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*R. R. Jaeger, S. T. Cohen, E. E. Egleston and W. R. Deal*

November 18, 1972


*AEC Research and Development Report*

**MOUND LABORATORY**
Miamisburg, Ohio
operated by

**MONSANTO RESEARCH CORPORATION**
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**U. S. ATOMIC ENERGY COMMISSION**
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## *NOTICE*



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## ABSTRACT

A process for coating $^{238}PuO_2$ particles with molybdenum is described in detail. The process is based on the hydrogen reduction of $MoCl_5$ in a fluid-bed reactor. $MoCl_5$ was chosen over $MoF_6$ because of the increased neutron flux which results from any fluoride impurity due to the $^{19}F(\alpha,n)^{22}Na$ reaction.

## INTRODUCTION

Mound Laboratory is engaged in the production of $^{238}PuO_2$ cermet fuel discs for use in thermoelectric generators. The material for the cermet discs is prepared by coating individual particles of $^{238}PuO_2$ with Mo in a fluid-bed reactor by the hydrogen reduction of $MoCl_5$. The coated particles are then vacuum hot pressed into the desired configuration.

## APPARATUS

The apparatus for the $MoCl_5$-$H_2$ process is illustrated in Figure 1. The vaporizer is five inches in diameter by six inches high (inside measurements). It is usually charged with two or three pounds of $MoCl_5$. The initial vaporizer was made of nickel-plated copper and is still in operation after one year of service. For convenience in handling the $MoCl_5$, a stainless steel beaker is used to hold the $MoCl_5$ charge inside the vaporizer. All lines between the vaporizer and fluid-bed are heated to 200-300°C by a heating tape. The argon to the vaporizer and the $H_2$ line are preheated to vaporizer temperature.

The fluid-bed reactor is made of 1.4 in. i.d. monel pipe and is routinely used to coat 200-230 g batches at deposition rates up to 0.7 g/min. The exact dimensions of the fluid-bed system are given in Figures 2, 3 and 4. The fluid-bed is heated by a two-stage furnace. Each stage is separately controlled.

The effluent gases exhaust from the fluid-bed into a copper-wool trap which is water cooled. This trap removes any solid material blown over during the operation, and also acts as a condenser for any unreacted $MoCl_5$. The copper-wool trap is followed by a scrubber to remove the HCl from the gas stream. Success was realized using any of the following as a scrubbing medium: water, molecular sieves, or soda-lime. Currently, soda-lime is preferred because of its ease of handling and long life.

After the run the coated particles are aspirated from the fluid-bed (Figure 5).

The entire apparatus is contained in an alpha fuels glovebox which is constantly purged with argon. The glovebox is also equipped with a combustible gas detector.

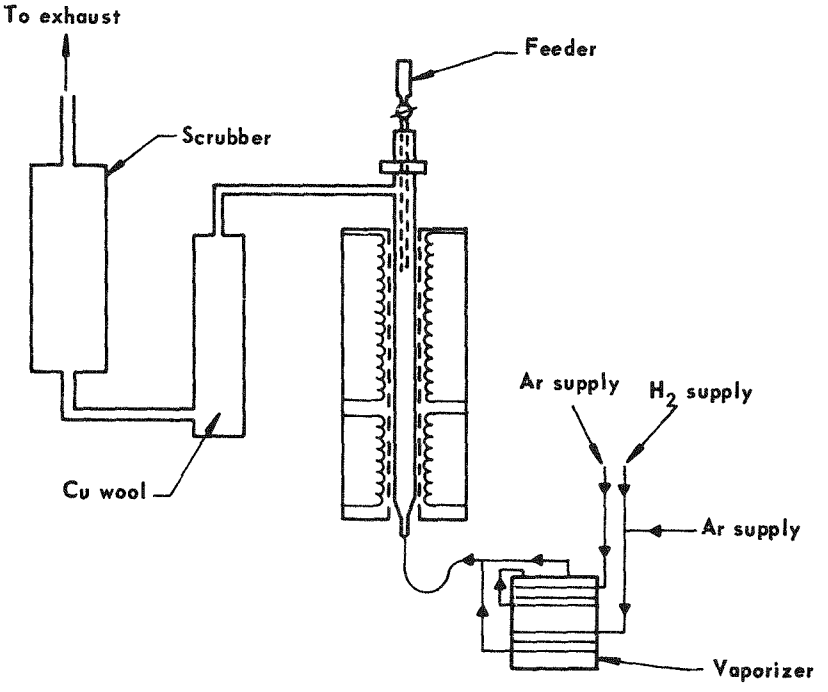


FIGURE 1 - Schematic of $MoCl_5$ chemical vapor deposition apparatus.

