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by *L. C. Ridenour*

TISOR, date *12-7-65*

DATE - April 19, 1965

PRELIMINARY STUDIES OF THE PREPARATION OF UO₂ MICROSPHERES BY A SOL-GEL TECHNIQUE

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1. INTRODUCTION

Uranium oxide microspheres are being prepared using adaptations of the methods used to prepare ThO_2 and $\text{ThO}_2\text{-UO}_2$ microspheres. Sol preparations to date have been on a relatively small scale, using laboratory rather than engineering development equipment. Batch sizes have been restricted to 300 g of uranium or less.

Although process development work is continuing, and is, in fact, not out of the laboratory in the sol preparation step, the large number of inquiries about the ORNL sol-gel process for UO_2 microspheres makes it desirable to make details of the process more widely available. The purpose of this report is to present process details and analyses made at various process steps for a series of experimental runs made using both natural and enriched uranium (approximately 97% ^{235}U).

Principal product shortcomings at the present state of development are high carbon content (about 10-fold too high at approximately 5000 ppm) and low crushing strength (variable, but sometimes as low as approximately 1 lb required to crush a 150- μ -diam sphere using a "standard" crush strength test). Development work is presently directed toward solving these problems.

2. PREPARATION OF A UO_2 SOL

The sols used in the preparation of UO_2 microspheres by the sol-gel technique were prepared by precipitation of hydrous U(IV) oxide and its subsequent dispersion. Sol preparation 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. In some preparations formic acid is added to the filtered solution. The hydrous oxide is formed by precipitating U(IV) with an NH_4OH -containing hydroxylamine solution. The precipitated hydrous oxide is removed by filtration and washed to remove excess electrolyte. The washed filter cake is then heated at 60 to 65°C to produce a fluid, stable sol. Precautions are taken to protect the material from air oxidation by the use of a blanketing gas (argon) during all stages of the process. Because it was desirable to work with enriched uranium, the sol preparations were carried out batchwise using 300 g of uranium in each preparation. Thus, several batches could be worked with concurrently in the same area without fear of criticality incidents.

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2.1 Preparation of U(IV) Nitrate Solution

In a typical preparation, 2520 ml of solution containing 0.4 M U-2.3 M NO_3^- -0.26 M urea was reduced with H_2 at one atmosphere pressure using 30 to 60 mg Pd as a Pd on thoria catalyst (for catalyst preparation, see Appendix). Reduction was carried out in a baffled 3-neck round bottom flask of 3-liter capacity equipped with a tru-bore stirrer. The solution was sparged with argon to remove reactive gases, and hydrogen was then bubbled through the solution at room temperature at a rate of 50 to 150 cc/min using a fritted gas-diffuser tube. Vigorous stirring was required; reduction was usually complete in 2 to 3 hr.

Completeness of reduction was determined by taking an aliquot of the solution, precipitating the U(IV) oxalate with excess oxalic acid, centrifuging, and adding a few drops of a 10% $\text{K}_4\text{Fe}(\text{CN})_6$ solution to the supernate. The absence of a brown color indicated greater than 99.9% reduction.

The reduced solution was allowed to stand several hours to permit the catalyst to settle. It was then filtered through a "fine" porosity fritted glass funnel. In some preparations the filtered solution is then transferred to the precipitation vessels. In the alternative method of preparation the solution was made 0.3 M in formic acid (formate/uranium ratio of 0.6) prior to precipitation.

2.2 Precipitation of Hydrous U(IV) Oxide

Precipitation of the hydrous oxide was carried out in 4-liter baffled beakers equipped with stainless steel stirrers. The beakers were fitted with gasketed plexi-glass covers with openings for the stirrer, pH electrodes, burette, and argon blanket inlet. For convenience, the U(IV) nitrate solution was split into two batches for precipitation. The hydrous oxide was precipitated with 3.0 M NH_4OH -0.5 M $\text{N}_2\text{H}_5\text{OH}$ solution added at a rate of 100 to 150 ml/min. Vigorous stirring was maintained during precipitation. Precipitation phenomena and character of the precipitate were different in the absence of formic acid (nitrate method) and presence of formic acid (formate method).

In the nitrate method a thickening stage is observed at an apparent pH* of about 4 and addition of the ammonia-hydroxylamine solution is stopped and stirring continued until fluidity is again achieved. Addition of base is continued to an apparent pH of 7. As stirring continues, the apparent pH drifts to lower values and more base is added to maintain apparent pH 7.0. Such additions are continued until the drift in 1 hr is less than 0.1 pH unit, at which time the precipitation is complete. Alternatively when pH 7.0 is reached, the suspension is allowed to age 15

*pH is measured with a glass electrode-calomel electrode system.

to 20 hr and the pH then adjusted to 7.0. In this case very little drift is observed with subsequent stirring. The precipitate is filtered on a 24-cm Buchner funnel using Whatman No. 42 paper. The cake is washed on the filter using 9 liters of wash water and is allowed to dry 10 to 15 min on the filter.

