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# SOL-GEL PROCESS — ENGINEERING-SCALE DEMONSTRATION OF THE PREPARATION OF HIGH-DENSITY UO<sub>2</sub> MICROSPHERES

B. C. Finney  
P. A. Haas

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

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ORNL-4802  
UC-25 -- Metals, Ceramics, and Materials

Contract No. W-7405-eng-26

CHEMICAL TECHNOLOGY DIVISION  
UNIT OPERATIONS SECTION

SOL-GEL PROCESS -- ENGINEERING-SCALE DEMONSTRATION OF THE  
PREPARATION OF HIGH-DENSITY  $UO_2$  MICROSPHERES

B. C. Finney  
P. A. Haas

NOVEMBER 1972

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ABSTRACT

A sol-gel process for the preparation of high-density  $\text{UO}_2$  microspheres in the size range 125 to 210  $\mu$  was demonstrated on an engineering scale. The process consists of preparing a 1 M  $\text{UO}_2$  sol by the CUSP process, forming the sol into gelled spheres in a nonfluidized column using hot 2-ethyl-1-hexanol as the dehydrating agent, and calcining the gelled spheres to dense  $\text{UO}_2$ . Eight batches of sol containing approximately 4 kg of  $\text{UO}_2$  each were prepared, and microspheres were produced in a microsphere forming column that was operated continuously for two one-week periods. Drying was carried out in glass product catchers; firing was done in alumina crucibles in a muffle furnace.

Four batches of sol were prepared the week prior to each microsphere forming run. Sols with  $\text{NO}_3^-/\text{U}$  mole ratios of 0.09 to 0.14,  $\text{HCOO}^-/\text{U}$  mole ratios of 0.38 to 0.47, and U(IV) contents of 85 to 87% were prepared following the standard CUSP operating path. Overall uranium material balances for the two demonstration runs were 102.2 and 104%, and the sol yields were 98 and 96.5%, respectively. No differences were noted in the microsphere forming properties of the various batches of sol.

The performance of the nonfluidized microsphere forming column was satisfactory. Minor difficulty was encountered with plugging of the two-fluid nozzle capillaries; however, this was minimized by installing glass frit filters in the sol feed line. An on-stream factor of 96% was attained for each run. The desired production capacity of approximately 3 kg of  $\text{UO}_2$  per day was attained during the second run. Operating conditions were established during the first run.

Results of the second run indicated an 86.8% yield of calcined microspheres in the size range 125 to 210  $\mu$ . The mean size varied from approximately 158 to 167  $\mu$ , with a standard deviation of approximately 10%. The O/U atom ratio was 2.003 to 2.005, and the carbon and iron contents were 24 to 60 and 12 to 46 ppm, respectively.

The feasibility of the CUSP nonfluidized-column processing method for the preparation of high-density  $\text{UO}_2$  microspheres has been demonstrated, and the process can be adapted to commercial use. However, additional development work is desirable in the area of multinozzle feeders in order to increase the capacity of the nonfluidized microsphere-forming column.

## 1. INTRODUCTION

The purpose of this work was to demonstrate the feasibility of a sol-gel process for preparing high-density  $\text{UO}_2$  microspheres in engineering-scale equipment. Microspheres of  $\text{ThO}_2\text{-UO}_2$  and  $\text{UO}_2$  are the proposed fertile and fissile fuel particles, respectively, for the High Temperature Gas-Cooled Reactors (HTGRs) developed by Gulf General Atomics (San Diego, California). Urania sols are also used to make  $\text{UO}_2\text{-PuO}_2$  microspheres. Irradiation tests have shown that  $\text{UO}_2\text{-PuO}_2$  microspheres may be potentially useful as fuel in LMFBRs. The engineering-scale demonstration of the sol-gel production of  $\text{ThO}_2\text{-UO}_2$  microspheres has been previously reported.<sup>1</sup>

The processing steps for the sol-gel production of  $\text{UO}_2$  microspheres are as follows: (1) preparation of a 1  $\underline{\text{M}}$  U(IV) feed by the hydrogen reduction of uranyl nitrate solution containing formic acid, (2) preparation of a 1  $\underline{\text{M}}$   $\text{UO}_2$  sol from the U(IV) feed by the Concentrated Sol Preparation (CUSP)<sup>2-5</sup> process, (3) forming the sol into gelled microspheres in a nonfluidized column using hot 2-ethyl-1-hexanol (2EH) as the dehydrating agent, (4) drying the gelled microspheres in an argon-steam atmosphere, and (5) firing the dried gel product in 4%  $\text{H}_2$ --argon to produce high-density  $\text{UO}_2$  microspheres.

The feasibility of the microsphere-forming operation had been demonstrated earlier in 5- to 6-hr runs; however, we needed to establish the capability for long-term, continuous operation and to identify any operating and equipment problems that might occur under sustained operation. Of paramount importance was our ability to demonstrate recycle of the 2EH. In this study, natural uranium was used; however, operation with enriched uranium would pose no problems.

Because of manpower limitations, sol preparation and microsphere forming could not be carried out simultaneously; consequently, the sol was prepared the week prior to each microsphere forming run. In each run, our objective was to operate the microsphere-forming column at a  $\text{UO}_2$  production rate of about 3 kg/day and produce acceptable calcined microspheres in the size range 125 to 210  $\mu$ .

## 2. PREPARATION OF SOLS

### 2.1 Process Description

The 1 M urania sols used to form microspheres in the two one-week demonstration runs were prepared by the Concentrated Urania Sol Preparation (CUSP) process, in which a 1 to 1.4 M crystalline urania sol is produced directly by solvent extraction. The handling of solids, which was required in some earlier urania sol processes is avoided, while the sol concentration step inherent in the earlier solvent extraction process for the preparation of dilute sols<sup>6-9</sup> is eliminated or minimized. Further, this process lends itself to closer control than can be imposed easily on the previous processes. In general, sols prepared by the CUSP process show greater reproducibility and have longer "shelf lives" than urania sols prepared by other solvent extraction methods.

In the CUSP process, a 1 M  $\text{UO}_2$  sol is prepared by continuously extracting nitrate at a controlled rate from a U(IV) nitrate-formate solution into an organic solvent of 0.25 M Amberlite LA-2,<sup>\*</sup> a secondary amine, in the mixed diluent 75 vol % diethylbenzene--25 vol % n- $\text{C}_{12}$ -paraffin.<sup>\*\*</sup> By following a prescribed conductivity-temperature-time relationship, stable 0.1 M urania sol comprised of highly crystalline colloidal particles

---

\* Product of the Rohm and Haas Company.

\*\* Product of the South Hampton Company. The  $\text{C}_{12}$  represents an average molecular weight of a mixture.

with a high U(IV) content is produced. The operating curve or path that is followed in preparing the sol is shown in Fig. 1; a typical chemical flowsheet is presented in Fig. 2.

The three nitrate extractions are carried out at different temperatures. An extraction is initiated by starting the solvent flow and is terminated by stopping the solvent flow. The first extraction is carried out at a temperature of 35 to 40°C; as the feed solution is heated from room temperature, there is a slight increase in conductivity. (Conductivity varies directly with temperature and free nitrate.) This extraction is continued until the conductivity is reduced to about 25,000 micromhos/cm, at which point the solvent flow is turned off. Prior to the second extraction, the solution is heated to 57-58°C, where crystallization of the  $\text{UO}_2$  to form colloentially suspended crystallites begins. At this point, the solvent flow is turned on and heating is continued until a temperature of 60 to 62°C is attained, where the major part of the extraction is performed. Crystallization is accompanied by a change in solution color from dark green to black, evolution of gas which is approximately 85 vol %  $\text{NO}$ , and an increase in conductivity. The gassing abates in 15 to 30 min, indicating that crystallization is essentially complete, and the extraction is continued until the conductivity decreases to approximately 20,000 micromhos/cm. The flow of solvent is then halted. The second extraction requires 45 to 60 min in order to ensure that crystallization is complete. Prior to the third extraction, the solution, which is a sol at this point, is cooled to about 25°C; a decrease in conductivity to about 10,000 micromhos/cm accompanies this cooling. Finally, in the third extraction, additional nitrate is removed until the conductivity is in the range of 3000 to 4500 micromhos/cm, which corresponds to a  $\text{NO}_3^-/\text{U}$  mole ratio of  $0.11 \pm 0.02$ .

Sol preparation time, which varies from 3.5 to 4 hr, is independent of batch size since nitrate must be extracted for prescribed periods of time. Various precautions must be taken during sol preparation. For example, the first nitrate extraction should require a minimum of 90 min, to allow time for the proper release of nitrate; otherwise, the  $\text{NO}_3^-/\text{U}$  mole ratio of the sol product will be too high, even though the conduc-

