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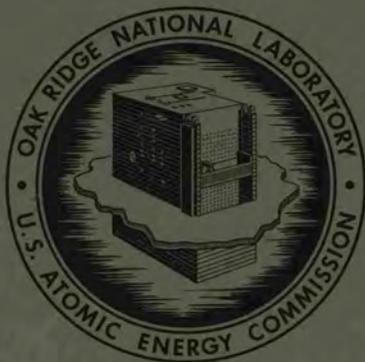
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MOUND ASSISTANCE PROGRAM;
DEVELOPMENT OF A SOL-GEL PROCESS AND
EQUIPMENT FOR THE PRODUCTION OF
DENSE $^{238}\text{PuO}_2$ MICROSPHERES

F. G. Kitts
R. E. Brooksbank
R. G. Haire
M. H. Lloyd



OAK RIDGE NATIONAL LABORATORY
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UNION CARBIDE CORPORATION
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U.S. ATOMIC ENERGY COMMISSION

Printed in the United States of America. Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road, Springfield, Virginia 22151
Price: Printed Copy \$3.00; Microfiche \$0.95

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ORNL-4565

Contract No. W-7405-eng-26

Chemical Technology Division

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MARCH 1971

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ABSTRACT

Microspheres of $^{238}\text{PuO}_2$, a potentially important isotopic power source, have been produced in kilogram quantities at Mound Laboratory using a plasma torch. During fiscal year 1967, a preliminary evaluation of the sol-gel process and product provided sufficient incentive for the U. S. Atomic Energy Commission to request Oak Ridge National Laboratory to determine the feasibility of producing $^{238}\text{PuO}_2$ microspheres by this route. As the ultimate objective of the program, Mound Laboratory was to be supplied with pretested equipment for incorporation into their process line.

The sol-gel process offers important advantages from the standpoints of product quality, process simplicity, and overall safety. It was found that satisfactory $^{238}\text{PuO}_2$ sols could be formed in the laboratory, using the $^{239}\text{PuO}_2$ flowsheet, if the feed was carefully prepared and a simple "aging" step was included. A remotely operated, neutron-shielded facility was constructed to process 200 g of plutonium per day. Successful demonstrations with ^{239}Pu were carried out in this facility and, although those with ^{238}Pu were less satisfactory, valuable experience was gained in preparing $^{238}\text{PuO}_2$ sol by remote means.

Equipment for the preparation of $^{238}\text{PuO}_2$ sols and conversion to dense microspheres was fabricated, installed in a stainless steel enclosure (box), and shipped to Mound Laboratory. After the box had been installed, ORNL personnel participated in a program of system checkout, continuing process development, and equipment modification. When difficulties were encountered due to the processing of larger batches of material, electron microscopy was utilized to identify two problem areas: (1) partial hydrolysis of the feed was preventing the formation of highly crystalline plutonium polymer, and (2) degradation of polymer was occurring during evaporation to dryness. The depolymerization process is similar to the simple dissolution of PuO_2 and is a function of time, temperature, and acid concentration. After several equipment improvements, the ORNL system that had been installed at Mound Laboratory proved to be capable of sustained operation; a total of 683 g of ThO_2 was processed in five

consecutive runs. It was concluded that $^{238}\text{PuO}_2$ sols and high-quality microspheres could be produced in the quantities required, and it was recommended that the facility supplied by ORNL be used for this purpose.

1. INTRODUCTION

Plutonium-238, with its 86-year half-life and its heat generation rate of greater than 1/2 watt per gram, is potentially an important isotopic power source. In dedicating the transuranium facilities at Oak Ridge National Laboratory, Glenn T. Seaborg, Chairman of the USAEC, mentioned various anticipated applications for ^{238}Pu power sources, including auxiliary power for space missions, pacemakers for heart patients, and possibly an "artificial heart that can be surgically implanted in the patient."¹

By late 1966, studies of various phases of the preparation and use of $^{238}\text{PuO}_2$ had been made at several locations. Mound Laboratory, Miamisburg, Ohio (Monsanto Research Corporation) was already engaged in the production of $^{238}\text{PuO}_2$ microspheres by a plasma torch method. Meanwhile, significant progress in applying sol-gel technology to the production of fast reactor fuel containing ^{239}Pu was being made at Oak Ridge National Laboratory (ORNL). The sol-gel process had been developed in detail from the standpoints of $^{239}\text{PuO}_2$ sol preparation² and subsequent microsphere formation.³ The need for $^{238}\text{PuO}_2$ microspheres presented a rare opportunity for adapting this technology.

The advantages of sol-gel-produced $^{238}\text{PuO}_2$ were recognized^{4,5} early in fiscal year 1967 when small quantities of ORNL-prepared $^{238}\text{PuO}_2$ microspheres were evaluated. This preliminary evaluation was favorable and revealed sufficient incentive to warrant rapid development of the sol-gel process to the point that representative product could be produced. Accordingly, late in 1966, the USAEC requested that a program be established at ORNL to demonstrate the feasibility of producing sol-gel $^{238}\text{PuO}_2$ microspheres for isotopic heat source applications.⁴ If successful, this method would provide an alternative procedure for the production of $^{238}\text{PuO}_2$ microspheres at Mound Laboratory.

The overall objective of the program to be carried out at ORNL was to supply Mound Laboratory with a system of pretested sol- and microsphere-producing equipment ready for installation in their process line. This overall objective was subdivided into steps as follows:

- (1) To develop a process for the preparation of $^{238}\text{PuO}_2$ microspheres.
- (2) To demonstrate the process on an engineering scale in a 150- to 200-g/day pilot plant.
- (3) To provide Mound Laboratory with a full-scale production system to prepare 50- to 250- μ microspheres with a process yield greater than 90%. (Nonrecoverable process losses were to be less than 1%, and individual particle densities were to be greater than 95% of theoretical.)
- (4) To provide Mound Laboratory with startup and technical assistance.
- (5) To upgrade the originally proposed system with process improvements as the technology developed.
- (6) To demonstrate the capability for an ^{16}O enriched product.

2. SUMMARY

Microspheres of $^{238}\text{PuO}_2$ produced by the sol-gel route have the desirable properties of high density (>94% of theoretical), high crushing strength (>1 kg/sphere), high yield in the desired 50- to 250- μ -diam range (>90%), excellent sphericity, and a glossy surface. The microspheres are easily washed, showing little tendency to be leached. In addition, they are stable over a wide range of temperatures, resistant to thermal shock, and amenable to oxygen exchange. From the standpoint of routine operation, the sol-gel process is attractive because the system consists primarily of solutions (i.e., it is a "solution" system). Such a system is easily adapted to remote operation and is flexible in that diluents (e.g., ThO_2 or ZrO_2) can be added and the product is available in several forms. The process is simple, and a high throughput and a high yield are obtained from small, compact equipment. The recycle of off-specification material requires only a minimum of additional effort. From the standpoint of safety, a solution system should be relatively simple to contain and present a reduced fire hazard. Radiation exposure is decreased by the self-shielding effect of hydrogenous liquids during processing, and the end

product requires less shielding for the reduced neutron dose rates that are effected by oxygen exchange.

Several $^{238}\text{PuO}_2$ sols were prepared in the laboratory by following the $^{239}\text{PuO}_2$ flowsheet when the free acid concentration in the feed was reduced to 2 M and a more dilute base (2 M NH_4OH) was used in the precipitation step. Initially, the sols were opaque and more viscous than $^{239}\text{PuO}_2$ sols, and the microspheres formed from them were characterized by deep pitting. However, sols of a superior quality have been produced by incorporating a simple "aging" step (in which the washed precipitate is refluxed in water for 2 hr) into the flowsheet. Aging improves crystallinity and increases resistance to radiolysis and chemical degradation. The use of this aging step resulted in 100% yields of dark-green, translucent sols that were more fluid than those made without the step; also, the NO_3^-/Pu mole ratios of these sols could be reduced to lower values than could those of sols produced by using the original flowsheet. Excellent microspheres were made from these sols.

A remotely operated, neutron-shielded facility was constructed in Bldg. 3019, Oak Ridge National Laboratory, to demonstrate the sol-gel process as a method for producing dense $^{238}\text{PuO}_2$ microspheres. The equipment, similar to that in the $^{239}\text{PuO}_2$ processing facility, was sized to process 200 g of plutonium per day. The equipment components were installed in a plywood mockup for vessel calibration and for hydraulic testing of the piping system before being permanently installed in the cell.

This facility, or sol-gel pilot plant, was initially operated with ^{239}Pu in order to check out the equipment and to establish operating parameters. This operation was successful, and good-quality microspheres were produced. Following this operating period, the cell face was shielded in preparation for the processing of ^{238}Pu .

The basic ^{239}Pu flowsheet was followed in working with ^{238}Pu (80% ^{238}Pu , 16% ^{239}Pu , and 4% other plutonium isotopes), except that conditions were often more stringently controlled. Of the five sol runs (50 to 160 g of plutonium per run) that were made, none was completely successful in preparing a sol suitable for microsphere preparation; however, each attempt contributed to a better understanding of the complex problems associated with the remote preparation of $^{238}\text{PuO}_2$ sols.

The sphere-forming equipment was successfully operated to produce $^{238}\text{PuO}_2$ microspheres from a sol (NO_3^-/Pu mole ratio, 0.18) that had been prepared in the laboratory. The microspheres were formed in 2-ethyl-1-hexanol (2EH) containing 0.3 vol % Ethomeen S/15, were dried in air at temperatures up to 140°C , and then calcined at 1200°C . The calcined product was characterized by a dimple, or "cherry pit," and, in general, had slightly less desirable physical characteristics than comparable $^{239}\text{PuO}_2$ products.

Equipment designed for preparing $^{238}\text{PuO}_2$ sols and for subsequently forming, drying, and firing $^{238}\text{PuO}_2$ microspheres to a dense final product was fabricated, installed in a stainless steel cubicle (or box), and shipped to Mound Laboratory. The box, which is 10 ft long, 7 ft 3 in. high, and 42 in. deep, was installed as part of a shielded production facility; it is to be operated remotely, using four model G manipulators. The production capacity of the unit is one batch of sol, containing 150 g of plutonium, per 24-hr period. The equipment was designed in accordance with the standard precipitation-peptization-denitration flowsheet for producing sol. Microspheres are to be made by forming droplets of sol in a two-fluid nozzle, fluidizing the droplets in a stream of 2EH in a tapered glass column until they are dried to a gel, drying the gel microspheres in hot air and steam at temperatures up to 160°C , and, finally, firing the microspheres in air at temperatures up to 1200°C .

The sol-forming equipment includes: (1) feed adjustment tank, (2) precipitation-peptization vessel, (3) high-nitrate sol evaporator, (4) denitration vessel, (5) final sol evaporator, and (6) sol surge tank. Separate filtrate (basic) and condensate (acid) waste systems (two tanks each) and vacuum and vessel off-gas systems are also included. An infusion pump meters the sol to the microsphere-forming column; a surge tank with a submerged centrifugal pump, a cooler, a filter, and a still for removing water from the 2EH comprise the system for recirculating the solvent. A surge vessel for gel microspheres, a dryer with associated steam generator, and a calciner constitute the remainder of the process equipment. The equipment was checked for operability after the final installation, and the box was closed and leak-checked prior to shipment to Mound Laboratory.

On receipt at Mound, the box was installed, shielding was erected, and the utilities and instrumentation were connected by Mound personnel. Instrumentation and operational checkouts were accomplished with the assistance of ORNL personnel. Then the box was closed and leak-checked; afterwards, it was reopened. ORNL personnel then assisted in a program involving: (1) system checkout, (2) continued process development, and (3) equipment modification.

Because of difficulties encountered in scale-up experiments at Mound, electron microscopy was introduced as a diagnostic tool to evaluate larger-scale sol preparations. Earlier studies had shown that both the formation and the retention of highly crystalline plutonium polymer are absolutely necessary for successful sol preparation. It was found that partial hydrolysis during feed preparation was the most probable cause for deficiency in polymer formation and that the high nitric acid concentration, high temperature, and long exposure times encountered in evaporation to dryness contributed to polymer degradation. Generally, the data indicate that depolymerization is similar to the simple dissolution of PuO_2 and is a function of time, temperature, and acid concentration. Later, in a run made at Mound, the digested precipitate was peptized at a low NO_3^-/Pu mole ratio (1.1) and a high plutonium concentration; this resulted in a low sol volume, a short evaporation time, and essentially a 100% yield.

Process development was continued during the fabrication and installation of the system, and several improvements were made in the equipment. These improvements should enable the facility to take advantage of the most recent advances in technology. For example, the high-nitrate sol evaporator was modified to permit vacuum distillation at temperatures of less than 100°C , and additions to the precipitator and waste system were made to permit continuous washing. Modifications to the microsphere-forming system included the substitution of an improved column, the addition of a filtration system, the provision for larger gel microsphere passages between vessels, and the addition of steam-treatment equipment to the dryer. The modified system was used to process 683 g of ThO_2 in five consecutive runs.

We concluded that the chemistry of $^{238}\text{PuO}_2$ sol preparation was sufficiently understood to produce high-quality $^{238}\text{PuO}_2$ microspheres in

the quantities required for the heat source program and recommended that the ORNL-supplied equipment be utilized for this purpose.

3. PRELIMINARY EVALUATION OF THE SOL-GEL PROCESS

The results of a comparison of methods for producing $^{238}\text{PuO}_2$ particles provided the incentive for establishing the $^{238}\text{PuO}_2$ sol-gel program at ORNL. This comparison included an evaluation of the sol-gel process and of the product obtained from this process. The evaluation, which was based on laboratory studies of $^{238}\text{PuO}_2$ and pilot-plant studies of $^{239}\text{PuO}_2$, is still valid, and is independent of the studies presented in this report. It is summarized here to provide perspective for the remainder of the report.

The general specifications for $^{238}\text{PuO}_2$ microspheres and the properties and capabilities of the microspheres that were being produced in 1966 using a plasma torch were described to us by Mound personnel.⁶ The ultimate criterion of good-quality microspheres is a uniformly high power density in a finished capsule. A high power density is achieved by the combination of a high microsphere density (>90% of theoretical) plus a high packing density (>65%); fines (material <50 μ in diameter) are to be avoided because they may accumulate to produce hot spots. A high particle crushing strength (>1000 g/sphere) is desirable to minimize the production of fines by particle attrition. An O/Pu atom ratio of 1.98 to 2.00 is required for good thermal conductivity. Other microsphere specifications arise from considerations for use in space applications (i.e., reentry or mission abort). The lower size limit (50 μ in diameter) was chosen so that microspheres would "fall out" and not be suspended in the atmosphere where they might more easily be ingested. The upper size limit (250 μ in diameter) should result in a good dispersion of the microspheres, rather than a local concentration as might be expected from larger sizes. The final product should have a low surface solubility in order to lessen the danger of spreading contamination.

At the inception of the program, Mound Laboratory was producing material in a density range of about 9.0 to 11.4 g/cc, or an average of about 10.0 g/cc (87% of the theoretical density of 11.46 g/cc). Crushing

strengths were 1000 to 1500 g/particle, averaging about 1300 g. An O/Pu atom ratio of 1.98 was set by the operating temperature. Mound had developed a standard surface cleanliness test, which was ultimately a solubility test. Representative microspheres were washed repeatedly in ethanol. The amount of radioactivity in the liquid was indicative of the level of surface cleanliness; however, as the washing continued, the count rate became constant, and zero could not be approached.

The yield of $^{238}\text{PuO}_2$ microspheres by the plasma torch method was only about 50%. There was a loss of 20 to 25% in feed preparation due to dusting, etc., and a 25 to 30% loss from vaporization, plating, over- and undersize material, etc. Fired material was solubilized for recovery by a 2-hr potassium pyrosulfate fusion at 800°C. The microsphere production rate required to fulfill commitments was 400 g/week. The plutonium contained approximately 20% ^{239}Pu and less than 2% impurities. Although a criticality limit of 2.5 kg was assumed, the heat generation rate of 0.55 w/g limits the practical batch size to 100 to 200 g of plutonium. Even for batches this small, radiation levels were high for manual operation; neutron doses (from α, \underline{n} reactions) of 6 to 20 mrem/hr were measured through 4 in. of Lucite.

Although the sol-gel and plasma torch products had not been completely evaluated and compared by an independent laboratory at this point in the program, enough $^{238}\text{PuO}_2$ sol-gel microspheres had been prepared to permit the preliminary determination of several parameters. These results provided the necessary information on acceptability and desirability of the sol-gel product and process.

3.1 Properties of the Product

Some of the most desirable properties of the sol-gel product are:

- (1) high density (97% of theoretical);
- (2) a particle surface that is clean, highly polished, and chemically inert;
- (3) high crushing strength (1200 g);
- (4) uniformity of size (i.e., 96% in desired size range);
- (5) stability under conditions of changing temperatures, and resistance to shock;
- (6) capability for oxygen exchange prior to densification.

3.1.1 Density

The density of particles of $^{239}\text{PuO}_2$ that were produced by using the sol-gel process has averaged 97% of theoretical. Current tentative specifications⁷ for material from the plasma torch process include a density of greater than 83% of theoretical. An obvious advantage of the higher particle density is a smaller fuel package, which will yield more power per unit volume. The density of the plasma-torch product generally ranges from 10 to 11.0 g/cc (87.4 to 96% of theoretical). Observations of workers preparing $^{238}\text{PuO}_2$ at Mound Laboratory indicated that densities higher than 11 g/cc were obtainable using sol-gel methods. The apparent density of $^{239}\text{PuO}_2$ microspheres submitted to Mound was found to be 11.33 ± 0.03 g/cc. The density decreased to 11.10 ± 0.03 g/cc after passage through a 10-kw plasma torch.

Photographs of the microstructures of typical $^{239}\text{PuO}_2$ and $^{238}\text{PuO}_2$ microspheres produced by the sol-gel process are presented in Figs. 1 and 2 respectively. High-pressure mercury porosimetry confirmed the apparent high density; the void volume existed primarily as microporosity. Imperfections visible in the $^{238}\text{PuO}_2$ photomicrograph are mainly inclusions; it is possible that they are silica since some glass equipment was used in preparing the sol.

3.1.2 Surface Characteristics and Leachability

Sol-gel PuO_2 microspheres are characterized by a high surface gloss and show no visible indications of cracking or other imperfections. Photographs of calcined and of uncalcined microspheres prepared from ^{239}Pu feed are shown in Fig. 3; calcined $^{238}\text{PuO}_2$ microspheres are shown in Fig. 4. Smear tests of $^{239}\text{PuO}_2$ and $^{238}\text{PuO}_2$ sol-gel product resulted in count-rates well below tolerable levels.⁸ The particles exhibit chemical inertness to most reagents, and their dissolution rate in HNO_3 -HF is slow.

Tests indicate that most of the leachable radioactivity can be washed off the surfaces of $^{238}\text{PuO}_2$ sol-gel microspheres. In three tests, 0.1-g samples of microspheres were cleaned and then soaked in 25 ml of water for 4 hr; this water was then analyzed by counting to determine the amount of leached radioactive material. The three cleaning methods used were water washing, soaking in 8 M HNO_3 at room temperature for 30 min, and boiling in 8 M HNO_3 for 5 min; the resulting leach-water activities were 2×10^4 , 4×10^3 , and $400 \text{ dis min}^{-1} \text{ ml}^{-1}$ respectively.⁹

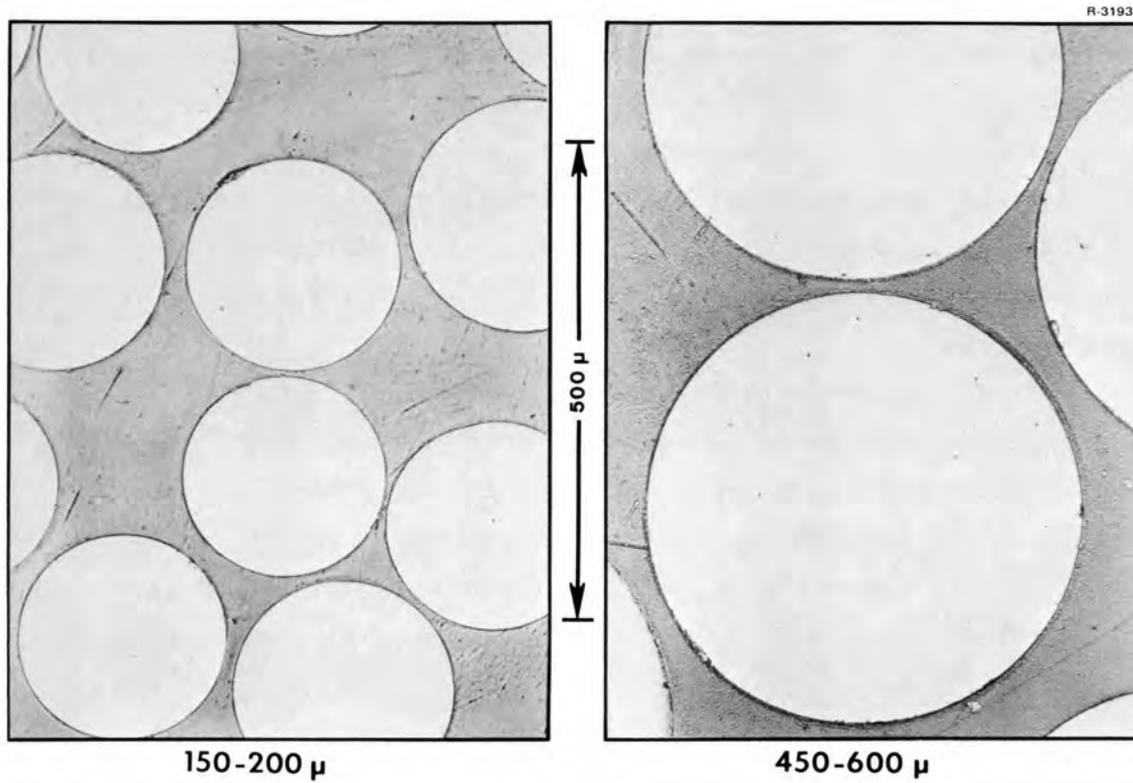


Fig. 1. $^{239}\text{PuO}_2$ Sol-Gel Microspheres Calcined at 1200°C .

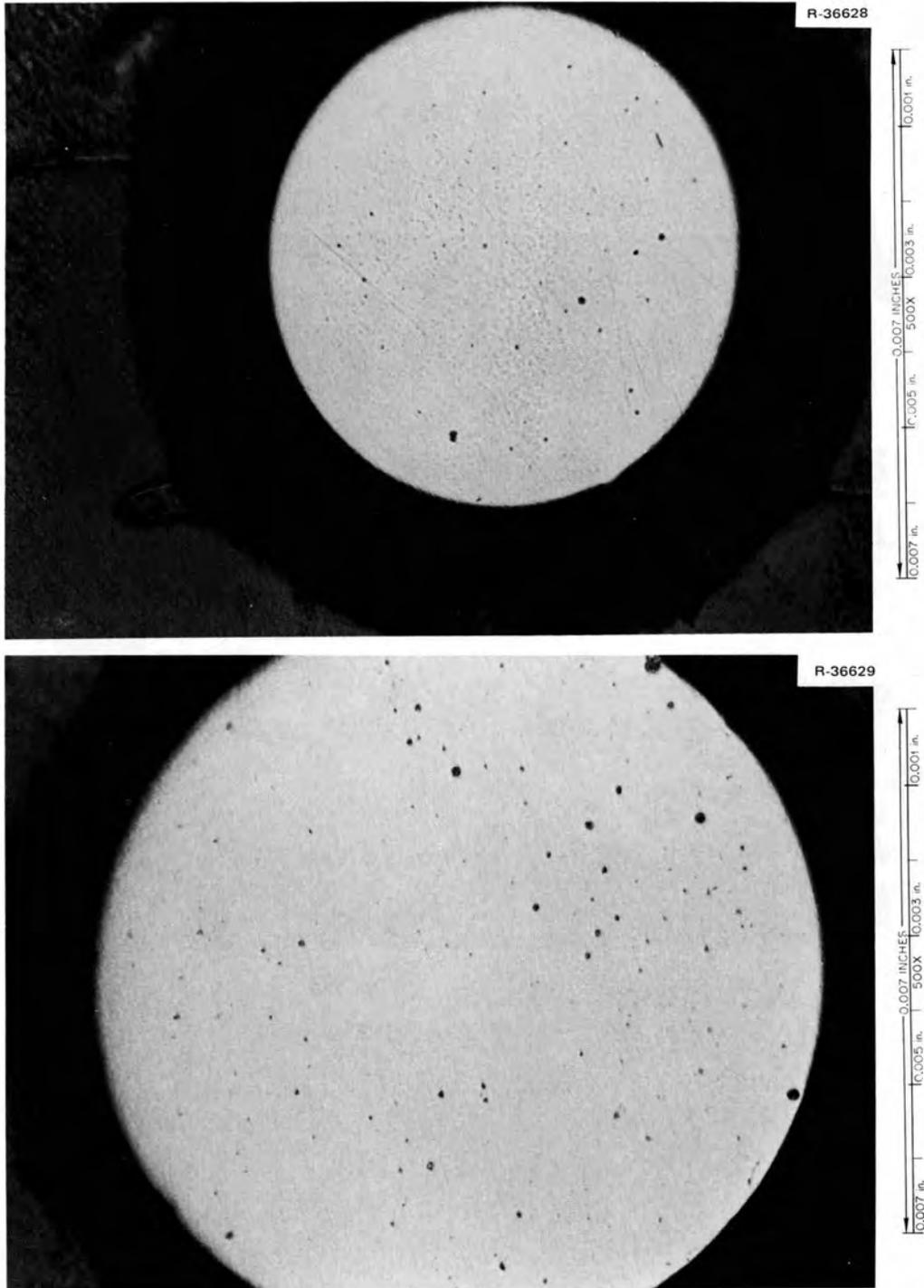


Fig. 2. Polished Sections of $^{238}\text{PuO}_2$ Microspheres.

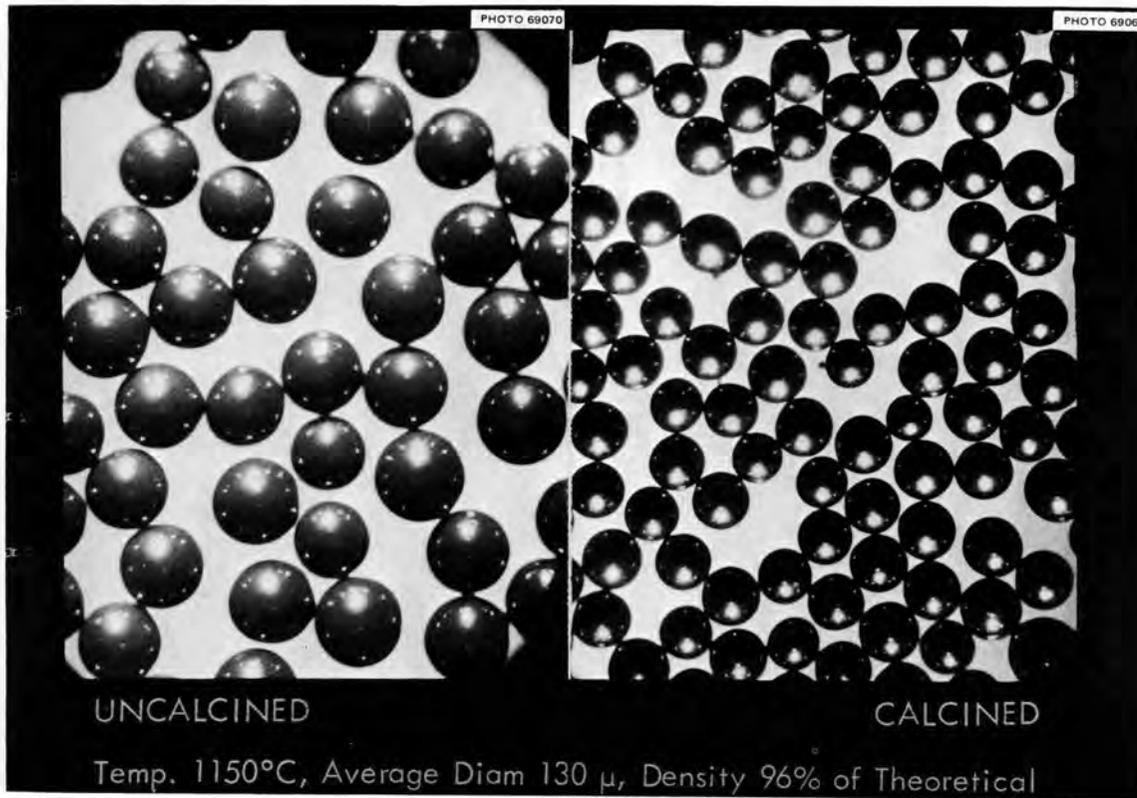


Fig. 3. Calcined and Uncalcined $^{239}\text{PuO}_2$ Microspheres.

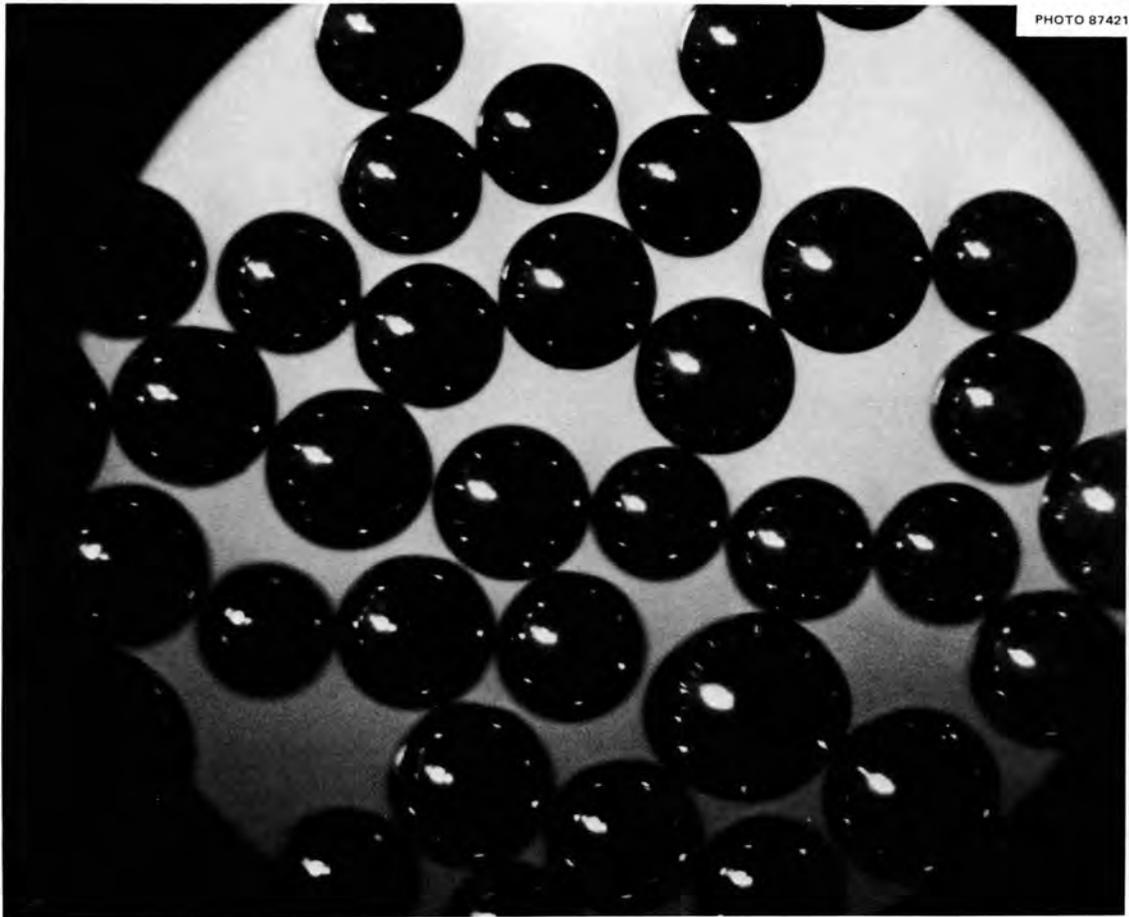


Fig. 4. Calcined $^{238}\text{PuO}_2$ Microspheres.

3.1.3 Crushing Strength

The average crushing strength of a 250- μ -diam $^{238}\text{PuO}_2$ microsphere was found to be 1200 g; the minimum value was 1050 g. The average crushing strength of $^{239}\text{PuO}_2$ microspheres of the same diameter was 550 g. When the latter microspheres were tested at Mound, the crushing strength, per microsphere, prior to plasma firing was found to be approximately 1 kg. After passage through the plasma torch, however, this value decreased to approximately 500 g.

These results show that the direct comparison of crushing strength data from various laboratories has not been feasible. At each site, different measuring devices were used, and different relative values were obtained. Mound Laboratory, Sandia Corporation, General Electric (Vallecitos), Douglas (Richland), and ORNL participated in a "round robin" series of crushing strength tests, using sized thoria, zirconia, and glass beads as standards. Measurements obtained for these standards by Mound, Sandia, and ORNL are shown in Table 1. The most consistent feature of these data is the correlation of crushing strength and particle size.

3.1.4 Size Range and Sphericity

The size of a given calcined microsphere is determined by the size of the sol droplet that is formed. In a two-fluid nozzle, this size may be changed by altering either the flow rate of the sol or the flow rate of the drying solvent. Extended production experience with $^{239}\text{PuO}_2$ led us to believe that at least 90% of the $^{238}\text{PuO}_2$ product microspheres would fall within the desired 50- to 250- μ size range. The maximum-diameter-to minimum-diameter ratio for individual sol-gel particles was essentially 1; tentative plasma torch specifications require that the ratio be no greater than 2.