## COATING PARAMETERS

The following conditions are typical for a given run:

| | |
|---|---|
| Weight of substrate $PuO_2$ | 200 g |
| Temperature of fluid-bed | 800°C |
| Temperature of vaporizer | 220°C |
| Hydrogen flow through fluid bed | 12 $ft^3$/hr |
| Argon flow through vaporizer | 4 $ft^3$/hr |
| Size of particles | 105-177 μm |
| Rate of deposition | 0.5 /min |
| Efficiency | >80% |

A deposition temperature of 700°C was used initially, and numerous batches were successfully coated at that temperature. However, from time to time, a few samples were observed to contain a definite third phase between the molybdenum and $^{238}PuO_2$ (Figure 6 vs. Figure 7). Electron microprobe studies[1] have shown this third phase to be a plutonium chloride species. Apparently, the $MoCl_5$ and/or HCl (reaction product) reacts in some cases with the $^{238}PuO_2$ before the surface of the $^{238}PuO_2$ is protected with a layer of deposited Mo. The deposition temperature was raised to 800°C to promote the $H_2$ reduction of $MoCl_5$, and thus, minimize the exposure time of the $PuO_2$ surface to chloride attack.

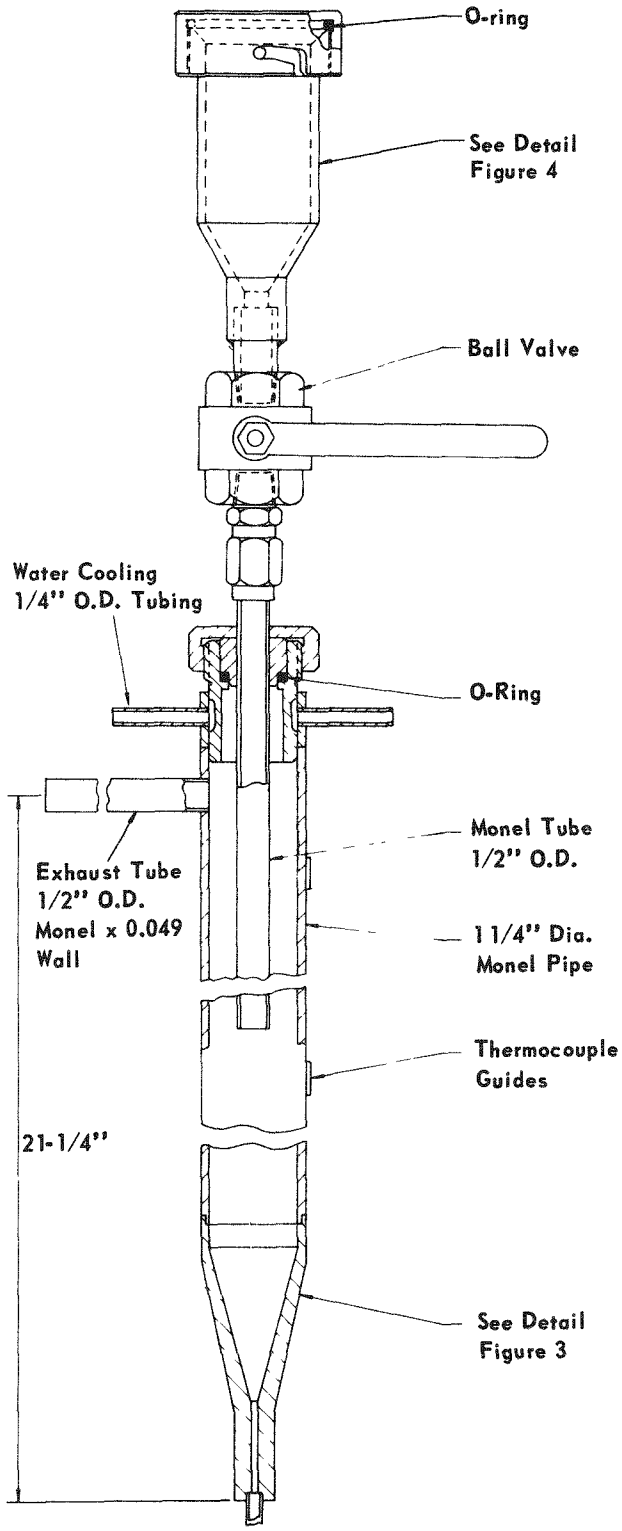


FIGURE 2 - Monel fluid-bed assembly for coating 200 g batches of $^{238}PuO_2$ by the $H_2$ reduction of $MoCl_5$.

