PROGRESS IN ALKALINE PEROXIDE DISSOLUTION OF LOW-ENRICHED URANIUM METAL AND SILICIDE TARGETS*

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ABSTRACT

This paper reports recent progress on two alkaline peroxide dissolution processes: the dissolution of low-enriched uranium metal and silicide (U_3Si_2) targets. These processes are being developed to substitute low-enriched for high-enriched uranium in targets used for production of fission-product ^{99}Mo. Issues that are addressed include (1) dissolution kinetics of silicide targets, (2) ^{99}Mo lost during aluminum dissolution, (3) modeling of hydrogen peroxide consumption, (4) optimization of the uranium foil dissolution process, and (5) selection of uranium foil barrier materials. Future work associated with these two processes is also briefly discussed.

INTRODUCTION

Technetium-99m (99mTc) is a medical isotope that has been used worldwide for diagnostic and treatment procedures. Currently, ^{99}Mo, the precursor of 99mTc, is almost exclusively produced from high-enriched uranium (HEU). Concerns over nuclear proliferation are driving research to replace HEU with low-enriched uranium (LEU). As a result, the Reduced Enrichment Research and Test Reactor (RERTR) program at Argonne National Laboratory (ANL) aims to develop LEU targets for production of fission-product ^{99}Mo [1].

As a part of this program, we are studying two LEU targets to replace the current HEU aluminide dispersion fuel target: uranium silicide (U_3Si_2) and uranium foil. This paper reports on the progress made during 1996 in developing alkaline peroxide dissolution processes for these LEU targets.

DISSOLUTION OF LEU SILICIDE TARGETS WITH ALKALINE PEROXIDE SOLUTION

Over the last several years, uranium silicide fuels have been developed as LEU targets for ^{99}Mo production [2]. Unlike UAl_x, U_3Si_2 does not readily dissolve in base. Therefore, target dissolution continues to be a primary development need for the replacement of conventional HEU aluminide with LEU silicide targets for ^{99}Mo production. In 1996, work continued on aluminum dissolution, including that in the cladding and fuel matrix, and uranium silicide dissolution.

Dissolution Kinetics of Uranium Silicide

We developed a U_3Si_2 dissolution rate model in the past year. The dissolution of uranium silicide in alkaline peroxide is proposed as:

$$U_3Si_2 + 25H_2O_2 + 10OH^- \rightarrow 2SiO_3^{2-} + 3UO_2(O_2H)_4^{2-} + 24H_2O \tag{1}$$

The dissolution kinetics of the U_3Si_2 particles was determined by use of the initial rate method. Experiments were carried out in an open, batch-reactor. Grap samples were taken at predetermined time intervals during dissolution and then analyzed by inductively coupled plasma-mass spectrometry (ICP-MS). The concentration of uranium was plotted against time. The initial reaction rate is the slope of a linear-regression fit for uranium concentration vs. time at the start (0.5-5 min) of each experiment.

Initial reaction rates were obtained for both comminuted and atomized U_3Si_2 particles [3,4]. The same mass of spherical atomized particles dissolved more slowly than the comminuted particles. This is due mainly to the surface area. The large surface area in the atomized particles is attributed to pore structure. It is believed that the internal surface of atomized particles was not effectively exposed to reactants during dissolution because the gas bubbles produced by the vigorous reaction inhibited the diffusion of reactants into the pores. However, the comminuted particles have a fine surface and not a porous structure. Thus, a reasonable effective surface area for the comminuted particles (200 cm^2/g) is about twice that of the atomized particles (100 cm^2/g). When the effective surface area is considered, the atomized and comminuted U_3Si_2 particles have similar uranium dissolution rates at 50°C.

The dissolution rate was found to vary with the initial base and peroxide concentration. A thermodynamic model for dissolution with an alkaline peroxide solution, developed by means of a software package called the Environmental Simulation Program (ESP) [5], predicts that hydrogen peroxide (H_2O_2) and hydroxyl ion (OH^-) are equilibrated with the peroxyl ion (O_2H^-) (Fig. 1). When the dissolution rate is plotted against the equilibrium O_2H^- concentration (Fig. 2), it is clearly shown that uranium dissolution rates depend most strongly on the equilibrium concentration of the peroxyl ion (O_2H^-). This effect can be explained by O_2H^- being required for uranium solubility and being a controlling factor in the dissolution.

