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Chemical Flowsheet Conditions for Preparing Urania Spheres by Internal Gelation

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Chemical Technology Division

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CHEMICAL FLOWSHEET CONDITIONS FOR PREPARING URANIA SPHERES BY INTERNAL GELATION

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ABSTRACT

Small, ceramic urania spheres can be prepared for use as nuclear fuel by internal chemical gelation of uranyl nitrate solution droplets. Decomposition of hexamethylenetetramine (HMTA) dissolved in the uranyl nitrate solution releases ammonia to precipitate hydrated UO_3. Previously established flowsheet conditions have been improved and modified at ORNL and have been applied to prepare dense UO_2 spheres with average diameters of 1200, 300, and 30 μm.

Acid-deficient uranyl nitrate (ADUN) solutions up to 3.4 M in uranium with NO_3^-/U mole ratios of 1.5 to 1.7 are prepared by dissolution of U_3O_8 or UO_3. Continuous mixing of metered, cooled ADUN containing urea and HMTA solutions provides a smooth, regulated flow of the temperature-sensitive feed solution. The gelation times for solution drops in organic liquids at 45 to 95°C depend on both the chemical reaction rates and the rates of heat transfer. The gel properties vary with temperature and other gelation variables. Gelation conditions were determined which allow easy washing, drying, firing, and sintering to produce dense UO_2 spheres of all three sizes. The 1200- and 300-μm UO_2 spheres were prepared by gelation in trichloroethylene at 50 to 65°C; 2-ethyl-1-hexanol was used as the gelation medium to prepare 30-μm UO_2 spheres. Washing and drying requirements were determined. The gel dried to 225°C contains about 95% UO_3; the remaining components are H_2O, NH_3, and NO_3^-, which are volatilized during firing to UO_2.

1. INTRODUCTION

The initial development emphasis for a fuel refabrication program at Oak Ridge National Laboratory (ORNL) has been focused on Sphere-Pac

fabrication for UO_2 fuels. The small ceramic spheres required for Sphere-Pac fabrication may be prepared by the gelation of liquid droplets using three general types of gel-sphere (also called sol-gel) processes. During 1978, 50- to 100-kg quantities of both depleted and enriched UO_2 spheres were prepared for use in fabrication development and irradiation tests. This report describes details of the chemical flowsheet conditions and requirements for preparation of these UO_2 spheres.

The current Sphere-Pac development program included an assessment of both domestic and foreign technology.[1] Three sizes of spheres having diameter ratios of about 40:10:1 were found to be necessary. Each of the three general types of gel-sphere processes had important advantages and disadvantages for their preparation. Results of the assessment[1] and various scouting tests[2,3] indicated that the large-size UO_2 spheres could not be prepared by application of published technology for two (water extraction from sols; external chemical gelation) of the three types of gel-sphere processes. The third type (internal chemical gelation) gave promising results for large- and intermediate-size UO_2 spheres but appeared to be unsatisfactory for the smallest-size product.

Improvements and modifications to previously published flowsheet conditions[4,5] for the internal chemical gelation process were developed and applied at ORNL to prepare dense UO_2 spheres with average diameters of 1200, 300, and 30 μm. In this process, decomposition of hexamethylenetetramine (HMTA) dissolved in uranyl nitrate solutions releases ammonia to precipitate hydrated UO_3. The internal gelation process was first

applied to the production of nuclear fuels and demonstrated for Sphere-Pac fabrication at KEMA*; their flowsheet conditions[4,5] are commonly termed "the KEMA process." Investigations of the KEMA and other internal gelation flowsheet conditions have been reported by other laboratories.[6-9] The conditions now being used at ORNL show important differences from and improvements to those established at KEMA.

This report is limited to a description of the internal gelation chemical flowsheet conditions now used to prepare UO_2 spheres at ORNL. Information on the equipment flowsheets is not presented here, but is included in the design report for an interim facility (10 kg of UO_2 per day).[10] The gel-sphere processes commonly require close duplication of process conditions or "recipes" because the feed liquids and gels are usually not at thermodynamic equilibrium. Some of the chemical flowsheet conditions used at ORNL appear to be essential to the results obtained. Therefore, the purpose of this report is to present and discuss these conditions in detail.

1.1 Generalized Internal Gelation Flowsheet

The schematic flowsheet for the internal gelation process is shown in Fig. 1. The chemical conditions are discussed in the order of process operations shown on the flowsheet. Although these operations are also valid for other internal gelation flowsheets, some of the chemical concentrations or ratios would differ.

The controlling characteristics of internal gelation result from the absence of mass transfer during the gelation step. The ammonia for

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*Keuring van Electrotechnische Materialen at Arnhem in the Netherlands.

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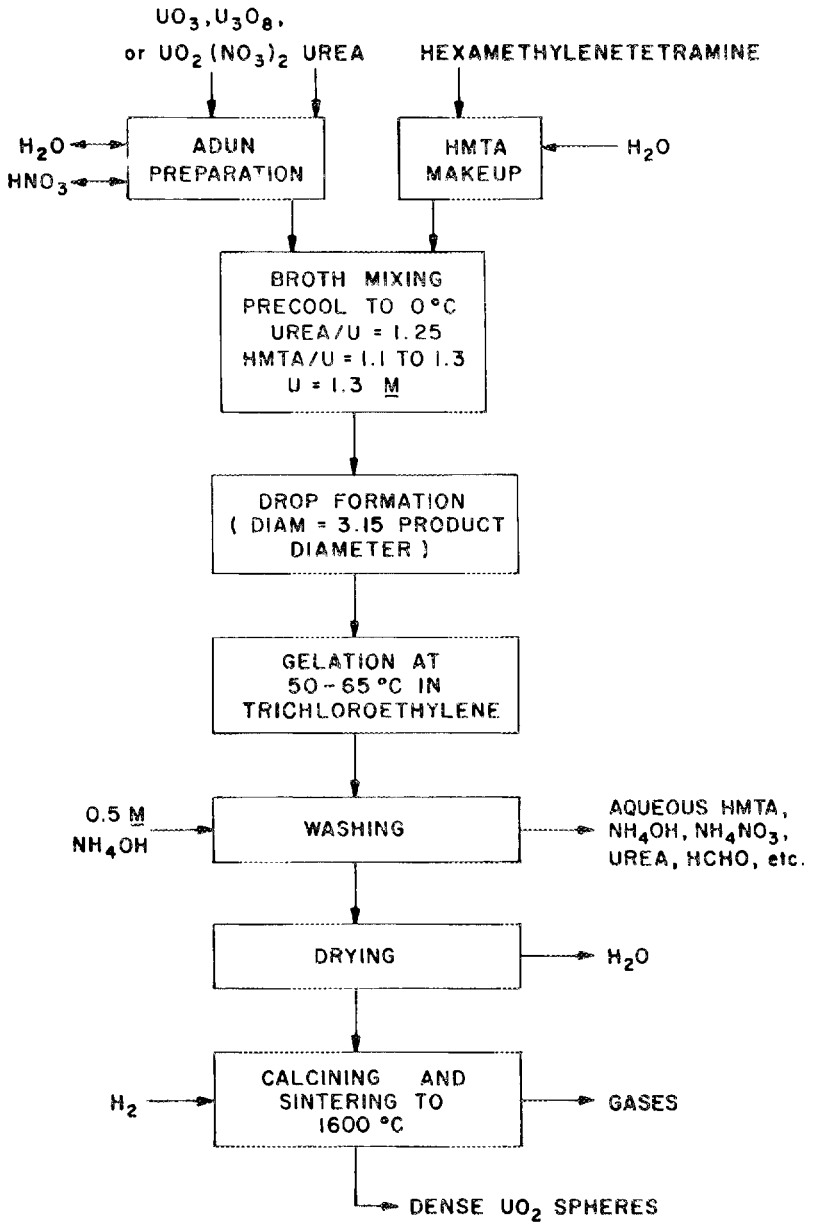

Fig. 1. Preparation of 200- to 1400-μm UO_2 spheres by internal gelation.

the chemical gelation is generated homogeneously without stresses or shell structures from concentration gradients. Since the heat transfer from the hot organic liquid is relatively rapid, the gelation times have only a small dependence on the droplet diameter. These advantages become increasingly important as the sphere diameter is increased. As a result, internal gelation appears to be the only practical gel-sphere process for preparing 1200-μm UO_2 spheres.

The KEMA type of internal gelation flowsheets have three significant problems not common to other types of gel-sphere processes: (1) the feed broth is sensitive to temperature and therefore has a limited life; (2) partially denitrated or acid-deficient metal nitrate feed solutions of high metal concentration are necessary to give good gel properties; and (3) gelation takes place in a warm, or hot, organic medium which must be removed from the spheres and recycled. Details of the chemical flowsheet conditions are selected to deal with these problems.

In the preparation of 1200-μm UO_2 spheres, the advantages of the homogeneous precipitation without mass transfer are more important than the disadvantages of internal gelation. The 300-μm spheres are easy to prepare; thus the process selection is determined by the need for 1200- and 30-μm products. The advantages and disadvantages of internal and external gelation processes were evaluated on a relative basis, as reported elsewhere.[11]

2. PREPARATION OF ACID-DEFICIENT URANYL NITRATE SOLUTIONS

The concentrations and compositions of uranyl nitrate solutions preferred for internal gelation are outside the range of those commonly

available. Dissolution of $UO_2(NO_3)_2 \cdot 6H_2O$ solids or simple evaporation of $UO_2(NO_3)_2 + HNO_3$ solutions does not give the required composition. Therefore, preparation of the feed solution is a crucial part of the overall chemical flowsheet.

2.1 Requirements

The acid-deficient uranyl nitrate (ADUN) solution should have NO_3^-/U mole ratios of 1.5 to 1.7 and uranium concentrations of ≥ 2.9 M. Since $UO_2(NO_3)_2$ is equivalent to a NO_3^-/U mole ratio of 2.0, the lower ratios correspond to compositions represented by $UO_2(OH)_x(NO_3)_{2-x}$, where x is 0.3 to 0.5. The most important reason for using acid-deficient solutions is to promote better gel-sphere properties, as discussed in Sect. 4. The acid deficiency is also necessary for high uranium concentrations. The solubility of uranium at room temperature increases from 2.4 M at a NO_3^-/U mole ratio of 2.0, or $x = 0$ in the chemical formula, to about 3.6 M at $x = 0.4$.

High uranium concentrations are required for practical continuous mixing of the temperature-sensitive feed. Accurate, dependable metering of HMTA solids would be very difficult, and the heat of dissolution and mixing of HMTA tends to result in premature gelation. Therefore, metering, precooling, and mixing of two solutions form the basis of the preferred procedure for preparing feed broth. The volume ratio of HMTA-ADUN solutions is about 1.0, and the uranium concentration in the ADUN must be double that in the mixed broth.

2.2 ADUN Solubility and Solution Properties

The ADUN solutions are three-component systems which may be represented as mixtures of $UO_3 + HNO_3 + H_2O$ or $UO_3 + UO_2(NO_3)_2 + H_2O$. ADUN solutions cannot be considered as part of a $HNO_3 + UO_2(NO_3)_2 + H_2O$ system because that system does not permit NO_3^-/U mole ratios below 2.0. From the Gibbs phase rule, an ADUN solution (no solid phase) has two degrees of freedom in addition to temperature and pressure. Therefore, the solution is completely specified if two other independent variables are measured or fixed. We commonly use molar concentration of uranium and NO_3^-/U mole ratio as the two convenient variables to specify an ADUN solution. For practical operation, the density and the pH can be measured to completely determine or specify an ADUN solution composition; however, the solution must be at equilibrium and at a known temperature and pressure. Some of the hydrolysis reactions of UO_2^{2+} are slow, and minutes or even hours are sometimes required to approach pH equilibrium following changes in concentration or temperature. Addition of a fourth component such as ammonia, NH_4OH, $Th(NO_3)_4$, or urea adds a degree of freedom and requires an additional measurement or composition to determine the solution properties.