3.1.5 Stability to Changes in Temperature, and Resistance to Thermal Shock

The sol-gel-produced $^{239}\text{PuO}_2$ that was shipped to Mound for evaluation was processed through a 10-kw plasma torch without any evidence of surface distortions. Although the density of the material decreased slightly on the first pass, it was reported that the same material was recycled through the torch seven times without distortion of the microspheres.

Three tantalum capsules, each containing 1.1 g of sol-gel-prepared plutonia microspheres, were subjected to temperatures of 1800°C for 5, 15,

Table 1. Comparison of Crushing Strength Data^{a,b} Obtained at Various Sites

Material	Run No.	Size (μ)	Mound Laboratory Values			Sandia Values			ORNL Values		
			Average	Maximum	Minimum	Average	Maximum	Minimum	Average	Maximum	Minimum
PuO ₂	1	420							860 (12)	1100	700
	3	420							825 (12)	1050	600
	8	300							533 (10)	780	380
	4	210							367 (9)	570	250
	9	210							318 (10)	530	230
	28	210							361 (12)	510	200
	31	210							448 (13)	600	300
	3	177							284 (9)	330	240
ThO ₂		590-710	>2770	>4563	1750				2472 (20)	4100	925
		420-500	1820	2829	563				1115 (20)	2050	300
		250-297	1104	2340	599				499 (20)	775	300
		177-210	615	870	254				343 (20)	625	175
		74-105	381	723	169				87 (20)	115	60
Glass		297-420	>3126 (2)	>3480	1844	4556 (9)	5715	2994	4167 (20)	7100	2400
		210-297	1929 (21)	2680	884	2780 (7)	4581	1179	3104 (20)	5450	1275
		105-210	2188 (20)	3027	779	2095 (23)	4581	953	3026 (20)	5875	1100
		125-177	892 (26)	1418	226	1303 (11)	2404	318	773 (20)	1535	200
ZrO ₂	I		1168 (20)	1922	805				1014 (20)	1910	500
	II		1548 (20)	2864	663				1419 (20)	3260	600
	III		1051 (20)	1730	675				1007 (20)	2600	300
	IV		902 (20)	1626	329				777 (20)	1300	400
	Air		1033 (20)	1735	528				858 (20)	2000	270

^aAll values are given in grams per microsphere.

^bFigures in parentheses indicate number of determinations.

and 25 min respectively. The material that was soaked for 5 min (Fig. 5) was readily poured from the capsule. With the longer soaking periods, some of the material adhered lightly to the capsule wall. The extended soaking period (25 min) effected sufficient sintering to produce a fairly solid mass of microspheres (Fig. 6). It is interesting to note that, in each instance, the microspheres remained intact. It was later learned that tantalum is not the most desirable metal for use with PuO_2 at 1800°C .

3.1.6 Oxygen Exchange

A technique has been developed at the Savannah River Laboratory (SRL) for preparing ^{16}O -enriched (or ^{18}O -depleted) $^{238}\text{PuO}_2$ using isotopic exchange with ^{18}O -depleted water vapor. This technique, which has been successfully demonstrated at SRL with samples of ORNL sol-gel material containing ^{239}Pu rather than ^{238}Pu , is believed to be a practical means for preparing $^{238}\text{PuO}_2$ microspheres that have the desired low neutron-emission rate.¹⁰

In the demonstration, isotopic exchange between water vapor and uncalcined $^{239}\text{PuO}_2$ microspheres was essentially complete within 30 min at a temperature of about 700°C . (Calcined microspheres were inert to oxygen exchange at temperatures up to 800°C , the maximum temperature used in the tests.)

The evaluation tests were performed by making batch equilibrations. Uncalcined plutonia microspheres in a platinum boat were heated in an evacuated quartz tube, outgassed, and then exposed to ^{18}O -depleted water vapor at a pressure of about 25 mm (absolute). The extent of the oxygen exchange was calculated on the basis of the ^{18}O analyses of the final water vapor and of the PuO_2 . (Complete exchange is defined as attainment of isotopic equilibrium.) In a typical experiment, 0.001 mole of uncalcined $^{239}\text{PuO}_2$ microspheres (0.204% of the oxygen was ^{18}O) was equilibrated sequentially with two 0.0139-mole aliquots of ^{18}O -depleted water vapor (0.007% ^{18}O) at 700°C . The ^{18}O assay of the $^{239}\text{PuO}_2$ after treatment was 0.027%.

Microspheres that had been subjected to the conditions necessary for isotopic exchange were calcined at 1150°C . There was no indication of any deleterious effect resulting from the isotopic exchange treatment. In any production process, oxygen exchange would be conducted after the microspheres had been dried, but prior to calcination.

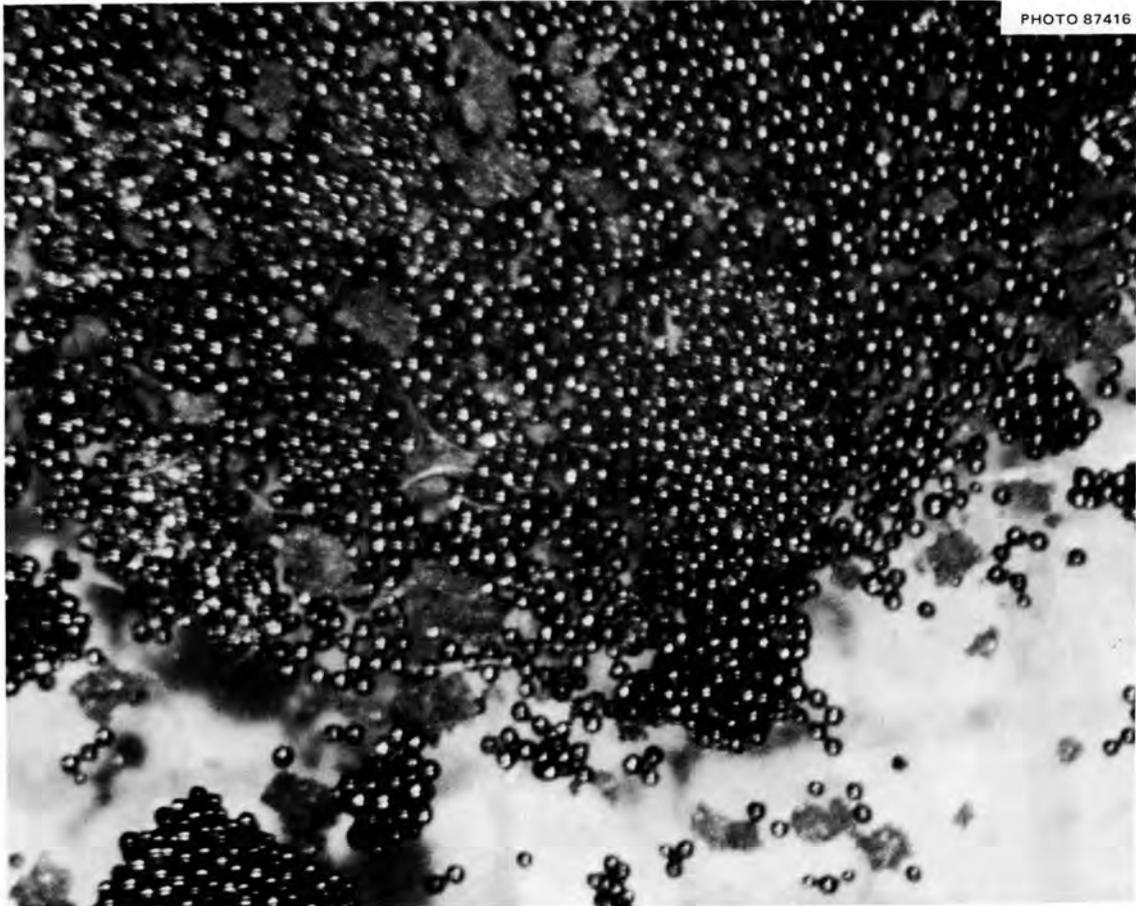


Fig. 5. $^{239}\text{PuO}_2$ Microspheres Soaked 5 min at 1800°C .

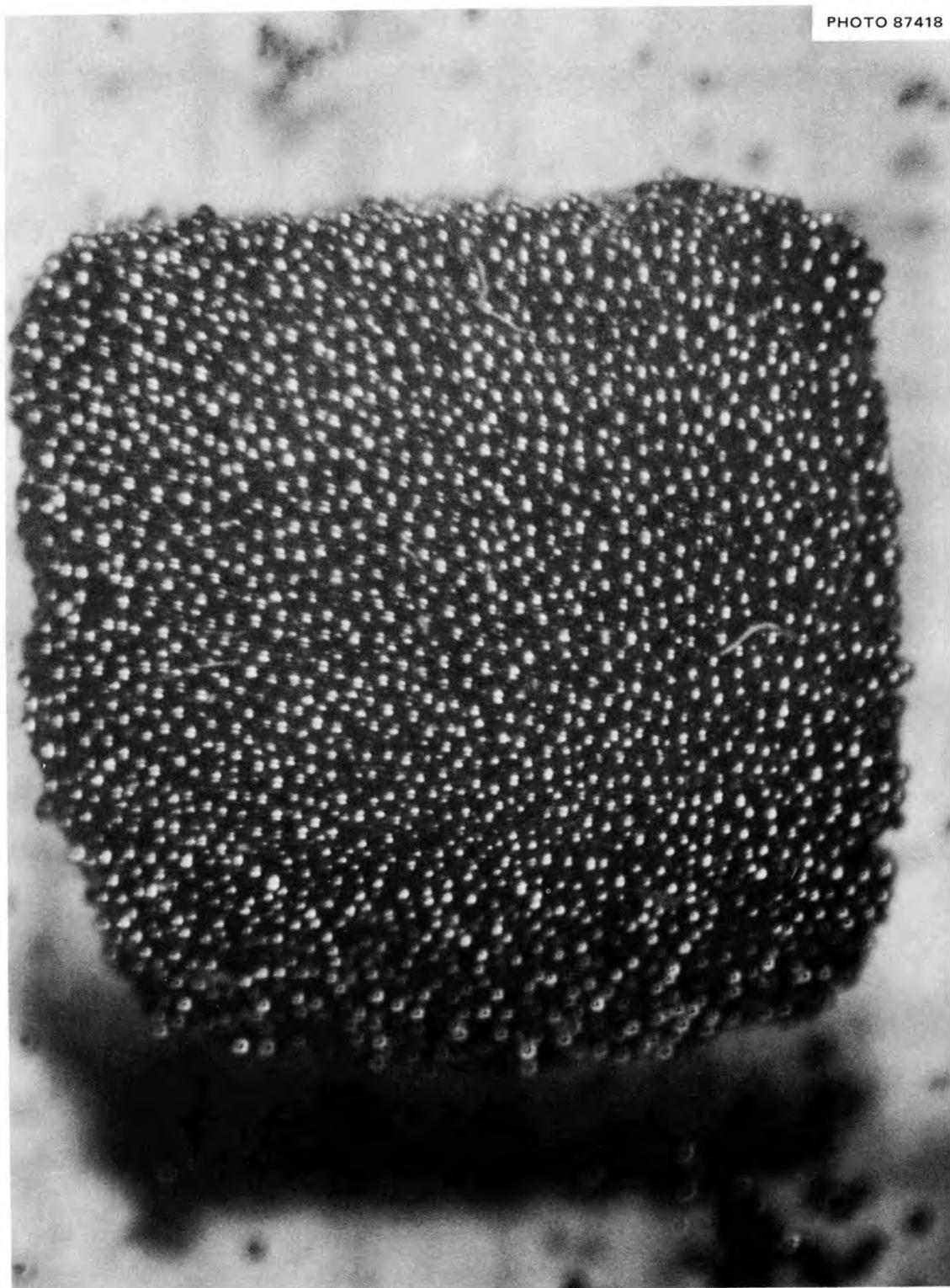


Fig. 6. $^{239}\text{PuO}_2$ Microspheres Soaked 25 min at 1800°C .

3.2 Process Considerations

In our equipment scale-up studies, we noted several important areas in which the sol-gel route may be superior to the method presently employed. As presently conceived, sol-gel offers the following:

1. The process is remotely operable; therefore, personnel exposure to radiation can be expected to be low.
2. The process features a contained "solution" system.
3. The yield of the process is expected to be high.
4. The cost of operation should be low since the equipment is small and compact and only a few operators are required.
5. The process can be operated to produce mixed sols ($\text{PuO}_2\text{-ThO}_2$, $\text{PuO}_2\text{-ZrO}_2$, etc.).
6. The process can be modified to produce shards and sinterable powders.
7. Size control of the particles produced is excellent.
8. Recycle of off-specification material requires only aqueous processing.

3.2.1 Remote Operation

The sol-gel process is designed for remote operation, which reduces operator exposure and thereby allows higher throughputs. One of the current problems at Mound Laboratory is the limited quantity of material that can be handled because of thermal effects and radiation exposures to hands. As currently envisioned, routine operations in the sol-gel box may be performed from a panel board. Manipulators are provided for transferring product to the conveyor system, operating process samplers, and making any minor changes that might be dictated by further developments.

3.2.2 "Solution" System

The sol-gel process features primarily a "solution" system, which lends itself to efficient quality control and accountability. The starting material is $\text{Pu}(\text{NO}_3)_4$, which is readily analyzed by acceptable coulometric ($\pm 0.5\%$) or potentiometric accountability methods. Side or waste streams may be analyzed with good precision by means of counting techniques. The final product may be weighed accurately as stoichiometrically pure PuO_2 . All of these factors make for good system material balances and reliable plutonium accountability.

3.2.3 Process Yield

The reported overall process yield using the plasma-torch method of microsphere preparation is approximately 60%. Losses are about evenly divided between feed preparation and torch operation. Yields using the sol-gel process have routinely been greater than 90% with semiengineering equipment. Process nonrecoverable losses have amounted to less than 0.1%.

3.2.4 Throughput and Process Simplicity

The use of small, compact equipment in the sol-gel process effectively reduces the size of the production unit from that necessary for a standard plasma torch line. The 10 x 7 x 4 ft sol-gel box results in a smaller overall system with a larger capacity than is presently possible with a plasma torch line.

3.2.5 Addition of Diluents

The addition of various sols, such as ThO₂ and ZrO₂, to PuO₂ sols to obtain a mixed-oxide product is feasible in the sol-gel process. The results of our chemical studies indicate that no difficulty should be encountered in mixing these sols and forming microspheres. We have routinely prepared UO₂-PuO₂, UO₂-ThO₂, and ThO₂-PuO₂ microspheres for use in fast reactor fuel studies.

3.2.6 Flexibility

After a sol has been prepared, it may be dried in different ways to yield the desired type of product. That is, plutonia sol (or a mixed sol) can be processed to yield microspheres, dense shards, sinterable powders, or "clays" that may be extruded. Shards may be sized and blended so that they will compact to different densities; microspheres of controlled porosity have also been prepared.¹¹

3.2.7 Size Control

Microsphere size may be controlled in various ways using the sol-gel process. For example, the solvent and sol feed ratios (to a two-fluid nozzle) may be adjusted to yield specific size ranges, or capillaries of different diameters can be used to feed the sol. These procedures have been successful in our 35-kg/day ThO₂ microsphere unit and in the engineering-scale ²³⁹PuO₂ system. Based on results of engineering studies, we expect that 96% of the product will be in the desired size range (50 to 250 μ).

3.2.8 Scrap Recovery

Undesirable or reject material produced from the plasma-torch method must be recycled by difficult salt fusion methods. Off-specification material from the sol-gel process may be dissolved with aqueous HNO_3 -HF mixtures and recovered by established anion exchange technology.

3.3 Safety Analysis

We believe that significant safety advantages would accrue, both in production and in application, from the use of sol-gel material. The aspects of containment, fire and radiation hazard, shielding, and product environment are reviewed.

3.3.1 Containment

One of the more important advantages in sol-gel operations is the avoidance of the dusting problem encountered in dry processing. Since the sol-gel process features a solution system, the equipment is easier to contain than other equipment, and containment is more effective. Furthermore, if containment is breached, the resulting hazard is less than with dry materials.

3.3.2 Fire Hazard

Since the sol-gel process features primarily a solution system, the process operations streams are isolated from the atmosphere of the box, and all equipment is serviced by the off-gas system. Such an arrangement essentially eliminates the PuO_2 dusting problem encountered in a typical torch process. The pressing and grinding operations used to prepare plasma feed stock almost certainly result in significant deposits of PuO_2 on filters. Even small quantities of $^{238}\text{PuO}_2$ (heat generation rate, 0.55 w/g), such as the deposits on these filters, would represent a serious fire hazard.

3.3.3 Radiation Hazard

In the preparation of $^{238}\text{PuO}_2$ sol, the dose rates measured through the shielding windows are significantly decreased by the self-shielding effect of the water associated with the $^{238}\text{PuO}_2$. This same beneficial effect is also derived from the hydrogenous drying solvent used in the microsphere-forming process. These factors result in lower operator exposures and, in turn, permit longer working times.

Soon after the microspheres have been dried to remove solvent, they are subjected to oxygen exchange treatment. Dose rates for the exchanged material are even lower than for the unexchanged material. This means that the individuals classifying the calcined product and fabricating the end-use item will also experience reduced exposures.

3.3.4 Product Shielding

The use of oxygen exchange, which is readily adaptable to the sol-gel process, reduces the shielding required for the final capsule. The ^{16}O -enriched $^{238}\text{PuO}_2$ neutron-emission rate advantage has been studied and reported by Mound and by SRL.

3.3.5 Internal Particle Voids

Internal voids weaken the structure of a particle and thus, in space applications, could lead to breakup of the particle upon reentry. Such breakups would, in turn, result in the dispersion of material smaller than $50\ \mu$ in diameter and increase the hazard of inhalation by the population. Obviously, higher-density particles have smaller void volumes and provide increased safety. However, even for particles of the same density (equal void fractions), the size of the internal voids, or "bubbles," is important. A void fraction dispersed in many small cells rather than a few large ones has a diminished weakening effect on the particle.

The void volume in sol-gel material consists almost entirely of micro-porosity (not visible at magnification of 500X). Plasma-torch material, on the other hand, contains larger bubbles, which are observable in photomicrographic sections. Even if both materials exhibited the same increase in void volume upon reentry, the material with the larger initial voids should be more likely to undergo degradation. Therefore, the use of sol-gel material with its higher density and smaller, dispersed voids should represent a lesser inhalation hazard.

4. DEVELOPMENT OF $^{238}\text{PuO}_2$ SOL PREPARATION TECHNIQUES

The first objective in our development of techniques for preparing $^{238}\text{PuO}_2$ sols was to determine if ^{238}Pu could simply be substituted for ^{239}Pu in our existing procedures. In the event that this was feasible, we planned to test the resulting $^{238}\text{PuO}_2$ sol for stability and for use in

forming good-quality microspheres. Our glove-box experiments were restricted to a maximum of 10 g of ^{238}Pu in each case because of containment limitations.

4.1 Preparation of $^{239}\text{PuO}_2$ Sol

Figure 7 presents the generalized flowsheet for preparing plutonia sol. (The digestion step shown was not used initially.) This is a flexible flowsheet, as shown by the ranges of concentrations over which it has been demonstrated; the batch size given is 150 g of plutonium. Prior to precipitation, a feed adjustment is made, if necessary, by passing NO gas through the $\text{Pu}(\text{NO}_3)_4$ solution to convert both Pu^{6+} and Pu^{3+} to the desired Pu^{4+} . To date, the $\text{Pu}(\text{NO}_3)_4$ that we have received has not required a plutonium valence adjustment. A minimum HNO_3 concentration of 1 M is maintained in the feed to prevent polymerization; however, sols have been successfully prepared starting with free HNO_3 concentrations as high as 3 M. In the precipitation step, as little as 48% excess NH_4OH has proved to be satisfactory as long as the concentration of this base in the final solution is at least 1 M. The $\text{Pu}(\text{NO}_3)_4$ feed solution is added to the NH_4OH solution at rates up to 30 cc/min. Moderate agitation is used to ensure rapid neutralization and precipitation of the $\text{Pu}(\text{OH})_4$. The NH_4NO_3 --excess NH_4OH solution is drawn off through a filter having 10- μ -diam openings. The precipitate is washed four times to remove NH_4^+ ; the filter cake is resuspended in each wash. Filtration time is about 30 min per wash. Plutonium losses to the total filtrate have been less than 0.01%. After the washing step, the precipitate is digested for 2 hr in H_2O at 95 to 100°C; this treatment stabilizes the crystalline structure and prevents depolymerization during subsequent steps. A high-nitrate sol is then formed by peptizing in dilute HNO_3 at a NO_3^-/Pu mole ratio of approximately 2. All of the steps including peptization are carried out in a single precipitation-filtration vessel that is 8 in. in diameter and has a porous stainless steel filter in the bottom. The high-nitrate sol passes out through the bottom of the vessel, leaving no solids on the filter.

A NO_3^-/Pu mole ratio of 1 or greater is necessary to accomplish peptization. Although ratios as high as 4 have been demonstrated, a ratio of 1.1 is sufficient to produce a sol upon heating to approximately 90°C. At

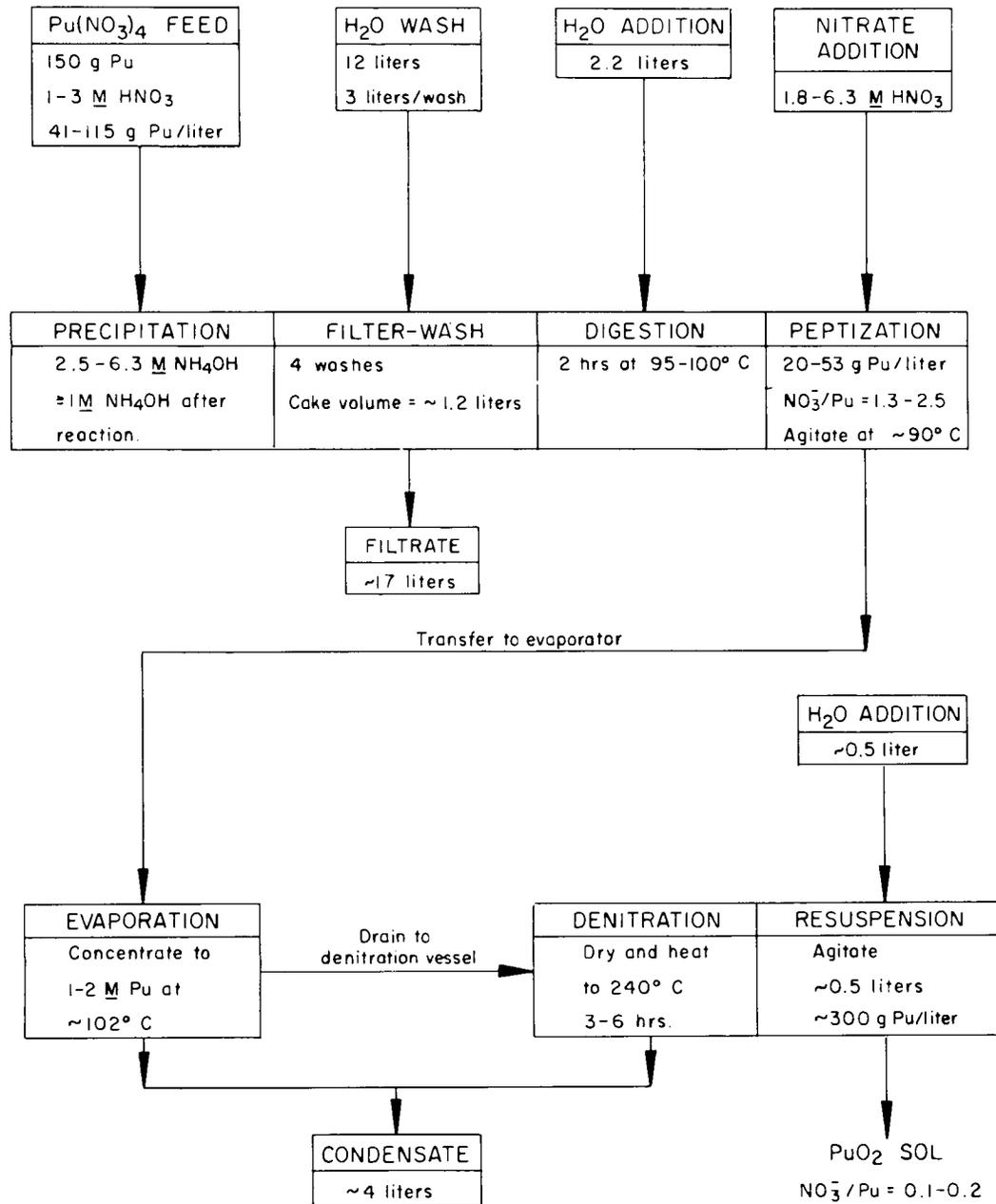


Fig. 7. Generalized Flowsheet for Preparing Plutonia Sol.

this point, a true sol (crystallite size, $<20 \text{ \AA}$) exists, but microspheres formed from this material would have a low density and a low resistance to crushing. To form a desirable product, a sol must have a NO_3^-/Pu mole ratio in the range of 0.1 to 0.2; the appropriate reduction in ratio is accomplished by thermal denitration (i.e., baking). Several other methods of precipitation and denitration were attempted; however none produced satisfactory results.¹²

In the thermal denitration step, the sol is evaporated to dryness at 100°C to form a thin, porous cake that remains intact through subsequent heating to 240°C . (The higher the temperature, the shorter the time required for denitration, as shown in Fig. 8.) Excess HNO_3 is evolved during evaporation, giving an initial NO_3^-/Pu mole ratio of 0.8 to 1.0 in the dry solid. In general, after 1 to 2 hr at 240°C , this ratio decreases to 0.2 to 0.3; usually an additional 2 to 3 hr is required to attain a final NO_3^-/Pu mole ratio of 0.1 to 0.15. Progress of the denitration is followed by periodically resuspending a weighed sample of the dry material and titrating with NaOH to determine the NO_3^- content. It is important that the heating of the solid be uniform in order to produce a homogeneous product. Denitration that is allowed to proceed until the NO_3^-/Pu mole ratio is appreciably less than 0.1 yields a form of PuO_2 that cannot be resuspended. The design of the denitration vessel allows independent control of temperatures of the top and bottom surfaces and limits radial gradients to about 2°C .

The denitration step promotes crystallite growth and agglomeration. After denitration, the average size of the crystallites is approximately 80 \AA ; these crystallites form agglomerates as large as 1000 \AA . Crystallite growth is desirable; however, the degree of agglomeration must be limited if a stable sol is to be obtained. Denitrated sol having a NO_3^-/Pu mole ratio in the range of 0.1 to 0.15 can be resuspended in water, using only mild agitation, to form sols having plutonium concentrations approaching 2 M ; more-concentrated sols may be produced by subsequent evaporation if desired.

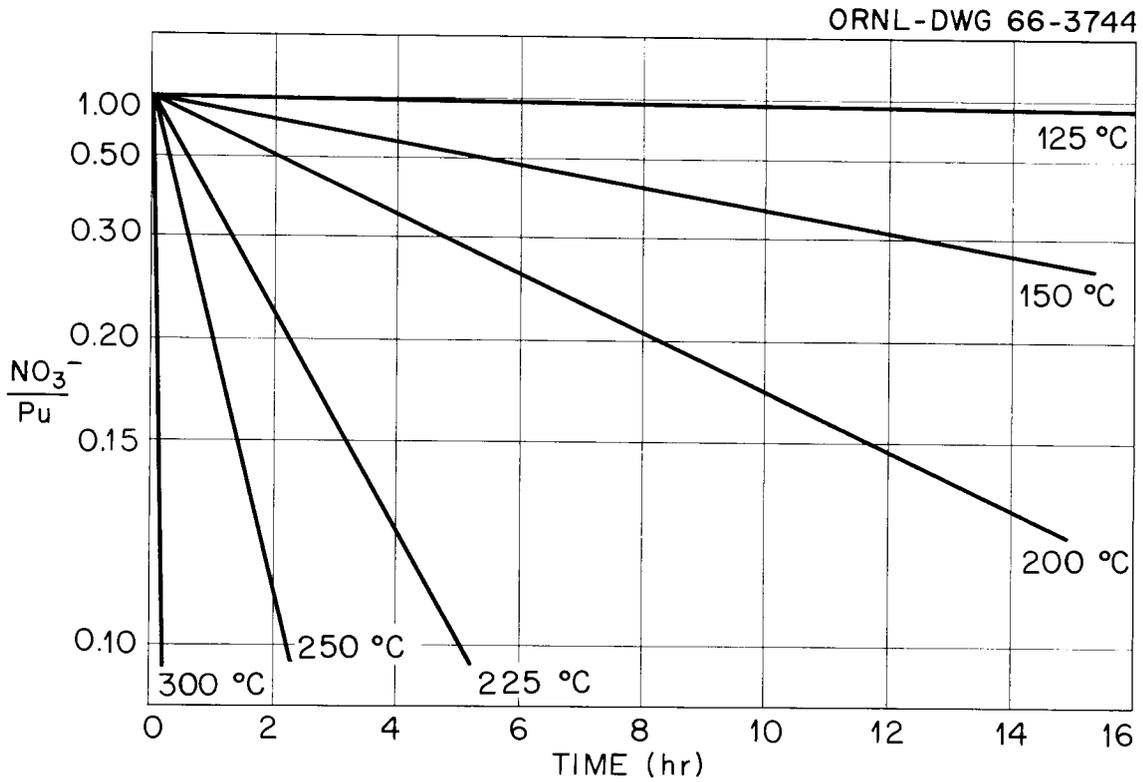


Fig. 8. Time Required for Thermal Denitration at Different Temperatures.

4.2 Adaptation of the Generalized $^{239}\text{PuO}_2$ Sol Preparation Flowsheet to $^{238}\text{PuO}_2$ Sol Preparation

Our initial philosophy for preparing $^{238}\text{PuO}_2$ sols was to proceed rapidly through the process to avoid radiolysis and self-heating effects. The starting material in each case was calcined $^{238}\text{PuO}_2$ powder. The oxide was dissolved in HNO_3 , and the valence of the plutonium was adjusted with nitric oxide. The resulting solution was then used in several experiments.

4.2.1 Acid in the Feed

Initially, ^{238}Pu solutions with high acid concentrations of 4 to 8 M HNO_3 were used to maintain valence stability and to allow convenient handling; however, thermal denitration of these preparations proved to be unsuccessful. In subsequent efforts, in which the acid concentration in the feed was reduced to 2 M, thermal denitration was successful, and good yields of $^{238}\text{PuO}_2$ sols with NO_3^-/Pu mole ratios of 0.15 to 0.20 were obtained. However, the sols were opaque and more viscous than desired, and microspheres prepared from them had surface imperfections that can be generally characterized as deep pits or holes. These effects were found to be independent of the type of surfactant used or of the surfactant concentrations in the drying solvent in the microsphere-forming column. Since microspheres of the desired quality could not be obtained with the existing plutonia sol preparation flowsheet, we decided to modify the flowsheet.

4.2.2 The Digestion, or Aging, Step

We found that $^{238}\text{PuO}_2$ sols of a superior quality could be made by incorporating an aging or digestion step into the original flowsheet. Aging was accomplished by refluxing the washed precipitate in water for about 2 hr prior to peptization with dilute HNO_3 . Although it was not immediately evident why this step was beneficial, the resulting improvement in final sol characteristics was very pronounced. The product sols were dark green and translucent, and were more fluid and had lower NO_3^-/Pu ratios than the sols prepared without this step. Process yields were increased to essentially 100%. Calcined microspheres (Fig. 4) that exhibited high density, excellent crushing strength, and good surface characteristics were readily prepared from these sols. The sols appeared to be stable on standing, showing no tendency to settle after several days. The only visible change

in the sols that were stored for periods of about one week was loss of water due to evaporation. Similar product improvements and process yields were obtained when the aging step was incorporated into the $^{239}\text{PuO}_2$ sol process.

4.3 Electron Microscopy of Aged and Unaged Sols

Concurrent with our efforts to prepare $^{238}\text{PuO}_2$ sols, experiments were initiated in collaboration with Dr. W. O. Milligan, of Baylor University, to delineate the colloidal characteristics of $^{239}\text{PuO}_2$ sols by electron microscopic and electron diffraction techniques. These experiments proved to be quite useful, both in increasing our understanding of the basic system and in defining the effects of the aging step. The results indicated that the plutonium hydroxide precipitate is a hydrous form of PuO_2 , since the first diffraction pattern obtained from washed precipitate is identical to PuO_2 patterns. The same diffraction pattern is obtained as the material is processed through the different steps of the flowsheet, that is, from the dispersed precipitate to the final denitrated sol. The absorption spectrum for the colloidal PuO_2 particles is identical to that reported in the literature for plutonium(IV) polymer.

4.3.1 Degree of Crystallinity

An electron micrograph of a high-nitrate plutonia sol prepared from an aged precipitate is shown in Fig. 9. This material, which is highly crystalline, is composed of small, symmetrical primary particles with diameters of 10 to 20 Å. The major difference between aged and unaged precipitates was found to be in the degree of crystallinity. This difference is most strikingly demonstrated by a comparison of electron diffraction patterns, as shown in Fig. 10. The definitive PuO_2 diffraction pattern, which is characteristic of amorphous particles, is obtained from unaged material.

We believe that the degree of crystallinity at this stage of processing of plutonia sols is important from two standpoints: (1) highly crystalline polymer is more resistant to depolymerization during concentration of the high-nitrate sol, and (2) it results in a more ordered crystallite growth during thermal denitration. Amorphous material is more easily depolymerized to ionic, noncolloidal plutonium forms that lead to undesirably large aggregates and erratic denitration.

