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**Preliminary Development of
Internal Gelation Flowsheets for
Preparing (Th,U)O₂ Spheres**

P. A. Haas
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PRELIMINARY DEVELOPMENT OF INTERNAL GELATION FLOWSHEETS
FOR PREPARING (Th,U)₂ SPHERES

Date Published: August 1981

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It is subject to revision or correction and therefore does not represent a
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CONTENTS

	<u>Page</u>
Abstract	1
1. Introduction	1
1.1 Product Specification	2
1.2 Scope of These Studies.	3
1.3 Characteristics of Internal Gelation Processes.	4
2. Process Development for Feed Prepared by Partial Neutralization With Ammonium Hydroxide.	8
2.1 Feed Preparation.	10
2.2 Gelation at 60 to 75°C (in Trichloroethylene)	11
2.2.1 HMTA Concentrations.	12
2.2.2 Broth Density Requirements	12
2.3 Aging and Washing	13
2.4 Drying.	14
2.5 Sintering and Product Properties.	16
2.6 Demonstration Run Conditions and Results.	19
3. Process Development for Feeds Prepared by Solvent Extraction of Nitrate and Addition of High Urea Concentrations	24
3.1 Acid-Deficient Metal Nitrate Solution Preparation	25
3.2 Effect of Urea.	26
3.3 Gelation in Perchloroethylene—Mineral Oil Mixtures at Temperatures Above 80°C	27
3.4 Aging and Washing	28
3.5 Drying.	29
3.6 Sintering and Product Properties.	29
3.7 Demonstration Run Conditions and Results.	29
4. Comparisons of the Two Flowsheets.	33
4.1 Feed Preparation.	33
4.2 Gelation, Washing, and Drying	33
4.3 Product Properties.	35
4.4 Remaining Development Requirements.	35
5. Conclusions and Recommendations.	36
6. References	38
7. Appendix: Tabulated Data.	40
7.1 Behavior after Mixing of the Th + U and HMTA Solutions.	45

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ABSTRACT

Internal gelation procedures were developed to prepare good, high-density (Th,U)O₂ spheres, 800- to 1200- μ m in diameter, as required for Sphere-Pac fabrication of nuclear fuels. Decomposition of hexamethylenetetramine (HMTA) dissolved in metal nitrate solution drops releases ammonia to solidify or gel the drops as hydrated metal oxides. The thorium-uranium nitrate feed solutions were made acid deficient by partial neutralization with NH₄OH or by solvent extraction of nitrate. For some feeds, gelation of drops was in trichloroethylene at 60 to 75°C. Feeds with high concentrations of urea as a complexing agent for metals required higher temperatures and were gelled in perchloroethylene-mineral oil mixtures at 80 to 95°C. Slow changes of concentration during washing with ammonia were important to prevent cracking of the 800- to 1200- μ m sintered spheres. The spheres were dried in steam atmospheres, calcined and then sintered in Ar-4% H₂ at 1450°C to give (Th,U)O₂ spheres with nearly theoretical density (>99%). The initial batches prepared with other washing and drying procedures showed severe cracking. These preliminary results demonstrated two practical chemical flowsheets, but additional development, including equipment flowsheets studies, would be necessary to justify final selection of a process.

1. INTRODUCTION

Sphere-Pac fabrication of nuclear fuels, as developed at Oak Ridge National Laboratory, has important advantages for remote operation, and these advantages are important for a thorium-uranium (Th-U) fuel cycle. The development of Sphere-Pac fabrication procedures¹ and of gel-sphere processes for UO₂^{2,3} have been reported. The development of gel-sphere processes to prepare (Th,U)O₂ spheres with metal ratios of Th/U = 3 was part of the continuing fuel refabrication program for application to LWRs. The most useful results for large (Th,U)O₂ spheres were from internal gelation processes, and this report describes these results.

The Sphere-Pac development program included an assessment of both domestic and foreign technology.⁴ 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 assessment⁴ and various scouting tests^{5,6} indicated that the large-size spheres of Th/U = 3 were very difficult to prepare by application of published technology for two (water extraction from sols; external chemical gelation) of the three types of gel-sphere processes. Few (Th,U)O₂ results have been reported for the third type (internal chemical gelation) as applied for preparation of Sphere-Pac UO₂ spheres.

The objective of this report is to describe the preliminary development of procedures for preparing good, high-density (Th,U)O₂ spheres, 800 to 1200 μm in diameter. The intermediate size of 200 to 300 μm in diameter are easy to prepare; thus, the process selection is determined by the need for large-and small-diameter products. The "fertile fines" concept using pure ThO₂ only as the small spheres might be used for Sphere-Pac Th-U fuels. If the fines must also be (Th,U)O₂, the Th-U feeds described in this report can probably be used with the same internal gelation procedures developed for UO₂ fines.^{2,3}

1.1 Product Specification

The primary product for these preliminary development studies is the large coarse (Th,U)O₂ spheres for a Sphere-Pac fabrication of nuclear fuel. Flowsheet conditions adequate for the large coarse size are very likely to allow easy preparation of the intermediate size. A Th/U ratio of 3.0 was used for all tests; variations over the range anticipated for most U-Th fuel cycles would probably require changes only in the broth concentrations.

The target specifications for the development studies were approximately as follows:

Composition:	(Th,U)O ₂
Th/U atom ratio:	3.0
Density:	≥99% of theoretical

Size:	>800 μm minimum 1000 to 1200 μm preferred
Shape and strength:	Very high fraction of good sphericity through fabrication. The degree and amount of nonsphericity allowable is not known
Carbon content and metallic impurities:	To meet nuclear fuel specifications for pellets
O/U ratio:	≤ 2.01
Other characteristics:	A solid solution of $\text{UO}_2\text{-ThO}_2$ would be preferred
Microstructure:	A homogeneous, fine-grained structure is desirable. The above specifications and the gel-sphere process characteristics probably assure a good microstructure without requiring a separate specification

1.2 Scope of These Studies

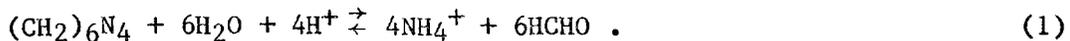
These studies determined two somewhat different internal gelation processes with promising results for preparation of the dense, 800- to 1200- μm $(\text{Th,U})\text{O}_2$ spheres. Process development is incomplete for both processes. Development for the $(\text{Th,U})\text{O}_2$ fuel cycle ended in 1979, and gel-sphere development for fuel refabrication in 1980 has been for $(\text{U,Pu})\text{O}_2$ compositions for FBR application. The information now available does not justify a final selection of either process variation. A process with ammonia neutralization and low urea concentrations in the feed has some simpler process steps and gave a slightly better demonstration result. Therefore it is described first. The alternative process, with extraction of HNO_3 and high urea concentrations, is described with respect to the differences between the processes. The two processes are compared with a listing of remaining development requirements and recommendations.

Since the $(\text{Th,U})\text{O}_2$ chemical and equipment flowsheets have many similarities to those developed for UO_2 ,^{2,3} some details are described briefly with references to the reports for UO_2 . In the body of the report, unsuccessful results are described only to the extent necessary to define the known limits of successful results. More complete descriptions of some development results are in the Appendixes.

1.3 Characteristics of Internal Gelation Processes

In these internal gelation processes, decomposition of hexamethylene-tetramine (HMTA) dissolved in metal nitrate solutions releases ammonia to precipitate hydrated metal oxides. The internal gelation process was first applied to the production of nuclear fuels and demonstrated for Sphere-Pac fabrication at KEMA;[†] their flowsheet conditions^{7,8} are commonly termed "the KEMA process." Investigations of the KEMA and other internal gelation flowsheet conditions have been reported by other laboratories.⁹⁻¹¹ Improvements and modifications to previously published flowsheet conditions^{7,8} for the internal chemical gelation process were developed and reported at ORNL² to prepare dense UO₂ spheres with average diameters of 1200, 300, and 30 μm.

The schematic flowsheet for the internal gelation process is shown in Fig. 1. The controlling characteristics of internal gelation result from the absence of mass transfer during the gelation step. The ammonia for chemical gelation is generated homogeneously without stresses or shell structures from concentration gradients. The overall reaction for decomposition of HMTA in an acidic medium is:



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 UO₂ spheres and has important advantages for large (Th,U)O₂ spheres. Spheres of 300 μm in diameter are easy to prepare, and selection of processes for Sphere-Pac preparation is determined by the need for >800- and 30-μm products.

The internal gelation studies for (Th,U)O₂ were made using the equipment and procedures available from preparation of UO₃ gel spheres.² The schematic equipment flowsheet is shown as Fig. 2. Batch mixing of the feeds was used for small tests, and continuous mixing was used for demonstration runs. For batch mixing, the two solutions were stored at the

[†]Keuring van Electrotechnische Materialen at Arnhem in the Netherlands.

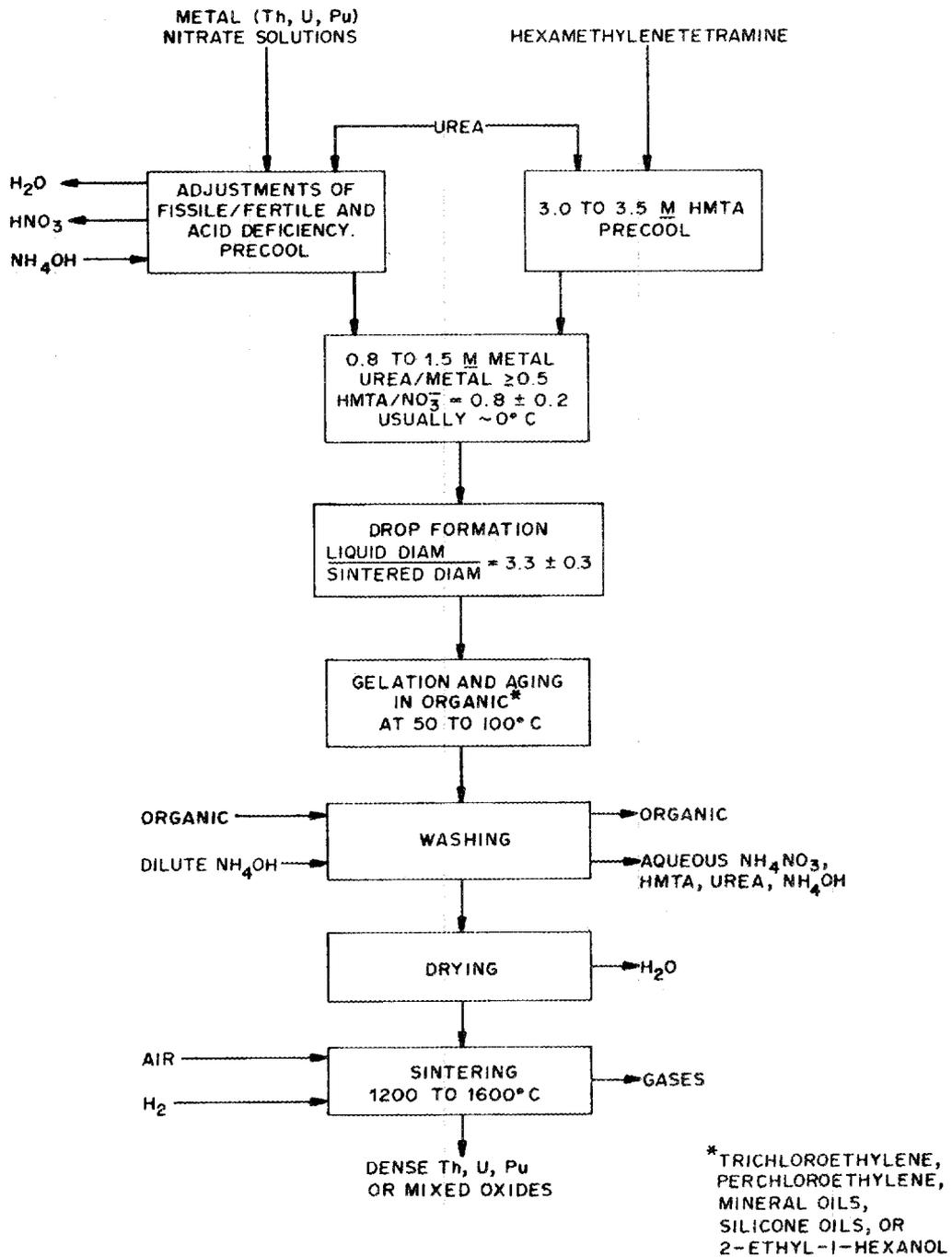


Fig. 1. Microsphere preparation by internal gelation.

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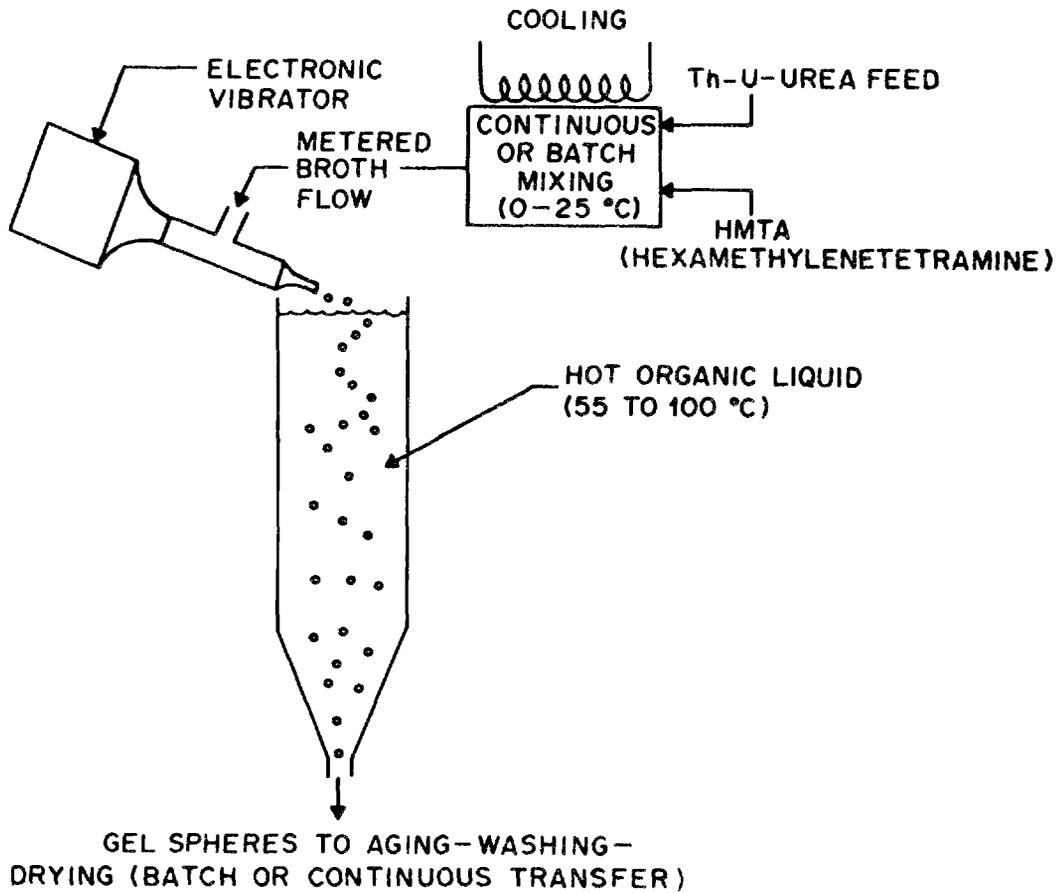
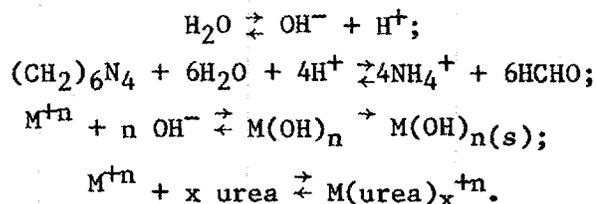


Fig. 2. Internal gelation procedures for $(\text{Th,U})\text{O}_2$ spheres.

desired mixing temperature (a refrigerator for mixing at $<2^{\circ}\text{C}$) overnight and then mixed in a vessel designed for air-pressurization. The broth feed rate to the drop formation was controlled by regulation of the air pressure to this vessel. The continuous mixing system uses capillary flow elements to meter each solution through precoolers (if needed) to a closed jacketed mixer.³ Mixing is by a magnetic stirrer bar. The broth flow rate is the sum of the two metered solution flow rates. Small batch gelations (up to 0.8 L of feed) were made in 4-L Pyrex beakers or graduates filled with the organic liquid medium with heat input through the vessel walls. Larger batches were prepared with continuous feed and with gelation in a 15-cm-diam by 120-cm-high column using cocurrent flow of hot organic liquid down through the column to a product collector. Drop formation was by use of single-fluid nozzles with vibration to give a controlled and uniform break-up of the jet into drops.³

For a practical internal gelation process, the broth should have (1) a long gelation time at a low temperature, so premature gelation does not occur in the feed system; and (2) a short gelation time at a higher temperature so that long fluidization times in the hot organic liquid are not required.