The limitations and requirements for our preparation and use of ADUN solutions would be most easily seen from the uranium solubility vs NO_3^-/U ratios, with temperature as a parameter. Unfortunately, the only detailed data are for approximately room temperature (Fig. 2). At temperatures near 0°C, the maximum ADUN solubility appears to be reduced to about 2.8 M uranium or less, giving a curve with approximately the

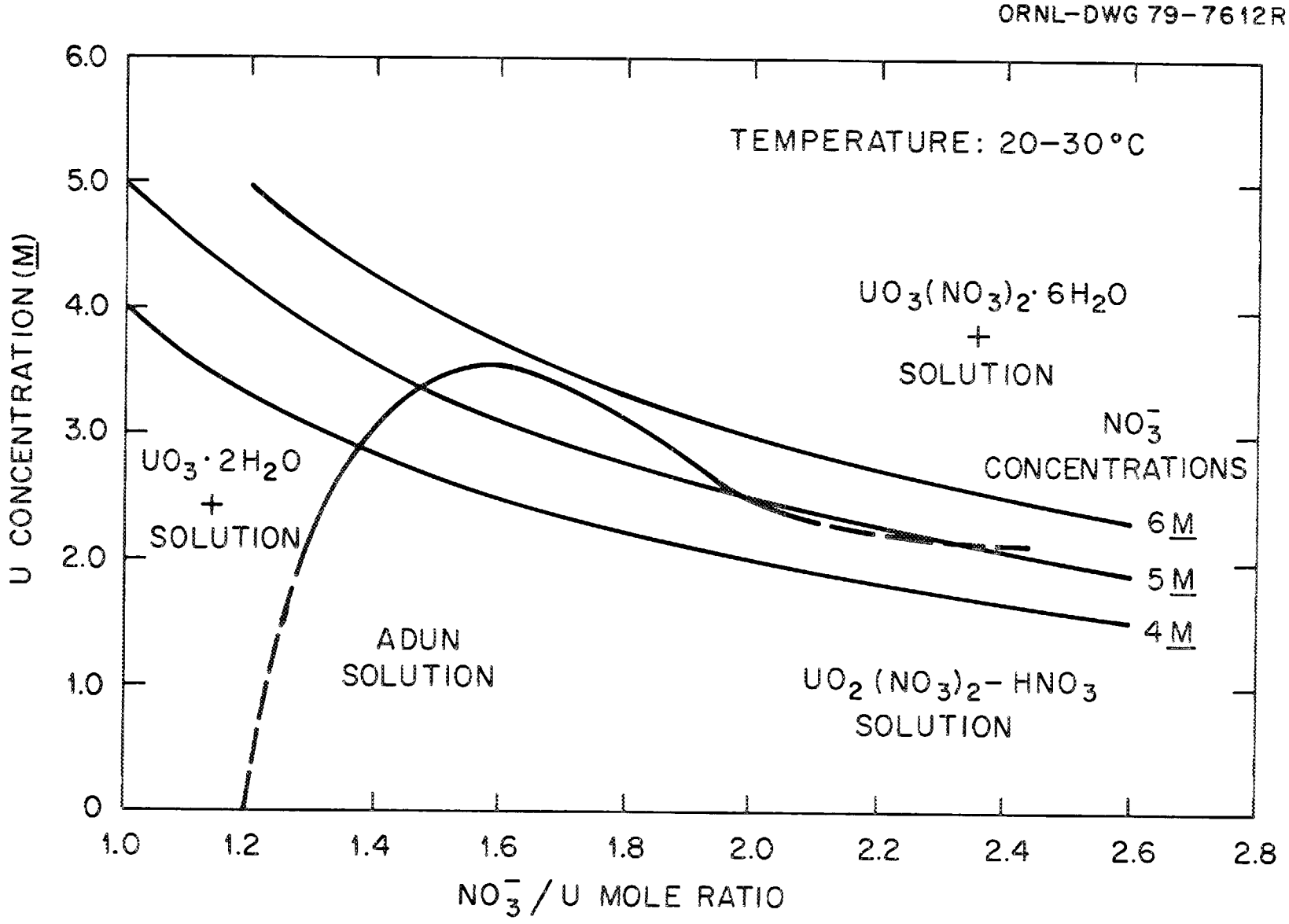

Fig. 2. Solubility of uranium(VI) vs NO_3^-/U mole ratio.

same shape as that shown in Fig. 2. As the temperature is increased to 60°C, the solubility for NO_3^-/U mole ratios less than 1.6 decreases, while that for NO_3^-/U mole ratios above 1.6 increases. Uranyl nitrate hexahydrate [$UO_2(NO_3)_2 \cdot 6H_2O$] melts at about 60°C, giving about 5.6 M uranium and 11.2 M NO_3 as one point on a solubility curve. At 100°C, only slight acid deficiencies are possible, and the solubility curve appears to be between NO_3^-/U mole ratios of 1.9 and 2.0 for the NO_3^- concentrations that give high uranium solubilities below 60°C.

The density of the ADUN solution is determined mainly by the uranium concentration. Botts, Raridon, and Costanzo[12] used the following equation to correlate experimental measurements for ADUN solutions:

$$\rho(\text{ADUN}) = \rho(H_2O) + 0.2659\ U + 0.0282\ NO_3, \tag{1}$$

where

$\rho(H_2O)$ = the density of H_2O at the same temperature, g/cm^3

U = the molarity of uranium,

NO_3 = the molarity of NO_3^-.

For NO_3^-/U mole ratios of 1.5 to 1.7, the effect of NO_3^- can be combined with the uranium concentration to give

$$\rho(\text{ADUN}) = \rho(H_2O) + 0.31\ U \tag{2}$$

and

$$U = 3.22\ [\rho(\text{ADUN}) - \rho(H_2O)]. \tag{3}$$

While the experimental data were obtained for uranium concentrations below 1.4 M, the correlations adequately represent our measurements

for higher concentrations and also give the density of $UO_2(NO_3)_2 \cdot 6H_2O$ crystals to within 0.3% of the handbook value.

The pH of an ADUN solution is dependent on both the NO_3^-/U mole ratio and the uranium concentration. For a resin-loading process dependent on NO_3^-/U mole ratio, pH measurements provided excellent process control.[13] Under acid-deficient conditions and at high uranium concentrations, the hydrolysis reactions of uranium are slow and measurements of pH must allow for such slow changes. We have extrapolated literature data for solutions 0.5 to 2.0 M in uranium to our ADUN feed concentrations (Fig. 3). A few experimental points in the shaded area of Fig. 3 agree with the extrapolations. Since the maximum uranium solubility at room temperature occurs within the preferred NO_3^-/U mole ratio range of 1.5 to 1.7, a high solution density ($\geq$2.05) is evidence of optimum acid deficiency. An ADUN solution can be diluted with water to concentrations at which the pH is more readily measured and more accurately correlated with NO_3^-/U mole ratios.

2.3 Dissolution of Uranium Oxides

The ADUN solutions used for our feed preparation have been prepared by dissolution of U_3O_8 or UO_3. The same procedure is equally effective for U_3O_8 from oxidation of UO_2 pellets or powder at 500°C, oxidation of scrap uranium metal chips, or calcination of UO_3. The dissolution of the UO_3 or U_3O_8 is simpler and easier than the denitration and concentration of uranyl nitrate solution.

Dissolution to give the required ADUN concentrations is readily achieved under the correct conditions, but impossible at other conditions.

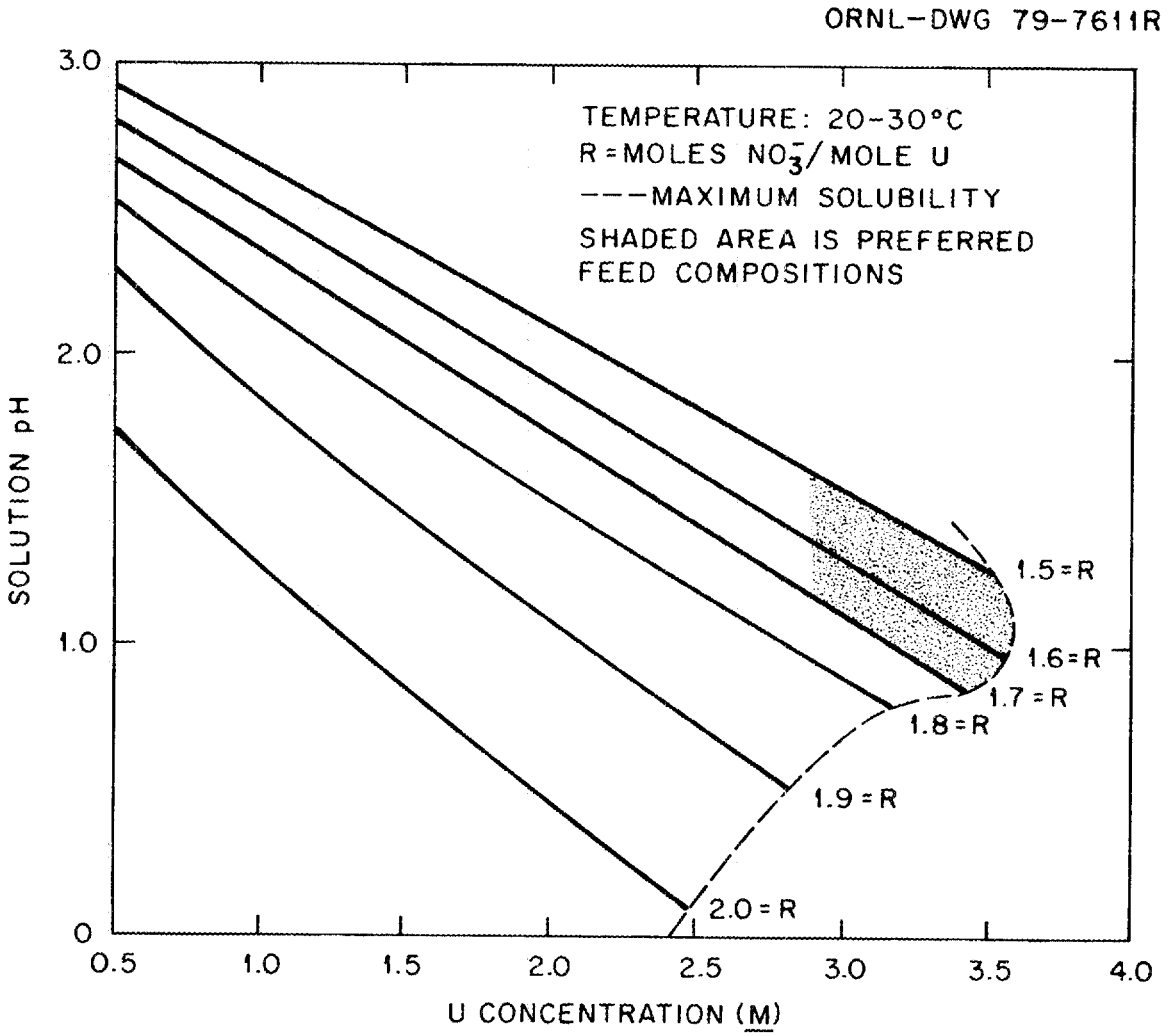

Fig. 3. The pHs of acid-deficient uranyl nitrate solutions.

The requirements can be explained by the peculiarities of uranium solubility. For example, the solubility of uranium is almost 50% greater for optimum acid deficiency than for stoichiometric $UO_2(NO_3)_2$. Figure 2 shows that a solution 3.5 M uranium and 5.6 M NO_3^- is stable (NO_3^-/U mole ratio of 1.6), but higher nitrate concentrations (additional HNO_3) will precipitate uranium. If ADUN is heated to near the boiling point, uranium is precipitated in a basic form, leaving a less acid-deficient solution of lower uranium and nitrate concentrations. ADUN solutions with uranium concentrations greater than 3 M will precipitate uranium as large yellow crystals at 0°C. Thus the uranium has a maximum solubility at both intermediate temperatures and intermediate NO_3^- concentrations. The uranium appears to precipitate from ADUN solutions in a basic form perhaps equivalent to $UO_2(OH)NO_3 \cdot xH_2O$. Some such precipitates are slow to dissolve, and they tie up UO_2^{2+} and NO_3^- in a ratio that causes the relatively narrow ADUN solubility peak to be bypassed.

A final requirement results from a common effect for the reaction of solids. A small fraction of the U_3O_8 or UO_3 is always less reactive and more difficult to dissolve than the bulk of the oxide; therefore, it is difficult to obtain the maximum uranium concentration by dissolving a residue of this least-reactive powder. In such cases, it is much more effective to completely dissolve a portion of the UO_3 or U_3O_8, add an excess of powder to saturate the solution, and then separate the excess oxide.

The optimum final NO_3^- concentration is about 5.6 M (Fig. 2). If U_3O_8 is used, up to 10% of the HNO_3 may be consumed to oxidize the U_3O_8 to U(VI). The reaction rates increase with temperature, but temperatures

above 70°C should be avoided because of the concomitant decrease in uranium solubility. Cooling is required to remove the heat of reaction. Controlled addition of concentrated HNO_3 to a UO_3 or U_3O_8 slurry is a simple way to avoid overheating. Small adjustments in the concentrations can be made by addition of small amounts of H_2O at the end.

A system for batch dissolution of U_3O_8 powder and preparation of ADUN solution was used in producing 20-kg batches of uranium. The system (Fig. 4) consists of a dissolver with agitator and temperature control, a solids settling vessel, and a receiving-blending tank. One hundred kilograms of UO_2 which had been oxidized for 3 hr at 500°C to U_3O_8 was dissolved in four batches over a five-day period. An excess of U_3O_8 was used, and the temperature was maintained between 50 and 60°C. The combined four batches of solution was 3.2 M in uranium with a NO_3^-/U mole ratio of 1.49; these were very close to the desired concentrations. The 1000 ppm of NO_2^- present after dissolution was destroyed by reaction with urea, and the solution was adjusted to 2.6 M in uranium and a NO_3^-/U mole ratio of 1.5, using nitric acid and water.

2.4 Formation and Decomposition of Nitrites

When U_3O_8 is dissolved in nitric acid, approximately 0.28 mole of nitrate is consumed per mole of uranium. By keeping the temperature below 60°C, the prepared ADUN contains on the order of 1000 ppm nitrite, which reacts quantitatively with urea in acidic solution to yield gaseous nitrogen and carbon dioxide. When this ADUN is mixed with a urea-HMTA solution and the resultant broth is dispersed into droplets, the gaseous products that are formed cause the droplets to crack; thus the nitrites must be removed before droplet formation.

