

PRODUCTION OF MO-99 USING LOW-ENRICHED URANIUM SILICIDE

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ABSTRACT

A process to recover Mo-99 from low-enriched uranium silicide is being developed at Argonne National Laboratory. The uranium silicide is dissolved in alkaline hydrogen peroxide. Experiments performed to determine the optimum dissolution procedure are discussed, and the results of dissolving a portion of a high-burnup ($>40\%$) U_3Si_2 miniplate are presented. Future work related to Mo-99 separation and waste disposal are also discussed.

INTRODUCTION

Molybdenum-99 is a precursor of Tc-99m, which is used in several medical applications. Since Mo-99 is not naturally abundant, it must be produced by one of two types of controlled nuclear reactions. One method produces Mo-99 by neutron bombardment of Mo-98; the Mo-99 is generated by the following nuclear reaction: $Mo-98 (n,\gamma) Mo-99$. This method produces Mo-99 with low specific activity and is not widely used [1]. Commercially, Mo-99 is being produced worldwide by the fission of U-235: $U-235 (n,f) Mo-99$. The Mo-99 is recovered by dissolving the irradiated target and separating the Mo-99 from the uranium and other fission products in the dissolver solution. The world's current supply of Mo-99 is almost exclusively produced from high enriched uranium (HEU).

In October 1992, the U.S. Congress passed an amendment to the Atomic Energy Act of 1954. This amendment prohibits export of HEU for use as a fuel or target in research or test reactors unless several conditions are met: (1) no alternative low-enriched uranium (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, whenever possible, an LEU fuel or target will be used in that reactor.

We are investigating the consequences of substituting LEU for HEU on target preparation and processing. The results of substituting LEU U_3Si_2 targets for HEU UAl_x alloys and aluminide targets during basic dissolution for Mo-99 recovery are discussed.

URANIUM SILICIDE TARGETS

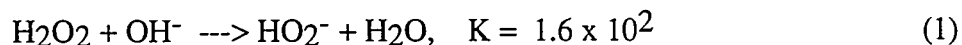
Over the last several years, uranium silicide fuels have been under development as LEU targets for Mo-99. The use of LEU silicide is aimed at replacing the UAl_x alloy in the HEU dissolution process practiced by the Institut National des Radioelements (IRE), Fluerus, Belgium

[2]; Comision Nacional de Energia Atomica, Buenos Aires, Argentina [3]; and the Atomic Energy Corporation of South Africa. The difficulty with using uranium silicide targets is that the conditions used to dissolve UAl_x targets are not applicable for the silicide targets. The targets do not readily dissolve in base. In acid, silica is precipitated in the dissolution process, and the Mo-99 cannot be recovered from the solution [4]. In 1987, Argonne workers [5] were able to dissolve uranium silicide in alkaline hydrogen peroxide at 70°C, dissolving 0.3 g U_3Si_2 in 100 mL of liquid. According to the original description, the target was initially placed in 3.0M NaOH to remove the cladding. Once the cladding was dissolved, the cladding solution was removed, and a 1:1 ratio of 3M NaOH and 30 wt % H_2O_2 was used to dissolve the remaining uranium silicide [5].

Two years later, the following optimized procedure was proposed to dissolve uranium silicide targets [6]. A steel dissolver vessel would be loaded with irradiated targets. Initially, the cladding and the aluminum in the fuel matrix were to be dissolved in 3M NaOH. (The addition of $NaNO_3$ was later suggested to keep hydrogen production to a minimum.) A gas sparge during the dissolution was proposed to remove the gaseous fission products and mix the dissolver contents. Once the cladding was dissolved, the flocculent in the solution would be removed from the dissolver, leaving the dense uranium silicide behind. This solution would be filtered, then returned to the dissolver. A 30 wt % solution of hydrogen peroxide would then be added dropwise until the uranium silicide was completely dissolved. Then, the dissolver solution would be heated to destroy the hydrogen peroxide complex and allow the dissolved uranyl hydroxide to precipitate. This solution would be filtered to recover the uranium, and then it would be acidified for subsequent recovery of Mo-99 in the same way as currently done for uranium aluminide targets. This project was discontinued in 1989 due to lack of funding, and no progress was made beyond this point for several years.

In recent work, we have only been able to partially reproduce the earlier procedure. Uranium silicide alone can be dissolved by the procedure described above. However, the cladding dissolution solution cannot be reused since we have not been able to filter or centrifuge it to remove the metal hydroxide alloying elements. Even if a pure aluminum alloy is used, and no flocculent is present in the dissolver solution (so that filtering is not required), we have been unable to dissolve even 0.1 g of silicide by the proposed scheme. This observation remained valid even if up to 500 mL of hydrogen peroxide was used in the attempt. Therefore, our current thinking is that the cladding solution cannot be reused in the subsequent silicide dissolution step; a fresh charge of sodium hydroxide solution must be used. In addition, we have found that stainless steel is unsuitable as a construction material for the dissolver vessel because of its rapid catalytic destruction of hydrogen peroxide.

