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DRYING OF ION-EXCHANGE RESINS FOR RESIN-BASED PREPARATION OF NUCLEAR REACTOR FUELS*

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ABSTRACT

The reference fuel kernel for recycle of ^{233}U to HTGRs (High Temperature Gas-Cooled Reactors) is prepared by loading carboxylic acid cation-exchange resins with uranium and carbonizing at controlled conditions. The loaded, dried resin must meet specifications for sphericity, composition, and other properties.

Microwave heating is used to give controlled and reproducible drying of 11-liter batches of uranium-loaded (4 kg of uranium) resin in a vessel of safe dimensions for nuclear criticality (12.7 cm ID). The dried resin must have a water content of 9 to 16 wt % to minimize handling problems. The microwave heating evaporates water throughout the resin bed, with preferential heating of the wettest resin, and allows short drying cycles.

As part of the resin feed preparation before uranium loading, the sodium-form resin is dried to allow separation of spheres from irregularly shaped material. A commercial, packaged fluidized bed dryer gives acceptable control and uniformity of drying.

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1. INTRODUCTION

The High-Temperature Gas-Cooled Reactors (HTGRs) use fissile particles which are small spheres of carbide or oxide fuel encased in pyrolytic carbon coatings. The Fort St. Vrain reactor, a 330-MW(e) HTGR constructed by the General Atomic Company for the Public Service Company of Colorado, uses the Th-^{233}U fuel cycle. The reference fuel kernel used for recycle of ^{233}U is prepared by loading carboxylic acid cation-exchange resins with uranium and carbonizing at controlled conditions.[1] A principal advantage is that many of the critical product properties (e.g., particle shape, size, and impurities) can be established and controlled for the feed resin before any uranium is present. Another advantage is that the uranium in the product can have any composition between UO_2 and UC_2 by controlling the conversion conditions after carbonization. The best performance during high burnup in a HTGR requires approximately 75% UC_2--25% UO_2.[2] Resin-based kernels are an alternate for the ^{235}U makeup fuel kernels.

The reference resin for ^{233}U recycle kernels is Amberlite IRC-72.* A typical fuel kernel of 60.0×10^{-6} g of uranium per sphere corresponds to a diameter of 715 μ for the wet, sodium-form resin or a diameter of 530 μ for the dried, uranium-loaded resin. About ± 10% is a common diameter range.

A flowsheet was developed to demonstrate the efficient preparation of the uranium-loaded resin using acid-deficient uranyl nitrate solution (Fig. 1).[3,4] For this demonstration, the resin feed was not processed to meet all specifications, and the procedures for drying the uranium-loaded resin would not meet the requirements for remote operation with ^{233}U. This paper reports

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the tests made to the equipment and the procedures that were used for the two resin drying operations. The process requirements had to be established for both operations before equipment and procedures could be selected.

When the resin-based kernel became the reference recycle fuel in 1974,[4] we conducted tests to determine the efficiency of microwave drying of both sodium-form and uranium-loaded resin. After the importance of controlled and uniform drying of the uranium-loaded resin was established, it was ascertained that microwave drying was apparently the best technique for meeting the in-cell requirements. Conventional fluidized bed equipment appeared adequate to meet the simpler requirements for drying the sodium-form resin.

Acknowledgement. The Metals and Ceramics Division at Oak Ridge National Laboratory developed the procedure for the carbonization and conversion of the uranium-loaded resin; they also established the requirements for dried, loaded resin.[2] Information concerning the development of resin-loading processes at the General Atomic Company contributed to our selection of microwave drying equipment.[5]

2. MICROWAVE DRYING OF URANIUM-LOADED RESIN

The uranium-loaded resin is dried to simplify handling and transfers and to meet the requirements for the carbonization feed. The uranium-loaded Amberlite IRC-72 contains 25 to 30 wt % water when drained briefly on a filter or screen. Our drying results are expressed as Loss On Drying in weight percent when dried to approximate equilibrium in ambient air at 110°C; that is, material dried to 110°C in air has 0 wt % LOD. Some of the water is chemically bonded or adsorbed so that zero LOD does not mean zero water content.

