DISSOLUTION OF LOW-ENRICHED UO_2/Al DISPERSION PLATES IN ALKALINE PEROXIDE SOLUTION

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ABSTRACT

A simple empirical model was developed to predict the rate of UO_2 dissolution in alkaline peroxide solutions. This showed that UO_2 could be dissolved in alkaline peroxide solutions at a rate high enough to be practical for use in the recovery of ^{99}Mo from irradiated UO_2/Al dispersion targets. Once it was shown that the rate of dissolution of UO_2 was sufficiently high to be useful, compacts of UO_2 and Al powder were dissolved, and the distribution of uranium and activation and fission products was measured through the various dissolution steps. These compacts simulate the “meat” of a UO_2/Al dispersion target. The test results show promise for the use of a low-enriched UO_2/Al dispersion target for the production of ^{99}Mo.

INTRODUCTION

Concerns over nuclear weapons proliferation are spurring research to develop methods for using low-enriched uranium (LEU) instead of high-enriched uranium (HEU) in research reactor fuels and targets. High-enriched uranium contains >20 wt % ^{235}U. In fact, the U.S. Congress passed an amendment, in October 1992, to the Atomic Energy Act of 1954 that prohibits export of HEU from the U.S. unless several conditions are met: (1) no alternative LEU fuel or target can be used, (2) the U.S. is actively developing an LEU fuel or target for that reactor, and (3) the proposed recipient of the HEU provides assurances that, when LEU fuel or targets can be used, they will be.

Technetium-99m, the daughter of ^{99}Mo, is the most commonly used medical radioisotope in the world. It is used in over nine million medical procedures annually in the U.S. alone and comprises 80% of all nuclear-medicine procedures [1]. Molybdenum-99 is typically produced by the thermal neutron fission of ^{235}U. The yield of ^{99}Mo from fissioning ^{235}U is ~6%. The targets are usually high-enriched (93% ^{235}U) uranium oxide, uranium-aluminum alloy, or uranium aluminide. After irradiation of the target, ^{99}Mo is recovered by dissolving the target and separating it from the uranium and fission and activation products [2-14].

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Molybdenum-99 can also be generated by neutron capture in targets of natural molybdenum or targets that have been enriched in ^{98}Mo. However, neutron capture produces ^{99}Mo of very low specific activity and is seldom used.

Substitution of LEU for HEU in the production of ^{99}Mo by fissioning ^{235}U requires modification of targets and, perhaps, processes. To yield equivalent amounts of ^{99}Mo, LEU targets must contain five to six times as much uranium as the HEU targets they replace. One way to increase the amount of uranium per target (and thus the amount of ^{99}Mo) is to use a denser form of uranium. Institutions recovering ^{99}Mo by alkaline separation processes typically use an HEU aluminide target. A target containing LEU silicide (U_3Si_2), which is about three times as dense as uranium aluminide, could serve as a substitute for the uranium aluminide target. However, dissolution of the uranium silicide in basic solutions is problematic [15]. In fact, we have discontinued development work on recovering ^{99}Mo from uranium silicide targets. Another alternative to the uranium aluminide target is a low-enriched UO_2 target. Uranium dioxide is about twice as dense as uranium aluminide, but loading the target to 40 vol % UO_2 will allow uranium loadings about three times greater than those of typical UAl_x/Al dispersion targets. Although twice as many targets would be required for LEU conversion, plate fabrication is a known technology, and this may be an option for some ^{99}Mo producers.

This paper reports the first step in establishing the feasibility of using this type of LEU target: dissolution of aluminum-clad low-enriched UO_2/Al dispersion target in basic solutions. Basic dissolution of a UO_2/Al dispersion target has several advantages: (1) it is compatible with facilities using existing basic dissolution processes (e.g., dissolution of uranium aluminide), (2) it separates the noble fission gases from iodine, and (3) uranium and many fission and activation products are not soluble in basic solutions. Dissolution in alkaline solution is the initial step required for separation of the ^{99}Mo in the irradiated target for many producers (Institut National des Radioéléments (IRE), Belgium; Atomic Energy Corporation of South Africa Limited (AEC), South Africa; Comisión Nacional de Energía Atómica (CNEA), Argentina; Mallinckrodt, Netherlands). One of the challenges to basic dissolution is that UO_2 dissolves very slowly in alkaline or alkaline/nitrate solutions. However, UO_2 dissolves in alkaline peroxide at rates required to dissolve a target in less than one hour. Previous work on the basic dissolution of both uranium silicide and uranium metal foils has shown that they catalyzed the auto-destruction reaction of hydrogen peroxide. Thus, they required significantly more peroxide than was stoichiometrically required to dissolve the uranium [16-17]. Fortunately, UO_2 does not catalyze the autodestruction reaction of hydrogen peroxide; therefore, peroxide consumption will be ^{2} 2% of that for dissolving uranium metal or silicide.

