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PREPARATION OF PLUTONIA-URANIA FUELS BY A SOL-GEL PROCESS

— Technical Report —

by
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ABSTRACT

The overall objectives of the Gel-Addition contract are to develop an economical process for producing particulate plutonia-urania fast reactor fuels by sol-gel and related processes and to demonstrate the process through the pilot plant stage. One of the specific objectives of this program is to obtain the irradiation data required to qualify vibratory compacted particulate fuel for LMFBR use. The selected fuels consist of 20% PuO_2-80% UO_2 in the form of spherical particles, such as those prepared by an ORNL sol-gel process, and angular particles, such as those prepared from crushed pellets.

In the sol-gel process for producing plutonia-urania fuels, separate sols of UO_2 and PuO_2 are prepared and blended in the appropriate ratio to obtain a mixed sol which is co-gelled into spherical particles and then fired to the mixed oxide. Nearly 2.2 kilograms of mixed-oxide microspheres were prepared with laboratory-scale equipment for the Gel-Addition irradiation program. The particles were prepared in two different diameter ranges—420 to 590 microns and less than 44 microns. In addition, two different uranium enrichments were used—0.26% and 20% ^{235}U.

The preparation of the sol-gel fuel and a complete description of the process used are summarized in this report. This program is supported by the U. S. Atomic Energy Commission under Contract No. AT(30-1)-3714.

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1. INTRODUCTION

Fuels for potential fast breeder reactor application are being developed, characterized, and tested in many laboratories. The major effort at this time is directed toward mixed PuO_2 - UO_2 in two physical forms—pellets and particles. To date, pelletized fuels have been studied far more thoroughly than have particulate fuels. However, numerous fuel pin failures seem to indicate that pelletized oxide fuels cannot provide a high enough burnup to make fast breeder reactors economically competitive with present thermal reactors. These pin failures may be caused by highly localized strains resulting from interaction between the fuel and cladding. Although the solution to the problem of fuel pin integrity involves understanding all phases of the interactions of fuel, cladding, and coolant, reducing the stress applied to the cladding by the fuel certainly would be an important advancement. In particulate fuels the concentration of voids per unit volume is at least 15%, compared with the normal 5 to 7% for high-density pellets. Since the average fuel temperature achieved in an LMFBR operation is not high enough to promote extensive sintering near the fuel-cladding interface, this zone of void space is essentially available for accommodation of swelling. Because of its potentially greater capacity to accommodate swelling, particulate fuel should exert fewer strains on cladding than pellet fuel. However, to date, sufficient data are not available to substantiate this potential advantage of particulate fuel.

In 1966 the AEC entered into the Gel-Addition contract with B&W to investigate the properties and irradiation characteristics of particulate fuels. Initially, the primary effort was directed toward demonstrating the feasibility of the Gel-Addition Process for preparing plutonia-urania fuels for fast reactor application. Basically this process involves contacting a single-component solid (UO_2) gel with an aqueous plutonium solution to form a mixed gel, which is then fired to the mixed oxide.

Material with a plutonium content that was sufficient for thermal fuels was readily prepared. However, numerous technical problems were encountered in attempting to prepare material with a plutonium content in the region of interest (15 to 25% Pu) for fast reactor fuels. Therefore, late in 1967 the primary emphasis of the Gel-Addition contract was shifted to fuel prepared by a sol-gel process, which involves preparing UO_2 and PuO_2 sols, blending the sols to obtain the desired Pu/U ratio, co-gelling the sols, and firing the gel to the mixed oxide. This report includes a detailed description of the sol-gel process for forming spherical mixed-oxide particles.

One of the specific objectives of the Gel-Addition contract is to obtain the irradiation data required to qualify vibratory-compacted particulate fuel for LMFBR use. Therefore, an irradiation testing program has been designed in which the performance of spherical particles prepared by a sol-gel process, angular particles prepared from crushed pellets, and pellets can be compared. This program is divided into three subtasks:

1. The time required for in-pile restructuring.
2. The manner in which sorbed gases are released.
3. Fuel performance in a fast neutron flux.

The exposures for the first two subtasks will be conducted in the BAWTR, and the EBR-II will be used for the third.

To date fuel has been prepared only for the irradiations under the first subtask, which were begun in late 1968. Included in this fuel order were nearly 2.2 kg of UO_2-20% PuO_2 sol-gel microspheres. The particles were in two different diameter ranges—420 to 590 microns and less than 44 microns—and contained two different uranium enrichments—0.26% and 20% ^{235}U. This material was prepared in three separate campaigns: The first was devoted to solving a number of process problems and preparing sufficient material for preliminary fabrication and irradiation testing. The second campaign involved the preparation of the spheres containing 20% PuO_2 in depleted UO_2. In the third campaign the spheres containing 20% PuO_2 in UO_2 enriched to 20% ^{235}U were prepared. The results from these three fuel preparation campaigns are summarized in this report.

2. RESULTS AND CONCLUSIONS

2.1. Preparation of UO_2 Sols

A total of 12.4 kg of uranium was converted in laboratory-scale equipment to stable UO_2 sol in 63 runs using a flow sheet based on the ORNL formate process. Three different ^{235}U contents were used—0.258, 19.68, and 93.16%. During these runs, three noteworthy problems arose:

1. Occasionally the reduction was allowed to proceed for too long.
2. A type 303 stainless steel stirring rod used in a few batches corroded severely in the region between the surface of the solution and the bottom of the bearing.
3. It was not possible to reduce the uranium in an enriched uranyl nitrate feed containing a uranium concentration of about 1 M.

However, the process was generally quite reliable when reasonable care was taken to minimize marked deviations from the flow sheet.

2.2. Preparation of PuO_2 Sols

A total of 1.4 kg of plutonium was converted to stable PuO_2 sol in 21 runs with laboratory-scale equipment using the ORNL precipitation-peptization flow sheet. It was shown that the conditions during the initial precipitation step must be rigidly controlled. The Pu(IV) feed must be less than 2 M in free acid, the ammonia precipitant must be less than 4 M, and the Pu(IV) feed rate must be slow (about 25 ml/min is satisfactory). If these conditions are not met, there is a strong tendency for the Pu(IV) to oxidize to Pu(VI) during the evaporation and/or thermal denitration step. Much time is required to prepare a stable PuO_2 sol after partial plutonium oxidation has occurred. In each of the final six batches, the conditions during the initial precipitation were rigidly controlled. No processing problems occurred during these runs, and the yield of plutonium as a stable sol was more than 95%.

2.3. Sol Blending

Mixed UO_2-20% PuO_2 sol was prepared for feed to the sphere-forming column by blending the appropriate quantities of UO_2 and PuO_2 sols. Over a period of seven days during the first run, the PuO_2 concentrated near the bottom of the container, even though the blended sol had been agitated continuously by a 2-inch magnetic stirring bar. This problem with sol segregation is thought to be caused by the use of a marginal-quality PuO_2 sol, in which there was a tendency for solids to settle, rather than to an inherent problem with the sol-gel process. Higher-quality PuO_2 sols were available during the latter part of this work. In addition, except for the first batch, the mixed sol was thoroughly agitated manually before any sol was withdrawn. The quality control results indicated that sol segregation did not occur after the first run.

2.4. Sphere Formation

About 1.4 kilograms of acceptable UO_2-20% PuO_2 spheres with a diameter of 420 to 590 microns were prepared in a 4-foot tapered glass column, and about 0.7 kilograms with a diameter of less than 44 microns were prepared by a stirred-pot technique. About 150 grams of mixed UO_2-PuO_2 sol-gel spheres were prepared routinely in an 8-hour day with the laboratory system by operating the column continuously and the stirred-pot on a batch basis. However, only about 50% of the input sol was recovered as acceptable mixed oxide microspheres.

With the laboratory-scale spheroidizing system, the mixed gel is exposed to air during a portion of the operation. This can lead to a product that is badly cracked and thus unacceptable. However, it was found that the amount of cracking can be limited by soaking the gel in concentrated NH_4OH for 15 to 30 minutes immediately after its removal from the column.

The mixed gel was fired by a carefully controlled cycle up to about 1250 C to form (U, 20% Pu)O_2 microspheres with a high density (>95% TD). After firing, the acceptable product for the Sphere-Pac process can be separated from the remaining material by screening it for size classification and then passing it over a roundometer which has a deflection from horizontal of less than five degrees to separate the rounds from the non-rounds.

2.5. Characterization of Microspheres

The average plutonium content of the microspheres prepared with depleted uranium was 19.6%. For the microspheres prepared with uranium enriched to 19.7% ^{235}U, the average plutonium content was 19.1%. The O/M ratio was measured as 1.985 for the coarse fraction and 1.975 for the fine fraction. The average moisture content was about 13 ppm for the coarse fraction and about 55 ppm for the fine fraction. The particle density of the coarse spheres was measured as about 96% TD. The sorbed gas content of the final product was in the region of 0.05 cc/g. The carbon and nitrogen contents each measured as about 12 ppm. About 6 ppm of chloride and 0.5 ppm of fluoride were detected. All of these results are well within the desired limits.

3. PREPARATION OF URANIA SOL

3.1. Process Selection

UO_2 sols can be prepared by either of the following general techniques:

> The precipitation of hydrous U(IV) oxide and its subsequent dispersion (or peptization).[1-5]
>
> The extraction of nitrate from an aqueous U(IV) solution containing less than the stoichiometric amount of nitrate by a water immiscible solution of a long-chain aliphatic amine.[2,3,6]

A precipitation-peptization technique was chosen for preparing UO_2 sols because, at the inception of this fuel preparation effort, it was more highly developed than solvent extraction techniques and more suitable to laboratory-scale operation. Of the several precipitation-peptization flow sheets available in the open literature, the ORNL formate method[1] was selected as the reference process for batch preparation of UO_2 sols because it was judged to be superior to the others.

Figure 3-1 is an outline of B&W's flow sheet for preparing UO_2 sols. The principal differences between the B&W and ORNL formate processes are that the B&W flow sheet calls for (1) a feed solution that is 1.0 $\underline{M}$ uranium rather than 0.5 $\underline{M}$ and (2) sol formation by placing the UO_2 filter cake in an ultrasonic bath rather than stirring and heating.

Other precipitation-peptization flow sheets for preparing UO_2 sols include the ORNL nitrate method,[1] an acid-deficient method,[2] and a chloride-stabilized method.[4] Each of these is similar to the method shown in Figure 3-1. The principal difference between the ORNL nitrate method and the selected flow sheet is that no formic acid is added to the uranous nitrate feed solution. As a result, it is difficult to prevent the oxidation of a large fraction of the U(IV) during processing. With the acid-deficient method, the NO_3^-/U mole ratio in the uranyl nitrate feed is about 2.0, compared with about 4.2 in the formate method. In addition, the hydrous oxide is washed completely free of electrolyte and then peptized by adding a controlled amount of electrolyte (HNO_3 and HCOOH). The acid-deficient flow sheet has been used principally for the engineering-scale preparation of urania sol. In the chloride-stabilized method, hydrous U(IV) oxide is precipitated from a uranous chloride solution. Less uranium oxidation occurs during sol preparation with this system than with the formate system. However, at the time of process selection, there was some concern that fuels prepared by this method could contain significant quantities of chloride and thus be incompatible with stainless steel fuel cladding.

3.2. Process Chemistry

The principal effort devoted to the preparation of UO_2 sols has been on the development of reliable engineering-scale processes, rather than on a thorough understanding of the basic chemistry. However, the data that are available do provide some insight into the phenomena taking place in preparing a UO_2 sol by the ORNL formate process and the properties of the sol.

Several chemical reactions apparently take place during the reduction step. It has been shown that ammonia is formed during the hydrogenation of solutions containing U(IV) and nitrate in the presence of 5% platinum-on-alumina catalyst.[5] However, there is no evidence of ammonia formation when nitric acid is treated under similar reaction conditions in the absence of uranium.[5] Therefore, U(IV) does play a role in the formation of ammonia during the reduction step, but the reaction mechanism is not clear. Since ammonia is formed during the reduction, it is probable that nitrite is also formed. The presence of nitrite in the reaction mixture is not desirable, because it results in virtually complete re-oxidation of the U(IV) in uranous nitrate solutions.[7] The destruction of nitrite by urea is well known and apparently occurs rapidly enough under the conditions of the reduction step to prevent nitrite from reacting with U(IV) to any significant extent.[8]

The precipitate formed by the addition of aqueous ammonia to the uranous nitrate solution has been shown by electron microscopy[9,10] to consist mainly of large, irregular-shaped aggregates of roughly spherical particles of hydrous UO_2. The primary particles are about 15 to 25

Å in diameter.[9] Electrolytes can be washed from the precipitate with distilled water. It has been shown[5] that a too-rapid washing results in inadequate removal of the nitrate ion and prevents the subsequent peptization of the hydrous UO_2. On the other hand, if the washing is too thorough, there will not be sufficient electrolyte present for peptization, and additional electrolyte must be added.[11] No technique for maintaining positive control of the electrolyte content of the hydrous UO_2 precipitate has been reported, but it is relatively easy to determine the necessary washing conditions by trial and error.

During the peptization step, the initially amorphous precipitate is converted to crystalline UO_2.[9,10] In addition, the conductivity of the aqueous phase surrounding the particles increases, indicating a loss of absorptive capacity by the solid phase for the electrolytes present.[12] From electron micrographs and electron diffraction patterns of a UO_2 sol prepared by the ORNL formate process, Hardy determined that the UO_2 was in the form of cubic crystallites with sides 10 to 20 Å long.[9,10] However, the crystallite size determined from x-ray line-broadening data is about a factor of five larger.[1] Based on turbidity and electron micrograph data,[9] the primary crystallites form aggregates which are about 800 Å in diameter and have a molecular weight of about 2×10^9. The conductivity of a stable sol is generally in the range of 2500 to 10,000 micromhos/cm,[12] and the apparent pH is generally in the range of 1.5 to 3.0.[1] About half of the conductivity can be attributed to the presence of free nitric acid.[12] The source of the remaining conductivity is not known.

Hardy has proposed a model for the physical and chemical constitution of the formate-containing sol particles.[9] According to this model, each crystallite contains 63 UO_2 molecules, of which 50 are in surface positions in normal face-centered cubic packing. Since chemical analyses have indicated the presence of 0.3 to 0.5 mole formate per mole uranium in the sol,[1] it was proposed that one formate ion bridges two surface uranium atoms. (This would correspond to a formate-to-uranium mole ratio of 0.40.) Thus the uranium is somewhat stabilized by coordination with formate ions and has less tendency to oxidize than in sols prepared by the ORNL nitrate method, in which no formate is added. There is about 0.08 to 0.18 mole nitrate per mole uranium in the sol.[1] By analogy with the particles in ThO_2 sols, Hardy assumes that the UO_2 crystallites have a positive surface charge. Thus, the nitrate ions may act as counter-ions.

3.2.1. Uranium Reduction

The most stable aqueous oxidation state of uranium is the hexavalent state. However, stable sols containing uranium solely as U(VI) are difficult to prepare because of the solubility of U(VI) in typical electrolytes used for peptization. In addition, the open literature contains very little information about preparing U(VI) sols. With uranium principally in the quadrivalent state, these problems are less severe. Therefore, the first step in the sol preparation involves reducing U(VI) to U(IV).

The U(VI) in a 0.8 to 1.3 $\underline{M}$ uranyl nitrate solution containing a nitrate-to-uranium mole ratio of 4.1 to 4.3 and a urea-to-uranium mole ratio of 0.5 is reduced to U(IV) with about 300 cc/min of free hydrogen at ambient temperature and pressure over 2.5 to 4.8 g of 5% platinum on Al_2O_3 catalyst per mole uranium. It was found that the catalyst obtained from Matheson, Coleman, and Bell resulted in shorter reduction times than that obtained from Engelhard Industries, Inc. It is not known whether the difference in activity is inherent to the nature of all the 5% platinum on Al_2O_3 catalyst prepared by each of these vendors or only to the nature of the particular batches used. The reduction is allowed to proceed until a ferrocyanide test for the presence of U(VI) gives a negative result. This test consists of treating an aliquot of the uranium solution with oxalate to precipitate the U(IV) and adding ferrocyanide to the supernate. If less than 99.9% of the U(VI) has been reduced, a brown precipitate forms.[13] The reduction time is highly dependent upon the mixing efficiency and, to some extent, on the mass of uranium reduced, the H_2 flow rate, and the quantity of catalyst used. In these runs the reduction time varied from about 3 to 14 hours. All operations following reduction are carried out under a nitrogen blanket to minimize re-oxidation to hexavalent uranium.

3.2.2. Catalyst Separation

The catalyst is readily separated from the mother liquor by filtration with a medium fritted glass filter. Over an extended period of use, it has been found that the catalyst activity decreases because of blockage of the surface by a small amount of black precipitate (probably uranous hydroxide).[14] The catalyst can be regenerated by washing with 1 to 2 M HNO_3 and then H_2O followed by air drying at 100 C.[15] However, in early sol-gel development work at B&W, it was found that this treatment was not always sufficient for complete regeneration. Therefore, during these runs the catalyst was rejected after each reduction.

3.2.3. Hydrous U(IV) Oxide Precipitation

Before precipitation, sufficient formic acid is added to obtain a formate-to-uranium mole ratio of 0.6 to 0.7. This is necessary to maintain a high U(IV) content in the precipitate.[16] The hydrous oxide is then precipitated with 3.0 M aqueous ammonia which contains 0.5 M hydrazine hydrate to ensure that there are no oxidants present and thus to minimize oxidation of U(IV) during precipitation. The precipitating solution is added to the uranous nitrate solution at a rate of about 5 ml/min until the apparent pH (as measured with a combination glass electrode) reaches a value of 7.5. To obtain a satisfactory and reproducible sol, it is necessary that the final pH during precipitation be carefully measured and closely controlled.

