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UO_2-ThO_2 AND UO_3-ThO_2 SOLS PREPARED BY PRECIPITATION-PEPTIZATION PROCESSES

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ABSTRACT

Co-precipitation methods are attractive for the preparation of mixed thoria-urania sols, as possible alternates to solvent extraction methods. Exceptionally stable sols (>18 mo.) resulted from the co-precipitation of thorium and U(IV) hydroxides in Th/U ratios of 1/1 and 3.5/1. Satisfactory microspheres were formed and calcined from one of these sols. A new co-precipitation method was developed for preparing 3 Th/1 U mole ratio sols using hexavalent uranium, featuring the attainment of low nitrate-to-metal ratios by a "seed sol" technique. The sols readily formed noncracking microspheres in 2-ethyl-1-hexanol by the conventional ORNL method and were fired to 99.5% of theoretical density and less than 1% porosity.

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1. INTRODUCTION

Developments in sol-gel processes at Oak Ridge National Laboratory for the preparation of aqueous colloidal oxide sols of thorium and uranium, and their conversion to ceramic nuclear fuels, have been reported by others.[1-6] In brief, thoria sols are made by peptizing steam-denitrated thoria with water and nitric acid, and urania sols are made by peptizing precipitated $U(OH)_4$ with nitric acid under an inert atmosphere. Both thoria and urania sols are suspended as liquid droplets in a column of upflowing 2-ethyl-1-hexanol, with suitable surfactants, until gelled to firm round beads. These beads, or microspheres, are removed from the column, further dried in superheated steam, and calcined at about 1150°C. Because of the colloidal nature of the gels, sintering to almost theoretical density and hardness takes place at this relatively low temperature of 1150°C, and the materials are suitable for use as ceramic fuels in nuclear reactors.

For some types of ceramic fuels, thoria-urania sol mixtures are used. These mixtures can be prepared in several ways, such as the peptizing of steam-denitrated thoria with uranyl nitrate solution, the co-denitration of uranyl and thorium nitrates followed by peptizing with HNO_3 (both methods for mixtures less than 10 mole % in uranium[1]), peptizing precipitated and washed thorium hydroxide with uranyl nitrate,[6,7] the blending of thoria and urania sols,[2,4,6] the co-precipitation of thorium and tetravalent uranium hydroxides from nitrate solution,[2,6,8] the co-precipitation of thorium and hexavalent uranium hydroxides,[8] and solvent extraction methods.[9,10] The present paper describes recent work at ORNL with the two co-precipitation methods, including scouting tests with the U(IV)-Th method and a more detailed account of the U(VI)-Th sol forming method. In the latter method, bead breakage, which was a problem with mixed sols of U(VI)-Th formed by means of hydroxide precipitation and peptization with nitrate, was eliminated by reducing the nitrate levels in the sols and using very slow microsphere heatup rates in the early firing stages. The co-precipitation methods were explored in order to develop alternate routes to the sol-mixing and solvent-extraction methods currently used.

2. ThO_2-UO_2 SOLS FROM THE CO-PRECIPITATION OF MIXED THORIUM AND URANOUS HYDROXIDES

The object of hydroxide precipitation from nitrate solution as a precursor to sol forming is to eliminate most of the nitrate anion without forming crystallites which are too large to be amenable to colloidal dispersion. In the microsphere-forming process at ORNL, the sol crystallite size, determined by x-ray line broadening, normally lies between about 30 A and 150 A, with values of about 50 to 80 A preferred. Thorium oxide produced by ignition in air consists of nondispersible crystallites of the order of hundreds to thousands of anstroms in size. Steam denitration in the ORNL rotary calciner at about 475°C produces a thoria powder of about 70 A, which is almost completely dispersible and can be made into microspheres up to about 1 mm in diameter. Thorium hydroxide precipitation normally results in crystallites below 30 A in size, which readily disperse to colloids, but the crystallites must be enlarged in some way for microsphere production. The tetravalent uranium hydroxide (or hydrated oxide) of McBride[3] readily forms aqueous sols with crystallites of about 50 A, without lengthy digestion. It therefore seemed worthwhile to investigate the properties of sols made from mixed precipitates, to see if acceptable size ranges could be achieved and thus by-pass the separate operation of the steam denitration of thorium nitrate.

Several of such mixtures were successfully made, based on the method of McBride, who advocated hydroxide precipitation from a vigorously stirred solution 0.5 $\underline{M}$ in [Th(IV) + U(IV)] nitrates, with optional addition of 0.6 mole of formic acid per mole of U, and using 3 $\underline{M}$ NH_4OH--0.5 $\underline{M}$ $N_2H_4 \cdot H_2O$ as the precipitant. Ammonia addition was normally stopped when pH 7.0 was reached. The nitrate solution contained 0.5 mole of urea per mole of uranium as a holding reductant, and the precipitation was carried out under argon. The mixed precipitate was washed on a Büchner funnel with water until nitrate removal ceased, and then either allowed to stand for several days at room temperature or heated to 65°C to form the sol. Table 1 summarizes the co-precipitation tests.

As Table 1 shows, several variations of the standard uranium preparation method were tried. Among the most interesting of the results were:

1. Sols in the Th/U range of 1/1 to 3.5/1 were stable indefinitely in closed containers, without a trace of precipitate.
2. Crystallites were large enough for probable success in microsphere production. Beads of 150 μ were made from one sol (CP-3) which, after firing to 1150°C in air, resisted a crushing load of about 1200 g. After hydrogen firing at 1250°C, the average resistance to crushing was about 540 g, which is adequate strength for reactor fuel.

