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LABORATORY AND ENGINEERING STUDIES OF SOL-GEL PROCESSES AT OAK RIDGE NATIONAL LABORATORY

R. G. Wymer

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

R. G. Wymer

For presentation at the Panel on Sol-Gel Processes to be held by the International Atomic Energy Agency, in Vienna, Austria, May 6-10, 1968.

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OAK RIDGE NATIONAL LABORATORY
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ABSTRACT

A brief description of a model for sols, based largely on studies on ThO_2 sols, is given. Processes based on solvent extraction of nitrate ion by secondary amines to prepare $\text{ThO}_2\text{--UO}_3$ and UO_2 sols are discussed, and the flowsheets and equipment used in preparing these sols are illustrated. A method suitable for preparing 150 g batches of PuO_2 as sol is described, along with the properties of the typical PuO_2 and $\text{UO}_2\text{--PuO}_2$ products. Demonstrated processes for preparing, drying, and firing microspheres of ThO_2 , $\text{ThO}_2\text{--UO}_2$ are described, and results of some experiments on low-energy compaction of microspheres in tubes to form fuel elements of predetermined density are discussed. Finally, miscellaneous sol-gel processes for preparing carbides, porous oxides, nitrides, and carbonitrides are briefly described.

INTRODUCTION

The work on sol-gel processes at Oak Ridge National Laboratory has been summarized recently in a series of our reports.^{1,2,3,4} In this paper much of what has already been reported is summarized, and recent observations and developments have been added. The emphasis is on the applied work rather than the basic work being carried out. Much remains to be done in both areas. The present emphasis is on exploiting sol-gel processes to produce improved fuels for fast breeder reactors, especially liquid-metal-cooled fast breeders, and for high-temperature gas-cooled reactors, especially those of the Fort St. Vrain (Public Service of Colorado) type. This emphasis is reflected in the order of presentation of the material. The order also reflects the state of the art at ORNL. Thoria and thoria-urania microspheres represent the products of the most highly developed processes; urania, the next; plutonia and plutonia-urania, the next; the carbides next, and the remainder fall into a sort of miscellaneous category.

PROPERTIES OF THORIA SOLS

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. 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.

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 powder 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.

In general, thoria sols are of two main types: the crystalline thoria sols, which are prepared from the steam-denitrated oxide, and hydrous amorphous thoria, which is produced by precipitation or dialysis of a solution of thorium nitrate or chloride at 25°C. The crystallite size of thoria 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. An 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.

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.

Figure 1 shows a graphic representation of nitric acid adsorption as reflected by solution depletion. It appears that thorium adsorbs nitrate in two forms: as ionic nitrate, and as a distorted "nitrato" species, with amounts of the latter increasing as the colloidal thorium is progressively dried.

The peculiarly strong adsorption of U(VI) on thorium is well known.⁷ If the U(VI) is adsorbed on pre-formed thorium 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

Detailed study of the electrophoresis of colloidal thorium has shown numerous, severe false-boundary and false-mobility effects due to traces of dissolved thorium nitrate or possibly other trace ionic contaminants. Further, it was only possible to obtain consistent trends of electrokinetic mobility with electrolyte composition for a given sample. Different thorium samples would sometimes give opposite trends. The electrokinetic behavior of thorium, and of other oxides as well, is apparently a very complex function of its preparative history, as has been suggested by others.⁹

$\text{ThO}_2\text{--UO}_3$ SOL PREPARATION BY SOLVENT EXTRACTION

The ability of amines to extract acids and metal complexes from aqueous solutions 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 colloidal suspensions containing thorium and uranium.¹⁰ 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.¹¹

In the solvent extraction process, $\text{ThO}_2\text{--UO}_3$ are prepared directly from aqueous solutions containing thorium and uranyl nitrates. The nitrate is removed from the aqueous solution by contacting it 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 first two extractions.

A typical flowsheet for the preparation of a sol having a Th/U atom ratio of about 3 is presented in Fig. 2. One volume of aqueous solution about 0.21 M in $\text{Th}(\text{NO}_3)_4$ and 0.07 M in $\text{UO}_2(\text{NO}_3)_2$ is contacted for at least 2 min with two volumes of 0.75 M 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 phase continuous.

ORNL-DWG 66-12570R

Fig. 1. Adsorption of HNO_3 on Colloidal ThO_2 .

ORNL DWG 67-6947

Fig. 2. Flowsheet for Preparation of $\text{ThO}_2\text{-UO}_3$ Sol by Amine Extraction of Nitrate.

After the initial contact, the phases are separated, and the aqueous phase, which has a $\text{NO}_3^-/\text{metal}$ ratio of about 1, 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 approximately 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.

Mixer-settlers are used as the contacting devices (Fig. 3). They are constructed of 3-in.-diam glass pipe and are geometrically safe for enriched uranium. Each mixer is divided into six compartments, with an agitator in each compartment. This minimizes bypassing and ensures efficient mixing. The solvent and the aqueous phases enter at the top and flow cocurrently through the mixer to the settler, which is a pipe tee located at the bottom of the mixer. The interface is maintained in the tee below the mixer to ensure an organic-continuous dispersion in the mixer, which is very important for preventing emulsions. The interface position is controlled by a simple jackleg and an adjustable weir on the aqueous outlet of the settler. The digester is merely an enlargement of the jackleg of the first-stage settler. The temperature is controlled by circulating heated water through the baffles in the mixers and through a coil in the digester.

The process was demonstrated at the design rate of 1 kg of $\text{ThO}_2\text{--UO}_3$ sol per hour. About 900 liters of 0.3 M sol was produced. The $\text{NO}_3^-/\text{metal}$ mole ratio was consistently less than 0.10. The crystallite size of the sol was 42-46 Å, which is slightly larger than that obtained in laboratory preparations.

The equipment has operated very smoothly. Organic-continuous dispersions were maintained without difficulty and interface control was very stable. Some emulsions accumulated in the first-stage settler during the early runs; however, coalescence occurred in subsequent stages such that the sol product contained less than 0.1 vol % solvent. During the latter runs, the scrub solution was recycled to the first stage, and virtually no emulsion was formed. Entrainment of aqueous in the solvent caused difficulties only for the solvent stream leaving the extraction section; it was directly dependent on the agitator speed in the mixer, ranging from 0.15% at 300 rpm to 0.8% at 600 rpm. Entrainment was the only significant cause of loss of metal, which usually amounted to about 0.1%. We believe this loss can be reduced by improved scrubbing of the solvent before regeneration. The efficiency of the mixers was 90 to 95% at agitator speeds of 300 to 500 rpm.

Batches of sol have been concentrated 5-fold (to 1.5 M) in a forced-circulation vertical-tube evaporator (Fig. 4). A high degree of turbulence and a large heat exchange area are used to minimize drying of the sol on the tubes. De-entrainment is accomplished by introducing the superheated sol tangentially into the body of the

Fig. 3. Mixer-Settlers Used for Continuous Preparation of $\text{ThO}_2\text{--UO}_3$ Sol by Amine Extraction of Nitrate.

Fig. 4. Forced-Circulation Evaporator for Concentration of Sols.

evaporator; additional de-entrainment occurs in the stripping section, where the vapor contacts the feed in a packed tower. Very few solids have formed, and no foaming has occurred, even with operation at a vacuum of 25 in. Hg. The concentrate is fluid and stable at all Th + U concentrations up to 1.5 M.

Seven kilograms of microspheres were formed, dried in a steam atmosphere, and calcined at 1150°C in an Ar atmosphere to form 350-500- μ -diam spheres. The microsphere forming column was operated with the surfactants 0.6 vol % Ethomeen S/15 and 0.5 vol % Span 80 in the 2-ethyl-1-hexanol. No microsphere cracking was detected at either the drying or calcining steps.