3.2.4. Filtration and Washing

The hydrous U(IV) oxide is readily filtered on Whatman No. 42 filter paper in a Büchner funnel. The filter cake is washed, in place, with demineralized water to remove excess electrolyte. Before it is used, the wash water is deaerated by boiling for about 15 minutes and then storing under nitrogen. A correct washing step is extremely important, since a filter cake that is either under-washed or over-washed will not yield a stable sol.[17] A satisfactory wash is obtained in the above-mentioned equipment with 30 to 40 ml of water per gram of uranium, provided the filter cake does not have gross cracks. Finally, the hydrous oxide is dried for 10 to 15 minutes by pulling nitrogen through it.

3.2.5. Sol Preparation

The washed and dried filter cake is transferred to a sealed flask and then peptized by placing the flask in a heated (60 to 65 C) ultrasonic bath overnight. The minimum time required for peptization has not been established, but it has been observed to be less than 6 hours. Because of its simplicity, the ultrasonic treatment for sol formation in a laboratory-scale operation is superior to stirring vigorously, as suggested in the ORNL flow sheet.[16] In the early sol-gel development work[18, 19] much difficulty was encountered in peptizing by the ORNL technique.

3.3. Apparatus Description

A laboratory-scale system (see Figure 3-2) was used in UO_2 sol preparation. Owing to the experimental nature of this system and the size of the fuel order, equipment selection was limited mainly to standard laboratory equipment. Thus it was possible to observe each step in the process visually and to make equipment modifications easily. In addition, the size of the equipment was restricted by space availability in the glove boxes, which were needed to maintain an inert atmosphere.

Uranium reduction (see section 3.2.1) takes place in a baffled, 2-liter reaction flask which is equipped with a four-neck head to accommodate the stirrer, gas dispersion tube, decanting dip tube and vent, and filling port (see Figure 3-3). Since the reaction flask is sealed and purged with nitrogen both before and after the reduction, a non-oxidizing atmosphere is maintained in the system without housing it in a glove box. Thus the potential hazard of using hydrogen in a confined glove box is eliminated.

After reduction, the catalyst is allowed to settle and the uranous nitrate solution is transferred into an inert-atmosphere glove box (see Figure 3-4) either by suction or by moving the entire reaction flask. Any suspended catalyst is removed by filtration through a medium-porosity glass filter. The solution is then transferred into a 4-liter beaker for precipitation. The appropriate quantity of formic acid to make the solution 0.6 $\underline{M}$ in HCOOH is added, and the beaker is jacked up to a fitted cover equipped with an inert gas purge, stirrer, pH electrode, and precipitant-addition line.

When precipitation is complete, the slurry is poured through Whatman No. 42 filter paper in a table-type Büchner funnel and washed in place. The cake is converted to a sol in a 500-ml freeze-drying flask suspended in an ultrasonic bath at about 60 C.

3.4. Experimental Results

Uranyl nitrate (UNH) solutions which were not enriched in ^{235}U were prepared from Fisher Certified Reagent Grade $UO_2(NO_3)_2 \cdot 6H_2O$ crystals, and UNH solutions enriched to 93.16% ^{235}U were prepared from UNH crystals obtained from Kerr-McGee Oil Industries, Inc. The 20% enriched material was prepared by isotopic dilution of fully enriched uranium, which was accomplished by mixing weighed quantities of enriched material as UNH solution with weighed solutions of reagent-grade UNH. The concentrations of both solutions were determined by coulometric analysis, using the standard analytical procedures available in our laboratories.

The isotopic dilution was performed with unusual care to guarantee a high degree of accuracy. Despite these precautions, the final isotopic analyses (see Table 3-1) indicated that the deviation from 20.00% was much larger than the expected errors in the work.

Table 3-1. Composition of Solutions Used in Isotopic Dilutions

Type of solution	^{235}U content, %	Uranium concentration, mg/g solution[a]
Non-enriched UNH stock	0.258 ± 0.009	206.5 ± 0.8
Non-enriched UNH stock	0.258 ± 0.009	199.7 ± 0.9
Enriched UNH stock	93.16 ± 0.08	214.8 ± 0.8
Enriched UNH feed (batches 102 - 108)	19.68 ± 0.02	207.4 ± 0.8
Enriched UNH feed (batches 109 - 112)	19.68 ± 0.02	205.5 ± 1.1

[a] Errors are for 95% confidence limits on the mean.

The preparation of the 20% enriched material could be considered as an isotopic dilution analysis check against coulometric titration, and the discrepancy indicated that there were unsuspected errors somewhere in the procedure. Because coulometric analysis has become an accepted standard, it was necessary to determine the origin of the errors. A careful recheck showed that the reagent-grade uranyl nitrate was not natural uranium as the supplier claimed, but actually depleted uranium (0.26% ^{235}U). The material had been taken as 0.71% ^{235}U for the isotopic dilution. A recalculation based on the correct isotopic analysis of the diluent uranium gave excellent correlation between the computed and measured ^{235}U content.

Uranium enriched to 20% ^{235}U was required for the finished fuel to produce an inpile linear heat rate near 20 kW/ft, rather than the 15 kW/ft rate available with natural uranium-20% plutonium mixtures. The difference in isotopic content between the target (20.00%) and actual (19.68%) values is of no importance in reactor performance, so the question of isotopic analysis is of interest only because of the analytical chemistry involved. No attempt was made to readjust the isotopic level.

A total of 63 UO_2 sol runs were made—51 with depleted uranium, 11 with uranium enriched to 19.68% ^{235}U, and one with uranium enriched to 93.16% ^{235}U. A total of 10.57 kg of depleted uranium, 1.742 kg of uranium enriched to 19.68% ^{235}U, and 53.7 g of uranium enriched to 93.16% ^{235}U were converted to stable, usable UO_2 sol during these runs. The composition of the stock UNH acid solutions is summarized in Table 3-2, and the run data from the sol preparation are summarized in Table 3-3.

Three noteworthy problems occurred during these runs. In batches 57, 66, 88, and 105 the reduction was allowed to proceed too long. (This has often been referred to as over-reduction.) As a result, the dark green U(IV) solution turned black. In earlier work[20] it had been shown that the pH of the over-reduced solutions was about 0.9, compared with a normal value of about 0.3 to 0.4. It has been shown[5] that some nitrate is reduced to ammonia during the catalytic reduction of uranium (in the presence of nitrate) by hydrogen, so it is not surprising that the pH of over-reduced solutions is relatively high. When over-reduction occurs, it is not possible to prepare a stable UO_2 sol with the usual flow sheet. Problems with over-reduction can apparently be eliminated through the use of oxidation-reduction electrodes (e.g., platinum electrode and a silver-silver chloride reference electrode) to monitor the potential, coupled with the automatic termination of the reaction at the appropriate time.[21]

Table 3-2. Composition of Stock Uranyl Nitrate Acid Solutions

Batch No.	Nitrate concentration, $\underline{M}$(a)	Uranium concentration, $\underline{M}$(a)	Nitrate/Uranium mole ratio(a)
51 - 56	5.34 ± 0.08	1.25 ± 0.10	4.27 ± 0.35
57 - 65	5.49 ± 0.08	1.29 ± 0.02	4.25 ± 0.10
66 - 76	5.36 ± 0.18	1.28 ± 0.02	4.19 ± 0.17
77 - 98	5.20 ± 0.04	1.25 ± 0.02	4.16 ± 0.06
99 - 101	5.26 ± 0.05	1.27 ± 0.01	4.14 ± 0.05
102 - 108(b)	5.48 ± 0.06	1.30 ± 0.01	4.22 ± 0.05
109 - 112(b)	5.49 ± 0.06	1.293 ± 0.006	4.25 ± 0.04
113(c)	≈4.25	≈1.0	≈4.25

(a) Errors are for 95% confidence limits on the mean.

(b) Contained 19.68 ± 0.02% ^{235}U.

(c) Contained 93.16 ± 0.08% ^{235}U.

Table 3-3. Data From Preparation of UO_2 Sols

Batch No.	Uranium reduced, g	Uranium concentration during reduction, M	Reduction time, h(a)
51	223.1	1.04	12.0
52(b)	223.1	1.04	9.0
53	223.1	1.04	9.0
54	223.1	1.04	NM
55	223.1	1.04	NM
56	111.6	1.04	NM
57(c)	230.2	1.08	<8.0
58	230.2	1.08	4.5
59	230.2	1.08	5.0
60	230.2	1.08	5.5
61	230.2	1.08	NM
62	230.2	1.08	8.5
63	230.2	1.08	8.0
64	230.2	1.08	8.5
65	144.3	1.08	10.0
66(c)	304.6	1.07	<16.0
67	304.6	1.07	14.0
68	304.6	1.07	7.7
69	304.6	1.07	6.3
70	304.6	1.07	7.5
71	304.6	1.07	NM
72	304.6	1.07	9.7
73	304.6	1.07	NM
74	304.6	1.07	NM
75	304.6	1.07	NM
76	198.0	1.07	NM
77	445.8	1.04	16.0
78(d)	445.8	1.04	>80
79	445.8	1.04	21.0
80	364.1	1.06	10.5
81	364.1	1.06	10.5
82	222.9	1.04	NM
83	364.1	1.06	8.5
84(e)	364.1	1.06	9.0
85	364.1	1.06	NM
86	364.1	1.06	8.5
87(f)	376.8	1.25	6.5
88(c)	376.8	1.25	<9.0
89(f)	376.8	1.25	8.0
90(f)	373.9	1.27	11.5
91(f)	373.9	1.27	NM
92	370.3	1.04	NM
93(g)	370.3	1.04	>16.0
94(g)	370.3	1.04	>34.5
95(g)	370.3	1.04	>19.5
96(g)	226.7	1.06	>9.5
97	226.7	1.06	3.8
98	226.7	1.06	4.0
99	370.3	1.04	8.0
100	370.3	1.04	7.5
101	370.1	1.04	6.0
102(h, i)	379.4	1.06	> 32
103(h, i)	379.4	1.06	> 31
104(i)	52.6	0.276	3.5
105(c, i)	157.9	0.830	< 5.0
106(i)	210.1	0.830	4.2
107(i)	252.0	0.826	3.5
108(i)	227.6	0.826	3.5
109(i)	249.9	0.822	3.5
110(i)	249.9	0.822	3.8
111(i)	249.9	0.822	3.8
112(i)	249.9	0.822	4.0
113(j)	53.7	0.54	1.2

(a) Wide variation partially due to equipment modifications at various times.

(b) Batch lost when a large excess of NH_4OH was added during the precipitation step.

(c) Over-reduction occurred.

(d) Catalyst had been used once previously; reduction did not proceed properly.

(e) Formic acid inadvertently omitted after reduction was completed.

(f) Stainless steel stirring rod used; sol rejected due to impurities.

(g) Reduction was incomplete due to malfunction of H_2-dispersing system.

(h) Reduction was not complete.

(i) Contained 19.68% ^{235}U.

(j) Contained 93.16% ^{235}U.

During the reduction of batches 87 - 91, a type 303 stainless steel stirring rod was used. Before the reduction of batch 91 was complete, the operator observed that the uranium solution was unusually dark in color. As a result, the entire reduction apparatus was disassembled and inspected. It was then discovered that the stirring rod was severely corroded in the region between the surface of the solution and the bottom of the bearing. The reason for the corrosion is not known at this time, but batches 87 - 91 were rejected because of the possibility of their having a high impurity level. All of the other UO_2 sol batches were prepared with a glass stirring rod.

This third problem occurred during the initial runs with UNH enriched to 20% ^{235}U. In batches 102 and 103, reduction was not complete using the normal conditions even after over 30 hours of running. However, when the UNH feed was diluted somewhat with deionized water, the reduction was complete in 3.5 - 4.0 hours. As far as is known, the only possible chemical difference between the enriched and natural UNH feed is the anion impurity level. (No anion specifications were included with the shipment of 93.16% enriched UNH from Kerr-McGee). So perhaps the reason for needing a more dilute UNH feed for preparing UO_2 sols enriched to 20% ^{235}U is related to anion impurities in the enriched UNH feed solution.

3.5. Conclusions

The flow sheet shown in Figure 3-1 for the preparation of UO_2 sol on a laboratory scale can be quite reliable if reasonable care is taken to minimize marked deviations from the stated conditions. Only two batches (102 and 103) of the 63 sol runs for this program failed for unknown reasons. Earlier experience with the flow sheet[22-26] indicated that most processing problems occur for these reasons:

1. The U(VI) is not reduced for the proper length of time; if the UNH solution is reduced either too long or not long enough, a stable sol cannot be prepared with this flow sheet.

2. A good inert atmosphere is not maintained above the U(IV) during processing and storage; this is extremely critical before the sol is formed; sols in storage have been stable with U(IV) content as low as 75%.[25-27]

3. The filter cake is not washed properly; improper washing resulted in a number of rejected sol batches in early work.[17]

No difficulty was encountered during sol storage as long as the sols were covered with an inert gas. On occasion, UO_2 sols have been stored for up to six months without any noticeable deterioration.

