1/22/68

222

OAK RIDGE NATIONAL LABORATORY
operated by
UNION CARBIDE CORPORATION
NUCLEAR DIVISION
for the
U.S. ATOMIC ENERGY COMMISSION

UNION
CARBIDE

ORNL- TM- 1978

Conf- 671008--4

ENGINEERING DEVELOPMENT OF SOL-GEL PROCESSES
AT THE OAK RIDGE NATIONAL LABORATORY

P. A. Haas
C. C. Haws, Jr.
F. G. Kitts
A. D. Ryon

DISCLAIMER

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Contract No. W-7405-eng-26

CHEMICAL TECHNOLOGY DIVISION

ENGINEERING DEVELOPMENT OF SOL-GEL PROCESSES
AT THE OAK RIDGE NATIONAL LABORATORY[*]

P. A. Haas, C. C. Haws, Jr., F. G. Kitts, and A. D. Ryon

For presentation at the CNEN symposium on "Sol-Gel Processes for
the Production of Ceramic Nuclear Fuels," Turin, Italy, October 2-3, 1967.

JANUARY 1968

OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee
Operated by
UNION CARBIDE CORPORATION
for the
U. S. ATOMIC ENERGY COMMISSION

THIS PAGE

WAS INTENTIONALLY

LEFT BLANK

CONTENTS

ENGINEERING DEVELOPMENT OF SOL-GEL PROCESSES
AT THE OAK RIDGE NATIONAL LABORATORY

P. A. Haas, C. C. Haws, Jr., F. G. Kitts, and A. D. Ryon

ABSTRACT

The development and application of equipment for sol-gel processes at the Oak Ridge National Laboratory are described. This report, along with associated reports on the development of chemical flowsheets,[1] on the irradiation and evaluation of products,[2] and on fabrication costs,[3] comprise a review of sol-gel studies at ORNL. Aqueous sols of thoria, urania, plutonia, or their mixtures were prepared by hydrothermal denitration, in precipitation-washing equipment, or in continuous solvent extraction apparatus. Sol drops were converted to gel spheres by extraction of water, or gel fragments were formed by evaporation of water. The gel particles were fired to give products of the desired densities and compositions.

SUMMARY

Thoria sols are prepared by steam denitration in a rotating stainless steel drum that is heated to 500°C. Fluidized beds appear promising for large-scale operation. An alternative preparation of ThO_2-UO_3 sols by solvent extraction, at rates up to 1 kg of oxide per hour, was demonstrated in continuous-flow equipment. In this method, an aqueous solution of thorium and uranyl nitrates is contacted with an organic phase consisting of a long-chain secondary amine (Amberlite LA-2) dissolved in a paraffin-type diluent. Denitration is accomplished by cocurrent flow through three mixer-settler stages; about 30% excess amine is used for the nitrate extraction. The aqueous phase leaving the first stage is digested at 100°C for 10 min. This forms the sol and releases more nitrate, which is extracted in the subsequent stages to produce a NO_3^-/metal ratio of about 0.1. The amine is regenerated with Na_2CO_3 in a mixer-settler and thus can be recycled.

Controlled mixing in all stages produces water-in-oil type dispersions that serve to prevent emulsions. Typical batches of sol were concentrated to 1.5 $\underline{M}$ by evaporation in a forced-circulation vertical-tube evaporator.

The production of pure urania sols requires U(IV) solutions as the starting materials. We produced U(IV) by catalytic aqueous-phase reduction of $UO_2(NO_3)_2$ with hydrogen at 300 psi. UO_2 sols were prepared by using several precipitation-washing-peptization flowsheets. Most of the UO_2 sols were prepared by a batch method that yielded up to 2 kg/batch. Continuous-method equipment that was designed to produce 3 kg of uranium per day was also operated.

Plutonia sols were prepared from $Pu(NO_3)_4$ solution by a batch precipitation-peptization method.

These sols were dispersed in 2-ethyl-1-hexanol (2EH) and then converted to gel spheres by extraction of water. To keep the sol drops and gel spheres fluidized without coalescence, clustering, or deposition on the vessel walls, surfactants were added to the 2EH. Operation was satisfactory over six-month periods for ThO_2 sols when 0.2 vol % Ethomeen S/15 and 0.05 vol % Span 80 were added to the initial 2EH charge, and 10 ml of Ethomeen S/15 and 2.5 ml of Span 80 per liter of 2.5 $\underline{M}$ thoria sol feed were added daily to the 2EH. Formation of the PuO_2 and PuO_2-ThO_2 microspheres required 0.5 vol % Ethomeen S/15 plus a small amount of Span 80 in the 2EH. The UO_2 and UO_2-PuO_2 microspheres required larger amounts of surfactants; 0.5 to 1.5 vol % Span 80 and 0.2 to 0.5 vol % Ethomeen S/15 were commonly used. The formation of microspheres from ThO_2-UO_3 sols that had been prepared by solvent extraction required the use of low surfactant concentrations to prevent cracking or distortions of shape; about 0.10 vol % Span 80 and 0.05 vol % Ethomeen S/15 were commonly used.

The gel spheres were first dried in argon or nitrogen containing admixtures of superheated steam; the presence of steam in the atmosphere during drying was found to promote removal of 2EH from the gel and to

reduce the amount of cracking. The temperature and the atmosphere were controlled while the gel was heated to the sintering temperature and then cooled to room temperature. Microspheres of thoria or plutonia, or of their mixtures, were fired in air. Mixtures containing up to 25% urania were fired in air and then exposed to hydrogen or argon-hydrogen at 1150° to ensure reduction to UO_2. We successfully prepared microspheres of ThO_2, UO_2, and PuO_2 (and of their binary mixtures) that had diameters of 1 to 700 μ, densities of 90 to 100% of theoretical, and relatively high resistances to crushing. The sol preparation and sphere forming equipment presently in operation has daily production capacities of greater than 10, 1, and 0.1 kg of ThO_2, UO_2, and PuO_2, respectively.

1. INTRODUCTION

This paper describes the engineering studies in which equipment was developed for sol-gel fuel preparation processes and was applied to the production of sol-gel products for use in fuel-cycle experiments. The studies of sol-gel chemistry and the development of chemical flowsheets are discussed by McBride[1]. Irradiation tests of these products are described by Olsen et al.[2]; Washburn et al.[3] report comparative fabrication costs. The engineering studies have been primarily concerned with the preparation of thoria, urania, and plutonia (and their binary mixtures), although many other oxide sols were also prepared in laboratory studies.[1] A primary current objective is to develop procedures and equipment of a type useful for remotely operated fuel preparation in the Thorium-Uranium Recycle Facility (TURF). Results are presented for the three operations common to our sol-gel processes: (1) preparation of an aqueous sol, (2) removal of water to give gel particles, and (3) firing at controlled conditions to remove volatiles, to sinter to a high density, and to effect any necessary reduction or chemical conversion.

Our first sol-gel flowsheet was developed for the preparation of dense fragments of thoria-urania for use as vibratorily compacted fuel.[4],[5] The thoria-urania sol was converted to gel by evaporation at 80 to 85°C in flat trays with forced circulation of air. The 2 $\underline{M}$ (Th + U) sol was loaded to 0.75-in. depths and gave gel fragments of 0.5 in. maximum dimensions. Evaporation produces an increasing concentration of the sol until gelation occurs. If the sol is not stable throughout this concentration range, precipitation or segregation of constituents can occur. If the sol is stable, evaporation is a very simple gelation procedure. However, since small spherical particles of high density oxide or carbide are the preferred fuel materials for many reactor designs, the processes of greatest current interest are those for producing small spherical particles (microspheres). The preparation of microspheres requires a special gelation procedure in which the water is extracted into an organic liquid.

2. SOL PREPARATION

Sol preparation procedures were developed for most of the metal oxides that are of interest for use as irradiation specimens or fuel elements. One objective was to obtain the same advantages of process simplicity and potential economy for these metal oxides as are obtained in the thoria sol-gel process; another was to demonstrate our ability to produce mixed-oxide products by starting with either mixed-oxide sols or pure sols.

The feed materials for our sol preparation procedures were nitrate salts or solutions. (The products of reactor fuel processing by solvent extraction are usually nitrate solutions, and any residual nitrate remaining in the sol or gel can be volatilized during calcination.) Conversion of the nitrate salt into an oxide sol requires the following four steps, which can be combined or accomplished in any suitable order:

1. Reducing or oxidizing to the optimum valence; U(IV) and Pu(IV) are preferred for urania or plutonia sols.

2. Converting the metal nitrate into a hydrated (or hydrous) oxide.

3. Removing excess nitrate and nonvolatile impurities. For example, NH_4NO_3 or $NaNO_3$ must be removed if the hydrous oxides are precipitated by NH_4OH or $NaOH$.

4. Dispersing the oxide as a stable aqueous sol.

The procedure for preparing thoria sols[1,5,6] is unique in that the colloidal particles are formed by steam denitration at a temperature approaching 500°C. For sols other than thoria, the colloidal state is formed in solutions or wet precipitates. Thoria-urania sols with U/Th ratios of less than 0.1 may be prepared by adding UO_3 or uranyl nitrate to thoria sols. The U(VI) is adsorbed on the surface of the thoria particles. Pure sols may be mixed to prepare materials having other compositions.

ThO_2 Sol Preparation

The preparation of dispersible ThO_2 by steam denitration of thorium nitrate was selected over other possible methods of preparation (such as hydroxide precipitation from thorium nitrate solutions, calcination of thorium oxalate, or thermal decomposition of thorium nitrate in air) because of its simplicity, ease of operation, and good quality control. Denitration is easily accomplished by superheated steam in a rotary calciner surrounded by a furnace. The rotary calciner gives good contact with the steam and eliminates local overheating effects. The off-gas condenses to give a dilute HNO_3 solution, and the ThO_2 product is a coarse, free-flowing powder. A 14 in. ID rotary denitrator has been used[6] to produce several hundred 14.5-kg batches of dispersible ThO_2. In the Kilorod program,[5] a 6-hr run time gave a ThO_2 product having a NO_3^-/Th mole ratio of about 0.03. Complete dispersion of the ThO_2 is obtained by adding 0.077 mole of nitrate per mole of ThO_2 (as either HNO_3 or $UO_2(NO_3)_2$) and heating, with agitation,

to 80 to 85°C for 0.5 hr. After prolonged standing, 0.5 to 1% of the ThO_2 will settle out as an undispersed "heel." Uranium/thorium atom ratios as high as 0.1 are obtained by absorbing U(VI), which is added as $UO_2(NO_3)_2$ or UO_3.

A 10-in.-diam fluidized-bed denitrator has been operated to produce dispersible ThO_2 at the rate of 100 lb/hr.[7] This product was dispersed by agitation with hot water and was excellent for the preparation of high-density ThO_2 fragments. The product from the fluidized-bed denitrator had a higher NO_3^-/U mole ratio than the optimum (0.11) for sol from rotary denitrator produced ThO_2. The sol made from a sample of fluidized-bed product was not suitable for the preparation of ThO_2 microspheres; the gel spheres cracked into fragments, as often occurs with high-nitrate sols. Higher temperatures and/or longer residence times in the fluidized bed would probably give a product having a lower NO_3^-/Th mole ratio and thus more suitable for the preparation of microspheres. The fluidized-bed denitration[7] could easily be operated on a large scale; the 10-in.-diam or 100-lb/hr unit was a pilot plant for a much larger denitrator that has since been built and operated successfully with uranyl nitrate.

The hydrothermal denitration is the preferred preparation process for ThO_2 sols because of the simple equipment flowsheet and the excellent properties of the sols. Thoria sols are easy to prepare and many other methods may be used. Much of our early sol-gel work was done with thoria sols that had been prepared by thermal decomposition of thorium oxalate at 650°C and dispersion of the ThO_2 with nitric acid.[4] The cost of oxalic acid and the necessity for careful precipitation and washing are significant disadvantages. Pure ThO_2 sols prepared by precipitation processes have cracked into small fragments during gelation and have, therefore, not been suitable for preparation of microspheres. Usable ThO_2-UO_3 and ThO_2-UO_2 sols have been prepared by precipitation-peptization processes.[8] Sols for preparing particles with controlled porosity were made by mixing $Th(NO_3)_4$ or UCl_4 solutions with $(NH_4)_2MoO_4$ solutions.[9]

ThO$_2$-UO$_3$ Sol Preparation

The most promising method of preparing mixed sols of ThO$_2$ and UO$_3$ is by solvent extraction (Fig. 1).[1] An aqueous solution of thorium and uranyl nitrates is denitrated by three stages of extraction with a long-chain amine (Amberlite LA-2) dissolved in a $\underline{n}$-paraffin. After the first stage the NO$_3^-$/metal mole ratio is about 1.0 in the aqueous phase. Digestion for 10 min at 100°C results in the formation of a sol and releases additional nitrate, which is extracted in the subsequent stages. The final NO$_3^-$/metal mole ratio is about 0.1. A small amount of uranium that is extracted in the first stage is removed from the solvent in a second cocurrent stage. The low nitrate concentration of the sol in stage 2 promotes uranium stripping. The third stage is countercurrent with respect to the first and second stages. The large excess of amine in the third stage gives a sol product having a lower nitrate concentration. Vigorous mixing can be used in the third stage since the solvent flows through the second stage before it is regenerated. The nitrate-loaded solvent leaving the second stage is scrubbed with water to remove entrained sol. The scrubbed solvent is then regenerated to free amine with sodium carbonate. None of the flow ratios are critical provided that an excess of both amine (30 to 50% excess was used) and Na$_2$CO$_3$ is used.