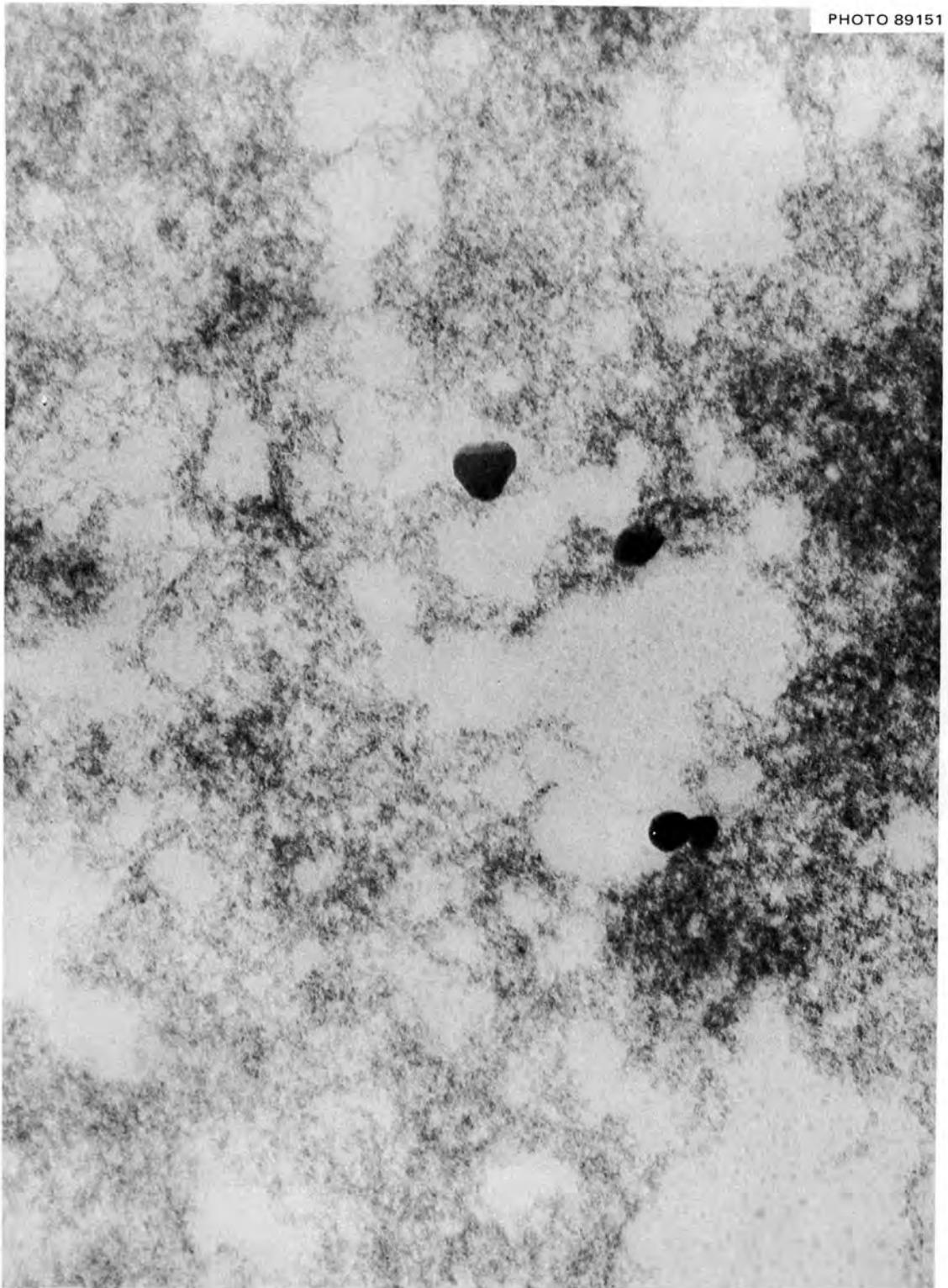


Fig. 9. High-Nitrate Plutonia Sol Prepared from an Aged Precipitate.

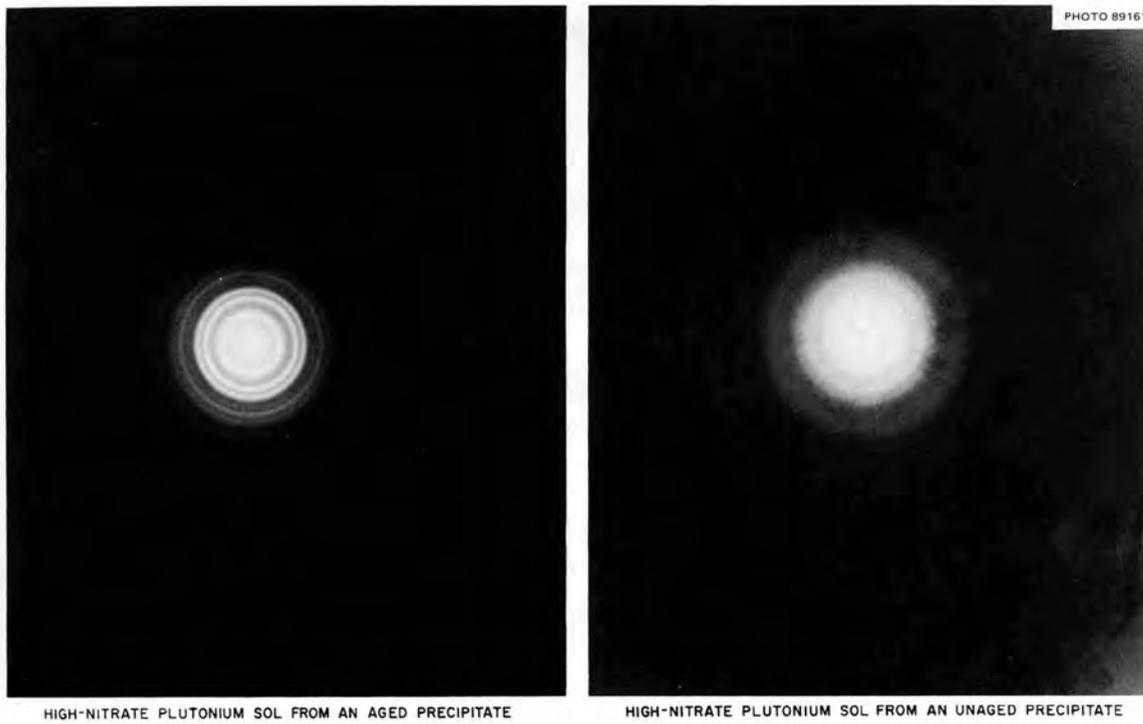


Fig. 10. Electron Diffraction Patterns for $^{238}\text{PuO}_2$ Sols.

4.3.2 Degree of Aggregation

During thermal denitration of a sol at elevated temperatures, the size of the crystallites in the sol increases to about 80 A (see Fig. 11). Examination of the crystalline material reveals that it consists, primarily, of symmetrical particles of 80 to 100 A (or particles about the same size as the crystallites); the electron diffraction pattern corresponds to that of PuO_2 . Large aggregates of the primary crystallites are also present. Micropore filtration experiments have indicated that unaged sols contain aggregates larger than 2000 A, whereas the aggregates in aged sols are smaller than 500 A.

4.3.3 Scale-up at Mound Laboratory

Laboratory scale-up experiments were conducted at Mound because facilities were available. The development group at ORNL collaborated closely with Mound personnel throughout the course of the work and performed small-scale experiments in support of the joint program.

In initial scale-up experiments, 25 g of ^{238}Pu was used in preparation runs made in laboratory equipment. Sols with final NO_3^-/Pu mole ratios of about 0.2 were obtained in the first two runs. This ratio seemed to be limiting, since no further decrease occurred with increased baking. Microspheres prepared from these sols were pitted. In the next two runs, the concentration of acid in the feed was decreased further (from 2 M to 1 M), and the NH_4OH concentration was decreased from 7 M to 2 M. These changes resulted in the production of sols with final NO_3^-/Pu mole ratios of 0.13 to 0.18. Good-quality microspheres were prepared from both products.

A final successful run was made in this series; in it, the concentration of acid in the feed was increased to 1.5 M. This was desirable because the preparation of stable feed at an acid concentration of 1 M is difficult, and this difficulty is accentuated as the batch size is increased.

Further scale-up studies made at Mound Laboratory are described in Sect. 7.1.

4.4 Investigation of Process Variables

In conjunction with these experiments at Mound, several significant small-scale experiments were performed at ORNL. It was recognized from previous work that successful sol preparation requires the formation and

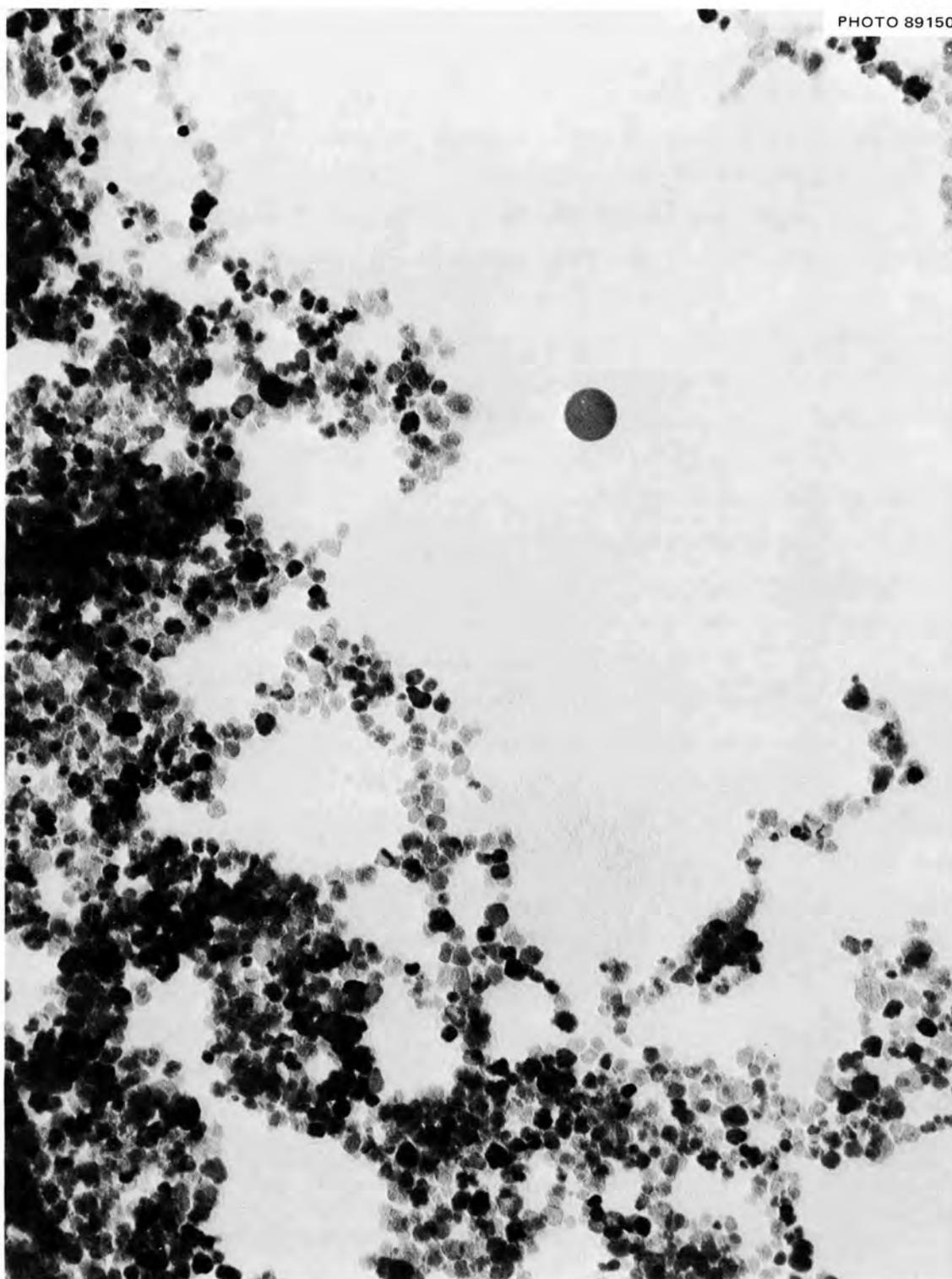


Fig. 11. Final Plutonia Sol Prepared from an Aged Precipitate.

retention of highly crystalline plutonium polymer.¹³ Therefore, primary efforts were directed at determining the effects of process variables on polymer formation and degradation.

4.4.1 The Two-Phase Region

As high-nitrate sols (made from aged precipitates) are concentrated by evaporation, an insoluble solid is formed and suspended in the boiling liquid when the nitrate concentration is between 0.5 and 5 M. When the nitrate concentration exceeds 5 M, a stable colloidal solution re-forms. This phenomenon is reversible; that is, the addition of water to 5 M solution will again produce two phases, and, if water is added to the settled solid phase after separation from the supernate, a stable colloidal solution is produced. This phenomenon was investigated because of concern over inadvertent thermal denitration of the solid phase when low aqueous volumes are attained in process equipment.

The solid phase was found to consist of crystalline polymer, which can be separated from the liquid (by filtration), dried, denitrated, and formed into excellent sol. Ionic forms and degraded polymer concentrate in the liquid phase. Attempts to form sols from solids obtained by evaporating the liquid phases to dryness were unsuccessful. Denitration was very rapid, and the resulting solids would not resuspend.

4.4.2 Effects of Peptization Ratio

Other experiments were designed to assess the effect of HNO_3 on plutonium polymer. During the evaporation of high-nitrate plutonia sols to dryness, plutonium polymer is exposed to high HNO_3 concentrations at elevated temperatures. Depolymerization could occur during this operation; also, the self-heating and radiolytic properties of ^{238}Pu would be expected to increase degradation in the case of $^{238}\text{PuO}_2$ sols. Since the amount of nitric acid in the system is determined by the HNO_3/Pu mole ratio used to peptize the aged precipitate, the effect of acid on depolymerization was evaluated as a function of peptization ratio. We investigated NO_3^-/Pu mole ratios from 1 to 4, and the amount of polymer degradation (which is evidenced by formation of ionic Pu^{6+}) was determined spectrophotometrically. High-nitrate $^{238}\text{PuO}_2$ and $^{239}\text{PuO}_2$ sols were examined immediately after peptization (approximately 0.1 M plutonium) and after evaporation to dryness.

Degradation was shown to occur principally during evaporation, as dryness was approached, and as the nitric acid concentration increased to greater than 5 M. Freshly peptized $^{238}\text{PuO}_2$ sol contained 1 to 2% ionic species (mainly Pu^{6+}), while less than 1% ionic species was observed for $^{239}\text{PuO}_2$ sols. The peptizing ratio had little effect on these values. The maximum amount of degradation was observed in samples that had been evaporated to dryness. In the case of ^{239}Pu preparations that had been peptized at NO_3^-/Pu ratios of 3 or less, the maximum amount of ionic species amounted to 2% of the plutonium. At a peptization ratio of 1, only 0.1 to 0.2% ionic species was observed; at a ratio of 4, more than 10% was found. The amount of ^{238}Pu polymer that decomposed was about three times the amount of ^{239}Pu polymer that decomposed under similar conditions. In these experiments, special care was exercised to avoid obtaining erroneous results. For example, hexavalent ^{238}Pu is sensitive to the dilution medium and to the time that is allowed to elapse after dissolution of the dried solids. Also, dissolution, in water, of the solids containing either ^{238}Pu or ^{239}Pu was avoided in order to prevent polymerization of any tetravalent plutonium. Dissolving the evaporated solids in 0.1 to 0.2 M HNO_3 just prior to spectrophotometric examination was found to be a satisfactory procedure.

4.4.3 Variation of Peptization Time with Nitrate Ratio

These experiments demonstrated the adverse effect of excess HNO_3 ; however, low NO_3^-/Pu mole ratios could be disadvantageous if longer digestion times were required to accomplish peptization at a given plutonium concentration. It was found, however, in experiments with both ^{238}Pu and ^{239}Pu , that lower ratios could be used without an appreciable extension of the peptization time if higher plutonium concentrations (and hence higher initial nitric acid concentrations) were employed. Peptizations at 0.45 M plutonium were demonstrated without incurring a two-phase region. Thus, in addition to the advantage of a lower NO_3^-/Pu ratio (e.g., 1.2), the volume of liquid to be evaporated is reduced to 22% of that required when a plutonium concentration of 0.1 M and a NO_3^-/Pu ratio of 2.5 are used. When ^{239}Pu is peptized at nitrate and plutonium concentrations much greater than 0.45 M, the plutonium is "peptized" as a two-phase system. While such mixtures will convert to a single phase upon evaporation and subsequently denitrate in a normal manner, the difficulty of handling the precipitate and two-phase mixture makes peptization in such solutions undesirable.

4.4.4 Effects of Iron and Fluoride Impurities

Experiments were performed to determine whether small amounts of fluoride (present from the dissolution of PuO_2) or iron (present as a contaminant) would create difficulties in the preparation of plutonia sols. About 3 wt % iron (as ferric nitrate) and 0.1 M HF were added to a nitric acid solution of ^{239}Pu . Feeds containing one or both of the contaminants were prepared and processed to form sol in the usual manner. No detrimental effects were observed in any of the preparations. Fluoride was removed during the precipitation and washing of the plutonium, while iron was carried through the process to the final sol. Sols containing iron had a brownish hue instead of the normal green color.

4.4.5 Self-Denitration of High-Nitrate $^{238}\text{PuO}_2$ Sol

The denitration of high-nitrate $^{238}\text{PuO}_2$ solids by self-heating effects was evaluated at two batch sizes. High-nitrate sols were prepared in the normal manner (using a NO_3^-/Pu peptizing ratio of 1.5) and evaporated to dryness. A 5-g portion was spread to a 1/16-in. bed depth, and a 15-g portion was arranged to a depth of 1/4 in. The NO_3^-/Pu mole ratio was checked periodically. Nitrate was lost in both samples, and the NO_3^-/Pu mole ratio decreased to 0.18 in one week. (Rates were not appreciably different for the two samples.) The apparent temperature, as measured by a thermocouple placed in the solids, did not exceed 120°C in either case. However, after one week, about one-half of the material would not resuspend to form a sol. While these results cannot be extrapolated directly to larger batches of ^{238}Pu , it must be inferred that, since denitration does occur in the solid state (even with small quantities of material at bulk temperatures at least 100°C less than the normal processing temperature for ^{239}Pu), the effect will be more pronounced in larger batches. Since the denitrated solids in this experiment were not satisfactory for preparing sol after one week, the holdup of high-nitrate $^{238}\text{PuO}_2$ solids for even a short period of time prior to thermal denitration is probably undesirable.

5. ENGINEERING DEVELOPMENT

A remotely operated, neutron-shielded facility was constructed in cell 4 of Bldg. 3019 at ORNL to demonstrate the sol-gel process as a method for producing dense $^{238}\text{PuO}_2$ microspheres. The system was designed as a remotely operated replica of the multiple glove-box facility used in the ^{239}Pu development program. The equipment was sized to process 200 g of plutonium per day.

5.1 The ORNL Pilot Plant

The facility described above was designed to convert acid plutonium nitrate feed to dense $^{238}\text{PuO}_2$ microspheres in the 50- to 250- μ -diam range. It included sol preparation equipment, microsphere-forming equipment, firing furnace, and classification equipment. Auxiliary systems such as cooling water, steam, vacuum, vessel off-gas, gas supply, and waste collection were also provided. A schematic flowsheet of the cell 4 equipment is shown in Fig. 12. After the equipment components had been fabricated, they were positioned in a plywood mockup of the cell, and the connective piping was installed; such a procedure was necessitated by space limitations in the cell itself. An overall view of the equipment in the mockup is shown in Fig. 13. More details may be seen in Figs. 14-16. After the vessels had been calibrated and the piping systems had been hydraulically tested in the mockup, the equipment was permanently installed in cell 4. Figure 17 is a front view of the facility; Fig. 18 is a view inside, parallel to the operating face.

5.1.1 Sol-Preparation Equipment

Since the ^{238}Pu was received as an oxide, both the dissolution and the complete conversion to Pu^{4+} (which was accomplished by bubbling NO gas through the warm, acid solution) had to be carried out in the valence adjustment vessel. From this vessel, the adjusted feed was metered into NH_4OH ($\sim 4 \text{ M}$) in the precipitator-filter-peptizer; batch washing, digestion and peptization were carried out in the same vessel (Fig. 19) following the precipitation step. The mother liquor (containing excess NH_4OH and reaction product NH_4NO_3) and multiple water rinses, were transferred by vacuum to the aqueous waste system. After the plutonium polymer had been peptized with HNO_3 , the high-nitrate sol (NO_3^-/Pu mole ratio ≈ 2) was

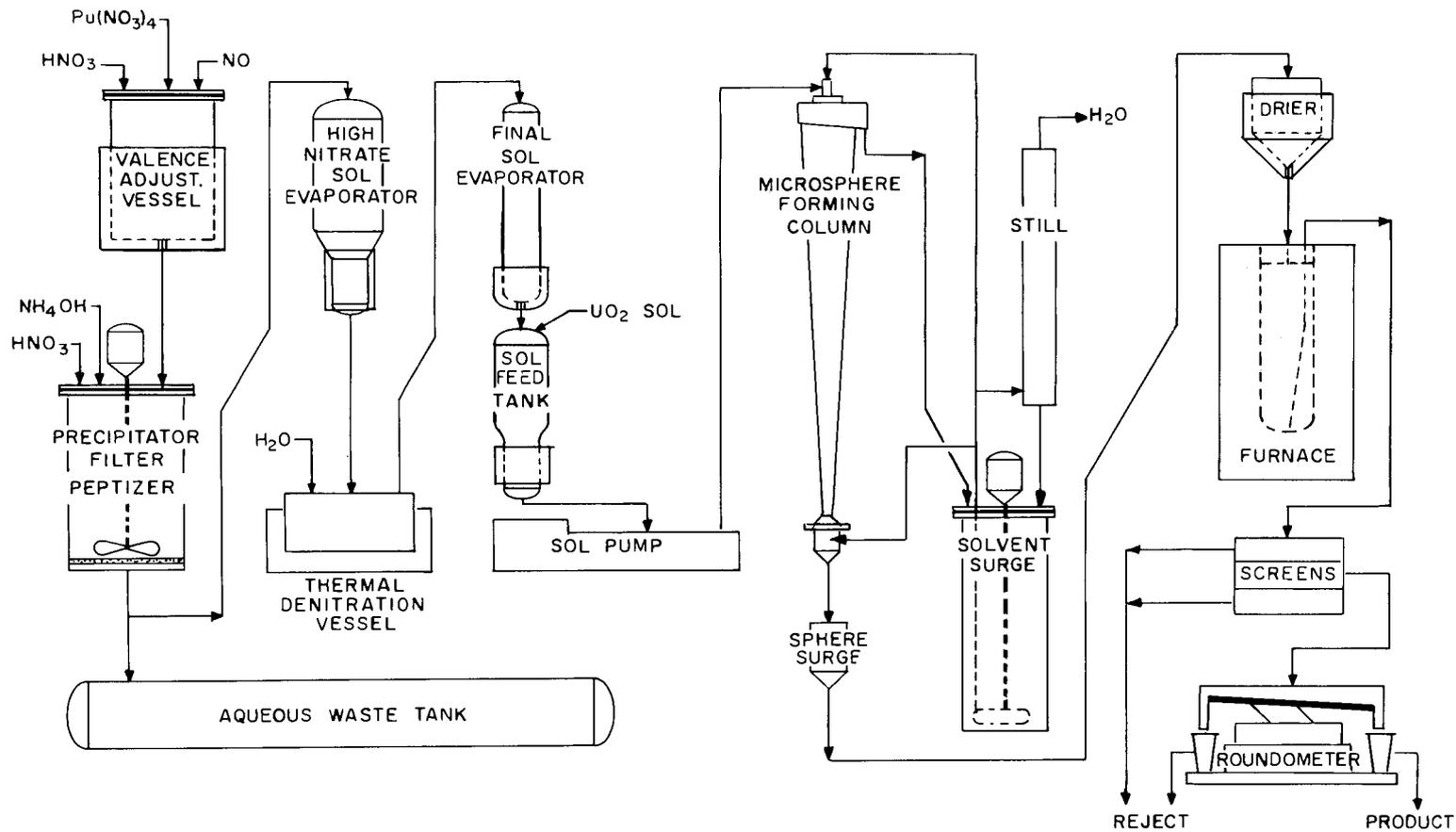


Fig. 12. Schematic Flowsheet of Shielded Equipment for Preparing PuO_2 Sols and Microspheres.

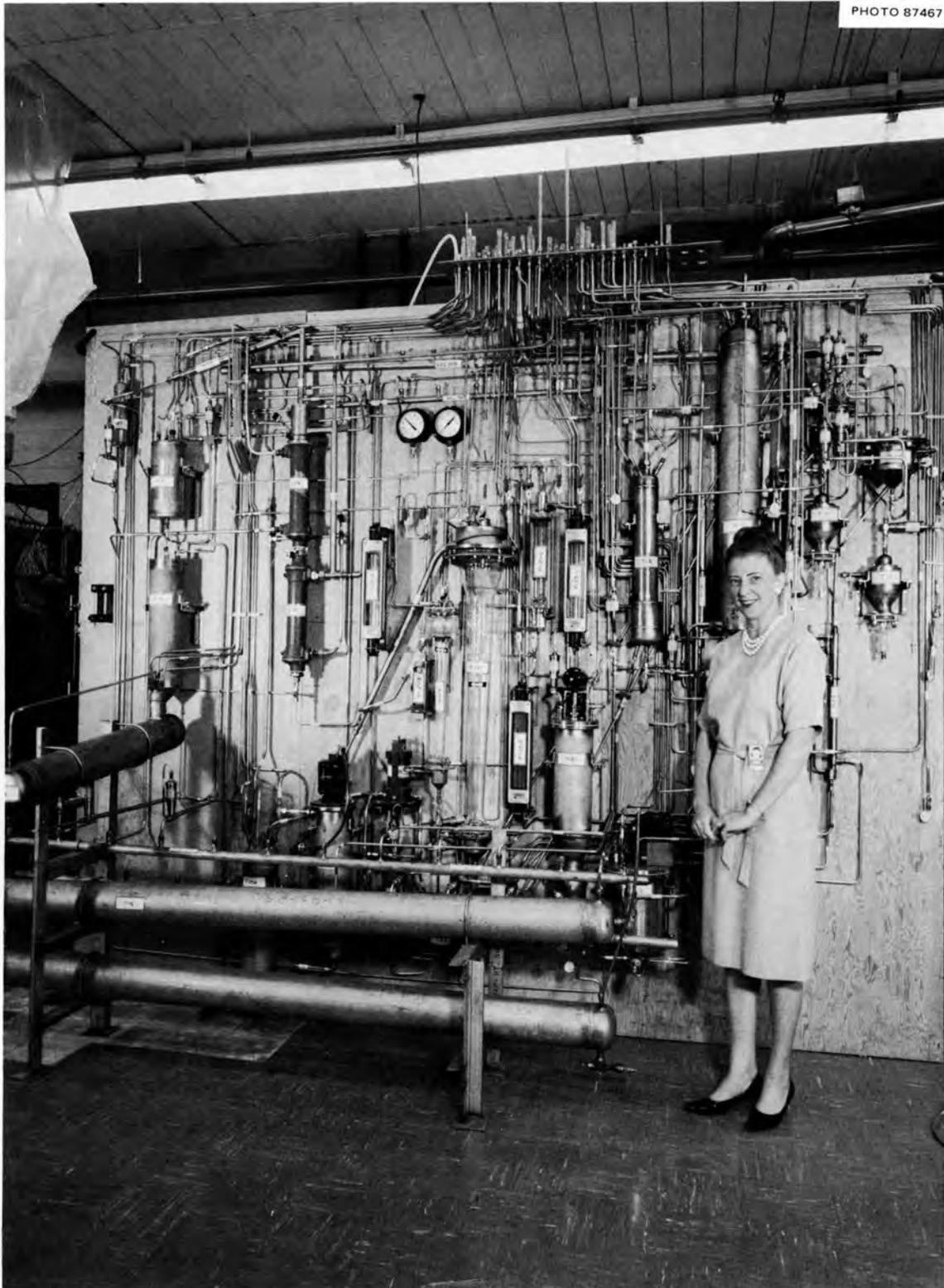


Fig. 13. ORNL Pilot Plant Mockup — Overall View.

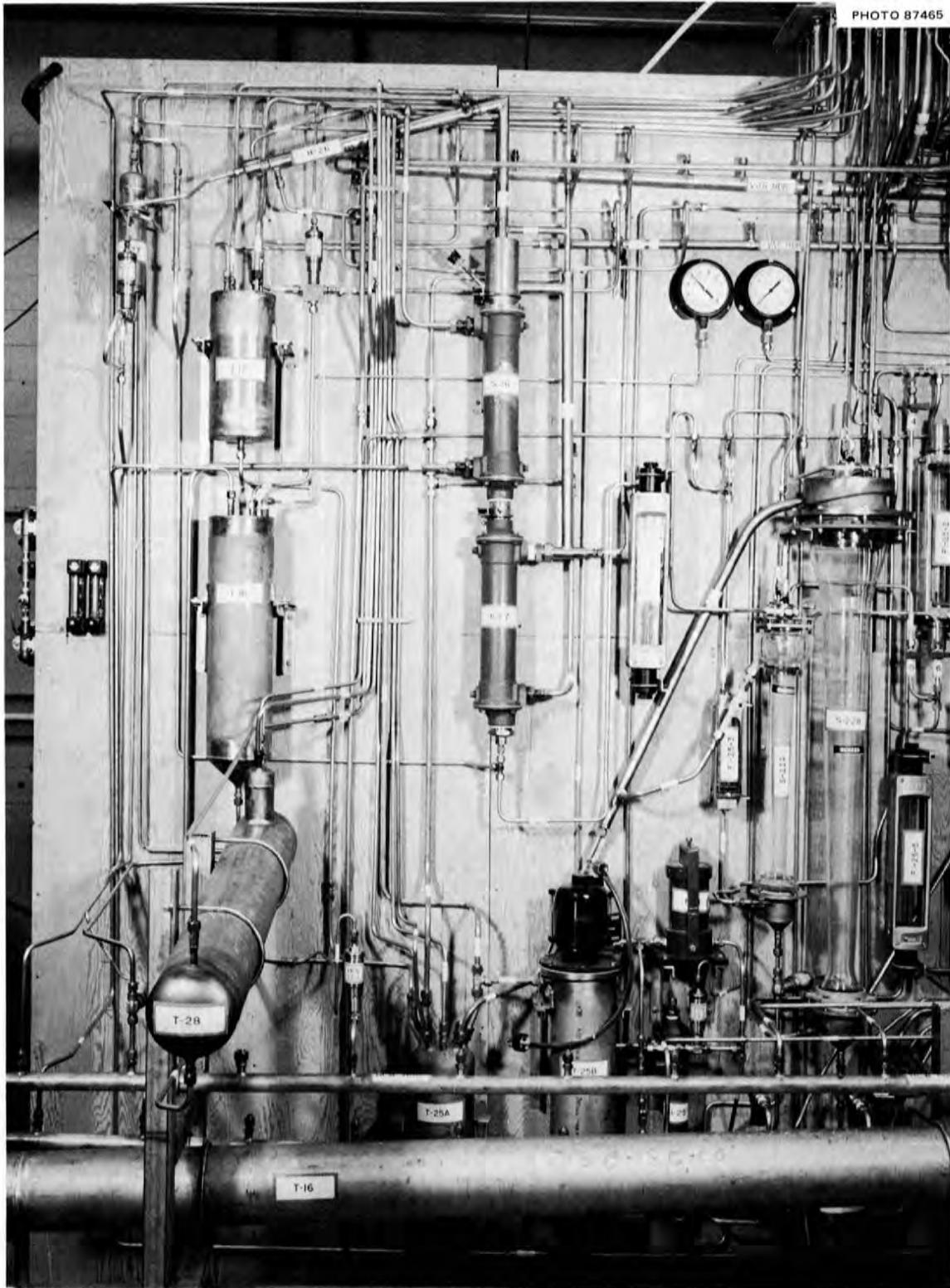


Fig. 14. ORNL Pilot Plant Mockup — Left Section.