The optimum water content for uranium loaded Amberlite IRC-72 appears to be 9 to 16 wt % LOD. Above 20% LOD, resin particles stick together from the effects of moisture. Uranium-loaded resin dried to less than 9% LOD shows detectable static charge effects, and these charge effects were extremely troublesome at 0 to 2% LOD. The addition of graphite powder to coat the resin can alleviate the charge effects, but the preferred method uses less complete drying of the resin to leave 9 to 16% LOD.

The resin is a porous plastic and an excellent insulator. The controlling requirement for drying this resin is the heat necessary to vaporize the water it contains. If the heat is supplied by a flowing gas, the water is evaporated and the gas is cooled until it becomes saturated with water vapor. When a heated gas is used, the drying is not uniform; almost complete drying occurs near the gas inlet before the resin is dry enough to flow freely or fluidize away from the inlet.

Fixed-bed drying utilizing upflow and downflow of steam-heated air was found to be unacceptable, because geometry restrictions for nuclear criticality resulted in nonuniform drying and long drying cycles. Fluidized bed drying was also rejected because of poor fluidization characteristics, long drying times, and geometry restrictions. Microwave drying of the uranium-loaded resin has yielded acceptable uniformity and much shorter drying cycles in a 12.7-cm-ID vessel.

Microwave drying has several advantages over conventional heating which relies primarily on conduction-convection. These advantages include instant on-off capability; moisture leveling (i.e., preferential heating of the wettest material); and shorter drying cycle without high temperatures. For this application with geometry restrictions, poor thermal conductivity of

the resin, and uniformity requirements, microwave heating has satisfied our requirements better than any other methods considered.

2.1 Description of Microwave Dryer

Following the loading of uranium as uranyl ion on the ion exchange resin, the fuel is transferred to the dryer as a slurry. Provisions for solids addition and withdrawal (as well as liquid or vapor only, through screens) is incorporated in a special flange assembly (Fig. 2). This flange has a conical (~ 45° slope), 120-mesh screen with a hole at the apex. A ball valve is secured to the plate to allow transfer of solids.

A schematic diagram illustrating the components of the microwave dryer system is shown in Fig. 3. The resin container is a Pyrex tube that has dimensions of 13.0 cm OD x 0.3 cm wall x 1.2 m long. The reference 4 kg of uranium on 11 liters of resin occupies approximately 75% of this column. The stainless steel, microwave cavity is 1.2 m high x 1.2 m wide x 0.9 m deep. The width and depth of the cavity, as well as the location of the glass column, was selected by the microwave manufacturer. A motorized mode stirrer is incorporated to level the energy distribution in the cavity. The power source is a 2.5-kW generator operating at 2.45 GHz. A circulator and dummy load are employed to prevent reflected power from damaging the power tube. Transmitted and reflected power monitors are also shown. A recirculating hot air system is operated during the drying cycle to reduce heat transfer from the resin to the surroundings. A 1-m length of flexible waveguide is used to facilitate connection of the cavity to the power source. For in-cell operation, the waveguide would be through a cell penetration with the power supply outside the cell.

2.2 Operating Procedures and Results

Following the washing of the resin to remove the excess uranyl nitrate solution that is used to transfer the resin, the excess interstitial water is removed by downflow of air at 28 slpm for 10 min. The microwave power is then supplied to the cavity and the air flow is increased to 113 slpm for one-half of the heating cycle, at which time the air is reversed and increased to 226 slpm. The air is passed through the bed to aid in water-vapor removal, but the primary purpose is to promote mixing of the material. At the onset of reversing the air flow, smooth fluidization is not observed; instead, slugging and channeling can be seen. This is due largely to the geometry configuration and also to the sticky phase during the drying cycle.

During a typical run, the column exit temperature rises from 25°C (the gas supply) to the steady-state operating temperature of approximately 75°C in less than 10 min. The saturated air leaving the resin bed is passed through a condenser and the condensate is collected. For the reference 11-liter batch the condensate rate is 2.8 liters/hr.

Development of a procedure (or determination of a positive signal) to obtain the desired moisture content on a reproducible basis is necessary. Initially, it was anticipated that the increase in the reflected power caused by removal of water from the resin might be used as the signal to determine when the desired moisture content was reached. However, experiments have shown that the reflected power is not very sensitive to the change in water content of the resin during a drying cycle. Due to the large load in the cavity, the reflected power remains fairly constant (typically, 50 to 70 W). This energy is absorbed by the dummy load. The temperature of the exit gas does not vary with the LOD of the resin until the resin is much drier than the required range of values.