Mixer-settlers were used as the contacting devices (Fig. 2). They are constructed of 3-in.-diam glass pipe and are geometrically safe for enriched uranium. Each mixer is divided into six compartments, with an agitator in each compartment. This minimizes bypassing and ensures efficient mixing. The solvent and the aqueous phases enter at the top and flow cocurrently through the mixer to the settler, which is a pipe tee located at the bottom of the mixer. The interface is maintained in the tee below the mixer to ensure an organic-continuous dispersion in the mixer, which is very important for preventing emulsions. The interface position is controlled by a simple jackleg and an adjustable weir on the aqueous outlet of the settler. The

ORNL DWG 67-6947
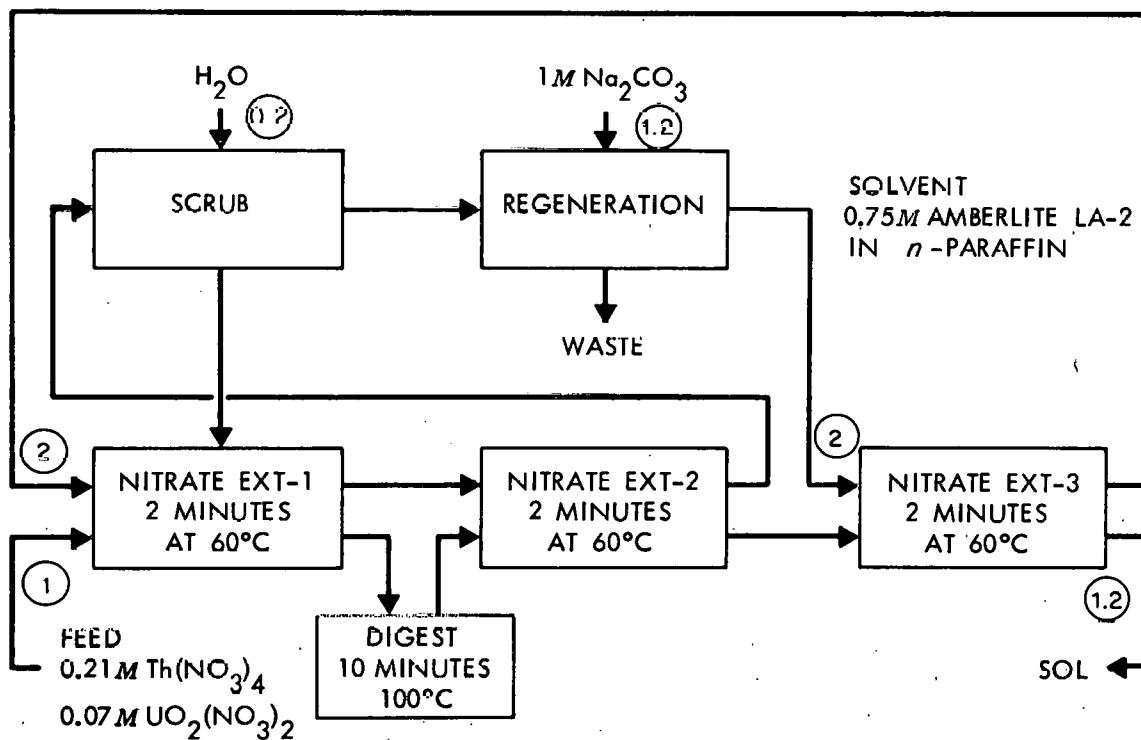
Fig. 1 Flowsheet for Preparation of Thoria-Urania Sol by Amine Extraction of Nitrate.
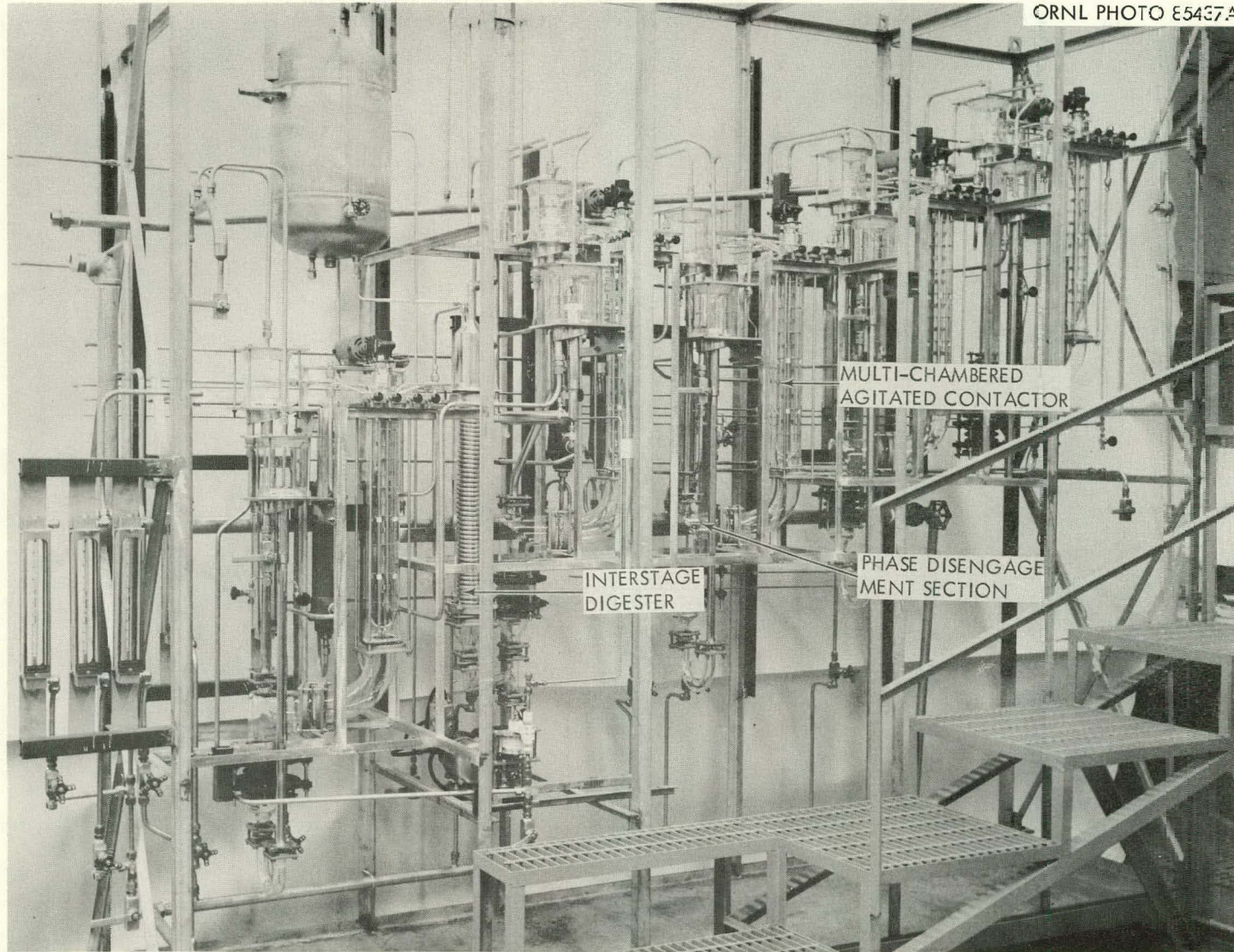
Fig. 2 Mixer-Settlers Used for Continuous Preparation of
Thoria-Urania Sol by Amine Extraction of Nitrate.

digester is merely an enlargement of the jackleg of the first-stage settler. The temperature is controlled by circulating heated water through the baffles in the mixers and through a coil in the digester.

The process was demonstrated at the design rate of 1 kg of ThO_2-UO_3 per hour. About 900 liters of 0.3 $\underline{M}$ sol was produced during the engineering study. The NO_3^-/metal mole ratio of this sol was consistently less than 0.10 (about half of that obtained in laboratory studies). The crystallite size of the sol was 42-46 A, which is slightly larger than that obtained in laboratory preparations.

The equipment has operated very smoothly. Organic-continuous dispersions were maintained without difficulty and the interface control was very stable. Some emulsions accumulated in the first stage settler during the early runs, however, coalescence occurred in subsequent stages such that the sol product contained less than 0.1 vol % solvent. During the latter runs, the scrub solution was recycled to the first stage, and virtually no emulsion was formed. Entrainment of aqueous in the solvent caused difficulties only for the solvent stream leaving the extraction section; it was directly dependent on the agitator speed in the mixer, ranging from 0.15% at 300 rpm to 0.8% at 600 rpm. Entrainment is the only significant cause of loss of Th + U, which usually amounted to about 0.1%. We believe this loss can be reduced by improved scrubbing of the solvent before regeneration. The efficiency of the mixers was 90 to 95% at agitator speeds of 300 to 500 rpm.

Several batches of sol have been concentrated to 1.5 $\underline{M}$ in a forced-circulation vertical-tube evaporator (Fig. 3). A high degree of turbulence and a large heat exchange area are used to minimize drying of the sol on the tubes. Deentrainment is accomplished by introducing the superheated sol tangentially into the body of the evaporator; additional deentrainment occurs in the stripping section, where the vapor contacts the feed in a packed tower. Very few solids have formed, and no foaming has occurred, even with operation at a vacuum of 25 in. Hg. The concentrate is fluid and stable at all Th + U concentrations up to 1.5 $\underline{M}$. Representative samples were formed into microspheres, which were dried and fired to produce dense ThO_2-UO_2.

ORNL PHOTO 87433A
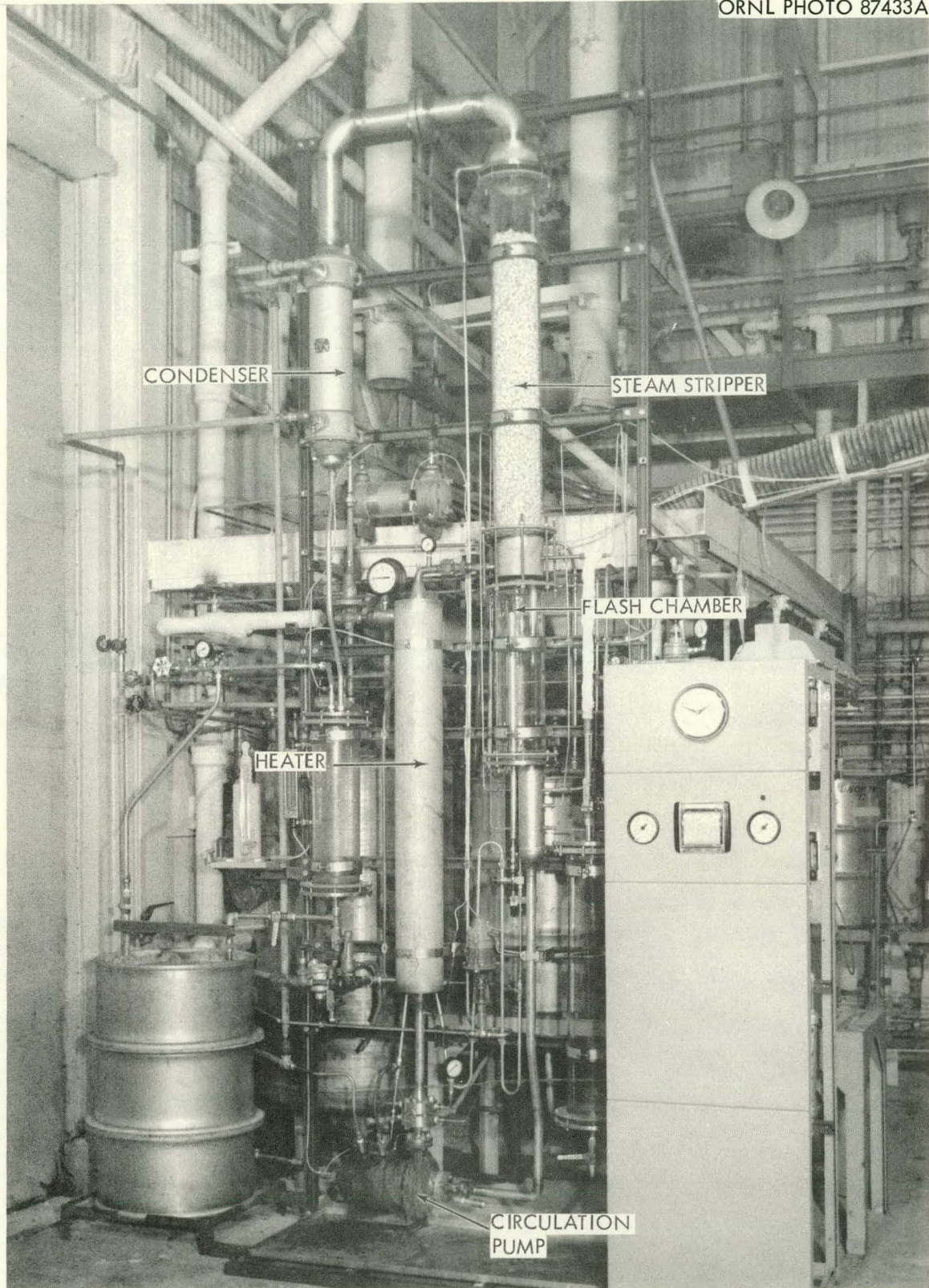
Fig. 3 Forced-Circulation Evaporator for Concentration of Sols.

Preparation of UO_2 Sols by Solvent Extraction

The equipment used in the preparation of ThO_2-UO_3 sol is also used to make UO_2 sol. The chemical flowsheet is very similar. A dilute solution of uranous nitrate (0.2 $\underline{M}$), stabilized with 0.1 $\underline{M}$ formic acid, is denitrated with 0.1 $\underline{M}$ Amberlite LA-2 in $\underline{n}$-paraffin. In the first stage the amine flow rate is controlled to reduce the NO_3^-/U ratio to about 1.0 (precipitation occurs at a ratio of less than 0.5). After the first stage, digestion for 30 min at 50°C allows the UO_2 sol to form and releases additional nitrate, which is extracted in the subsequent stages. The design capacity of the equipment is 0.2 kg of UO_2 per hour.

Several attempts to make UO_2 sol were unsuccessful because the uranous nitrate feed contained too much NH_4^+, which caused premature gelation of the sol. (The NH_4^+/U ratio should be less than 0.02 to avoid gelation.[1]) The NH_4^+ concentration depends on the method used for reducing uranyl nitrate. Satisfactory feed has been prepared in batch reduction equipment using finely divided platinum catalyst in a stirred reactor or by circulating the uranium solution through a fixed bed of catalyst pellets. In both cases, the reduction is monitored and stopped when the uranium is reduced; thus very little NH_4^+ is produced. The UO_2 sol prepared from such feed has been evaporated to a UO_2 concentration as high as 3.0 $\underline{M}$ without gelling. In this instance, the NH_4^+/U mole ratio was < 0.015; and the NO_3^-/U mole ratio was 0.10. Gelling is also caused by a low NO_3^-/U mole ratio; however, this can be prevented by adjusting the flow rate of amine or by adding nitric acid to the sol to give a NO_3^-/U mole ratio of 0.10. Satisfactory microspheres have been made from the concentrated sol without difficulty.

Preparation of UO_2 Sols by Precipitation

While several flowsheets have been developed for preparation of UO_2 sols by precipitation, each requires the same principal operations:

(1) reduction of uranyl nitrate to uranous nitrate by H_2 in the presence of a catalyst,

(2) precipitation of uranous hydroxide by ammonia,

(3) washing to remove NH_4NO_3, NH_4OH, and other solutes,

(4) dispersion with NO_3^-.

Each operation was tested in two or three different types of equipment. A number of flowsheet-equipment combinations were tested, but only those of most general interest will be described here.

The flowsheets developed in laboratory studies had three routine applications: preparation of UO_2 irradiation specimens, preparation of urania sol for development of the process for forming microspheres, and development of remotely operated equipment for the preparation of urania sols in TURF. The flowsheets for these applications differ.