In the formate method the U(IV) nitrate solution is made 0.3 M in formic acid (formate/uranium=0.6) prior to precipitation of the hydrous oxide. The 3.0 M NH_4OH -0.5 M $\text{N}_2\text{H}_5\text{OH}$ is added at 100 to 150 ml/min. The precipitate is apple green, and no thickening stage is observed at apparent pH 4. Addition of base is continued until pH 7 is reached. Negligible drift is observed on subsequent stirring, and the precipitate is put directly on the filter. As in the nitrate method, the precipitate is filtered on a 24-cm Buchner funnel using Whatman No. 42 paper, washed on the filter using 9 liters of wash water and allowed to dry 10 to 15 min on the filter. Formic acid is added prior to precipitation to maintain a high U(IV) content in the precipitate. The relationship of percent U(IV) to initial formic acid concentration is shown in Table 1. The 0.3 M formic acid concentration used in the preparations was chosen because it gave relatively high U(IV), good product yield, no thickening stage and negligible pH drift.

2.3 Conversion of Precipitate to Sol

In both the nitrate and formate methods the washed filter cakes are transferred to glass thimbles of about 1200 ml capacity and heated at 60 to 65°C under argon for several hours to form stable sols. Heating is carried out in dewar-type heating jackets heated by refluxing vapors of boiling methyl alcohol. The cake is stirred vigorously during the heating period and transforms into a fluid sol. Alternatively, the filter cake may be allowed to stand several days at room temperature, during which time "liquefaction" occurs without heating.

The filter cake from the nitrate method is black and liquefies to a black sol. The filter cake from the formate method is green in the interior with a thick brown-black layer on its surface. The cake from the formate method (unlike that from the nitrate method) forms a fluid green suspension on agitation at room temperature. The green suspension is converted to a black sol on heating for several hours or on standing several days at room temperature.

In general, the formate-method sols may be made more concentrated, have higher U(IV) contents, and drain more readily from the glass walls of the containing vessels than the nitrate-method sols. Tables 2 and 3 give information on typical preparations. A flowsheet is given in Fig. 1.

2.4 Additions of Sm to Sols

The effect on properties of the fired product UO_2 of deliberately added adulterants was determined by adding samarium. Uranium dioxide spheres containing

NITRATE METHOD

FORMATE METHOD

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Fig. 1. Flowsheets for the Preparation of Nitrate and Formate Sols.

450 ppm Sm_2O_3 were prepared by simply adding $\text{Sm}(\text{NO}_3)_3$ solution to the UO_2 sols prior to sphere formation. The $\text{Sm}(\text{NO}_3)_3$ solution was prepared by dissolving 800°C fired Sm_2O_3 in excess nitric acid and removing the excess acid by repeated evaporations. Samarium nitrate additions to the sols rather than to the U(IV) nitrate solutions prior to precipitation was chosen because precipitation of $\text{Sm}(\text{OH})_3$ would not have been complete at pH 7, and it was feared that Sm carrying would be incomplete.

Table 1. Effect of Formic Acid Concentration on % U(IV)

Preparation Designation	Initial Formic Acid Conc. <u>M</u>	U(IV) in Precipitate %	U(IV) in Sol %
NU-VIII-3	0	80.9	79.7
NU-XVI-3	0.1	89.2	86.1
NU-XX-3B	0.17	88.4	-
NU-XXIII-3	0.2	93.2	86.5
NU-XX-3A	0.33	92.0	-
NU-XV-3	0.5	97.2	89.4

Table 2. Properties of Nitrate-Method Sols

Preparation	Yield,* %	Specific Gravity, g/cc	Uranium Conc., <u>M</u>	U(IV) Content, %	NO_3^-/U Ratio
NU-XIV-3	93	1.257	1.02	81	0.06
NU-XIX-3	91	1.246	1.01	82	0.07
NU-XXII-	91	1.256	1.03	83	0.07
47-70-93	89	1.321	1.28	80	0.05
47-71-93	91	1.248	1.04	78	0.08
47-4-93	93	1.245	1.01	-	0.07
47-44-93	81	1.306	1.25	80	0.07
47-67-97	88	1.273	1.05	78	0.06

*Losses are primarily those associated with transfers of cakes and sols.

Table 3. Properties of Formate-Method Sols

Formic Acid/U Ratio in Precipitation Step: 0.6

Preparation	Yield, [*] %	Sol Specific Gravity, g/cc	Uranium Conc., <u>M</u>	U(IV) Content, %	NO ₃ ⁻ /U Ratio	COOH ⁻ /U Ratio
NU-XXIX-3	96	1.317	1.23	87	0.13	0.44
47-500-97	92	1.464	1.99	85	0.02	0.35
47-29-97	94	1.319	1.27	85	0.07	0.38
47-19-97	-	1.404	1.61	86	0.11	0.31

* Losses are primarily those associated with transfers of cakes and sols.