Both Th and U easily form complexes, and NH_4^+ , NO_3^- , urea, HMTA, and HMTA decomposition products may react with these metals and each other. Therefore, the number of chemical reactions possible during internal gelation is very large. Nevertheless, the observed effects for our internal gelation conditions can be explained by four primary reactions, where M^{+n} is the metal species:



Complexing of the metal anion by urea makes it unavailable for other reactions and prevents premature precipitation. The HMTA is a very weak base and reacts with HNO_3 to form a nitrate salt. After mixing of the HMTA and Th-U urea solutions, the indicated pH values exceed 4.0 in <6 s even at 0°C , where the broths remain fluid. The rates of reactions and the equilibrium

constants are both temperature dependent. For both U and Th, the solubility for acid-deficient conditions decreases as the temperature increases above 40°C. The reaction for decomposition of HMTA is reversible, and accumulation of NH_4^+ and HCHO decomposition products results in a higher H^+ concentration (i.e., a lower pH) at equilibrium. The interaction of these effects is complex and difficult to predict.

Some acid deficiency of an internal gelation feed broth seems highly desirable for practical operation. For $\text{Th}/\text{U} = 3$, the stoichiometric nitrate/metal ratio is 3.5 mol/mol. As a first approximation, the HMTA required for gelation is specified by an $\text{HMTA}/\text{NO}_3^*$ mole ratio, where the NO_3^* is defined as the total NO_3^- concentration minus the NH_4^+ concentration. The $\text{HMTA}/\text{NO}_3^*$ has an allowable range with (1) an upper limit that gives premature thickening at 0°C, and (2) a lower limit that does not give a firm gel in the hot organic forming media. If the NO_3^* is reduced either by removing the NO_3^- from the solution or by adding NH_3 or NH_4OH to form NH_4NO_3 , less HMTA is needed for gelation. With less dilution by HMTA solution, the broth metal concentration can be higher. The gels usually show better properties with less shrinkage and cracking during washing and drying as the metal concentration is increased. Studies with stoichiometric nitrate solutions were therefore very limited.

2. PROCESS DEVELOPMENT FOR FEED PREPARED BY PARTIAL NEUTRALIZATION WITH AMMONIUM HYDROXIDE

The chemical flowsheet studies that resulted in this ammonia neutralization process were started with the intention of using conditions for $(\text{Th},\text{U})\text{O}_2$ that were similar to those we had developed for UO_2 .² The UO_2 flowsheet has a feed that is 25% acid deficient; that is, NO_3^*/U is ~1.5, or ~75% of the stoichiometric ratio of 2.0. This solution is equivalent to an average composition of $\text{UO}_2(\text{OH})_{0.5}(\text{NO}_3)_{1.5}$. Thorium nitrate can also be stable as an acid deficient solution, and a 25% acid deficient solution would correspond to an average composition of $\text{Th}(\text{OH})(\text{NO}_3)_3$. As the acid deficiency increases above 25%, U will precipitate as hydrated UO_3 while Th can form clear, stable thoria sols for up to 90% acid deficiency. For Th-U mixtures, sol formation becomes more difficult as the U content increases, but clear-red sols are easily prepared for $\text{Th}/\text{U} = 3$ (see ref. 12). A 25%

acid deficiency would correspond to a $\text{NO}_3^*/(\text{Th} + \text{U})$ ratio of $(0.75)(3.5)$ or 2.63. The program requirements and scouting experimental studies reduced the feed compositions variables to:

1. $\text{Th}/\text{U} = 3.0$ atom/atom,
2. $\text{Urea}/\text{U} = 2.0$ mol/mol or $\text{urea}/(\text{Th} + \text{U}) = 0.5$,
3. $\text{NO}_3^*/(\text{Th} + \text{U})$ of 3.1 mol/mol,
4. Adjustment of $\text{NO}_3^*/(\text{Th} + \text{U})$ ratio by addition of NH_4OH or NH_3 to $\text{Th}(\text{NO}_3)_4\text{-UO}_2(\text{NO}_3)_2\text{-HNO}_3$ solutions.

The reasons for these selections will be stated briefly. The Th/U ratio of 3 is typical of that required for the final fuel composition.

The presence of urea is necessary to prevent the precipitation and separation of U-rich solids when the Th-U solutions are mixed with HMTA. The urea/U ratio of 2 [$\text{urea}/(\text{Th} + \text{U}) = 0.5$] eliminated or delayed the precipitation so it was not troublesome, while a ratio of 1 was sometimes inadequate. Since the ratio of 2 did not seem to have any detectable disadvantages, it was used thereafter without further testing of other values. Additional tests of urea as a process variable were the basis of the alternate flowsheet reported in Sect. 3.

For a practical internal gelation process, the broth should have a long gelation time at a low temperature, so premature gelation does not occur in the feed system, and a short gelation time at a higher temperature, so that long fluidization times are not required. If all other compositions are fixed, the practical HMTA concentrations will be limited to a range. The higher concentration limit is that which gives premature thickening or gelation at the feed system temperature (0°C with refrigeration). The lower concentration limit is that at which gelation is incomplete or inadequate in the hot organic liquid. The scouting experimental studies showed that this range became smaller or narrowed as the Th-U feeds were made more acid deficient. For $\text{urea}/\text{U} = 2$ mol/mol, there was no useable HMTA concentration for $\text{NO}_3^*/(\text{Th} + \text{U}) = 2.5$ mol/mol and 2.8 was very sensitive or difficult to use. The advantages of low $\text{NO}_3^*/(\text{Th} + \text{U})$ ratios or high acid deficiencies were discussed in section 1.3. The $\text{NO}_3^*/(\text{Th} + \text{U})$ ratio of ~ 3.1 was selected as a compromise and fixed for the study of washing, drying, and sintering behavior.

During scouting experimental tests, some acid-deficient feeds with no NH_4^+ were prepared by dissolving UO_3 in $\text{Th}(\text{NO}_3)_4$ solutions. For the same $\text{NO}_3^*/(\text{Th} + \text{U})$ ratios, the gel-sphere properties were slightly better for $\text{NH}_4^+(\text{Th} + \text{U})$ ratios of 0.5 to 1.0 than for $\text{NH}_4^+ = 0$. Higher NH_4^+ concentrations did not give any further improvement. This result is fortunate for convenience of feed makeup. The Th and U nitrate solutions from purification processes can be easily concentrated by evaporation to contain small excesses of HNO_3 . The adjustment of acid deficiency by the addition of NH_4OH or NH_3 is very simple and gives the preferred amount of NH_4NO_3 for $\text{NO}_3^*/(\text{Th} + \text{U}) = 3.1$. While the presence of this amount of NH_4^+ is not necessary to good gel properties, the easy adjustment of acid deficiency by ammonia addition is a very important process advantage. Therefore, broth preparation without ammonia addition was not tested further.

2.1 Feed Preparation

Adjustment of acid deficiency by neutralization was done by mixing $\text{Th}(\text{NO}_3)_4$ and $\text{UO}_2(\text{NO}_3)_2$ solutions and then adding concentrated NH_4OH solution with good agitation at 60 to 90°C. Use of NH_3 gas avoids dilution but requires special mixing apparatus.¹² A precipitate forms at the point of ammonia addition and then disappears as it is mixed with the bulk liquid. For <50% acid deficiency, the ammonia addition can be made at room temperature. For higher acid deficiencies and particularly for Th-U mixtures, heating is necessary to accomplish the conversion of precipitates into stable colloidal particles. The preferred $\text{NO}_3^*/(\text{Th} + \text{U})$ ratio of 3.1 mol/mol (see Sect. 2.) is only 11% acid deficient, and room temperature mixing is adequate. Urea (urea/U = 2 mol/mol) is added after adjustment of the acid deficiency. The maximum stable Th + U concentrations for these feeds at 30°C are ~2.6 M. Higher concentrations or other temperatures may remain stable for days as a result of super-saturation effects but will eventually form deposits of large crystals. The acid deficiency can be checked by pH measurements; the pH values after urea addition with 2.4 to 2.6 M Th + U, but before mixing with HMTA, should be 0.8 to 1.2 at 25°C. The pH values before urea addition are 0.6 to 1.0 for the preferred acid deficiencies.

The solubility of HMTA is ~3.8 M at 10°C and decreases as the temperature increases. Since there is a heat of solution, easy preparation of

3.4 or 3.5 M HMTA requires cooling to $\sim 10^{\circ}\text{C}$. The 3.4 M HMTA solution can be used at 10 to 30°C with no difficulty. A solid hydrate is stable at temperatures below 10°C , but solutions can usually be super-cooled to 0°C before hydrate solids are formed.

The concentrations can be checked by density measurements. For concentrations, (HMTA) or (Th + U), in moles per liter, and solution densities, ρ , in grams per cm^3 :

$$(\text{HMTA}) = 31.4 [\rho(\text{HMTA}) - \rho(\text{H}_2\text{O})],$$

$$(\text{Th} + \text{U}) = 2.83 [\rho(\text{Th} + \text{U}) - \rho(\text{H}_2\text{O})].$$

The $\rho(\text{H}_2\text{O})$ is the density of water at the same temperature, and (Th + U) refers to the preferred acid-deficient solution of Th and U, including urea.

2.2 Gelation at 60 to 75°C (in Trichloroethylene)

The gelation procedures and equipment developed for $\text{UO}_2^{2,3}$ were used with minor modifications for (Th,U) O_x spheres (Fig. 2). The feed HMTA and Th-U solutions (see Sect. 2.1) were cooled to $\sim 0^{\circ}\text{C}$ and mixed. The maximum temperature of the trichloroethylene (TCE) is limited to $< 78^{\circ}\text{C}$ by the boiling point of the TCE- H_2O azeotrope. For the gelation of Th-U broths in TCE, the effects of increased TCE temperatures were always either favorable or indeterminate. Therefore, there were no reasons to limit the TCE temperatures to improve the gel properties as preferred for some sizes of uranium-gel spheres.

For drop formation, the single-fluid nozzles with vibration operate better with the Th-U broth than with U broths for internal gelation. The multiple-orifice nozzles for small-coarse sizes were operated at 27,000 to 250,000 cycles/min with good drop formation and no significant difficulty from unequal flows. The single nozzles for large-coarse sizes were operated with broth feed rates of 53 to $65 \text{ cm}^3/\text{min}$.

Gelation tests were made with about 0.03 vol% Span 80 in the starting TCE for the large-coarse size and 0.1 vol% Span 80 for the small-coarse size. The depletion of Span 80 for continuous-column operation was slow; however, the longest test for 220- μm small-coarse size showed a need for Span addition (some clustering and sticking) near the end of the test.

2.2.1 HMTA concentrations

The Th + U broths are much more sensitive to HMTA concentrations than are pure U broths, and this sensitivity increases as the acid deficiency increases. For 10 to 15% acid deficiency and urea/U of 2 mol/mol, the allowable ratio of HMTA/NO₃^{*} has an adequate range ($\sim 0.70 \pm 0.04$ mol/mol) to allow practical operation.

For these Th + U feeds, the volume ratios of HMTA solution to (Th + U) solution for test operation were determined empirically. Small samples were mixed with several volume ratios covering the range of expected values (1.3, 1.45, 1.6 as a typical set). The pH values were determined 2 to 5 min after mixing. By graphical interpolation, the volume ratio was selected to give a pH of ~ 4.2 , or slightly lower if this value resulted in thickening in <10 min at room temperature. For the preferred feed concentrations, the empirical tests consistently gave HMTA/NO₃^{*} ratios close to 0.70 mol/mol, and this is an adequate criteria without the empirical test.

2.2.2 Broth density requirements

For preparation of large-coarse sizes, distortion of the drop to give a nonspherical particle is an important problem. For TCE or other organic liquids of low viscosity, the drop density should be 0.01 to 0.1 g/cm³ more than the density of the organic medium. For these Th-U broths, the densities of some compositions were so low that the drops floated in pure TCE. Therefore, some tests were made in mixtures of TCE and 2-ethyl-1-hexanol (2EH). At gelation temperatures of $\sim 70^\circ\text{C}$, the densities of mixtures can be estimated from additive volumes at 1.38 g/cm³ for TCE and 0.80 g/cm³ for 2EH. For continuous column operation, a mixed organic composition of 7/8 TCE -1/8 2EH was maintained without difficulty and had a good density for the large drops of 0.98 M Th + U. This organic liquid drained from 600- to 4000- μm gel spheres completely enough that an organic removal wash was not required. Less uniform spheres of <500 μm (av diam) required an isopropyl alcohol wash mixture.

For the most common compositions and additive volumes of the HMTA and Th + U feeds, the broth density, $\rho(\text{broth})$ is

$$\rho(\text{Broth}) = 0.421(\text{Th} + \text{U}) + \rho(\text{H}_2\text{O}).$$

In this equation, (Th + U) indicates the total metal concentration in moles per liter (mol/L). For hot TCE, the allowable broth concentrations for densities of 1.40 to 1.48 g/cm³ are 0.95 to 1.15 M (Th + U). Since the TCE density is higher at room temperature, broth drops of 1.04 M (Th + U) or less would float at room temperature. Some water is lost during gelation, and the gel spheres have a slightly higher density than the broth feed. The practical concentrations without solubility problems are 2.6 M (Th + U) and 3.4 M HMTA to give:

$$\frac{[2.6 \frac{\text{mol Th + U}}{\text{L}}][3.1 \frac{\text{NO}_3^*}{\text{Th + U}}][0.69 \frac{\text{HMTA}}{\text{NO}_3^*}]}{3.4 \frac{\text{mol HMTA}}{\text{L}}} = 1.64 \frac{\text{L HMTA}}{\text{L Th + U}}$$

$$\frac{2.6}{1 + 1.64} = 0.98 \text{ M (Th + U) in broth.}$$

Therefore, the broth drops will settle in hot TCE, but not in cold TCE.

2.3 Aging and Washing

The preferred feed concentrations and the gelation conditions gave gel spheres of excellent appearance in the hot TCE, but the aging and washing conditions were critical to preserving this good appearance. Aging in hot TCE appeared to result in less cracking during washing and drying. Gradual cooling in TCE before draining and washing seemed to reduce the amount of surface spalling and dusting. Therefore, the best overall conditions were to leave the 4.0-L batches of gel spheres in the product collectors filled with TCE and covered with a lid for ~90 min. During this time, the product collector cooled to about half way between the gelation temperature and room temperature. Some controlled program of aging temperatures might be superior, but the above conditions seemed better than either a longer cool-down time or a flow of hot TCE at the gelation temperature.

The gel spheres ooze or occlude clear solution as they age in warm organic liquid with up to 20% decrease in sphere volume. This clear solution may be a source of surface dust on the dried spheres.

In general, washing produced only minor problems for the small gel spheres (200- to 300- μm diam at theoretical density), but became increasingly more troublesome as the sphere size increased. The washing procedures

developed for UO_3 gel spheres proved to be unsatisfactory for the large (800- to 1200- μm diam at theoretical density) ThO_2 - UO_3 gel spheres. Cracking or crazing of a significant fraction of gel spheres was usually the result.