A simple, empirical model was developed to predict the rate at which UO_2 will dissolve in alkaline peroxide solutions. Once it was shown that UO_2 would dissolve at acceptably high rates in alkaline peroxide solutions, compacts of aluminum powder and UO_2 were prepared and dissolved. These compacts simulate the “meat” of an aluminum-clad UO_2/Al dispersion target. Some compacts were then irradiated to low burnup, and the distribution of uranium and activation and fission products through the various dissolution steps was measured. Miniplates were also prepared for future development work.

DISSOLUTION OF UO_2

As stated previously, the initial step in the recovery of ^{99}Mo is dissolution of the irradiated target (which includes the UO_2). Dissolution of UO_2 was measured as a function of hydroxide and peroxide concentrations. Rates were measured by adding solutions of sodium hydroxide and hydrogen peroxide to a 125 mL Erlenmeyer flask containing UO_2 powder (-100 to +200 mesh). The sodium hydroxide and hydrogen peroxide were heated to 50°C before adding them to the Erlenmeyer flask. The reaction between hydrogen peroxide and sodium hydroxide is highly exothermic, which causes the solution to heat up. Due to the problems associated with the self-heating of the sodium hydroxide/hydrogen peroxide reaction, the temperature of the system needs to be monitored. For that purpose, a Teflon-coated thermocouple was placed into a holed stopper, and then the assembly was placed on top of the Erlenmeyer flask; an additional hole had been drilled through the stopper to allow gas to escape. At specified times, samples were taken from the flask, and the concentrations of peroxide and uranium measured. The mass of uranium dissolved was determined from the concentration of uranium in the dissolver solution.

Once the uranium and peroxide concentration of each sample had been determined, the rate of reaction was calculated by fitting a line through the "cumulative mass of uranium dissolved" vs. time data. The cumulative mass of U dissolved per unit area is calculated by:

$$CM_j = \frac{[U]_j \bullet (IV - \sum_{n=0}^{j-1} AV_n) + \sum_{n=0}^{j-1} [U]_n \bullet AV_n}{\text{Average}\left\langle SA_j , SA_{j-1} \right\rangle}$$

Where:

CM_j = Cumulative mass of U dissolved to the $j^{\underline{th}}$ sample per unit area (mg UO_2/cm^2).
$[U]_j$ = Concentration of uranium in the $j^{\underline{th}}$ sample of the dissolver solution (mg UO_2/cm^3).
IV = Initial volume of solution in the dissolver (cm^3).
AV_n = Volume of the $n^{\underline{th}}$ sample removed from the dissolver (cm^3).
SA_j = Total surface area of the UO_2 at the $j^{\underline{th}}$ sample (cm^2).

The surface area is calculated by assuming that UO_2 powder is composed of uniform (e.g., all have the same radius) spheres. Unfortunately, the UO_2 used in most of these experiments was not 100% dense (ρ = 10.96 g/cm^3). To compensate for the porosity of the UO_2, the density was measured under ethanol and found to be 5.39 g/cm^3. It was also assumed that, as the UO_2 dissolved, all the spheres decreased in size at the same rate and had an initial specific surface area of 109 cm^2/g. The total surface area at the $j^{\underline{th}}$ point (SA_j) in cm^2 is calculated using the total number of UO_2 particles (Pt) and the radius of a partially dissolved particle (r_j):

$$SA_j = 4\pi \bullet Pt \bullet r_j^2$$

The total number of UO_2 particles Pt, is calculated from:

$$Pt = \frac{IM \bullet SSA^3 \bullet \rho^2}{36\pi}$$

where:

IM = Initial mass of UO_2 powder (g).
SSA = Specific surface area of UO_2 (109 cm^2/g).
ρ = Density of UO_2 (5.39 g/cm^3).

The radius of a partially dissolved sphere r_j (cm), is calculated from:

$$r_j = \left[\frac{3 \bullet \left(IM - DM_j\right)}{4\pi \bullet \rho \bullet Pt}\right]^{\frac{1}{3}}$$

The mass of UO_2 dissolved to the j^{th} point DM_j (mg UO_2), is calculated from:

$$DM_j = [U]_j \bullet (IV - \sum_{n=0}^{j-1} AV_n) + \sum_{n=0}^{j-1} [U]_n \bullet AV_n$$

where:

$[U]_j$ = Concentration of uranium in the jth sample of the dissolver solution ($mg\ UO_2/cm^3$).
IV = Initial volume (cm^3).
AV_n = Volume of the nth sample removed from the dissolver (cm^3).