The first step in recovering Mo-99 from a silicide target is to remove the aluminum cladding. This procedure was developed in the fifties at Oak Ridge National Laboratory (ORNL) [7], and slight variations of it are practiced all over the world. Thus, this well-developed procedure can be easily adapted to the new LEU silicide targets. The problem is that methods to dissolve the silicide itself need to be established. Experiments to optimize the silicide dissolution process are in progress at our laboratory. During the dissolution process, two chemical reactions are occurring, the autodestruction of hydrogen peroxide and the dissolution of uranium silicide. A literature search revealed very little data about the autodestruction of hydrogen peroxide in sodium hydroxide solutions. One source simply identified that the autodestruction reaction is catalyzed in base, but no quantitative data were given [8]. A limited kinetic study of dilute hydrogen peroxide (0.01M) in 0.5-6.0M NaOH at room temperature indicated that hydrogen peroxide was stable in highly basic solutions [9]. This stability was attributed to the following equilibria:



We have completed experiments to quantify the autodestruction rate in various NaOH solutions over the temperature range 70-100°C. The autodestruction reaction is exothermic, and its kinetics must be understood to optimize the U₃Si₂ dissolution and design a dissolver with the proper heat transfer characteristics so that the dissolution process can be safely controlled.

OPTIMIZED PROCEDURE FOR ALUMINUM CLADDING DISSOLUTION

Aluminum cladding alloys used in the production of Mo-99 in Europe and the USA are shown in Table 1. Both of these types of alloys are easily dissolved in NaOH-NaNO₃ mixtures. Most of the alloying elements will precipitate, but the sodium aluminate will remain in solution under the optimized dissolution conditions of molar ratios Al:NaOH:NaNO₃ of 1.00:1.66:1.47.

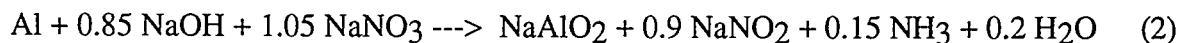
Table 1. Composition Range of Common Cladding Alloys (wt %) [10]

Designation	Cr	Cu	Mg	Mn	Si
Al 5052 ^a	0.15-0.35	0.1	2.2-2.8	0.1	-
Al 6061 ^b	0.04-0.35	0.15-0.4	0.8-1.2	0.15	0.4-0.8

^aCommon use in Europe.

^bCommon use in United States and Argentina.

The ORNL procedure is claimed to minimize hydrogen production and also prevent the precipitation of sodium aluminate [7]. The overall stoichiometry of the dissolution is:



The published dissolution rate data in boiling NaOH solutions can be correlated with the following equation:

$$\text{Rate} = k [\text{NaOH}]^{1.54} \quad (3)$$

Where,

$$k = 5.26 \text{ mg Al/cm}^2 \cdot \text{min} \cdot \text{M}^{1.54} \text{ at the boiling temperature}$$

$$\text{Rate} = \text{Al dissolution rate, mg Al/cm}^2 \cdot \text{min}$$

To test this procedure, 3.77 g of Al6061 (60.5 cm² surface area exposed) was dissolved in 77.3 mL of 3M NaOH and 3M NaNO₃. The dissolver was a 250 mL jacketed glass beaker with a glass sparger. The heat transfer fluid set point was initially 70°C, and the vessel contents were mixed by nitrogen sparging. Within 1 min of introducing the cladding material, the dissolver solution was boiling, 104°C. Within 5 min, no undissolved cladding was visible in the vessel, and the boiling subsided. This dissolution rate is consistent with the published results. A sample of the dissolver liquid was evaluated by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) to determine the concentrations of the dissolved alloying elements and the aluminum (Table 2). As shown in Table 2, the dissolver liquid contains a significant concentration of alloying elements. Care was taken to avoid suspended solids in the liquid sample sent for ICP-AES, even though this sample could not be filtered.

Table 2. Composition of Final Dissolver Solution

Element	Concentration in Dissolver Liquid (mg/L)
Al	55700 ^a
Cr	85
Cu	110
Mg	500
Mn	44
Zn	69
Si	b

^aEquivalent to an Al concentration of 2.06M.

^bSilicon not determined due to interference from dissolution of the glassware in strong base.

After dissolution, the flocculent of metal hydroxide alloying elements in the cladding solution forms a gelatinous precipitate that cannot be filtered or centrifuged. These flocculent impurities must be removed, since they catalyze the autodestruction of hydrogen peroxide in the subsequent silicide dissolution. Upon acidification, the flocculent particles are easily dissolved and will likely not interfere with the subsequent Mo-99 recovery. Depending on the size of the silicide particle, between 8 and 30% of the Mo-99 produced will be lost to the cladding dissolution solution due to fission recoil. Thus, economic concerns dictate that Mo-99 must be recovered from this solution.

AUTODESTRUCTION OF HYDROGEN PEROXIDE IN SODIUM HYDROXIDE SOLUTIONS

The autodestruction of hydrogen peroxide:



was observed to have a first-order dependence on the concentration of hydrogen peroxide:

$$\frac{d[\text{H}_2\text{O}_2]}{dt} = -k [\text{H}_2\text{O}_2] \quad (5)$$

Where,

$[\text{H}_2\text{O}_2]$ = concentration of hydrogen peroxide, mol/L

t = time, min

k = first-order rate constant, min^{-1}

Equation 5 can be integrated with the initial condition $[\text{H}_2\text{O}_2] = [\text{H}_2\text{O}_2]_0$ at $t=t_0$:

$$\ln \frac{[\text{H}_2\text{O}_2]}{[\text{H}_2\text{O}_2]_0} = -k (t - t_0) \quad (6)$$

To determine k , we measured the isothermal destruction of a completely mixed batch of hydrogen peroxide in a sodium hydroxide solution over time. The slope determined from $\ln [H_2O_2]/[H_2O_2]_0$ vs. time equals to $-k$. Since this equation has the form $y=mx$, a least squares fit of the data was used to statistically minimize the errors in the measurements of $[H_2O_2]$.