Table 1. Sols Made from Co-Precipitated U(IV)-Th(IV) Hydroxides

Sol Code	Mole Ratio, Th/U	Nitrate Method Variations	Mole Ratio, $NO_3^-/(Th + U)$ Added	Mole Ratio, $NO_3^-/(Th + U)$ Found	$\underline{M}$ (Th + U)	% U(V) in U	Crystallite Size (A)	Sol Stability
CP-1	1/1	Spontaneously peptized at 1/2 normal wash volume on suction filter	0	0.46	0.78	51	42	>18 mo.
CP-2	1/1	Formate method, pptd. at 50°C	0.08	0.23	0.68	50	53	>18 mo.
CP-3	1/1	Formate method, 25°C	0	0.36	0.68	54	54	>18 mo.
CP-4	1/1	Dup. of CP-1, drier cake	0	0.18	0.92	54	40	>18 mo.
CP-5	1/19	Pptn. pH 8.0, fast filtering*	0.14	0.12	0.95	69	-	Thickened in 2 mo.
CP-6	1/19	Pptn. pH 7.0, fast filtering*	0.24	0.13	0.87	73	53	-
CP-7	3.5/1	Slow filtering	0.04	0.59	0.83	49	50	>18 mo.
CP-8	1/99	Pptn. pH 7.5, fast filtering*	0.16 0.23	- -	~1.0 ~1.0	- -	- -	Formed gel in 4 d. Formed gel in 2 d.
CP-9	1/99	Pptn. pH 7.5, fast filtering*	0.04	-	~1.0	-	-	Formed gel in 2 mo.
CP-10	1/19	Pptd. at 10°C	Liquefied on filter, batch lost					
CP-11	3.5/1	Pptd. at pH 8.5	0.10	0.51	0.76	32	50	>18 mo.

*Fast filtering -- factors of 5 to 10 times faster than filtering rate of pure $U(OH)_4$ precipitated at pH 7.0.

3. Nitrate-deficient filter cakes, such as those prepared at 50°C or at a pH higher than 7, formed stable sols when sufficient nitrate was added as dilute HNO_3 to complete the peptization.
4. Nitrate contents tended to be higher in these co-precipitation sols than in pure uranium sols. In the nitrate method for pure U sols, the NO_3^-/U ratio normally is 0.05-0.08, and in the formate method it is approximately 0.18.[3] Our mixtures had nitrate ratios as high as 0.59.
5. The percentage of U(IV) in total U, normally more than 85 in pure urania sols, here was only about 50, due to spontaneous oxidation of the tetravalent to hexavalent uranium by the nitrate, even in an argon atmosphere. This produced nitric oxide and a drop in pH, probably according to the reaction:

$$3\,U^{4+} + 2\,NO_3^- + 2\,H_2O \rightarrow 3\,UO_2^{2+} + 2\,NO\uparrow + 4\,H^+ \quad .$$

The nitric oxide sometimes pressurized the containers, which required periodic venting. The gas was obviously nitric oxide, since it was colorless in the glass containers and turned instantly to brown NO_2 in air when vented.

6. The spontaneous peptizing and liquefaction of batch CP-10, precipitated at 10°C and washed partially free of nitrate on the filter, shows a tendency toward high nitrate retention in the precipitate. This was probably due to the increased surface area known to be associated with low-temperature

precipitations. This low-temperature effect had been observed previously with pure uranium preparations and will be discussed further in a forthcoming report.

7. Sols from these co-precipitated hydroxides were sometimes too dilute at 0.7-1.0 M for microsphere formation, but it was found that they could be concentrated, without damage, to 1.5-2.0 M by evaporation under vacuum.

3. ThO_2-UO_3 SOLS BY CO-PRECIPITATION OF HYDROXIDES

The precipitation of mixed U(IV)-Th(IV) hydroxides for the preparation of the thoria-urania sols described above requires the reduction of uranyl to uranous nitrate as a preliminary step. The mixing of UO_2 sols with ThO_2 sols made from steam-denitrated thoria, which is another useful method for preparing mixed sols at ORNL, in addition requires the thoria denitration and thoria sol preparation steps. Co-precipitation of U(VI)-Th(IV) hydroxides from mixed uranyl and thorium nitrates would bypass both the uranium reduction and the thorium steam-denitration steps. The hydroxide co-precipitation method has been employed at KEMA,[8] apparently with some limitations on its usefulness, and at the Houdry Process Corporation in the United States.[11] At ORNL, 3/1 thoria-urania sols prepared by co-precipitation were formed into nearly theoretically dense nonporous microspheres in the 250-μ size range, without sphere cracking or pitting. No internal gelation was used, and no washing of the gel for nitrate removal was required.

Our process, which produces dense noncracking microspheres, has the following interesting features:

1. Carbon dioxide, normally strongly absorbed by thorium hydroxide, and a precipitating agent for thoria sols, is excluded by the use of an inert blanketing gas in the entire series of operations.[12]
2. Precipitation of the mixed hydroxides is made by "reverse strike", i.e., the nitrate solution (0.5 $\underline{M}$) is added to the ammonium hydroxide solution (3 $\underline{M}$), a typical rate of addition being 18 min for a half-mole batch.
3. The temperature during precipitation is maintained at 80 ± 5°C.
4. The ammonia is present in 70% excess, assuming that all nitrate is replaced by hydroxide.
5. The fast-settling yellow precipitate is filtered by suction and washed with 10 to 12 cake volumes of water at 80 ± 5°C, containing about 5 ml of concentrated NH_4OH per liter to prevent peptization and promote nitrate removal. The filtering and washing normally take about 2.5 hr for a half-mole batch, using an 18-cm Büchner funnel. The NO_3^-/(Th + U) mole ratio is thus reduced in the filter cake to about 0.003, and the NH_4^+/(Th + U) mole ratio to 0.05. The ammonium diuranate content of the cake is hence very small, and the ammonium nitrate is almost completely removed.
6. We then expel the remaining ammonium ion, as ammonia, from the mixed hydroxides, to a residual level of 10-30 ppm, by boiling the hydroxides as a water slurry for about 2.5 hr, or until the pH of the evolved steam decreases from its initial value of 9-10 to about 6. The hydroxides have a crystallite size of <30 A, measured by x-ray line broadening. An electron micrograph at 69,000X illustrating the flocculated pattern is shown in Fig. 1.

