

Chapter for IAEA TECODOC

Converting Targets and Processes for Fission-Product ⁹⁹Mo From High- to Low-Enriched Uranium

by

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CONVERTING TARGETS AND PROCESSES FOR FISSION-PRODUCT ⁹⁹MO FROM HIGH- TO LOW-ENRICHED URANIUM

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Abstract

Most of the world's supply of ⁹⁹Mo is produced by the fissioning of ²³⁵U in high-enriched uranium targets (HEU, generally 93% ²³⁵U). To reduce nuclear-proliferation concerns, the U.S. Reduced Enrichment for Research and Test Reactor Program is working to convert the current HEU targets to low-enriched uranium (LEU, <20% ²³⁵U). Switching to LEU targets also requires modifying the separation processes. Current HEU processes can be classified into two main groups based on whether the irradiated target is dissolved in acid or base. Our program has been working on both fronts, with development of targets for acid-side processes being the furthest along. However, using an LEU metal foil target may allow the facile replacement of HEU for both acid and basic dissolution processes. Demonstration of the irradiation and ⁹⁹Mo separation processes for the LEU metal-foil targets is being done in cooperation with researchers at the Indonesian PUSPIPTEK facility. We are also developing LEU UO₂/Al dispersion plates as substitutes for HEU UAl_x/Al dispersion plates for base-side processes. Results show that conversion to LEU is technically feasible; working with producers is essential to lowering any economic penalty associated with conversion.

1. INTRODUCTION

The Reduced Enrichment for Research and Test Reactor (RERTR) Program was established in 1978 at the Argonne National Laboratory (ANL) by the Department of Energy (DOE), which continues to fund the program and to manage it in coordination with the Department of State (DOS), the Arms Control and Disarmament Agency (ACDA), and the Nuclear Regulatory Commission (NRC). The primary objective of the program is to develop the technology needed to use low-enriched uranium (LEU) instead of high-enriched uranium (HEU) in research and test reactors, and to do so without significant penalties in experimental performance, economics, or safety aspects of the reactors. Research and test reactors utilize nearly all the HEU that is used in civil nuclear programs, and eliminating their dependence on this material will significantly reduce nuclear proliferation concerns. The RERTR program continues to receive strong support from many international organizations that contribute to this effort.

Most of the HEU used in research reactors is contained in their fuel elements; therefore, a large fraction of the RERTR program activities has been concentrated on developing suitable LEU alternatives for research reactor fuels. However, a non-negligible, wide-spread, and expanding utilization of HEU in research reactors is due to its use in targets for the production of ⁹⁹Mo through fission. Technetium-99m, the daughter of ⁹⁹Mo, is the most commonly used medical radioisotope in the world. It is relied upon for over nine million medical procedures each year in the U.S. alone, comprising 70% of all nuclear-medicine procedures. Most ⁹⁹Mo is produced in research and test reactors by the irradiation of targets containing HEU. Because the worldwide effort to fuel research and test reactors with LEU instead of with HEU has been so successful, HEU is now used only for ⁹⁹Mo production in some countries. In addition, while there are only a few major producers of ⁹⁹Mo, many nations with developing nuclear programs are seeking to become producers of ⁹⁹Mo, both for domestic and foreign consumption. Therefore, an important component of the U.S. RERTR program's goal of reducing world commerce in HEU is the development of means to produce ⁹⁹Mo using LEU. Initial development work was carried out from 1986 to 1989, when the effort was halted by lack of funding. The DOE authorized resumption of this work in 1993. The two principal aspects of the work are (1) target development and (2) chemical process testing and modification.

As we did for fuel development and testing, the RERTR Program is developing international partnerships for the ^{99}Mo development work. These partnerships are especially important because, at the present time the U.S. does not have facilities suitable for irradiating targets. An agreement was signed with the Indonesian National Atomic Energy Agency (BATAN) in November 1994, and our joint work is well underway. A second agreement was signed with the Korea Atomic Energy Research Institute in December 1996.

Currently, targets for the production of ^{99}Mo are generally either (1) miniature Al-clad fuel plates [1-9] or pins [10,11] containing U-Al alloy or UAl_x dispersion fuel similar to that used, at least in the past, to fuel the reactor or (2) a thin film of UO_2 coated on the inside of a stainless steel tube [12,13]. The ^{99}Mo is extracted first by dissolving either the entire Al-clad fuel plate or pin or by dissolving the UO_2 and then performing a series of extraction and purification steps. Both acid and basic dissolutions are used, and each producer has its own process. The highly competitive nature of the business and the stringent regulations governing the production of drugs make each producer reluctant to change its process. Therefore, the RERTR program's strategy is to minimally modify the most widely used and potentially most useful existing processes.

To yield equivalent amounts of ^{99}Mo , the LEU targets must contain five to six times as much uranium as the HEU targets they replace. Substituting LEU for HEU in targets will require, in most cases, changes in both target design and chemical processing. Three major challenges have been identified: (1) to modify targets and processing as little as possible, (2) to assure continued high yield and purity of the ^{99}Mo product, and (3) to limit economic disadvantage. Keeping the target geometry the same, thereby minimizing the effects of LEU substitution on target irradiation, necessitates modifying the form of uranium used. Changing the amount and form of the uranium in the target necessitates modifying at least one or, possibly, two target processing steps--dissolution and initial molybdenum recovery.

One of the issues raised in connection with using LEU to produce ^{99}Mo is the greater amount of ^{239}Pu generated. The ^{239}Pu is generated through neutron capture by the ^{238}U . About 30 times more ^{239}Pu is generated in an LEU target vs. an HEU target for an equivalent amount of ^{99}Mo . However, because significantly more ^{234}U is present in HEU than in LEU as a consequence of the enrichment process, total alpha contamination of an irradiated LEU target is less than 20% higher than that of an equivalent HEU target. Table I shows calculated ^{99}Mo and ^{239}Pu yields and alpha contamination from uranium isotopes in comparable HEU and LEU irradiated targets.

Our progress in target and process development is summarized in this paper.

TABLE I. COMPARISON OF TYPICAL HEU AND LEU TARGETS FOR THE PRODUCTION OF FISSION-PRODUCT ^{99}Mo

	HEU	LEU ^a
^{235}U Enrichment, %	93	19.75
^{235}U , g	15	18.5
Total U, g	16.1	93.7
^{99}Mo yield ^b , Ci	532	545
Total Mo, mg	9.8	10.0
^{239}Pu ^c , μCi (mg)	30 (0.44)	720 (12.)
$^{234}, ^{235}, ^{238}\text{U}$, μCi	1280 ^d	840 ^e
Total ? , μCi	1310	1560

^aAssumes the LEU target irradiation was done in an LEU-fueled reactor.

^bAt the time target leaves the reactor core.

^cAssuming all ^{239}Np has decayed to ^{239}Pu .

^dBased on a ^{234}U isotopic content of 1.0 wt%.

^eBased on a ^{234}U isotopic content of 0.12 wt%.

2. CURRENT STATUS OF FISSION-PRODUCT ^{99}Mo PRODUCTION

Except for fission-product ^{99}Mo produced by the Australian Nuclear Science and Technology Organization (ANSTO), which uses uranium enriched to power-reactor fuel levels, all major producers use HEU targets. Table II compares targets and processes used worldwide. The RERTR response to each HEU target and process is also summarized in this table.

TABLE II. COMPARISON OF CURRENT PROCESSES FOR ^{99}Mo PRODUCTION (ACID VS. BASE DISSOLUTION)

	Process	
	Acid Dissolution	Base Dissolution
Current Target	<p>Target (1)--UO_2 (HEU) on inside of stainless-steel (SS) cylinder (Cintichem) by Indonesian National Atomic Energy Agency (BATAN), and Sandia National Laboratories (SNL), USA</p> <p>Target (2)--Extruded Al-clad U/Al-alloy pins (HEU), AECL/Nordion, Canada</p> <p>Target (3)--UO_2 pellets (2% ^{235}U), ANSTO, Australia</p>	<p>Aluminum-clad UAl_x/Al-dispersion-fuel plates (HEU)--Institut National des Radioéléments (IRE), Belgium; Comisión Nacional de Energía Atómica (CNEA), Argentina; Atomic Energy Corporation of South Africa Limited (AEC), South Africa; Mallinckrodt, Netherlands</p>
Dissolving Reagent	Nitric acid solution (Cintichem process combines with sulfuric acid)	Sodium hydroxide solution, often with sodium nitrate to avoid H_2 formation
Initial Molybdenum Recovery Step	<p>Target (1)--Precipitation of Mo by ? -benzoin oxime followed by dissolution in basic solution for further purification</p> <p>Targets (2) and (3) sorption of Mo by alumina column</p>	Acidification to recover radioiodine and sorption of Mo by (1) alumina or (2) anionic exchange
Advantages	<p>Target (1)</p> <ul style="list-style-type: none"> Target cylinder acts also as dissolver vessel--only irradiated UO_2 is dissolved, producing a low volume of waste solution. Initial Mo recovery is fast with excellent yield and decontamination while concentrating product. <p>Target (2)</p> <ul style="list-style-type: none"> Targets are prepared in similar manner to fuel pins. Targets are miniature fuel pins; therefore, behavior in the reactor is well known. <p>Target (3)</p> <ul style="list-style-type: none"> The low enrichment is not a proliferation problem. Preparation of UO_2 pellet is a well-known technology. 	<p>General</p> <ul style="list-style-type: none"> Dissolving in base will release the noble fission gases, while retaining radioiodine in the dissolver solution. Fission gases can be recovered separately from iodine. A second step, lowering the pH of the solution, will release iodine isotopes into the gas phase, allowing their separate recovery. Dissolution of target by base acts as a Mo decontamination step. Basic solution causes precipitation of uranium, other actinides, and many fission products as insoluble hydroxides, which can be filtered from the solution containing the soluble MoO_4^{2-} species. Targets are essentially miniature fuel plates; therefore, they are easily fabricated, and their behavior in the reactor is well known.

TABLE II. COMPARISON OF CURRENT PROCESSES FOR ^{99}Mo PRODUCTION (ACID VS. BASE DISSOLUTION)

	Process	
	Acid Dissolution	Base Dissolution
Disadvantages	<p>Targets (1), (2), and (3)</p> <ul style="list-style-type: none"> Noble fission gases and iodine gas are released together during uranium dissolution. <p>Target (2)</p> <ul style="list-style-type: none"> Large quantity of aluminum must also be dissolved, leading to a large volume of waste solution. Because reactor fuel will be LEU in the future, targets will need to be made in a dedicated line--separate from that for fuel. <p>Target (3)</p> <ul style="list-style-type: none"> Large amount of uranium must be dissolved for ^{99}Mo yield--due to low ^{235}U enrichment. 	<p>General (continued)</p> <ul style="list-style-type: none"> Entire target is dissolved. A large quantity of aluminum must be dissolved with the uranium, resulting in a large waste volume.
Major Technical Challenges to LEU Substitution	<p>General</p> <ul style="list-style-type: none"> To make as little modification to target geometry and processing as possible while increasing the uranium content ~5 times To produce ^{99}Mo with same or higher specific activity and purity To obtain same or higher yields of ^{99}Mo and, in some cases, other fission products To maintain or decrease waste-volume generation To maintain or increase safety of disposed radioactive waste To maintain or decrease treatment required for safe waste disposal To limit economic penalty To limit concerns from the greater amount of ^{239}Pu in LEU by showing its effective decontamination from ^{99}Mo product To obtain Reactor Operator acceptance of LEU target design To obtain Process Safety Officer acceptance of modified process and equipment To obtain U.S. Federal Drug U 	<p>General</p> <ul style="list-style-type: none"> To make as little modification to target geometry and processing as possible while increasing the uranium content ~5 times To produce ^{99}Mo with same or higher purity and specific activity To obtain same or higher yields of ^{99}Mo and, in some cases, other fission products To maintain or decrease waste-volume generation To maintain or increase safety of disposed radioactive waste To maintain or decrease treatment required for safe waste disposal To limit economic penalty To limit concerns from greater amount of ^{239}Pu in LEU by showing its effective decontamination from ^{99}Mo product To obtain Reactor Operator acceptance of LEU target design To obtain Process Safety Officer acceptance of modified process and equipment To obtain U.S. Federal Drug

TABLE II. COMPARISON OF CURRENT PROCESSES FOR ⁹⁹Mo PRODUCTION (ACID VS. BASE DISSOLUTION)

	Process	
	Acid Dissolution	Base Dissolution
	Administration (FDA) or equivalent national authority approval of the ⁹⁹ Mo product from LEU	Administration (FDA) or equivalent national authority approval of the ⁹⁹ Mo product from HEU
Major Technical Challenges to LEU Substitution (Continued)	Specific for Target (1)	Specific
	<ul style="list-style-type: none"> Electrodeposition of UO₂ limited by electrochemistry and equipment. Too thick layers of UO₂ may cause sintering and, therefore, difficult or incomplete dissolution of UO₂. If a fully-loaded HEU (~20-g ²³⁵U) Cintichem target is used, it is unlikely that an equivalent LEU target can be made using electrodeposited UO₂. 	<ul style="list-style-type: none"> The density of UAl_x is not high enough to allow keeping target geometry the same while accommodating ~5 times the amount of uranium per target. Alternative, high-density forms of uranium are needed to keep target geometry the same. Use of alternative forms of uranium may also call for changes in the dispersion medium and the cladding material (both currently aluminum).
	Specific for Target (2)	<ul style="list-style-type: none"> The thickness of the cladding may also need to be decreased. If radical changes to the HEU target are necessary to achieve similar ⁹⁹Mo yields, opposition could be strong. Changes to the fuel, the dispersion medium, and the cladding will all affect processing.
	Target (3) is already LEU.	
Means to Convert to an LEU Target	Target (1)	U₃Si₂
	<ul style="list-style-type: none"> Use of LEU metal is a strong alternative due to its high density and thermal conductivity, easy dissolution by nitric acid under conditions similar to that for UO₂, and ease of making into a foil. Initial development was on electrodeposition of U metal on Ni-coated stainless-steel cylinders to give a target/dissolver duplicating the current UO₂-coated one. Concerns that electrodeposition from molten salt was too “high tech” for some potential users shifted R&D to a mechanically formed target. 	<ul style="list-style-type: none"> Because U₃Si₂'s density is higher than that of UAl_x, LEU targets of the same geometry can be fabricated to produce same ⁹⁹Mo yield as HEU. Because U₃Si₂ is harder than UAl_x, cladding must be converted from pure Al to a stronger alloy (Al-6061). Alloying elements complicate target dissolution by precipitating as hydroxides. The U₃Si₂ cannot be dissolved by NaOH solutions or NaOH solutions containing NaNO₃. Therefore, the cladding and aluminum powder in the fuel meat are dissolved in one step,

TABLE II. COMPARISON OF CURRENT PROCESSES FOR ⁹⁹Mo PRODUCTION (ACID VS. BASE DISSOLUTION)

Process		
	Acid Dissolution	Base Dissolution
Means to Convert to an LEU Target (Continued)	Target (1) (Continued) <ul style="list-style-type: none"> • The LEU target is based on holding a uranium-metal foil between two concentric cylinders with different thermal expansion coefficients. The foil will be provided good thermal contact with the outer, water-cooled cylinder by the higher expansion of the inner cylinder. • The outer cylinder is zirconium. Inner cylinders being tested are Al, Mg, 304 SS, and zirconium. Water cooling of outer and no cooling of inner cylinder is still likely to provide some differential thermal expansion, in a target with both cylinders fabricated from zirconium. • Because the U foil bonded to the walls of the target during irradiation, 10-15 μm fission-product-absorption barriers have been added to the U foil. Potential barriers are Ni, Cu, Zn, and Fe. All dissolve quickly in acid; Ni, Zn, and Fe have no activation-products which could generate problems with ^{99}Mo purity. Copper has one major activation product that requires a decontamination factor (DF) of 3300; tracer experiments confirm that this DF can be met. • Adjusted U has been used in targets to minimize the grain size in the foil. An Fe concentration of 450 ppm and Al of 1000 ppm and given a β quench to obtain a 10-20-μm grain size. • Targets with adjusted U, a 304 SS inner cylinder, and Zn or Cu fission-barriers on both sides of the U foil have been irradiated and disassembled successfully. • Early targets have used 10-15 μm Cu, Zn, or Ni foils wrapped around the U foil as fission barriers. In the future, Ni, Zn, or Cu will be electroplated onto the U foil. • A Zn/U compound formed during irradiation dissolves significantly slower in nitric acid than either of the two metals. Conditions for dissolution must be modified to account for this lower dissolution rate. 	U_3Si_2 (Continued) <ul style="list-style-type: none"> • and a second step is required using a more powerful reagent to dissolve the U_3Si_2. • Because 15-25% of the ^{99}Mo is lost to the aluminum matrix due to fission recoil, it must be recovered from both solutions. • Alkaline hydrogen peroxide will dissolve U_3Si_2 at acceptable rates. However, mechanical means must be employed to break up the agglomerated U_3Si_2 particles following irradiation for rapid dissolution. • An aggressive dissolution solution using concentrated fluoride will dissolve irradiated U_3Si_2 targets in a single step [8]; fluoride complicates waste treatment and disposal. • Future work should either (1) build on the dissolution process using concentrated fluoride described by Sameh [8], (2) look at other aggressive dissolution reagents, or (3) look at other forms of U. U-Metal Foils <ul style="list-style-type: none"> • Alkaline peroxide will dissolve U foil at acceptable rates. Means have been developed to minimize peroxide autodestruction. • The need for metal barriers in the foil target has complicated basic dissolution. Only Zn can be dissolved in base. Dissolution of Zn in basic sodium nitrate gives high rates. Sodium hydroxide with peroxide dissolves Zn more slowly, but at rates comparable to U dissolution. • Although the Zn/U compound formed during irradiation does not dissolve significantly in basic nitrate solutions, it does dissolve at a higher rate than U or Zn in alkaline peroxide and should not cause dissolution problems.