Figure 3-1. B&W Flow Sheet for the Preparation of UO_2 Sols

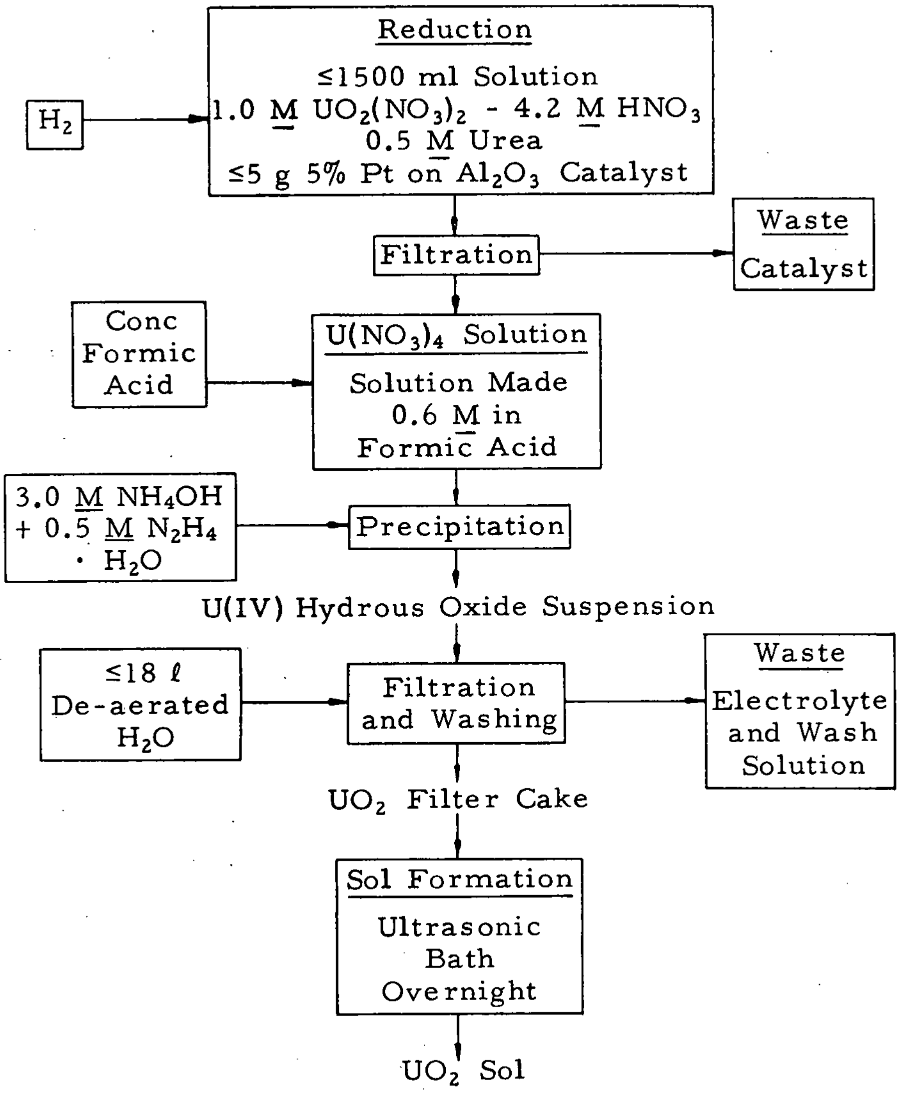


Figure 3-2. UO_2 Sol Preparation Facilities

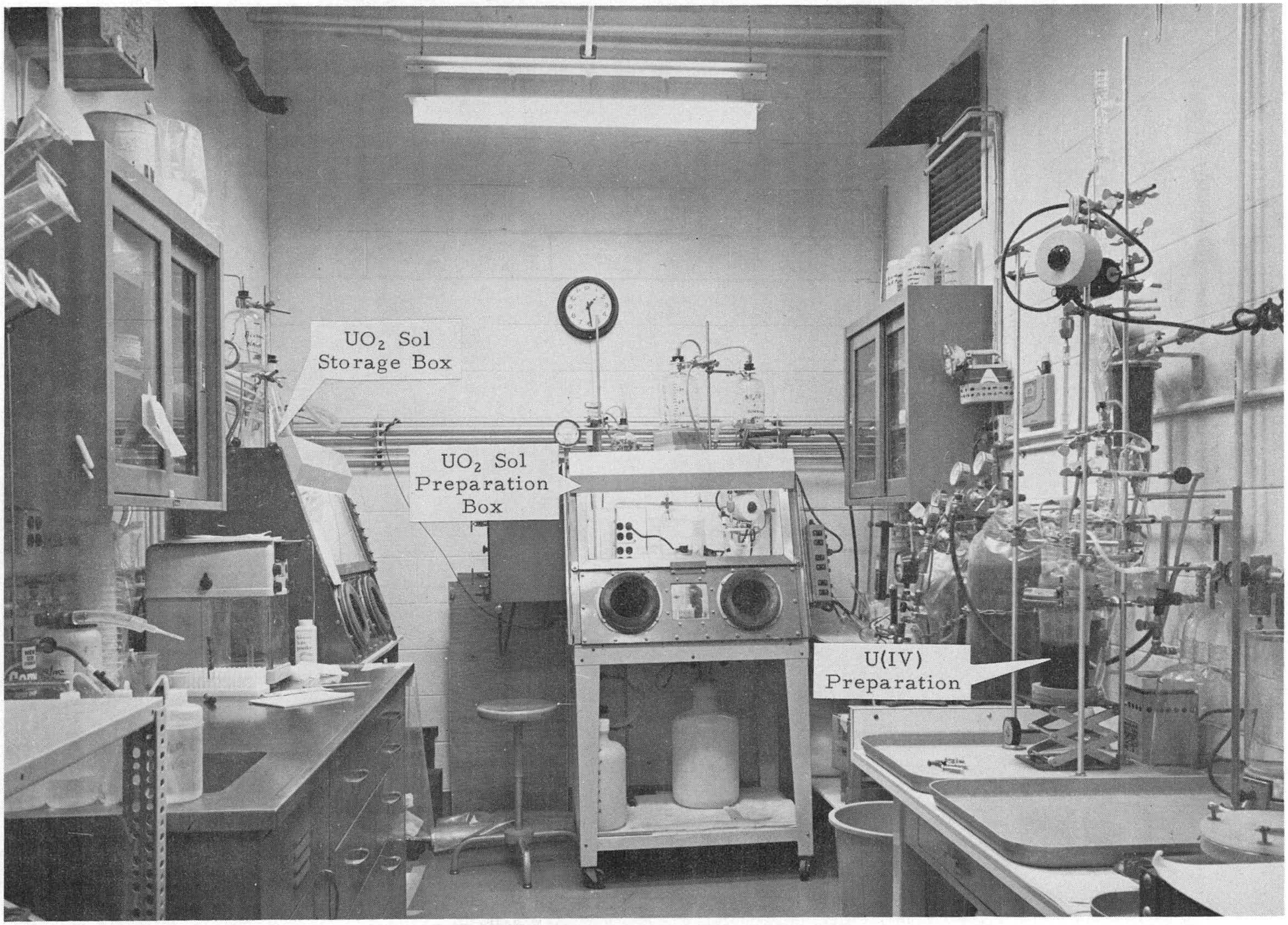


Figure 3-3. Uranyl Nitrate Reduction System

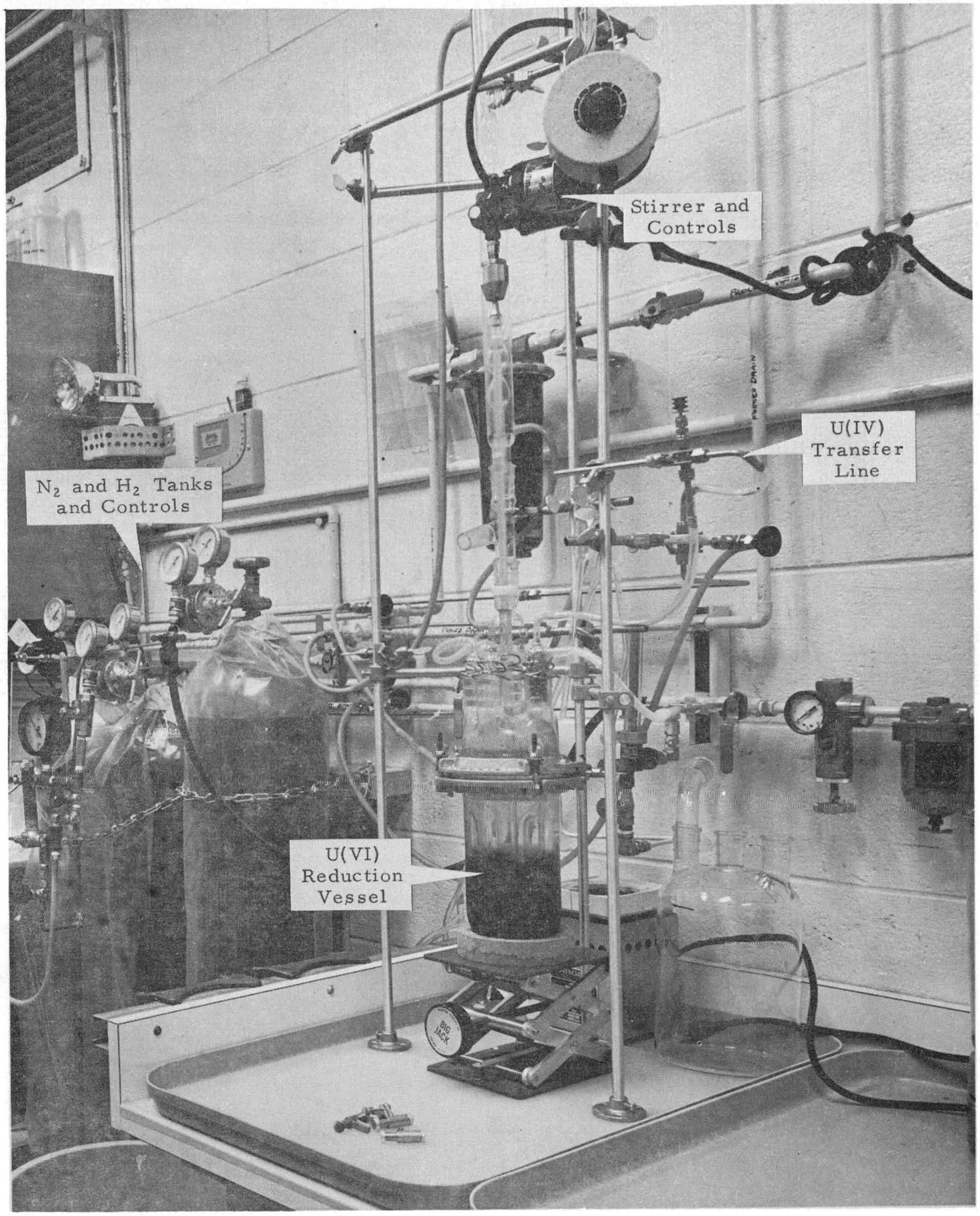
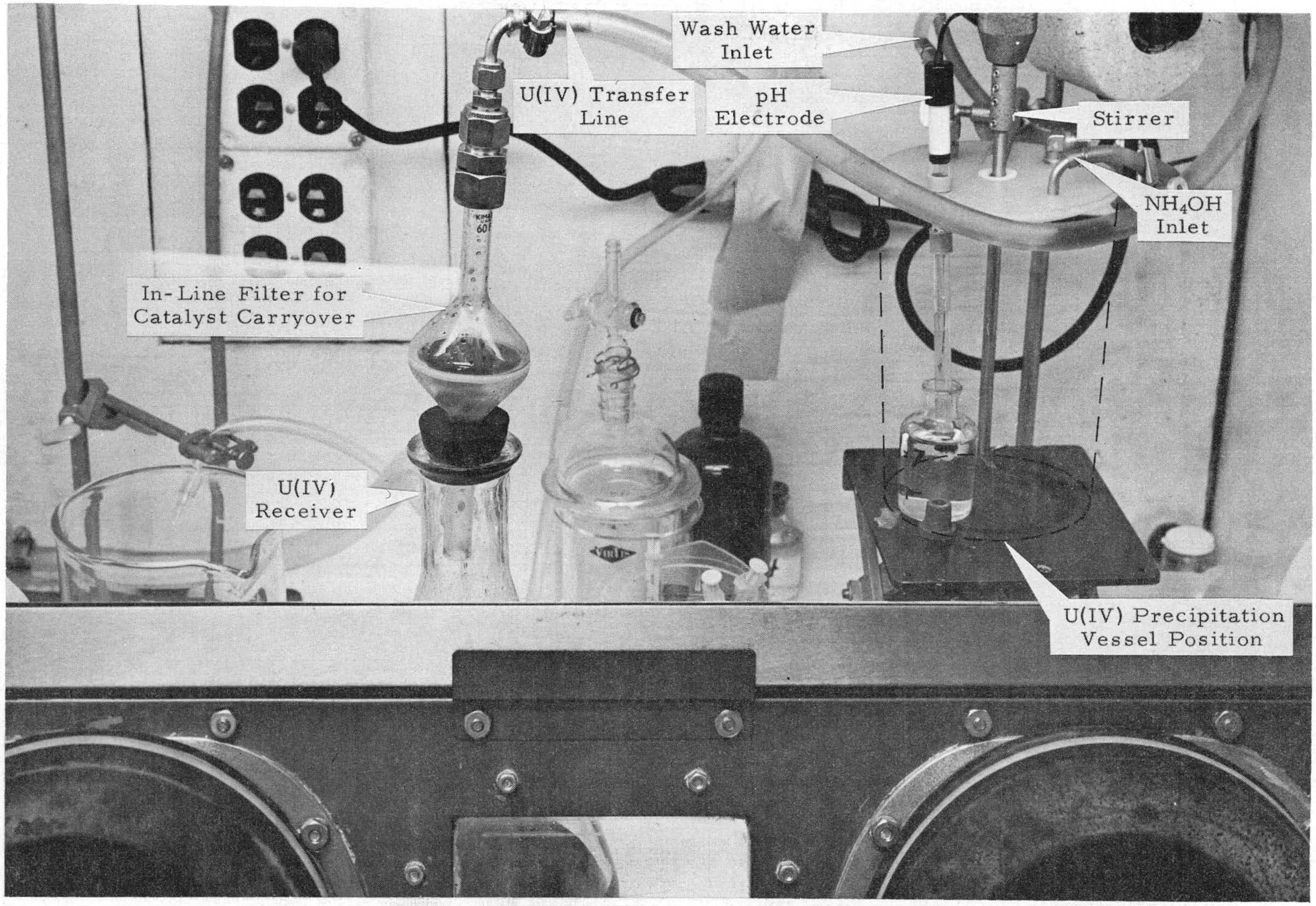


Figure 3-4. UO_2 Sol Preparation Box



4. PREPARATION OF PLUTONIA SOL

4.1. Process Selection

The PuO_2 sols were prepared in batches using the ORNL precipitation-peptization flow sheet.[28] At the time of process selection, this was the only reliable flow sheet available in the open literature. Figure 4-1 is an outline of this process. Added details are discussed in the following section.

4.2. Process Chemistry

During the precipitation step a substance called "Pu(IV) polymer" is formed. The distinctive absorption spectrum for Pu(IV) polymer has been shown to be the dominant spectral characteristic at all stages of the process.[28] However, it is very misleading to refer to the initial precipitate as the Pu(IV) polymer with no further identification. If the initial conditions are varied, there can be a number of differences in the behavior of the polymer in subsequent steps, even though the initial precipitate appears to be identical under most conditions (section 4.4 includes a discussion of these differences). Therefore, it is necessary to precipitate what could be called the "right kind" of Pu(IV) polymer. Unfortunately at this time, the properties of this polymer that distinguish it from other forms of Pu(IV) polymer are not known.

In order to peptize the digested precipitate, it is necessary to add at least one mole HNO_3 per mole plutonium.[28] However, if the nitrate level is then reduced by thermal decomposition to as low as 0.1 mole nitrate per mole plutonium, it is possible to form a stable sol by merely adding water. It has been shown that during baking, there is an increase of the crystallite size from about 20 to about 90 Å, as well as aggregation of crystallites.[28] Apparently the preparation of PuO_2 sols with low nitrate concentrations is strongly dependent on the crystallite size and/or the aggregate size.

4.2.1. Plutonium Precipitation

Before precipitation, the free nitric acid in the $Pu(NO_3)_4$ feed is adjusted to 1.0 $\underline{M}$ by adding the appropriate quantity of 0.5 $\underline{M}$ HNO_3. It should be noted that 0.5 $\underline{M}$ HNO_3, rather than water, is used to adjust the acid strength of the feed to prevent premature hydrolyzation of Pu(IV). The adjusted $Pu(NO_3)_4$ feed is then added at 25 to 30 ml/min to moderately agitated 4.0 $\underline{M}$ NH_4OH to precipitate hydrous Pu(IV) oxide. The total quantity of 4 $\underline{M}$ NH_4OH used is such that it is twice the calculated stoichiometric quantity needed to neutralize all the free nitric acid in the feed. It is extremely important to keep the free acid strength of the $Pu(NO_3)_4$ feed and the concentration of the NH_4OH at low values. Otherwise, there is a strong tendency for the Pu(IV) in the hydrous oxide to partially oxidize to Pu(VI) during ensuing steps (probably during evaporation and/or denitration), and the formation of a stable PuO_2 sol will be nearly impossible.[29] This oxidation is apparently no problem with feed solutions containing free $HNO_3 < 2$ $\underline{M}$ and $NH_4OH < 4$ $\underline{M}$.[28]

4.2.2. Electrolyte Removal

The hydrous Pu(IV) oxide precipitate is separated from the precipitation mixture by filtration on a Whatman No. 42 filter paper. The excess electrolyte cannot be readily removed by washing the precipitate in place; so the precipitate is placed in a beaker, 1 to 2 liters of demineralized H_2O are added, the mixture is vigorously stirred for at least 15 minutes, and the precipitate is recovered by filtration. This washing procedure is repeated until the pH of the effluent is less than 7.5. Three to five washes are usually sufficient. In the early batches more than five washes were required. However, in these runs the free acid and ammonia molarities in the feed solutions were too high, and a large amount of the Pu(IV) oxidized to Pu(VI) during processing.[30] In addition, the volume of the filter cake was only about half as much as in later runs. Thus it appears that high acid and/or ammonia concentrations during the initial precipitation result in the preparation of a form of hydrated Pu(IV) oxide that can be readily oxidized during the drying procedure and/or thermal denitration and which cannot be easily washed free of electrolyte.

4.2.3. Digestion

The washed precipitate is digested by refluxing in water for about 2 hours. This step results in more stable and more reproducible sols than can be obtained without digestion.[28]

4.2.4. Peptization

Sufficient 1 M HNO_3 is added to the aged precipitate to increase the NO_3^-/Pu mole ratio to about 2. This mixture is then digested at about 90 C for 1 to 2 hours or until the precipitate peptizes. The occurrence of peptization is readily apparent, because the slurry changes color from a light, milky green to a translucent, emerald green. If peptization does not occur within 2 hours, additional 1 M HNO_3 is added to increase the NO_3^-/Pu mole ratio by about 0.25, and digestion is continued. With a few batches, it was necessary to add even more nitric acid to obtain a stable sol. It should be noted that if the hydrous Pu(IV) oxide precipitate is allowed to dry during any previous step, peptization will not occur readily. It should also be noted that HNO_3 concentrations of greater than 1 M are avoided in order to minimize any tendency for the Pu(IV) polymer to depolymerize during peptization.

4.2.5. Denitration

The plutonium sol produced through nitrate addition is a stable colloidal dispersion. However, the high nitrate levels render it unsuitable for fuel particle preparation.[28] Therefore, the nitrate concentration is lowered by evaporating the sol to dryness and then thermally denitrating (baking) the dried gel. During the drying operation, the temperature of the system must be limited to minimize the tendency for the Pu(IV) polymer to depolymerize. This is especially important when the system is near dryness, since the HNO_3 becomes concentrated.

After drying, the lustrous black gel is baked until the NO_3^-/Pu mole ratio is between 0.1 and 0.2. The mole ratio should be below about 0.2 to minimize problems with fuel particle preparation and must be above about 0.1 to form a stable colloidal suspension. It should be noted that nitrate removal is a function of temperature and time. Laboratory results[31] relating temperature and time to the removal of NO_3^- show that at 200 C nearly 20 hours are required to obtain a NO_3^-/Pu mole ratio of 0.1, whereas at 250 C only about 2 hours are required, and at 300 C about 15 minutes are required. Thus, since it is extremely important to keep the NO_3^-/Pu mole ratio above 0.1 and the required baking time is strongly dependent on the baking temperature, either the dried gel must be stirred so that none of the powder can remain on a hot spot for several minutes, or the thermal denitrator must be constructed so that very even heating can be obtained.

The NO_3^-/Pu mole ratio can be rapidly determined periodically during the baking operation by removing a precise amount of dried gel (about 0.5 g), adding a few ml of H_2O to peptize, and titrating with 0.1 <u>M</u> NaOH to pH 9. Then, by assuming that the dried gel contains 85 wt % Pu and that the milliequivalents of base required are equal to the milliequivalents of nitrate present, the NO_3^-/Pu mole ratio can be calculated. The values obtained by this technique agree reasonably well with NO_3^- determination by the Kjeldahl method.[32]

4.2.6. Redispersion

The final low-nitrate PuO_2 sol is prepared by redispersing the denitrated powder in water and concentrating to about 1 M plutonium. The sol is then allowed to stand for one day, and any solids which have separated from the sol are removed by decantation.

In a number of the early runs in this program stable sols could not be formed through water addition. Instead, a clear red-brown liquid layer containing Pu(VI) separated from the solids. To remove the Pu(VI), it was necessary to slurry the powder a number of times with H_2O, allow it to settle, and decant the supernate containing Pu(VI). This decreased the sol yield and increased the process time to unacceptable levels. A more complete discussion of this problem is included in section 4.4. At this point it is important only to recognize that a stable PuO_2 sol can be prepared even after it is discovered that ionic Pu(VI) has been inadvertently formed, provided the Pu(VI) is removed.

4.3. Apparatus Description

The PuO_2 sol was prepared in a laboratory-scale system. Like the UO_2 sol preparation process, the equipment for PuO_2 sols was restricted to standard laboratory equipment, and equipment size was limited by the space available in the glove box.

Precipitation takes place in an 8-liter stainless steel beaker which is equipped with a variable-speed stirring motor and a 500-ml buret for adding the $Pu(NO_3)_4$ feed (see Figure 4-2). After precipitation is complete, the mixture is filtered through Whatman No. 42 filter paper in a Büchner funnel, and the filtrate is collected in a 2-liter flask for pH measurement. The filter cake is then transferred back into the 8-liter stainless steel beaker for washing. All of the filtrate is stored in a closed 18-liter polyethylene tank during the run to minimize ammonia buildup in the glove box atmosphere.

The washed filter cake is digested in a 3-liter distilling flask equipped with a reflux condenser and a heating mantle (see Figure 4-3). The digested slurry is then returned to the stainless steel beaker for peptization.

The high-nitrate sol is transferred to the distilling flask and evaporated to dryness. The dried powder is denitrated in a 4-liter stainless steel beaker on a sand bath. The beaker is large enough so that the powder forms a thin layer on its bottom. In addition, there is an insulated cover on the beaker. Thus, with periodic mixing, it is possible to maintain relatively uniform heating of the powder.