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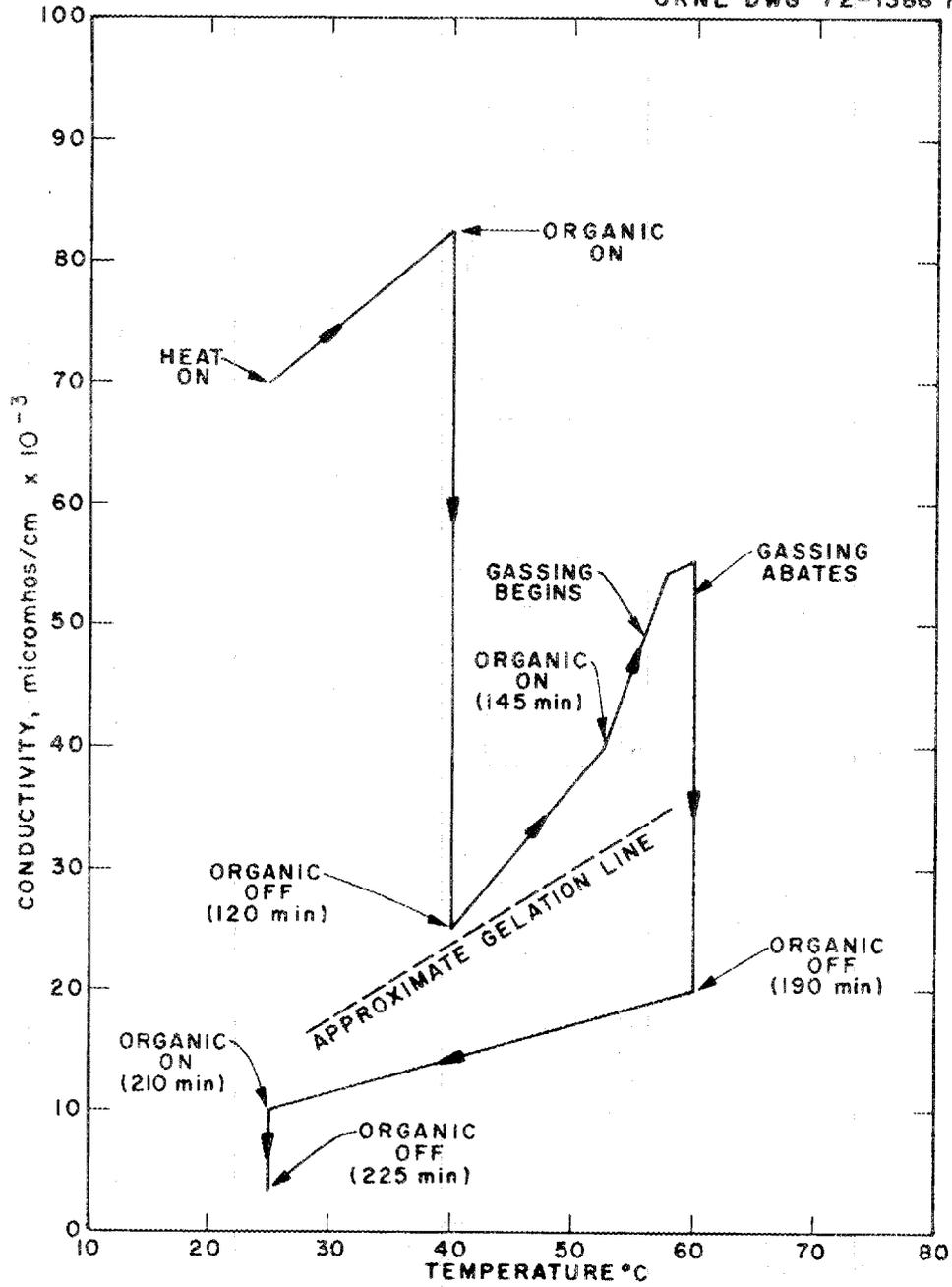
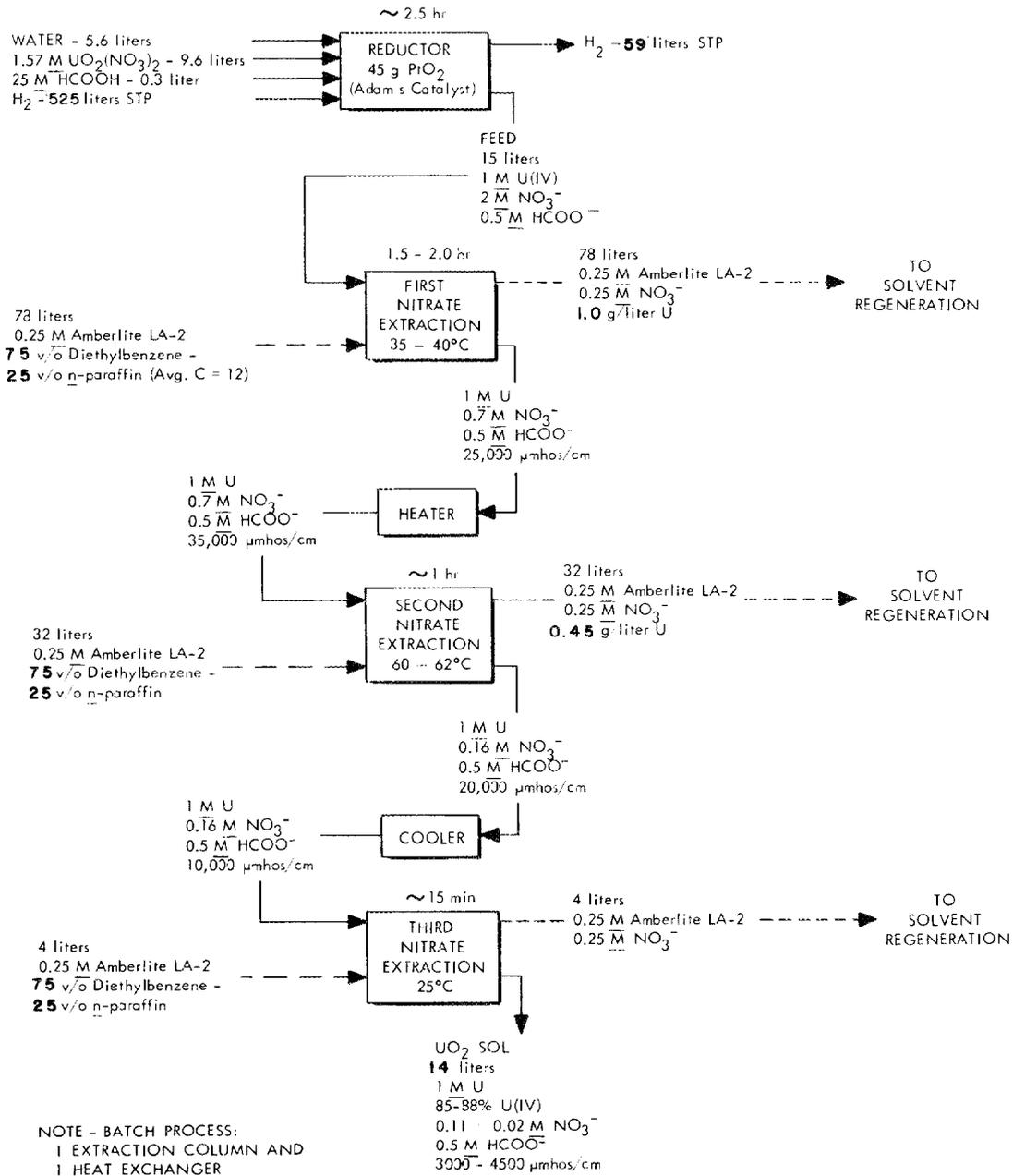


Fig. 1. Operating Curve for the Production of CUSP UO<sub>2</sub> Sols on an Engineering Scale.

Fig. 2. Chemical Flowsheet for Preparing  $\text{UO}_2$  Sol by the CUSP Process.

tivity is in the proper range. However, care must be taken not to prolong the first nitrate extraction excessively since thickening or possibly gelation can result from overextraction. During the second extraction, favorable oxidizing conditions are present (elevated temperature, and release of NO); consequently, this extraction, while sufficiently long to ensure complete crystallization, should not be unnecessarily extended to minimize the oxidation of U(IV) to U(VI).

In preparing the feed, water, concentrated uranyl nitrate solution that is stoichiometric in nitrate ( $\text{NO}_3^-/\text{U}$  mole ratio = 2), and formic acid are mixed in the proper proportions to give a solution that is 1 M in  $\text{UO}_2^{2+}$ , 2 M in  $\text{NO}_3^-$ , and 0.5 M in HCOOH (Fig. 2). Approximately 1.3 to 1.4 moles of  $\text{H}_2$  are consumed per mole of uranium reduced, and the feed to the sol preparation equipment is 1 M in U(IV), 2 M in  $\text{NO}_3^-$ , and 0.5 M in HCOOH. Approximately 65, 25, and 5% of the nitrate is extracted during the first, second, and third extractions, respectively; the extraction times are controlled by regulating the solvent flow rate. The sol product is approximately 1 M in uranium [85 to 88% U(IV)],  $0.11 \pm 0.02$  M in  $\text{NO}_3^-$ , approximately 0.5 M in  $\text{COOH}^-$ , and has a conductivity of 3000 to 4500 micromhos/cm.

## 2.2 Equipment and Procedures

An equipment flowsheet for the preparation of  $\text{UO}_2$  sol by the CUSP process is presented in Fig. 3. The order in which the equipment is discussed corresponds to the sequence of process steps.

### 2.2.1 Feed Preparation

The U(IV) feed is prepared in the batch slurry uranium reductor shown in Fig. 4. The uranyl nitrate solution (1 M in  $\text{UO}_2^{2+}$ , 2 M in  $\text{NO}_3^-$ , and 0.5 M in HCOOH) is reduced with  $\text{H}_2$  at atmospheric pressure using a commercially available platinum catalyst ( $\text{PtO}_2$ , "Adams Catalyst"). The extent of reduction is monitored by the U(IV)/U(VI) redox potential, using platinum vs glass electrodes. When the uranium reduction is nearing completion, the slope of the potential-vs-time graph decreases rapidly

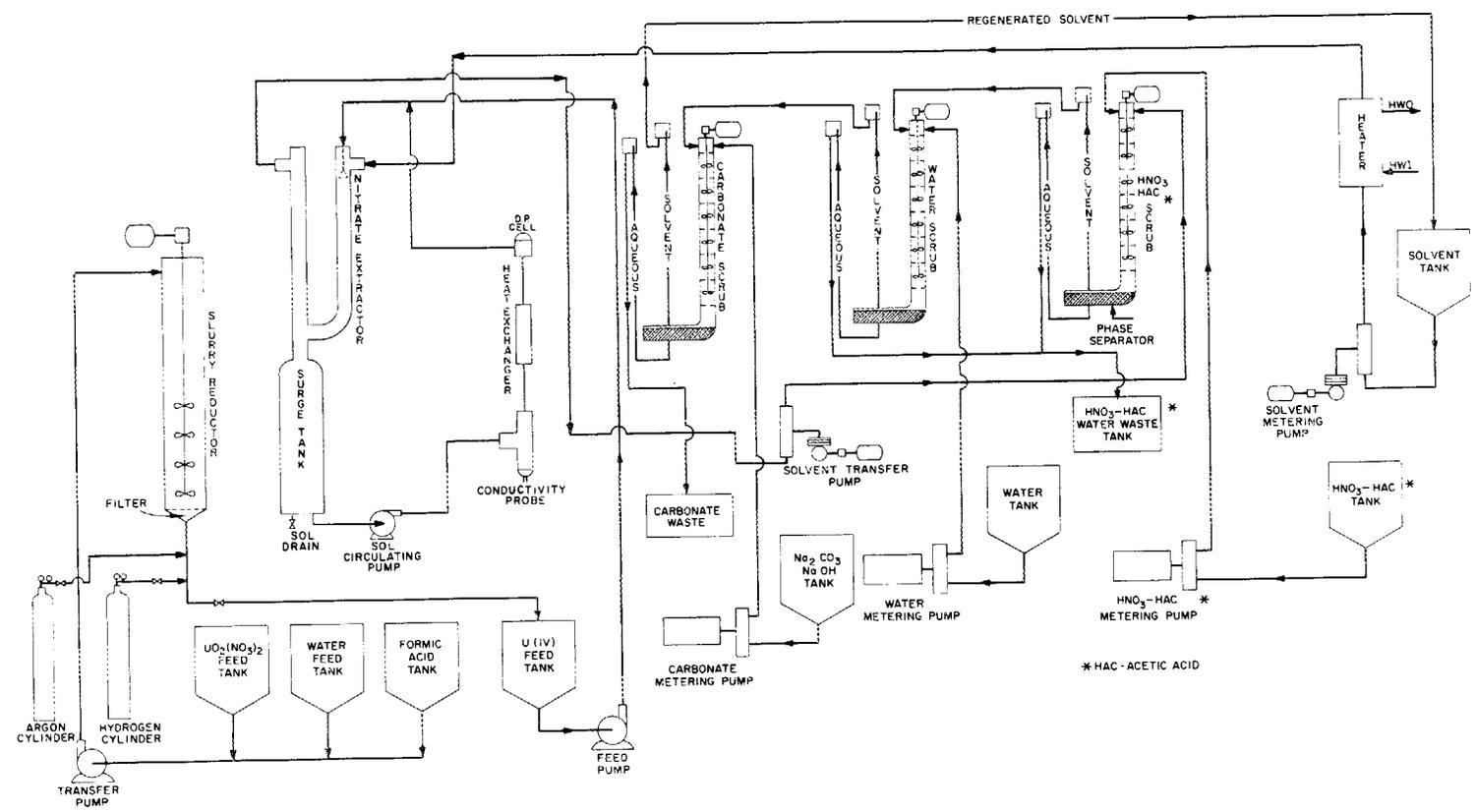


Fig. 3. Equipment Flowsheet for the Preparation of  $UO_2$  Sol by the CUSP Process.