TABLE II. COMPARISON OF CURRENT PROCESSES FOR ^{99}Mo PRODUCTION (ACID VS. BASE DISSOLUTION)

	Process	
	Acid Dissolution	Base Dissolution
Means to Convert to an LEU Target (Continued)	Target (2) <ul style="list-style-type: none"> The AECL is moving independently on LEU conversion. Cooperation with the RERTR Program is on an informal, periodic discussion basis. 	UO₂ <ul style="list-style-type: none"> Dispersion-fuel plates with UO₂ loadings up to 40 wt% can provide ~3X the U loading of the UAl_x target--that is about one-half of the ²³⁵U needed for an equivalent LEU target. The UO₂ can be dissolved in basic peroxide at acceptable rates. As an added advantage over U₃Si₂ and U metal, it does not catalyze the autodestruction of H₂O₂. Therefore, its dissolution requires substantially less H₂O₂ and is easier to control.
	Target (3) <ul style="list-style-type: none"> Not applicable 	Advanced Fuels <ul style="list-style-type: none"> To allow all research and test reactors to convert to LEU fuel, RERTR is developing fuels that will provide higher U loadings [14]. Alloys of U with Mo or with a combination of Zr and Nb are being tested with densities 32-47% higher than that of U₃Si₂. Due to their lowering the specific activity of the ⁹⁹Mo, Mo alloys are not appropriate for ⁹⁹Mo production. If LEU-Nb-Zr alloys are found to be successful as fuels, they should be tested for use in ⁹⁹Mo production.
Status of LEU Process Development	Target (1) <ul style="list-style-type: none"> Test irradiations of targets continue to optimize their design for consistent removal of the U foil from the target for processing. The need for fission barriers in targets is established. Zinc, Cu, and Ni are being tested; so far Zn- and Cu-foil-barrier targets have been successful. Zinc barriers have been electroplated on U foil successfully. Copper electroplating is underway, and that of Ni is yet to be begun. No work has been done using adjusted U. Dissolution of uranium foil has been developed for unirradiated U foil. Tests in Indonesia confirm that irradiated LEU foil dissolves as fast or faster than unirradiated U foil. 	U₃Si₂ <ul style="list-style-type: none"> Dissolution by a two-step process is developed to the point where a full-scale demo is needed. Rates and mechanisms of dissolving (1) aluminum in cladding and the fuel matrix and (2) silicide particles are understood. It is clear that the reason irradiated silicide is slow to dissolve is the bonding of silicide particles during irradiation. A physical means to break up the fused silicide particles before or during dissolution is needed for successful processing. We have not yet designed means to do this. Use of alloyed-aluminum cladding necessitates a solids-separations step following cladding dissolution. Hydroxide precipitates of alloying elements are suspended in the spent cladding-dissolver solution. Separation of this low-density precipitate from the high-density U₃Si₂ can be accomplished.

TABLE II. COMPARISON OF CURRENT PROCESSES FOR ⁹⁹Mo PRODUCTION (ACID VS. BASE DISSOLUTION)

	Process	
	Acid Dissolution	Base Dissolution
Status of LEU Process Development (Continued)	Target (1) (Continued) <ul style="list-style-type: none"> We have no dissolution experience for adjusted U. Tracer-level experiments have shown that Ni, Cu, or Fe fission barriers should not affect dissolution or processing. If a Zn barrier is chosen, conditions must be developed to dissolve Zn/U layer and to show Zn will not affect processing. Use of a dissolver solution of HNO₃ alone (rather than a mix of HNO₃ and H₂SO₄) has been developed to cut waste treatment and disposal costs. Tracer-level demonstrations in the U.S. showed that LEU substitution will not adversely affect recovery or purity of ⁹⁹Mo product. Indonesian tracer-level demos using (1) ~1000X more activity and (2) the actual solution volumes, reagents, and equipment for a full-size target verified earlier U.S. results and showed the effectiveness of the improved counting and data-analysis methods that were developed. Design, fabrication, and testing of an experimental dissolver for the full-scale demonstration has been completed. A multi-use production dissolver is yet to be designed. Agreement was reached with SNL that irradiating and processing of LEU-oxide Cintichem targets will be in the test ⁹⁹Mo-product-acceptance matrix. Targets are being fabricated at Los Alamos National Laboratory. 	U₃Si₂ (Continued) <ul style="list-style-type: none"> Conditions were found to keep silica in solution during acidification of the dissolver solution prior to I and Mo recovery but must be verified under actual process conditions. Conditions are known for destroying peroxide and allowing uranium to precipitate following target dissolution. (Precipitation of uranium is necessary prior to acidification and use of an alumina column to recover Mo.) The procedure must still be optimized. Conditions for alumina recovery of Mo have been determined but must be verified under process conditions. Full-scale demo yet to be done.
	Target (2) <ul style="list-style-type: none"> Status not known. 	U-Metal Foil <ul style="list-style-type: none"> Dissolution of U foil with a Zn barrier <i>may</i> require a two-step process. Rate and mechanism of U-foil dissolution by alkaline peroxide are understood and modeled. Effects of adjusted uranium not yet measured. Zinc that has not reacted with U dissolves quickly in basic nitrate solutions. Dissolution rate using alkaline peroxide may also be adequate. Dissolver design is only conceptual. Zinc is the only material currently acceptable as a barrier for base-side processes. The Zn/U compound formed by heat treating is quickly dissolved by alkaline peroxide. Conditions are known for destroying peroxide and allowing uranium to precipitate following target dissolution. Procedure still to be optimized. Following dissolution and peroxide destruction, steps for the recovery and purification of molybdenum that were developed for HEU should be appropriate for LEU metal. Must still be verified.
		UO₂ <ul style="list-style-type: none"> Dissolution of UO₂ by alkaline peroxide has been optimized and modeled.

TABLE II. COMPARISON OF CURRENT PROCESSES FOR ⁹⁹Mo PRODUCTION (ACID VS. BASE DISSOLUTION)

	Process	
	Acid Dissolution	Base Dissolution
Status of LEU Process Development (Continued)	<p>Target (3)</p> <ul style="list-style-type: none"> Not applicable. 	<p>UO₂ (Continued)</p> <ul style="list-style-type: none"> Conditions for dissolving UO₂/Al dispersions in a two-step process have been developed and tested using heat-treated and low-burnup compacts. Dispersion-fuel miniplates of UO₂/Al loaded to 40 vol% U have been prepared. <p>Advanced Fuels</p> <ul style="list-style-type: none"> No work has yet been done.
Planned Development Activities	<p>Target (1)</p> <ul style="list-style-type: none"> At least one full-scale demonstration will be done in Indonesia during 1997. Following successful demonstration, we will tackle specific tasks necessary for conversion: (1) design and fabrication of the multi-use dissolver, (2) waste treatment and disposal, and (3) economic comparison of production from HEU and LEU. <p>Target (2)</p> <ul style="list-style-type: none"> Continued informal communication with AECL staff. <p>Target (3)</p> <ul style="list-style-type: none"> No plans. 	<p>U₃Si₂</p> <ul style="list-style-type: none"> A decision has been made to suspend R&D activities on this fuel. <p>U-Metal Foils</p> <ul style="list-style-type: none"> Destruction of peroxide following dissolution will be optimized for the % recovery and filterability of the U/OH precipitate. Dissolver system to be developed. Effects of LEU on ⁹⁹Mo recovery and purification will be studied using low-burnup targets. A technical partnership will be established for full-scale demonstration. <p>UO₂</p> <ul style="list-style-type: none"> Samples of miniplates will be irradiated to low burnup and used in tracer studies to test dissolution and ⁹⁹Mo recovery and purification. Tasks will parallel those of U foil. <p>Advanced Fuels</p> <ul style="list-style-type: none"> As alloys are found acceptable for fuels, they will be tested as ⁹⁹Mo-production targets.

3. TECHNICAL CHALLENGES TO LEU CONVERSION

Although technical challenges are far from the only impediments to conversion from HEU to LEU, they are the most clearly addressed. They also most clearly define economic factors. The RERTR program's research and development activities need to address all aspects of production but to focus limited resources on technical areas that will give the best return on investment. Molybdenum production can be broken up into the following areas:

- Target fabrication
- Irradiation
- Postirradiation disassembly
- Target dissolution
- Separation and purification of ^{99}Mo
- Waste treatment and disposal

In the case of target development, this requires (1) not modifying target geometry, (2) using materials and fuels that are acceptable to reactor operators, and (3) developing targets that require simple, "low-tech" fabrication methods. In the case of processing it means focusing on target dissolution and the first molybdenum recovery/purification step. The primary differences between LEU and HEU targets shown in Table I (greater amounts of uranium and $^{239}\text{Np}/\text{Pu}$ in the LEU target) should only affect dissolution and primary molybdenum recovery. If dissolution of the LEU target is properly designed, the molybdenum fraction should be chemically identical following these two steps.

Waste treatment and disposal have often been neglected in the past but, due to increasing regulations and costs associated with radioactive waste disposal, are becoming an extremely important concern to producers. Modifications to processing required by conversion to LEU could actually be to economic advantage if waste treatment is given proper consideration.

4. LEU TARGET DEVELOPMENT

Target R&D activities are almost completely centered on the uranium-foil target. This target is being developed for both acid- and base-side processing. Fabrication of dispersion-fuel plates for U_3Si_2 and UO_2 has no show-stopping technical issues that need to be addressed. Both are acceptable reactor fuels and are fabricated commercially. Achieving as high as possible uranium loadings is an issue for molybdenum production targets and for reactor fuels. The following sections discuss progress in developing the uranium-foil target and electrodeposition of fission barriers for this target.

4.1. Uranium-foil target

Until 1989, Cintichem, in Tuxedo, NY, produced about one-half of the world's ^{99}Mo supply using targets consisting of high-enriched UO_2 coated on the inside of stainless steel tubes. The same targets are used, under license, in Indonesia today. The standard "Cintichem" target contains up to 25 g of UO_2 , or up to 20 g of ^{235}U . Because of concerns that the UO_2 coating thickness could not be increased nearly enough to produce an LEU target with an equivalent ^{235}U content, we had begun to develop electrodeposited metallic uranium targets [15]. However, since we were seeking a target that could be fabricated using "low-tech" methods, we have developed a concept using uranium-metal foils [16, 17].

We have concentrated on the target design illustrated in Fig. 1, where a thin (~130- μm thick) uranium metal foil is sandwiched between slightly tapered inner and outer tubes. The taper is currently 5/1000. In our preferred design, the inner tube is made of a material with a larger thermal expansion coefficient than that of the outer tube material. This differential thermal expansion should assist in maintaining good thermal contact between the foil and the tubes. We have chosen zirconium for the outer tube and, as discussed below, have tested aluminum, magnesium, and stainless steel for the inner-tube material in the differential-thermal-expansion design. Zirconium is also being tested in a design without differential thermal expansion based on differing materials. Aluminum, magnesium, or zirconium is preferred owing to their low neutron absorption cross sections.

Assembly of the target is accomplished by rolling the uranium foil around a mandrel, placing the foil over the inner tube, and inserting the inner tube and foil into the outer tube. A press is used to seat the foil firmly between the tapered inner and outer tubes. Then, the end fittings are welded on, and the assembly is filled with helium gas and sealed. The taper and the greater shrinkage of the inner tube upon cooling after irradiation facilitate disassembly, which is

accomplished by cutting off the two ends with a mechanized tubing cutter and using a press to push the inner tube, and the uranium foil, out of the outer tube.

A basic design criterion is to be able to separate the irradiated foil from the tubes, so that only the foil need be dissolved to recover the molybdenum, thereby minimizing waste volume. In our first test, targets with thin oxide layers were produced on the inner and outer tubes to serve as diffusion barriers to inhibit diffusion bonding of the uranium to the tubes. As will be discussed later, we have added fission-fragment-absorbing barriers between the uranium foil and the target tubes. Several targets of this type have been irradiated in the Indonesian RSG-GAS reactor operating at 22.5 MW. Postirradiation examinations have been performed in the adjacent BATAN hot cell facility, under a cooperative research agreement between BATAN and Argonne National Laboratory.

One such target, with a zirconium outer tube and an aluminum inner tube, was irradiated and examined during the summer of 1995. In spite of a thin aluminum-oxide barrier between the uranium foil and the inner tube, which had proven to be sufficient to prevent reaction during thermal testing at elevated temperature, the uranium reacted with the aluminum during irradiation and could not be removed from the inner tube. Metallography showed no apparent interaction of the uranium with the zirconium outer tube, on which a thin zirconium oxide barrier had been placed. Therefore, zirconium appeared to be a suitable target-tube material.

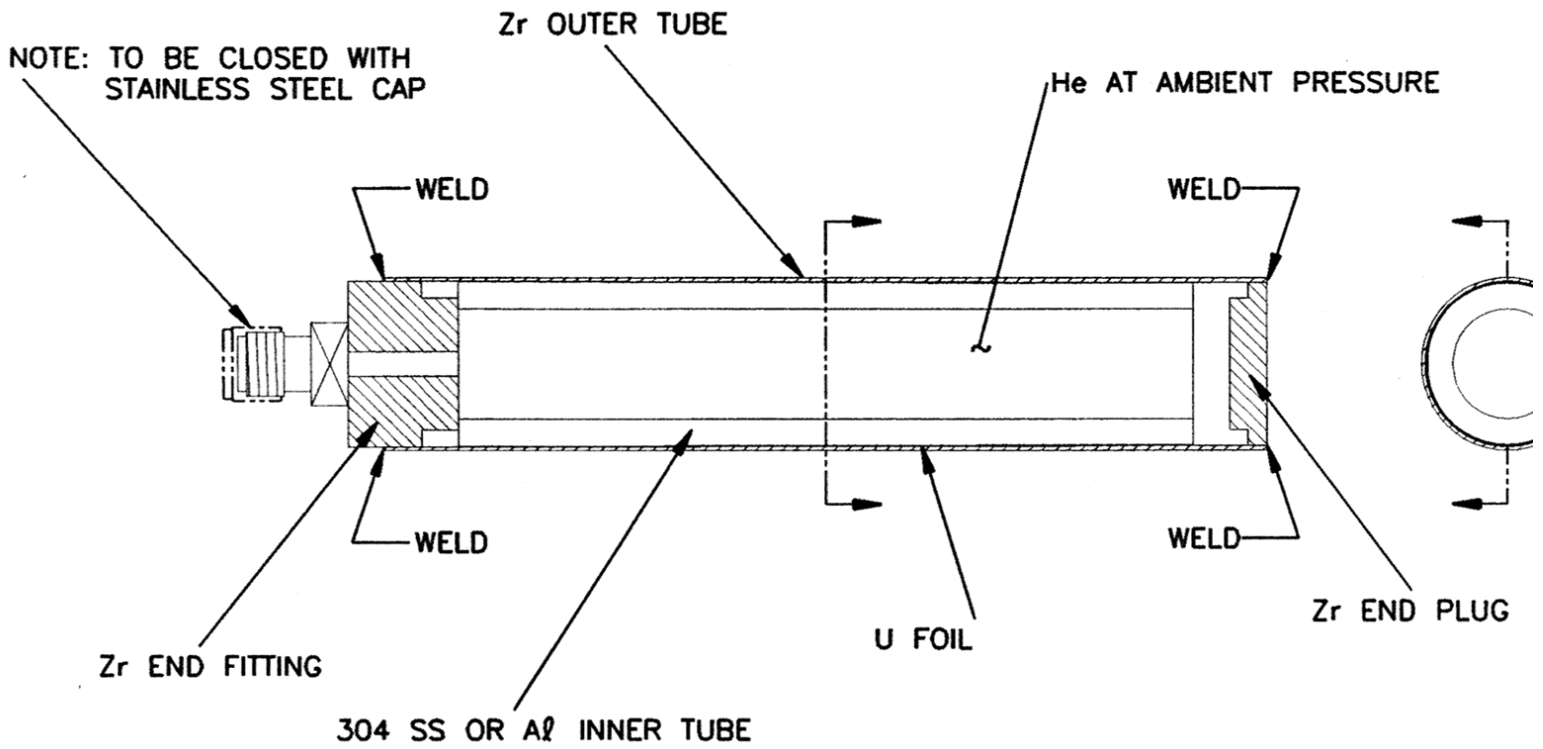


FIG. 1. Uranium metal-foil target.

Three additional test targets were irradiated between November 1995 and March 1996 to explore different materials for the inner tube of the target. In one, we coated the aluminum with zirconium by flame spraying, thereby retaining all the features of the first design while adding a zirconium layer between the uranium and aluminum to prevent interaction. In a second target the inner tube was made from magnesium, which also has a larger expansion coefficient than zirconium but forms no compounds with uranium. The third target had a zirconium inner tube. Obviously, the thermal expansion difference was not present in this combination; however, we believe that adequate thermal contact was assured by the assembly process with the tapered tubes. This test was added to verify the apparent nonbonding of uranium foil and zirconium.

Postirradiation examinations performed during April and May of 1996 showed that the uranium foil was bonded to the inner tube of each of these targets. The tentative explanation is that the high fission rate in the uranium and correspondingly high recoil atom flux at the uranium-target tube interface lead to an efficient atomic intermixing at the interface. It appears that bonding by this mechanism will occur with any material. A potential solution to this bonding is inclusion of a thin (10-15 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 electroplated onto uranium or made into foils, (2) low thermal-neutron cross sections for radioisotope formation, 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 and zinc for dissolution in base.

Based on the experience gained during the first two series of tests, a third set of irradiations was performed during August 1996. To achieve a smaller grain size and, hence, a more-uniform dimensional change in the uranium during irradiation, we added small amounts of iron and aluminum to produce an "adjusted" uranium alloy containing ~450 ppm iron and ~1000 ppm aluminum. The uranium was reduced to foils by a combination of hot and cold rolling. Following rolling, a β quench (690°C for 5 min followed by air cooling) was completed to eliminate texture in the foils. We irradiated four targets to test two basic concepts:

1. The inner tube material of one target was changed to austenitic stainless steel. This material was chosen because it will not dissolve in the acid used to dissolve the uranium and because its use will retain the thermal expansion difference since 300 series stainless steel has 2 to 2.5 times the expansion coefficient of zirconium. We expected the uranium foil to bond to the stainless steel inner tube and to be pulled loose from the zirconium outer tube during cooling and disassembly (as was the case for the targets with aluminum and magnesium inner tubes), so that the uranium could be dissolved off the inner tube by placing the entire inner tube into the dissolver. However, the inner tube and foil could not be extracted from the outer tube, indicating some amount of bonding of the uranium foil to the zirconium outer tube.
2. Thin recoil-absorbing barrier foils of ~10- μm thickness were placed between the uranium and one or both target tubes. We expected these barrier foils to bond to the uranium by recoil mixing but not to the target tubes, since the fission fragments will not penetrate the barrier. Since the barrier foils must be dissolved with the uranium foil, only certain materials such as nickel, copper, iron, and zinc are acceptable. We tested both nickel and copper. In one target an aluminum tube with unoxidized surfaces was used, and nickel foils were placed on both sides of the uranium foil. The inner tube with foils was easily extracted, but the foils could not be removed, indicating bonding, presumably by diffusion, of the nickel to the aluminum. We think that introduction of an aluminum oxide layer will prevent such bonding. The other two targets used a stainless steel inner tube. In one a nickel barrier foil was introduced only between the uranium and the zirconium outer tube. The inner tube with foils was easily extracted, and, as expected, the uranium bonded to the inner tube. The uranium and nickel could be dissolved as described above. The final target contained copper barrier foils placed on both sides of the uranium foil. The inner tube with foils was easily extracted, and the foil sandwich was easily removed from the inner tube.