4.4. Experimental Results

Plutonium nitrate solutions were obtained from Atlantic Richfield Company (ARHCO). These were of high chemical purity and had a plutonium content of about 200 to 260 g/ℓ and a free acid molarity of about 3.0 to 6.5. All other chemicals used during processing were reagent grade.

A total of 21 PuO_2 sol runs were made; Table 4-1 summarizes the run data. In the early runs, each batch of powder was divided into smaller sub-batches during the thermal denitration step, so that even if one sub-batch was excessively baked, a reasonable sol yield would still be possible. However, with constant vigilance and frequent determination of the NO_3^-/Pu mole ratio, it was possible to avoid any problems due to excessive baking. As experience with this flow sheet was gained, the time required for denitration was reduced considerably.

Table 4-1. Summary of Batch Preparation of Pu(IV) Sols

	Pu feed solution										
Batch No.	Pu, g/ℓ	Free acid, M	Pu input, g	4 M NH_4OH, ℓ	No. of washes	Vol H_2O per wash, ℓ	NO_3^-/Pu mole ratio to peptize	Baking time, h[a]	Final NO_3^-/Pu mole ratio[a]	Yield of denitrated powder, g	Pu recovered as sol, %[b]
1	186.8	4.41	100	1.54[c]	13	1.0	1.90	11.5	0.15	28.1	24
								16.5	0.15		
								15.5	0.15		
2	186.8	4.41	102	1.35[c]	4	1.0	2.22	6	0.25	121.9	102
								3.5	0.20		
3	249.9	4.41	110	1.02[c]	9	1.0	1.99	2.75[d]	NM	0[d]	0[d]
								2.75[d]	NM		
4	240.1	6.3	109	1.33[c]	8	1.0	2.27	4	0.25	25.5[e]	20[e]
								3.5	0.25		
								3.5	0.25		
5	240.1	6.3	101	1.23[c]	8	1.5	1.88	3	0.14	70[e]	59[e]
								4	0.11		
								2	0.17		
6	120	3.6	101	1.28[f]	7	3.0	1.99	6	0.18	71[e]	60[e]
7	120	3.6	1.01	1.28[f]	12	2.0	2.50	8	0.11	76.3[e]	64[e]
								8	0.16		
10	29.5	1.0	100.9	11.3	13	2.0	1.54	5.7	0.15	60[e]	51[e]
								6.0	0.18		
11	55.6	1.0	98.7	2.5	5	1.0	1.84	7.0	0.15	106	91
12	55.9	1.0	99.1	2.5	5	1.0	1.83	4.0	0.19	1.08	93
13	55.7	1.0	98.9	2.5	5	1.0	1.84	1.2	0.09	109	94
14	56.2	1.0	197.5	5.0	3	2.0	2.63	3.0[g]	0.70[g]	0[g]	0[g]
15	56.5	1.0	100.3	2.5	3	1.5	2.33	2.0[g]	1.0[g]	0[g]	0[g]
16	55.7	1.0	98.9	2.5	4	1.5	2.02	3.0	0.09	105	91
17	55.7	1.0	98.8	2.5	5	1.5	2.06	2.0	0.12	110	95
18	55.4	1.0	99.2	2.5	5	1.5	1.87	1.0	0.15	119	101
19	51.6	1.0	99.1	2.5	5	1.5	1.87	0.6	0.07	105	99
20	57.2	1.0	76.3	1.9	5	1.0	2.57	0.5	0.15	89	99
21	54.7	1.0	131	3.1	4	2.0	1.85	0.6	0.15	147	95
22	56.2	1.0	99.5	2.5	5	1.5	1.87	0.2	0.15	112.6	96
23	56.2	1.0	99.5	2.5	5	1.5	1.87	0.3	0.15	76.5[h]	65[h]

---

[a] Initial batches were divided into smaller sub-batches during thermal denitration.

[b] Assuming denitrated powder is 85 wt % plutonium.

[c] Concentrated NH_4OH used.

[d] Between 2.5 and 2.75 hours, color of powder changed from shiny black to dull green; upon resuspending, Pu(VI) observed and batch discarded.

[e] Yield reduced because of Pu(VI) formation.

[f] 8 M NH_4OH used.

[g] Baking discontinued because powder would not resuspend.

[h] Yield reduced because of in-box spill during processing.

The principal problem during these runs was the formation of Pu(VI). As pointed out in section 4.2.1, the formation of Pu(VI) can be suppressed by reducing the acid content of the Pu(IV) feed to ≤2 M and reducing the initial concentration of the precipitating solution to ≤4 M aqueous ammonia. However, this information was not available before the initial seven runs were completed, and the acid and ammonia concentrations were well above the desired levels during these early runs. There was no Pu(VI) formation in the first two batches, even though they were prepared with high acid and base concentrations. The reason for the lack of Pu(VI) formation in batches 1 and 2 is not known, but the rate of $Pu(NO_3)_4$ addition in the initial precipitation step was much slower than in the other batches. So perhaps the type of PuO_2 polymer formed during a slow precipitation at high acid and base concentrations is as resistant to oxidation as the polymer formed at low acid and base levels.

The formation of Pu(VI) apparently occurs during evaporation of the high-nitrate PuO_2 sol and/or the thermal denitration step, because Pu(VI) is not observed until after water is added to the denitrated powder to form the final PuO_2 sol. However, several differences have been noted in the behavior and the appearance of the material throughout the processing when lower acid and base concentrations are used:

1. The aqueous Pu(IV) oxide precipitate is a much darker green color.
2. The volume of the filter cake is nearly twice as large (about 0.9 ℓ for a 100-g plutonium batch).
3. Fewer washes are required before the pH of the effluent is below 7.5.
4. The precipitate peptizes more rapidly.

In addition, the PuO_2 sol can be made more concentrated.

In batch 10 the precipitate was washed 13 times until the effluent pH reached 7.9 (compared with the usual value of 7.5). In addition, some Pu(VI) was observed during the first attempt to suspend the denitrated powder, and the PuO_2 settled out. After decanting the supernate, the sol formed properly; no additional Pu(VI) was observed. One possible explanation for the large number of washings is the fact that some NH_3 was present in the glove box atmosphere. Thus, enough ammonia could have dissolved in the water during the washing procedure to raise the pH above 7.5 before filtering. Although the reason for Pu(VI) formation in this case is not clear, the same effect was observed on a previous occasion when washing, peptization, and denitration were carried out in the presence of gaseous ammonia.[33] During the following 13 runs, ammonia was excluded from the box atmosphere, and neither an excessive amount of washing nor Pu(VI) formation was encountered.

In batches 14 and 15, the partially denitrated powder would not peptize upon water addition. Normally, during the initial precipitation, Pu(IV) is added to the ammonia at a rate of 25 to 30 ml/min. However, owing to an equipment malfunction during each of these two runs, plutonium addition rates in excess of 100 ml/min were obtained for a short period of time. Three other differences from the normal operating conditions were also noted:

1. Fewer washings were required.
2. A larger quantity of HNO_3 and a longer period of time were required to peptize the filter cake.
3. During the evaporation to dryness, a large quantity of the precipitated solids turned from black to green before all of the sol was dry.

These observations indicate that an undesirable form of the hydrous Pu(IV) oxide is prepared if the rate of precipitation is too rapid.

In each of the last six batches, the conditions during the initial precipitation step were rigidly controlled, and no problems were encountered. Thus it seems that the successful preparation of stable PuO_2 sols by the precipitation-peptization flow sheet depends strongly on having the proper conditions for the preparation of the hydrated Pu(IV) oxide.

The amount of plutonium recovered as sol during a normal run with the flow sheet is in excess of 90%. The low yield in batch 1 was probably due to small losses during each of the many transfers and filtrations and to the large number of samples taken for NO_3^-/Pu determination during the baking. The excessive number of washes was probably due to inadequate mixing during each wash. The low yield in batch 23 was caused by an in-box spill during processing.

4.5. Conclusions

The flow sheet shown in Figure 4-1 can be used on a laboratory scale for the preparation of stable PuO_2 sol. It has been shown that it is imperative that the initial precipitation be performed under the proper conditions; otherwise the type of polymer formed will not readily yield a satisfactory sol. Although it is not necessarily obvious when a process error has been made during precipitation, often there are enough differences in the way the material behaves in subsequent steps to indicate that there has been an error.

The other critical step in the flow sheet is thermal denitration. It is quite difficult to bake batches as large as 100 grams properly with the equipment shown in Figure 4-3. Therefore, an engineered system based on an ORNL design[28] has been built for future work (see Figure 4-4). This thermal denitrator allows independent control of the temperatures of the top and bottom surfaces and thus has the capability of providing very uniform heating.