A relationship between the average water content (LOD) of the dried material and a drying factor has been established experimentally. The drying factor, which uses units of kilowatt-minutes per liter of loaded resin, enables the operator to obtain the desired water content for a given batch size by selecting the heating time and the input power (typically, 2.5 kW). The drying factor is normalized per unit volume because the batch size may vary.

Typical results are shown in Table 1. Samples for moisture content analysis were taken from the bottom, middle, and top of the column. Uniform moisture content within the batch and from batch to batch is quite good, with differences varying less than 2%. To determine the duration of microwave heating, the drying factor is multiplied by the batch size and divided by the microwave input power. To obtain an average LOD of 13%, the drying factor is 9.0 kW-min per liter of resin. Thus, the microwave heating cycle is 40 min for the reference 11-liter batch when utilizing 2.5 kW of microwave power. Approximately 60% of the total water (2 liters) is removed during the microwave heating cycle. An additional 0.2 liter of water is collected during the cooldown portion of the drying cycle prior to removal of the resin from the column by gravity.

3. FLUIDIZED BED DRYING OF SODIUM-FORM RESIN

The commercial Amberlite IRC-72 resin does not meet the HTGR specifications for shape and uniformity of size. It is a nominal -20 +50 mesh and contains about 10 wt % of nonspherical particles, whereas the size and shape of the resin feed to the uranium loading process are strictly limited. Therefore, the resin is subjected to classification processes to eliminate unwanted resin prior to uranium loading.

One of the processes used is shape separation, in which the spherical resin beads are separated from the nonspherical beads on a vibrating plate. Shape separation must be performed on dry resin, since the particles must be free rolling; excessive moisture tends to agglomerate the beads. Prior to shape separation, the resin is wet screened to about a 10% range of diameters. The resin must be dried between the wet screening and shape separation operations. The LOD of the resin must be lowered to approximately 10% or less, but the resin must not be dried to the point of excessive static charge development or resin damage. The wet, drained resin has a moisture content of approximately 3.8 kg of water per kilogram of dry resin, or an LOD of 79%. To reach an LOD of 10%, 3.7 kg of water per kilogram of dry resin must be removed.

3.1 Description of Fluidized-Bed Dryer Equipment and Procedure

Currently, fluidized bed drying is employed to dry the sodium-form resin; fixed bed, rotary drum, and microwave drying had been tested previously.[4] Although the resin dried in the fixed bed and rotary drum tests, it tended to agglomerate into large clusters. Microwave drying resulted in some of the resin being charred. Fluidized bed drying was selected and confirmed to be a suitable alternate method offering acceptable control of drying temperature and product dryness; it also maintained an agitated bed to keep the particles from forming clusters.[4] The carboxylic acid resins in the sodium form were dried to 100°C, and were rewet with no detectable change in exchange capacity; under the same conditions, hydrogen-form resins show a loss of capacity. Conditions and procedures for use of a pilot-plant scale, fluidized bed dryer were tested as a problem for the MIT School of Chemical Engineering Practice at Oak Ridge.[6]

The fluidized bed drying is performed in a commercial, packaged drying unit,* as shown schematically in Fig. 4. The product container, with a capacity of 82 liters, is filled with wet resin and sealed pneumatically into the dryer. The electrically driven blower pulls room air through the bed at 375 to 565 slps, and the air is heated at the inlet by the finned-tube steam heater. The inlet air temperature can range from ambient to 110°C. The temperature is controlled with a proportional controller and an air-actuated valve on the steam inlet. Air flow and fluidization is controlled by a damper which directly precedes the blower.

A typical drying run begins with the loading of the wet resin into the bed. After the product container is sealed into the dryer, the air flow is started and the inlet air temperature is set. While drying can be done at almost any temperature, 93°C is preferred because it results in a short drying time with no damage to the resin. The damper is manipulated to produce a well-agitated bed. Due to the sticky nature of the wet resin, a smooth, fluidized bed cannot be achieved. There is always a good deal of slugging, channeling, and expulsion of material from the bed.