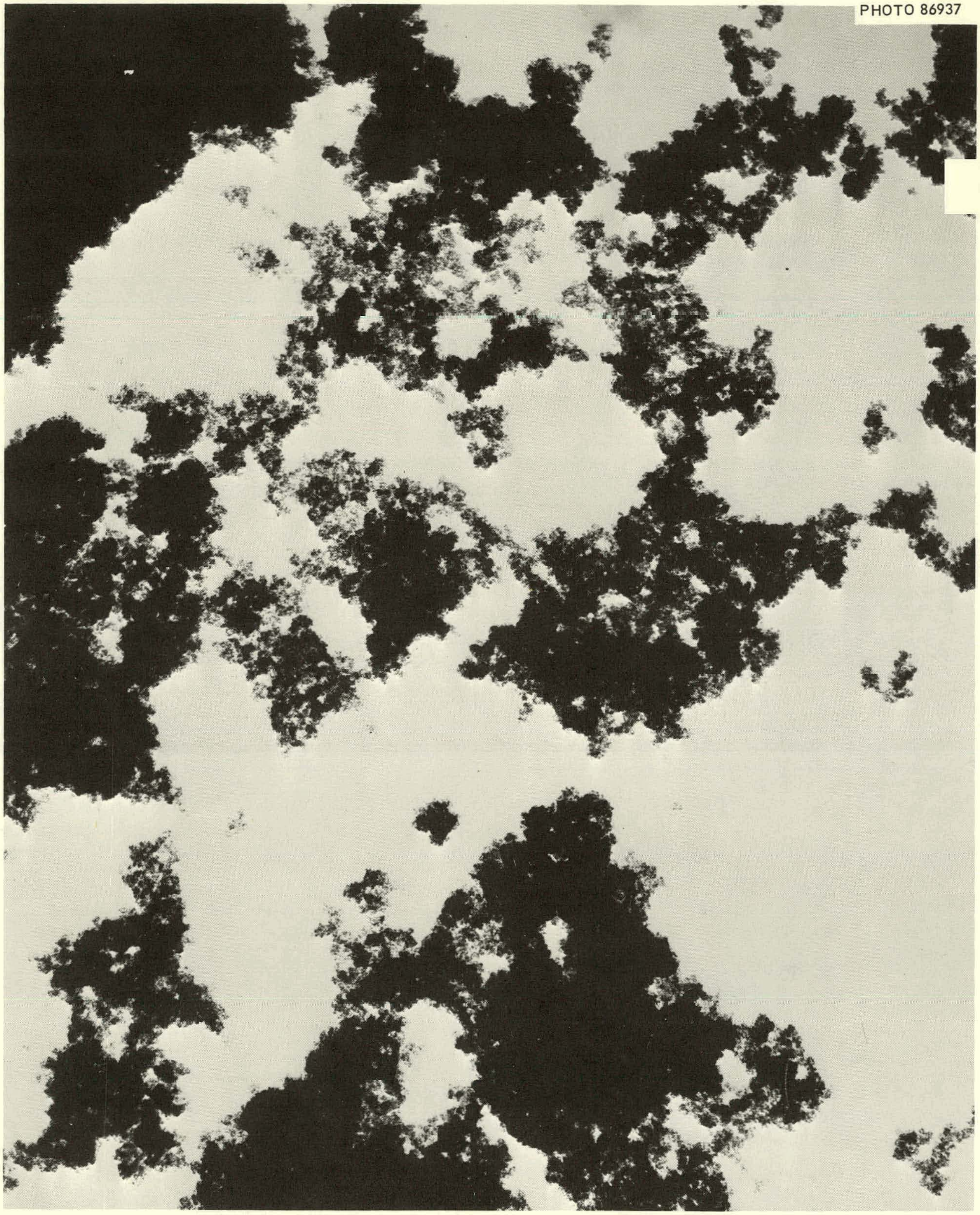

Fig. 1. Flocculated 3 Th/1 U(VI) Hydroxides (69,000X).

7. With the nitrate thus washed out of the hydroxide mass, it is now possible to peptize to a low-nitrate sol, which is essential for the prevention of pitting and cracking in the microspheres. We have found that when nitrate is left in the hydroxide, due to using other methods of precipitation and washing, the nitrate ratio required for peptizing to a sol is higher than is the case when starting from a denitrated hydroxide (e.g., 0.6 to 0.8 vs 0.13). The lowest nitrate ratio we have obtained by direct boiling of nitric acid with the denitrated hydroxide is 0.19 in 12 hr. Even lower ratios of 0.13 to 0.14 are obtained by a three-step "seed sol" peptization process for these 25 mole % UO_3--75 mole % ThO_2 sols, as follows:

   a) One-third of the hydroxide slurry is boiled for a few minutes with enough nitric acid to yield a nitrate-to-metal ratio of 0.13 to 0.14, computed on a whole-batch basis. Traces of CO_2 introduced by the ammonia and water washes are expelled because of the low pH, and a clear red sol quickly forms, with a nitrate-to-metal ratio of about 0.40.

   b) Half of the remaining hydroxide is added, with continued boiling for about 20 min, until peptized also. The nitrate ratio is now about 0.20.

   c) The last of the hydroxide is now added to the "seed sol", and boiling is continued under reflux for about 8 hr, or until the sol is a clear dark red. This sol can be concentrated by evaporation until saturated at about 1.5 M (Th + U). Figure 2 is a typical electron micrograph of such a sol, with an x-ray crystallite size of 44 A, showing that the amorphous masses of crystallites have grown from their original size of <30 A at precipitation and have dispersed.