3. FORMATION OF URANIA GEL MICROSPHERES

The process for conversion of aqueous sols into gel oxide microspheres previously developed for thorium sols was used for urania sols without changes except where the previously developed procedures were inadequate. In this process, the sol is dispersed into drops of controlled diameter in a drying solvent and the drops are supported in the solvent while water is extracted and a solid gel is formed. Essentially all the urania microsphere products were prepared by dispersion of the urania sol into drops with a two-fluid nozzle and fluidization of the drops in a column during extraction of water. Sols may also be dispersed into drops and suspended during drying by mechanical agitation. This procedure appears useful for preparing microspheres having diameters less than 50 μ , and of rather wide particle size range. Other dispersion techniques which appear promising are the use of multiple orifices in a rotating device and of electrodynamic effects.

The conversion of urania sols into gel microspheres involves three operations, which are carried out in a single column system. First, the sol is dispersed into drops which will give a final product within the desired size range. The size of the drops needed is calculated from the sol concentration and the size range specified for the UO₂ product. Any drops outside the desired size range will be waste or recycle material. Second, the sol drops are suspended in the solvent while water is extracted and gellation occurs. Experiments with thorium sols have shown that formation of hollow spheres or cracking into fragments occurs when the water is removed too rapidly. The rate of extraction of water depends on the organic solvent used:

2-ethylhexanol was used for the formation of urania microspheres. Acceptable drying times have been from several minutes for $<100\ \mu$ diameter sol droplets to 20 minutes or more for $\sim 1000\ \mu$ sol droplets. The third operation is the separation of the gel microspheres from the organic liquid. Solvent is recovered for reuse by removal of the water (and perhaps nitrate) extracted from the sol. While the recovery step is simple in principle, about 1000 kg of solvent is processed through the recovery operations for each kg of urania microspheres produced.

3.1 System Description

Urania gel microspheres were formed continuously in a column system of six inch maximum diameter (Fig. 2). The sol feed vessel was blanketed with Ar and the column top and solvent tanks were supplied with an Ar purge to prevent oxidation of the U(IV) sol by oxygen from the air. The sol was pumped at variable, but accurately controlled rates from the feed tank to the two fluid dispersion nozzles by automatic infusion-withdrawal pumps. These pumps use variable speed motors, multispeed transmissions, solenoid valves, and standard hypodermic syringes to give positive displacement pumps of non-pulsating flow. This accurately metered, non-pulsating flow was necessary to the control of the drop diameter by the two-fluid nozzles. The principles of operation and the results for these nozzles are described in detail in Sect. 3.3.

The sol drops were fluidized in a tapered glass column during drying and gellation. In order to maintain good fluidization and to avoid coalescence, clustering, and deposition on the column wall, the addition of surfactants to the organic solvent and the use of a special column configuration were necessary. The gel microspheres had a higher density and thus a higher settling velocity in the solvent than the sol drops. The column was designed to use this higher settling velocity to permit continuous dropping out of gel spheres while sol drops were fed in the top of the column. This continuous operation of the column is practical only when uniform sol drops are formed and the column is designed to discharge preferentially the particles with the highest settling velocities. The gel microspheres which settled out of the fluidized bed in the column were collected on a closed fritted glass filter and the 2-ethylhexanol was drained off under an Ar purge.

The useful life of the 2-ethylhexanol appears to be limited by the accumulation of impurities. The water and the nitrate extracted from the sol were removed by distillation and ion exchange, respectively (see Sect. 3.5). With this solvent treatment, the system has been operated with thorium sols at rates up to 300 cc/hour and with continuous periods of operation of up to 72 hours. The urania sols were limited to 300 g U per batch for convenience and criticality control during sol preparation. The column system is of critically safe geometry. The decomposition of surfactants or accumulation of impurities not removed in the distillation or ion exchange columns may limit the solvent life.

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Fig. 2. Gel Microsphere Forming Column and Solvent Recovery System.

3.2 Solvent and Surfactant Selection

The drying solvent for all preparations of urania microspheres was 2-ethylhexanol. The 2-ethylhexanol had the best combination of properties of all solvents considered for preparation of thoria microspheres and the same requirements apply for urania microspheres.

To prevent the sol droplets from coalescing and sticking to each other, a surfactant is dissolved in the organic phase. One-tenth to 0.5 vol % surfactant in the organic liquid is sufficient. The following three surfactants are representative of the types which have worked satisfactorily for certain sols and certain size droplets: Ethomeen S/15 (Armour), Amine 0 (Geigy), and Span 80 (Atlas). Ethomeen S/15 and Amine 0 have been successful in forming thoria spheres in all sizes. Span 80 can only be used for thoria sols in the size range of 100 to 300 microns. Larger drops distort into non-spherical shapes when Span 80 is used, probably because the Span 80 gives an appreciably lower interfacial tension. For a thoria-8 wt % urania sol, Ethomeen S/15 proved to be unsatisfactory and Span 80 worked perfectly for sizes up to 1000 microns. A surface active agent is necessary to make the process work; however, the type of surfactant required is not highly predictable for a new sol and a particular particle size range.