In addition, it is important to assure that the substrate is at operating temperature (800°C) before it is exposed to the chloride. Thus, the fluidizing gas flow ($H_2$ + Ar) is established with the argon bypassing the vaporizer ($MoCl_5$ flow off). The $^{238}PuO_2$ particles are then dropped in from the feeder and allowed to reach operating temperature. The argon flow is then switched to route through the vaporizer ($MoCl_5$ flow on).

## OPERATION OF SYSTEM

1. The glovebox is checked for air leaks by closing all supply and exhaust lines. The exhaust valve is opened until a negative pressure of 1.5 to 2.0 in. of water is obtained. The exhaust valve is then closed. The glovebox should maintain this negative pressure for at least one minute.

2. The argon purge through the glovebox is adjusted to a minimum of 10 $ft^3$/min.

3. The combustible gas detector is checked to be sure it is operational.

4. The controller for the vaporizer heating mantle is turned on and set at 220°C. The controller for the heating tape on the $MoCl_5$ transport line is turned on and set at 200 to 300°C.

5. The argon flow through the fluid-bed reactor is adjusted to 10-15 $ft^3$/hr.

6. The controllers for the two-stage, fluid-bed, reactor furnace are activated and allowed to reach operating temperature of 800°C.

7. The previously weighed substrate material is transferred to the hopper (feeder) on the fluid-bed.

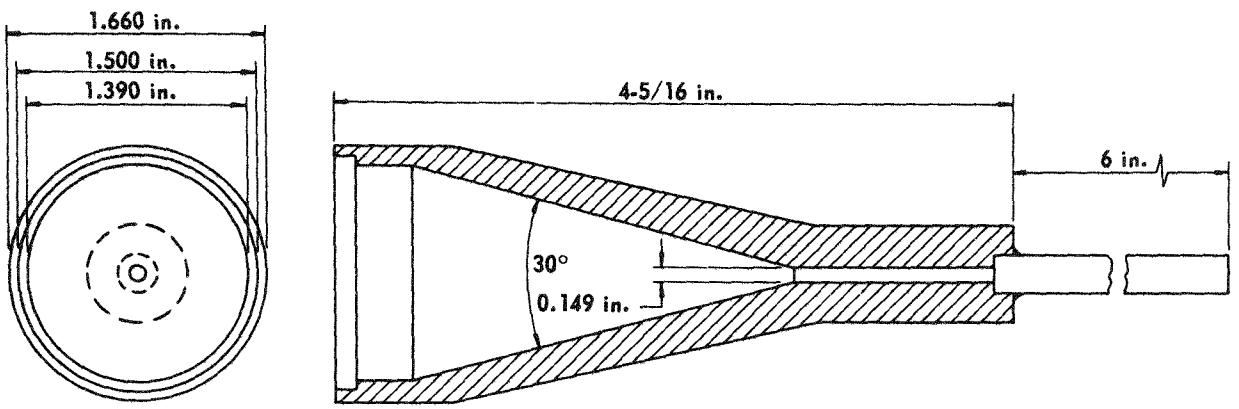


FIGURE 3 - Details of cone section of fluid-bed assembly.

