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ABSTRACT

Most of the world's supply of ^{99m}Tc for medical purposes is currently produced from ^{99}Mo derived from the fissioning of high enriched uranium (HEU). Substitution of low enriched uranium (LEU) silicide fuel for the HEU alloy and aluminide fuels used in current target designs will allow equivalent ^{99}Mo yields with no change in target geometries. Substitution of uranium metal for uranium oxide films in other target designs will also allow the substitution of LEU for HEU.

Efforts performed in 1989 focused on (1) fabrication of a uranium metal target by Hot Isostatic Pressing uranium metal foil to zirconium, (2) experimental investigation of the dissolution step for U_3Si_2 targets, allowing us to present a conceptual design for the dissolution process and equipment, and (3) investigation of the procedures used to reclaim irradiated uranium from Mo-production targets, allowing us to further analyze the waste and by-product problems associated with the substitution of LEU for HEU.

INTRODUCTION

Technetium-99m for medical purposes is a decay product of ^{99}Mo, which is produced in research reactors from the fissioning of ^{235}U or from neutron capture in ^{98}Mo. This continuing effort is related only to fission-product ^{99}Mo. Presently, ^{99}Mo is produced using a variety of

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target designs that contain HEU (~93% ^{235}U). These designs include fuel plates,[1-4] rods,[5] and cylinders with a film of UO_2 electroplated on the inside surface.[6,7]

This paper presents the results of our continuing investigations on the consequences of substituting LEU for HEU on target preparation and processing. Earlier reports have discussed the substitution of electrodeposited uranium films for uranium oxide films in fabricating cylindrical targets[8-10] and effects on irradiated-target processing caused by uranium-metal substitution for UO_2[8] and U_3Si_2 substitution for U-Al alloy or aluminide fuels by basic[9,11] and acidic[11] dissolution. We have extended our investigation of uranium-metal target fabrication to include HIPping (Hot Isostatic Pressing) uranium metal foil onto zirconium. In the area of target processing, we have continued our studies of basic dissolution of uranium silicide targets. A conceptual design of the equipment and procedure for this process step are described. An important concern in the substitution of LEU for HEU is that approximately six times the uranium must be processed and recovered for the same ^{99}Mo yield. We have performed a literature review of possible uranium-recovery technologies and will report in this paper how these processes and the associated equipment needs will be affected by the larger amounts of uranium that must be recovered.

FABRICATION OF LEU METAL TARGETS

A current design for an HEU target is a hollow cylindrical can with a thin layer of UO_2 coated to the inside wall. Molybdenum recovery is accomplished by adding an acid solution into the target cylinder that dissolves the irradiated UO_2 from the cylinder wall, removing the concentrated solution from the cylinder, and processing the solution to recover the ^{99}Mo from the uranium and other fission products in solution.[6,7]

Because the UO_2 surface density is, in some cases, close to the current HEU target's practical fabrication limit, a new target design and/or a much denser film material is required for the larger amounts of uranium necessary for an LEU target.[8] To this end, our efforts have concentrated in past years on developing a cylindrical target with a thin layer of electrodeposited uranium metal on the inside surface.[8-10] During this year, other methods have been considered. After review of the possible fabrication techniques, HIPping was selected to be used in a first attempt to bond a thin uranium foil to a support structure of Zircaloy-2 tubing. An experimental target assembly has been designed to test the proof-of-concept. The components of the assembly are shown schematically in Fig. 1. Part A outlines the support mandrel for the uranium foil target, and Part B defines an outer pressure distribution sleeve for the HIPping operation. A flow chart of the fabrication steps for the target is shown in Fig. 2. Processes relating to the cleaning, assembly, electron-beam welding, and HIPping (Fig. 2) are adapted from those used at ANL for the production of Zr-clad U-metal targets for the Intense Pulsed Neutron Source (IPNS).

All of the necessary hardware, including the uranium foil, are currently ready for cleaning and assembly. The assembled units are to be electron-beam welded peripherally around the top and bottom to create

the hermetic seal required for successful HIP bonding. With the concept illustrated in Fig. 1, the inner Zr core would have to be machined away after irradiation in order to expose the U foil to a dissolving solution. This is clearly not an economically sound practice for production targets. The geometry presented here is only intended to demonstrate proof-of-concept. Subsequent design iterations will require a tubular inner core or liner which is configured in such a way as to be easily removed. Further, provisions need to be made for adding top and bottom covers much like some of the production targets in use today. Such design changes will be incorporated into the hardware for future HIP experiments.