The first reproducible sol-gel flowsheet for urania was applied to the preparation of microspheres for irradiation specimens. More than 10 kg of enriched urania was made into sols. Criticality control was achieved by limiting the batch size to 300 g of U. Laboratory apparatus was practical for this batch size; therefore all the enriched UO_2 presently in irradiation specimens was prepared in batch laboratory apparatus by using the flowsheet with precipitation to a pH of 7 to 7.5.

Most of the natural-urania sols were prepared in a batch apparatus (1 kg UO_2/batch) using flowsheets with precipitation to a pH of 8.1 to 9. Precipitation, washing, and dispersion were all done in a single vessel which had a 12-in.-diam porous stainless steel plate as the bottom and a slow-speed, paddle-type agitator. Supernates (present after precipitation and after each of four washing steps) were removed by filtration. Washing was achieved by agitating 10 liters of H_2O with the 5 liters of slurry or cake remaining on the filter. Peptization was accomplished by agitation and heating after the addition of HNO_3 and $HCOOH$.

The reduction of uranyl nitrate to uranous nitrate is a preliminary step that is relatively independent of the remaining precipitation-peptization flowsheet. Reduction at atmospheric pressure, using a finely divided catalyst, was used for batch preparations in laboratory

apparatus. For larger-scale operations, most of the reductions were done at 300 psig, using platinized-alumina pellets. Operation was continuous; flow of the feed was controlled by a diaphragm pump. We presently use a batch method for reduction that involves recirculation through a fixed bed of platinized alumina spheres. This system provides the control necessary to avoid reduction of NO_3^- to NH_4^+ and also gives acceptable capacities at 0 to 30 psig. Continuous operation of a once-through fixed-bed unit required a pressure of 200 to 300 psi to give satisfactory reduction rates. The batch, fixed-bed (Fig. 4) operation provides rates of 0.5 to 3 moles of U per hour per kg of catalyst (or, per liter of bed volume, since the bulk volume is ~ 1 kg/liter). We plan to use this type of system for remote operation.

Precipitation was done in vessels with simple, slow-speed paddle agitators under an Ar atmosphere. For batch operation, the NH_4OH solution was added over a period of about 0.5 hr until the desired pH was obtained. In the case of continuous operation, both NH_4OH solution and U(IV) feed solution were metered into the precipitator; the precipitate slurry overflowed into the next process vessel. Two continuous precipitators (all the U feed solution was fed to the first, and about half of the NH_4OH was fed to each) were also used. The type of precipitation equipment was a relatively unimportant variable, although it appeared to have small effects on the settling characteristics and the dispersibility of the precipitate.

Most of the NO_3^- and NH_4^+ after precipitation are easily washed out; the NO_3^- or the NH_4^+ concentrations are approximately equal in the supernate and precipitate. Small amounts of the NO_3^- at pH $\leq$ 7.5 or NH_4^+ at pH > 9.0 are absorbed and are not easily removed. Because the precipitate has a large volume (~ 0.3 $\underline{M}$ U) unless concentrated by filtration or other treatments, either multiple washes or countercurrent washing is necessary to reduce the NO_3^-/U and NH_4^+/U ratios by factors of 10^2 to 10^3 without excessive waste volumes. For the batch preparations, four or five washing steps were used, with separation of the supernate by filtration and/or decantation. Continuous washing

ORNL DWG 67-6889 R 1

OXIDATION-
REDUCTION
ELECTRODES

Ar

OFF
GAS

0-30 PSIG GAGE

PRESSURE
CONTROL
VALVE

SPRING

10 MESH SCREENS

1/4-in. GLASS RASCHIG RINGS

3-in. DIAMETER BED OF 1/8-in.
CATALYST SPHERES, 0.5 %
Pt ON ALUMINA

U
SOLUTION
TANK

GAS SPARGER (Porous S.S.)

Ar

H₂

COOLING
WATER

FLOWMETER

FLOW CONTROL
VALVE

CENTRIFUGAL
PUMP
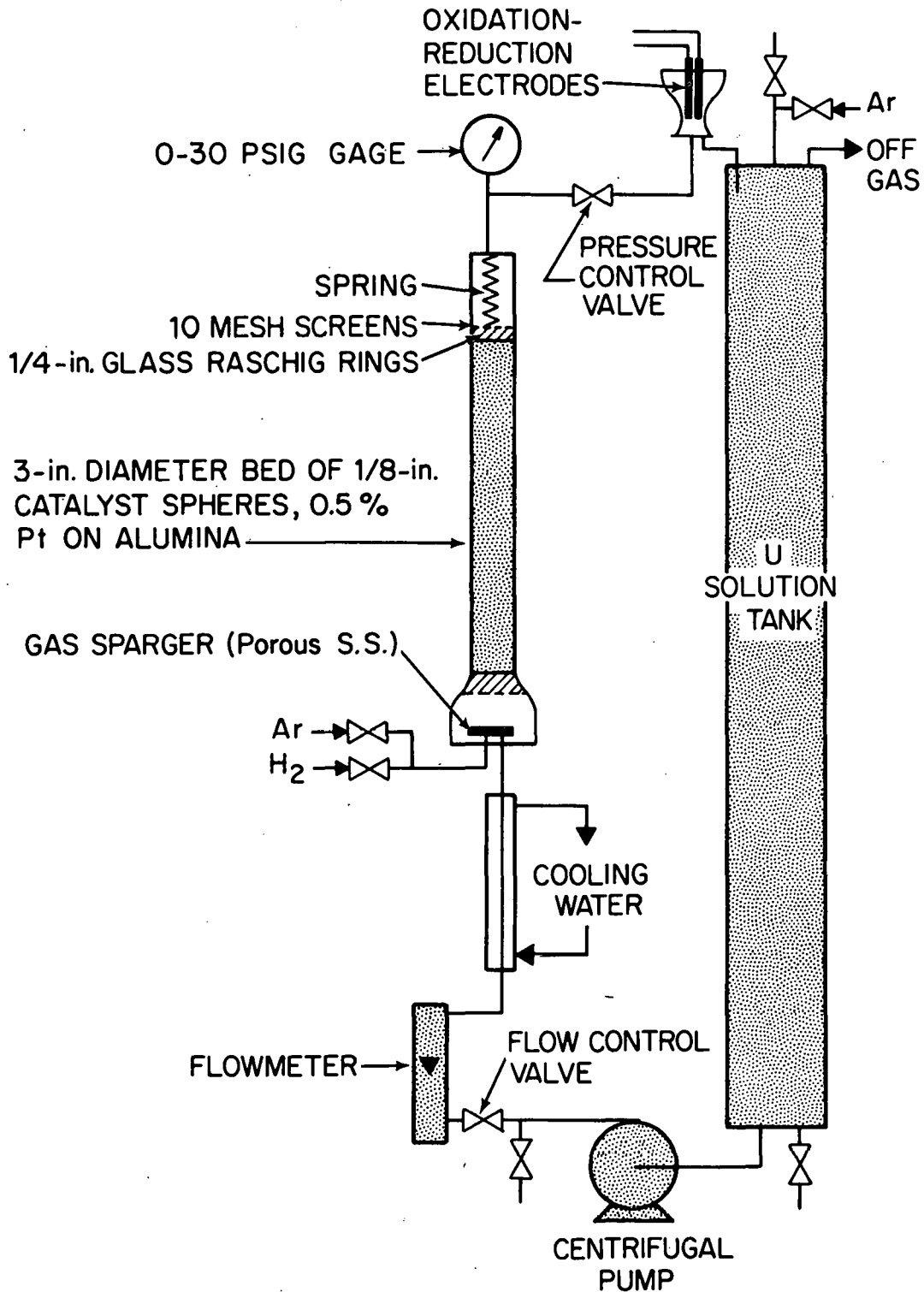
Fig. 4 Batch, Fixed-Bed Uranium Reduction Apparatus.

equipment of two types was tested.[10] One was six countercurrent mixer-decanter stages (Fig. 5). The wash water flowed by gravity while the precipitate was transferred by gas operated pumps. The second was a twelve foot high, 4 in. ID column with countercurrent flow of precipitate and wash solution. The mixer-decanter system gave stage efficiencies of 53 to 87% with the higher values when the pump flows were adjusted to minimize back mixing. The countercurrent column gave 3.3 to 5.2 transfer units or HTU values of 2.3 to 3.6 feet based on the precipitate phase. The same chemical flowsheets, the same precipitators, and the same peptizer-concentrator equipment could be used with either the wash column or the mixer-decanter washer. As compared to the mixer-decanter, the wash column had advantages of mechanical simplicity and less accumulation of solids, but disadvantages of much greater height requirements and less-positive mixing.

The washed precipitate is dispersed into a sol by agitation, heating to 60°C, and addition of HNO_3 and $HCOOH$ to give NO_3^-/U mole ratios of about 0.16 and $HCOO^-/U$ mole ratios of 0.2 to 0.4. The most difficult requirement is to concentrate from about 0.2 $\underline{M}$ U (in the washing equipment) to about 1 $\underline{M}$ U for preparation of microspheres. Excessive heating may result in precipitation or oxidation of the uranium. In batch equipment, the precipitate is vacuum filtered until the volume of cake is small enough to give the required sol concentration. In order to use continuous peptizers with the continuous washers, washed precipitate that was 0.2 to 0.3 $\underline{M}$ in uranium was fed into the peptizers, and the sol was concentrated by continuous, forced-circulation, vacuum evaporators (Fig. 5) with an inert atmosphere at 60°C.[10] The choice of equipment for the preparation of urania sol would depend on the design criteria for a particular application. Important considerations would be the production rate, criticality control criteria, head-room limitations, and the provisions for recycle between processing operations.

ORNL DWG. 67-1484
R1

0.5 M U(IV), NO$_3^-$, COOH$^-$

3.0 M NH$_4$OH
0.5 M N$_2$H$_4\cdot$H$_2$O

DECANTERS
(24" STRAIGHT SIDE)

0.01 M N$_2$H$_4\cdot$H$_2$O

pH 7.8

4"

4"

4"

4"

4"

5"

PRECIPITATORS
(4" ϕ x 12" HIGH)

WASH
SOLUTION
TO WASTE

3 M HNO$_3$

WATER

PRODUCT
(0.7 M UO$_2$ SOL)

STEAM

60°C   60°C

PEPTIZERS
(4" ϕ x 12" HIGH)

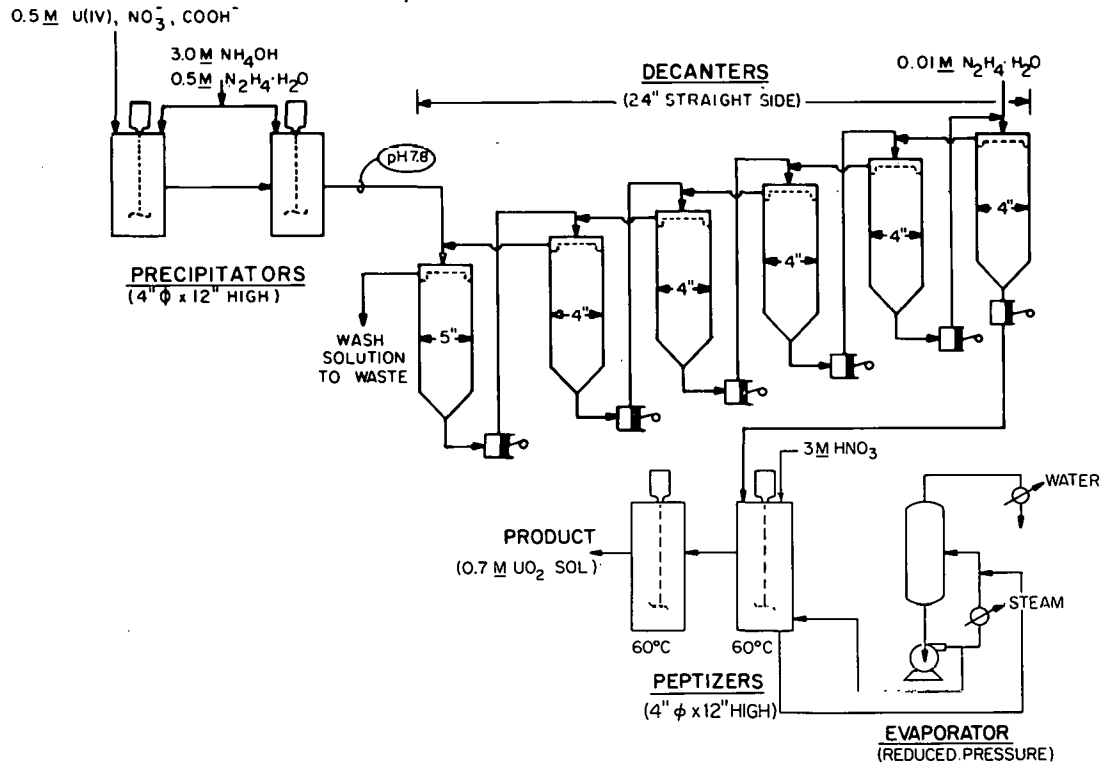EVAPORATOR
(REDUCED PRESSURE)

Fig. 5 Precipitation-Peptization-Continuous Countercurrent
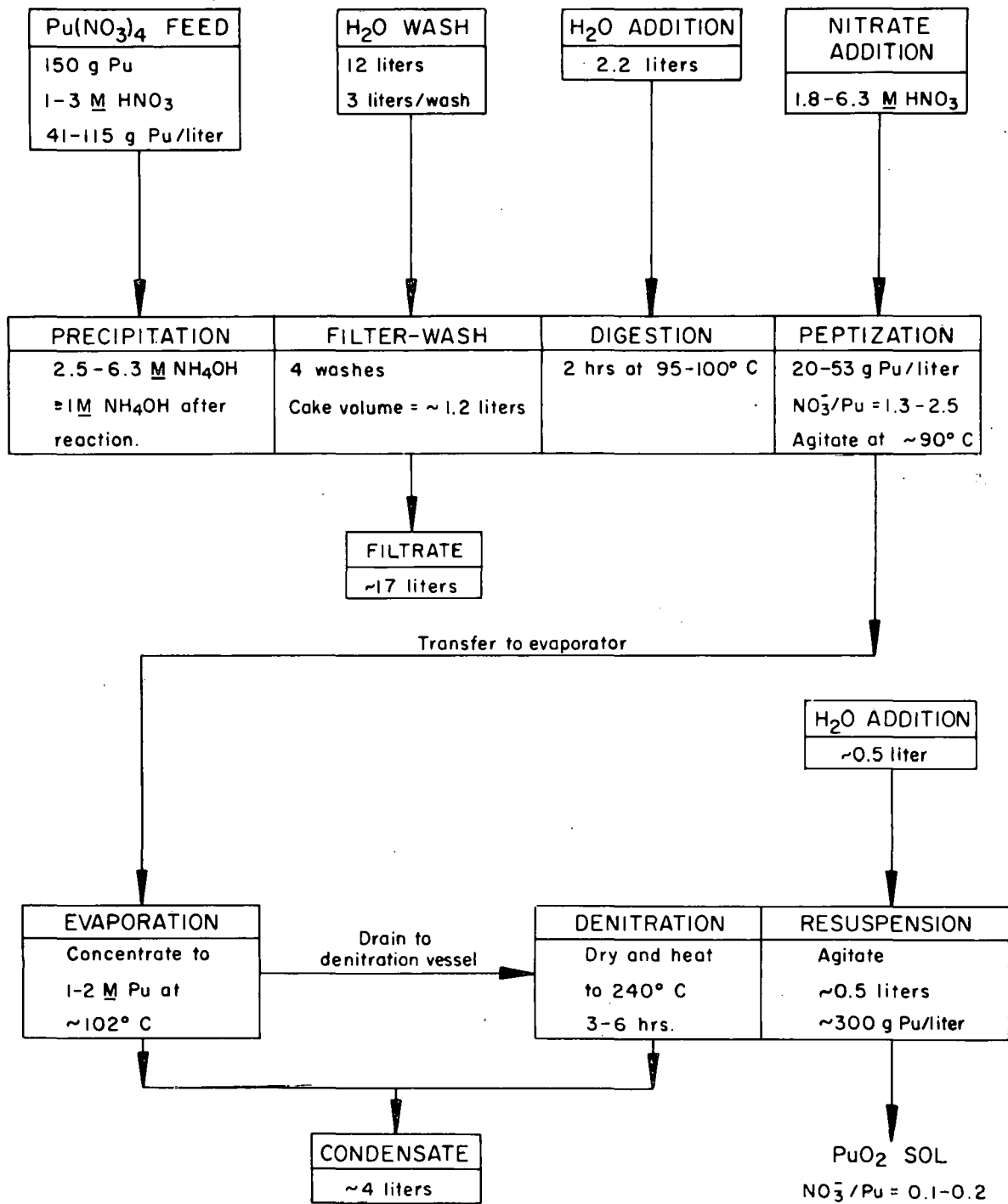Decantation (P^{2}C^{2}D) Apparatus for Preparation of UO$_2$ Sols.