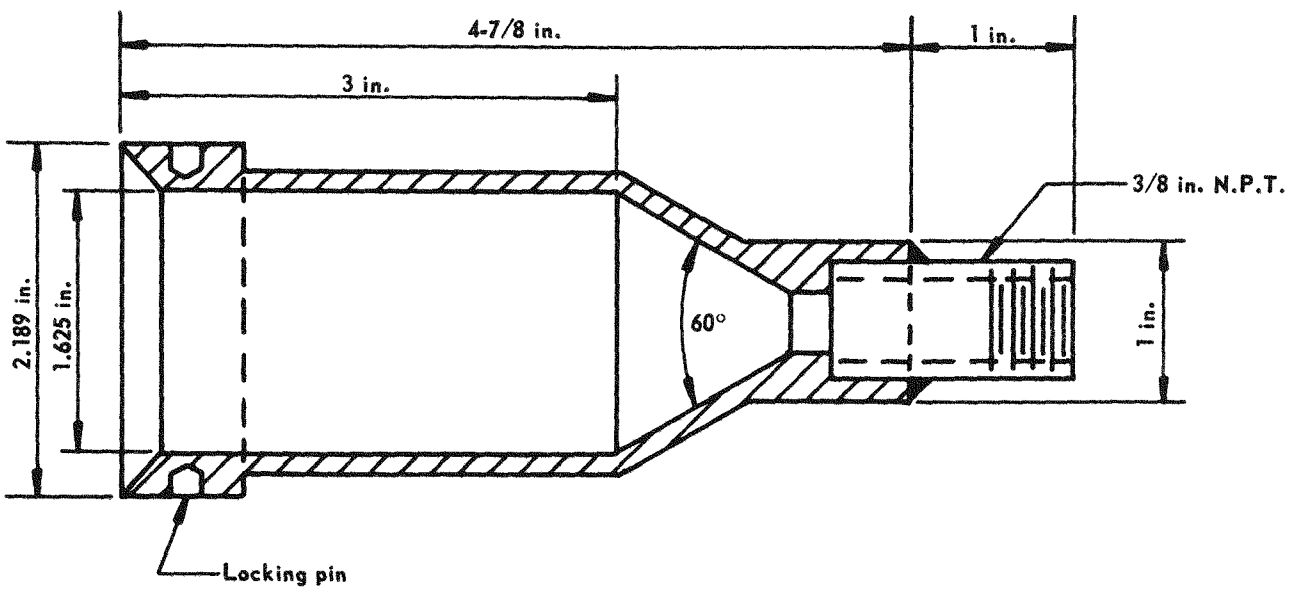


FIGURE 4 - Details of feeder for fluid-bed assembly.