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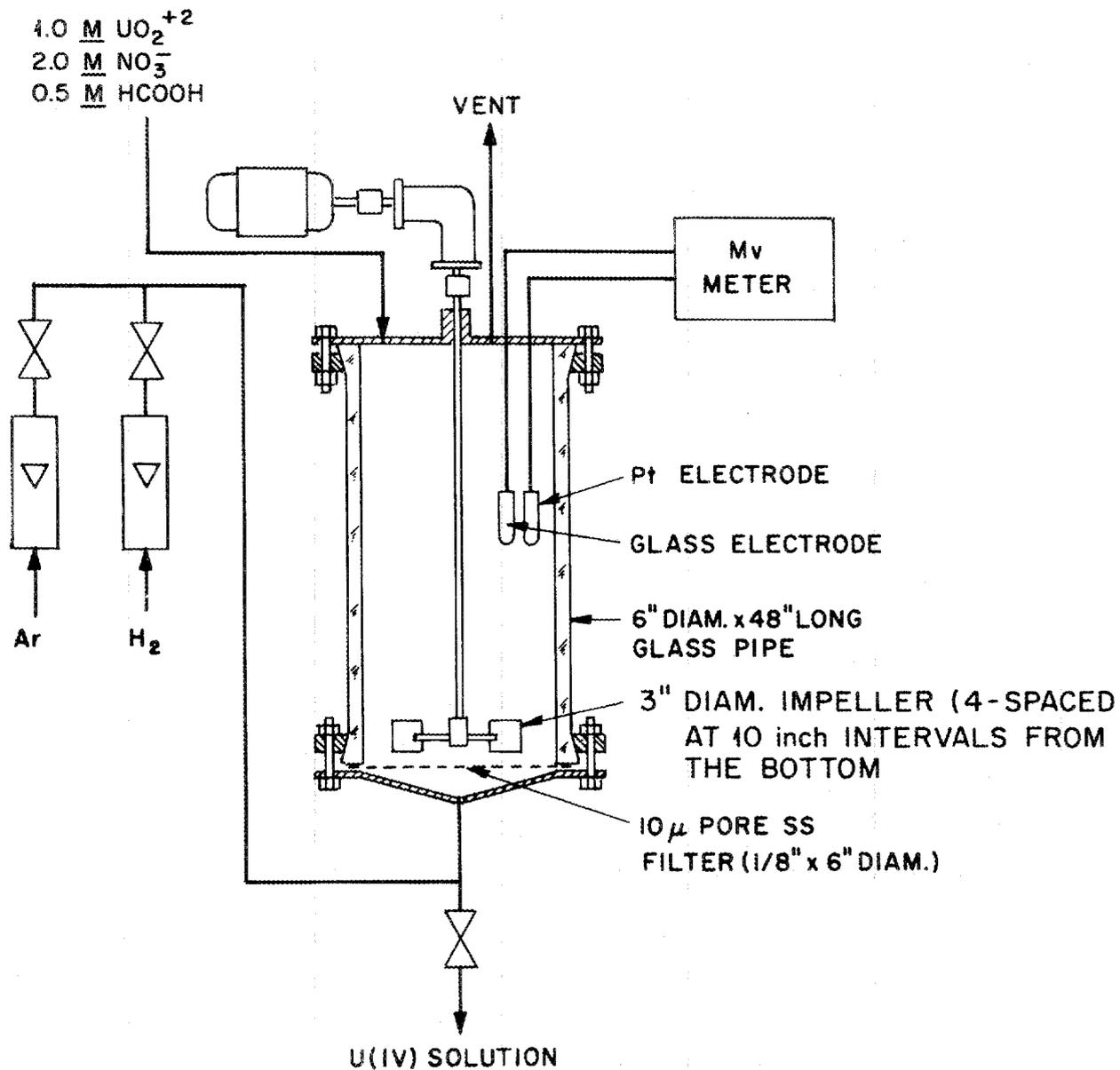


Fig. 4. Batch Slurry Uranium Reductor.

and abruptly approaches zero (Fig. 5). At this point, the hydrogen flow is turned off. Vigorous agitation is required to ensure uniform reduction since a continuing flow of  $H_2$  in the absence of uranyl ions produces ammonia. More than about 0.01 mole of ammonia per mole of uranium promotes early gelation and gives an erroneous conductivity. Conductivity is the major process control variable in the extraction steps. A period of 2 to 2.5 hr is required to reduce 15 liters of 1 M uranyl nitrate solutions ( $\sim 4$  kg of  $UO_2$ ).

When reduction is complete, the U(IV) feed solution is drained from the reductor; and the catalyst, which has been reduced to metallic platinum, is caught on the 10- $\mu$ -pore stainless steel filter. The catalyst is subsequently washed with water and reoxidized with 5 M  $HNO_3$ .

#### 2.2.2 Preparation of Sols by Solvent Extraction

The sol preparation equipment (Fig. 6) has a 15-liter aqueous-phase capacity ( $\sim 4$  kg of  $UO_2$ ) and consists of a spray column nitrate extraction contactor, a solvent reservoir, an aqueous-phase surge tank, a centrifugal pump, a conductivity probe, a heat exchanger, a differential pressure cell, and a spray header to disperse the aqueous phase into drops. The aqueous phase is circulated (3 to 4 liters/min) cocurrent with the solvent down the contactor. During the extraction periods, the solvent flows continuously to the nitrate extraction contactor and the spent solvent is sent to the solvent cleanup and regeneration system.

Following sol preparation, the sol and solvent are drained separately and the equipment is washed out successively with dilute  $HNO_3$  ( $\sim 3$  M) and with water. Some accumulation of solids occurs at the solvent-sol interface, primarily during the crystallization phase. These solids tend to cling to the equipment during draining, resulting in a loss of uranium to the equipment wash solution (see Sect. 2.3) equivalent to approximately 2 to 4% of the uranium in the feed solution, and a loss to the solvent wash (dilute  $HNO_3$ ) of approximately 0.5%. The uranium can be recovered from these acidic-wash solutions.

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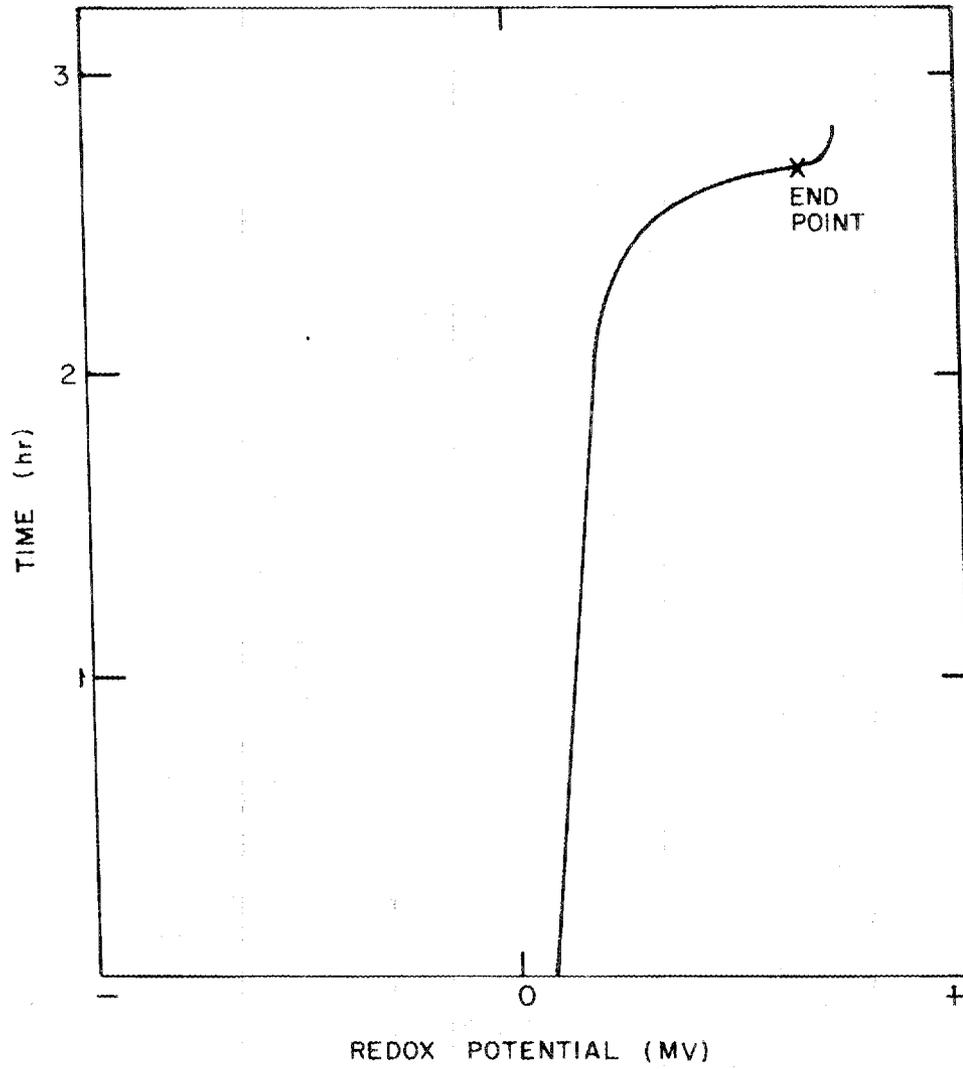


Fig. 5. Plot of Redox Potential vs Time for the Reduction of a 1 M  $\text{UO}_2(\text{NO}_3)_2$  -- 0.5 M  $\text{HCOOH}$  Solution.

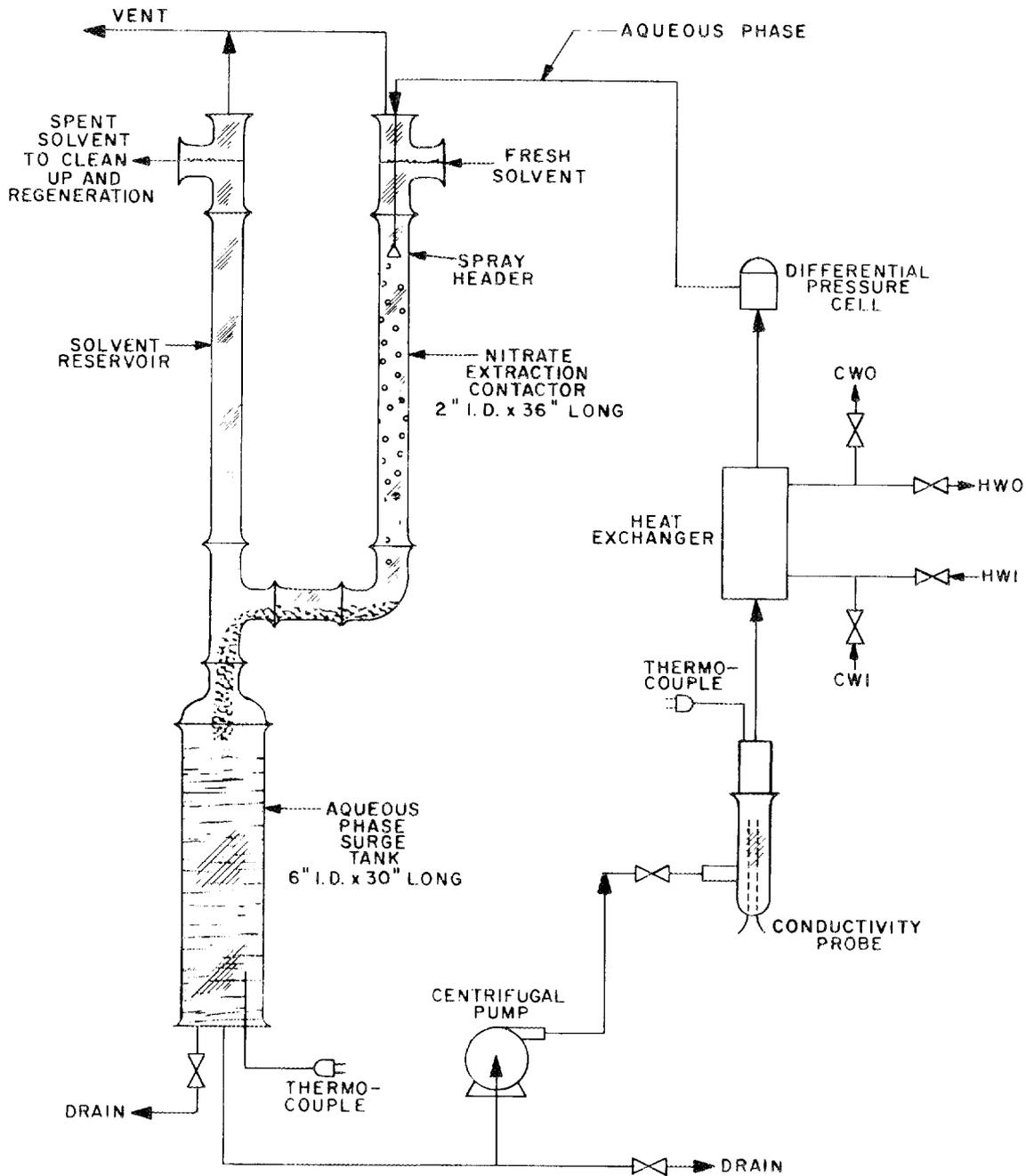


Fig. 6. Equipment Flowsheet for Preparing  $UO_2$  Sol by the CUSP Process.  
(Capacity, 15 liters of aqueous phase or  $\sim 4$  kg of  $UO_2$ ).