PuO$_2$ Sol Preparation

More than forty plutonia sols (50 to 150 g of Pu per batch)
containing over 3000 g of Pu have been prepared using the standard
procedure (precipitation, washing, peptization, denitration, and
resuspension). These preparations demonstrated the operability of
equipment and the reproducibility of the flowsheet, and provided sol
for the formation of mixed-oxide and plutonia microspheres. A typical
flowsheet for the formation of Pu sol is shown (Fig. 6). This is a
flexible flowsheet, as shown by the ranges of concentrations over which
it has been demonstrated. Prior to the operations shown on the
flowsheet, an adjustment of the valence of the plutonium (to Pu^{4+}) is
made, if necessary by bubbling NO gas through the Pu(NO$_3$)$_4$ solutions.
A minimum HNO$_3$ concentration of 1 $\underline{M}$ is maintained in the feed to
prevent polymerization; free HNO$_3$ concentrations as high as 3 $\underline{M}$ were
successfully used.

The Pu(NO$_3$)$_4$ feed solution is added to NH$_4$OH at rates as high as
30 cc/min, with moderate agitation, to ensure rapid neutralization and
precipitation of the Pu(OH)$_4$. As little as 40% excess NH$_4$OH proved to
be satisfactory as long as the concentration of NH$_4$OH in the final
solution was $\geq$1 $\underline{M}$. The NH$_4$NO$_3$ and the excess NH$_4$OH are removed through
a porous stainless steel (grade G) filter. The precipitate is then
washed thoroughly (four washes), with resuspension of the filter cake
in each wash. A high-nitrate sol is then formed by peptizing the
washed cake in dilute HNO$_3$ at a NO$_3^-$/Pu mole ratio of about 2. All the
steps just mentioned were carried out in an 8-in.-diam precipitation-
filtration vessel having a porous stainless steel filter in the bottom
(Fig. 7). Filtration time is about 20 min per wash. Four such washes
gave adequate NH$_4^+$ removal. The high-nitrate sol was removed through
the bottom of the vessel leaving no solids on the filter (10 μ).

A minimum NO$_3^-$/Pu mole ratio of 1 is necessary for forming colloidal
plutonia particles (i.e., sol). Although ratios as high as 4 have been
used, a ratio of 2 is sufficient to bring about sol formation upon
heating to about 90°C. Under these conditions, a true sol

Pu(NO₃)₄ FEED	H₂O WASH	H₂O ADDITION	NITRATE ADDITION
150 g Pu	12 liters	2.2 liters	
1-3 $\underline{M}$ HNO₃	3 liters/wash		1.8-6.3 $\underline{M}$ HNO₃
41-115 g Pu/liter			

PRECIPITATION	FILTER-WASH	DIGESTION	PEPTIZATION
2.5-6.3 $\underline{M}$ NH₄OH	4 washes	2 hrs at 95-100° C	20-53 g Pu/liter
≅1$\underline{M}$ NH₄OH after	Cake volume = ~1.2 liters		NO₃⁻/Pu = 1.3-2.5
reaction.			Agitate at ~90° C

FILTRATE

~17 liters

Transfer to evaporator

H₂O ADDITION

~0.5 liter

EVAPORATION		DENITRATION	RESUSPENSION
Concentrate to	Drain to	Dry and heat	Agitate
1-2 $\underline{M}$ Pu at	denitration vessel	to 240° C	~0.5 liters
~102° C		3-6 hrs.	~300 g Pu/liter

CONDENSATE

~4 liters

PuO₂ SOL

NO₃⁻/Pu = 0.1-0.2

Fig. 6   Typical Flowsheet for PuO₂ Sol Preparation.

ORNL Dwg 67-6043

TO CONDENSER
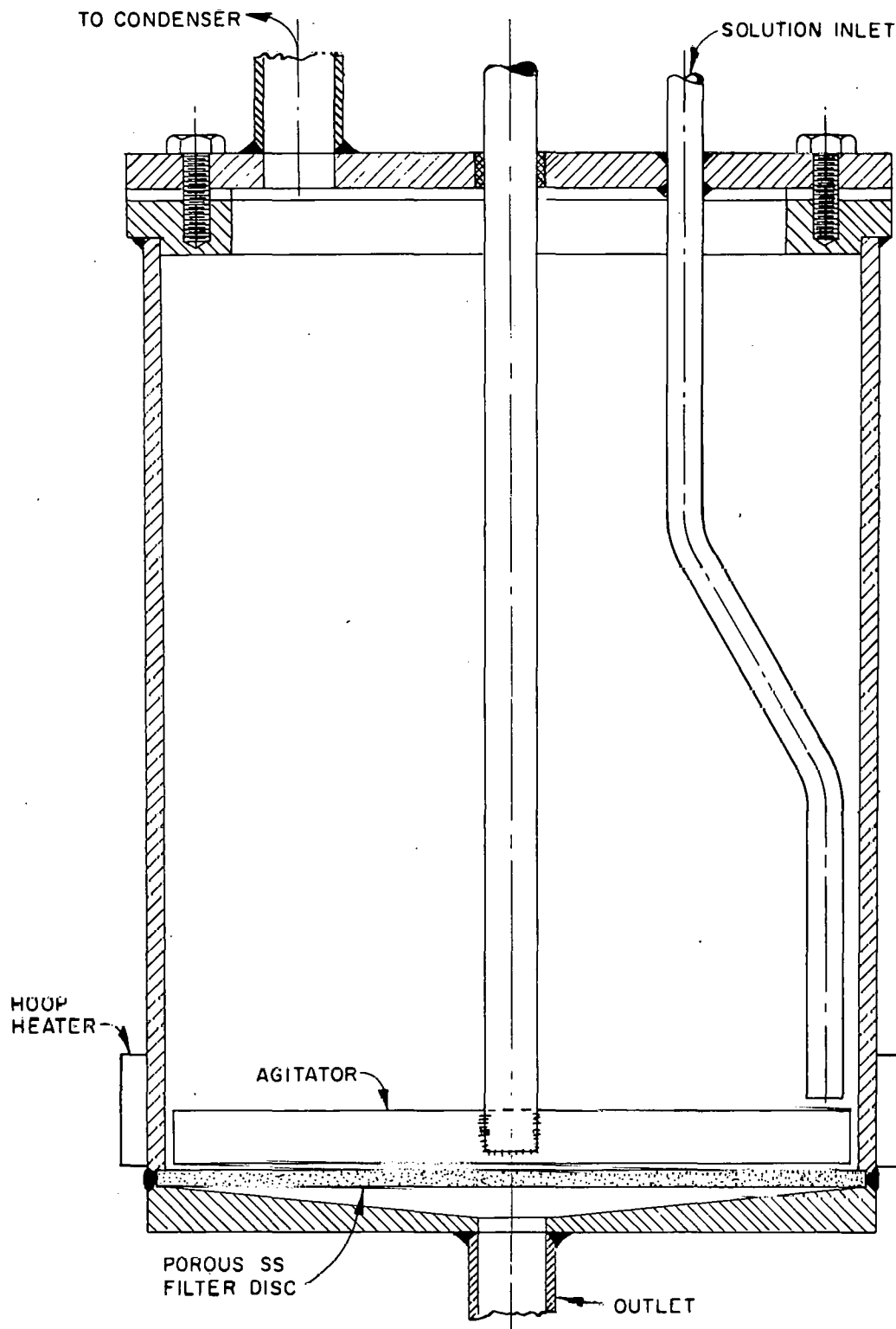
SOLUTION INLET

HOOP
HEATER

AGITATOR

POROUS SS
FILTER DISC

OUTLET

Fig. 7 Vessel for the Precipitation, Filtration, and Peptization
of PuO_2 Sol.

(crystallite size, ~20 A) exists; however, microspheres formed from this material have low densities and strength.

The NO_3^-/Pu ratio of the sol must be reduced to 0.1 to 0.2 by thermal denitration (or baking) and resuspension before the sol will form dense microspheres. This is a crucial step requiring careful control of temperatures and time; the higher the temperature, the shorter the time required. The sol is first evaporated to dryness at 100°C and then heated to a temperature of about 240°C. A thin, porous cake is formed as the sol dries and is maintained intact throughout the cycle. During the reduction to dryness, excess HNO_3 is evaporated such that the initial NO_3^-/Pu mole ratio in the dry solid is 0.8 to 1.0. Usually this ratio will be 0.2 to 0.3 after the solid is heated for 1 to 2 hr at 240°C; another 2 to 3 hours is required to reach the desired 0.1 to 0.15. Progress of the denitration is followed by 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 obtain a uniform product. If the denitration is allowed to proceed until the NO_3^-/Pu mole ratio is less than 0.1, the PuO_2 cannot be resuspended as a sol. A diagram of the denitration vessel, which allows independent control of the temperatures of the top and bottom surfaces and limits radial gradients to ~2°C, is shown in Fig. 8. Crystallite growth and agglomeration also occur during baking. After the denitration step, the basic crystallite size is ~ 80 A, with agglomerates as large as 1000 A. The amount of agglomeration must be limited to ensure a stable sol, although the basic crystallite growth is no detriment. Material having NO_3^-/Pu mole ratios of 0.1 to 0.15 can be resuspended by mild agitation in water to give plutonium concentrations as great as 2 M; more concentrated sols may be produced by evaporation after resuspension.
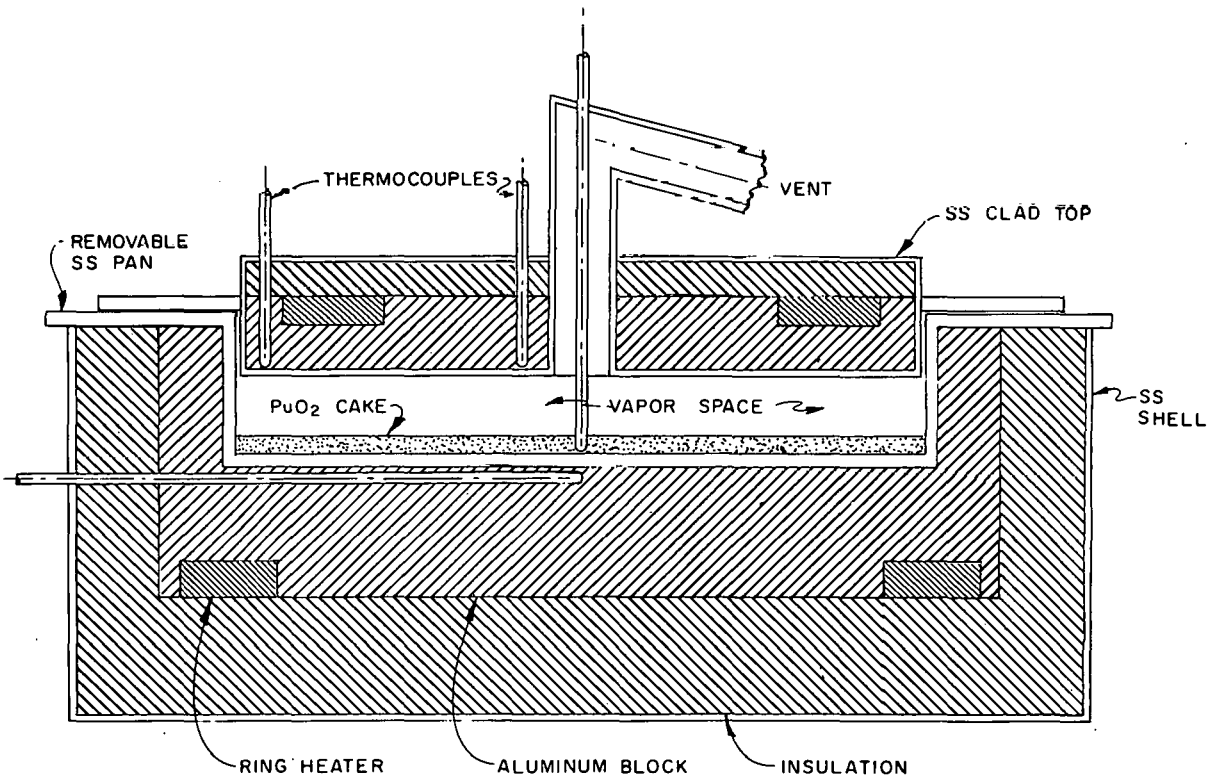
ORNL Dwg 67-6044

Fig. 8 Vessel for the Thermal Denitration of PuO₂ Sol.

3. PREPARATION OF MICROSPHERES

A process was developed for converting sols into spherical gel beads of 10 to 1000 μ in diameter. (Small spherical particles are the preferred shapes for dispersion fuel or fuel that is to be coated with pyrolytic carbon.) In this process, droplets of sol are gelled by extraction of water into an organic liquid such as 2-ethyl-1-hexanol (2EH). The following five 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.