The latter two targets demonstrated the viability of the fission-fragment-barrier concept. Another series of tests was performed in Indonesia during April and May 1997 to test additional barrier-material/target-tube-material combinations. In all of these tests, an oxide diffusion barrier was placed on the target tube surfaces. One of the targets contained copper barrier foils and a stainless steel inner tube, a combination that was successful during the previous test. The remaining targets contained other combinations of copper, nickel, and zinc barrier foils and stainless steel, aluminum, and zirconium inner tubes. None of the targets containing copper or nickel barriers and stainless steel or aluminum inner tubes was successful during this irradiation; the foils were stuck to the stainless steel tubes and the targets with aluminum inner tubes could not be disassembled. The outer surfaces of the copper and nickel barrier foils were speckled, whereas the foil surface in the previously successful target was shiny.

However, the target containing zinc barrier foils and a stainless steel inner tube did work; the uranium/barrier foil combination was easily removed from the inner tube. Its surface was shiny, as expected. We now theorize that the uranium foils were rougher than in the previous experiment and that the protruding uranium grains penetrated into the copper and nickel barrier foils to such a depth that the barrier thickness was reduced below the $\sim 7\text{-}\mu\text{m}$ fission fragment range in a number of spots. The zinc barrier foil, which was $5\text{ }\mu\text{m}$ thicker than the copper and nickel foils, apparently was thick enough to absorb the recoils. We must await results of metallographic examinations to be performed in Indonesia to confirm this explanation.

As before, the viability of the fission-fragment-barrier concept has been confirmed, but a number of design details must be addressed to produce a reliable target. We will be examining ways to minimize roughness of the uranium foils. We have also begun to optimize the target. We will be studying (1) the use of aluminum or other low-neutron-absorbing materials for the inner tube in order to decrease the reactivity penalty of the target, (2) the minimization of the thicknesses of the target tubes in order to minimize waste and neutron absorption, and (3) the plating of barrier materials on the uranium foils rather than use of foils in order to minimize fabrication costs.

4.2. Electrodeposition of fission barriers

Electroplating fission barriers on the uranium foil should make target preparation simpler and more economical. Commercial sources for the baths and supplies are available (e.g., Starlite Technical Service, Inc., 1319 W. North Avenue, Chicago, IL 60622, USA), and literature was available for electrodepositing nickel on uranium metal. A survey of the literature on electroplating uranium located a modest number of papers on the electroplating of nickel on uranium for the purpose of preventing or reducing the surface corrosion of uranium [18-23]. Plating of other elements was not found, but the principles involved in plating nickel should be applicable to the other metals in which we are interested. These are, in addition to nickel, zinc, copper, and, possibly, iron. All the publications agree that the uranium surface must be rough (i.e., have small finger-like projections) for the nickel to adhere. The interface is not a metal bond because uranium oxidizes so readily, but the nickel is attached mechanically. This agrees with earlier experience of one of the authors, who electroplated coatings on uranium in the late 1940s.

We have used plating methods reported in the literature, modifying them as needed as we gain experience. The literature indicates that we must provide a roughened, clean surface. The general method for preparing the uranium surface for nickel plating is to (1) degrease the surface, (2) remove the uranium oxide coating, then (3) etch the surface in a metal chloride salt solution (sometimes containing hydrochloric acid) or a hydrochloric acid/sulfuric acid solution. Because the uranium foils we are attempting to electroplate are only $130\text{-}\mu\text{m}$ thick, surface preparation has been extremely challenging. We must balance surface roughness against dissolution of the foil. We have used an alkaline zincate bath for plating zinc, an alkaline copper phosphate bath for plating copper, and a nickel sulfamate plating bath for plating nickel. The specific procedure we use consists of:

- Degreasing with xylene
- Removing the xylene by rinsing in methanol
- Rinsing with water to remove any methanol
- Dissolving the oxide layer with 8 M HNO_3 (pickling)
- Rinsing with water
- Etching in concentrated ferric chloride solution at 40°C [other chlorides that have been used are those of Sn(II), Ni(II), and Li(I)]
- Rinsing with water
- Immersing in 8 M HNO_3 until a metallic surface is obtained
- Rinsing with water
- Electroplating

To minimize oxidation of the uranium surface, the foil is placed in the plating bath with the power supply already on. The success of the procedure was followed by measuring the foil thickness with calipers (0.0001 in.), by weighing the foil before and after treatment, and by performing a microscopic examination. Samples were taken after etching, after electroplating, and, sometimes, after the pickling. In both the pickling and etching steps, uranium is dissolved. Attempts were made to minimize these losses while preparing a surface that produces a continuous, well-bonded barrier metal after electroplating. Zinc plates ($12\text{-}\mu\text{m}$ thick) have been prepared with a current density of $\sim 0.12\text{ A/cm}^2$ at ~ 1 volt for 15 minutes.

Scanning electron micrographs of an early attempt at plating uranium with zinc barriers are shown in Figs. 2 through 4. These figures, which show cross sections of the plated foil, reveal a number of interesting features about the zinc plate and the etching and plating process. In these figures, the lightest band across the picture is the uranium foil. The zinc plate is seen as a darker color on either side of the uranium. The black portion is the

background--the epoxy matrix holding the foil. Figure 2 shows that the surface of the uranium is considerably deteriorated, containing great variations in thickness as well as some pockets that have been generated by etching. This situation was suspected because of the considerable mass loss from the foil in etching without a proportional loss in thickness. Figure 3 shows a section of foil in which the nodular character of the Zn plate is rather pronounced. Plating began at a number of active sites, which are surrounded by sites that are inactive. As seen, this condition produces a very uneven plate, with the thickness of the Zn plate varying from 0 to 18 μm , with the average being $\sim 8 \mu\text{m}$.

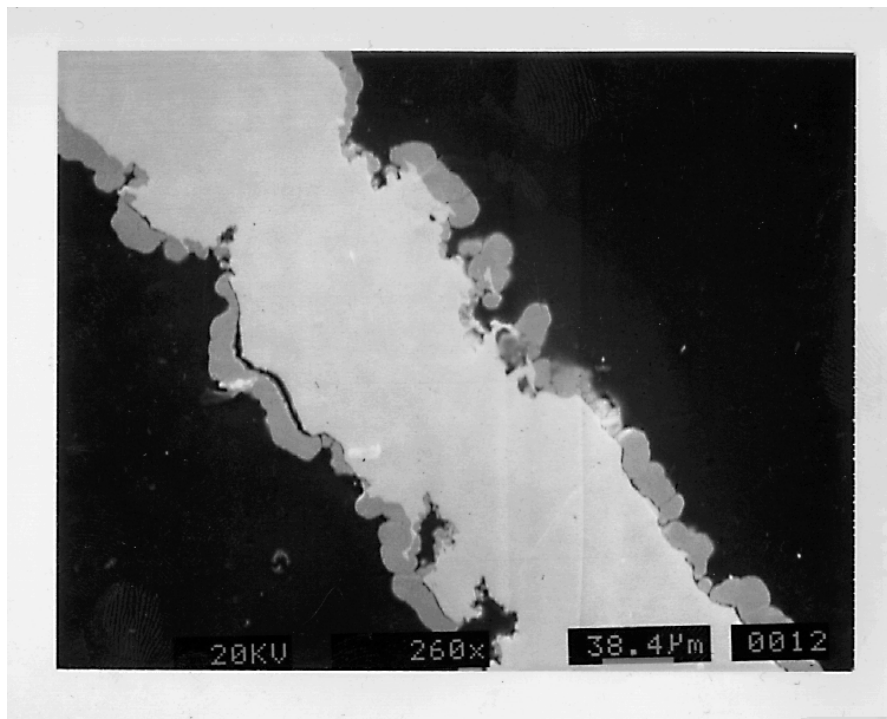


FIG. 2. SEM photograph showing wide variation in Zn plate.

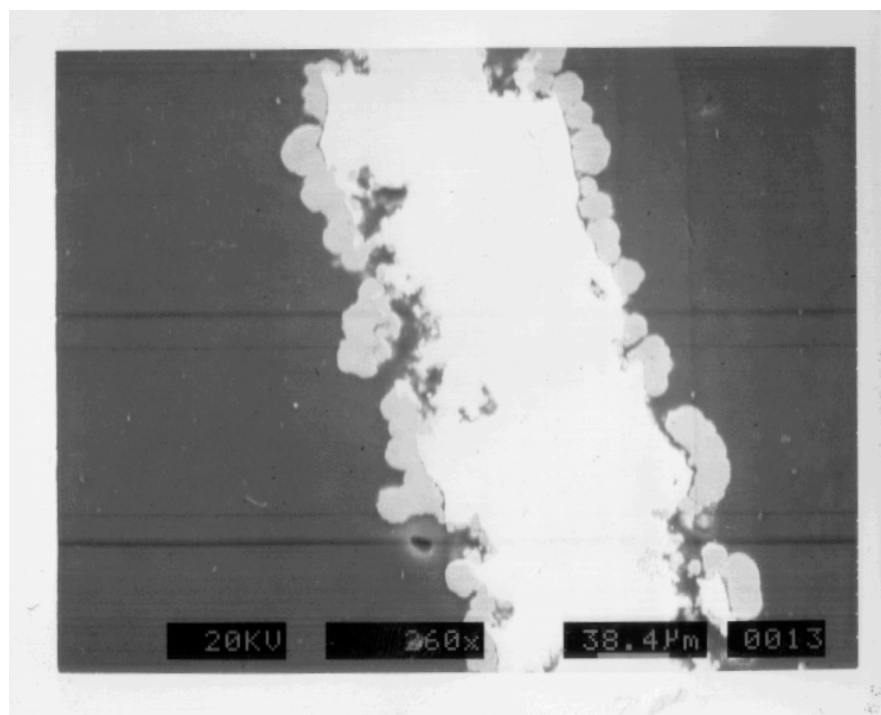


FIG. 3. SEM photograph showing nodular nature of Zn plate.

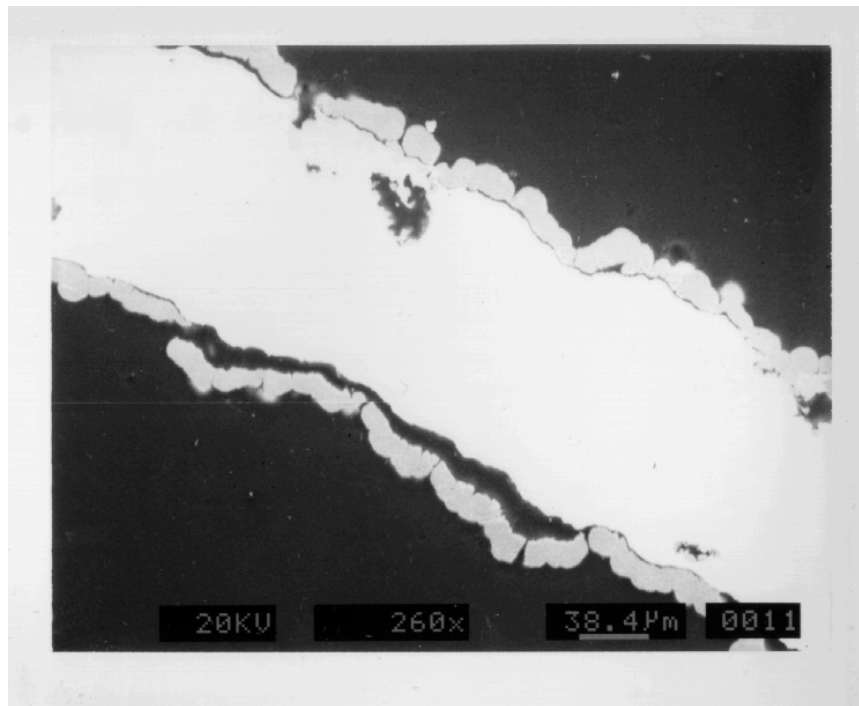


FIG. 4. SEM photograph showing separation of Zn plate from U foil.

Figure 4 shows a section where the separation of the Zn plate from the U foil is especially pronounced. This separation had been visually seen as flaking of the plate when the foil was bent. This flaking occurred on the side of the foil where the Zn plate was in compression, and that is also the case in the photograph. Flaking on the side of the foil on the outside of the bend, where the Zn was in tension, was not visually observed and was much less pronounced than on the compression side, although there are some indications of it on the tension side in the figure. Adhesion of the plate is a factor, but some separation of the plate from the foil will be acceptable provided the plate does not develop gaps or fall off the foil during bending. Figure 5 is an optical micrograph of another early plate. The plating was slightly more uniform (average of 12 μm), but surface etching dissolved far too much of the uranium. Figure 6 shows an optical micrograph of a cross section of the as-received uranium foil, 130 μm thick.

Surface preparation is a compromise between optimal conditions for making a uniform and well-bonded plate and etching away a high fraction of the LEU surface. The best conditions found to date remove about 25 μm of the 130- μm uranium foil. We will deal with the loss in uranium by preparing 150- μm foils. Figures 7a and 7b show zinc-plated uranium foils that meet the criteria of ≈ 25 μm uranium loss and uniform, well-bonded zinc electrodeposits. We have yet to produce copper-plated uranium foils that look this good. We are planning to electroplate Zn, Cu, and, time permitting, Ni barriers on LEU foils, which will be irradiated in the Indonesian reactor in September 1997.

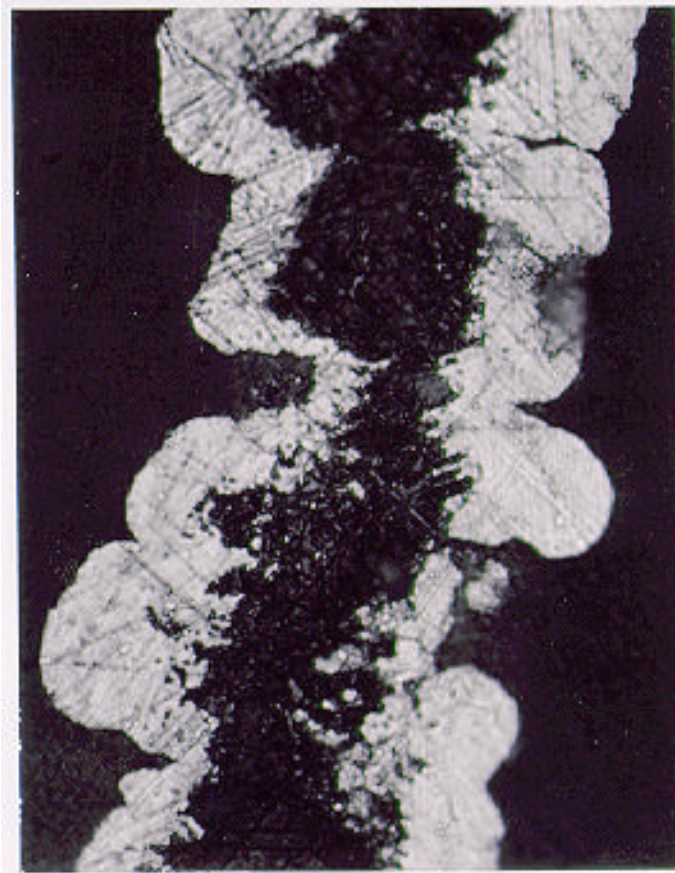


FIG. 5. Early Zn-plated uranium foil showing considerable loss of uranium during etching.