Figure 4-1. Flow Sheet for the Preparation of PuO_2 Sols

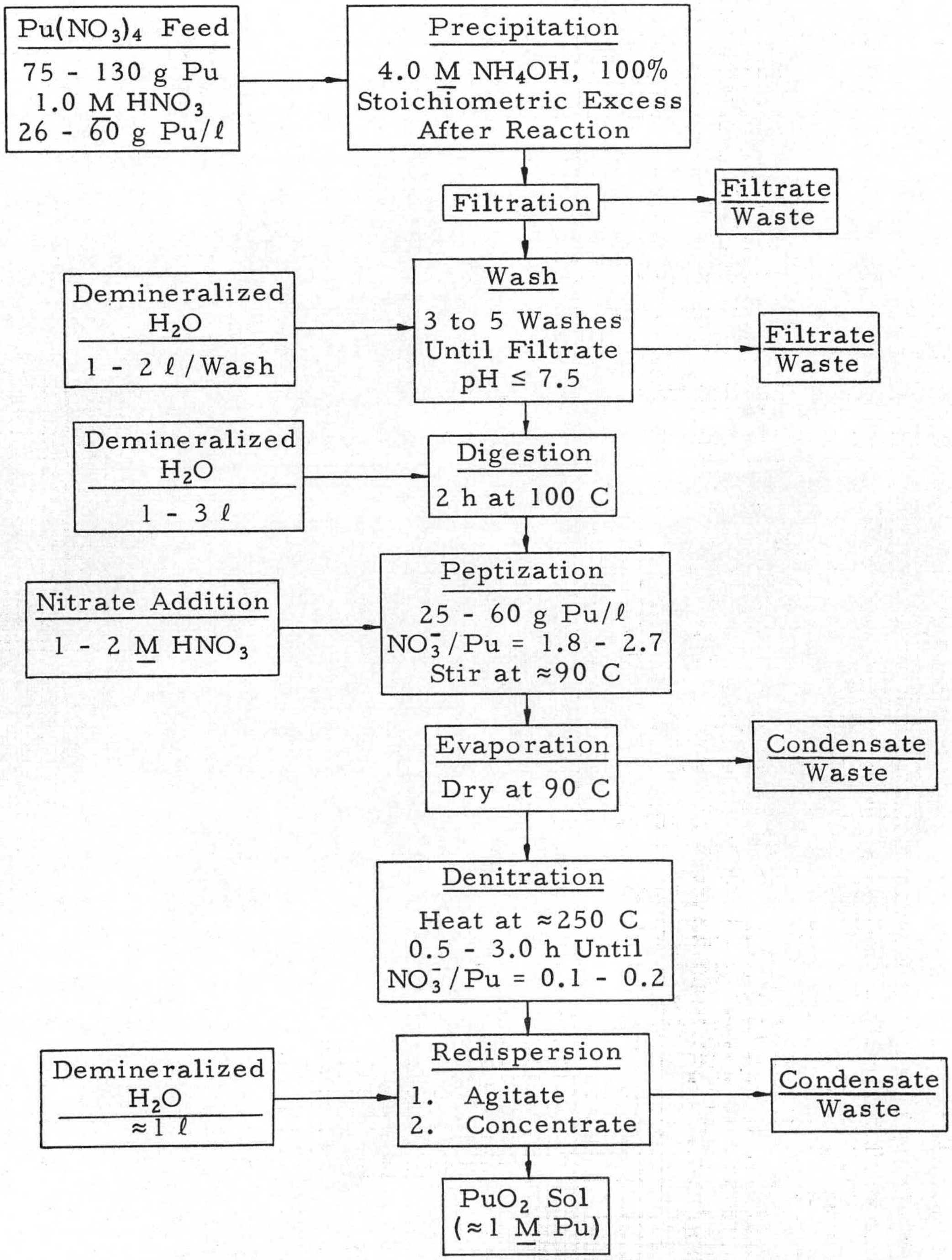


Figure 4-2. Pu(IV) Precipitation Equipment

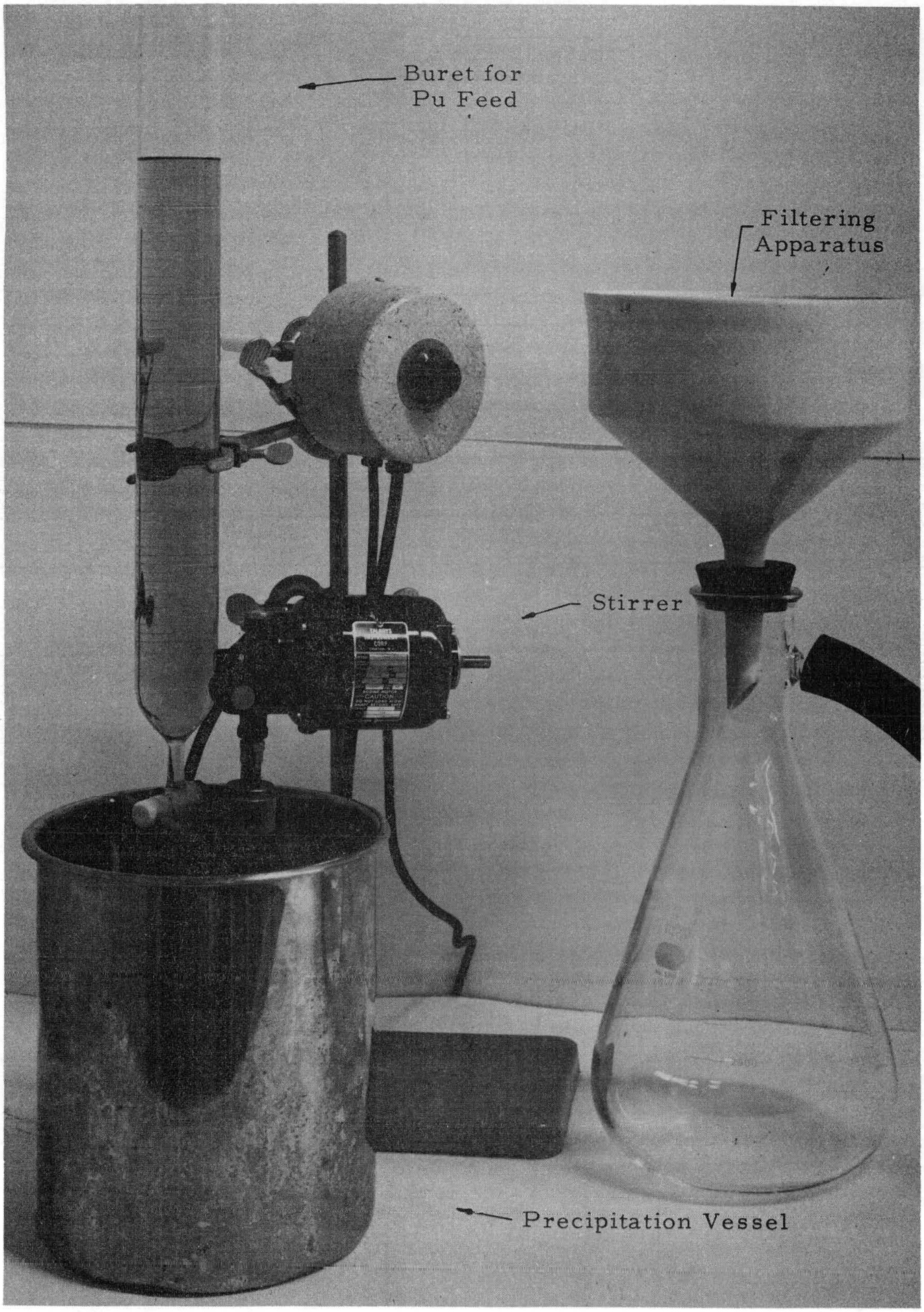


Figure 4-3. PuO_2 Sol Preparation Equipment

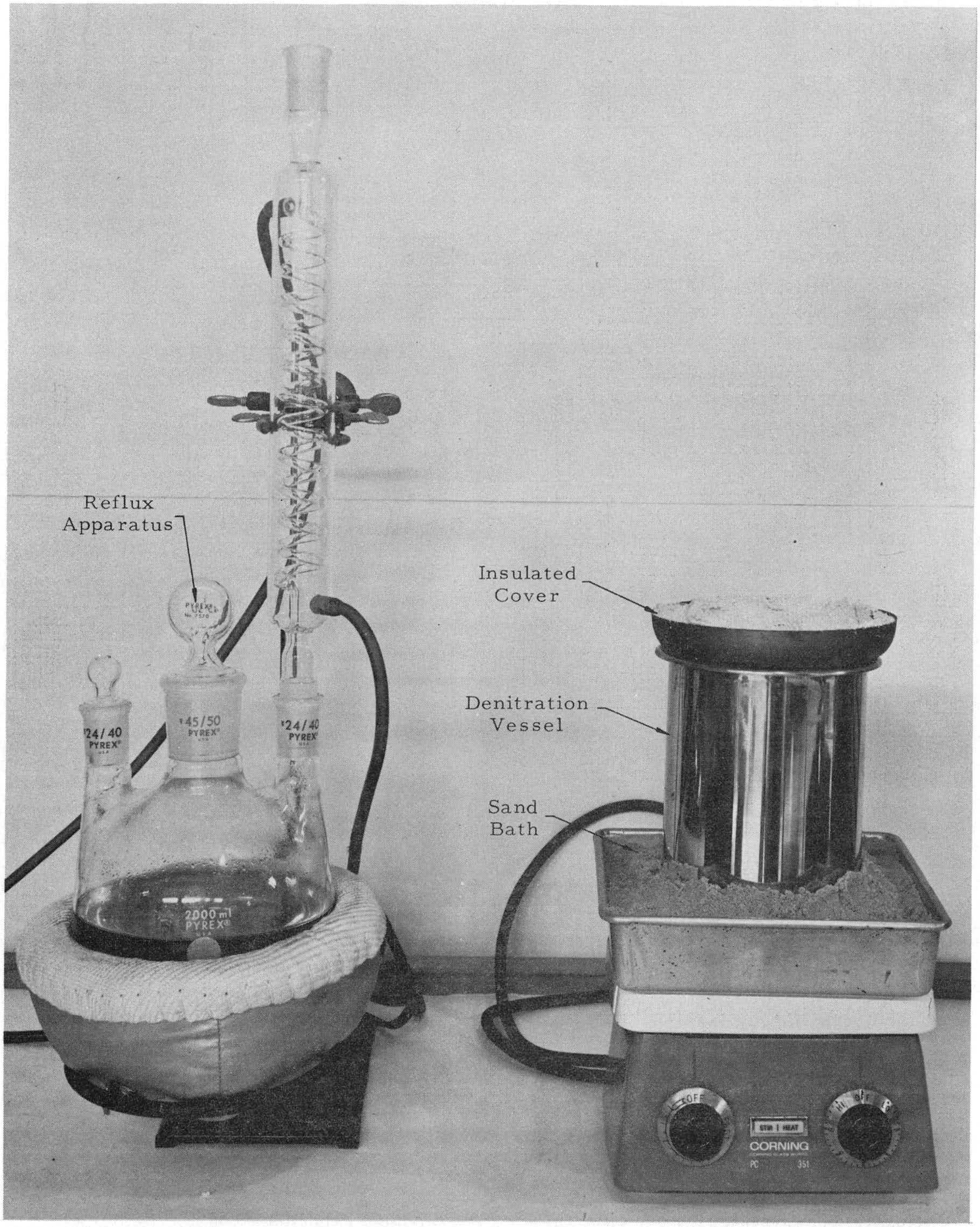
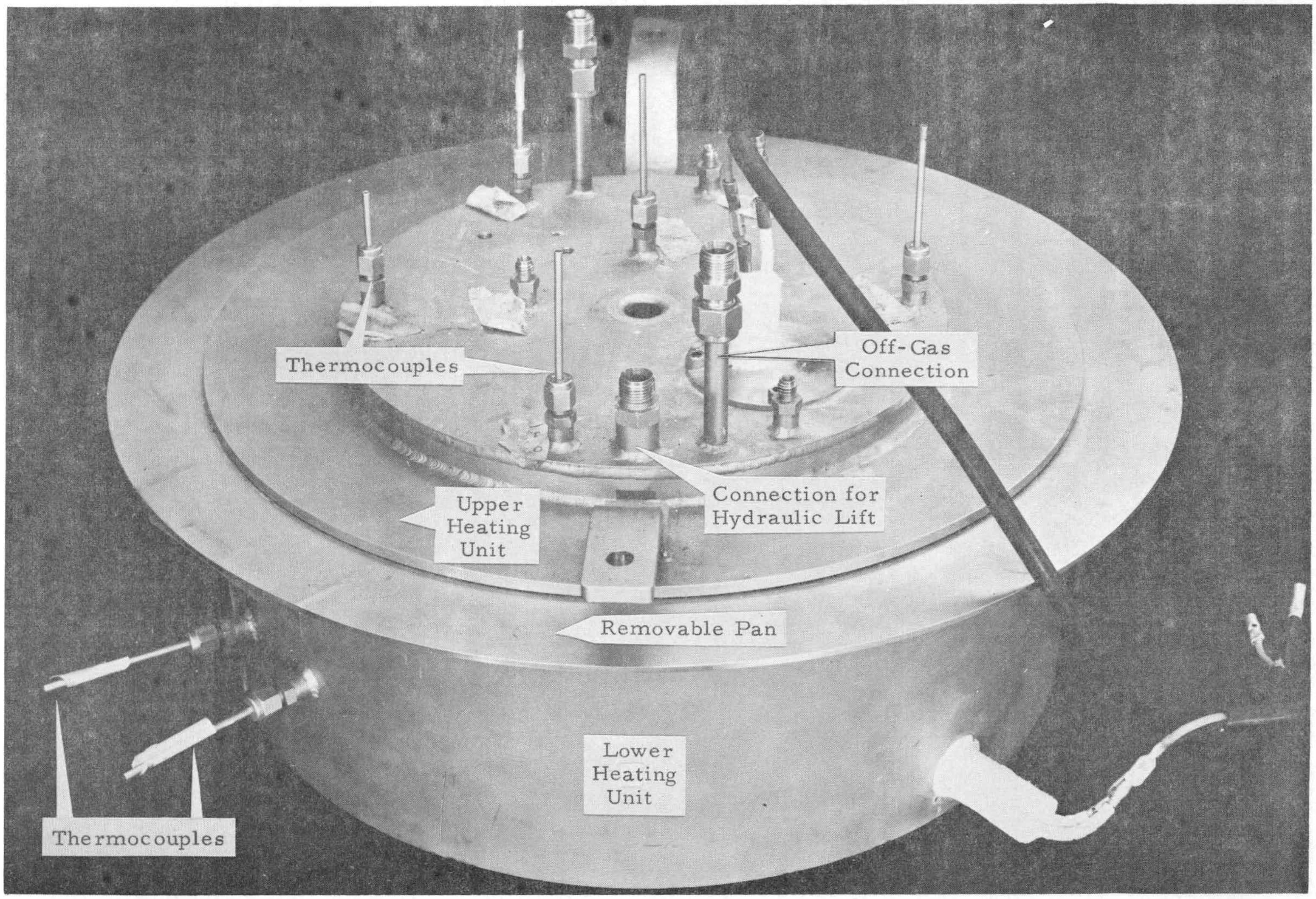


Figure 4-4. System for Thermal Denitration of PuO_2 Sols



5. SOL BLENDING

In an effort to have a sol feed with uniform properties and to minimize the analytical requirements, several batches of a given type of sol were blended. The procedure involved pouring each batch into a container which was then closed tightly and vigorously agitated manually for 3 to 5 minutes. Next, each sol blend was analyzed for its wt % of metal. On the basis of these analyses the quantity of each sol necessary to prepare a UO_2-20% PuO_2 sol was calculated. Then, under an N_2 atmosphere, the appropriate quantity of UO_2 sol was weighed into a glass container which could be closed tightly. After this container was transferred to the sphere-preparation box (air atmosphere), a pre-weighed amount of PuO_2 sol was added quantitatively, and the container was thoroughly purged with argon, closed tightly, and manually agitated for 5 minutes.

During the first of the three sphere-forming campaigns, a 2-inch magnetic stirring bar was placed in the sol container to provide continuous agitation, and a 1/2-inch layer of kerosene was carefully poured on top of the mixed sol to protect the UO_2 from air oxidation. However, the quality control analyses showed that the PuO_2 sol slowly became concentrated near the bottom of the container during the first 7 days of operation. This indicated that the PuO_2 sol contained particles that were large enough to settle over an extended period of time and that a magnetic stirrer cannot provide adequate axial mixing if there is any tendency for sol segregation to occur. Therefore, in the remainder of the first sphere-forming run, the stock sol blend was manually agitated for 3 to 5 minutes just before each withdrawal, and the sol container was continuously purged with argon to minimize the oxidation of U(IV). A sample was withdrawn from every third or fourth sphere batch for analysis. The results from this quality control are summarized in Table 5-1. It should be noted that since only a single determination was made for each sample, the range of Pu/(Pu + U) values and the average deviations from the means are consistent with the accuracy of these measurements. Therefore, the modified procedure described above was used throughout the last two sphere-forming campaigns. From the data in Table 5-1, it is apparent that no measurable sol segregation occurred after the initial problem.

Table 5-1. Quality Control Results

	No. of samples	Pu/Pu + U, % Range of values	Mean value[a]
1st campaign (2nd half)	17	18.3 - 21.4	19.7 ± 0.75
2nd campaign	44	17.4 - 21.9	19.5 ± 0.56
3rd campaign	12	18.4 - 19.7	19.1 ± 0.38

(a)Errors listed are the average deviation from the mean value.

Since close control of the fissile content in nuclear fuels is of prime importance, sol segregation cannot be tolerated. If segregation occurs due to an inherent incompatibility of PuO_2 and UO_2 sols, it would be highly questionable whether the sol-gel process could be seriously considered as a potential nuclear fuel preparation method. However, the segregation observed in this work appears to be related principally to the formation of PuO_2 particles which are non-colloidal in size. Three observations tend to support this conclusion:

1. The first seven batches of PuO_2 sol were a light, milky green in color, whereas the others were a translucent, emerald green. This indicates that the colloidal particles in the early runs (when the segregation problem occurred) were larger than those in the later runs.

2. If a freshly prepared PuO_2 sol is allowed to stand for a day or longer, a small quantity of solid particles settles out. This is probably due to nonuniform baking and thus perhaps to a NO_3^-/Pu mole

ratio in a portion of the powder which is too low to allow peptization. In most runs the solids were removed by decanting the stable PuO_2 sol; however, several batches had been used before the problem of settling was recognized.

3. The plutonium content of a grab sample of spheres from early in the initial run was measured at about 27%, whereas the plutonium content of both the mixed sol and the spheres on the day the segregation problem was discovered was measured at only about 8%. Since the mixed sol was being removed from the bottom of its container, it is apparent that PuO_2 rather than UO_2 was settling out of the sol.

From this work it appears that segregation of PuO_2 from UO_2 in a mixed sol prepared by the method discussed earlier poses no serious problem in fuel preparation, provided it is recognized that the problem can occur and that appropriate precautions are exercised. Presumably, current flow sheet development studies will eliminate this problem completely.

6. SPHERE FORMATION

The basic process used to form the urania-plutonia microspheres involved (1) dispersing aqueous sol droplets of controlled diameter into an organic desiccant, (2) fluidizing the droplets until enough water was removed to form rigid gel particles, and (3) firing the gel to the mixed oxide. However, different techniques were needed for the two sizes required. To prepare the large microspheres (oxide diameter of 420 to 590 μ), sol droplets were injected with a two-fluid nozzle into a 4-foot tapered glass column and fluidized by a counter-current flow of 2-ethyl-1-hexanol (2-EH) until dry. To prepare the small microspheres (oxide diameter <44 μ), sol droplets were injected with a syringe into a pot and fluidized by stirring the 2-EH rapidly.

6.1. Additives to Organic Desiccant

It is not possible to prepare truly spherical particles by injecting aqueous sol into pure 2-EH. Surfactants must be added to the 2-EH to prevent the sol droplets from clustering or sticking to the walls of the column and to prevent the formation of gel particles with a concave side (often called "cherry-pitted") or an irregular shape (often called "raisin-shaped"). Experience has shown that 0.3 to 0.7 vol % Span-80 (Atlas Chemical Industries) will prevent clustering, sticking, or the formation of cherry-pitted particles, and that 0.3 to 0.7 vol % Ethomeen S/15 (Armour Industries) will prevent the formation of raisin-shaped particles. A scouting experiment[26,35] performed in an effort to find optimum surfactant levels in 2-EH showed that the concentrations must be varied depending on the nature of a given sol. Therefore, until the interactions involved in forming spherical particles with this type of system are better understood, a trial-and-error technique must be used to determine the necessary quantities of surfactants for a given run. This involves selecting a surfactant level, preparing a few grams of microspheres, examining the spheres under a microscope, and then readjusting the surfactant concentrations until the desired product is obtained. Generally the appropriate conditions can be found after three or four trial batches.

In addition to surface active agents, it is necessary to add water to the 2-EH before use. It has been found that unless 2-EH contains about 0.5 vol % or more water, the gel particles obtained are cracked.[26,35] Presumably, this phenomena is caused by the surface of the sol droplet drying too rapidly and thus becoming too rigid to shrink properly as the interior dries. The water content of the 2-EH can be allowed to increase up to its 3.1 vol % solubility limit.[36] However, a higher water content requires a longer drying time for the sol droplets. Therefore, the water concentration in 2-EH is generally not allowed to exceed about 1.5 vol %.

6.2. Formation of Large Microspheres

Figure 6-1 shows the laboratory-scale sphere-forming system. The right-hand side of the glove box (see Figure 6-2) contains the equipment for preparing large microspheres. The sol injection system consists of a two-fluid nozzle and a 50-ml syringe equipped with a constant-speed drive mechanism. In the nozzle the sol is fed through a stainless steel needle into the center of a stream of 2-EH flowing concurrently with the sol. The organic drive fluid then accelerates the sol until it breaks up into sol drops with diameters 2 to 2.5 times greater than the minimum sol-stream diameter by a varicose mechanism.[37,38] Next, the droplets are discharged into the tapered column in which the 2-EH is recirculated counter-currently to the sol flow, so that the droplets are fluidized (see Figure 6-3). As water is extracted from the aqueous droplets into the organic phase, the sol is converted to a gel. As the density of the particles increases due to water extraction, they are fluidized at a lower level in the column until finally the velocity of the 2-EH is not sufficient to maintain fluidization, and the particles drop through the throat of the column into the collection vessel. Thus it is possible to operate the column continuously.

With the laboratory system, both the sol and the gel are exposed to air during part of the operation. Therefore, the UO_2 sol is partially oxidized during processing. During the first of the three fuel preparation campaigns,[38] oxidation gave rise to two serious problems:

1. A large fraction of the spheres were cracked and thus rejected from the final product.
2. The surfactant levels in the 2-EH had to be adjusted frequently to obtain a spherical product, probably because of the changing properties of the sol resulting from oxidation.

It has been found that the first problem can be minimized if the gel is soaked in concentrated NH_4OH for 15 to 30 minutes immediately after its removal from the column. Samples of UO_2 gel subjected to this treatment have subsequently been washed with ethanol and air-dried with no observable cracking. Other samples of NH_4OH-soaked UO_2 gel that were dried under argon have subsequently been exposed to air for periods of up to 24 hours with no apparent damage.

The problem with oxidation of the sol can be minimized by not allowing the mixed sol to remain in a glove box with an air atmosphere for a great length of time. It was found that a continuous argon purge of the mixed-sol storage vessel protects the U(IV) sufficiently for at least two days, so that no readjustment of the surfactant levels is necessary.[39]

Another problem encountered, especially during the second campaign, was extremely long column drying times (up to 3 hours).[40] Since this campaign occurred during the summer months, the long drying time was attributed to absorption of moisture from the humid summer atmosphere into the 2-EH (see reference 41 for a discussion of water pickup by 2-EH).

As a result of these difficulties, the column operating procedures were changed several times, and those listed below were adopted as being adequate for the purpose of this work:

1. The surfactants (Span 80 and Ethomeen S/15) are premixed in the 2-EH to the desired concentrations.

2. The water concentration in 4 liters of 2-EH is brought up to 0.4 vol %, and this organic is placed in the glove box storage tank.

3. Eight batches of mixed sol (50 ml each) are injected into the column through a two-fluid nozzle. (Fresh sols are introduced into

the box and mixed each day.) After each batch of mixed sol is injected, an additional 4 liters of pre-mixed 2-EH containing 0.1 vol % H_2O are added to the storage tank. When the 16-liter tank is filled, 12 liters of 2-EH are pumped out to allow further addition of dry organic.

4. The total column residence time of the spheres is about 1.5 to 2 hours, at which time they drop through the throat. After all the spheres have dried in the column, they are soaked about 15 minutes in concentrated NH_4OH, washed with ethanol, and pre-dried with argon. Then they are dried overnight in a vacuum oven (150 C, 15 inches Hg) under nitrogen.

6.3. Formation of Small Microspheres

The equipment used in the preparation of small microspheres and in cleaning gel particles is shown in Figure 6-4. The sol injection system is a 50-ml syringe which feeds sol directly into a pot of rapidly stirred 2-EH. The sol is then broken up into droplets by the turbulence and the shear forces of the organic.

The following procedures were used in preparing the small microspheres:

1. The surfactants are pre-mixed in the 2-EH to the desired levels, and the water concentration is brought up to 0.5 vol %.

2. About 4 liters of the pre-mixed organic are added to the pot.

3. Next, 75 ml of mixed sol are injected into the stirred organic, and stirring is continued for 20 minutes. After allowing the spheres to settle for 30 minutes, the bulk of the organic is pumped out of the pot. The remaining organic is decanted off the spheres.

4. The spheres are then soaked in concentrated NH_4OH for about 15 minutes, washed with ethanol, and pre-dried with argon. Finally, they are dried overnight in a vacuum oven (150 C, 15 inches Hg) under nitrogen.

6.4. Firing and Classification

The gel spheres were fired in batches in a box furnace built by the Hevi-Duty Heating Equipment Company (Figure 6-5). An automatic program controller which can regulate the heating, cooling, and gas flow cycles is connected to the furnace. Before firing the mixed gel, several tests were run with UO_2 gel. In each test, several small gel samples (15 to 20 g) from different batches were fired to determine the effects of sphere history on the quality of the final product. It has been indicated that a final product with lower carbon content can be prepared by exposing the gel to air before firing.[42] Therefore, a number of the gel samples were treated in this manner.

The firing cycle is necessarily complicated because of the need to oxidize the carbon in the gel without oxidizing the gel to such a degree that the spheres crack. In addition, the carbon must be removed before a great deal of sintering occurs, or else a low-density product will result. Then, after carbon removal, the metal must be reduced to obtain an O/M ratio of about 2.00. The firing cycles tested were based on those suggested by ORNL studies.[43-45] From the results of seven test runs, the following firing cycle was selected for sintering the mixed gel:

Under CO_2 Atmosphere

Heat to 450 C at 50 C/h.
Heat to 600 C at 25 C/h.
Heat to 900 C at 50 C/h.
Hold at 900 C about 2 h.

Under N_2-6% H_2 Atmosphere

Heat to 1250 C at 200 C/h.
Hold at 1250 C for 4 h.
Cool to room temperature.

This cycle is based on the conclusions derived from the test firings:

1. The carbon content in the product does not seem to be dependent on the gel-sphere history.

2. Rapid heating (more than about 50 C/h) at temperatures below about 600 C results in a porous product which appears to have a relatively high carbon content (>100 ppm).