We believe that the function of the O_2H^- as a rate-controlling factor is surface related: O_2H^- is required to produce an activated complex on the uranium surface and to allow the dissolution to proceed. Thus, a kinetic model for uranium dissolution can be developed by assuming that the total uranium on the surface of the U_3Si_2 particles ($[U_s]$) exists in three distinct states: the unreacted surface ([A]); the reactive complex of A with O_2H^- ($[B] = K_1[A][O_2H^-]_{eq}$); and a second, unreactive complex of A with OH^- ($[C] = K_2[A][OH^-]_{eq}$). Then, the expressions for the reactive complex [B] can be solved from the relation $[U_s]=[A]+[B]+[C]$, as shown in Eq. 2:

$$[B] = [U_s]\,\frac{K_1[O_2H^-]_{eq}}{1 + K_1[O_2H^-]_{eq} + K_2[OH^-]_{eq}} \tag{2}$$

A uranium dissolution rate model developed from Eq. 2 is shown in Eq. 3:

$$R_u = \frac{1}{S}\frac{dU}{dt} = k_a[B] = k_a\,\frac{K_1[O_2H^-]_{eq}}{1 + K_1[O_2H^-]_{eq} + K_2[OH^-]_{eq}} \tag{3}$$

where R_u is the uranium dissolution rate ($mg \cdot cm^{-2} \cdot min^{-1}$), S is the particle surface area (cm^2), and U is the uranium concentration in solution (mol/L). The constants k_a, K_1, and K_2 were determined as 0.65, 1.2, and 550, respectively, from the data collected during dissolution of atomized and comminuted particles at 50°C. The constant k_a can be treated as the Arrhenius form ($k_a = A_i \exp(-E_{a_i}/RT)$) with a modified pre-exponential constant A_i and activation energy E_{a_i}, where i denotes atomized (AT) or comminuted (CO) particles. Equation 3 is then converted to

$$R_u = A_i \exp\left(-E_{a_i}/RT\right) \cdot \frac{K_1[O_2H^-]_{eq}}{1 + K_1[O_2H^-]_{eq} + K_2[OH^-]_{eq}} \qquad (4)$$

The following constants were determined from the experimental data: A_{AT}, A_{CO}, $E_{a_{AT}}$, and $E_{a_{co}}$ are 5.10×10^8 mg $U \cdot cm^{-2} \cdot min^{-1}$, 1.84×10^{12} mg $U \cdot cm^{-2} \cdot min^{-1}$, 5.5×10^4 $kJ \cdot mol^{-1}$, and 7.7×10^4 $kJ \cdot mol^{-1}$, respectively.

The calculated curves for the dissolution of U_3Si_2 particles as a function of temperature and O_2H^- concentration are plotted with experimental data in Fig. 2. In the figure, the predicted dissolution rates at the three temperatures (40, 50, and 60°C) fit the data well in the desired processing concentration range (0.3-3M O_2H^-).

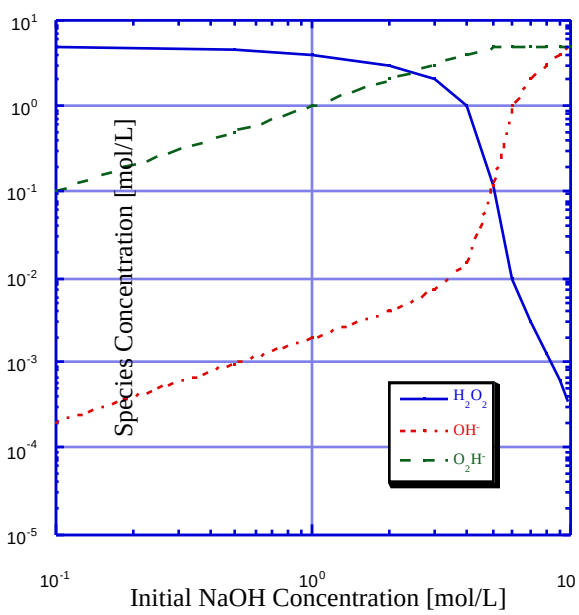

Figure 1. Variation in Equilibrium Concentrations of O_2H^-, OH^-, and H_2O_2 for an Initial 5.0M H_2O_2 and Variable Initial NaOH Concentrations