Nitrate Sols. — With 0.6 vol % Amine 0 in 2-ethylhexanol, the nitrate sols behaved very similarly to the thoria sols. Using Ethomeen S/15 as the surfactant, the urania droplets would dry partially and then stick to each other. These clustered particles were detrimental to the continuous operation of the column. Span 80 was even less satisfactory because of the distortion of large drops to give non-spherical shape and because it appeared to decompose in the distillation system.

Formate Sols. — No single satisfactory surfactant was found for formate sols, but 0.5 vol % Amine 0 and 0.5 vol % Span 80 together were satisfactory. Span 80 by itself resulted in non-spherical shapes with "cherry-pitting" or cherry-shaped particles as the most common effect. The Amine 0 by itself permitted excessive clustering of particles. These clusters dropped out of the column too quickly and decreased the yields of good microspheres.

3.3 Sol Drop Formation

Sol drops of controlled diameters were initially formed in the tapered column system by discharging sols through a small orifice. To eliminate the undesirably

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small orifice sizes required for free-fall drop formation, a two-fluid nozzle is currently being used to form the drops (see Fig. 3). The sol is introduced in the center of a flowing organic stream which acts as the drive fluid. The continuous sol flow is accelerated to the drive fluid velocity and then breaks up by a varicose mechanism to give sol droplets with diameters 2 to 2.5 times greater than the minimum sol stream diameter.⁽¹⁾ A nozzle length of 10 in. has been used to ensure droplet formation before discharge into the tapered column. Assuming a "varicose" mechanism for droplet formation, the sol droplet diameter, D , can be related to the sol flow rate, f , and the maximum drive fluid velocity, $V_{\max}$, by the following equation:

$$D = k \sqrt{\frac{4f}{\pi V_{\max}}} = \frac{2k}{\sqrt{\pi}} \sqrt{\frac{f}{V_{\max}}}$$

where k should be a constant having a value between 2.0 and 2.5 for a particular system. Theoretically the sol droplet diameter should be independent of the sol entry tube diameter. In order to form uniformly-sized droplets with a two-fluid nozzle, the drive fluid flow must be laminar, and therefore the sol should be injected in such a manner as to minimize disturbances.

A typical calculation of the required organic drive fluid flow rate under two-fluid nozzle conditions for preparing microspheres of a specified size follows:

Given Conditions:

Sol concentration: 1.5 moles uranium/liter

UO₂ microsphere diameter sought: 150 microns

Nozzle drive fluid size: 0.0791 cm² cross section area

Density of calcined UO₂ = 10.8 g/cc

$\underline{M}$ of calcined UO₂ = $\frac{(10.8)(1000)}{267} = 40.4$ moles/liter

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Fig. 3. Two-Fluid Nozzle for Forming Sol Droplets.

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$$\text{Shrinkage in going from sol to calcined } \text{UO}_2 = \sqrt[3]{\frac{40.4}{1.5}} = \sqrt[3]{26.9} = 3.0$$

$$\text{Diameter of sol droplets} = (150 \text{ microns})(3.0) = 450 \text{ microns}$$

From the eqn. for D:

For $k = 2.4$, $f = 1.23 \text{ cc/min}$ (an arbitrary but reasonable feed rate in the present equipment)

$$0.0450 \text{ cm} = 2.4 (1.13) \sqrt{\frac{1.23 \text{ cc/min}}{V_{\max}}}$$

$$0.0166 \text{ cm} = \sqrt{\frac{1.23 \text{ cc/min}}{V_{\max}}}$$

$$2.76 \times 10^{-4} \text{ cm}^2 = \frac{1.23 \text{ cc/min}}{V_{\max}}$$

$$V_{\max} = 4450 \text{ cm/min}$$

$$\text{Organic drive fluid flow rate} = \frac{(4450)(0.0791)}{2} = 176 \text{ cc/min}$$

The two-fluid nozzle gives uniform particles and a high yield in a relatively narrow diameter range. This uniformity is necessary to long-term, continuous operation of the column and is very desirable in order to avoid recycle of off-size product. The size yield of five different urania product batches with a total urania weight of 1160 g was 76 wt % in the size range of 125 to 177 microns.

3.4 Fluidization in the Column

A schematic flow diagram of the tapered column system being used to produce urania gel spheres is shown in Fig. 4. This figure also includes the dimensions of the tapered column. The organic liquid, 2-ethylhexanol, is pumped by a centrifugal pump through a Cuno Micro-Klean filter and into the bottom of the tapered glass column. For the work discussed in this report, all of the organic liquid entered the column system tangentially, creating a swirl in the lower half of the column. The organic liquid then flowed upward through the column and was recycled to the pump. A small stream of organic was taken through the 0 to 0.2 gpm rotameter (176 cc/min

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Fig. 4. Gel Microsphere Forming Column.