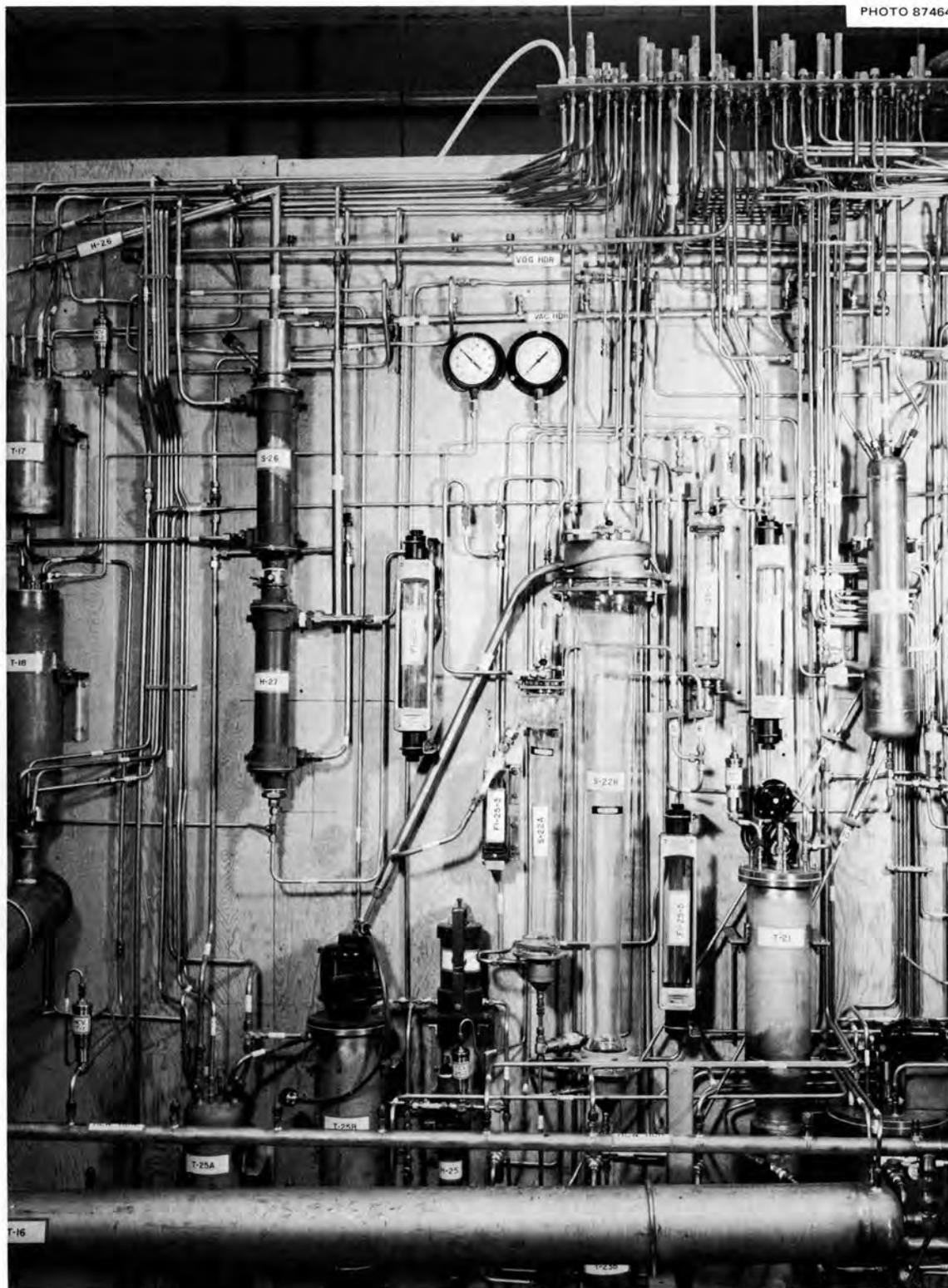


Fig. 15. ORNL Pilot Plant Mockup — Center Section.

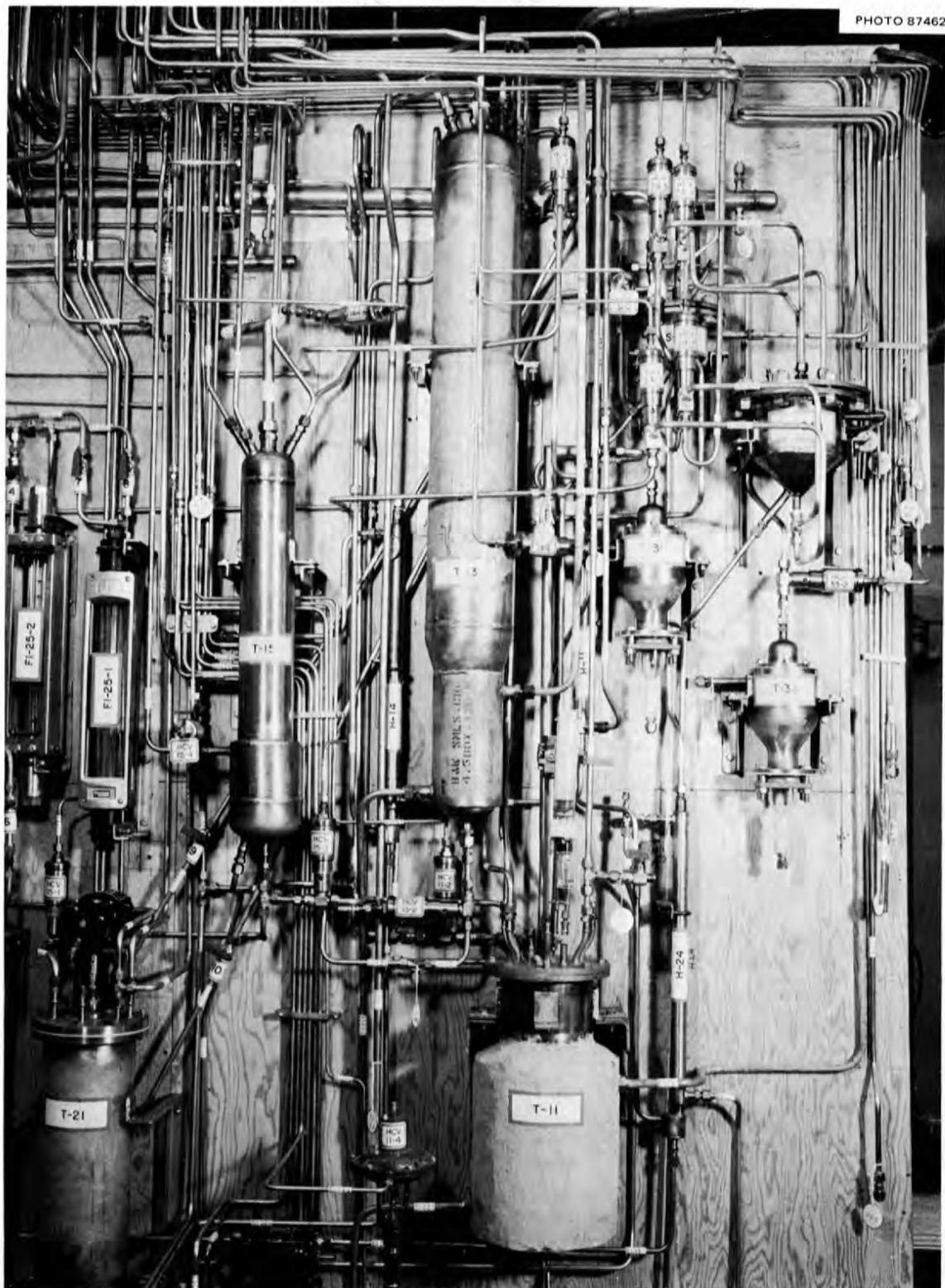


Fig. 16. ORNL Pilot Plant Mockup — Right Section.

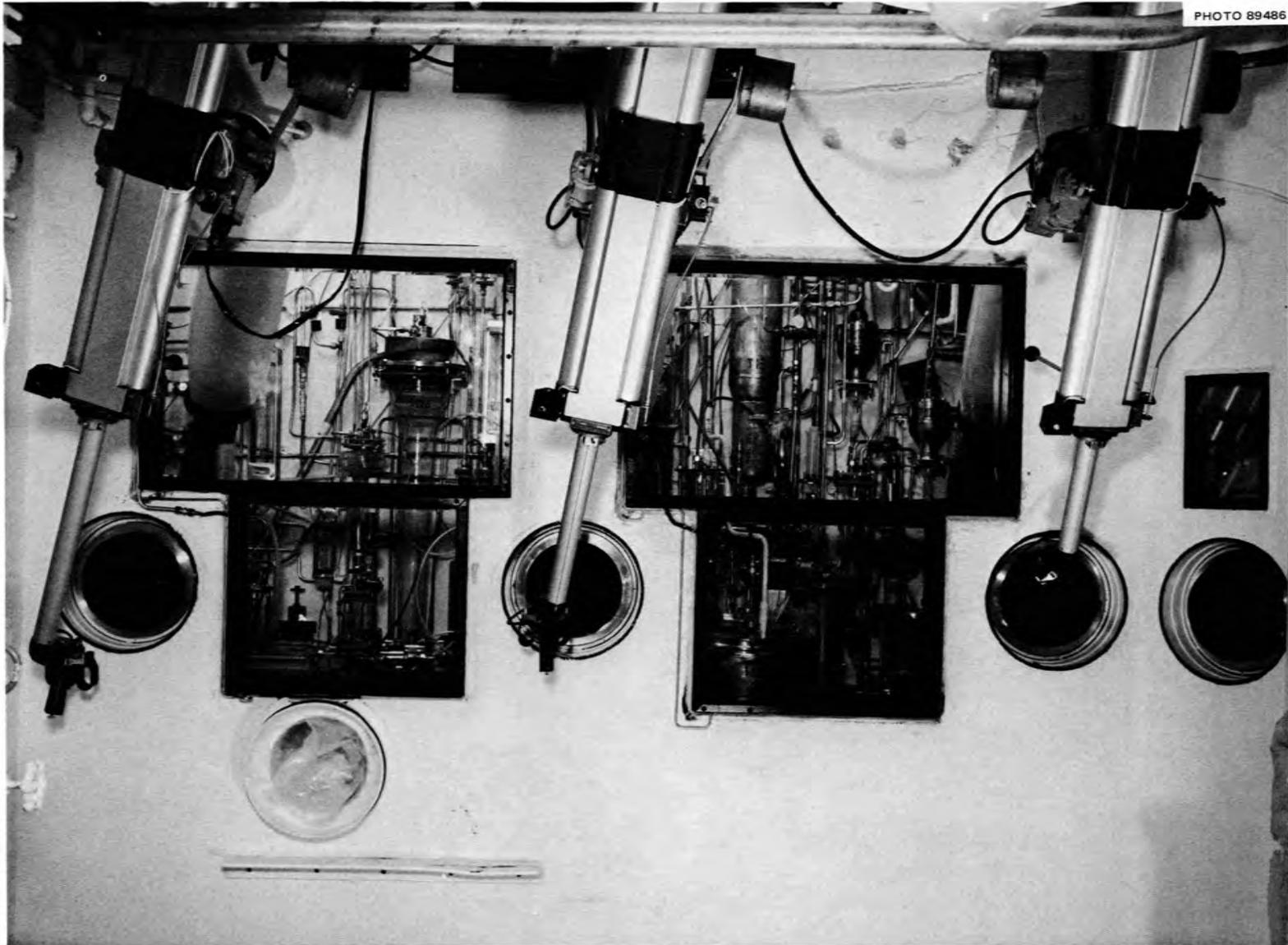


Fig. 17. ORNL Pilot Plant - Front View.

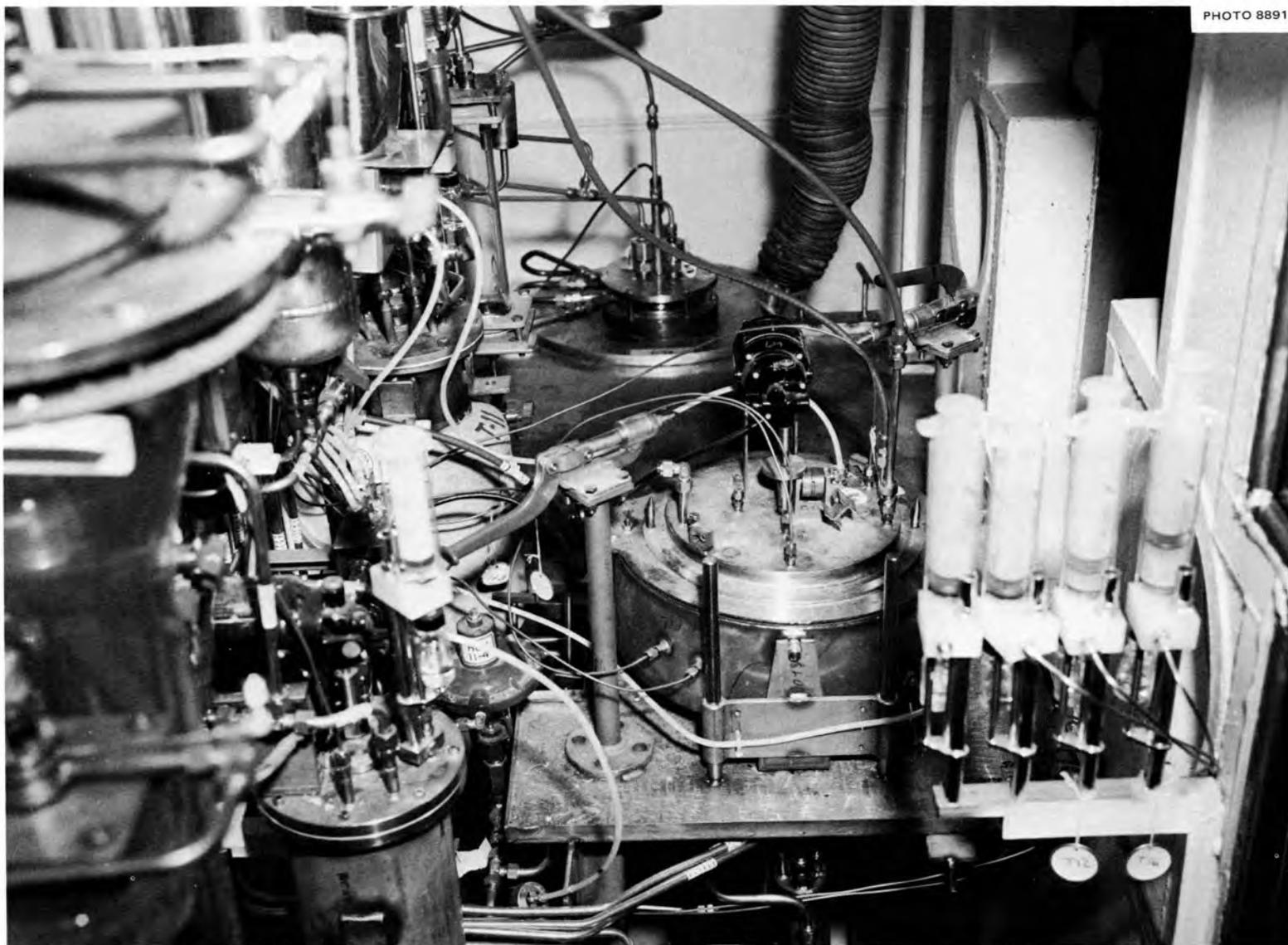


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Fig. 18. ORNL Pilot Plant — Side View from Inside the Cell.

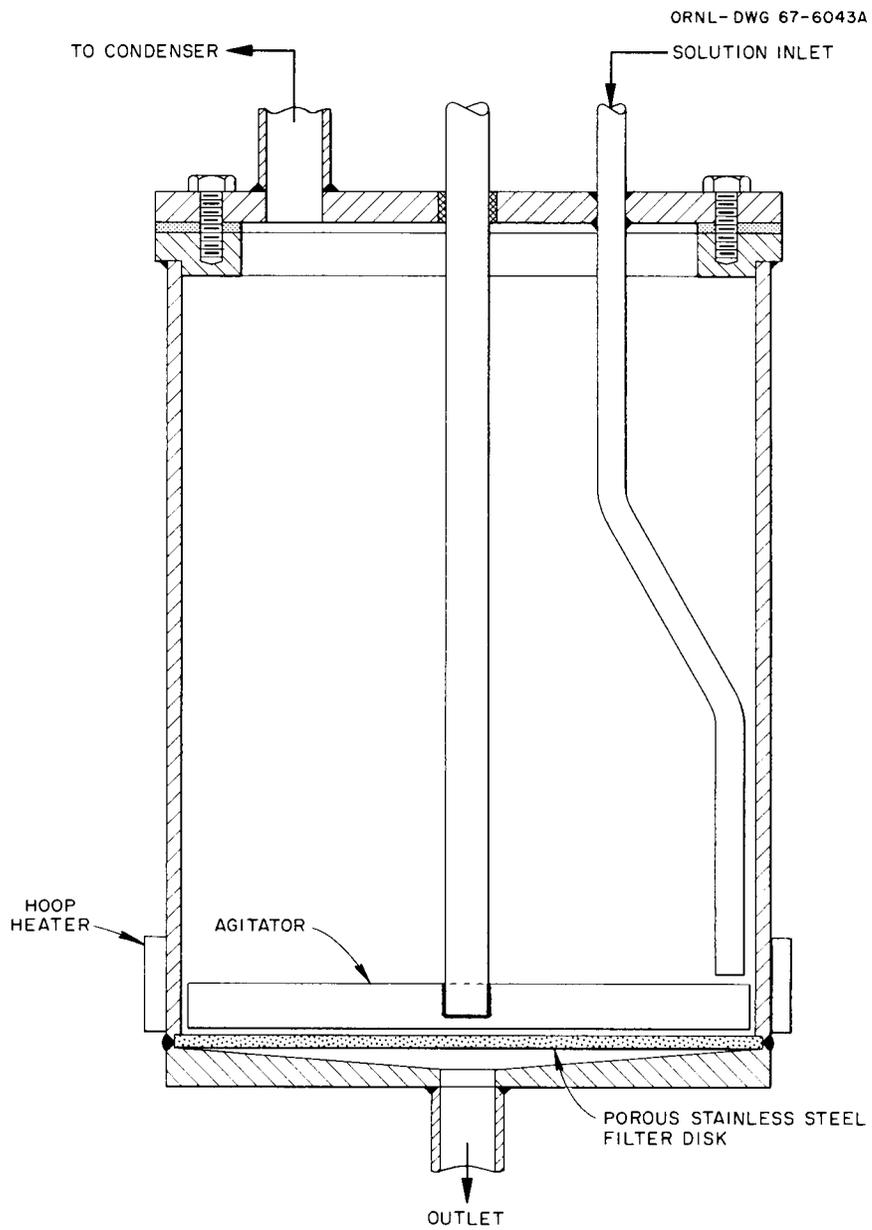


Fig. 19. Vessel for the Precipitation, Filtration, and Peptization of PuO_2 Sol.

transferred by vacuum to the evaporator. Here the volume was reduced to about 0.5 liter, which could be drained into the thermal denitration vessel (an electrically heated, flat-bottomed, pan-like vessel with a capacity of about 1 liter, Fig. 20). The dilute nitric acid condensate from the evaporator also was collected in the aqueous waste system.

In the thermal denitration vessel, the concentrated high-nitrate sol was fumed to dryness, and the resulting thin cake was heated to 240°C and held for about 4 hr; at this time, the NO_3^-/Pu mole ratio should have been in the range 0.11 to 0.14. Only the addition of water and mild agitation were necessary for resuspension. The sol was then transferred by vacuum into the final sol evaporator. This vessel was provided for the concentration of sols that were resuspended at plutonium concentrations lower than desired for microsphere forming. The vessel also provided additional surge or storage capacity since cooling water could be circulated through its steam jacket.

The sol was transferred, by gravity, from the final sol evaporator to the sol feed tank. This vessel merely held the finished sol (with cooling) until it was pumped (by the sol pump) to the two-fluid nozzle at the top of the microsphere-forming column.

5.1.2 Microsphere-Forming Equipment

In the microsphere-forming column, droplets of sol are gelled by the extraction of water into an organic liquid such as 2-ethyl-1-hexanol (2EH). To prepare finished microspheres, the following six operations are required:

- (1) dispersion of the sol into droplets,
- (2) suspension in an immiscible liquid that will extract water to cause gelation,
- (3) separation of the gel microspheres from the 2EH,
- (4) recovery of the 2EH,
- (5) drying of the gel microspheres, and
- (6) firing to the dense oxide.

The size of the product microsphere is determined in the first step. In the second step, the extraction of water causes gelation and thus converts the droplet of sol into a solid sphere. (Interfacial tension holds the droplet in a spherical shape.) There is a maximum practical drop size

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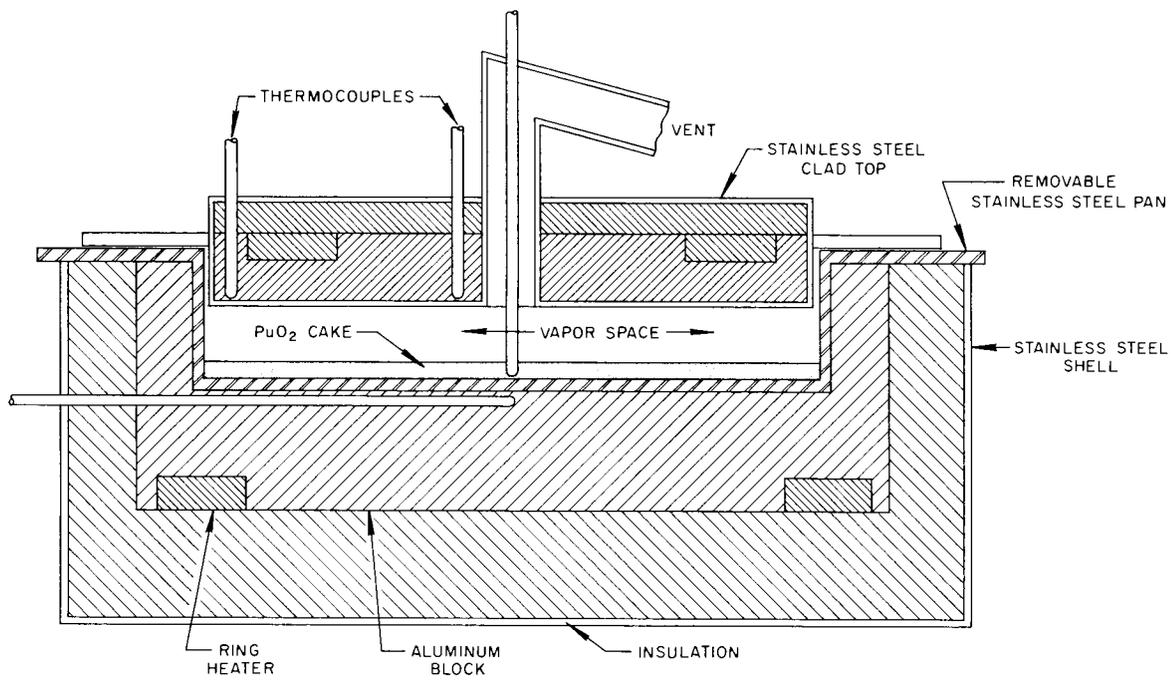


Fig. 20. Vessel for the Thermal Denitration of PuO_2 Sol.

since product microspheres made from very large drops will be distorted in shape. A surfactant must be added to the 2EH to prevent the coalescence of sol drops with each other, the sticking of sol drops to the vessel walls, and the clustering of partially dried drops. These first two are the key processing steps; the four remaining operations are simple in principle.

The first four process operations are performed continuously in a recirculating solvent system. The sol is dispersed into droplets, via a two-fluid nozzle, in the enlarged top of the tapered forming column. These droplets are suspended or fluidized by a recirculated, upflowing stream of 2EH. As the water is extracted and the droplets shrink and gel into solid microspheres, the settling velocity increases. The column configuration and the fluidizing flow rates are selected to permit the gelled particles to drop continuously from the bottom of the column at the same average rate that sol droplets are being dispersed at the top of the column. The separation of the gel spheres from the 2EH is accomplished by discharging the sphere-surge vessel into the dryer and draining off the liquid through a woven wire cloth. Another stream of the drying solvent is directed through a still, where water is distilled continuously from the 2EH at the same average rate that it is extracted from the sol in the forming column.

In the dryer, a stream of air and steam is passed through the bed of spheres as the temperature is slowly increased to approximately 180°C. About 4 g of water (as steam) per gram of oxide is usually sufficient to thoroughly remove the residual organics. After drying, the batch is pneumatically conveyed to the firing furnace. The simple firing schedule calls for heating to 1200°C in air, at 300°C/hr, and then holding at this temperature for about 2 hr.

After cooling, the spheres are pneumatically removed from the furnace through a dip tube and a cyclone separator. Sizing is done with conventional 8-in.-diam screens; the screens are emptied and cleaned by hand. The particles are separated according to sphericity by passing them over a continuously vibrated flat plate that is inclined very slightly from the horizontal. The essentially round particles roll downward counter to the vibration, while those of more irregular shapes are conveyed up the incline and collected as rejects.

5.2 $^{238}\text{PuO}_2$ Sol Preparation Attempts

The most significant engineering development phase of the program was the operation of the pilot plant (in cell 4, Bldg. 3019) designed for a ^{238}Pu throughput of 150 g/day. Following a shakedown operational period using ^{239}Pu as a stand-in for ^{238}Pu , we made a series of five runs involving 500 g of ^{238}Pu (80% ^{238}Pu , 16% ^{239}Pu , and 4% other plutonium isotopes).

The basic steps of the ^{239}Pu flowsheet were followed in the pilot-plant work with ^{238}Pu ; however, as a result of our previous experience with this isotope, more stringent control of conditions was applied at times. Of the five runs (50 to 160 g of plutonium per run), none was completely successful in producing a sol suitable for microsphere preparation. However, each of the attempts contributed to a better understanding of the special difficulties of remote preparation, the limitations of the physical equipment, and the special radiolytic problems inherently associated with ^{238}Pu (specific activity, 3.8×10^{10} dis min^{-1} ml^{-1} ; heat generation, 0.55 w/g). Several procedural modifications were made during the campaign to improve the quality of the product and to facilitate operation.

5.2.1 Corrosion Product Contamination

The ^{238}Pu used in the ORNL pilot-plant program was supplied as the 600°C-calcined oxide by Mound Laboratory. This material was dissolved in refluxing 15 M HNO_3 -0.01 M HF , and the resulting solution was concentrated by evaporation to 4.8 M HNO_3 . The plutonium was adjusted to the tetravalent state by bubbling NO gas through the solution. Thirteen hours was required for this preliminary feed preparation.

For the first run, this feed stock was subsequently adjusted to a plutonium concentration of 50 g/liter and an acid concentration of 2.3 M. The plutonium was then precipitated by slow addition of the feed to 4 M NH_4OH (175% of that required for reaction). Samples of the raffinate and of the filtrate from four water washes of the precipitate showed that plutonium losses in this step were negligible.

The precipitate was then peptized by digestion at 0.25 M HNO_3 . After peptization, the color of the resulting product indicated the presence of impurities. These impurities were identified as stainless steel corrosion products, principally iron, which was present in an amount equivalent to 34 wt % of the plutonium. The solids were denitrated at 240°C for 1 hr, and the run was terminated at this point.

We ran some corrosion tests on the stainless steel dissolver system with 15.8 M HNO₃ and with 15.7 M HNO₃--0.02 M HF. The tests that included HF were made both with total reflux and with no reflux. The corrosion rate was significant in each case; however, it was greater with total reflux. Since there was reflux in the 3-ft length of uninsulated off-gas line leading to the condenser, it was not certain whether the 309 SCb dissolver itself had been attacked. The results indicated that most, if not all, of the corrosion occurred in the 304 SS off-gas line and condenser system. The corrosion rate with HNO₃ alone was about 5% of that observed with HNO₃ and HF, and was considered to be unimportant. It was concluded that the use of HF during dissolution in this system would result in excessive amounts of corrosion products in the dissolver solution. A final corrosion test was made with 6 M HNO₃ at 60 to 70°C, with NO gas being bubbled through the solution (simulating valence adjustment conditions); in this 8-hr test, no detectable corrosion products were found.

5.2.2 Oxidation, Analytical, and Equipment Difficulties

In the second run using ²³⁸Pu, 65.4 g of plutonium (80% ²³⁸Pu) was dissolved in a 1-liter glass flask. The plutonium valence was adjusted to the tetravalent state by bubbling NO gas through the dissolver solution for 14 hr while the temperature of the solution was maintained between 60 and 70°C. The acid concentration of the solution was subsequently adjusted to 2.0 M by the addition of 0.4 M HNO₃; in this step, the plutonium concentration was decreased to 31 g/liter. The plutonium was then precipitated by adding the solution to a 75% excess of 4.2 M NH₄OH. The precipitate was washed with four 3-liter volumes of water. Plutonium losses to the combined filtrates were negligible.

After the precipitate had been digested in water for 2 hr, peptization in 0.17 M HNO₃ (NO₃⁻/Pu mole ratio of 2.0) was attempted; however, after 4 hr at 95°C, peptization had still not occurred. Additional acid was then added to increase the NO₃⁻/Pu mole ratio to 2.5, and the peptization procedure was continued. After 26 hr, peptization was achieved, but the color of the cake was a light brownish-green instead of the translucent dark green that had been expected. Five percent of the plutonium in the peptized solution was found to be in the hexavalent state.

The peptized material, plus precipitator flushes, was concentrated in the evaporator to a volume of about 370 ml (1.3 \underline{M} Pu), and was subsequently transferred to the thermal denitration vessel. After drying at 115°C, the cake was glassy black and resuspended easily in 200 ml of H₂O. The cake was dried again at 115°C and then heated to 235°C over a period of 3-1/2 hr. After this drying period, the cake was cooled immediately; its appearance again was glassy black. A sample of the cake would not completely resuspend, although its NO₃⁻/Pu mole ratio was 0.36. Heating at 240°C for an additional hour did not change the appearance of the cake; however, none of a sample of this cake would resuspend, even though the NO₃⁻/Pu mole ratio was only 0.125. Abnormalities in the run included the long period required for peptization and the physical appearance of the peptized material (containing 5% hexavalent plutonium). The baked material looked normal, but would not resuspend.

In a third attempt to prepare a ²³⁸PuO₂ sol, the following changes were initiated: (1) a lower-impurity-content stock material (75 ppm instead of 1000 ppm of iron), (2) a slower, uniform feed rate to the precipitator (13.5 ± 1.5 instead of 20 ± 15 ml/min), (3) a lower feed temperature (~20°C instead of >50°C), (4) washing to a pH of less than 8 (eight 3-liter batch washes were required, as compared with the previously used four), and (5) fuming to dryness in the denitrator at 95°C instead of boiling.

The concentrated high-nitrate sol contained two phases and would not resuspend in water after drying to 115°C or after baking to 220°C, although the NO₃⁻/Pu mole ratio was greater than 0.60. A material balance for the run accounted for 100% of the 68 g of plutonium; 88% of this quantity was found in the denitration vessel at the termination of the run.

5.2.3 Rapid, Nonuniform Denitration

The fourth run (64 g of total Pu; 51 g of ²³⁸Pu) was made using essentially the same procedure as that used in the previous run. Minor changes were as follows: (1) The feed rate to the precipitator was increased to 25 ml/min (instead of <15 ml/min). (2) The acid concentration of the feed was reduced to 1.4 \underline{M} . (3) A 130% excess of 3.2 \underline{M} NH₄OH was used for precipitation. (4) The agitator in the precipitator was operated at 660 rpm (vs 330 rpm) during precipitation and subsequent precipitate washing. (5) Continuous, favored over batchwise, washing of the precipitate was carried out. For continuous washing, the precipitator volume was

held at 2.0 ± 0.5 liters, while water was added at the rate of 125 ml/min and drawn off at approximately the same rate; the agitator ran continuously to prevent the precipitate from forming a cake. The washing, which was completed after approximately 25 liters of water had passed through the precipitator, required 3-1/3 hr. The effectiveness of washing was monitored by measuring the pH of the effluent wash water intermittently. The pH fell below 8 after about 12 liters of water had been added, and reached 3.1 after 25 liters; this was unexpected since we had thought that a pH of 7 was the minimum to be encountered during this procedure.

Peptization was first attempted at a NO_3^-/Pu mole ratio of 1.50 (0.25 M HNO_3); it was finally completed at a NO_3^-/Pu mole ratio of 1.75 after a total of 5-1/2 hr. The volume of the high-nitrate sol was reduced in the evaporator only to the extent required to give a final plutonium concentration of approximately 0.35 M (instead of ~ 2 M) before the suspension was transferred to the denitration vessel and fumed dry. The denitration was carried out at 220°C instead of 240°C.

This run was performed in an orderly fashion; no equipment difficulties or delays were experienced. All stages of the run prior to the denitration step were very encouraging. The cake was glassy black in appearance and resuspended easily after 1 hr at 220°C; the NO_3^-/Pu mole ratio was 0.45. After 4 hr at 200°C, the appearance of the cake was unchanged; however, attempts to resuspend a sample failed. The NO_3^-/Pu mole ratio was checked by the in-cell titration method and found to be about 0.24, although analysis of a later sample showed it to be only 0.061. To further augment this discrepancy, approximately 20% of the batch resuspended in water to form an inferior sol (light green, large particles) in which the NO_3^-/Pu mole ratio was found to be 0.41. It was concluded that the most probable cause of the rapid, nonuniform denitration was a high flow of humid air through the denitration vessel; the source of this air was the vessel off-gas system (normal vacuum, 3 in. H_2O). The intended purpose of the off-gas connection was simply to remove the denitrator fumes; however, this connection has been found to induce a much higher flow of air than that used in the denitration vessel in our developmental facility.

In the last ^{238}Pu run, we recycled the material that had been recovered from the denitration vessel following the preceding run (i.e.,

~58 g of total Pu). This run was to be carried out under identical conditions as the previous run, with the exception that the denitration was to be accomplished without the off-gas sweep. However, as described below, the run was plagued with equipment problems and the results prior to the denitration step were markedly different from those in the previous run.

Although the plutonium precipitate was washed continuously for 6-1/2 hr (39 liters), the pH of the effluent wash water never fell below 9. After peptization, which required 8-1/2 hr at a NO_3^-/Pu mole ratio of 2.0, the suspension was still a cloudy brown color. The dried cake in the denitration vessel was black, but was crusty and cohesive instead of granular.

After denitration at 220°C for 50 min, only about one-half of the material would resuspend even though a titrated sample showed a NO_3^-/Pu mole ratio of approximately 0.15. Denitration was discontinued, and re-suspension of the entire batch was attempted. Approximately 30% of the initial batch formed a brown sol having a NO_3^-/Pu mole ratio of 0.46. Although these analyses are similar to those in the previous run, no conclusions can be drawn concerning the effect of an air sweep on denitration since the runs were so dissimilar in the earlier stages.

5.2.4 Confirmatory Tests with ^{239}Pu

After the termination of the ^{238}Pu program, a few tests were run with ^{239}Pu to confirm that the difficulties we were experiencing were due to differences in the behavior of the two isotopes.