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. This is the key process step. The interfacial tension holds the drop in a spherical shape. The maximum droplet size is limited since very large drops will distort. A surfactant must be added to the 2EH to prevent coalescence of the sol drops with each other, coalescence of the sol drops on the vessel walls, and/or clustering together of partially dried drops. The remaining three operations are simple in principle.

The initial development of the process for the preparation of ThO_2 microspheres and its application to UO_2 or UO_2-ZrO_2 sols have been previously reported.[11,12] Our recent work has included the operation of a microsphere pilot plant, which includes procedures and equipment required for a remote facility, the application of the process to a variety of sols on a larger scale, and the continued development of dispersers for sols.

Microsphere Preparation in the CPDL and TURF

Full-scale prototype units for microsphere preparation in a remotely operated Thorium-Uranium Recycle Facility (TURF) have been

operated during the last two years to produce ThO_2 microspheres. Our objectives in prototype operations were: (1) to improve and, wherever possible, to simplify existing equipment and operations, (2) to obtain data on the reliability and the behavior of both the equipment and the process over extended operating periods, (3) to adapt the equipment to the exacting requirements of remote operation, and (4) to provide 100-kg batches of ThO_2 microspheres for use in large-scale pyrocarbon-coating experiments.

The prototype equipment in the Coated Particle Development Laboratory (CPDL) incorporates all chemical and physical operations that are essential for the conversion of aqueous sols into microspheres. The design capacity is 1 kg/hr of oxide spheres. The improved equipment flowsheet presently used (Fig. 9) provides fewer items of equipment and simplified controls than earlier pilot plant flowsheets. The first four process operations (see above) are done continuously in a tapered glass column (Fig. 9). The sol is dispersed into droplets that are released into the enlarged top of the tapered column. These droplets are suspended or fluidized by a recirculated, upflowing stream of the 2EH. As the water is extracted and the droplets 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 out continuously while sol droplets are being formed in the top of the column. Then the separation of the gel spheres from the 2EH is accomplished by discharging the product collector into a dryer and draining off the liquid through a woven wire cloth. The gel spheres are dried and calcined batchwise. Fresh or purified 2EH is continuously added to the column; this displaces a stream of wet 2EH to a recovery system. Water is removed from the 2EH by distillation.

Extended, stable operation of the column was demonstrated with ThO_2. As of January 1 of this year, the entire system had been emptied and filled twice with 2EH, and 300 kg of 210- to 250-μ-diam and 20 kg of 500- to 590-μ-diam ThO_2 microspheres were prepared. Each charge
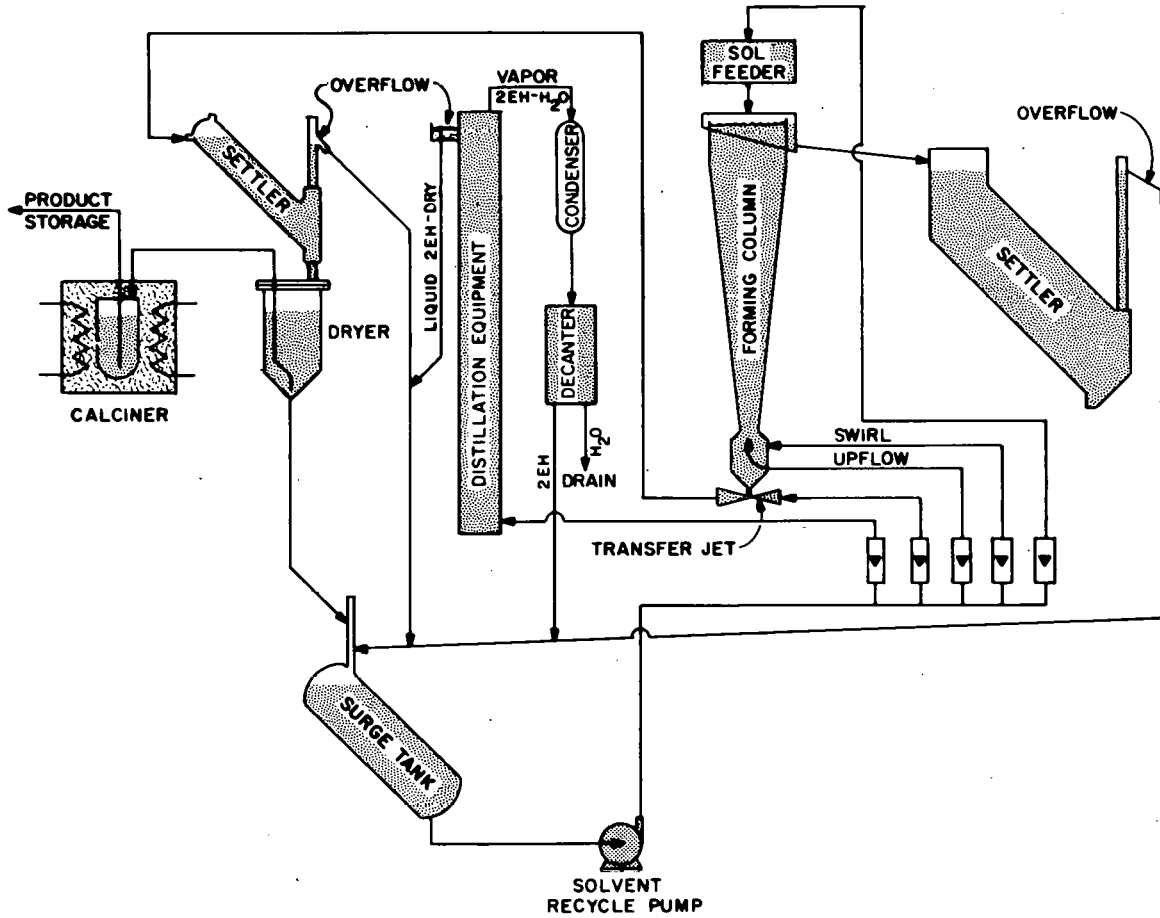
Fig. 9 CPDL Microsphere Preparation: Improved and Simplified
Equipment Flowsheet.

(about 45 gal) was used for 6 months, equivalent in our operating mode to about 300 hr of operation in the column-distillation system. Operation was smooth throughout both periods; actually, the solvent could have been used for a longer period of time, if necessary or desired. The largest monthly production was 137 kg of ThO_2 microspheres (during April of this year).

Surfactants must be added to the 2EH to prevent coalescence of droplets, sticking of droplets on column walls, and clustering of partially dried drops. Each time the column was filled with fresh 2EH, 0.3 vol % Ethomeen S/15 and 0.07 vol % Span 80 were added. Satisfactory column operation was maintained by adding 10 ml of Ethomeen S/15 and 2.5 ml of Span 80 per liter of sol fed. Excessive Span 80 concentrations result in distortion of large sol droplets and thus non-spherical gel particles; therefore, the maintenance-additions of Span 80 were discontinued while making 400 μ ThO_2 microspheres.

Samples of 2EH were analyzed for nitrate, amine, total nitrogen, and thorium periodically throughout each of the six-month periods. Results of these analyses made over the last four months that the second charge was used (Table 1) showed no trend with time for the three suspected degradation products. Only the thorium (ThO_2) concentration built up steadily throughout the period, causing turbidity of the solvent. This buildup was the result of occasional equipment malfunction. Turbidity hindered visual observations of microspheres through the column walls and was the primary reason for discarding both the 2EH loadings. The thoria causing the turbidity was present as extremely fine particles (300 A), which settled out upon long standing (~ 15 days), leaving clear 2EH.

A method for monitoring the extent of column loading was needed for remote operation. A bubbler tube was installed with its lower tip placed in a sidearm off the column bottom. The back pressure from this bubbler is transmitted to a recorder. As the column is loaded with microspheres, the back pressure increases to about 4 in. of water and then levels off. This plateau has been used as a means of controlling the loading of the column.

Table 1. Concentrations in the 2-Ethyl-1-Hexanol Charge of
the CPDL Microsphere Column over a Four-Month Period

Nitrate ion	$(1.5 \text{ to } 4) \times 10^{-4}$ $\underline{M}$, no trend with time
Total nitrogen	$(2.0 \text{ to } 5) \times 10^{-4}$ $\underline{M}$, no trend with time
Amine	$(6.0 \text{ to } 10) \times 10^{-4}$ $\underline{M}$, no trend with time
Thorium	$(2.0 \text{ to } 7) \times 10^{-4}$ $\underline{M}$, increasing with time

The present geometry of the glass column (Fig. 10) appears to be nearly optimum for producing microspheres in the size ranges of interest. The 500- to 590-μ-diam particles settle in a sharply defined zone in the tapered section just above the throat; the stainless steel top section gives ample settling capacity for the 210- to 250-μ-diam particles.

A filter was placed in the 2EH circuit to remove suspended fines; it was also effective in removing small gelled particles. Use of filtration, in an overall sense, was not satisfactory since operational upsets allowed soft, half-gelled sol to enter the circulating system and to immediately plug the filter element. A large settler (Fig. 9) is now used to remove any entrained sol or gel particles before they reach the pump.

A liquid-driven (2EH) jet was mounted on the bottom of the forming column to transfer the microspheres continuously to the dryer. This transfer method has worked satisfactorily.

A prototype dryer design is shown in Fig. 11. The ThO_2 microspheres enter the settler with the 2EH transfer fluid. Part of the 2EH flows down through the stainless steel wire cloth in the dryer bottom, while the rest overflows the settler. Both streams combine and return to the column circuit. The microspheres remain on the screen. The settler was installed to allow the transfer jet to operate at constant pressure, since the pressure drop across the bed of microspheres increases as the dryer is filled. When the dryer is filled with

ORNL DWG 67 6888

OVERFLOW SECTION
6-in. I.D.
(STAINLESS STEEL)

18 in.

4-in. I.D.

18 in.

4-in. I.D.

63 in.

GLASS COLUMN
SECTION

32 in.

2-in. I.D.