3. Gross cracking in the gel does not "heal" during the firing.

4. Air exposure of the gel for several hours before firing does not appear to result in a lower carbon content in the product nor does it appear to produce a higher particle density. In addition, the air exposure causes a large number of gel spheres to crack.

5. Particle densities of 95% TD or higher are possible with the selected firing cycle.

6. O/M ratios near 2.00 can be readily attained with the selected firing cycle if good exposure of the entire sample to the furnace atmosphere is permitted and a temperature ≥1200 C is held for at least four hours.

7. The carbon content can be reduced to less than 30 ppm with the selected firing cycle.

After firing the mixed-gel microspheres, the oxide was screened to separate the desired sizes from the remainder of the product. The coarse sphere fraction was then passed over a roundometer (Wald Industries, Inc.) which had a deflection from horizontal of less than 5 degrees to separate the rounds from the non-rounds (see Figure 6-6).

6.5. Experimental Results

In order to dry the gel spheres, to sinter them to oxide, and then to classify the product, it is necessary to transfer the material three times between laboratory units established for maintaining criticality control. Therefore, to increase the accuracy of these fissile material transfers, an empirical value for the weight loss by the gel during conversion to oxide was sought by weighing several batches of material. The data from these measurements are summarized in Table 6-1. These data show large differences in the weight losses of separate batches of material. Although the batches were treated under the same nominal conditions, each one was treated separately. Therefore, at least a portion of the discrepancies in weight loss could be attributed to changes in the treatment, such as the length of the NH_4OH or ethanol soak or the temperature or pressure in the oven. However, probably a more important factor is a variation in the residence time of the droplets in 2-EH. This would be expected to give rise to a variation in the water content of the gel and, thus, to a variation in the gel weight loss.

Table 6-1. Weight Losses by (U, 20% Pu)O_2 Gel

Sphere size	Weight of pre-dried gel, g[a]	Weight of dried gel, g[b]	Weight loss during drying, %	Weight of sintered oxide, g	Weight loss during sintering, %	Total weight loss, %
Coarse	489.2	431.5	12	391.9	9.2	20
Coarse	220.2	191.3	13	162	15	26
Coarse	602.3	--	--	400	--	34
Coarse	662.0	--	--	513	--	23
Fine	121.4	110.3	9.1	100.1	9.2	18
Fine	195.3	--	--	136	--	30
Fine	130.2	--	--	92	--	29

(a)Pre-dried gel has been soaked in concentrated NH_4OH, washed with ethanol, and dried in flowing argon at ambient conditions.

(b)Dried gel has been subjected to the treatment above and dried overnight in an oven under N_2 (15 inches Hg, 120 C).

The size distribution of the column-prepared spheres from the first sphere-forming campaign is shown in Table 6-2. A total of 56.2% of the spheres were of the desired size. In the third campaign 80% of the spheres were 420 to 590 microns in diameter. This marked improvement in performance is undoubtedly related to increased experience with the column operation. With the laboratory system in use, it is questionable whether much more than 80% of the spheres can be formed with the desired diameter because of a lack of precise control of the sol feed rate and the 2-EH flow rate through the two-fluid nozzle. However, an improved performance would be expected from a carefully engineered system.

Table 6-2. Size Distribution of Column-Prepared Spheres[a]

Diameter, μ	Amount of oxide, g	Amount of oxide, %
>590	40.3	10.3
420 - 590[b]	219.5	56.2
297 - 420	92.0	23.5
210 - 297	24.8	6.3
<210	14.5	3.7

[a] First campaign only.

[b] Desired size.

The rejection of material from passing over the roundometer varied from 10 to 30%. Most of these rejects were grossly cracked spheres. The cracking is probably due to partial oxidation of the gel from air exposure during processing. If this is the case, a system designed to prevent air exposure would greatly reduce the production of non-round or cracked particles.

Another type of material loss occurred during preparation of the gel particles. Of the sol introduced into the sphere-forming column, 10 to 30% was washed out of the top into the 2-EH storage tank. Part of this loss was related to the formation of very small particles due principally to occasional breakup of input droplets, but most was due to difficulties in operating such a small column on a continuous basis. If the counter-current flow of 2-EH is too high, the low-density, initial sol droplets are washed out the top of the column; however, if the flow is too low, gel spheres fall through the throat of the column into the receiving vessel before they are sufficiently dry and then stick together in one large mass. As a result the 2-EH flow rate was kept high enough to ensure adequate drying of the gel spheres, and rather large losses of initial sol droplets were tolerated. Experience at B&W on other projects has shown that large columns can be operated easily with almost no sol loss.

In preparing the small microspheres, 15 to 40% of the input sol to the pot of stirred 2-EH was not recovered. This is mainly because this fraction of the material does not settle before the 2-EH is decanted from the bulk of the spheres. Since better techniques for the preparation of small microspheres are currently being developed at the Oak Ridge National Laboratory, no effort was made to minimize this source of material loss.

The quantity of material recovered from each of the campaigns is summarized in Table 6-3. It should be noted that the coarse product scrap includes all off-sized material and rejects from the roundometer. Since the necessary degree of particle roundness has not been determined, some of this material could be suitable for the Sphere-Pac fuel rod fabrication process. The fine product scrap includes only the off-sized material, because for particles this small, it is not possible to separate the rounds from the non-rounds with the type of roundometer used.

The low yield of fine spheres in the first campaign was caused by too low a stirring speed of the 2-EH. As can be seen, there were very few rejects in the last two campaigns when a higher stirring speed was used.

Table 6-3. Quantities of Sol-Gel Material Prepared for Gel-Addition Irradiation Program

Campaign	420 - 590-μ rounded product, g	Coarse product scrap, g[a]	Usable coarse product, %	<44 μ product, g	Fine product scrap, g[b]	Usable fine product, %
1[c]	179	213	46	35	65	35
2	644	688	48	462	10	98
3[d]	536	539	50	210	18	92

[a] All off-sized material and rejects from roundometer are included as scrap.

[b] Only off-sized material is included as scrap.

[c] Data do not include losses incurred when sol segregation led to unusable product (see section 3.4).

[d] Uranium was enriched to 20% ^{235}U.

6.6. Conclusions

It has been demonstrated that up to 150 grams of mixed UO_2-PuO_2 sol-gel microspheres can be prepared routinely in an 8-hour day with the laboratory sphere forming system. However, it appears that the total process efficiency with this system is limited to only about 45 to 50%. The main reason for the low efficiency seems to be the lack of positive control of the atmosphere, moisture content of the organic desiccant, feed rates, and injection system. A unit operations system is currently being constructed (see Figure 6-7) in which problems with these factors should be substantially diminished.

It has been demonstrated that with a given stock batch of sol, the necessary column conditions to prepare acceptable microspheres remain constant.

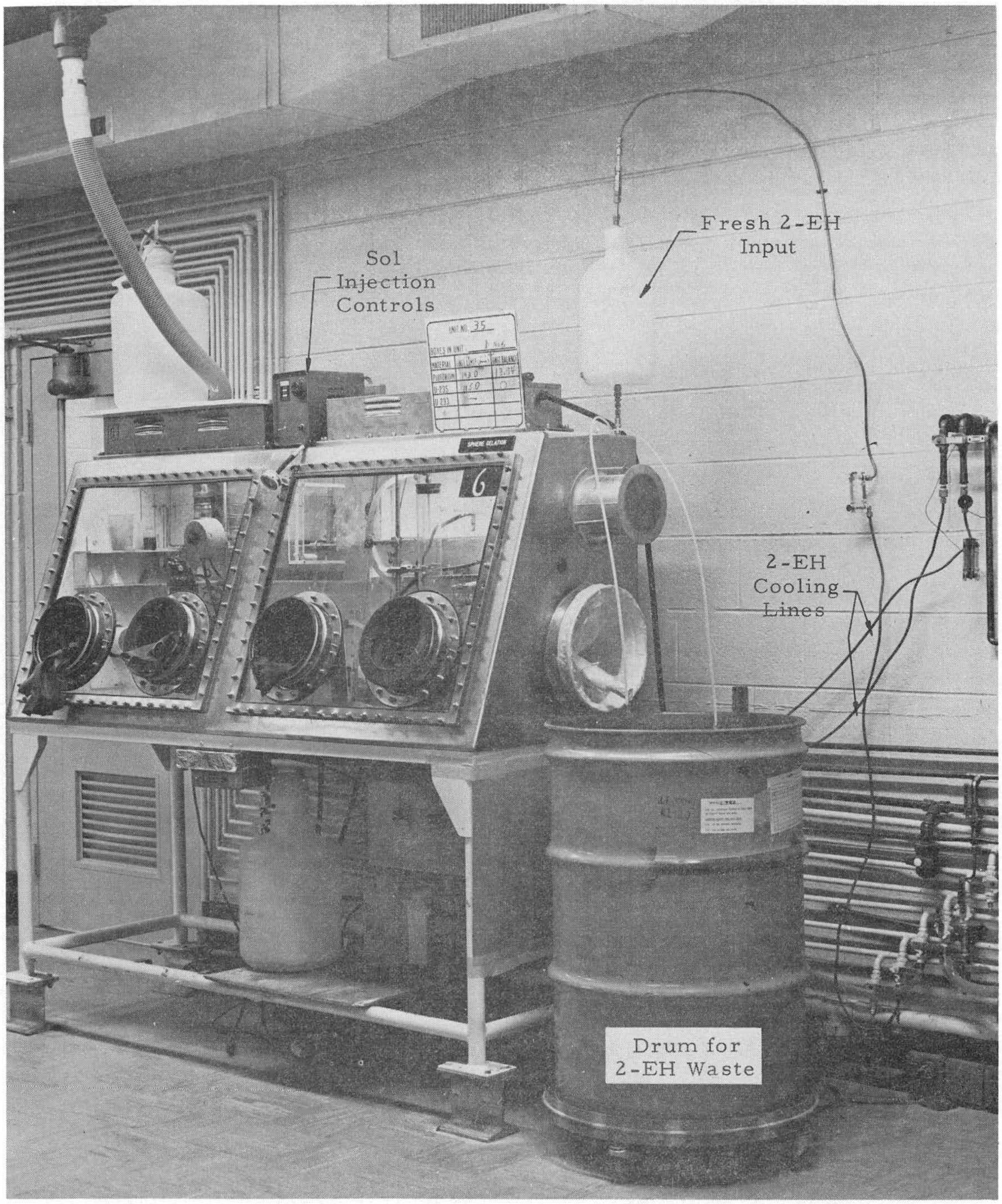


Figure 6-1. UO_2-PuO_2 Gel Sphere Preparation Box

Figure 6-2. System for Preparation of Large Microspheres

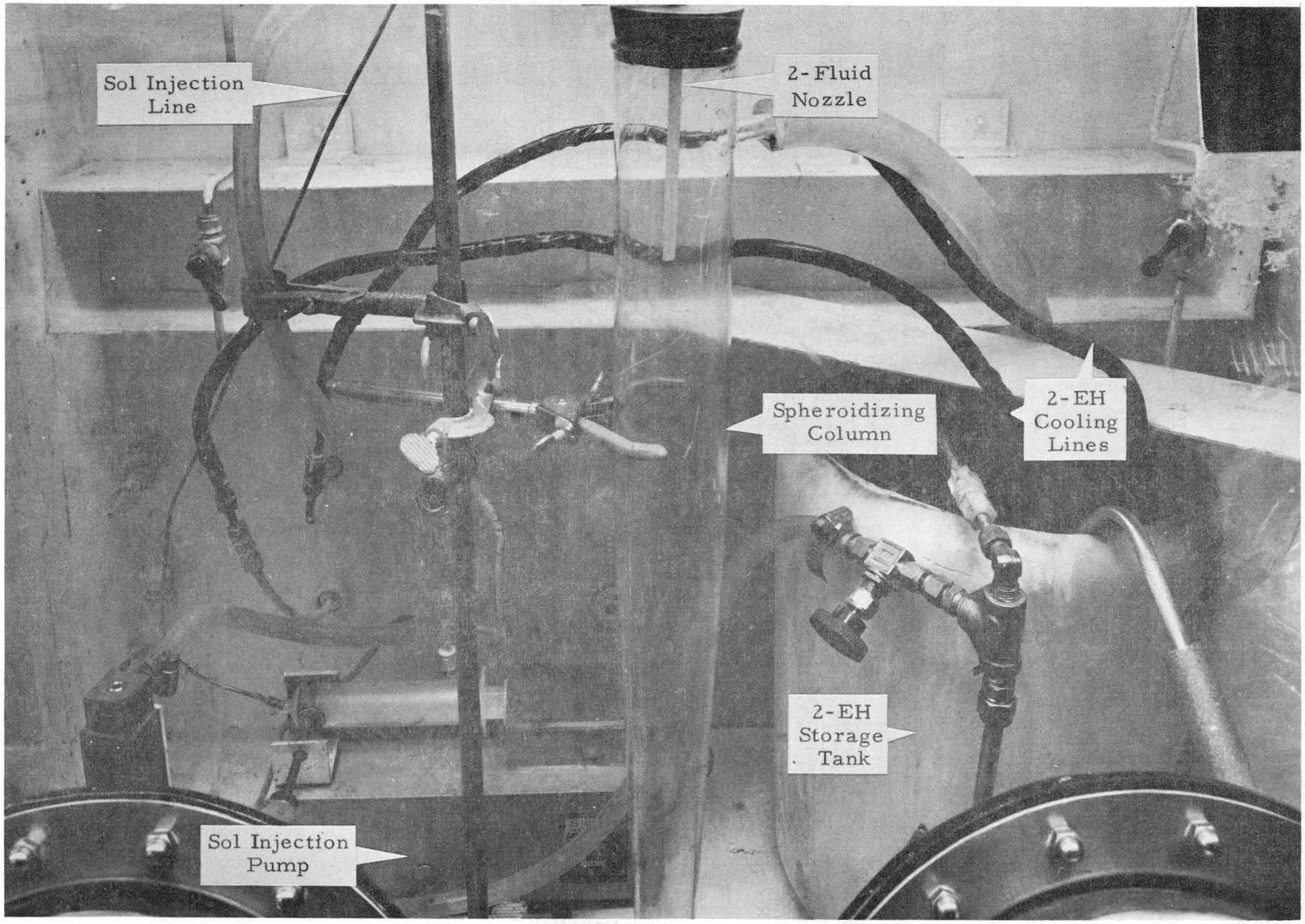


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Figure 6-3. Sol Droplets Fluidized in Tapered Column

