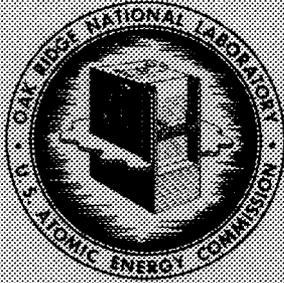


ORNL
MASTER COPY

26



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



ORNL-TM-1980

J.P.M.

LABORATORY STUDIES OF SOL-GEL PROCESSES AT THE
OAK RIDGE NATIONAL LABORATORY

J. P. McBride

NOTICE This document contains information of a preliminary nature and was prepared primarily for internal use at the Oak Ridge National Laboratory. It is subject to revision or correction and therefore does not represent a final report.

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

- A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or
- B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

ORNL-TM-1980

Contract No. W-7405-eng-26

CHEMICAL TECHNOLOGY DIVISION

LABORATORY STUDIES OF SOL-GEL PROCESSES AT THE
OAK RIDGE NATIONAL LABORATORY*

Compiled by J. P. McBride

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

SEPTEMBER 1967

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

*Research sponsored by the U. S. Atomic Energy Commission under contract
with the Union Carbide Corporation.

CONTENTS

	<u>Page</u>
Abstract	1
Summary	1
Introduction	4
Thoria Sol-Gel Process	5
Properties of Thoria Sols	7
Thoria-Urania Sol Preparation by Solvent Extraction	13
Sol-Gel Preparation of Thoria-Urania Microspheres Containing High Concentrations of Uranium	19
Sol-Gel Preparation of Porous Thoria from ThO_2 -C Sols	25
Urania Sol-Gel Process	25
Urania and Urania-Zirconia Sol Preparation by Precipitation-Peptization	26
Urania Sol Preparation by Solvent Extraction	32
Preparation of U(IV) Solutions	36
Properties of Urania Sols and Gels	39
Drying and Firing of Urania Gels	46
Plutonia Sol-Gel Process	51
Zirconia Sol-Gel Process	58
Miscellaneous Sol-Gel Processes	60
Sol-Gel Preparation of ThO_2 and Thorium Uranium Dicarbide	60
Sol-Gel Preparation of Uranium Nitride	64
Preparation of Lanthanide Oxide Microspheres by Sol-Gel Methods	66
Status of Americium-Curium Sol-Gel Process	68

LABORATORY STUDIES OF SOL-GEL PROCESSES AT THE
OAK RIDGE NATIONAL LABORATORY

Compiled by J. P. McBride

ABSTRACT

Sol-gel processes are being developed for preparing the oxides, carbides, and nitrides of thorium, uranium, plutonium, zirconium, and their mixtures. This paper presents the status of the laboratory studies being made at the Oak Ridge National Laboratory (ORNL) in support of this effort, and is primarily concerned with sol preparation, sol characterization, and drying and firing of gel products. Of the sol-gel processes studied, those involving the preparation of pure ThO_2 and ThO_2 -3% UO_3 are the most advanced and most completely reported. Hence, only brief mention is made of these processes. In the interest of completeness, ORNL work on the sol-gel preparation of oxides of the rare earths and the transplutonium elements is referenced.

SUMMARY

Sol-gel processes have been, or are being, developed for preparing the oxides, carbides, and nitrides of thorium, uranium, plutonium, zirconium, and their mixtures. This paper presents the status of the laboratory studies being made at the Oak Ridge National Laboratory (ORNL) in support of this effort, and is primarily concerned with sol preparation, sol characterization, and drying and firing of gel products.

Fundamental studies were conducted, using pure thoria sols that had been prepared from hydrous amorphous thoria and microcrystalline thoria by peptization with nitric acid. The nature of the fundamental sol particle was delineated by using a variety of techniques, including light scattering, viscometry, electron

microscopy, and x-ray diffraction, as well as surface area measurements of dried gel. Surface adsorption properties of sol particles were investigated by means of pH and conductivity measurements. Thoria sols were found to exhibit a wide range of rheological behavior--thixotropy, rheopexy, pseudoplasticity, and viscoelasticity--depending on the sol and electrolyte concentrations and the particle (or agglomerate) shapes. However, concentrated thoria sols ($\leq 4 \text{ M}$) that exhibited Newtonian flow behavior at low-to-moderate rates of shear were readily prepared.

A simple solvent extraction process was developed for preparing thorium-uranium oxide sols, with U/Th atom ratios as high as 2, directly from aqueous thorium-uranium nitrate solutions. The nitrate is extracted by a long-chain aliphatic amine that is dissolved in an inert diluent. Greater than 98% of the "extractable" nitrate is removed in two extraction stages, with an intervening digestion step, to yield 0.2 to 0.3 M sols with NO_3^- /metal mole ratios that vary from 0.33 to 0.15. The latter ratio decreases as the U/Th atom ratio increases from 0 to 2. The dilute sol may be dried to gel fragments, or it may be evaporated to a metal oxide concentration of 1 to 2 M and then formed into microspheres. The fragments (or spheres) are dried, calcined in air at 1150°C , and, finally, fired in an Ar-4% H_2 atmosphere to produce the desired ceramic product. This process has been demonstrated in engineering-scale equipment.

Dense ThO_2 -- UO_2 microspheres having U/Th atom ratios of 0.15 to 0.85 were prepared by simply mixing thoria and urania sols and then forming the mixed sol into microspheres. A method was developed for preparing ThO_2 -- UO_3 sols, with a Th/U mole ratio of 3, by coprecipitation of the oxides from thorium-uranyl nitrate solutions. The preparation of dense ThO_2 -- UO_2 microspheres from these sols was demonstrated on a laboratory scale. Other approaches to the preparation of thorium-uranium sols included coprecipitation of the tetravalent hydrous oxides, peptization of thorium hydroxide precipitates with uranyl nitrate, and addition of UO_3 to nitrate-stabilized thoria sols that had been prepared from the hydrous oxide.

Porous microspheres and shards of ThO_2 were prepared by incorporating carbon in ThO_2 sols, forming the gels, and then burning out the carbon.

Various methods of preparing concentrated UO_2 sols ($\geq 1 \text{ M}$) were developed, the principal ones being (1) precipitation and subsequent peptization of the hydrous oxide and (2) removal of nitrate from U(IV) nitrate-formate solution. In laboratory-scale preparations by the first method, the hydrous oxide is precipitated at pH 7.5 from a U(IV) nitrate-formate solution (NO_3^-/U mole ratio = 4.6; HCOO^-/U mole ratio = 0.6), collected by filtration, and washed, in place, to obtain the NO_3^-/U mole ratio required for sol formation; then the filter cake is heated at 60 to 63°C to spontaneously produce a stable fluid sol. In engineering-scale preparations, the hydrous oxide is first precipitated at pH 9 (NO_3^-/U mole ratio = 2.0; HCOO^-/U mole ratio = 0.5 to 1.0); then the resulting precipitate is washed free of electrolyte by decantation and is subsequently peptized with HNO_3 and HCOOH by heating at 60 to 63°C. To date, the results of the laboratory process have been more reproducible than those of its engineering counterpart.

The second method, a solvent extraction process, for the preparation of urania sol is similar to that developed for thoria-urania sol. Nitrate is extracted with a long-chain amine from a dilute (0.2 M) and partially hydrolyzed U(IV) nitrate-formate solution. The extraction is carried out in two extraction stages, with an intervening digestion step at an elevated temperature.

Laboratory studies included the adaptation of the laboratory method of urania sol preparation to the preparation of urania-zirconia sols, attempts to prepare U(IV) solutions by catalytic reduction with hydrogen (a necessary first step in urania sol preparation), characterization studies of urania sols and gels, and an investigation of drying and firing conditions that are necessary for the production of oxide products having near-theoretical densities and low carbon contents.

A sol-gel process for preparing dense microspheres of PuO_2 was developed. In this process, the hydrous oxide is precipitated from plutonium nitrate solution, washed free of electrolyte, and peptized with nitric acid to give a nitrate-rich plutonia sol. The nitrate content is then reduced, and plutonia crystallites are grown by a drying and baking step. The residue is resuspended in water to give the final sol, which is

1 to 3 M in plutonium and has a NO_3^-/Pu mole ratio of 0.1 to 0.15. The plutonia sols are compatible with thoria and urania sols, and the ability to produce dense plutonia, as well as homogeneous plutonia-urania and plutonia-thoria, microspheres, at any desired ratio of the metal oxides, has been demonstrated.

Concentrated zirconia sols (≤ 3.4 M) were prepared by autoclaving zirconyl nitrate solutions at 200°C to promote hydrolysis and to grow zirconia crystallites. The resulting slurries were peptized by successive decantation-washing procedures to give nitrate-rich zirconia sols. Their nitrate contents were reduced to acceptable levels (NO_3^-/Zr mole ratios between 0.1 and 0.2) by solvent extraction with a long-chain amine dissolved in an inert diluent. Gel microspheres were prepared in the usual manner and fired in air at 1100°C to yield dense, porcelain-white zirconia spheres.

The sol-gel preparation of ThC_2 and $\text{ThC}_2\text{-UC}_2$ microspheres was demonstrated on a laboratory scale. Carbon black was dispersed in ThO_2 and $\text{ThO}_2\text{-UO}_3$ (Th/U mole ratio of 3) sols at a C/metal mole ratio of 4; gel microspheres were formed from the resulting sols; and the carbides were obtained by firing the gels in vacuum or in an argon atmosphere at temperatures up to 2000°C . Studies of the preparation of metal oxide-carbon sols showed that the thoria and urania sols were unique in their ability to disperse carbon blacks to produce stable oxide-carbon sols. Initial results of the preparation of uranium mononitride microspheres from $\text{UO}_2\text{-C}$ sols were promising.

INTRODUCTION

The development of the thoria sol-gel process and the success that has been achieved in the preparation of dense sol-gel thorium oxide and thorium oxide containing small amounts of uranium oxide for use as fuel for nuclear reactors naturally led to the consideration of sol-gel processes for preparing other materials that form hydrosols and have nuclear application. Accordingly, sol-gel processes have been, or are being, developed for preparing the oxides, carbides, and nitrides, not only

of thorium but also of uranium, plutonium, zirconium and their mixtures. In addition, work has been directed toward the development of sol-gel processes for the preparation of rare-earth oxides for use in control rod and heat source applications and the preparation of oxides of americium and curium for use as neutron targets in the production of higher-molecular-weight actinides. This paper presents the status of the laboratory studies being made at the Oak Ridge National Laboratory (ORNL) in support of this effort and is primarily concerned with the work on thorium, uranium, plutonium, and zirconium. In the interest of completeness, however, the ORNL work on the sol-gel preparation of the rare-earth oxides and the transplutonium elements is referenced. Sol preparation methods, methods of characterizing sols, and drying and firing studies of gel products are described.

THORIA SOL-GEL PROCESSES

The sol-gel process for the preparation of pure ThO_2 and ThO_2 -3% UO_3 is the most advanced and most completely reported;¹⁻³ hence, only brief mention will be made of it. The basic chemical flowsheet (Fig. 1) has been satisfactorily demonstrated on an engineering scale. In the Kilorod program, for example, over 1000 fuel rods of ThO_2 containing 3% $^{233}\text{UO}_2$ were prepared by vibratorily compacting sol-gel oxide shards into Zircaloy tubes.⁴

Recent laboratory studies of sol-gel processes for the preparation of thoria-based fuels have been concentrated on the development of alternative methods of sol preparation, such as solvent extraction, and a means of increasing the urania content to more than 10%, the apparent upper limit that is associated with the basic process. In addition, a considerable effort has been directed toward a fundamental study of the nature of thoria sols.

ORNL-LR-DWG 74842R1

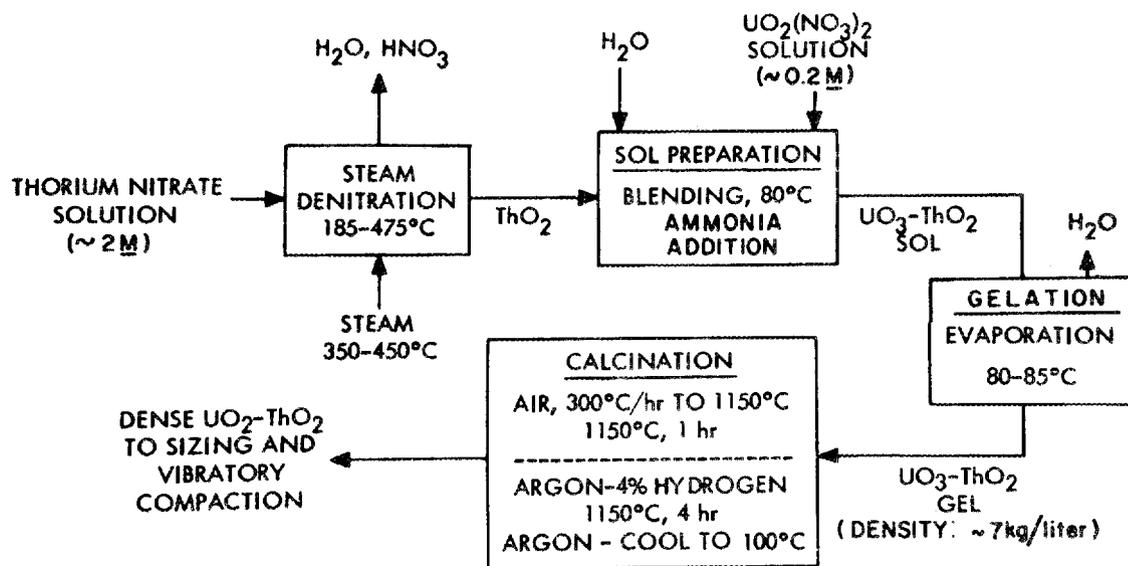


Fig. 1. Schematic Flowsheet for the Thoria Sol-Gel Process.

Properties of Thoria Sols

K. H. McCorkle

Much of our understanding of the nature of sols, as well as the physical chemistry of sol-gel processes, stems from fundamental studies of the colloidal properties and the surface chemistry of thoria sols and gels, which were carried out at ORNL or were sponsored by ORNL under subcontract to various universities. A large part of this work, particularly as it is related to the nature of thoria sols, is summarized and interpreted in a comprehensive and well-documented doctoral thesis.⁵ More recently, the work has been supplemented by detailed studies of rare-earth oxide sols.⁶ From these studies has emerged a model that the concentrated sols that are suitable for the preparation of dense ceramic materials are composed of well-formed crystallites having a well-defined surface stoichiometry for the adsorption of ions from solution. In addition, the rheologically significant particle appears to be a loosely bound aggregate or floc containing several crystallites, the shape and average size of the floc being mainly determined by the surface chemistry of the crystallites and the electrolytic environment. The concept of a definite, well-defined surface stoichiometry is ideally represented by thoria sols; but it is felt that other oxide sols also show this property to some degree, and the concept has proved to be useful in the development of sol-gel processes for urania, plutonia, zirconia, and the rare-earth oxides. Indeed, while the method for preparing each of the latter sols has differed from that for preparing thoria and is more or less unique, the crystallite sizes and electrolyte requirements for stable sols, in each case, are about the same as those for thoria.

The thoria sols of interest, with regard to use as fuel for nuclear reactors, are those consisting of thoria in nitric acid solutions. Several groups other than those at ORNL have worked with colloidal thoria. These include workers in the Netherlands⁷ and Italy,⁸ as well as the Babcock and Wilcox Company,⁹ Diamond Alkali Company,¹⁰ du Pont Company,¹¹ W. R. Grace Company,¹²⁻¹⁴ and Mallinckrodt Chemical Company¹⁵ in the United States.

Most of the results obtained in the thoria sol-gel studies at ORNL have been, or are in the process of being, published.^{1-5,16-20} Very often, part of the thoria sol preparation process also involves uranium in some form; however, the corresponding pure thoria sol can usually be made by simply omitting the uranium and possibly adjusting the peptizing anion concentration. At ORNL, thoria to be used for dispersion to sols has been prepared in a variety of ways; however, the largest quantities have been made by passing steam at a pressure of 1 atm over a thin layer of thorium nitrate at a temperature that is gradually increased to 485°C. The thoria power thus produced has a $\text{NO}_3^-/\text{ThO}_2$ mole ratio of about 0.025 and contains about 1% H_2O . When this thoria is stirred vigorously at 80°C in sufficient dilute nitric acid to give a $\text{NO}_3^-/\text{ThO}_2$ mole ratio of 0.11, a stable thoria sol results within a few hours.

Most of the ORNL studies of the colloidal properties of thoria sols have been made with sols of the type just described, although some work has been done, for comparison, on sols that were prepared from calcined thorium oxalate or hydrous precipitated thoria. In general, thoria sols are of two main types: the hydrous amorphous thoria sols (sometimes called "thorium hydroxide" sols), and the crystalline thoria sols, which are prepared from the steam-denitrated oxide.

Properties of Particulate Thoria Sols

Hydrous amorphous thoria is produced by precipitation or dialysis of a solution of thorium nitrate or chloride at 25°C. This type of colloid is a stringy polymer of variable composition.²¹ The polymer is unstable toward crystallization, forming fluorite-structure thoria.^{22,23} The ultimate crystallite is irregularly centrosymmetric, with both cubic and octahedral faces being present.²⁴

The crystallite size of thoria that is prepared by steam denitration of thorium nitrate was found, by x-ray line broadening and electron microscopy, to be about 80 Å. The presence of an anisometric floc in crystalline thoria sols has been confirmed viscometrically. Figure 2 shows a plot of reduced viscosity (defined as $(\eta_{\text{sol}} - \eta_{\text{H}_2\text{O}})/\eta_{\text{H}_2\text{O}}$) vs solids volume fractions of a crystalline thoria sol. These

ORNL DWG. 67-9753

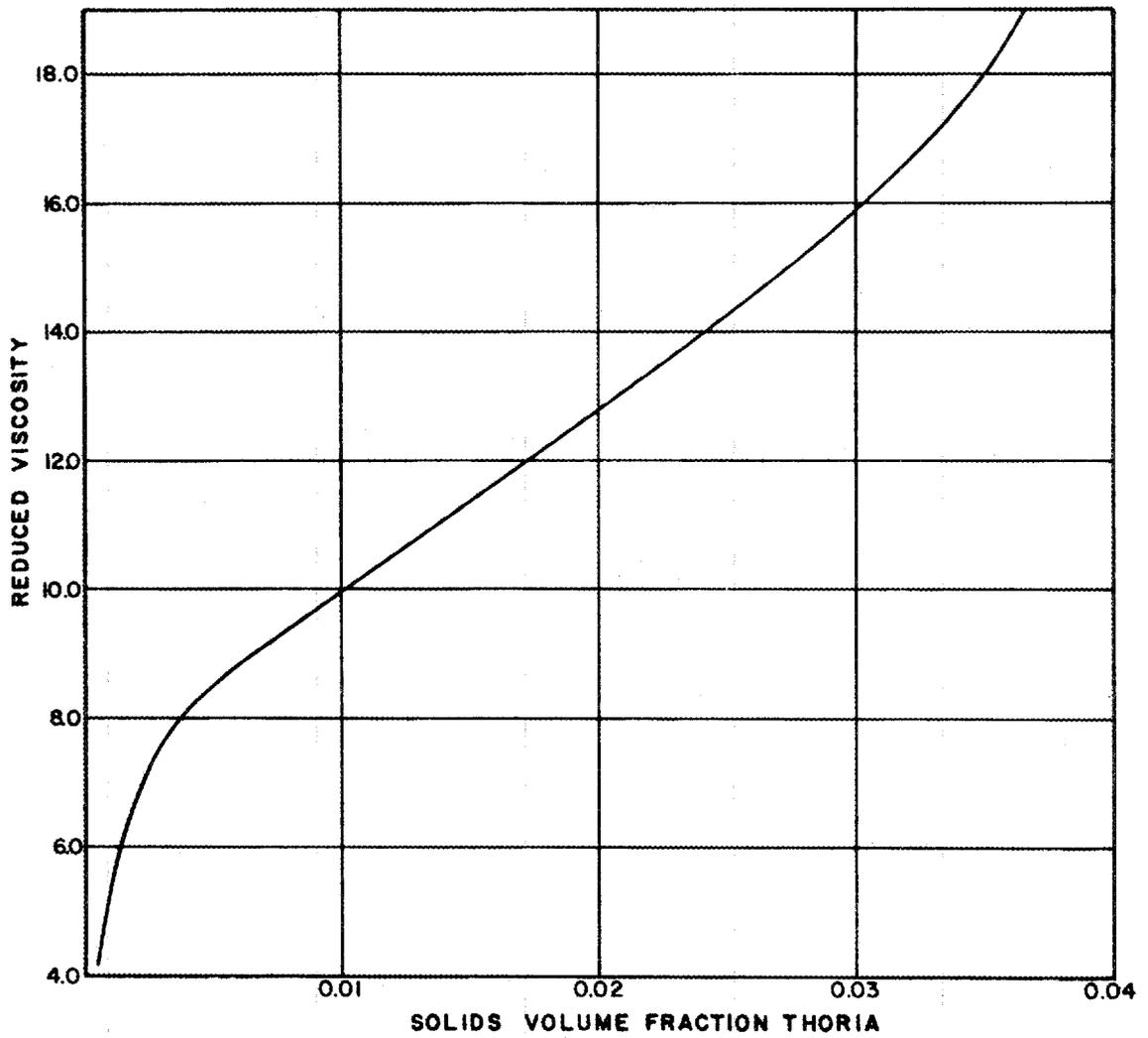


Fig. 2. Reduced Viscosity of Thoria Sol (pH 2; Thoria Calcined at 650°C) as a Function of Solids Volume Fraction.

flocs may be described as equivalent prolate spheroids by the method of Simha.²⁵ Apparently, the floc of crystallites is about six times longer than it is broad, and tends to come apart at very high dilutions. Another indication that the flocs of crystallites are not tightly bonded is that the area calculated from the x-ray crystallite size is, within experimental error, the same as that measured by the BET area.

Surface Chemistry of Colloidal Thoria

Thoria rapidly adsorbs water and a variety of other chemical species that are generally acid or amphoteric. Completely dispersed thoria is probably rapidly and completely hydrated. Acid metal oxides, as a class, are adsorbable. For monomeric acids, a saturation value of 4 to 6 micromoles per square meter of ThO_2 surface is obtained.