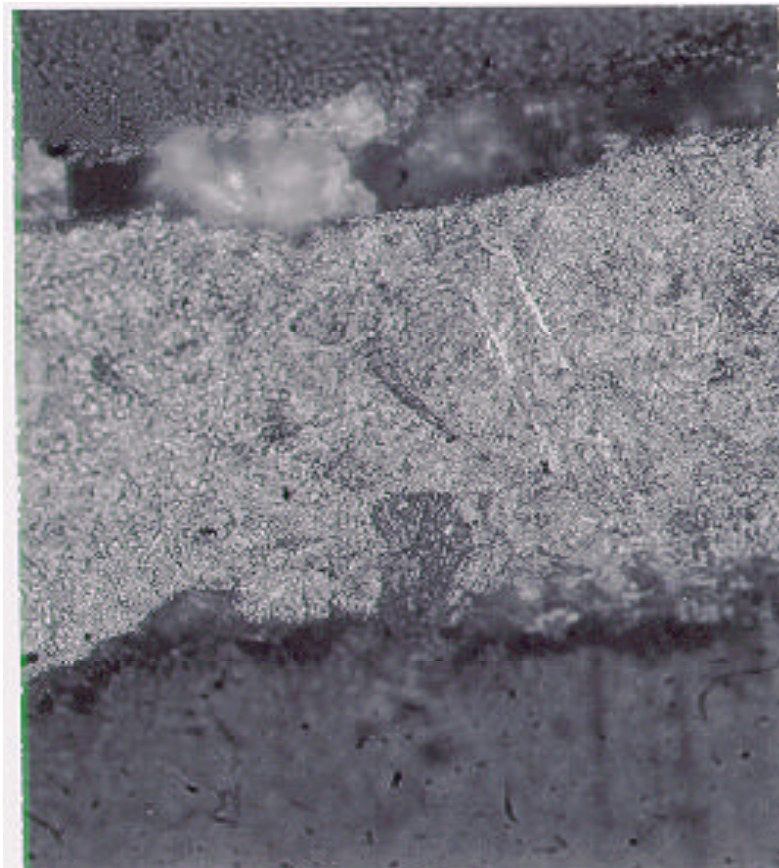
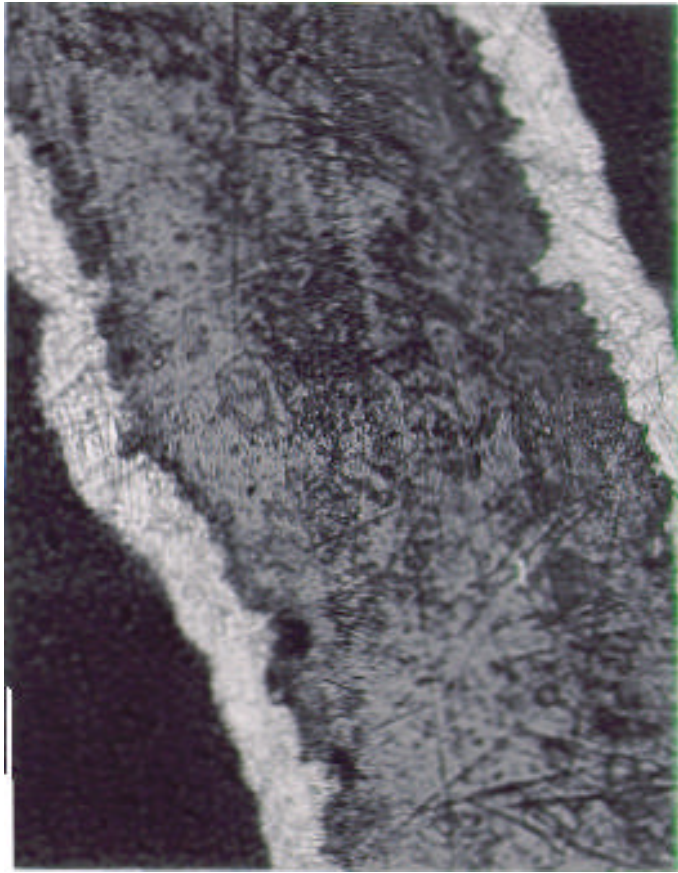
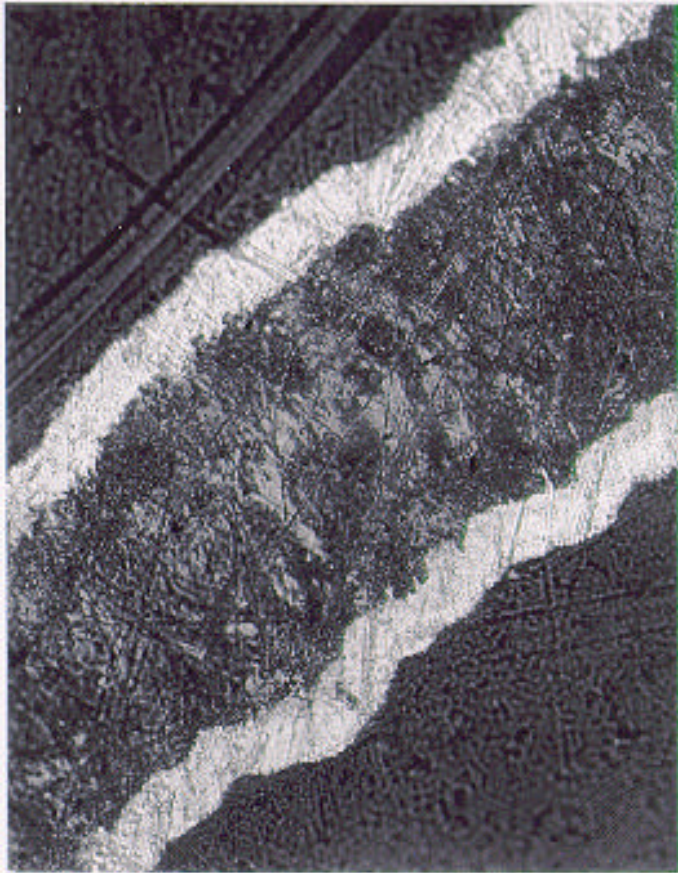


FIG. 6. Optical-microscope photograph of as-delivered uranium foil.



a



b

FIG.7. Two examples of acceptable zinc-plated uranium foils.

5. LEU PROCESS DEVELOPMENT

Throughout the period of our involvement to convert ^{99}Mo production from HEU to LEU, R&D activities have been divided between base- and acid-side processing. Meeting our objective of converting all production of fission-product ^{99}Mo from HEU to LEU necessitates such an approach. This section will be first broken up into base and acid dissolution processes. The next division for each subsection will be made by the two important processing steps for conversion--(1) irradiated target dissolution and (2) the initial molybdenum recovery/purification step. In the case of base-side processing, one further division will be made to discuss the three potential LEU targets- (1) $\text{U}_3\text{Si}_2/\text{Al}$ dispersion fuel, (2) uranium foil, and (3) UO_2/Al dispersion fuel.

5.1. Acid-side processing

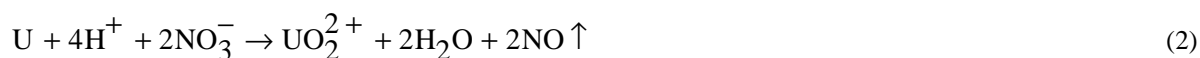
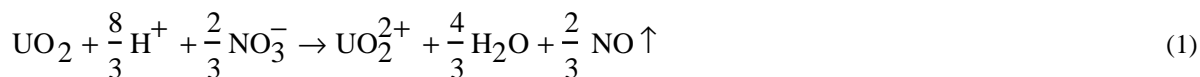
Most of the world's supply of ^{99}Mo is produced in the NRU reactor at the AECL's Chalk River Laboratories in Chalk River, Ontario, Canada. It is recovered from irradiated aluminum-clad extruded pins of U/Al alloy by first performing a partial mechanical-decladding and then dissolving the target in nitric acid. The ^{99}Mo is separated from the uranium and other fission products by using an alumina column. Although AECL's conversion from HEU to LEU is vital to meeting the goals of the RERTR program, we have not yet developed a formal program with the AECL or Nordion to assist them in conversion. Our hope is that as we demonstrate the technical and economic feasibility of conversion, such a cooperation will develop. Our efforts directed to acid-side processing have, therefore, been entirely focused on the Cintichem process, which is currently being used by the Sandia National Laboratories and the Indonesian Radioisotope Production Centre located at the PUSPIPTTEK Laboratory in Serpong, Indonesia. When the RERTR program first became involved with converting ^{99}Mo production from HEU to LEU, Union Carbide was producing ^{99}Mo at their U.S. reactor in Tuxedo, NY. Cintichem, which took over these operations, produced about half the world's supply of ^{99}Mo before it shut down operations in 1989.

A formal agreement has been in place between ANL and BATAN for about three years to convert the Cintichem process, which BATAN licensed in the late 1980s. Argonne and SNL have cooperated informally for about a year on LEU conversion, and a formal agreement will be signed in the third quarter of 1997. Under this agreement, irradiation and processing of LEU-oxide targets will be added to their test matrix for product acceptance. The LEU-oxide targets are being fabricated at the Los Alamos National Laboratory (LANL), the current fabricator of HEU targets for SNL. Because the United States DOE now owns the licensing rights to the Cintichem process, the RERTR program expects that the LEU-modified Cintichem process can be made available to established and new ^{99}Mo producers under reasonable terms and conditions.

5.1.1. Target dissolution

The Cintichem HEU target is a closed cylinder with an electrodeposited layer of UO_2 on its inner wall. Following irradiation, the target is opened, a cocktail of nitric and sulfuric acid is added, and the target is heated to dissolve uranium and the fission products. Following a degassing step, which removes most of the iodine and noble fission gases, the solution is removed from the target cylinder for further processing. For the LEU-foil target, a slightly different procedure will be followed. After the irradiated uranium foil is removed from its target, it will be placed in a multi-use dissolver and heated. Following dissolution, the resulting solution will be removed from the dissolver and processed by a similar procedure as used for the HEU target.

One of our conversion goals is to make the composition of the spent dissolver solution from the LEU target act as much as possible like that from the current HEU target. Because a comparable LEU target will contain 5-6 times more uranium than an HEU target, the spent LEU dissolver solution must have a higher volume, a higher uranium concentration, or both. Also, because the dissolution of uranium metal is a six-electron oxidation compared to only a two-electron oxidation for UO_2 , more of the oxidant (e.g., nitric acid) needs to be present initially. The reactions for oxidation of UO_2 and U metal are shown below:



Hydrogen ion can be supplied by sulfuric and/or nitric acid. As seen in Eqs. 1 and 2, the major reduction product of nitric acid is NO. Because (1) up to six times more uranium will be dissolved and (2) uranium metal dissolution will generate three times the amount of NO than for UO_2 dissolution, gas pressures produced and solution volumes used during dissolution were important design criteria for the LEU dissolver.

Uranium-foil dissolution was initially studied as chemical R&D in 1994 [24]. The chemical studies moved into engineering studies in the following years [25, 26]. In 1994, we verified that uranium metal would dissolve in nitric/sulfuric acid mixtures at rates comparable to UO_2 . We also measured the heat of dissolution in this system to be 1.10×10^3 kJ/mol-U. In 1995, we measured activation energies for uranium-foil dissolution by the mixed nitric/sulfuric acid system and found it to be 44 kJ/mol-U. Rate-vs.-temperature data are shown in Fig. 8. We also verified (1) that the stoichiometry of Eq. 1 is valid, (2) that no H_2 evolves during dissolution, and (3) that the rate is dependent on hydrogen-ion concentration but nearly independent of whether the hydrogen ion is supplied by sulfuric or nitric acid.

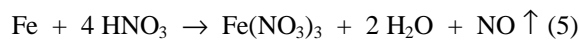
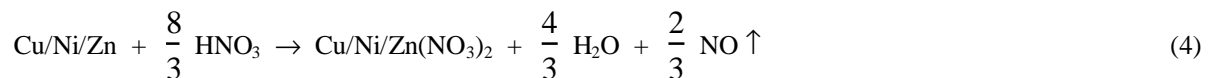
To calculate the rate of dissolution for uranium foil as a function of temperature and the concentrations of HNO_3 and H_2SO_4 , all data on dissolution rates were extrapolated to 92°C based on the activation energy of the reaction. Then, the rate of uranium dissolution at 92°C (R_{U92}) was obtained by a least-squares fit of the data using Eq. 3:

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

where the a values are coefficients that were adjusted by using a least-squares fit, x is the molar concentration of HNO_3 , and y is the molar concentration of H_2SO_4 . 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 in Eq. 3 yielded the contour plot given in Fig. 9, which shows how the uranium dissolution rates vary in the expected range of operation. A typical reaction path is indicated by the dashed arrow going from point A to point B in Fig. 9. The initial solution would be 3 M HNO_3 and 2M H_2SO_4 ; after reacting to generate a 1M UO_2^{2+} solution, the spent dissolver solution would contain 1M HNO_3 and 1M H_2SO_4 . During dissolution, the initial rate that uranium dissolves will be much higher than the final rate. This contour plot also shows that a much simpler correlation can be made to fit the data. The rate at 2 M H_2SO_4 is approximately equal to that at 4M HNO_3 ; the rate at 1M H_2SO_4 is approximately equal to that at 2 M HNO_3 ; etc. The dissolution rate can be simply correlated to the total hydrogen ion concentration in the dissolver solution. This relationship does break down, however, if not enough nitrate ion is present to oxidize the uranium. This revelation led us to consider using a dissolver solution containing nitric acid alone to eliminate problems that sulfate ion causes in waste treatment and disposal.¹

The next step was to design a closed dissolver that could be used in the PUSPIPTEK hot cells to dissolve the irradiated foil. The design we chose had the same dimensions as the Cintichem target, thus allowing it to be used in the device now used to heat and rotate the HEU target/dissolver. A series of experiments was run at ANL and PUSPIPTEK where various sized pieces of 130- μm depleted uranium (DU) foil were dissolved in 80 mL of 3M HNO_3 and 2M H_2SO_4 with a steady-state temperature of $102 \pm 2^\circ\text{C}$ (Fig. 10). The initial spike in the pressure is caused by the high heat of dissolution (1.10×10^3 kJ/mol-U). The heat released during uranium dissolution causes rapid heatup of the solution and even faster dissolution of the uranium foil. Testing showed that dissolution with HNO_3 alone provided almost identical dissolution times, pressure spikes, and final pressures for the same total hydrogen-ion concentrations as the mixed-acid systems. Figure 11 is a correlation of mass of uranium dissolved vs. final pressure in the dissolver. Some of the points are for UO_2 dissolution; in these cases, the uranium mass was divided by three to account for 1/3 less NO being formed per mole. The model fits the data quite well at 103°C . However, at 25°C , the model pressure is above the observed pressures. This deviation is attributed to the solubility of NO in the dissolver solution. This solubility increases as temperature decreases.

The need for barrier materials further complicates dissolution. However, the perturbation is minor. The overall dissolution reactions for metal barriers of Cu, Ni, Zn, and Fe using nitric acid alone are shown in Eqs. 4 and 5:



Dissolution rates for Cu, Ni, and Fe were measured over a variety of conditions in a covered, but unsealed, centrifuge tube in a constant-temperature bath. The results indicate that all three metals dissolve faster than

¹ Studies of the primary ^{99}Mo recovery step (discussed in section 5.1.2.) also showed no penalty for eliminating H_2SO_4 .

uranium: Ni is five times faster, Cu is 190 times faster, and Fe is 560 times faster. Zinc,² which was studied later as a potential barrier for the base-side processes, dissolves very quickly in nitric acid. Equations 4 and 5 and the ideal gas law were used in calculating the dissolution pressure for a two-sided barrier on a typical 18-g U-foil target³ with barrier dimensions of 76 x 102 x 0.010 mm, a dissolver temperature of 103°C, and a gas volume of 282 mL. The results indicate an increase in the final dissolver pressure of about 30 psig for the barrier foils, over that for U alone. Thus, the dissolver pressure will be increased about 10% by the presence of a two-sided barrier. This pressure increase is within the design limits of the stainless-steel dissolver, so that any of these four barrier materials (Zn, Cu, Ni, Fe) can be used without affecting the operation of the U-foil dissolver. In two tests, Ni foil was used in the closed (sealed) stainless-steel dissolver. The results of these tests were very similar. The pressure-time plots (not shown here) indicated that the Ni dissolved easily, as expected. The final gas pressure for this piece of Ni foil was expected to be 159 psia. Instead, a much lower pressure, about 40 psia, was actually realized. The difference in these two pressures may be due to NO gas solubility in the dissolver solution.

Researchers at BATAN attempted to dissolve the irradiated Zn-barrier LEU foil that was successfully removed from the target. They used conditions that should have completely dissolved the foil in 30 min. Following this procedure, the gas pressure generated during dissolution and the radioactivity levels in the spent dissolver solution both were far lower than expected. This may be due to (1) the formation of a U-Zn compound at the Zn-foil/U-foil interface during irradiation and (2) this compound dissolving at a lower rate than either uranium or zinc. To test this theory, we heated a zinc-plated DU foil at 375°C overnight. This formed a U/ Zn intermetallic that did dissolve at a rate substantially lower than either metal alone. We are undertaking a set of experiments to quantitate the rate of dissolution for this compound. Although we have been developing the Zn-barrier foils for basic dissolution, using it for acid-side processing is certainly possible if the dissolution rate can be easily handled by increasing dissolver temperature.

Further details on this topic can be found in references 24-26. The dissolver has been set up and tested in the PUSPIPTEK hot cell and is ready for the process demonstration of a fully irradiated foil scheduled for September 1997.

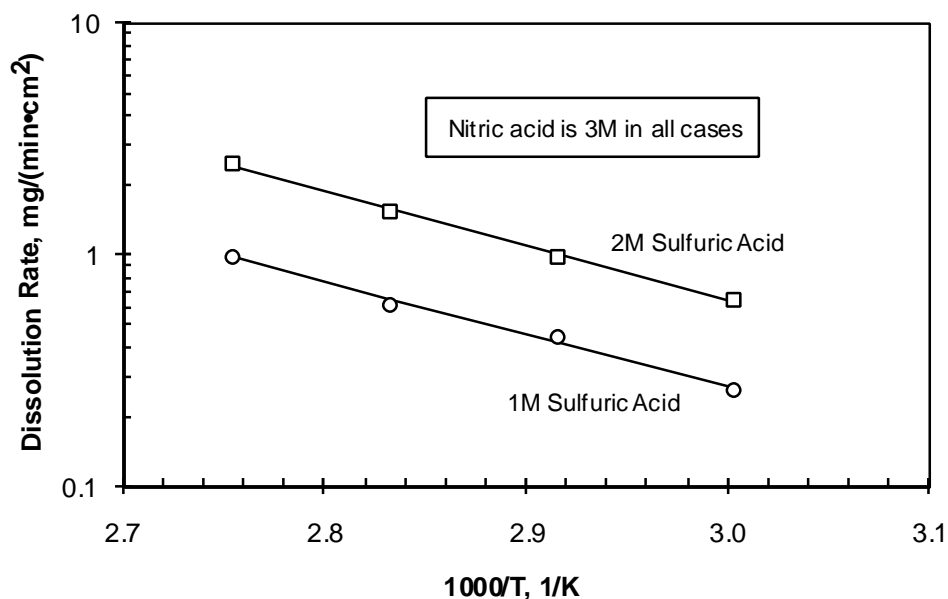


FIG. 8. Effect of temperature on the dissolution rate of uranium foil at two solution compositions.

² Complications of using Zn barriers due to its low melting point and reaction with uranium near its melting point will be discussed in section 5.2.1.3.

³ An 18-g LEU target contains approximately as much ²³⁵U as a typical HEU target being used by BATAN.

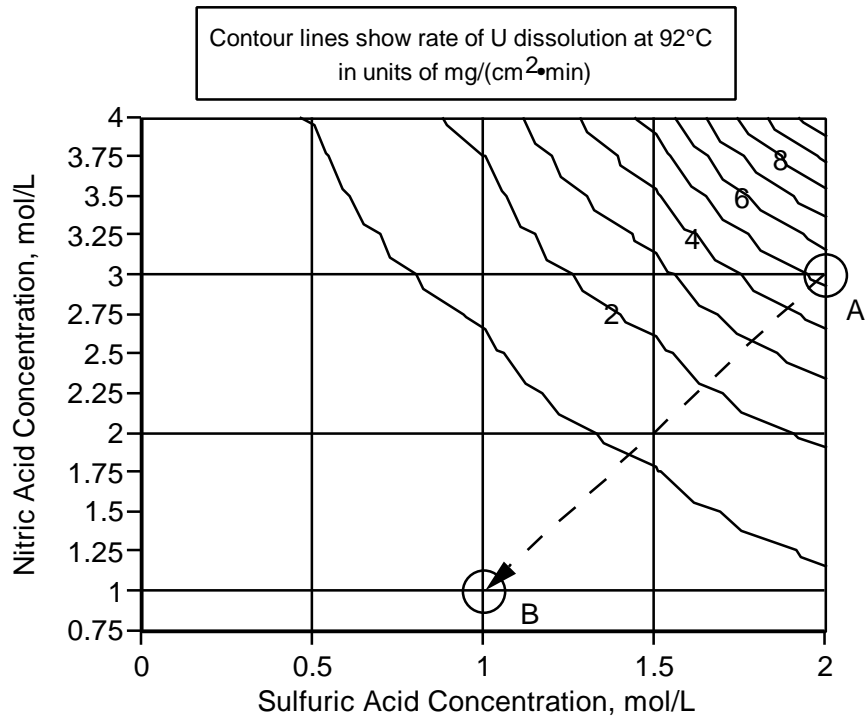


FIG. 9. Modeled effect of the concentration of nitric acid and sulfuric acid on the dissolution rate of uranium foil.