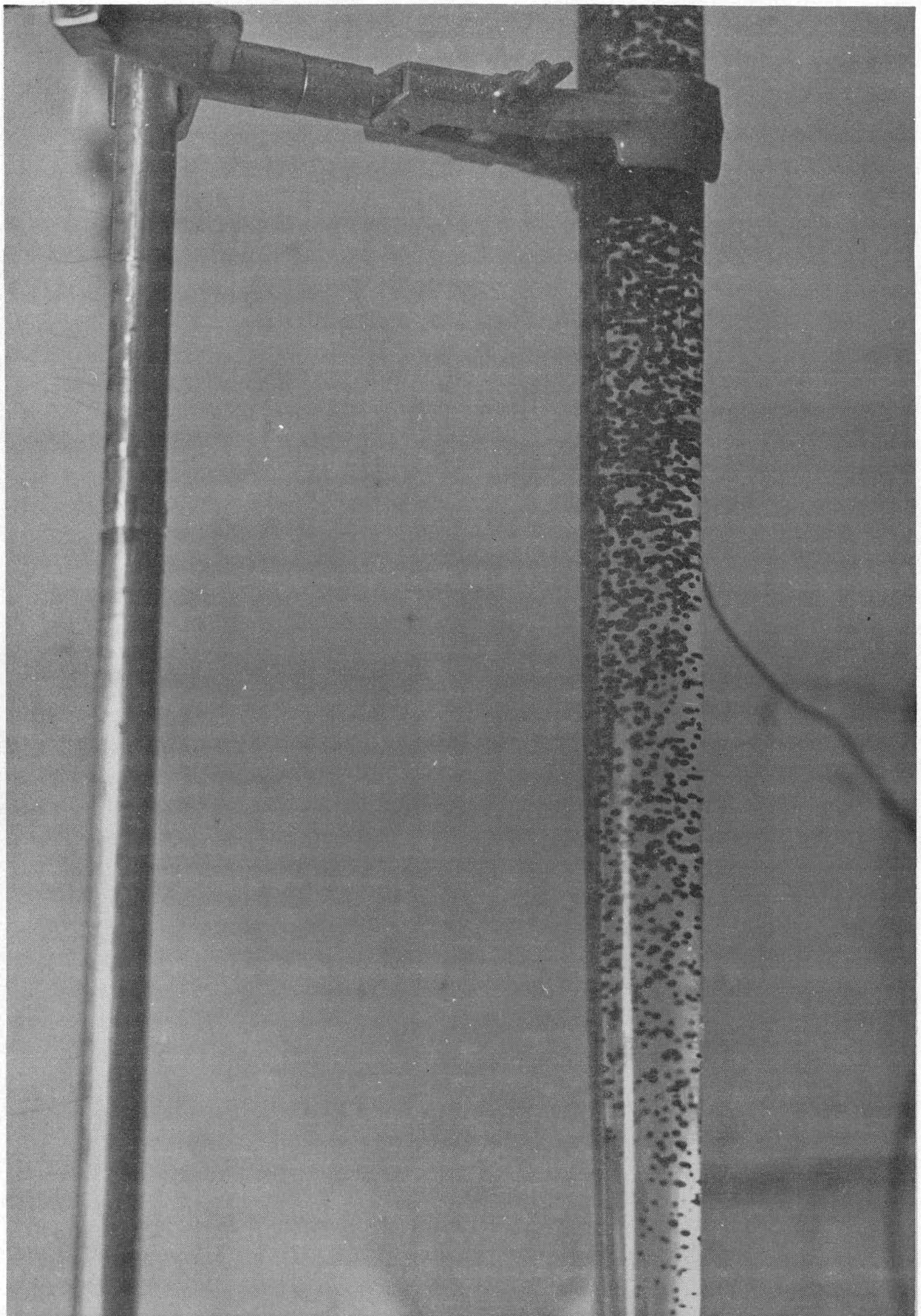


Figure 6-4. Equipment for Preparation of Small Microspheres

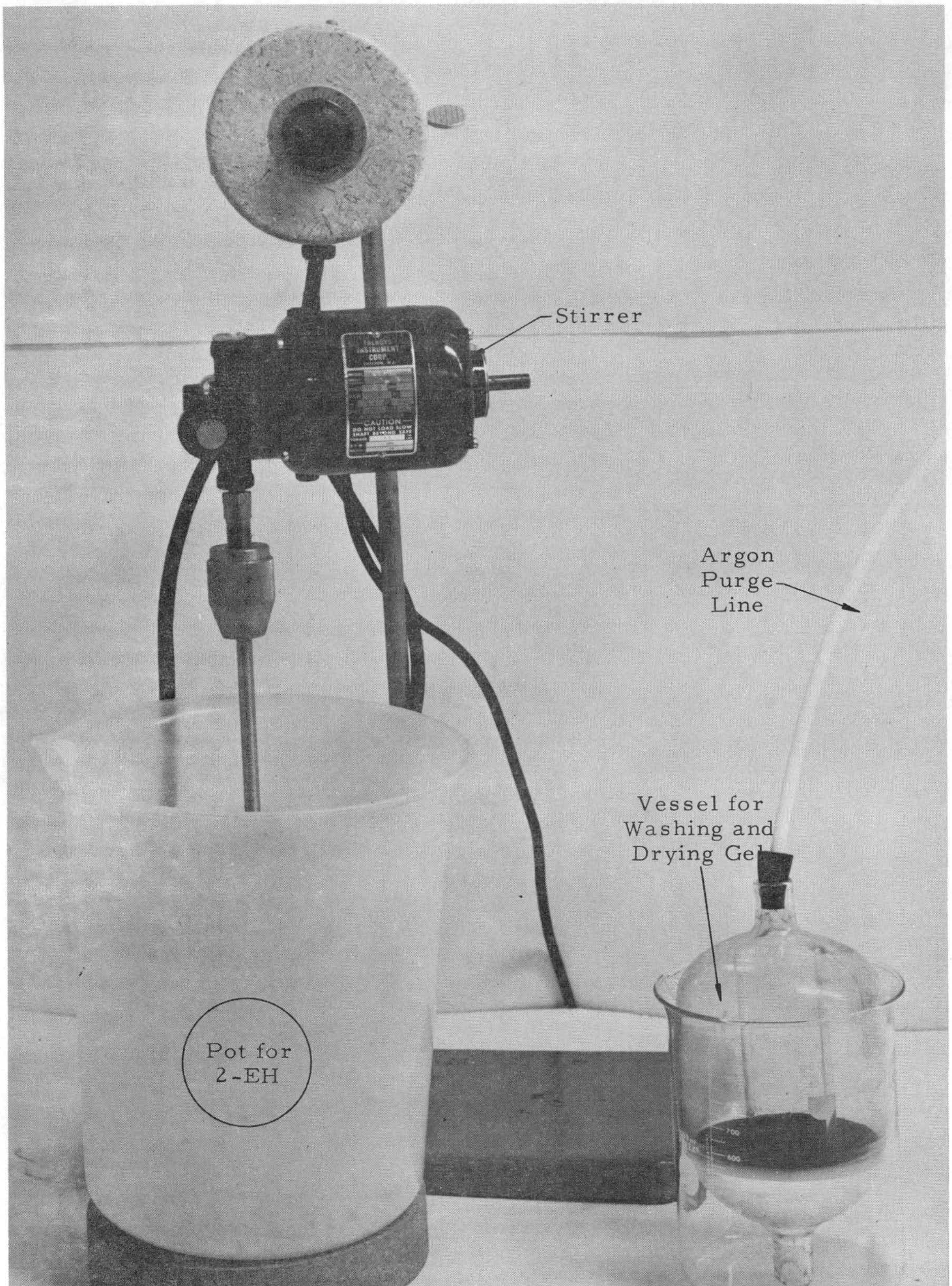


Figure 6-5. Furnace and Controls

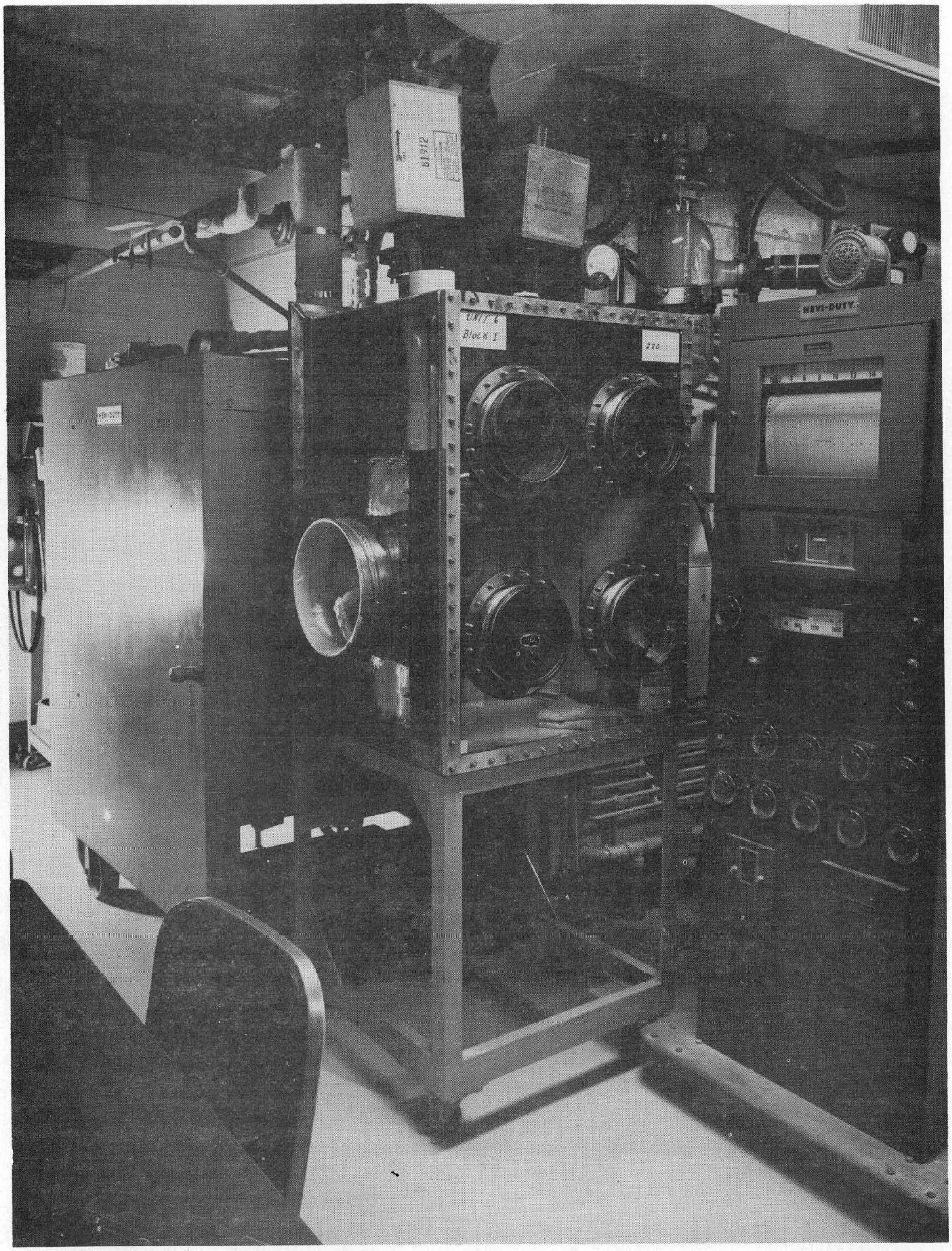


Figure 6-6. Roundometer and Screens

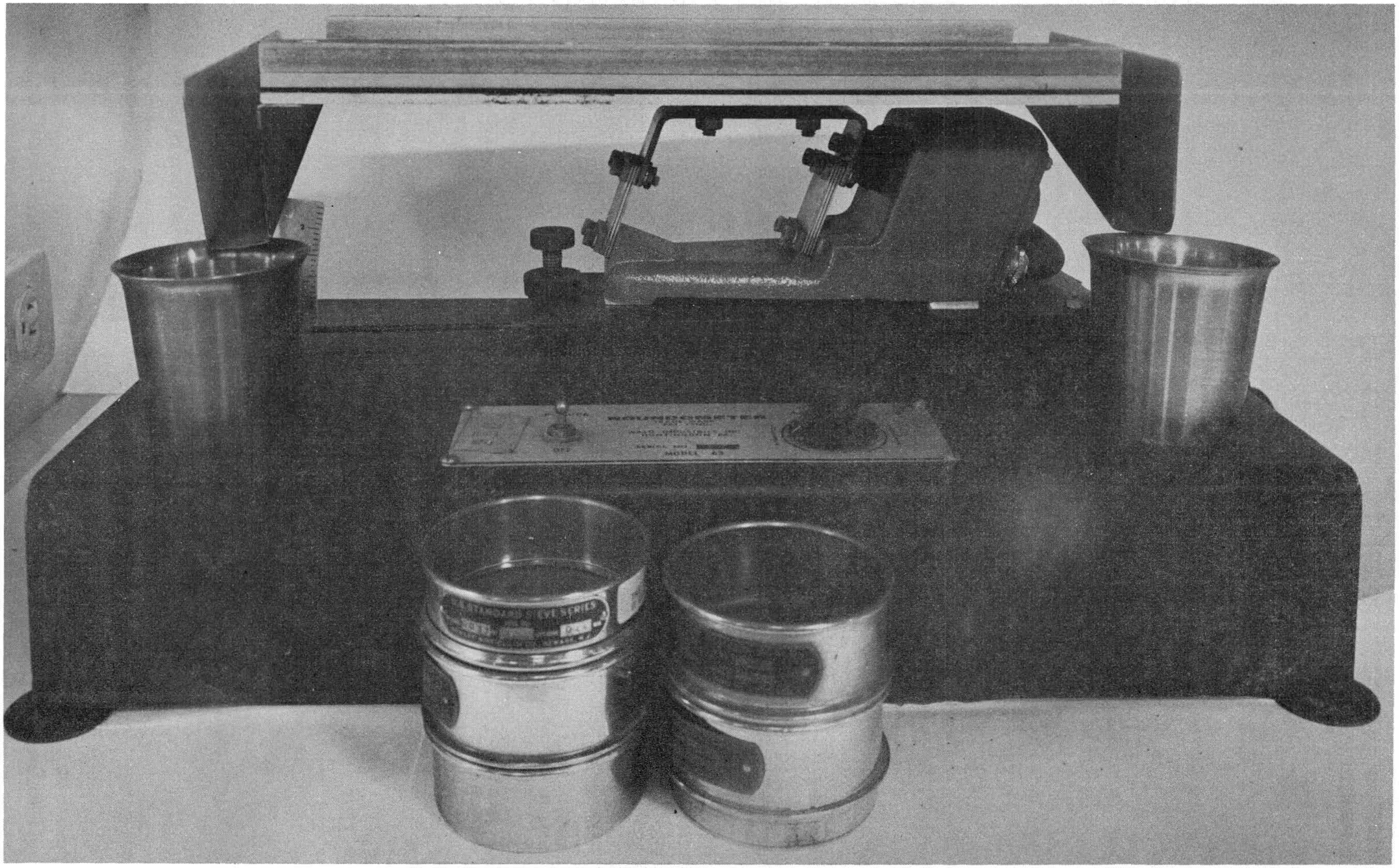
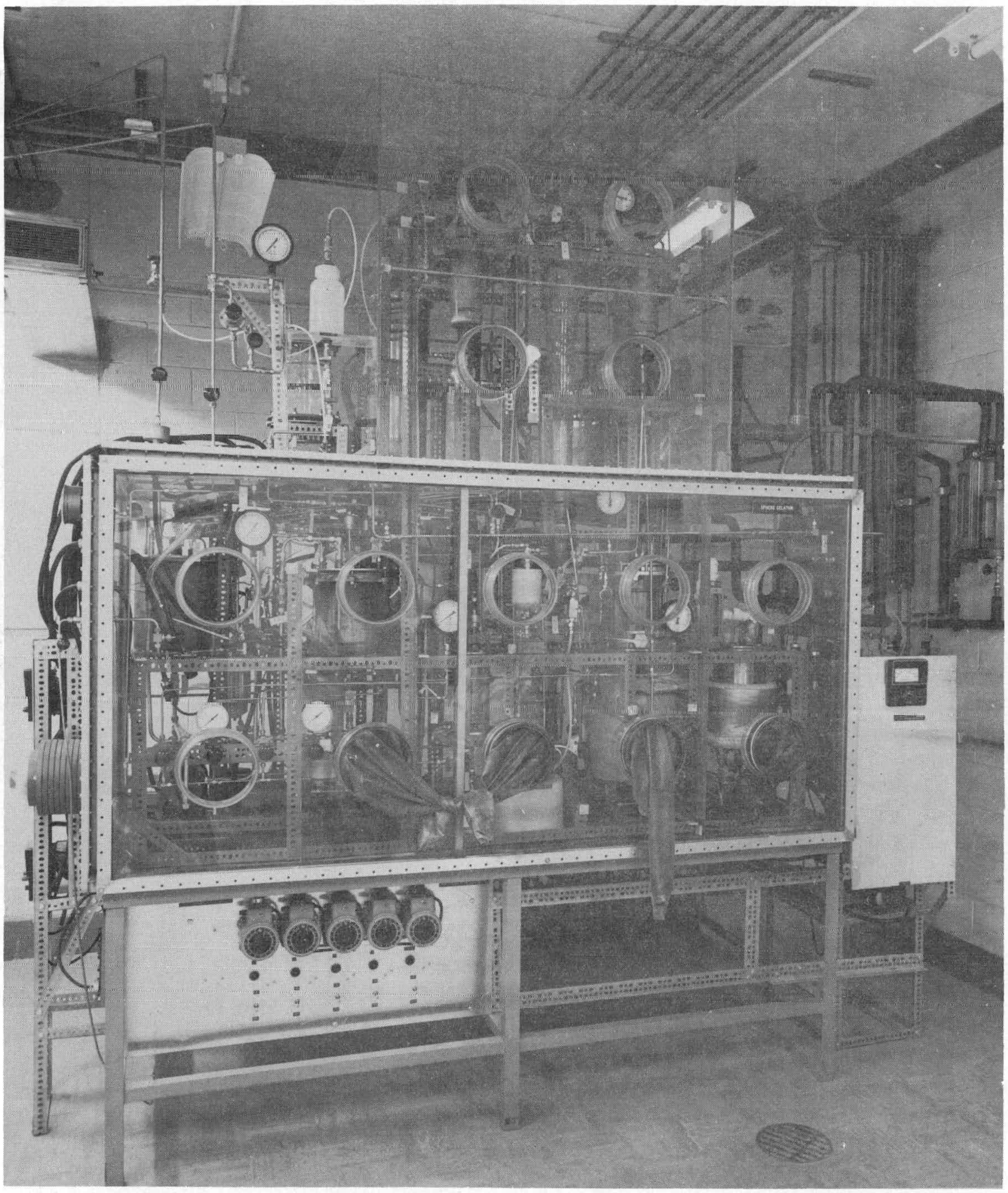


Figure 6-7. Unit Operations Gelation System



7. CHARACTERIZATION OF MICROSPHERES

The UO_2-PuO_2 microspheres are loaded into fuel rods using a vibratory compaction technique often referred to as the Sphere-Pac process. A discussion of this process and the experimental results obtained with these microspheres are presented in a companion report.[46] Before the microspheres were loaded, sufficient analyses were performed to demonstrate that their quality was adequate for irradiation testing.

7.1. Plutonium Content

The plutonium and uranium contents in the microspheres were determined by controlled-potential coulometry:[26,47,48] the results are summarized in Table 7-1. Within experimental error, these data agree with the results from the quality control analyses listed in Table 5-1. The plutonium content in the spheres containing 20% ^{235}U is somewhat low because of an error in the initial UO_2 sol analysis which was not confirmed until that campaign was about 50% complete. Since the lower plutonium content can be tolerated in the irradiation testing program, all of the spheres with 20% ^{235}U were prepared with about 19.1% plutonium.

7.2. Oxygen Stoichiometry

The O/M atom ratios shown in Table 7-1 were determined by microthermogravimetry.[46,49] These data indicate that the oxygen content of the microspheres is within the desired O/M range of 1.95 to 1.99.

7.3. Moisture Content

The moisture in the microspheres was determined with a modified CEC Type 321 AMA Solids Moisture Analyzer.[46,50,51] It should be recognized that there is now no widely accepted standard method for determining the moisture content of nuclear fuels. As would be expected, the total moisture determined depends on storage and handling conditions, such as humidity. Thus, different results are usually obtained from samples of the same material when the samples are withdrawn and analyzed at different times. The data shown in Table 7-1 were obtained on several different days in an effort to establish limits on what the moisture content in the encapsulated fuel could be. In addition, the analyses were performed at two different temperatures, the lower being the lowest known to be employed in other laboratories and the higher being near the upper limit of moisture evolution. (Very little additional moisture evolution has been detected at temperatures up to about 900 C.)[51] From these results, it appears that the moisture content of a blend of sol-gel spheres in which 75% of the spheres are 420 to 590 microns in diameter and 25% are less than 44 microns in diameter is within the fuel specification limit of 50 ppm.

7.4. Particle Density

The particle density of the coarse fraction microspheres was determined by a vibratory compaction technique.[46] This involves placing the sample in a tube having a diameter greater than 10 times the maximum spherical particle diameter, vibrating the tube until the spheres are packed in a minimum volume, determining the packed-bed volume, and finally calculating the particle density with the assumption that a single size particle is present. Ayer has shown theoretically that, under these conditions, 100%-dense spherical particles will fill 63.5% of the packed-bed volume.[52] However, experimental data indicate that only 62.5% of the packed-bed volume is filled by 100%-dense spherical particles of a single diameter.[53] The densities shown in Table 7-1 have been calculated using both values for the percent of the total bed volume filled by the particles. No attempt was made to determine the density of the spheres smaller than 44 microns in diameter because this fraction contains such a wide range of particle sizes that reasonably accurate results are impossible. The data indicate that the particle density is adequate for the purposes of the current phase of the Gel-Addition Irradiation Program. However, further development studies are needed to find suitable conditions for increasing the particle density.