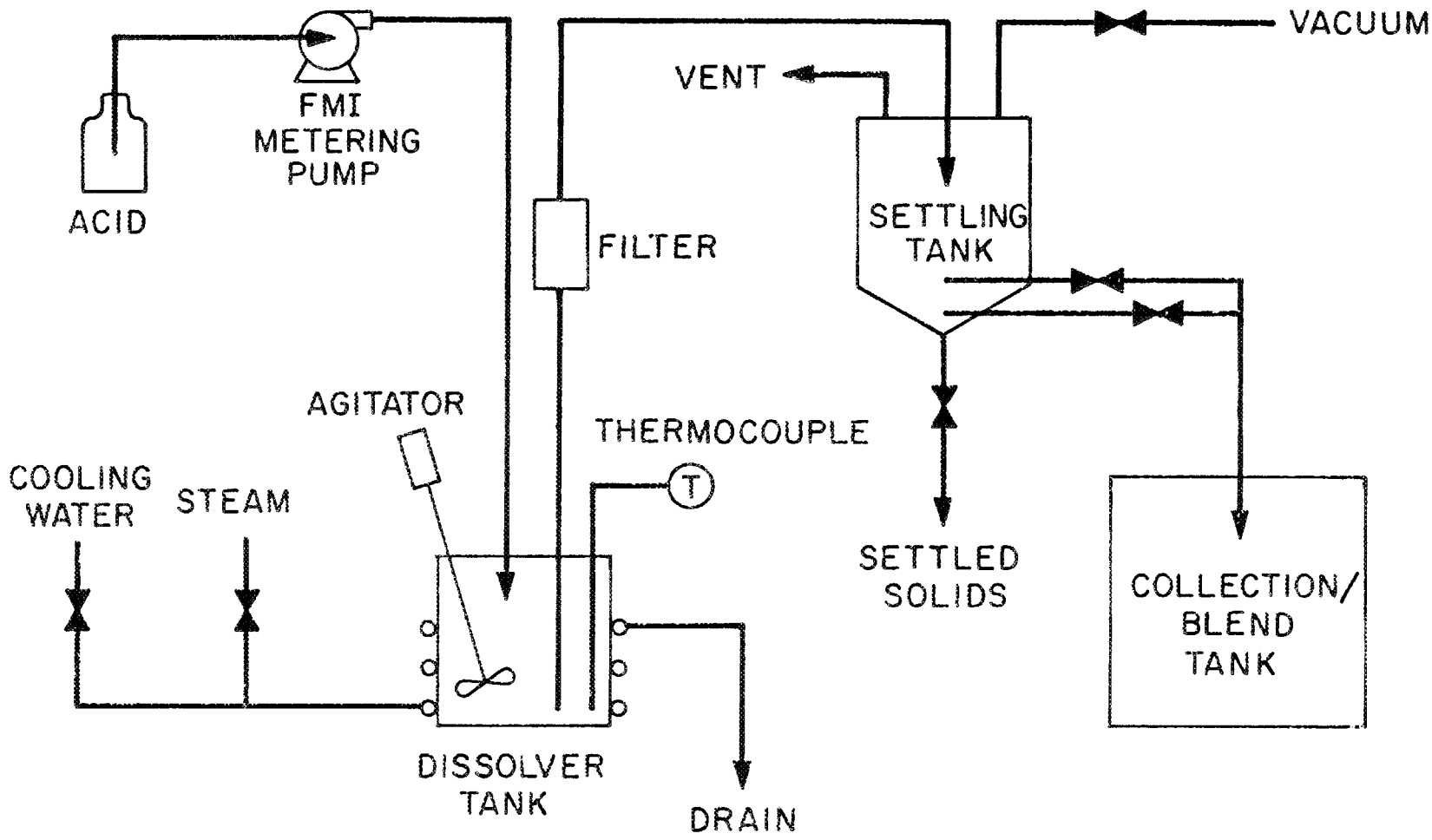

Fig. 4. Batch dissolution equipment for preparation of acid-deficient uranyl nitrate.

By using dissolution temperatures of about 80°C, the nitrite concentration is reduced to less than 10 ppm, which is acceptable. However, the resulting NO_3^-/U mole ratio is increased to 1.6 to 1.7, which gives a soft gel (see Sect. 4.4).

Since the reaction between nitrite and urea is one source of cracked spheres, the problem can be avoided by destroying the nitrite with urea prior to mixing with HMTA and dispersion into droplets. Addition of urea to ADUN at a urea-to-uranium mole ratio of 1.25, followed by stirring at about 50°C for 24 hr, reduces the nitrite content to less than 1 ppm. The addition of urea to the ADUN solution has the additional advantage of preventing crystallization of ADUN at a temperature of 0°C.

2.5 Other Procedures to Give Acid-Deficient Feed

If uranium oxide is available as a feed material, then dissolution to the final concentration is the preferred procedure for preparing the acid-deficient metal nitrate feed. If the refabrication process uses both nitrate solutions from reprocessing and fresh uranium, then the fresh uranium could be supplied as UO_3 or U_3O_8 and dissolved in the metal nitrate--nitric acid solutions to give acid-deficient feed. However, the practicality of this approach cannot be determined until details of the fuel reprocessing and recycle flowsheets are specified.

Solvent extraction by a liquid organic amine has been demonstrated as a viable method for the preparation of ADUN.[13] The extraction and regeneration reactions, where R_2NH represents the Amberlite (A-2)* secondary amine, are:

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*Trademark of the Rohm and Haas Company.

$$R_2NH + HNO_3 \rightarrow R_2NH_2NO_3 \tag{4}$$

and

$$R_2NH_2NO_3 + NaOH \rightarrow R_2NH + NaNO_3 + H_2O\ . \tag{5}$$

At high nitrate and/or uranium concentrations, excessive amounts of uranium are extracted as negatively charged complexes; therefore, the nitrate removal would have to be done at moderate uranium concentrations ($\leq$0.4 M). Since uranium precipitates when ADUN is heated to 100°C, the concentration would have to be accomplished by vacuum evaporation at 60°C. Nitrate extraction and vacuum evaporation to give a uranium concentration of 3.2 M and a NO_3^-/U mole ratio of about 1.5 have been demonstrated separately, but they have not been applied in combination to the preparation of feed for internal gelation.

Addition of NH_4OH or ammonia to uranyl nitrate solutions can produce acid-deficient conditions, as described by the following reaction:

$$UO_2(NO_3)_2 + 1/2\ NH_4OH \rightarrow UO_2(OH)_{0.5}(NO_3)_{1.5} + 1/2\ NH_4NO_3. \tag{6}$$

Internal gelation tests using this type of ADUN solution have been reported.[7] The NH_4NO_3 has undesirable effects on the UO_3 gel properties (discussed in Sect. 4). The uranium concentration is limited by the initial solubility of $UO_2(NO_3)_2$ and by the salting out or common ion effect of the NO_3^- present as NH_4NO_3. Nevertheless, the addition of ammonia is very simple and should be investigated further if $UO_2(NO_3)_2$ feed solutions must be used.

A vacuum-distillation procedure has been developed for preparing internal gelation feed solutions from $UO_2(NO_3)_2 \cdot Pu(NO_3) \cdot HNO_3$ solutions.[14]

Steam-stripping is a well-known procedure for making $Th(NO_3)_4$ solutions acid deficient, that is, producing NO_3^-/Th mole ratios less than 4. Attempts to achieve a controlled partial denitration of $UO_2(NO_3)_2$ solutions were not successful and do not appear to merit further study.

3. GELATION TIMES AND BROTH PREPARATION

To ensure practical operation of an internal gelation process, the broth should have a long gelation time at a low temperature, so that premature gelation in the feed system is avoided, and a short gelation time at a higher temperature, so that long fluidization times are not required. The maximum high temperature must be below the boiling point of the broth to prevent formation of vapor bubbles. The minimum low temperature is limited by freezing or solid-phase formation.

In our internal gelation flowsheet, the rate of gelation is controlled by the slowest rate(s) of three processes: (1) the heat transfer required to bring the broth up to gelation temperature, (2) the decomposition of HMTA to release ammonia, and (3) the precipitation of hydrated UO_3 by ammonia. The precipitation of the hydrated UO_3 appears to be relatively rapid; therefore, the first two rates are controlling.

3.1 Decomposition of HMTA

The decomposition of HMTA in an acidic medium can be written as:

$$(CH_2)_6N_4 + 10H_2O \rightleftarrows 4NH_4OH + 6HCHO \ . \qquad (7)$$

The reverse reaction is used to prepare HMTA, and the equilibrium pH is about 9. The equilibrium pH is much lower in the presence of NH_4NO_3

produced by precipitation of UO_3 from ADUN. For small broth droplets, the rate of heat transfer is rapid (see Sect. 3.3) and the experimentally observed gelation times appear to be controlled by the decomposition of HMTA. The gelation times for these small droplets seem to vary from less than 1 sec at 50°C to several minutes at 40°C. These estimates are based on the suspension times required to avoid distortions or clumping of settled droplets.

A high HMTA concentration is required to effect gelation. If the HMTA concentration is low, the HMTA decomposition reaction can reach equilibrium with products before enough decomposition takes place. Most of the useful internal gelation results are for HMTA/NO_3^- mole ratios of 0.75 $\pm$0.15, in which nitrate that is preneutralized by addition of NH_4OH is <u>not</u> included in the HMTA/NO_3^- ratio. Complete decomposition of the HMTA would give 2.4 to 3.6 moles of ammonia per mole of NO_3^-, while the stoichiometric ratio would be 1.

3.2 Settling Rates

One limit on the gelation times is that gelation should occur during free fall through a reasonable length of column. Since the settling velocity is strongly dependent on size, the largest size is limiting. The characteristics of large-coarse spheres are as follows:

Diameter	4000 μm
Density difference	0.1 g/cm^3 (or less)
Trichloroethylene (TCE) viscosity	0.4 cP
Maximum settling velocity[a]	9.2 cm/sec

[a]Value for 0.05 g/cm^3 density difference is 6.1 cm/sec.

Since 300-cm-high columns would be quite practical, gelation times could be as long as 300/9.2 or 30 sec. For fines, the settling velocities in 2-ethyl-1-hexanol (2EH) are less than 1 cm/sec, and the gelation times could be much longer for reasonable column heights. Additional settling velocities are tabulated in Table 1 as part of the heat-transfer calculations.

3.3 Heat-Transfer Calculations

The amount of heat to be transferred is primarily that required to heat the droplet from about 0°C to the gelation temperature. The resistances are those inside the droplet and the organic liquid film around the droplet. The organic medium is equivalent to a constant-temperature heat source.

The heat-transfer coefficients for the films around spheres are commonly correlated by:[15]

$$(Nu) = 2.0 + 0.6(Re)^{1/2}(Pr)^{1/3} , \tag{8}$$

where

Nu = the Nusselt number,

Re = the Reynolds number,

Pr = the Prandtl number.

When film coefficients are calculated for our gelation conditions, the range of values is surprisingly small. The droplet diameter appears in both Nu and Re and changes the settling velocity in Re. Therefore, the effect of diameters is small over the range of small- and large-coarse sizes and becomes important only for fines in which the final term in

Table 1. Heat-transfer coefficients and times for organic gelation medium films

	TCE[a]	2EH[b]	Silicone oil[c]
Large-coarse (0.4-cm-diam) droplets			
Settling velocity, cm/sec	9.2	32.5	7.1
Nusselt No.	32.2	42.1	14.5
Reynolds No.	1290	520	8.4
Prandtl No.	2.77	29.1	372
Organic film coefficient, cal/sec·cm^2·°C	0.027	0.044	0.013
Heat-transfer time,[d] sec	4.5	2.8	9.0
Small-coarse (0.1-cm-diam) droplets			
Settling velocity, cm/sec	2.83	6.67	1.46
Nusselt No.	10.4	11.5	4.85
Reynolds No.	99	26.7	0.43
Prandtl No.	2.77	29.1	372
Organic film coefficient, cal/sec·cm^2·°C	0.034	0.048	0.018
Heat-transfer time,[d] sec	0.9	0.6	1.7
Largest fraction of fines (0.02-cm-diam) droplets			
Settling velocity, cm/sec	0.45	0.76	0.05
Nusselt No.	3.5	3.4	2.23
Reynolds No.	3.15	0.61	0.003
Prandtl No.	2.77	29.1	372
Organic film coefficient, cal/sec·cm^2·°C	0.058	0.071	0.041
Heat-transfer time,[d] sec	0.10	0.09	0.15

[a]TCE = trichloroethylene.

[b]2EH = 2-ethyl-1-hexanol.

[c]At 95°C, the density is 0.93 g/cm^3 and the viscosity is 0.34 g/cm·sec.

[d]Heat-transfer time is calculated for infinite conductance inside the droplet and for 5/6 or 83% of the temperature change to equilibrium.

Eq. (8) is less than the constant term 2.0. The small density difference between TCE and the droplets results in a lower settling velocity in TCE as compared with 2EH; therefore, the more viscous 2EH has a higher film coefficient, and a high-viscosity silicone oil gives only a slightly lower film coefficient than TCE. Calculated values are included in Table 1 for three sizes of droplets. The times were calculated for the film as the only heat-transfer resistance (i.e., infinite conductance inside the droplet) and for 5/6 or 83% of the temperature change to equilibrium.

The times required for heat transfer inside the droplet can be estimated by results for conduction in a solid sphere. Any convection in the droplet before it thickens would shorten these times. Generalized results are available as charts of dimensionless temperature ratios vs Fourier number and dimensionless radial position.[16] The thermal diffusivity of the spheres is assumed to be that of water (0.00144 cm^2/sec). Calculated values for three sizes of droplets using the temperature-response charts of Schneider[16] are tabulated in Table 2. Schneider also provides charts to combine the effects of external film resistance and conduction inside a solid sphere.[16] Results for the combination of the two heat-transfer resistances are also tabulated.