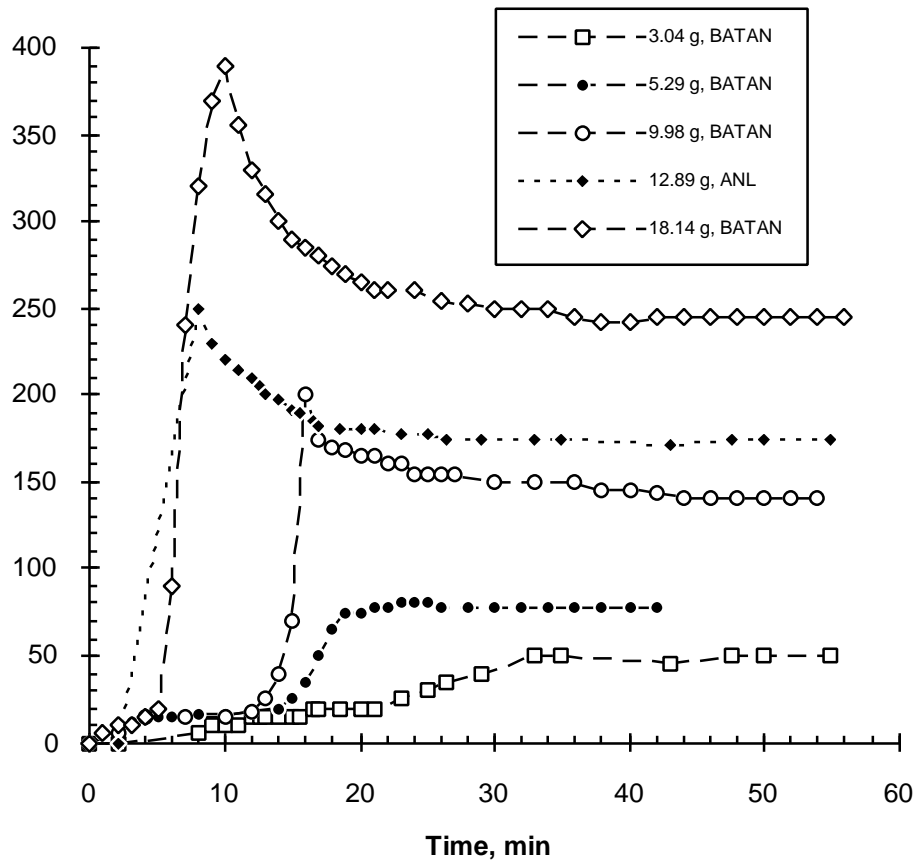


FIG. 10. Variation of pressure with time during dissolution of uranium foil in the stainless-steel dissolver.

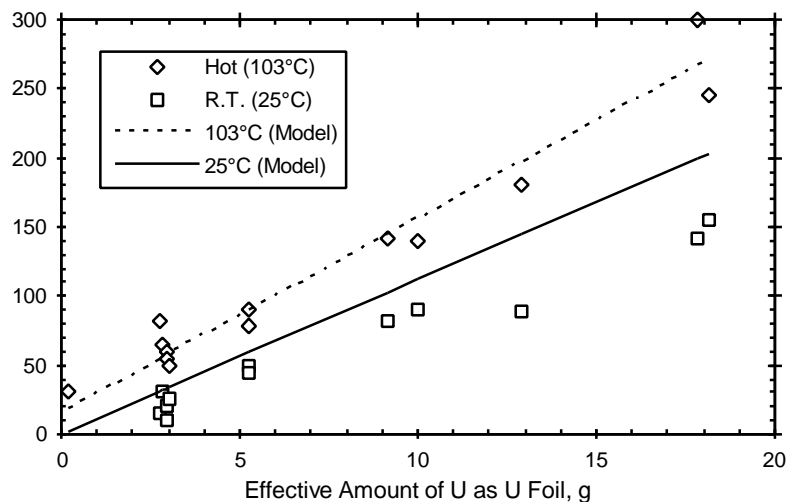


FIG. 11. Effect of uranium mass on final dissolver pressure at room temperature (R.T.) and 103°C.

5.1.2. Target processing

The major concern in defining the spent dissolver solution needed for the LEU-modified Cintichem process is to make it compatible with the primary molybdenum recovery and purification step. If this step is successful, differences between HEU and LEU targets are of no consequence to the rest of the process. The initial step in the Cintichem process is the precipitation of Mo(VI) by α -benzoin oxime (? -BO--see Fig. 12). This step is derived from a standard analytical method for molybdenum [27-29]. The standard procedure requires molybdenum in 1 M sulfuric acid. Molybdenum precipitation is quantitative, and the precipitate contains very low levels of impurities. Most of our efforts have been focused on this step and on how the yield and purity of ^{99}Mo are affected by the variations in concentrations of uranium, nitric acid, and sulfuric acid.

Early R&D [30, 31] was based on our knowledge of the Cintichem process found in patents [13, 14]. Later R&D [32-35] was based on a firm knowledge of the process due to our cooperative project with BATAN and SNL. Details of the work presented below can be found in these publications. The following summarizes the most important aspects of this work.

A series of experiments was performed to measure the effect of acid (Table III) on the recovery of molybdenum. The conclusion to these studies is that if the hydrogen-ion concentration of the spent dissolver solution is held between 0.5 and 5 M (whether from HNO_3 or H_2SO_4), molybdenum recovery will be essentially quantitative. Another set of experiments (Table IV) showed that uranium concentration has no perceptible effect on molybdenum yield. We also determined a range of concentrations for ? ? BO and molybdate that yielded quantitative recovery. The upshot of this work is that there is wide latitude in the composition of the spent dissolver solution. We, therefore, chose to (1) use only nitric acid and (2) keep the volume of the dissolver solution low and its uranium concentration high. Although the spent dissolver solution from LEU targets will contain 5-6 times more uranium, the uranium will be at 2-3 times higher concentrations than for the HEU target. Therefore, the LEU feed to the ? -BO precipitation will be about twice that for the HEU target.

Although the ? -BO precipitation has been our primary concern, we have looked at the entire process. A rather complete description of the process can be found in a document released by SNL [36]. Following precipitation and washing, the ? -BO/Mo precipitate is destroyed with alkaline peroxide, and the molybdenum is dissolved in base (as molybdate). The molybdenum solution is further purified by passing it through a column of silver-coated charcoal; performing a silver-iodide precipitation; passing it through a second column containing silver-coated charcoal, hydrated zirconium oxide, and activated charcoal; and finally passing it through a 0.2 μm filter.

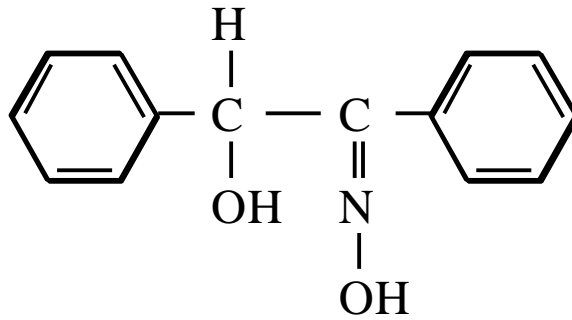


FIG. 12. Chemical form of alpha benzoin oxime.

TABLE III. MOLYBDENUM RECOVERY VS. SOLUTION COMPOSITION

[HNO ₃], <u>M</u>	% Mo Recovery	[H ₂ SO ₄], <u>M</u>	% Mo Recovery
0.1	90	0.1	100
0.5	100	0.5	100
1.0	100	1.0	98
2.0	100	2.0	95
4.0	100	4.0	93
6.0	88	6.0	98
8.0	-	8.0	8.7

TABLE IV. MOLYBDENUM RECOVERY VS. URANIUM CONCENTRATION

[UO ₂ (NO ₃) ₂], <u>M</u>	[H ₂ SO ₄], <u>M</u>	% Mo Recovery	
		Precipitate ^a	Filtrate ^b
0.5	1.0	100 ± 2	99.5 ± 0.1
1.0	1.0	100 ± 2	99.3 ± 0.1
1.5	1.0	100 ± 2	99.1 ± 0.1
2.0	1.0	98 ± 2	98.4 ± 0.1
0.5	2.0	-	99.1 ± 0.1
1.0	2.0	-	99.3 ± 0.1
1.5	2.0	-	99.0 ± 0.1

^a Based on neutron activation analysis (NAA) of molybdenum in the solid.

^b Based on NAA of molybdenum in the filtered solution.

The allowed levels for radiochemical impurity in ⁹⁹Mo product are very low, ranging from 10⁻¹ to 10⁻⁷ μCi/mCi-⁹⁹Mo. Therefore, each purification step must work effectively. The gamma-emitting isotopes that are analyzed in the ⁹⁹Mo product are tabulated in Table V. Using the ORIGEN2 computer code, we calculated the activities of these radioisotopes in an 18-g LEU target at 24 h after discharge from the Indonesian reactor (RGS-GAS), following a 120-h irradiation at full power (second column of Table V). Columns 3 through 5 contain decontamination factors measured in our tracer experiments for each processing step, the ⁹⁹Mo-BO precipitation and two polishing steps (purifications 1 and 2). The predicted impurity levels in units of μCi/mCi-⁹⁹Mo in the irradiated LEU target are listed in the last column. The calculations show that, except for ¹⁰³Ru, the desired radioisotopic decontamination levels can be met easily. Because ¹⁰³Ru contamination is not a concern in the current Cintichem product from HEU targets and because substitution of LEU will not affect the fission yield, this ¹⁰³Ru result may indicate a limitation of our tracer experiments more than a problem with LEU substitution. Experiments have also been performed to follow the behavior of uranium and plutonium in the individual Cintichem processing steps. Decontamination factors for both should be more than adequate for meeting alpha impurity levels in the ⁹⁹Mo product.

TABLE V. CALCULATED IMPURITY LEVELS OF A FULLY IRRADIATED LEU TARGET AND THE ⁹⁹Mo PRODUCT^a

Nuclide	Calculated Target Activity,	Measured Decontamination Factors ^b			Calculated Product Impurity Level,
	Ci	Precipitation	Purification 1	Purification 2	μCi/mCi- ⁹⁹ Mo
Ba-140	292	>516	>162	>165	<3.6E-05
Ce-141	121	>1116	328	419	<1.3E-06
Ce-143	685	>3354	313	641	<1.7E-06
I-131	186	51	28	41	5.3E-03
I-133	628	91	35	51	6.3E-03
I-135	104	121	38	43	8.8E-04
La-140	224	>2409	>104	>149	<1.0E-05
Mo-99	697	1.04	1.05	1.08	—
Nb-95	4.7	4	>13	>9.5	<1.7E-02
Nb-97	480	11	56	1410	9.2E-04
Nd-147	119	208	>62	>59	<2.6E-04
Np-239	1610	>1770	>247	>333	<1.9E-05
Pm-151	45	103	>16	>21	<2.1E-03
Rh-105	102	>276	>34	>46	<4.0E-04
Ru-103	54	113	1.3	3.7	1.7E-01
Sb-127	13.6	>41	1.3	>10	<4.3E-02
Sr-89	65.7	—	—	—	<2.3E-07 ^c
Sr-90	0.39	—	—	—	<1.4E-09 ^c
Sr-91	209	>3452	235	>586	<7.4E-07
Sr-92	2.65	>2101	>71	>63	<4.7E-07
Te/I-132	464	>5083	327	657	<7.1E-07
Y-93	258	>1294	511	822	<8.0E-07
Zr-95	70	13	27	>49	<6.8E-03
Zr-97	447	17	23	>41	<4.6E-02

^aBasis is an 18-g LEU target, 24 h after discharge from the RGS-GAS reactor, following a 120 -h irradiation at full power.

^bRatio of activity in the molybdenum solution before and after treatment.

^cPredicted from ⁹¹Sr behavior.

Development of LEU metal-foil targets has led to the use of thin (10-15 μm) metal barriers between the uranium foil and the target walls. Three metals (Cu, Fe, and Ni) were selected as primary candidates for the barrier material on the basis of their physical, chemical, and nuclear properties.⁴ The nuclear properties of interest are the radioisotopes generated in the barrier during target irradiation and their activity levels, which must be removed from molybdenum during processing. By the use of ORIGEN2, we calculated the radioisotopes generated in Fe, Ni, and Cu barriers during LEU target irradiations in the RGS-GAS reactor. The results of these calculations show that only a copper barrier would generate enough radioactivity to be of concern. For its primary activation product, ⁶⁴Cu, to be less than 0.1 μCi/mCi-⁹⁹Mo in the molybdenum product, its overall decontamination factor must be >3100.

Neither the barrier materials nor their neutron-activation products are reported to interfere with the precipitation of molybdenum by ?-BO [27-29]. Experiments were run to verify the noninterference of these metal ions by using solutions prepared to simulate dissolving the barrier-clad uranium foil in nitric acid. In the same experiments, we measured the amount of each barrier metal that carried with the molybdenum precipitate. Table VI shows the results of these experiments. The molybdenum recovery was high for all experiments, as were the measured decontamination factors. It is likely that the differences in the decontamination factors are more an indication of how well the precipitate was washed in each experiment rather than chemical differences in the barrier-metal ions.

⁴ Zinc, which was primarily selected for base-side process targets, is not discussed below.

TABLE VI. EFFECTS OF BARRIER MATERIALS ON γ -BO PRECIPITATION^a

	Cu	Fe	Ni
Molybdenum Recovery, %	99 ± 3	96 ± 3	96 ± 3
Decontamination Factors	1680	258	660

^aSolution contained 0.75M HNO₃, 1.5M UO₂(NO₃)₂, and the concentration of Cu, Ni, or Fe corresponding to a 10- μ m barrier on either side of the uranium foil.

The decontamination factors measured for Fe and Ni are more than high enough to meet impurity requirements for the molybdenum product. However, the removal of ⁶⁴Cu may require additional decontamination, since the measured value after γ -BO precipitation (Table VI) is below the required value of >3100. For this reason, we tested the removal of copper by the two polishing steps; these tests showed that the overall decontamination factor for the two polishing steps should be >10,000. A combination of all three steps should, therefore, effectively reduce ⁶⁴Cu contamination to well below regulatory concern.

Testing and development activities are continuing at Argonne National Laboratory and the University of Texas to support modification of the Cintichem process for use with LEU targets and to assist BATAN researchers at the PUSPIPTEK Radioisotope Production Center, who are preparing to demonstrate this process on a fully irradiated LEU target. Our collaboration with BATAN is vital to developing and validating this process. Their results continue to show that substitution of LEU in the Cintichem process will be successful and have advanced our progress toward the full-scale demonstration to be done by BATAN. Our unofficial, but soon to be official, cooperation with SNL will move full development of the LEU Cintichem process even faster. Processing of LEU oxide targets will be demonstrated at SNL in the next year.

In summary, our experimental results predict that replacing the current dissolution cocktail, which contains both nitric and sulfuric acids, with nitric acid alone will not compromise the effectiveness of the Cintichem process. In our tracer experiments with this substitution, molybdenum recovery and purity were not degraded. Removal of sulfuric acid from the dissolver solution will decrease waste treatment and disposal costs and increase the stability of the disposed waste form. On the basis of measured decontamination factors from our tracer experiments, molybdenum produced from processing fully irradiated LEU targets is predicted to meet radiochemical purity limits. Its yield will be equivalent to that currently produced from HEU. Likewise, addition of barrier materials will not affect the process. A full-scale demonstration of process will take place in the near future at PUSPIPTEK.

5.2. Base-side processing

As seen in Table II, ⁹⁹Mo production by IRE, CNEA, Mallinckrodt, and the AEC is all done by irradiating HEU UAl_x/Al-dispersion plates and dissolving the plates in base. The three LEU targets we are studying as the HEU replacement are U₃Si₂/Al and UO₂/Al dispersion plates and a uranium-metal foil with a zinc barrier. For all three targets, base alone is not sufficient to dissolve the uranium fuel; addition of hydrogen peroxide is necessary to achieve acceptable dissolution rates. In processing the two dispersion-fuel targets, the entire target is dissolved before molybdenum can be recovered. In the LEU-metal target, only the uranium foil (and the fission barrier) must be dissolved. The spent dissolver solution will be essentially identical for the two LEU dispersion targets and much like that of the current HEU target.⁵ The dissolver solution from the foil target will not have the very high aluminum content like those from the dispersion-fuel targets. However, the dissolver solution from the foil target will contain a significant concentration of zinc. Once dissolved, processing will likely be the same for all three targets. Experimentation on base-side molybdenum recovery and processing steps was done with U₃Si₂ targets; these studies were performed in 1987 and 1988 [31, 37].

5.2.1. Target dissolution

The discussion of target dissolution is divided into three parts--one for each target type. Because the dissolution reagents are the same (NaOH and H₂O₂), the dissolution studies have much in common. In all cases, the purpose of our efforts was first to show the feasibility of target dissolution, then to optimize the dissolution process, and finally to design a dissolver.

⁵ The consequences of dissolving LEU rather than HEU targets on the volume and compositions of the feed to the primary ⁹⁹Mo recovery step are discussed in section 5.2.2.

5.2.1.1. U₃Si₂/Al dispersion plates

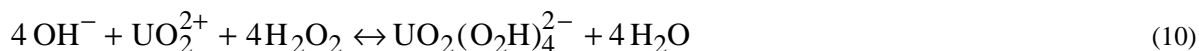
We first began to look at U₃Si₂-target dissolution and processing in 1987, and it was the program's major emphasis through 1989 [31, 37, 38], when all RERTR-⁹⁹Mo efforts were stopped due to funding problems. Research and development directed toward U₃Si₂ targets began again in 1993 and continued through 1996 [39-43]. A decision was made late in 1996 to suspend this work and to expend limited resources on development of the uranium-metal and UO₂/Al-dispersion targets. The following summarizes the status of U₃Si₂ dissolution; for details, the reader is directed to the above-cited works.

An important side reaction that occurs during the silicide dissolution process is the autodestruction of hydrogen peroxide:⁶



A literature search revealed very little data about the autodestruction of hydrogen peroxide in sodium hydroxide solutions. One source simply revealed that the autodestruction reaction is catalyzed in base, but no quantitative data were given [44]. A limited kinetic study of dilute hydrogen peroxide (0.01 M) in 0.5-6.0M NaOH at room temperature indicated that hydrogen peroxide was stable in highly basic solutions [45]. Experiments at ANL showed the autodestruction of H₂O₂ was first order with respect to H₂O₂ in alkaline solutions between 70 and 100°C. In general, autodestruction of H₂O₂ is catalyzed by metallic surfaces and, in some cases, metal ions in solution.