3.2 Results

Three drying periods are observed. In the first period, the bed is warmed to equilibrium with the fluidizing air. In the second period, the drying reaches a constant rate, and the outlet air temperature remains constant at 38 to 43°C. Finally, a falling-rate period is entered. The resin suddenly shrinks in volume by a factor of 4.3, and begins to fluidize more evenly. The outlet temperature begins to climb, and, at an outlet temperature of 82°C, the dryer is shut down and the product is removed. At this

*Model FA-75 Fitzaire Fluid Bed Dryer, The Fitzpatrick Company.

point, the resin has an LOD of 10 to 13%. The elapsed time of drying ranges from 1 to 2 hr depending on the batch size, atmospheric conditions, and the initial wetness of the resin.[6]

4. REFERENCES

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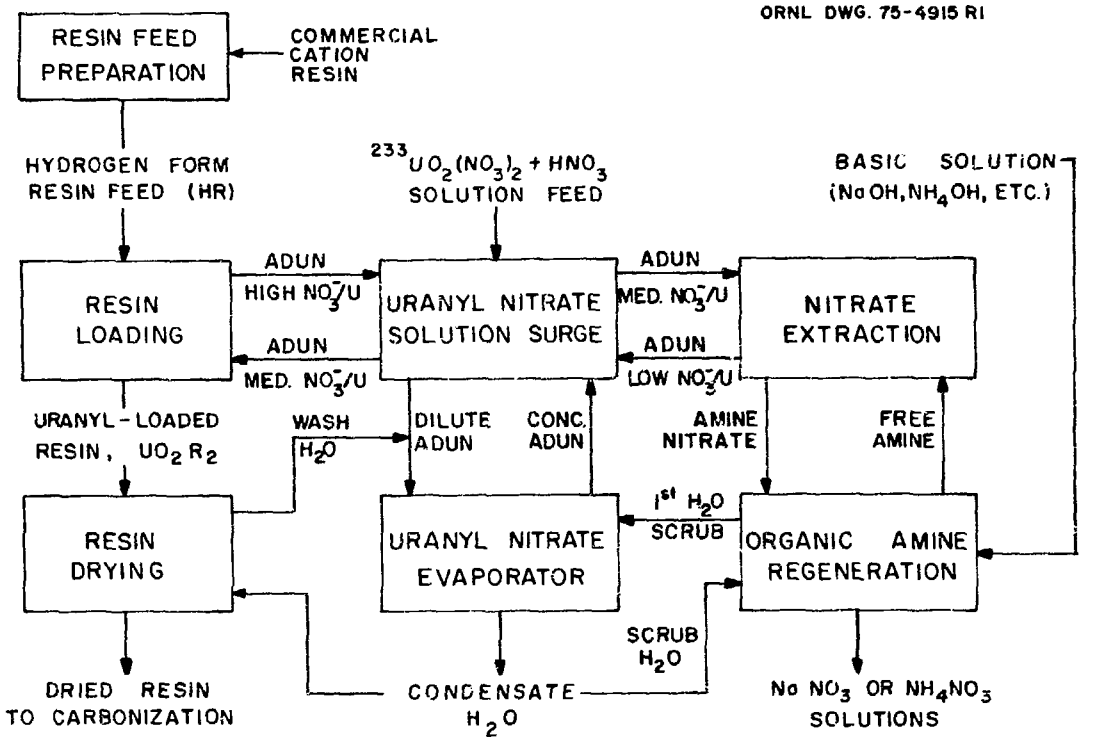
Table 1. Drying of uranium-loaded resin with microwave heating

Air Flow: 113-slpm downflow for one-half of time at power; 113-, 142-, or 226-slpm upflow for one-half of time at power and for 30 min cooldown