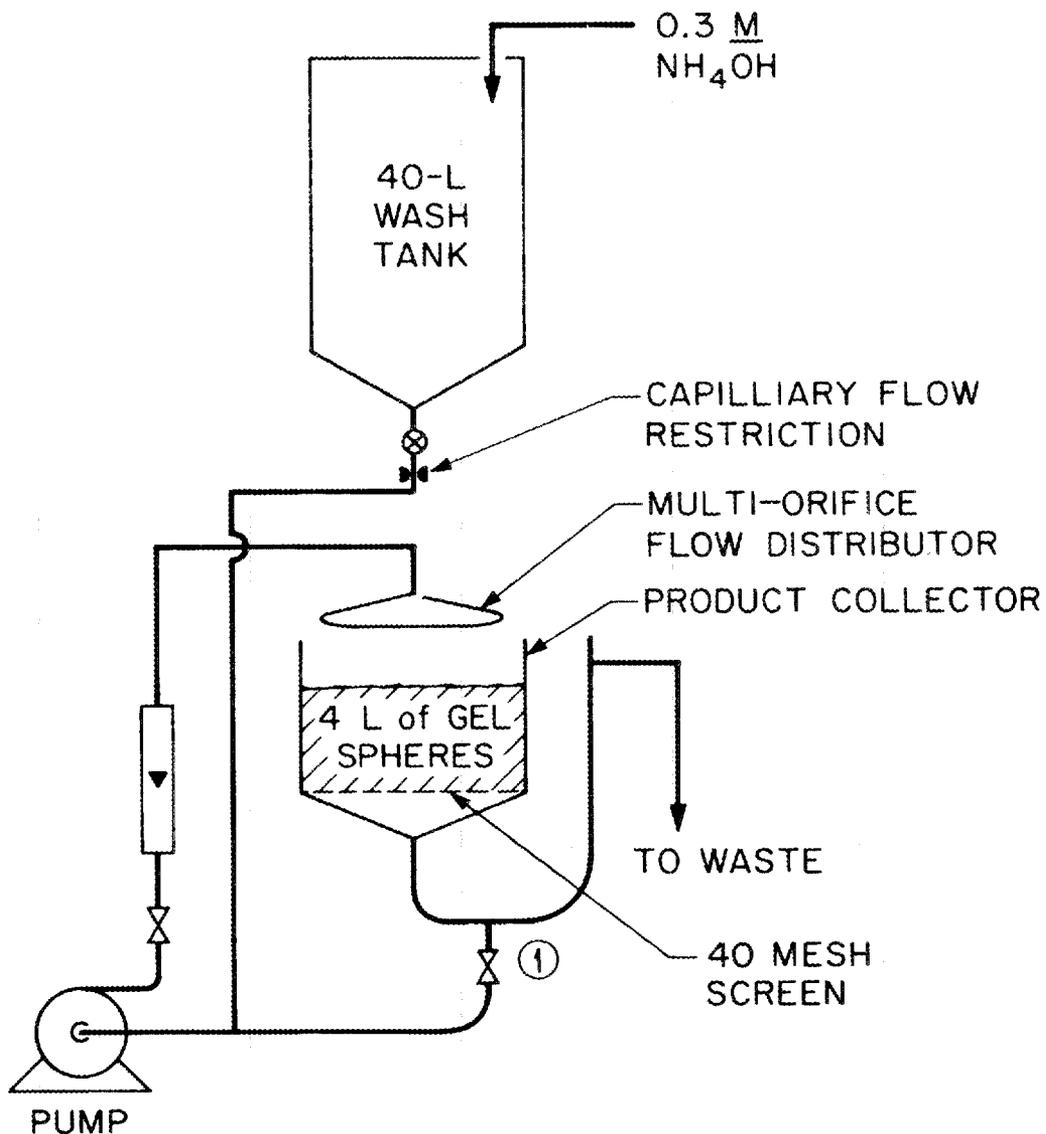
Damage to the gel was eliminated for spheres made from the ammonia-neutralized broth with a low urea content by careful control of the ionic strength of the wash solution. First the gel spheres were immersed in a salt solution with approximately the same ionic strength as the gel spheres to minimize osmotic stresses. This salt solution (1.06 M NH_4NO_3 --0.167 M NH_4OH) was recirculated through the fixed bed of gel spheres (see Fig. 3). The soluble salts were slowly leached out of the gel spheres by gradually diluting this recirculating wash solution with a flow of dilute NH_4OH . The volume of wash in the recirculating system was maintained constant by means of an overflow of excess solution. After ~2 h of washing in this manner, the ionic strength is close enough to that of fresh dilute NH_4OH to allow a final period with once-through flow of the wash solution to remove the remaining small amount of leachable solids. After 2 h of once-through flow, the conductivity levels out to a constant value, indicating leaching has ceased.² This washing procedure was developed after several trials and resulted in a satisfactory sintered product for this flowsheet.

This wash procedure required ~10 L of fresh dilute NH_4OH for every liter of bulk gel spheres. This ratio generates a lot of waste effluent, but the washing has not been optimized. The effluent from several of the batch washes has been noted to contain precipitate usually flushed from the system in the first few minutes. Most likely this precipitate was material on the surface of the gel spheres that weeped or oozed during aging.

2.4 Drying

The drying procedures tested were those found useful for UO_3 gel spheres.² 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 bulk of the water is evaporated at 100°C, with heat transferred from an oven at a higher temperature (usually 175 to 250°C) to the gel in an atmosphere of its own vapor. The individual spheres remain at 100°C for

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FOR RECIRCULATION, VALVE ① OPEN AND PUMP ON;
FOR STRAIGHT-THROUGH WASH, VALVE ① CLOSED
AND PUMP OFF WITH GRAVITY FLOW.

Fig. 3. Gel wash station with recirculation.

varying times (from a few minutes for a small sample such as a monolayer to >24 h at the center of 4-L 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.

Steam drying with the spheres at 100°C for most of the water removal is preferred over air-drying. Some batches were successfully steam dried, but the same material showed excessive cracking for air-drying. This cracking sometimes occurred during drying and sometimes occurred when the dried spheres were cooled in air. For cracking during and after cooldown, the spheres would break explosively or "popcorn." This "popcorn" cracking could be prevented by heating the spheres to ~250°C without any cooling or exposure to air. The air-drying tended to give higher gel densities but did not show any significant effect on the sintered density. Since the cracking is a major process problem, the 100°C or steam-drying condition is clearly superior.

Kerrigan and Lee¹³ pyrolyzed our gel and determined the compositions of gases evolved by use of a mass spectrometer. Peaks for water evolution differ from those previously observed for UO₃ gels. Peaks for CO₂ evolution were at higher temperatures for (Th,U)O_x. The abstract for this report reads as follows:

The pyrolysis of thoria-urania gel microspheres at programmed heating rates has been studied by time-of-flight mass spectrometry. The gaseous decomposition products were monitored, and reaction mechanisms for the pyrolysis reactions were proposed from the data. A nonisothermal kinetic method was used for determining activation energies of components released from the pyrolyzed gels. The approximate activation energies for the release of NH₃, hydrated H₂O, CO, and CO₂ were 70.7, 73.2, 103, and 134 J/mol respectively. Differences in pyrolysis reactions were noted between (Th-U)O₂ gels and UO₂ gels.¹³

2.5 Sintering and Product Properties

Because of the large number of batches of (Th,U)O₂ in this study, each batch was sintered using only one schedule. A very conservative schedule

using slow heating rates was used to prevent as much particle breakage as possible. This schedule consisted of heating from room temperature through the low temperatures to gently remove volatiles and prevent cracking (a rate of $100^{\circ}\text{C}/\text{h}$ up to 600°C). After 600°C was reached, the heating rate was increased to $300^{\circ}\text{C}/\text{h}$ up to 1450°C , where the sample was held for 4 h. The atmosphere used during the entire schedule was Ar-4% H_2 . This treatment was always sufficient to sinter particles to very near theoretical density (>99%). However, the majority of the batches cracked quite severely during one of the washing, drying, or sintering operations.

Each batch was characterized to compare all variations of the different flowsheets. Besides density by porosimetry with mercury, each batch was also characterized for cracking both before and after sintering. Cracking was determined using shape separation and a careful ceramographic examination after sintering. The cracking behavior could be divided into three categories, which are internal cracks, major cracks, and surface spalling. Internal cracks in several particles are shown in Fig. 4(a) and are thought to occur during either washing or drying. Major cracks are shown in Fig. 4(b), and these cracks extend from the particle surface toward the center of the sphere. These particles normally remain intact and are not removed by shape separation. Figure 4(c) shows surface spalling where a thin layer around the outside surface is peeled away from the rest of the particle. Variables involved in the washing and drying procedures were examined to determine the cause of cracking which occurred during processing of large (>800 μm) microspheres [smaller microspheres (<300 μm) showed little cracking]. The degree of cracking appeared to be dependent on the type of washing procedure used; the three major procedures tested were (1) a recirculating wash, (2) a once-through wash, and (3) a recirculating wash followed by a once-through wash. The once-through wash changed concentrations at a rapid rate, and a large percentage of the microspheres cracked during washing. The recirculating wash was more gentle, and spheres survived the washing step. However, when the uncracked microspheres from the recirculating wash were dried and sintered, a large percentage of the batches cracked. Data from the spectrometer indicated that large amounts of water and carbon dioxide were being released and possibly cracking the spheres.

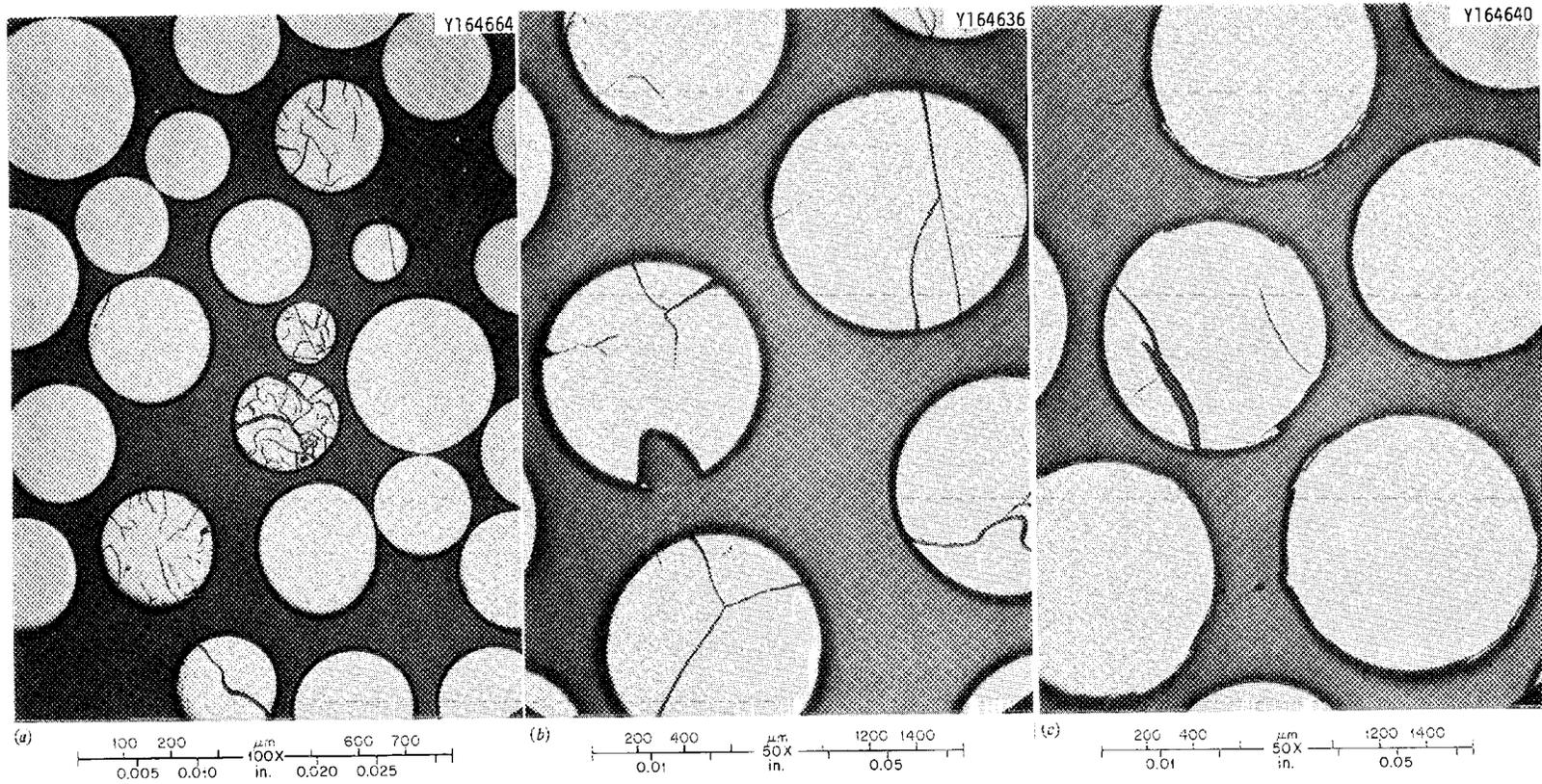


Fig. 4. Typical cracking exhibited by $(\text{Th,U})\text{O}_2$ batches, (a) internal cracks, 100x, (b) major cracks, 50x, (c) surface spalling, 50x.

The third type of wash procedure using the recirculating wash followed by the once-through wash produced acceptable yields of >90% after sintering for a limited number of batches. No noticeable cracking occurred during sintering of these particles.

During the search for an acceptable (Th,U)O₂ flowsheet, only a small number of batches survived the processing operations without cracking. Several batches produced using the ammonia neutralization flowsheet were sintered with very few of the particles cracking. Figure 5 shows ceramographic cross sections of two such batches. Careful examination of the entire ceramographic sample showed that only 5 to 10% of the particles have cracks. The particles that failed had radial cracks extending from the surface toward the center of the sphere. The grain size of these batches was considerably smaller than typical UO₂ batches (Fig. 6). These batches were of very high quality before sintering because <5% of the particles were rejected during a separation of nonspherical shapes. The overall yield from this flowsheet was over 90%. A more detailed description of the specific runs that were made appears in Table 7.3 of the Appendix.

2.6 Demonstration Run Conditions and Results

The final experimental tests made were intended to demonstrate the reproducible preparation of good, large (Th,U)O₂ spheres. The largest part of the experimental tests were with one feed composition and one sintering procedure with variations in aging, washing, and drying conditions to reduce cracking. The best conditions during these tests were for batches X21-2 and X21-3, and the conditions were reproduced for batches X22-2 and X23-2 (Table 1). The first batches in new TCE (X21-1, X22-1) and variations in aging, washing, and drying conditions (X21-4, X21-5, X22-4, X22-5) gave more cracking.