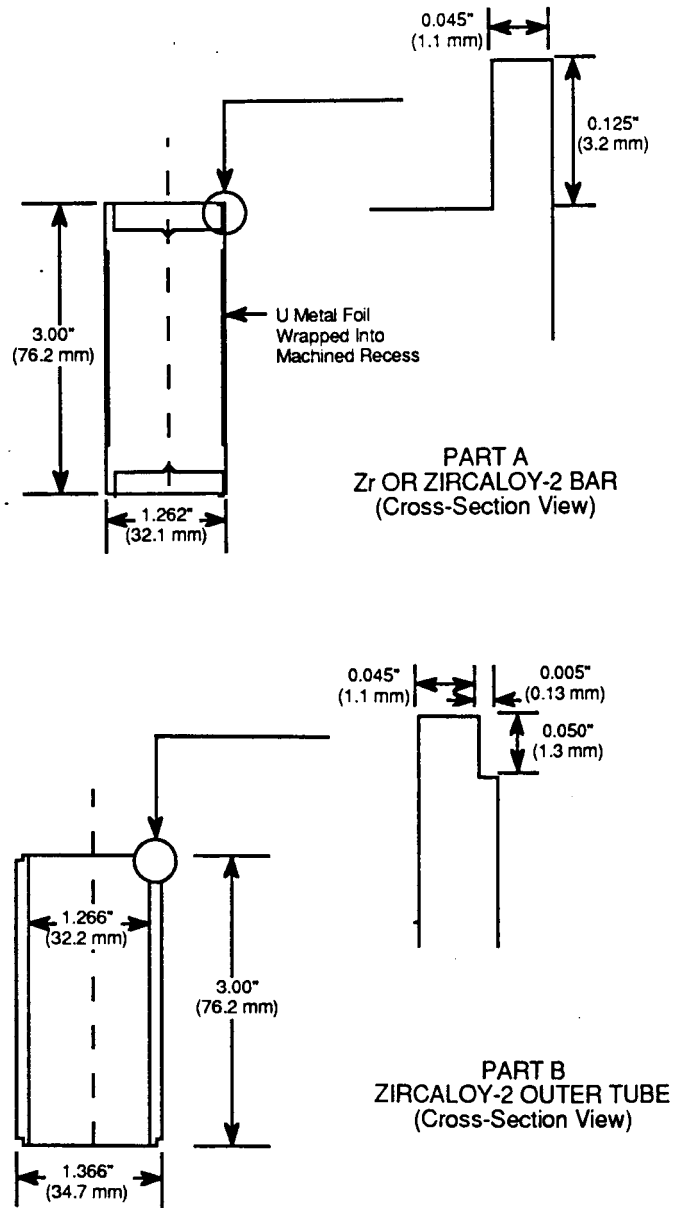

Fig. 1. Components for HIP Bonding U-Metal Foil to Zircaloy-2 Tubing

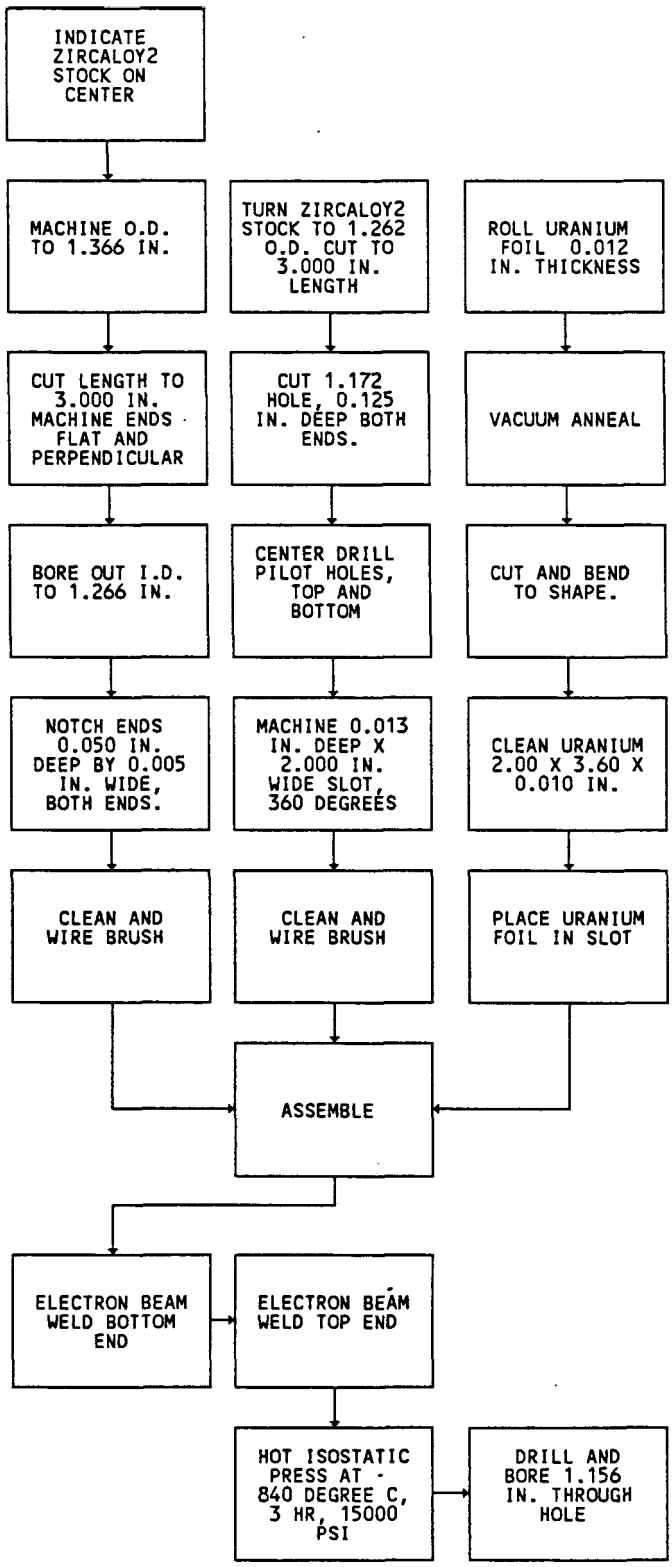

Fig. 2. Flow Chart for Fabrication of Uranium-Metal Targets

Other procedures for bonding U metal foil to the inside of Zircaloy-2 will also be addressed. An alternative procedure, for example, may be to combine appropriate materials in a configuration such

that, upon heating in a vacuum, the differential thermal expansion properties of the materials will generate the pressure required to produce a uranium/Zircaloy-2 bond.

BASIC DISSOLUTION OF U_3Si_2 TARGETS - EXPERIMENTAL RESULTS

The foremost benefit of using basic digestion of irradiated uranium targets for ^{99}Mo production is the high degree of separation achieved during this step. As ^{99}Mo is dissolved during target digestion, it is purified from U, Np, Pu, and many of the fission products that have insoluble hydroxide salts. A second benefit is that radioxenon can be collected separately from radioiodine (recovered during acidification). Although these benefits will remain when LEU-silicide fuel is substituted for HEU-aluminide fuel, the LEU dissolution will be more complex.

At the 1988 RERTR meeting,[11] we discussed results of dissolution of low-burnup LEU-silicide targets. Based on these results, we 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 using 3M NaOH solution. During this step, many of the alloying elements from the cladding (in our case, 6061 Al) would precipitate as hydroxides. The U_3Si_2 could then be dissolved separately with basic hydrogen peroxide. On heating the peroxide solution, UO_3 would precipitate and could be separated with many of the fission products from iodine and molybdenum.