Fig. 2. Sol from 3 Th/1 U(VI) Hydroxides (69,000X).

Figure 3 shows typical gel microspheres after being formed and partially dried in 2-ethyl-1-hexanol containing 1.1% H_2O, 0.3% Span 80, and 0.5% Ethomeen S-15. These perfect spheres contrast sharply with the distorted and coated spheres from another sol with a much higher $NO_3^-/(Th + U)$ ratio of 0.78 and a crystallite size of 40A (Fig. 4). This latter sol had retained too much nitrate in the hydroxide precipitate because it was precipitated at pH 7 instead of by reverse strike with an ammonia excess.

Figure 5 shows 140°C-dried beads, still perfectly shaped, made from low-nitrate sol, and Fig. 6, by contrast, shows another lot of dried beads from a high-nitrate sol, with extensive pitting and breakage.

Furnace firing studies on the dried microspheres from low-nitrate sols revealed breakage problems here also, however. Figure 7 shows the sudden breakage encountered between 200 and 250°C when temperature rise rates of about 300°C/hr were used. Less frequent breakage occurred at lower rise rates, and at a rate of 20°C/hr in this critical temperature region the breakage ceased. Figure 8 shows microspheres fired in air at 1140°C for 4 hr. The light reflections on the black surfaces reveal their high brilliance and gloss. Density of this material in mercury at 1 atm is 101.8%, and at 15,000 psi, 102.6% of theoretical, computed as a solid solution of UO_2 in ThO_2. We do not yet know if these higher-than-theoretical densities are due to analytical errors or to some other unidentified factor. The crush resistance between parallel flat plates of tungsten carbide is about 2500 g for the 250-μ size fraction. Porosity is less than 1%.

This ability of the beads to be fired in air is of importance in burning out the organic carbon introduced by the 2-ethyl-1-hexanol and the surfactants, but for

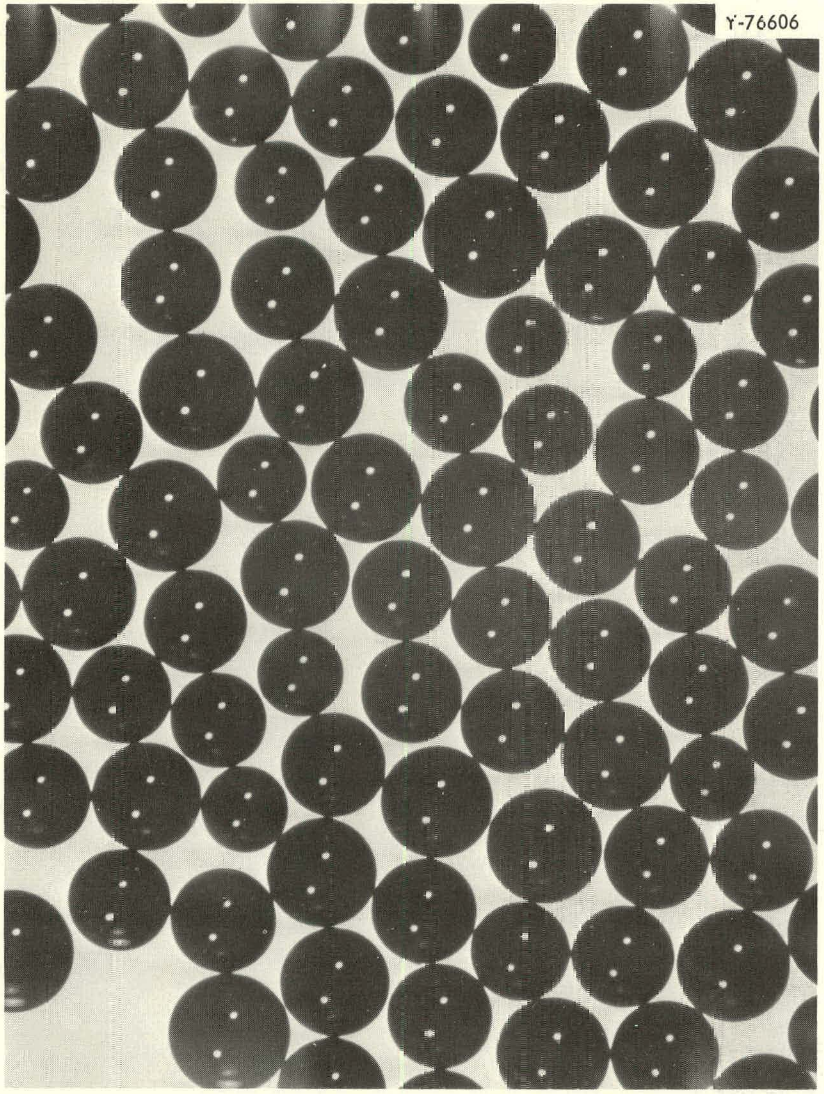

Fig. 3. Gel Microspheres from 3 ThO_2/UO_3 Sol with $NO_3^-/(Th + U)$ Mole Ratio of 0.13 (33X).