Conditions for run X22 to prepare large-coarse spheres were as follows:

HMTA solution:	3.42 <u>M</u> HMTA
Th + U solution:	Th/U = 3.0
	(Th + U) = 2.5 <u>M</u>
	NO ₃ ⁻ /(Th + U) = 3.6 mol/mol

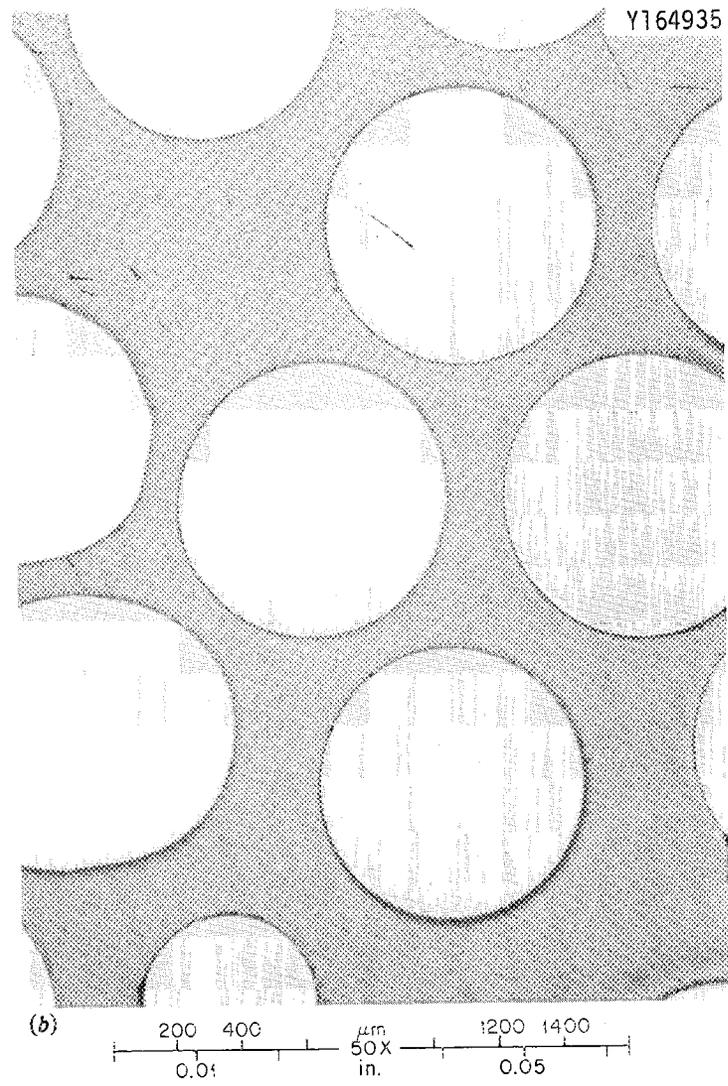
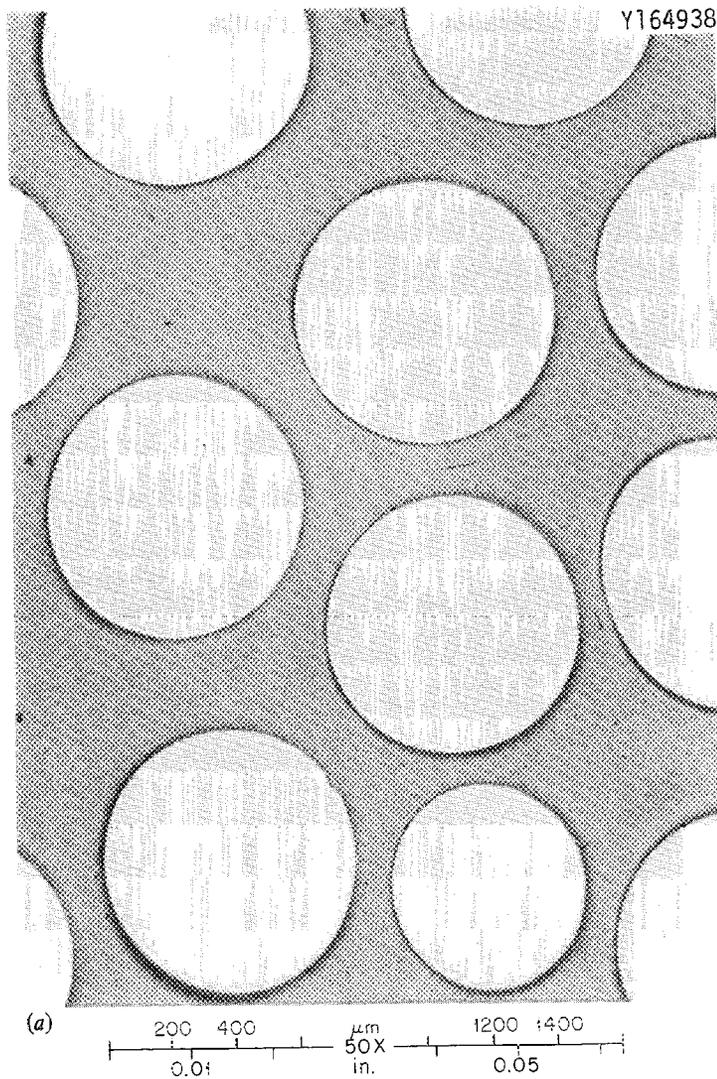


Fig. 5. Two batches of $(Th,U)O_2$ produced by ammonia neutralization exhibit very few cracked microspheres after sintering.

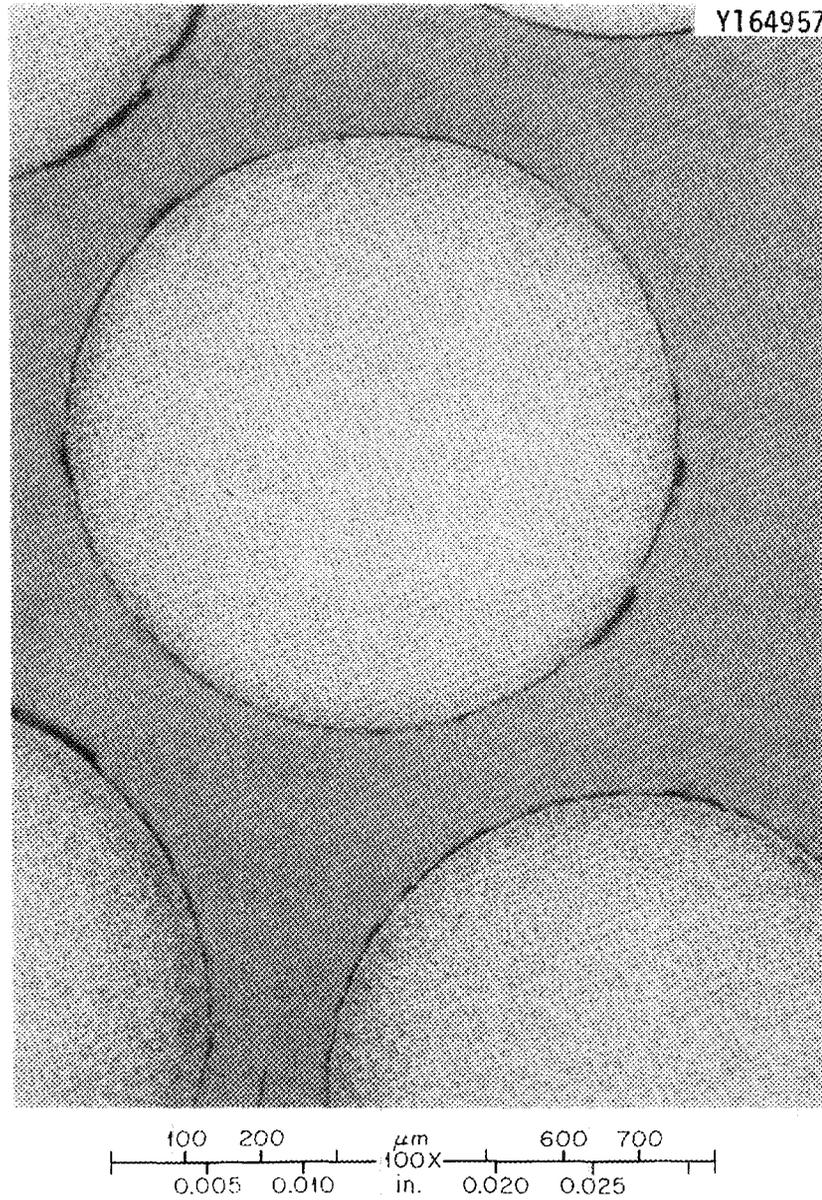


Fig. 6. $(\text{Th,U})\text{O}_2$ microsphere produced by ammonium hydroxide neutralization shows very fine grain size.

Table 1. Demonstration Test Results with Ammonia Neutralization

Drop Diameter: 3200 μm

Sintered Diameter: 950 μm

Organic Medium: TCE containing 0.03 vol % Span 80 at 72°C

HMTA/NO₃* = 0.69 or 0.70 mol/mol

Product batch No.	Other variables	Appearance of dried gel	Total shape reject (%)	Observations from ceramography
X21-1	First product in new TCE	>10% cracked	--	
X21-2	Accidental spill, short aging	Some junk	23	5-10% major cracks
X21-3A	None	Acceptable	3	5-10% major cracks
X21-3B	Air dry to 125°C	>30% cracked	7	80% hairline cracks
X21-4A	Aged with hot TCE flow	More surface dusting	-	
X21-4B	Aged with hot TCE flow	More surface dusting	15	10% major cracks
X22-1	First product in new TCE	More surface defects	14	25% major cracks
X22-2	None	Acceptable	4	15% major cracks
X22-3A	None	Acceptable	4	20% major cracks
X22-3B	None	Acceptable	4	20% major cracks
X22-4A	Aged overnight in TCE	Acceptable	16	20% major cracks
X22-4B	Aged overnight in TCE	Acceptable	-	
X22-5A	Aged with hot TCE flow	More surface defects	3	75% surface spalling
X22-5B	Aged with hot TCE flow	More surface defects	-	

$$\text{NH}_4^+ / (\text{Th} + \text{U}) = 0.5 \text{ mol/mol}$$

$$\text{NO}_3^* / (\text{Th} + \text{U}) = 3.1$$

11% acid deficient

$$\text{Urea}/\text{U} = 2.0 \text{ mol/mol}$$

$$\text{density} = 1.909 \text{ g/cm}^3$$

$$\text{pH} = 0.8$$

HMTA/(Th + U) solution volume ratio: 1.58

HMTA/NO₃^{*} unneutralized = 0.70 mol/mol

Organic medium: TCE containing 0.03 vol% Span 80

TCE temperatures: 75°C at column inlet

69°C at column middle

62°C in product collector

Broth feed rate: 43.5 cm³/min

Nozzle vibration frequency: 2500 cycles/min

Observed drop residence time in column: 28 s

Calculated drop diameter: 3220 μm

Calculated dense-sphere diameter: 950 μm

Observed gel-sphere diameter: 3200 μm

For this chemical flowsheet, the gel spheres leaving the gelation column are of excellent appearance, sphericity, and uniformity of texture. This is true for the ranges of both the small-coarse (500-to 1000-μm drops) and large-coarse (3000-to 4000-μm drops) sizes. Microphotographs of large-sphere cross sections and grain sizes are shown in Figs. 5 and 6.

The mechanical operation of the equipment, including drop formation and transfers and handling of gel spheres, did not cause any problems. Overall, the equipment performed as well, and perhaps slightly better, for this mixed oxide than for our standard UO₃ gel.

In summary, the process variables that appeared to contribute to the best results were:

1. A slightly preneutralized broth with total NO₃⁻/(Th + U) of about (3.1 + n) mol/mol and NH₄⁺/(Th + U) of n mol/mol, where n is 0.3 to 0.7. The pH values after urea addition, but before mixing with HMTA, are 0.8 to 1.2.

2. An HMTA concentration that gives a broth pH of 4.1 ± 0.1 at 10 to 15°C for 2 to 5 min after mixing.
3. Gelation in a trichloroethylene at ~70°C.
4. Initial washing with a high recirculation of wash solution so the wash pH changes slowly from an initial value of 5.2 to 8 over a 1 h or longer period.
5. Completion of washing by downflow of dilute (0.3 M) NH₄OH solution.
6. Drying in a steam atmosphere in an oven at ~170°C.

Cracking during washing and drying is the major problem, and this cracking increases greatly as the sphere diameter increases. The controlled wash concentrations, items 4 and 5 above, were required to allow preparation of the large-coarse sizes (>2700- μ m drop or >800- μ m-dense spheres). Variations in the other four conditions listed can also result in increased cracking. Conditions 1 and 2 give a combination of good broth stability at below 10°C and good gelation behavior and properties. Most other broth compositions either give premature thickening of the broth or give slow gelation or soft gels. The drying conditions, item 6, give better surface appearance and less cracking than air atmosphere or 250°C.

3. PROCESS DEVELOPMENT FOR FEEDS PREPARED BY SOLVENT EXTRACTION OF NITRATE AND ADDITION OF HIGH UREA CONCENTRATIONS

These chemical flowsheet conditions evolved from small-scale studies of a wide range of feed compositions. The Th-U feeds were Th(NO₃)₄-UO₂(NO₃)₂-HNO₃ solutions as mixed or with varying amounts of acid deficiency by extraction of HNO₃, as described in Sect. 3.1 below. The acid deficiencies were adjusted further by additions of NH₄OH or HNO₃. The mole ratios of urea to (Th + U) and HMTA to NO₃^{*} in the broth were also varied over wide ranges. The gelation behavior and gel properties were observed for small samples in test tubes or bottles with temperature as a variable (Appendix, Table 7.4).

These small-scale tests greatly narrowed the ranges of possible process variables. Conditions which resulted in no gelation, in soft-mushy gels, or in immediate gelation during mixing of the HMTA with the Th-U were eliminated from further testing.

Some gels of good appearance were obtained for three different Th-U feeds: (1) $\text{Th}(\text{NO}_3)_4\text{-UO}_2(\text{NO}_3)_2$ solutions, (2) $\text{Th}(\text{NO}_3)_4\text{-UO}_2(\text{NO}_3)_2$ solutions partially neutralized by addition of NH_4OH to give acid deficiency, and (3) acid-deficient solutions prepared by solvent extraction of nitrate. Some of the (2) conditions correspond to the flowsheet conditions already described in Sect. 2 of this report. Gel-sphere preparation was tested for conditions (1) and (3) and for those condition (2) variables not already tested during the Sect. 2 studies of this report (Appendix, Table 7.5). Most of the conditions resulted in severe cracking of the gel spheres during aging, washing, and drying (Appendix, Table 7.6). Limited tests of variations in aging, washing, and drying conditions did not reveal any easy answers for the cracking problems. Some results for acid-deficient feed prepared by solvent extraction of nitrate showed the least cracking, and the most detailed aging, washing, and drying tests were made using the conditions for these best results. The descriptions in the remainder of this section are principally for this feed with information from the scouting tests in the Appendix.

3.1 Acid-Deficient Metal Nitrate Solution Preparation

Both thorium nitrate and uranyl nitrate can be denitrated by solvent extraction (SOLEX) of nitric acid into using an organic amine. The equipment and procedures of SOLEX are described in detail elsewhere.^{14,15} The same equipment used for making the SOLEX sols was used in the present study. A slower, more controlled denitration procedure was used with continuous recycle of a batch of feed until the target acid deficiency was achieved. Both thoria sols and thoria-urania sols were produced and tested in this manner. The thoria sols were mixed with acid-deficient uranyl nitrate (ADUN) to achieve the desired Th/U mole ratio of 3. Most of the SOLEX feeds were prepared in this manner, though the thoria-urania sols gave similar results. The general observations on acid deficiency in Sect. 1.3 also apply to these SOLEX preparations.

The sols are usually stable at higher heavy-metal concentrations than their corresponding nitrate solutions. However, the maximum concentration is a function of the relative amount of uranium present and the extent of acid deficiency. The thoria sol used in most of the tests ($\text{NO}_3^-/\text{Th} = 2.07$)

was only 1.6 M Th, but remained fluid when evaporated to 5 M Th (the stability over long periods of time at this concentration is questionable), whereas the solubility of $\text{Th}(\text{NO}_3)_4$ at 25°C is 2.7 M.

The Th-U broths are quite sensitive to the HMTA content. In fact, for the level of acid-deficiency [$\text{NO}_3^-/(\text{Th} + \text{U}) = 2$] being discussed for the SOLEX sol feed, the stability is practically nonexistent, even at low temperatures (<0°C). Adding HNO_3 [$\text{NO}_3^-/(\text{Th} + \text{U}) = 3$] enhanced the stability such that gelation was delayed 30 to 40 min at <0°C. However, urea is an effective stabilizing agent with urea/(Th + U) mole ratios of 2.0 to 3.75 giving stability for several hours at room temperature and a ratio of 5.4 giving stability for several days at room temperature. A urea/(Th + U) mole ratio of 2.0 proved to be only marginally successful in making good product. Better results were obtained with a urea to (Th + U) mole ratio of 3.75. An optimum ratio probably exists between these two. These large amounts of urea cause a small amount of precipitation or crystallization in the SOLEX sols urea in a few days.

In summary, the feed preparation procedure for SOLEX is to denitrate dilute $\text{Th}(\text{NO}_3)_4$ solutions and $\text{UO}_2(\text{NO}_3)_2$ solutions either together or separately by solvent extraction of HNO_3 with an organic amine. The dilute, acid-deficient solutions are concentrated by evaporation. If the solutions are denitrated separately, they are then mixed to make up the required Th/U mole ratio. Subsequent additions of the required amount of urea results in Th+U concentrations of 1.4 to 1.6 M (using the most typical sol concentration).