Adsorption studies of water,^{26,27} nitric acid,^{16,28-30} gaseous carbon dioxide,³¹ phosphates,³² silicates,³³ organics,³⁴ and U(VI)^{8,17,28,35} have been made by solution depletion. Many other ionic adsorptions have been deduced from electrokinetic studies.^{29,36-38}

Figure 3 shows what is thought to be the best graphic estimate of nitric acid adsorption by solution depletion.² It appears that thoria adsorbs nitrate in two forms: as ionic nitrate, and as a distorted "nitrate" species, with the latter increasing as the colloidal thoria is progressively dried.³⁹

The peculiarly strong adsorption of U(VI) on thoria is well known.⁴⁰ If the U(VI) is adsorbed on preformed thoria crystallites, the expected 4 to 6 micromoles of uranium per square meter of surface are adsorbed. If, however, the crystallites are formed in the presence of U(VI), the U(VI) content appears to exceed this value by as much as 100%.⁸

Some of the problems inherent in the determination of ionic adsorption on thoria by electrokinetics are indicated by the data in Fig. 4.^{29,36-38,41,42} In general, these values of "zeta potential" imply only about one-fifth of the adsorption of HNO_3

ORNL-DWG 66-12570R

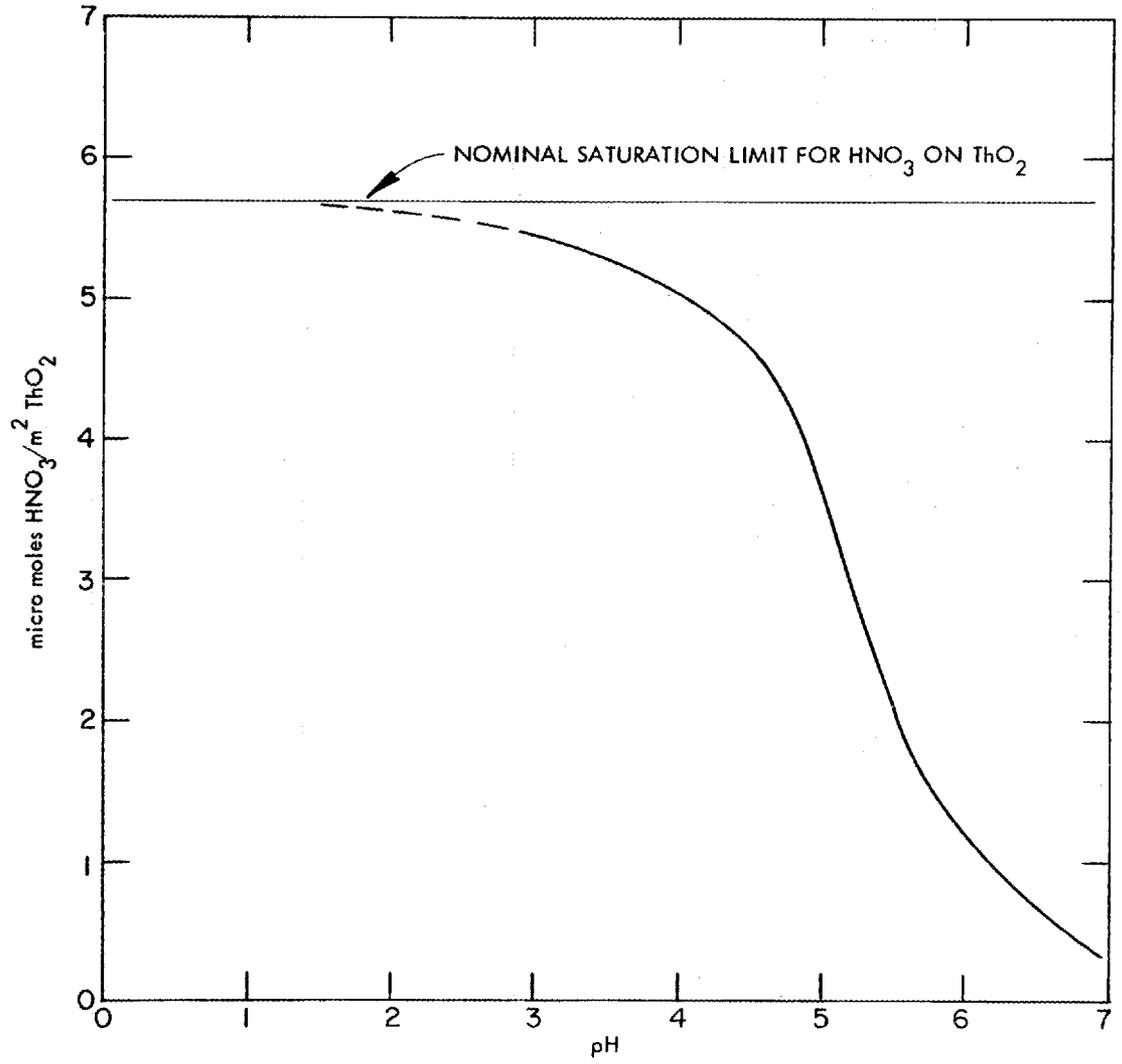


Fig. 3. Adsorption of HNO₃ on Colloidal ThO₂.

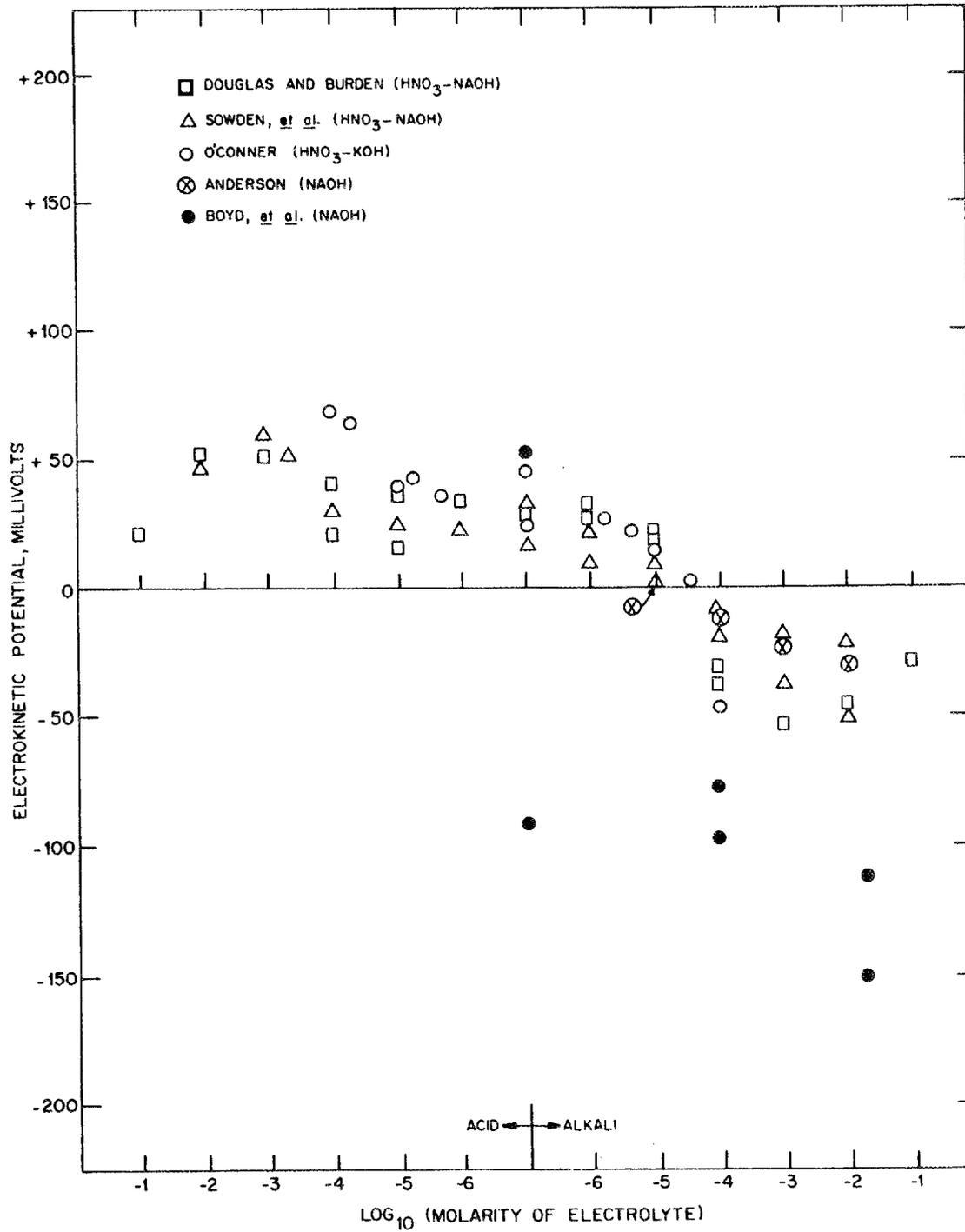


Fig. 4. Summary of Electrokinetic Data Obtained for Thoria Sols.

that the best solution depletion results give. Detailed study of the electrophoresis of colloidal thoria has shown numerous, severe false-boundary and false-mobility effects due to traces of dissolved thorium nitrate or possibly other trace ionic contaminants.⁴² Further, it was possible to obtain consistent trends of electrokinetic mobility with electrolyte composition only for a given sample. Different thoria samples would sometimes give opposite trends. The electrokinetic behavior of thoria is apparently a very complex function of its preparative history, as has been suggested by others.^{37,43}

The theoretical connection between fundamental physical chemistry and the macrorheology of colloidal thoria will probably involve some parameter akin to the zeta potential;⁴⁴ however, this relationship is, at best, still very obscure⁴⁵ and is probably related to what Overbeek calls "anomalous flocculation."⁴⁶ Thoria colloids are capable of exhibiting some remarkable anomalies of flow, considering the supposed simplicity of the ultimate crystallites. Figure 5, taken from Sturch,⁴⁷ illustrates rheopexy, thixotropy, and pseudoplasticity.

Thoria-Urania Sol Preparation by Solvent Extraction

J. G. Moore

The ability of amines to extract acids and metal complexes from aqueous solutions⁴⁸ provided the basis for the development of the process in which amines were used for the partial denitration of thorium and/or uranium⁸ and for the preparation of certain colloidal suspensions containing thorium and uranium.⁴⁹ More recently, it was utilized in a two-stage solvent extraction process that was developed at ORNL for the preparation of thorium-uranium oxide sols.⁵⁰

In the solvent extraction process, sols are prepared directly from aqueous solutions containing thorium and uranyl nitrate. The nitrate is removed from the aqueous solution by two contacts with a long-chain aliphatic amine dissolved in an inert diluent. The aqueous phase is digested at 95 to 100°C during the interval between the two extractions.

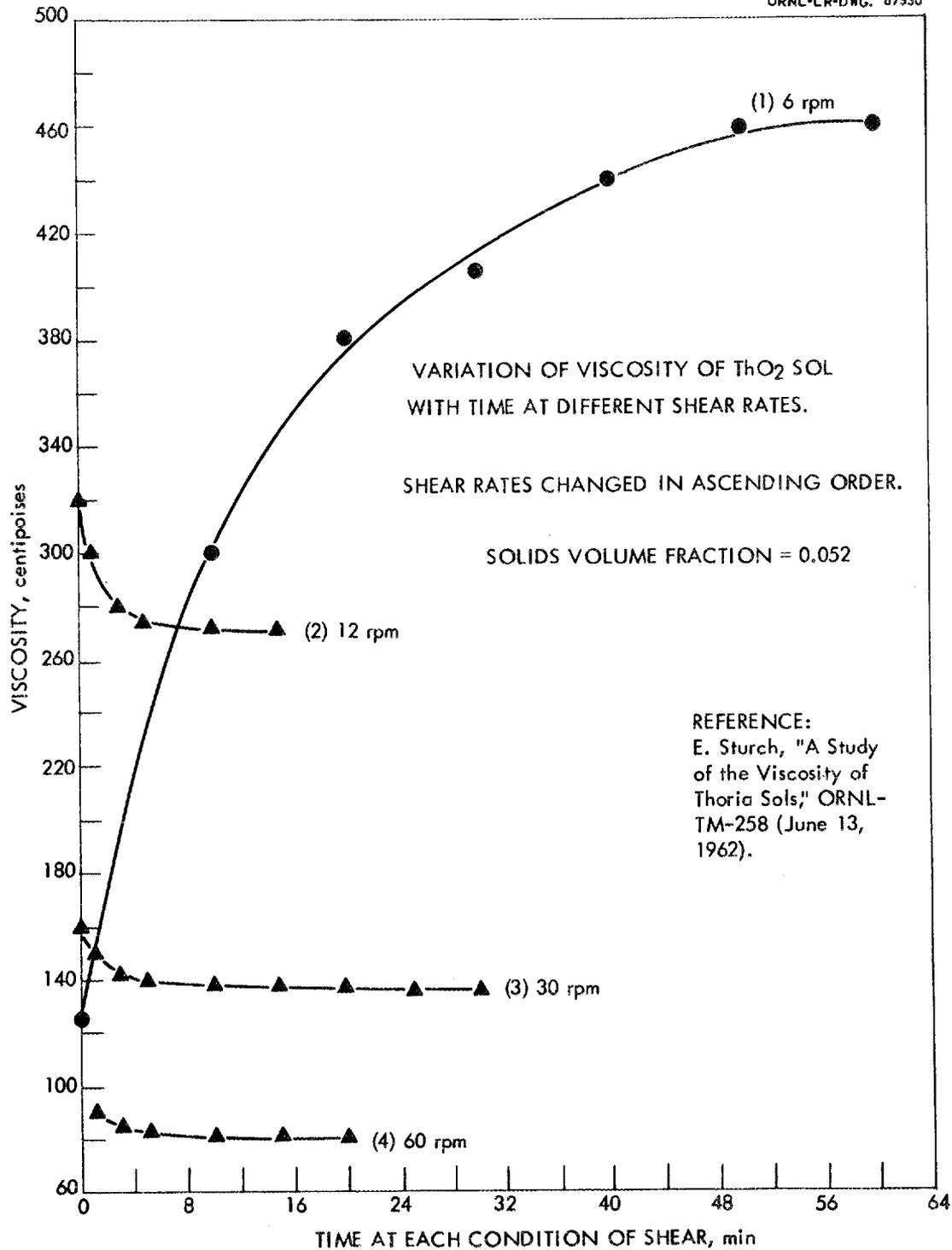


Fig. 5. Variation of Viscosity of ThO_2 Sol with Time at Different Shear Rates.

A typical flowsheet for the preparation of a sol and, subsequently, oxide microspheres having a Th/U atom ratio of about 3.5 is presented in Fig. 6. One volume of aqueous solution about 0.21 M in $\text{Th}(\text{NO}_3)_4$ and 0.06 M in $\text{UO}_2(\text{NO}_3)_2$ is contacted for at least 2 min with 1.9 volumes of 0.75 Amberlite LA-2 (a commercial, extensively branched secondary amine, n-lauryltrialkylmethyl amine) in n-paraffin. To ensure rapid phase separation, the extraction is made at 50 to 60°C with the organic as the continuous phase.

After the initial contact, the phases are separated, and the aqueous phase is heated for at least 10 min at 95 to 100°C. This heat treatment causes the aqueous to change from a yellow solution to a dark red sol containing ~10- to 40-Å crystallites. Also, more nitrate is released for extraction in the second stage. Although the flowsheet shown uses cocurrent flow, countercurrent flow is equally effective. In any event, operation of the second stage is identical to that of the first; but, after the phases are separated in the second stage, the organic is regenerated and the aqueous is concentrated.

Sols were prepared also by using amines such as Primene JM-T, 1-nonyldecylamine, ditridecyl P and Adogen 364; however, most of the development work was done with Amberlite LA-2: approximately 1.2 to 1.5 moles of amine per mole of initial nitrate to ensure complete removal of the extractable nitrate. Other diluents were also examined, but, for convenience, most of the studies were made with 0.6 to 0.75 M amine solutions in n-dodecane (or its commercial equivalent n-paraffin).

Laboratory tests showed that, after the first extraction, the $\text{NO}_3^-/(\text{Th} + \text{U})$ mole ratio in the aqueous phase decreased linearly from about 0.70, for pure thorium nitrate solutions, to about 0.25, for thorium nitrate containing about 50 mole % uranyl nitrate. The $\text{NO}_3^-/\text{metal}$ mole ratio in the sol product after all extraction stages also decreased linearly as the uranium content increased to 25 mole %; it then remained constant at about 0.16 mole of nitrate per mole of total metal (Fig. 7).

The total metal concentration in the aqueous phase was maintained at less than 0.6 M to prevent the formation of solids during the first extraction. Although these solids liquefy on heating, they could be troublesome in a continuous process.

ORNL DWG 67-9774

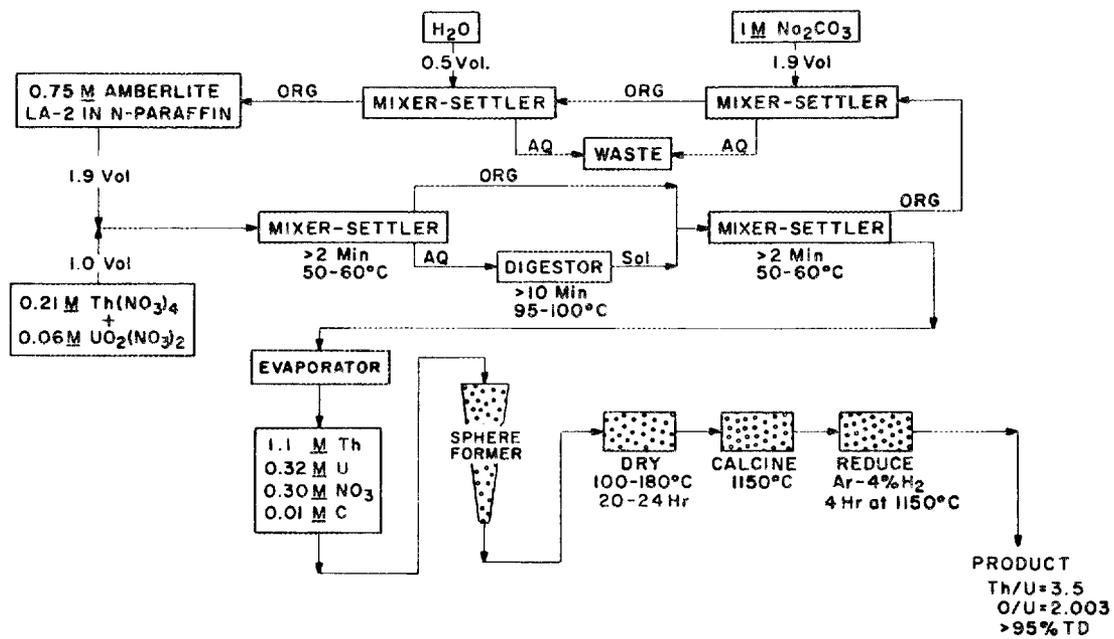


Fig. 6. Solvent Extraction Process for the Preparation of Thoria—Urania Microspheres.

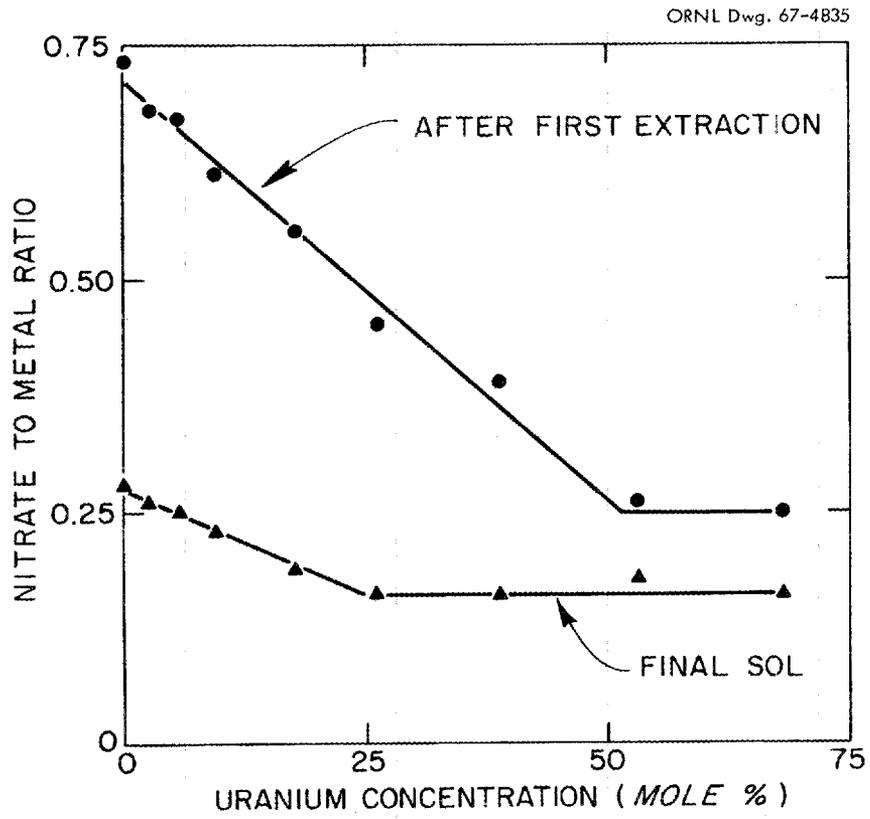


Fig. 7. Effect of Uranium Concentration on the $\text{NO}_3^-/(\text{Th} + \text{U})$ Mole Ratio in Thoria-Urania Sols.

The organic amine nitrate generated in the extraction step is reconverted to free amine by contacting it with an aqueous solution containing about 1.05 moles of sodium carbonate per mole of amine. The organic phase is then washed with water to ensure that carbonate is not carried over into the extraction stages.

The dilute sol from the second extraction stage flows to an evaporator, where it is concentrated to a sol that is 1 to 2 M in total metal. This sol can be formed into microspheres or dried into gel fragments. In the particular example cited above (see Fig. 6), the final sol was 1.10 M in thorium, 0.32 M in uranium, 0.30 M in nitrate, and 0.01 M in carbon of an unspecified form. Spheres were formed by injecting droplets of this sol into a column of 2-ethyl-1-hexanol containing 0.5 to 1 vol % H₂O, 0.03 to 0.15 vol % Span 80, and 0.03 to 0.15 vol % Ethomeen S-15. The Span 80 prevented clustering of the partially gelled spheres, and the Ethomeen S-15 prevented coalescing. The droplets were usually allowed to remain in the column for about 30 min.

The gelled spheres were dried overnight at 100°C, held at 170 to 180°C for about 5 hr, and then calcined in air at 1150°C. Finally, the uranium was reduced in Ar-4% H₂ for 4 hr at 1150°C. The resulting spheres were shiny black and had an O/U atom ratio of 2.003. Open porosity was less than 1%; the density was greater than 95% of the theoretical density of the oxide solid solution. Individual spheres 150 to 350 μ in diameter resisted crushing forces of 940 to 2000 g.

The solvent extraction flowsheet has been used to prepare sols, in the laboratory, from aqueous thorium nitrate containing up to 68 mole % uranyl nitrate. Sols having compositions (Th/U mole ratios 3 to 4) that are currently of interest in the preparation of reactor fuels have been made in engineering studies at the rate of 1 kg/hr. In addition, the complete process has been demonstrated, on a laboratory scale, by the preparation of gram quantities of ThO₂-UO₂ ceramic spheres containing 17 to 26 mole % UO₂.