Hydrogen peroxide is also consumed in the dissolution of the U₃Si₂. The following equations describe the dissolution of U₃Si₂ in alkaline peroxide based on the assumption that it is an intermetallic compound:



Equation 11 is an overall reaction for Eqs. 7 through 10:



Due to catalyzed autodestruction, the actual H₂O₂ consumption is 10-100 times greater than that predicted by Eq. 11.

We developed a U₃Si₂ dissolution-rate model that can be used in designing a target dissolution procedure. Dissolution rates of U₃Si₂ particles were determined using the initial rate method. A large set of experiments started with ~5.4M H₂O₂ and varied base concentrations at 40, 50, and 60°C. The uranium dissolution rates were normalized to U₃Si₂ particle mass. These normalized rates were then plotted versus initial base concentration (Fig. 13). The uranium dissolution reaction reaches a maximum at approximately 1.5 M NaOH for each temperature with both comminuted and atomized U₃Si₂ particles.⁷ The reaction rate doubles for a 10°C increase in temperature. The spherical atomized particles dissolve more slowly than the comminuted particles, mostly due to surface area. The atomized and comminuted U₃Si₂ particles have similar uranium dissolution rates at 50°C when surface area is considered. The different activation energies for the two particle types show that more than surface area differences are relevant in the dissolution kinetics of atomized and comminuted U₃Si₂ particles.

⁶ Both uranium metal and U₃Si₂ catalyze this autodestruction, making it orders of magnitude more important than in the dissolution of UO₂, which does not catalyze this reaction.

⁷ Most experiments used jagged comminuted powder, crushed from larger pieces and possessing mostly a single-phase structure [46]. Later experiments used atomized powder, spherical particles produced by quenching of molten U₃Si₂ in an inert atmosphere [47].

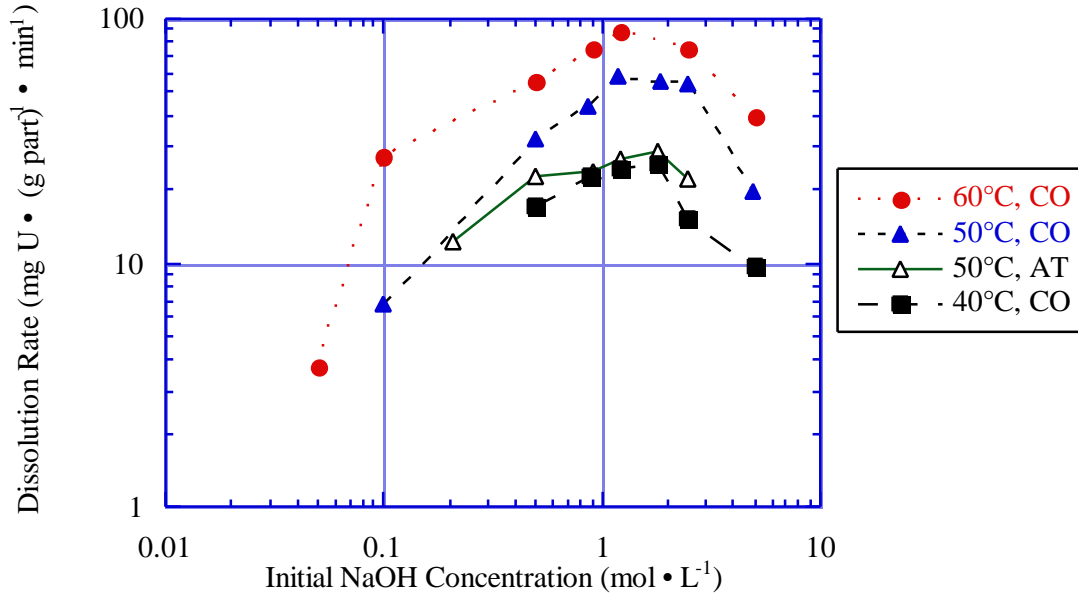


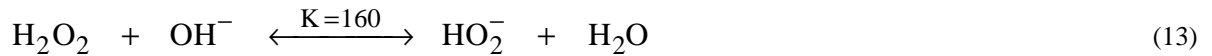
FIG. 13. Variation in uranium dissolution rate normalized to mass of particles (g part) with initial NaOH concentration. The data series in legend give reaction temperature and comminuted (CO) or atomized (AT) particles.

The dissolution activation energies of comminuted and atomized particles were determined by using the Arrhenius equation:

$$k = A \exp(-E_a/RT) \quad (12)$$

where k is the rate constant, E_a is the activation energy, R is the universal gas constant, T is the absolute temperature, and A is a pre-exponential factor. The reaction mechanism is probably the same for the base range of 0.5-2.5M NaOH, resulting in the same E_a for each particle type. Arrhenius plots are made by plotting the natural logarithm of the uranium dissolution rate constant against the inverse of the temperature ($1/T$). The slope of the line determines E_a and the y-intercept determines A . Table VII lists the experimentally determined activation energies for comminuted particles dissolved in 0.5-2.5 M NaOH and 5.2M H_2O_2 . As shown, the average activation energy is 77 ± 15 kJ/mol. The activation energy of the comminuted particles is 40% higher than that of the atomized particles. Differences between their activation energies may be explainable by how they are prepared. The comminuted particles are cooled slowly and contain a single crystalline phase. The atomized particles are condensed quickly from molten U_3Si_2 and contain many different crystalline phases. One or more of these phases has a lower activation energy.

The equilibrium shown in Eqs. 13 and 14 significantly decreases the concentrations of H_2O_2 and OH^- from their as-prepared values:



or

$$160 = \frac{[HO_2^-][H_2O]}{[H_2O_2][OH^-]} = \frac{[HO_2^-]}{[H_2O_2][OH^-]} \quad (14)$$

Figure 14 plots the equilibrium concentrations of O_2H , OH^- , and H_2O_2 for a fixed initial peroxide concentration of 5.2M H_2O_2 and variable initial OH^- concentrations. In basic solution the equilibrium H_2O_2 concentration is always less than the initial concentration, and its concentration in high-base solutions is significantly less than in low-base solutions. The maximum peroxide destruction rate occurs at approximately the equilibrium base concentration of 0.1M OH^- , which corresponds to a starting concentration of ~1.2M NaOH.

TABLE VII. EXPERIMENTAL ACTIVATION ENERGY FOR COMMINUTED U_3Si_2 PARTICLES DISSOLVED IN NaOH AND 5.2M H_2O_2 .

[NaOH], mol/L	Activation Energy, kJ/mol
0.5	80
0.9	84
1.2	71
1.8	55
2.5	93
Mean	77 ± 15

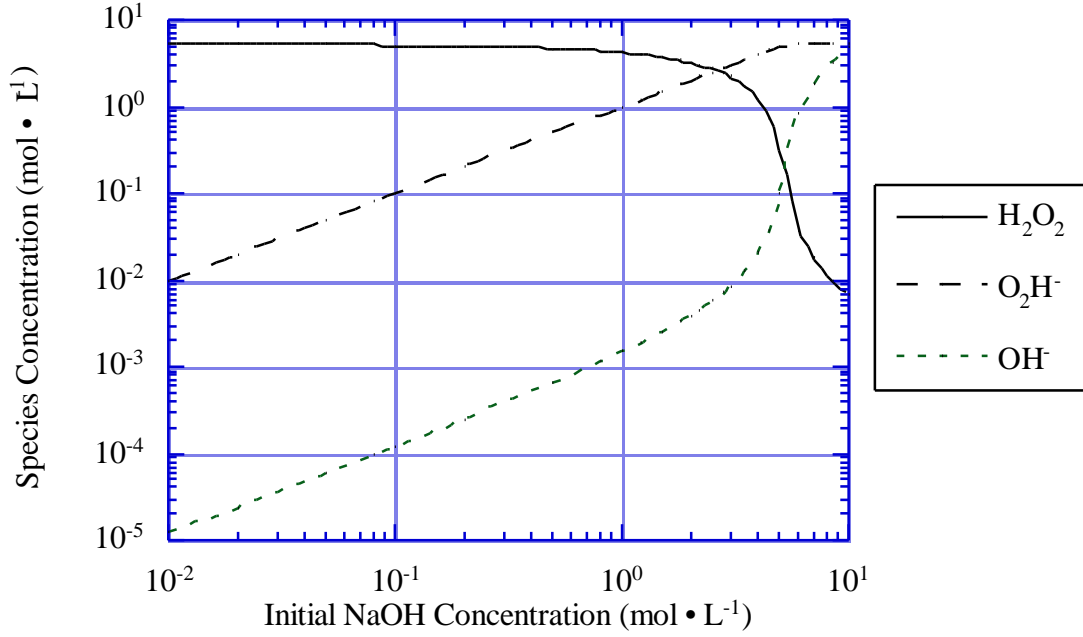


FIG. 14. Calculated variation in equilibrium concentrations of O_2H^- , OH^- , and H_2O_2 for an initial 5.2M H_2O_2 and variable initial OH^- concentration based on Eq. 14.

A model for uranium-silicide 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, as described by

$$[U_s] = [A] + [B] + [C] \quad (15)$$

where A is the unreacted surface available for reaction, B is the reactive complex from the reaction of A with equilibrium O_2H^- , and C is the unreactive surface produced from the reaction of A with equilibrium OH^- . The complexes B and C are produced by reactions described in Eqs. 16 and 17, where K_1 and K_2 are equilibrium constants:



The expressions for [B] and [C] can be substituted into Eq. 15 and solved for [B]:

$$[B] = [U_s] \frac{K_1 [O_2H^-]_{eq}}{1 + K_1 [O_2H^-]_{eq} + K_2 [OH^-]_{eq}} \quad (18)$$

Eventually, through a series of fast reactions, complex B becomes the soluble form of uranium that we measure. A uranium dissolution rate model was developed from Eq. 18 and the rate data. Equation 19 gives the uranium dissolution rate R_u as functions of the particle type, and OH^- and O_2H^- concentrations:

$$R_u = A_i \exp\left(\frac{-E_{a_i}}{RT}\right) \cdot \frac{K_1 [O_2H^-]_{eq}}{1 + K_1 [O_2H^-]_{eq} + K_2 [OH^-]_{eq}} \quad (19)$$

The constants K_1 and K_2 were determined by curve fitting of the 50°C data to be 1.2 and 550. The constants for the modified pre-exponential constant A_i and activation energy E_{a_i} (where i denotes AT or CO particles)-- A_{AT} , A_{CO} , $E_{a_{AT}}$, and $E_{a_{CO}}$ --are $5.10 \times 10^8 \text{ mg U}\cdot\text{cm}^{-2}\cdot\text{min}^{-1}$, $1.84 \times 10^{12} \text{ mg U}\cdot\text{cm}^{-2}\cdot\text{min}^{-1}$, $5.5 \times 10^4 \text{ kJ}\cdot\text{mol}^{-1}$, and $7.7 \times 10^4 \text{ kJ}\cdot\text{mol}^{-1}$, respectively. This temperature-dependent dissolution model for the dissolution of U_3Si_2 particles (Eq. 19) is plotted with experimental data in Fig. 15. The temperature dependence in the exponential fits the data well. The curves fit the data in the desired processing concentration range 0.3-3 M O_2H^- . Dissolution rates outside this range are too low for processing an irradiated target.

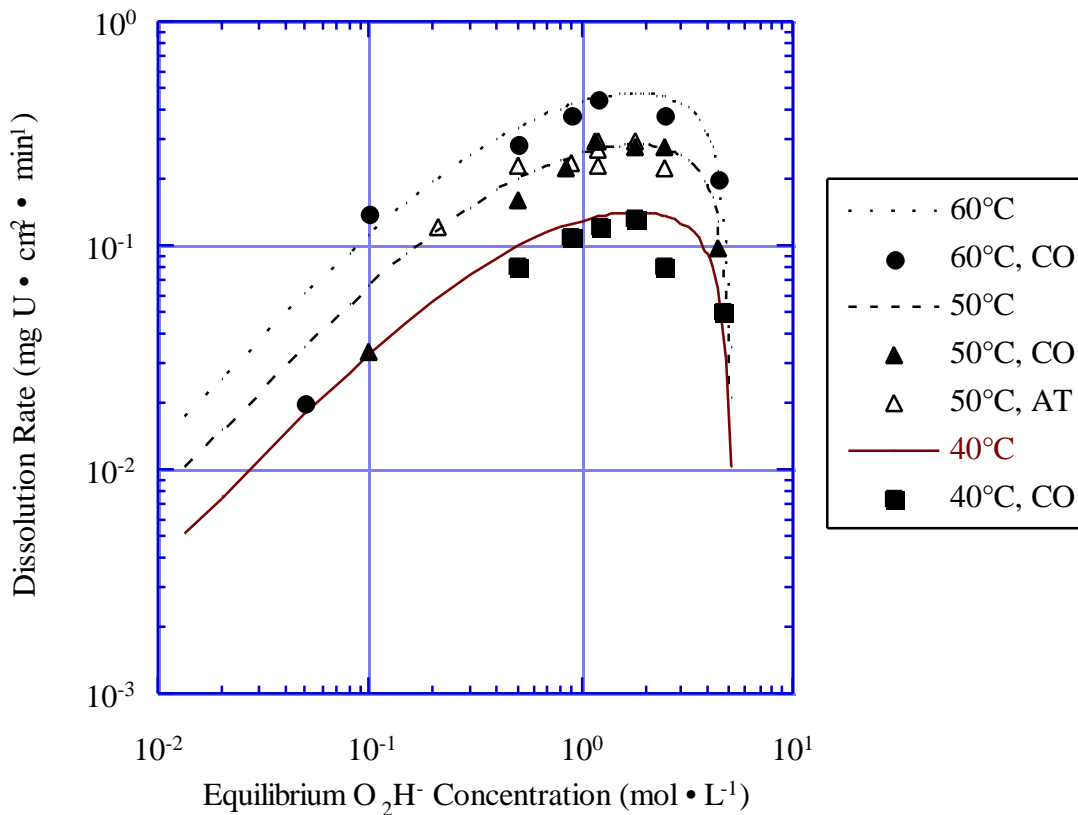


FIG. 15. Variation of uranium dissolution rate with equilibrium peroxy ion concentration. Data points are denoted by dissolution temperature and particle type (atomized or comminuted), while the empirical model curves generated from Eq. 19 are denoted by temperature only.

In conclusion, equilibrium concentrations of peroxy and hydroxyl ions were used to develop a model for the alkaline peroxide dissolution of U_3Si_2 particles used in dispersion fuel and targets. The uranium dissolution rate reaches a maximum when the equilibrium peroxy-ion concentration approaches $\sim 1.5\text{ M } O_2H^-$, but the rate changes little over the broader range of $0.5\text{--}2.5\text{ M } O_2H^-$. This peroxy-ion range corresponds to initial concentrations of $0.5\text{--}2.5\text{ M } OH^-$ with $5.2\text{ M } H_2O_2$ and indicates that the uranium dissolution process is insensitive to small changes in reactant concentrations.

Dissolving unirradiated U_3Si_2 particles is well understood, but we still have a long way to go for dissolving irradiated targets. The current process for basic dissolution involves dissolving the entire target in $NaOH/NO_3^-$ solution. During the dissolution, uranium and various fission products precipitate as hydrated hydroxide salts. This mixture is diluted and filtered, and molybdenum is recovered from the solution using a column.

In 1987 through 1989 [31,37,38], our results suggested that the targets be digested in a two-step process. In the first step, the aluminum-alloy cladding and the aluminum powder in the fuel meat would be dissolved in $3\text{ M } NaOH$ solution. During this step, many of the alloying elements from the cladding (in our case, 6061 Al) would precipitate as hydroxides. The hydroxide slurry would be removed from the U_3Si_2 , which could then be dissolved separately with basic hydrogen peroxide. On heating the peroxide solution, peroxide would be destroyed, uranium and many of the fission products would precipitate from the highly basic solution, and the soluble iodine and molybdenum would be separated from them in the filtrate. The two dissolver solutions would be combined for further processing. This scheme is based on three observations:

- Molybdenum-99 loss from the U_3Si_2 fuel due to fission recoil into the aluminum matrix will be in the $\sim 20\%$ range and is likely to represent too high an economic penalty to be ignored.
- The dissolution/digestion rate of U_3Si_2 is too low ($<1\%/day$) in basic solution alone for its practical use in ^{99}Mo -target processing.
- Cladding precipitates must be removed from the dissolver before U_3Si_2 can be dissolved by basic hydrogen peroxide. If they are not, they cause robust autodestruction of hydrogen peroxide before it even contacts the U_3Si_2 particles on the bottom of the dissolver vessel.

In the studies performed in 1988, targets were irradiated in the ANL 180-kW JANUS reactor for 80 min at 1/4 power--a burnup of only $10^{-5}\%$. This burnup produced 0.9 mCi of ^{99}Mo and enough of the other fission products and ^{239}Np to measure the yield and decontamination of ^{99}Mo through the various steps of the proposed processing scheme. These experiments were performed in glassware at the laboratory-scale level. The next step, to demonstrate this scheme at production levels by using a target with appropriate burnup, was not taken because funding for this project was suspended.

To make a step in that direction, we tested this process using an irradiated miniplate sample that was being stored at ANL following its post-irradiation examination. The miniplate sample that we tested had undergone $\sim 42\%$ burnup in the 30 MW Oak Ridge Reactor (ORR). This miniplate contained uranium enriched to 19.84% ^{235}U before irradiation. Since the miniplate was nearly 9 years old, the short-lived fission products, including ^{99}Mo , had completely decayed. 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 with 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 by Gerard Hofman and colleagues at Argonne [48] 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 $2\text{-}\mu\text{m}$ thick at 40% burnup.
- The new layer can be represented by the chemical formula $U(Al,Si)_3$, 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, hydro fluoric acid, and citric acid etched the unaltered U_3Si_2 but did not attack the $U(Al,Si)_3$ 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. However, 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. Heat-treated, unirradiated plates showed the same effect and confirmed that a physical means to break up the fuel meat will be an essential part of target dissolution.

Design of a dissolver system for a two-step process that also provides physical desegregation is a difficult technical problem. This among other problems led us to suspend activity in this area and look toward other targets.

5.2.1.2. Uranium-foil targets

We first dissolved uranium foil in alkaline peroxide in 1988 [37]. Dissolution studies for uranium metal began in earnest in 1995 and are continuing today [42, 49-51]. Studies were moving toward engineering and dissolver design, but chemical aspects were reopened when the use of a zinc fission -recoil barrier became necessary (see section 5.2.1.3).