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flow rate for the example of section 3.3) and used as a drive fluid in the two-fluid nozzle. The sol was metered by a syringe pump to the two-fluid nozzle and dispersed into droplets. The droplets fell through the up-flowing organic until the droplets reach their fluidizing velocity. As water was extracted from the aqueous droplets into the organic liquid, the sol set to a rigid gel and the gelled particles, being more dense than sol droplets, required a higher fluidizing velocity. This column system was operated continuously by adjusting the organic fluidizing flow to allow the gelled spheres to fall through the minimum column cross-sectional area. This permitted product removal without interfering with column operation.

For the desired size of urania microspheres the organic liquid flow rate up through the column for fluidization was about 0.8 gpm. This flow rate corresponded to an average upward velocity at the minimum column cross-sectional area of 0.082 ft/sec. The organic liquid entered the bottom of the tapered column tangentially through a 3/16-in.-ID opening. The 0.8 gpm flow rate corresponded to a tangential organic entrance velocity of 9.3 ft/sec. The swirl induced in the fluidizing organic stabilized the bed of sol and of gelled spheres, allowing a continuous removal of gelled product from the column. The Stokes terminal velocity for a gelled particle is about 1.4 times greater than that for a newly formed sol droplet. This difference in fluidizing velocities allows the sol droplets to be suspended in the upper portion of the column while the gelled particles are dropping out of the bottom. For an upward organic flow with no rotation, the sol droplets and gelled particles were in a continuous motion up and down the column, and a flow instability was produced which allowed both sol drops and gelled spheres to fall out of the fluidized bed.

The conditions in the column tended to oxidize the U(IV) in the nitrate sols. With no argon atmosphere over the organic phase or no resin column to remove NO_3^- in the solvent recovery system, the U(IV) content of the gelled spheres (as removed from the column) was 62%. With an argon atmosphere and a resin column in the solvent recovery system, the U(IV) content was 73%. For a formate sol, the U(IV) content of the gelled spheres was 82% with the argon atmosphere and the resin column in use.

3.5 Solvent Recovery

To operate the sphere forming column continuously it is necessary to remove a side stream of organic liquid and reduce its water content by distillation. This was done with a steam-heated still operating with an organic liquid temperature of 150°C (see Fig. 2). The dry organic liquid from the still contained about 0.5 wt % water. It was cooled to room temperature and metered to the suction side of the column pump. The wet and dry organic liquid flow rates to the still and to the column were each 0.5 liter/min. These flow rates kept the water content in the column below 1.0 wt % for a sol flow rate up to 2.5 cc/min. An organic liquid flow rate of 0.5 liter/min was recycled from the wet organic tank to a 3-in.-diam column containing 1.5 lb of Dowex 1-X8 ion exchange resin (hydroxide form). This resin removed any nitrate

which had been extracted from the sol. With the resin column in operation, the NO_3^- content in the column organic was between 0.005 and 0.05 mg/ml. The removal of NO_3^- from the organic liquid seemed to be necessary both because the NO_3^- buildup in the organic apparently caused clustering of the nitrate sol droplets and because the NO_3^- buildup apparently increased the extent of oxidation of U(IV) to U(VI).

Very little information was obtained about the problems arising from long-term recycle of the organic liquid since most of the sol batches were formed in unused solvent. There is evidence that the Span 80 loses its effectiveness upon recycling through the distillation system. Also, some results for long-term recycle of organic liquid during formation of thoria microspheres show decreasing product densities with recycle time. This may be due to accumulation of impurities in the solvent.

4. DRYING GEL MICROSPHERES

Drying of the gelled microspheres was studied as a function of drying gas, drying time, and temperature. This study is by no means complete, and many variables remain to be explored. Drying microspheres to remove sorbed alcohol and water prior to calcination is more desirable than a 1-step drying and calcination process in the high temperature furnace. The use of separate equipment for low temperature drying is much simpler and cheaper. Complete removal of the 2-ethylhexanol and formate in the drying step would be very desirable as it would then be virtually impossible to have carbon as an impurity in the final calcined product. In the present stage of development, carbon is a major impurity and is found in amounts ranging up to 0.6%.

4.1 Drying Apparatus

The apparatus used in the drying studies is shown in Fig. 5. Wet gel spheres were placed on the fritted disk, and blanket gas was passed through the fritted disk and hence through the bed of gelled spheres. The entire vessel was heated by a heating mantle. Batches of UO_2 microspheres up to 300-g size could be conveniently dried in this apparatus.

In future work steam-stripping will be extensively studied as a function of steam flow rate, temperature, and time. Also, extensive studies are planned on methods for soaking out the 2-ethylhexanol (B.P. = 185°C) with more volatile liquids such as acetone and methanol which would then be easier to strip out of the gel spheres on drying.