This two-step process would be clearly advantageous if (1) the concentrated aluminum solution from the first step is handled separately, (2) the solution resulting from dissolving the uranium silicide contains all the fission products, and (3) only the silicide solution needs to be treated for recovery of iodine and molybdenum. Results of 1988 work, however, indicated that loss of ^{99}Mo from the fuel particles due to fission recoil is substantial, and that the two-step dissolution must be modified to recover the molybdenum lost to the decladding solution. Results of this year's study on the dissolution are discussed below, followed by our conceptual design of the procedure and equipment needed for dissolution of uranium silicide targets for ^{99}Mo production.

Mo-99 Loss Due to Fission Recoil

Loss of ^{99}Mo to the first dissolution step of an irradiated U_3Si_2 miniplate occurs when fission energy carries the fission products out of the fuel-particle boundaries into the surrounding aluminum. The measured 19% experimental loss of ^{99}Mo was nearly the same as the calculated loss of 20%, assuming a particle size distribution of 0 to 150 μm.[11] To verify this effect, three compacts were irradiated in the ANL Janus reactor. Each compact was prepared with sieved U_3Si_2 particles and aluminum powder; the size distribution of U_3Si_2 in each compact is shown in Table 1. After irradiation, each compact was digested separately in 3M NaOH. The resultant solutions (including washes of the silicide particles containing small amounts of black precipitate) were counted for gamma activities. They were subsequently

filtered through Whatman 41 paper and recounted. The U_3Si_2 particles were dissolved in 1.5M NaOH/15%H_2O_2 and also gamma counted.

Table 1. Calculated and Experimental Loss of ^{99}Mo, ^{131}I, and ^{239}Np to Sodium Hydroxide Dissolving Solution

U_3Si_2 Particle Size Range (μm)[a]	Calc. Loss (%)[b] Recoil to Al Matrix			Exp. Loss (%) to Filtered Al Fraction[c]		
	^{99}Mo	^{131}I	^{239}Np	^{99}Mo	^{131}I	^{239}Np
125-150 (138)	8.8	7.2	0	10.4	6.7	0.7
73-88 (81)	15.0	12.2	0	18.2	12.7	1.7
40-45 (43)	28.3	23.0	0	30.1	19.8	2.2

[a] Sphere diameters for which the losses were calculated are in parentheses.