As stated above, to calculate the average reaction rate, the slope of the best fit line through the "CM_j vs. t" data is used. Only the first several points of data were used to calculate this slope. Figure 1 shows a few typical data sets used to calculate this slope. Data after the initial few points in an experiment were excluded for several reasons:

1.) They were not in the linear portion CM_j vs. t data; this indicates that the assumptions made (concentrations of hydroxide and peroxide are constant, particles are spherical, all particles dissolve at same rate, etc.) were no longer valid.

2.) All of the uranium had essentially dissolved; that is the principal cause of the linearity problems noted in #1 above.

3.) The temperature of the dissolver solution had deviated significantly from 50°C. The exclusion criteria were somewhat subjective and based on experience with the system, but as a rule of thumb, points were excluded when T>65°C and T<40°C.

4.) The point at t=0 was excluded in every experiment because the conditions--concentration of sodium hydroxide, concentration of hydrogen peroxide, and concentration of uranium (assumed=0)--were calculated rather than measured.

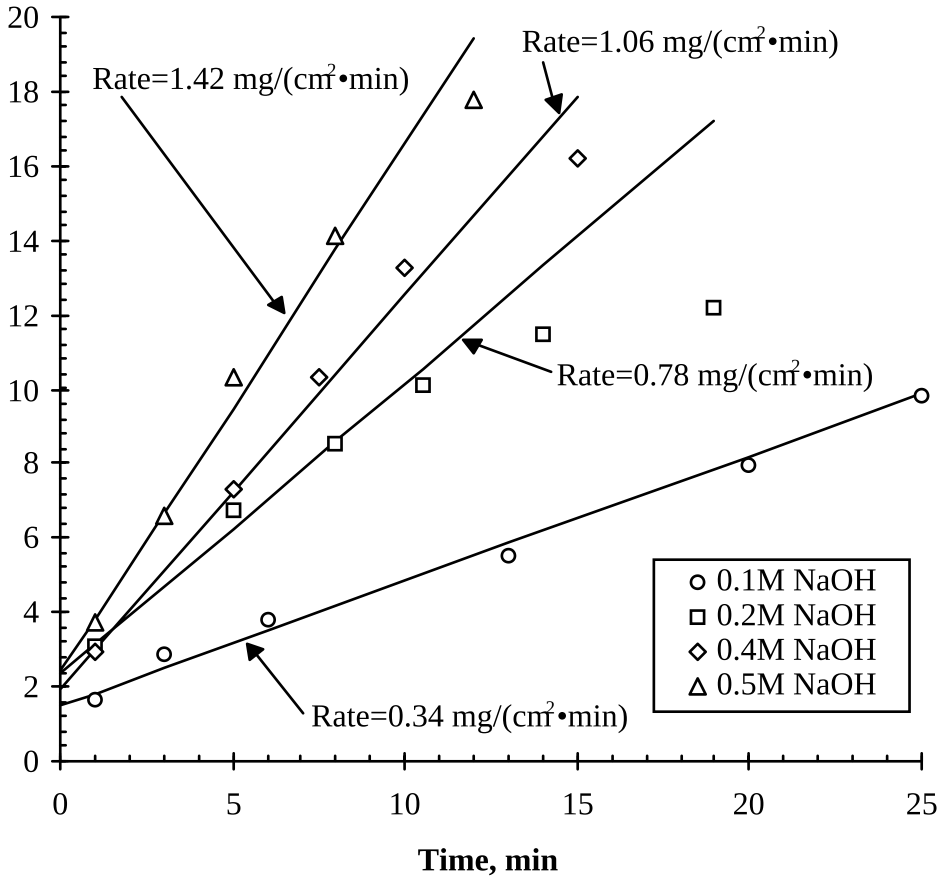

Figure 1. Sample UO_2 Dissolution Rates

From these experiments, an empirical rate model was generated of the form:

$$r = k \bullet [H_2O_2]_i^{0.5}[OH^-]_i^{0.5}$$

where k is an empirical rate constant, and $[H_2O_2]_i$ and $[OH^-]_i$ are the initial hydrogen peroxide and base concentrations, respectively. A plot of dissolution rate vs. $[H_2O_2]_i^{0.5}[OH^-]_i^{0.5}$ is shown in Fig. 2. As seen in Fig. 2, a fairly linear relationship is present over several orders of magnitude. The slope of the best fit line is equal to the rate constant, k=1.26. Figure 2 also shows that as $[H_2O_2]_i^{0.5}[OH^-]_i^{0.5}$ increases the scatter in the data increases. This larger scatter might be caused by the temperature tending to vary more widely as the concentrations of hydroxide and peroxide increase.