Fig. 5. Gel Microsphere Drying Apparatus.

4.2 Drying Results

A variety of drying conditions were tested for effectiveness of removing 2-ethylhexanol from gelled microspheres (Table 4). The most effective of the procedures for removing the alcohol were steam-stripping using mixtures of steam and either H_2 or CO , and boiling methanol extraction followed by drying under Ar or H_2 . Steam-stripping appeared to be slightly more effective. Drying under argon at $150^\circ C$ best preserved the U(IV) content of the gel, but the carbon content was about a factor of 3 higher than with steam-stripping. Vacuum drying at $100^\circ C$ was not a very effective procedure. After drying at $100^\circ C$ for 75 hr, the gelled microspheres still contained about 5 wt % carbon. Thermogravimetric analysis showed that the bulk of the volatile material was removed at temperatures in the 100 to $200^\circ C$ range (Fig. 6). The maximum differential weight loss occurs at $165^\circ C$. Two other distinct peaks occur at $300^\circ C$ and $450^\circ C$ and are as yet unexplained.

Since the preliminary studies on drying indicated that exhaustive studies were needed to optimize the drying step, it was decided that early evaluation of the final product of calcined spheres was desirable before these studies were undertaken. Thus, for convenience, the procedure of drying under argon at $150^\circ C$ for 18 to 24 hr was selected. Besides, there was the possibility that most of the remaining sorbed alcohol could be driven off during the heat-up stage of calcination. The seven enriched UO_2 preparations listed in Table 5 of the next section utilized the argon drying procedure and typically contained 5 wt % carbon after drying.

5. CALCINING DRIED GEL MICROSPHERES

The calcination of UO_2 microspheres was studied principally as a function of gaseous atmospheres and, to a lesser extent, the heat-up rate and calcination temperatures. It was reasoned by analogy with previous work on the calcination of sol-gel thoria that near-theoretical density and adequate strength could be achieved for UO_2 by calcination at 1050 to $1200^\circ C$. It was known that a blanket of reducing gas, preferably Ar-4% H_2 , was necessary at the final calcination temperature to prevent oxidation and so assure a pure UO_2 product.

5.1 Calcination Procedure

The UO_2 microspheres were calcined in high-purity Alundum boats inside a 2-1/4-in.-ID furnace tube of high-purity Alundum. The boats had about a 300-g capacity for dried gel spheres. Temperature control was maintained by Wheelco controllers and the temperature was measured with platinum thermocouples. Heat rates were controlled by either variac transformer or a proportional temperature controller which uses a cam device.

Fig. 6. Thermogravimetric Analysis of NUX XV-3 Wet Gel Microspheres.

Table 4. Drying of

Sol Code	Drying Code	Drying Gas	Temp. °C
NU II-3	A-11	Argon	1200
	A-12	Argon	1200
	A-13	Argon	1200
	A-14	Argon	1200
	A-15	Argon	1200
NU IV-3	B-11	Argon	120-150
	B-21	H ₂ + Steam	100-120
	B-31	CO + Steam	100-120
	B-41	Argon	120-150
NU V	C-11	CO	150-170
	C-12	CO + Steam	100-120
	C-13	H ₂ + Steam	100-120
	C-14	CO bubbled thru CH ₃ OH then Dry CO	90 200
	C-16	Same as C-4	
	C-16 2	CO	150-170
NU VI	D-1	CH ₃ OH wash; ^a dry H ₂	120
	D-2	" " " "	120
	D-31	" " " "	120
	D-32-H ₂	H ₂	170
	D-32-CO	H ₂	170
	D-31-Dr	CO + N ₂ H ₄ + Steam then CO	145 150-170
NU VIII	E-1	CH ₃ OH wash; ^a Ar-4% H ₂	120
	E-2	" " " "	120
	E-1Me	CH ₃ OH wash; ^a Argon	120
		then Argon	200
	E-IRA-400	CH ₃ OH wash; ^a Ar-4% H ₂	120
	E-IRA-1450	" " " "	120
	E-IRA-150	CH ₃ OH wash; ^a Ar	150
	E-IDr-150	" "	150
NU XV-3	3 M	Ar	150
	3 Sm	Ar	150
NU XXII-3	3-60	Ar	150
	3 C	Ar	150
	3 Sm	Ar	150
NU XXV-3	3 VP	Vacuum	25
		then Vacuum	100
	3 Sm 3 Sm 5 D		

^aExtracted with boiling CH₃OH for 4 hr in Soxhlet extraction.