Sol-Gel Preparation of Thoria-Urania Microspheres Containing High Concentrations of Urania

A. B. Meservey and W. D. Bond

Since the urania content of thoria-uranium microspheres that are prepared by the basic process appeared to be limited to 10%,¹⁷ other sol-gel methods for preparing thoria-uranium microspheres containing all proportions of thoria and uranium were investigated. These included processes involving (1) the mixing of ThO_2 and UO_2 sols and (2) coprecipitation methods for sol preparation using thorium nitrate and either uranous or uranyl nitrate solutions.^{51,52} The first approach, which is preferred, has been used in the laboratory-scale preparation of a variety of ThO_2 - UO_2 fuel compositions of interest.

Sol-Gel Process via ThO_2 - UO_2 Sols

Two methods of preparing UO_2 - ThO_2 sols of high uranium content were investigated: coprecipitation (and subsequent peptization) of the hydrous oxides from nitrate solutions of thorium and U(IV), and simple mixing of UO_2 sols that had been prepared by the laboratory flowsheet for uranium sol preparation⁵³ (see the section on Uranium Sol-Gel Process) with ThO_2 sols that had been prepared by steam denitrated thoria. The coprecipitation approach was not studied extensively; a simple laboratory demonstration was made to show that sols having a Th/U atom ratio of 3 could be prepared and formed into microspheres. The latter were fired to a high-density product. Kilogram quantities of the sol were prepared by the mixed-sol approach; microspheres were formed and evaluated, and irradiation test specimens were prepared.

In the mixed-sol approach, the ability to satisfactorily control fuel composition was demonstrated by the preparation of 150-g quantities of thoria-uranium microspheres with different Th/U atom ratios and different uranium enrichments (Table 1). To obtain the various enrichments, a UO_2 sol prepared from 93.18% enriched uranium was mixed with a sol made from natural uranium. The mixed thoria-uranium sol

Table 1. Properties of Fired ThO₂-UO₂ Microspheres Prepared from Mixed ThO₂-UO₂ Sols

Diameter: 250-297 μ

Firing Conditions: Ar-4% H₂ to 650°C at 300°C/hr; CO₂ to 1100°C at 200°C/hr; Ar-4% H₂ at 1100°C for 4 hr

Prep. Code	Th/U Weight Ratio		Uranium Enrichment		Density		Surface Area (m ² /g)	C (ppm)	Gas Release to 1200°C in Vacuum (cm ³ /g)
	Desired	Measured	Desired (%)	Measured (%)	(g/cm ³)	% of Theoretical			
OL-2	0.3333	0.3337	43.5	43.3	10.34	96.5	0.004	<20	0.02
OL-3	1.000	1.005	65.3	65.04	10.31	98.3	0.006	30	0.01
OL-4	1.857	1.886	93.18	--	10.08	97.5	0.005	--	0.011

was formed into gel microspheres under standard operating conditions. About 40 to 60% of these microspheres were in the desired 210- to 297- μ -diam range (after firing) and were of excellent quality; they were characterized by high densities and low carbon contents. The process was further demonstrated by the preparation of $\text{ThO}_2\text{-UO}_2$ sols and fired microspheres having Th/U atom ratios of 0.05 and 19, respectively.

Kilogram quantities of $\text{ThO}_2\text{-UO}_2$ microspheres having Th/U atom ratios of 4.8 and 3.4 were prepared by using highly enriched urania sol; these microspheres, after being coated with pyrolytic carbon, were used in irradiation tests in the Dragon reactor.⁵⁴ The spheres were characterized by high density, high crush resistances, and essentially "geometric" surface areas (Table 2). X-ray diffraction measurements showed that solid solution was achieved. The spheres produced by the 1400°C firing in H_2 were amber-colored and transparent, an effect that was not produced in the 1100°C firings in Ar-4% H_2 . Photomicrographs of typical metallographic sections of the 1400°C-fired spheres are shown in Fig. 8.

A number of interesting color effects were noted throughout the course of the firings. After the 1100°C firing, approximately equal number of pale green microspheres, all nontransparent, were obtained. The density was 97 to 98% of theoretical; the O/U atom ratio was <2.006. It was decided to refire the spheres in pure hydrogen in the event that the colors were caused by minor variations in the O/U atom ratio or the degree of solid solution among the individual spheres. After being fired to 1400°C in hydrogen, all of the spheres were converted to an amber-colored transparent type. These color effects have also been noted when kilogram quantities of 300- μ -diam $\text{ThO}_2\text{-UO}_2$ microspheres having Th/U atom ratios of 9 and 3 were fired.

Sol-Gel Process via $\text{ThO}_2\text{-UO}_3$ Sols

A coprecipitation method was developed for the preparation of $\text{ThO}_2\text{-UO}_3$ sols and was demonstrated in the laboratory through the final calcination to obtain dense $\text{ThO}_2\text{-UO}_2$ microspheres having a Th/U atom ratio of 3.⁵¹ Other precipitation

Table 2. Analyses of Fired $\text{UO}_2\text{-ThO}_2$ Microspheres (97.6% Enriched Uranium)

	Sample Number ^a		
	3371-78-1400 ^b	3371-80-1400	3371-82-1400
Firing Procedure: First Firing: Ar-4% H_2 at 300°C/hr to 850°C; CO_2 at 200°C/hr to 1100°C; hold 1.25 hr at 1100°C and reduce for 2 hr in Ar-4% H_2 at 1100°C; cool to 25°C in Ar.			
Second Firing: The 210-297 μ fraction from the first firing was fired to 1400°C and reduced 4 hr in H_2 ; cooled to 25°C in Ar.			
Sol Preparation Number	47-27-97	47-27-97	47-49A-97
Th/U Atom Ratio	3.41	3.41	4.79
U, %	10.95	10.95	8.18
Th, %	37.3	37.3	39.2
Hg Porosimetry:			
Density, g/cc	10.13	10.17	10.11
Density, % theoretical	99.3	99.7	99.6
Porosity, %	<1	<1	<1
Resistance to Crushing, g	1152	1008	907
Surface Area, ^c m^2/g	0.004	0.003	0.004
X-Ray Crystallite Size, A	1537	1280	1348
Lattice Parameters	5.5679	5.5680	5.5679
Carbon, ppm	<10	<10	<10
Aluminum, ppm	100	110	110
Gas Release to 1200°C in Vacuum:			
Total vol, cc/g	0.011	0.007	0.007
Composition, vol %			
H_2	91.4	68.8	81.1
H_2O	0.69	5.24	2.16
$\text{N}_2 + \text{CO}$	7.92	13.4	16.2
Ar	--	0.26	0.27
CO_2	--	12.0	0.27
O_2	--	0.26	--

^aAll analyses on 1400°C-fired material.

^bContained some "cherry-pitted" spheres.

^cCalculated geometric surface area of 210- to 297- μ -diam spheres is $2.0\text{-}2.8 \times 10^{-3} \text{ m}^2/\text{g}$.

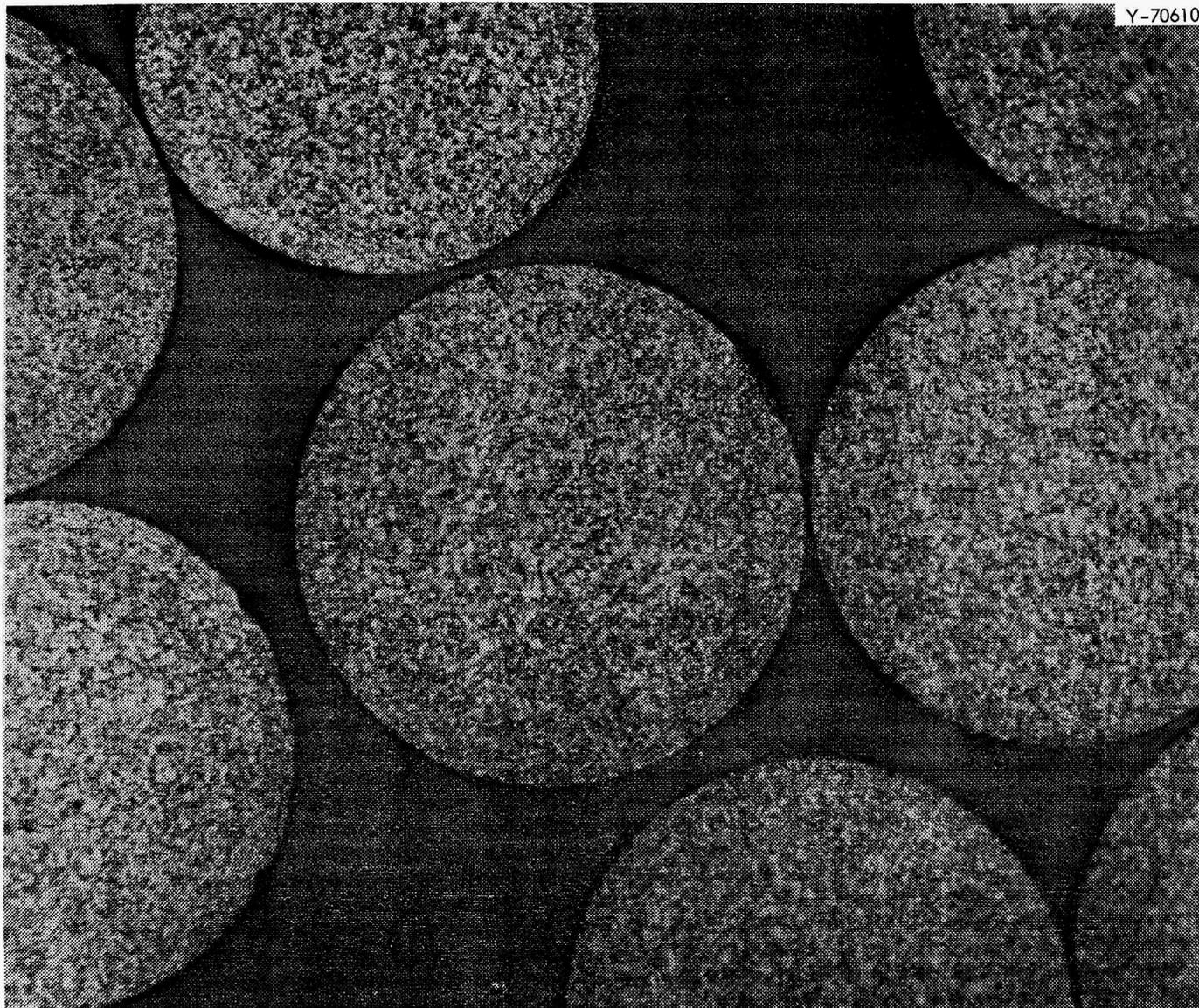


Fig. 8. Metallographic Sections of Sol-Gel $\text{ThO}_2\text{-UO}_2$
Preparation 3371-82-1400, etched with $\text{H}_3\text{PO}_4\text{-HF}$; grain structure
is visible.

approaches were attempted, including: (1) peptization of thorium hydroxide precipitates with uranyl nitrate, and (2) addition of UO_3 to ThO_2 sols that had been prepared from precipitated thorium hydroxide. Although sols could be readily formed by these methods, the NO_3^- /metal ratios of the sols were higher than those obtained by the coprecipitation method, and difficulty was encountered in forming gel microspheres by the usual techniques.

The coprecipitation method consists in coprecipitating the hydrous oxides in excess ammonia at $80 \pm 5^\circ\text{C}$ by a "reverse strike" procedure, washing the hydrous oxide filter cake until it is free of nitrate, boiling the aqueous slurry of the filter cake to remove residual ammonia, and then dispersing to sol with nitric acid. In a typical laboratory-scale preparation of sol (0.5-mole batches of the mixed oxides), a $0.5 \text{ M } \text{UO}_2(\text{NO}_3)_2\text{-Th}(\text{NO}_3)_4$ solution was added at a nearly constant rate, over a 20-min period, to a 75% excess of $3 \text{ M } \text{NH}_4\text{OH}$; the precipitation temperature was maintained at $80 \pm 5^\circ\text{C}$. The precipitate was then washed essentially free of nitrate, using ten filter cake volumes of about $0.08 \text{ M } \text{NH}_4\text{OH}$ at $80 \pm 5^\circ\text{C}$. The washing procedure reduces the $\text{NO}_3^-/(\text{Th} + \text{U})$ mole ratio to about 0.003; the $\text{NH}_4^+ / (\text{Th} + \text{U})$ mole ratio is 0.05. The concentration of the remaining NH_4^+ is reduced to 10 to 30 ppm by boiling an aqueous slurry of the filter cake until the pH of the evolved steam is decreased from its initial value of 9 to 10 to about 6. X-ray measurements indicate that the crystallite size of the hydrous oxides is $<30 \text{ \AA}$.

A three-step process is used in dispersing the hydrous oxides to a sol in order to attain NO_3^- /metal mole ratios that are suitable for sphere forming:

1. One-third of the hydroxide slurry is boiled with sufficient nitric acid to give a NO_3^- /metal mole ratio of 0.40, and a clear, red sol quickly forms.
2. Another one-third of the slurry is added to the red sol and boiled for about 20 min; this treatment peptizes all of the added hydroxides and provides a NO_3^- /metal mole ratio of 0.20.
3. The remaining slurry is then added, and boiling is continued at reflux temperature for about 8 hr or until the sol attains a clear, dark red color.

The final $\text{NO}_3^-/(\text{Th} + \text{U})$ mole ratio of the sol is 0.13 to 0.14. The sol is then concentrated by evaporation to 1.5 M (Th + U). X-ray measurements indicate that the crystallite size of the dispersed particles of the sol is 40 to 45 Å.

The sol was readily formed into microspheres by the standard method (using 2-ethyl-1-hexanol containing 1.1% H_2O , 0.3% Span 80, and 0.5% Ethomeen S/15). The gel spheres were fired in air to 1200°C and then contacted for 4 hr with Ar—4% H_2 to yield a reduced product of near-theoretical density. Temperature rise rates greater than 20°C/hr caused cracking during the heating to 300°C; however, the cracking could be entirely eliminated by using a slower rise rate. Fired spheres of 177 to 250 μ in diameter resisted crushing loads of about 1700 g.

Sol-Gel Preparation of Porous Thoria from ThO_2 -C Sols

K. J. Notz and W. D. Bond

Laboratory studies of the preparation of ThO_2 shards and microspheres of controlled porosity up to about 50% have been made⁵⁵ by incorporating carbon black in ThO_2 sols, forming ThO_2 -C gel microspheres or shards, and subsequently burning out the carbon to leave voids. The primary variables are the C/ ThO_2 mole ratio and the firing cycle. The best control and the maximum porosity for a given carbon content were obtained when the mixed gel was first densified at about 1400°C in argon and then the carbon was burned out in air at 800°C. The amount of porosity introduced by this method is nearly equal to the volume of the carbon incorporated in the gel. In the case of shards, this method gave porosities of up to 64% and pore sizes of 120 to 2000 Å. The porosities obtained with microspheres were about 8% higher than shards at a given C/ ThO_2 mole ratio.

URANIA SOL-GEL PROCESS

The development of a sol-gel process for the preparation of pure urania microspheres was prompted by the potential use of the latter as fuel for thermal reactors

and as a fast-reactor fuel (containing plutonia), in which urania would be the bulk constituent. More than 100 kg of urania microspheres have been prepared in laboratory- and engineering-scale equipment; also, kilogram quantities of urania sols have been mixed with plutonia sol and used to form urania-plutonia microspheres that are suitable for irradiation testing as fast-reactor fuels.

Chemical development of the urania sol-gel process proceeded in two phases. The first comprised the development of a laboratory process for preparing aqueous urania sols by a precipitation-peptization method and the production of kilogram quantities of urania microspheres, some containing highly enriched urania.^{53,56} The second phase consisted in modifying the laboratory process to make it more amenable to engineering scaleup and developing a solvent extraction process for large-scale production of urania sol.^{56,57} Laboratory studies included the adaptation of the laboratory method for preparing urania sol to the preparation of urania-zirconia sols, work on the preparation of U(IV) solutions by catalytic reduction with hydrogen (a necessary first step in urania sol preparation), characterization studies of urania sols and gels, and an investigation of drying and firing conditions necessary for the production of UO_2 products of near-theoretical density and low carbon content.

Urania and Urania-Zirconia Sol Preparation by Precipitation-Peptization

J. P. McBride, K. H. McCorkle, W. L. Pattison

Laboratory Preparation of Urania Sol

The laboratory preparation of a urania sol (see Fig. 9)⁵³ begins with the preparation of a uranous nitrate solution by the catalytic reduction, with hydrogen, of a uranyl nitrate solution containing excess nitric acid. The solution is filtered to remove the catalyst. Then formic acid is added to the filtered solution, and the hydrous oxide is formed by precipitating U(IV) with ammonium hydroxide containing hydrazine. The precipitate is collected by filtration and washed, in place, to remove excess electrolytes. The washed filter cake is then heated at 60 to 65°C to produce a fluid, stable

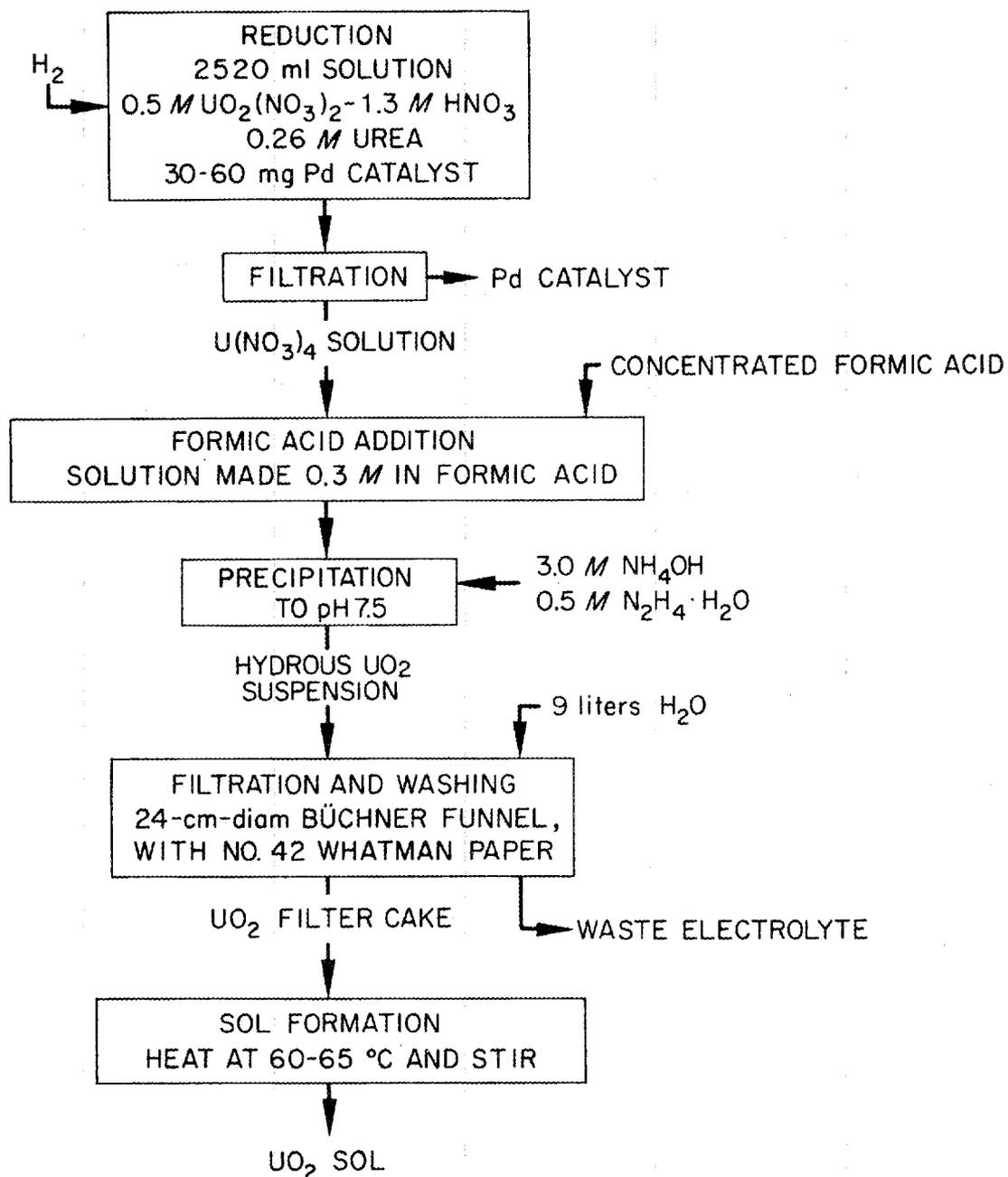


Fig. 9. Flowsheet for the Laboratory Preparation of Urania Sol.

sol. Precautions are taken to protect the material from air oxidation by the use of a blanket gas (argon) during all stages of the process. Sol concentrations of 1.2 to 1.6 M U can be achieved (Table 3).⁵⁶

In order that the washed filter cake can be liquefied to a sol by heating, ammonium hydroxide must be added in the precipitation step until a pH of 7 to 8 is achieved. The addition of formic acid to the U(IV) nitrate solution is necessary in order to maintain a high U(IV) content (more than 85% of the total uranium) in the precipitate and the subsequent sol. In the absence of formic acid, the U(IV) content of the hydrous oxide would be only about 80% of the total uranium, compared with more than 99% for the original U(IV) nitrate solution. In addition, formic acid simplifies pH control in the precipitation step and accelerates the washing of the filter cake.

Table 3. Urania Sols Prepared by the Laboratory Preparation Method

Specific Gravity (g/cc)	Uranium Concentration (M)	U(IV) Content (% of U)	NO ₃ ⁻ /U Ratio	HCOO ⁻ /U Ratio
1.317	1.23	87	0.13	0.44
1.319	1.27	85	0.07	0.38
1.369	1.48	86		0.45
1.373	1.49	84	0.14	0.45
1.404	1.61	86	0.11	0.31
1.405	1.62	87	0.11	

Engineering-Scale Flowsheet for Urania Sol Preparation

The development of a process for the continuous production of kilogram quantities of urania sol (enriched in ²³⁵U) in criticality-proof equipment required modification of the laboratory process. The filtering and washing steps in the laboratory

process presented criticality and handling problems and made the production of sols having a prescribed NO_3^-/U ratio difficult. Hence, attention was directed toward the development of a process in which the hydrous oxide was precipitated, washed completely free of electrolyte by decantation, and peptized by the addition of a controlled amount of peptizing electrolyte.