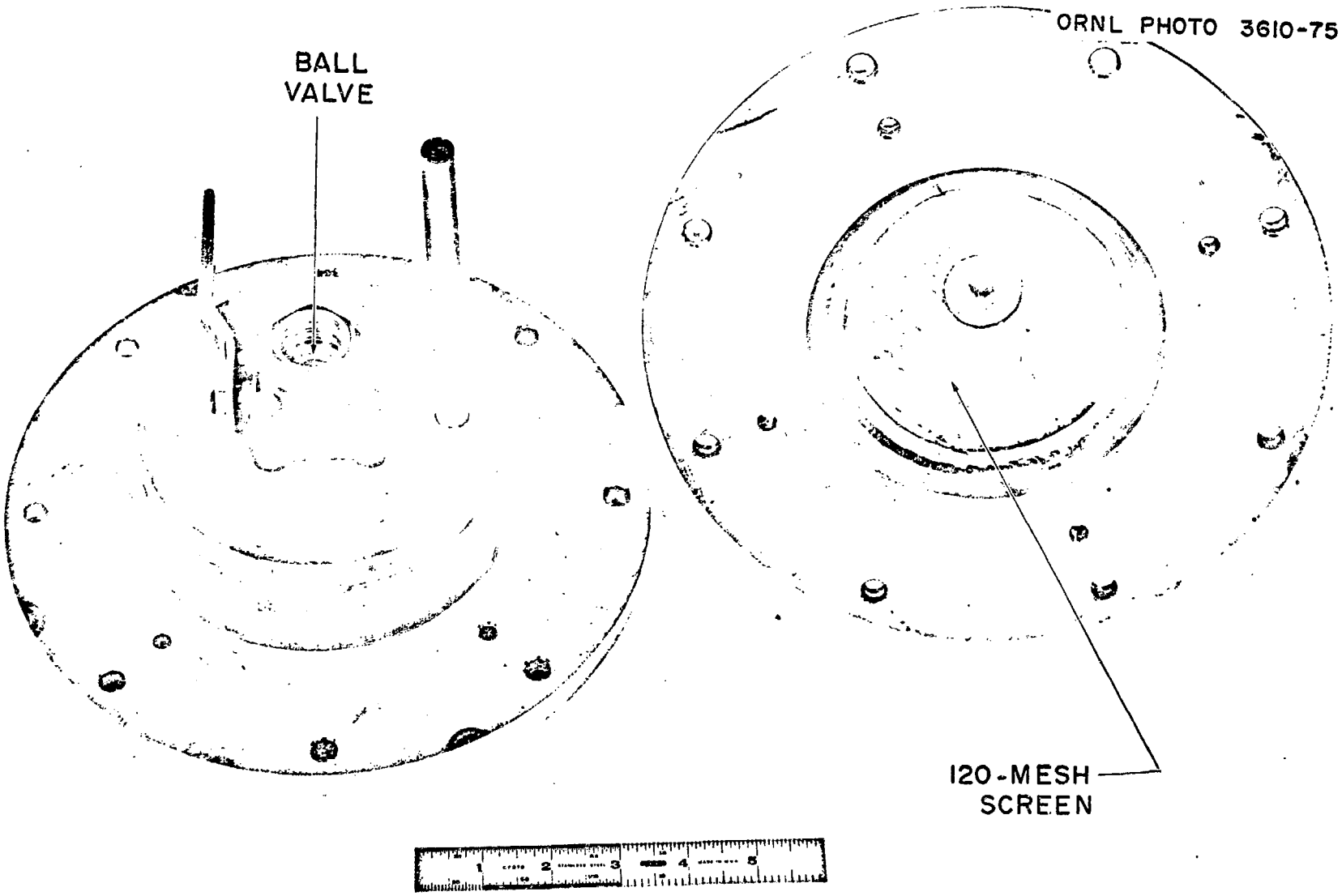
Drying factor kW-min / liter resin	Wet resin volume (liters)	LOD (wt %)[a]				Condensate volume (liters)	Power	
		Bottom	Middle	Top	Average		min	kW
8.0	11.5	7.7	15.6	13.2	14.4	2.08	46	2.0
	11.1	14.7	15.2	14.7	14.9	2.14	44.5	2.0
	11.5	15.5	16.2	15.1	15.6	2.08	37	2.5
8.8	9.65	14.2	15.3	15.4	15.0	1.81	34	2.5
9.0	11.1	12.5	13.4	13.4	13.1	2.30	42	2.5
	11.4	14.0	14.5	12.3	13.6	2.67	41	2.5
	11.1	13.6	13.3	13.2	13.4	1.98	40	2.5
9.3	9.65	13.6	14.6	13.6	13.9	1.83	36	2.5
9.5	10.25	10.2	12.7	12.4	11.8	2.02	39	2.5
	12.0	15.8	14.2	11.6	13.2	2.50	46	2.5

[a]LOD = Loss On Drying.