[b] Assumes a fission fragment range of 8.1 μm for ^{99}Mo and 6.6 μm for ^{131}I.

[c] The concentrations of ^{99}Mo and ^{131}I were the same before and after filtering. The loss of ^{239}Np to the unfiltered solution was 4% for all three fractions.

Calculations of ^{99}Mo loss from the U_3Si_2 particles into the aluminum matrix are based on the following equation:[12]

$$f = 0.5\ (3\lambda/D - \lambda^3/D^3)$$

where f is the fraction of fission products,
D is the diameter of the particle (sphere), and
λ is the fission fragment range, based on data from Frank[13] and Northcliffe and Schilling.[14]

The calculated losses for ^{99}Mo and ^{131}I are in good agreement with experimental values (Table 1). Certainly, there is a strong dependence of ^{99}Mo loss on the U_3Si_2 particle size.

The behavior of ^{239}Np in these samples should be indicative of that of uranium and other species that are not fission products. Because ^{239}Np is not formed by fission, it does not have the recoil energy necessary to release it from the fuel particles and can be used as a marker for the behavior of other materials. The loss of neptunium to all three dissolver solutions was 4%. Filtering the solutions through a rather coarse filter paper (designed to retain 20-25 μm particles) removed the larger fines. The amount of true fines left in the solution after filtration appears to be inversely proportional to the average particle size of the sieved fractions.

Rates of U_3Si_2 Dissolution by NaOH Solutions

Another way to interpret the ^{239}Np results is that some dissolution of the fuel particles is occurring during dissolution of the aluminum. To explore this possibility, experiments were run to (1) verify results

of earlier experiments of the low solubility of the U_3Si_2 in hot sodium hydroxide solutions, (2) measure the effect on dissolution rate of the particle size of the uranium silicide, and (3) measure the effect on dissolution rate of the concentration of sodium hydroxide. In these experiments, 0.5 g of uranium silicide particles with diameters in the ranges 40-45 μm, 73-88 μm, and 125-150 μm were heated at 70°C with 30 mL of a basic solution. The base was either 3M or 6M sodium hydroxide; some solutions also contained 0.2M sodium carbonate. (Sodium carbonate would act to increase the solubility of uranium(VI) in the NaOH solution.) Results of this study, which are illustrated in Fig. 3 and 4, are:

(1) the rate of U_3Si_2 dissolution was very low, and dissolution of the fuel by the basic solution used to dissolve the cladding material will be only a few tenths of a percent at most;

(2) increasing the concentration of sodium hydroxide increased the extent of fuel dissolution, but, even with 6M sodium hydroxide, dissolution of the fuel was minimal; and

(3) the effect of particle size on the rate of uranium silicide dissolution was imperceptible within experimental uncertainties.