The current flowsheet for the engineering-scale preparation of urania sol is shown in Fig. 10. A U(IV) solution is prepared by the catalytic reduction, with hydrogen, of a $0.5 \text{ M } \text{UO}_2^{2+}$ solution that is 1 M in NO_3^- and 0.25 M in HCOO^- . After reduction and catalyst removal, concentrated formic acid is added to the resulting solution to provide a HCOO^-/U mole ratio of 0.6 to 1.0 (The adjustment is necessary because part of the original HCOO^- is destroyed in the reduction step). The hydrous oxide is then precipitated by the addition of $3.5 \text{ M } \text{NH}_4\text{OH}$ or $3.0 \text{ M } \text{NH}_4\text{OH}-0.5 \text{ M } \text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ to pH 9.0. The resulting precipitate is washed free of electrolyte by decantation by using either H_2O or $0.01 \text{ M } \text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$. The washed precipitate is resuspended, HNO_3 and HCOOH are added, and the suspension is stirred at 60 to 63°C until peptized. The use of hydrazine in the precipitation and washing steps and the addition of formic and nitric acid in the peptization step, apparently controls aging mechanisms in the precipitate and increase the sol yields.⁵⁷

In general, although the sols prepared by the engineering flowsheet are fluid when prepared, they are not as stable or as consistent in their properties as those prepared by the laboratory flowsheet. More recent studies suggest that precipitation at pH 7.5, washing with $0.01 \text{ M } \text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$, and peptization with HNO_3 alone will yield a sol that more nearly resembles those routinely prepared by the laboratory method. The hydrazine wash removes all the HNO_3 from the hydrous oxide precipitate but leaves a residual HCOOH content similar to that observed in the sols prepared in the laboratory.

Urania-Zirconia Sol Preparation

The laboratory method for preparing urania sol by precipitation-peptization was adapted to the preparation of urania-zirconia sols. Zirconyl nitrate or zirconia

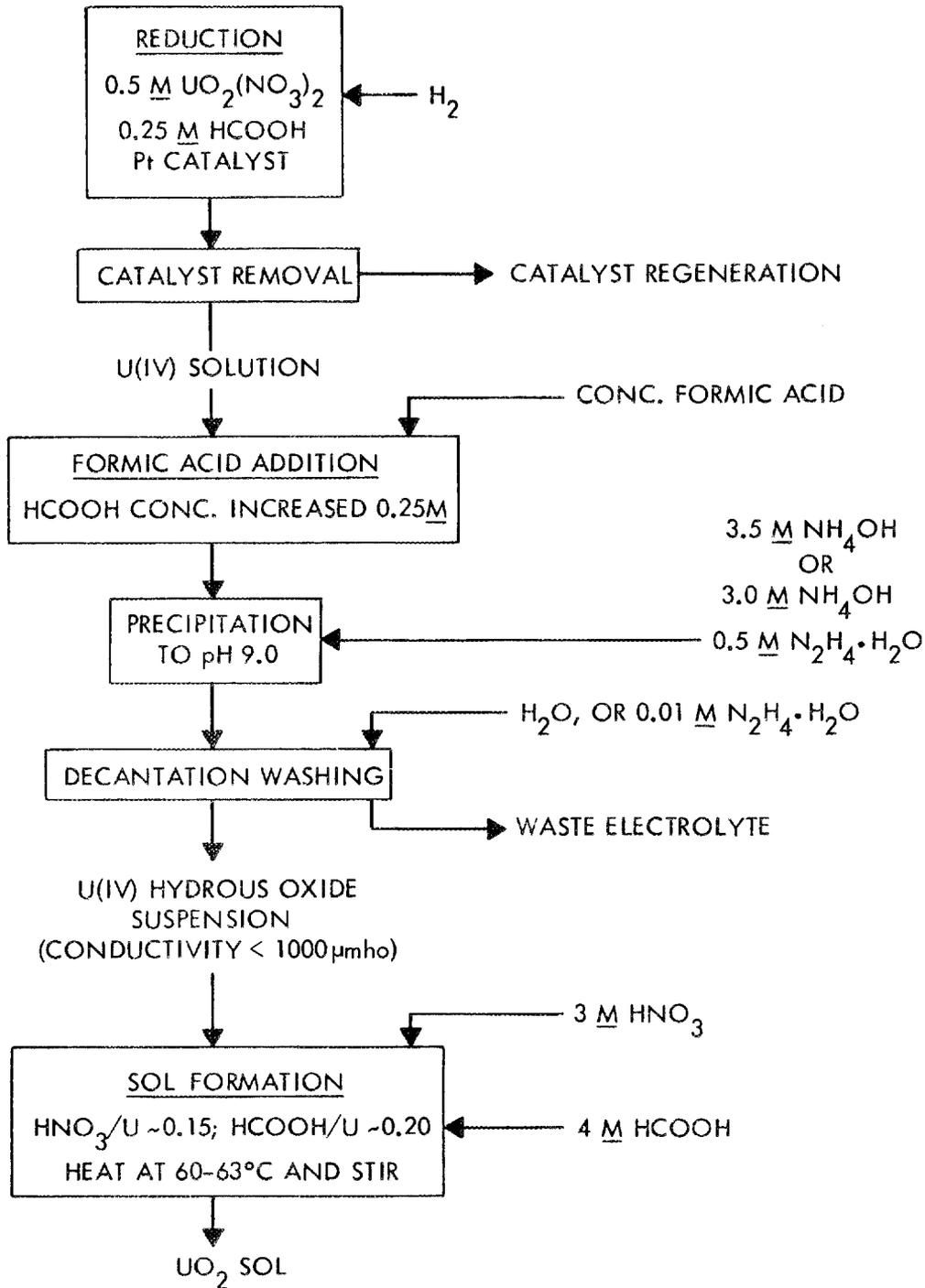


Fig. 10. Flowsheet for the Engineering-Scale Preparation of Urania Sol.

sol was added to the U(IV) solution (Zr-U atom ratio = 0.3) prior to precipitation; then the hydrous oxides were coprecipitated, collected by filtration, and washed in place. The moist filter cake was heated at 60 to 63°C in argon to form the sol. When zirconia sol was used as the starting material, it was prepared by titrating a zirconyl nitrate solution to a pH of 1.5 to 1.7 with ammonium hydroxide and boiling to produce an opalescent ~ 0.5 M zirconia sol.

Table 4 shows the properties of urania-zirconia sols that were prepared by the coprecipitation technique. In preparing NU-11-3Z, the uranium in a 0.5 M $\text{UO}_2(\text{NO}_3)_2$ —0.14 M $\text{ZrO}(\text{NO}_3)_2$ solution that was 1.3 M in excess HNO_3 and contained a small amount of urea was reduced catalytically with hydrogen. Then the hydrous oxides were coprecipitated. In the preparation of NU-13-3Z, the uranium in a 0.5 M uranyl nitrate solution that was 1.3 M in excess HNO_3 was reduced with hydrogen, as in the preparation of a pure UO_2 sol. Zirconia sol was added prior to precipitation. NU-27-3Z and NU-28-3Z were prepared similarly except that formic acid was added to the solution prior to precipitation of the mixed hydrous oxides to provide HCOO^-/U mole ratios of 0.6 and 0.8, respectively. All the urania-zirconia sols retained their fluidity longer than pure UO_2 sols; no instability was observed after storage for more than 2.5 years under an inert atmosphere.

Table 4. Analyses of Urania-Zirconia Sols Prepared by Coprecipitation

Preparation	Specific Gravity (g/cc)	U Conc. (M)	Zr Conc. (M)	U(IV) Content (% of U)	$\text{NO}_3^-/(\text{U}+\text{Zr})$ Mole Ratio	$\text{HCOO}^-/(\text{U}+\text{Zr})$ Mole Ratio
NU-11-3Z	1.262	0.89	0.20	72 ^a	0.20	-
NU-13-3Z	1.242	0.92	0.27	82	0.10	-
NU-27-3Z	1.204	0.67	0.22	85	0.16	0.36
NU-28-3Z	1.244	0.82	0.27	91	0.11	0.49

^aPossible oxidation during filtration.

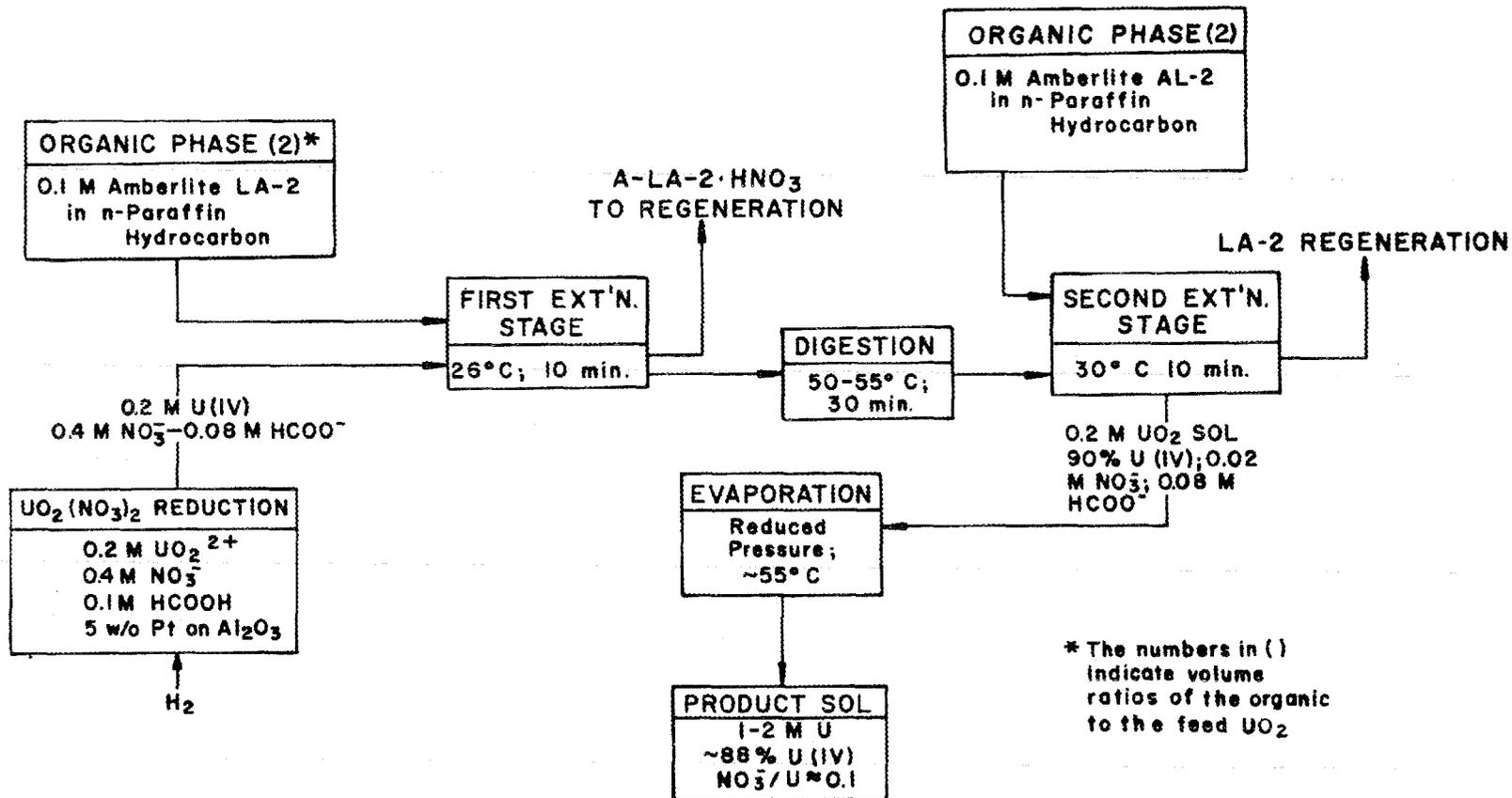
Portions of NU-13-3Z and NU-28-3Z were formed into gel microspheres in the usual manner by dispersing the sols into drops in a drying solvent and firing the gelled spheres in a hydrogen atmosphere. After a 4-hr firing at 1150°C, the NU-13-3Z product had a density of 10.5 g/cc and a specific surface area of 0.007 m²/g. The 149- to 177- μ -diam fraction resisted a crushing load of 1490 g. Microspheres formed from the NU-28-3Z sol had a density of only 8 g/cc after firing 4 hr at 1200°C. The 177- to 149- μ fraction resisted a crushing load of 921 g; refiring at 1400°C in hydrogen increased this crushing resistance to >2000 g.

Urania Sol Preparation by Solvent Extraction

L. E. Morse

A solvent extraction process analogous to that developed for the preparation of thorium-urania sols was developed for the preparation of urania sols. The process involves the extraction of NO₃⁻ from an aqueous U(IV) solution, containing less than the stoichiometric amount of NO₃⁻ and HCOO⁻, into a solution of a long-chain secondary amine (Amberlite LA-2, *n*-lauryltrialkylmethyl amine) in a *n*-paraffin hydrocarbon (NPH), *n*-dodecane, or its commercial equivalent. The extraction is carried out in two extraction stages. Approximately half of the extracted NO₃⁻ is removed in the first stage; the remainder is removed in the second. In the interval between extractions, the aqueous phase is digested at an elevated temperature. The extraction of the NO₃⁻ causes the U(IV) to undergo progressive hydrolysis, which leads to the formation of a dilute sol. The dilute sol is then concentrated by evaporation at reduced pressure to a concentration that is suitable for microsphere formation. Precautions are taken to protect the uranium from oxidation by the use of a blanketing gas (argon) during all stages of the process.

A flowsheet for the process is shown in Fig. 11. A U(IV) solution is prepared by catalytically reducing, with hydrogen, the uranium in a 0.2 M UO₂²⁺-0.4 M NO₃⁻-0.1 M HCOO⁻ solution by using a platinized-alumina powder containing 5 wt % Pt. The time required to prepare 2500 to 2600 ml of the U(IV) solution



33

Fig. 11. Flowsheet for Urania Sol Preparation by Solvent Extraction with a Secondary Amine.

containing 1.5 g catalyst is about 2 hr. During the reduction, about 25% of the HCOO^- is lost such that the solution used in the sol preparation is 0.2 M in total U (99% U(IV), 0.4 M in NO_3^- , and ~ 0.075 M in HCOO^-).

One volume of the U(IV) solution is added to two volumes of stirred 0.1 M Amberlite LA-2 in NPH diluent, and the phases are equilibrated for 10 min at 25 to 50°C. After separation, the aqueous phase is transferred to a digestion vessel and maintained at 50 to 55°C for 0.5 hr with stirring. The digested aqueous phase is then added to two volumes of stirred fresh organic and equilibrated for 10 min at 25 to 35°C. The separated dilute urania sol is removed and stored under argon. The composition of the aqueous sol at this point is approximately 0.2 M total U [88% U(IV)]—0.02 M NO_3^- —0.075 M HCOO^- . The residual NO_3^- concentration is governed by the total amine concentration and the prevailing equilibria, whereas HCOO^- does not extract under the conditions described. The entire extraction cycle is carried out in an inert atmosphere. When the extractions were made at temperature above ambient, the organic phase was preheated.

The dilute sol must be concentrated until it is about 1 M in total U in order to be useful for the preparation of microspheres. Fluid, stable sols having uranium concentrations of 1.3 to 1.5 M have been obtained in the laboratory.

Microsphere formation, drying, and firing were studied only to the extent necessary to show that acceptable urania microspheres could be made from a urania sol that had been prepared by solvent extraction. Briefly, microspheres were formed by injecting droplets of a concentrated urania sol into a column of 2-ethyl-1-hexanol containing the surfactants Ethomeen S/15 and Span 80. The microspheres were dried in steam and argon and then fired to dense UO_2 by heating to 1250°C in argon—4% H_2 . The microspheres had a density that was 98% of theoretical at 210 psi Hg, an O/U atom ratio of 2.006, and a carbon content of 0.09%.

Table 5 shows typical analyses obtained at various stages of the process.

The digestion step between the extractions is essential in order to avoid precipitation (which would occur if all the NO_3^- to be extracted were removed in one

Table 5. Process Analyses in the Preparation of UO_2 Microspheres

	Total U (M)	U(IV) (% of U)	moles/liter		moles/mole total U	
			NO_3^-	HCOO^-	NO_3^-	HCOO^-
UO_2^{2+} Solution	0.204	--	0.40	0.105	1.96	0.52
U(IV) Solution	0.204	>99.44	0.40	0.074	1.96	0.36
Dilute Sol	0.21	89.96	0.025	0.076	0.12	0.37
Concentrated Sol	1.39	88.18	0.17	0.51	0.12	0.37
	% U	O/U	% NO_3^-	% C	Hg Density (210 psi)	He Density
UO_2 Gel Microspheres Dried at 164°C	83.00	2.35	0.66	0.42	--	--
UO_2 Microspheres Calcined at 1250°C	88.10	2.006	--	0.091	10.75	11.0

or several stages at room temperature). In a two-stage process, it was convenient to extract the NO_3^- in approximately equal fractions such that a single amine concentration could be employed; however, it was possible to extract as much as 75% of the total NO_3^- in the first stage without causing precipitation. Sols have also been prepared from uranium solutions containing three and four moles of NO_3^- per mole of uranium (HCOO/U mole ratio ~ 0.5).

Preparation of U(IV) Solutions

W. L. Pattison and J. P. McBride

The U(IV) solutions used in urania sol preparation by the precipitation-peptization method were prepared by the catalytic reduction with hydrogen, of the uranium in $0.5 \text{ M } \text{UO}_2(\text{NO}_3)_2 - 0.25 \text{ M } \text{HCOOH}$ solutions. In the laboratory, the reductions are carried out in a stirred, baffled flask, using finely divided palladium-on-thoria or platinum-on-alumina catalysts, and hydrogen is added through a sintered-glass gas diffuser tube. Progress of the reduction was followed by measuring the redox potential with a platinum electrode and a silver-silver chloride reference electrode.

Figure 12 shows the curve of the potential obtained, using a platinum electrode and a silver-silver chloride reference electrode, during the preparation of a U(IV) solution of the composition $0.5 \text{ M } \text{U} - 1.0 \text{ M } \text{NO}_3^- - 0.25 \text{ M } \text{HCOOH}$. A sharp break in the curve is observed between 96 and 100% U(IV). If a saturated calomel reference electrode had been used, the potentials would have been more negative by about 44 mv. The presence of hydrogen has a marked effect on the potential observed at the platinum electrode. The potentials shown in Fig. 12 were made with hydrogen flowing into the solution at 1 atm (to keep the solution saturated with hydrogen). When hydrogen is removed and an argon blanket is substituted, the potential observed in a 100% U(IV) solution is about -100 mv. Measurements of potential were made repeatedly and reproducibly, to follow the progress of the reduction, during the laboratory-scale preparation of uranous nitrate-formate solutions; they were also used in estimating U(IV) concentrations in solutions that were prepared in stainless steel equipment.

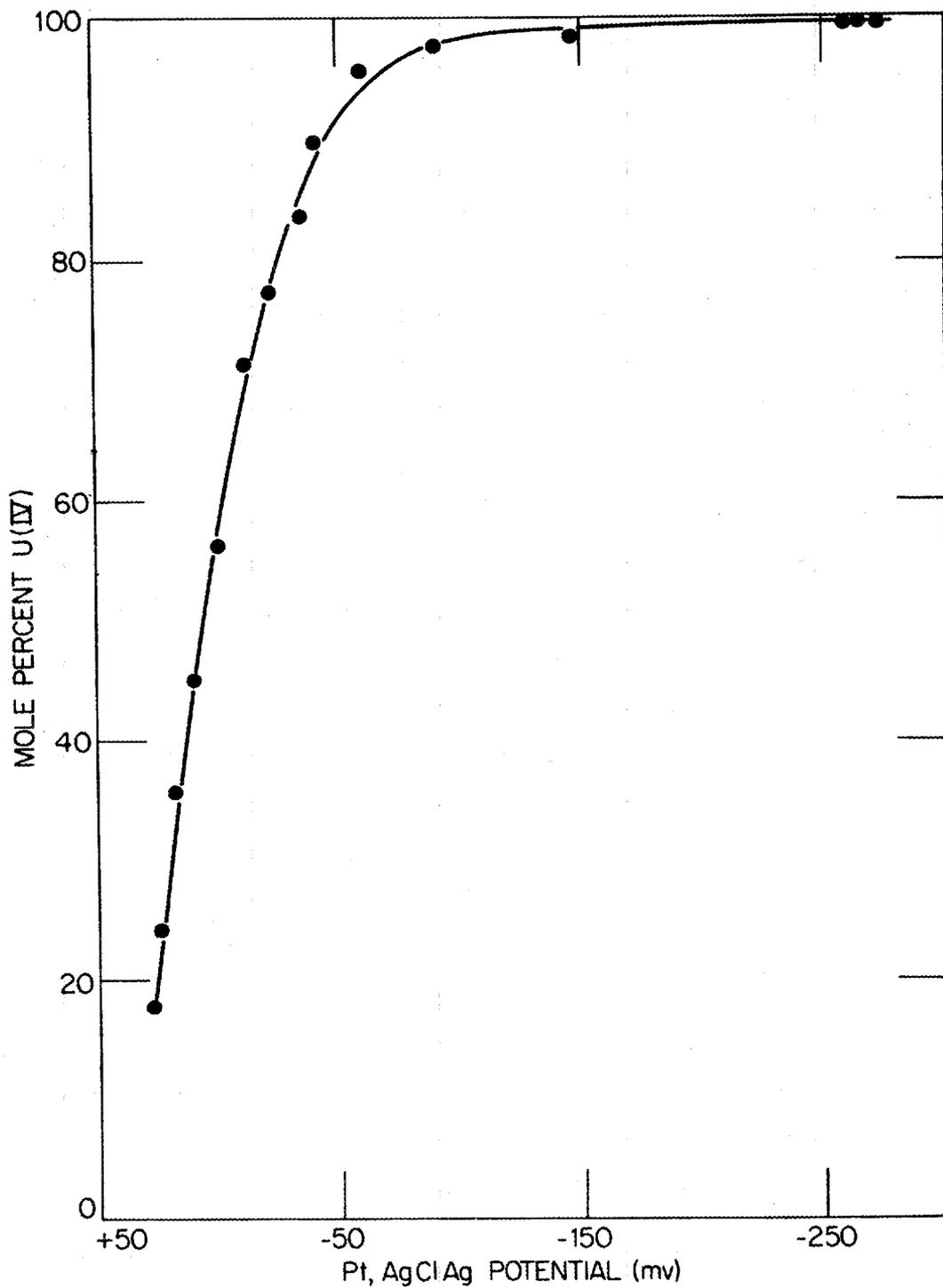


Fig. 12. Redox Potentials Under Hydrogen at 1 atm of Pressure During the Preparation of a U(IV) Solution from a Solution of the Composition $0.5 \text{ M } \text{UO}_2^{2+} - 1.0 \text{ M } \text{NO}_3^- - 0.25 \text{ M } \text{HCOOH}$.

Three slurry catalysts were evaluated, by means of the laboratory reduction apparatus for possible use in the preparation of U(IV) solutions: Adams Catalyst (PtO_2), platinized-alumina powder (5 wt % Pt), and the palladium-on-thoria powder (2 wt % Pd) used in the early developmental studies of the urania sol process.⁵³ Use of 2.58 g of the Adams Catalyst and 2.5 g of the platinized-alumina powder permitted complete reduction in 3 hr. When the palladium-on-thoria catalyst, which contained an amount of palladium equivalent to the amount of platinum in the platinized-alumina powder, was used, reduction required about 6 hr. All catalysts required settling overnight before the U(IV) solution could be decanted free of suspended catalyst. In view of the favorable results obtained with the platinized-alumina powder, further studies were made with this catalyst.