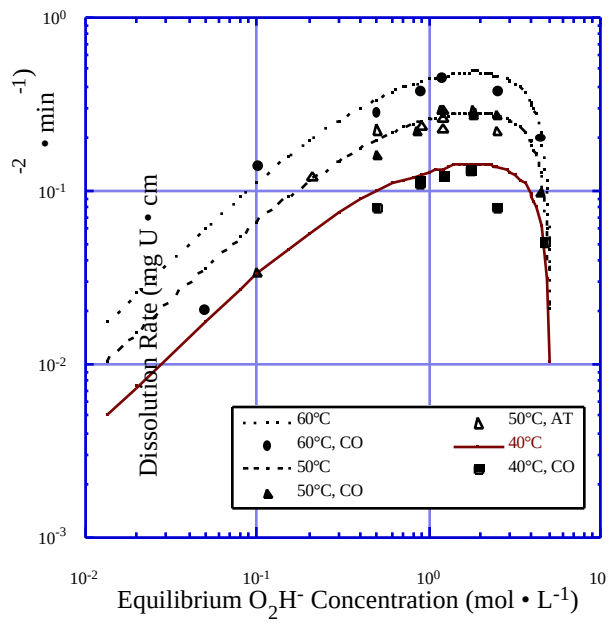

Figure 2. Variation of Uranium Dissolution Rate with Equilibrium Peroxyl Ion Concentration. Data points are denoted by dissolution temperature and particle type, (CO or AT); empirical model curves are denoted by temperature only.

Distribution of Molybdenum-99 in Irradiated Uranium Silicide Targets

We currently employ a two-step method to dissolve uranium silicide targets. The first step uses a mixture of sodium hydroxide and sodium nitrate to dissolve aluminum alloy (AL6061) cladding and matrix aluminum powder. The second step dissolves U_3Si_2 with an alkaline peroxide solution.

Earlier experiments [2] showed that, after initial treatment with $NaOH/NaNO_3$, a wafer of the fuel meat remained if the target was irradiated or heat-treated. It was not clear if the matrix aluminum in the meat dispersion had dissolved. If matrix aluminum did not dissolve, fission product loss to the cladding would amount to only a few percent, allowing this solution to be disposed. However, if the aluminum in the dispersion dissolved, a large quantity of the ^{99}Mo would be lost to the decladding solution. The distribution of ^{99}Mo in cladding aluminum, matrix aluminum, and U_3Si_2 particles after irradiation was determined to decide if the initial cladding removal solution contains sufficient ^{99}Mo to necessitate its recovery. A 300 mg U_3Si_2 target containing 100 mg of uranium (~20 mg ^{235}U) was irradiated at 100 kW for 5 min in the Lazy Susan facility of the TRIGA reactor at the University of Illinois at Urbana-Champaign (UIUC).

The target was dissolved in three fractions: easily dissolved cladding and matrix aluminum, breaking up the fuel meat wafer, and the U_3Si_2 particles. The cladding was removed with 10 mL of 3M NaOH-3M $NaNO_3$ at 75°C. After the cladding was dissolved, the target meat remained intact and was continuously treated with 15 mL of 3M NaOH-3M $NaNO_3$ for 30 minutes until it broke apart. Finally, the U_3Si_2 particles were sequentially dissolved in six batches with 2mL of 1.5M NaOH-5MH_2O_2 solutions.

The resulting solutions from each of these dissolution steps were counted with a high-purity germanium detector, and the results are summarized in Table 1. It was found that approximately 26% ^{99}Mo was lost in the aluminum cladding dissolution, and approximately 9% of the ^{99}Mo was dissolved during the fuel meat treatment. The U_3Si_2 particles contained the balance (~65%) of the ^{99}Mo. Other base-soluble isotopes (^{131,133,135}I, ^{135}Xe) have similar levels in the aluminum decladding solution. Only 10-15% of other isotopes and 6.8% of the absorption product were found in the aluminum decladding solution. Because ^{239}Np would not recoil, the 6.8% may be seen as the fraction of full or fine particles that were dissolved or suspended in the decladding solution. The conclusion drawn from this experiment is that a significant amount of the ^{99}Mo fission product will be lost during decladding and must be recovered.

Table 1. Fraction of Isotopes Released during Dissolution of Cladding, Matrix Aluminum, and U_3Si_2 Particles. All values in percent.