The experimentally observed gelation times are in good agreement with the heat-transfer times for large-coarse (0.4-cm-diam) droplets. The rate of gelation for this size is probably determined by the rate of heat transfer. Film resistance around the sphere is the slowest heat-transfer rate, but the conduction inside a solid sphere is

Table 2. Heat-transfer times allowing for conduction in solid spheres[a]
(Nomenclature and results obtained from ref. 16)

	Large-coarse (0.4-cm-diam) droplets	Small-coarse (0.1-cm-diam) droplets	Fines (0.02-cm-diam) droplets
	Infinite film coefficient		
Fourier No. = $\alpha\Theta/r^2$	0.11	0.11	0.11
Heat-transfer time,[b] sec	3.1	0.19	0.008
	TCE[c] film coefficient		
Biot No. = hr/k	3.75	1.18	0.40
Fourier No. = $\alpha\Theta/r^2$	0.30	0.67	1.60
Heat-transfer time,[b] sec	8.3	1.2	0.11
	2EH[d] film coefficient		
Biot No. = hr/k	6.11	1.67	0.49
Fourier No. = $\alpha\Theta/r^2$	0.21	0.54	1.40
Heat-transfer time,[b] sec	5.8	0.94	0.10
	TCE film coefficient and $k \to \infty$		
BiFo = $h\Theta/\rho Cr$	0.60	0.60	0.60
Heat-transfer time,[b] sec	4.4	0.90	0.10

[a]Assume thermal diffusivity of H_2O or $\alpha = k/\rho C_p$, cm^2/sec, is 1.44×10^{-3}.

[b]Heat-transfer time is calculated for 5/6 or 83% of the equilibrium temperature change at 80% of radius.

[c]TCE = trichloroethylene.

[d]2EH = 2-ethyl-1-hexanol.

significant. For the small-coarse (0.1-cm-diam) and fines (<0.02-cm-diam) droplets, conduction inside the droplet is so fast that the heat-transfer time for conduction does not significantly affect the overall gelation time. The heat-transfer times calculated for the organic films for these droplet sizes are 0.1 to 1.0 sec. We believe that the gelation times are longer than this and that they are controlled, therefore, by the chemical reactions; however, we have not made the quantitative measurements that would be necessary for confirmation.

3.4 Observed Results

Relative gelation times have been determined experimentally in two ways: (1) observation of the time required for the clear yellow broth drops to change to a completely opaque yellow while suspended in or falling through the organic liquid and (2) observation of the suspension time required to prevent settled spheres from sticking together or showing contact marks. For large-coarse (0.4-cm-diam) droplets, both times are in reasonable agreement with the 8 sec shown in Table 2. For the small, coarse (0.1-cm-diam) droplets, the experimentally observed times generally seem to be longer (typically several seconds) than the 1.2 sec shown in Table 2. The precision of these estimated times are ± 1 sec at best. Therefore, the 0.1-sec time shown for the 0.02-cm-diam droplets cannot be confirmed by these observations. Fines have been discharged and collected in shallow settlers with good results (gelation in less than 0.5 sec). Dispersion of the broth feed stream to form spherical droplets probably requires more than 0.01 sec. Therefore, gelation times for the fines appear to be within the broad range of 0.02 to 0.5 sec.

The reaction of ADUN-urea solution with NH_4OH appears to be very fast. For the external gelation processes, solution droplets form surface gel layers in less than 0.02 sec in ammonia gas. The NH_4OH generated by homogeneous decomposition of HMTA should react more rapidly because mass transfer is not required.

The controlling rates for our internal gelation droplets appear to be as follows. For droplet temperatures below 40°C, the HMTA decomposition is controlling. For large-coarse droplet sizes in hot TCE, the rate of heat transfer is controlling, with the TCE film resistance being larger than the resistance inside the droplet. As the droplet size decreases, the heat transfer is accelerated and is completely controlled by the TCE film resistance. We do not know whether the HMTA decomposition or the heat-transfer rates are controlling for the small-coarse and fines droplets.

3.5 Continuous Mixing Requirements

Continuous mixing of stable feed streams is the preferred procedure to minimize the effects of the temperature sensitivity and the limited life of the broth. The continuous system can be small to limit the inventory of perishable broth and to allow cleanout without large volumes of waste. The control of droplet or product diameter requires a metered broth flow,[10] and it is easier to meter stable solutions to coolers and a closed mixer than to operate a refrigerated metering system for the perishable broth.

For continuous mixing, ADUN and HMTA solutions are metered and cooled separately before being blended in a cooled, closed mixer.

Initially, urea was added to the HMTA solution because this resulted in a nonradioactive makeup operation for the urea. When the release of gaseous urea-nitrite decomposition products was observed (Sect. 2.4), urea was added to the ADUN solution to allow reaction and outgassing before continuous mixing.

Continuous mixing requires the use of solutions because metering and cooling of slurry or solid feed streams are not practical. The uranium and HMTA concentrations must be near the solubility limits in order to attain final broth densities greater than the density of TCE. For a NO_3^-/U mole ratio of 1.6 and a urea/U mole ratio of 1.25, the solution densities are represented as follows:

$$\rho(\text{ADUN + urea}) = \rho(H_2O) + 0.327\ U \tag{9}$$

and

$$U = 3.06\ [\rho(\text{ADUN + urea}) - \rho(H_2O)]\ . \tag{10}$$

All concentrations are in moles per liter, and all solution densities are in grams per cubic centimeter. For HMTA solutions,

$$\text{HMTA} = 31.4\ [\rho(\text{HMTA}) - \rho(H_2O)]\ . \tag{11}$$

If the HMTA has the same additive volume (equivalent to 0.77 cm^3/g) after mixing, the broth density for urea-uranium and HMTA-uranium of 1.25, and the 1.6 NO_3^-/U ratio would be as follows:

$$\rho(\text{broth}) = \rho(H_2O) + 0.3623\ U \tag{12}$$

and

$$U = 2.76\ [\rho(\text{broth}) - \rho(H_2O)]\ . \tag{13}$$

The uranium concentration must exceed 1.25 M to ensure settling in TCE. The solubility of HMTA varies from about 3.5 M at room temperature to 3.7 to 3.8 M at 0°C. Complete dissolution of all HMTA solids is slow and difficult for HMTA concentrations greater than or equal to 3.2 M. Therefore, the HMTA solutions have either been 3.1 M HMTA or have been saturated with an excess of HMTA solids. Starting with an ADUN solution of 3.3 M in uranium and an HMTA solution of 3.1 M HMTA, the broth has a maximum uranium concentration of 1.33 M, or a density of 1.48 g/cm^3. Therefore, continuous mixing of broth for gelation in HMTA requires the highest practical solution concentrations. Continuous mixing of solutions could not give the higher concentrations specified for some other internal gelation flowsheets. The high broth densities are not required for 2EH or for mixtures containing mineral oil, and lower uranium concentrations are practical.

4. GEL-SPHERE PROPERTIES VS GELATION CONDITIONS

The effects of gelation conditions on the properties of the gel are very complex. The effects of differences in gel properties frequently become apparent during drying without being observed in the earlier process operations. There is considerable uncertainty, as well as disagreement, concerning the results obtained in precipitating uranium from uranyl nitrate solutions by NH_4OH. The NO_3^-/U mole ratio is known to be an important variable. In addition, urea forms complexes with the uranyl ion and changes the precipitation behavior. In the internal gelation process, the ammonia needed for gelation is formed by the decomposition of HMTA; thus the decomposition and other reactions

of HMTA are important. Internal gelation combines all of these variables in a single process. Only a narrow range of gelation conditions has been tested, and the conditions that allow solidification of solution droplets into good-quality gel spheres are even more limited.

Conditions outside the range shown to be acceptable can give the following results:

1. Solidification occurs too rapidly to permit convenient formation of spherical liquid drops.
2. Not enough NH_4OH is produced to adequately precipitate the uranium; that is, a large fraction of the uranium remains in solution.
3. The precipitated uranium separates from a supernate, leaving two phases instead of a homogeneous solid.
4. The gel is too soft, allowing the spheres to distort or break from their own weight or from mild mechanical impacts.

The formation of a strong gel sphere is not a sufficient test of acceptable gel properties. Some gel properties are not conducive to washing, drying, calcining, and sintering without promoting cracks or other unacceptable defects. Finally, the gel properties may deteriorate with time or with process treatments.

Our understanding and selection of process conditions are strongly dependent on data reported by the original developers of the KEMA process[4,5] and on process variations and improvements studied elsewhere.[6-9] In the following sections, information from these sources is combined with our results at ORNL and reinterpreted without detailed acknowledgments or references.

4.1 Precipitation of Uranium(VI) by NH_4OH

The composition and structure of precipitates in the UO_3^--NH_3-H_2O system continue to be the subject of considerable controversy. There is reasonable agreement that precipitation gives a complex mixture of compounds with an apparent composition of $UO_3 \cdot xNH_3 \cdot (2-x)H_2O$. A true ammonium diuranate corresponding to x = 1.0 does not actually exist. Cordfunke[17] claimed to establish four compounds equivalent to values of 0, 1/3, 1/2, and 2/3 for x. Stuart and Whateley[18] interpret their results to indicate that x varies continuously (instead of having discrete, fixed values) and that the ammonia is present as NH_4^+. In either case, the true molecular structures are those of complex hydrated uranyl hydroxides. Stuart and Whateley propose a cation exchange mechanism starting with a $UO_2(OH)_2 \cdot H_2O$ solid when no ammonia is included. Some of the results we obtained in preparing ADUN (Sect. 2) indicate that basic nitrate compounds can precipitate as solids with $UO_2(NO_3)_y(OH)_{2-y} \cdot H_2O$ and y of about 1 as a possible example. Explanations of the chemistry of ADUN solutions commonly postulate the presence of hydrolyzed species such as $[UO_2(OH)]^+$ and $[(UO_2)_2(OH)_2]^{2+}$. If the $UO_2(NO_3)_y(OH)_{2-y} \cdot H_2O$ is washed to equilibrium with dilute NH_4OH, the NO_3^- should first be replaced by OH^- to give NH_4NO_3 in the wash solution and a $UO_2(OH)_2 \cdot H_2O$ precipitate. Continued washing should produce the apparent $UO_3 \cdot xNH_3(2-x)H_2O$ composition with an x of 1/3 or less. Compounds with higher values of x are possible only at high NH_4OH concentrations and would not be expected to form during our process conditions.

4.2 Reactions of Urea

We have not investigated urea concentration as a process variable, but the discussion by Kanij, Noothout, and Votocik[5] appears to be consistent with our experience. The primary purpose of adding urea is to complex the uranyl ion and prevent premature precipitation of uranium. The urea complex affects the rate of uranium precipitation by NH_4OH and the characteristics of the precipitate. Kanij claims that urea increases the decomposition rate of HMTA. Urea reacts with nitrite to give gaseous products, as described in Sect. 2.4. Two other reactions of urea are possible, but are probably not important for our usual internal gelation conditions. These are: (1) Urea can react with formaldehyde (from the decomposition of HMTA) to yield condensation products which can eventually grow into insoluble urea-formaldehyde resins. (2) Urea can hydrolyze under acidic conditions to form ammonia and CO_2. This hydrolysis, although very slow in comparison with the hydrolysis of HMTA, may limit the long-term stability of ADUN-urea solutions.

4.3 Reactions of HMTA

The primary reaction of HMTA is hydrolysis:

$$(CH_2)_6N_4 + 10H_2O \rightleftarrows 6HCHO + 4NH_4OH \ . \qquad (14)$$

The reverse reaction is used to prepare HMTA by adding an excess of NH_4OH, and the decomposition is favored by low solution pH. The undecomposed HMTA, which is only mildly basic, is a weaker complexing agent for

uranyl than is urea. Increasing the temperature will increase the rate or extent of HMTA decomposition, thus providing a convenient means of controlling the precipitation rate for internal gelation processes. The temperature also affects the equilibrium, in that some mixtures which remain fluid at room temperature will solidify at 60 to 100°C.

4.4 Effects of Concentrations

The feed solution has four major components: uranium, NO_3^-, HMTA, and urea. The concentrations are conveniently given in terms of molarity in the case of uranium and in molar ratios (moles component/mole uranium) for the other three. If the solution is partially preneutralized or made more acid deficient by addition of NH_4OH, the concentration of this component is also given as moles per mole of uranium. Droplets suspended in warm or hot organic liquids to promote the gelation reactions may give one of the four poor results listed at the beginning of Sect. 4, or they may give strong gel spheres. The strong gel spheres may contain different crystalline phases, have different crystallite sizes, or consist of relatively noncrystalline polymers.

The uranium concentration is determined by solubility limitations and broth mixing requirements and thus is not used as a variable to control the gel properties. A high uranium concentration is preferred, but it is limited by two factors, as discussed for broth preparation. Solubility limitations result in uranium concentration limits of $\leq$1.5 M for mixing of solutions. Uranium concentrations of 1.5 to 2 M might be tested by careful dissolution of solid HMTA in ADUN, but such

concentrations are not practical for routine use. In the gelation of very large spheres, the organic-liquid density should be only slightly lower than the solution droplet density since larger differences cause distortions into nonspherical shapes. Therefore, the uranium concentration for large spheres should be about 1.3 M when the gelation medium is TCE and 1.8 M when tetrachloroethylene is used.

The primary effect of increasing urea concentrations is to allow higher HMTA concentrations without premature precipitation. If the urea concentration is too low, not enough HMTA can be used to give good gel properties. High urea concentrations tend to require higher HMTA concentrations, and both concentrations are limited by solubility limits. Baran's results[7] for ADUN solutions ($NO_3^-/U = 1.5$) show a wide range of permissible HMTA concentrations if the urea/U mole ratio is about 1.25. Urea/U ratios of 2.0 to 2.5 appear to be necessary for uranyl nitrate solutions (or $NO_3^-/U = 2.0$). Other gelation results confirm good gel properties at these two ratios without any systematic study of urea/U ratio as a variable. Many test results are reported with HMTA-urea solutions of equal molarities (3 M HMTA--3 M urea is common), and the urea/U and HMTA/U ratios are changed by varying the volume ratio of (HMTA + urea)/U solutions. The results are believed to be much more dependent on the HMTA/U ratio than on the urea/U ratio.