With both the palladium-on-thoria catalyst and the platinized-alumina powder, uranium reduction rates were linear with time, indicating a zero-order dependence on U(VI) concentration and suggesting that the transfer of hydrogen to the surface of the catalyst was probably rate-controlling under the conditions of the experiments. With the Adams Catalyst the rate was linear over most of the range, with a slight tailing-off near the end of the reduction. This was probably the result of flocculation of the catalyst and loss of catalyst surface. In other experiments, gross flocculation of the Adams Catalyst was found to occur during the reduction. Hydrogen consumption rate was also linear with time; however, the mole ratio of hydrogen consumed to uranium reduced (H_2/U) varied (using the platinized-alumina powder) from 1.0 to 1.4. Analyses of the reduced solution showed that only a negligible amount of NO_3^- had been lost from the system during reduction. No correlation was observed between the relative hydrogen consumption and the loss of formate. Presumably, the formate disappears by two processes: catalytic decomposition, and catalytic reduction to volatile species that are sparged from the system by the hydrogen not consumed in the reduction process.

The platinized-alumina powder used in the various reductions was recovered by filtration, and washed first with 1 to 2 M nitric acid and then with water. The washed powder was dried in air at $\sim 100^\circ\text{C}$ and reused. No significant loss in specific catalytic activity was observed.

Properties of Urania Sols and Gels

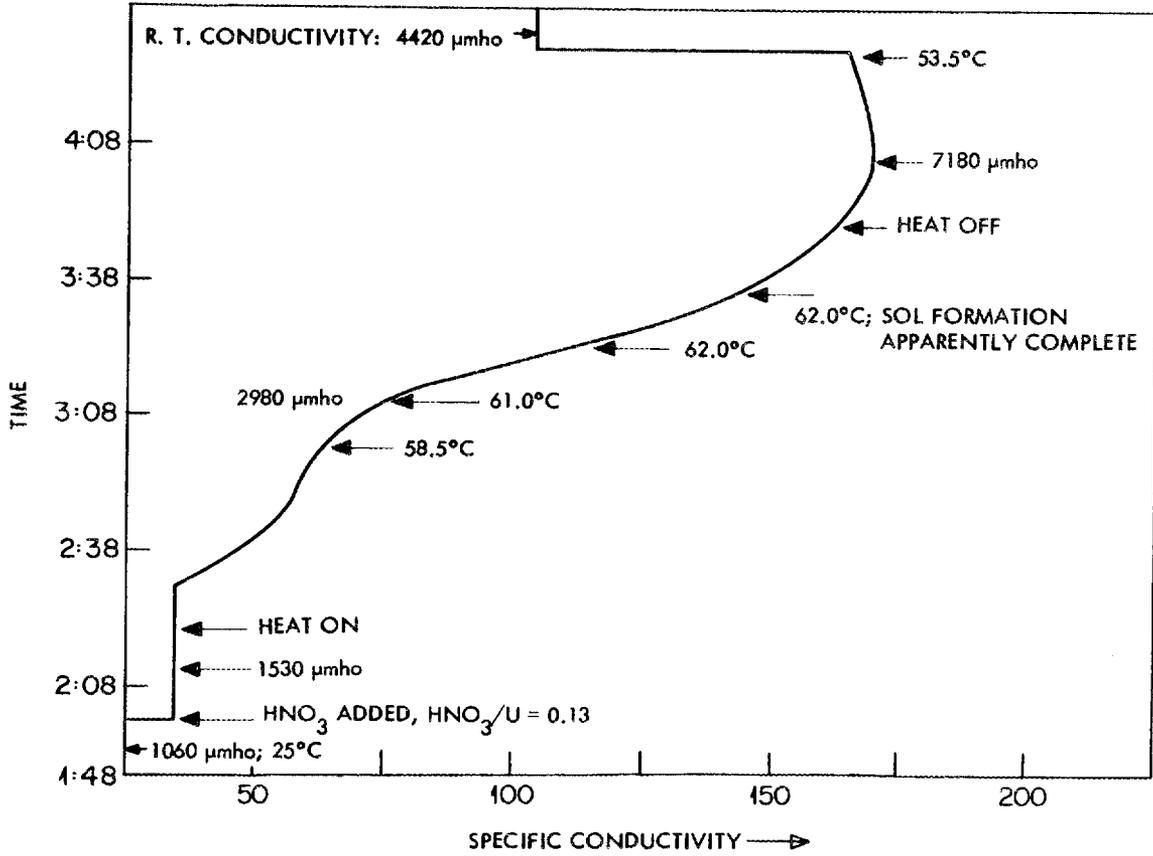
K. H. McCorkle, W. L. Pattison, and J. P. McBride

Urania sols produced by the laboratory flowsheet (see Fig. 9) are generally characterized by low viscosity and tend to thicken and sediment upon aging for several months. Urania sols prepared by the engineering flowsheet (see Fig. 6) show varying degrees of stability. While some have remained fluid as long as four months, many have thickened, gelled, or sedimented appreciably in times as short as four days. The most common behavior exhibited by these sols, particularly if their urania concentration exceeds 1 \underline{M} , has been thixotropy, with a setting time of several days. They become fluid when shaken vigorously, but re-gel after standing for 24 hr or longer.

In both of the preceding sol preparation methods, the sols are finally prepared by heating the precipitated urania to about 62°C for 1 hr or longer. Crystallization of the initially amorphous precipitate occurs during this step, causing loss of absorptive capacity for the electrolytes present. The rate of desorption of the electrolytes into the water solution surrounding the particles during recrystallization can be followed by measuring the conductivity of the solution, as shown in Fig. 13. Until the temperature rises to about 55 to 60°C, the increase in conductivity is due mainly to the increase in temperature; when the temperature exceeds 60°C, however, crystallization of the urania occurs rapidly, releasing adsorbed electrolyte. An electron micrograph of particles of a sol that was prepared by the laboratory method is presented in Fig. 14; Fig. 15 shows its electron diffraction pattern, which indicates that the particles consist of crystalline UO_2 .⁵⁸

The size of the crystallites that are produced in sols prepared by the engineering flowsheet depends on precipitation conditions. When the precipitating reagent was 3.5 \underline{M} NH_4OH , the crystallites of urania in the sol were 62 to 84 Å in diameter, regardless of whether hydrazine (0.02 \underline{M}) was used in the wash water. When the hydrazine was incorporated in the precipitating reagent (3.0 \underline{M} NH_4OH —0.5 \underline{M} N_2H_4), the crystallites had diameters of 90 to 96 Å. An aggregate size of about

ORNL Dwg. 66-12344



FORMING DATA ON SOL UNR-9-N (10/12/66)

Fig. 13. Typical Conductivity Curve Obtained During the Formation of a Urania Sol.

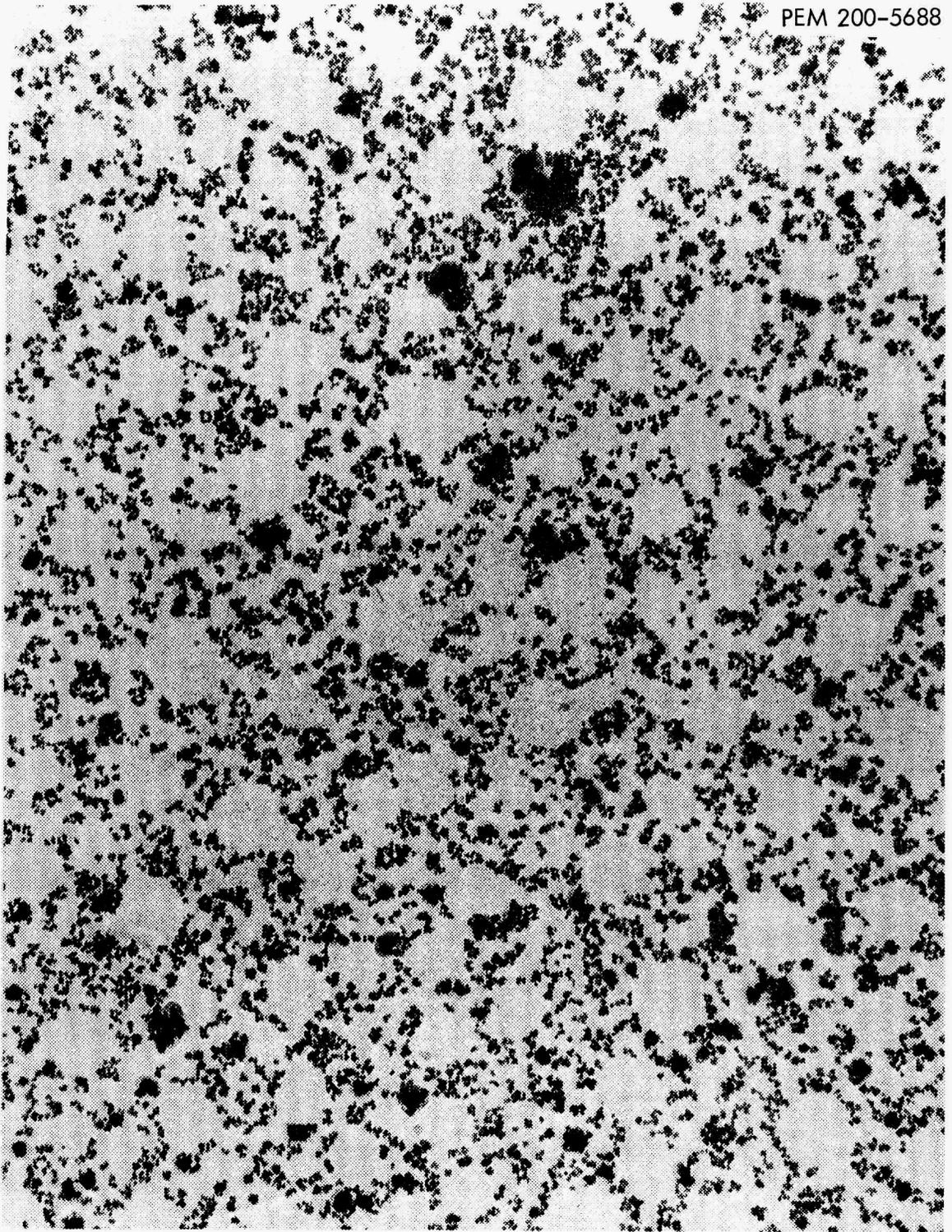


Fig. 14. Electron Micrograph of Urania Sol Prepared by Laboratory Method.

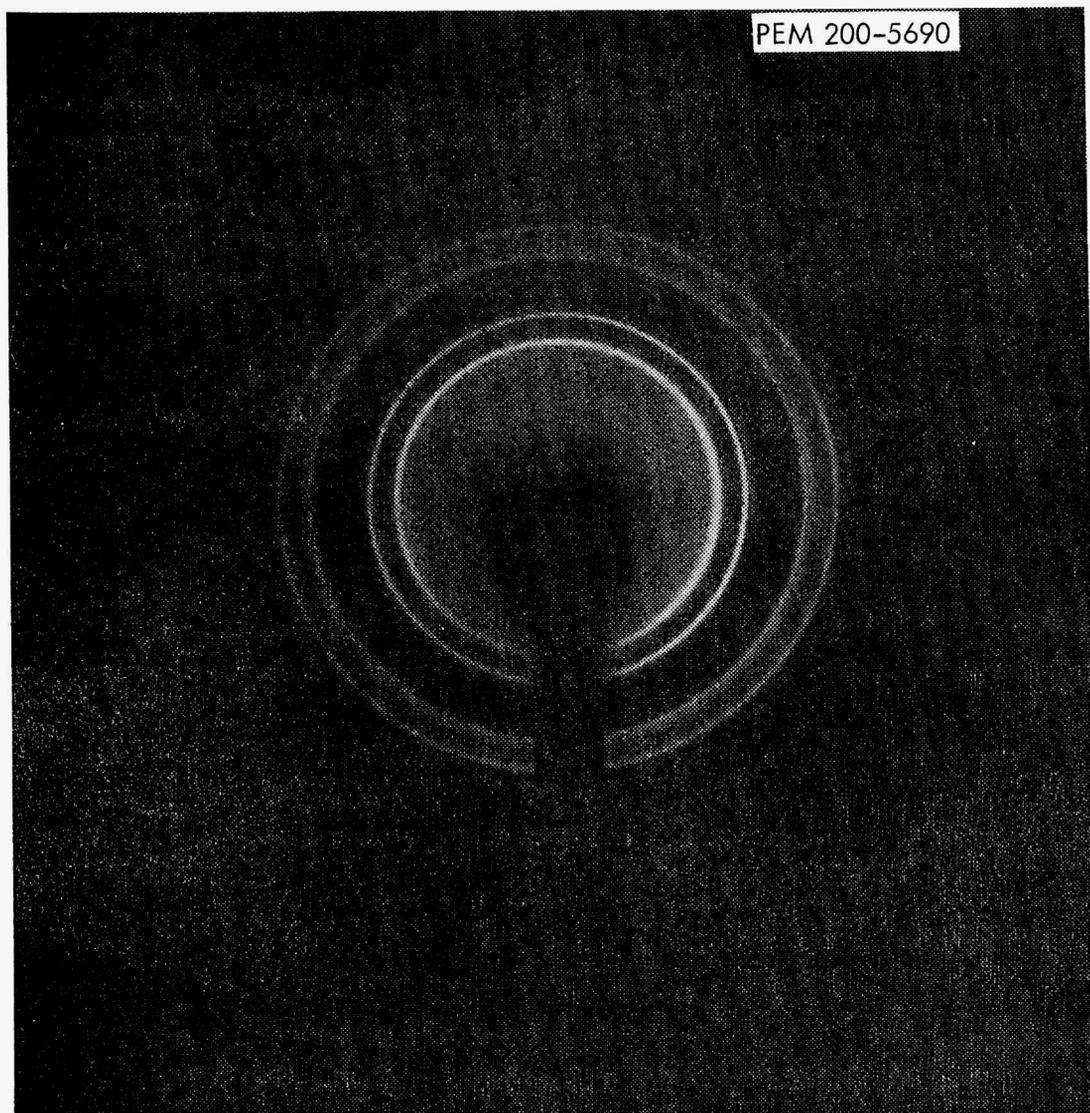


Fig. 15. Electron Diffraction Pattern of Urania Sol Prepared by Laboratory Method.

800 Å was calculated from the turbidities or apparent absorption spectra of diluted sols.⁵⁸

The crystallite size of colloidal urania does not correlate with the pore size of the dried urania gel, as measured by N₂ condensation. This behavior is in contrast with that of crystalline colloidal thoria, for which the pore diameter is approximately one-third of the crystallite size. Table 6 shows a comparison of the average pore size with the crystallite size of urania gels.

Table 6. Pore and Crystallite Sizes of Urania Gels

Preparation	Crystallite Diameter (Å)	Pore Diameter (Å)	Pore/Crystallite Diameter Ratio
N1-110	69	76	1.1
N2-110	67	56	0.84
E1-110	52	38	0.73
E1-170	57	33	0.58

The crystallite size of urania gel does not reliably correspond with the BET area of the gel, as the pore size data suggest. However, the discrepancies in BET areas do not correspond with the discrepancies in the porosity data. Table 7 shows a comparison of crystallite size, measured BET area, and the area calculated from the crystallite size by using the following equation, which was obeyed by crystalline thoria gels:

$$A = 6/\rho D ,$$

where A = area, ρ = density, and D = diameter of the crystallite.

Table 7. Crystallite Size and BET Area of Urania Gels

Preparation	Crystallite Diameter (A)	Calculated Area (m ² /g)	BET Area (m ² /g)
N1-27	63	87	107
N1-110	69	79	50.1
N2-110	67	81	81.6
E1-110	52	105	60.4-70.1
E2-170	57	96	64.8-82.9

Not all the discrepancies are necessarily caused by variation in the gel themselves. Replicate BET area measurements of the gel sample E2-170 gave, respectively: 64.8, 82.9, 66.7, 78.9, and 80.4 m²/g. For thoria gels, replicate BET area measurements generally agree within 5%.

The stability and viscosity of urania sols possess only approximate quantitative relationship to the electrolyte composition of the sols. Conductivities of the most stable sols range from 2500 to 10,000 micromhos/cm; the apparent pH range is 1.7 to 2.5. About half of this conductivity is due to free HNO₃; the origin of the other half is obscure. Analyses of sol centrifugates indicate that it does not stem from sol particle conductivity and that the amounts of dissolved uranium salts present are insufficient to account for the discrepancy. Attempts to explain the discrepancy by assuming that the Donnan EMF falsifies the pH, as is true in the case of thoria, were not confirmed experimentally by the comparison of the pH values of sols and centrifugates.

Comparisons of the pH's and conductivities of sols diluted 1024-fold confirm the presence of a neutral, conducting electrolyte even at the highest dilutions. These data further imply that the neutral, dissolved species is either progressively ionized as a function of dilution or is progressively desorbed along with the nitric acid, from the surfaces of the sol particles as dilution increases.

It seems likely that at least part of the difficulty in relating sol stability and viscosity with electrolyte content lies in the experimental inaccessibility and in the sensitivity to air of the surface oxidation states of colloidal urania particles. For sols prepared by either type of precipitation-peptization method (laboratory or engineering flowsheet), the amount of overall urania oxidation may vary between 9 and 17% U(VI) without having a consistent effect upon the stability or viscosity of the sol. If an additional atmospheric oxidation of 1% occurs in sols having a uranium concentration higher than about 0.8 M , an increase in viscosity on the order of tens of centipoises occurs. If an atmospheric oxidation of 3 to 4% occurs, the sol is converted to a gel. Oxidation prior to forming the urania crystals in the sol is not necessarily a surface phenomenon, but oxidation occurring after crystallization probably takes place on the surface, radically altering the flocculative state.

Viscometric measurements of sols that have been prepared under conditions defined in the laboratory flowsheet and then diluted to solids volume fractions of 0.033 to 0.004 imply the presence of anisometric flocs. The reduced viscosity was 1.32 ± 1.7 over the concentration range. If the shape of the particle is prolate spheroidal, the axial ratio of the flocs should be 10, as predicted by the method of Simha.²⁵ The determination of the floc shape is approximate because the prolate spheroid shape is assumed and because the urania sols have exhibited thixotropy and pseudoplasticity at solids volume fractions as low as 0.008. Rheopectic behavior has been observed at low shear (7.6 sec^{-1}) in a urania sol at a solids volume fraction of 0.012 and a NO_3^-/U mole ratio of 0.05. The approximate ranges of viscosities of the sols depend more on the method of preparation and the recent shear history than on specific composition variables. The viscosities of the sols prepared by the laboratory flowsheet were 0.9 to 1.5 centipoises at uranium concentrations of up to 1.3 M (0.033 solids volume fraction). The viscosities of sols prepared by conditions of the engineering flowsheet were 0.9 to 1.5 centipoises at uranium concentrations as low as about 0.3 to 0.5 M , depending on the recent shear history. At uranium concentration of 0.6 to 0.8 M , viscosities of the latter sols were 10 to 100 centipoises; at 1 M they frequently gelled.

Drying and Firing of Urania Gels

W. D. Bond

Drying and firing studies of sol-gel UO_2 have been made in a variety of atmospheres to establish conditions that will yield products having low carbon contents (<100 ppm) and near-theoretical densities (>95%). Products having the desired properties were obtained by drying and firing the spheres to 1000°C in an H_2O -0.2 vol % Ar atmosphere. Final reduction was accomplished in an Ar-4% H_2 atmosphere for 2 to 4 hr. Other atmospheres tested included CO_2 , argon, Ar-4% H_2 , and O_2 ; however, none of these gave results that were reproducible with respect to density and carbon removal when different gel preparations were used. Differential thermal analysis (DTA), thermogravimetric analysis (TGA), and measurements of shrinkage rate, crystallite growth, and surface area were used as guides in studying the effect of gaseous atmospheres on sintering and carbon removal.^{53,59,60} The source of the carbon is the drying solvent used in the microsphere forming column. The sorbed organic materials must be removed prior to sintering to consistently achieve a high-density product. If these materials are not removed, they are often trapped within the pores, giving a product that has a high carbon content and a density less than 95% of theoretical.

The formic acid that is present in the UO_2 sol (and also in the gel microspheres) is not difficult to remove. Analysis of shards prepared by evaporating UO_2 sols in argon and firing in Ar-4% H_2 showed that the final product contained <30 ppm of carbon and had a density 97 to 100% of theoretical. Comparison of TGA curves for shards and gel microspheres shows that formic acid is decomposed at 250 to 400°C .

The removal of the sorbed organic materials is limited, with regard to kinetics, at moderate temperatures. Since these materials are very strongly sorbed, heating in an inert atmosphere or vacuum for prolonged periods does not provide sufficient removal. Instead, one must use a gaseous atmosphere that can either oxidize the sorbed organic compounds to a more volatile species or displace them. In the

H₂O atmosphere the sorbed organic species are not removed below 450°C; for example, they were not completely removed after "soaking", with 5 to 10 g of H₂O (as gas) per gram of microspheres, for periods of 4 to 24 hr until a temperature of greater than 450°C was reached (Table 8). At any fixed temperature, the rate of removal became very slow (a few ppm per gram of steam) after about 3 g of H₂O per gram of gel microspheres had been used, and rapidly diminished thereafter. Experiments indicated that the removal of the sorbed organic species was more dependent on the total amount of steam used than on the steam flow rate.

Table 8. Soaking of Gel Microspheres in Gaseous H₂O

Conditions: Heated to temperature at 100°C/hr after drying first in argon to 105°C for 4 to 24 hr; 10- to 50-g samples; flow rates linear

Temperature (°C)	Quantity of H ₂ O (g of H ₂ O/g of gel)	Net Carbon ^a (wt %)
110	3	2.9
110	18	2.7
210	5	1.0
350	5	0.6
450	10	0.1-0.02
850	10	0.001-0.005
1000	10	0.001-0.005

^aNet carbon is defined as total carbon minus the formate carbon.

The following heating schedule in H₂O (gas) was used to consistently produce a product having a uniform black color, a density of 95 to 99% of theoretical, a carbon content of <50 ppm, and an O/U atom ratio of <2.005.

- (1) The gel spheres are dried in a flowing stream of H₂O vapor to 200°C at 50°C/hr and held for 4 to 6 hr; 10 to 15 g of H₂O per gram of gel spheres is used. The spheres are then heated to 1000°C at 300°C/hr, using 5 g of H₂O per gram of gel. Flow rates of about 300 scfh for steam and 0.7 scfh for argon are generally used in firing 50- to 100-g batches of UO₂.

- (2) At 1000°C, the sample is reduced in a stream of Ar-4% H₂ (1 scfh) for 2 to 4 hr.