The first tests with ^{239}Pu were made with a split batch of high-nitrate sol that had been prepared in the glove-box facility. Results of these tests showed that, when the thermal denitration vessel in the pilot plant was being operated without an off-gas sweep, it essentially duplicated the operating characteristics of the oven in the glove-box facility. With an off-gas sweep, a fairly good ^{239}Pu product was prepared even though denitration was more rapid and more nearly complete than without the sweep.

The final test involved the preparation of a 100-g batch of $^{239}\text{PuO}_2$ sol in the pilot plant. In preparing this sol, we used the flowsheet that we believed was most suitable for preparing $^{238}\text{PuO}_2$ sol; conditions were almost identical to those used in the fourth ^{238}Pu run described above.

Despite delays caused by equipment problems (which probably would have resulted in an unsatisfactory ^{238}Pu product), a good high-nitrate sol was prepared. This sol was denitrated without an off-gas sweep. The NO_3^-/Pu mole ratios, as a function of time at 240°C , were entirely consistent with denitration curves that had been obtained in laboratory development work. After 4 hr at 240°C , the NO_3^-/Pu mole ratio was 0.15. The final sol contained 78 g of plutonium, and the overall material balance was 98%.

5.3 Formation of $^{238}\text{PuO}_2$ Microspheres

The sphere-forming equipment in cell 4 was successfully operated to produce $^{238}\text{PuO}_2$ microspheres from a sol (NO_3^-/Pu mole ratio, 0.18) prepared in laboratory equipment. The microspheres were formed in 2EH containing 0.3 vol % Ethomeen S/15. The gel microspheres were first dried in air at temperatures up to 140°C and then calcined at 1200°C . The final product was characterized by a dimple, or "cherry pit," and, in general, had slightly less desirable physical characteristics than the comparable $^{239}\text{PuO}_2$ product.

A $^{238}\text{PuO}_2$ sol was prepared in cell 4, Bldg. 4507, starting with 32 g of plutonium (80% ^{238}Pu) in the form of oxide. The sol was prepared using techniques developed during earlier work on smaller batches, except that the precipitate was washed in a continuous countercurrent washer. The suspended precipitate was washed for 2 hr; this resulted in a final pH of less than 8 for the wash water. The NO_3^-/Pu mole ratio during peptization was 2.5; the denitrated sol had a NO_3^-/Pu mole ratio of 0.18.

The final sol, containing 25.5 g of plutonium, was transferred to cell 4, Bldg. 3019, and was formed into microspheres in the permanent cell equipment. The principal difficulty encountered during microsphere formation involved gassing of the sol in the sol pump; this gas tended to fill the horizontal-drive syringes, increasing the surge capacity and resulting in an uneven feed of the sol to the two-fluid nozzle at the top of the microsphere-forming column.

The product was dried in air to 140°C and calcined at 1200°C in air without incident. The microsphere transfer systems appeared to operate satisfactorily, except that considerable difficulty was encountered in removing the microspheres from the furnace. This difficulty is attributed to

the high static charge of the product after calcination. A total of 16.5 g of calcined oxide was recovered from the furnace; the size distribution was as follows:

<u>Diameter (μ)</u>	<u>Condition</u>	<u>% Yield</u>
<50 (fines)	Composite	8.6
50-250	Rounded fraction	36.4
50-250	Reject fraction	27.1
>250	Rounded fraction	14.3
>250	Reject fraction	13.6

The microspheres from the rounded fractions were characterized by dimples or "cherry pits" of various sizes. Other physical measurements made on the rounded fraction of 50- to 250- μ -diam spheres were as follows:

Crush strength (20 determinations)	570 g/sphere
Bulk density*	9.96 g/cc
10,000-lb density*	10.94 g/cc
Pore volume*	0.0090 cc/g
Surface area*	0.0680 m ² /g
Carbon content	300 ppm

5.4 Equipment Deficiencies

During the series of five ²³⁸PuO₂ sol-preparation runs, equipment limitations became apparent as several permanent components failed or became unreliable; these difficulties contributed to the failure of a run in at least three instances. Equipment deficiencies in cell 4 are listed below. In each case, a brief statement is made concerning (1) the effect of the deficiencies on the process, and (2) the improvements expected by using the Mound box.

We believe that ²³⁸PuO₂ preparation must proceed as rapidly as possible from the precipitation step to the start of baking, without allowing the precipitate to form a cake. The following three difficulties were related to this requirement.

* Value calculated from mercury porosimetry measurements.

- (1) The air-operated feed metering valve between the dissolver and precipitator in cell 4 had to be operated either fully closed or open; thus it was not possible to control the feed flow rate to the precipitator. In the Mound system, this valve could be replaced in case of failure.
- (2) The agitator in the precipitator was unreliable. When it failed to operate, the precipitate settled, causing intolerable delays in washing and/or peptization. In the Mound system, this agitator could be replaced in case of failure.
- (3) The cell 4 vacuum system used for filtration was unreliable and in three runs caused extensive delays in washing the precipitate. Extensive overhaul will be required to make this system operable. The Mound box is connected to a dependable "house" vacuum source.

The following three problems were associated with process development or process monitoring.

- (1) The volume measuring equipment in the precipitator did not operate properly, and spurious measurements of the volumes were obtained during continuous washing and peptization. Since these are critical steps, it is necessary to have exact control of the operating conditions. The same basic volume measuring equipment is used at Mound; however, this equipment can be checked for these difficulties and modified prior to use if required.
- (2) Samples obtained from the vacuum transfer tank were not representative of the wash effluent; therefore, the effectiveness of washing could not be followed. The Mound system has an in-line sampler for sampling the flowing wash liquid.
- (3) The small tanks made it impossible to operate at the optimum concentrations for a full-scale batch. This should not be a problem in the Mound equipment since the tank volumes are about twice as large as those in cell 4.

Two miscellaneous difficulties, as well as a very serious problem that has not been explained fully, are described below.

- (1) The stainless dissolver system in cell 4 introduced corrosion products during plutonium oxide dissolution. To solve this

problem, a makeshift glass dissolver system was used in the latter runs. Feed material at Mound will consist of high-purity solutions produced directly from an ion exchange process.

- (2) A three-way valve at the bottom of the precipitator failed, allowing a flow in either direction whenever vacuum was applied to either of two receivers. This increased the probability of operator error. In the Mound system, this three-way valve has been replaced by two two-way valves in accessible locations for easy replacement in case of failure.
- (3) The material balance in the last run was low by more than 25%. It is possible that the filter in the precipitator may have permitted passage of solids, which would not necessarily show up in waste samples unless these solids were redissolved. This possibility has not been confirmed; however, as a precaution, it was decided that no further runs with ^{238}Pu would be made in this equipment.

5.5 Transfer of Program

Since the deficient components, described above, were in such a state of deterioration that a successful ^{238}Pu demonstration appeared unlikely and repair or replacement by remote means was impossible, further attempts to prepare $^{238}\text{PuO}_2$ sol were abandoned. Then, because most of the extensive changes recommended for the pilot plant had already been incorporated into the Mound system, a decision was made¹⁴ to transfer all the process demonstration work to Mound. Further, ORNL engineers proposed that the demonstration runs be performed in the sol-gel cubicle (box) provided by ORNL. During startup, it was agreed that ORNL would provide engineers and technicians to operate the equipment and chemists to determine optimal run conditions and to analyze and evaluate the runs while they were in progress. Details of the cooperative program were to be worked out with representatives from Mound Laboratory. ORNL engineers also recommended a $^{239}\text{PuO}_2$ sol run and one or more small-scale (50 to 60 g) $^{238}\text{PuO}_2$ sol runs prior to a full-scale demonstration with $^{238}\text{PuO}_2$. Although the introduction of ^{239}Pu into the system might be somewhat objectionable because of possible isotopic contamination, it was felt that the successful preparation of a

sol with this isotope would be helpful in identifying possible equipment problems not related to the radiation effects introduced by ^{238}Pu . Small-scale $^{238}\text{PuO}_2$ sol runs would aid in the determination of possible adverse radiation effects and in the optimization of critical variables.

It was decided that development work on the larger-scale flowsheet would be done in shielded glove boxes at Mound rather than in the manipulator-operated ORNL equipment, even though the latter equipment might have proved advantageous in some ways.

6. FABRICATION OF THE MOUND FACILITY

Equipment for the preparation of $^{238}\text{PuO}_2$ sols and the conversion of these sols to dense $^{238}\text{PuO}_2$ microspheres was fabricated, installed in a stainless steel cubicle, and shipped to Mound Laboratory, Miamisburg, Ohio, in November 1967. The system, having a nominal capacity of 150 g of plutonium per batch (each requiring about 24 hr of operation), is contained in a box that is 10 ft long, 7 ft 3 in. high, and 42 in. deep. The equipment was designed to prepare sol by using the standard flowsheet as described in Sect. 4.1. Microspheres are to be made by fluidizing sol droplets in a stream of 2EH in a tapered glass column until gelled, drying in hot air and steam to a minimum temperature of 160°C , and firing by heating in air to 1200°C . Operation in this facility should have several advantages over operation in glove boxes. Manual operations have been minimized, and those remaining will be performed with manipulators; this will reduce personnel exposures. All transfers of solution will be made using gravity or vacuum techniques, and solids will be conveyed hydraulically or pneumatically. Heat will be provided by steam, which will give more effective control and cooler heat-transfer surfaces while eliminating overheating and element burnout; this should especially benefit the microsphere-forming operation by reducing the rate of surfactant degradation in the solvent still.

6.1 The Stainless Steel Enclosure

A pictorial view of the stainless steel box is shown in Fig. 21; construction prints from which it was fabricated may be found in the Appendix. It is of all-welded, sheet, and angle construction. It was

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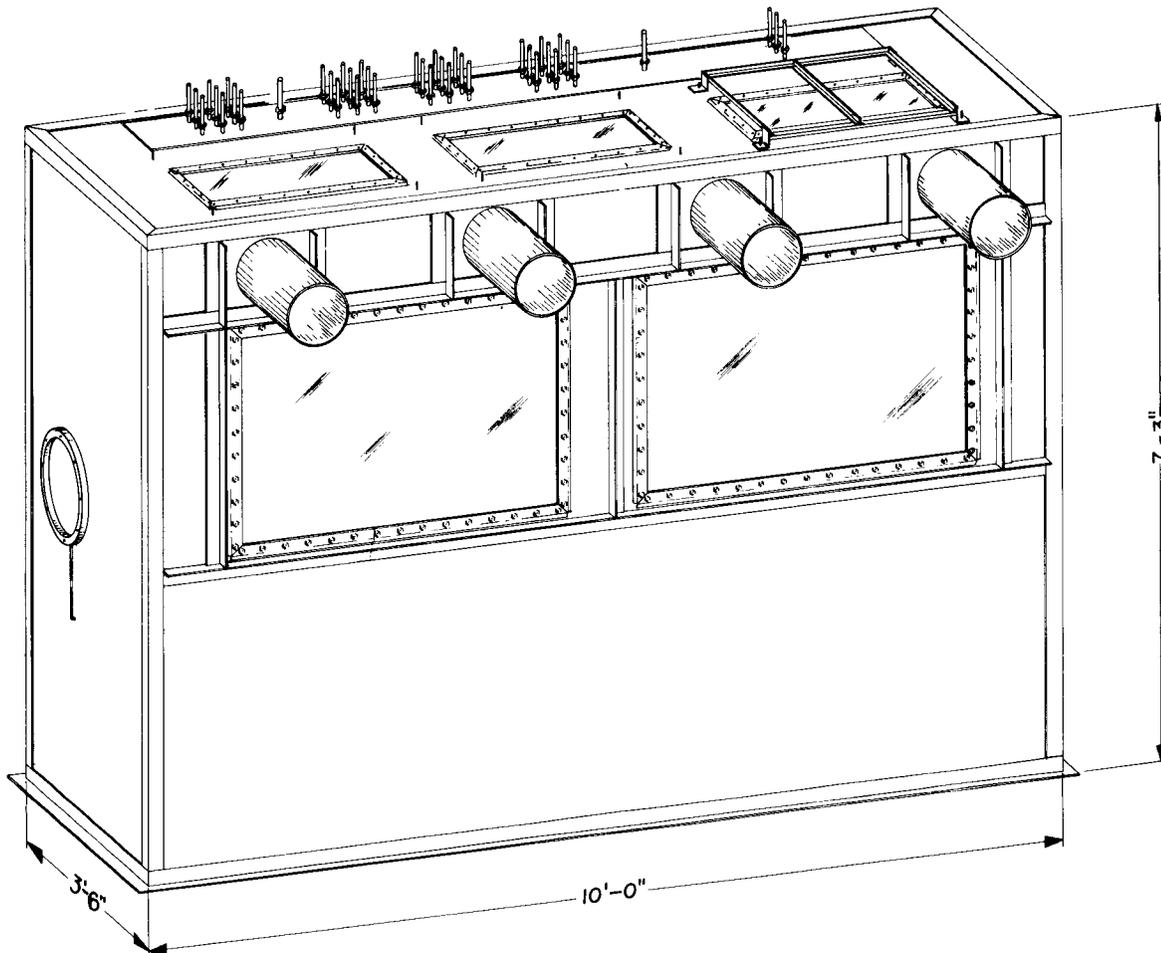


Fig. 21. Mound Manipulator Box.

built at ORNL as specified by Mound so that it could be integrated directly into their hood line. The four projections from the front of the box are mounting tubes for the four model G manipulators that will be used to operate the equipment inside the box. The front ends of these tubes will fit essentially flush with the front face of the water-filled neutron-shielding tanks when they are erected in front of the box. Fittings located at each end of the box will permit the box to be connected to other facilities via a conveyor system.

Figure 22 shows the box with equipment and instrumentation at Mound before the shielding was installed. The housing of the conveyor system is visible at the extreme top of the photograph. The unique system used by Mound to filter the air entering the box is not shown. The filter medium is contained in a number of cylindrical cartridges, in series, with rubber rings that seal against the inside of the pipe containing them; fresh cartridges are inserted from outside the box, and "hot" cartridges are discharged inside the box.

Since ^{238}Pu is a highly radioactive and mobile material, the most important function of the enclosure is to contain the material and thus prevent the spread of contamination. Since stainless steel and glass are impervious to ^{238}Pu , the most vulnerable points are the penetrations of the box; these will be discussed in three categories.

6.1.1 Process and Instrumentation Lines

All lines that were expected to carry plutonium of any concentration, as well as those which might easily become contaminated in routine or irregular operation, penetrated the top of the box as specified by Mound. These included feed, product, salvage, aqueous waste, process gas, funnel addition and instrumentation lines - a total of 39. The actual penetrations were 3/8-in.-diam pipe couplings centered in the box wall and welded (see drawing M12196 CD 080 D R3, Appendix). Type CMT or "drilled out" 3/8-in. tubing compression fittings were screwed into each end of the couplings. This allowed the tubing to be continuous through the box wall and therefore forced any contamination from within the box to pass two seals (screwed or compression) before escaping to the outside. All of the lines were equipped with block valves just below the ceiling of the box; those that connected to dip tubes were provided check valves between the block valve and the respective vessel (see Fig. 23).

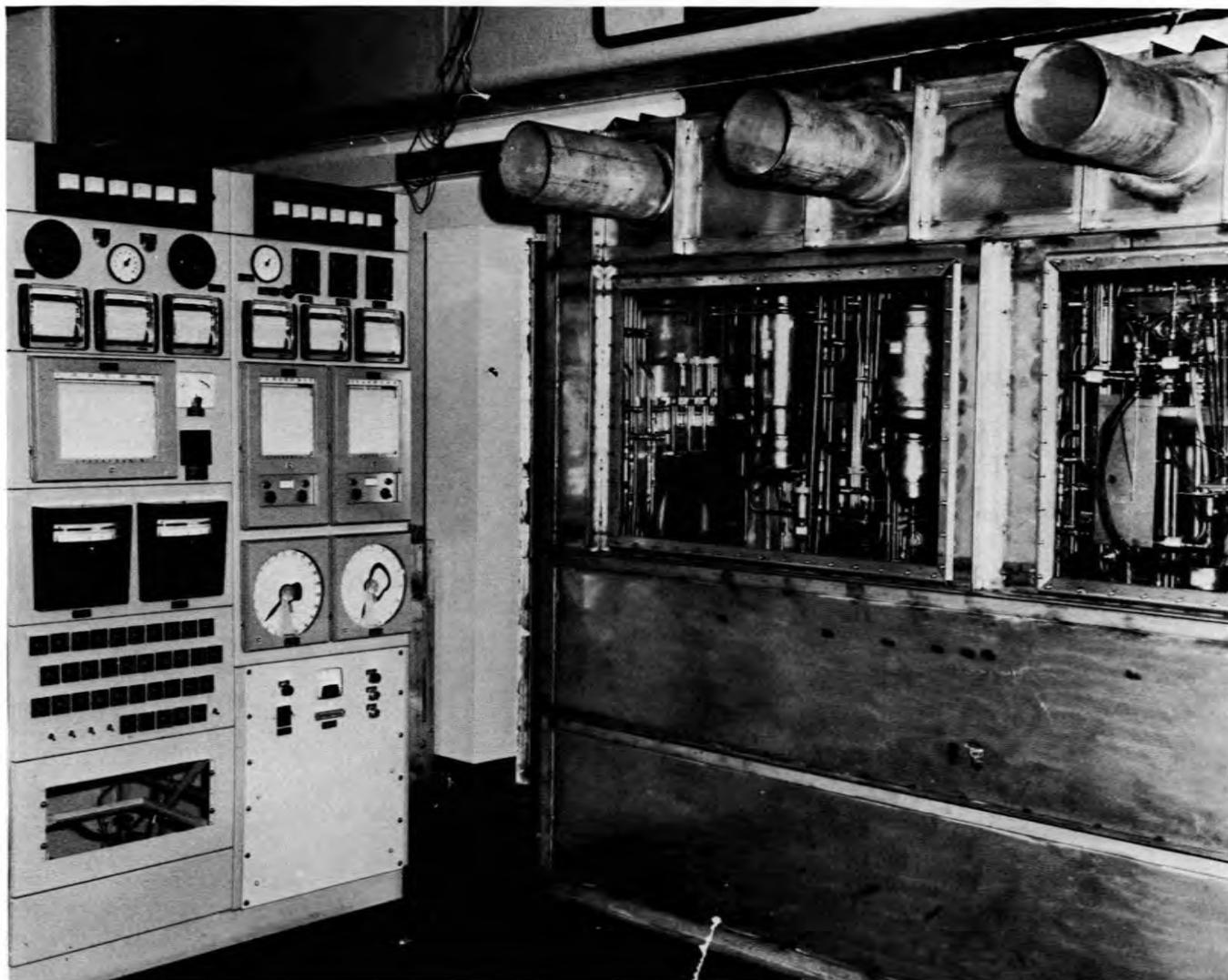


Fig. 22. ORNL System with Instrumentation, During Installation at Mound.

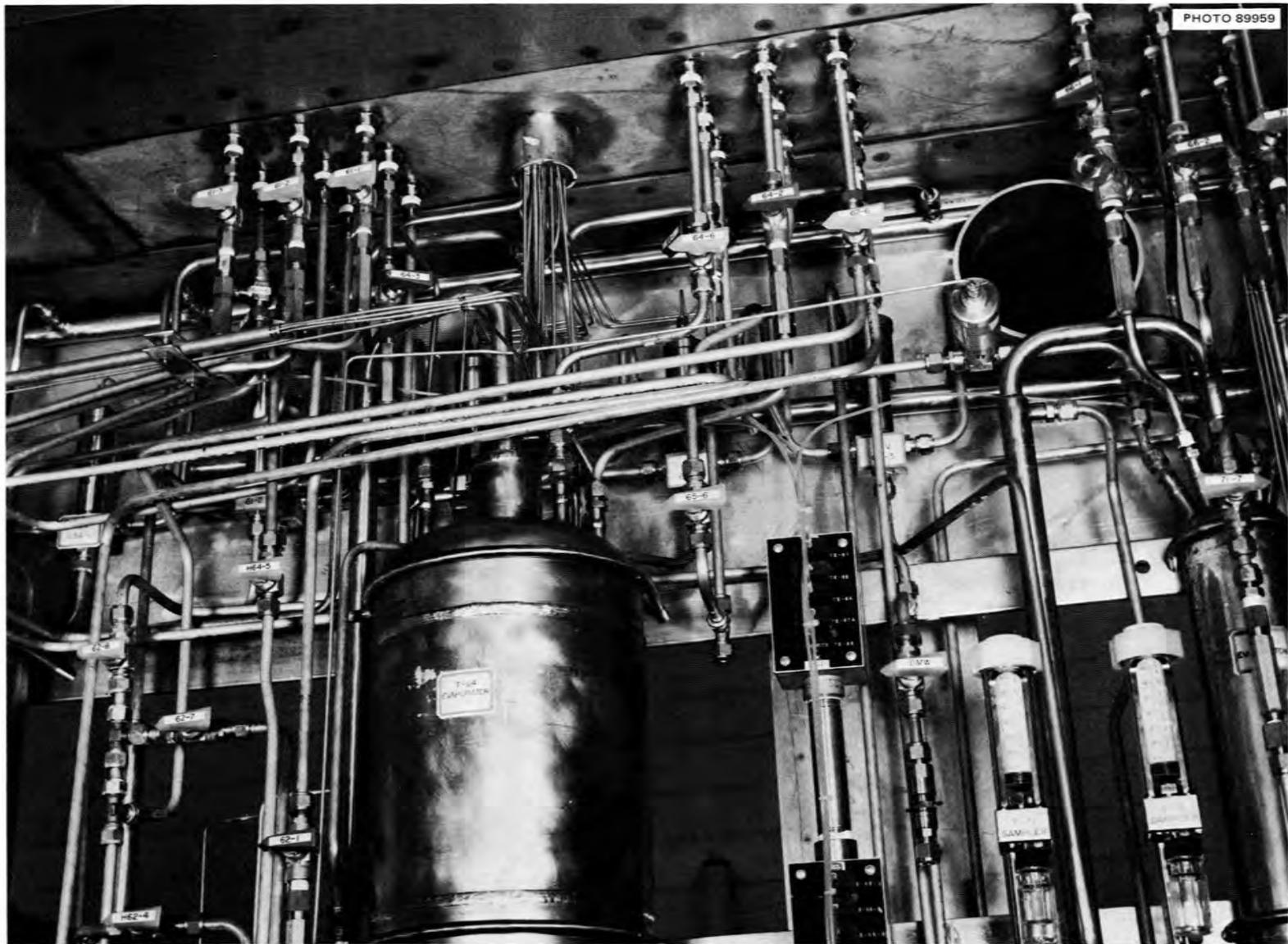


Fig. 23. ORNL System — Block and Check Valves.

The 1/8-in. tubing lines supplying pressurized air to actuate the remote valves also penetrate the top, through 2-in. pipe sleeves. Before use with radioactive materials, these sleeves will be sealed with epoxy resin.

6.1.2 Service Lines

All electrical, utility, and reagent lines, including those for power supply, controlled voltage, thermocouples, steam, condensate, chilled water supply and return, vacuum (VAC), and vessel off-gas (VOG), penetrate the back wall of the box under the center window (see Dwg. M12196 CD 083 E R3, Appendix). These lines and manifolds, of all-welded construction inside the box, terminate in female pipe threads for connection outside the rear wall of the box. All electrical conductors, from the furnace power supply cables to the tiny thermocouple leads, penetrate the box through standard GUAB fittings. Within these fittings, the wires are stripped of insulation and the bare conductors are sealed in a mass of epoxy resin.

6.1.3 Gasketed Closures

Box penetrations sealed by rubber gaskets include the two front viewing-windows, three rear windows, three top windows, end ports, access panels under the outside rear windows, and the top penetration plate that runs almost the full length of the top of the box.

All the window closures are constructed similarly, except for the overall size. All the windows use an extrusion with a "U"-shaped cross section, which is slipped over the edge of the glass; this seal is made of a special rubber formulation, with which Mound Laboratory has obtained excellent results in past installations. This assembly is placed against the outer surface of the box wall, centered over the opening, and secured by tightening an outer flange which compresses both layers of rubber (see Dwg. M12196 CD 055 E R5, Appendix). A bracket to support a fluorescent fixture is installed over each of the three top windows.

The panels that cover the access ports and the top penetration plate are the same in principle, but different in size. A continuous flat gasket, of a special formulation, forms the seal between the box wall and the stainless steel panel that serves as the outer flange. Both the gasket and the panel fit over studs capacitance-welded to the wall or the top of the box.

6.2 Sol Preparation Equipment

The equipment in the Mound box was designed to carry out the standard flowsheet shown in Fig. 7. The detailed equipment flowsheet is given in Dwgs. F12196 CD 053 E R5 and F12196 CD 054 E R3 (Appendix); a greatly simplified schematic showing the most important items of equipment is shown in Fig. 24. Both of the drawings have been updated to show the changes discussed in Sect. 7.2. The equipment is basically similar to that of the cell 4 pilot plant; however, since it was designed for remote maintenance (manipulators) and easier operation, reliability and operability should be greatly improved.

From the inception of the project, it was assumed that Mound would supply $\text{Pu}(\text{NO}_3)_4$ feed of the proper acid concentration. With this provision, only the addition of H_2O_2 just prior to precipitation would be required for valence adjustment in T-61. An air-operated control valve meters the feed into well-agitated excess NH_4OH in T-62. Photographs of these vessels are shown in Figs. 25-27. Figure 25 shows T-61 from a front opening, while Fig. 26 shows T-61 from the rear, along with the metering valve and the top flange of T-62 with its agitator motor (black, barely visible). Figure 27 shows the bottom of T-62 through one of the rear access panels.

After precipitation, the reaction mixture (excess NH_4OH and product NH_4NO_3) is transferred by vacuum through the porous stainless steel disk in the bottom of T-62. (A schematic of the T-62 vessel is shown in Fig. 19.) This vessel was designed in such a manner that the precipitate is retained through the washing and digestion steps but is passed completely after peptization with nitric acid. The waste solutions from the precipitation and washing steps are pulled into the basic aqueous waste system, which is comprised of T-63A and T-63B. These are two tanks of identical construction but with different nozzle arrangements. Waste is collected in T-63A, then sampled and held in T-63B while awaiting analytical results, and finally transferred to waste or salvage (depending on the values reported).

After peptization, the high-nitrate sol and water rinses pass through the filter and are transferred by vacuum up to the T-64 evaporator (see Figs. 23 and 26). Here simple evaporation is carried out until the batch has been reduced to a volume that can be accommodated by T-65. The

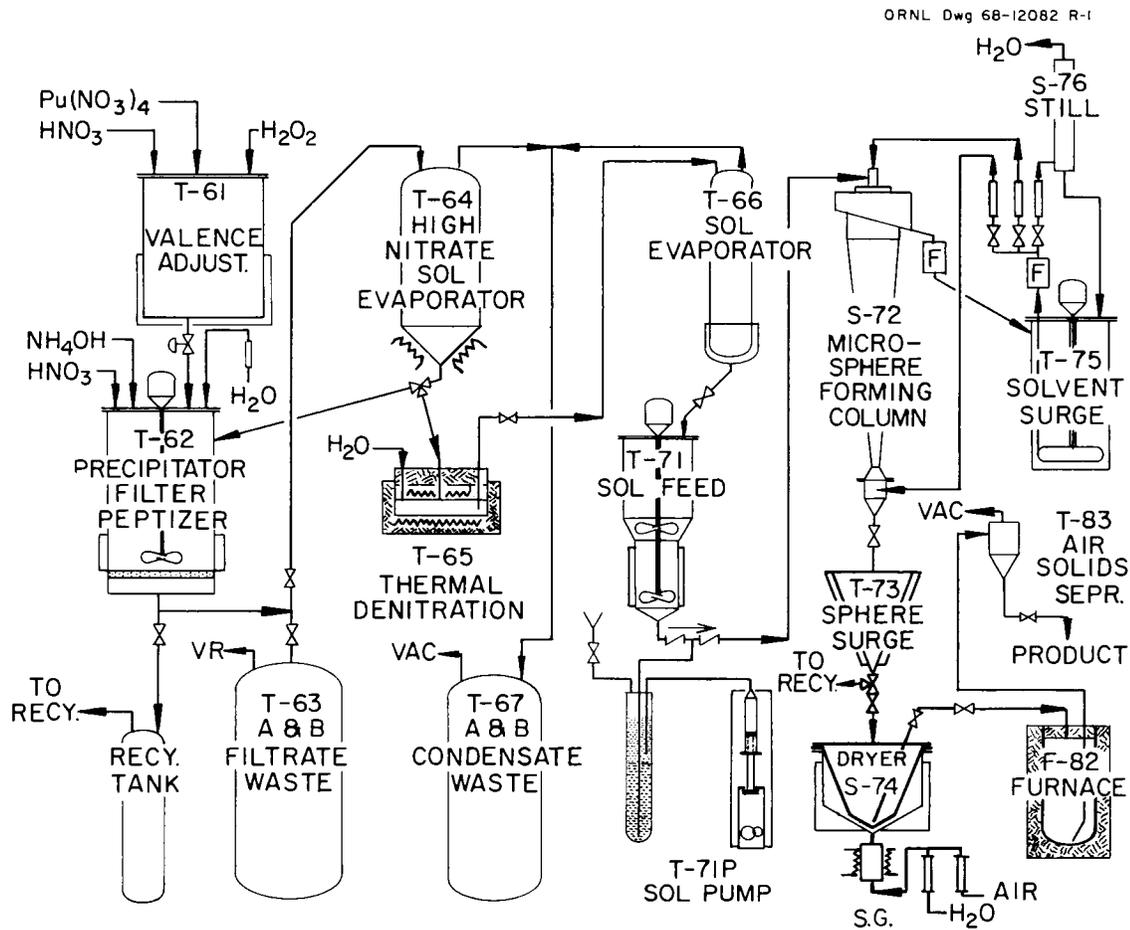


Fig. 24. Schematic of Equipment for $^{238}\text{PuO}_2$ Sol Preparation and Microsphere Formation.

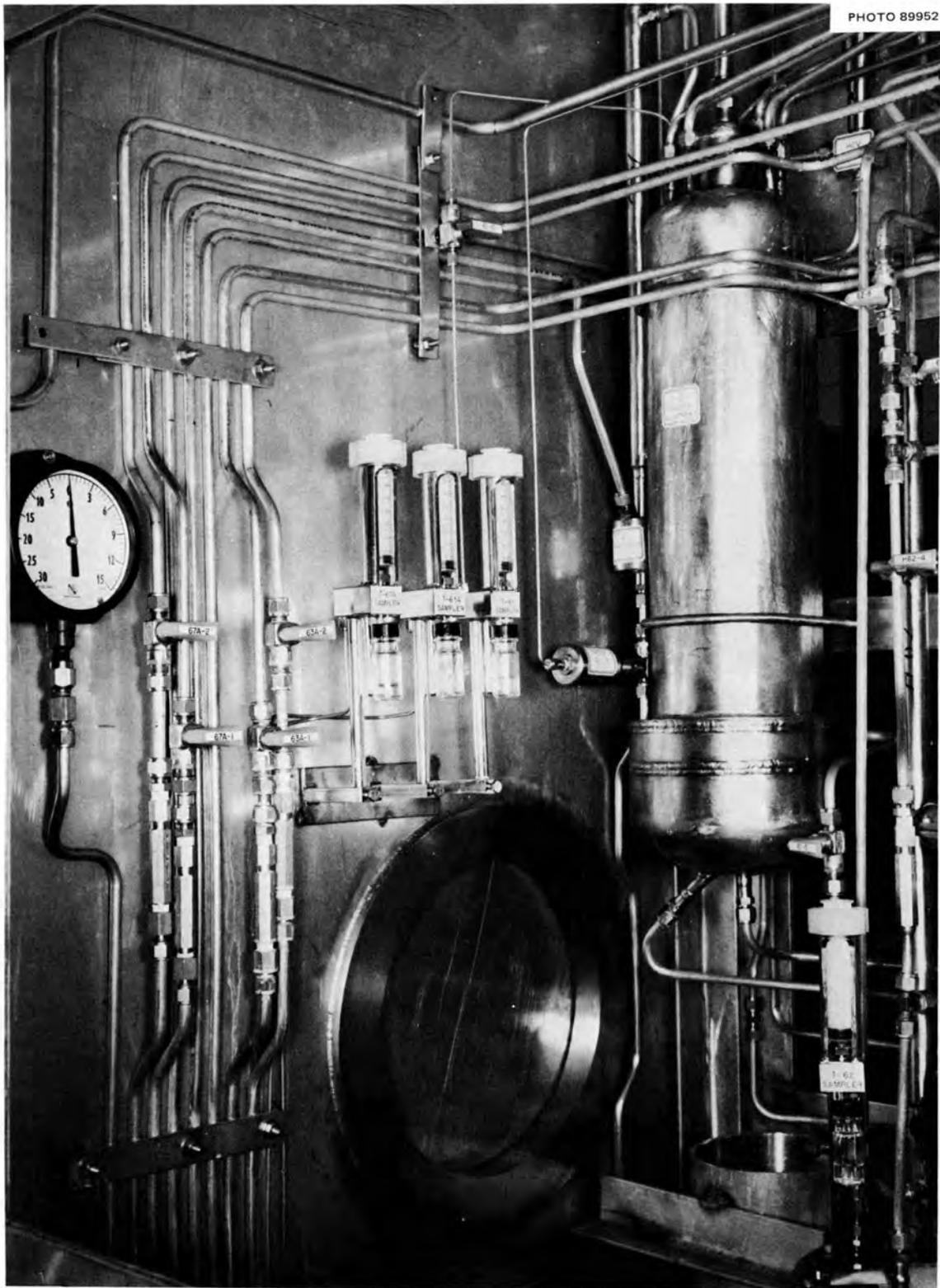


Fig. 25. ORNL System - Valence Adjustment Vessel, T-61.



Fig. 26. ORNL System — Rear of T-61, Metering Valve, and Top of T-62.