Engineering studies of the amine extraction process are now being extended to include high specific alpha activity materials, e.g., ^{233}U . Towards this end, an alpha enclosure containing amine extraction equipment (the Pu Solex Development Laboratory) has been designed and built.¹² This laboratory will permit the preparation of concentrated hydrosols containing fissionable isotopes at a rate of about 1 kg/day. Three stages of amine extraction with two stages of digestion are permissible. Three contactors without the interstage digestion are available for amine regeneration. These six contactor assemblies are mounted on a frame with the services located between the hydrosol forming stages and the amine regeneration stages. The assembled unit fits onto a track inside an alpha enclosure to facilitate equipment modifications (Fig. 5).

A second alpha enclosure of identical design contains the vacuum evaporator. This critically safe vacuum evaporator is designed for batch operation, and is capable of removing about 4 liters of condensate per hour. It is very similar to the evaporator described earlier.

UO_2 SOL PREPARATION BY SOLVENT EXTRACTION

The development of a sol-gel process for the preparation of urania microspheres was prompted by their potential use as thermal and fast reactor fuels, in which urania would be the bulk constituent. A solvent extraction process analogous to that developed for preparation of $\text{ThO}_2\text{--UO}_3$ sols was developed for preparation of UO_2 sols. The process has been successfully scaled up and operated continuously in engineering experiments. A total of 40 runs has been made, each producing about 2 kg of UO_2 in the form of dilute (about 0.2 M) sol. Laboratory studies have been continued to characterize the sol and aid in the engineering studies. Some of the operating parameters affecting sol properties that were studied are: nitrate-to-uranium ratio during digestion; digestion temperature; and method of preparing the U(IV) solution.

Fig. 5. Amine Extraction Equipment Alpha Enclosure.

The reference flowsheet for the preparation of UO_2 sol by solvent extraction (Fig. 6) was developed from laboratory batch studies.¹³ It consists of extracting nitrate from an aqueous solution of U(IV) nitrate-formate with a long-chain amine (e.g., Amberlite LA-2, Rohm and Haas Company) dissolved in a paraffin diluent. Digestion of the nitrate deficient solution thus formed results in formation of the UO_2 sol. Final nitrate adjustment is obtained in subsequent extractions. The amine is regenerated by contact with sodium carbonate and is recycled.

Preparation of U(IV) Solution

During the laboratory studies, the U(IV) solution was prepared by contacting $0.2 \text{ M } \text{UO}_2(\text{NO}_3)_2$ — $0.1 \text{ M } \text{HCOOH}$ with hydrogen using 5% Pt on Al_2O_3 powder as the catalyst. Although this procedure usually produced good results, it did not appear very practical for the larger engineering tests because of the time required for settling and filtration for removal of the catalyst. Several alternative methods of reduction were tried. The first method was continuous reduction in a pressurized fixed bed of Pt on Al_2O_3 pellets. Attempts to make sol using U(IV) from this reductor failed because of the formation of viscous sol in the second extraction stage. The next reduction method tried was batch operation of the fixed catalyst bed at nearly atmospheric pressure. This allowed better control of the reduction, and the resulting sol was improved; no thickening of the dilute sol occurred. However, the sol could not be concentrated (by vacuum evaporation) to 1 M without getting thick or setting up as a gel. The U(IV) solution contained a nitrogen-bearing basic material which acted like ammonia during chemical analysis but degraded on standing. The fact that ammonia can cause thick sol was demonstrated in laboratory tests by adding ammonia (mole ratio $\text{NH}_3/\text{U} = 0.02$) to the laboratory prepared U(IV) solution, which then was formed into sol by the usual batch extraction technique.

Our preferred reduction method now is based on use of a slurry-type reductor wherein finely divided PtO_2 catalyst is suspended in a well-mixed uranium nitrate solution and hydrogen is introduced through a sparger. The PtO_2 is reduced to metal, which becomes flocculated in the presence of excess hydrogen, so that when the reduction of the uranium is nearly complete the catalyst settles very rapidly and is readily retained on a filter. The filter is a flat disc of porous stainless steel (10μ pore) which forms the bottom of the reductor. The reduction is monitored by measuring the redox potential of the solution using a Pt electrode vs a reference glass electrode system. (Other reference electrodes, such as silver-silver chloride or calomel, will work but are not as rugged and free of trouble as glass.) The end point is readily detected as a sharp break in emf which occurs when reduction has progressed to between 96 and 100% U(IV). The feed composition was fixed at $0.6 \text{ M } \text{UO}_2(\text{NO}_3)_2$ containing about $0.4 \text{ M } \text{HNO}_3$ and $0.3 \text{ M } \text{HCOOH}$ so that NO_3^-/U was 2.6, and HCOOH/U was 0.5.

Fig. 6. Preparation of UO₂ Sol by Solvent Extraction.

The slurry reductor has been tested both in a laboratory unit of 1.6 liter capacity and a larger unit of 14 liter capacity to supply feed for the engineering tests of the solvent extraction sol process. A total of about 10 kg of U was reduced in the small reductor, thus demonstrating the feasibility of the slurry catalyst. The large reductor was designed and built using the laboratory data. The results of 20 runs, producing a total of 40 kg U(IV), show excellent performance. The Pt catalyst has shown no sign of loss in activity or in ease of filtration (gravity filtration time was 12 min for 14 liters). Greater than 99.5% U reduction was easily obtained, very little ammonia was formed ($\text{NH}_3/\text{U} \leq 0.002$), and less than 10% of the HCOOH was destroyed. The rate of U reduction with 30 g of PtO_2 ranged from 2 moles/hr when only a small excess of hydrogen was used (96% utilization) to 3.3 moles/hr at 77% hydrogen utilization.

Figure 7 is a schematic representation of the reduction equipment used to prepare feed for the engineering scale solvent extraction equipment. Table 1 shows the effect of agitator speed and H_2 flow rate for a fixed feed and catalyst concentration.

Preparation of Sol

The equipment for the engineering study of the sol preparation process is the same as was used for the preparation of $\text{ThO}_2\text{--UO}_3$ sol.¹⁴ It uses mixer-settlers as the contacting devices for extraction, water scrub, and amine regeneration. The mixer-settlers are geometrically safe with regard to criticality. The design capacity of the equipment is 6 liters of sol per hour; capacity is set by the size of the digester and the flowsheet requirement of about 1-hr residence time in the digester.

The operation of the solvent extraction equipment with the reference flowsheet has been very good (during 20 runs about 1000 liters of 0.2 M UO_2 sol has been produced). Table 2 summarizes some operating conditions and sol product properties. No emulsion or entrainment problems have occurred. The entrainment of solvent in the sol product has been consistently less than 0.01 vol %. A small entrainment of sol in the used solvent is removed by a water scrub stage to prevent loss of uranium to the regeneration waste. Although three extraction stages have been used in most of the runs, only two are needed because the nitrate content of the sol changes very little in the third stage. The stage efficiency has been consistently greater than 90% at a mixer speed of 500 rpm.

Variation of U concentration from 0.15 to 0.3 M (the reference concentration is 0.2 M) did not cause any trouble, and good sol was produced; however, two attempts to run at 0.5 M U were unsuccessful because the sol became thick in the second extraction stage.

The digestion temperature was found to be an important variable. At 50°C the sol product contains a significant amount of amorphous UO_2 (determined by

ORNL DWG 68-4113

Fig. 7. Batch Slurry Uranium Reductor.

Table 1. Batch Reduction of 0.6 M $\text{UO}_2(\text{NO}_3)$ —0.3 M HCOOH 0.3 M HNO_3
Solution (14 liters) in a Stirred Slurry Catalyst (30 g PtO_2) Reductor.