5. Calcination of Microspheres - Preliminary Studies

Calcination Conditions		Cool-Down Conditions			Carbon, ppm	Surface Area, m ² /g	Volume %, Porosity	
		A - Ar to Room Temp	Crush Strength, g (Ave. of 10)	Density				
		B - To 800°C in H ₂ , then to Room Temp in Ar		Toluene				Hg
% H ₂	4	A	675	9.7	7.64			
	4	A	352					
	4	A	564					
% H ₂ + H ₂ O	4	A	275					
% H ₂	4	A	587					
% H ₂	4	B	129	9.68		30	3.7	
	4	B	1336 ± 125	10.4	11.37	300	3.7	
	4	B	1267 ± 330	10.6	10.62	150	3.3	
	4	B	1352 ± 230	10.2	10.56	200	6.95	
	4	B	587 ± 148	9.9	9.92	100	9.9	
	4	B	338 ± 136	10.3	11.03	760	5.3	
	4	B	579 ± 125	10.2		440	7.0	
	4	B	748 ± 155	9.84	10.57		11.0	
	4	B	407 ± 129	9.7	10.11		11.7	
	4	B	646 ± 130	9.89			10.5	
	4	B	280 ± 125			11,600		
	4	B	697 ± 157	10.3		2,920		
	4	B	704 ± 129	10.2		3,730		
	4	B	855 ± 160	10.5		2,830		
	4	B	647 ± 64	10.3	10.27	3,140		
	4	B						
	4	B	909 ± 131	10.9		5,100	<1	
	4	B	677 ± 153	9.8		4,500		
	1/2	2						
	1/2	1	B	664 ± 225	10.8 (He 10.7)	710		
	1/2	2	B	654 ± 219	9.7	5,600		
	1/2	2						
	1/2	1	B	824 ± 314	9.98	6,400		
	1/2	4	B	1389 ± 271	10.47	10.53	2,750	
		4	B	1170 ± 233	10.56	10.37	2,100	
		3	B	668	9.8		3,420	.018
		3	B		10.36		2,890	2.3
		4	B	1132	9.94		4,600	.011
	4	B	336	10.4		9,200	15.1	
	4	B		10.1		9,500	9.72	
	4	B					0.012	
	4	B		9.44				
	4	B		9.54			0.011	

5.2 Calcination Results

A variety of calcination procedures was tested for gelled microspheres in preliminary studies (Table 5). This was necessary mainly because low temperature drying procedures of gelled microspheres did not completely remove the sorbed 2-ethylhexanol. It was hoped that some combination of gaseous atmosphere and heat-up rate would remove the sorbed alcohol at temperatures below about 500°C and thus prevent the presence of carbon impurity in the final product. Typically, the dried gel microspheres contained about 5 wt % carbon. Thermogravimetric analysis showed that although the principal amounts of sorbed materials were removed at temperatures below about 500°C, smaller, but yet significant, quantities of volatiles were evolved at temperatures up to 900°C (Figs. 7 and 8). Three distinct peaks in the differential weight loss curve appear at 250, 450, and 850°C. The peak at 850°C can be explained by thermal decomposition of U_3O_8 , but the other peaks are unexplainable on information we have obtained to date.

Carbon monoxide was added in the cool-down step as insurance against oxidation of the UO_2 by trace amounts of O_2 impurity in argon. Cooling under CO in this temperature range was thought to be preferable to cooling under hydrogen since H_2 is known to chemisorb below 800°C. The argon used in the laboratory preparations is currently being purified by flowing the tank argon over activated copper metal; the CO step will be eliminated as soon as the purification method is proven.

Seven batches of enriched gelled microspheres of 200 to 300 g per preparation were calcined according to the above procedure (Table 6). About 450 ppm Sm was added to these preparations. Crush strengths attained after firing were 600 to 800 g and carbon contents were 0.2 to 0.4 wt %. Uranium analyses showed an essentially pure U(IV) product. Average percentage of the total UO_2 weight that was present in the desired 125 to 177 μ range (80 to 120 mesh) was 77.5% for the seven batches. Average percentages for the oversize (greater than 177 μ) and for the undersize (less than 125 μ) were 10.7 and 11.9, respectively, of the total UO_2 weight.

All of the calcination procedures tested showed near equal effectiveness except for procedures in which air was used (Table 5). Heat-up in air to 1100 to 1200°C was the only procedure that was consistent in removing carbon from the final product; however, the microspheres had low crush strengths and low densities. Typically, all other procedures gave fairly good crush strengths but carbon contents were high (1000 to 12,000 ppm). The B and C series had carbon contents in the 100 to 700 ppm range, whereas almost all others had carbon contents in the 3000 to 6000 ppm range. This difference is not understood. The variability of product characteristics when all variables of preparation were apparently constant is not understood (compare D-1, D-2, D-3-1 in Table 5; also E-IRA-150 with E Dr-150 and NU XV-3 μ and 3 Sm).