For the ORNL flowsheet, gel properties improve as the NO_3^-/U mole ratio decreases; however, the feed broth becomes less stable at ratios below 1.5. The uranium solubility is a maximum for NO_3^-/U mole ratios of 1.5 to 1.7, and this range appears optimum for internal gelation.

At ratios below 1.5, the solution is close to precipitation and the acceptable range of other process variables is reduced. As the NO_3^-/U mole ratio increases, more NH_4NO_3 must be formed before precipitation or gelation takes place. This can be accomplished by preneutralization of the uranyl nitrate solution using NH_4OH, or the ammonia can be obtained from decomposition of HMTA. When the additional ammonia comes from HMTA decomposition, more HMTA is required to replace that being used and the gelation process is retarded. The lower initial pH increases the initial rate of HMTA decomposition, and the increase in gelation time may be small. The additional NO_3^- gives a softer gel that is more difficult to wash and handle, independent of whether the additional NO_3^- is present as NH_4NO_3 in the feed or is reacted with ammonia from decomposition of HMTA.

The HMTA concentration, which is usually given in terms of an HMTA/U mole ratio (as specified at the beginning of this section), is the most important concentration variable. An HMTA/NO_3^- mole ratio is probably more logical when the NO_3^- that is preneutralized with NH_4OH is <u>not</u> included. The best HMTA/NO_3^- mole ratios are around 0.8. This gives HMTA/U ratios of about 1.25 at a NO_3^-/U mole ratio of 1.55 and HMTA/U ratios of 1.6 at a NO_3^-/U mole ratio of 2.0. Work at ORNL has shown that the HMTA/NO_3^- ratio of 0.8 is also optimum for gelation of acid-deficient solutions of mixed thorium-uranium nitrates. At low HMTA concentrations, the equilibrium pH is not high enough for practical gelation rates or gel properties.

4.5 Effects of Gelation Temperatures

Apparently, gelation temperature has not been a variable in most of the internal gelation studies reported. Formation of gas bubbles in the gel becomes troublesome when the gelation temperature is near the boiling point of the feed solution. As a result, nearly all tests reported by others were made at 85 to 95°C in order to use the maximum temperatures possible without formation of gas bubbles.

Our results indicate that gelation temperature has an important effect on gel properties and that the relationship is not a simple, single optimum. The gelation temperature should be defined as the temperature of the broth droplet or solution while gelation is taking place. As discussed for gelation times, the time required to heat 3800-μm droplets is significant; therefore, the gelation takes place at a temperature lower than the organic-liquid temperature. For the smaller sizes (1000- and 100-μm droplets), the temperature of the droplets is very close to the organic-liquid temperature when gelation occurs. The cold broth and heat losses to the surroundings result in significant temperature changes; thus the bulk organic temperatures are lower than the inlet organic temperatures.

As the gelation temperatures decrease below 50°C, the gelation rates become inconveniently slow for a gelation column. However, usable fines (100-μm average droplet diameter) have been prepared with an organic-liquid temperature as low as 40°C and with a 40-cm settling height after droplet formation. Broth samples at 25°C will give firm gels in 5 to 30 min, depending on the composition and

previous history. Temperatures above 50°C are not necessary for good gel properties at the ORNL flowsheet concentrations.

When the gelation temperature is raised to 70°C, the characteristics of the gel are changed. Both the rate of HMTA decomposition and the equilibrium pH are temperature-dependent. The results are most easily detected for small droplets ($\leq$100 μm). At the higher temperatures, the freshly formed small spheres are a clear, transparent yellow and have an excellent appearance like small glass marbles. These spheres soften rapidly and change to an opaque yellow during washing in NH_4OH solution. Depending on size, gelation temperature, amount of dehydration by the organic liquid used as the forming medium, total wash time, and other variables, the softening can progress until the gel is an unusable cake. The effects of higher gelation temperatures for larger spheres were more apparent for other organics with higher boiling points. Acceptable gel spheres were obtained at 74°C, using tetrachloroethylene and the standard broth composition; however, a soft gel which eroded during washing was produced at 85 and 95°C. A slightly improved product was obtained when the HMTA/U mole ratio was increased to 1.4 or 1.55, but it was still inferior to that produced in TCE at less than 70°C.

In the preparation of small-coarse (1000-μm) droplets, the higher gelation temperatures will produce a dried gel having a softened and poor-quality surface without complete loss of sphericity. For the largest (3900-μm) droplets and at the maximum temperatures practical for TCE (∿75°C), the heat-transfer times are long enough that gelation takes place before the droplets reach 70°C. Tests in other organics

at higher organic temperatures gave dried gel with less desirable properties; thus, we must conclude that either the higher temperatures give poor results or that TCE is a superior organic liquid.

The temperature of the organic liquid also affects the degree of dehydration of the gel surface, and this can cause confusion with regard to the primary effect of the temperature. The gel sphere--organic is a two-phase system with a minimum-boiling azeotrope. Therefore, TCE with gel spheres boils below 80°C to dehydrate the surface by vaporization of water. If a high-boiling organic is used as the forming medium, the boiling point of the azeotrope is near 98°C and the gel is dehydrated as the temperature increases toward that boiling point.

Our feed-broth composition produces better gel properties if gelation takes place at 50 to 55°C, as compared with temperatures greater than 70°C. The largest droplets (3900-μm) gel at droplet temperatures significantly below the TCE temperature; therefore, they do not clearly show any unsatisfactory results from excessive TCE temperatures. Dehydration of the gel surface improves the behavior of the wet gel spheres. For this reason, intermediate temperatures appear to give the poorest result since they give a poor type of gel precipitate as compared with the product typically produced at lower temperatures and less dehydration, or perhaps less complete precipitation, as compared with the product obtained at higher temperatures.

4.6 Effects of Organic Medium

The organic liquid functions as more than just a heat source and suspension fluid. The interfacial tension and the density difference

between the broth and organic liquid determine whether the droplet is spherical or elongated. Water is extracted from the droplet surface. The water may be soluble in the organic (2.5 vol % in 2EH), or it may vaporize as a low-boiling azeotrope. The azeotropic boiling point for TCE is below 80°C, while it would be about 98 to 99°C for organics with boiling points above 130°C.

Hydrocarbons such as mineral oil or n-paraffin (a purified kerosene) seem to result in gels with soft surfaces which erode during washing. When large-coarse spheres are first formed in new TCE, they are frequently characterized by a softer surface and more extensive cracking. After good-quality gel spheres had been prepared in TCE, higher gelation temperatures were tested by using several other organic liquids. The different organic mediums gave variations in results, and none of the products were as good as those formed in TCE at lower temperatures. A normal paraffin and 1,1,2-trichloroethane gave soft gels which fell apart or eroded during washing. Tetrachloroethylene gave a rough surface with detectable erosion during washing. Silicone oil gave an acceptable product, but TCE is preferred.

Ease of removal of the organic from the spheres is an important process advantage. For the large-coarse and small-coarse droplets (3900 and 960 μm as wet gel), TCE removal is achieved by brief (5- to 15-min) exposures to a downflow of air. Any small amounts of TCE trapped via the washing procedure are preferentially vaporized during drying without causing decomposition of liquid TCE on the dried gel. Removal of TCE from fines is much less complete because of their small

and varied diameters. All other organic liquids used as gelation mediums have higher boiling points than water and require organic washes for removal from the gel spheres. The high viscosities of silicone oil and mineral oils make their removal more difficult. In the work at ORNL, we have usually used 50 vol % isopropyl alcohol plus 50 vol % ammonia solution to remove organics. Other alcohols, TCE, and CCl_4 have been used elsewhere.

In summary, the properties of the organic liquid have significant, but incompletely understood, effects on the quality of the gel spheres. Dehydration of the gel by 2EH greatly facilitates the washing and drying of fines. The density and high interfacial tension of TCE are good for preparation of the largest spheres. The TCE yields products with better surface properties than do hydrocarbons, silicone oil, or high-boiling (>110°C) chlorinated ethanes and ethylenes.

The tendency of droplets to stick to each other or to the surfaces of process vessels before gelation is completed is greatly reduced by small additions of a surface-active compound. We commonly use Span 80, a sorbitan monooleate ester. In the preparation of the large-coarse spheres, Span 80 can be present at a concentration as low as 0.01 to 0.05 vol %, and it is depleted slowly. For small-coarse and fines droplets, Span 80 is added continuously at rates of about 0.001 and 0.03 liter per liter of broth feed. If the Span 80 additions are stopped or are inadequate, the small-coarse or fines droplets will cluster as flocs or clumps; these may separate without detectable affect on the dried or sintered spheres. After further depletion

occurs, the gel may begin sticking to vessel walls. The addition rates required are approximately proportional to the surface area of the spheres or inversely proportional to the diameter. However, we do not have any other measurements to verify the presence of a surface layer of Span 80 on the gel spheres.

4.7 Preferred Conditions

The gelation conditions for the 1200-, 300-, and 30-μm UO_2 spheres are summarized in Table 3. Two sets of values are shown for each size: (1) the conditions recently used to prepare more than 50 kg each of depleted and enriched products and (2) the range of conditions which are believed to permit trouble-free operation without a significant effect on the quality of the product. Conditions outside these ranges either give poorer results or have not been tested. The detailed discussions in other sections include information for some conditions other than those that are preferred.

5. GEL-WASHING REQUIREMENTS

Washing the gel spheres (1) physically displaces the gelation medium, (2) leaches NH_4NO_3 and other soluble constituents from the gel, and (3) allows additional reaction with NH_4OH to give an improved composition and structure for drying and sintering. A high-density organic forming medium can be displaced by the downflow of gas or NH_4OH solution. When the forming medium has a high viscosity or boiling point (e.g., tetrachloroethylene, 2EH, or silicone oils), a preliminary wash with a more volatile organic (CCl_4 for tetrachloroethylene, isopropyl alcohol for 2EH, and CCl_4 or hexane for silicone oils) is desirable. The principal

Table 3. Preferred gelation conditions for three sizes of UO_2 spheres

	Large-coarse (1200-μm) UO_2 spheres		Small-coarse (300-μm) UO_2 spheres		Fines (30-μm) UO_2 spheres	
	Applied	Range	Applied	Range	Applied	Range
Feed broth						
Uranium, moles/liter	1.3	1.25-1.5	1.3	1.25-1.5	1.3	1.1-1.5
HMTA/uranium mole ratio	1.25	1.1-1.4	1.25	1.1-1.4	1.15	1.1-1.3
Urea/uranium mole ratio	1.25	1.0-1.5	1.25	1.0-1.5	1.25	1.0-1.5
Temperature, °C	-1	-6-4	-1	-6-4	-1	-6-4
Organic gelation medium						
Name	Trichloroethylene		Trichloroethylene		2-ethyl-1-hexanol	
Temperature (in column), °C	64	55-70	54	50-60	50	48-55
Initial Span 80, g/liter of organic	0.1	0.05-0.5	0.5	0.2-1.0	2.0	1.0-10
Span 80 addition, g/liter of broth feed	<1.0	<1.0	1.0		30	
Column height, cm	180	>100	180	>50	60	>30
Organic removal	Air flow to vacuum for 10 min		Air flow to vacuum for 10 min		0.5 liter per liter of 50% isopropyl alcohol plus 50% 3.0 M NH_4OH	

part of the washing is accomplished by using 0.1 to 0.5 M NH_4OH solutions. The total wash volumes required for slow wash rates are those necessary to dilute the NH_4NO_3, urea, and HMTA by a factor of about 1000. The minimum times required for fast wash rates are those for mass transfer in the gel spheres with low concentrations in the wash solution around the spheres.

5.1 Theoretical Considerations of Nitrate Removal During Washing

The minimum times and wash volumes are determined by the requirements for leaching soluble constituents (NH_4NO_3, urea, HMTA, and formaldehyde) from the gel. Physical displacement of the organic forming medium and additional reaction with NH_4OH can be accomplished in shorter times or by smaller wash volumes. The NH_4NO_3 must be removed to prevent cracking of the product during drying and calcining, and the nitrate content of the wash effluent can be determined at desired intervals by simple measurements. Therefore, we have investigated the washing of nitrate from the gel spheres and assumed that nitrate removal is the controlling requirement.

The mass-transfer considerations for washing the gel spheres are very similar to those for stripping porous ion exchange resins. Results for the more common case of loading a resin can also be applied by recognizing that the direction of mass transfer and the breakthrough curves are reversed, and that the equilibrium and feed concentrations are zero. Our usual washing conditions are based on the use of a 23-cm-diam, 9- to 10-cm-long fixed bed. When very high wash flow rates are used, the rate of washing is controlled by the rate of mass transfer

(diffusion-controlled) inside the gel sphere. When very low wash flow rates are used, the gel and the wash liquid are close to equilibrium; thus the wash volume (or time) required in this case is controlled by the equilibrium distribution between the two components. The most practical way of avoiding both excessive waste volumes and excessive times is to stipulate the use of intermediate flow rates in the wash conditions.