The hydrogen peroxide autodestruction reaction was carried out in a 1000 mL glass round-bottom flask. Attached to the flask was a 40 cm Allihn condenser to ensure that vaporized water and hydrogen peroxide were returned to the flask. A thermometer was inserted into the liquid to monitor the temperature. A 380 W heating mantle was used to manually control the temperature at various set points. The destruction of hydrogen peroxide is exothermic and is a function of the composition of the peroxide solution [8]. Heats of reaction between 94 and 99 kJ/mol are reported for this reaction in water. The heat of mixing is not included in this number since it is negligibly small compared to the heat of reaction (0.4-1.2 kJ/mol). The autodestruction reaction heats up the reaction mixture during the rate experiments. Temperature control within 1°C was possible during the course of the experiments. A glass shaft and Teflon impeller were used to mix the reactor contents after addition of reagents. During the experiments, the generation of oxygen gas bubbles, caused by the decomposition of hydrogen peroxide, was adequate to mix the flask contents.

Initially, the flask was filled with 30 mL of a sodium hydroxide solution and heated to 10°C less than the required reaction temperature. The experiment was started by adding 40 mL of 30 wt % hydrogen peroxide to the flask. Since the peroxide was stored at 0°C, initially the flask contents cooled slightly, then as the reaction began, the flask contents heated up as high as 95°C. Within a few minutes, the contents cooled to the required temperature of 70, 80, or 90°C. The temperature was then maintained at this temperature by adjusting the heating mantle. Once the set point temperature was reached, a clock was started, and 0.1-0.2 mL grab samples were removed at set time intervals up to 120 min. The grab samples were quickly cooled to 0°C in an ice water bath to slow the reaction before they were introduced into 50 mL of 1M H_2SO_4 and 0.15M KI for titration with 0.1M sodium thiosulfate. This allowed us to determine the hydrogen peroxide concentration [11]. Once the concentration vs. time data were obtained, the rate constant was derived from Eq. 5.

Typical experimental data plot as straight lines on a logarithmic scale; two examples are shown in Figure 1. The straight line indicates that the data fit a first-order dependence well.

The rate constants were calculated and are displayed on an Arrhenius plot in Figure 2. The Arrhenius form for rate constant is:

$$k = A \exp\left(\frac{-E_a}{RT}\right) \quad (7)$$

Where,

k = first-order rate constant, min^{-1}

A = collision frequency, min^{-1}

E_a = activation energy, J/mol

R = universal gas constant, J/(mol•K)

T = temperature, K

This exponential temperature dependence plots as a straight line, as shown in Figure 2. The activation energy for the reaction can be determined by the slope of the line, and the collision frequency by the intercept at $1/T = 0$. This equation can be used to predict the temperature dependence of the autodestruction reaction.

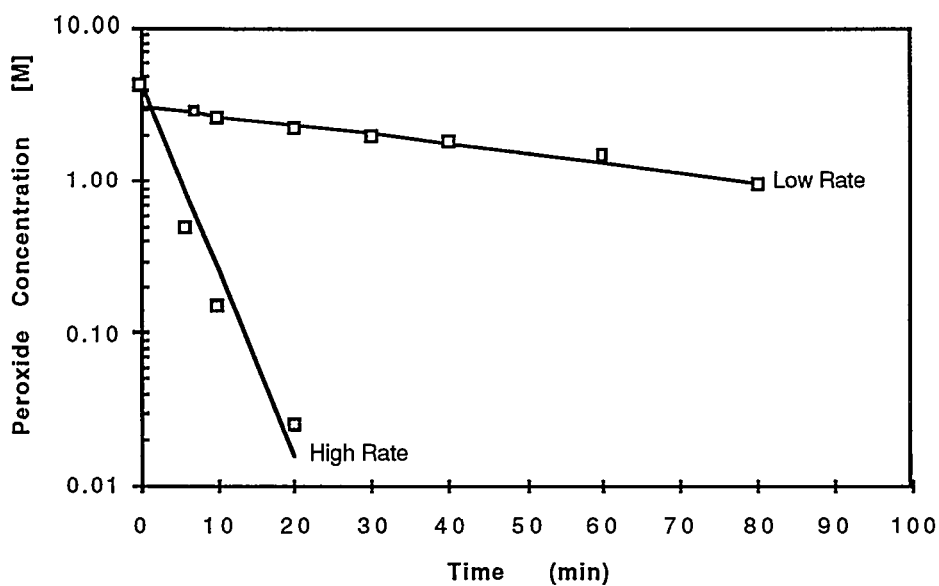


Figure 1. Plot of Typical Concentration vs. Time for Destruction of Hydrogen Peroxide in NaOH Solutions. Shown are the lowest rate in 2.57M NaOH at 70°C , and the highest measured rate in 0.128M NaOH at 90°C .