COLUMN
THROAT

SETTLER

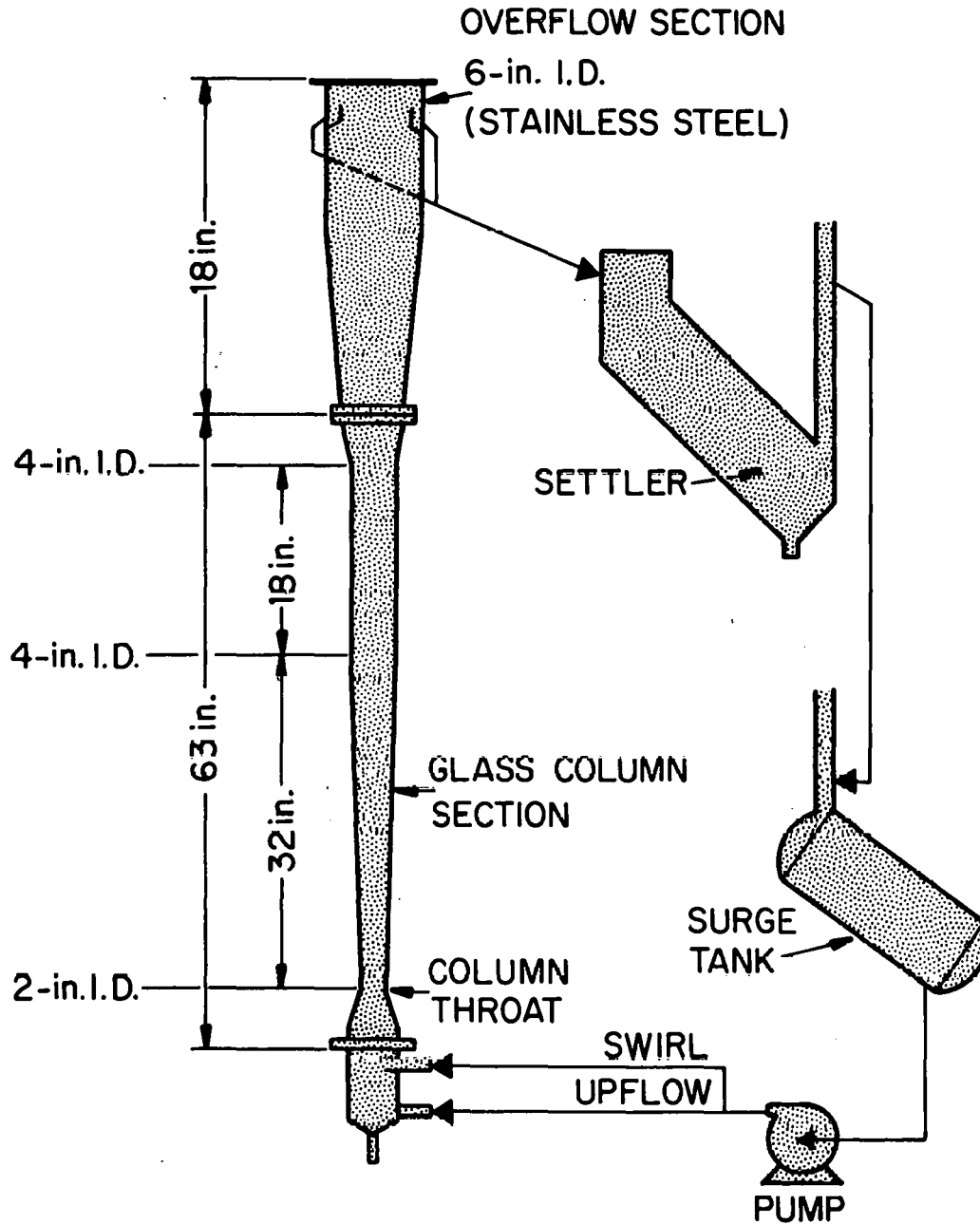SURGE
TANK

SWIRL

UPFLOW

PUMP

Fig. 10 CPDL Microsphere Column: Configuration and Dimensions.
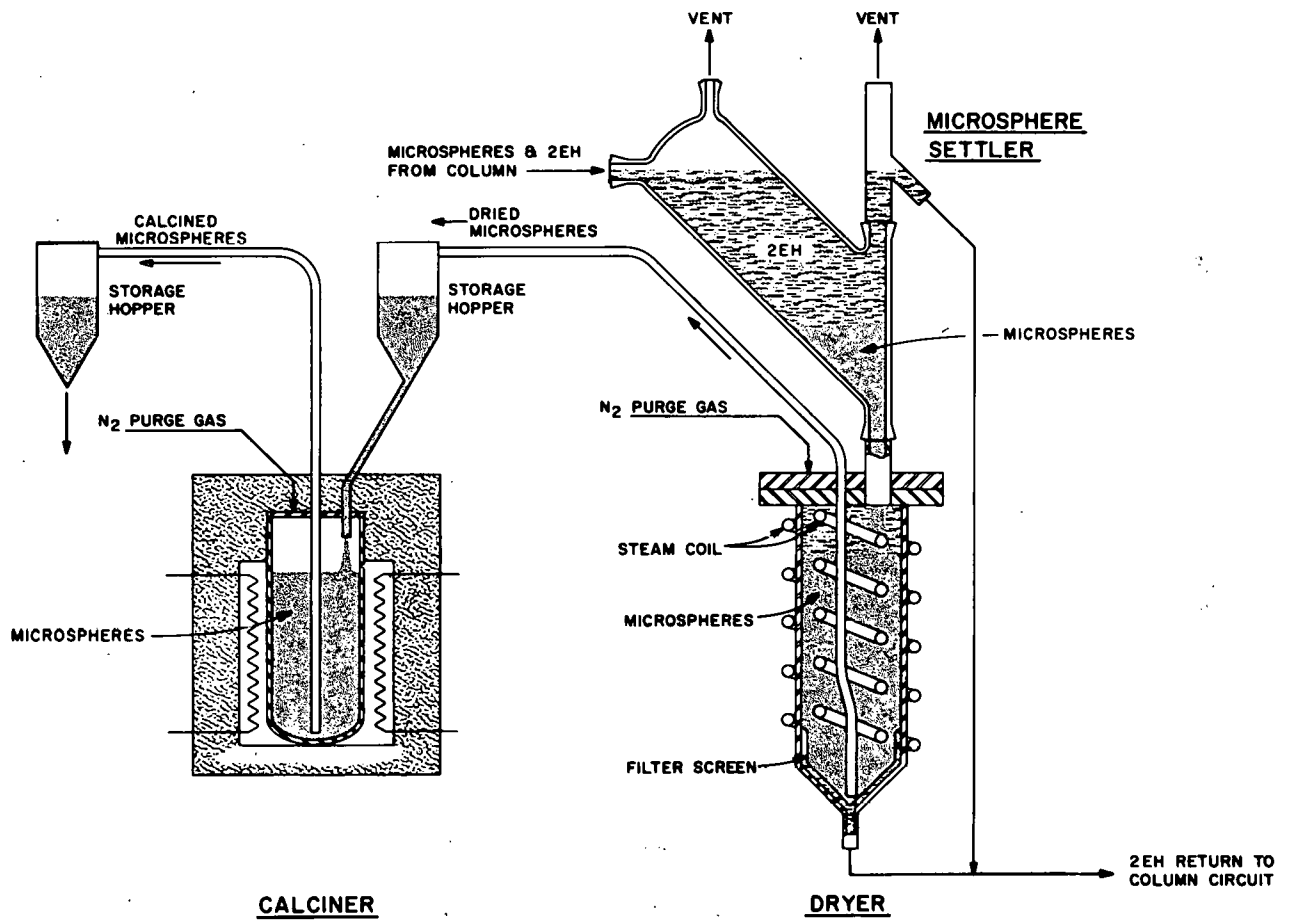
ORNL DWG 67-3686 R I

Fig. 11   Schematic Arrangement of Microsphere Dryer and Calciner.

microspheres, excess 2EH is blown down through the screen with nitrogen, the steam is turned on, and the bed is allowed to dry (150 to 250°C). After drying, microspheres are transferred pneumatically to the calciner station.

In the conceptual design of the remotely operated calciner (Fig. 11), the charge is contained in a crucible that is fixed in the furnace. The charge will be loaded by gravity and discharged pneumatically. The present calciner is actually a muffle furnace containing crucibles that are loaded manually.

The use of the liquid and pneumatic microsphere transfer systems represents a significant improvement in our flowsheet, serving to eliminate mechanical transfer of canisters, or crucibles, within the cell.

Preparation of Thoria-Urania Microspheres from Solvent Extraction Sol

The ThO_2-UO_3 sols prepared by amine extraction of nitrate (Th/U ratios, 3 to 5) were formed into gel spheres using Span/Ethomeen volume ratios of about 2. Span 80 alone tended to give wrinkled or "raisin" surfaces, while Ethomeen S/15 alone tended to give deep dimples or "cherry pits." Small-scale tests with freshly prepared sol and new 2EH required low total surfactant concentrations ($\leq 0.2\%$) to prevent cracking of the gel spheres into fragments. This cracking did not occur for surfactant concentrations as large as 0.8 vol % in larger-scale tests with aged sol (storage period, 1 to 3 months) and 2EH that had been used 20 to 40 hours. The drying and firing conditions were similar to those used for microspheres prepared from ThO_2 sols containing small amounts of $UO_2(NO_3)_2$ or UO_3.

UO_2 Microspheres

The equipment developed for use in preparing ThO_2 microspheres is provided with an inert gas blanket to prevent oxidation of UO_2 during preparation of urania microspheres; otherwise it remains unchanged.

The initial concentrations and the additions of surfactant to the 2EH are less predictable for UO_2 sols than for ThO_2 sols. The UO_2 sols are more prone to stick, coalesce, or cluster, and require more careful control of the surfactant concentrations. Also, the urania sols, which are prepared by several flowsheets, have many more composition variables (Th $\underline{M}$ and NO_3^-/Th ratio for ThO_2 sols, as compared to U $\underline{M}$, NO_3^-/U, O/U, $COOH^-$/U and NH_4^+/U ratios for UO_2 sols).

The UO_2 sols generally required the presence of both Span 80 and Ethomeen S/15 in the 2EH, as well as much higher total surfactant concentrations than for ThO_2 sols. A total surfactant concentration of about 1 vol % and a Span/Ethomeen volume ratio of 4 were as satisfactory as any other concentrations for most UO_2 sols. A Span 80 concentration of ≥ 0.5 vol % was necessary to minimize sticking and clustering. High total surfactant concentrations or high Span/Ethomeen volume ratios tended to result in badly distorted particles having the appearance of raisins. High Ethomeen S/15 concentrations seemed to favor production of particles having a deep dimple or "cherry pit" on one side. High surfactant concentrations appeared to contribute to cracking of the spheres in some cases.

PuO_2, PuO_2-UO_2, and PuO_2-ThO_2 Microspheres

Equipment for the forming, drying, and calcination of microspheres containing PuO_2 was operated to produce 4 kg of 5-20% PuO_2--UO_2, 1.5 kg of 5% PuO_2--ThO_2 and 3 kg of PuO_2. Batch sizes were 50 to 150 g, and densities generally were $\geq 95\%$ of theoretical. The equipment is installed in two 6-ft glove boxes; the first is used for sol mixing, microsphere forming, and drying; the second for calcination and size classification. To obtain mixtures, the two pure sols are prepared separately and then blended to the desired proportions; thus, any Pu/Th or Pu/U atom ratio can be easily achieved. The PuO_2 and PuO_2-ThO_2 sols are formed into spheres using the procedure that is routinely used for ThO_2 spheres. Plutonia-urania mixtures, like urania, must be processed in an inert atmosphere until after firing.

Microspheres containing PuO_2 are prepared by using equipment and procedures similar to those developed for thoria microspheres. The principal difference in equipment is that a smaller size is required for use in glove boxes. The primary differences in procedures involved the surfactant systems used in the drying solvent and the degree of atmosphere control required. The PuO_2 and PuO_2-ThO_2 sols were formed by using 0.3 to 0.5 vol % Ethomeen S/15 alone as the surfactant. The 20% PuO_2--UO_2 spheres were formed, using a surfactant system of 0.3 to 0.6 vol % Ethomeen S/15 and 0.3 to 0.6 vol % Span 80; however, it was found later (during the preparation of 15% PuO_2--UO_2) that a less-concentrated system, 0.1 vol % Ethomeen S/15--0.4 vol % Span 80, was more satisfactory. Plutonia and ThO_2 sols and mixtures require no atmospheric protection, and their gels are fired in air.

The types of material produced, size ranges, total weights, number of batches, and physical properties are shown in Table 2. No significant differences were observed in the range 5-20% PuO_2 in urania; densities of all materials, except for fines, were $\geq$ 95% of theoretical. Analytical data (Hg porosimetry) for fines are variable and of uncertain accuracy. Carbon levels were less than 100 ppm in all cases and surface areas, except for fines, were generally $\leq$ 0.05 m^2/g. Crushing resistance for the coarse material was about 1 kg/sphere.

Figure 12 shows the uniform shapes and glossy surfaces of PuO_2 microspheres. A few surface cracks may be seen in the largest spheres for both PuO_2 and PuO_2-UO_2 but not with PuO_2-ThO_2. Cross sections of PuO_2 spheres of two sizes (Fig. 13) show sharp edges, which are consistent with low surface areas. No internal voids are observed, although a small amount of microporosity can be detected.

A larger system for preparing PuO_2 and PuO_2-UO_2 microspheres was fabricated and installed (Fig. 14). The design capacity is 1 kg of microspheres per day and 200 g of Pu (as PuO_2 sol) per day.

Table 2. PuO_2-Containing Microspheres Prepared in Glove Box Facility, Building 3019

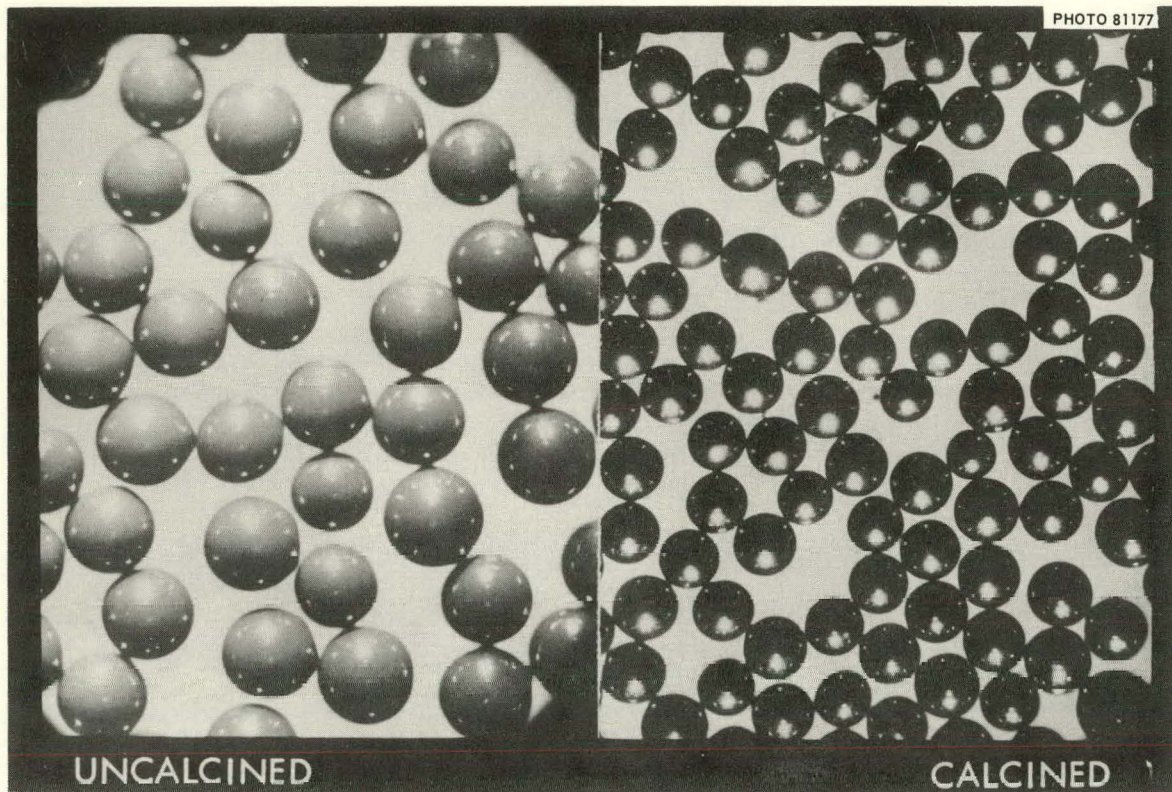| Type of Material	Size Range (μ)	Total Wt (g)	No. of Batches	Density by Hg Porosimetry			Carbon (ppm)	Surface Area	
				Bulk (g/cc)	10,000 psi (g/cc)	Theoretical (%)		Gas Adsorption Method (m^2/g)	Calculated (m^2/g)
20% PuO_2--$^{235}UO_2$	300-600	1900	23	10.3	10.5	95	< 10	0.02	--
	< 44	340	5	~6	9.0	82	< 10	0.04	0.08
15% PuO_2--$^{238}UO_2$	300-600	970	11	10.5	10.6	97	< 90	--	0.06
	< 44	234	4	5.6	~9.2	~84	< 100	--	0.5
5% PuO_2--$^{238}UO_2$	300-600	496	3	--	--	--	--	--	--
5% PuO_2--ThO_2	300-600	1148	5	9.48	9.84	97	< 10	0.02	--
	< 44	403	4	~6	~9.5	~94	--	0.17	--
PuO_2	250-600	251	4	11.13	11.22	98	< 30	0.02	0.03
	50-250	571	7	11.06	11.19	98	< 70	0.01	0.02
	< 44	43	1	--	--	--	--	--	--

Fig. 12 Plutonia Gel and 1150°C Sintered Microspheres. Average
Diam: 130 μ; Density: 96% of Theoretical.
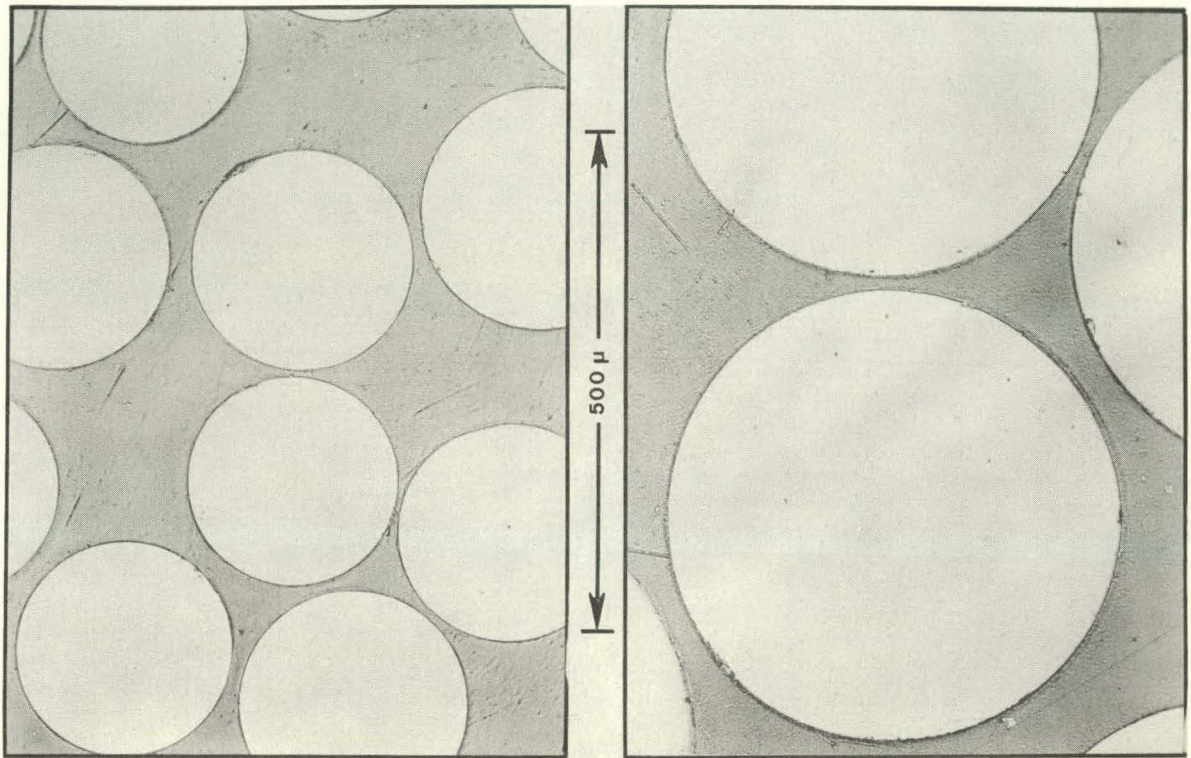
35

Fig. 13   PuO$_2$ Sol-Gel Microspheres Calcined at 1200°C.