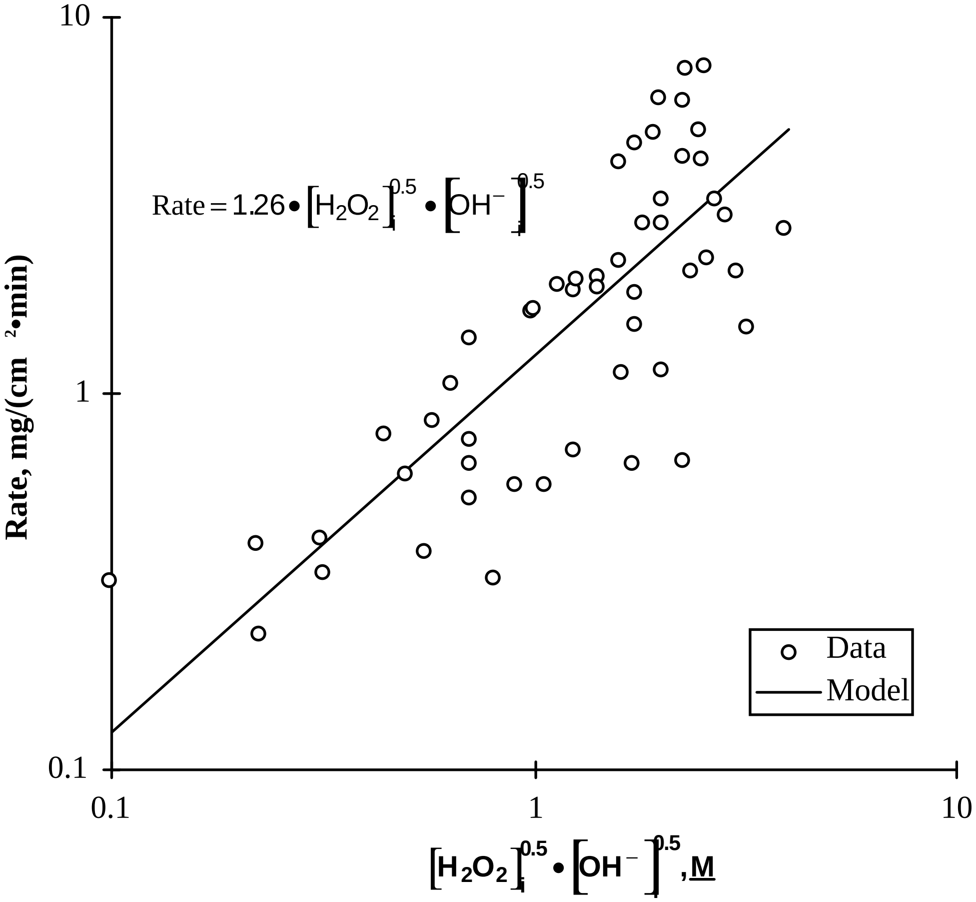

Figure 2. Rate Data for the Dissolution of UO_2 in Alkaline Peroxide

DISSOLUTION OF UO_2 COMPACTS

Once it was shown that UO_2 would dissolve at acceptably high rates in alkaline peroxide solutions, compacts of aluminum powder and UO_2 were prepared and dissolved. These compacts simulate the "meat" of an aluminum-clad UO_2/Al dispersion target. Some compacts were then irradiated to low burnup, and the distribution of uranium and activation and fission products was measured through the various dissolution steps.

Qualitative experiments were performed to determine the overall process for dissolving a simulated UO_2/Al dispersion target. The simulated targets were prepared by mixing UO_2 (-100 to +200 mesh; 74-149 µm) and aluminum powder (-325 mesh; ^{2}44 µm) and pressing them into a compact (see Fig. 3). For dissolving these simulated targets the first step was to dissolve the aluminum associated with the compact using an alkaline nitrate solution. Base insoluble impurities in the aluminum generated a light, fluffy precipitate. The supernatant and light, fluffy precipitate were removed, and the remaining UO_2 solids were washed with dilute sodium hydroxide and then with water. The light, fluffy precipitate was also seen in the wash solutions. The UO_2 was washed with water until no more light, fluffy precipitate was seen. After washing, the UO_2 was dissolved in a 0.5$\underline{M}$ sodium hydroxide/5.0$\underline{M}$ hydrogen peroxide solution. Uranium forms a base-soluble complex with peroxide. The solubility of this complex was measured and found to be about 37 g UO_2/L. In order for the uranium to precipitate the peroxide in the solution must be destroyed. Peroxide was destroyed by adding potassium permanganate solution until a slight pink color remained in the supernatant.