Table 7-1. Characterization of Sol-Gel Microspheres

Property measured	Specification	Sample A	Sample B	Sample C	Sample D	Sample E(a)	Sample F(a)
Sphere size range, μ	420 - 590	420 - 590	--	420 - 590	--	mixture	mixture
	<44	--	<44	--	<44	mixture	mixture
^{235}U content, wt % U(b)	≤0.71	0.258 ± 0.009	0.258 ± 0.009	--	--	0.258 ± 0.009	--
	20.0 ± 0.5	--	--	19.68 ± 0.02	19.68 ± 0.02	--	19.68 ± 0.02
Pu/(Pu + U), %(b)	20.0 ± 0.5	19.52 ± 0.32	19.71 ± 0.17	19.00 ± 0.11	19.20 ± 0.17	19.57 ± 0.34(c)	19.05 ± 0.15(c)
O/M, atom ratio(b)	1.97 ± 0.02	1.976 ± 0.005	1.987 ± 0.002	1.974 ± 0.003	1.983 ± 0.004	1.979 ± 0.005(c)	1.976 ± 0.004(c)
Moisture (range), ppm oxide							
at 100 C	--	5.5 - 9.1	20.7 - 33.0	3.5 - 6.4	10.2 - 28.3	--	--
at 600 C	--	11.2 - 18.0	49.1 - 69.6	9.1 - 16.7	41.1 - 57.3	--	--
Moisture (average), ppm oxide	<50						
at 100 C	--	6.9	26.0	5.0	20.2	11.7(c)	8.8(c)
at 600 C	--	14.2	59.0	11.7	50.5	25.4(c)	21.4(c)
Sorbed gas (range), cc/g	< 1	--	--	--	--	0.036 ± 0.039	0.028 - 0.078
Particle density, % TD(b)	>95						
using assumption(d)	--	95.8 ± 0.6	--	97.3 ± 0.7	--	--	--
using assumption(e)	--	96.2 ± 0.9	--	97.8 ± 0.9	--	--	--
Carbon, ppm oxide(b)	<150	NA	NA	12 ± 2	NA	--	--
Nitrogen, ppm oxide(b)	<200	NA	NA	12 ± 4	NA	--	--
Chloride, ppm oxide(b)	<25	NA	NA	6 ± 2	NA	--	--
Fluoride, ppm oxide(b)	<25	NA	NA	0.5 ± 0.2	NA	--	--

(a) Samples E and F are as-loaded mixtures.

(b) Errors are for 95% confidence limits on the mean.

(c) Calculated from results for samples A - D.

(d) Calculated with the assumption that 63.5% of the total packed-bed volume is filled by particles.

(e) Calculated with the assumption that 62.5% of the total packed-bed volume is filled by particles.

NA: not available.

TD: theoretical density.

7.5. Sorbed Gas Content

The sorbed gas content of the sol-gel microspheres was measured by placing a sample under a high vacuum, heating to 1600 C, measuring the pressure change, and finally calculating the volume of gas evolved from the pressure change.[46] The samples used for this measurement contained 75% 420- to 590-micron spheres and 25% <44-micron spheres, the same mix as was used in fuel rod fabrication. These data are summarized in Table 7-1. The measured values are well within the fuel specifications of less than 1 cc/gram.

7.6. Carbon Content

The carbon content of the microspheres was determined with a modified LECO Low Carbon Analyzer.[54] With this method, the carbon is separated from the nuclear fuel material by burning in an oxygen atmosphere and the evolved CO_2 is measured with a gas chromatograph. The carbon content shown in Table 7-1 is well below the specification of less than 150 ppm.

7.7. Nitrogen Content

Nitrogen is separated from the microspheres by a modified Kjeldahl technique and determined by a constant current coulometric titration. The nitrogen content shown in Table 7-1 is well below the specification of less than 200 ppm.

7.8. Halogen Content

The halogens are separated from the microspheres by pyrohydrolysis and determined with ion selective electrodes.[55] The data shown in Table 7-1 indicate that the chloride and fluoride content is well within the fuel specification of less than 25 ppm each.

7.9. Trace Metallic Impurities

The trace metallic impurities were determined with a Baush and Lomb Dual Grating Spectrograph by a d-c arc, carrier distillation method. The results are shown in Table 7-2.

Table 7-2. Trace Metallic Impurities in Sol-Gel Microspheres

Specification		Sample	
Element	Concentration, ppm oxide	Element	Concentration, ppm oxide
Aluminum	<500	Aluminum	270
Boron	<5	Beryllium	<0.5
Cadmium	<1	Boron	1.5
Chromium	<250	Cadmium	<1
Iron	<500	Chromium	<20
Magnesium	<23	Copper	41
Nickel	<500	Iron	550
Plutonium	<100	Lead	<1
Sodium	<500	Magnesium	23
Vanadium	<500	Manganese	3
Cu + Zn + Si + Ti	<800	Molybdenum	<25
Ag + Mn + Mo + Pb + Sn	<200	Nickel	<20
		Silicon	≈250
		Tin	3
		Silver	<1
		Sodium	21
		Titanium	<15
		Vanadium	<1
		Zinc	<20

7.10. Ceramographic and Alpha Autoradiographic Examination

Samples of the product were examined microscopically to determine whether the sol-gel microspheres contained any gross porosity or cracks. The sphere samples were prepared for examination by mounting in room-temperature-setting resin, grinding on a lap, and polishing with 0.5-micron diamond paste on nylon cloth in a vibratory polisher.[46] Figures 7-1 through 7-4 show the microstructures of typical spheres. (It should be noted that the small dark particles in Figures 7-1 and 7-2 are not $(U,Pu)O_2$ microspheres but alumina which was added to the mounting compound.) These photographs show that the microspheres have a high density and are generally free from gross porosity or cracking.

Alpha autoradiographs were prepared by placing cellulose-nitrate-covered glass slides face-down on the ceramographic mount with aluminum foil as a filter between the specimen and the cellulose nitrate.[56,57] After about 15 minutes' exposure, the cellulose nitrate slides were treated with NaOH. Figures 7-5 and 7-6 are typical alpha autoradiographs of the microspheres. These photographs show that the plutonium is uniformly distributed within the microspheres.

Figure 7-1. Ceramographic Section of Fired 420- to 590-μ-Diameter (Depleted U, Pu)O_2 Spheres

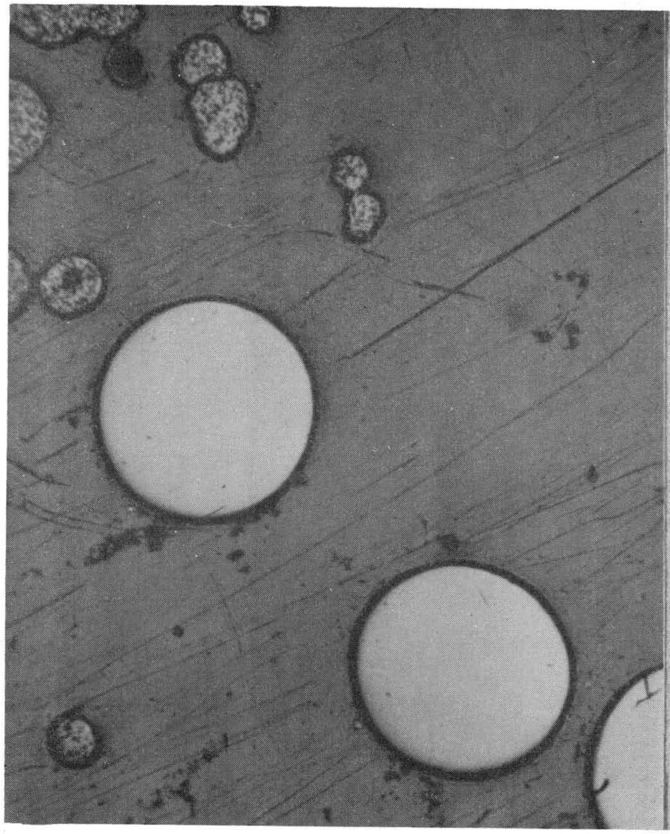

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Figure 7-2. Ceramographic Section of Fired 420- to 590-μ-Diameter (20% ^{235}U, Pu)O_2 Spheres

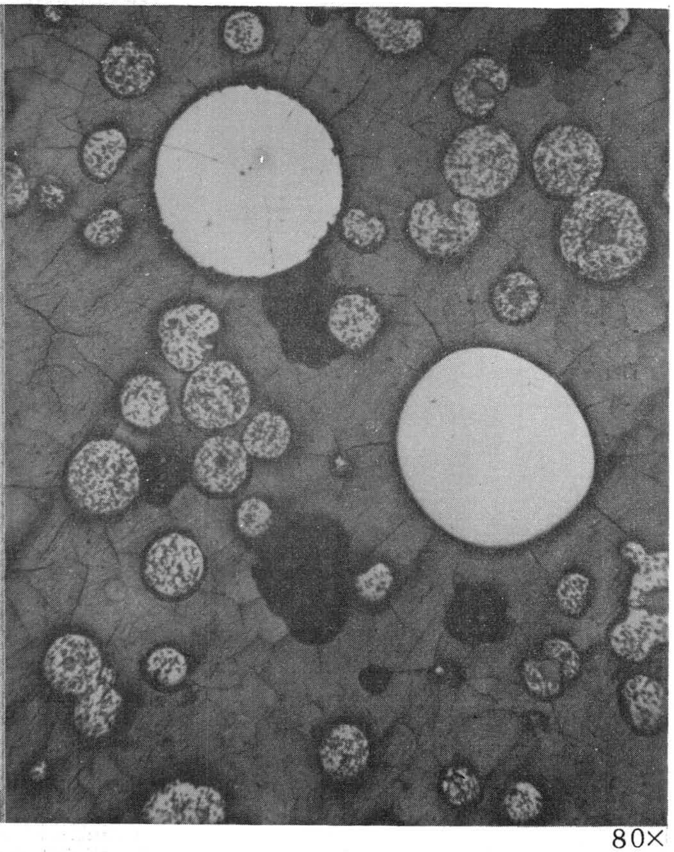
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Figure 7-3. Ceramographic Section of Fired 44-μ-Diameter (Depleted U, Pu)O_2 Spheres

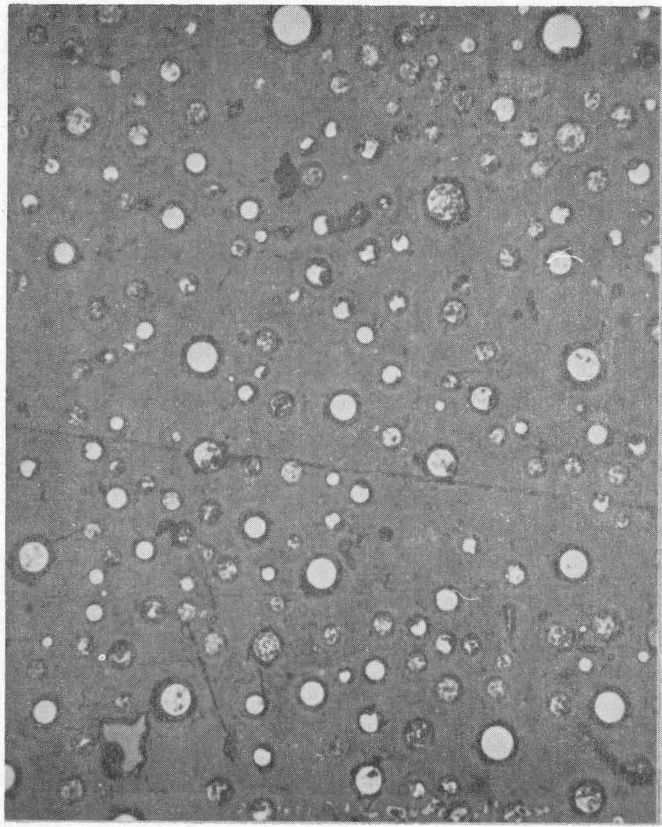

400×

Figure 7-4. Ceramographic Section of Fired 44-μ-Diameter (20% ^{235}U, Pu)O_2 Spheres

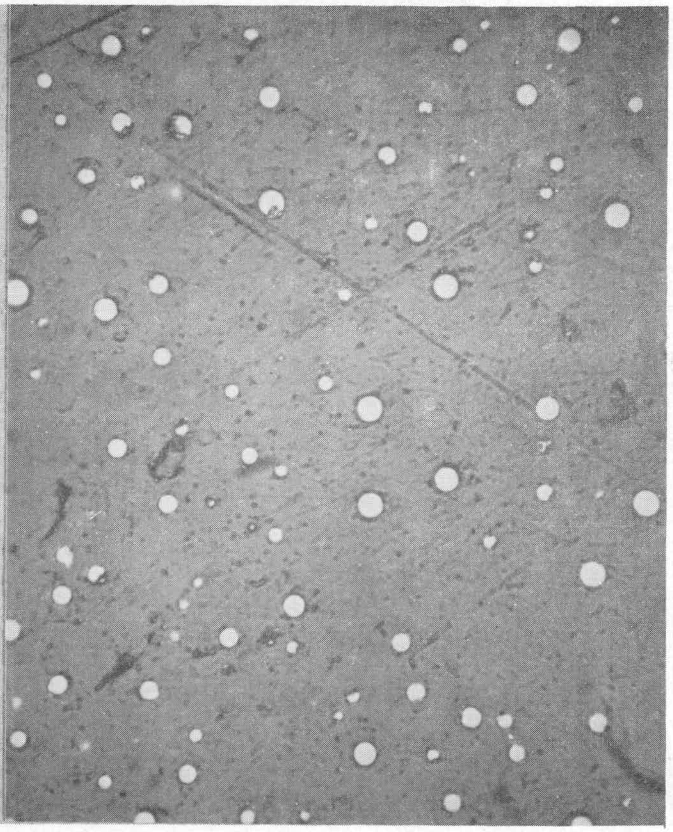

400×

Figure 7-5. Alpha Autoradiograph of Fired 420- to 590-μ-Diameter (Depleted U, Pu)O_2 Spheres

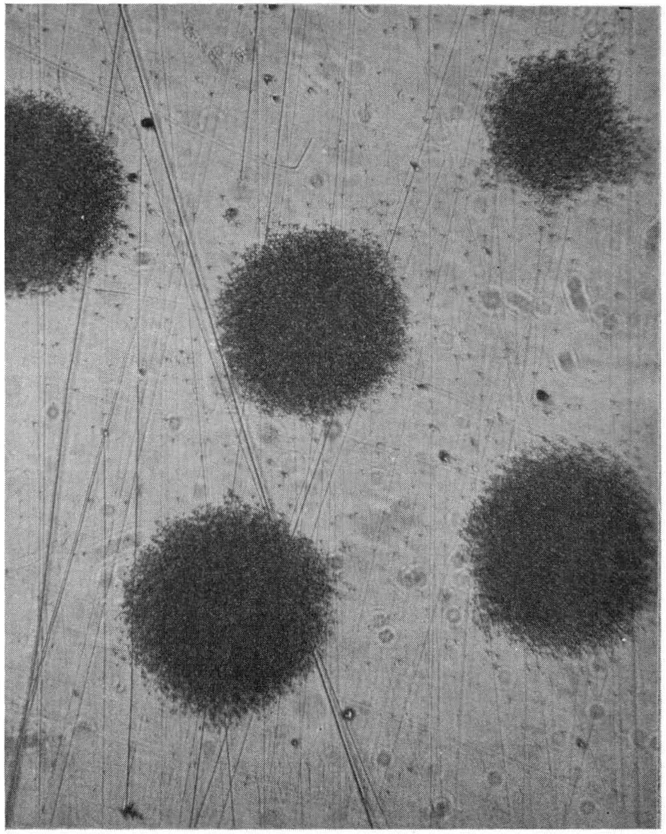
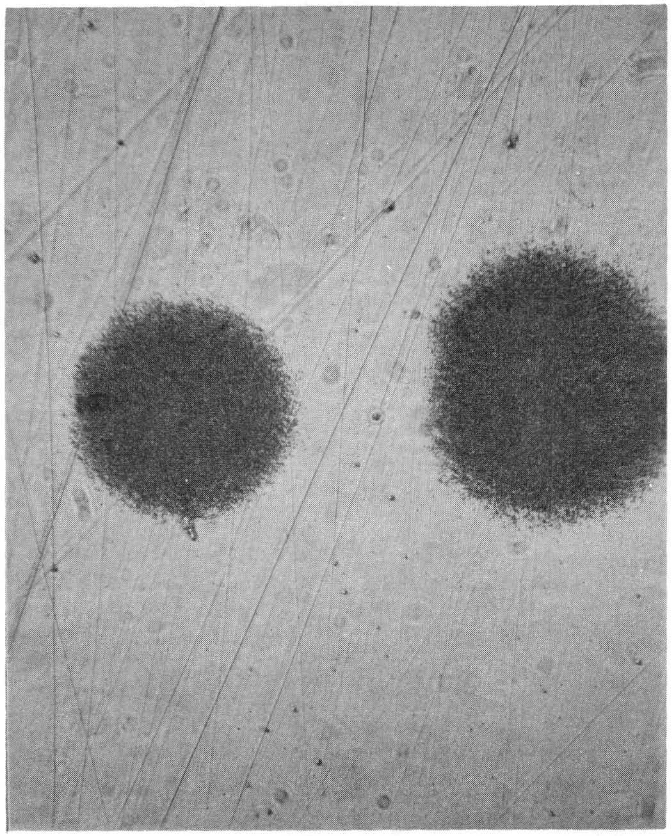


Figure 7-6. Alpha Autoradiograph of Fired 420- to 590-μ-Diameter (20% ^{235}U, Pu)O_2 Spheres



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