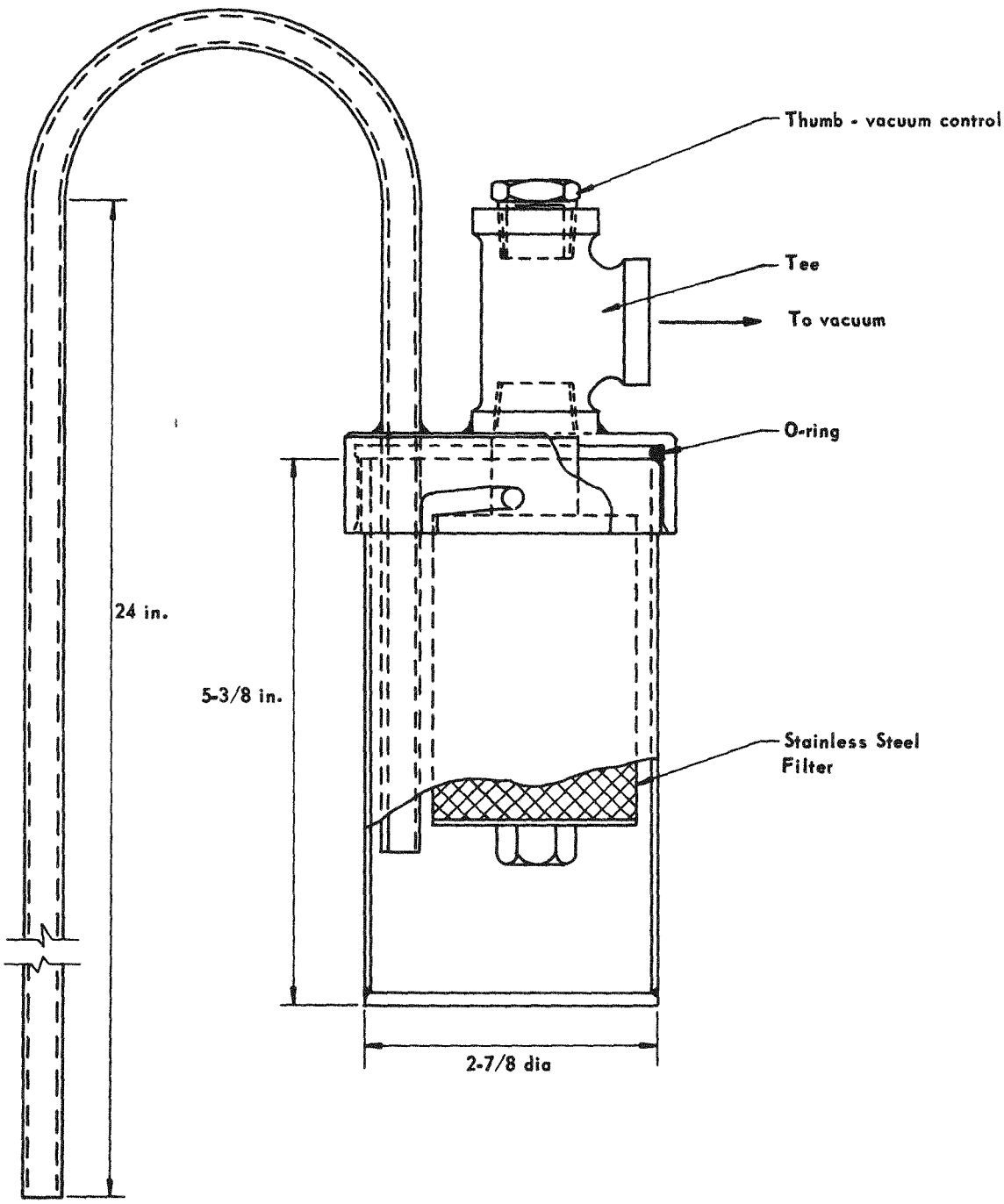


FIGURE 5 - Aspirator for removing coated particles from fluid-bed.

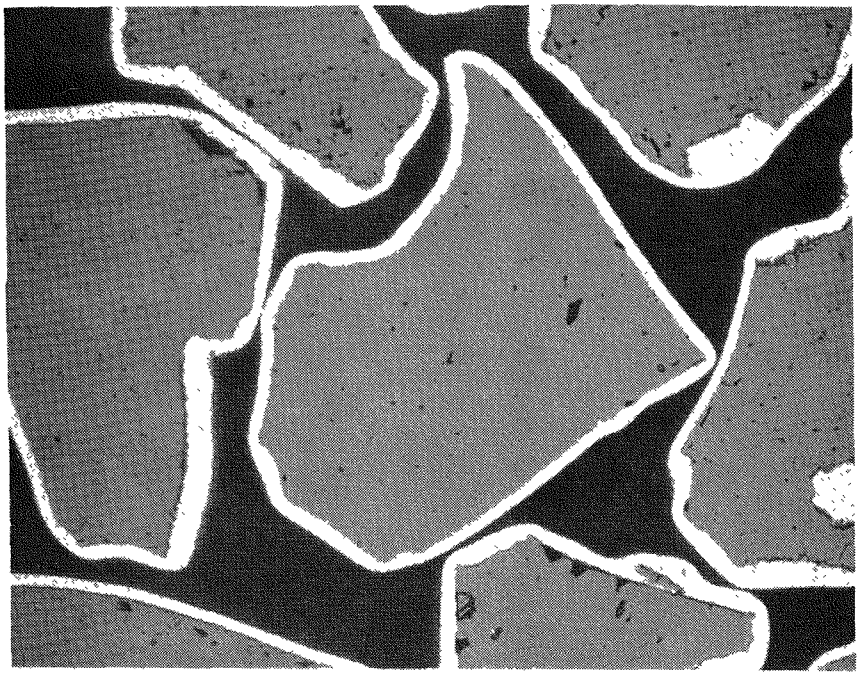

FIGURE 6 - Photomicrograph of cross-section of Mo coated $^{238}PuO_2$ particles. Note there is no reaction zone between Mo and $^{238}PuO_2$. (250X)