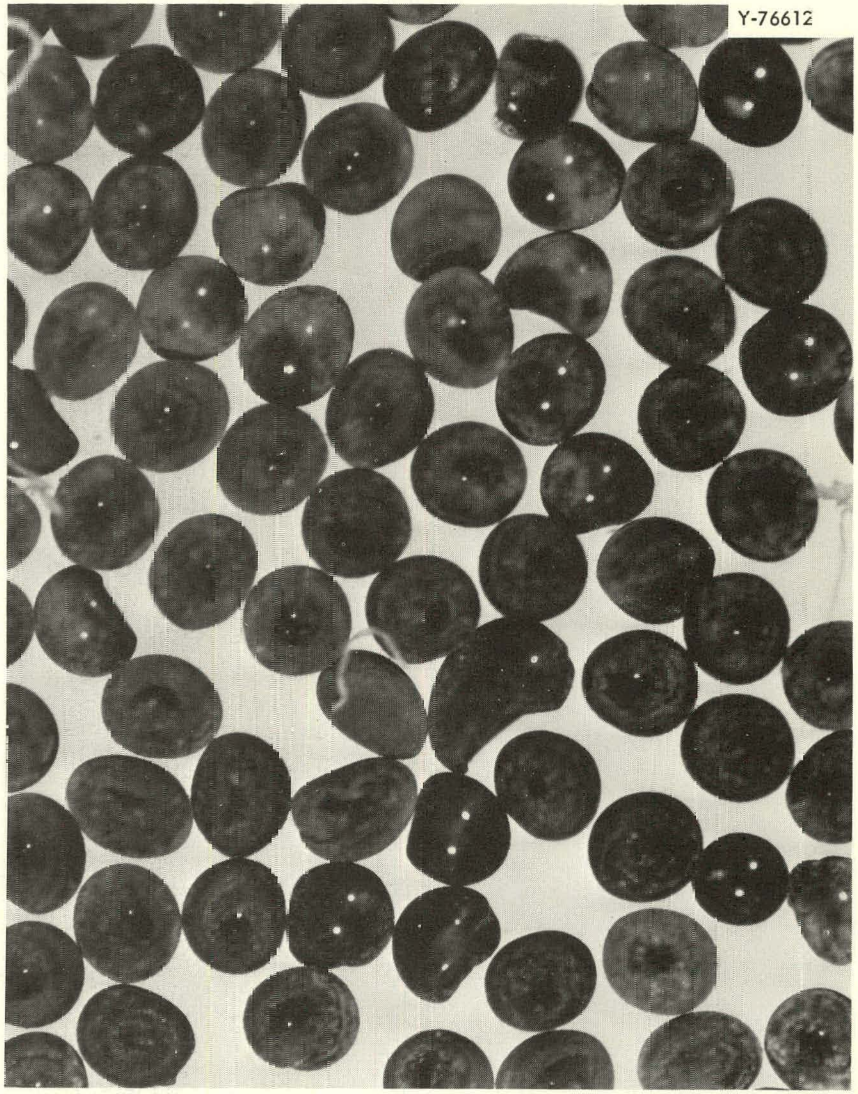

Fig. 4. Gel Microspheres from 3 ThO_2/UO_3 Sol with $NO_3^-/(Th + U)$ Mole Ratio of 0.78 (33X).

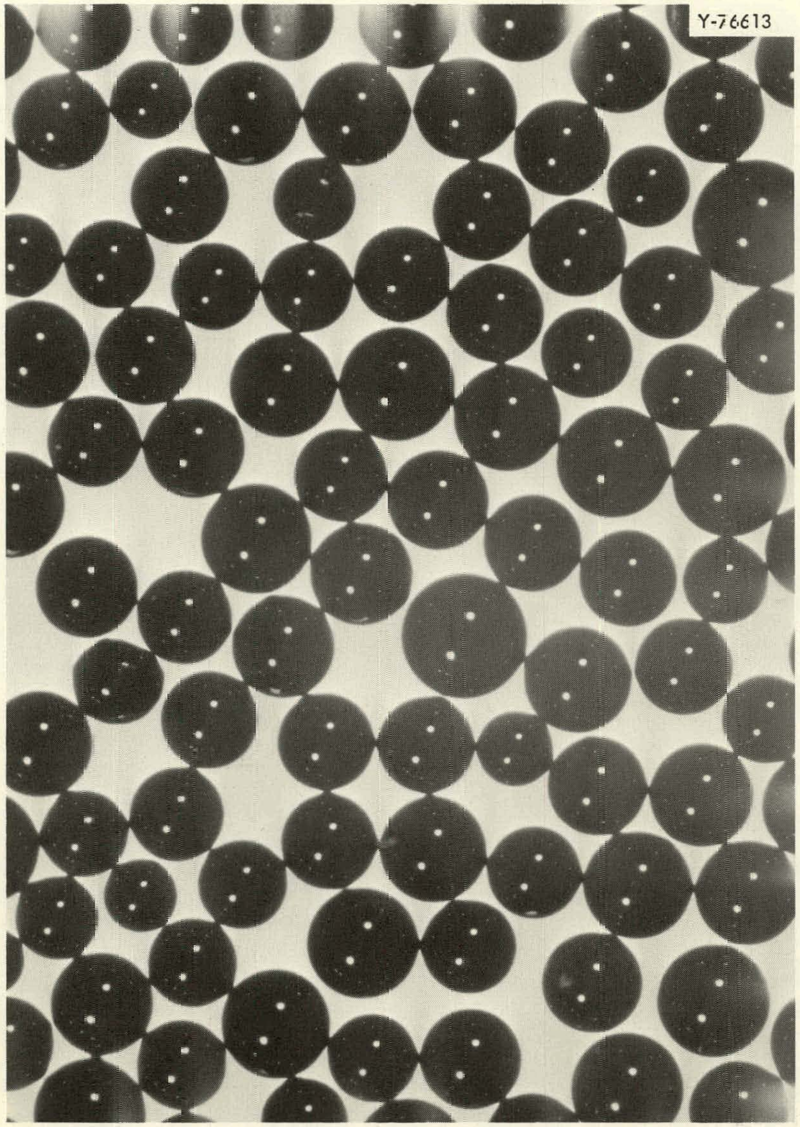

Fig. 5. Gel Micropheres of Fig. 3, Dried at 140°C (33X).