Agitator Speed (rpm)	Excess H_2 (%)	Reduction Rate (mole U/hr)
570	12	1.9
820	12	2.5
1070	12	2.8
1070	4	2.0
1070	12	2.8
1070	22	3.7

Table 2. UO_2 Sol Formation by Solvent Extraction in Continuous-Flow Engineering Tests

Run No.	Excess Amine (%)	Digestor Temp. ($^{\circ}\text{C}$)	Dilute Sol, NO_3^-/U mole ratio	Shelf Life of 1 M Sol (day) [*]
15	50	50	0.17	13
16A	50	50	0.26	50
16B	50	65	0.08	90
17	50	50	0.27	43
18	50	50	0.24	40
19	70	50	0.24	60
20	50	60	0.09	35
21	50	60	0.09	36
22	50	60	0.10	60
23A	65	60	0.17	25
23B	65	50	0.24	-
24	50	50	0.24	50
27	20	60	0.13	50
28	20	60	0.14	50
29	50	60	0.10	50
30	50	60	0.09	10
31	50	60	0.09	25
32	50	60	0.09	15
33	50	70	0.07	8
35	50	60	0.10	-
36	50	60	0.09	-

^{*}Shelf life refers to the number of days the sol remained fluid. In some cases, the sol thickened after the interval listed; in others, it gelled. In all cases the sol had been concentrated from the concentration given in column 4 to 1 mole/liter.

x-ray diffraction). This sol gels at about 0.5 M if evaporated immediately after preparation; however, after aging overnight it can be evaporated to greater than 1.0 M and will remain fluid for over 30 days. When the digestion temperature is increased to 60°C, the sol contains more UO_2 crystallites, and the fresh sol can be concentrated without gelling. To minimize oxidation of the uranium at the higher digestion temperature, the laboratory flowsheet was modified by using an excess of amine in the first stage. This results in the nitrate being extracted down to a NO_3^-/U less than 0.5. At a digester temperature of 70°C, the sol has a shorter shelf life after concentration; perhaps because too much oxidation of uranium occurs, even at the low nitrate-to-uranium ratio. The digester temperature also affects the nitrate-to-uranium mole ratio in the sol product; it averages 0.24 when digestion is carried out at 50°C, 0.10 when carried out at 60, and 0.07 when carried out at 70°C. The amount of amine in excess of the stoichiometric quantity required to extract the nitrate from the feed has very little effect on the nitrate content of the sol over the range of 20 to 70% excess. The average size of the UO_2 crystallites is 35 to 40 Å and does not seem to be dependent on either digester temperature or length of the aging period.

Evaporation of Sol

The dilute sol must be concentrated to about 1 M U to facilitate forming microspheres. Vacuum evaporation is used to avoid over heating the sol. The temperature is kept below about 35°C. The sol is quite sensitive to oxidation, and exposure to air is a common cause of thickening or, in extreme cases, flocculation of the sol.

Seven batches (each 2 kg U) of dilute sol have been successfully concentrated in the forced circulation vertical tube evaporator¹⁵ to yield 1 M sol for use in making microspheres. The evaporation has been very smooth without foaming or scaling at the design boilup rate of 15 liters/hr and at an absolute pressure of 30 torr. The shelf life of the large batches of concentrated sol has not been as good as product from the small laboratory evaporator. We believe this is caused by some inleakage of air and resultant oxidation of uranium in the large evaporator. In several runs where large leaks were discovered, the sol thickened overnight, while in other runs the sols were still fluid after 30 days.

PuO_2 SOL PREPARATION

A sol-gel process for the preparation of dense oxide forms of PuO_2 has been developed and tested on a 150-gram scale. The sols produced by this method are 1 to 3 M in plutonium and have NO_3^-/Pu of 0.1 to 0.15. They are stable for many months and are compatible with thorium and urania sols that have been prepared at

Oak Ridge National Laboratory. Dense PuO_2 , as well as $\text{PuO}_2\text{--UO}_2$ or $\text{PuO}_2\text{--ThO}_2$ microspheres at any desired Pu/U or Pu/Th atom ratio have been produced.

A total of 7.4 kg of Pu was converted into stable PuO_2 sols during the past year. Approximately 90% of this was formed into PuO_2 microspheres of greater than 94% theoretical density. The remainder was mixed with UO_2 sols and formed into microspheres for fuel fabrication studies. These preparations demonstrated the operability of equipment and the reproducibility of the flowsheet, and provided sol for the formation of mixed-oxide and plutonia microspheres. The present flowsheet for the preparation of Pu sol is shown in Fig. 8. Prior to the operations shown on the flowsheet, an adjustment of the valence of the plutonium (to Pu^{4+}) is made, if necessary, by bubbling NO gas through the $\text{Pu}(\text{NO}_3)_4$ solutions. A minimum HNO_3 concentration of 1 M is maintained in the feed to prevent polymerization of the plutonium; free HNO_3 concentrations as high as 3 M have been used successfully.

The $\text{Pu}(\text{NO}_3)_4$ feed solution is added to NH_4OH at rates as high as 30 cc/min, with moderate agitation, to ensure rapid neutralization and precipitation of the $\text{Pu}(\text{OH})_4$. As little as 40% excess NH_4OH proved to be satisfactory as long as the concentration of NH_4OH in the final solution was $\geq 1 \text{ M}$. The NH_4NO_3 and the excess NH_4OH are removed through a porous stainless steel (G porosity) filter. The precipitate is washed thoroughly (four washes), with resuspension of the filter cake in each wash. A high-nitrate sol is then formed by peptizing the washed cake in dilute HNO_3 at a NO_3^-/Pu mole ratio of about 2. All the steps just mentioned are carried out in an 8-in.-diam precipitation-filtration vessel having a porous stainless steel filter in the bottom (Fig. 9). Filtration time is about 20 min per wash. Four such washes give adequate NH_4^+ removal. The high-nitrate sol is removed through the bottom of the vessel, leaving no solids on the filter.

A minimum NO_3^-/Pu mole ratio of 1 is necessary for forming plutonia sol. Although ratios as high as 4 have been used, a ratio of 2 is sufficient to bring about sol formation upon heating to about 90°C . Under these conditions, a sol having approximately 20 Å crystallites exists. However, microspheres formed from this material have low densities and low strength.

The NO_3^-/Pu ratio of the sol must be reduced to 0.1 to 0.2 by thermal denitration (or baking) and resuspension before the sol will form dense microspheres. This is a crucial step requiring careful control of temperature and time. The sol is first evaporated to dryness at 100°C and then heated to a temperature of about 240°C . A thin, porous cake which forms as the sol dries is maintained intact throughout the cycle. During the reduction to dryness, excess HNO_3 is evaporated such that the initial NO_3^-/Pu mole ratio in the dry solid is 0.8 to 1.0. Progress of the denitration is followed by resuspending a weighed sample of the dry material and titrating with NaOH to determine the NO_3^- content. It is important that the heating of the solid be uniform in order to obtain a uniform product. If the denitration is allowed to proceed until the NO_3^-/Pu mole ratio is less than 0.1, the PuO_2 cannot be resuspended

Fig. 8. Flowsheet for Preparation of PuO_2 Sol.

Fig. 9. Vessel for the Precipitation, Filtration, and Peptization of PuO_2 Sol.

as a sol. Laboratory results relating temperature and time to the removal of NO_3^- from the cake being denitrated are shown in Figs. 10, 11, and 12. A diagram of the denitration vessel, which allows independent control of the temperatures of the top and bottom surfaces and limits radial gradients to approximately 2°C , is shown in Fig. 13. Crystallite growth and agglomeration also occur during baking. After the denitration step, the basic crystallite size is approximately 80 Å. These form agglomerates as large as 1000 Å. The amount of agglomeration must be limited to ensure a stable sol. Material having NO_3^-/Pu mole ratios of 0.1 to 0.15 can be resuspended by mild agitation in water to give plutonium concentrations as great as 2 M; more concentrated sols may be produced by evaporation after resuspension.