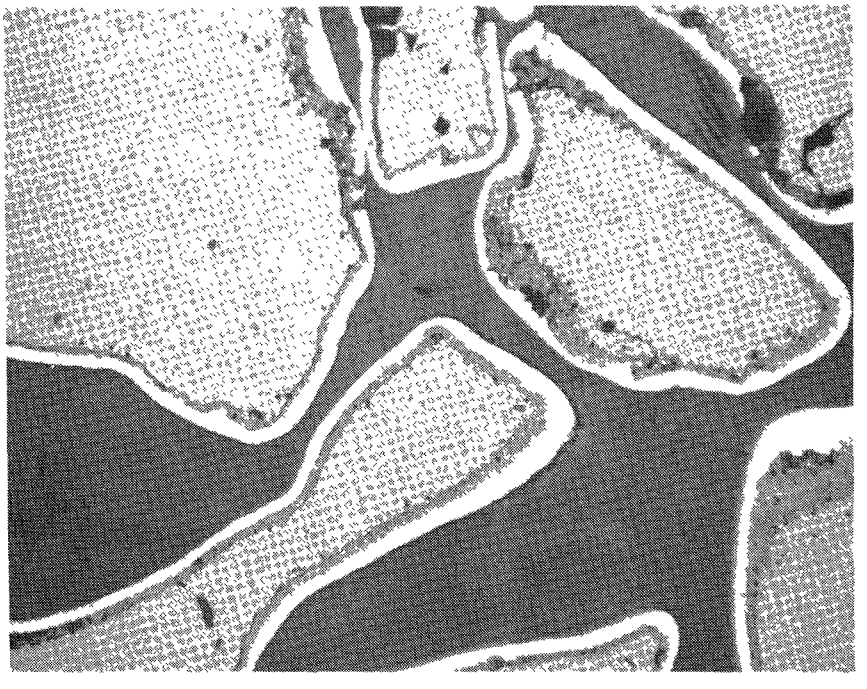

FIGURE 7 - Photomicrograph of cross-section of Mo coated $^{238}PuO_2$ particles. Note reaction zone between Mo and $^{238}PuO_2$. (250X)

8. The argon and hydrogen flows through the fluid-bed are adjusted to the following:

| Particle Size | $H_2$ Flow | Ar Flow (By-Pass Vaporizer) |
|---|---|---|
| 105-177 μm | 12 $ft^3$/hr | 4 $ft^3$/hr |
| 177-250 μm | 20 CFH $ft^3$/hr | 4 $ft^3$/hr |

9. The time required to coat material is calculated from the following equation:

$$\text{time} = \frac{(w/o)(Gp)}{(1-w/o)(Dy)} ,$$

where w/o = weight percent Mo required

GP = weight of $PuO_2$ being coated

Dy = deposition rate of Mo.

Dy is usually about 0.5 g/min, but the best rate is that obtained empirically from the previous run carried out under the same conditions.

10. The substrate material in the hopper is dropped into the fluid-bed.

11. Approximately five minutes after the substrate is dropped into the fluid-bed (when the substrate temperature reaches 800°C), the argon flow is routed through the vaporizer.

12. Maintain the above established flows for the period of time calculated in Step 9.

13. Turn off the flow of argon through the vaporizer after the proper elapsed time, and immediately increase the hydrogen flow through the fluid-bed by about 4 $ft^3$/min.

14. Maintain fluid-bed furnace temperature for at least an additional 15 min after the $MoCl_5$ is shut off.

15. Turn off furnace controller on fluid-bed; however, continue the $H_2$ flow until the cone temperature is below 300°C.

16. Switch simultaneously from hydrogen to argon (about 10 $ft^3$/hr) and maintain this flow for a minimum of 5 min to purge all $H_2$ from the system.

17. Aspirate the coated particles from the fluid-bed.

18. Screen coated particles to remove any large Mo flakes.

19. Weigh and record weight of coated particles.

## REFERENCE

1. R. R. Jaeger and S. T. Cohen, "Molybdenum Coating of $ThO_2$ and $^{238}PuO_2$ Particles," in Proceedings of the Third International Conference on Chemical Vapor Deposition, F. A. Glaski (ed.), American Nuclear Society, Hinsdale, Ill., 1972, pp. 500-512.