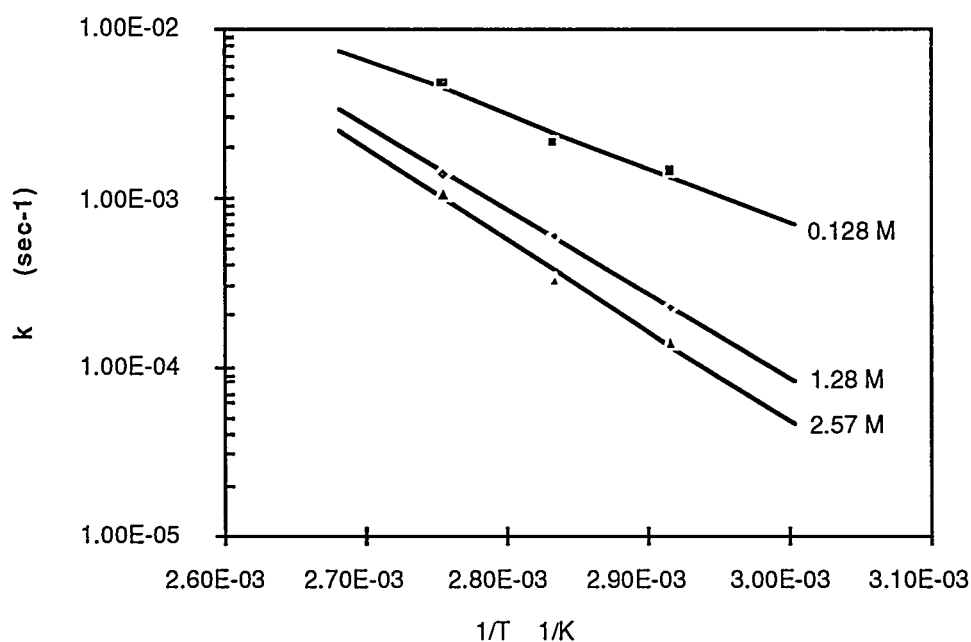


Figure 2. First-Order Rate Constants for Destruction of Hydrogen Peroxide in NaOH Solutions. The three lines are for different NaOH concentrations, as shown.

The activation energies and collision frequencies from the least squares fit to the data are reported in Table 3. The results for water on glass and stainless steel can be found in the literature [12]. In both water and in dilute base, the activation energies are about the same as shown in Table 3. Thus, the rate of increase of these reactions with temperature is about the same in water or dilute base. At higher base concentrations, the activation energy is larger. Thus, the rate of increase of these reactions with temperature is more rapid in higher base. In water, a 30 wt % solution of hydrogen peroxide is slightly acidic (pH of about 4). Thus, the activation energy does not seem to depend on pH over this small range. The difference in the rate constants is due to the large difference in the collision frequencies. For base, the collision frequencies are larger, indicating a much larger destruction rate at these conditions. For the glass vessels reported in the literature, the collision frequency was independent of the surface area of the glass vessel. In stainless steel, the collision frequency depended on the surface area of the exposed steel, indicating a surface catalytic effect.

Table 3. Activation Energies and Collision Frequencies for Hydrogen Peroxide Destruction

Condition	E _a (kJ/mol)	A (min ⁻¹)
Water on glass ^a	66.9	2.4 E+05
Water on stainless steel ^a	61.9	1.5 E+07
0.128M NaOH	60.5	1 E+08
1.28M NaOH	95.9	6 E+12
2.57M NaOH	104.1	6 E+13

^aFrom Ref. [12].

As shown in the table, the activation energy for hydrogen peroxide destruction in aqueous solutions is 61-67 kJ/mol, which is substantially less than the energy to break the O-O bond, 200 kJ/mol. Thus, the rate-controlling step in the reaction probably does not involve the breakage of the O-O bond [12]. The activation energy in 0.128M NaOH was similar to the result in water; however, the activation energy in high NaOH concentrations was substantially larger, which contributes to greater stability of hydrogen peroxide in more concentrated NaOH solutions. If the dissolution had been done in water alone, the destruction rate of hydrogen peroxide would also be lower still in the temperature range studied (70-90°C). The highest destruction rate was found in 0.128M NaOH. When hydrogen peroxide in sodium hydroxide is contacted with stainless steel, the autodestruction rate is about 200 times more rapid than with glass in > 2M NaOH at 70°C. This result eliminates the use of stainless steel as a construction material for the dissolver.