ORNL Dwg. 67-6045
R-1
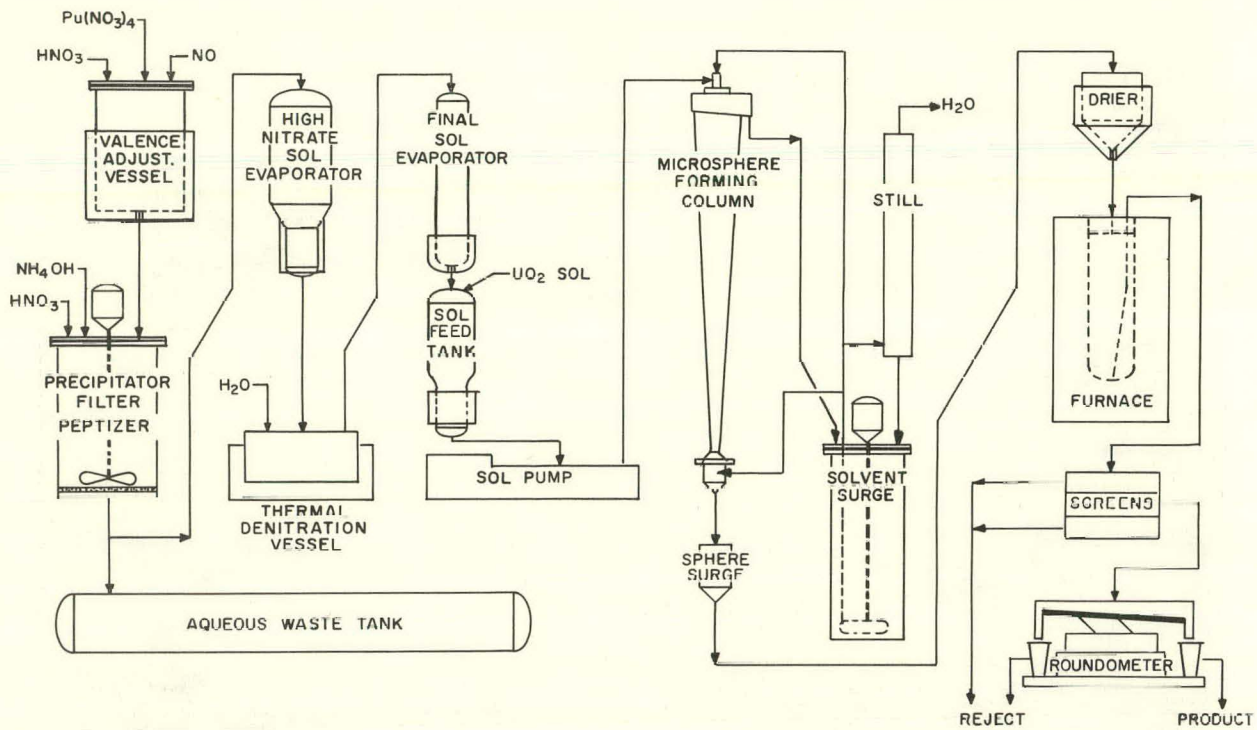

Fig. 14 Schematic Flowsheet of Sol Preparation and Microsphere Forming Equipment, PuO_2 and Mixed Oxide Sols, Cell IV, Bldg. 3019.

Development of Dispersion Devices

Many column operating difficulties would be minimized if sol droplet sizes were uniform; therefore, a variety of sol dispersion devices have been tested. Sol droplets can be formed from a larger mass of sol by applying one or more forces, such as gravity, centrifugal field, shear, inertia, interfacial tension, and electrostatic repulsion. To obtain uniform droplet size and controlled diameters, both the force and the configuration of the sol (where the force is applied) must be uniform and one or both of these factors must be controllable. For all dispersers tested, a uniform configuration is obtained by feeding the sol through orifices or capillaries that are 0.004 to 0.030 in. in diameter.

Two-fluid nozzles (Fig. 15) have proved to be the most useful sol dispersion devices.[11,12] They are reliable, give a uniform product, and are easily controlled over the sol droplet size range of interest (200 to 2000 μ in diameter). With single two-fluid nozzles, 90 wt % of the product consistently had diameters within ± 15% of the mean diameter (Table 3). The capacity of single two-fluid nozzles was unacceptably low for pilot plant operations. Therefore, multiple arrays of two-fluid nozzles arranged in parallel were tested; the sol and the 2EH were fed to their respective feed locations from single pumps. Two arrays tested consisted of 6 and 11 parallel two-fluid nozzles. The yield within ± 10% of the mean diameter for extended periods of operation were 70% (for the 6-nozzle arrangement) and 50% (for the 11-nozzle arrangement).

Sol droplets formed from capillaries that are mechanically connected to, and vibrated by, a loudspeaker (Fig. 15) are more uniform at optimum conditions than those from any other disperser. A simple sinusoidal displacement of the capillary tip appears to be the best vibratory wave shape. Secondary vibrations cause nonuniform drops. The best results are obtained with a continuous, approximately sinusoidal liquid stream that breaks at the midpoint position with

Table 3. Sizes of Calcined Thoria Microspheres from Three Dispersers

Sol feed: Thoria sols 3.0 $\underline{M}$ in Th; diameters of sol droplets were
2.35 times those of theoretically dense ThO_2 product

	Two-Fluid Nozzles		Vibrating Capillaries			Free-Fall Drop Method
Number of feed capillaries	Single	Two	Single	Four	Four	19
Capillary diameter, μ	250	425	425	480	480	400
Sol feed rate, cc/min	1.2	9.9	1.2	19.2	9.6	9.6
Vibration frequency, cps	---	---	40	200	50	---
Predicted mean size, μ	270[a]	230[a]	33c[b]	310[b]	390[b]	---
Amount of sample, g	540	10,200	---	314	720	480
Mesh[c] or diameter size of product, wt %:						
30/35 or 500-590 μ						97.9
35/40 or 420-500 μ					0.1	0.8
40/45 or 350-420 μ			0.2		61.9	1.1
45/50 or 297-350 μ	2.9	0.2	98.3	30.4	37.6	
50/60 or 250-297 μ	92.0	3.0	1.5	62.6	0.4	
60/70 or 210-250 μ	0	85.8		7.0		
-70 or < 210 μ	5.3	10.9				

[a] Calculated from equation developed for two-fluid nozzle.

[b] From number of drops per cycle and flow rate.

[c] From use of U. S. Sieve Series screens.

ORNL DWG 66-10982

SOL

2 EH
DRIVE
FLUID

LOUDSPEAKER

SOL

SOL

PLASTIC
BUCKET

2EH

VARIABLE FREQUENCY
POWER SUPPLY

VOLTS   FREQUENCY

2EH

2EH

a. TWO-FLUID NOZZLE

b. VIBRATING CAPILLARY

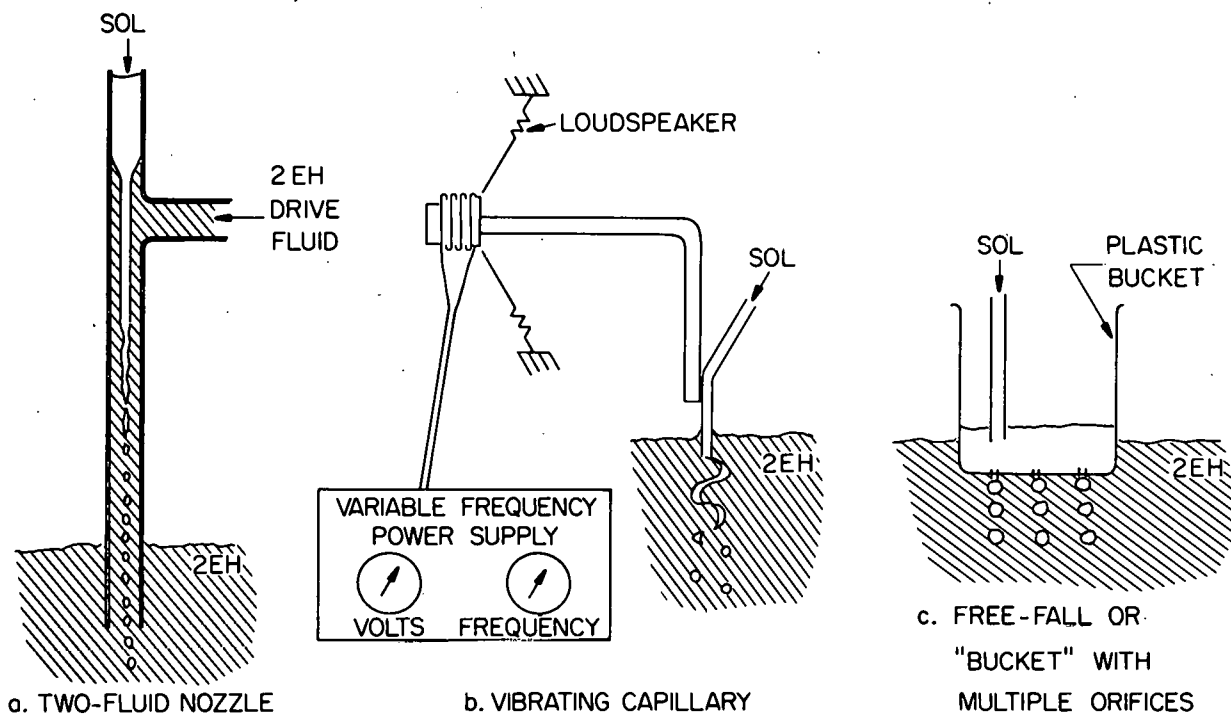c. FREE-FALL OR
"BUCKET" WITH
MULTIPLE ORIFICES

Fig. 15 Devices for Dispersion of Sol as Drops in 2-Ethyl-1-
Hexanol (2EH).

respect to amplitude (Fig. 16). The amplitude for this type of operation varied from 1/4 in. at 20 cps to 1/32 in. at 200 cps and was obtained by 1.5 to 4.0-v inputs to commercial loudspeakers. Results for single capillaries are somewhat better than those for multiple capillaries (Table 3).

The free-fall drop mechanism and the relationship between droplet size, orifice size, and interfacial tension are well known. The use of plastic buckets with a large number of holes (Fig. 15) provides a practical capacity and avoids droplet size variations caused by variable wetting of the orifice by the sol. This disperser is useful for large drops only; the orifice sizes necessary to produce drops smaller than 1000 μ in diameter are too small to be practical. The interfacial tension between the sol and the 2EH depends on the amounts of surface-active agents present and thus causes variations in droplet size.

4. DRYING AND FIRING

Drying and firing are necessary to remove volatile constituents, to effect chemical reactions, and to sinter the particles to a high density. Both the temperature and the atmosphere are controlled while the gel is heated to the sintering temperature and then cooled to room temperature. Particles containing UO_2 or carbides must be protected from oxygen. The drying and firing conditions were initially determined empirically, with little theoretical understanding of the mechanisms involved. The cracking of particles, the densification during sintering, and the amount of carbon and gases in the calcined product can vary greatly depending on the conditions used. The drying and firing conditions preferred for engineering studies are outlined below and some equipment will be described. More detailed studies of the drying and sintering mechanisms are reported elsewhere.[1,13]

Thoria or thoria-urania fragments have been fired principally in standard muffle furnaces with time-controlled temperatures and
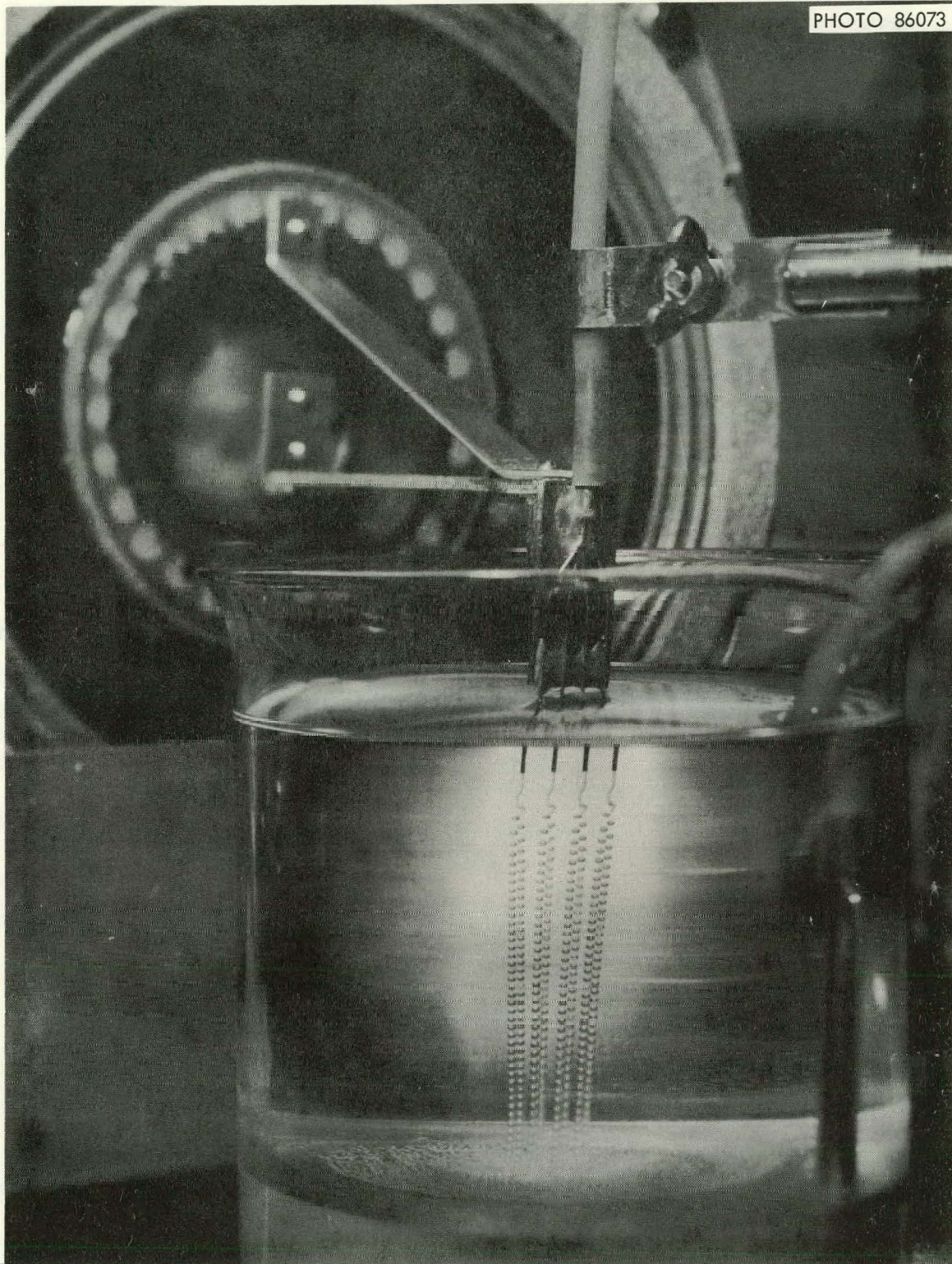
Fig. 16 Dispersion of a ThO$_2$--25% UO$_2$ Sol by a Vibrating Capillary Disperser. Four capillaries are vibrated at 90 cps to form 950-μ-diam droplets.