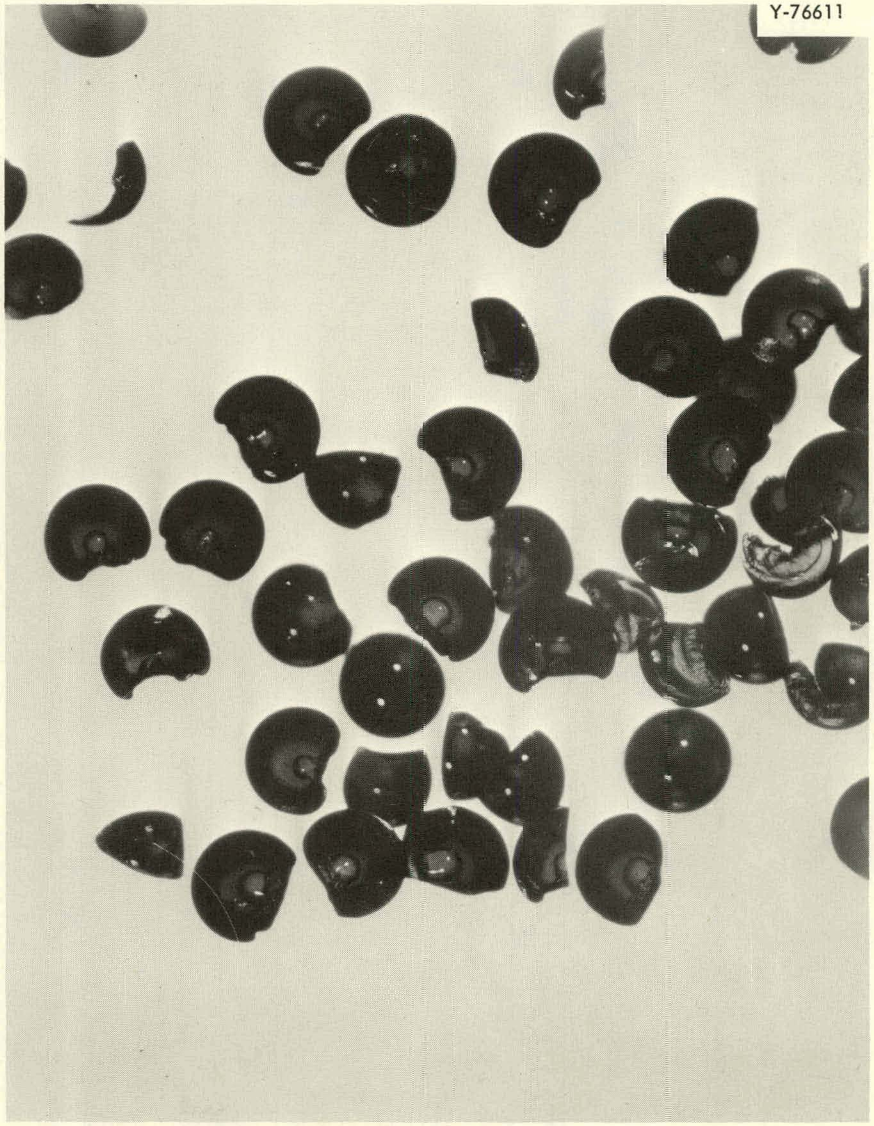

Fig. 6. Gel Microspheres from Same Sol as Fig. 4, with 1.5% H_2O Added to the 2-ethyl-1-hexanol (33X).