Equations and numerical solutions reported by Rosen[19,20] appear to be applicable to the washing of gel spheres in a fixed bed. However, such application requires values of the effective diffusion coefficient for NH_4NO_3 in UO_3 gel and the effective equilibrium constant in terms of the gel/wash liquid concentration ratio at equilibrium. Values were measured experimentally by determining nitrate concentrations in solution vs time for three batch mixings of large-coarse gel spheres with NH_4OH solutions. The concentrations at equilibrium indicate that the equilibrium constant is 0.85 in units of (NO_3^- per cm^3 of gel/NO_3^- per cm^3 of wash). This is a reasonable value if the precipitated urania has little affinity for nitrate; the washed UO_3 gel is greater than 90 vol % water. The half-life for approaching the equilibrium concentration varied from 6 to 7 min, indicating a diffusion coefficient for NH_4NO_3 of 0.66×10^{-5} cm^2/sec. The theoretical value[15] at infinite dilution in water is 1.93×10^{-5} cm^2/sec. The lower value (by a factor of 3 for the gel) appears to be reasonable. Since these results are based on nitrate analyses of the solutions, any nitrate present in the gel in a form that washes out at a low or zero rate would not be

detected. An examination of material balances and old nitrate analyses of washed gel shows that more than 95% of the nitrate originally in the gel is easily washed out.

From the above results, the minimum wash times for very large wash volumes would be about 45 and 70 min to reduce the washable nitrate contents by factors of 100 and 1000 respectively. The wash volumes as determined by using results reported by Rosen[20] and our standard wash conditions would be about four and six volumes of wash per volume of gel to give the same nitrate reductions (factors of 100 and 1000). We tend to require somewhat higher ratios, probably as a result of some nonuniform flows through the fixed beds. Since the equilibrium distribution is favorable, the wash/gel volume ratio could be as low as 2 or 3 when only a moderate number of countercurrent stages are used.

5.2 Conditions and Results for Washing of Large-Coarse and Small-Coarse Spheres

Formed spheres are gelled in hot TCE and collected in a 23-cm-diam, screen-bottom product catcher capable of holding about 4 liters (bulk volume) of spheres (∿650 g of uranium). Once the product catcher is full, the TCE is drained through the screen; this is followed by a few minutes of air flow to vacuum to complete the removal of TCE. The product catcher is then transferred to a washing rig which has four stations (Fig. 5). Each station consists of a 50-liter plastic bottle, a ball valve, a short length of capillary tubing, and a spiral multiholed distributor. The 0.5 M NH_4OH wash solution is made up in a 250-liter tank. Forty liters of this solution are subsequently pumped

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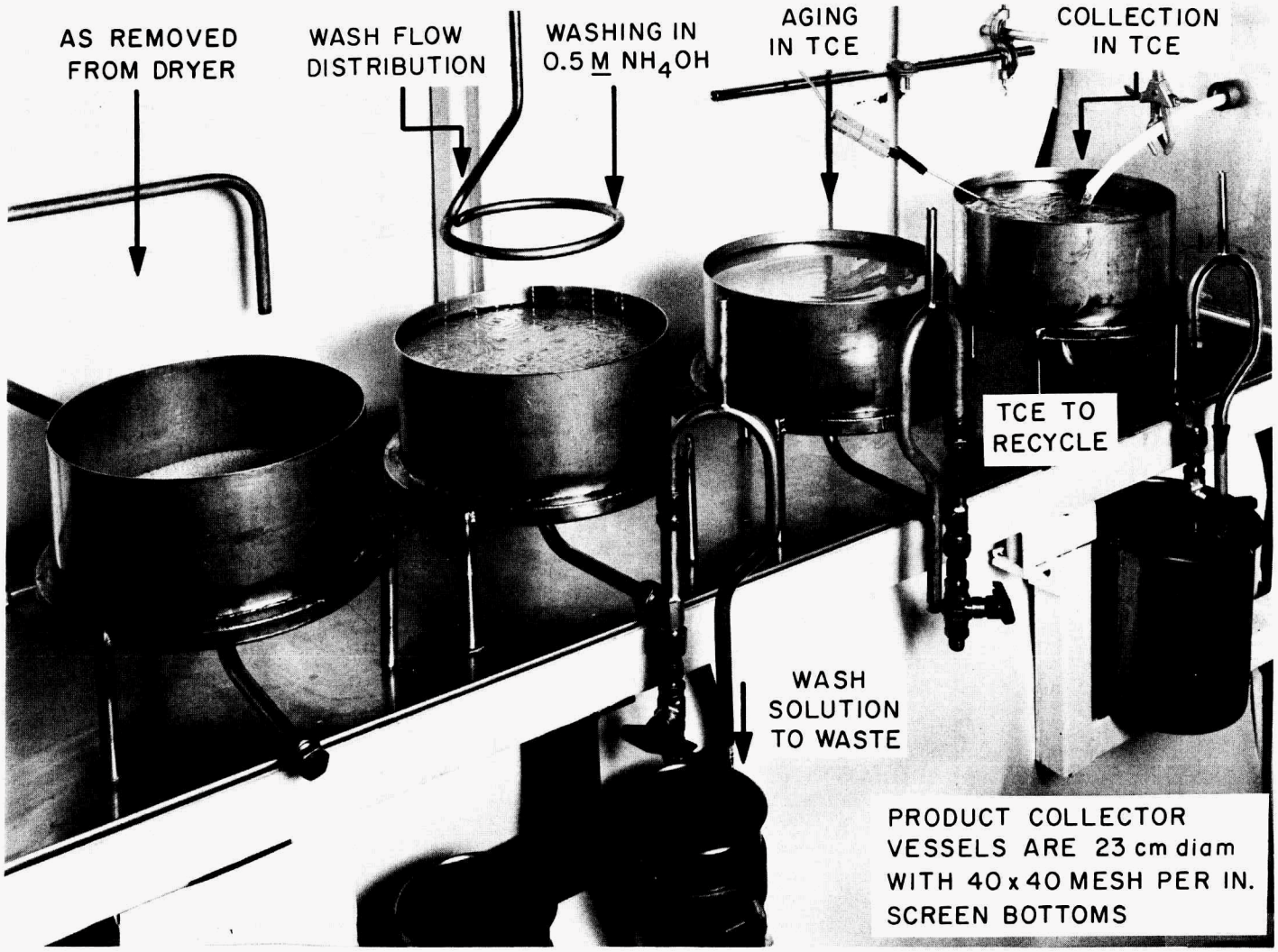

Fig. 5. Collection, aging, and washing of urania gel spheres.

to each plastic bottle, from which it drains downward and through the spheres in the product catcher. Inlet flows are regulated by the capillary tubing and the exit flow by overflow weirs to maintain set levels in the wash vessel.

A yellow discoloration, indicative of uranium, is apparent in the effluent initially obtained in the washing of small-coarse spheres. This discoloration usually disappears after a few minutes of washing. However, the discoloration did not disappear for material gelled at 75°C; at the end of 4 hr, uranium was present at a concentration of 1500 ppm, as compared to 50 ppm for material gelled at 50°C. Samples taken of effluent from the washing of large-coarse spheres show less than 1 ppm uranium present at the end of 4 hr, but the concentration increases to 50 ppm when the spheres are allowed to stay in the wash overnight.

The extent of washing has been monitored as a function of time by using a conductivity meter. The conductivity, which is due mainly to the presence of nitrate ions, peaks after about 30 min of washing for a batch of large-coarse spheres containing a total of 600 g of uranium and then declines to the value for pure 0.5 $\underline{M}$ NH_4OH after 2 hr. For 400 g of uranium of small-coarse spheres, the peak again occurs about 30 min after washing is initiated and declines to the pure wash value within 1 hr. Comparison of the resulting curves with similar curves determined by a nitrate-specific ion electrode is shown in Figs. 6 and 7 for the large-coarse and small-coarse sphere washing respectively. The nitrate and conductivity curves exhibit the same behavior as the

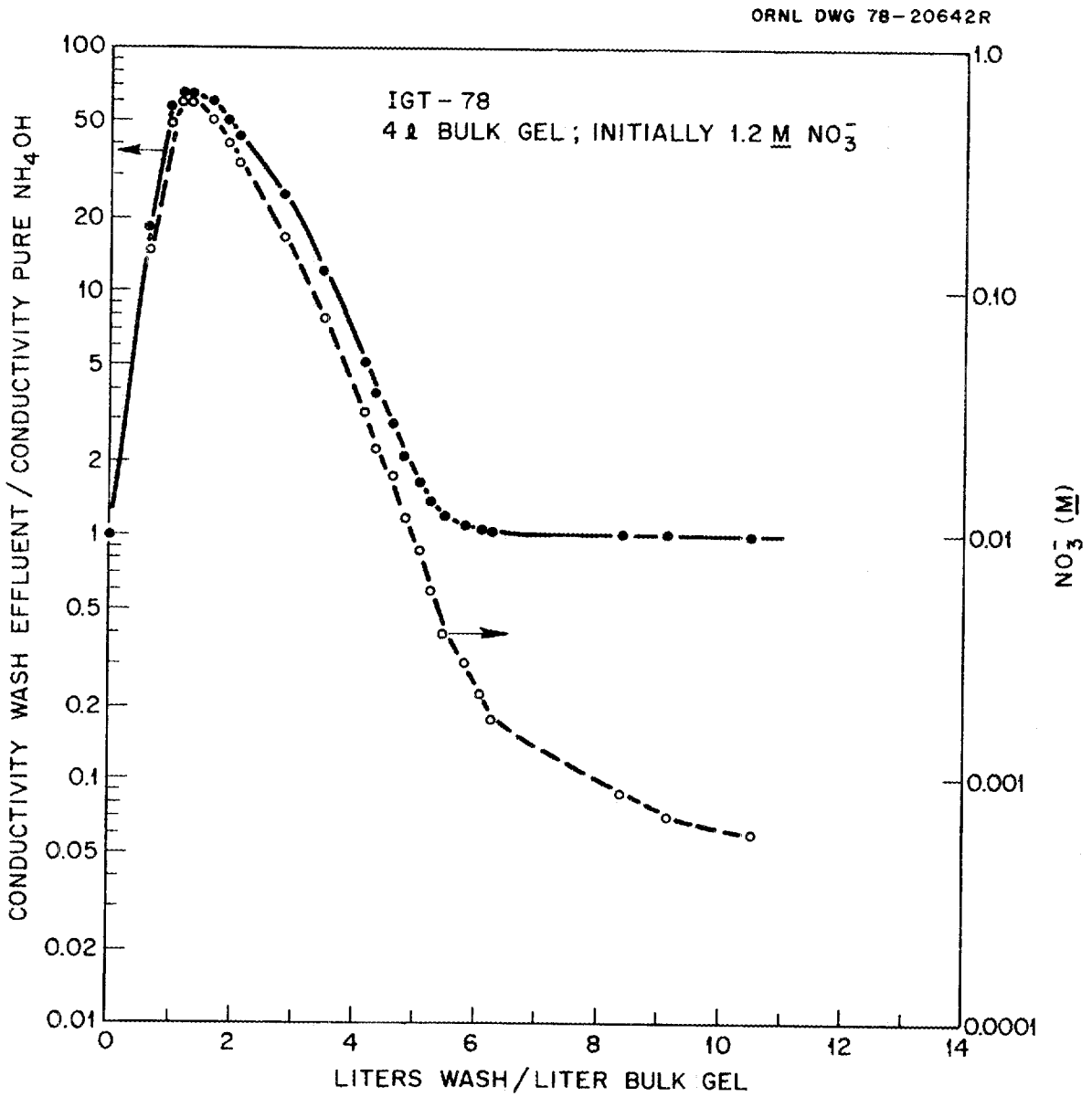

Fig. 6. Washing of large-coarse spheres — conductivity and nitrate analysis of wash effluent.

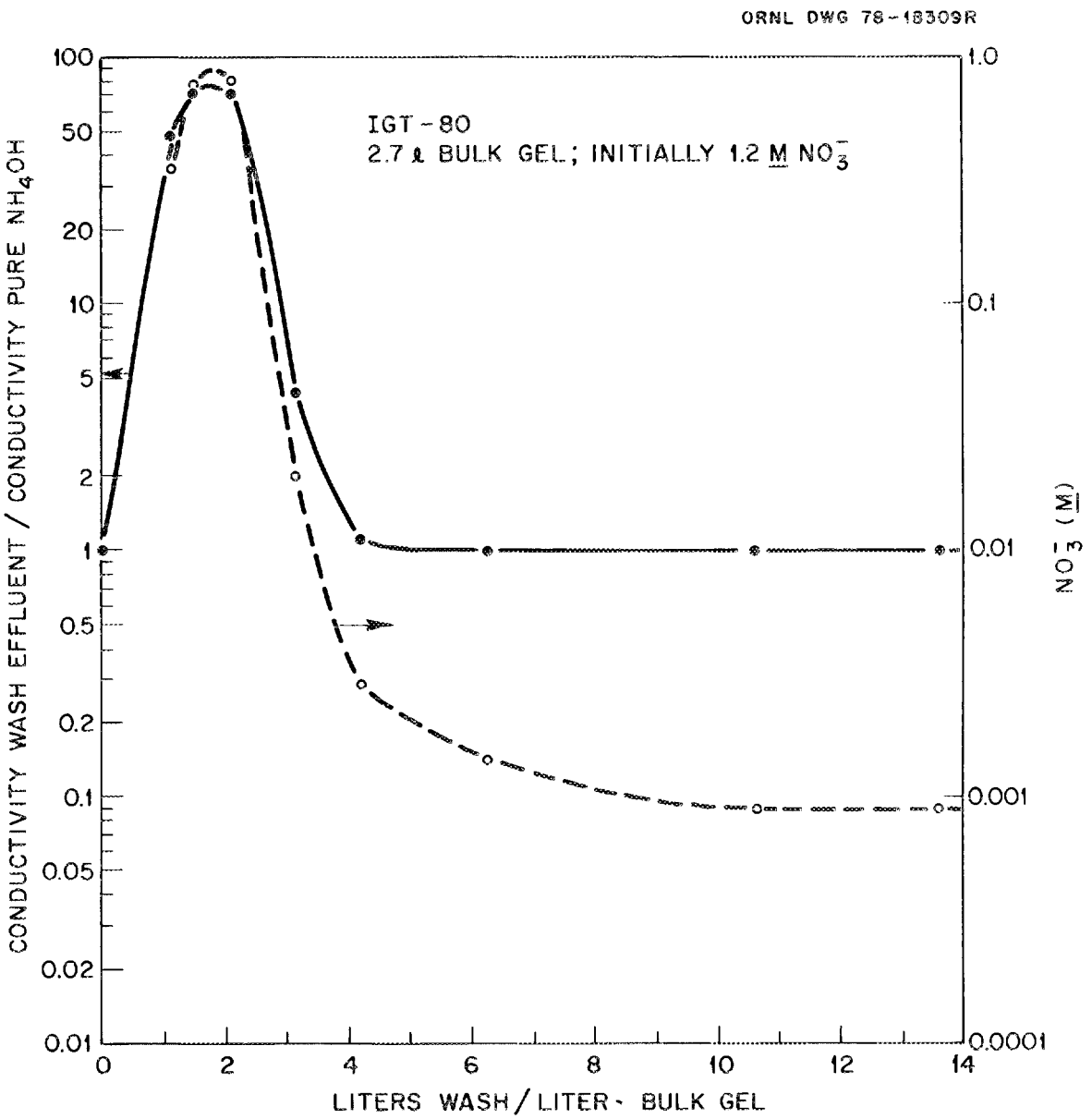

Fig. 7. Washing of small-coarse spheres — conductivity and nitrate analysis of wash effluent.

wash proceeds (liters of wash per liter of bulk gel is equivalent to time). Note that, as the nitrate content drops below 0.01 M, the conductivity curve levels off at the value for pure wash solution, while the nitrate curve continues to drop to <0.001 M. Thus, batches of spheres are typically washed for 30 min (5 to 6 liters of wash) beyond the time required for the conductivity of the wash effluent to reach that of the pure wash solution.