atmospheres.[5] The dried gel is heated in air to 1150°C at a rate of
300°C/hr. The charge is held at 1150°C for 4 hr; if urania is present,
an Ar--4% H_2 atmosphere is used to reduce it to UO_2. A continuous,
vertical tube, moving-bed calciner was successfully operated with
thoria--3% urania fragments.[14] The temperature profile along the
tube is carefully controlled so the moving charge undergoes the correct
temperature-time program. The countercurrent flow of gas up the tube
provides excellent utilization of hydrogen and helps maintain the
required temperature profile. The moving-bed type of calciner appears
to be practical for large production ($\geq$ 50 kg day), while batch
units appear more attractive for small-scale preparation.

The factors that minimize cracking of microspheres are those that
minimize composition gradients within the gel microspheres. The
drying conditions were the important variable, and the most efficient
drying conditions for microspheres required superheated steam to final
drying temperatures of 200°C.[1,13] As compared with thoria-urania
fragments, microspheres may require more-complicated firing cycles
to remove organic compounds and carbon.[1,13] All microsphere
calcinations have been done in batch furnaces with time-controlled
temperatures and atmospheres. The conditions in Table 4 were
successfully used for firing gel microspheres in muffle furnaces.
Argon--4% H_2 is used to avoid the explosive hazards of
pure H_2. If hydrogen is present throughout cooldown, excessive amounts
of it may be adsorbed. The firing of urania microspheres requires a
controlled oxidation during the firing cycle. Excessive oxidation
results in low final densities. Apparently the UO_2 structure is lost
if oxidation is excessive and sintering does not occur at the usual
temperature for sol-gel oxides, even though the urania is again
reduced to UO_2. If a reducing or inert atmosphere is used throughout
the drying and firing, the fired microspheres will have high (10^3 to
10^4 ppm) carbon contents and low densities. The effects of drying
and firing conditions on sol-gel urania have been extensively investi-
gated in laboratory studies.[1] No universally optimum conditions were

found. The ThO_2, PuO_2, and ThO_2-PuO_2 microspheres are simply fired in air, which removes carbon as volatile oxides. The ThO_2-UO_3 microspheres are also fired in air to remove carbon, but reduction with hydrogen and cooldown in argon are necessary to give ThO_2-UO_2 microspheres.

Table 4. Conditions for Firing Microspheres

Temperature ($^\circ$C)	Time	Atmospheres Used for:		
		ThO_2 or PuO_2	ThO_2-UO_3	UO_2[a]
25	16 hr	--	--	Air
25 to 100	300°C/hr	Air	Air	Air
100 to 1150	300°C/hr	Air	Air	Ar
1150	4 hr	Air	Ar--4% H_2	Ar--4% H_2
1150 to < 100	< 500°C/hr	Air	Ar	Ar

[a]UO_2 conditions would also be usable for UO_2-ThO_2 or UO_2-PuO_2.

ACKNOWLEDGMENT

6. REFERENCES

1. J. P. McBride (compiler), <u>Laboratory Studies of Sol-Gel Processes</u>
    <u>at the Oak Ridge National Laboratory</u>, ORNL-TM-1980 (September 1967).

2. A. R. Olsen <u>et al</u>., <u>Fabrication and Irradiation Testing of Sol-Gel</u>
    <u>Fuels at Oak Ridge National Laboratory</u>, ORNL-TM-1971 (September 1967).

3. T. N. Washburn <u>et al</u>., <u>Comparative Evaluation of Sol-Gel Fuel</u>
    <u>Fabrication Costs</u>, ORNL-TM-1979 (September 1967).

4. D. E. Ferguson, O. C. Dean, and P. A. Haas, <u>Preparation of Oxide</u>
    <u>Fuels and Vibratory Compaction by the Sol-Gel Process</u>, CEND-153,
    (vol I), pp 23-38; also, ORNL-TM-53 (November 20, 1961).

5. C. C. Haws, J. L. Matherne, F. W. Miles, and J. E. Van Cleve,
    <u>Summary of the Kilorod Project--A Semiremote 10-kg/day Demonstration</u>
    <u>of $^{233}UO_2$-ThO$_2$ Fuel Element Fabrication by the ORNL Sol-Gel</u>
    <u>Vibratory-Compaction Method</u>, ORNL-3681 (August 1965).

6. D. E. Ferguson, "Sol-Gel Technology in the Nuclear Reactor Fuel
    Cycle," Progress in Nuclear Energy, Process Chemistry, vol. 4
    (to be published).

7. E. N. Nelson, <u>Fluid-Bed Denitration of Thorium Nitrate</u>, U. S.
    Atomic Energy Commission, MCW-1511 (January 19, 1966).

8. A. B. Meservey, <u>UO$_2$-ThO$_2$ and UO$_3$-ThO$_2$ Sols Prepared by Precipitation-</u>
    <u>Peptization Processes</u>, ORNL-TM-1782 (March 20, 1967).

9. T. A. Gens, <u>Preparation of Uranium and Thorium Oxide Microspheres</u>
    <u>with Controlled Porosity by a Sol-Gel Process</u>, ORNL-TM-1530
    (May 31, 1966).

10. A. R. Irvine, J. M. Chandler, P. A. Haas, and K. H. McCorkle,
    "The Design and Performance of Continuous Process Equipment for
    Preparation of Urania Sol," Transactions of the American Nuclear
    Society, San Diego, California, June 11-15, 1967.

11. P. A. Haas and S. D. Clinton, "Preparation of Thoria and Mixed
    Oxide Microspheres," <u>Ind. Eng. Chem.</u>, <u>Prod. Res. Develop.</u> <u>5</u>
    (3) 236-244 (1966).

12. P. A. Haas, S. D. Clinton, and A. T. Kleinsteuber, "Preparation
    of Urania and Urania-Zirconia Microspheres by a Sol-Gel Process,"
    <u>Canadian J. Chem. Engr.</u> <u>44</u> (6), 348-353 (1966).

13. P. A. Haas, F. G. Kitts, and H. Beutler, "Preparation of Reactor Fuels by Sol-Gel Processes," presented at AIChE National Meeting, Salt Lake City, May 21-24, 1967; to be published in "Nuclear Engineering Series" by the American Institute of Chemical Engineers.

14. C. C. Haws, Jr., <u>Cold Testing of a Vertical-Tube Furnace for Continuously Calcining 35 kg of Sol-Gel Derived ThO$_2$-UO$_2$ per Day</u>, ORNL-3895 (to be published).

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

47

ORNL-TM-1978

INTERNAL DISTRIBUTION

1-3.	Central Research Library	79.	E. L. Long, Jr.
4-5.	ORNL--Y-12 Technical Library Document Reference Section	80.	A. L. Lotts
		81.	H. G. MacPherson
6-25.	Laboratory Records	82-86.	J. P. McBride
26.	Laboratory Records, ORNL RC	87.	R. W. McClung
27.	ORNL Patent Office	88.	K. H. McCorkle
28.	R. E. Adams	89.	D. L. McElroy
29.	G. M. Adamson, Jr.	90.	A. B. Meservey
30.	H. Beutler	91.	C. S. Morgan
31.	S. E. Bolt	92.	J. G. Moore
32.	E. S. Bomar	93.	J. P. Moore
33.	W. D. Bond	94.	L. E. Morse
34.	G. E. Boyd	95.	K. J. Notz
35.	R. E. Brooksbank	96.	A. R. Olsen
36.	K. B. Brown	97.	P. Patriarca
37.	J. M. Chandler	98.	W. L. Pattison
38.	S. D. Clinton	99.	W. H. Pechin
39.	J. H. Coobs	100.	J. W. Prados
40.	C. M. Cox	101.	R. B. Pratt
41.	F. L. Culler	102.	J. M. Robbins
42.	J. E. Cunningham	103.	J. T. Roberts
43.	D. E. Ferguson	104.	M. W. Rosenthal
44.	R. B. Fitts	105.	A. D. Ryon
45.	J. H. Frye, Jr.	106.	R. Salmon
46-66.	P. A. Haas	107.	J. L. Scott
67.	R. G. Haire	108.	J. D. Sease
68.	R. L. Hamner	109.	J. G. Stradley
69.	W. O. Harms	110.	O. K. Tallent
70.	F. E. Harrington	111.	D. B. Trauger
71-72.	C. C. Haws, Jr.	112.	W. E. Unger
73.	M. R. Hill	113.	T. N. Washburn
74.	A. R. Irvine	114.	A. M. Weinberg
75.	F. G. Kitts	115.	J. R. Weir
76.	J. A. Lane	116.	M. E. Whatley
77.	J. M. Leitnaker	117-127.	R. G. Wymer
78.	M. H. Lloyd		

EXTERNAL DISTRIBUTION

128-132. F. W. Albaugh, Battelle, PNL
133-136. R. J. Allio, Westinghouse Atomic Power Division
137. A. Amorosi, Argonne National Laboratory, LMFBR Program Office
138. R. D. Baker, Los Alamos Scientific Laboratory
139. R. W. Barber, AEC, Washington
140. L. Brewer, University of California, Berkeley
141. L. Burris, Argonne National Laboratory, LMFBR Program Office
142. V. P. Calkins, GE, NMPO
143. W. Cashin, Knolls Atomic Power Laboratory
144. S. Christopher, Combustion Engineering, Inc.
145. D. B. Coburn, General Atomic
146. D. F. Cope, RDT, SSR, AEC, ORNL
147. G. W. Cunningham, AEC, Washington
148. C. B. Deering, RDT Site Representative, ORNL
149. E. Dewell, B&W, Lynchburg, Virginia
150. G. K. Dicker, Division of Reactor Development and Technology, AEC, Washington
151. D. E. Erb, Division of Reactor Development and Technology, AEC, Washington
152. E. A. Evans, GE, Vallecitos
153. W. C. Francis, Idaho Nuclear Corporation
154. T. A. Gens, Linde Division, Union Carbide Corporation, Tonawanda, New York
155. A. J. Goodjohn, General Atomic
156. R. G. Grove, Mound Laboratory
157. D. H. Gurinsky, BNL
158. A. N. Holden, GE, APED
159-161. J. S. Kane, Lawrence Radiation Laboratory, Livermore
162. H. Kato, U. S. Department of the Interior, Bureau of Mines
163. L. K. Kellman, Argonne National Laboratory, LMFBR Program Office
164. E. A. Kintner, Fuel Fabrication Branch, AEC, Washington
165. J. H. Kittel, ANL
166. E. J. Kreih, Westinghouse, Bettis Atomic Power Laboratory
167. W. J. Larkin, AEC, Oak Ridge Operations
168. J. A. Leiberman, AEC, Washington
169. P. J. Levine, Westinghouse Advanced Reactor Division, Waltzmill Site, Madison, Pa.
170. J. J. Lombardo, NASA, Lewis Research Center
171. F. D. Lynch, Babcock & Wilcox
172. J. II. MacMillan, Babcock & Wilcox
173. R. Mayfield, ANL
174. M. McGurty, GE, NMPO
175. W. H. McVey, AEC, Washington
176. E. Moncrief, B&W, Lynchburg, Virginia
177. J. Morabito, AEC, Washington

EXTERNAL DISTRIBUTION

178. M. Nevitt, ANL
179. E. O. Nurmi, B&W, Lynchburg, Virginia
180. R. E. Pahler, Division of Reactor Development and Technology, AEC, Washington
181. S. Paprocki, BMI
182. D. Ragone, General Atomic
183. W. E. Ray, Westinghouse Advanced Reactor Division, Waltzmill Site, Madison Pa.
184. W. E. Roake, Battelle, PNL
185. B. Rubin, Lawrence Radiation Laboratory, Livermore
186. J. W. Ruch, AEC, ORO
187. F. C. Schwenk, Division of Reactor Development and Technology, AEC, Washington
188. W. F. Sheely, Division of Research, AEC, Washington
189-191. J. M. Simmons, Division of Reactor Development and Technology, AEC, Washington
192. E. E. Sinclair, AEC, Washington
193. L. E. Steele, Naval Research Laboratory
194. R. H. Steele, Division of Reactor Development and Technology, AEC, Washington
195. A. Strasser, United Nuclear Corporation
196. J. A. Swartout, UCC, New York, N. Y.
197. A. Toboada, Division of Reactor Development and Technology, AEC, Washington
198. A. Van Echo, Division of Reactor Development and Technology, AEC, Washington
199. R. Van Tyne, Illinois Institute of Technology Research Institute
200. B. Vondra, NUMEC, Apollo, Pa.
201. C. E. Weber, Atomics International
202. J. F. Weissenberger, RDT, OSR, GE, NMPO
203. G. W. Wensch, Division of Reactor Development and Technology, AEC, Washington
204. G. A. Whitlow, Westinghouse Advanced Reactor Division, Waltzmill Site, Madison, Pa.
205. M. J. Whitman, AEC, Washington
206. E. A. Wright, AEC, Washington
207. Laboratory and University Division, AEC, ORO
208-222. Division of Technical Information Extension