### 2.2.3 Solvent Cleanup and Regeneration

Some uranium is lost to the solvent, primarily during the first and second nitrate extractions. This uranium, which amounts to approximately 0.5% (see Sect. 2.3) of the uranium in the feed, is in the form of entrained sol and is present as a colloidal suspension. The particles are well dispersed, carry a slight negative charge, cannot be removed by filtration or adsorption on silica gel or activated carbon, and are not effectively removed by the standard solvent treatments. A slight loss of amine (approximately 0.06 to 0.10 mole per kilogram of  $\text{UO}_2$  prepared as a 1 M sol) also occurs during sol preparation. The amine concentration can be satisfactorily maintained at an essentially constant value by periodic additions of Amberlite LA-2 to the solvent storage tank. A three-stage solvent treatment system consisting of two cleanup stages and a regeneration stage was found to be satisfactory (see Fig. 7). A 1 M  $\text{HNO}_3$ --0.4 M  $\text{HC}_2\text{H}_3\text{O}_2$  scrub and a water wash are used to clean up the solvent; a 1 M  $\text{Na}_2\text{CO}_3$ --1 M  $\text{NaOH}$  scrub is used for regeneration. Essentially all the uranium in the solvent is removed in the cleanup acidic effluent, from which recovery can be readily accomplished.

The solvent extraction contactors used in the solvent treatment system are mixer-settlers of the type shown in Fig. 8.<sup>10</sup> Each mixer-settler is made of 3-in.-diam glass pipe to permit observation of the process streams and the operating characteristics. It is divided into six compartments, each of which has a mixing impeller; the six impellers are mounted on a common shaft with a variable-speed drive. The aqueous and organic phases enter at the top and flow cocurrently down through the six compartments to give the effect of mixing vessels in series. This arrangement ensures good stage efficiency. The mixer is designed in such a manner that the aqueous phase is dispersed into the organic phase. (The organic phase is maintained continuous to minimize emulsification.) At shutdown, the aqueous phase drains out of the vessel; consequently, only the organic phase is present at startup, and the aqueous stream is easily dispersed as it enters. Each mixer is equipped with two U-shaped sections of stainless steel tubing through which hot water can be circulated.

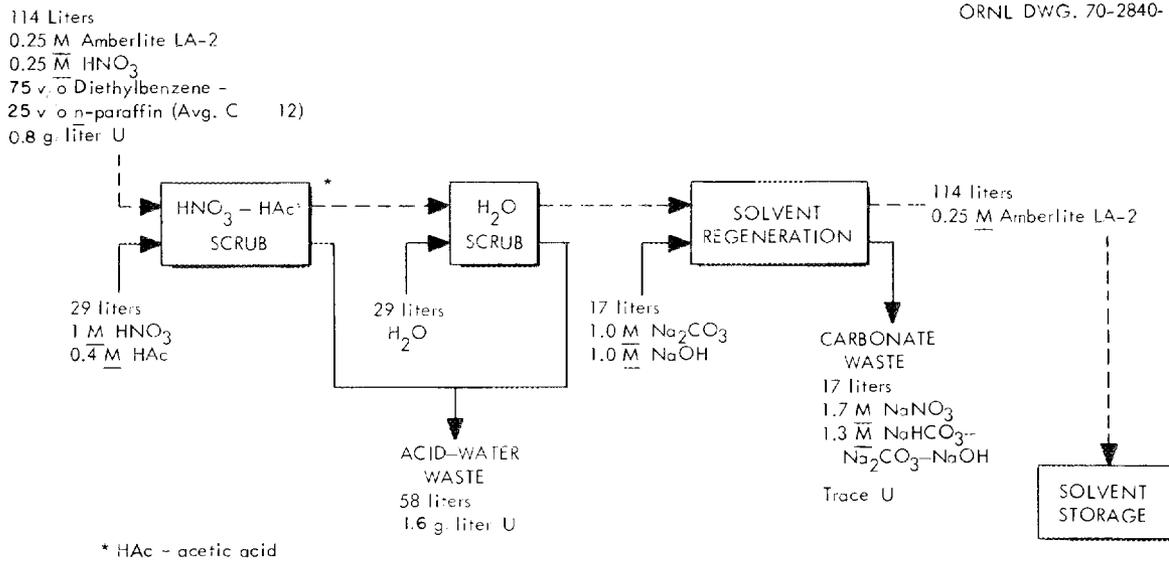


Fig. 7. Chemical Flowsheet for Solvent Cleanup and Regeneration in the CUSP Process.

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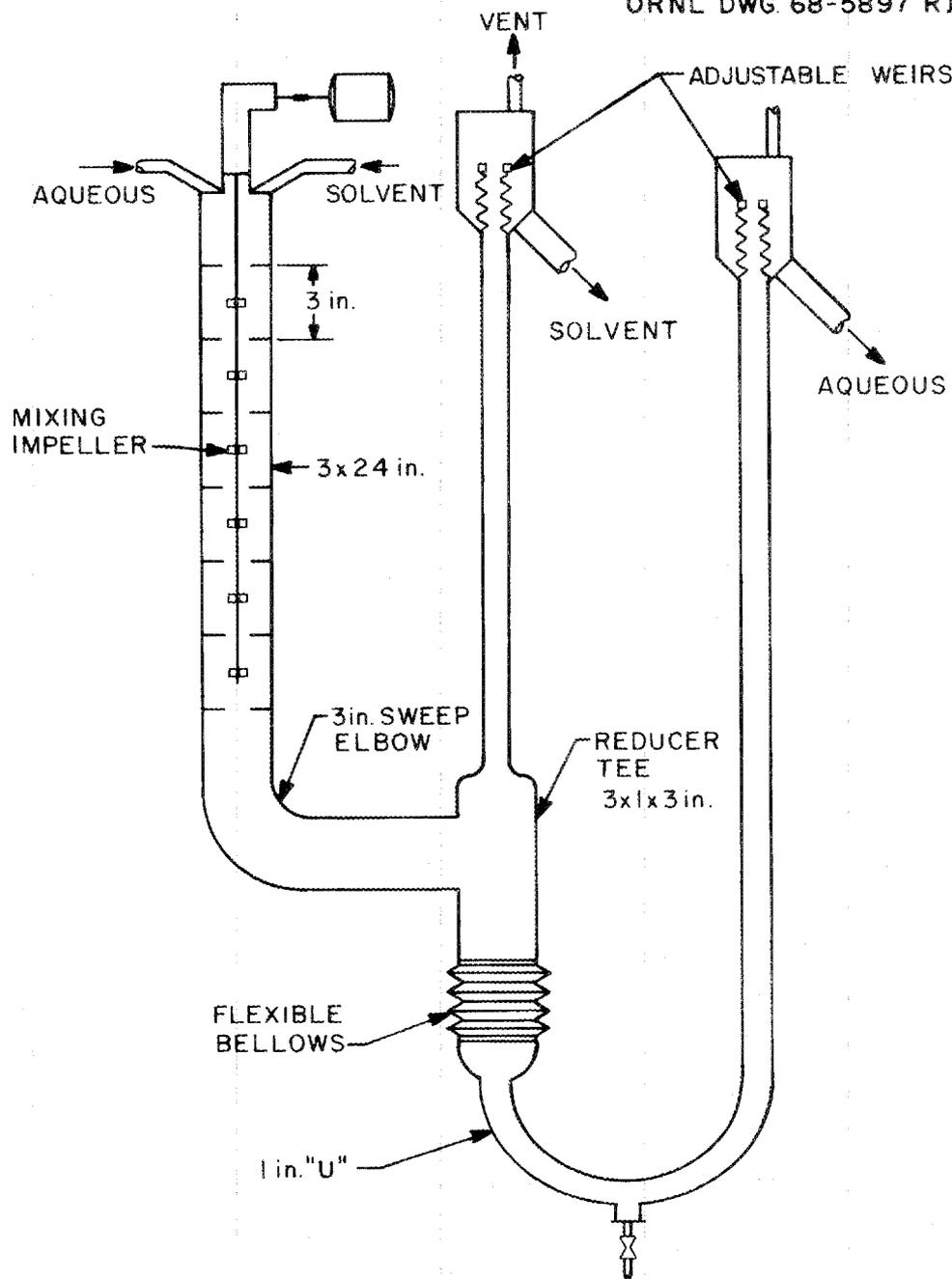


Fig. 8. Mixer-Settler Stage.

Phase separation occurs in the section located below the mixer. The position of the interface is controlled by adjustable weirs on both the aqueous and the organic overflow lines. The nominal volumetric capacity of the mixing section is 2.0 liters; that of the settler is 2.8 liters of organic phase and 1.5 liters of aqueous phase.

### 2.3 Results and Material Balances

Eight batches of sol ( $\sim 4$  kg of  $UO_2$  per batch, four batches per run) were prepared for the two demonstration runs. Some of the chemical and physical properties of the batches of sol are presented in Table 1. As seen, the reproducibility of these properties is excellent. A 15-liter batch of sol ( $\sim 4$  kg of  $UO_2$ ) was prepared on each of four days during the week preceding each demonstration run. The sols were fed to the microsphere forming step in the order of their preparation. There was no discernible difference in the microsphere forming characteristics of the various sols.

The uranium material balances for the U(IV) feed and sol preparation runs are presented in Table 2. The loss of 0.5 to 0.6% of the uranium during feed preparation is due to washing the catalyst after the feed has been drained from the reductor. Although it was not done in these runs, the wash water could be added to the U(IV) feed, which would result in 6 to 7 vol % dilution of the feed and essentially a zero uranium loss from this step. The overall uranium recoveries of 102.2% for run 1 and 104% for run 2 are calculated from many weights and analyses. Based on previous experience and a number of material balances, it would appear that the sol yields of 98 and 96.5% are probably a little high, perhaps by 2 to 4%. It is estimated that recoveries of 92 to 96% would be obtained for a large number of repetitive batches. As mentioned previously, the largest uranium losses are to the solvent acid and water scrubs and to the extraction equipment and solvent acid washes. These are acidic solutions from which the uranium can be recovered easily.

Table 1. Properties of CUSP  $UO_2$  Sols Prepared for Demonstration Runs 1 and 2

	U (mg/ml)	U(IV) Content (%)	$NO_3^-/U$ Mole Ratio	$HCOO^-/U$ Mole Ratio	$NH_4^+/U$ Mole Ratio	$Na^+/U$ Mole Ratio	Conductivity at 25° C (micromhos/cm)	pH
NFC-DR-1								
SCLHB-95	246	86	0.14	0.44	0.0023	0.0023	3990	--
-96	259	85	0.12	0.38	0.0018	0.0017	3591	--
-97	251	87	0.13	0.36	0.0016	0.0012	3397	--
-98	249	87	0.12	0.39	0.0013	0.0026	3466	--
NFC-DR-2								
SCLHB-99	253	86	0.10	0.40	0.0021	0.0053	3078	2.44
-100	254	87	0.11	0.40	0.0017	0.0023	2884	2.53
-101	253	85	0.09	0.47	--	0.0040	3010	2.53
-102	255	87	0.11	0.40	0.0025	0.0033	3477	2.57

Table 2. Uranium Material Balances for Feed and Sol  
Preparation for Demonstration Runs 1 and 2

	Run 1		Run 2	
	U (g)	U (%)	U (g)	U (%)
Reduction				
In:				
Conc. $\text{UO}_2(\text{NO}_3)_2$ Soln.	14,280	100.0	14,280	100.0
Out:				
U(IV) feed	14,199	99.4	14,209	99.5
Waste	81	0.6	71	0.5
Sol Preparation and Solvent Regeneration				
In:				
U(IV) feed	14,199	100.0	14,209	100.0
Out:				
Sol	13,927	98.0	13,712	96.5
Acid scrub	101	0.7	235	1.7
H <sub>2</sub> O scrub	91	0.6	141	1.0
Carbonate scrub	34	0.2	70	0.5
Extractor acid wash	317	2.2	543	3.8
Solvent acid wash	71	0.5	75	0.5
Total	14,541	102.2	14,776	104.0

### 3. PREPARATION OF MICROSPHERES

The ORNL sol-gel processes for preparing microspheres from actinide oxide sols, including the design and operation of the equipment, have been previously described.<sup>1,10,11</sup> In general, conversion of a sol to dense microspheres requires the following six process operations:

- (1) Dispersion of the sol into drops containing the same amount of oxide as the fired sphere.
- (2) Suspension of the sol drop in an organic liquid, usually 2EH, while water is extracted to cause gelation.
- (3) Separation of gel microspheres from the organic liquid.
- (4) Recycle of the organic liquid for reuse.
- (5) Drying of the gel microspheres.
- (6) Firing the dried microspheres at controlled conditions to remove volatiles, to sinter to a high density, and to reduce or make chemical conversions (e.g., from oxide to carbide).

The first four operations were carried out in a continuous column system (Fig. 9) in this demonstration. The last two were done batchwise.