Nuclide	Cladding Al	Matrix Al	Silicide	Nuclide	Cladding Al	Matrix Al	Silicide
Nd-147	13.5	8	78.4	I-132	16.4	9.5	74.1
Ce-141	14.2	8.9	76.8	I-133	24.5	8.6	66.9
Mo-99	25.9	9	65.1	Ba-140	10.7	7.8	81.5
Te-132	13.9	9	77.1	Sr-91	12.1	8.6	79.4
Xe-135	24.6	15.6	59.8	I-131	22.7	8.4	68.9
Y-93	13.7	8.5	77.8	Nb-97	14.7	8.3	77.1
Np-239	6.8	6.6	86.6	Sb-127	15.9	11.5	72.5
Ce-143	13.7	8.7	77.6	Zr-95	14.4	8.2	77.4
Rh-105	17.8	9.8	72.3	Te-131m	13.8	9.9	76.4
Pm-151	12.8	7.5	79.7	Y-92	13.9	8.1	78
Zr-97	14.7	8.3	77	I-135	26.5	8.2	65.3
Ru-103	18.8	10.3	71	La-140	10.8	8.2	81.1

DISSOLUTION OF LEU FOIL TARGETS WITH ALKALINE PEROXIDE SOLUTION

Since 1995, dissolution of LEU metal foil with alkaline peroxide solution has been studied at ANL as an option for ^{99}Mo production in replacement for processing of the HEU aluminide targets. A LEU-foil dissolution kinetics model was proposed in the same year [6]. During 1996, work was focused on reducing the consumption of hydrogen peroxide during uranium foil dissolution in alkaline peroxide solution and optimizing the uranium dissolution process.

Consumption of Hydrogen Peroxide

Dissolution of uranium metal in an alkaline hydrogen peroxide solution involves a complex process in which hydrogen peroxide is consumed by several competing reactions. The uranium surface catalyzes H_2O_2 auto-destruction; the rate is orders of magnitude less without the foil present. As a result, a tremendous amount of hydrogen peroxide is depleted during uranium metal dissolution, leading to increased process waste and creating problems in process control. Thus, better understanding the kinetics of hydrogen peroxide decomposition has become a very important factor for reducing the hydrogen peroxide consumption during uranium dissolution.

Experimental work was conducted in an open, batch-type reactor under isothermal conditions. This work was described in detail earlier [6]. The initial reaction rate was also employed in this study. The concentration of hydrogen peroxide in the dissolution solution was determined by using a standard procedure of titrating liberated iodine with sodium thiosulfate ($Na_2S_2O_3$) solution.

Figure 3 shows the experimental data for the overall disappearance rates of hydrogen peroxide over a broad range of base concentrations. The depletion of hydrogen peroxide essentially follows the kinetic trend of uranium dissolution and can be divided into two regimes, depending on the hydroxide concentration [6]. In the high-base regime (above 0.2M, indicated by a solid line in Fig. 3), the equilibrium hydrogen peroxide concentration solely controls the rate of hydrogen peroxide disappearance. In other words, the rate of peroxide decomposition is independent of base concentration, and hydroxide ions affect only the acid/base equilibrium between H_2O_2 and O_2H^- . While in the low-base regime (below 0.2M, indicated by the dotted line in Fig. 3), both the hydrogen peroxide and hydroxide concentrations affect the rate of peroxide decomposition. Note that one group of data, shown by the upper rectangle, has a common condition of high hydrogen peroxide concentrations and does not follow the trend for the uranium dissolution. This may be explained by the overall rate of hydrogen peroxide decomposition not being solely controlled by the uranium surface under the condition of high peroxide concentration.

Based on the above experimental observations, an empirical kinetics model of the overall disappearance of hydrogen peroxide (Rp) is proposed:

$$R_p = A_p \exp\left(-\frac{E_a}{RT}\right)\left(\frac{K_a [OH^-]^{n''}}{1 + K_a [OH^-]^{n''}}\right)[H_2O_2]^n_{equilibrium} \qquad (5)$$

Values for K_a, n, and n" were determined to be 20.4, 0.25, and 2, respectively, from the previous uranium dissolution model [6]. The following values were obtained from the experimental data: the pre-exponential factor, A_p, 5.06 x 10^7; and the activation energy, E_a, 76.4 ± 10% kJ/mol.

