of solution in the vicinity of the foil and the solubility of NO and NO₂ in the solution. If the dissolver is tilted so that the foil is completely covered with solution, the dissolver still seems to work. The dissolver orientation will be explored further to determine if there are any drawbacks to more vertical positions and if such a dissolver needs to be rotated at all. For the few tests done, the 304 stainless-steel dissolver worked well, with no visible corrosion problems. It needs to be determined what the life of the 304 stainless-steel dissolver will be and if another metal would be more cost effective for a production dissolver.

Since the amounts of the oxides of nitrogen (NO_x) gases evolved during the LEU dissolution with metal foil are greater than those for the HEU dissolution with UO₂, and since these gases are mixed with the volatile radionuclides, it is not known whether the gas traps that are used for HEU are suitable for LEU processing. Additional studies are required to ensure that fission gases are trapped effectively and are not released into the environment before they decay away.

SUMMARY

The composition of the dissolver solution (cocktail) and the temperature required to achieve a quick dissolution of irradiated LEU-metal foil targets were established in small-scale dissolver tests using depleted uranium foils in the place of LEU foils. These experiments were done with a glass apparatus containing 30 to 700 mg of uranium in 3 mL of the dissolver cocktail. The results indicated that the cocktail should have a composition of 3M nitric acid and 2M sulfuric acid, and the dissolver temperature should be 97 to 102°C. A key point is that no hydrogen is evolved in the dissolution process, and therefore, explosive gas mixtures will not be formed.

Using the process chemistry and the results of the small-scale dissolver tests, we developed a correlation giving the rate of uranium dissolution over a wide range of temperatures (25 to 95°C) and concentrations for nitric acid (0.75 to 16M) and sulfuric acid (0 to 2M). This correlation was employed to develop a model for the dissolution of uranium foil as a function of time and temperature. The model worked fairly well for tests where a small amount of uranium foil was dissolved in a test tube in a constant temperature bath. The model gave conservative dissolution times for the stainless steel dissolver, where the heat of uranium dissolution apparently plays an important role. Ways in which the dissolution model can be improved were identified.

Through a knowledge of the process chemistry, the results of the small-scale dissolver tests, and the calculations with dissolver model, a stainless-steel dissolver was designed, built, and tested for 5-mil-thick (0.13 mm) uranium foils with masses from 0.2 to 18 g. This dissolver was designed to use existing Cintichem equipment. Tests showed that the uranium foil was dissolved in 30 to 60 min with uranium concentrations up to 1.0M so that basic process goals were met. Remote-handling features were incorporated into the dissolver, making it usable in a shielded-cell facility. The dissolver minimizes the amount of nitric and sulfuric acid used. This, in turn, minimizes the solution volume that must be processed to recover the ⁹⁹Mo from the uranium, fission products, and other materials. The dissolver can be reused so that the amount of solid waste generated is reduced.

Overall, small-scale dissolver tests were used in the design of the stainless-steel dissolver for irradiated LEU targets. It was tested by dissolving depleted uranium metal of the same mass and thickness as the LEU target and found to work well.

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