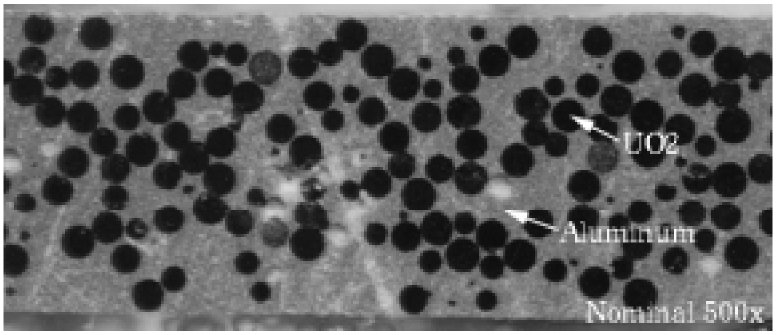

Figure 3. UO_2/Al Powder Compact

This process worked well for the UO_2/Al powder compacts and was used on compacts irradiated to a low burnup. The distribution of fission products was then measured during the various dissolution steps. Results are shown in Table 1. As shown in Table 1, a small amount of ^{99}Mo is freed during the dissolution of the aluminum. This is due to recoil of the ^{99}Mo out of the UO_2 particle during fission. It may be necessary to recover this ^{99}Mo. However, note that after the destruction of the peroxide, uranium and base-insoluble fission and activation products precipitate (e.g., Ce, Zr, Ba, La, Np), leaving the base-soluble fission products in solution (e.g., Mo, I). A small amount of ^{99}Mo is also lost during this step. It could be that MnO_2, formed during the permanganate destruction of the peroxide, adsorbs the ^{99}Mo. Selection of a different method of destroying the peroxide should alleviate this problem.

Table 1. Distribution of Uranium and Fission and Activation Products as a Percentage of the Initial Amount Present

Isotope	Aluminum Dissolution[a]		UO_2 Washings[b]		UO_2 Dissolution[c]	H_2O_2 Destruction[d]
	Liquid (%)	Solid (%)	Liquid (%)	Solid (%)	(%)	(%)
Mo-99	5.9	0.5	0.2	1.4	92.0	83.8
U	0.1	2.0	0.1	6.8	89.1	1.9
Sr-91	0.4	6.9	0.2	1.7	90.8	N/A
Sr-92	6.1	1.2	0.2	1.3	91.2	N/A
Zr-95	5.6	1.5	1.1	2.1	89.7	3.6
Zr-97	5.6	0.9	0.2	1.4	91.9	N/A
Ru-103	6.8	1.5	0.3	1.3	90.1	79.4
Te-132	6.4	1.6	0.4	1.6	90.0	1.3
I-131	6.9	1.3	0.2	1.3	90.3	68.7
I-133	6.3	1.4	0.2	1.3	90.9	66.2
I-135	6.1	1.1	0.3	1.8	90.8	N/A
Ba-140	0.6	5.3	0.1	1.8	92.1	<4.1
La-140	0.6	7.4	0.1	1.7	90.2	<5.7
Ce-141	0.4	6.5	0.1	2.0	91.0	<5.6
Ce-143	0.5	5.7	0.0	1.9	91.9	0.8
Np-239	0.0	0.2	0.0	1.6	98.2	21.2

[a] Both the clear supernatant and the fluffy precipitate were analyzed.

[b] The dilute sodium hydroxide and water washes were combined. The light, fluffy precipitate was analyzed separately from the clear liquid.

[c] Analysis of the resultant solution after the alkaline peroxide dissolution of the UO_2.

[d] Analysis of the resultant supernatant after the peroxide had been destroyed using potassium permanganate.

CONCLUSIONS AND FUTURE WORK

This work has demonstrated that an aluminum-clad UO_2/Al dispersion target can be successfully dissolved in an alkaline peroxide solution. After dissolution of the target and destruction of the peroxide, recovery of the ^{99}Mo would be nearly identical to the current processes, which employ basic dissolution. Therefore, a low-enriched UO_2/Al dispersion target could potentially be used for the production of ^{99}Mo. Two aluminum-clad miniplates have been fabricated from UO_2/Al powder compacts containing 40 vol % UO_2. Next year, cores from these miniplates will be irradiated to a low-level burnup, and the effects of this LEU target on the ^{99}Mo recovery and purification process will be tested. For full-scale demonstration of this target, we will also be seeking a commercial partner that now uses a basic dissolution process to recover ^{99}Mo.

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