KINETICS OF URANIUM SILICIDE DISSOLUTION

The kinetics of uranium silicide dissolution was determined by the initial rate method [13]. The dissolution was done in a 250 mL jacketed glass beaker. Temperature was controlled by circulating a 50/50 mixture of propylene glycol and water in an external beaker jacket from a Brinkman RMS-6 refrigerator/heater. By this method, temperature of the flask contents was easily controlled within 1°C during the experiments. The temperature of the beaker contents was monitored by a thermometer. The liquid phase was continuously stirred with a magnetic stirrer. The stirring was not adequate to suspend the dense silicide particles, but the liquid phase was completely mixed. During a typical experiment, the hydrogen peroxide and sodium hydroxide

mixture was initially thermally equilibrated in the flask. When the silicide was introduced, the first sample was taken, and the clock was started. Grab samples were taken at predetermined intervals during a 10-min experiment. The grab samples were analyzed for hydrogen peroxide by titration and for dissolved uranium by inductively coupled plasma mass spectroscopy (ICP-MS). During the experiment, the heat generated by the autodestruction of hydrogen peroxide was continuously removed by the circulating heat-transfer fluid. At temperatures higher than 60°C, the heat released by the autodestruction reaction was greater than the capacity of the jacketed beaker to remove the heat; the liquid temperature reached the boiling point, and the dissolution could not be controlled so that accurate initial rate experiments could not be completed.

Typical experimental data are plotted in Figures 3 and 4. These experiments were started in 5M hydrogen peroxide, using 1 g U_3Si_2 with 270-352 mesh particles at 60°C. As shown in Figure 3, the dissolution rate for uranium is higher in 1.28M base than 5.14M base. For longer times than shown in the figure, the hydrogen peroxide is very rapidly consumed, and once the peroxide runs out, the dissolution of the uranium stops. Thus, higher base concentrations allow one to dissolve more uranium due to the longer lifetime of hydrogen peroxide in the dissolver solution. The substantially lower depletion rate of hydrogen peroxide in higher NaOH solutions is illustrated in Figure 4.

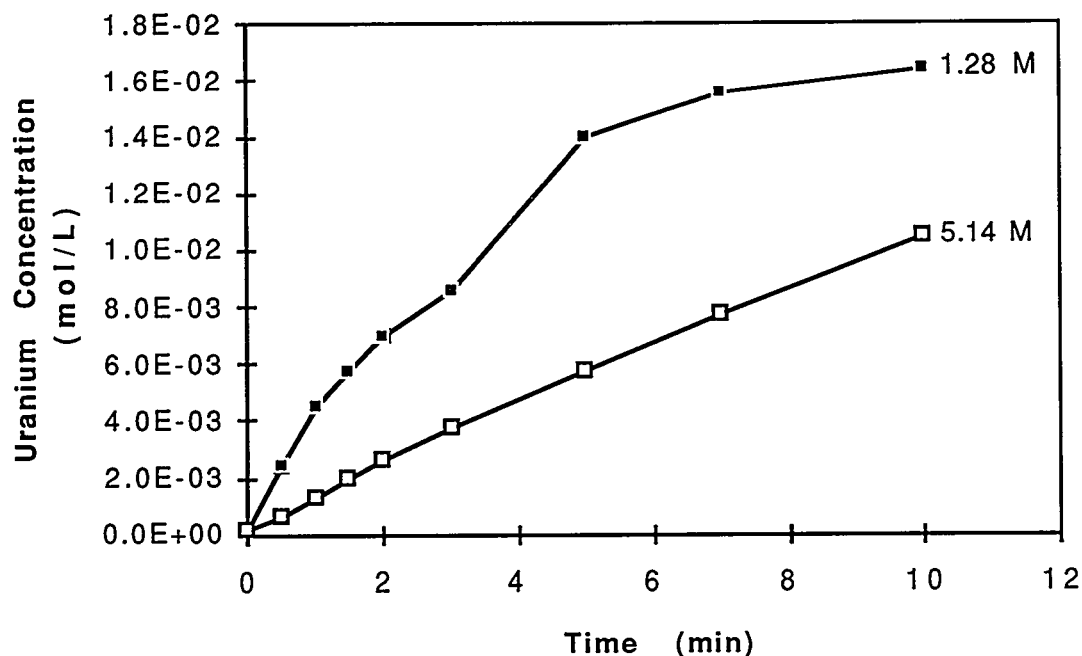


Figure 3. Initial Rate Results for Uranium Silicide Dissolution at 60°C and Two NaOH Concentrations. Uranium silicide in 270-325 mesh particles.