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. They can also be mixed with thoria or urania sols and formed into microspheres or fragments. Formation of gel microspheres from these sols is accomplished by using the procedures developed for thoria sols.

Microspheres have been prepared 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 600 μ in diameter can be obtained. After calcination at 1150°C , these products are characterized by high density, low surface 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 from 300- to 600- μ -diam microspheres. Crushing loads for microspheres calcined at 1150°C average above 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 $\text{UO}_2\text{--}20\%\text{ PuO}_2$ 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 $\pm 1.5\%$.

Fig. 10. Denitration of Plutonium by Baking at Different Temperatures.

Fig. 11. Denitration of Plutonium by Baking at 250°C.

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Fig. 12. Variation of k with Temperature.

Fig. 13. Vessel for the Thermal Denitration of PuO₂ Sol.

MICROSPHERE PREPARATION

The initial development of the process for the preparation of ThO_2 microspheres and its application to UO_2 or $\text{UO}_2\text{-ZrO}_2$ sols have been previously reported.^{16,17} Our work has included the operation of a microsphere pilot plant, with procedures and equipment required for a remote facility, the application of the process to a variety of sols on a larger scale, and the continued development of dispersers for sols.

Full-scale prototype units for microsphere preparation in a remotely operated facility have been operated during the past two years to produce ThO_2 microspheres. The prototype equipment incorporates all operations that are essential for the conversion of aqueous sols into microspheres (see Fig. 14). The design capacity is 1 kg of oxide spheres per hour. The improved equipment flowsheet presently used requires fewer equipment pieces and is simpler to control than earlier pilot plant flowsheets. The sol is dispersed into droplets that are released into the enlarged top of the tapered column. These droplets are suspended or fluidized by a recirculated, upflowing stream of the 2-ethyl-1-hexanol (2EH). As the water is extracted and the droplets gel into solid microspheres, the settling velocity increases. The column configuration and the fluidizing flow rates are selected to permit the gelled particles to drop out continuously while sol droplets are being formed in the top of the column. Separation of the gel spheres from the 2EH is accomplished by discharging the product collector into a dryer and draining off the liquid through a woven wire cloth. The gel spheres are dried and calcined batchwise. Fresh or purified 2EH is continuously added to the column; this displaces a stream of wet 2EH to a recovery system. Water is removed from the 2EH by distillation.

The entire system has been emptied and filled twice with 2EH, and 300 kg of 210- to 250- μ -diam and 20 kg of 500- to 590- μ -diam ThO_2 microspheres have been prepared. Each charge of 2EH (about 45 gal) was used for 6 months (equivalent in our operating mode to about 300 hr of operation in the column-distillation system). Operation was smooth throughout both periods; the solvent could have been used for a longer period of time, if necessary or desired. The largest monthly production was 137 kg of ThO_2 microspheres.

Surfactants must be added to the 2EH to prevent coalescence of droplets, sticking of droplets on column walls, and clustering of partially dried drops. Each time the column was filled with fresh 2EH, 0.3 vol % Ethomeen S/15 and 0.07 vol % Span 80 were added. Satisfactory column operation was maintained by adding 10 ml of Ethomeen S/15 and 2.5 ml of Span 80 per liter of sol fed. Excessive Span 80 concentrations result in distortion of large sol droplets and thus in nonspherical gel particles; therefore, the additions of Span 80 were discontinued while making 400 μ ThO_2 microspheres.

Samples of 2EH were analyzed for nitrate, amine, total nitrogen, and thorium periodically throughout each of the two 6-month periods. Results of analyses obtained during the last four months of the second 6-month period showed no trend with time

Fig. 14. Improved and Simplified Equipment Flowsheet for Microsphere Preparation.

(see Table 3). Only the thorium (ThO_2) concentration built up steadily throughout the period, causing turbidity of the solvent. This buildup was the result of occasional equipment malfunction. Turbidity hindered visual observations of microspheres through the column walls and was the primary reason for discarding both the 2EH loadings. The thorium causing the turbidity was present as extremely fine particles (300 Å), which settled out upon long standing (~15 days), leaving clear 2EH.

To monitor the extent of column loading, a bubbler tube was installed with its lower tip placed in a sidearm off the column bottom. As the column loaded with microspheres, the back pressure increased to about 4 in. of water and then leveled off. This plateau has been used as a means of controlling the loading of the column.

The present geometry of the glass column (Fig. 15) appears to be nearly optimum for producing microspheres in the size ranges of interest. The 500- to 590- μ -diam particles settle in a sharply defined zone in the tapered section just above the throat; the stainless steel top section gives ample settling capacity for the 210- to 250- μ -diam particles.

A filter was placed in the 2EH circuit to remove suspended fines; it was also effective in removing small gelled particles. Use of filtration, in an overall sense, was not satisfactory since any operational upsets allowed soft, half-gelled sol to enter the circulating system and to plug the filter. A large settler (Fig. 16) is now used to remove any entrained sol or gel particles before they reach the pump.

A liquid-driven (2EH) jet was mounted on the bottom of the forming column to transfer the microspheres continuously to the dryer. This transfer method has worked satisfactorily.

A prototype gel microsphere dryer design is shown in Fig. 16. The ThO_2 microspheres enter the settler with the 2EH transfer fluid. Part of the 2EH flows down through the stainless steel wire cloth in the dryer bottom, while the rest overflows the settler. Both streams combine and return to the column circuit. The microspheres remain on the screen. The settler was installed to allow the transfer jet to operate at constant pressure, since the pressure drop across the bed of microspheres increases as the dryer is filled. When the dryer is filled with microspheres, excess 2EH is blown down through the screen with nitrogen, the steam is turned on, and the bed is allowed to dry (150 to 250°C). After drying, microspheres are transferred pneumatically to the calciner.

In the conceptual design of the remotely operated calciner the charge is contained in a crucible that is fixed in the furnace. The charge will be loaded by gravity and discharged pneumatically. The present calciner is actually a muffle furnace containing crucibles that are loaded manually.

Table 3. Analyses of Species Present in the 2-Ethyl-1-Hexanol Used
in a Microsphere Column over a 4-Month Period

Species	Concentration Range	Comment
Nitrate ion	$(1.5 \text{ to } 4) \times 10^{-4} \text{ M}$	No trend with time
Total nitrogen	$(2.0 \text{ to } 5) \times 10^{-4} \text{ M}$	No trend with time
Amine	$(6.0 \text{ to } 10) \times 10^{-4} \text{ M}$	No trend with time
Thorium	$(2.0 \text{ to } 7) \times 10^{-4} \text{ M}$	Increasing with time

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Fig. 15. Microsphere Column: Configuration and Dimensions.

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Fig. 16. Schematic Arrangement of Microsphere Dryer and Calciner.

The use of the liquid and pneumatic microsphere transfer systems represents a significant improvement in our flowsheet, serving to eliminate mechanical transfer of canisters, or crucibles, within the cell.