3.2 Effect of Urea

The effect of the urea is to complex the heavy-metal components, thus stabilizing the broth. Urea in small amounts is required even for stoichiometric nitrate contents or broths containing excess acid to prevent premature or preferential precipitation of uranium. For the preferred acid-deficient broths, a urea/(Th + U) mole ratio of 0.5 is sufficient for only 10 to 15% acid deficiencies. However, for greater acid deficiencies, the stable range of HMTA concentrations becomes vanishingly small. Addition of HNO_3 to the SOLEX sols to produce a final $\text{NO}_3^-/(\text{Th} + \text{U})$ mole ratio of 3 improved their stabilities

only slightly (gelation in 30 min rather than 1 min at 0°C). However, increasing the urea content to a urea/(Th + U) mole ratio of 3.756 improved the broth stability dramatically. Not only could the broths be mixed at room temperature, but the HMTA could be added as a solid. These broths remain fluid several hours at room temperature.

Acid deficiencies are limited to 70% or less, even with the high urea contents. Higher acid deficient broths give only weak, mushy gels.

3.3 Gelation in Perchloroethylene—Mineral Oil Mixtures at Temperatures Above 80°C

The gelation procedures and equipment used for these tests were not very different from those for TCE (see Sect. 2.2). Either HMTA crystals or solution were mixed at room temperature with the acid-deficient Th-U solution containing large amounts of urea. The added stability of these high-urea broths either required higher temperatures or longer suspension times in the forming medium for satisfactory gelation. Since the suspension time was limited by the available equipment, higher temperatures were used. Even using the maximum temperatures of ~95°C (to prevent bubble formation by water vaporization from the liquid drops), suspension times as long as 1 or 2 min were required for some broths. Because these temperatures are greater than the boiling point of trichloroethylene, an alternative medium was required. Perchloroethylene (PERC), with its boiling point of 121°C was selected. Since the density of PERC is significantly higher than most of the broths used, PERC-Mineral oil mixtures were used to give the optimum forming-medium densities. Span 80 was used as described in Sect. 2. An organic wash of TCE was required to remove the PERC-Mineral oil from the spheres prior to the aqueous wash.

As explained in Sect. 2.2.2, the broth density should be 0.01 to 0.1 g/cm³ greater than the forming-medium density. Mineral oil was added to the PERC to match the broth density for each test. The densities of the PERC-mineral oil mixtures can be estimated from the additive volumes. The density of mineral oil at room temperature is 0.872 g/cm³ and of PERC is 1.623 g/cm³. The density of PERC at 100°C is 1.484 g/cm³. Assuming a 0.001 g/cm³ change for every 2.5°C gives a mineral oil density of 0.842 g/cm³ at 100°C. The mineral oil contents never exceeded 25 vol %. The

density of the mixed broth for the most common urea and HMTA concentration ranges are adequately estimated by:

$$\rho(\text{Broth}) = 0.41 (\text{Th} + \text{U}) + \rho(\text{H}_2\text{O}).$$

In this equation, (Th + U) indicates the total metal concentration in moles per liter (mol/L). The coefficient of 0.41 is slightly lower than that for ammonia neutralization broths because sols prepared by solvent extraction have lower ammonium and nitrate concentrations.

The broths lose their sensitivity to HMTA at the high urea contents. The HMTA to NO_3^* mole ratios as high as 1.0 were used at times to speed up gelation in the hot organic forming medium (since suspension times of 1 or 2 min were required). To minimize washing and waste problems, lower HMTA/ (NO_3^-) ratios down to 0.8 mol/mol were commonly used.

3.4 Aging and Washing

Cracking during washing, drying, and sintering was a problem for all feed concentrations and gelation conditions tested. The amounts of cracking were dependent on the washing and drying conditions. Wet gel spheres made from SOLEX-sol, high-urea broths were damaged less by the established wash procedure for UO_3 spheres than were the spheres made from the other Th-U broths. Nevertheless, despite an extensive search, a salt solution could not be found that eliminated damage during washing for these high-urea gel spheres (Appendix, Table 7.3). Solutions of NH_4NO_3 , urea, and NH_4OH were investigated. Based on an assertion that 70% PuO_2 -30% UO_2 gel spheres must be washed in a Soxhlet apparatus,¹⁶ Soxhlet extraction was tried. Washing in this manner proved quite successful, eliminating virtually any sign of damage in the washed gel spheres. Further investigation demonstrated that the mechanics of the Soxhlet apparatus were responsible for its success. Duplication of its results could be achieved by very slow washing in the apparatus illustrated in Fig. 3. First, the PERC-Mineral oil mixture must be rinsed from the gel spheres using TCE. After pulling air through the bed for 15 min to evaporate the TCE, the washing is started. The bed of gel spheres is left drained of liquids, and the dilute NH_4OH is slowly (40 L/8 h) dripped onto the gel spheres. The liquid level in the bed slowly builds up until the spheres are covered and the wash solution is

overflowing. After this the wash proceeds in a once-through manner until the effluent conductivity indicates washing is complete. The results for eight wash conditions and four gels are compared (Appendix, Table 7.6).

3.5 Drying

The drying conditions and results were the same as those described in Sect. 2.4. In general, the dried spheres from SOLEX sols with high urea contents had glossy surfaces, free of surface dust or powder. The ammonia neutralized feeds frequently give a surface dust, as reported in Sect. 2.4.

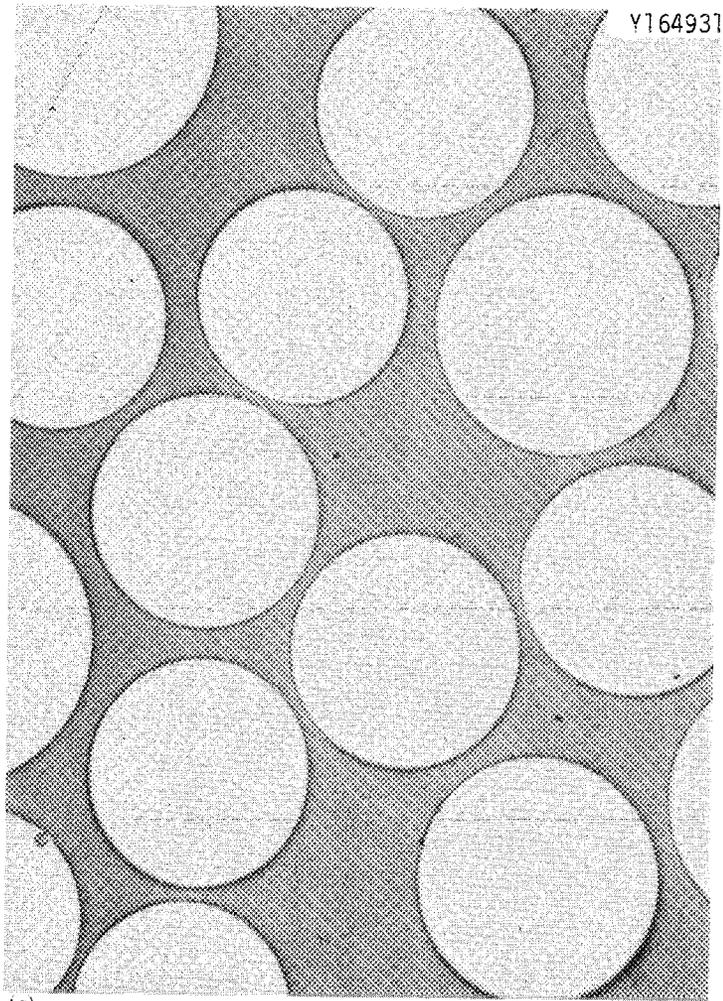
3.6 Sintering and Product Properties

A few batches produced using the extraction of nitric acid flowsheet also produced uncracked microspheres after sintering (Fig. 7). These batches were of high quality after drying, with <5% of the particles rejected because of shape separation. A ceramographic examination of the batch after sintering revealed that ~5% of the particles had radial cracks running from the outside surface toward the center of the sphere. These cracks were not severe enough to cause the particles to be rejected by shape separation; therefore, the cracking could have occurred during any of the washing, drying, or sintering operations. The final yield for these batches was ~90% (see Table 7.7 of the Appendix for complete characterization). The grain size of all these mixed-oxide batches was extremely small.

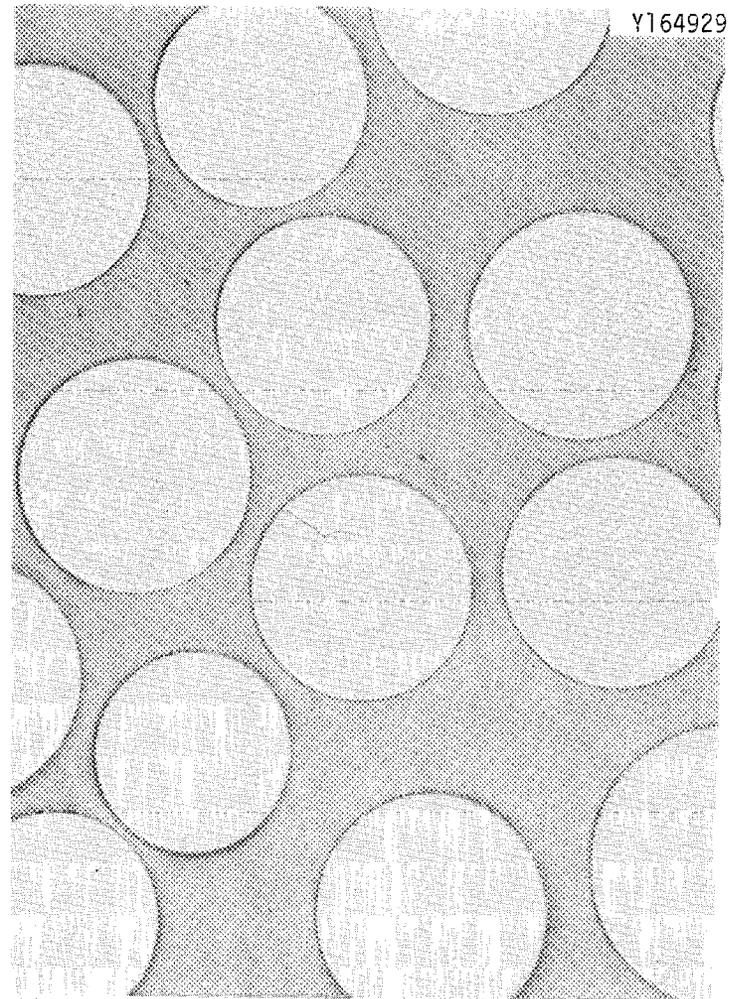
It is important to note that most batches produced cracked particles. Only a specific set of forming conditions, washing procedures and drying conditions produced batches that survived all processing steps including sintering without cracking. More details on the characterization of all particle batches produced using these flowsheets, including the forming conditions, are shown in the Appendix (Table 7.7).

3.7 Demonstration Run Conditions and Results

The final experimental tests were intended to provide a comparison of the reproducibility and quality of large (Th,U)O₂ spheres from this



(a) 200 400 μm 1200 1400
0.01 50X in. 0.05



(b) 200 400 μm 1200 1400
0.01 50X in. 0.05

Fig. 7. Sintered batches of $(\text{Th,U})\text{O}_2$ produced by the thorium solex sol preparation scheme exhibit only 5 to 10% cracked particles.

flowsheet as compared to those for the flowsheet of Sect. 2. The feed concentrations and the other conditions were as follows:

1000 mL Th SOLEX sol: Th = 1.55 M
 $\text{NO}_3^-/\text{Th} = 2.07 \text{ mol/mol}$
 (48% acid deficient)
 density = 1.510 g/cm³
 pH = 2.69

177 mL ADUN: U = 2.9 M
 $\text{NO}_3^-/\text{U} = 1.65 \text{ mol/mol}$
 (17.5% acid deficient)

478 g urea: urea/(Th + U) = 3.8 mol/mol
 548 g HMTA: HMTA/ NO_3^- = 0.96 mol/mol
 PERC containing 14 vol % mineral oil and 0.03 vol % Span 80
 Column temperatures: 99°C at column top
 93°C at column middle
 Broth feed rate: 24.4 cm³/min for small coarse
 29.0 cm³/min for large coarse
 Nozzle vibration frequency: 22,800 cycles/min for small coarse,
 four holes
 865 cycles/min for large coarse
 Observed residence time in column and transport line: 90 s
 Calculated drop diameter: 800 μm; 4000 μm
 Calculated dense sphere diameter: 240 μm; 1215 μm
 Observed gel sphere diameter: 300 μm; 4000 μm

For this recipe, the wet gel spheres are smooth and spherical, and the gel is tough and resilient. The gel spheres were aged at least 20 min based on observations for urania gel spheres and Th-U gel spheres from NH_4OH -neutralized broths. Such aging did not appear to change the results on the dry gel spheres although some wet gel spheres were observed to turn slightly cloudy or opaque with aging. Microphotographs of a product batch are shown as Fig. 7. Results are tabulated in Table 2.

Table 2. Demonstration test results for solvent extraction of nitrate
 Organic liquid medium: PERC - 14 vol %; Mineral oil - 0.03 vol % Span 80
 Organic temperature: 95°C
 Feed compositions: Urea/(Th + U) = 3.75, NO₃-(Th + U) = 2.0 to 2.2
 Steam drying temperature: 170°C

Product Batch No.	Other variables or comments	Appearance after drying	Shape reject after drying (%)	Calculated sintered size ^a (μm)	Observations from ceramography
MGT-201 B	Batch mixing of broth	Acceptable	2.6 1.1 1.6	775 1125 1270	5% major cracks 10% major cracks 30% major cracks
MGT-218	Batch mixing of broth	10% cracked	11.3	990	60% major cracks
MGT-219-2	Continuous mixing of broth	5% cracked	4.6	1190	30% major cracks
MGT-219-3	Continuous mixing of broth	3% cracked	3.2	990	20% major cracks
MGT-221	SOLEX thoria-urania sol	5% cracked	4.9	1020	5% major cracks
MGT-222	SOLEX thoria-urania sol	5% cracked	4.0	1020	5% major cracks

^aCalculation made for 100% of theoretical density.

4. COMPARISONS OF THE TWO FLOWSHEETS

The most important comparison is with respect to the ability to meet product specifications. Differences in yields, wastes, process complexity, or any other factors cannot justify the selection of a process that does not give specification products. The information from the development studies does not allow a final selection with respect to product specifications. The process with ammonia neutralization gave a slightly better demonstration run result, but all products showed a worrisome amount of internal cracks. While the strength and densities of the best batches are believed adequate for product specifications, any discovery that would completely eliminate the cracks would be a major and perhaps controlling advantage for that flowsheet.

4.1 Feed Preparation

The feed preparation operations for the two flowsheets are given in tabular form (Table 3). Both are shown to start with dilute metal nitrate solutions. The solvent extraction of nitrate requires dilute solutions. Therefore, availability of concentrated solutions (solid nitrate salts or oxides which could be dissolved in HNO_3) would eliminate the concentration step for ammonia neutralization, but not for solvent extraction of nitrate. The solvent extraction of nitrate requires a complex system with multiple process operations.^{14,15} The waste from the solvent extraction is a NaNO_3 solution. Otherwise, the feed preparation steps are all very simple mixing, dilutions, or evaporation steps with water, nitric acid, and heat as the waste products.

4.2 Gelation, Washing, and Drying

Both flowsheets require the same basic operations, and the differences in complexity are not large. The use of TCE as the organic medium for ammonia-neutralized feed is somewhat simpler. The use of a PERC-mineral oil mixture is a small complication because as the composition must be measured and controlled. The need for a wash by a more volatile organic (TCE) to remove the PERC-mineral oil from the gel spheres is an added process step. The wash procedures tested for both flowsheets were batch operations. Continuous washing would be preferred for a large-scale operation, but the acceptability of continuous-wash procedures is completely untested.

4.3 Product Properties

Product specifications are given in Sect. 1.1. With the exception of increased cracking as the sphere size increases, both flowsheets appear to meet all product specifications very well. The total shape reject (after drying plus after sintering) was ~5% for the ammonia-neutralization demonstration runs and 5 to 10% for the runs for the alternative flowsheet with extraction of HNO_3 . The limited results leave an uncertainty as to whether this is a real difference.

4.4 Remaining Development Requirements

This development of gel-sphere processes for a Th-U fuel cycle for LWR application was ended as a result of program changes. The information now available does not justify a final selection between the two process flowsheets. Additional chemical flowsheet studies would be needed for selection of a final flowsheet. Then equipment development studies would be necessary to allow design and evaluation for pilot plant or production applications.