Dissolution of LEU metal foil with alkaline peroxide solution followed by recovery and purification of ^{99}Mo has been studied at ANL as an option for replacement for the HEU aluminide targets. An LEU-foil dissolution kinetics model was proposed in 1995. 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. In 1997, work has focused on dissolving uranium foil with zinc fission barriers.

Unlike the well-documented acid process, dissolution of uranium metal with alkaline peroxide solutions has received little study. The stoichiometry of uranium metal dissolution by alkaline peroxide is shown in Eq. 20:



In the early 1940s, L. Warf [52] reported that "X (the X stands for uranium) metal dissolved in $H_2O_2 + Na_2O_2$, $NaOH + H_2O_2$, and $Na_2O_2 + H_2O$ slowly, and in $NaOH + Na_2O_2$ very slowly." In their review papers, both Gindler [53] and J. C. Warf [54] mentioned that uranium metal dissolves in a sodium hydroxide solution containing hydrogen peroxide or in a sodium peroxide water mixture, and they both cited L. Warf's report [52]. Larson [55] reported that uranium metal reacts at a moderate rate with a sodium hydroxide/hydrogen peroxide mixture to form a clear solution that is highly colored by the uranyl peroxide complex. However, the kinetics of dissolution of uranium metal foil in alkaline peroxide solutions was basically unknown. The following describes kinetic studies of uranium dissolution in alkaline peroxide solutions. The rate of uranium dissolution was determined by using depleted uranium (DU) foil under various chemical conditions. Much of this study parallels the work and the discussion of the alkaline peroxide dissolution of U_3Si_2 . Differences in data treatment reflect differences in perspectives of the principal investigators.

The rate of uranium dissolution versus the equilibrium hydrogen peroxide concentration is shown in Fig. 16 (a log-log plot). Three sets of data were obtained at three fixed base concentrations (0.2, 1.0, and 5.0 M) with varying initial hydrogen peroxide concentration (from 1.0 to 4.0 M), and the other data set was from experiments in which initial (total) hydrogen peroxide concentration was constant ($\sim 3.5 M$), while the base concentration varied from 0.01 to 5 M . Figure 16 clearly indicates that the uranium dissolution data over a broad range of base concentrations can be divided into two groups. The first group, shown by the dashed line on the right-hand side, includes only three data points at base concentrations of 0.01, 0.05, and 0.09 M . The second group, the solid line, covers the remaining 20 data points (some data points overlie each other, only 18 can be seen) at base concentrations = 0.2 M . On this basis, we concluded that two types of uranium dissolution can be distinguished, a low-base and a high-base process, and that the transition from low-base to high-base process takes place at a base concentration of about 0.2 M .

We believe that, in the low-base process (i.e., below 0.2 M base), alkali content is the main factor that controls the rate of reaction. An increase in base concentration significantly promotes the rate of uranium dissolution. As shown in Fig. 16, the equilibrium hydrogen peroxide concentration of the three data points in this group varied very little, but the rate of uranium dissolution varied significantly. It is obvious that this dramatic change in the dissolution rate was caused by different base concentrations.

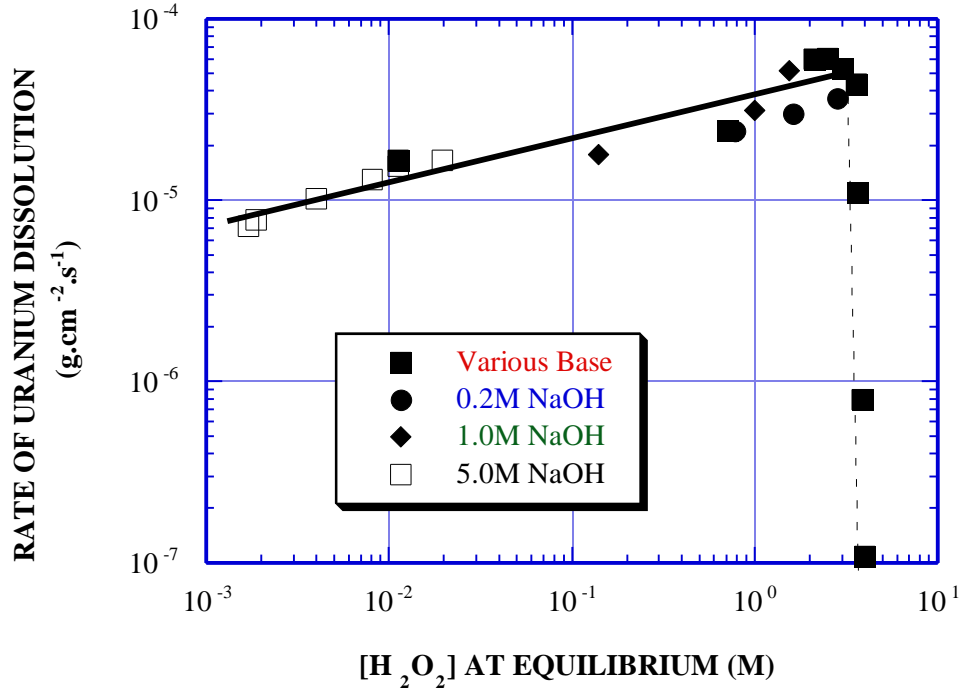


FIG. 16. Effect of equilibrium hydrogen peroxide concentration on rate of uranium dissolution (U Surface Area = 2 cm^2 , Temp. = 60°C).

On the other hand, in the high-base process (i.e., above 0.2 M base), the rate of uranium dissolution is solely controlled by the equilibrium hydrogen peroxide concentration. Figure 16 indicates that, for base concentrations from 0.2 to 5.0 M , the rate of uranium dissolution increased as the equilibrium hydrogen peroxide concentration was increased. All 20 data points fell near or on the same straight line when the uranium dissolution rate was plotted against the equilibrium hydrogen peroxide concentration (in a log-log plot). The slope of the line was 0.25 , and the correlation coefficient of the line was 0.89 . Therefore, uranium dissolution in the high-base process is a one-fourth order reaction with respect to the equilibrium hydrogen peroxide concentration.

Based on the experimental observations and discussions above, we proposed the empirical kinetics model as shown in Eq. 21:

$$R_u = A \left(e^{\frac{-E_a}{RT}} \right) \left(\frac{K_a [\text{OH}^-]^{n'}}{1 + K_a [\text{OH}^-]^{n'}} \right) [\text{H}_2\text{O}_2]_{\text{equilibrium}}^n \quad (21)$$

where R_u is the rate of uranium dissolution ($\text{g}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$), T is the temperature in Kelvin, E_a ($=48.8 \text{ kJ/mol}$) is the activation energy, A ($=1.65 \times 10^3$) is the pre-exponential factor, R is the gas constant, n ($=0.25$) is a constant, n' ($=2$) is a constant, K_a ($=20.4$) is a constant, $[\text{OH}^-]$ is the initial (total) hydroxide concentration, and $[\text{H}_2\text{O}_2]_{\text{equilibrium}}$ is the equilibrium concentration of hydrogen peroxide. The mechanism of uranium dissolution is unknown and is out of the scope of this investigation. A factor of $\{K_a[\text{OH}^-]^{n'}/(1+K_a[\text{OH}^-]^{n'})\}$ was introduced into the model because we believe that OH^- groups are adsorbed on the uranium surface to form an activated compound (Eq. 22) and that uranium dissolution proceeds from a reaction of the activated compound (U^*) with hydrogen peroxide.



Details of how this dissolution model was generated can be found in reference [50]. The predicted rates of

uranium dissolution with the model (Eq. 20) were plotted against the experimental data, as shown in Fig. 17. The figure indicates that, in general, the model is good, except that it underestimates the rate of uranium dissolution by approximately 40% at base concentrations of about 0.2M. Notice that a base concentration of 0.2M falls right at the transition point between the low-base and the high-base processes. More parameters are needed to improve the accuracy of this model when applied near the transition regime. However, practical conditions for dissolution are at higher base concentrations.

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 autodestruction; the rate is orders of magnitude less without the foil present [51]. 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.

Figure 18 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 [51]. In the high-base regime (above 0.2M, indicated by a solid line in Fig. 18), 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 dashed line in Fig. 18), both hydrogen-peroxide and hydroxide concentrations affect the rate of peroxide decomposition. Note that one group of data, shown by the two rectangles, 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.

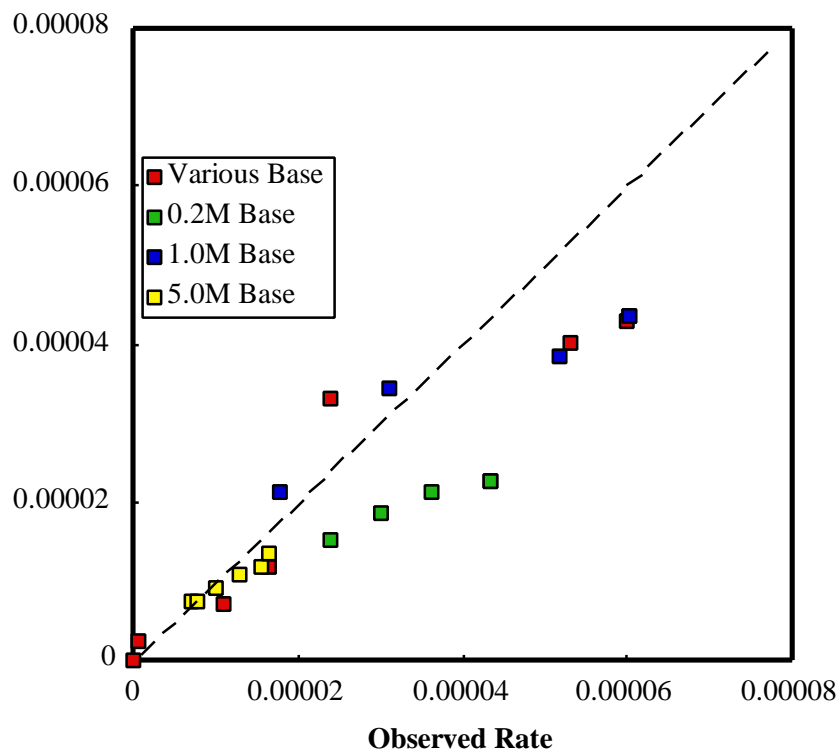


FIG. 17. Predicted vs. observed rate of uranium dissolution.

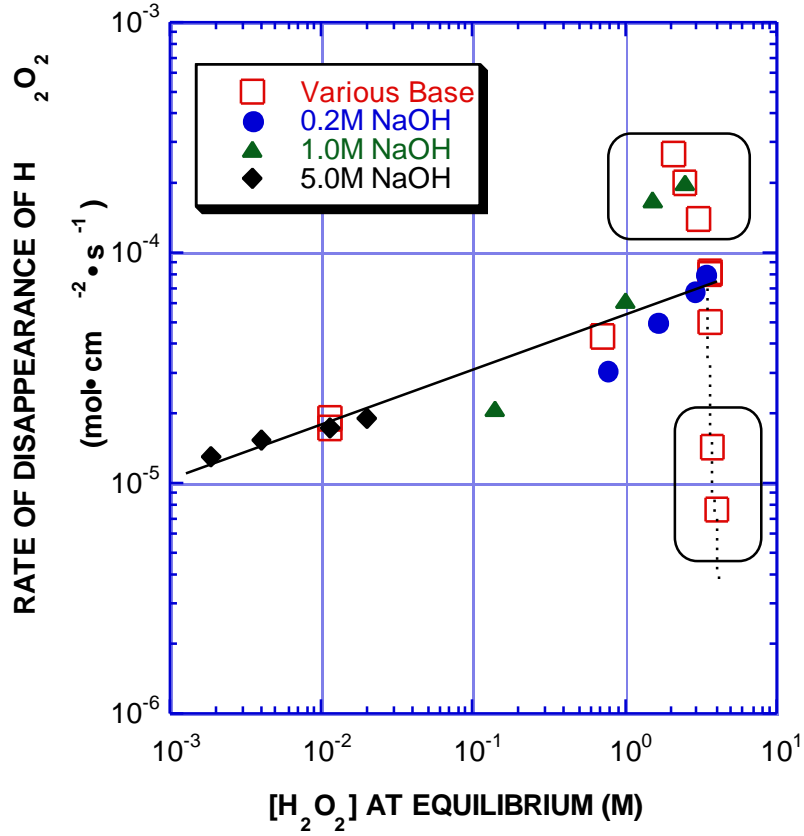


FIG. 18. Effect of equilibrium H_2O_2 concentration on its depletion rate at $60^\circ C$.

Based on the above experimental observations, an empirical kinetics model of the overall disappearance of hydrogen peroxide (R_p) was developed that parallels that for uranium metal dissolution:

$$R_p = A_p \exp\left(-\frac{E_a}{RT}\right) \left(\frac{K_a [\text{OH}^-]^{n'}}{1 + K_a [\text{OH}^-]^{n'}} \right) [\text{H}_2\text{O}_2]_{\text{equilibrium}}^n \quad (23)$$

Values for K_a , n , and n' were determined to be 20.4, 0.25, and 2, respectively, from the uranium dissolution model [50]. The following values were obtained from the experimental data: the pre-exponential factor, A_p , 5.06×10^7 ; and the activation energy, E_a , $76.4 \pm 10\%$ kJ/mol.

In this model, the overall disappearance rate of hydrogen peroxide is essentially governed by two terms, OH^- concentration and H_2O_2 concentration. In the high-base regime, the hydroxide ion concentration term becomes near constant. This reveals that the overall consumption of hydrogen peroxide in the high alkaline solution was 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. 19. However, this model underestimates the rate of hydrogen peroxide decomposition by 6 to 98% over the regime of base concentrations studied.

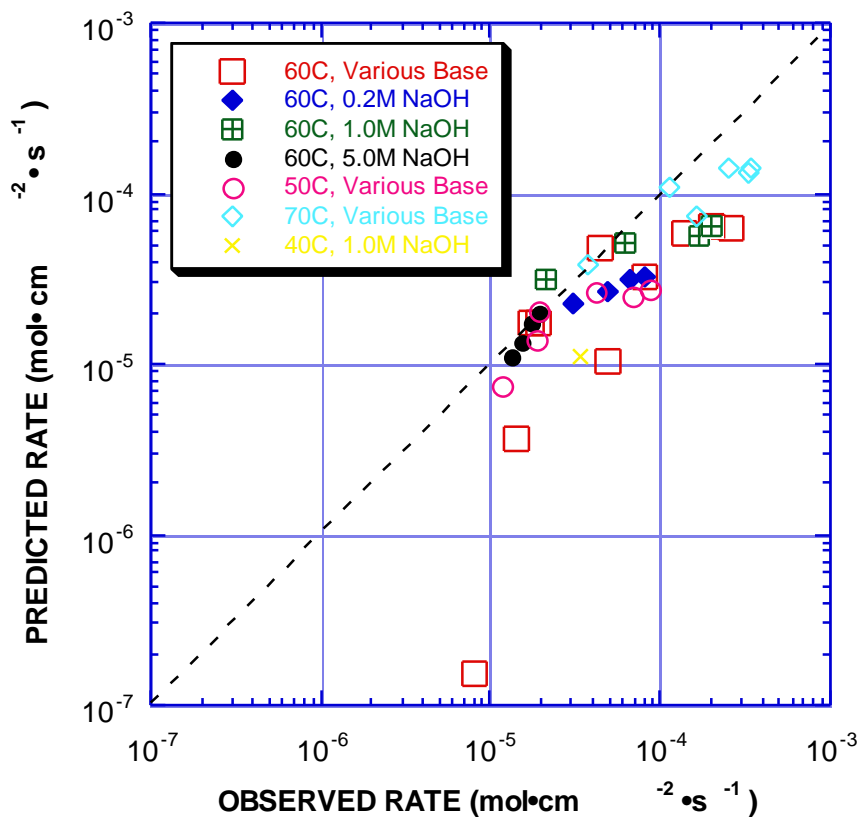


FIG. 19. Predicted rates versus observed rates for depletion of H_2O_2 .

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

An optimized procedure has been developed to reduce the HPCR by using sequential additions of alkaline peroxide [42]. 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 to 5 times the stoichiometric ratio. Because many small -volume additions were actually used in this optimized procedure to frequently replace the dissolving solution or continuously replenish hydrogen peroxide, this 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 between 50 and 90°C 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.

Low-enriched uranium metal foils appear to be a viable alternative to the current HEU dispersion -plate targets. Modeling of uranium metal dissolution and 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. 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 . At this stage of development, we conclude 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. Future work on the dissolution of uranium metal foil will also be concerned with designing the dissolver/off-gas system and integrating ⁹⁹Mo recovery and purification steps to the dissolution. Complications due to the need of a base-soluble fission barrier are discussed in the following section.

5.2.1.3. Zinc fission barriers

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. Neither Cu, Ni, nor iron dissolve in base. Therefore, a challenging task in process development was identifying a suitable metal for a barrier material that could dissolve in alkaline solution and meet other mechanical and chemical criteria. A literature survey found the following elements that dissolve in alkaline solutions: aluminum, zinc, beryllium, gallium, tin, arsenic, niobium, and tantalum. Aluminum dissolves at about the same rate as uranium metal in 5.0 M H₂O₂/1.5M NaOH solution at 70°C. However, there is a strong concern that uranium would react with aluminum during the target irradiation. Germanium and rhenium, although not amphoteric, are reported to dissolve readily in dilute hydrogen peroxide. Of the elements mentioned above, the toxicity of beryllium metal and the low melting point of gallium (30°C) preclude their use. Arsenic is classified as a non-metal and may not have sufficient metallic properties to be made into a foil. Zinc is an active electropositive element and forms a strong anion with oxygen. It also dissolves readily in sodium-hydroxide/nitrate solution. Work on barrier materials for targets to be processed by dissolution in base has, therefore, focused on zinc.⁸

Three methods of forming the zinc barrier were considered: (1) pressing together zinc and uranium foils, (2) hot dipping the uranium target in molten zinc, and (3) electroplating the zinc onto the uranium foil. One of the most important constraints on the barrier is that it should be of relatively uniform thickness of not much greater than 15 μm to minimize the material to be dissolved after irradiation. Use of pre-formed zinc foil pressed onto the uranium target was eliminated by the high cost and porous nature of the zinc foils thinner than 20 μm. Hot dipping provides a coating of rather poorly controlled thickness, and thicknesses less than 20 μm are unlikely. Electroplating of zinc, on the other hand, seems to provide a relatively simple and inexpensive process with good control over the thickness.⁹

The first task was to develop means to dissolve the zinc barriers. Three types of solutions for dissolving zinc were studied: NaOH, NaOH/H₂O₂, and NaOH/NaNO₃. A variety of solutions containing NaOH or NaOH/H₂O₂ showed dissolution rates less than the desired 2 mg/(cm²•min). On the other hand, a variety of solutions containing NaOH and NaNO₃ gave dissolution rates well above that. A solution of 2.5M NaOH/1M NaNO₃ at 70°C is our standard for rapid dissolution of pure zinc metal. Experiments have confirmed that a zinc coating electroplated onto the uranium-foil surface is also dissolved rapidly by this solution. Analysis by energy dispersive spectroscopy (EDS) of the foils left after dissolution showed that all of the zinc plate was dissolved from the uranium. Liquid scintillation counting of the dissolution solution showed that virtually none of the uranium foil was dissolved with the zinc.