The $\text{ThO}_2\text{-UO}_3$ sols prepared by amine extraction of nitrate (Th/U ratios = 3 to 5) were formed into gel spheres using Span-80/Ethomeen S/15 volume ratios of about 2. Span 80 alone tended to give wrinkled or "raisin" surfaces, while Ethomeen S/15 alone tended to give deep dimples or "cherry pits." Small-scale tests with freshly prepared sol and new 2EH required low total surfactant concentrations ($\leq 0.2\%$) to prevent cracking of the gel spheres into fragments. This cracking did not occur for surfactant concentrations as large as 0.8 vol % in larger-scale tests with aged sol (storage period, 1 to 3 months) and 2EH that had been used 20 to 40 hours. The drying and firing conditions were similar to those used for microspheres prepared from ThO_2 sols containing small amounts of $\text{UO}_2(\text{NO}_3)_2$ or UO_3 .

The UO_2 sols can be formed into gel microspheres in the equipment developed for use in preparing ThO_2 microspheres. However, provision must be made for an inert gas blanket to prevent oxidation of the UO_2 during microsphere preparation. The UO_2 sols are more prone to stick, coalesce, or cluster, and require more careful control of the surfactant concentrations than ThO_2 or $\text{ThO}_2\text{-UO}_3$ sols. Also, the urania sols have many more composition variables. The UO_2 sols generally require the presence of both Span 80 and Ethomeen S/15 in the 2EH. High total surfactant concentrations or high Span/Ethomeen volume ratios tend to result in badly distorted particles having the appearance of raisins. High Ethomeen S/15 concentrations seem to favor production of particles having a deep dimple or "cherry pit" on one side. High surfactant concentrations also appear to contribute to the cracking of the spheres in some cases.

Equipment for the forming, drying, and calcination of microspheres containing PuO_2 was operated to produce 5-20% $\text{PuO}_2\text{-UO}_2$, 5% $\text{PuO}_2\text{-ThO}_2$ and PuO_2 . Batch sizes were 50 to 150 g, and densities generally were $\geq 95\%$ of theoretical. The equipment is installed in two 6-ft glove boxes; the first is used for sol mixing, microsphere forming, and drying; the second, for calcination and size classification. To obtain mixtures, the sols are prepared separately and then blended to the desired proportions; thus, any Pu/Th or Pu/U atom ratio can be easily achieved. The PuO_2 and $\text{PuO}_2\text{-ThO}_2$ sols are formed into spheres using the procedure that is routinely used for ThO_2 spheres. Plutonia-urania mixtures, like urania, must be processed in an inert atmosphere. After firing, the microspheres may be handled in air, but prolonged exposure to moist air is not advisable because of a slight hygroscopicity of the fired spheres.

Microspheres containing PuO_2 are prepared using equipment and procedures similar to those developed for thorium microspheres. The primary differences were the use of glove boxes for containment and somewhat different surfactant requirements for optimum microsphere formation. The PuO_2 and $\text{PuO}_2\text{-ThO}_2$ sols were formed by using 0.3 to 0.5 vol % Ethomeen S/15 as the surfactant. The 20%

$\text{PuO}_2\text{--UO}_2$ spheres are best formed using a surfactant system of 0.1 vol % Ethomeen S/15—0.4 vol % Span 80. Plutonia and ThO_2 sols and mixtures require no atmospheric protection, and the gel spheres are fired in air.

Some types of material, size ranges, and physical properties are shown in Table 4 for materials produced in the glove box facility. No significant differences were observed in the range 5–20% $\text{PuO}_2\text{--UO}_2$. Crushing resistance for the coarse material was about 1 kg/sphere.

A larger, shielded system for preparing PuO_2 and $\text{PuO}_2\text{--UO}_2$ microspheres has been fabricated and installed (Fig. 17). The design capacity is 1 kg of microspheres per day and 200 g of Pu (as PuO_2 sol) per day. The equipment is basically the same as that described earlier for PuO_2 sol preparation and microsphere forming.

Development of Dispersion Devices

Many column operating difficulties would be minimized if sol droplet sizes were absolutely uniform. A variety of sol dispersion devices have been tested to achieve this. Sol droplets can be formed by applying one or more forces, such as gravity, centrifugal field, shear, inertia, interfacial tension, and electrostatic repulsion. To obtain uniform droplet size and controlled diameters, both the force and the configuration of the sol (where the force is applied) must be uniform, and one or both of these factors must be controllable. For all dispersers tested, a uniform configuration is obtained by feeding the sol through orifices or capillaries that are 0.004 to 0.030 in. in diameter.

Two-fluid nozzles (Fig. 18) have been our most-used sol dispersion devices.^{16,17} They are reliable, give a very uniform product, and are easily controlled over a wide sol droplet size range (200 to 2000 μ). With single two-fluid nozzles, 90 wt % of the product consistently had diameters within $\pm 15\%$ of the mean diameter (Table 5). The capacity of single two-fluid nozzles was unacceptably low for pilot plant operations. Therefore, multiple arrays of two-fluid nozzles arranged in parallel were tested; the sol and the 2EH were fed to their respective feed locations from single pumps. Two arrays tested consisted of 6 and 11 parallel two-fluid nozzles. The yields within $\pm 10\%$ of the mean diameter for extended periods of operation were 70% for the 6-nozzle arrangement and 50% for the 11-nozzle arrangement.

Sol droplets formed from capillaries that are vibrated by an electrodynamic device (Fig. 19) are more uniform at optimum conditions than those from any other disperser. The best results are obtained with a continuous, approximately sinusoidal liquid stream that breaks at the midpoint position with respect to amplitude (Fig. 18). The amplitude for this type of operation varied from 1/4 in. at 20 Hertz to 1/32 in. at 200 Hertz and was obtained by 1.5 to 4.0-v inputs to commercial loudspeakers.

Table 4. Examples of PuO_2 -Containing Microspheres Prepared in a Glove Box Facility

Type of Material	Size Range (μ)	Density by Hg Porosimetry			Carbon (ppm)	Surface Area	
		Bulk (g/cc)	10,000 psi			Gas Adsorption Method (m ² /g)	Calculated (m ² /g)
			(g/cc)	Theoretical (%)			
20% PuO ₂ - ²³⁵ UO ₂	300-600	10.3	10.5	95	<10	0.02	-
15% PuO ₂ - ²³⁸ UO ₂	300-600	10.5	10.6	97	<90	-	0.06
5% PuO ₂ - ²³⁸ UO ₂	300-600	-	-	-	-	-	-
5% PuO ₂ -ThO ₂	300-600	9.48	9.84	97	<10	0.02	-
PuO ₂	250-600	11.13	11.22	98	<30	0.02	0.03
	50-250	11.06	11.19	98	<70	0.01	0.02

Fig. 17. Schematic Flowsheet of Shielded Sol Preparation and Microsphere Forming Equipment for PuO_2 and Mixed Oxide Sols.

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Fig. 18. Devices for Dispersing Sol in Gelling Media.

Table 5. Sizes of Calcined Thoria Microspheres from Three Dispersers

Sol feed: 3 M ThO₂; diameters of sol droplets were 2.35 times those of theoretically dense ThO₂ product

	Two-Fluid Nozzles		Vibrating Capillaries			Free-Fall Drop Method
No. of feed capillaries	Single	Two	Single	Four	Four	19
Capillary diameter, μ	250	425	425	480	480	400
Sol feed rate, cc/min	1.2	9.9	1.2	19.2	9.6	9.6
Vibration frequency, cps	-	-	40	200	50	-
Predicted mean size, μ	270 ^a	230 ^a	330 ^b	310 ^b	390 ^b	-
Amount of sample, g	540	10,200	-	314	720	480
Mesh ^c or diameter size of product, wt %:						
30/35 or 500-590 μ						97.9
35/40 or 420-500 μ					0.1	0.8
40/45 or 350-420 μ			0.2		61.9	1.1
45/50 or 297-350 μ	2.9	0.2	98.3	30.4	37.6	
50/60 or 250-297 μ	92.0	3.0	1.5	62.6	0.4	
60/70 or 210-250 μ	0	85.8		7.0		
-70 or <210 μ	5.3	10.9				

^aCalculated from equation developed for two-fluid nozzle.^bFrom number of drops per cycle and flow rate.^cFrom use of U. S. Sieve Series screens.