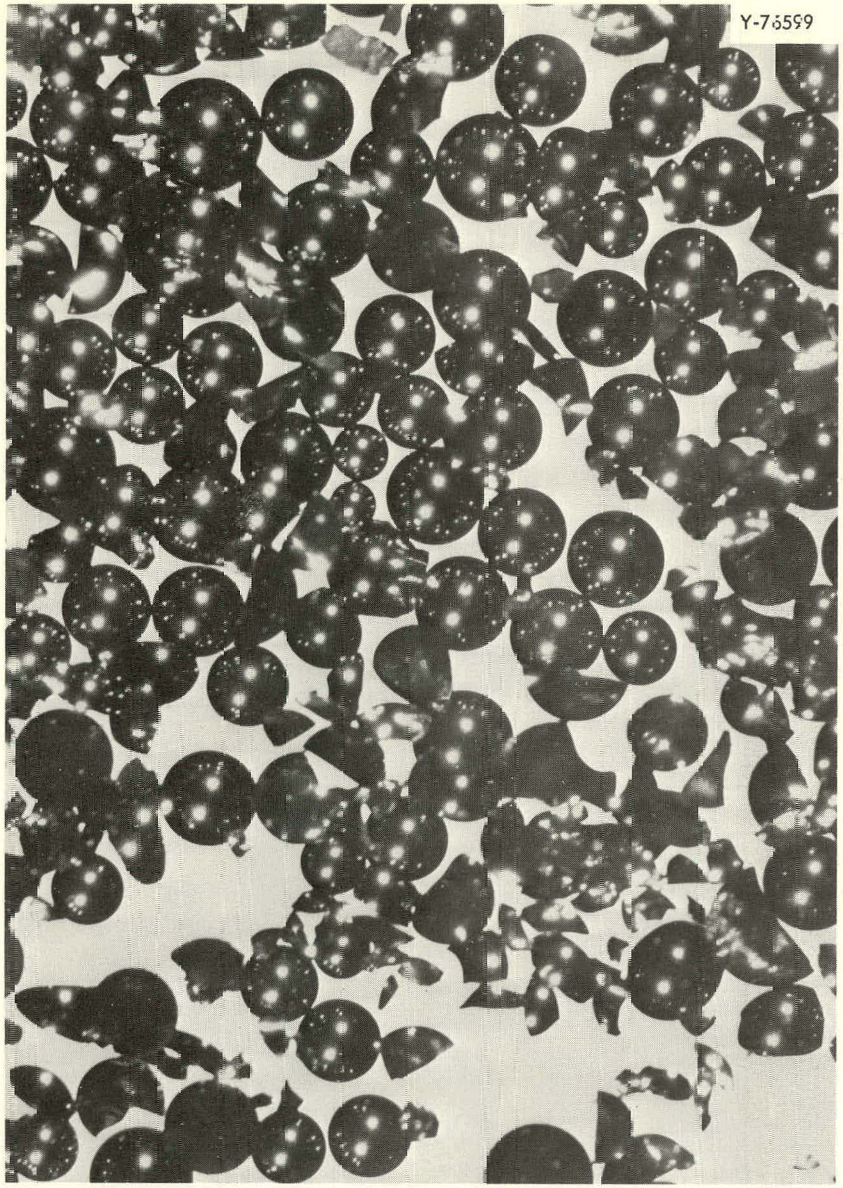

Fig. 7. Breakage of Low Nitrate Microspheres at 200–250°C at Temperature Rise of 300°C/hr (33X).

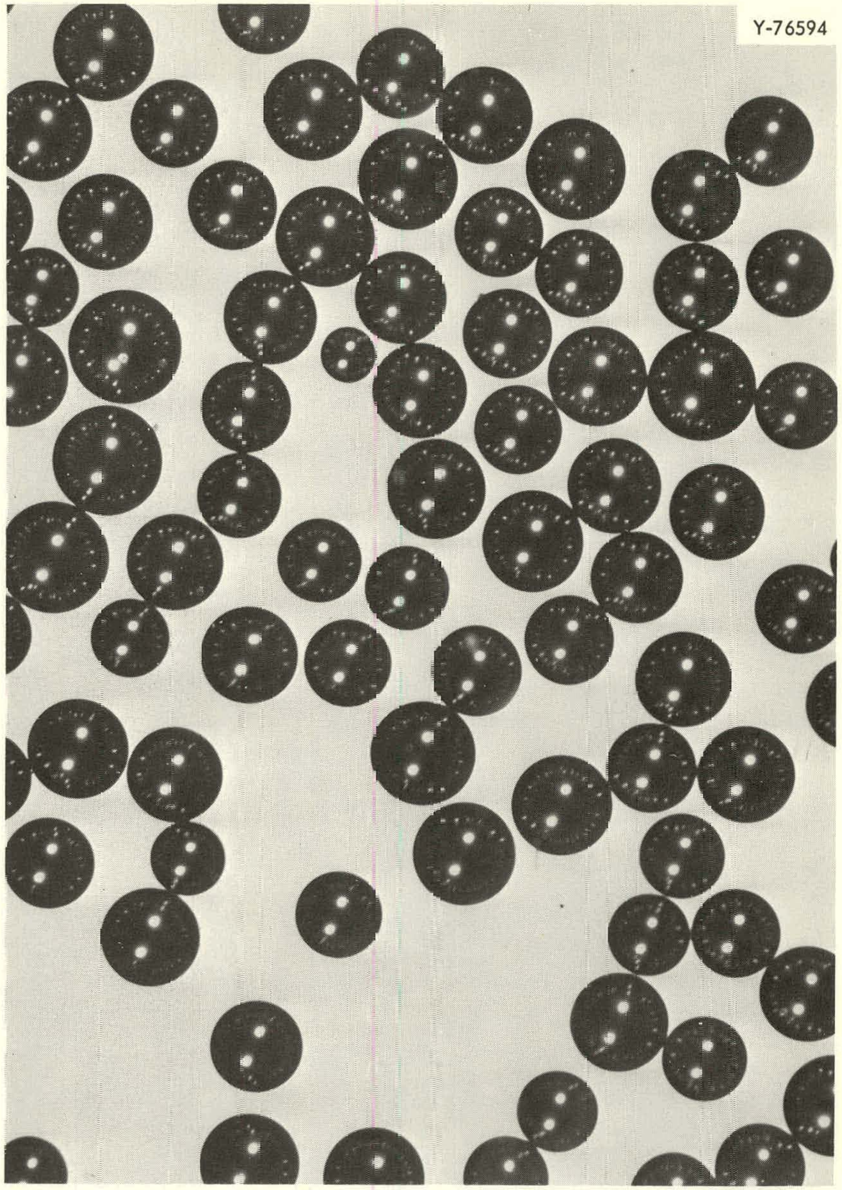

Fig. 8. 3 ThO_2/UO_3 Microspheres Fired in Air 4 hr at 1140°C (33X).

reactor fuels the microspheres must be fired afterward in hydrogen in order to reduce uranium oxides to UO_2. Figure 9 shows the 177- to 250-μ size fraction (-60 +80 mesh) after hydrogen firing at 1200°C. The density of these beads is 99.5% of theoretical, the crush resistance about 1700 g, and the porosity still less than 1%.

It is thus apparent that both the U(IV)- and U(VI)-thorium co-precipitation routes in the range of about 25 mole % uranium show promise as alternative paths to mixed thoria-urania microspheres.

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Assistance from members of other divisions included electron microscopy by T. E. Willmarth, microsphere photography by J. C. Gower, x-ray crystallite size determinations by R. L. Sherman, and chemical analyses by W. R. Laing.