In routine operations, we have washed the large-coarse (1200-μm-diam) spheres and the small-coarse (300-μm-diam) spheres with ten volumes of wash per volume of gel at a flow rate of 18 liters/hr. Once covered by wash solution, the small-coarse spheres must be stirred to remove any trapped air so that channeling of the wash solution is avoided. Both sizes of spheres have an initial tendency to float on the wash surface but are easily submerged for complete contact with the wash solution.

5.3 Conditions and Results for Washing of Fines

The washing of fines generally presents more problems than the washing of larger-size spheres because of difficulties in displacement of the organic forming medium and nonuniform flows through the fixed beds. These problems are somewhat offset by the shorter wash times required for a given wash solution volume as a result of higher mass-transfer rates in the gel.

In the interim engineering-scale fines system, in which 2EH is used as the preferred organic forming medium, fines are collected batchwise and transferred to filter-bottom containers for subsequent

washing, giving 23-cm-diam, 10-cm-long fixed beds. Excess 2EH is initially removed from the bed by vacuum. An initial isopropyl alcohol wash to displace residual 2EH is followed by the principal part of the wash using 0.5 M NH_4OH solution. The following wash schedule has proved to be satisfactory for batches of fines containing 4 liters of bulk gel:

Wash step	Liters wash per liter gel	Composition
1	1.5	50% isopropyl alcohol--50% 1.5 M NH_4OH
2	5.0	0.5 M NH_4OH
3	0.3	75% isopropyl alcohol in water

The bed is stirred for about 1 min upon initial contact with wash solutions 1 and 2. Because wash solution is passed through the fixed bed using vacuum, constant wash rates are difficult to maintain and thus vary from 1 to 2 hr for the overall operation. A final isopropyl alcohol rinse (step 3) is used to partially displace water from the surface of the spheres with a more volatile liquid in order to enhance drying rates in air.

6. EFFECTS OF WET AGING AND DRYING PROCEDURES

While many gel-sphere processes require careful control of drying conditions, the internal gelation conditions described in the previous sections produce UO_3 spheres that are easy to dry. The properties of the dried gel vary with the drying conditions, but these differences are only partially understood. Some of the effects persist through calcination

and sintering. Cracking of the spheres, distortion into nonspherical shapes, and clustering or caking of spheres into strong agglomerates are examples of effects that can remain after sintering and result in an unacceptable product. Other effects observed or measured in the dried gel have no noticeable influence on the properties of the dense UO_2 spheres. The density of the dried gel, the weight loss during calcining, and the uniformity and darkness of the gel color can show wide variations without affecting the dense UO_2. Clustering and cracking may persist through sintering, as noted above, or the clusters may separate into acceptable spheres.

The water in the wet gel is vaporized at a rate determined by the rate at which heat is supplied for this operation. For steam-drying, the water is evaporated at 100°C with heat transferred from an oven at a higher temperature (usually 225 to 250°C) to the gel in an atmosphere of its own vapor. The individual spheres remain at 100°C for varying times (from a few minutes for a small sample such as a monolayer to >24 hr at the center of 4-liter batches). For air-drying, the water is evaporated at the wet bulb temperature of a large flow of dry air. This temperature can be as low as 14°C for air supplied at room temperature and as high as 20°C for warm or hot air at 60 to 80°C when the air is heated by low-pressure steam in a heat exchanger. Intermediate temperatures could be used with steam-drying in a vacuum oven or with higher hot-air temperatures for air-drying, but neither of these has been tested.

Burrell and Lee[21] pyrolyzed our gel and determined the compositions of gases evolved by use of a mass spectrometer. Peaks for water evolution

were ascribed to coordinated water at about 100°C, dehydration [$UO_2(OH)_2 \rightarrow UO_3 + H_2O$] at about 250°C, and decomposition of organics or self-reduction of U(VI) at about 330°C. A broad peak for ammonia occurred at 200 to 250°C.

6.1 Cracking

Some occurrences of cracking remain unexplained; however, for all known causes, the amount of cracking increases greatly with diameter. Therefore, only cracking of the large-coarse spheres is discussed here.

When all known causes of cracking are avoided, the probability of preparing a high-quality product is good. Since there were a few cases in which small amounts of cracking could not be readily explained, however, additional information or experience is needed to determine whether some causes remain unrecognized. The usual causes of cracking include the following:

1. Inadequate time in hot TCE to complete gelation before washing. A holdup of 20 min in hot TCE appears to be a minimum requirement. Samples of large-coarse spheres with closely controlled, short aging times show cracking of all spheres aged for 4 min or less and 50% cracking of spheres aged for 8 min (Fig. 8). The aging time for batch washing is much less than the wash time and is accomplished without any additional process complexity. For continuous washing, this time requires an additional holdup vessel located between the gelation column and the wash system.
2. Insufficient washing with NH_4OH. Washing requirements are discussed in Sect. 5. The wash/gel volume ratio, the uniformity of washing, or the time may be inadequate.

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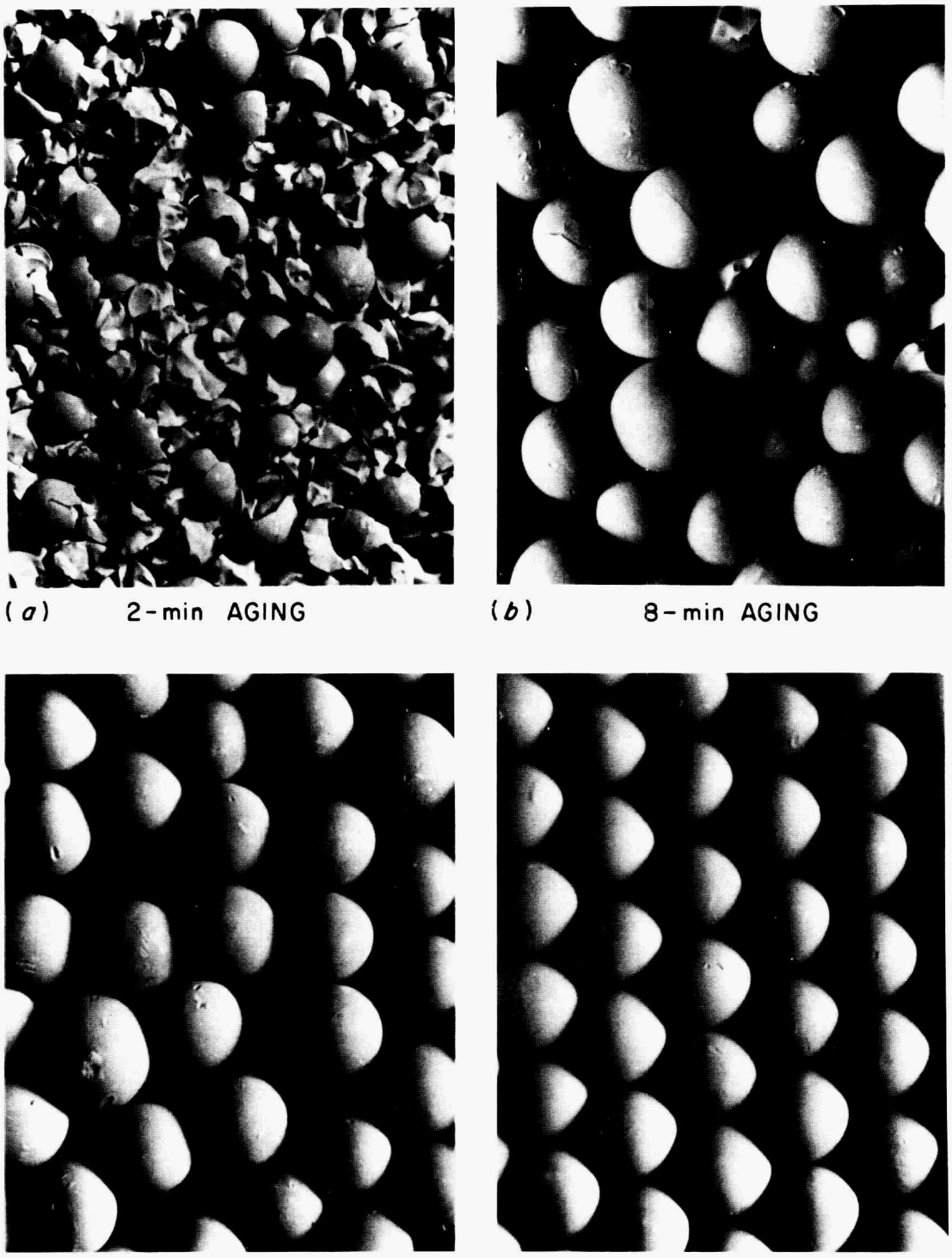

Fig. 8. Dried gel spheres with aging times in hot TCE as a variable.

3. Rewetting dry gel by liquid water. This effect is variable with high fractions of cracked spheres for some cases and less than 2% for others. When large batches of spheres are steam-dried in an oven, the steam produced at the surface layer may be condensed by cold gel in the interior of the batch and then drained back into the dried gel.
4. Upsets in feed flow which give high or low HMTA/U ratios during gelation.
5. Excessive aging which also produces distortion of the gel spheres.
6. Drying by 80°C air followed by exposure to room air. The spheres could be observed to "pop" or shatter over a period of several hours. This type of cracking was eliminated by completing the drying to 225°C in an oven without cooling or exposure to room air.
7. Contact of wet gel spheres with the tray used to contain the spheres during drying. The spheres touching the tray showed a high fraction of cracking, while the bulk of the spheres did not. Monolayers of spheres showed much less evidence of cracking than the surface layer. It appears that a large temperature gradient or heat flux through the gel sphere may cause the cracking, while a more rapid temperature rise without a high heat flux has no effect.
8. Mechanical damage by stirring, violent impacts, or large pressure drops. Such damage is possible but thus far has not been significant as a cause of cracking. Instead, the damage takes the form

of smears, nicks, pockmarks (where spheres press together), scratches, or other excessive surface defects before cracking occurs.

6.2 Distortions of Shape

Changes that occur during the aging of wet gel tend to result in distortions that produce nonspherical shapes in the dried product. These distortions appear as very rough surfaces with ridges and valleys and also as ellipsoidal shapes. The overall appearance is that of a lopsided baseball of an old type that was wrapped with coarse string and then dipped in latex, leaving the ridges from the string wrapping visible. This effect, which occurs slowly at room temperature, is much more rapid at 100°C. Aging at room temperature for 1 to 3 days, either in TCE or after the NH_4OH wash, commonly yielded 2 to 10% distorted particles for the large-coarse spheres. For drying in steam at atmospheric pressure, the gel is heated to 100°C and then held at that temperature until the water is evaporated. Some 4-liter cans of both large-coarse and small-coarse spheres showed high (50 to 100%) degrees of distortion after drying in steam. This unexpected result may be attributed to combinations of aging before drying, the poor configuration for heat transfer, and overloaded drying ovens.

The distortion effect has been avoided with little difficulty after its primary cause was recognized. The aging occurs in several different media but is not easily detected in the wet gel; therefore, it is easy to mistakenly believe that one particular condition is to blame. Basically, the wet gel changes with time, and the rate of change is

very temperature-dependent. The same change occurs in TCE, in the NH_4OH wash, in gel drained of wash solution, or in wet gel in air at 15 to 30°C or in steam at 100°C. Up to 24 hr at room temperature or 4 hr at 100°C appears to be acceptable for the large-coarse spheres and our preferred gelation conditions. Tripling these aging times is likely to produce significant distortion, while the results for intermediate times are unpredictable. The small-coarse spheres are much less sensitive to aging. Fines prepared with some dehydration in 2EH have never shown any evidence of this distortion.