Fig. 19. Dispersion of a ThO_2 -25% UO_2 Sol by a Vibrating Capillary. Four capillaries are vibrated at 90 Hertz to form 950- μ -diam droplets.

The free-fall drop mechanism and the relationship between droplet size, orifice size, and interfacial tension are well known. The use of plastic buckets with a large number of holes provides a practical capacity and avoids droplet size variations caused by variable wetting of the orifice by the sol. This disperser is useful for large drops only; the orifice sizes necessary to produce drops smaller than 1000 μ in diameter are too small to be practical. The interfacial tension between the sol and the 2EH depends on the amounts of surface-active agents present.

DRYING AND FIRING

Drying and firing of both microspheres and shards of gel are necessary to remove volatile constituents, to effect chemical reactions, and to sinter the particles to a high density. Both the temperature and the atmosphere are controlled while the gel is heated to the sintering temperature and then cooled to room temperature. Particles containing UO_2 or most carbides must be protected from oxygen. Cracking of particles, densification during sintering, and the amount of carbon and gases in the calcined product can vary greatly depending on the conditions used.

ThO_2 and $\text{ThO}_2\text{--UO}_2$

Thoria or thoria-urania fragments have been fired principally in standard muffle furnaces with time-controlled temperatures and atmospheres.¹⁸ The dried gel is heated in air to 1150°C at a rate of 300°C/hr. The charge is held at 1150°C for 4 hr; if uranium is present, an Ar--4% H_2 atmosphere is used to reduce it to UO_2 . A continuous, vertical tube, moving-bed calciner was also successfully operated with thoria--3% urania fragments. The temperature profile along the tube is carefully controlled so the moving charge undergoes the correct temperature-time program. The countercurrent flow of gas up the tube provides excellent utilization of hydrogen and helps maintain the required temperature profile. The moving-bed-type calciner appears to be practical for large production (≥ 50 kg day), while batch units appear more attractive for small-scale preparation.

The most efficient drying conditions for microspheres required superheated steam to final drying temperatures of 200°C.¹ The conditions in Table 6 were successfully used for firing gel microspheres in muffle furnaces. Argon--4% H_2 is used to avoid the explosive hazards of pure H_2 . If hydrogen is present throughout cool-down, excessive amounts of it may be adsorbed.

Table 6. Conditions for Firing ThO_2 , $\text{ThO}_2\text{--UO}_3$ and PuO_2 Microspheres

Temperature (°C)	Time	Atmospheres Used for:	
		ThO_2 or PuO_2	$\text{ThO}_2\text{--UO}_3$
25	16 hr	-	-
25 to 100	300°C/hr	Air	Air
100 to 1150	300°C/hr	Air	Air
1150	4 hr	Air	Ar-4% H_2
1150 to <100	<500°C/hr	Air	Ar

UO₂ Drying and Firing

Drying and firing studies of sol-gel UO₂ 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 spheres to 1000°C in H₂O—0.2 vol % Ar. Final reduction was accomplished in Ar—4% H₂ for 2 to 4 hr. Other atmospheres tested included CO₂, Ar, Ar—4% H₂, and O₂; however, none of these gave results that were reproducible with respect to density and carbon removal when a variety of 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.^{19,20,21} The source of the carbon is the drying solvent and surfactants used in the microsphere forming column. The sorbed organic materials must be removed prior to sintering to achieve a consistently 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 present in UO₂ sol (and also in the gel microspheres) is not difficult to remove. Analysis of shards prepared by evaporating UO₂ sols in argon and firing in Ar—4% H₂ 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.

Since the organic materials are very strongly sorbed, heating in an inert atmosphere or vacuum for prolonged periods is not sufficient. A gaseous atmosphere that can either oxidize the sorbed organic compounds to a more volatile species or displace them is needed. In an 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 7). 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.

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,

Table 7. 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.

using 5 g of H_2O 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 UO_2 .

- (2) At 1000°C , the sample is reduced in a stream of Ar-4% H_2 (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 H_2O per gram of UO_2 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 H_2O , particularly in the firing region above 600°C , can be decreased substantially from the quantities listed in Table 7.

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.¹⁹⁻²² Differential thermal analysis (DTA), thermogravimetric analysis (TGA), and measurements of crystallite growth, shrinkage rate, and surface area showed that gaseous atmospheres of H_2O or CO_2 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 UO_2 crystallites or a very strong surface adsorption of CO_2 was also occurring. The gain in sample weight during sintering in the CO_2 was found to be 0.25%. Thermogravimetric measurements also indicated that the carbon compounds were not removed by CO_2 at appreciable rates until a temperature of about 550°C was reached. With H_2O , 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 CO_2 . Thermogravimetric measurements indicated that either a very rapid surface oxidation of the UO_2 crystallites or a strong surface adsorption of the H_2O 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 H_2O than with CO_2 .

In Ar-4% H_2 , 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 UO_2). Studies of carbon removal and sintering are continuing.

PuO_2 Drying and Firing

During the past year the gel microsphere drying technique was modified to include steam drying at 95 to 105°C over a period of 4 to 5 hr to remove the residual drying solvent, and then continuing the flow of steam up to 150 to 170°C for 5 to 6 hours. Approximately 3 to 4 g of steam/g Pu was passed through the bed of microspheres. This technique results in microspheres of slightly higher density, and a process advantage is realized in that steam suppresses or eliminates the thermal excursion occasionally observed in drying deep beds of gel. To reduce micro-porosity in the finished microsphere, the firing technique was modified to include passing humidified air over the microsphere bed throughout the firing step.

LOW-ENERGY MICROSPHERE PACKING (SPHERE-PAC)

High-density microspheres of $(\text{U,Pu})\text{O}_2$ are ideally suited for fuel rod fabrication by the Sphere-Pac process. We are developing the Sphere-Pac fabrication process to produce fuel rod loadings with smear densities in the range of 80 to 90% of theoretical.^{3,23} The process involves pouring a large size-fraction of microspheres into the cladding tube and vibrating the tube to settle the poured bed, then infiltrating this bed with a fine size-fraction of microspheres. The bed of large size microspheres is restrained during addition of the small-size fraction.

These studies yielded samples of about 85% of packing density for characterization and irradiation testing.

We are now attempting to form sphere beds in the higher density range (88% and higher) by blending two sizes of large spheres to form the initial poured bed prior to infiltration with the fine-size fraction. The blending studies are carried out by placing about 60 g of coarse and medium size spheres in a 3.5-cm-diam 120-cc bottle, rolling the bottle at 275 rpm for times up to 5 min, pouring the blended spheres into a 1.07-cm-ID graduated tube, and packing the unrestrained bed by vibrating for from 1 to 120 min. Blending is found to be complete after about 1 min, and the poured bed is fully settled after about 1 min of vibration. The conditions of vibration were 60 cps with about 7 g acceleration of the bed.

Figure 20 illustrates our results on blended bed volume packing (P_v) as a function of the volume percentage coarse and medium spheres for three sphere diameter ratios. These results agree well with those obtained by McGearry²⁴.

and extend them to lower diameter ratios and smaller size spheres. The data obtained from the maximum density point (~65% coarse and 35% medium) on these curves may be used to calculate the efficiency (P_E) of the medium size spheres in filling the void available to them around the coarse spheres. In order to calculate this efficiency on a uniform basis, we assume an artificial packing efficiency for the coarse spheres of 63.5%. This is the limit for packing efficiency of a single size sphere in a large tube as presented by Ayer.²⁵

Using this basis for the packing efficiency of smaller spheres in a packed bed of large spheres, the data in Fig. 21 was obtained. Some data from the work of McGeary and Ayer is also shown in this figure. The agreement is excellent for diameter ratios up to 8 or 10. Above this range, Ayer's work deviates significantly from our findings and those of McGeary.