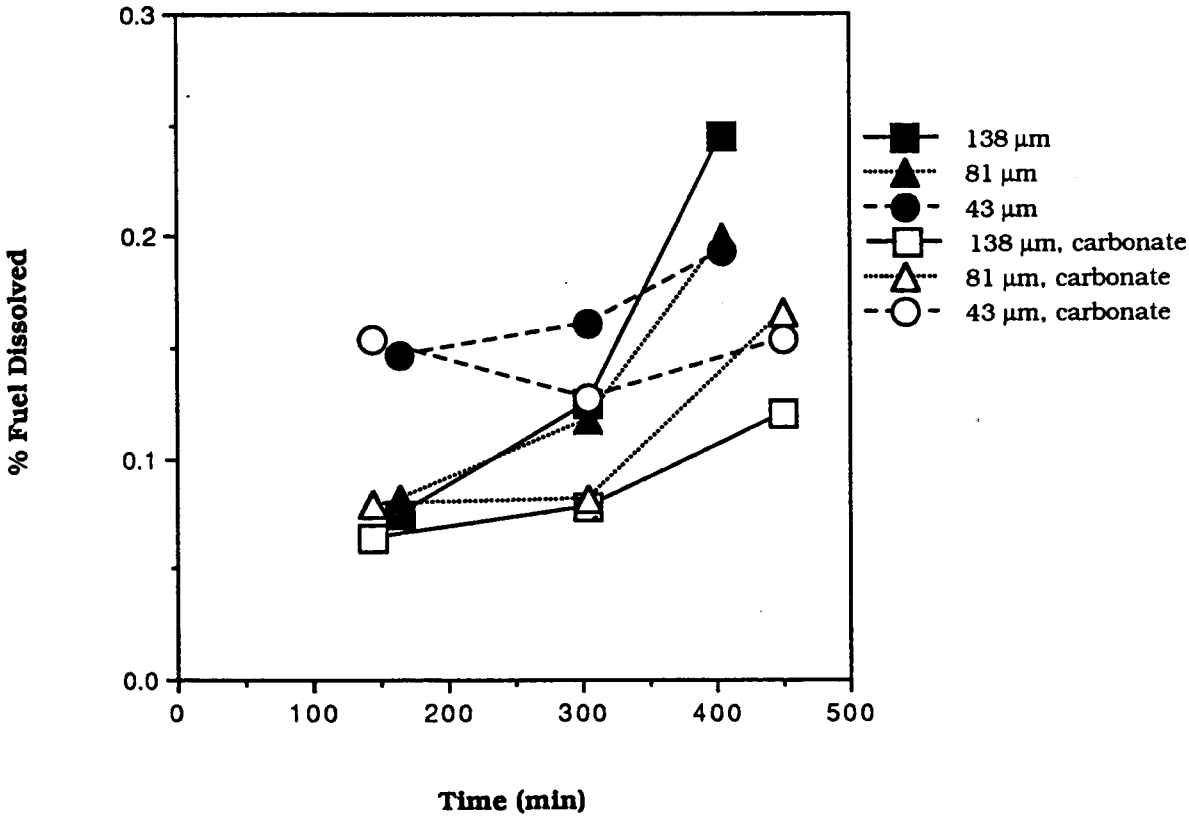

Fig. 3. Dissolution of Uranium Silicide by 3M Sodium Hydroxide at 70°C vs Time and Particle Size

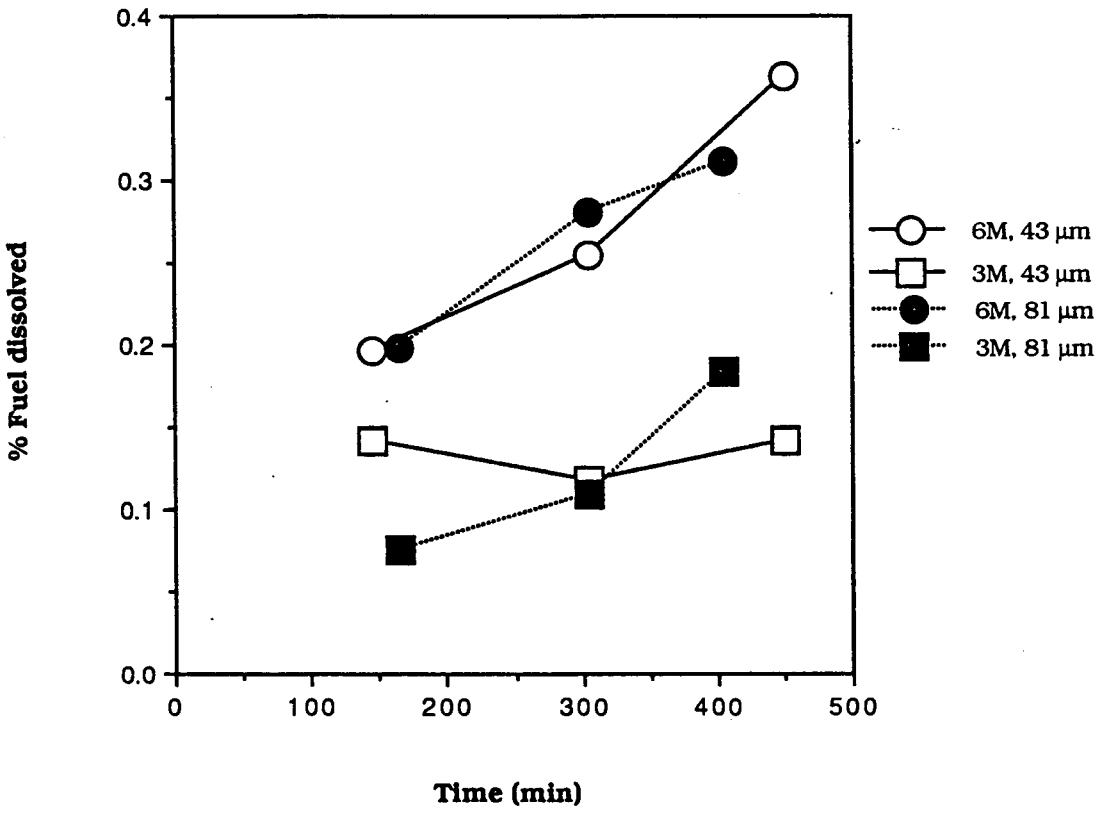

Fig. 4. Dissolution of Uranium Silicide Particles (43 μm and 81 μm) by 3M and 6M Sodium Hydroxide at 70°C