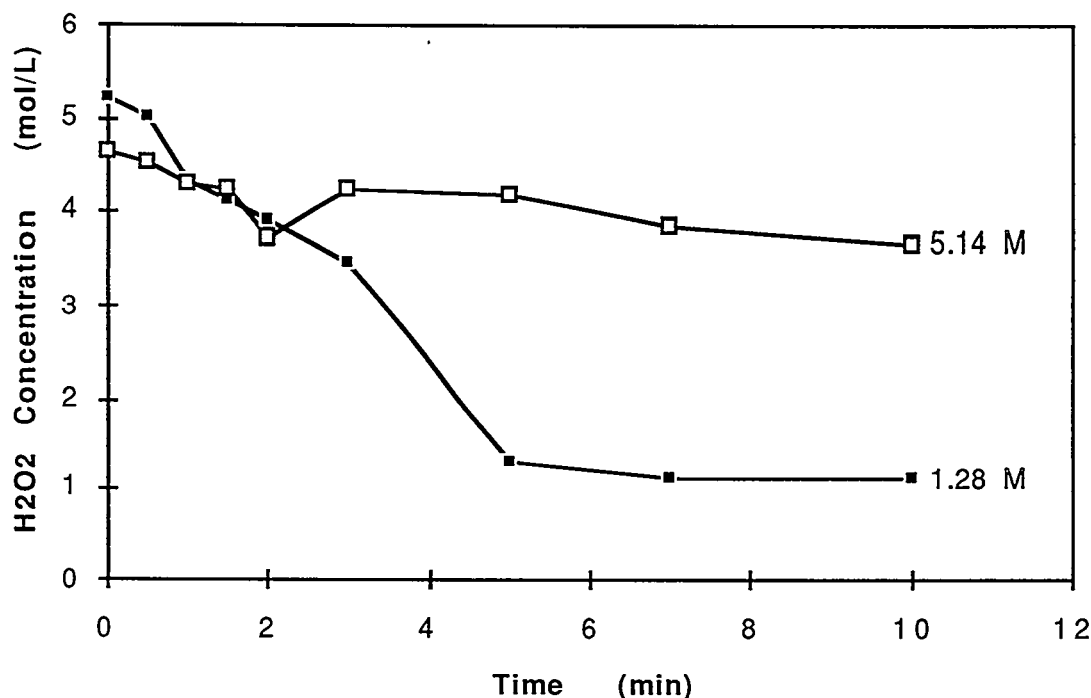


Figure 4. Initial Rate Results for Hydrogen Peroxide Depletion at 60°C and Two NaOH Concentrations. Uranium silicide in 270-325 mesh particles.

The results from the reaction-order experiments with 2.57M NaOH at 50° and 60°C are shown in Figure 5. These results indicate that the reaction order with respect to hydrogen peroxide is two in 2.57M NaOH. Also shown in the figure by the dashed line are the results for 5.14M NaOH at 60°C. At the higher base concentration, the order of the reaction with respect to hydrogen peroxide concentration is 1.3. The effect of the NaOH concentration on the order of the reaction will be investigated further. The present results indicate that the dissolution rate can be correlated by Eq. 8. The dissolution rate constant was determined by dividing the dissolution rate by the hydrogen peroxide concentration to the second power. Thus, the dissolution rate can be correlated by the following expression.

$$\frac{d[U]}{dt} = k_d A [H_2O_2]^2 \quad (8)$$

Where,

[U] = uranium concentration, mg/L

t = time, min

$k_d A$ = dissolution rate constant, mg U/L•min•g U₃Si₂ [H₂O₂]²

[H₂O₂] = concentration of hydrogen peroxide, M

The initial rate experiments also indicated the following trends:

- The silicide dissolution rate is directly proportional to the surface area of the particles. Therefore, as the particle size decreases, the increased surface area will result in an increased dissolution rate. Depending on the base concentration, a 35% decrease in the

particle size will increase the dissolution rate by a 50-75%. This effect is quantified by the variable "A" in Eq. 8.

- The rates of the reactions increase with temperature, as expected. The rate of increase depends on the base concentration being tested. In 5.14M base, a 10°C increase in temperature increases the silicide dissolution rate 300%, and the peroxide depletion rate 150%. Thus, higher temperatures favor the dissolution reaction over the peroxide destruction reaction.
- The order of $[H_2O_2]$ dependency for both the dissolution reaction ($[H_2O_2]^2$) and the peroxide autodestruction ($[H_2O_2]$) did not change with temperature.

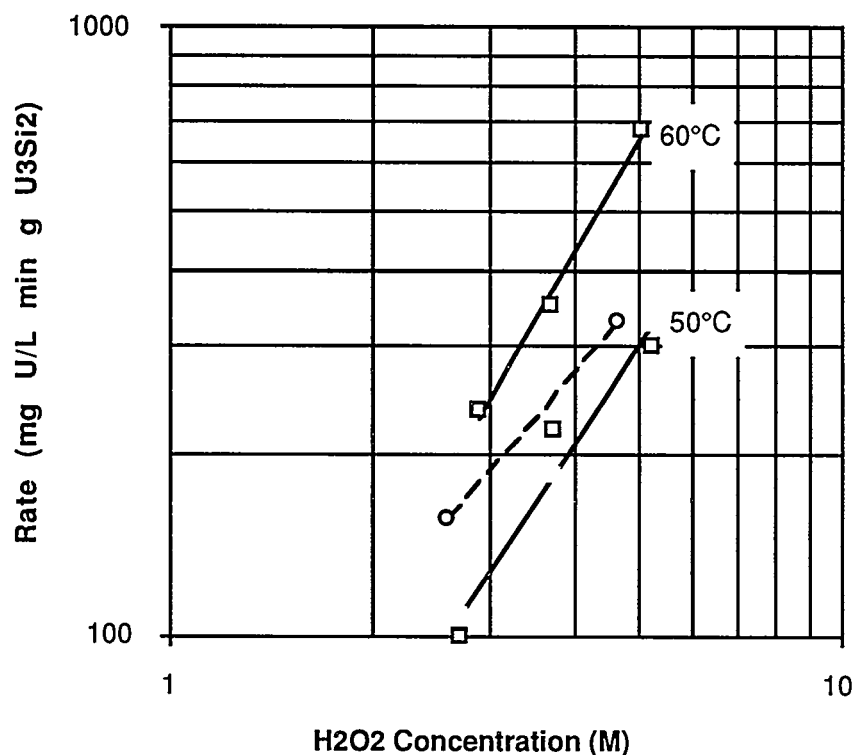


Figure 5. Plot Used for Determining Reaction Order for U₃Si₂ Dissolution. Solid lines, 2.57M NaOH, 50° and 60°C; dashed line, 5.14M NaOH, 60°C.