The investigation of promising chemical flowsheet variables is believed to be reasonably complete for both flowsheets. The reproducibility of the product quality should be determined for continuous gelation and small adjustments of the washing conditions. Continuous washing conditions, perhaps with recycle flows to slow down concentration changes, might give optimum control of wash concentrations and also minimize waste volumes. As mentioned earlier, any significant difference in the ability to meet product specifications would be controlling for process selection. If products from both flowsheets meet specifications, then the selection would probably be on the basis of process complexity, including waste handling. The complex solvent extraction system to remove HNO_3 , the organic wash to remove PERC-mineral oil, and larger amounts or more complex compositions of waste are significant differences.

For the selected process, engineering development studies would be required to develop pilot-plant and production-scale equipment for all process operations, including waste handling. Continuous aging, washing and drying operations would be preferred, but batch operations may be required for control of the sequence of chemical conditions. Such engineering studies are

now in progress for UO_2 gel-sphere processes, and many of the development results for UO_2 will be applicable to $(Th,U)O_2$. Since the completeness and the applicability of the UO_2 process results cannot be predicted, a detailed specification of $(Th,U)O_2$ development requirements is not justified. Waste handling will be a major process development problem. Recycle of waste or reject $(Th,U)O_2$ is likely to be more difficult than recycle of UO_3 or UO_2 because $(Th,U)O_x$ is more difficult to dissolve.

5. CONCLUSIONS AND RECOMMENDATIONS

Internal gelation flowsheet conditions were determined to prepare good, high-density $(Th,U)O_2$ spheres ($Th/U = 3$), 800 to 1200 μm in diameter, as required for Sphere-Pac fabrication of nuclear fuels. The starting conditions tested were those previously developed for UO_2 spheres, but modifications and close duplication of process conditions or "recipes" are necessary to prevent severe cracking. Slow changes of concentration during washing with ammonia solutions are important to minimize cracking. The intermediate size, 200 to 300 μm in diameter, is easily prepared using the same chemical flowsheet conditions, but the preparation of $(Th,U)O_2$ fines ($<45 \mu m$ in diameter) remains to be demonstrated.

The gelation conditions and the required feed compositions are closely related. For $Th/U = 3$, the stoichiometric nitrate/metal ratio is 3.5 mol/mol and some acid deficiency is highly desirable for practical operation. Two different feed compositions and gelation conditions gave useful products. For both, concentrated HMTA (hexamethylenetetramine) solutions were mixed with acid-deficient $Th(NO_3)_4-UO_2(NO_3)_2-NH_4NO_3$ -urea solutions to prepare the feed broths. For one feed composition, $Th(NO_3)_4-UO_2(NO_3)_2$ solutions containing 2 to 10% excess nitric acid were made 10 to 15% acid-deficient by the addition of ammonia. Urea concentrations of 0.5 mol/mol $(Th + U)$ were used to prevent premature precipitation when this feed was mixed with HMTA solutions at 0 to 5°C. Gelation of the drops was in trichloroethylene at 60 to 75°C. For the other feed compositions, solvent extraction of HNO_3 was used to prepare acid-deficient thorium or thorium-uranium nitrate solutions. Higher urea concentrations were used [2 to 3.75 mol/mol $(Th + U)$], and the mixed broths with HMTA added were stable at

room temperature. Gelation required higher temperatures of 80 to 95°C and were done in perchloroethylene-mineral oil mixtures.

Slow changes of concentration during washing were necessary to minimize cracking of 800- to 1200- μm product spheres. A recirculating wash procedure and a slow addition wash procedure were developed. Steam atmosphere drying with the spheres at 100°C for most of the water removal gave less cracking than air-drying with the spheres at the wet bulb temperatures for large air flow rates.

A conservative calcining and sintering schedule was used without optimization of conditions. Heating was at 100°C/h up to 600°C, 300°C/h for 600 up to 1450°C, and 4 h at 1450°C. The atmosphere was Ar-4% H₂ throughout. All products were sintered to near theoretical (>99%) density for (Th,U)O₂. The preferred gelation-washing-drying conditions were necessary to avoid severe cracking, and ~5% cracking of the largest sizes resulted at the best conditions.

Process development is incomplete for both processes, and the information now available does not justify a final selection of processes. For any immediate application without further development, the ammonia neutralization flowsheet should be used, principally because of some simpler operations. If the development program is resumed, both flowsheets should be tested further using continuous sphere preparation and small variations in feed compositions and washing conditions. Some remaining development requirements are discussed as Sect. 4.3.

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7. APPENDIX: TABULATED DATA

The body of this report defines and describes conditions which give useful results for preparation of large-coarse (Th,U)O₂ spheres. More detailed tabulations of experimental data, particularly for conditions which did not give useful products, are in this Appendix.

Twenty-two column gelation runs (Table 7.1) were made to prepare 3.5-L batches of mixed-oxide (Th/U = 3) gel spheres using feeds prepared by ammonia neutralization. Six runs were small-coarse sizes (400-to 1000- μ m drops) to test several washing and drying conditions and to supply products for calcining and sintering tests. Fourteen runs were for the large-coarse size (2700-to 3600- μ m drops). Two were for fines sizes. All runs gave good gel spheres in the organic-forming medium. Six of the large-coarse-size products were found to be excessively cracked during the investigation of the washing and drying requirements. Initial improvements gave good dried gel spheres that cracked excessively during sintering. Additions of organic polymers to the broth (polyvinyl alcohol, Methocel K100) gave softer gels and more cracking during washing and drying as compared to spheres containing no polymer. Two batches of large-coarse spheres (3200 μ m), prepared with the use of all the improved conditions, gave good dense spheres without excessive cracking. These results are tabulated in Tables 7.2 and 7.3.

The large batch of Th-U feed solution used for most column runs had the following concentrations:

$$\begin{aligned} \text{Th/U} &= 2.994 \text{ atom/atom} \\ \text{Th} + \text{U} &= 2.42 \text{ M} \\ \text{NH}_4^+(\text{Th} + \text{U}) &= 0.54 \text{ mol/mol} \\ \text{NO}_3^-(\text{Th} + \text{U}) &= 3.7 \text{ mol/mol} \\ \text{Urea/U} &= 2.0 \text{ mol/mol} \\ \text{pH} &= 1.2 \end{aligned}$$

The HMTA solutions used were made to 3.5 M HMTA by mixing at 10°C. The optimum volume ratio of these two solutions (to give pH = 4.2 in 2 min at 15°C) was 1.47 volume HMTA/volume Th + U. The mixed broth is then 0.98 M (Th + U) and has a density of 1.41 g/cm³.

Table 7.1 Gelation conditions for $(\text{ThU})\text{O}_2$ with ammonia neutralization of feed

Feed concentrations: Th + U: 0.98 + 0.03 M
 HMTA/ NO_3^- : 0.69-0.71 mol/mol
 Acid deficiency: 10 to 14%

Run No.	Forming conditions		Temp (°C)	Typical wet gel diam (µm)	Comments; results
	Organic				
557	2EH		82	200	Fines size, clustered.
X01	TCE-13%	2EH	71	2600	
X02	TCE-13%	2EH	72	500 700	Small-coarse size.
X03	TCE-13%	2EH	72	1000	Small-coarse size.
X04	TCE-13%	2EH	71	3600	
X05	TCE-13%	2EH	63	3500	Polyvinyl alcohol in feed; salted out.
X06	TCE-13%	2EH	67	3400	No NH_4^+ in feed; cracked.
X07	TCE-13%	2EH	67	3200	
X08	TCE-13%	2EH	68	3400	
X09	TCE-13%	2EH	68	3500	First test of recirculating wash.
X10	TCE-13%	2EH	70	3200	Methyl cellulose additive in feed.
X11	TCE-13%	2EH	68	660	Small-coarse size.
X12	TCE-13%	2EH	68	3200	
X13	TCE-13%	2EH	68	430	Smallest uniform size practical.
X14	TCE-13%	2EH	68	960	Small-coarse size.
X15	TCE-13%	2EH	71	3700	
X16	TCE-13%	2EH	72	300	Fines size, clustered.
X17	TCE-13%	2EH	72	400	Fines size.
X18	TCE		72	3100	No 2EH and continuous broth mixing.
X19	TCE		72	750	Small-coarse size.
X20	TCE		72	3100	Recirculating wash, then once-through.
X21	TCE		72	3100	Recirculating wash, then once-through.
X22	TCE		72	3100	Duplicate of run X21.

Table 7.2. Washing-drying results for $(\text{ThU})\text{O}_x$ with ammonia neutralization of feed

Product No.	Typical dry gel diam (μm)	Washing-drying conditions, results	Conclusion
557	80	Isopropyl alcohol, steam dry to 240°C	$(\text{ThU})\text{O}_x$ clusters much worse than UO_3
X01	1000	>30% cracked	New organic may give poor result
X02	280	Good appearance	Looks good for this size
X03	375	Good appearance	Looks good for this size
X04	1400	~90% cracked	Gel cracks during washing
X05	1400	Excessive cracking	Polyvinyl alcohol additive not useful
X06	1300	>20% cracked	No NH_4^+ in feed not helpful
X07	1200	Initial wash was NH_4NO_3 - very dilute NH_4OH ; cracked during cooling	Change in initial wash concentration prevents cracking in wash
X08	1300	First wash with recirculation (20 min)	Better than no recirculation
X09A	1300	Steam atm dry to 160°C	Excellent dried gel appearance
X09B	1250	Steam atm dry to 250°C	~2% cracked.
X10	1300	Off-shape, lots of cracking	Methyl cellulose additive not useful
X11	250	Recirculating wash now standard	Excellent dried gel
X12	1300		Some surface chips or roughness
X13	220	Isopropyl alcohol; no recirculation	Poor appearance compared to X11
X14	400		Excellent dried gel
X15	1500		Steam dry, >3% cracked; air dry, >30
X16	150	Isopropyl alcohol; no recirculation	} $(\text{ThU})\text{O}_x$ clusters much worse than UO_3 }
X17	150	Isopropyl alcohol; no recirculation	
X18-1	1200	>10% cracked	New organic may give poor results
X18-2	1200	Standard conditions, excellent	Better in used organic
X18-3	1200	Aged in hot TCE; ~2% cracked	Extra aging not helpful
X18-4	1200	Aged in hot TCE; >30% cracked	Hot gel into cold wash caused cracking

Table 7.2 (continued)

Product No.	Typical dry gel diam (μm)	Washing-drying conditions, results	Conclusion
X19-1	300	Excellent	
X19-2	300	Excellent	
X19-3	300	Excellent	
X19-3B	300	Dried as thin layers, open tray	Air-drying gives higher density, transparent
X20-A	1200	Dried in open tray, oven at 120°C	Drying not complete
X20-B	1200	Dried in open tray, oven at 150°C	{ Much more cracking in open tray (i.e., air atm drying) }
X20-C	1200	Dried in covered tray, oven at 150°C	
X21-1	1200	Recirculating once-through now standard	New organic may give poor results
X21-2	1200	Acceptable	Short aging poor (spill during change)
X21-3A	1200	Acceptable	
X21-3B	1200	Air atm dry to 125°C, >30% cracked	
X21-4A	1200	Aged in hot TCE, surface dusting	Long hot aging may be poor
X21-4B	1200	Aged in hot TCE, surface dusting	Long hot aging may be poor
X22-1	1200	Standard is 1-1/2 hr cooldown in TCE	New organic may give poor results
X22-2	1200	2 hr recirculating-2 hr once-through	
X22-3A	1200	for wash, steam atm dry oven at 175°C	
X22-3B	1200	2, 3A, and 3B better than 1.	
X22-4A	1200	Overnight in TCE	Little effect from aging in cold TCE
X22-4B	1200	Overnight in TCE	Little effect from aging in cold TCE
X22-5A	1200	Aged in hot TCE, some surface defects	Hot TCE to wash, may be poor
X22-5B	1200	Aged in hot TCE, some surface defects	Hot TCE to wash, may be poor

Table 7.3 Characterization of (Th,U)O₂ Produced by Ammonia Neutralization

Feed concentrations:
 Th + U: 0.98 ± 0.03 M
 Urea/U: 2.0 mol/mol
 NH₄⁺/(Th + U): 0.5 to 0.54 mol/mol

Chem. Tech. batch	M&C batch	Sintering run	Forming conditions ^a (°C)	Washing conditions ^b	Drying conditions (°C)	As-Dried density (g/cm ³)	Shape reject after drying (%)	As-Dried size (µm)	Hg density after sintering (g/cm ³)	Shape reject after sintering (%)	Observations from ceramography
X-03	J-935	S-426	TCE + 13% ZEH 74*	OT	210° steam	2.91	1	375	10.20	5	50% major cracks
X-04	J-936	S-417	TCE + 13% ZEH 73*	OT	240° steam	2.64	47	1200	10.23	47	95% major cracks
GT-557	J-937	S-393	ZEH 82°	OT	240° steam	3.01		75	10.21	75	Clustered in groups of 5-10 particles
X-09	J-938	S-418	TCE + 13% ZEH 68*	R	170° steam	2.40	15	1350	10.20	58	50% surface spalling, 10% major cracks
X-09B	J-939	S-419	TCE + 13% ZEH 68*	R	240° steam	3.20	2	1250	10.16	31	100% surface spalling
X-11	J-940	S-427	TCE + 13% ZEH 68*	R	170° steam	2.84	1	250	10.17	2	50% surface spalling plus cracks
X-12	J-941	S-420	TCE + 13% ZEH 68*	R	170° steam	2.73	52	1200	10.22	74	80% surface spalling
X-13	J-942	S-424	TCE + 13% ZEH 68*	OT	Warm air then 165°	3.54	1	220	10.14	1	100% major cracks
X-14	J-944	S-425	TCE + 13% ZEH 68*	R	170° steam	2.93	1	350	10.20	90	80% surface spalling
X-15	J-945	S-421	TCE + 13% ZEH 71*	R	170° steam	2.80	9	1400	10.16	35	80% surface spalling plus cracks
X18-1	J-954	S-433	TCE 72°	R	170° steam	2.63	10	1225		90	100% major cracks
X18-2	J-955	S-434	TCE 72°	R	170° steam	2.61	2	1160		90	100% major cracks
X18-3	J-956	S-435	TCE 72°	R	170° steam	2.57	17	1190		90	100% major cracks
X19-1	J-957	S-438	TCE 72°	R	170° steam	2.45	1	280	10.22	1	3% internal voids, no cracking
X19-2	J-958	S-439	TCE 72°	R	170° steam	2.56	1	280	10.21	1	3% internal voids, no cracking
X19-3	J-959	S-440	TCE 72°	R	170° steam	2.54	2	280	10.21	1	3% internal voids, no cracking
X19-3B	J-960	S-441	TCE 72°	R	170° open tray	3.15	1	280	10.20	1	3% internal voids, 20% major cracks
X21-2	J-966	S-456	TCE 71°	R + OT	160° steam	2.34	22	1250	10.21	1	5-10% major cracks
X21-3A	J-967	S-457	TCE 71°	R + OT	160° steam	2.43	2	1250	10.19	1	5-10% major cracks
X21-3B	J-968	S-458	TCE 71°	R + OT	125° open tray	2.79	6	1200	10.20	1	80% hairline cracks
X21-3C	J-969	S-459	TCE 71°	R + OT	125° steam	2.41	5	1260	10.20	1	20% major cracks
X21-4B	J-970	S-460	TCE 71°	R + OT	125° steam	2.38	14	1250	10.19	1	10% major cracks
X22-1	J-1063	S-666	TCE 70°	R + OT	180° steam	2.60	12.5	1250		1	25% major cracks
X22-2	J-1064	S-710	TCE 70°	R + OT	180° steam	2.53	3.0	1250		1	15% major cracks
X22-3B	J-1065	S-702	TCE 70°	R + OT	195° steam	2.67	2.7	1250		1	20% major cracks
X22-3A	J-1066	S-667	TCE 70°	R + OT	180° steam	2.47	2.4	1250	10.20	1	20% major cracks
X22-4A	J-1067	S-668	TCE 70°	R + OT	185° steam	2.52	14.6	1250	10.21	1	20% major cracks
Z22-5A	J-1069	S-670	TCE 70°	R + OT	180° steam	2.62	2.2	1250	10.22	1	75% surface spalling

^aTrichlorethylene (TCE) 2-ethyl hexanol (ZEH).

^bOnce-through (OT), recirculating (R).