Dissolution of an Unirradiated Target

Because of the loss of ^{99}Mo from the targets during dissolution of the aluminum cladding and matrix, we looked at adding 30% hydrogen peroxide directly to the basic solution to dissolve the fuel. This addition was made after all the aluminum in the target had been dissolved. The presence of the precipitated hydroxides from the aluminum-alloy cladding acted to catalyze the autodestruction of the hydrogen peroxide, forming large quantities of gas (presumedly O_2) with no peroxide reaching the bottom of the beaker to dissolve the U_3Si_2. This result leads to the conclusion that a one-step process for dissolving the complete target using hydrogen peroxide is not feasible; the precipitate must be removed before uranium silicide can be dissolved.

BASIC DISSOLUTION OF U_3Si_2 TARGETS--CONCEPTUAL DESIGN

The experimental results discussed above lead to the following conclusions:

- ^{99}Mo loss due to fission recoil is likely to represent too high an economic penalty to be ignored.

- The dissolution/digestion rate of U_3Si_2 is too low in basic solution 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.

Based on these conclusions, the conceptual dissolver system shown in Figs. 5 and 6 was developed.

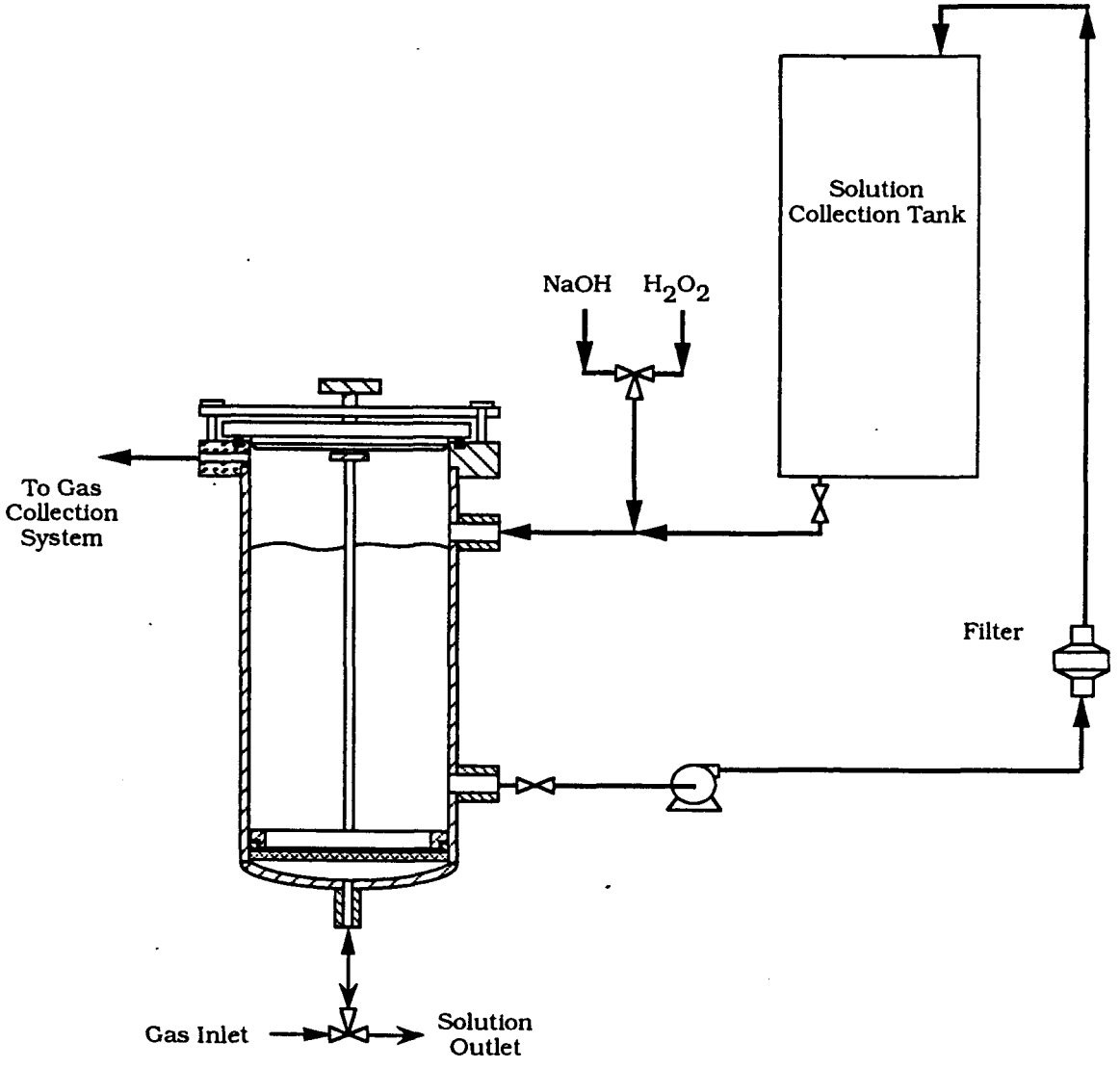

Fig. 5. Schematic of the U_3Si_2-Target Dissolver System

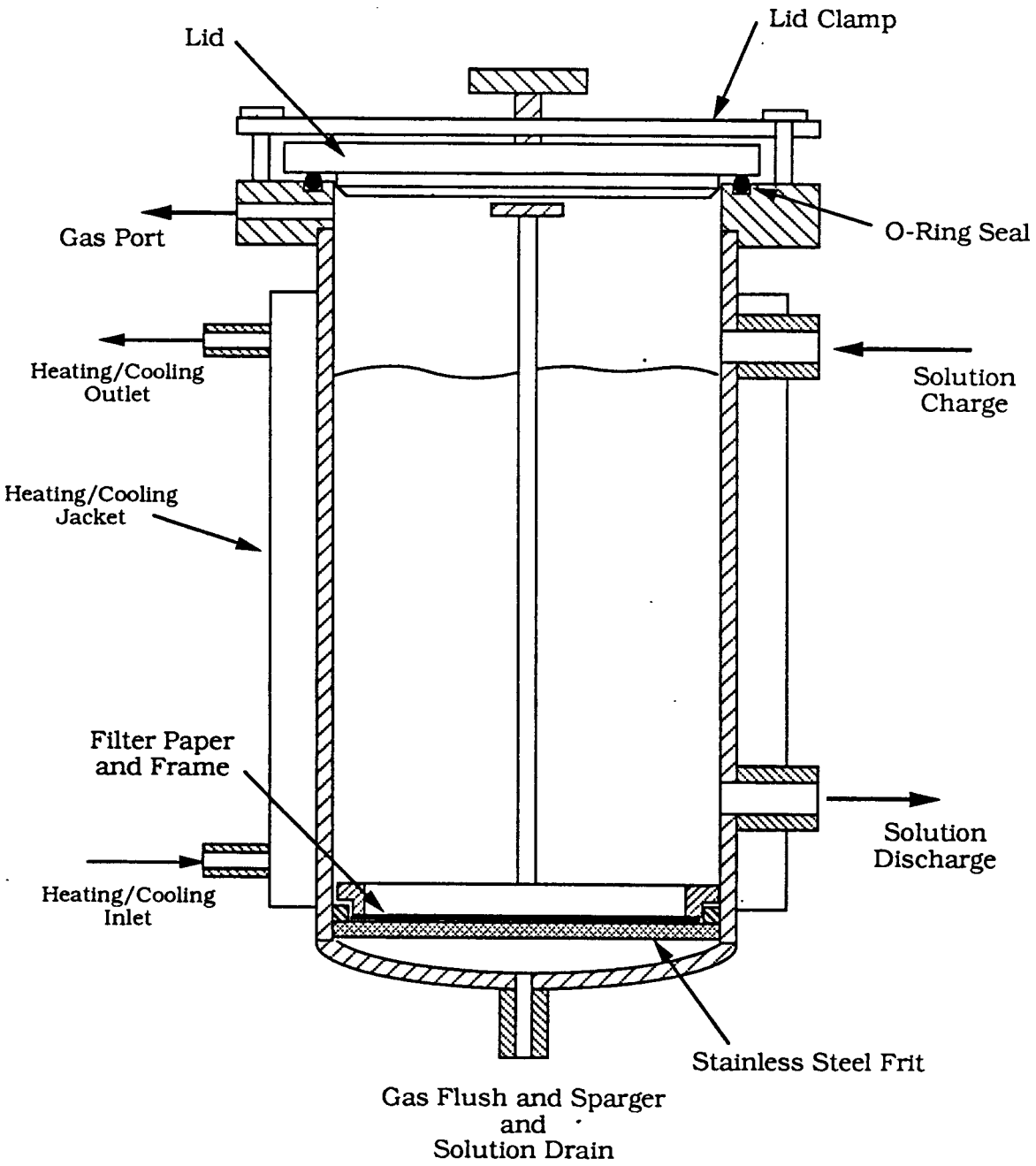

Fig. 6. Schematic of the U_3Si_2-Target Dissolver

With this arrangement, the irradiated target(s) will be charged into the dissolver through its removable lid. A solution of ~3M sodium hydroxide (perhaps with $NaNO_3$ to limit H_2 production) will then be added to the dissolver through a port in the dissolver's side. (The dissolver can be cooled or heated as needed by a thermostated jacket surrounding it.) A gas sparge at the bottom of the reactor may be used to purge gaseous fission products and mix the contents. The cladding and the aluminum powder in the fuel meat will dissolve, leaving a flocculent precipitate and the dense uranium silicide particles. At the completion of this step, the basic aluminum solution and the flocculent will be pumped from the dissolver, and the dense fuel particles will be left