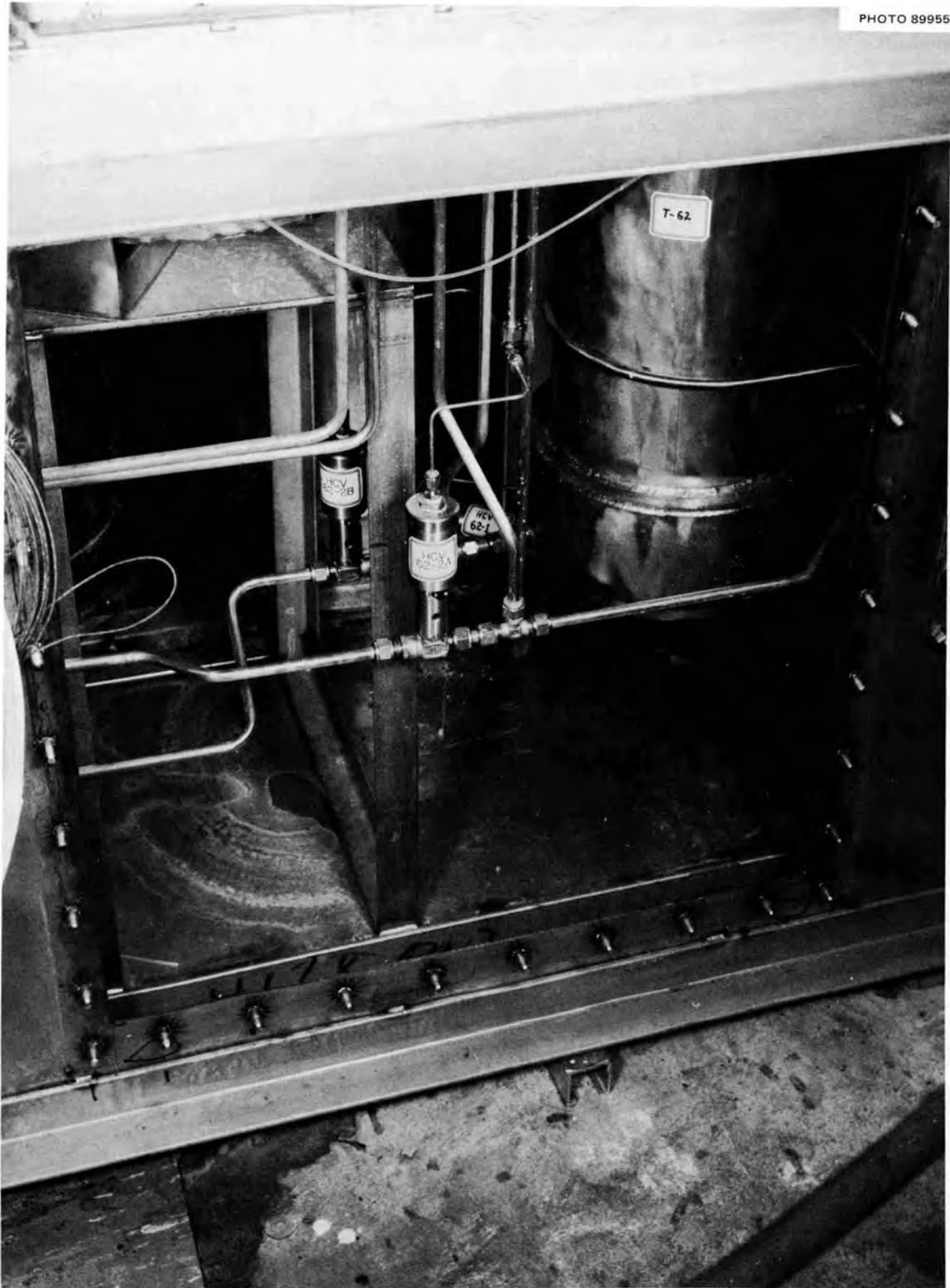


Fig. 27. ORNL System — Bottom of T-62.

condensate from the two evaporators (T-64 and T-66) is collected in the acid waste system T-67A and T-67B. These two tanks are similar and function in the same way as the basic waste tanks, although they are somewhat smaller (see Fig. 28). Three of the four waste tanks (T-67A and -67B and T-63B) are visible on the left. Normally, a "counter top" (removed from its brackets for these photographs) obscures these tanks from view.

The thermal denitration vessel, T-65 is an electrically heated stainless steel pan (see Figs. 20 and 29) in which the concentrated high-nitrate sol is fumed to dryness and the resulting cake is heated to 220-240°C for 2 to 4 hr to reduce the NO_3^-/Pu mole ratio to 0.10-0.15. The vessel shown gave even heating with a steady-state temperature variation of only $\pm 1^\circ\text{C}$ over the surfaces adjacent to the PuO_2 cake. After thermal denitration, only the addition of water and mild agitation are necessary for resuspension. The final sol and water rinses are then transferred by vacuum into T-66, the final sol evaporator and concentrated to the desired level. A view of T-66 from the rear is shown in Fig. 30. From T-66, the sol flows by gravity to the sol feed tank T-71 (Fig. 29). Both of these latter vessels have lines for the return of material to salvage.

6.3 Sol Pumping Equipment

The sol pumping equipment is the "interface" between the sol preparation equipment (aqueous) and the sphere-forming equipment (organic). It withdraws sol from the T-71 sol feed tank and discharges it into the drying solvent (2EH with surfactants) in the top of the microsphere-forming column. The sol pumping system (including the two-fluid nozzle) is one of the most important systems in the microsphere-forming operation because the yield of product cannot exceed the percentage of sol droplets formed in the proper size range. The size of these droplets, which, in turn, determines the size of the calcined product, is dependent on the rates at which the sol and solvent flow through the two-fluid nozzle. The constancy of these flows determines the uniformity of droplet sizes. The solvent flow rate can be controlled relatively easily by throttling the output of a centrifugal pump with a needle valve. Thus the yield is a direct function of the efficiency of the sol pumping system.

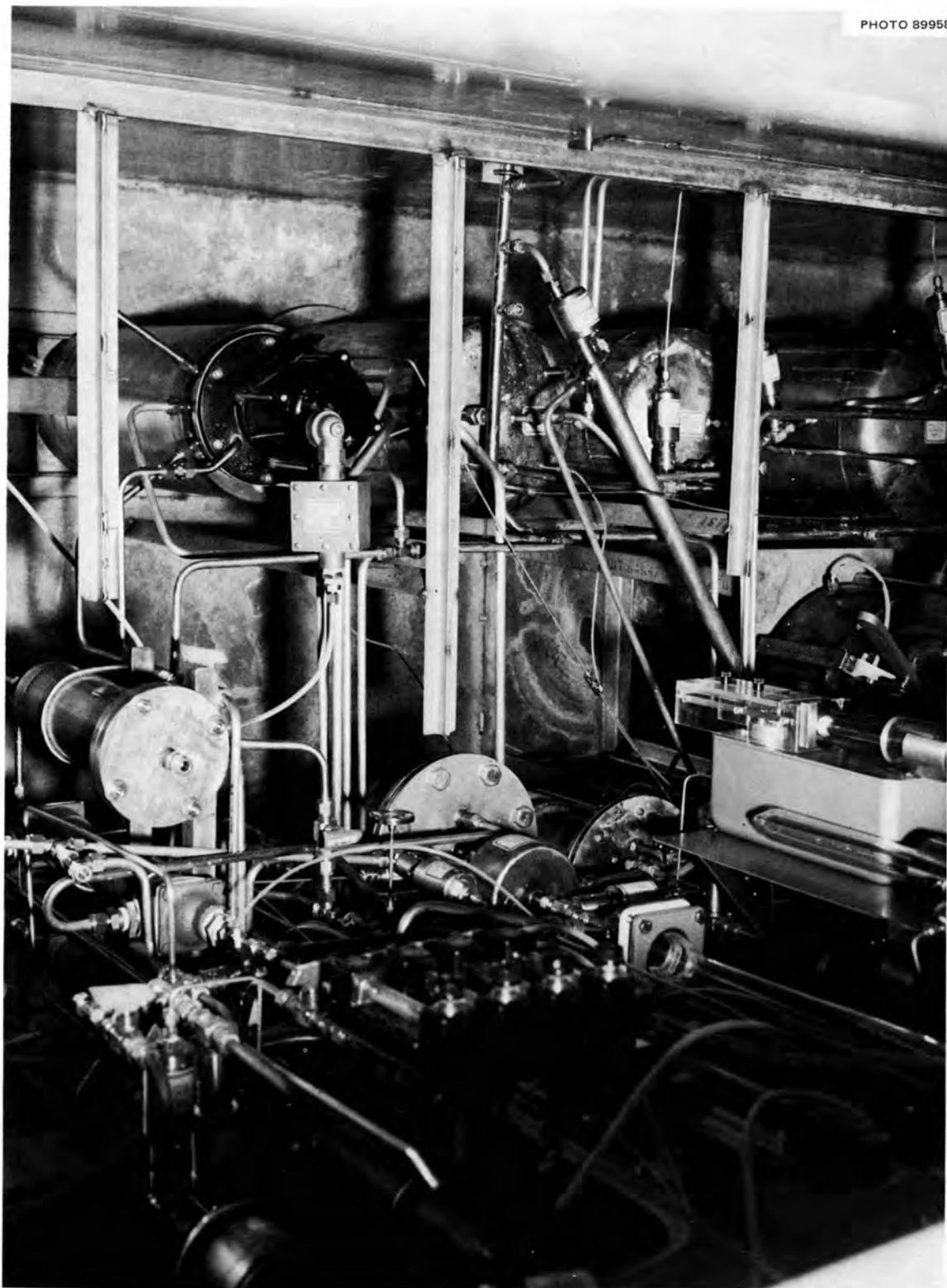


Fig. 28. ORNL System — Waste Tanks.

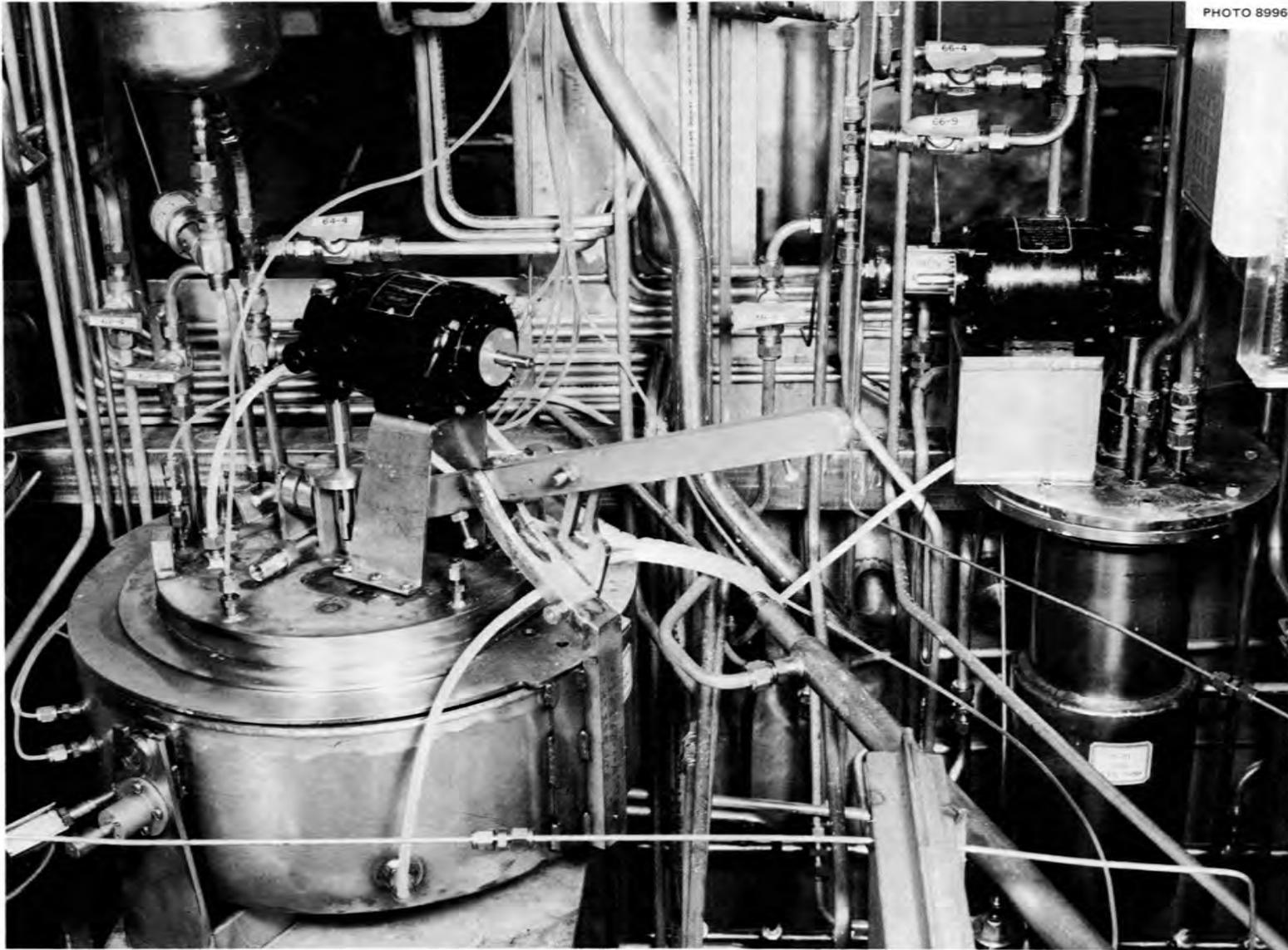


Fig. 29. ORNL System — Thermal Denitration Vessel, T-65.

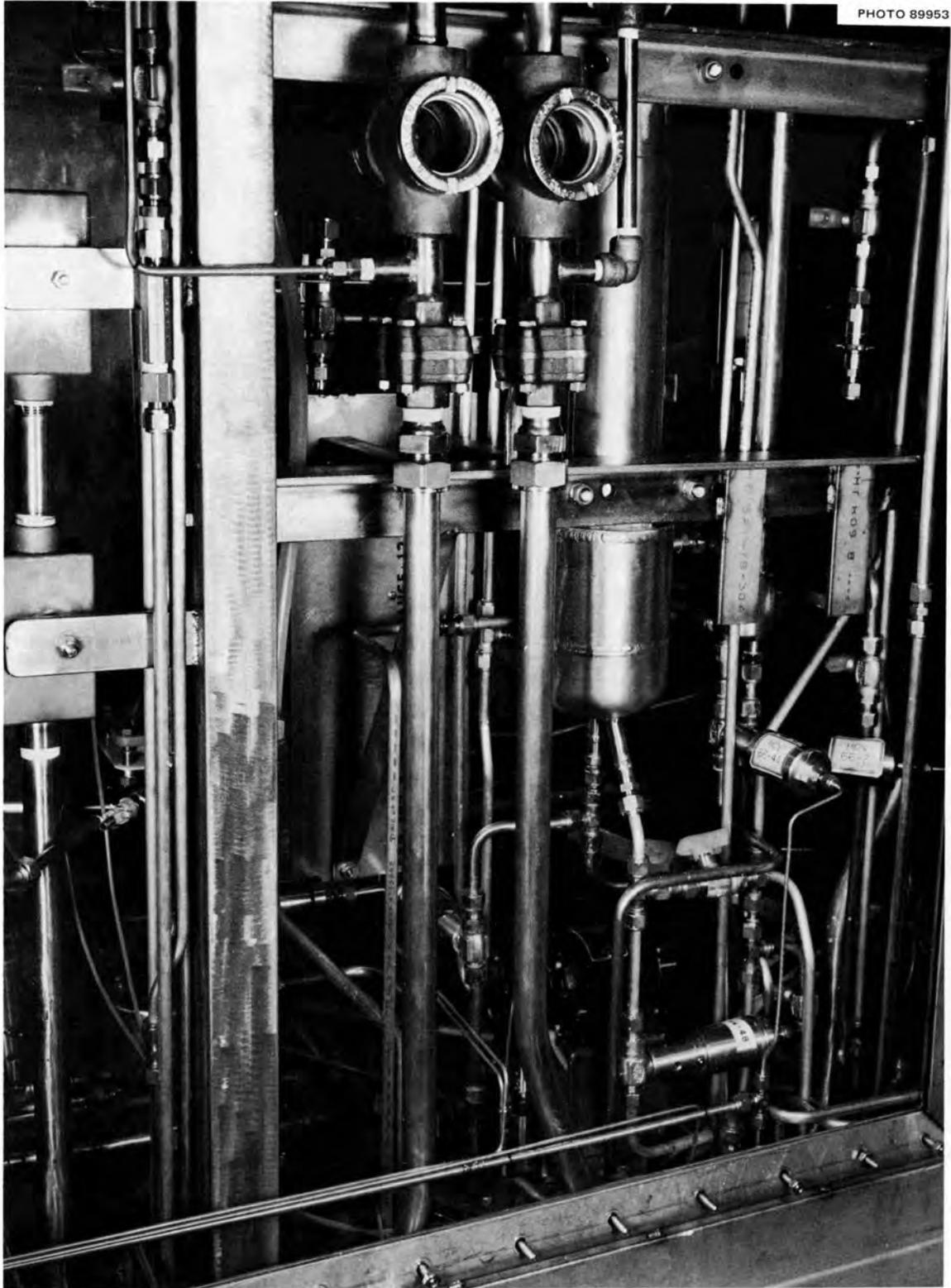


Fig. 30. ORNL System - Final Sol Evaporator, T-66 (Rear).

To achieve constancy of flow at the low flow rates required (1 to 3 cc/min), an infusion or syringe-type pump was chosen; the use of an indirect or displacement method of pumping also seemed logical because, in this method, no elastomeric seal would be required to contact the $^{238}\text{PuO}_2$ sol. The pump is shown schematically as T-71P in Fig. 24; the hardware may best be seen in Fig. 31. The pump, basically a standard variable-speed, reversible, external-gear infusion pump, has been modified radically and amplified to give the required flexibility and versatility. The liquid pumped by the syringe is water-saturated 2EH; a fixed volume of this fluid cycles between the syringe and the displacement pot, a 12-in.-long, 1-in.-ID glass tube in which a 2EH- $^{238}\text{PuO}_2$ sol interface is always visible. Three air-operated valves are included in the system for controlling the pump; these valves admit sol to the displacement tube (V_1), allow sol to be pumped to the two-fluid nozzle (V_2), and vent the displacement tube (V_3). During normal cycling, 2EH is pumped into the displacement tube at the desired rate (1 to 3 cc/min), which is set by a rheostat on the pump control; during pumping, sol is displaced through V_2 to the two-fluid nozzle (V_1 and V_3 are closed). At the end of the forward stroke, a limit switch opens V_1 , closes V_2 , and causes the plunger of the syringe to be withdrawn at the maximum rate (~ 30 cc/min for the size of syringe supplied). After a preset travel, the limit switch causes the valves to reverse and the pumping cycle to be repeated.

One of the major difficulties encountered in the accurate pumping of $^{238}\text{PuO}_2$ sols is the generation of gas within the sol itself. When sol is admitted to a syringe that is discharging upward, the gas collects near the tip and results in bubbles and intermittent flow to the two-fluid nozzle; this was one of the chief considerations that led us to use displacement pumping. Gas generated in the displacement tube is trapped against the top flange above the 2EH layer. When a significant volume of gas has accumulated, the pump control is switched from the CYCLE mode described above to the VENT mode. This closes V_1 and V_2 , opens V_3 , and causes the pump to run forward at maximum speed, thus rapidly displacing the gas from the tube. Upon return to CYCLE, normal pumping is resumed. A small reservoir, which can be vented manually, was incorporated in the two-fluid nozzle to trap gas generated in the line from the displacement tube.

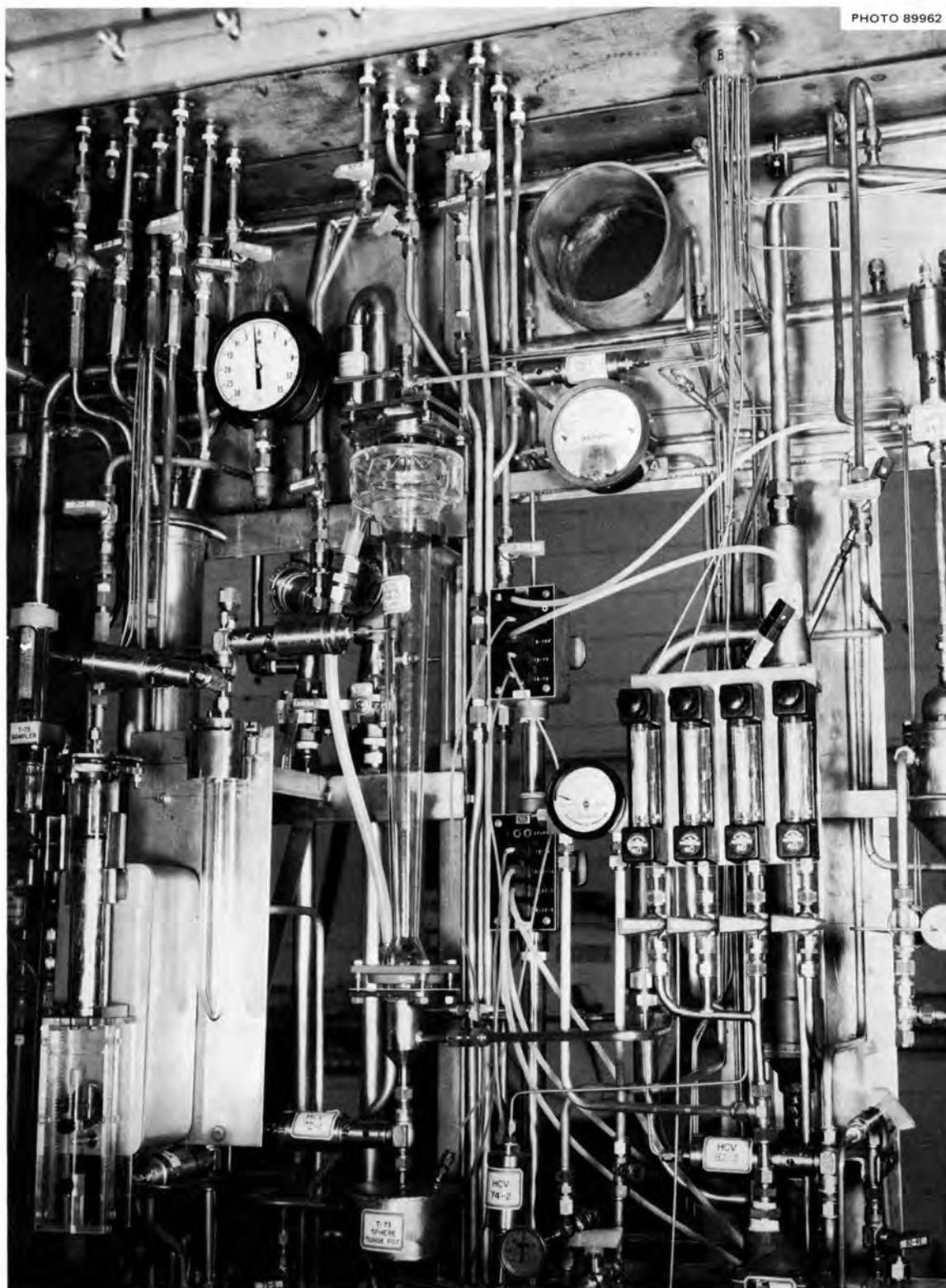


Fig. 31. ORNL System - Sol Pump, Syringe, Drive, and Displacement Tube.

For complete flexibility, a third mode, MANUAL, was provided. In this mode, the three valves may be either opened or closed by individual switches, the direction of flow may be selected (fill or pump), and the speed may be chosen (maximum or controlled). Different combinations of conditions are required for irregular operation, charging of saturated 2EH, cleanout, etc.

6.4 Microsphere-Forming Equipment

The microsphere-forming column is of the conventional ORNL design. It has a 7/8-in.-diam throat (minimum) that tapers to a diameter of 1-7/8 in. over a height of 16 in. and enlarges to a diameter of 3-1/2 in. at the point of solvent overflow. Since the column (S-72), the sphere surge vessel (T-73), the dryer (S-74), and the block valves have the same vertical axis (see Fig. 32), the microspheres that drop continuously through the column throat can fall by gravity through T-73 and into the conical basket of the dryer if all the valves are open. In normal operation, a batch of microspheres is accumulated in water-jacketed T-73; then these microspheres, along with solvent, fall into the dryer. This solvent is then drawn off through the screen that forms the bottom of the dryer basket.

Water is removed from the 2EH at the same average rate that it is extracted from the sol by passing a side stream of the 2EH through a continuous still. This still may be operated at any temperature in the range of 130 to 180°C as long as the flow rate of 2EH is adjusted accordingly. The amount (wt %) of water remaining in the effluent from the still is determined by the operating temperature. The entire stream flowing through the still must be heated to its boiling point, but only a small percentage of it must be vaporized. When condensed, this overhead stream separates into two phases; a phase separator routes the water to waste and returns a small stream of water-saturated 2EH to the still. With the proper choice of operating temperature and flow rate to the still, the concentration of water in the 2EH inventory can be controlled in a narrow range (± 0.1) within the limits 0.7 to 2.0 wt %. Generally, a low still temperature is desirable to minimize surfactant degradation. In this respect, the steam-heated still in the Mound box is superior to an electrically heated still;

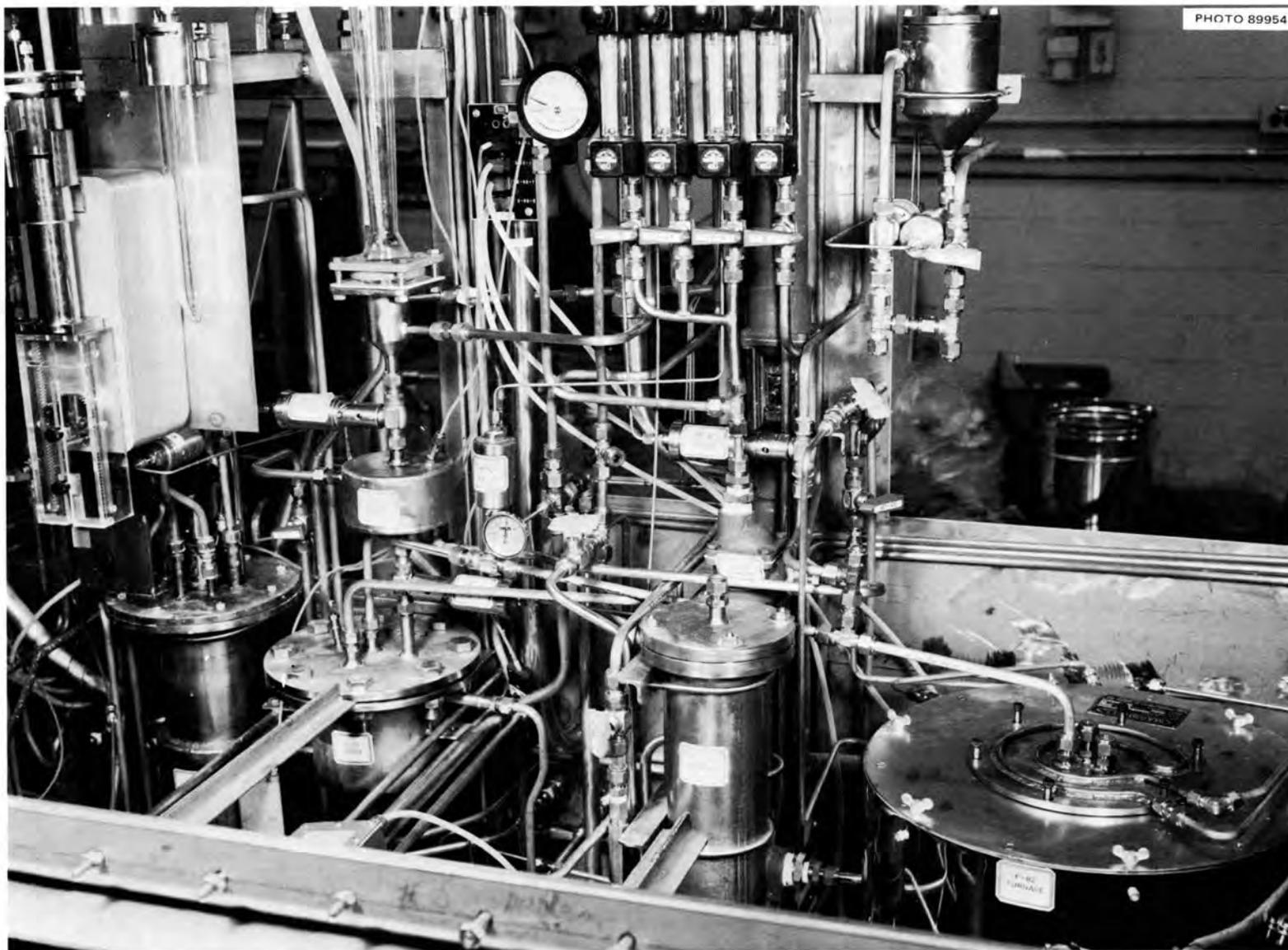


Fig. 32. ORNL System — Column Throat, Sphere Surge Vessel, and Dryer.

the maximum wall temperature is limited by the steam pressure and is not dependent on the rate of solvent flow past the heated surface.

In addition to the overhead condenser and phase separator, the still itself consists of three shell-and-tube heat exchangers. The actual boiling takes place inside the tubes of one exchanger with regulated steam in the jacket; the hot, dry solvent leaving this main exchanger is passed through the shell of a second exchanger, which has cool, wet, incoming solvent flowing upward in its tubes. Finally, the dry solvent flows through a water-jacketed cooler, which decreases its temperature to that desired for the system. This equipment may be seen in Figs. 31 and 33.

Gel microspheres are dried by passing argon up through the microsphere bed while admitting steam to the dryer jacket. The temperature is gradually increased (over about 4 hr) until at least 160°C is reached. After drying, the microspheres are conveyed out of the dryer pneumatically through a permanently installed dip-tube and connective piping directly into the F-82 firing furnace. This furnace is of the vertical-tube type with an alumina crucible and a heating element that is capable of operating at 1250°C in air. The furnace has cooling coils on the top flange, the outer cylindrical shell, and both shell ends. The top of the furnace is viewed from a front window in Fig. 32; a rear view is seen through one of the access ports in Fig. 34.

Microspheres are fired to near-theoretical density by heating to 1200°C in air at rates of 40 to 300°C/hr. It is during the early part of this heatup (400 to 800°C, prior to complete sintering) that oxygen exchange may be accomplished. Neutron emission rates from the (α, n) reactions in $^{238}\text{PuO}_2$ can be reduced to less than one-half by multiple equilibrations of the gel microspheres with H_2^{16}O vapor containing 0.01% ^{17}O and 0.01% ^{18}O .¹⁰ Such treatment would be carried out in the F-82 furnace using the appropriate time-temperature schedules. The ^{16}O handling equipment, located outside the box, was the responsibility of Mound Laboratory and required only penetrations and connective piping within the box.

After being fired, the dense microspheres are removed from the furnace by pneumatic transfer through a dip tube and collected in a cyclone separator. From this receiver, the batch is drained into a Mound product container for transport to other equipment for further processing and

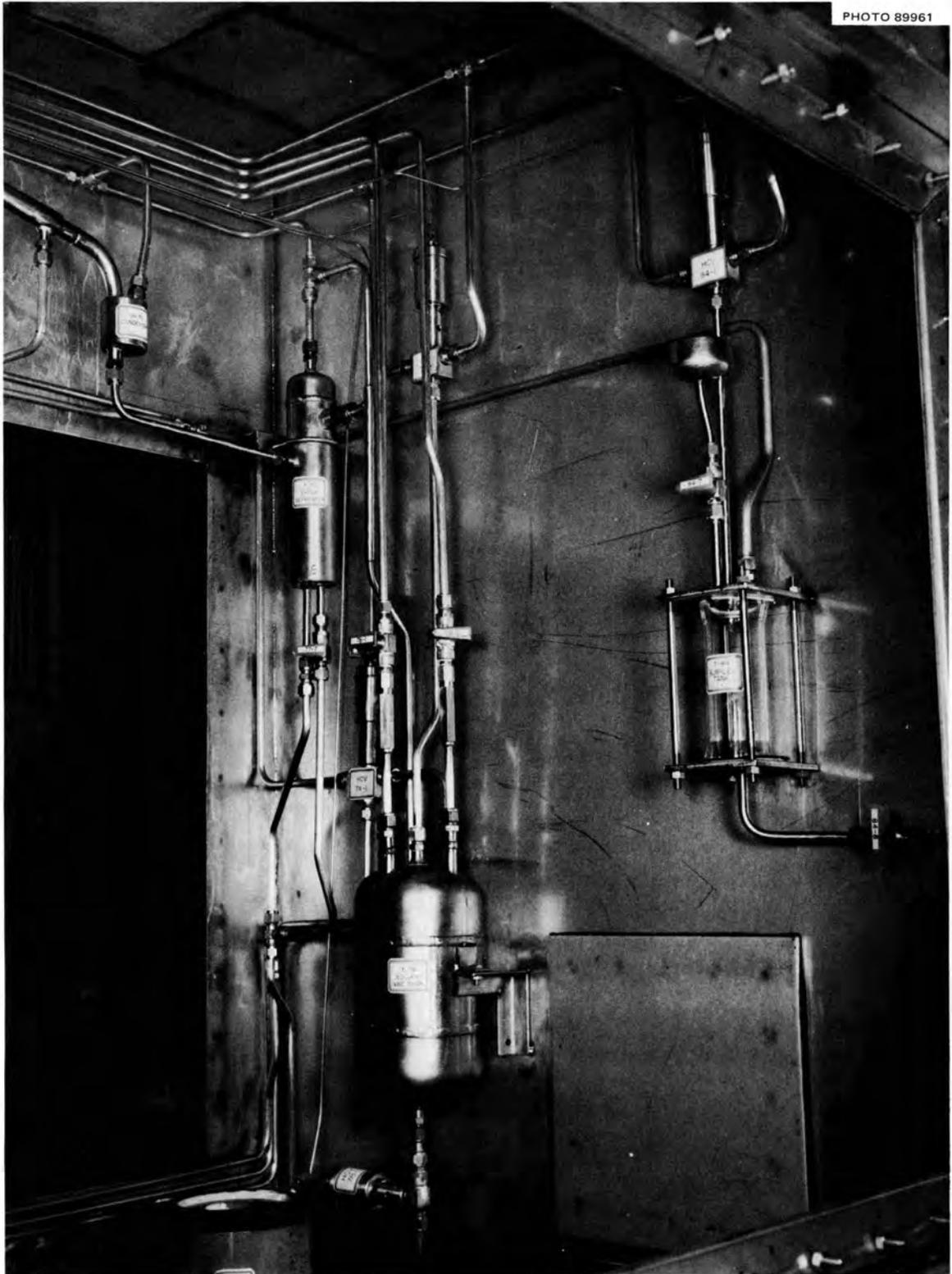


Fig. 33. ORNL System — Still Condenser and Phase Separator.