The major differences in this demonstration of  $\text{UO}_2$  microsphere preparation, compared with earlier demonstration runs, were the use of sol prepared by the CUSP process and the formation of microspheres in a non-fluidized column. In addition, the column height was 28 ft vs the 10-ft column previously described<sup>12</sup>, and the temperature of the 2EH was 50 to 80°C in the nonfluidized column (vs 25 to 35°C for the fluidized columns). Our experience with CUSP sols has shown that both recycle of the 2EH and drying and firing of the  $\text{UO}_2$  microspheres formed in the recycled 2EH have been very troublesome. Therefore, recycle of the 2EH was a principal point to be demonstrated.

#### 3.1 Equipment and Procedures

The equipment flowsheet (Fig. 9) shows components for the first four process operations. This equipment was installed in a location where it was convenient to install the 28-ft-high column (Fig. 10). The drying and firing operations were carried out in laboratory-scale equipment that was available from microsphere preparation development studies.

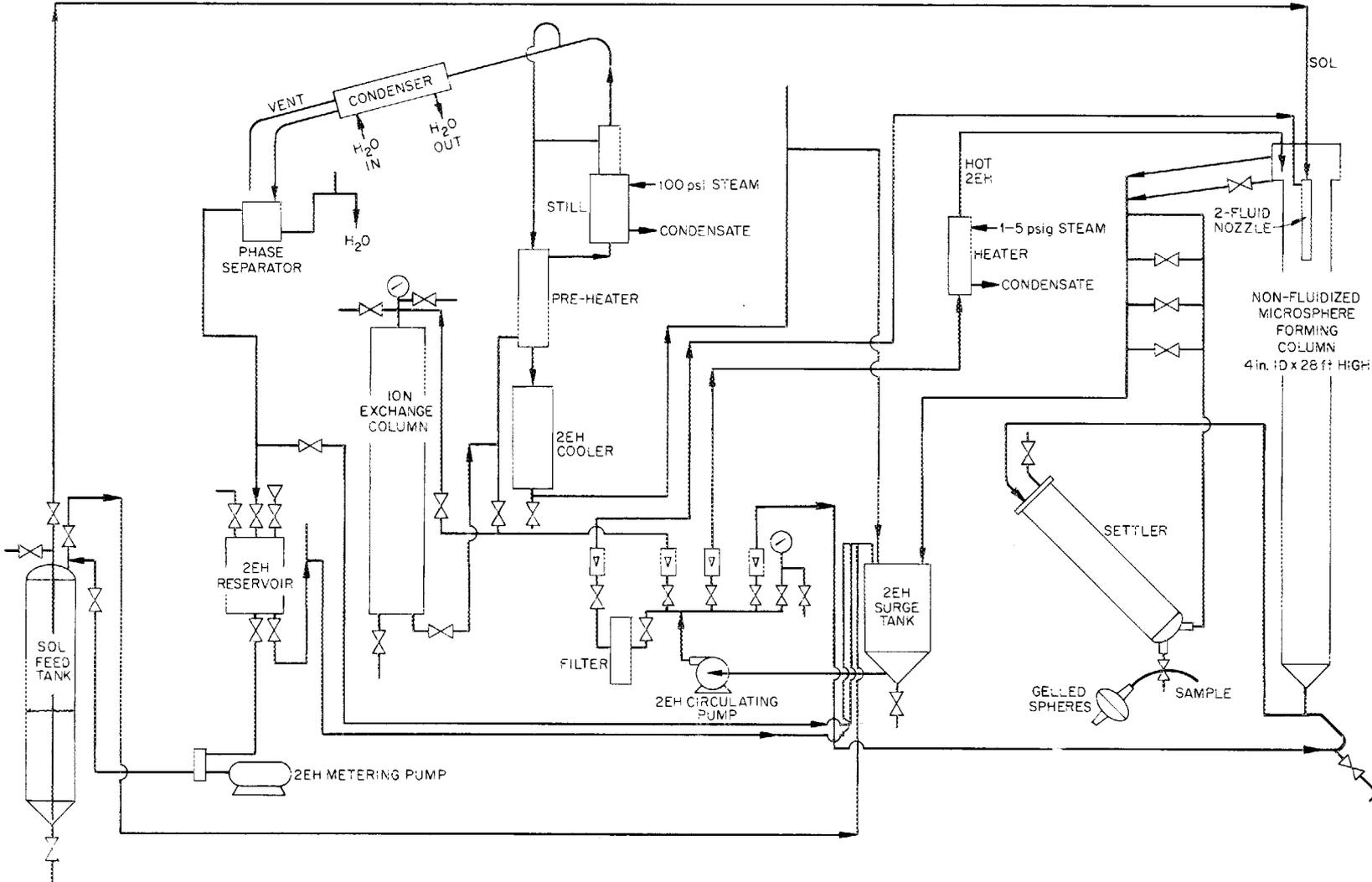


Fig. 9. Equipment Flowsheet for the Nonfluidized Microsphere-forming Column.

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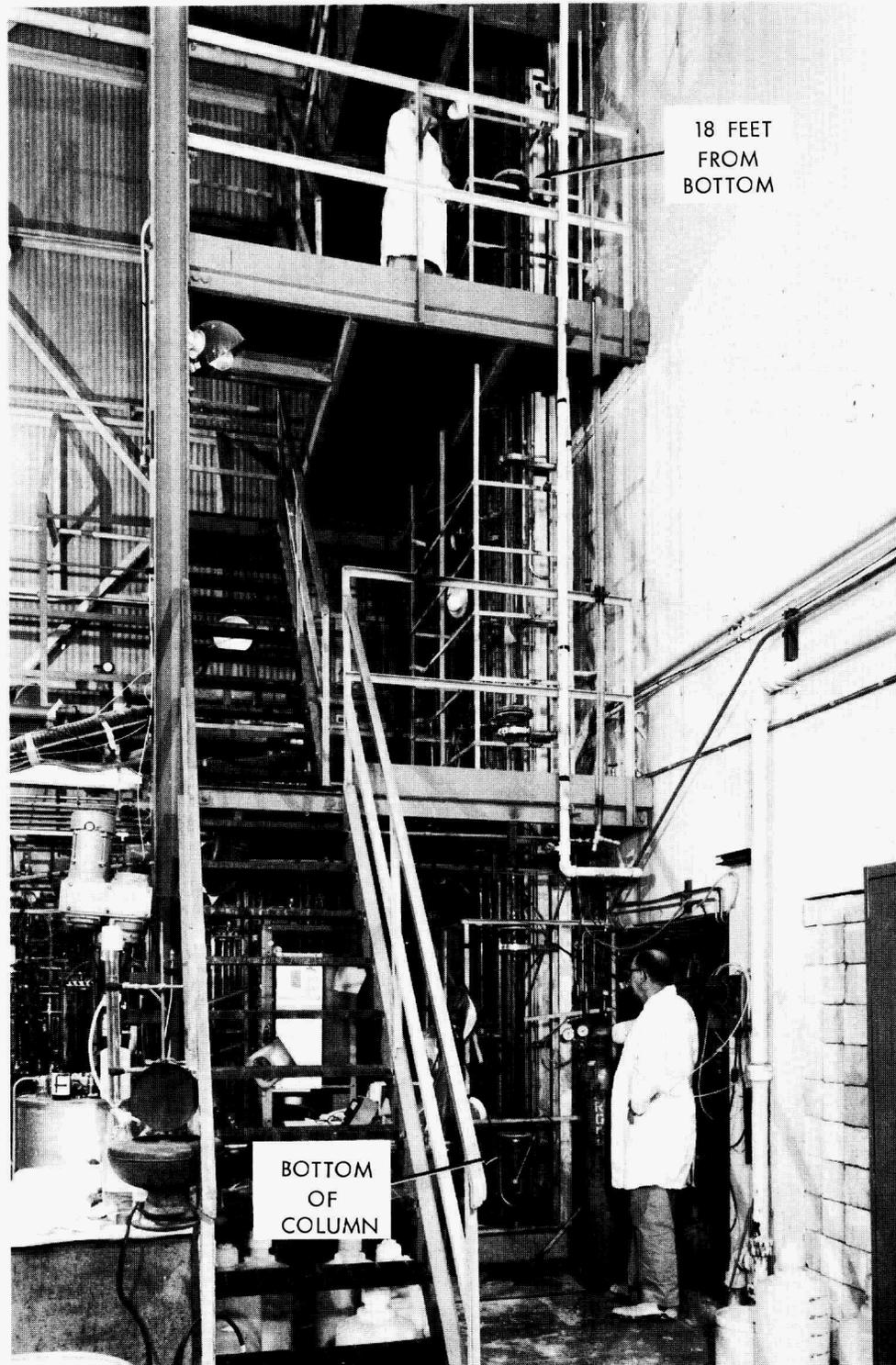


Fig. 10. Bottom 20 ft of the 28-ft-high Nonfluidized Column Used for the Formation of Sol-Gel Microspheres.

### 3.1.1 Nonfluidized Microsphere Forming Column

The 28-ft column was assembled from two 10-ft and two 4-ft lengths of 4-in.-ID Pyrex pipe. The 2EH sol or gel microspheres flow cocurrently downward and then through a 3/8-in.-OD tubing line to a 6-in.-ID by about 48-in.-long Pyrex pipe settler (Fig. 11). This is either vertical or slanted downward in the direction of flow throughout to avoid accumulation of gel microspheres. Valves in the overflow from the settler are adjusted to control the 2EH level in the column. The 2EH is circulated by a canned rotor pump, with rotameters and manually adjusted valves for flow control. This equipment was troublefree throughout the demonstration run.

The principal limitation with regard to the nonfluidized preparation of microspheres is that the sol drops introduced into a nonfluidized column must be small enough to gel before they settle to the bottom. The required column heights are dependent on mass transfer and on the settling velocity. Clinton has investigated and correlated mass transfer as a function of sol drop size and organic liquid variables.<sup>13</sup> The settling velocities may be calculated using Stokes' equation or a drag coefficient. Both the sol-drop size and the density vary with time. Thus, mass transfer and the settling velocity also vary with time, and analytical solutions are not possible. However, the time and free-fall distance as a function of sol drop variables and alcohol variables can be conveniently calculated using a computer program.

Calculations were made, using a computer program for mass transfer, to determine the effects of varying the 2EH temperature. The conditions were selected to apply to the 28-ft-high nonfluidized column with our usual  $\text{UO}_2$  or  $\text{ThO}_2$  sols. The calculated values are for a water concentration driving force,  $\Delta C$ , of 0.010 g/ml or 1.0 vol % (i.e., the water concentration in the 2EH was approximately 1 vol % less than saturation). The gelation times (Fig. 12), or the free-fall distances (Fig. 13), are inversely proportional to  $\Delta C$ ; therefore, the values for other water concentrations can be easily calculated. For example, the times (or distances) for 1.8 vol %  $\text{H}_2\text{O}$  in the 2EH at 28°C ( $\Delta C = 0.005$ ) would be twice those shown for 1.3 vol %  $\text{H}_2\text{O}$  in the 2EH at 28°C ( $\Delta C = 0.010$ ). For