Due to radioactive-decay heat generated within the irradiated LEU, a concern arose regarding whether or not a zinc barrier would melt during transport of the target from the reactor pool to the processing hot cells. The biggest hindrance to the transfer of heat from the target is the relatively small surface area from which heat can be transferred. Sample calculations were made for natural convection in the air immediately after the target leaves the cooling pool and for the possibility that the target will be placed in a cask and shipped over a 24 -hour time frame. Although exact temperatures to be experienced by the zinc barriers cannot be predicted, calculations show that temperatures in the range of 300-400°C are likely. Although this is very close to zinc's melting point (420°C), it is expected that the melting point of zinc will not be reached. However, when a zinc-plated uranium foil was heat treated at 375°C overnight in an evacuated glass tube, an intermetallic U/ Zn compound was formed.

The intermetallic U/ Zn compound is visually distinct from the unheated zinc-plated uranium foil when viewed through a microscope with a magnification of about 440X. Figures 20a and b are micrographs of the Zn-plated DU foil shown in Fig. 5 following this heat treatment. With this intermetallic compound, the interface between the zinc and the uranium is almost indistinguishable, whereas it had been pronounced before. Notice the dendrite formations along the edge of the foil in Fig. 20a. Even if the target is held at low overall temperatures during transport, the fission-product recoil that the zinc barrier is designed to absorb will cause localized heating and most likely cause the formation of this intermetallic compound at the U/ Zn interface.

⁸ As discussed in section 4.2., a zinc fission-barrier is also being considered for acid-side processing targets. This would have the advantage of developing just one target for all processes.

⁹ Zinc plating is described in section 4.2.

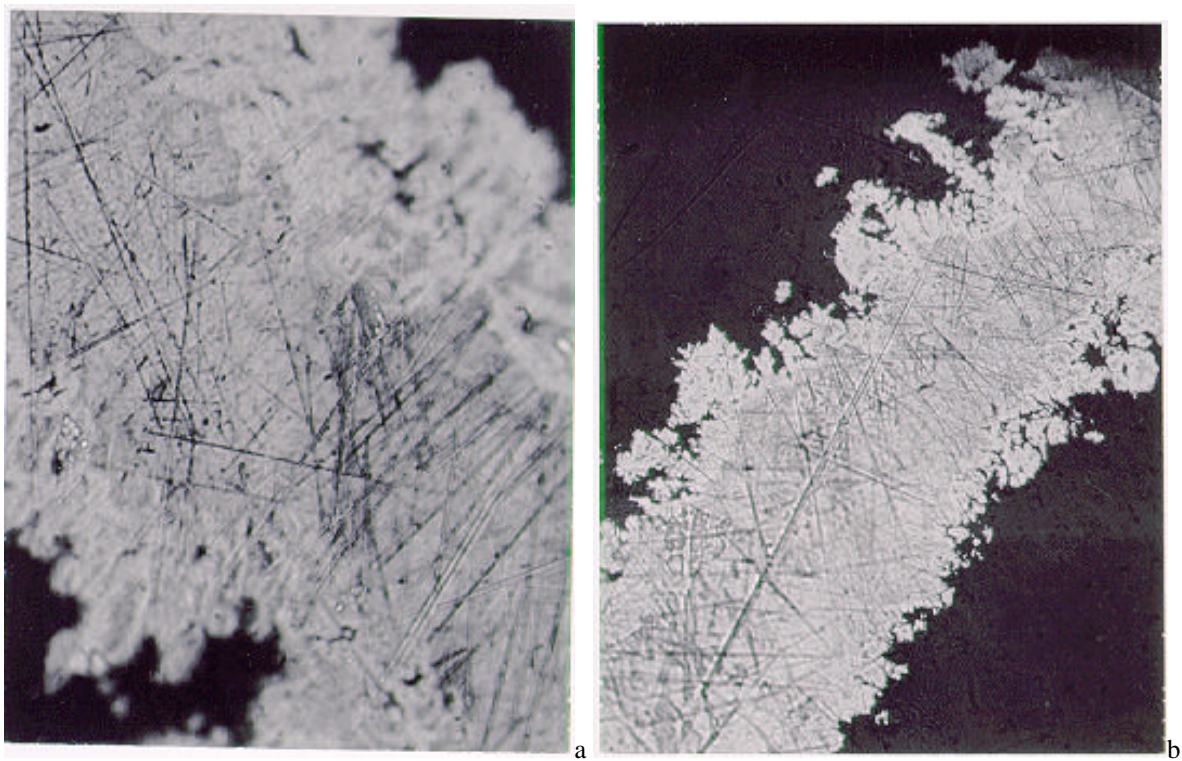


FIG. 20. Two sections of Zn-plated DU foil after heating at 375°C overnight (compare to FIG. 5).

Solutions suitable for dissolving the intermetallic U/Zn compound were pursued. Attempts to dissolve the zinc from this foil showed that this intermetallic would not dissolve as the zinc plate had from the unheated foils (at 70°C with 50 mL of 2.5M NaOH and 1M NaNO₃). A solution of 8M HNO₃ at 70°C dissolved the intermetallic compound but too slowly to be useful.¹⁰ On the other hand, a solution of 1.5 M NaOH/5M H₂O₂ appears to dissolve the intermetallic compound faster than it does pure zinc or pure uranium. This solution may be useful for this task, although more experimental work is necessary to clarify the rate of dissolution.

5.2.1.4. UO₂/Al dispersion plates

Work on the alkaline -peroxide dissolution of UO₂/Al dispersion plates is new in 1997. This is the first report of our activities. The density of UO₂ is greater than uranium aluminide, and if the UO₂/Al dispersion is loaded to 40 vol%, an LEU target could contain about three times more uranium than an HEU aluminide target of equivalent geometry. Between five and six times more uranium is needed for an equivalent substitution of LEU for HEU in a ⁹⁹Mo-production target. Although these LEU targets will contain about one-half the ²³⁵U of HEU aluminide targets, (1) expertise is already available for their fabrication, (2) dissolution and processing chemistry will be simpler than that for U₃Si₂, and (3) the time to develop the processing method will be significantly shorter than that for either the U₃Si₂ or uranium-foil targets. Therefore, they may be useful as interim LEU targets while development of the uranium-foil targets is still underway.

Work on recovering ⁹⁹Mo from a UO₂/Al dispersion target by dissolution in alkaline peroxide solution is underway. Dissolution data were collected by separately adding hydrogen peroxide and a solution of sodium hydroxide to particles of UO₂. All solutions had an initial temperature of 50°C. Typically the reaction between the base and the peroxide caused the temperature to increase rapidly on mixing. From these experiments an empirical rate model was generated of the form:

$$R_U = k \cdot [H_2O_2]_i^{0.5} \cdot [OH^-]_i^{0.5} \quad (24)$$

where R_U is the rate of uranium dissolution in units of mg/(cm²•min) k is an empirical rate constant, and $[H_2O_2]_i$ and $[OH^-]_i$ are the initial hydrogen peroxide and base concentrations, respectively, in mol/L. A plot of rate vs.

¹⁰ As discussed in section 5.1.1., BATAN researchers appeared to have had some difficulty in dissolving an irradiated zinc-barrier target in nitric acid.

$[H_2O_2]_i^{0.5} \cdot [OH^-]_i^{0.5}$ is shown in Fig. 21. As seen in Fig. 21, a fairly linear relationship is present. The slope of the best fit line is equal to the rate constant, $k = 1.26 \text{ mg-L/mol-cm}^2\text{-min}$. Final uranium concentrations as high as 0.35M have been attained in spent dissolver solutions. Uranium precipitates when the peroxide is destroyed.

Pressed compacts of aluminum powder and UO_2 have been prepared. The compacts are similar to the “meat” of a UO_2/Al dispersion target. (Figure 22 shows a micrograph of one of these compacts and a drawing showing how the dispersion plate would look.) Dissolution experiments were completed using these compacts. First the aluminum in the compact was dissolved with a solution of 3M sodium hydroxide and 3M sodium nitrate. The aluminum was easily dissolved, and the remaining UO_2 was free-flowing particulate. The UO_2 particles were washed several times with water to remove any residue from the aluminum dissolution. Finally, the UO_2 was easily dissolved in a solution of 0.5M sodium hydroxide and 5.0M hydrogen peroxide.

To simulate the reaction between the aluminum matrix and UO_2 during irradiation [56]:



several compacts were heat treated under vacuum at 350°C for 6 and 24 hours. For these compacts, the aluminum could also be easily dissolved, and the remaining UO_2 was also a free-flowing particulate that was easily dissolved in alkaline peroxide. This behavior was vastly different and superior to heat-treated uranium silicide particles, which formed a solid monolith that was difficult to dissolve. Results from low-burnup irradiations of these targets showed that (1) fission-product behavior was as expected based on the UO_2 particle size, and (2) the reaction between UO_2 and the aluminum matrix had no effect on dissolution of the uranium. Although the effects of the longer heating were observed by the swelling and near disintegration of the 24-hour compact, the 6- and 24-hour heat-treated compacts gave the same results following irradiation. In both cases, about 8% of fission products dissolved with the aluminum matrix, while less than 0.2% of the ^{239}Np was found in this solution. (Because ^{239}Np is an activation product and not a fission product, it would remain in the uranium particle after formation. Its low concentration in the aluminum dissolver solution is, therefore, indicative of the small amount of uranium that dissolved.)

Two additional UO_2/Al powder dispersion compacts were prepared. These compacts have been formed into miniplates. Cores punched from the miniplate will be used to study the dissolution of clad miniplates in basic peroxide solutions. In addition, these cores will be irradiated to a very low burnup using either the ANL Intense Pulsed Neutron Source (IPNS) or the University of Texas reactor. Irradiation of the targets will allow us to conduct tracer-level experiments of the target dissolution and ^{99}Mo recovery and purification steps.

5.2.2. Target processing

Work on base-side processing for the recovery and purification of ^{99}Mo was begun in 1987 and concluded in 1988 [31,37]. All this work was based on use of the LEU silicide targets and the IRE process [2,3]. Conclusions that can be derived from this work are:

- Silica gel formed from acidification of the spent dissolver solution could be a severe problem to molybdenum recovery but can be controlled by keeping silica's concentration below $\sim 0.1\text{M}$. Even at lower concentrations, soluble silicate decreases the sorption of Mo(VI) onto alumina.
- Uranium precipitation following dissolution by alkaline peroxide must be nearly quantitative so that uranium in solution will not interfere with Mo(VI) sorption on alumina. This means that peroxide destruction must be complete, allowing uranium hydroxides to precipitate.

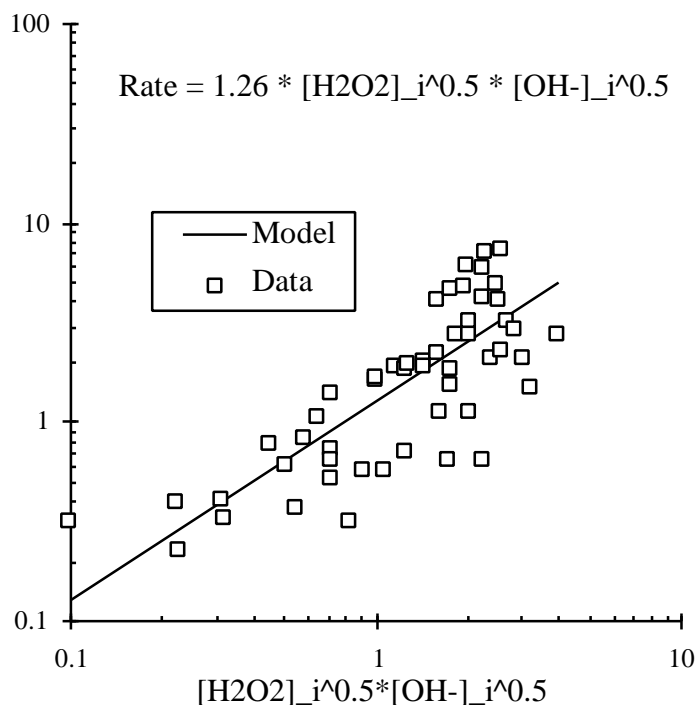


FIG. 21. Rate data and model fit for the dissolution of UO₂ in alkaline peroxide. Initial temperature of reagents was 50°C.

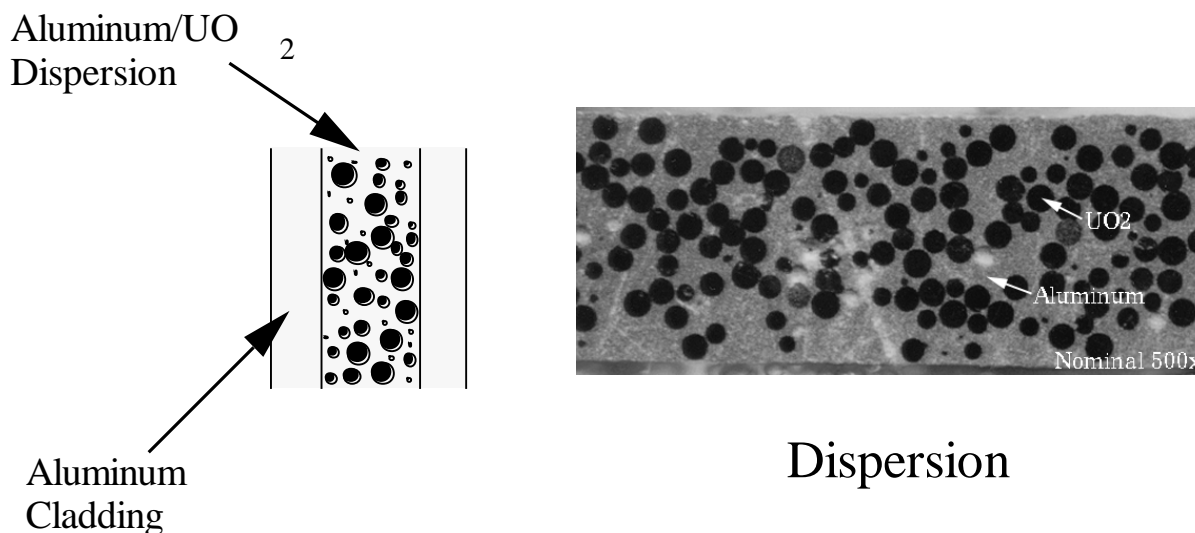


FIG. 22. Illustration of a UO₂/Al-dispersion plate and micrograph of a UO₂/Al-dispersion compact.

- In spite of these two potential problems, experiments where U₃Si₂ miniplates were irradiated to low burnup showed that the LEU target would give satisfactory performance using the modified dissolution followed by the standard HEU process. Molybdenum recovery was high, and purification was as expected when the two-step dissolution was followed by acidification and molybdenum sorption on an alumina column.

Because the spent dissolver solutions of LEU foil or oxide targets will not contain significant concentrations of silica, the major concern of U₃Si₂ processing will be eliminated. Because of the need for zinc fission barriers, the feed to the primary recovery step from foil target will contain significant quantities of zinc, which may affect the recovery. However, it will not contain the extremely high concentrations of aluminum found in the plate-type targets.

In the IRE process, three 4.2-g uranium targets are dissolved in 1.6 L of base. This produces a spent dissolver solution near saturation in NaAlO_2 (2.1M). The volume of the feed to the primary molybdenum-recovery step would be increased significantly by two of the three LEU targets. With the IRE process,

- Dissolution of a silicide target (with 5 times the uranium) would require about twice the solution volume due to its being a two-step process. The volume to dissolve the aluminum would be the same for the HEU and LEU-silicide targets. The uranium silicide could be dissolved in about 50% of that volume. Rinse solutions would account for the remaining volume. The feed to the primary recovery step might need to be increased further to keep silica in solution.
- Dissolution of two LEU oxide targets (each containing about three times the amount of uranium) would generate about three times the volume of the HEU target. A two-step process is also required for their dissolution. Twice the aluminum would require twice the volume to dissolve it. Dissolution of the UO_2 would require about 50% of that volume, with the remainder due to rinse solutions.
- Dissolution of the LEU-foil target would require the same or less volume than the HEU target to dissolve the Zn-coated LEU foil. Approximately 50% of the HEU-target volume would be to dissolve the uranium, another 20% to dissolve the zinc, and the remainder for rinse solutions.

Once conditions for LEU target dissolution are firm, we will need to reinvestigate the effects of these compositional and volume differences on the primary molybdenum-recovery step.

6. PLANNED R&D ACTIVITIES

We will continue our development activities on both acid- and base-side processes. The LEU-modified Cintichem process needs to be demonstrated on a commercial scale before it can be accepted. Demonstrations are planned at both the Indonesian PUSPIPTEK facility and Sandia National Laboratories. Sandia will actively take part in obtaining FDA approval for LEU Cintichem-type targets, while BATAN will assist in developing economic factors related to the conversion to LEU.

Target fabrication for LEU foils still needs to be optimized in terms of both (1) reproducibly successful disassembly following irradiation and (2) ease of fabrication. The effectiveness of electrodeposited fission barriers must also be demonstrated.

A commercial partner must be acquired for the base-side processing. The partner will assist in (1) refining our design of the dissolution system, (2) focusing our development activities, and (3) demonstrating processing of irradiated full-scale targets.

The RERTR Program wishes to work with all current and future producers of ^{99}Mo to assure that, ultimately, no HEU is needed for ^{99}Mo production.

7. CONCLUSIONS

Conversion of fission-product ^{99}Mo production from HEU to LEU has been proven technically feasible. However, full-scale demonstrations and partnerships with producers world-wide are needed to (1) complete development activities, (2) clarify economic disincentives to conversion, and (3) gain acceptance of the targets, processes, and ^{99}Mo product from LEU. The U.S. Department of Energy and the RERTR Program are committed to eliminating HEU as reactor fuel and as target material for radioisotope production.

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