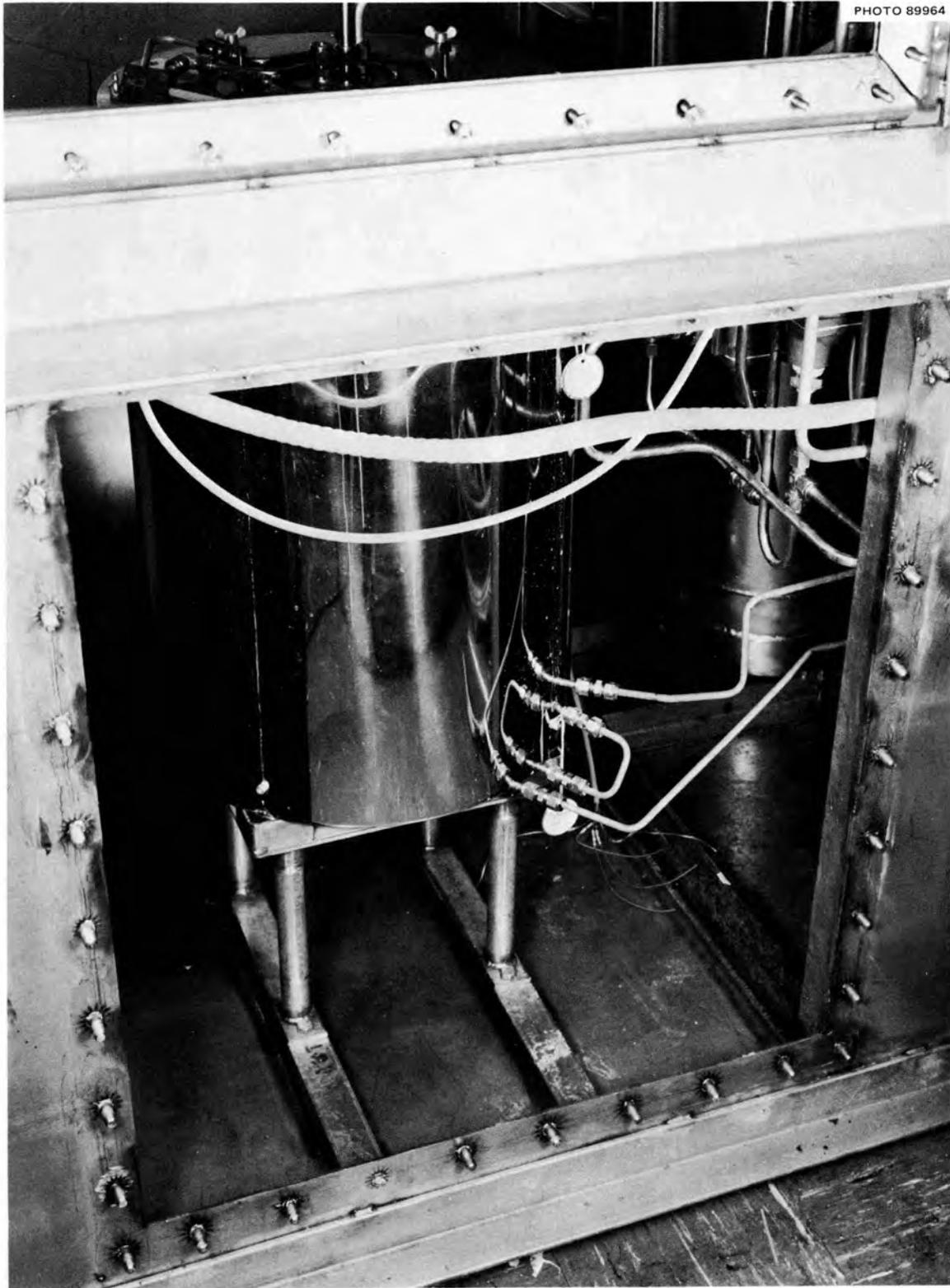


Fig. 34. ORNL System — Bottom of Firing Furnace.

evaluation. Equipment for sizing and shape-separation was not included in the box, since it was already available in the Mound complex.

6.5 Miscellaneous Equipment

Some equipment is common to both the sol preparation and microsphere-forming systems; most notable are the VAC and VOG systems, valves (two- and three-way, air-operated and manual), and samplers. The VAC and VOG headers, traversing the central two-thirds of the box high against the rear wall, may be seen in Figs. 23 and 31. The risers, cutoff valves, and "bull's-eye" sight glasses are shown from the rear in Fig. 32. Each vessel is connected to the VOG system; in the systems that are also served by VAC, the connections are through air-operated three-way valves. (The vessel is always connected to either the VAC or the VOG system but cannot be connected to both at the same time.) The three-way valve has the configuration of a tee, with the VAC and the VOG systems connected to the "run" and the vessel connected to the side outlet. This may be seen clearly in Fig. 33. A ball with a right-angle port is positioned at the intersection. One leg of the 90° port is always aligned with the vessel connection (vertical), and an 180° rotation of the ball by the air-operator causes the other leg of the 90° port to align with either the VAC or the VOG connection.

All of the valves in the system, except one diaphragm-operated metering valve, are of the ball type and have Teflon seats. The most common valve has 3/8-in. tubing fittings and a bore of approximately 1/4 in. The same valve is used in both manual and air-operated applications. In the operators, the linear travel of a spring-loaded piston is translated into rotational motion by lugs on the skirt of the piston operating in angular slots. Valves were located to minimize exposure to solids or liquids containing high concentrations of ^{238}Pu . In instances where this was impossible (such as for drain or block valves at the bottoms of vessels), the valves were positioned for easy replacement.

Each major vessel was provided with a liquid sampler of the type shown schematically in Fig. 35. Three of these samplers are shown clearly in Fig. 25. A 35-ml syringe is used to provide an easily controlled vacuum with which to withdraw the sample. The sample receiver is a glass

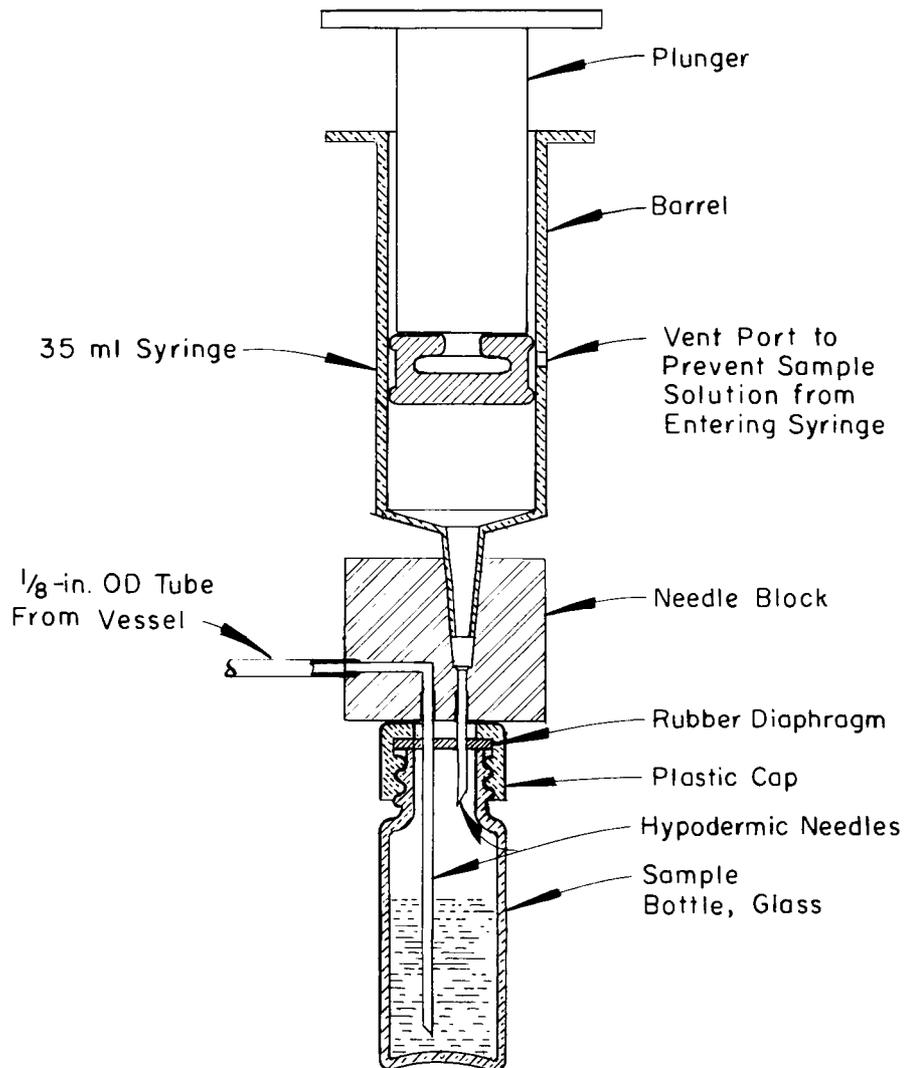


Fig. 35. Schematic of Liquid Sampler.

bottle (volume, ~20 ml) with a rubber diaphragm sealed over the top opening by a drilled, plastic screw cap. The rubber reseals when the needles are withdrawn; therefore, the same bottle can be used to transmit the sample to the analytical laboratory. A vent port in the syringe barrel prevents overfilling. The plunger may be operated repeatedly, if desired, to provide recirculation; the distance from the lower needle to the bottom of the bottle determines the minimum volume of a recirculated sample.

6.6 Instrumentation

The instrument panel for the sol-gel equipment can be seen in Fig. 22. The temperatures in the major process vessels are measured by thermocouples and then printed out on the 12-point, strip-chart recorder, which is located slightly below eye level on the left panel. Above this is a row of six liquid-level and density recorders; these quantities are measured by bubblers in the vessels and differential-pressure cells located in the access corridor behind the box. Alarms (principally for liquid level) are located at the tops of both panels. The two autotransformers (top left) are operated in conjunction with the two temperature controllers (below the strip chart) to regulate the heating elements in the thermal denitration vessel. The four rows of toggle switches position the air-operated valves. The control system for the sol pump (described in Sect. 6.3) normally occupies the hole at the bottom of the left panel.

The three speed controllers for agitator motors, as well as the control and indicator for the $\text{Pu}(\text{NO}_3)_4$ feed metering valve, are located at the top of the right panel. The left programmer and recorder-controller actuate a steam valve to maintain the desired temperature in the jacket of the sphere dryer. The programmer and recorder-controller on the right, in conjunction with the power supply at the bottom, execute firing cycles in F-82. The temperature of this furnace F-82 is also indicated on the dial next to the strip chart. Below the dial is a thermocouple selector switch for checking and intermittently recording temperatures not routinely recorded.

6.7 Leak Checking

The Mound box was temporarily closed and checked for leaks before being shipped. Prior to helium leak-testing, the box was evacuated to

-8.2 in. H₂O and was backfilled with helium to a pressure of 3.8 in. H₂O. The box was then purged for 1 hr under these conditions; helium entered the top of the box, and the air was displaced through a temporary header at the bottom of the box. A Veeco leak detector, Model MS-9 AB (sensitivity, 3×10^{10} cc/sec) was used for the test; it was standardized using a standard leak tube having an 8.3×10^{-7} cc/sec leak rate. The testing was conducted by qualified technicians under the supervision of the ORNL Inspection Engineering Department. Except for the three windows in the top of the box (which were closed by aluminum plate), the regular safety plate glass windows were installed for the test.

The results of the test were encouraging. No leakage could be detected on the front or either end of the box. No window leaks were observed; also, there was no evidence of leakage on any of the weld joints. Small leaks through openings such as electrical and thermocouple junction boxes were found; however, these were scheduled to be sealed with epoxy resin at Mound.

7. ASSISTANCE TO MOUND LABORATORY

The full-scale Mound production system was designed and fabricated at ORNL. After preliminary testing of the system at ORNL, the box was shipped to Mound and installed in the PP building there. The shielding was erected, and the utilities and instrumentation were connected by Mound personnel. Instrumentation and operational checkouts were accomplished with the assistance of ORNL personnel; then the box was closed and leak checked. Afterward, when it was reopened, ORNL personnel assisted in the program of (1) checking out the system, (2) continuing process development, and (3) modifying the system to incorporate as many of the recent improvements as time permitted.

7.1 Continued Development with Larger Batches at Mound Laboratory

As Mound personnel increased the size of ²³⁸PuO₂ sol batches stepwise from 5 to 50 g of plutonium, satisfactory results became increasingly difficult to achieve. The processing of larger batches in laboratory facilities was not permissible; consequently, it was decided to continue the studies in shielded, glove-box facilities rather than in the manipulator-operated ORNL equipment. Mound's developmental sol-forming facility

utilized an existing precipitation vessel, a porous stainless steel filter funnel, and an 8-in.-diam denitration vessel that had been supplied by ORNL and used earlier in the smaller-scale laboratory studies at Mound.

The microsphere-forming equipment was patterned after that in the ORNL system. It incorporated one of the improved forming columns (supplied by ORNL and described in Sect. 7.3) and a solvent still and a pump tank, both of which were fabricated at Mound Laboratory from ORNL prints. A furnace that was normally used in another process was utilized for firing the dried gel spheres.

7.1.1 Electron Microscopy of $^{238}\text{PuO}_2$ Sols Produced at Mound

The introduction of electron microscopy as a diagnostic tool in the evaluation of larger-scale (50 g of ^{238}Pu) sol preparation enabled us to isolate two principal problem areas in the process. Recognition of these difficulties led to minor process changes that resulted in the successful preparation of $^{238}\text{PuO}_2$ sols and microspheres in batches containing up to 120 g of ^{238}Pu .

After success at the 25-g level, the next stage of development involved a series of experiments at Mound in which 50 g of plutonium was used per batch. In these runs, Mound personnel attempted to duplicate all conditions that produced good-quality sols in the 25-g runs. However, in three consecutive attempts, sols that did not produce good-quality microspheres were made. A fourth run yielded a sol from which satisfactory microspheres could be formed; however, microspheres could not be prepared from the product sol obtained in the fifth run.

At this point, in close collaboration with Mound personnel, electron microscopy was introduced as a diagnostic tool to evaluate sol preparations. The microscope available at Mound had a magnification of only 35,000. A magnification this low did not allow unambiguous interpretation of particle size, but it was possible to evaluate the crystallinity of plutonium polymer at various stages in the process by examination of electron diffraction patterns. Sols were examined at three or more key points during preparation; samples of the high-nitrate sol prior to evaporation, the dried sol before baking, and the final denitrated sol were taken.

Later at ORNL, a Philips 300 electron microscope was used to obtain micrographs of high-nitrate and denitrated $^{238}\text{PuO}_2$ sols. These micrographs demonstrated that there were no fundamental differences in crystallinity or particle size between $^{238}\text{PuO}_2$ sols and $^{239}\text{PuO}_2$ sols. The results substantiated previous findings which indicated that (1) the failure to produce crystalline polymer and (2) the degradation of crystalline polymer during the evaporation of high-nitrate sol to dryness had been the two principal problems encountered during scale-up experiments.

Crystallinity in the High-Nitrate Sol. — In the first 50-g run examined, it was found that, immediately after peptization, the high-nitrate sol was amorphous rather than crystalline as desired. Diffraction patterns demonstrating this difference are shown in Fig. 36. Denitrated sol prepared from this material gave results characteristic of sols prepared from amorphous polymer, that is, erratic denitration during baking and uncontrollably pitted microspheres. A second 50-g experiment was designed to determine whether longer aging times of the washed hydroxides would produce crystalline polymer. The washed hydroxide was boiled for 6 hr (instead of 2 hr, which had previously been considered sufficient); a portion of the hydroxide was peptized and examined by diffraction after each 2-hr period of aging. In this experiment, the polymer was crystalline after the initial 2 hr. Crystalline polymer was also obtained in subsequent experiments after only 2 hr of aging. It now appears that the presence of amorphous polymer at this early stage can result from hydrolysis or partial hydrolysis of the plutonium feed during adjustment to a low acid concentration or subsequent storage at a low acid concentration. This effect has almost certainly been responsible for some of the difficulties experienced during scale-up experiments. This finding definitely identified feed adjustment as a critical area in the flowsheet.

Degradation of PuO_2 Polymer. — A run made with the hydroxide that had been aged for 6 hr did not form sol, although the polymer in the high-nitrate sol was highly crystalline. Electron diffraction patterns again strongly suggested that the PuO_2 polymer had degraded. In Fig. 37, diffraction patterns for this sol are compared with those for a 10-g control batch. The loss of diffraction pattern in the dried high-nitrate sol for the 50-g



AMORPHOUS POLYMER

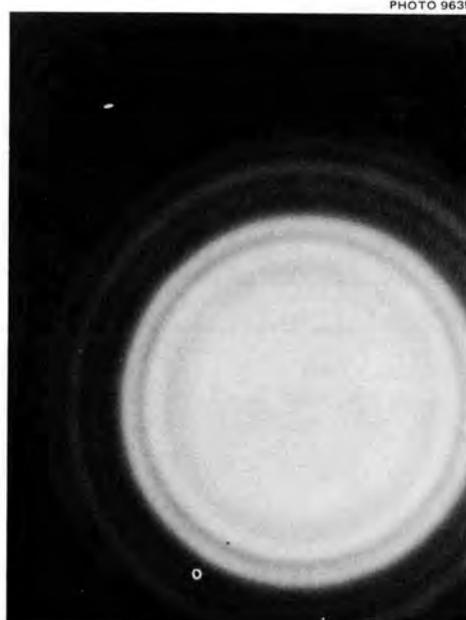


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CRYSTALLINE POLYMER

Fig. 36. Diffraction Patterns of High-Nitrate $^{238}\text{PuO}_2$ Sols.

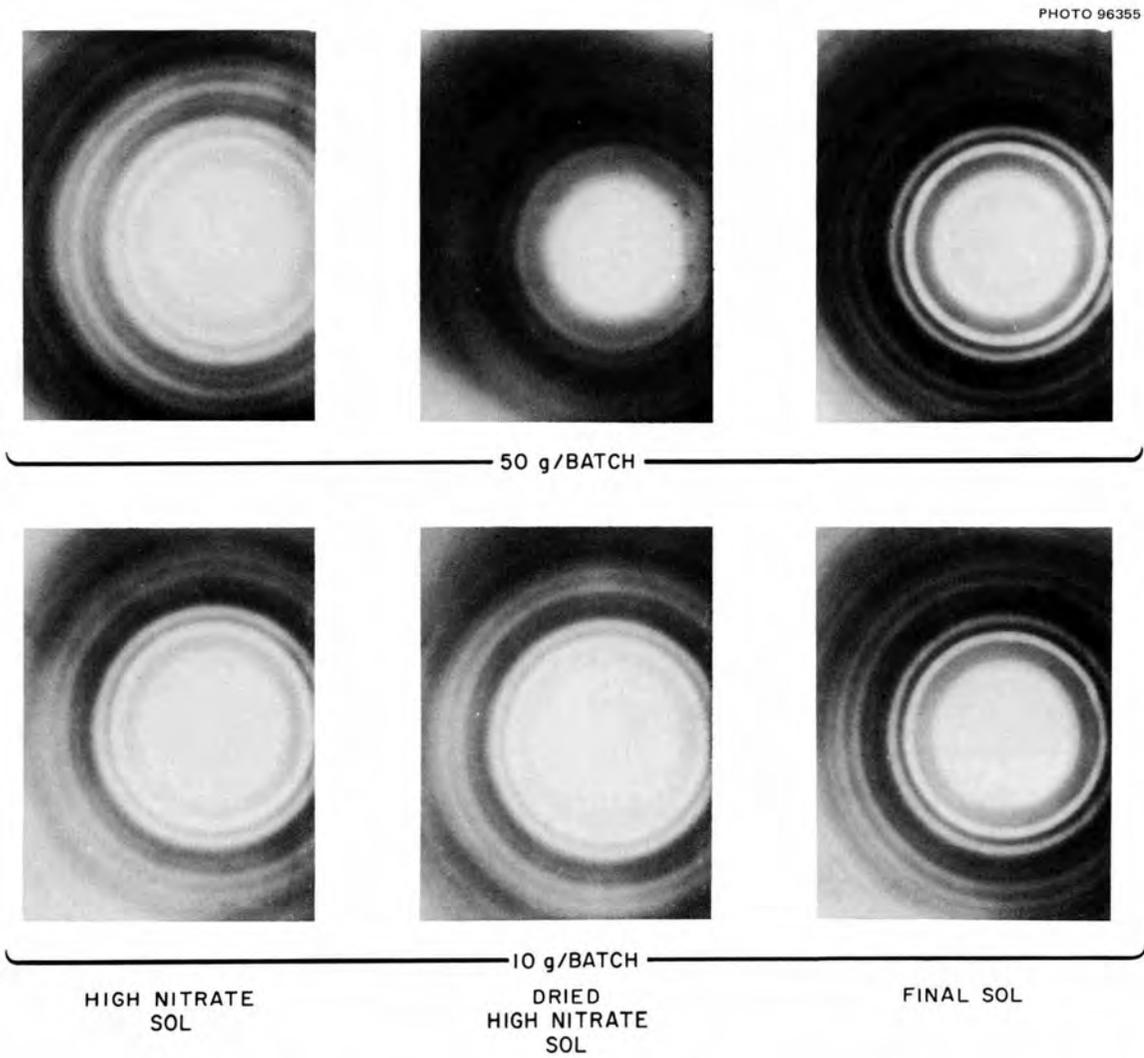


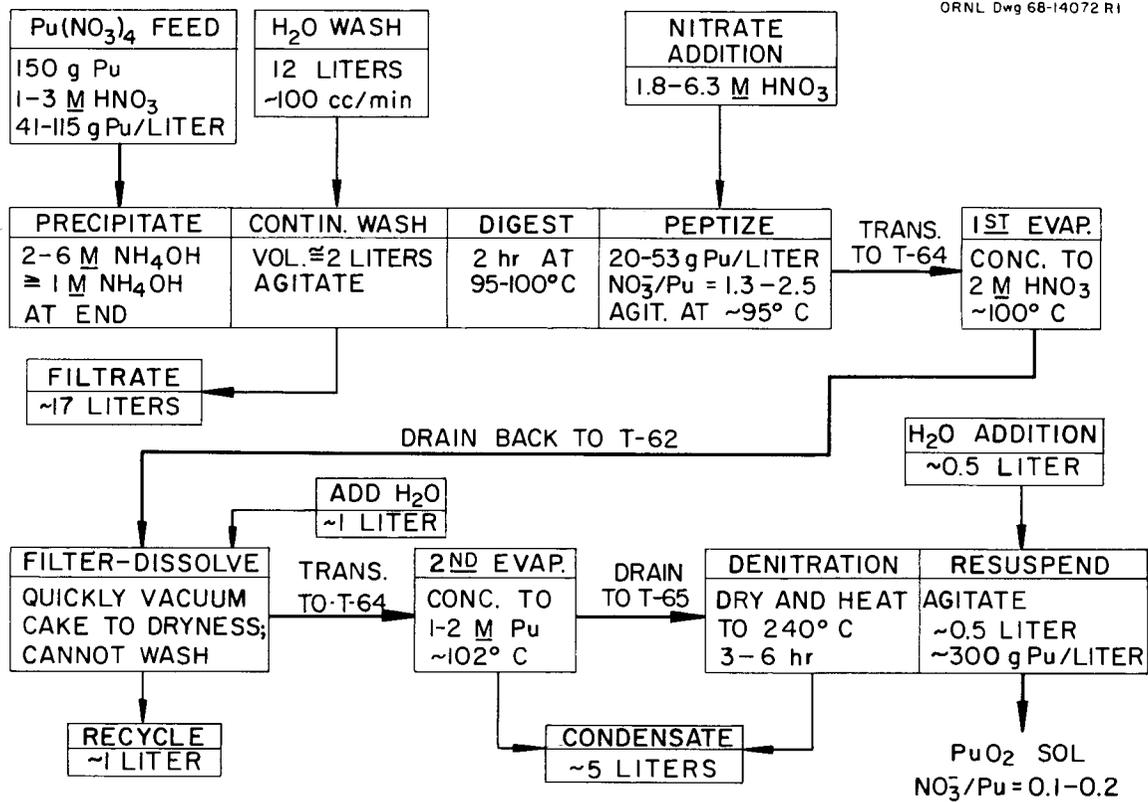
Fig. 37. Diffraction Patterns for Sol Preparations.

batch indicates that the initially crystalline sol had undergone severe degradation to ionic forms of plutonium as it was subjected to a high concentration of HNO_3 in evaporating to dryness. Baking gives increased crystallinity for two reasons: (1) the size of the crystallites increases during baking, and (2) ionic forms of plutonium present in the dry material convert to PuO_2 at the baking temperature. Although an indication of crystallinity at this point is necessary if a good-quality sol is to be prepared, it provides no guarantee that good-quality sol will be produced.

7.1.2 "Dropout" Process

The two-phase region encountered during the evaporation of high-nitrate sol suggested a method for avoiding contact with strong acid, that is, separation of the polymeric solids by filtration when maximum precipitation occurs. We have termed this the "dropout" process. Mound investigated this technique with both 10- and 50-g batches of ^{238}Pu . Their results correlated well with those from small-scale experiments at ORNL. Mound investigators found that, for both batch sizes, maximum precipitation occurs at a nitrate concentration of about 2 M and that as much as 80% of the plutonium can be recovered by filtration. The filtered precipitate readily disperses in water, and the resulting sol can be dried and baked in the usual manner. A schematic flowsheet embodying this principle is shown in Fig. 38. In the experiments at Mound, both the precipitate and the supernate were processed; the solid fraction formed excellent low-nitrate sol in 100% yield, and good-quality microspheres were readily produced. As in our small-scale experiments, the supernate fraction contained a high percentage of ionic plutonium and did not produce sol.

These results confirmed that the primary difficulty in scale-up experiments is polymer degradation by HNO_3 during evaporation to dryness. The fact that degradation is more pronounced in 50-g runs than in 10-g runs indicates that contact time between polymer and HNO_3 is also an important variable. In these experiments, the time required for evaporation to dryness increased with batch size, and it is likely that the temperature also increased due to radiolytic self-heating effects. In general, the data, considered collectively, indicate that depolymerization is similar to simple dissolution of PuO_2 and is, therefore, a function of time, temperature, and acid concentration.



"DROP OUT" FLOWSHEET FOR PLUTONIA SOL PREPARATION

Fig. 38. "Dropout" Flowsheet for Plutonia Sol Preparation.

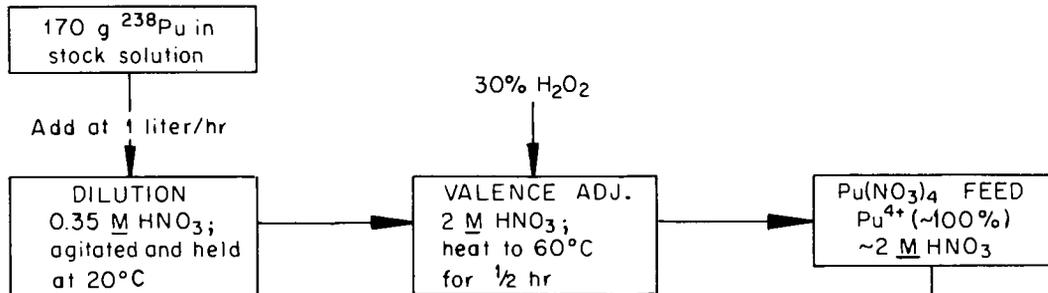
7.1.3 "Straight-Through" Runs

These concepts were further evaluated in experiments with larger batches containing 75 to 120 g of ^{238}Pu . A series of six $^{238}\text{PuO}_2$ sol runs was made at Mound Laboratory, and two comparable $^{239}\text{PuO}_2$ sol runs were made at ORNL. These experiments were designed to evaluate "straight-through" operation (i.e., with no overnight breaks) from feed preparation to resuspension, vacuum evaporation (reduced temperature), and the effects of excess peptizing acid as process variables. They also provided an opportunity to evaluate various analytical procedures for possible use as routine quality control techniques. These runs were designed to further substantiate the concept that the formation and retention of highly crystalline plutonium polymer are required for successful sol preparation.

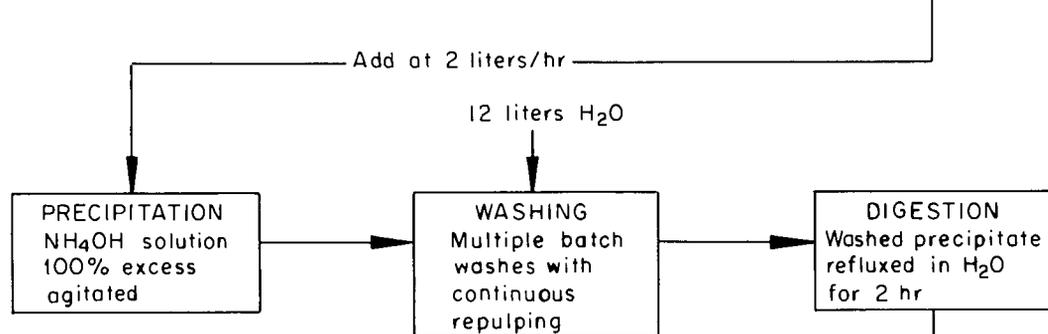
In the experiments at Mound, six continuous runs were made; numerous samples were taken at key steps in the process in efforts to evaluate crystallite size, polymer crystallinity, and polymer degradation as functions of process variables. Analyses of these samples were performed by solution spectroscopy, electron diffraction, and electron microscopy. In three of the runs, a high NO_3^-/Pu mole ratio (2.5) was used for peptization, while a low ratio (~ 1.1) was used in the remainder. In high-nitrate runs, the time required for evaporation was proportionately longer since a larger volume had to be evaporated. Other aspects of the six runs were similar; a "dropout" separation was used to obtain the highest-quality sol possible. Subsequent to these experiments, two "straight-through" runs at ORNL were made with ^{239}Pu . In these two runs, the low-acid and high-acid flowsheets were compared. A good-quality sol that was readily converted into microspheres was obtained in each case. Results obtained in these runs supported our previous conclusions and substantiated the advantages of the low-acid flowsheet.

Some time after this series of experiments, Mound personnel made a successful low-acid run with 170 g of ^{238}Pu in which the "dropout" separation was omitted. This is obviously a double advantage because it gives a higher yield and eliminates the plutonium recycle that is necessary with the "dropout" procedure. This preferred $^{238}\text{PuO}_2$ sol-preparation procedure, known as the low-nitrate, no-"dropout" (LNND0) flowsheet, is shown in Fig. 39.

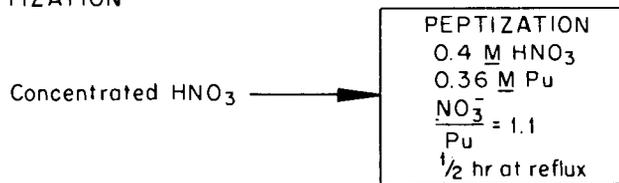
I. FEED ADJUSTMENT



II. PRECIPITATION, WASHING, AND DIGESTION



III. PEPTIZATION



IV. THERMAL DENITRATION

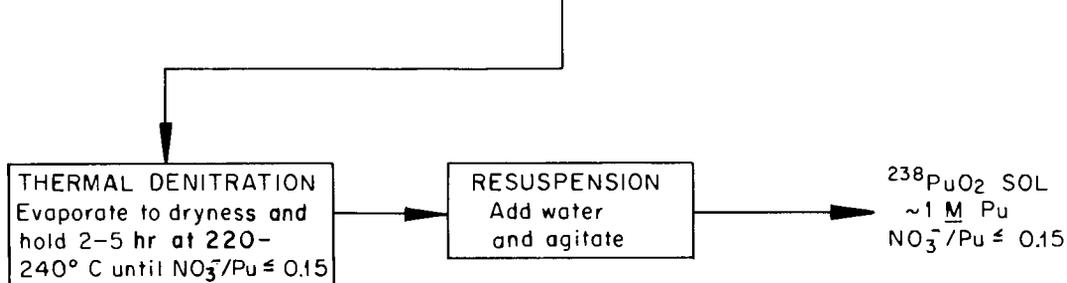


Fig. 39. The LNNDO Flowsheet for $^{238}\text{PuO}_2$ Sol Preparation.

As a result of the experiments described above, we believe that the chemistry in the $^{238}\text{PuO}_2$ sol-preparation process is now sufficiently understood to produce high-quality microspheres in high yield in the batch sizes required for the heat source program.