The gelation of small samples in test tubes or bottles was observed visually for over 80 broth compositions (Table 7.4). The tests with SOLEX thoria or thoria-urania sols determined the conditions tested for gel-sphere preparation as reported in Sect. 3. The tests with ammonia-neutralized feeds showed that urea/(Th + U) mole ratios of ≥ 2 gave broth compositions that remained fluid for long times at room temperature. The tests with nitrate solutions gave some good gelation results.

The scouting tests of gel-sphere formation gave firm, smooth spheres in the organic forming medium for all three types of feed broths (Table 7.5). However, the gel spheres from nitrate solution feeds all cracked excessively during washing (Table 7.6). The gel-spheres from some SOLEX feeds and some NH_4OH neutralized feeds were washed with no or a few cracks after washing (Table 7.6 and 7.7). Results for sintered products using SOLEX feeds are in Table 7.8.

7.1 Behavior after Mixing of the Th + U and HMTA Solutions

Measurements of pH and fluid properties vs time after mixing were made for some of the broth compositions. The experiments were relatively crude with respect to good temperature control and good mixing. Figure 7.1 gives the viscosity, pH, conductivity, surface tension, and temperature as a function of time for the SOLEX sol feed. The properties of the solutions prior to HMTA addition were also measured and are given in Table 7.9. The urea addition was endothermic, causing the temperature to drop to 14°C . However, the HMTA dissolution was exothermic, as indicated in Fig. 7.1. The surface tension profile is quite flat, but as the feed thickened and gelled the surface tension became impossible to measure because of the rapidly increasing viscosity. The pH and conductivity demonstrate similar behavior, with an initial rapid change followed by a long period of no change or slow change. The viscosity experiences a small jump as the HMTA is dissolved, followed by a long quiescent period and then a period of rapidly increasing viscosity. Based on these observations, only the viscosity and pH were monitored in the remaining tests.

Several attempts to monitor the properties of the NH_4OH -neutralized feed failed because of local gelation. In contrast to the SOLEX sol feed,

Table 7.4. Test tube studies of gelation behavior vs broth composition

Type of feed	NO ₃ * (Th + U) (mol/mol)	Urea (Th + U) (mol/mol)	HMTA/NO ₃ * (mol/mol)	Results or comments	Number of tests
SOLEX	0.3-1.7	0.4-1.7	1.0-5.	Weak, mush gels.	4
	1.9-2.1	0.3-0.5	0.8-1.1	Gelled below room temperature	2
		1.1-1.3	0.6	Gelled slowly at 75°C	2
		1.4-2.1	0.71-1.0	Gelled slowly at 0 or 25°C.	4
		3.9, 5.5	0.9, 2.6	Gelled rapidly at 75°C. Gelled slowly at room temperature	2
NH ₄ OH neutralized (NO ₃ */Th + U = 3.0 before neutralization)	0.5	2.0	0.7	Weak, mush gel	1
	2.0	1.7	0.9	Gelled in 4 min at 25°C.	1
	1.-2	2.0	0.47-0.70	Gelled slowly at 25°C	5
NH ₄ OH neutralized (NO ₃ */Th + U = 3.9 before neutralization)	3.1	2.0	0.85	Gelled in <5 min at 25°C	2
		3.7	0.75	Gelled in 4.5 h at 25°C	1
		4.9, 24	0.75	Stable >8 h at 25°C	2
Nitrate solutions	3.0	0	0.55-0.66	Weak, mushy gels at 95°C	3
		0	0.75-1.97	Gelled in 7 to 60 min at 0 or 25°C	8
		2.1	0.82-1.02	Gelled in 1 to 14 min at 25°C	3
		3.6	0.63, 0.72	Stable at 0°C	2
		3.6-3.9	0	0.77-1.62	Gelled in 6-90 min at 0 to 25°C
	3.6-3.9	3.5	0.77-0.87	Gelled in 3-46 min at 25°C	3
		1.0	0.70-0.87	Gelled slowly at 25°C	4
		2.0	0.77-0.90	Gelled slowly at 25°C	4
		3.7-3.8	0.77-0.90	Stable >8 h at 25°C Gelled quickly at >75°C	4
		4.1-4.3	0	0.20-0.60	No gel or weak gel at 75-98°C
	3.6-3.9	0	0.82-1.03	Gelled in <30 min at 25°C	12
		2.1-2.2	0.75-0.87	Gelled in 2-90 min at 25°C	3
		2.8	0.70	Gelled in 4 min at 75°C	1
		3.6-3.9	0.77-0.9	Stable >8 h at 25°C Gelled <6 min at 75°C	5
		5.4, 7.4	0.85, 0.87	Gelled at 90°C	

Table 7.5. Scouting experiments for gel-sphere formation

Type of fuel and HMTA/NO ₃ *	Urea/Th + U (mol/mol)	NO ₃ */Th + U (mol/mol)	Broth stability	Sphere formation		Results; sphere properties
				Medium ^a	Temperature	
SOLEX	0	0.6	Precipitation	-	-	Weak, semi-gel
	0.3	0.3	Good	TCE, MX	75, 95°C	Weak, semi-gel
	0.5	2.5	Good	MX	66	Firm, smooth
	0.5	2.9	Gelled in 4 min at 25°C	MX	75	Firm, smooth
	0.5	3.0	Gelled at 0-3°C	TCE	68, 70	Firm, smooth
	2.0	2.0	Good	MX	93-98	Firm, smooth
	2.0	3.0	Good	MX	98	Firm, smooth
	3.5, 3.6	2.2, 2.0	Thickened at 25°C	MX	98	Firm, smooth
	3.8	2.0	Good	MX	98, 95	Firm, smooth
	4.0	3.0	Good	TCE	77	Gelled too slowly
				MX	98	Firm, smooth
				MX	98	Soft
	NH ₄ neutralized 0.6-0.9 mol/mol	0.5	3.2	Gelled in 20 min at 25°C	MX	98
2.0		1.0	Good	MX	98	Firm, smooth
		1.5	Good	MX	98	Firm, smooth
		2.0	Thickened in 2-5 hr at 25°C	MX	95-98	Firm, smooth
3.7		3.1	Good	MX	95	Seven tests Firm, smooth
Nitrate solution 0.7-1.0	0	3-4.1	Good at 0°C	MX	90-95	Soft
	0.3	3.6-3.8	Good at 0°C	MX	50, 75, 95	Firm, smooth
	0.5	3.9	Good	MX	70	Poor gelation
					90, 98	Firm, smooth
	0.7	3.0	Stable at 0°C	MX	55	Firm, smooth
		4.1	Stable at 0°C	MX	95	Soft
	1.0	3.9	Stable at 25°C	MX	95	Firm, smooth
	2.0	3.9	Stable at 25°C	MX	90	Firm, smooth
	3.0	3.7	Stable 6 hr at 25°C	MX	95	Firm, smooth
	3.6-3.7	3.9	Stable >8 hr at 25°C	MX	90-98	Firm, smooth Eight tests

^aMX indicates perchloroethylene—mineral oil mixtures.

Table 7.6. Washing studies (immersing gel spheres in special salt solutions)

Test No.	Wash solution			Results
	NH ₄ OH (M)	NH ₄ NO ₃ (M)	Urea (M)	
13	0	0	0	Many cracks within a few min
46	0	3.8	9.8	Few cracks within a few min
43	0	6.6	8.8	Few cracks within 10 min
48	0	6.7	10.5	Few cracks within 20 min
45	0	7.0	9.0	Few cracks within 20 min
47	0	8.3	9.0	Few cracks within 30 min
8	0.05	0	0	Many cracks within a few min
17	0.1	0.1	0	Many cracks within a few min
5	0.1	0.55	0	Few cracks within a few min ^a
25	0.1	1.1	0	Many cracks within a few min
4	0.1	1.64	0	Many cracks within a few min
16	0.1	3.28	0	Many cracks within a few min
18	0.1	3.5	0	Many cracks within a few min
6	0.15	0	0	Few cracks within a few min ^a
19	0.15	0.44	0	Many cracks within a few min
20	0.15	0.88	0	Many cracks within a few min
24	0.15	0.94	0	Many cracks within a few min
2	0.15	1.09	0	Few cracks within a few min
21	0.15	1.09	0	Few cracks within a few min
22	0.15	1.09	0	Many cracks within a few min
23	0.15	1.09	0	Few cracks within a few min
3	0.15	2.2	0	Few cracks within a few min ^a
14	0.15	2.2	0	Many cracks within a few min
15	0.15	4.4	0	Many cracks within a few min
7	0.2	0.55	0	Few cracks within a few min ^a
12	0.2	2.9	0	Many cracks within a few min
1	0.3	0	0	Many cracks within a few min
9	0.3	4.4	0	Many cracks within a few min
44	3.1	8.3	5.1	Few cracks within a few min
42	3.3	4.8	10.0	Few cracks within 10 min
40	4.5	6.1	8.1	Few cracks within 20 min
37	5.0	4.0	3.0	Many cracks within a few min
29	5.0	7.0	0	Many cracks within 10 min
41	5.1	7.0	5.7	Few cracks within 10 min
39	7.0	6.7	5.0	Few cracks within 6 min
31	7.2	9.8	0	Few cracks within a few min
34	7.3	6.9	1.0	Few cracks within a few min
33	7.3	6.9	3.0	Few cracks within a few min
10	7.4	0.88	0	Many cracks within a few min
11	7.4	4.4	0	Many cracks within a few min
35	7.4	4.4	3.0	Few cracks within a few min
36	7.4	4.4	6.0	Few cracks within 8 min
26	7.4	7.0	0	Few cracks within a few min
27	8.0	Saturated ^b	0	No cracks after 9 min

Table 7.6 (continued)

Test No.	Wash solution			Results
	NH ₄ OH (M)	NH ₄ NO ₃ (M)	Urea (M)	
32	9.0	4.4	0	Many cracks within a few min
30	9.0	7.0	0	Few cracks within a few min
38	9.8	4.0	3.0	Many cracks within a few min
28	10.4	5.6	0	Many cracks within a few min
MGT-211 NH ₄ OH neutralized gel spheres ^c				
4	0	6.6	7.2	No cracks visible after 30 min
1	0.3	0	0	No cracks visible after 25 min
2	1.7	1.1	0	Few cracks after 10 min
3	7.2	9.8	0	No cracks visible after 21 min
MGT 213 Solex sol gel spheres ^d				
5	0	0	0	Few cracks in 1 h
2	0	7.6	8.2	No cracks after 20 h
3	0.17	1.1	0	Few cracks within 15 min
9	0.3	0	0	Few cracks in 1 h
12	0.5	0	0	Few cracks in 1.5 h
13	0.5	1.0	0	No cracks after 21 min
15	0.5	1.0	0	Gel weakened, gaping cracks after heating at 50-60°C
1	7.2	9.8	0	No cracks after 21 h

^aObservational techniques masked internal cracks.

^bCounting undissolved NH₄NO₃, 10 M NH₄NO₃.

^cThese spheres were opaque, so internal cracks could not be observed.

^dSome of these were also opaque, making some observations difficult.

Table 7.7. Qualitative evaluation of damage for different washing methods

Wash method	Gel-sphere batch No.			
	202	211	212	213
0.3 M NH_4OH straight-through	Medium	Bad	Bad	Very light
<u>Recirculating</u>				
1.06 M NH_4NO_3^- 0.167 M NH_4OH	Fair	Fair	Bad	Fair
7.2 M NH_4OH - 9.8 M NH_4NO_3	Fair	Bad	Bad	Bad
9 M urea-8.2 M NH_4NO_3	Light	Medium	Bad	Fair
<u>Soxhlet extraction with 3% NH_4OH^a</u>				
Recycle	Fair	Light	Fair	Light
Once-through	Fair	Fair	Light	Very light
<u>Soxhlet extraction approximations^a</u>				
0.5 M NH_4OH recirculation plus H_2O	-	-	-	Medium
Slow straight-through	-	Fair	Light	Very light

^aGel spheres washed by Soxhlet techniques were dried at 110°C; others were dried at 170°C.

Table 7.8. Washing,^a drying, and sintering results for SOLEX feeds
 Sintered product densities: 99 or 100% of theoretical density

Batch No.	Wash method	Drying temp. (°C)	Dry product			Sintered product		
			Bulk density (g/mL)	Subjective evaluation	Diameter (µm)	% shape rejection	Subjective evaluation	% shape rejection
<u>Sorex Sol</u>								
213, Wash 7	A	110	2.46	Few cracked	1400	23	100% broken	-
Wash 8	B	110	1.29	Few cracked	2000 + 600	28	60% cracked	-
Wash 10	C	170	2.13	Most cracked	2000 ± 300	39	-	-
Wash 14	D	170	2.29	Many cracked	2200	41	-	-
Wash 17	E	110	2.25	Some broken	1800	18	-	-
219, P.C.2	F	170	2.25	5% cracked	1700	5	30% cracked	-
P.C.3	F	170	2.31	3% cracked	1400	3	20% cracked	-
222	E	170	2.51	5% cracked	1400	4	5% cracked	-
221	E	170	2.54	5% cracked	1400	5	5% cracked	-
					350	3	5% cracked	-
					1100	3	5% cracked	-
201 A	C	170	2.16	5% cracked	1700 + 100	2	70% cracked	-
					1100	3	5% cracked	-
B	G	170	2.29	5% cracked	1600	1	10% cracked	-
					1800	2	30% cracked	-
218	E	170	2.33	10% cracked	1400	11	60% cracked	-

Table 7.8 (continued)

Batch No.	Wash method	Drying temp (°C)	Dry product				Sintered product	
			Bulk density (g/mL)	Subjective evaluation	Diameter (µm)	% shape rejection	Subjective evaluation	% shape rejection
<u>Solex Sol + HNO₃</u>								
189	G	150	-	Some cracks	1800 ± 1200	-	-	-
184	G	150	3.40	Some cracks in larger	1300	-	-	-
183	G	245	2.82	10% broken and split	900	-	-	-
193	G	170	2.74	<5% cracked	500	<1%	-	2
196	G	170	2.34	None cracked	800 ± 300	13	-	2
			2.34	Some cracked	1400 ± 300	19	-	2
			2.32	Some cracked	2000 ± 300	59	100% cracked	22
212,	Wash 1	A	110	Some broken	1800	63	100% broken	-
	Wash 2	G	170	Most cracked	2000	20	40% cracked	-
	Wash 3	B	110	Few cracked	1900	53	75% cracked	-
197	G	170	2.34	5% cracked	600	<1%	-	3

^aWash methods:A - Soxhlet extraction, recycle, starting with 3% NH₄OH.B - Soxhlet extraction, once-through, starting with 3% NH₄OH; followed by straight-through wash at 40 L/4h with 0.3 M NH₄OH.C - Recirculating wash starting with 1.06 M NH₄NO₃ + 0.167 M NH₄OH and adding 0.3 M NH₄OH, followed by straight-through wash of 0.3 M NH₄OH.D - Same as C, except started with 7.2 M + 9.8 M NH₄NO₃.E - Straight-through wash at 40 L/8h starting with a drained bed using 0.3 M NH₄OH.F - Wash as in E for 2 h, but finish wash at 10 L/h for 2 h using 0.3 M NH₄OH.G - Straight-through wash at 40 L/4h using 0.3 M NH₄OH or 0.5 M NH₄OH.H - Same as C, except started with 9 M urea + 8.2 M NH₄NO₃.I - Soxhlet extraction, once-through with continuous feed of 3% NH₄OH.J - Soxhlet extraction, once-through with one batch of 3% NH₄OH.