Using this information on blended bed densities and packing efficiencies, we have developed a graphical construction which may be used to correlate and generalize all of our information relating to the Sphere-Pac fabrication procedure. This is shown in Fig. 22 where the horizontal axis represents the volume packing of spheres in a container or bed (packing efficiency) and the vertical axis represents the void volume associated with this volume packing. If a 45° operation line is established between the two zero points of the axes then the void volume associated with any packed volume may be determined by reading up and then across (line A-B-C). If we now construct a line joining the volume packing efficiency of a given size sphere (% of available void volume filled by spheres) to the void volume zero point, the horizontal distance between this line and the operation line is always proportional to the packing efficiency multiplied by the void volume associated with that packed bed density. Thus, the line A-D represents the packing of a single size sphere in a large tube or in a packed bed (according to Ayer) where the diameter of the sphere is less than approximately 1/25 that of the smallest sphere in the packed bed.

This curve may be used to illustrate the effect of serial infiltrations with spheres having d_1/d_2 greater than 25. We will obtain 63.5% packing with the coarse spheres. If we then infiltrate a small size sphere at this same efficiency, we obtain from point E an 87% dense bed, and a second infiltration produces a 95% dense bed. This type of line must also be plotted for the packing of spheres of varying diameter ratio with respect to the bed. These data are shown by the dotted lines for spheres of 1/4, 1/7, and 1/10 the size of the spheres in the bed, and are obtained from the plot of P_E vs d_1/d_2 (Fig. 21).

We may now see the effects of using a blended bed, or the effect of infiltration at less than the optimum 63.5% packing efficiency. If a d_1/d_2 ratio of 4.0 is used for a blended bed, the bed density (volume packing) is increased to 72%, point F. Infiltration with spheres 1/10 the size of the medium fraction

Fig. 20. Volume Packing of Blended Spheres of Two Sizes for Various Diameter Ratios.

Fig. 21. Packing Efficiency of Small Spheres in a Packed Bed of Large Spheres.

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Fig. 22. Analysis of Sphere-Pac Beds.

produces an 88% dense bed, point G. This is exactly the density which we have obtained and reproduced by this technique. We have also produced 86.5% dense beds by infiltration of a blended bed ($d_1/d_2 = 3.4$) with the 10/1 size ratio of medium to small. This is the density predicted by the graphical correlation for these conditions.

From the above discussion it may be seen that to produce a 90% dense fuel, we must use either a double infiltration with very carefully controlled sphere sizes or a blended bed at d_1/d_2 of about 5.8/1, followed by a single infiltration. This requires investigation of the behavior of beds blended at this diameter ratio. They tend to segregate.

The Sphere-Pac process is a promising technique for bulk oxide fuel fabrication over the range of 80 to 90% volume fuel loading. The use of blended beds to raise the fuel column to the 90% dense range is an attractive approach since it would eliminate the need for more than one infiltration step and be quicker and easier to control than a double infiltration approach.

Our experience with irradiation tests on Sphere-Pac fuels at this time is limited. We have examined twelve test rods fabricated by this process, all at relatively low burnup levels, with a maximum of 16,000 Mwd/tonne. One group of four rods with a peak burnup level of 40,000 Mwd/tonne has been removed from the reactor, but has not been examined. There are fourteen additional test rods in-reactor in uninstrumented tests and one 2-rod instrumented test. With the exception of the two rods discussed at Turin,³ which failed during a power transient under severe overpower conditions (50 kw/ft), all rods have performed well. Based on the microstructures of the uninstrumented fuel rods and some preliminary in-reactor thermal conductivity measurements in the instrumented tests, it appears that the Sphere-Pac beds have in-reactor thermal conductivities essentially equivalent to pellet fuel rods with the same loading density. In-reactor fuel restructuring is also similar to pellets. The data are still too meager to report on relative fission gas release rates.

PREPARATION OF ThC_2 AND $\text{ThC}_2\text{-UC}_2$

The dicarbides of thorium and of thorium-3% uranium have been prepared by the sol-gel process. In this process, carbon-containing sols are prepared by dispersing carbon black in ThO_2 or $\text{ThO}_2\text{-3% UO}_3$ 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 $\text{ThC}_2\text{-20% UC}_2$ microspheres is in progress.

Extensive studies of the preparation of oxide-carbon sols have been made, since fluid, stable hydrosols containing the required amounts of carbon are essential to the process. In addition, an understanding of the interactions between the oxides and carbon in our presently used oxide-carbon sols will be useful in preparations of other sols of future interest such as $\text{PuO}_2\text{-C}$, $\text{UO}_2\text{-PuO}_2\text{-C}$, and $\text{UO}_2\text{-ZrO}_2\text{-C}$. Results to date have shown that the oxide crystallites in ThO_2 , UO_2 , or $\text{ThO}_2\text{-UO}_3$ sols disperse carbon aggregates by a strong interaction with them. This interaction results in very intimate association of the oxide and carbon, with the oxide acting as a protective colloid. The extent of adsorption of the oxide depends primarily on the relative surface areas of the oxides and the carbon. Some colloidal oxides do not show this strong type interaction.^{1,3} For example, ZrO_2 and $\text{Eu}(\text{OH})_3$ as currently prepared at ORNL, boehmite (AlOOH : duPont Baymal), and silica (duPont Ludox) do not. These colloidal oxides do not disperse carbon to the extent that the ThO_2 , UO_2 , or $\text{ThO}_2\text{-UO}_3$ sols do. Plutonia sols prepared at ORNL interact sufficiently to produce a mixed sol containing the amount of carbon required for carbide or nitride conversion.

Electron microscopic techniques, viscosity, electrophoretic and specific surface measurements are employed in studies of the oxide-carbon interactions.

Urania and $\text{ThO}_2\text{-UO}_3$ sol behaviors are virtually identical to that of thorium sol. The extent to which carbon was dispersed by all of these sols was dependent upon the relative surface area of the oxide and carbon and was demonstrated by viscometric titration.

Stable, fluid sols containing carbon in sufficient quantity to produce mono- or dicarbides or to produce porous oxides could be prepared from the UO_2 , ThO_2 , or $\text{ThO}_2\text{-UO}_3$ sols produced at ORNL. The amounts of dispersed carbon required to produce monocarbides and dicarbides from these oxides are 3 and 4 moles of C per mole of oxide, respectively. The amount of carbon required to produce porous oxides over the range of 10 to 60% porosity is 0.5 to 6 moles C per mole of oxide.

The most important variables in the sol-gel method of preparation of ThC_2 are the firing conditions during conversion, and control of the carbon content in the $\text{ThO}_2\text{-C}$ gel. To obtain densities >90% of the theoretical density of ThC_2 (9.6 g/cc), the conversion must be effected under a controlled CO overpressure at temperatures where a critical balance among rate of chemical conversions, grain growth, and sintering is maintained. If porous carbides are the desired product, the reactions are carried out under vacuum. Product densities of 91 to 93% are obtained when the reaction is carried out at a controlled rate under argon until nearly complete, and then vacuum is applied to complete the reaction. The argon sweep gas contained about 4000 ppm CO, which was maintained by controlled diffusion out of the sample crucible. An infrared inline CO analyzer (Beckman Model 315) was used to monitor the progress of the reactions. This conversion

technique also produced $(\text{Th}_{0.78}, \text{U}_{0.22})\text{C}_2$ and UC microspheres that were 90–93% of theoretical density in a few demonstration runs.