Studies are being made to determine the feasibility of shortening the firing schedule and decreasing the amount of steam. Preliminary results indicated that a temperature of 850°C may be sufficiently high to achieve near-theoretical density and low carbon content (<50 ppm). Tests indicate that 3 g of H₂O per gram of UO₂ in the temperature range 200 to 1000°C is not sufficient for obtaining a product that has the characteristics just mentioned. However, we believe that the quantity of H₂O, particularly in the firing region above 600°C, can be decreased substantially from the quantities listed in Table 8.

The effect of a variety of atmospheres and soaking conditions on the sintering of UO_{2+x} gels and the removal of carbon have been studied.^{53,59-61} Differential thermal analysis (DTA), thermogravimetric analysis (TGA), and measurements of crystallite growth, shrinkage rate, and surface area showed that gaseous atmospheres of H₂O or CO₂ promote sintering in the region where the carbon-bearing volatiles are being removed. Carbon dioxide promotes a very rapid sintering of the UO_{2+x} gels, as is evidenced by: (1) DTA, which showed that the release of surface energy began at 400°C and rose to a sharp maximum at 500°C, (2) x-ray measurements, which showed rapid crystallite growth in this temperature region, and (3) surface area measurements, which showed a tenfold decrease in surface area. Thermogravimetric measurements indicated that either a very rapid surface oxidation of the UO₂ crystallites or a very strong surface adsorption of CO₂ was also occurring. The gain in sample weight during sintering in the CO₂ was found to be 0.25%. Thermogravimetric measurements also indicated that the carbon compounds were not removed by CO₂ at appreciable rates until a temperature of about 550°C was reached. With H₂O, however, the rate of sintering did not become significant until a temperature of 450°C was reached, and then it increased more slowly from 450 to 550°C than was observed with CO₂. Thermogravimetric measurements indicated that either a very rapid surface oxidation of the UO₂ crystallites or a strong surface adsorption of the H₂O was taking place. Carbon removal occurred at

appreciable rates at 450 to 550°C. All these data strongly suggest that removal of the sorbed organic materials prior to sintering could be more easily accomplished with H₂O than with CO₂.

In Ar-4% H₂, sintering occurred over a higher and much broader temperature range (600 to 900°C); however, at these higher temperatures, hydrocarbons are decomposed, leaving free carbon within the gel, unless sufficient excess oxygen is present in the UO_{2+x} to react with the sorbed materials or their decomposition products. Thermogravimetric studies indicated that air could be employed to remove the carbon, by combustion of the sorbed organics at 150 to 200°C, with subsequent firing in argon to 1000 to 1200°C to give a product having a low carbon content. Since this type of reaction is highly exothermic, the rate must be controlled by limiting the quantities of the reactants (to prevent excessive temperature rises and oxidation of the UO₂). Definitive studies of carbon removal and sintering are continuing.

Atmospheres of CO₂, air, Ar, Ar-3% H₂O, and Ar-4% H₂ have been tested, using a variety of soaking conditions (Table 9), to determine their effectiveness in yielding a product with a high density and a low carbon content. After the soaking periods, Ar-4% H₂ was used for final reductions at 1100 to 1200°C. Soaking for periods of up to 20 hr at 400 to 600°C in CO₂, Ar-3% H₂O, Ar or Ar-4% H₂ did not yield final products that were reproducible with regard to density and carbon content when different gel microsphere preparations were employed. The length of the soaking cycles did not appear to affect the properties significantly; variations observed were probably due to differences in individual gel preparations. Argon (or Ar-4% H₂) was effective in removing carbon only from gels having O/U atom ratios of 2.35 or greater. Argon was generally more effective than Ar-4% H₂, presumably because the excess oxygen in the UO_{2+x} was better maintained at the higher temperatures. Since typical gels from the UO₂ sol-gel process have O/U atom ratios of 2.15 to 2.25, some means of controlling the oxidation state must be employed in order to use Ar or Ar-H₂ atmospheres to remove the carbon. Thus far, it has not been possible to accomplish this, in a reproducible manner, by presoaking in air to 200°C.

Table 9. Effects of CO₂, Ar, Ar-4% H₂, Ar-3% H₂O, and Air on the Sintering of UO₂

Conditions: Gel microspheres dried at 150 to 200°C in H₂O-Ar atmosphere [(1 to 3) g of H₂O per gram of UO₂] and cooled to room temperature prior to firing; diameter, ~400 μ; O/U atom ratio = 2.15 to 2.25; gels were soaked in the atmospheres indicated and then reduced at 1100 to 1200°C in Ar-4% H₂ for 2 to 4 hr.

Soaking Atmosphere	Conditions		Density (% Theor.)		Carbon Content (ppm)	
	Temp. (°C)	Time (hr)	Range	Average	Range	Average
CO ₂ ^a	25-950	25	85-97	90-95	10-800	100
CO ₂ ^a	450-850	2-16	85-97	90-95	10-800	100
CO ₂ ^a	400	20	85-97	90-95	10-800	100
Ar	25-1200	4-24	90-99	93-95	1000-4000	2000
Ar-4% H ₂	25-1200	4-24	85-96	90-95	2000-8000	4000
Ar-3% H ₂ O	25-1200	4-24	90-99	95	10-800	100
Air ^b	25-200	3	93-99	95	10-100	30

^a Ar-4% H₂ atmosphere in temperature region above maximum soaking temperature, using rise rates of 300°C/hr to 1200°C.

^b Argon atmosphere from 200 to 1200°C at 300°C/hr.

PLUTONIA SOL-GEL PROCESS

M. H. Lloyd, R. G. Haire, and O. K. Tallent

A sol-gel process for the preparation of dense oxide forms of PuO_2 has been developed and tested on an engineering scale. Primary emphasis during this work was on the development of a process for preparing a plutonia sol that would be compatible with other actinide sols and would afford versatility in forming techniques. These objectives require a nitrate medium and a stable plutonium colloid of low nitrate content. The sol process described here utilizes the polymerization behavior of tetravalent plutonium to produce crystallites of colloidal size and to maintain valence stability. The final sols produced by this method are 1 to 3 \underline{M} in plutonium and have NO_3^-/Pu mole ratios of 0.1 to 0.15. They are stable for many months and are compatible with thoria and urania sols that have been prepared at Oak Ridge National Laboratory. Dense PuO_2 , as well as homogeneous $\text{PuO}_2\text{-UO}_2$ or $\text{PuO}_2\text{-ThO}_2$ microspheres at any desired Pu/U or Pu/Th atom ratio have been produced on an engineering scale.

Description of the Sol-Gel Process

The flowsheet for the plutonia sol process is shown in Fig. 16. Hydrous plutonia is precipitated from a plutonium nitrate solution (that is 1 to 3 \underline{M} in excess HNO_3) by slow addition of the plutonium solution to a 100% excess of NH_4OH , with simultaneous rapid stirring. The plutonia is recovered by filtration, the filter cake is resuspended in water, and the suspension is filtered. Three washings are usually sufficient to reduce the pH of the filtrate to less than 8.0, which indicates satisfactory removal of contaminant ions. The freshly precipitated plutonia is aged by refluxing in water for 1 to 2 hr and then peptized by digestion with dilute HNO_3 . Complete peptization, which is characterized by a change from an opaque light-green slurry to a nearly transparent dark-green suspension, requires a minimum NO_3^-/Pu mole ratio of 1. At this NO_3^-/Pu ratio, a peptization time of about 4 hr at 80°C is necessary. Higher nitrate concentrations, however, can be used to reduce

ORNL DWG 67-6958

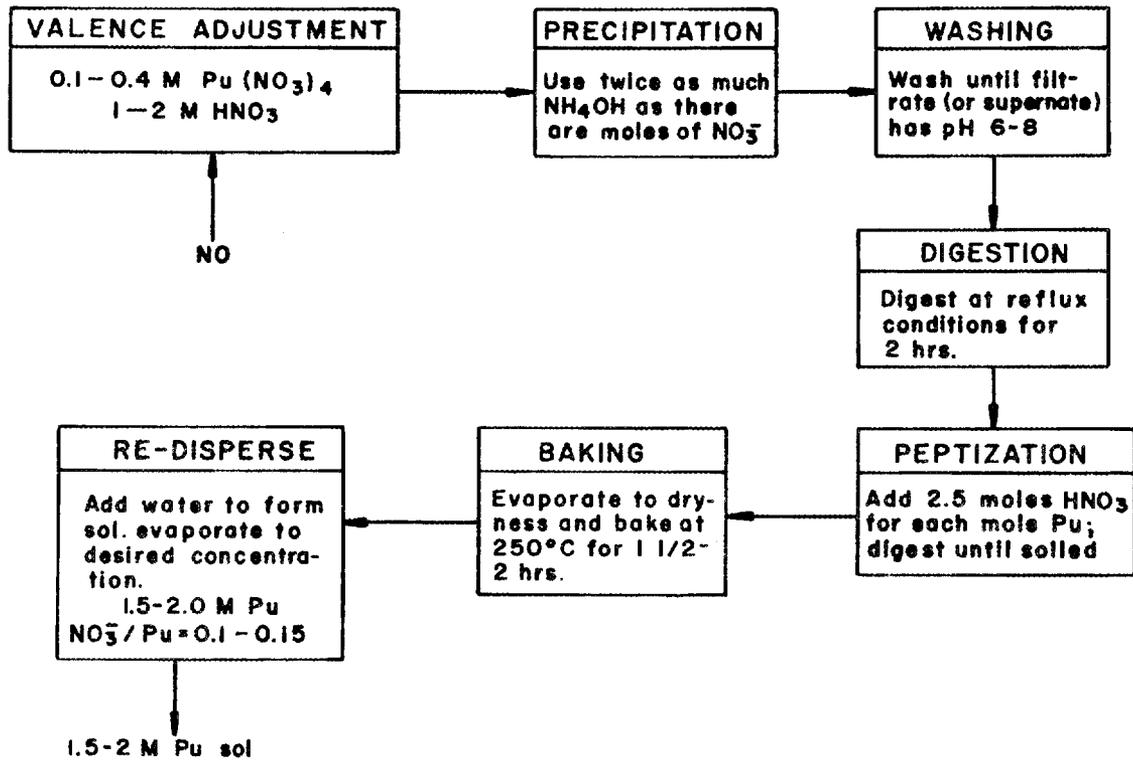


Fig. 16. Flowsheet for Plutonia Sol Preparation by Precipitation-Bake Process.

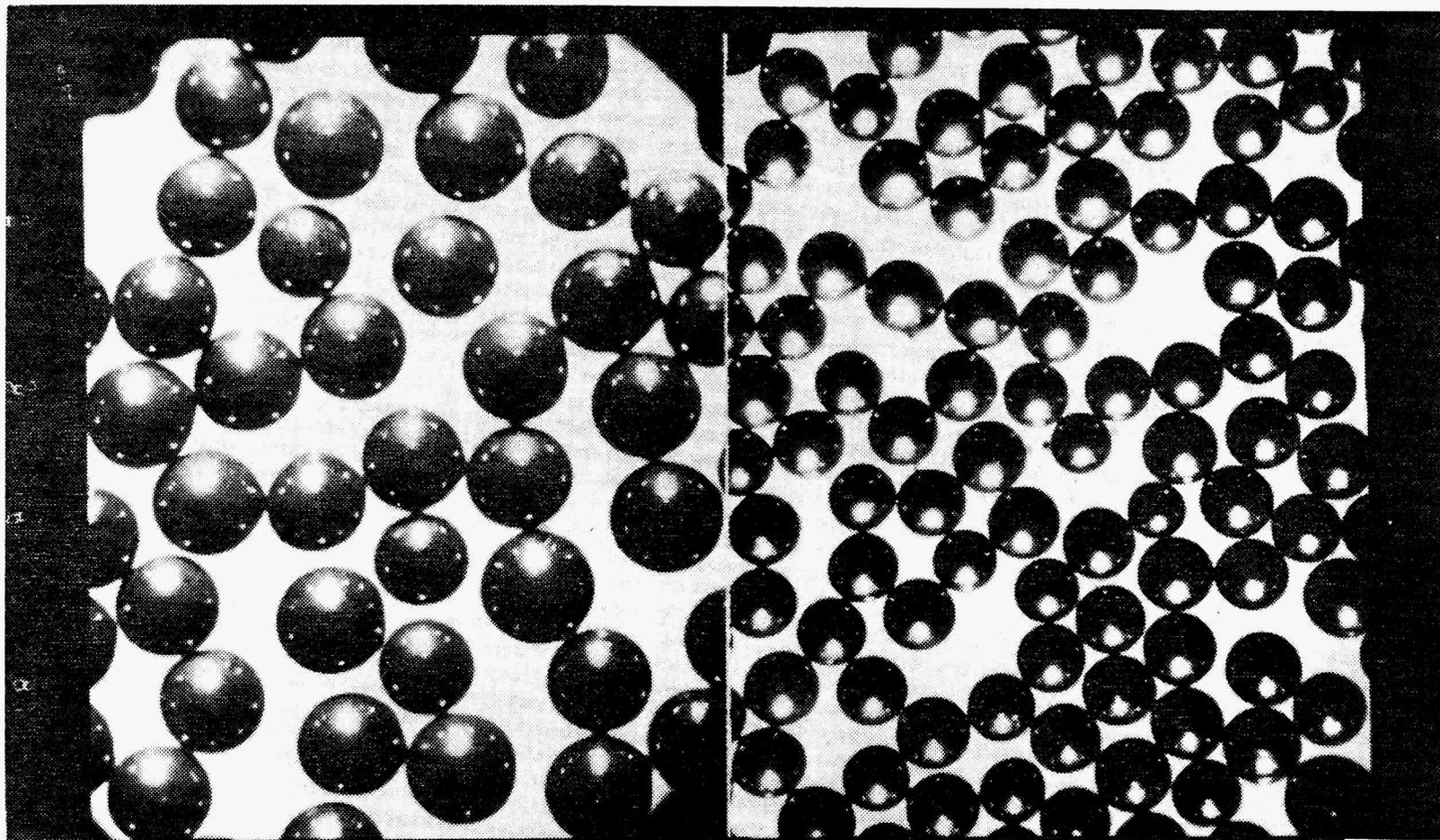
the peptization time and temperature; for example, at NO_3^-/Pu mole ratios of 2 or more, peptization requires only 10 to 15 min at room temperature.

The plutonia sol produced during peptization is a stable colloidal dispersion that is not suitable for fuel-particle preparation until the nitrate concentration has been reduced. This is accomplished by evaporating the sol to produce a gel, then baking the dried gel at 250°C for about 2 hr. Nitrate removal is a function of both time and temperature, and excessive baking will result in material that cannot be redispersed. For this reason, very uniform heating of plutonia solids is required during nitrate removal. The final sol is prepared by resuspending the baked gel in water and evaporating to the desired plutonium concentration. Sols with plutonium concentrations in excess of 2 M and with NO_3^-/Pu mole ratios between 0.1 and 0.15 are obtained.

Demonstration of the Process

Numerous small-scale batches (5 to 20 g of plutonium per batch) of plutonia sol have been prepared in the laboratory, while a small pilot facility has been used to prepare large batches (50 to 150 g of plutonium per batch) of sols having uniform characteristics. These preparations demonstrated the operability of engineering-scale equipment and the reproducibility of the standard flowsheet. Plutonia sols can be dried and calcined to dense hard fragments, or they can be formed into microspheres that are subsequently calcined to dense oxide spheres (see Fig. 17). They can also be mixed with thoria or urania sols and formed into microspheres or fragments. Formation of gel microspheres from sols is accomplished by using procedures that were developed at ORNL for thoria.

Microspheres of uniform size have been prepared, on both laboratory and engineering scales, from mixed $\text{PuO}_2\text{-ThO}_2$ sols containing 2, 5, 10, 20, 30, 50, and 80 wt % PuO_2 and from mixed $\text{PuO}_2\text{-UO}_2$ sols containing 5, 15, 20, 25, and 50 wt % PuO_2 . Calcined microspheres that are 50 to 600μ in diameter can be obtained. After calcination at 1150°C , these products are characterized by high density, low surface



UNCALCINED

CALCINED

Fig. 17. Plutonia Gel, and Microspheres Sintered at 1150°C.
Average diameter: 130 μ ; density: 96% theoretical.

area, and high resistance to crushing. Mercury porosimetry indicates densities of 95 to 99% of the theoretical crystal density for typical products. Surface areas of $0.02 \text{ m}^2/\text{g}$ are obtained for 300- to 600- μ -diam microspheres. Crushing loads for microspheres calcined at 1150°C average about 550 g for a 250- μ -diam microsphere, and increase to greater than 1 kg for a 500- μ -diam sphere. Crush resistance is approximately the same for microspheres calcined at 1600°C or 1150°C .

X-ray analysis indicated a crystallite size of 1000 Å for PuO_2 spheres that had been calcined in air at 1150°C . Crystallite size increases with temperature; for example, 1700-Å crystallites were observed in material that had been calcined for 0.5 hr at 1550°C . It was found that $^{239}\text{PuO}_2$ microspheres can be washed free of smearable alpha contamination. Calcined spheres were water-washed, dried in air, and smeared. Extensive contact with 50 to 100 spheres produced counts on the order of $20 \text{ dis min}^{-1} \text{ smear}^{-1}$.

The homogeneity of UO_2 -20% PuO_2 microspheres was investigated using the electron microprobe technique. Since no plutonium standard was available, analysis was limited to uranium. Data obtained indicated the presence of a homogeneous mixture having a uniform distribution of urania. The maximum deviation of the uranium concentration over the entire surface of the sectioned microspheres was $\pm 1.5\%$. Figure 18 shows polished sections of fired microspheres of PuO_2 and UO_2 -20% PuO_2 illustrating low porosity, high density, and product homogeneity.

Discussion of Process Variables for Plutonia Sol Preparation

During early developmental work spectral analysis established that the sol that forms during peptization of the hydroxide consists of "Pu(IV) polymer." Plutonia sol retains the polymer spectrum throughout all stages of preparation.

It was recognized that this polymeric form stabilized the valence of the plutonium (in the tetravalent state) and that crystallites formed by polymerization were of colloidal dimensions; however, the high nitrate demand (one mole of nitrate per mole of plutonium) required for the total conversion of precipitated plutonium to a stable polymeric colloid required a subsequent nitrate removal step in the sol process.

R-33774

R-33600

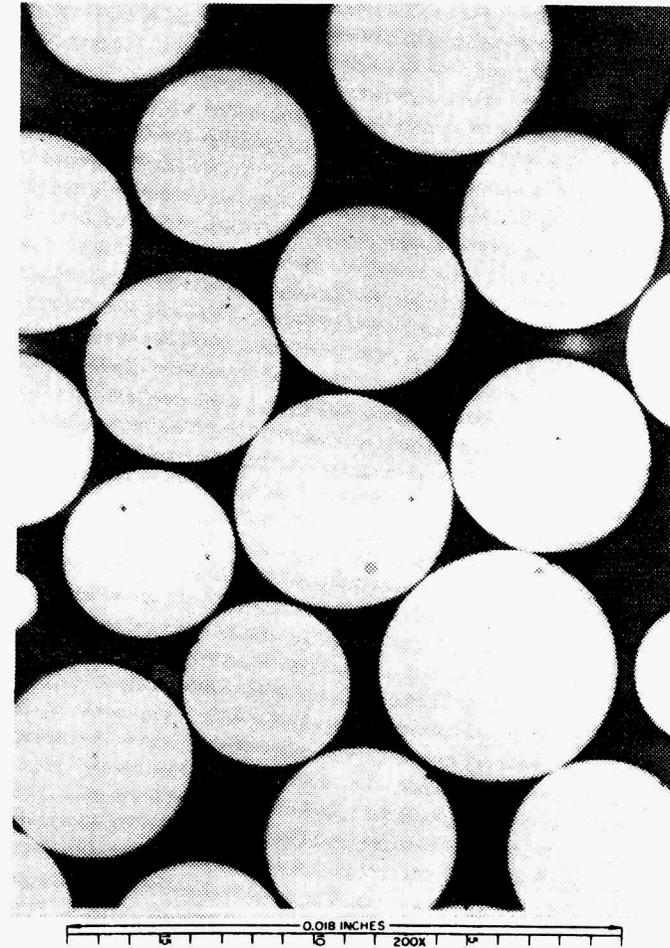
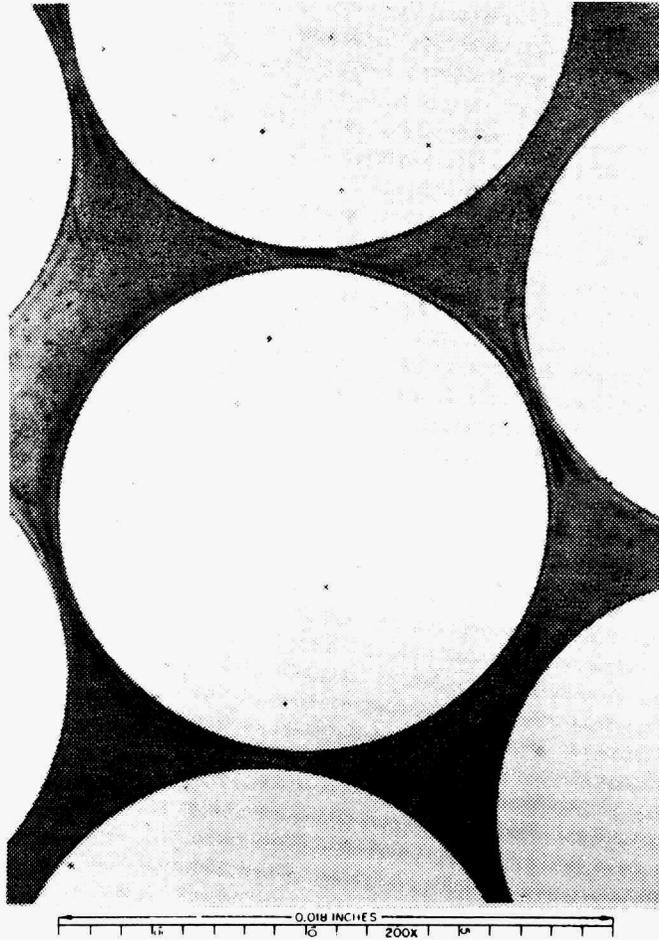


Fig. 18. Polished Sections of Fired UO_2 -20% PuO_2 (A) and PuO_2 (B) Microspheres at 200X.

While nitrate can be removed by thermal methods (e.g., "baking" the dried polymeric colloid at temperatures of 100 to 300°C), adequate control requires knowledge of the kinetic rates for nitrate removal. The solids must be heated uniformly to obtain a final sol having a low nitrate concentration and to prevent excessive product losses.

During denitration, both crystallite growth and agglomeration of crystallites occurred. These phenomena appear to be intimately associated with the preparation of plutonia sols of low nitrate contents. X-ray line broadening techniques indicate crystallite growth from 20 Å in high-nitrate sols to about 80 Å in final sols. Micro-pore filtration and centrifuge experiments show a range of micelle sizes in the final sol, with some aggregates as large as 1000 Å. Fractionation of final sols by high-speed centrifugation has given three to four aggregate fractions; x-ray analysis of such fractions indicate that crystallite size is not a function of aggregate size. These data suggest that although both crystallite growth and agglomeration occur during baking, only the latter limits the baking time.