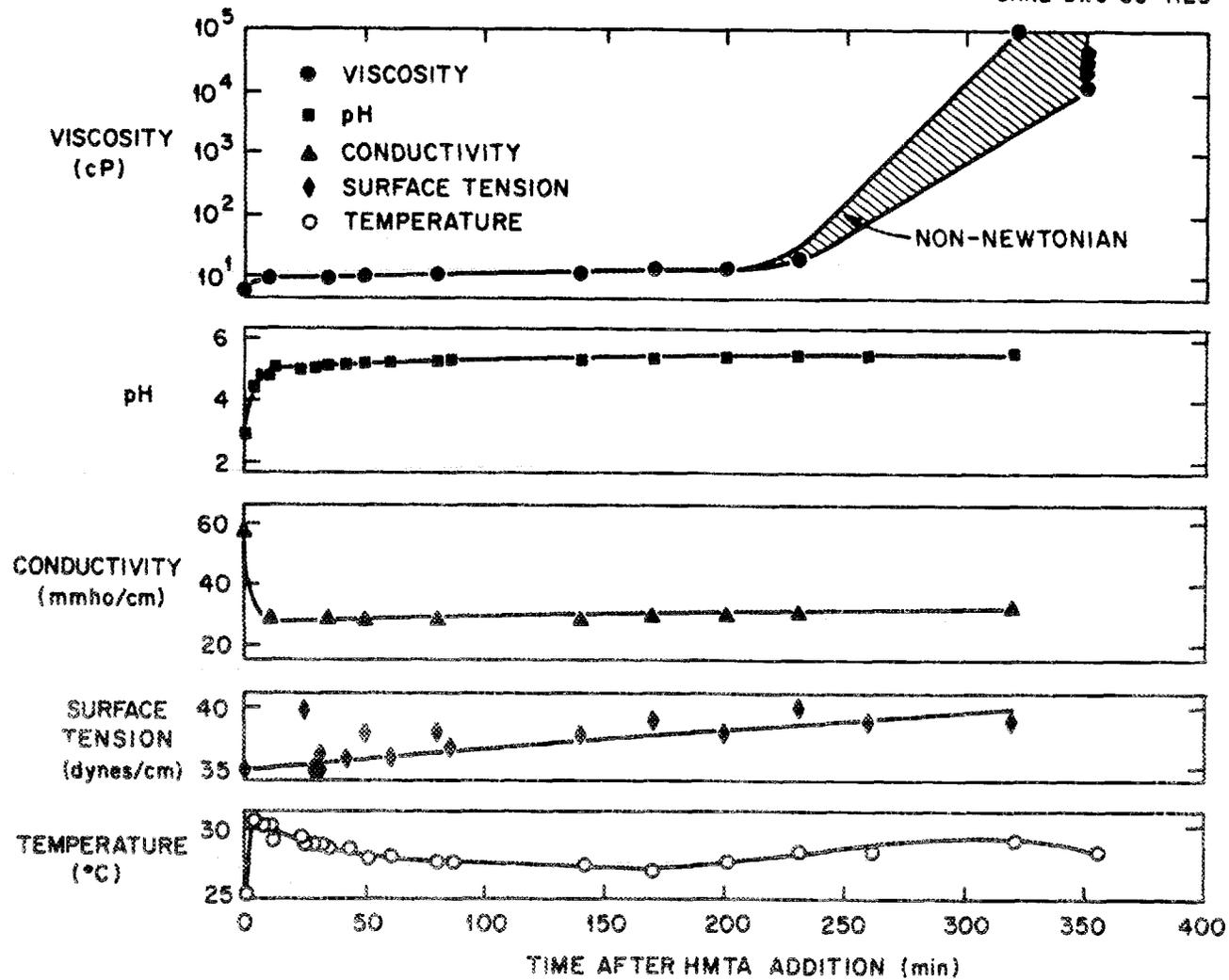


Fig. 7.1. Time record of fluid properties for test No. 1 (solex sol feed).

Table 7.9. Properties of solutins used in feed makeup

	Temperature °C	Density g/mL	Surface tension dyne/cm	pH	Conductivity mmho/cm	Viscosity cP
<u>Test No. 1 Solex Sol Feed</u>						
ADUN	25	1.94	59.4	1.03	48.3	10.6
Th Solex sol 108A	24	-	34.4	2.35	76.3	6.1
Th sol + ADUN (25% U)	25	-	42.1	2.35	73.5	6.35
Th sol + urea $\frac{\text{urea}}{\text{Th} + \text{U}} = 3.75$	16	-	36.0	3.99	54.0	7.3
<u>Test No. 2 NH₄-Neutralized Feed</u>						
Th-U-9	25	-	-	0.44	-	19.1
HMTA solution	24	-	-	6.8	-	8.03

the HMTA not only must be added as a solution at low temperatures, but vigorous mixing is required at the moment of addition or local regions of gelation will occur. Once the HMTA is well mixed, the feed is fairly stable, even at room temperature (though not as stable as the high urea feeds). Thus for these tests, the solutions were chilled ($<5^{\circ}\text{C}$), mixed vigorously, and then placed in the bath (25°C). The feed thickened so quickly that non-Newtonian behavior was observed by the time (10 min) the first viscosity measurements were taken and the viscosities were in the tens of thousands cP and increasing. The viscosity remained measurable at 10^4 to 10^6 cP for at least 2 h (when measurements were ceased), depending on the spindle and rotation rate used on the Brookfield viscometer.

Figure 7.2 illustrates the viscosity behavior for the SOLEX sol feed (tests No. 1 and 8) and for the NH_4OH -neutralized feed (test No. 6). Although the viscosity behavior was similar for the two tests shown for the SOLEX sol feed, the viscosity-time curve was not reproduced exactly.

Figure 7.3 is a short time plot of the pH behavior of the two feeds. The delay of almost 1 min in the response seen in test No. 6 is indicative of the poor mixing in these experiments. Once the HMTA solution is well mixed in this test, the pH stabilizes in a matter of seconds. The total stabilization time for test No. 1 is about the same as test No. 6, but the difference in the shapes of the two curves can be attributed to the fact that HMTA was added as a solid in test No. 1.

Figure 7.4 is a long time plot of the pH behavior for the SOLEX sol feed. Note that the pH gradually increases to as high as 7 after the initial large jump. The change in the curve at ~ 400 min is probably a problem with the pH meter and not real.

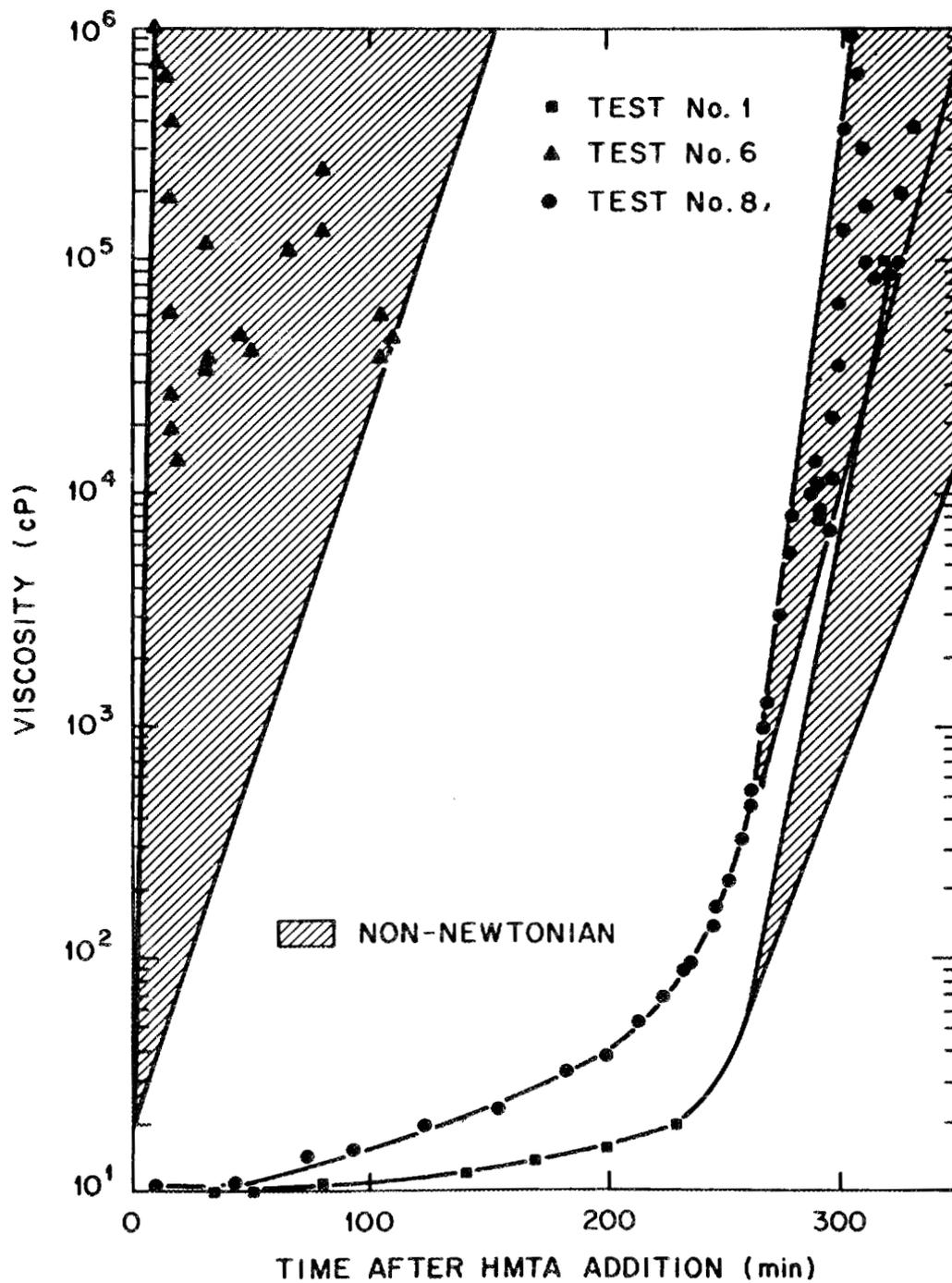


Fig. 7.2. Viscosity behavior after HMTA addition

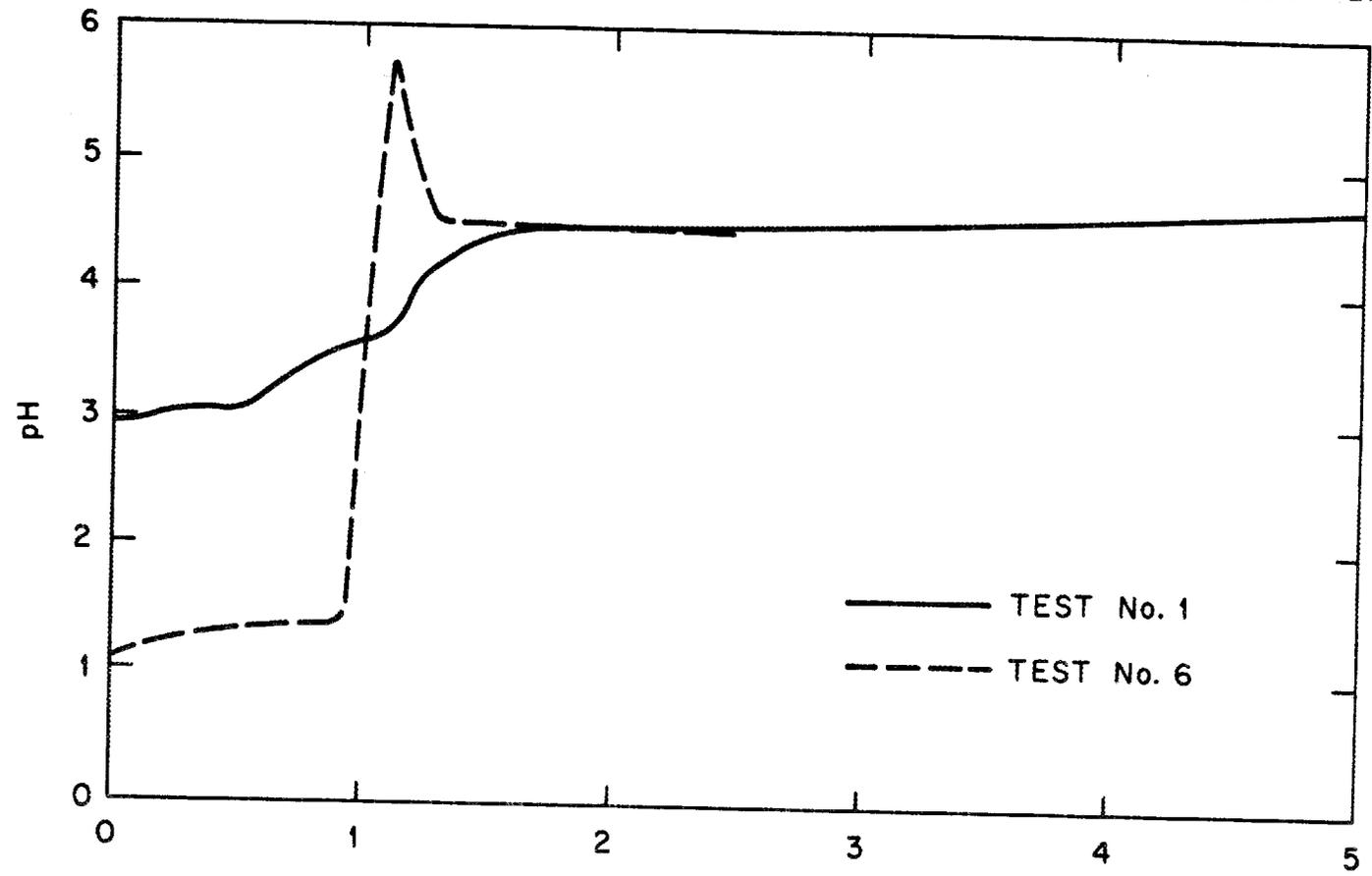


Fig. 7.3. Behavior of pH immediately following HMTA addition.

Time after HMTA addition (min)

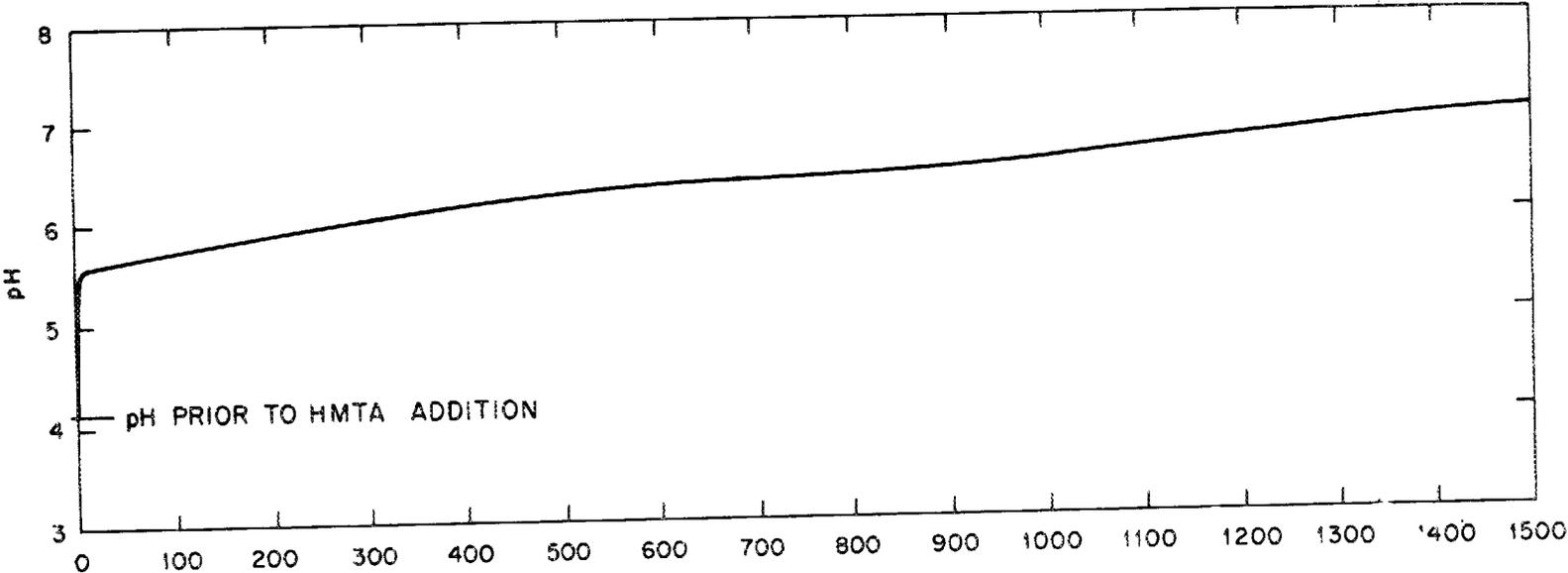


Fig. 7.4. Behavior pH for test No. 8 several hours after HMTA addition.

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