In this model, the overall disappearance rate of hydrogen peroxide is essentially governed by two terms, hydroxyl ion (OH^-) concentration and hydrogen peroxide (H_2O_2) concentration. In the high-base regime, the hydroxide ion concentration term becomes near constant, independent of the hydroxide concentration. This reveals that the overall consumption of hydrogen peroxide in the high alkaline solution was determined to be a 1/4-order function of the equilibrium hydrogen peroxide

concentration. While in the low-base regime, the hydroxide concentration term becomes a second-order function of the hydroxide concentration. The hydroxide ion plays a key role in forming an activated complex on the uranium surface to allow the reaction to proceed. It follows that the hydroxide concentration tends to be an important factor in the rate of hydrogen peroxide decomposition, along with the hydrogen peroxide concentrations. This pattern fits the experimental data well, as shown in Fig. 4. However, this model underestimates the rate of hydrogen peroxide decomposition by 6 to 98% over the regime of base concentrations studied.

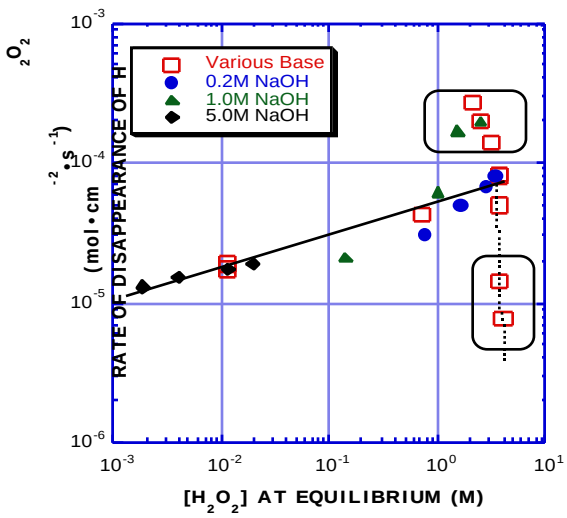

Figure 3. Effect of Equilibrium H_2O_2 Concentration on its Depletion Rate at 60˚C

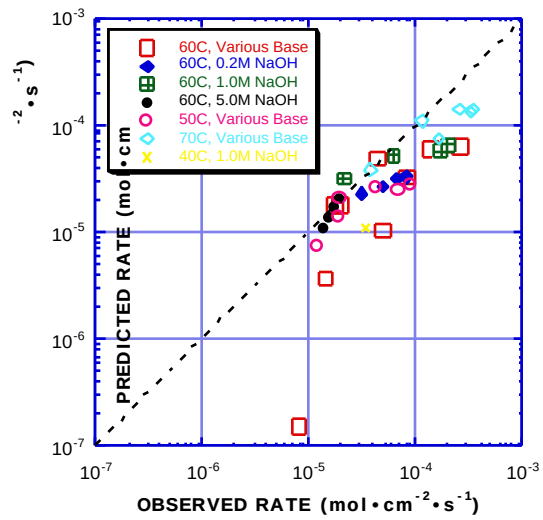

Figure 4. Predicted Rates versus Observed Rates for Depletion of H_2O_2

Optimization of Uranium Foil Dissolution Process

In an open, batch-type reactor, most of the available hydrogen peroxide is consumed by unwanted auto-decomposition. The hydrogen peroxide consumption ratio (HPCR, moles of hydrogen peroxide consumed per mole of uranium dissolved) was approximately 600 in our previous work. It is critical in this process development to reduce the consumption of hydrogen peroxide to make the process practical.

An optimized procedure has been proposed to reduce the HPCR by using sequential additions of alkaline peroxide. In this sequential procedure, multi-batch processing was employed to replace single-batch processing and thereby avoid decomposition of hydrogen peroxide that remained in the reactor. Results showed that the HPCR could be significantly reduced in a laboratory-scale reactor from 100 times to five times the stoichiometric ratio. Because a large number of small-volume additions was actually used in this optimized procedure to frequently replace the dissolving solution or continuously replenish hydrogen peroxide, it opens up the possibility of substituting a plug flow reactor for the multi-batch reactor configuration in the dissolver system.

The HPCR could be further reduced by optimizing the dissolution parameters. We performed a series of experiments to correlate the sodium hydroxide concentration with the uranium dissolution rate and HPCR. The results showed that both the HPCR and the dissolution time were reduced when the base concentrations increased. The effect of dissolution temperature on the uranium dissolution consumption and dissolution time was also determined. As expected, the dissolution time was reduced as temperature increased. However, the HPCR was minimized at 70°C. This probably is due to the

competing reactions of uranium dissolution and hydrogen peroxide decomposition, each being affected differently by temperature changes.