From a process standpoint, a baking temperature that would permit some latitude in baking time and would still accomplish rapid removal of nitrate is desired; 250°C appears to meet these requirements. At 250°C, a baking time of 1.5 to 2 hr will provide a product with the desired NO_3^-/Pu mole ratio (e.g., at 1.5 hr, the NO_3^-/Pu mole ratio is about 0.14; at 2 hr it is about 0.11).

To obtain reproducible values for the baking rates, it was necessary to periodically mix the solids. The laboratory equipment consisted of a machined stainless steel flat-bottomed dish, 8-in. in diameter, that was bolted to an aluminum block in which heaters were mounted. Sol with a high nitrate concentration was evaporated in this dish and then baked at the desired temperature. In each batch (containing 50 to 100 g of plutonium), the solids formed a layer about 1/8-in. thick, giving a high surface-to-depth ratio and uniform heating. It was found by drying high-nitrate sols of different NO_3^-/Pu mole ratios that the dry solid obtained always had an initial NO_3^-/Pu mole ratio of approximately 1. Thus, a higher NO_3^-/Pu mole ratio

can be used in the peptization of the plutonium precipitate without causing problems in the subsequent nitrate removal step.

Further developmental work is planned in order to investigate other possibilities of sol formation; in the interim, however, the present process affords a satisfactory method for preparing a plutonia sol that is compatible with the urania and thoria sols that have been produced at ORNL.

ZIRCONIA SOL-GEL PROCESS

J. P. McBride and W. L. Pattison

The objective of the studies of the zirconia sol-gel process was the preparation of concentrated sols, of low electrolyte content, that were capable of being mixed with urania sols in all proportions and that could be used to form dense microspheres. Previous attempts to prepare zirconia sols involved two approaches: destruction of the nitrate in zirconyl nitrate solution with formaldehyde, and precipitation of hydrous zirconia and subsequent peptization with nitric acid.⁵⁶ Neither of these was successful in producing concentrated sols of low nitrate content. Concentrated zirconia sols of low nitrate content were prepared, however, by autoclaving zirconyl nitrate solutions at 200°C to promote crystallite growth and zirconia precipitation, removing the bulk of the nitrate by centrifugation and decantation, peptizing the recovered solids by addition of water, and decreasing the nitrate content of the zirconia sol to the desired level by solvent extraction. This method was based on work described in a patent by G. B. Alexander and J. Bugosh.⁶² A 1-liter stainless steel autoclave containing a gold liner was used in these experiments; it was operated in an upright position.

Experiments carried out in the autoclave at 150, 175, 185, 190, and 200°C, using 1 M $ZrO(NO_3)_2$ solutions, indicated that a temperature of 200°C would be required to promote the desired zirconium hydrolysis and crystallite growth. Subsequent autoclavings were, therefore, done at 200°C, using 1 M and 2 M $ZrO(NO_3)_2$ solutions.

In a typical sol preparation, a 1 M $\text{ZrO}(\text{NO}_3)_2$ solution was autoclaved for 5 hr at 200°C. The resulting slurry was centrifuged and the clear supernate was poured off. Distilled water was added to the cake to produce a ~1.5 M slurry. The latter was centrifuged, and the slightly cloudy supernate was decanted. More water was added to the cake to increase the slurry volume to about 250 ml. The result was a stable, milky-white sol with a zirconium concentration of 1.6 M and a NO_3^-/Zr mole ratio of 0.44. The two centrifugations removed a total of 0.87 mole of nitrate, with a loss of only 0.032 mole of zirconium. At lower autoclave temperatures, nitrate removal was less complete and the loss of zirconium was greater.

Even though the 200°C autoclaving and subsequent treatment produced a stable sol, the NO_3^-/Zr mole ratio (0.44) was still thought to be too high for the successful preparation of gel microspheres from the sol. It was decided to lower the nitrate concentration further by amine extraction. One volume of 1.6 M sol was contacted for 30 min with four volumes of 0.1 M Amberlite LA-2 in *n*-dodecane at room temperature. The NO_3^-/Zr mole ratio was decreased from 0.44 to 0.2. No precipitation or gelation occurred, and the separation of both phases was excellent; only very small quantities of emulsified crud were observed at the interface.

Formation of Zirconia Microspheres

By using the 1.6 M sol prepared by the 200°C autoclaving of a 1 M zirconyl nitrate solution, gel microspheres were prepared in the usual manner; that is, droplets of the sol were dispersed into a column of 2-ethyl-1-hexanol containing 0.2 vol % Ethomeen S-15 and 1 vol % Span 80. The spheres were allowed to remain in the column for 30 min and were then dried in air overnight at 110°C. The dried spheres were yellow-white and showed only slight cracking.

A second batch of microspheres was prepared from one of the more-concentrated sols prepared by autoclaving a 2 M zirconyl nitrate solution (3.37 M in Zr; NO_3^-/Zr mole ratio, 0.14) and using the forming conditions just described. While drying in the column, the spheres, which were bluish-white in color at first, became translucent.

Upon drying for 48 hr at 110°C in air, they turned yellow; however, no cracking was observed. The diameters ranged from 300 to 500 μ . On firing in H_2 at 1150°C for 3 to 4 hr the spheres densified and became black in color; only slight cracking was noted. Firing in air at the same temperature yielded hard porcelain-white spheres that showed little or no cracking.

MISCELLANEOUS SOL-GEL PROCESSES

Sol-Gel Preparation of ThC_2 and Thorium-Uranium Dicarbide

K. J. Notz and W. D. Bond

The dicarbides of thorium and of thorium—3% uranium have been prepared by a sol-gel process. In this process, sols are prepared by dispersing carbon black in ThO_2 or ThO_2 —3% UO_3 sol. Gel microspheres are formed from the final sol and are then converted to dicarbide microspheres by firing at 1800 to 2000°C. Thorium dicarbide microspheres with densities that are 91 to 93% of theoretical have been prepared by this method; the preparation of UC and $(Th,U)C_2$ microspheres is in progress.

Initial work⁶³ showed that carbon could be incorporated in thoria and thoria—3% UO_3 sols and the resulting mixed sols could be formed into microspheres and converted to ThC_2 or $(Th,U)C_2$ by firing at 1600 to 1750°C in vacuum or flowing argon. These studies suggested that the major problems to be solved would involve minimizing the free carbon content, decreasing the porosity, and attaining high density. Conversions of 98% and densities as high as 89% of theoretical were attained in this study. The reaction $ThO_2 + 4C \rightarrow ThC_2 + 2CO$ was shown to be kinetically favorable, with ThO_2 —C gels, 98% conversion being attained at 1650°C under vacuum. Kinetic studies showed the reaction to be a pseudo first-order type with an activation energy of about 112 kcal/mole of ThO_2 .

Further studies^{20,64-68} have demonstrated that good conversion of $\text{ThO}_2\text{-C}$ gel microspheres and a high-density final product can be obtained by carrying out the conversion and sintering at a controlled rate; also, methods for the preparation and characterization of metal oxide—carbon sols have been improved. To achieve the proper balance between conversion and sintering, the reaction is carried out in argon until it is nearly complete; then vacuum is applied to complete the reaction. In six runs, products having densities greater than 90% of theoretical were obtained (Table 10). The argon sweep gas contained about 4000 ppm of CO, which was maintained by a controlled diffusion of CO out of the sample crucible. An infrared in-line CO analyzer (Beckman model 315) was used to monitor the reaction. The densities were 91 to 93% of the theoretical value (9.60 g/cc). Open porosities were about 1%; closed porosities were 6 to 8%. Porosity is evident in the sectioned spheres (Fig. 19). The free carbon and oxygen contents are reasonably low; reduction to lower levels may be difficult. In the runs conducted at 1950°C or higher, the free carbon content ranged from 700 to 1900, and the oxygen content ranged between 300 to 1100 ppm. Further studies, which are aimed at decreasing these values, are being made. Attempts to convert gel shards of $\text{ThO}_2\text{-C}$ to ThC_2 by the technique used for conversion of microspheres gave products of high porosity. Initial preparations of $(\text{Th}_{0.88}, \text{U}_{0.22})\text{C}_2$ microspheres by the sol-gel route gave results that are equivalent to those obtained for ThC_2 .

Dispersion of the carbon into the oxide sols by ultrasonic agitation was more successful than dispersion by ball-milling or recirculation in a centrifugal pump loop. The surface area of the carbon black affects final sol properties: If the surface area is too high ($>1000 \text{ m}^2/\text{g}$), the mixed sol is too viscous; if it is very low ($<30 \text{ m}^2/\text{g}$), the mixed sol is difficult to prepare. For convenience in handling, pelletized carbon black is preferred. Spheron 9 (Cabot Corporation) appears to have optimum properties for sol preparation; it is a channel black having a surface area of $105 \text{ m}^2/\text{g}$. Microspheres can be formed from the metal oxide—carbon sols by the usual method (drying in 2-ethyl-1-hexanol containing Ethomeen S/15 and Span 80).

Table 10. Properties of 200- μ -diam Thorium Dicarbide Microspheres

Run No.	II-146	II-148	II-150	III-14	III-16	III-18
Max. temp., °C	2050	1950	1850	1975	1975	2030
Time at temp., hr	1	2.5	4	2.5	2.5	4 ^a
X-ray diffraction ^b						
ThO ₂	?	nd	?	nd	nd	nd
ThC	v. wk.	nd	wk.	v. wk.	v. wk.	v. wk.
ThC ₂	P	P	P	P	P	P
Thorium, %	90.93	91.25	90.88	91.23	91.23	91.45
Total carbon, %	9.09	8.74	8.85	8.57	8.52	8.65
Oxygen, %	0.096	0.045	0.360	0.033	0.032	0.106
Σ (material balance)	100.12	100.04	100.09	99.83	99.78	100.21
Free carbon, %	0.12	0.12	0.47	0.066	0.106	0.186
C/Th atom ratio	1.92	1.83	1.83	1.81	1.79	1.80
Density, ^c g/cc						
Particulate	>8.75	8.83	8.75	>8.91	>8.76	>8.97
Hg intrusion	8.84	8.95	8.87	9.00	8.84	9.06
Helium	-	-	-	9.04	8.77	9.10
Open porosity, ^d %	<1	1.3	1.4	<1	<1	<1
Resistance to crushing, ^e g	700	790	940	800	700	-

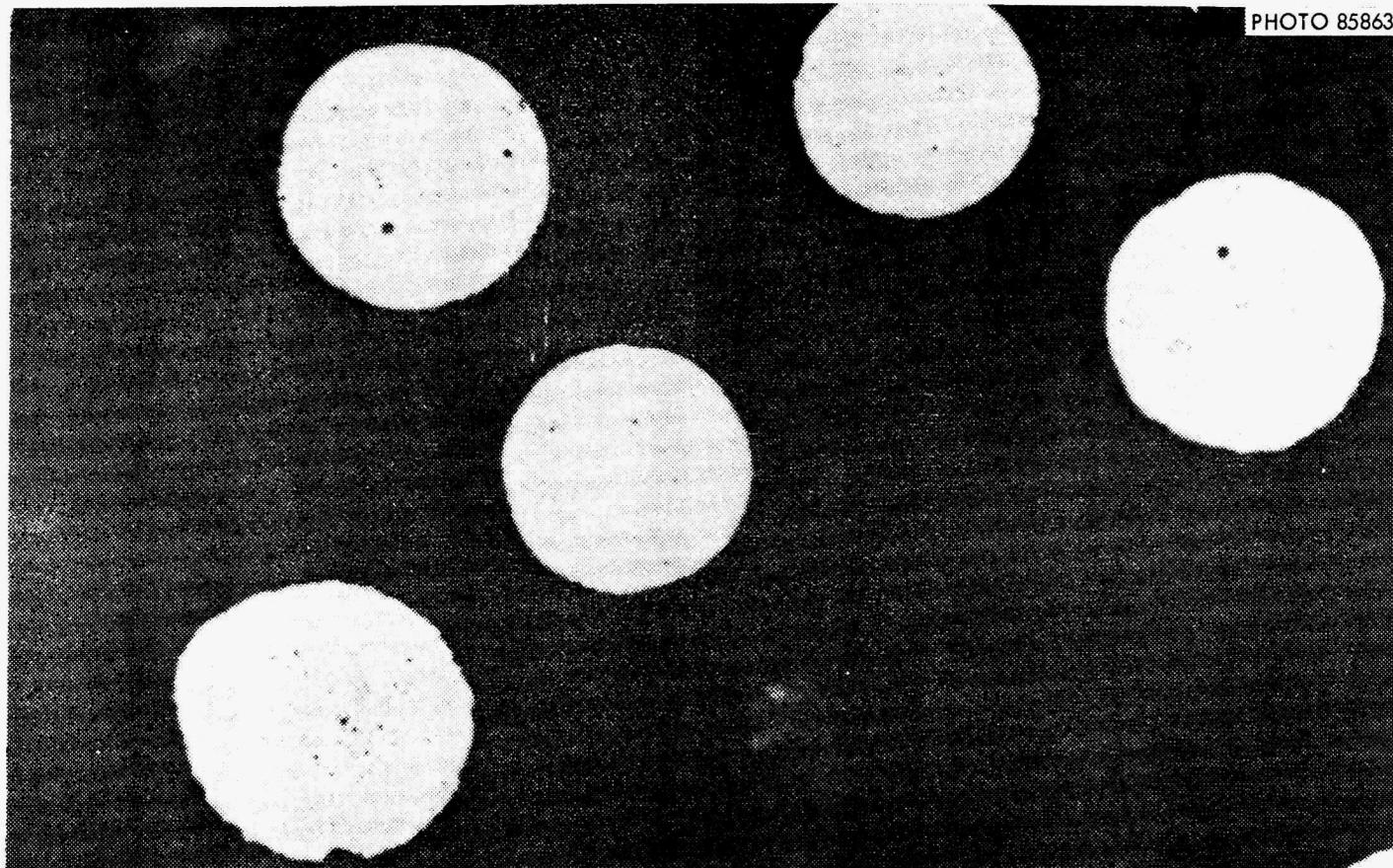
^aTemperature was gradually increased from 1700 to 2030°C during the 4 hr.

^b"P" indicates phase present; v. wk., very weak; ?, may be present; nd, not detected.

^c"Particulate" density means the bulk density of single spheres; "Hg intrusion" density is the density after subtracting the volume occupied by Hg at 15,000 psi. The difference between these two values is the "open porosity" for pores >120 Å. The helium density subtracts all open pore volumes, including those <120 Å.

^dDefined above.

^eCorrected to 240- μ -diam sphere by assuming that resistance to crushing is proportional to the square of the diameter.



200 MICRONS

2050°C



1 HR

Fig. 19. Polished Sections of Thorium Dicarbide Microspheres.

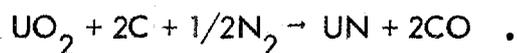
Electron-microscopic studies showed that an intimate mixture of thoria and carbon was achieved in the $\text{ThO}_2\text{-C}$ sols.⁶³ This early work suggested that perhaps the carbon black particles (130 A in diameter) were dispersed into the component crystallites (20 A) on the surface of the thoria since no particles larger than 100 A could be observed in electron photomicrographs. However, more recent work^{64,66,67} showed that, although electron microscopy indicates that the carbon is dispersed to individual crystallites, this is not the case. It now appears that the thoria is sorbed on the surface of the carbon aggregates and acts as a protective colloid. This surface sorption makes detection of the carbon aggregates difficult unless conditions are properly chosen. Confirmation that the thoria was sorbed on the surface of the carbon aggregates and that the surface aggregates of carbon black were not dispersed into the ultimate particle or crystallite was obtained in (1) electron-microscopic studies of $\text{ThO}_2\text{-C}$ sols that contained less thoria than required to saturate the adsorption sites on the carbon, (2) dissolution of the ThO_2 and recovery of carbon aggregates virtually identical in size and shape to the initial aggregates, and (3) surface area measurements of $\text{ThO}_2\text{-C}$ gels. The adsorption of the metal oxide on the carbon aggregates (and the formation of a stable metal oxide-carbon sol) is characteristic of ThO_2 and UO_2 sols; the same type of interaction, however, was not observed with Al_2O_3 , ZrO_2 , or SiO_2 sols. Viscometric measurements indicated that complete dispersion of the carbon was achieved at C/metal-oxide mole ratios that were characteristic of their respective surface areas.

Sol-Gel Preparation of Uranium Nitride

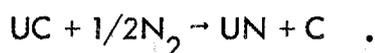
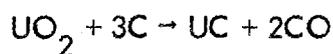
T. A. Gens, D. M. Helton, and S. D. Clinton

Initial studies of the preparation of UN microspheres from $\text{UO}_2\text{-C}$ gel microspheres were promising.⁶⁹ In the preliminary experiments, $\text{UO}_2\text{-C}$ gel microspheres having a C/ UO_2 mole ratio of 2.8 were converted to $\text{UN}_{0.92}\text{C}_{0.13}$ by firing the $\text{UO}_2\text{-C}$ gel in nitrogen to 1600°C. The density of the final product was 13.7 g/cc. It is expected that conversion to the nitride will improve with adjustment of the C/ UO_2 mole ratio to the proper value and with optimization of the firing schedule.

The sol-gel approach for preparing nitride microspheres consists in dispersing high-surface-area carbon black in a UO_2 sol, forming gel microspheres by dispersing droplets of the sol in 2-ethyl-1-hexanol, and then converting the microspheres to nitride by firing to a high temperature. There are two possible approaches to conversion of the $\text{UO}_2\text{-C}$ gel to UN: (1) The spheres are heated in a stream of nitrogen to form a nitride according to the following reaction:



(2) The monocarbide is formed first; it is then reacted with nitrogen according to the following reactions:



The second method leads to the presence of free carbon in the UN product. In one preliminary test in which conversion was accomplished by the second method at 1600°C , carbon could not be removed from the $\text{UN}_{0.81}\text{C}_{0.40}\text{O}_{0.24}$ product with hydrogen at 1000°C without destruction of the microspheres. The hydrogen treatment caused the spheres to crumble and powder. It is apparent that, with either method, careful control of the C/U and the C/O atom ratios must be exercised to achieve a relatively pure UN product that is free of carbon and oxide impurities. Actually, UO_2 sols are UO_{2+x} sols, where x may vary from 0.15 to 0.25; this must be taken into account when the amount of carbon required for the reaction is calculated.

Test conversions were made of $\text{UO}_2\text{-C}$ gel microspheres having a C/ UO_2 ratio of 2.3. A $\text{UO}_2\text{-C}$ sol was prepared by dispersing Spheron 9 carbon black (BET surface area = $105 \text{ m}^2/\text{g}$) into a UO_2 sol, by means of an ultrasonic generator probe, while the sol was cooled by an ice bath. The required weight of carbon (2.3 moles per mole of U) was added to a 0.83 M UO_2 sol, and the resultant sol was diluted with water to a UO_2 concentration of approximately 0.55. The $\text{UO}_2\text{-C}$ sol was formed

into gel microspheres in a sphere forming column, using 94.5 vol % 2-ethyl-1-hexanol—5 vol % 2-octanol and 0.5% Amine "O"; the spheres were dried in argon at 120°C for 16 hr.

Attempts to convert the $\text{UO}_2\text{-C}$ gel microspheres to nitride by heating at 1600°C for 2 hr in a stream of nitrogen were unsuccessful as a result of the formation of an impervious nitride coating on the spheres. This thin, mirror-like coating of UN impeded the entry of nitrogen. It was found, however, that the coating could be made permeable to nitrogen by cooling in nitrogen to 950°C and then reheating to 1600°C. Presumably, $\text{UN}_{1.6}$ formed, then decomposed on reheating to make the coating permeable. By starting with $\text{UO}_2\text{-C}$ gel microspheres containing exactly enough carbon to remove all of the oxygen as CO, it should be possible to prepare essentially pure UN.

PREPARATION OF LANTHANIDE OXIDE MICROSPHERES BY SOL-GEL METHODS*

C. J. Hardy, S. R. Buxton, and M. H. Lloyd

Lanthanide oxide microspheres have been produced with a controlled size in the diameter range 50 to 500 μ , a density of up to 98% of the theoretical crystal density, a low surface area (0.01 to 0.1 m^2/g), and a high resistance to crushing (up to 3 kg for 500- μ -diam spheres). Hydroxide sols and gels were used as intermediates, and the resulting spheres were calcined at a relatively low final temperature (1000 to 1500°C), which depended on the crystal form required.

Sols were prepared by precipitating the lanthanide hydroxides from lanthanide nitrate solutions with ammonium hydroxide, washing the precipitates thoroughly, and heating them for 1 hr at 80°C. These sols were concentrated by evaporation until they were 2 to 3 M in the metal ion and contained 0.06 to 0.25 mole of residual nitrate per mole of metal ion; then they were formed into gel microspheres of

*This section is a reproduction of the abstract of ref. 6.

controlled size by partial dehydration with a long-chain alcohol in a tapered column. The gel spheres were dried further in vacuum at 120°C, heated to 500°C in vacuum to decompose the residual nitrate, and finally calcined to oxide microspheres at 1000 to 1500°C in air.

Spectroscopic methods were used to rapidly determine the nitrate and metal ion concentrations in the sols, to study the form of bonding of the components (e.g., nitrate) of the sols and gels, and to estimate the sizes of the aggregates of colloidal particles. Electron microscopy and electron diffraction measurements showed that the initial precipitates of lanthanide hydroxides consisted of amorphous particles of 30 to 60 Å in diameter. When aged in the mother liquor, these particles changed into crystalline sheets up to several hundred angstroms in width; when thoroughly washed and aged in water, they changed into rods, tubes, or rolled sheets up to several thousand angstroms in length. Randomly arranged bundles of these rod-shaped crystals were present in microspheres of the lanthanide hydroxide gels. Electron micrographs of replicas of etched polished surfaces of the dense oxides obtained by heating the gels to 1450°C showed 5- to 10- μ -wide grains that contained oriented crystalline units that were 0.2 to 0.5 μ wide. These units were probably polycrystalline because x-ray line-broadening measurements indicated a crystallite size of 500 to 700 Å.

Lanthanide oxides in this form have potential industrial value; for example, europium oxide in cermets could be incorporated in reactor control rods, and europium, promethium, and thulium oxides might be used in radioactive heat sources. The method of preparation is also applicable to the production of sols, gels, and oxides of the transplutonium elements, of which americium and curium are of interest for incorporation in targets for the High Flux Isotope Reactor at Oak Ridge to produce transcurium isotopes.

STATUS OF AMERICIUM-CURIUM SOL-GEL PROCESS

R. D. Baybarz, M. H. Lloyd, and J. D. Hoeschele

The development of a sol-gel process for preparing dense Am-Cm oxides for incorporation into targets for the High Flux Isotope Reactor is continuing. Preliminary and process feasibility demonstrations have been made.⁷⁰

To date, ^{241}Am and mixed ^{243}Am - ^{244}Cm sols, gels, and oxide microspheres have been prepared by the standard lanthanide sol-gel procedure⁶ and/or a slight modification of this method. The first procedure utilizes centrifuging to accomplish washing, whereas the modified procedure uses a sintered-glass filter. The essential advantage of the latter is one of simplification; that is, it eliminates all handling during the washing and just prior to the sol forming step since washing and digestion can be accomplished on the filter itself.