OPTIMIZED URANIUM SILICIDE DISSOLUTION PROCEDURE

A summary of the initial rate results at 50 and 60°C is given in Table 4. By using an Arrhenius form, these rates can be extrapolated to higher temperatures. Experiments to verify this extrapolation are planned. As shown in the table, the dissolution rate decreases with increasing hydroxide concentration. However, the hydrogen peroxide depletion rate also decreases with increasing base concentration. At low base concentrations, hydrogen peroxide rapidly decomposes, and although the silicide dissolution rate is initially high, it drops to zero as soon as the hydrogen peroxide is consumed; hydrogen peroxide must be present to dissolve the silicide, and these conditions are favored at higher base concentrations. In addition, when the dissolution is

complete, the dissolver solution must be acidified before being fed to an alumina column for Mo-99 removal. Thus, higher base concentrations require more acid to recover Mo-99. The optimum base concentration will be high enough to keep hydrogen peroxide in solution long enough to dissolve the silicide, but low enough to minimize the acid consumption prior to recovering the Mo-99 by ion chromatography. The optimum base concentration to meet these criteria is about 5M NaOH.

Table 4. Summary of Initial Rate Results (5M H₂O₂, 270-325 mesh U₃Si₂ Particles)

NaOH (<u>M</u>)	U Dissolution Rate (mol U/L•min•mol U ₃ Si ₂)		H ₂ O ₂ Depletion Rate (mol H ₂ O ₂ /L•min•mol U ₃ Si ₂)	
	50 °C	60 °C	50 °C	60 °C
1.28	1.42	3.68	153	793
2.57	1.23	3.02	-	647
5.14	0.42	1.23	128	185

The effect of temperature is also shown in Table 4. In the 5.14M base case, a 10°C increase in temperature increases the uranium dissolution rate 300%, while the hydrogen peroxide rate increases only 150%. Thus, silicide dissolution is favored over hydrogen peroxide destruction as the temperature increases. Extrapolation of these results indicates at 100°C, near the boiling point, dissolution rates as high as 180 mol U/L•min•mol U₃Si₂ and depletion rates of 270 mol H₂O₂/L•min•mol U₃Si₂. These are about the highest rates obtainable in an atmospheric dissolver. Even higher rates could theoretically be obtained in a pressurized dissolver, but because of the large amount of gas generation caused by peroxide destruction, such a device is impractical.

The dissolver design is limited by the foaming of the dissolution solution at these conditions. If too much hydrogen peroxide (our preliminary work has used up to 5M H₂O₂) is mixed with sodium hydroxide (5M) near the boiling point, the foaming caused by the gas evolution is so great that the contents may be dispersed outside the dissolution vessel. Thus, the problem becomes one of limiting the amount of solution (5M hydrogen peroxide and 5M NaOH) which is added to that batch, so that foam generation can be controlled.

By using the optimized condition described above, quantities of up to 3 g of uranium silicide can be dissolved in less than 1 h. The resulting solution will exceed the uranium concentration required so that the LEU targets will produce a Mo-99 concentration equivalent to current HEU processes. In fact, we have been able to reach concentrations of uranium approaching 0.16M during the dissolution process.

We have found that the following procedure gives the best conditions for dissolving an unirradiated target. After the cladding solution is removed, the jacketed flask is heated to 90-95°C, then for the first 3 g of silicide, 5 mL of 30 wt % hydrogen peroxide (9.56M) and 5 mL of 10M NaOH are added to the dissolver. This combination produces close to the optimum 5M H₂O₂-NaOH. The solution foams, and within about 3 min, the foaming subsides and a dark red uranium solution is produced. Since the dissolution is second order with respect to hydrogen peroxide concentration, high concentrations of peroxide are needed to achieve rapid dissolution. To avoid dilution, the solution is removed from the dissolver and 10 mL of 30 wt % hydrogen peroxide (9.56M) and 10 mL of 10M NaOH are added to the dissolver. More reagents can be added because the foaming is reduced with subsequent reagent additions. As before, the solution foams, and within about 3 min, the foaming subsides and a dark red uranium solution is produced. This solution can be removed from the dissolver and the process repeated until the

entire target is dissolved. We have found that it takes about 150 mL of reagents to dissolve 3 g of U_3Si_2 .

These dissolution kinetics are ideal for a plug-flow reactor configuration. We plan to use a jacketed glass filter as a dissolver to test this concept.

DISSOLUTION OF HIGH BURNUP TARGET

Because irradiated uranium silicide targets could behave differently, we tested this process using an irradiated miniplate sample that was stored at Argonne following its post-irradiation examination. The miniplate sample that we used had undergone 42.2% burnup in the 30 MW Oak Ridge Reactor (ORR). This miniplate contained uranium enriched to 19.84% ^{235}U before irradiation. Since the miniplate is nearly 9 years old, the short-lived fission products, including ^{99}Mo , have completely decayed. However, several stable molybdenum isotopes and the long-lived fission products and actinides still remain in the U_3Si_2 miniplates.