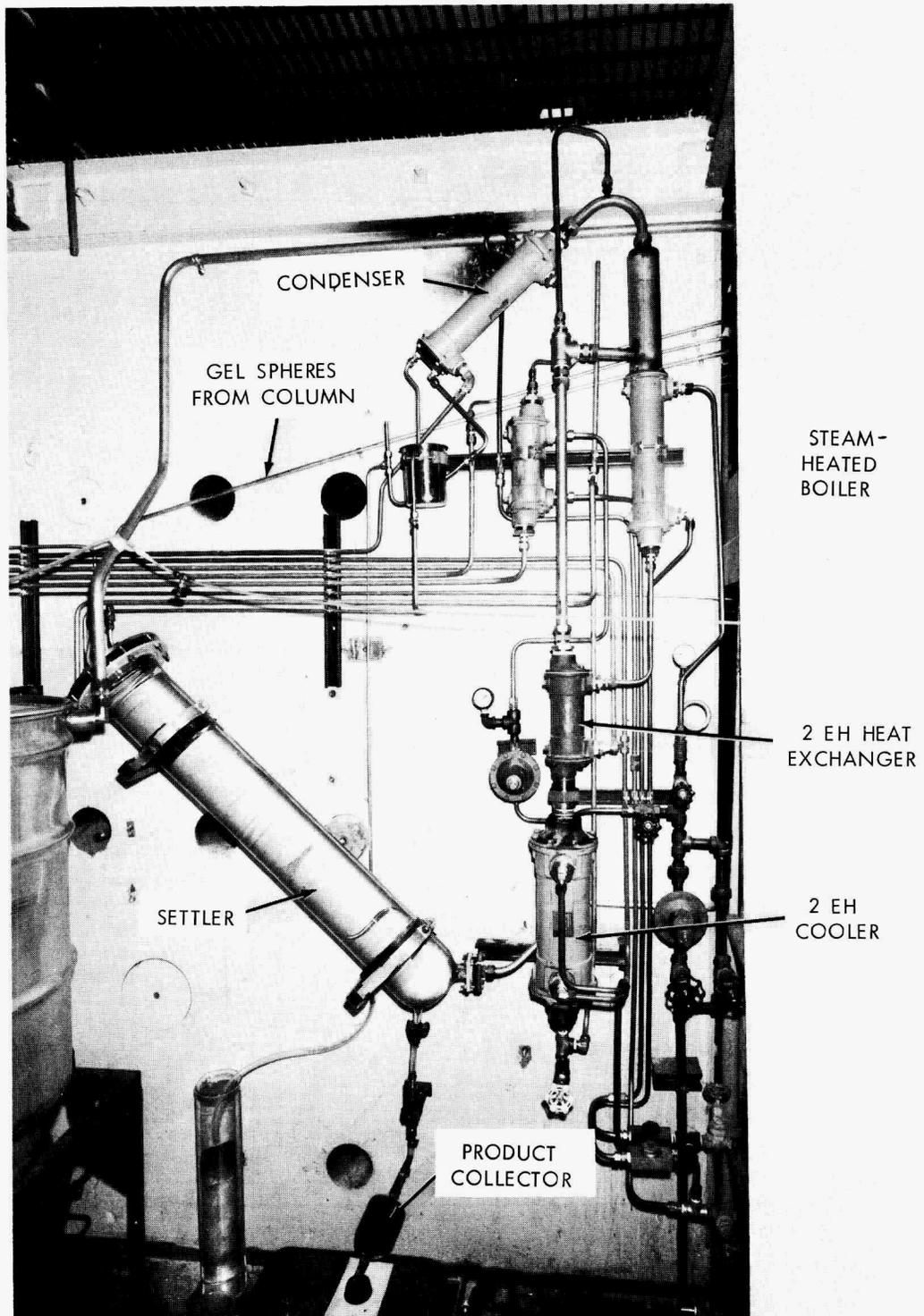


Fig. 11. Still and Product Settler for the Nonfluidized Column for the Formation of Sol-Gel Microspheres.

ORNL-DWG 71-5521

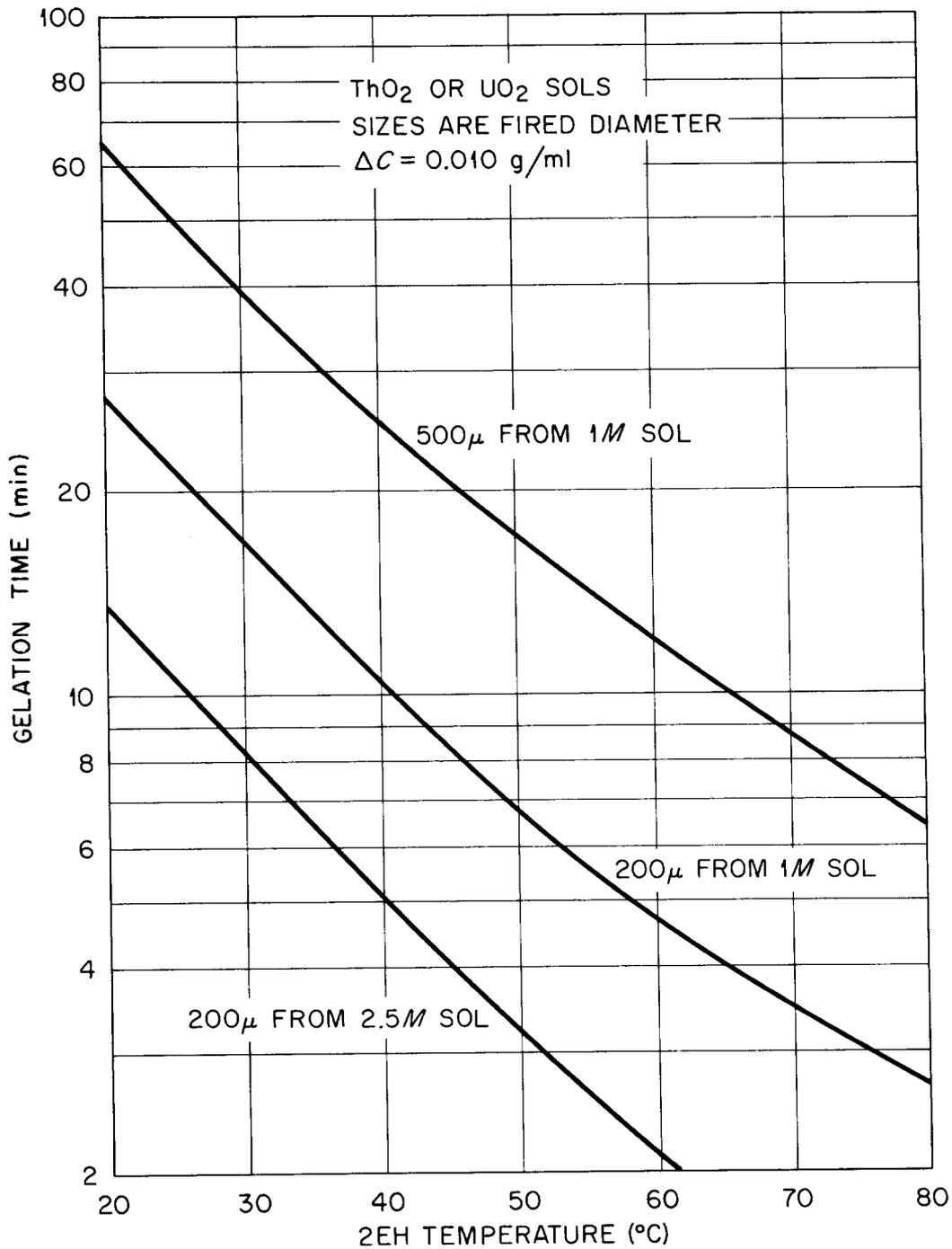


Fig. 12. Calculated Gelation Times for Various Sol Molarities and Fired Sphere Diameters as a Function of 2EH Temperature in Nonfluidized Columns.

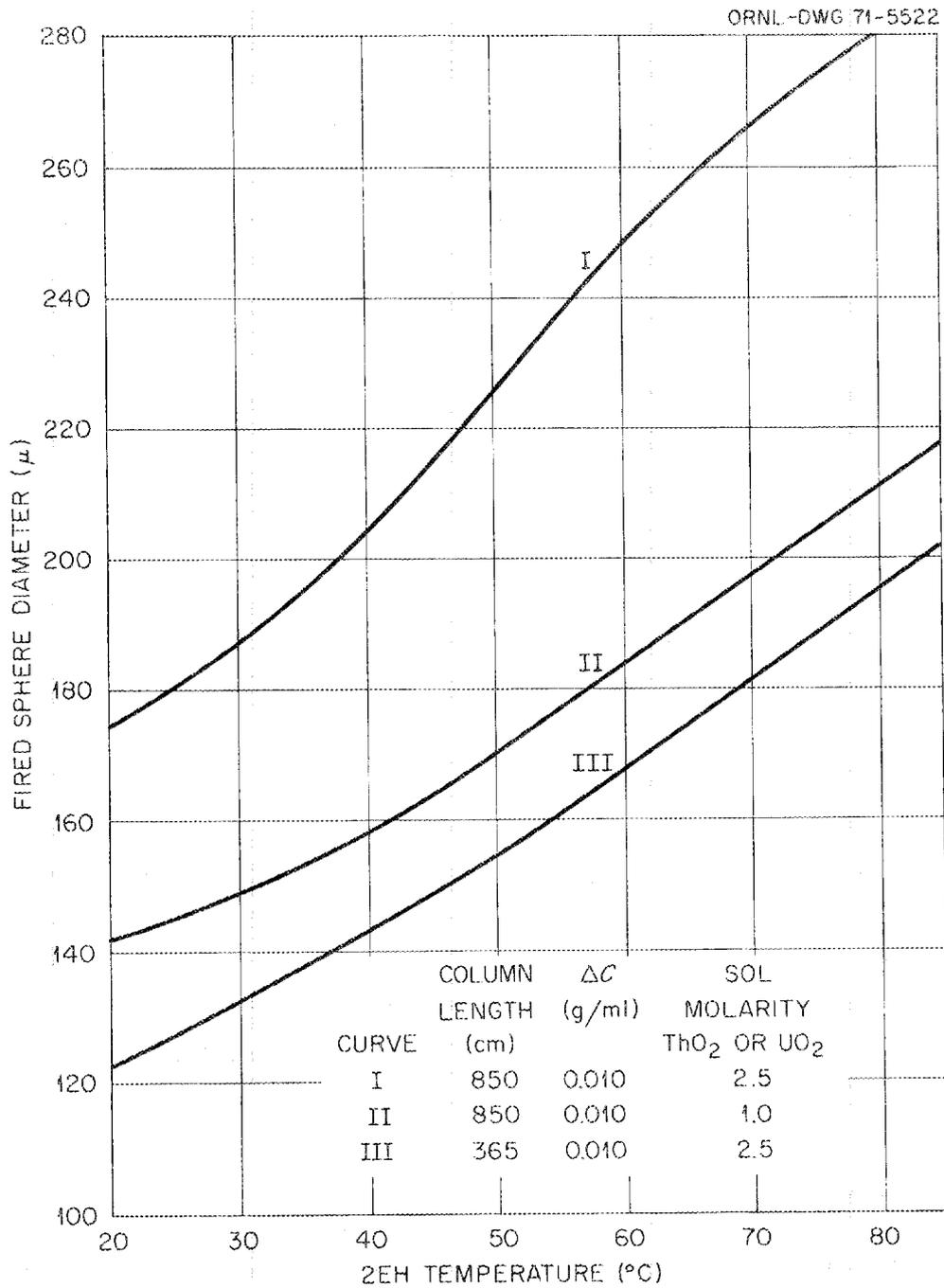


Fig. 13. Calculated Fired Sphere Sizes Attainable for Various Column Lengths and Sol Molarities as a Function of Temperature in Nonfluidized Columns Containing 2EH.

the 28-ft (850-cm) column, the sizes of the fired spheres increased from 180  $\mu$  to 280  $\mu$  for 2.5  $\underline{M}$   $\text{ThO}_2$  sol, and from 145  $\mu$  to 210  $\mu$  for 1.0  $\underline{M}$   $\text{UO}_2$  sol, as the 2EH temperature increased from 25°C to 80°C. While the rate of water extraction increased by a factor of 7 or 8, the allowable sphere size only increased by about 50% as the 2EH temperature increased from 25°C to 80°C. This can be explained by the increase in settling velocity as the temperature increases. Under the same column conditions, the allowable initial sol drop sizes are generally about 5% larger for 1  $\underline{M}$   $\text{UO}_2$  sol than for 2.5  $\underline{M}$   $\text{ThO}_2$  sol; however, the drops of the more dilute sol shrink to a smaller final size. While the thoria sol is more concentrated initially and is, therefore, closer to gelation, the higher density and the higher settling velocity for a  $\text{ThO}_2$  sol drop, as compared with those for a  $\text{UO}_2$  sol drop of the same initial size, require a larger free-fall distance before gelation is complete.

Heated 2EH is supplied to the top of the column, and the temperature down the column decreases as heat is lost to the surroundings. This temperature gradient is favorable since it gives rapid extraction of water at the top, where the sol is fluid, and slower extraction at the bottom, where gelation occurs. It may be seen from Fig. 13 that the 28-ft column requires a 2EH temperature of 80°C for  $\Delta C = 0.010$  g/ml in order to prepare 210- $\mu$  fired spheres from a 1  $\underline{M}$   $\text{UO}_2$  sol. Use of a lower temperature would be adequate if the  $\Delta C$  were larger, but this is impossible since heated 2EH is required to produce 150- to 210- $\mu$   $\text{UO}_2$  spheres. The residence time of the  $\text{UO}_2$  in the nonfluidized column (2 to 5 min in hot 2EH) is much less than that of the 2EH (more than 30 min); thus, the 2EH flow rate has only a small effect.