6.3 Clustering and Caking

Clustering and caking are problems observed only for the fine spheres; in fact, they are the controlling factors with respect to selection of flowsheet conditions for fines. The fine spheres, with their wide range of sizes, probably exhibit more clustering and caking than would occur in a uniform-size product of the same average diameter. Therefore, a concerted effort to achieve better uniformity in fines preparation of size would be recommended. The changes with aging that promote shape distortion in larger spheres (Sect. 6.1) also give a softened surface that tends to cake, but distortions of these larger spheres become excessive before extensive caking occurs.

Three flowsheet conditions are important to minimize the clustering and caking of fines. These conditions involve earlier steps of the gelation (and have been discussed previously); however, their effects do not become obvious until the gel spheres are dried. Therefore, they are listed again below.

1. The surface of the gel sphere should be dehydrated to harden the gel and make it less sticky. Formation in 2EH that is not saturated with water is preferred. TCE can provide some removal of water, but hydrocarbons or other organic liquids with low water solubilities and higher boiling points cannot. Dehydration as a separate process operation that occurs after gelation has been used elsewhere, but it appears to be an unnecessary process complexity.
2. Gelation should take place at 48 to 55°C to provide the optimum gel properties. Heat transfer for the fines spheres is so rapid that the organic temperature in the column is the gelation temperature. (The inlet organic temperature must be higher to compensate for the heat transfer to the cold droplets and to the surroundings.) Below 48°C, decomposition of the HMTA is not rapid or sufficiently complete. Temperatures above 55°C tend to give gel properties which allow softening in the NH_4OH wash.
3. Nonuniform washing resulting from pockets of organic forming liquid or from channeling of wash liquid results in caking of the poorly washed gel.

The aging changes that result in shape distortions for the larger spheres (Sect. 6.1) appear to contribute to caking of fines. The first two flowsheet conditions listed above are much more important. However, gel fines formed in TCE are less dehydrated than those formed in 2EH and must be dried by air flow, while those formed in 2EH may be dried either by air flow or in steam at 100°C.

6.4 Density of Dried Gel

The densities of the gel spheres show large variations (dependent on the drying conditions), but the densities of the sintered UO_2 show little or no dependence on the gel densities. The values reported here are bulk densities measured when the gel spheres were poured into a container. The gel spheres usually contain about 38 vol % voids; thus the true gel densities are about $(1 - 0.38)^{-1}$, or 1.61 times these bulk densities.

Steam-drying with the gel held at a temperature of 100°C during vaporization of water gives densities of 0.7 to 1.0 g/cm^3. Air-drying with the gel at 14 to 20°C during vaporization of water gives densities of 1.3 to 1.6 g/cm^3, if drying is completed without excessive gel aging. Large batches of fines frequently required either lengthy drying periods (>72 hr) or transfer of the partially dried gel to an oven to steam-dry for removal of the final 10% of the water. These fines showed intermediate densities. It seems probable that the same aging effects that result in distortions of the dried gel particles (Sect. 6.1) also reduce the densities of the products. If this is true, the temperatures and times are important, while the atmosphere of steam as compared with air is not. The results in Table 4 are typical for our flowsheet conditions, but may not be representative of those obtained when using gelation conditions that would give different gel properties.

6.5 Other Characteristics of Dried Gel

The maximum temperature during drying determines (1) the color of the dried gel and (2) the remaining volatiles or weight loss during

Table 4. Typical bulk densities of dried UO_3 spheres[a]

Organic medium	Mean diam as dense UO_2 (μm)	Drying conditions			Bulk density (g/cm^3)	
		Type	Atmosphere	Temperature during water evaporation (°C)	Typical	Range
TCE[b]	1200	Oven	Steam	100	0.76	0.73-1.0
		Warm air	Air	∿20	1.45	1.35-1.47
		Air	Air	14	1.5	1.41-1.58
	300	Oven	Steam	100	0.76	0.65-1.05
		Warm air	Air	∿20	1.42	1.36-1.47
		Air	Air	14	1.4	1.06-1.44
	40-100	Air	Air	14	1.4	1.3-1.5
2EH[c]	80-200	Oven	Steam	100	0.8	0.61-0.9
		Warm air	Air	20	1.4	
	20-60	Oven	Steam	100	0.74	0.68-0.77
		Warm air	Air	20	1.44	1.33-1.52
		Combined	Air, steam	14, then 100	1.0	0.7-1.3

[a]Chemical flowsheet conditions: standard broth compositions; final drying temperature, 220 to 250°C.
[b]TCE = trichloroethylene.
[c]2EH = 2-ethyl-1-hexanol.

calcining. Variations in these two gel properties do not seem to affect the properties of the sintered UO_2 spheres. The color of the dried UO_3 gel varies from an opaque light or medium yellow below 100°C to an opaque medium orange at 250°C. For our internal gelation flowsheets, the dried gel spheres are never glassy or transluscent, and they are never red in color.

Some of the gel spheres that have been dried at temperatures above 200°C exhibit varying dark shades over or with the color of the UO_3 gel. These are believed to be traces of decomposition products of Span 80 or other organic materials. The spheres from a few batches of fines are dark gray or almost black in bulk but appear to be yellowish-black when examined microscopically. When batches of fines are air-dried and then heated in an oven to 225-250°C, the spheres near the surface of the batch are commonly orange, while those at the center are dark gray. Large spheres may show spots or semicircles on the surface, with colors varying from black to gray to dark brown or purple. These color variations do not seem to affect the sintering behavior or the properties of the product UO_2 spheres.

The wet, washed gel contains about 3 g of volatile material per gram of UO_3, where the volatile material is mostly water, small amounts of ammonia and nitrate, and traces of other materials. After 95% of the volatiles have been removed, leaving about 15 wt % volatiles in the gel, the gel has a dry appearance and the important properties have been fixed. Continued drying to 225-250°C increases the removal of volatiles to 98-99% and gives the color changes and variations previously

described. Exposure of this dried gel to room air results in weight gains that can be as large as 1 to 2 wt % for fines. These changes and variations do not seem to affect the properties of the final sintered product.

6.6 Drying via Microwave Heating

Tests with microwave heating of the washed UO_3 gel were made with a home-kitchen type of oven. Drying of samples in Pyrex dishes was rapid and relatively uniform as the moisture content decreased from 3 g of water to about 0.2 g of water per gram of UO_3. When exposure to microwave energy was continued, a hot spot would develop and grow until a 1- to 3-cm-diam area was glowing brightly. This area would reach a steady-state size without any change in the remaining UO_3. Additional tests have shown that the coupling with the microwave energy appears to require reduced valences of uranium. Several different samples of dry UO_3 did not show any significant heating when exposed in the microwave oven. All of the UO_2 and U_3O_8 samples heated strongly. The hydrated gel samples first tested apparently underwent small amounts of reduction from traces of ammonia and organic materials remaining in the gel after washing. Once overheating began, U(VI) was converted into U_3O_8 until all the microwave energy was being transformed into heat and radiated at a steady-state temperature. Tests with well-insulated samples of urania show fusion (temperatures >2200°C) in a 600-W, home-kitchen type of microwave oven. These results, although unexpected, may be useful for other applications. A result that illustrates this effect occurred when a 10.3-g sample of UO_2 spheres was placed in a cylindrical

cavity in a small cube cut from a zirconia brick. The cube was centered in a 600-ml Pyrex beaker filled with bubble ZrO_2 insulation. After 15 min (0.15 kWhr) of microwave exposure, about one-third of the UO_2 spheres had fused into a chunk, and some of the bubble zirconia insulation was sintered to the zirconia cube.

6.7 Calcining and Sintering

Calcining and sintering conditions and results have not yet been reported in the open literature, but the preferred conditions and typical results are briefly described here.[22]

One product catcher full of dried spheres (gel weight, ∿800 to 900 g) is loaded into a stainless steel tray to a depth of about 1 in. As many as ten of these trays are then heated under flowing argon--4% hydrogen at 100°C/hr to 450°C for 1 hr. This process eliminates most of the residual water, ammonium salts, and organics, without any significant particle shrinkage or reduction. The particles are then removed from the protective atmosphere and loaded into molybdenum trays, again to a depth of about 1 in., and sintered under pure hydrogen in a cold-wall-design, tungsten-element furnace. They are heated rapidly (3 hr) to 1600°C and held for 4 hr; then they are cooled at the natural furnace cooldown rate (∿3 hr). This step completely eliminates the volatile species, reduces the UO_3 to UO_2, and sinters the particles to a high-density product.

Several kilogram-size batches of UO_2 of the three standard sizes (i.e., large-coarse, small-coarse, and fines) were prepared by internal gelation and characterized in depth. Each batch of product spheres

exhibits chemical compositions and impurity contents well within the ASTM/ANSI specification for sintered UO_2 pellets, except for gas release and moisture content. The latter parameters are expected to be higher for spheres than for pellets due to the greater surface area of the spheres. Before the spheres are loaded into rods, however, a simple low-temperature vacuum outgassing step will decrease the moisture and gas levels sufficiently to meet specifications.

Typical results of the chemical characterization of the UO_2 batches are as follows:

Uranium	88.2 wt %
Oxygen/uranium ratio	1.98 to 2.00
Density	99+% of theoretical
Carbon	4 to 7 ppm, by weight
Metallic impurities	$\leq$100 ppm total; $\leq$10 ppm individual
Chlorine, fluorine	$\leq$5 ppm each
Gas release at 1600°C	$\leq$0.085 cm^3 per gram of uranium
Moisture content	$\leq$0.004 wt %

7. SUMMARY AND CONCLUSIONS

Improvements and modifications to the previously established flowsheet conditions for internal gelation were developed and applied at ORNL to prepare dense UO_2 spheres with average diameters of 1200, 300, and 30 μm. The gel-sphere processes generally require close duplication of process conditions or "recipes."

Details of the chemical flowsheet conditions were selected, in part, to control three problems associated with the internal gelation process: (1) the feed solution or broth is temperature-sensitive and must be

mixed at temperatures around 0°C to prevent premature gelation; (2) partially denitrated or acid-deficient metal nitrate feed solutions of high metal concentration are required to produce good gelation behavior; and (3) gelation takes place in a warm, or hot, organic liquid which must be removed from the spheres and recycled.

The ADUN solutions are three-component systems which may be represented as mixtures of UO_3, HNO_3, and H_2O. In the absence of a solid phase, the ADUN solutions have two degrees of freedom in addition to temperature and pressure. We use the molar concentration of uranium and the NO_3^-/U mole ratio as two convenient variables to specify the composition of an ADUN solution. In normal operations, monitoring the density and the pH can provide a convenient means of process control. For densities in grams per cubic centimeter and concentrations in molarities, the relationships are defined as:

$$\rho(\text{ADUN}) = \rho(H_2O) + 0.2659\ U + 0.0282(NO_3)\ . \qquad (15)$$

For NO_3^-/U mole ratios of 1.5 to 1.7, the relationship can be approximated by:

$$U = 3.22\ [\rho(\text{ADUN}) - \rho(H_2O)]\ . \qquad (16)$$

The NO_3^-/U mole ratios are estimated from pH measurements by use of a graphical correlation. The ADUN solutions for gelation feed were prepared by dissolution of U_3O_8 or UO_3. Solutions with a uranium concentration of about 3.5 M and a NO_3^-/U ratio of 1.6 were consistently prepared by use of excess uranium oxides at the optimum temperature

and nitrate concentration. (Uranium has a maximum solubility at both intermediate nitrate concentrations and intermediate temperatures.)

The rate of gelation and the gel properties depend on the gelation conditions. For the large-coarse (0.4-cm-diam) droplets, the gelation times are approximately the same as the times calculated for heat transfer from the organic liquids to the droplets. In the case of fines, the times calculated for heat transfer are 0.1 sec or less, and the gelation times are probably controlled by the reactions of HMTA. The best internal gelation results are for HMTA/NO_3^- mole ratios of 0.75 ± 0.15, in which nitrate preneutralized by addition of NH_4OH is not included.

Only a narrow range of gelation conditions has been tested, and the practical conditions for preparation of good-quality gel spheres are even more limited. Some gel properties result in deleterious changes (cracking, distortion, etc.) during washing, drying, calcining, or sintering. Precipitation in ADUN solutions by ammonia is reported to produce compounds of the apparent composition $UO_3 \cdot xNH_3 \cdot (2-x)H_2O$. For our internal gelation conditions, x is probably near zero during gelation but should increase, with one-third as a maximum during washing with NH_4OH solutions. Urea is added to the ADUN to prevent premature precipitation of uranium. For continuous mixing of solutions, the uranium and HMTA concentrations must be near the solubility limits to give the desired mixed concentrations.

The effect of temperature on gelation is based on the droplet temperature during gelation. The gelation rates become inconveniently

slow for a gelation column at temperatures below 50°C, but 50°C will give good gel properties. At 70°C or higher, the characteristics of the gel are less desirable. Therefore, the preferred organic-liquid temperatures increase from 50 to 55°C for fines, where heat transfer is rapid, to about 65°C for large-coarse droplets.

Dehydration of the gel surface by the organic liquid is important for the preparation of fines and also appears to be desirable for larger-size product; however, it can confuse the primary effect of gelation temperature. The preferred forming organic medium for fines is 2EH, because it provides more dehydration of the gel surface than does TCE. The high density and higher interfacial tension of TCE are necessary to keep the 0.4-cm droplets spherical during gelation. The 0.1-cm droplets can be gelled in either 2EH or TCE, but TCE allows easier separation and washing.

The minimum wash times and volumes are determined by the requirements for leaching soluble constituents from the gel. Empirically determined wash procedures and measurements for removal of NH_4NO_3 from the gel agree with literature models and calculations for stripping ion exchange resins.

Wet aging and drying effects are complex and only partly understood, but many variations in the dried gel do not result in any differences in the sintered UO_2 spheres.

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