The primary benefit to using a sample with a high burnup is to measure the effects on the dissolution step of changes in the fuel caused by the high degree of fissioning. High burnup of the fuel significantly changes its chemical composition. For example, the chemical composition of the target is modified from that of unirradiated or low-burnup fuels by lowering the uranium content of the fuel, producing ^{28}Si from ^{27}Al , producing ^{31}P from ^{30}Si , and causing the formation of fission products and transuranic elements. Such chemical compositional changes coupled to radiation damage to the fuel caused by energy input (about 200 MeV/fission) form new compounds, especially along the contact between the U_3Si_2 fuel particles and the aluminum matrix. The formation of new compounds in highly irradiated fuels was studied earlier by Gerard Hofman and colleagues at Argonne [14] using both optical and electron microscopy techniques on polished metallographic specimens. The salient aspects of their findings are summarized below:

- A new layer caused by the interaction of uranium silicide with aluminum was formed as a result of high levels of irradiation. The thickness of the layer increased with the duration of irradiation. The layer was about 2- μm thick at 40% burnup.
- The new layer can be represented by the chemical formula $\text{U}(\text{Al},\text{Si})_3$, where the Al and Si can form a series of solid solutions represented by the end members UAl_3 and USi_3 . At 40% burnup, the chemical composition of the layer is about 65 mol% Al, 25 mol% Si, and 10 mol% U.
- A mixture of nitric acid, hydrofluoric acid, and citric acid etched the unaltered U_3Si_2 but did not attack the $\text{U}(\text{Al},\text{Si})_3$ layer.

Unlike the unirradiated target, the irradiated miniplate did not dissolve readily by use of our optimized procedure. The decladding procedure did work as expected. But after the cladding was removed, the silicide fuel looked like a monolith, not the particles we obtained during the unirradiated testing. This monolith was resistant to dissolution. Even after the monolith was broken into pieces, the dissolution was very slow. We used 800 mL of 5M NaOH-5M H_2O_2 over a 10 h period (only 150 mL was expected to be used in less than 1 h). A substantial portion of the miniplate did dissolve. Samples from the liquid dissolver solution are being analyzed so that a material balance can be completed. We suspect that the miniplate did not dissolve due to the formation of a surface layer of $\text{U}(\text{Al},\text{Si})_3$, and we plan to test this hypothesis by using annealed unirradiated targets later this year.

DEVELOPMENT OF URANIUM SILICIDE PROCESS

During the next year we plan to make considerable progress to evaluating the technical and economic feasibility of an LEU silicide process for Mo-99 production. The highest priority is to develop a dissolution procedure for irradiated targets. In addition, the following issues will be studied.

Acidification of the cladding solution. The cladding solution must be acidified to allow recovery of the Mo-99 by ion chromatography. The HEU processes in use at the IRE acidify the dissolved solution (cladding and fuel are dissolved in one step) to 1M by using concentrated nitric acid. Work at Argonne has shown that Mo-99 is better recovered with 0.5M nitric acid [15]. Experiments to verify this procedure are planned.

Recovery of the uranium. Once the silicide target is dissolved, the uranium can be recovered as sodium diuranate by destroying the peroxide complex. We have finished a limited amount of experimental work to develop this procedure. More experiments are planned to determine the parameters that control this process, including the effect of carbonates on interfering with the uranium precipitation. Processes for recycling the recovered uranium and their cost effectiveness will be investigated.

Acidification of the dissolver solution. Early work at Argonne has shown that the silicon concentration must be less than 0.1M in the acidified dissolver solution [5]; this prevents precipitation of gelatinous silica. Concentrated nitric acid will be used to acidify this solution.

Ion chromatography recovery of Mo-99. This procedure has been used at the IRE on HEU targets for more than 10 years. A detailed description of the process is given elsewhere [2]. Unlike the IRE, the LEU process will produce a slightly different composition solution. Experiments are planned using an irradiated miniplate to determine the material balance for molybdenum, uranium, activation products, and fission products. These experiments will employ the new optimized dissolution procedure and the published ion chromatographic procedure to recover the Mo-99.

Waste disposal. The liquid and solid wastes generated from the process must be characterized and disposed of. A material balance on the optimized process will be done, and the waste streams identified.

CONCLUSIONS

The first roadblock to the use of LEU silicide targets instead of the conventional HEU UAl_x alloys for Mo-99 production is the dissolution of the target. In base, the uranium silicide does not readily dissolve. However, the silicide can be dissolved in alkaline peroxide. The optimum conditions for silicide dissolution appear to be 5M NaOH-5M H_2O_2 at boiling temperatures. The kinetics of the dissolution process favor a plug-flow reactor configuration. Using these optimum conditions we have been able to successfully dissolve significant quantities of unirradiated uranium silicide in less than 1 h. Irradiated targets are not readily dissolved by this procedure. It is suspected that the formation of a $U(Al,Si)_3$ surface layer interferes with the dissolution. This possibility will be studied further during the next year. Downstream of the dissolution, the solutions recovered will produce a Mo-99 yield equivalent to current HEU processes. Work remains to be done on the process downstream of the dissolution, including ion chromatographic recovery of Mo-99 and waste disposal.

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