Control of the carbon-to-metal oxide mole ratio in the gel starting material is most important for good conversion and attainment of high density. When the initial carbon-to- ThO_2 mole ratio was too low, objectionable amounts of mono-carbide were formed; when it was too high, a highly porous product was obtained. Excess carbon contents of 0.50 to 2.58% in ThC_2 resulted in highly porous products. A mole ratio of carbon-to-oxide of 3.9 to 4.0 appears optimum for preparing dense ThC_2 . In practice, the carbon-to-metal oxide ratio must be adjusted empirically. This adjustment is necessary because of pickup of additional carbon by the sorption of the carbon-bearing organic materials in the sphere-forming process, and because of the reaction of carbon with the nitric acid during firing of the gel. A few attempts were made to remove the additional carbon imbibed during sphere formation by oxidizing it with air on a recording thermogravimetric balance where the rate of reaction could be carefully monitored; however, the degree of oxidation was found to be difficult to control. We have not yet tried removing the sorbed organic material by treating with steam to 600°C ; this is a method found to be effective for organics from UO_2 gel spheres.

A few experiments on the conversion of $\text{ThO}_2\text{--UO}_3\text{--C}$ gel spheres to $(\text{Th}_{0.78}, \text{U}_{0.22})\text{C}_2$ spheres gave very encouraging results (Table 8). The products were solid solutions of the monoclinic ThC_2 structure with slightly contracted parameters due to the uranium content. A reaction temperature of 1900°C was sufficient for complete reaction, whereas approximately 2000°C was necessary for ThC_2 . The presence of the uranium permits conversion at a lower temperature and also seems to promote a desirable sintering pattern. Densities were 76 to 94% of the theoretical value, depending on the original carbon content. Even at the higher porosities, the spheres had a uniform cross section and the pores were approximately $1\ \mu$ in diameter. Preliminary results equally as encouraging as those obtained in preparing $(\text{Th}, \text{U})\text{C}_2$ were obtained on converting $\text{UO}_2\text{--C}$ gel spheres to UC and UC–UN microspheres.

PREPARATION OF POROUS OXIDES

We have shown that ThO_2 microspheres or shards of controlled porosity can be prepared from $\text{ThO}_2\text{--C}$ gels by volatilizing the carbon by air oxidation after the oxide structure has been preset by firing to 1400°C in argon.^{1,13,26} The amount of porosity could be controlled by varying the amount of carbon; the volume of porosity introduced was nearly equal to the volume of carbon added. In subsequent work, the technical feasibility of preparing porous $\text{ThO}_2\text{--UO}_2$ and UO_2 by this same approach was demonstrated. For the $\text{ThO}_2\text{--UO}_2$ preparations, $\text{ThO}_2\text{--UO}_3\text{--C}$ gels were employed and air oxidation was used to volatilize the carbon. However, in the porous

Table 8. Analyses of $(\text{Th}_{0.78}\text{U}_{0.22})\text{C}_2$ Microspheres
(Conversions in argon at 1900°C)

	Run Number		
	IV-82	IV-84	IV-86
<u>Carbon-to-metal mole ratio of</u>			
<u>reactants:</u>			
Desired	3.90	3.95	4.00
By analysis	4.00	4.06	4.15
<u>Composition of product</u>			
% Thorium	70.3	69.7	69.4
% Uranium	20.4	20.2	20.0
% Carbon	8.87	9.02	9.37
% Oxygen	0.081	0.127	0.173
Material balance (Σ of above)	99.65	99.05	98.94
% Free carbon	0.097	0.264	0.146
<u>Mercury density of product, g/cm³</u>			
1 atm	9.45	8.92	7.75
10,000 psi	9.56	9.09	8.65

UO₂ preparations, CO₂ or H₂O was the preferred reactant for removing the carbon because air caused too much oxidation of the UO₂.

Experiments on preparation of 60% porous ThO₂-22% UO₂ indicated that higher porosities were obtained with ThO₂-UO₃-C gel shards than would have been expected by analogy with ThO₂-C gel shards of the same oxide to carbon ratio. The amount of carbon which produced 47% porosity in ThO₂ produced 59% porosity in ThO₂-UO₂. Also, the pore sizes in the ThO₂-UO₂ were 400 to 800 Å in diameter, whereas the size was about 400 Å in the ThO₂.

In our attempts to prepare porous UO₂ in a way that prevented excessive air oxidation of the UO₂, two methods for removing carbon from the prefired UO₂-C have been tested: the reaction H₂O + C ⇌ CO + H₂ and the Boudouard reaction (CO₂ + C ⇌ 2CO). Both require a temperature of about 1000°C to remove the carbon at a practical rate. Technical feasibility of porous UO₂ preparation by this approach was demonstrated by removing carbon from a gel sample of shards containing 6 moles of carbon per mole of urania. Although in these experiments only 80% of the original carbon was reacted, a 48 vol % porous product was produced.

PREPARATION OF UN AND UN-UC MIXTURES

Initial studies of the preparation of UN microspheres from UO₂-C gel microspheres were promising.²⁷ In the preliminary experiments, UO₂-C gel microspheres having a C/UO₂ mole ratio of 2.8 were converted to UN_{0.92}C_{0.13} by firing the UO₂-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/UO₂ 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 back in a UO₂ 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 UO₂-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 to 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 UO_2 -C gel microspheres having a C/ UO_2 ratio of 2.3. A UO_2 -C sol was prepared by dispersing Spheron 9 carbon black (BET surface area = 105 m²/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 UO_2 -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 UO_2 -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 UO_2 -C gel microspheres containing exactly enough carbon to remove all of the oxygen as CO, it should be possible to prepare essentially pure UN.

SOME PROPERTIES OF LANTHANIDE OXIDE SOLS PREPARED BY SOL-GEL METHODS

Lanthanide sols were prepared by precipitating the 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.

Spectroscopic methods were used to 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 and x-ray analyses showed that the initial precipitates of lanthanide hydroxides consisted of amorphous particles of 30 to 60 Å in diameter. When aged in water, these particles changed into rods or tubes, up to several thousand angstroms in length. In the periodic arrangement of the lanthanide elements, the trends of decreasing ionic radii and basicity with increasing atomic number are well known; similar trends are expected for the actinides. The results of the studies on the sol-gel preparations reflect these systematic changes. It has been found that the lanthanides can be divided into two groups on the basis of their crystallization behavior; namely, the time required for crystallization, and the crystalline structure or form obtained. The first group would consist of the elements lanthanum through dysprosium. It is characterized by shorter crystallizing times and needle or rod-like crystalline structures that range up to 7000 Å in length and several hundred angstroms in width. The remaining lanthanide elements fall into the second group; they have much longer crystallizing times and form predominately sheets that are up to 7000 Å on each side. In each group the crystallizing time and size of the crystalline forms increase as the ionic radii of the elements decrease.

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.²⁸

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 or a slight modification of it. The first procedure utilizes centrifuging to accomplish washing, whereas the modified procedure uses a sintered-glass filter. The essential advantage of the latter is that it eliminates solids handling.

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.²⁸ 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.

An ^{243}Am - ^{244}Cm sol (20% ^{243}Am) has been prepared by the centrifuge technique; however, we have now developed a process based on filtration and washing which produces sol suitable for forming into microspheres. This process is shown in Fig. 23. With the actinide elements americium and curium, needle or rod-like structures are obtained, and the diffraction patterns are isomorphous with the first group of lanthanides.

* M(III) DENOTES THE MIXTURE OF TRI-VALENT AM AND CM.

Fig. 23. Preparation of ^{243}Am - ^{244}Cm Sols, Gels, and Oxide Microspheres.

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