The conclusions are that (1) HPCR can be significantly reduced by using a multi-stage batch reactor, (2) the optimum composition and temperature are 5.0M H_2O_2/1.5M NaOH and 70°C, respectively, and (3) significant difficulties, such as reactor size and resident time, still need to be resolved.

Barrier Materials Dissolution

Post-irradiation examination of the ANL LEU-foil test targets showed that bonding of the uranium-metal foil to the target walls was occurring during irradiation. Because of this, it was impossible to remove the foil from the target. A potential solution to this bonding is inclusion of a thin (10-μm) metal barrier between the foil and the target walls. A literature review was undertaken to choose metals that would have the mechanical and chemical attributes suitable for barriers. Important chemical properties were (1) ease of dissolution, (2) noninterference with the recovery of molybdenum from the dissolution, and (3) noninterference with the purification of the ^{99}Mo product. Other important factors were (1) the ability to be electroless plated on uranium or made into foils, (2) low absorption yield of radioisotopes during target irradiation, and (3) low cost.

Based on these criteria and mechanical properties, the best choices for a barrier metal are nickel, iron, and copper for the process of uranium foil target dissolution with acidic solution. However, none of them was dissolved in our tests with either 1.5M NaOH or 5.0M H_2O_2/1.5M NaOH solution at 70°C. As a result, a challenging task in the process development has become identification of a suitable metal as a potential barrier material in the neutron irradiation that can dissolve in alkaline solution and meet other mechanical and chemical criteria.

Aluminum is one of the best-known elements. An experiment has proved that aluminum could dissolve at about the same rate as uranium metal with 5.0M H_2O_2/1.5M NaOH solution at 70°C. However, there is a strong concern that uranium would react with aluminum in the target irradiation. Similar to aluminum, zinc is also an active electropositive element and forms a strong anion with oxygen. It is also expected to dissolve readily in sodium hydroxide solution.

A literature survey has found other metals as candidate barrier materials. The following elements were found to dissolve in alkaline hydroxide solutions: zinc, beryllium, gallium, tin, arsenic, niobium, and tantalum. Germanium and rhenium, although not amphoteric, are reported to dissolve readily in dilute hydrogen peroxide. Chromium may be amphoteric, but this is unclear in the literature. Of the elements mentioned above, the toxicity of beryllium metal and the low melting point of gallium may preclude their use. Arsenic is classified as a non-metal and may not have sufficient metallic properties to be made into a foil. Future work is needed to select barrier materials for targets to be processed by dissolution in base. Zinc will be the first barrier metal tested.

CONCLUSIONS

Progress has been made to facilitate the transition from HEU to LEU in targets for ^{99}Mo production. This paper has summarized the current status of the development of two types of targets, LEU silicide and LEU foil, that are meant to be dissolved with alkaline peroxide solution.

During 1996, effort continued on developing a process for dissolving silicide targets with alkaline peroxide solutions and recovering pure ^{99}Mo. The dissolution kinetics model developed in this study was used to evaluate the effects of hydrogen peroxide, base concentrations, and operating conditions. The results will help provide fundamental knowledge for use in the dissolver system design. An experiment found that a significant amount of the ^{99}Mo was transferred from the uranium silicide particles to the aluminum matrix by fission recoil, and then lost to the decladding

solution. Obviously, this solution cannot be discarded as waste. Future work on this process will concentrate on developing improved mechanical means to break up the fuel meat wafer and, perhaps, more powerful dissolution reagents. We may also decide to abandon research in this area and concentrate on metal foil targets.

As an alternative process, the dissolution of LEU metal foil with alkaline peroxide solution has been studied in three areas this year. The first area, modeling of hydrogen peroxide decomposition, was undertaken to develop an in-depth understanding of the process, and the results should be invaluable in the design of the dissolution process and equipment. In the second area, optimization of the dissolution process and minimization of radioactive process waste were achieved by developing a sequential procedure and optimizing the process variables to avoid the rapid decomposition of H_2O_2. The third area, selection of materials that could be used as a fission-recoil barrier between uranium metal and the target walls during irradiation, has been initiated. This is expected to be the most critical area in process development. Future work on the dissolution of uranium metal foil will also be concerned with designing the dissolver/off-gas system and integrating ^{99}Mo recovery and purification steps to the dissolution.

ACKNOWLEDGMENT

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