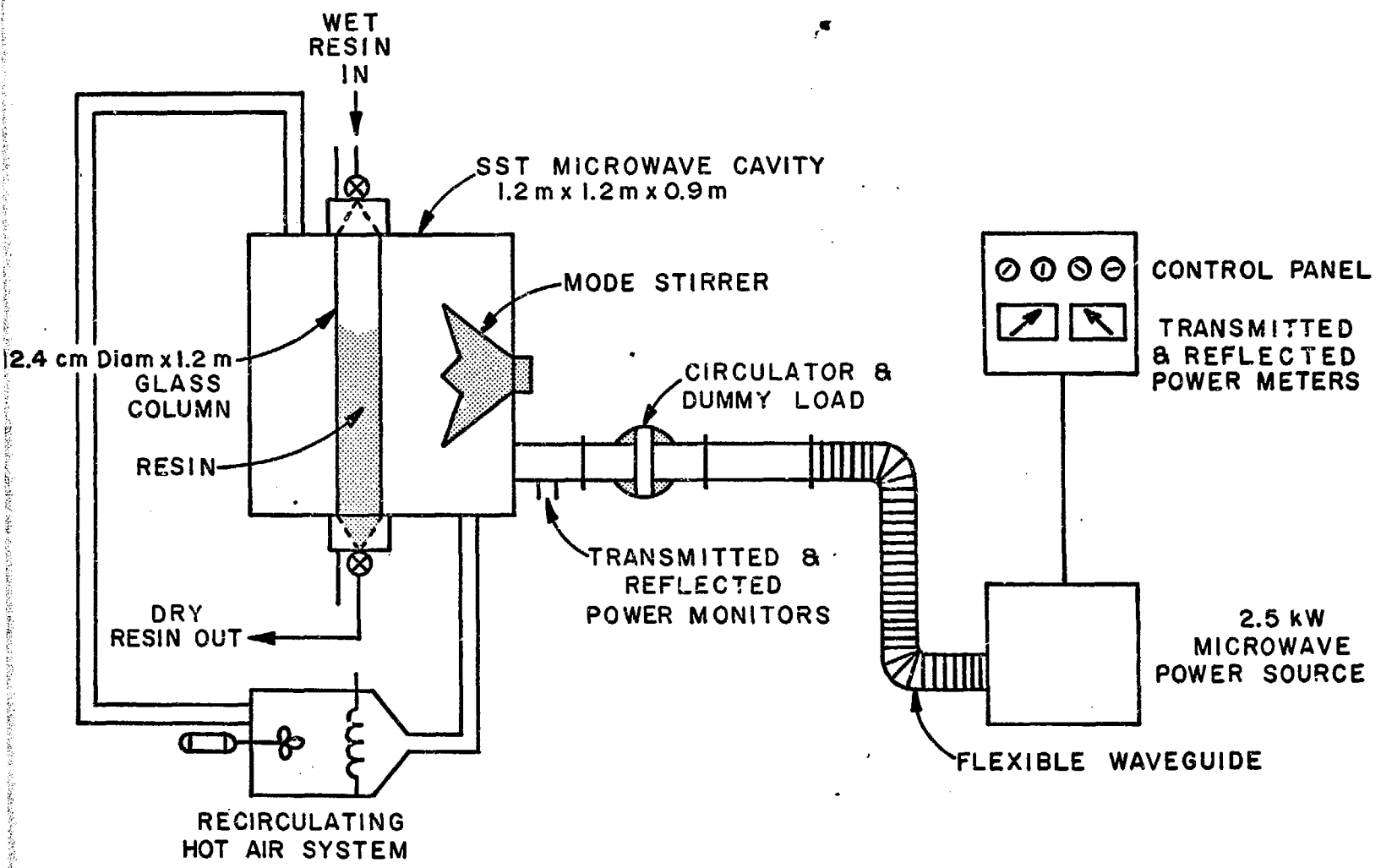
"ADUN" INDICATES ACID-DEFICIENT URANYL NITRATE ($NO_3/U<2$, MOLES/MOLE)

ORNL PHOTO 3610-75



END SECTIONS OF RESIN DRYER IN MICROWAVE CAVITY

ORNL-DWG 76-569



MICROWAVE HEATED DRYER
FOR URANIUM LOADED, ION EXCHANGE RESIN

ORNL-DWG 76-570

FLUIDIZED BED DRYER USED
FOR ION EXCHANGE RESIN