### 3.1.2 Sol Feed System

The sol was fed by displacement from a feed tank by a metered stream of 2EH and was then dispersed into drops by using a glass two-fluid nozzle. These items of equipment have been described previously.<sup>11</sup> The only mechanical difficulty with this arrangement involved the low-speed operation of a variable-speed motor for the 2EH metering pump. This difficulty was eliminated by replacing the motor and gear reducer with one having a more suitable range.

The two-fluid nozzle was intended to be operated with laminar flow of the 2EH drive fluid in order to give varicose breakup of the sol.<sup>11</sup> The desired capacity of 3 kg of UO<sub>2</sub> per 24-hr day required relatively high drive fluid flows, which tend to result in small satellite drops or in turbulent operation (which produces nonuniform drop sizes). The diameter of a 1 M UO<sub>2</sub> sol drop is 3.4 times the diameter of the fired UO<sub>2</sub> sphere. For example, a 170-μ fired sphere requires an initial 575-μ sol drop, which should result from varicose breakup of a 275-μ- or 0.011-in.-diam sol stream. Demonstration run 1 was made using nozzles with 0.018-in.-diam capillaries. While the 2EH drive fluid accelerates the sol stream to give the desired average sol drop or sphere size, there were many small drops with poor overall uniformity. The uniformity was greatly improved in demonstration run 2, which was made using nozzles with 0.013-in.-diam capillaries. However, use of the 0.013-in.-diam capillaries caused some difficulties with plugging and slow increases in pressure drop. The frequency of nozzle plugging was greatly diminished by simply installing a glass frit filter in the sol line to the nozzle.

For nozzles of this type and 1 M UO<sub>2</sub> sol, the varicose breakup equation<sup>11</sup> can be expressed in the following forms:

$$S = k(ID) \sqrt{F/f},$$

$$k = (S/ID) \sqrt{f/F},$$

where S is the mean diameter of the sol drop; ID is the inside diameter of the nozzle; F and f are sol and 2EH flow rates, respectively; and k is a dimensionless constant, which should be equal to about 1.5.<sup>11</sup>

Using the mean diameters of the fired spheres described in Sect. 3.2 and Table 5, and a sol drop diameter 3.4 times the fired diameter, substitution gives:

$$k = (3.4) (0.0158/0.34) \sqrt{575/7.4} = 1.40,$$

$$k = (3.4) (0.0167/0.34) \sqrt{575/7.0} = 1.53.$$

The other results would also give reasonable agreement with the varicose breakup equation.

### 3.1.3 Recycle of 2-Ethyl-1-hexanol

The composition of the organic liquid is the principal operating variable during the conversion of a specified sol into gel microspheres by an ORNL sol-gel process. Problems such as sticking, clustering, coalescence, cracking, or distortions can be effectively controlled by varying this composition.<sup>11</sup> In a demonstration run, the overall procedure must contain provisions for maintaining proper control of the organic composition throughout the run. A satisfactory steady-state composition is the ultimate objective.

The selection of the organic liquid composition and the recycle treatments was based on tests with CUSP sols in both fluidized-bed and nonfluidized columns. The primary organic liquid for all tests in the 28-ft column was 2EH. While isoamyl alcohol extracts water rapidly and leads to gelation in shorter columns than 2EH, all of the product  $UO_2$  particles greater than 100  $\mu$  in size exhibit severe distortions. Hexyl alcohols (2-methylpentanol and mixtures) show intermediate properties, but our limited results with these alcohols did not appear promising for forming 200- $\mu$ -diam  $UO_2$  spheres.

The water extracted by the 2EH is removed by a single-stage distillation using small shell-and-tube heat exchangers (Figs. 9 and 11) and steam at about 100 psia. With steam at this pressure, the 2EH returned to the system contains about 0.4 vol % water. For the demonstration run flow rates, the steady-state water contents would be about 0.6 vol % at the top of the column and 0.9 vol % at the bottom.

Two variables that can be initially adjusted to and maintained at acceptable values are the surfactant composition and the pH. Formic acid extracted from the CUSP sols and any degradation products of surfactants or 2EH contribute to coalescence, clustering, or cracking of the  $UO_2$  spheres; therefore, these must be limited to low concentrations. An overall objective was to demonstrate the simplest acceptable alcohol recycle procedure consistent with the control of these variables.

Removal of formic acid is required when CUSP sols are used because its presence causes unacceptable amounts of clustering, coalescence, or sticking of  $UO_2$  spheres. We used a weak-base ion exchange resin (Amber-

lyst A-21) to remove the formic acid from the 2EH, following the procedures reported previously.<sup>14</sup> Use of this ion exchange resin also removes any nitrate that has been extracted from the sol and maintains a pH of 5 to 7 for the 2EH (as measured with a glass electrode -- calomel electrode system) if other treatments, such as HNO<sub>3</sub> addition, are not used.

Clustering, sticking, and coalescence of sol drops or gel spheres are much less troublesome in nonfluidized columns than in fluidized-bed columns. Therefore, many surfactant concentrations give good results initially. We wanted to select a concentration that minimized long-term problems stemming from the accumulation of degradation products. The removal of nitrate by the ion exchange treatment is favorable since it prevents deleterious surfactant reactions in the still. Pure 2EH or 2EH containing 0.1 to 0.5 vol % Ethomeen S/15 or Pluronic L-92 was usually satisfactory for the CUSP UO<sub>2</sub> sols in the nonfluidized column. However, it occasionally gave undesirable doublet or partially coalesced drops. Low concentrations of Span 80\* were more consistently effective in preventing doublets, although they tended to cause surface roughness or dimples. The ion exchange step has been shown previously to hydrolyze or otherwise change Span 80; surprisingly, however, the modified Span 80 remains effective in preventing doublets in the nonfluidized column and, in addition, does not cause the surface roughness or dimples observed when fresh Span 80 is used. Therefore, the demonstration run was made with 0.1 to 0.3 vol % Span 80 that had been modified by flowing through the ion exchange resin system.

The 2EH was used for more than 250 hr of UO<sub>2</sub> microsphere preparation and still appears suitable for continued use. Regeneration of the ion exchange resin column indicates accumulation of about 18% of the formic acid and 8% of the nitrate in the sol feed. (Both absorbed and "free" formate and nitrate are present in the sol, but only the free ions are transferred with the water to the 2EH during dehydration of the sol.) These acids are subsequently removed in the ion exchange column. The pH of the 2EH during steady-state operation was about 6.0. The operation of

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\* A sorbitan monooleate ester distributed by Atlas Chemical Industry.

the still to remove water and the ion exchange treatment to remove formate and nitrate required little attention and caused no difficulties. Normal makeup of the 2EH that is removed with the gel product in the still condensate, or during regeneration of the ion exchange resin, might provide enough dilution to maintain any long-term accumulation of impurities at an acceptable steady-state level.

#### 3.1.4 Drying and Firing

Drying and firing of the gel  $\text{UO}_2$  microspheres involve some significant and complex structural changes. The gel microspheres have a density less than 40% of that of the final product, and must lose up to 15% of their original weight. Results of differential thermal analyses<sup>15</sup> indicate some of the changes that take place during drying and firing. The volatile constituents include water, nitrate, formate, 2EH, and surfactants. The  $\text{UO}_2$  must be protected from excessive oxidation during drying and firing. Finally, the uranium oxide must be reduced from about  $\text{UO}_{2.2}$  to  $\text{UO}_{2.01}$ . As a preliminary to the drying operation, argon is blown down through the gel spheres to remove adherent 2EH.

The overall drying-firing program, starting with gel microspheres that are wet with 2EH was as follows:

- Drying: Argon flows, at 25 to 110°C, for 1 to 2 hr
  - Argon + steam flow, at 110 to 180°C, for about 4 hr
  - Argon + steam flow, at 180°C overnight
- Firing: To 500°C at 100°C/hr in argon
  - Over the range 500 to 1100°C at 300°C/hr in argon
  - At 1150°C for 4 hr in Ar--4%  $\text{H}_2$
  - Over the range 1150°C to <100°C for >36 hr in argon

The purpose of the steam was to promote removal of organics and thus avoid leaving excessive carbon in the fired spheres. We used 0.5 to 1 g of steam per gram of  $\text{UO}_2$ . Although the higher temperatures with steam are more effective for carbon removal, they tend to make the  $\text{UO}_2$  gel become more reactive and more sensitive to oxidation. Therefore, we chose 180°C as the maximum temperature, so that we would have less difficulty with

oxidation during the transfer from the drying equipment to the firing furnace. The Ar--4% H<sub>2</sub> reduces uranium oxides to UO<sub>2</sub>. The long cool-down is characteristic of our furnace; however, faster cooling, as high as 20°C/min, would not affect the spheres. Use of an argon atmosphere is necessary during cooling because any O<sub>2</sub> present would oxidize the UO<sub>2</sub>, and also because H<sub>2</sub> is absorbed at intermediate temperatures. The dense UO<sub>2</sub> spheres are not reactive with air below 100°C.

The drying and firing equipment consisted of small, laboratory-scale batch units that had been used for other sol-gel development studies. The product collectors and dryers (Fig. 11) were Pyrex vessels fabricated from 600-ml filter funnels with coarse-porosity filter frits. These dryers were placed in a laboratory oven and connected both with an argon supply and with steam from a distillation flask. The firings were made in alumina crucibles in a commercial muffle furnace that had been modified to improve control of the atmosphere.

### 3.2 Results and Material Balances

The size distributions (weight percent) of the calcined microspheres produced during the two demonstration runs are shown in Tables 3 and 4. The nonfluidized microsphere-forming column was operated continuously. The first run (duration, 116 hr), was made in three parts. The first part was made using two glass two-fluid nozzles (0.018-in.-ID sol feed capillaries) with independent sol feed systems and a sol flow rate of approximately 3 cc per minute per nozzle. The size distribution of the composite of six batches of calcined microspheres (a total of 5834 g) was: <125 μ, 16.7 wt %; 125-210 μ, 73.6 wt %; and >210 μ, 9.8 wt %. The >210-μ fraction resulted from larger microspheres that had not been sufficiently dried after falling through the column and subsequently stuck together; the <125-μ fraction was formed as the result of satellite formation, which is inherent in the operation of the two-fluid nozzle when microspheres in the 150- to 200-μ size range are produced. The production rate for part 1 was approximately 2.5 kg of UO<sub>2</sub> per day.

Table 3. Size Distribution (wt %) of UO<sub>2</sub> Microspheres Produced  
During Nonfluidized Column Demonstration Run 1

Batch No.	Size (μ)					
	-125	125-149	149-177	177-210	210-250	+250
Part 1 <sup>a</sup>						
1	13.9	5.1	35.3	36.5	3.7	5.4
2	17.1	5.1	34.0	32.5	0.7	10.5
3	16.4	6.6	36.1	26.1	0.7	14.1
4	15.2	5.0	36.0	32.8	0.6	10.4
5	20.7	7.1	42.6	24.0	1.2	4.4
6	16.6	4.8	34.2	36.8	0.7	6.9
Total weight, g	972.1	325.4	2119.8	1846.6	73.0	496.9
% of grand total	16.7	5.6	36.3	31.7	1.3	8.5
						
73.6						
Part 2 <sup>a</sup>						
1	20.0	6.6	42.5	28.5	0.9	1.5
2	18.1	5.9	40.7	35.0	0.3	0.1
3	22.5	12.6	48.0	15.0	0.5	1.4
Total weight, g	494.2	194.9	1072.1	681.1	13.3	23.9
% of grand total	19.9	7.9	43.2	27.5	0.5	1.0
						
78.6						
Part 3 <sup>a</sup>						
1	18.8	9.3	37.3	18.5	4.6	11.6
2	28.7	9.3	31.2	15.2	4.7	10.9
Total weight, g	296.4	119.0	443.2	218.5	58.0	144.9
% of grand total	23.2	9.3	34.6	17.1	4.5	11.3
						
61.0						

<sup>a</sup>NOTE: Part 1 -- Two glass two-fluid nozzles (∅0.018-in.-ID sol feed capillaries) with independent feed systems were used; sol flow rate, ∼3 cc per min per nozzle.