behind. This slurry will be pumped through a filter (or a continuous centrifuge) as the solution is stored in a collection tank. Part of the solution will be returned to the dissolver to act as a wash for removing the rest of the precipitates from the silicide particles. After this washing operation is completed, a fraction of the basic aluminum solution will be returned to the dissolver, and a 30% H_2O_2 solution will be administered dropwise to the dissolver as the uranium silicide is dissolved. After dissolution of the U_2Si_2, the dissolver will be heated to destroy the excess peroxide and, thus, to precipitate UO_3. The solution is then removed from the dissolver through the gas sparge outlet, as the UO_3 and base-precipitated fission products are separated by filtration. The basic aluminum solution will be passed into the dissolver and through the filtered UO_3 before being combined with the earlier effluent. The solution and the uranium precipitate will then be treated in the same manner as is currently done for uranium aluminide targets.

RECOVERY OF BY-PRODUCT URANIUM

In comparison to basic dissolution of U_3Si_2, when irradiated uranium oxide, aluminum alloy, or metal is dissolved in acid, the entire feed material enters solutions. This is followed by a separation of ^{99}Mo from the solution containing uranium and other fission products. The waste from the ^{99}Mo-recovery step is essentially the original solution containing the uranium, plutonium, and the bulk of the fission products, less the ^{99}Mo. Subsequent purification steps on the separated ^{99}Mo should produce small volumes of low activity waste. The uranium remaining in the dissolver solution is valuable and should be recovered. In some cases, it could be packaged and sent to a reprocessing facility.

After the ^{99}Mo has been removed from the solution, the residual dissolver solution is handled to recover the uranium. Based on the reference HEU oxide and LEU metal targets discussed in an earlier report,[8] the LEU metal target will require approximately six times the amount of uranium for the same ^{99}Mo yield and, therefore, six times the volume of waste solution will be generated. The recovery of the ^{99}Mo requires immediate processing of the target to forestall undue losses of product. However, recovery of the uranium has no time constraint, and it may be advantageous to allow some radioactive decay before processing.

There are several techniques for recovering the uranium.[15-18] The uranium may be precipitated from the solution as the peroxide[15,16] or the diuranate,[15,17] or it may be retrieved by drying and/or denitrating the solution in a batch denitrator.[15,18] When the uranium is precipitated from the target solution, the bulk of the associated radioactivity remains in solution and creates a radioactive waste that must be disposed of. On the other hand, if the uranium solution is evaporated to dryness, the bulk of the radioactivity remains with the uranium and can be returned with the uranium to a reprocessing facility.

The impact of handling the increased volume of solution will depend upon the equipment size and the cycle times. For example, if one week's accumulation of uranium waste solution is processed in one eight-hour day at full capacity, the increased volume of solution could be

accommodated by running the equipment six days a week, with the added cost due to the increased operating time. If the uranium recovery requires operation for five days at eight hours a day, larger size equipment would have to be installed to handle the increased volume of solution.

With the larger amount of ^{238}U in LEU targets, the plutonium content of the reference LEU target is approximately 26 times the amount in the HEU target./8/ Laboratory experiments have demonstrated that ^{99}Mo can be adequately separated from Pu. If drying/denitrating the uranyl nitrate solution is chosen for uranium recovery, plutonium will remain with the uranium and will be returned with it to the reprocessing facility.

SUMMARY

Work has been performed in three areas this year to facilitate the transition from HEU to LEU in targets for ^{99}Mo production. The first area, fabrication of a uranium metal target by HIPping uranium foil to the inner wall of a cylindrical Zircaloy tube, is in the conceptual-design and proof-of-principle stage, and additional work must be done to produce a functional target. Other means of producing this target are also being pursued.

The second area, development of a procedure for basic dissolution and processing of LEU silicide targets, is ready for demonstration on a full-size, full-burnup target. A conceptual design of the dissolver has been completed, and plans are being made for a demonstration in 1990.

The third area, a reinvestigation of the effects of LEU substitution on uranium recovery from target processing, corroborates earlier statements./8/ Because approximately six times the amount of uranium will need to be processed and recovered than for current HEU targets, there will be an economic penalty due to the increased amount of uranium recovery. Depending on the method used to recover this uranium, manpower costs could be larger, or, if equipment and facilities are already highly utilized, capital expenditures must also be made to handle the increased load.

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