A 1.5-kg batch of UO_2 microspheres of 125 to 177 μ particle size was prepared by combining calcined gel microspheres from the B, C, D, and E series listed in Table

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Table 6. Calcination of Enriched UO_2 MicrospheresCalcination Conditions: Heat-up: 300°C/hr to 1150 in H_2 Calcine: 1150°C for 4 hr in H_2 Cool-down: to 800°C in H_2 , 800°C to 600°C in CO ,
to room temperature in argon

Original Sol	Total Wt, g	Screen Analyses, wt %			Product Analyses				Crush Strength, * g
		>177 μ	125-177 μ	<125 μ	Total U, %	U IV %	C, ppm	Sm, ppm	
47-72-97	197.6	2.8	81.0	16.2	87.67	85.37	2400		583
47-31-97	179.3	5.0	79.8	15.2	87.62	87.9	1800		662
47-500-97	246.0	22.3	72.9	4.8	87.02	86.99	4600		831
47-67-97 #2	170.7	51.7	37.4	10.9	88.02	88.05	2400		666
47-67-97 #2R*	103.6	4.3	75.6	20.9	88.26	88.38	4300		627
47-67-97 #3	130.1	3.3	86.6	10.2	88.01	88.12	1900		675
47-40-97	237.5	24.8	68.9	6.3	87.99	87.92	2000		356
47-29-97	236	12.1	78.0	9.9	87.20	87.82	4000		1039
Average** =		10.7	77.5	10.5					

*Refire of 47-67-97-2 to 1200°C; all other conditions same

**47-67-97-2 excluded from average

Fig. 7. Thermogravimetric Analysis of Dried B-41 Gel Microspheres.

Fig. 8. Thermogravimetric Analysis of Dried C-11 Gel Microspheres.

7. The carbon content ranged from about 3000 to 8000 ppm, and average crush strengths varied from about 600 to 1150 g. Metallographic examination of the W-9 product showed a grainy structure.

The following schedule was selected for preparation of several enriched batches of UO_2 of 300-g size as it was found to be as effective as any of the other procedures tested and was convenient for laboratory scale preparations.

Heat-up: 300°C/hr under H_2 to 1150°C

Calcine: 1150°C for 4 hr under H_2

Cool-down: to 800°C under H_2 ; 800 to 600°C under CO ; 600°C to ambient under argon

Calcination studies in future work will be aimed at lowering the carbon content in the final product to less than 100 ppm. It is hoped that the drying studies outlined in Section 4.3 will allow attainment of this goal by using our present calcination procedure. However, if this does not work out, the following methods for removing carbon will be studied.

- (1) Firing in CO_2 through the 500 to 900°C range to remove carbon by the reaction, $\text{CO}_2 + \text{C} = 2 \text{CO}$.
- (2) Firing in steam through the 400 to 800°C range to remove carbon by the reaction $\text{H}_2\text{O} + \text{C} = \text{CO} + \text{H}_2$.

Table 7. Natural UO_2 Microspheres (1.5 kg Preparation of 125-177 μ Size)

Calcination Procedure: Heat at 300°C/hr to 1200°C under H_2 ; calcine at 1200°C under H_2 for 2 hr; cool to 800°C under H_2 and from 800°C to ambient under argon

Code	Sub-Code	Wt Used, g	Crush Strength, g			Carbon (Fired Product) ppm	Carbon Dried Gel wt %	Density			Vol % Porosity	Surface Area m^2/g
			Minimum	Average	Maximum			Toluene	Hg	Tap		
W-1 + 2	W-1 W-1 W-1 + 2	371	328	717	1262	4800	5.98					
W-3		123	219	654	869	5050						
W-4 + 5	W-4 W-5 W-4 + 5	175.1 182.5				7700 6160	6.01 6.05					
W-6 + 8		147.1	500	790	1100							
W-9		159.2	382	595	787	8800						
W-10*	BFA Special E-1	152.9	401	1155	1823	4200 4800		9.78	9.38	10.6	<1	0.009
W-11	D-3-2-CO D-3-2-H ₂ D-3-1 E-2	53.6	470 382 397 346	855 704 697 677	1109 899 990 958	3140 2830 3730 4500						
W-12	Undersize <125 μ	94.2										
W-13	Oversize >177 μ	69.0										
TOTAL		1527.6										

*Densities were determined on this sample as follows: toluene - 9.78 g/cc
Hg - 9.38 g/cc
tap - 10.6 g/cc

Vol porosity: <1
Sp. Surface Area: 0.009 m^2/g

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APPENDIX

Palladium Catalyst Preparation

The Pd catalyst was prepared by refluxing 650°C fired ThO_2 (from thorium oxalate) with a $\text{Pd}(\text{NO}_3)_2$ solution at a ratio of 0.05 g $\text{Pd}(\text{NO}_3)_2$ to 1 g ThO_2 to form a sol. Hydrogen was then bubbled through the suspension to reduce the Pd, destroy the nitrate and form a black, slow settling suspension. A typical preparation used 100 g ThO_2 and 5 g $\text{Pd}(\text{NO}_3)_2$ in a liter of solution. Aliquots of the reduced catalyst suspension were used in the preparation of the U(IV) nitrate solutions. Details of the preparation are given in U.S. Patent No. 3,023,085.

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