Part 2 -- One glass two-fluid nozzle (∅0.018-in.-ID sol feed capillaries) was used; sol flow rate, ∼3 cc/min.

Part 3 -- One glass two-fluid nozzle (∅0.018-in.-ID sol feed capillaries); 2EH flow in turbulent region; sol flow rate, ∼6 cc/min.

Table 4. Size Distribution (wt %) of UO<sub>2</sub> Microspheres Produced During Nonfluidized Column Demonstration Run 2<sup>a</sup>

Batch No.	Size (μ)					
	-125	125-149	149-177	177-210	210-250	+250
1	11.8	6.7	75.8	5.7	0.07	0.03
2	14.7	7.1	73.4	4.5	0.09	0.09
3	14.4	7.4	68.5	9.3	0.3	0.15
4	15.3	9.0	67.5	8.1	0.1	--
5	17.9	8.6	65.6	7.6	0.2	0.09
6	10.1	5.4	74.2	10.2	0.1	--
7	10.3	7.2	71.6	10.6	0.2	0.07
8	13.3	7.6	67.7	10.3	0.6	0.4
9	11.7	6.6	71.3	9.9	0.5	0.1
10	9.7	7.1	64.6	16.3	0.7	1.6
11	12.4	6.6	70.7	9.8	0.3	0.2
12	14.7	13.5	67.1	4.4	0.1	0.1
13	9.7	7.1	79.1	4.0	--	--
14	10.8	19.1	55.9	13.3	0.8	0.1
Total weight, g	1542.4	1020.2	8356.2	1066.5	35.8	25.2
% of grand total	12.8	8.5	69.4	8.9	0.3	0.2
		86.8				

<sup>a</sup>One glass two-fluid nozzle (~0.013-in.-ID sol feed capillaries) was used; sol flow rate, ~7.3 cc/min.

Some difficulty was encountered in controlling the sphere size from one of the nozzles during part 1. Thus the faulty nozzle was removed from the system, and part 2 was made using only one two-fluid nozzle and a sol flow rate of approximately 3 cc/min. The size distribution of the composite of three batches of calcined microspheres (a total of 1280 g) was: <125  $\mu$ , 19.9 wt %; 125-210  $\mu$ , 78.6 wt %; and >210  $\mu$ , 1.5 wt %. The amount of the <125- $\mu$  fraction was about the same as in part 1; however, there was a marked decrease in the amount of material in the >210- $\mu$  fraction (1.5 wt % as compared with 9.8 wt %). The production rate for part 2 was approximately 1.4 kg of  $UO_2$  per day.

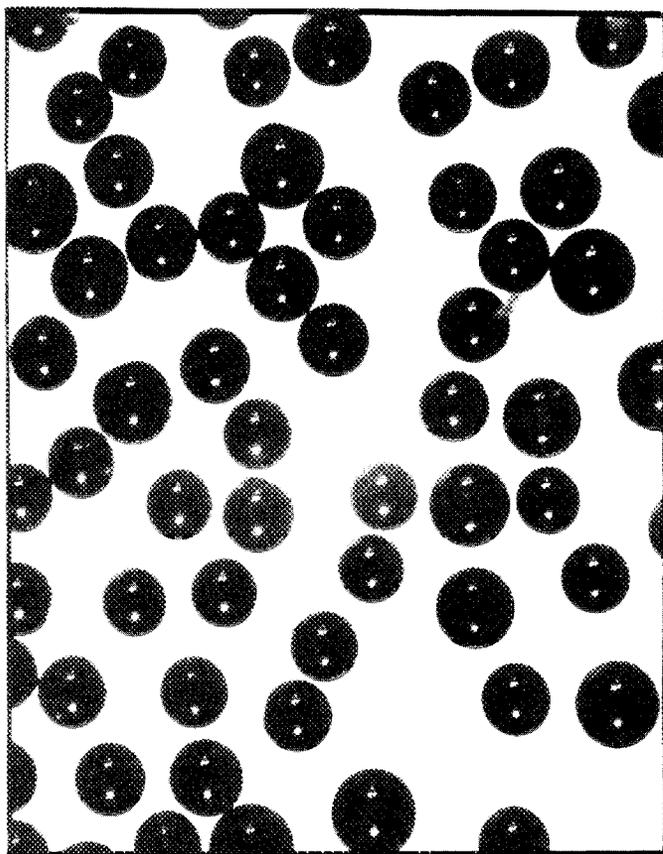
Part 3 was made using one two-fluid nozzle and a sol flow rate of approximately 6 cc/min. The size distribution of the composite of two batches of calcined microspheres (a total of 1280 g) was : <125  $\mu$ , 23.2 wt %; 125-210  $\mu$ , 61 wt %; and >210  $\mu$ , 15.8 wt %. Because of an operational error, this part of the run was made with the nozzle alcohol flow in the turbulent range. The result was a loss of control of sphere size, as indicated by the size distribution.

The second run (duration, 104 hr), was made using one two-fluid nozzle (0.013-in.-ID sol feed capillaries) and a sol flow rate of approximately 7 cc/min. The size distribution of the composite of 14 batches of calcined microspheres (a total of 12,330 g) was: <125  $\mu$ , 12.8 wt %; 125-210  $\mu$ , 86.8 wt %; and >210  $\mu$ , 0.5 wt %. The production rate for the run was approximately 2.9 kg of  $UO_2$  per day.

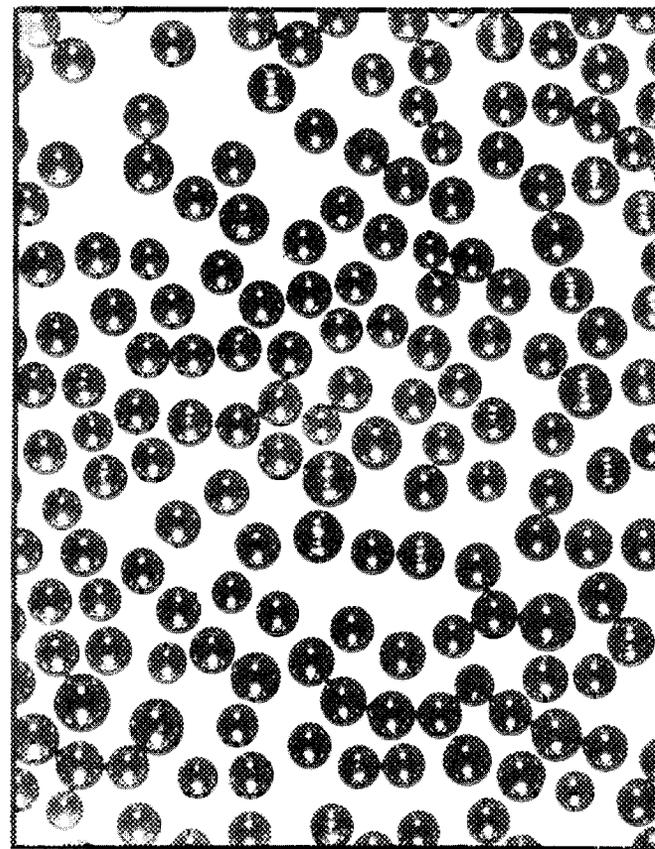
Some of the chemical and physical properties of the calcined microspheres (see Table 5) are as follows: density, 97 to 100% of theoretical; O/U atom ratio, 2.003 to 2.005; roundness ratio ( $D_{max}/D_{min}$ ), 1.02 to 1.03; carbon content, 24 to 60 ppm, and iron content, 12 to 46 ppm. The size control was quite good, especially for run 2, in which the standard deviation was approximately 10%. There was very little surface porosity, as indicated by the small surface area (0.008 to 0.4  $m^2/g$ ) and the low gas release ( $\sim 0.004$  cc/g). Photomicrographs of the dried and calcined microspheres (see Fig. 14) indicates that the spheres are round, and that cracking and surface imperfections did not represent a problem.

Table 5. Summary of Physical and Chemical Properties of Calcined UO<sub>2</sub> Microspheres Produced During Nonfluidized Column Demonstration Runs 1 and 2

	Run 1		Run 2	
	Batch 1-2	Batch 2-3	Batch 3	Batch 7
Weight of calcined product, g	924.8	628.5	1132.5	727.2
125- to 210- $\mu$ -diam fraction, g	662.7	475.4	965.0	649.9
125- to 210- $\mu$ -diam fraction, wt%	71.6	75.6	85.2	89.4
Mean size, $\mu$	174.0	155.0	158.0	167.0
Standard deviation, $\mu$	32.0	19.0	15.0	16.0
Roundness ratio, $D_{\max}/D_{\min}$	1.03	1.03	1.02	1.02
Density, % of theoretical	98.0	97.0	98.6	100.0
BET surface area, m <sup>2</sup> /g	0.04	0.015	0.009	0.008
O/U atom ratio	2.0028	2.005	2.0051	2.005
Carbon content, ppm	30	40	60	24
Iron content, ppm	31	46	33	12
Gas release to 1200°C, cc/g	0.0046	0.004	0.004	0.004
Average crushing strength, g	1623	1286	1435	1444



Gel Spheres Dried at 170°C in Steam-Argon  
(a)



Spheres Calcined for 4 hr at 1130°C in 4% H<sub>2</sub>-Argon  
(b)

0.033"

Fig. 14. Photomicrographs of (a) Dried and (b) Calcined UO<sub>2</sub> Microspheres.

Because of the nature of the operation of the nonfluidized microsphere-forming column, essentially no uranium loss occurs; however, some waste, 2.7 and 2.2 wt %, was generated during the demonstration runs. This waste resulted from sphere samples that were dried in air for size and shape examinations.

#### 4. CONCLUSIONS

Based on the results of the two one-week demonstration runs described in this report and on previous developmental experience, we have drawn the following conclusions with regard to the preparation of high-density  $\text{UO}_2$  microspheres from CUSP sols in a nonfluidized forming column when hot 2EH is used as the dehydrating agent.

1. The U(IV) feed can be routinely prepared in a batch slurry uranium reductor. Vigorous agitation is required for a uniform reduction, and the completion of the reduction can be determined by monitoring the redox potential. Sols prepared from feed that had been aged for at least 24 hr prior to sol preparation had U(IV) concentrations 2 to 3% higher than sols prepared from fresh feeds.
2. CUSP is an instrumented batch process for preparing 1 to 1.4 M  $\text{UO}_2$  sols that are fully crystalline and have U(IV) concentrations of 85 to 87%. Reproducible sols can be prepared in relatively simple equipment by following the standard operating path. Some uranium is lost to the organic solvent; a loss also occurs as the result of equipment cleanout between batches. Uranium in the waste solutions can be recovered easily. The sol yield varies from 92 to 98%.
3. The operation of the nonfluidized microsphere forming column was quite satisfactory at the capacity attained during the second week's run (i.e., ~3 kg of  $\text{UO}_2$  per day). Although the production capacity of the 4-in.-ID column has not been established, it is greater than 3 kg of  $\text{UO}_2$  per day. Some difficulty was encountered with plugging of the glass two-fluid nozzle capillaries;

however, this was greatly minimized by installing a glass frit filter in the sol line. The 2EH was recycled, and good-quality, round spheres were prepared by small periodic additions (~0.1 vol %) of Span 80. It was necessary to make two additions during the demonstration runs. An on-stream factor of 96% was attained for each run.

4. Additional development work is required, primarily in the area of multinozzle feeders; however, we believe that the feasibility of the CUSP--nonfluidized column process for the preparation of high-density  $\text{UO}_2$  microspheres has been demonstrated and that the process can be adapted to commercial use.

#### 5. ACKNOWLEDGMENTS

The success of the demonstration runs was the result of the work of many individuals. The sol preparation and microsphere forming equipment was efficiently operated by R. D. Arthur, V. L. Fowler, E. R. Johns, K. Ladd, D. A. McWhirter, C. H. Tipton, and D. E. Willis.

We wish to express our appreciation to the groups of W. R. Laing and G. R. Wilson of the Analytical Chemistry Division for performing the chemical analyses and to C. B. Pollock of the Metals and Ceramics Division for performing the metallurgical tests and making measurements.

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