7.2 Equipment Modifications

Developmental work associated with the formation of sols and microspheres was continued during the fabrication and installation of the system, and several equipment improvements that should enable the facility to take advantage of the most recent advances in technology were made. A few of the improvements are described below; the list is by no means complete.

7.2.1 Sol-Preparation Equipment

The bottom of the evaporator was modified from a jacketed cylinder to a 45° cone to allow concentration to smaller volumes without exposing a portion of the heat-transfer surface. The bottom section of this cone, including the outlet tubing, was machined from bar stock so that no weld would be subjected to the high plutonium and HNO_3 concentrations that would be present here. A conical shell ($\sim 1/16$ in. thick) was also machined to fit the outside surface of the bottom of the cone. A Calrod heating element was then wound on (and attached to) the outside of this conical shell, thus providing us with an easily replaceable, heavy-duty heating element. Also, the substitution of resistance heating for steam and the addition of vacuum capability to the condensate tank made vacuum distillation (at temperatures less than 100°C) in the evaporator more practicable.

The mounts and shaft connectors of agitator motors were modified to facilitate remote replacement and alignment. With the new design, the activation of a toggle clamp replaces the previously required tedious operation of removing and replacing screws. Torque is transferred by a flexible coupling that requires no attachment and only approximate alignment.

Continuous Washing. — It was suggested that continuous washing should be attempted in order to avoid possible cake overheating and radiolytic effects. Although the equipment was designed for conventional batch washing of the PuO_2 precipitate, continuous downflow washing could be carried

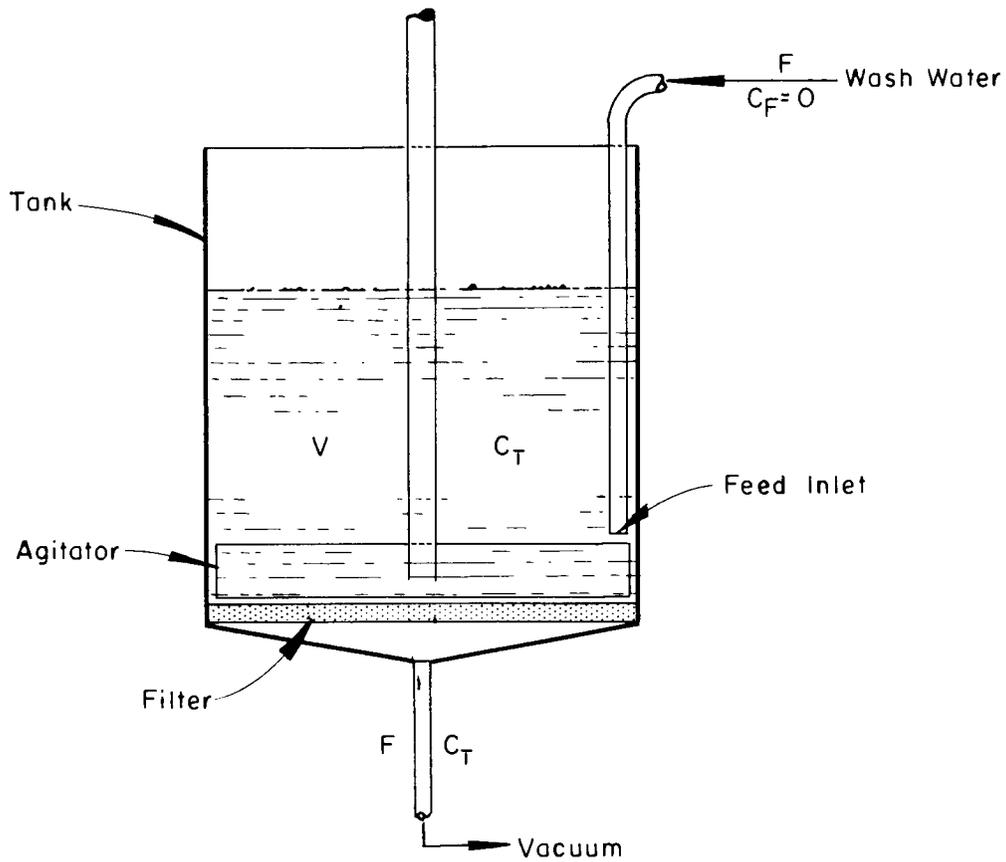
out in the same equipment with minor revisions. Calculated results indicate that continuous washing is feasible and might yield lower electrolyte concentrations in a shorter time, and with a smaller volume of waste, than batch washing. A model of the system is shown in Fig. 40.

The excess NH_4OH reagent and the NH_4NO_3 that is formed during the precipitation reaction can be washed from the precipitate to acceptable levels in reasonable times, possibly shorter than with batch washings, using the setup illustrated in Fig. 40. Agitation is continuous; filtrate is drawn into the waste tank at a rate proportional to the vacuum, and wash water is added at a rate sufficient to maintain a constant reading on the level-recording instrument. The concentration of NH_4^+ in the filtrate (and tank) at any time is found by evaluating the expression

$$\frac{C_T}{C_0} = e^{-\frac{F}{V} t},$$

which is the solution of the applicable differential equation. Apparently, for more rapid washing, we must maximize F/V ; we may make F larger or V smaller, within limits. The smallest volume that will permit effective mixing is probably about 2 liters. If we assume that all but 1.0 liter of the reaction mixture ($\sim 1 \text{ M } \text{NH}_4\text{OH}$ and $\sim 1 \text{ M } \text{NH}_4\text{NO}_3$) is removed initially, dilution to this 2-liter volume before the continuous washing begins gives $C_0 = 1 \text{ M } \text{NH}_4^+$, and the value of the exponential may be read directly as $\text{M } \text{NH}_4^+$. The average flow rate realized in batch washings in $^{239}\text{PuO}_2$ sol preparations at ORNL was approximately 67 cc/min, although scouting tests with continuous washing indicate flow rates greater than 100 cc/min should be easily attainable.

Table 2 shows calculated results obtained by using three assumed flow rates, $C_0 = 1 \text{ M}$, and a constant tank volume of 2 liters. A conservative flow of 60 cc/min, along with a realistic 100 cc/min, was chosen. The third value, 46 cc/min, was chosen for convenience in extrapolation (the concentration is reduced by one-half every 30 min). From experience with $^{239}\text{PuO}_2$ sols, it is believed that washing until the NH_4^+ concentration in the filtrate is less than 0.001 M should be sufficient. The above mathematical treatment assumes removal of electrolytes by bulk dilution; however, the rate of washing must also be considered. It is expected that the actual



- C Concentration of NH_4NO_3 or NH_4OH (moles/liter) at time t (perfect mixing assumed)
 C_0 Initial value of C_T at time = 0
 F Feed and filtrate flow rate (liters/min)
 V Volume of liquid in tank (liters) = constant
 t Time of flow (min)

Fig. 40. Model for Continuous Washing.

Table 2. NH_4^+ Molarity in Filtrate as a Function of Time

t (min)	$\frac{F}{V} = \frac{\text{Feed and filtrate rate (liters/min)}}{\text{Volume in tank = constant = 2 liters}}$		
	0.030/min	0.050/min	0.023/min
30	0.407	0.224	0.500
60	0.166	0.050	0.250
120	0.027	0.0025	0.0625
180	0.0046	0.000125	0.0156
240	0.00075		0.004
300	0.000125		0.001

concentration will follow an exponential curve quite satisfactorily at high concentrations where bulk dilution is being effected but will depart from it as diffusion within the agglomerated precipitate becomes rate limiting.

Modifications to permit continuous washing were made; a vacuum regulator was installed on the filtrate tank, and a means to permit the continuous addition of water was provided for the precipitator-filter.

"Dropout" Filtration. — Before it was shown that the dropout separation would probably not be necessary, the ORNL system was modified to permit this filtration to be performed using the existing filter in the bottom of T-62. The addition of a recycle tank (with vacuum service) to collect the plutonium-containing filtrate (about 20% of the batch) and a piping change at the bottom of the T-64 evaporator (see Fig. 24) were the only changes required. The flowsheet shown in Fig. 38 indicates how the modified equipment is to be operated.

7.2.2 Sphere-Forming Equipment

Preliminary tests of the microsphere-forming equipment with ThO_2 sol by Mound personnel showed the need for a filter for removing fine sol droplets that are entrained in the solvent overflowing the top of the forming column. To solve this problem, a filter assembly with a replaceable, porous stainless steel element was supplied by ORNL. Upon Mound's recommendation, the entire line of equipment for handling wet gel spheres (i.e., the column bottom, surge vessel, dryer top, and two shutoff valves) was replaced in order to provide a larger flow passage (9/16 vs 5/16 in. in diameter) and to add an "abort" valve for removing off-specification material.

Laboratory studies and the preparation of kilogram quantities of $^{239}\text{PuO}_2$ microspheres at ORNL had indicated the desirability of contacting the gel microspheres with steam prior to densification; the capability for steam treating the gel spheres during drying was incorporated by adding a rotameter for water addition and a steam generator to the dryer purge-gas line and by modifying the dryer basket to ensure passage of the steam through the bed of spheres.

The detailed flowsheets and operational procedures (runsheets) were revised to reflect these modifications, and a simplified "operational flow-sheet" was prepared.

7.3 Sustained Operation with ThO_2 Sol

The program did not call for a ^{239}Pu checkout of either the sol-preparation or microsphere-forming equipment; however, it was convenient for the latter equipment to be thoroughly checked by operation with ThO_2 sol. Personnel from both sites cooperated in this effort, and the technology of microsphere forming by sol-gel methods was transferred from ORNL to Mound personnel. Runsheets and procedures were tested for validity. After Mound had installed the new and modified components supplied by ORNL (see Sect. 7.2.2), a series of five runs was made by ORNL personnel to check the capability of the system for sustained operations. In each run, a 1.5 M ThO_2 sol was pumped into the microsphere-forming column at the rate of approximately 2 ml/min until 136.6 g of ThO_2 had been fed to the system. After 3 to 4 hr of continuous column operation, the gel microspheres were batch-transferred into the dryer, where they were contacted with superheated steam (>4 g of H_2O per gram of ThO_2) at temperatures increasing to 200°C . They were then transferred into the furnace, heated to 1200°C (in an 8-hr program), and held at that temperature for 3 hr.

The results of these five runs are summarized in Table 3. From 80.4 to 128.5 g of product was obtained in each run. Of the total product, greater than 94% passed the test for roundness. Approximately 88% of the product from the first four runs was in the 74- to 250- μ -diam range; a total of less than 1 g was smaller than 74 μ . A small quantity of thoria (<10 g per run) was recovered from the solvent overflow piping near the top of the column; 13 g was recovered after the fifth run, but this included the total accumulation in the column "gutter." In a partial

Table 3. Product Characterization and Material Balances for
ThO₂ Runs at Mound Laboratory

	Run No.					Partial Cleanout
	TX-13	TX-14	TX-15	TX-16	TX-17	
Input						
ThO ₂ as sol, g	136.6	136.6	136.6	136.6	136.6	0
Product						
Dense ThO ₂ , g	100.1	128.5	82.4	96.2	80.4	0
Round, %	97.8	99.6	89.0	94.6	86.1	
Size range, %						
>250 μ	2.5	9.2	22.5	18.1	Not separated	
177-250 μ	32.3	82.7	25.6	24.1		
125-177 μ	59.2	6.5	37.9	37.4		
74-125 μ	6.0	1.6	14.3	20.4		
Other ThO ₂ recovered, g	8.4	0	6.3	6.3	13.3	110.3
ThO ₂ not recovered, g	28.1	8.1	47.9	34.1	42.9	-110.3
Cumulative unrecovered, g	28.1	36.2	84.1	118.2	161.1	50.8

cleanout of the equipment after five runs, 110 g of ThO₂ was recovered from the new filter in the organic overflow line. Only 51 g of ThO₂, or 7.4% of the input, remained unaccounted for.

The thoria recovered after the runs consisted of fine particles that had been swept out of the top of the column. The results of run TX-14 suggested a possible solution to this problem. In this run, larger particles were produced, and 94% of the input was recovered as product. Unfortunately, the sol disperser (two-fluid nozzle) was inadvertently altered early in run TX-15, and all succeeding products were substandard.

The problem of fines entrainment was solved by expanding the disengaging section at the top of the forming column. The bottom and fluidizing sections were left unaltered; however, with an increase of less than 4 in. in overall height, we were able to more than double the cross-sectional area at the point of solvent overflow and to almost triple the distance from the top of the fluidizing section to this point. Two columns of this type and improved two-fluid nozzles were supplied to Mound by ORNL.

All of the equipment will be cleaned thoroughly prior to operation with $^{238}\text{PuO}_2$; this will prevent ThO_2 contamination of the product and, hopefully, will reveal the location of the unaccounted for ThO_2 .

8. CONCLUSIONS AND RECOMMENDATIONS

Based on a preliminary evaluation of laboratory-produced $^{238}\text{PuO}_2$ microspheres, we believe that sol-gel is an advanced method, with meaningful process advantages, for producing a superior product with significantly lower neutron emission rates. If a more thorough evaluation of representative product should reveal some deficiency in this material, the sol-gel process could still be used to provide an extremely uniform feed material retaining many of its primary advantages. We believe that equipment supplied to Mound by ORNL is of sound design and construction and capable of producing dense $^{238}\text{PuO}_2$ microspheres by the modified chemical flowsheet. Since the ORNL system has not yet been placed in service, further elaboration would be mere conjecture. However, a great deal of work was done both at ORNL and Mound toward the development of a flowsheet for the large-scale (150 to 200 g) preparation of plutonia sol. A summary of our interpretation of this effort is presented in the following paragraphs.

Experience that has been accumulated from various investigations of the plutonia sol-gel process over a period of several years strongly suggests a relatively simple model for the representation of plutonia behavior during sol preparation. This model requires the formation of highly crystalline plutonia polymer during the precipitation and digestion steps, and retention of this form throughout subsequent processing. Collective experience to date indicates that adherence to the concepts implied by this model is required for optimum sol preparation, regardless of the isotopic composition of the plutonium. Retention of the polymeric form during evaporation of the high-nitrate sol to dryness is essential. Depolymerization during evaporation is analogous to simple dissolution; therefore, the rate should be a function of time, temperature, and acid concentration. In the case of ^{238}Pu , this rate is further increased by the radiolytic and thermal properties of the isotope. The final effects of depolymerization are rapid, erratic nitrate loss and irreversible crystallite aggregation, resulting in low yields and unstable sols.

Electron microscopy, electron diffraction, and micropore filtration experiments have demonstrated that crystalline plutonia polymer consists of extremely small (5- to 20-Å) crystallites having lattice constants identical to those of PuO_2 . Those primary crystallites do not irreversibly associate to a significant extent at any stage in the sol-gel process. During the thermal denitration step, crystallite growth occurs. Processing runs made under optimum conditions have been found to provide crystallites that are about 80 Å in diameter and are essentially unassociated or aggregated.

Strict adherence to flowsheet specifications during precipitation, washing, and aging is required to obtain crystalline polymer. A pure Pu^{4+} feed solution with a low free-acid concentration (1 to 2 M) is required for the production of crystalline polymer. Since $^{238}\text{Pu}(\text{NO}_3)_4$ can hydrolyze under these conditions, the preparation of the feed must be closely controlled. Each feed should be sampled at the time of precipitation to verify the absence of Pu^{6+} and hydrolysis products and to ensure a low free-acid concentration. Particular attention should be given to ensure essentially complete removal of NH_4NO_3 after precipitation. Since the effect of incomplete washing is not clearly defined, we recommend that either the washed precipitate or the peptized high-nitrate sol be analyzed for both NH_4^+ and NO_3^- . We recommend that micro-Kjeldahl be utilized as the major method for analyzing for nitrate. It can also be used to analyze for NH_4^+ , which we believe is essential.

The aged precipitate should be dispersed using the smallest amount of HNO_3 that is consistent with a reasonable processing time. With 150-g batches of ^{239}Pu , NO_3^-/Pu mole ratios of 1.1 and plutonium concentrations of 0.4 M have produced improved sols. The obtaining of electron diffraction patterns of the high-nitrate sol to determine crystalline characteristics should be continued as a standard quality control procedure to aid in interpreting run results and in isolating trouble areas. After HNO_3 is added to peptize the aged precipitate, every effort should be made to minimize degradation of the polymer by limiting its exposure to HNO_3 , especially at elevated temperatures. The high-nitrate sol should be evaporated at a reduced pressure to give a boiling temperature of about 80°C. The total cycle time from peptization through thermal denitration should be minimized.

The thermal denitration of $^{238}\text{PuO}_2$ sol does not appear to be a particularly troublesome operation; however, evaluation is difficult because sol behavior during denitration is a strong function of the condition of the high-nitrate sol to be denitrated. High-nitrate sols with consistent characteristics would be required to thoroughly evaluate possible difficulties in this area. At present, we do not believe that allowing the dried sol to stand overnight prior to denitration should be considered a safe practice until we have demonstrated that such a procedure does not introduce a significant variable. The temperature presently being used for baking (230°C) appears to be sound; however, lower temperatures could be tried. Thermal denitration should be achieved at the lowest temperature that is consistent with reasonable processing times. Also, the composition of the gas phase in contact with the solid material should be considered an important variable. The presence of ionic material during thermal denitration can lead to high losses; it also probably adversely affects microsphere formation. Although we do not know how much ionic material can be tolerated, 10% has been demonstrated to result in a very poor-quality sol. Continued experiments to relate the concentrations of ionic material to sol quality should be very helpful.

Microsphere formation is a strong function of the feed sol; this step should become less troublesome as the quality of the sol is improved. Attention to small details, which may not appear to be significant, is very important in this operation. We have no knowledge at present concerning microsphere-forming behavior as a function of storage time of the final sol. Data for sols of various ages would allow us to correlate microsphere formation with age, spectral data, nitrate analysis, and electron microscopic examination. It is known that the water and surfactant contents and the apparent pH of the drying solvent are very important variables; thus the continuous monitoring of these variables would be very helpful in assessing the conditions in the forming column at any given time.

9. ACKNOWLEDGMENTS

This report describes the work of many people at ORNL and mentions the efforts of many at Mound Laboratory. Although it was not our purpose to document the work of Mound personnel, reference to some of their

investigations and findings was necessary in order to clearly delineate the ORNL role in this joint undertaking.

Grateful acknowledgment is made of the contributions of the following individuals at ORNL: F. E. Harrington, who designed the vessels and layouts for both cell 4 and the Mound box; A. J. Farmer, draftsman; C. G. Shorter and J. A. Yount, both of Plant and Equipment Division, who installed the vessels and piping in both installations (under the supervision of R. P. Beard, Plant and Equipment Division, by direction of W. R. Whitson); R. E. Toucey, Instrumentation and Controls Division, who designed the instrumentation for both installations; and C. V. Williams, Instrumentation and Controls Division, and R. J. Shannon, who checked out the instrumentation of the ORNL system at Mound; C. W. Martin, who helped in checking out the operation of the entire ORNL system at Mound; J. R. Parrott, R. W. Horton, and F. R. Chattin, who supervised the operation of the ORNL pilot plant by R. J. Shannon, C. W. Martin, and D. R. Taylor; S. A. McCosh and O. K. Tallent, who performed many of the laboratory sol-preparation experiments; J. W. Cooper, Analytical Chemistry Division, who supervised the analytical group; and D. A. Costanzo, also of the Analytical Chemistry Division.

At Mound, the effort was coordinated, from its inception, by R. E. Vallee. Laboratory sol preparations were made by W. H. Smith, D. L. Plymale, B. R. Kokenge, R. F. Heidelberg, and technician R. L. Deaton. Engineering-scale preparations were by E. Byrge, A. B. Combs, and T. C. Elswick under the direction of D. R. Rogers. S. M. Freeman assisted in the design of the enclosure for the ORNL system, which was installed under the direction of J. V. Insley, Jr., and D. L. Balsmeyer. J. J. Goldin and Calvin Kidd, Jr., checked out the box equipment, helped with modifications, and carried out developmental work related to the forming of microspheres. The analytical group was headed by W. R. Amos. J. S. Griffo (Space Nuclear Systems), E. A. Walker, Don Ofte, and L. R. Willett were the USAEC representatives who coordinated the work.

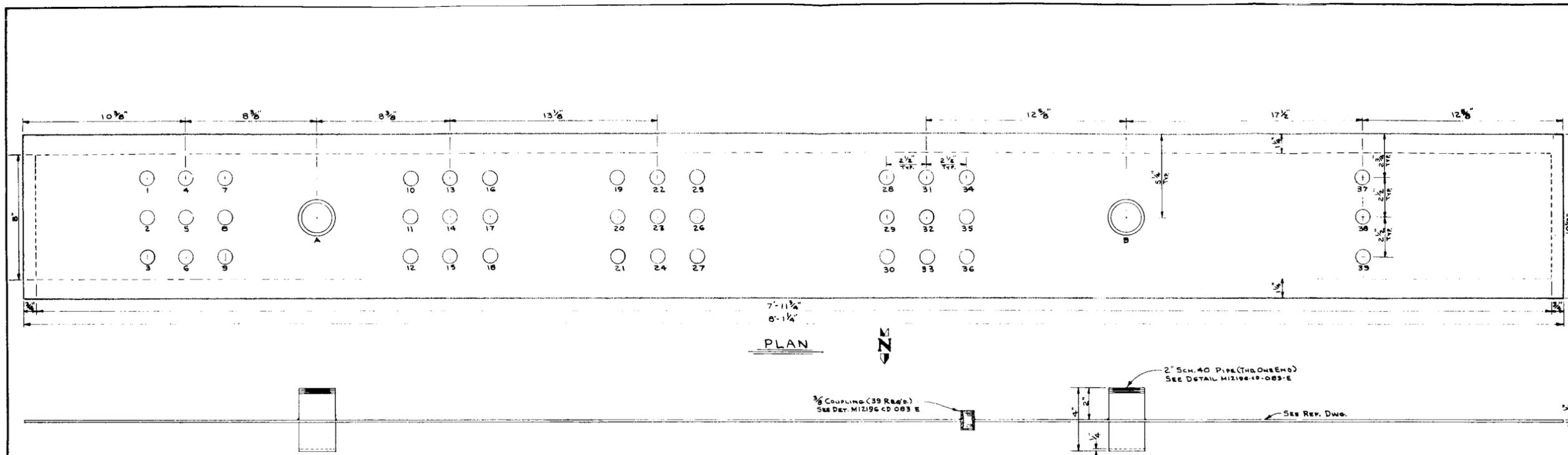
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1

11. APPENDIX





HOLE No.	TYPE FITTING	LINE No.	SERVICE	HOLE No.	TYPE FITTING	LINE No.	SERVICE
1	Gyrolok CMT	T6103-38T	Pu Nitrate Addition, TCI	32	Gyrolok CMT		
2		T6104-38T	S. A. Gas Purge, T61	33		T7501-38T	Outlet To Incinerator
3		T6162-38T	GR. Lo T61	34		T7561-38T	LL Lo T-75
4		T6360-38T	LL HI T-63A	35		T7504-38T	SA. T75, T78 P-71
5		T6760-38T	LL HI T-67A	36		T7804-38T	Purge Gas From F-82
6		T6161-38T	LL Lo T-61	37		T7860-38T	LL HI T-78
7		T6361-38T	LL Lo T-63A	38		T7861-38T	LL Lo T-78
8		T6462-38T	GR. R. Lo T-64				
9		T6160-38T	LL & DR HI, T61				
10		T6761-38T	LL Lo T-67A				
11		T6460-38T	LL & DR HI, T64				
12		T6404-38T	SA. T-64				
13		T6260-38T	LL HI T-62				
14							
15		T6461-38T	LL Lo T-64				
16		T7102-38T	T638, T71, T66 To Waste OR SALVAGE				
17		T6261-38T	LL Lo T-62				
18							
19							
20			SPARE				
21		T6660-38T	LL & DR HI, T66				
22		S4-38T	T638 & T678 To Waste OR SALVAGE				
23		T7161-38T	LL Lo T-71				
24		T6661-38T	LL Lo T-66				
25							
26		T6662-38T	GR. Lo T-66				
27		T7160-38T	LL HI To T71				
28		T7860-38T	LL HI T78				
29		T7802-38T	Purge To F-82				
30							
31		S7403-38T	Purge To S-74				

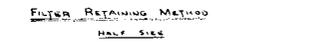
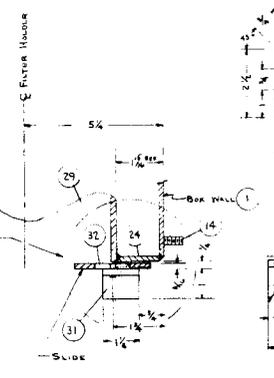
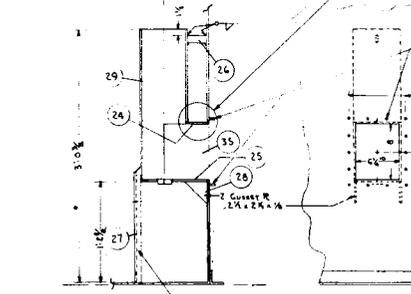
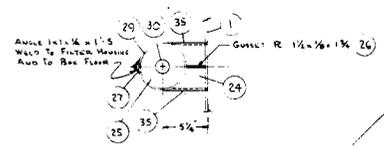
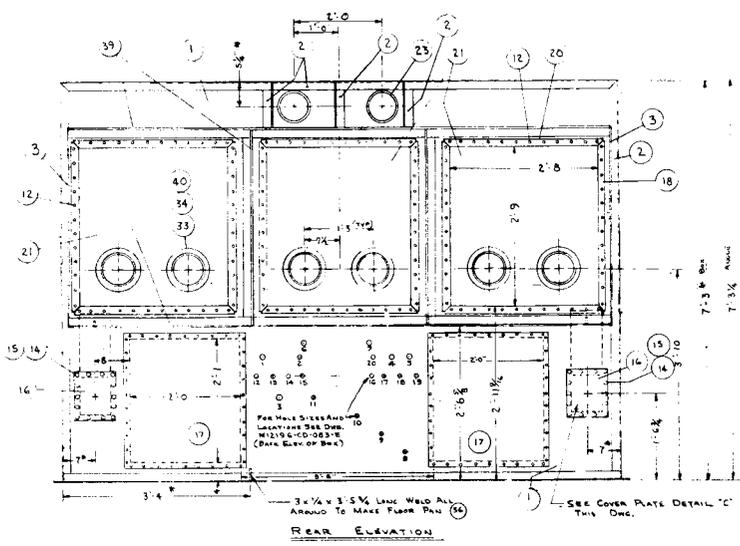
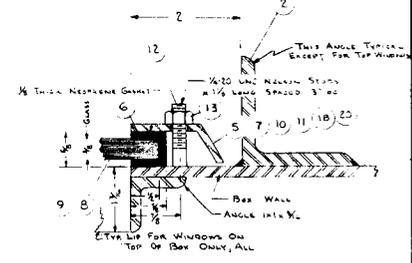
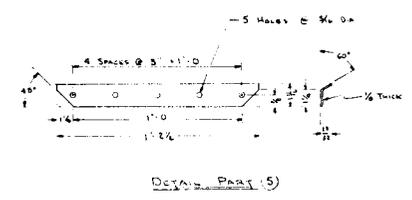
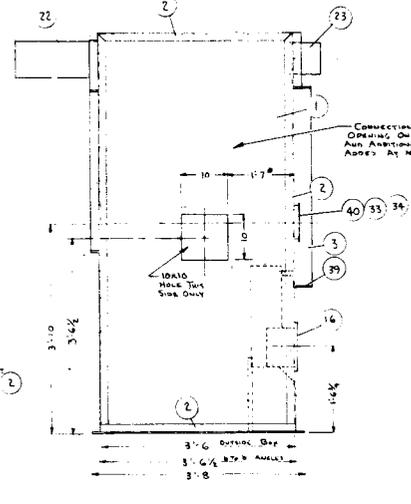
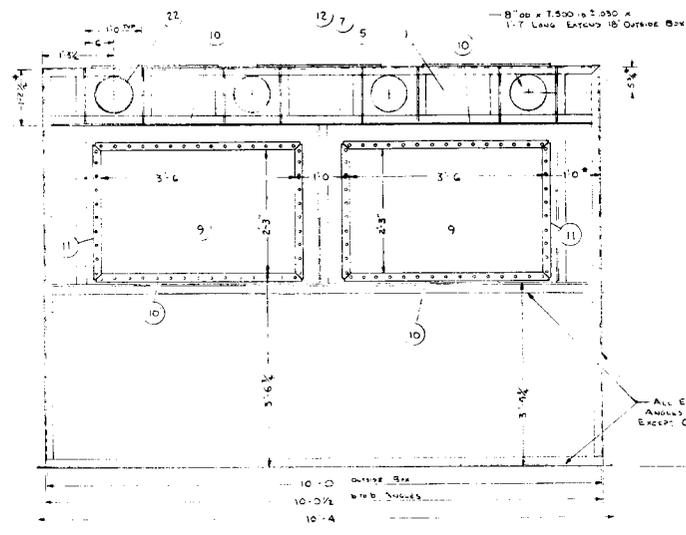
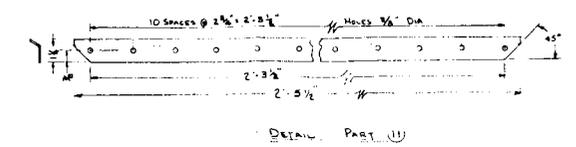
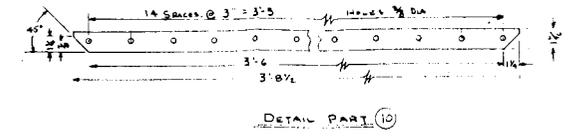
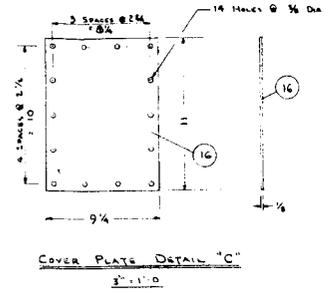
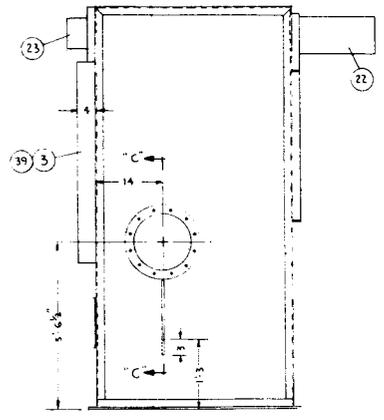
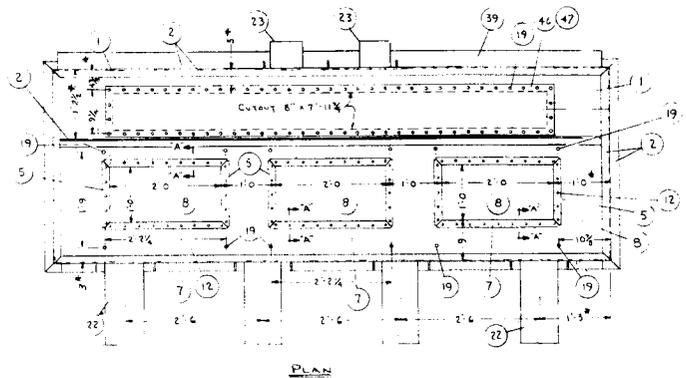
SLEEVE "A"		
HOLE No.	LINE No.	SERVICE
1	T6365-18T	Air To HCV G3A-1
2	T6168-14T	Air To HCV G14 A & B
3	T6365-18T	Air To HCV G3 B-1
4	T6665-18T	Air To HCV G6-1
5	T6166-14T	Air To HCV G1-1
6	T6766-18T	Air To HCV G7A-1
7	H6165-18T	Air To HCV G1-2
8	T6266-14T	Air To HCV G2-2 A & B
9	H6466-18T	Air To HCV G4-2
10	H6167-18T	Air To HCV G1-3
11	T6468-14T	Air To HCV G4 A & B
12	T6765-18T	Air To HCV G7B-1
13	H6667-18T	Air To HCV G6-3
14	H6467-18T	Air To HCV G4-3
15	T6366-18T	Air To HCV G3B-2
16	T6465-18T	Air To HCV G4-1
17	T6265-18T	Air To HCV G2-1
18	H6466-18T	Air To HCV G6-2
19	T6766-18T	Air To HCV G7B-2
20	T6366-18T	Air To HCV G3A-2

SLEEVE "B"		
HOLE No.	LINE No.	SERVICE
1	T6465-18T	Air To HCV 84-1
2	T7565-18T	Air To HCV 75-1
3	S7465-18T	Air To HCV 74-1
4	T7868-18T	Air To HCV 78-1
5	T7865-18T	Air To HCV 78-2
6	T6669-18T	Air To HCV G6-5
7	F8265-14T	Air To HCV 82-2
8	F8267-18T	Air To HCV 82-1
9	S7266-18T	Air To HCV 72-1
10	T6668-14T	Air To HCV G6-4A & B
11	T7365-18T	Air To HCV 73-1
12	T8365-18T	Air To HCV 83-1
13	T8366-18T	Air To HCV 83-2
14	PT167-18T	Air To HCV 71-1
15	PT165-18T	Air To HCV 71-2
16	PT167-18T	Air To HCV 71-3
17	SPARE-14T	
18	S7465-18T	Air To HCV 74-2
19	F8266-18T	Air To HCV 82-3
20	SPARE-14T	
21	TT169-18T	Air To HCV 71-4

NO.	REVISIONS	DATE	APPD	APPD
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2	AS BUILT		R.B.W.	1/29/67
1	GEN. REV.		A.J.V.	9-6-67

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 FRACTIONS ± _____
 DECIMALS ± _____
 ANGLES ± _____
 SCALE: 4" = 1'-0"

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MOUND BOX SHEET #2	M 12196	CD	OBO	E
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