 ^{241}Am Sol Preparations

Americium-241 sols have been prepared by both centrifugal and filtration methods. The sols are orange-brown in color, translucent, iridescent, and stable, exhibiting no sediment for as long as six weeks, and are capable of being concentrated to nearly 2 M.⁷⁰ Americium hydroxide shows no tendency to peptize during extensive washing; however, if a washed hydroxide is allowed to stand for a day or two, it will spontaneously convert to a sol.

Americium hydroxide sols with americium concentrations as low as 0.36 M have been formed into nearly perfect spheres of uniform size. The gel spheres were calcined at 1175°C to give stable, strong, dense oxide microspheres.

Mixed ^{243}Am - ^{244}Cm Sol Preparations

A ^{243}Am - ^{244}Cm sol (20% ^{243}Am) has been prepared by the centrifuge technique; however, as yet, all attempted preparations by the filter method have

failed. The sol prepared via the centrifuge route, at a 4-g level, spontaneously converted to a fluid sol having a high NO_3^-/Cm mole ratio (0.7) and a metal concentration of 0.37 M. The sol was introduced into standard sphere forming equipment without difficulty, and fairly uniform particles were produced. The product, however, consisted of hollow hemispheres, although the appearance of the surface was satisfactory and the spheres retained their shape during calcination.

Baybarz⁷¹ prepared Am-Cm sols via the centrifugation approach by first washing out all the nitrate with 7 M NH_4OH and then adding the amount of 1 M HNO_3 calculated to give a NO_3^-/Cm mole ratio of 0.15 to 0.25. The slurry was then digested at 70°C for 1 to 2 hr to produce the sol. Severe foaming occurred, but was quenched by adding methanol. Extensive agglomeration of sol droplets during column drying was eventually controlled by varying the drying mixture and surfactants. The microspheres obtained had to be calcined at a temperature greater than 1050°C to eliminate the tendency to disintegrate to a fine powder.

Work in the immediate future will be concerned with the filtration approach and will attempt to increase the efficiency of the hydroxide washing step in order to reduce the nitrate ratio to desired levels.

REFERENCES

1. D. E. Ferguson, O. C. Dean, and D. A. Douglas, "The Sol-Gel Process for the Remote Preparation and Fabrication," Third United Nations International Conference on the Peaceful Uses of Atomic Energy, Vol. 10/CONF.2.6/P/237.
2. D. E. Ferguson, "Sol-Gel Technology in the Nuclear Reactor Fuel Cycle," Progress in Nuclear Energy, Process Chemistry, Vol. 4, Pergamon, New York (to be published in January 1968).
3. O. C. Dean, C. C. Haws, A. T. Kleinstaubler, and J. W. Snyder, "The Sol-Gel Process for Preparation of Thorium Base Fuels," Proceedings of the Thorium Fuel Cycle Symposium, Gatlinburg, Tennessee, Dec. 5-7, 1962, USAEC, Division of Technical Information, TID-7650 (Paper No. 22).
4. C. C. Haws, J. L. Matherne, F. W. Miles, and J. E. Van Cleve, Summary of Kilorod Project - A Semiremote 10 kg/day Demonstration of $^{233}\text{UO}_2\text{-ThO}_2$ Fuel Element Fabrication by the ORNL Sol-Gel Vibratory Compaction Method, ORNL-3681 (August 1965).
5. K. H. McCorkle, Surface Chemistry and Viscosity of Thorium Sols, ORNL-TM-1536, (July 1966); doctoral thesis, The University of Tennessee, Knoxville, Tennessee.
6. C. J. Hardy, S. R. Buxton, and M. H. Lloyd, Preparation of Lanthanide Oxide Microspheres by Sol-Gel Methods, ORNL-4000 (August 1967).
7. F. W. Van der Bruggen, M. E. A. Hermans, J. B. W. Kanij, A. J. Van der Plas, and H. S. G. Slooten, "Sol-Gel Processes for Spherical Thorium-Containing Fuel Particles," Thorium Fuel Cycle, Proceedings of the Second International Symposium, Gatlinburg, Tennessee, May 3-6, 1966, USAEC, Division of Technical Information (in press).
8. G. Cogliati, R. De Leone, G. R. Guidotti, R. Lanz, L. Lorenzini, E. Mezi, and G. Scibona, "The Preparation and Dense Particles of Thorium and Uranium Oxide," Third United Nations International Conference on the Peaceful Uses of Atomic Energy, Vol. II, A/CONF. 28/P/555 (1964).
9. E. J. Kosiancic, R. H. Dodd, and C. J. Halva, "Direct Preparation of Thorium-Uranium-233 Fuel by the Sol-Gel Process," Thorium Fuel Cycle, Proceedings of the Second International Symposium, Gatlinburg, Tennessee, May 3-6, 1966, USAEC, Division of Technical Information (in press).
10. T. L. O'Connor, J. Walter, P. H. McNally, and N. W. Rosenberg, "Improvements in or Relating to Actinide Metal Oxide Sols," British Patent No. 924,999, to Diamond Alkali Company, June 17, 1959.

11. D. C. Yates, "Process for Preparing Thoria Aqua Sols," U.S. Patent No. 3,162,605, to E. I. du Pont de Nemours and Company, Jan. 26, 1962.
12. W. T. Barrett, S. Park, M. G. Sanchez, G. Burnie, and M. C. Vanik, "Sols of Actinide Metal Oxides," Patent No. 3,164,554, to W. R. Grace Co., May 2, 1960.
13. F. R. Hurley, M. Tecotzky, and M. C. Vanik, "Sols d'oxyde de Thorium-Oxyde d'Uranium et Procèdes Pour Leur Preparation," French Patent 1,279,655, to W. R. Grace Co., Jan. 5, 1961.
14. F. T. Fitch and Jean G. Smith, "Process for Preparing Sols," U.S. Patent No. 3,186,949, to W. R. Grace Co., Dec. 5, 1962.
15. E. N. Nelson, Fluid Bed Denitration of Thorium Nitrate, Mallinckrodt Chemical Company, Report MCW-1511 (Jan. 19, 1966).
16. D. E. Ferguson, Fuel Cycle Development: Semi-Annual Progress Report for Period Ending March 31, 1961, ORNL-3142 (July 18, 1961).
17. D. E. Ferguson, Status and Progress Report for Thorium Fuel Cycle Development for Period Ending Dec. 31, 1962, ORNL-3385 (Oct. 14, 1963).
18. R. G. Wymer and D. A. Douglas, Jr., Status and Progress Report for Thorium Fuel Cycle Development for Period Ending December 31, 1963, ORNL-3611 (July 1965).
19. R. G. Wymer and D. A. Douglas, Jr., Status and Progress Report for Thorium Fuel Cycle Development for Period Ending December 31, 1964, ORNL-3831 (May 1966).
20. R. G. Wymer and D. A. Douglas, Jr., Status and Progress Report for Thorium Fuel Cycle Development for Period Ending December 31, 1965, ORNL-4001 (Oct. 1966).
21. A. Dobry, S. Guinand, and A. Mothieu-Sicaud, *J. Chim. Phys.* 50, 501-6 (1953).
22. U. S. Atomic Energy Commission, "Fundamental Nuclear Energy Research," Supplemental Report to the Annual Report to Congress, p. 261 (1965).
23. R. Prasad, M. L. Beasley, and W. O. Milligan, Aging of Hydrous Thoria Gels, (unpublished report), Baylor University, Waco, Texas (1965).
24. E. Ryshkewitch, Oxide Ceramics, p. 408, Academic, New York, 1960.

25. R. Simha, "The Effect of Shape and Interaction on the Viscosity of Dilute Solutions of Large Molecules," Proc. 1st Int. Rheol. Congress, Amsterdam, Netherlands, pp. II-68 — II-76, North-Holland, 1948.
26. H. F. Holmes, Reactor Chemistry Division Information Meeting, Abstracts of Papers, May 15, 1964, Oak Ridge, Tennessee.
27. H. F. Holmes and C. H. Secoy, *J. Phys. Chem.* 69, 151-58 (1965).
28. R. C. Sowden, K. E. Francis, and R. B. Harper, *Journal of Nuclear Science and Engineering* 16, 1-24 (1963).
29. Reactor Chem. Div. Ann. Progr. Rept. Jan. 31, 1962, ORNL-3262, pp. 99-104 (May 4, 1962).
30. Reactor Chem. Div. Ann. Progr. Rept. Jan. 31, 1963, ORNL-3417, pp. 121-24 (May 1, 1963).
31. C. H. Pitt and M. E. Wadsworth, Carbon Dioxide Absorption on Thoria, and a Kinetic Study of CO₂ Desorption from Thoria, Tech. Reports No. I and No. II, Dept. of Metallurgy, Univ. of Utah (1958).
32. D. R. Vissers, "The Sorption of Orthophosphate on Crystalline Metal Oxides" (to be published in the *Journal of Catalysis*).
33. G. Spaepen, R. J. Wimber, and M. E. Wadsworth, Adsorption of Silicic Acid on Thoria-Determined by Infrared Spectroscopy, Tech. Report No. V, Dept. of Metallurgy, Univ. of Utah (June 30, 1959).
34. H. R. Bradford and M. E. Wadsworth, Adsorption of Organic Acids on Thoria, Tech. Report VI. Thoria Surface Chemistry Project, Dept. of Metallurgy, Univ. of Utah (1959).
35. Homogeneous Reactor Quarterly Progress Reports, covering periods from Jan. 31, 1958 to Oct. 31, 1959, Oak Ridge, Tennessee, ORNL-2561, ORNL-2654, ORNL-2606, and ORNL-2879.
36. P. J. Anderson, *Trans. Faraday Soc.* 54, 130-38 (1958).
37. H. W. Douglas and J. Burden, *Trans. Faraday Soc.* 55, 350-62 (1959).
38. D. J. O'Connor, "The Ion Exchange and Ion Adsorption Properties of Thoria," AERE C/M 230, Harwell, England (1955).
39. C. J. Hardy, unpublished data, Oak Ridge National Laboratory (1965); guest scientist, AERE, Harwell, England.

40. B. Szilard, *Compt. rend.* 143, 1145-51 (1906).
41. C. M. Boyd, H. P. House, and O. Menis, Microelectrophoretic Determination of the Zeta Potential of Thorium Oxide, ORNL-3836 (1959).
42. F. J. Smith and N. A. Krohn, Electrophoretic Behavior of Thoria in Nitric Acid, unpublished data, Oak Ridge National Laboratory.
43. H. F. Holmes, C. S. Shoup, and C. H. Secoy, "Electrokinetic Phenomena at the Thorium Oxide-Aqueous Solution Interface," *J. Phys. Chem.* 19, 3155 (1965).
44. P. J. Anderson and P. Murray, "Zeta Potentials in Relation to the Rheological Properties of Oxide Slips," AERE M/R 2482, Harwell, Great Britain (Jan. 1958).
45. E. Matijevic and J. L. Stryker, *J. Colloid Interface Sci.* 22, 68 (1966).
46. J. Th. G. Overbeek, Colloid Science, Vol. 1, p. 335, ed. by H. R. Kruyt, Elsevier, New York, 1952.
47. E. Sturch, A Study of the Viscosity of Thoria Sols, ORNL-TM-258 (June 13, 1962).
48. E. L. Smith and J. E. Page, "The Acid-Binding Properties of Long-Chain Aliphatic Amines," *J. Soc. Chem. Ind. London* 67, 48-51 (1948).
49. British Patent 924,999 (1959).
50. J. G. Moore, Sol-Gel Process for Preparing ThO_2 - UO_3 Sols from Nitrate Solutions by Solvent Extraction with Amines, ORNL-4095 (in press).
51. A. B. Meservey, UO_2 - ThO_2 and UO_3 - ThO_2 Sols Prepared by Precipitation-Peptization Processes, ORNL-TM-1782 (Marc. 20, 1967).
52. A. B. Meservey, Preparation of Sols and Microspheres of ThO_2 , UO_2 , ThO_2 - UO_2 and ThO_2 - UO_3 by Sol-Gel Techniques, ORNL-4177 (in preparation).
53. J. P. McBride (Compiler), Preparation of UO_2 Microspheres by a Sol-Gel Technique, ORNL-3784 (February 1966).
54. W. D. Bond et al., Preparation of $^{235}\text{UO}_2$ - ThO_2 Microspheres by a Sol-Gel Method, ORNL-TM-1601 (August 1966).
55. K. J. Notz, Preparation of Porous Thoria by Incorporation of Carbon in Sol, ORNL-TM-1780 (in preparation).
56. Chem. Tech. Div. Ann. Progr. Rept. May 31, 1966, ORNL-3945 p. 160 (September 1966).

57. Chem. Tech. Div. Ann. Progr. Rept. May 31, 1967, (ORNL-4145 (in preparation)).
58. C. J. Hardy, The Electron Microscope, Electron Diffraction, and Spectrophotometric Examination of Hydrous Uranium Dioxide Precipitates and Sols, ORNL-3963 (August 1966).
59. R. G. Wymer and J. H. Coobs, "Preparation, Coating, Evaluation, and Irradiation Testing of Sol-Gel Oxide Microspheres," Proceedings of the British Ceramic Society (February 1967).
60. P. A. Haas, F. G. Kitts, and H. Beutler, "Preparation of Reactor Fuels by Sol-Gel Processes," paper presented at the American Institute of Engineers National Meeting at Salt Lake City, Utah, May 21-24, 1967; to be published in Nuclear Engineering Series by the A.I.Ch.E.
61. R. G. Wymer and A. L. Lotts (Compilers), Fuel Cycle Ann. Progr. Rept. 1966 (in preparation).
62. G. B. Alexander and J. Bugosh, "Concentrated Zirconia and Hafnia Aquasols and Their Preparation," U.S. Patent 2,984,628, to du Pont Co., May 16, 1961.
63. J. L. Kelly, A. T. Kleinstuber, S. D. Clinton, and O. C. Dean, "Sol-Gel Process for Preparing Spheroidal Particles of the Dicarbides of Thorium and Thorium-Uranium Mixtures," Ind. Eng. Chem., Process Design Develop. 4, 212 (1965).
64. K. J. Notz, Mixed Sols of Carbon Black with Thoria and with Other Oxides, ORNL-TM-1982 (in preparation).
65. K. J. Notz, A Sol-Gel Process for Preparing Dense Microspheres of ThC₂, ORNL-TM-1983 (in preparation).
66. K. J. Notz, "Dispersal of Carbon Blacks to Individual Crystallites," J. Phys. Chem. 71, 1965 (1967).
67. K. J. Notz, "Correction to Dispersal of Carbon Blacks to Individual Crystallites," submitted for publication in J. Phys. Chem.
68. K. J. Notz, A Sol-Gel Process for Preparation of (Th,U)C₂ Carbide, ORNL-TM-1984 (in preparation).
69. T. A. Gens, D. M. Helton, and S. D. Clinton, Laboratory Preparation of Uranium Nitride Microspheres by a Sol-Gel Technique, ORNL-3879 (November 1965).
70. M. H. Lloyd, R. D. Baybarz, S. R. Buxton, and C. J. Hardy, Transuranium Quarterly Prog. Rept. Oct. 31, 1965, ORNL-3965, pp. 23-5.

71. R. D. Baybarz, "Preparation of Curium Hydroxide Sol-Gel Spheres as an Intermediate to CmO_2 Microsphere Preparation," *Inorg. Nucl. Chem. Letters* 2, 129-32 (1966).

INTERNAL DISTRIBUTION

- | | | | |
|--------|-------------------------------|----------|------------------|
| 1-3. | Central Research Library | 79. | E. L. Long, Jr. |
| 4-5. | ORNL — Y-12 Technical Library | 80. | A. L. Lotts |
| | Document Reference Section | 81. | H. G. MacPherson |
| 6-25. | Laboratory Records | 82-186. | J. P. McBride |
| 26. | Laboratory Records, ORNL RC | 187. | R. W. McClung |
| 27. | ORNL Patent Office | 188. | K. H. McCorkle |
| 28. | R. E. Adams | 189. | D. L. McElroy |
| 29. | G. M. Adamson, Jr. | 190. | A. B. Meservey |
| 30. | H. Beutler | 191. | C. S. Morgan |
| 31. | S. E. Bolt | 192. | J. G. Moore |
| 32. | E. S. Bomar | 193. | J. P. Moore |
| 33. | W. D. Bond | 194. | L. E. Morse |
| 34. | G. E. Boyd | 195. | K. J. Notz |
| 35. | R. E. Brooksbank | 196. | A. R. Olsen |
| 36. | K. B. Brown | 197. | P. Patriarca |
| 37. | J. M. Chandler | 198. | W. L. Pattison |
| 38. | S. D. Clinton | 199. | W. H. Pechin |
| 39. | J. H. Coobs | 200. | J. W. Prados |
| 40. | C. M. Cox | 201. | R. B. Pratt |
| 41. | F. L. Culler | 202. | J. M. Robbins |
| 42. | J. E. Cunningham | 203. | J. T. Roberts |
| 43. | D. E. Ferguson | 204. | M. W. Rosenthal |
| 44. | R. B. Fitts | 205. | A. D. Ryon |
| 45. | J. H. Frye, Jr. | 206. | R. Salmon |
| 46-66. | P. A. Haas | 207. | J. L. Scott |
| 67. | R. G. Haire | 208. | J. D. Sease |
| 68. | R. L. Hamner | 209. | J. G. Stradley |
| 69. | W. O. Harms | 210. | O. K. Tallent |
| 70. | F. E. Harrington | 211. | D. B. Trauger |
| 71. | C. C. Haws, Jr. | 212. | W. E. Unger |
| 72. | D. M. Helton | 213. | T. N. Washburn |
| 73. | M. R. Hill | 214. | A. M. Weinberg |
| 74. | A. R. Irvine | 215. | J. R. Weir |
| 75. | F. J. Kitts | 216. | M. E. Whatley |
| 76. | J. A. Lane | 217-227. | R. G. Wymer |
| 77. | J. M. Leitnaker | | |
| 78. | M. H. Lloyd | | |

EXTERNAL DISTRIBUTION

- 228-232. F. W. Albaugh, Battelle, PNL
- 233-236. R. J. Allio, Westinghouse Atomic Power Division
- 237. A. Amorosi, Argonne National Laboratory, LMFBR Program Office
- 238. R. D. Baker, Los Alamos Scientific Laboratory
- 239. R. W. Barber, AEC, Washington
- 240. L. Brewer, University of California, Berkeley
- 241. L. Burris, Argonne National Laboratory, LMPFB Program Office
- 242. V. P. Calkins, GE, NMPO
- 243. W. Cashin, Knolls Atomic Power Laboratory
- 244. S. Christopher, Combustion Engineering, Inc.
- 245. D. B. Coburn, General Atomic
- 246. D. F. Cope, RDT, SSR, AEC, ORNL
- 247. G. W. Cunningham, AEC, Washington
- 248. C. B. Deering, RDT Site Representative, ORNL
- 249. E. Dewell, B&W, Lynchburg, Virginia
- 250. G. K. Dicker, Division of Reactor Development and Technology, AEC, Wash.
- 251. D. E. Erb, Division of Reactor Development and Technology, AEC, Wash.
- 252. E. A. Evans, GE, Vallecitos
- 253. W. C. Francis, Idaho Nuclear Corporation
- 254. T. A. Gens, Linde Division, Union Carbide Corporation, Tonawanda, N.Y.
- 255. A. J. Goodjohn, General Atomic
- 256. R. G. Grove, Mound Laboratory
- 257. D. H. Gurninsky, BNL
- 258. A. N. Holden, GE, APED
- 259-261. J. S. Kane, Lawrence Radiation Laboratory, Livermore
- 262. H. Kato, U. S. Department of the Interior, Bureau of Mines
- 263. L. K. Kellman, Argonne National Laboratory, LMFBR Program Office
- 264. E. A. Kintner, Fuel Fabrication Branch, AEC, Washington
- 265. J. H. Kittel, ANL
- 266. E. J. Kreih, Westinghouse, Bettis Atomic Power Laboratory
- 267. W. J. Larkin, AEC, Oak Ridge Operations
- 268. J. A. Leiberman, AEC, Washington
- 269. P. J. Levine, Westinghouse Advanced Reactor Div., Waltzmill Site,
Madison, Pa.
- 270. J. J. Lombardo, NASA, Lewis Research Center
- 271. E. D. Lynch, Babcock & Wilcox
- 272. J. H. MacMillan, Babcock & Wilcox
- 273. R. Mayfield, ANL
- 274. M. McGurty, GE, NMPO
- 275. W. H. McVey, AEC, Washington
- 276. E. Moncrief, B&W, Lynchburg, Virginia

EXTERNAL DISTRIBUTION

- 277. J. Morabito, AEC, Washington
- 278. M. Nevitt, ANL
- 279. E. O. Nurmi, B&W, Lynchburg, Virginia
- 280. R. E. Pahler, Division of Reactor Development and Technology, AEC, Wash.
- 281. S. Paprocki, BMI
- 282. D. Ragone, General Atomic
- 283. W. E. Ray, Westinghouse Advanced Reactor Division, Waltzmill Site,
Madison, Pa.
- 284. W. E. Roake, Battelle, PNL
- 285. B. Rubin, Lawrence Radiation Laboratory, Livermore
- 286. J. W. Ruch, AEC, ORO
- 287. F. C. Schwenk, Division of Reactor Development and Technology, AEC, Wash.
- 288. W. F. Sheely, Division of Research, AEC, Washington
- 289-291. J. M. Simmons, Division of Reactor Development and Technology, AEC, Wash.
- 292. E. E. Sinclair, AEC, Washington
- 293. L. E. Steele, Naval Research Laboratory
- 294. R. H. Steele, Division of Reactor Development and Technology, AEC, Wash.
- 295. A. Strasser, United Nuclear Corporation
- 296. J. A. Swartout, UCC, New York, N.Y.
- 297. A. Toboada, Division of Reactor Development and Technology, AEC, Wash.
- 298. A. Van Echo, Division of Reactor Development and Technology, AEC, Wash.
- 299. R. Van Tyne, Illinois Institute of Technology Research Institute
- 300. B. Vondra, NUMEC, Apollo, Pa.
- 301. C. E. Weber, Atomics International
- 302. J. F. Weissenberger, RDT, OSR, GE, NMPO
- 303. G. W. Wensch, Division of Reactor Development and Technology, AEC, Wash.
- 304. G. A. Whitlow, Westinghouse Advanced Reactor Division, Waltzmill Site,
Madison, Pa.
- 305. M. J. Whitman, AEC, Washington
- 306. E. A. Wright, AEC, Washington
- 307. Division of Research and Development, AEC, ORO
- 308-322. Division of Technical Information Extension