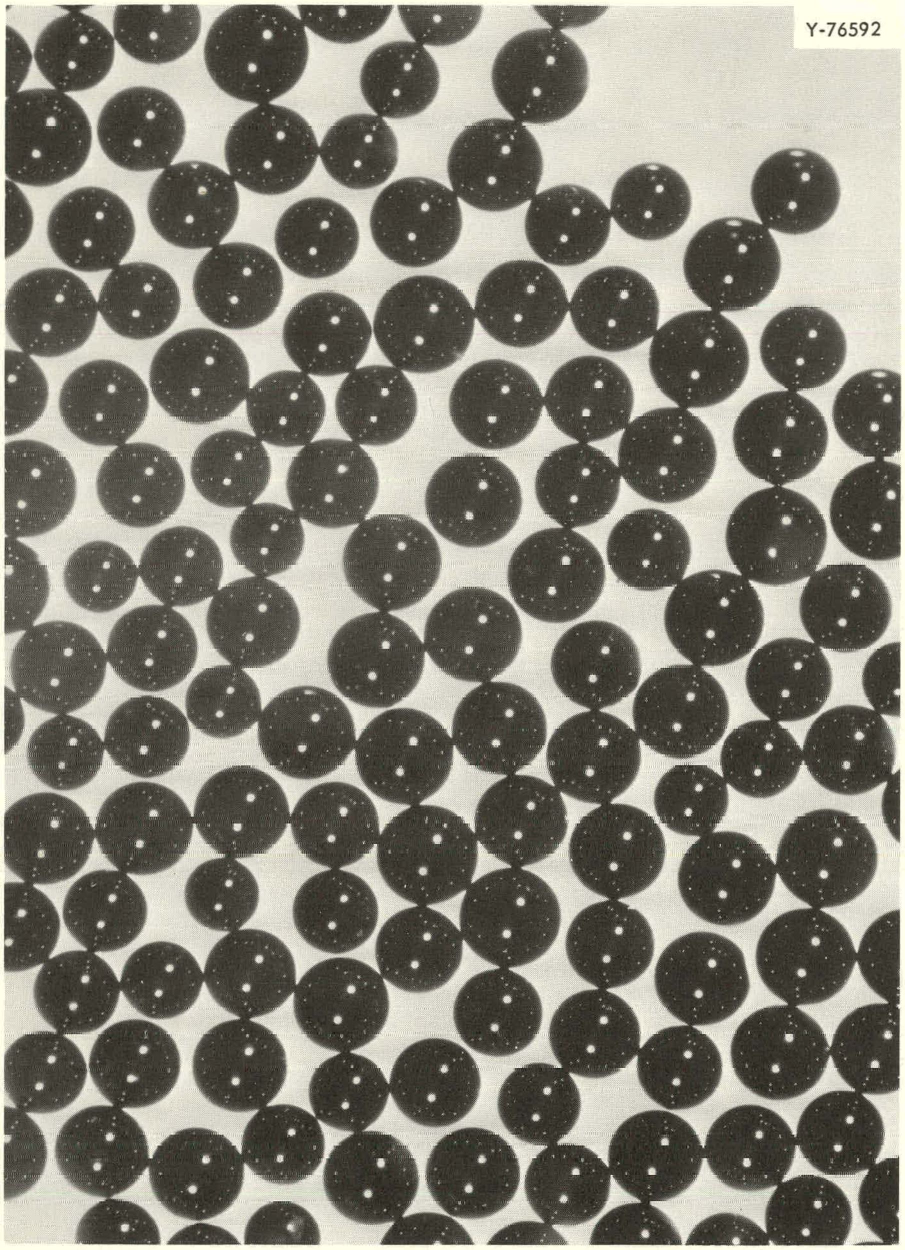

Fig. 9. Same Microspheres as in Fig. 8, Fired 4 hr in Argon + 4% H_2 at 1200°C. Sieve fraction of 177–250 μ (33X).

5. REFERENCES

1. D. E. Ferguson, O. C. Dean, and D. A. Douglas, "The Sol-Gel Process for the Remote Preparation and Fabrication of Recycle Fuels," A/Conf. 28/P/237, Proc. Intern. Conf. Peaceful Uses At. Energy, 3rd, Geneva, 1964 (1965).

2. R. G. Wymer and D. A. Douglas, Jr., Status and Progress Report for Thorium Fuel Cycle Development for Period Ending Dec. 31, 1965, ORNL-4001 (October 1966).

3. J. P. McBride, Preparation of UO_2 Microspheres by a Sol-Gel Technique, ORNL-3874 (February 1966).

4. W. D. Bond, S. D. Clinton, P. A. Haas, A. T. Kleinsteuber, and A. B. Meservey, Preparation of $^{235}UO_2$-ThO_2 Microspheres by a Sol-Gel Method, ORNL-TM-1601 (Aug. 8, 1966).

5. P. A. Haas, S. D. Clinton, and A. T. Kleinsteuber, "Preparation of Urania and Urania-Zirconia Microspheres by a Sol-Gel Process," Can. J. Chem. Eng., p. 348 (December 1966).

6. Chemical Technology Division Annual Progress Report for Period Ending May 31, 1966, ORNL-3945 (September 1966).

7. M. E. A. Hermans and H. S. G. Slooten, "Preparation of UO_2 and ThO_2 Powders in the Subsieve Range," A/Conf. 28/P/634, Proc. Intern. Conf. Peaceful Uses At. Energy, 3rd, Geneva, 1964 (1965).

8. F. W. van der Brugghen, M. E. A. Hermans, J. B. W. Kanij, A. J. Noothout, Th. van der Plas, and H. S. G. Slooten, "Sol-Gel Processes for Spherical Thorium Containing Fuel Particles," KEMA, Ch-E/PV-6/66 (21 April 1966), Thorium Fuel Cycle, Proceedings of the Second International Symposium, Gatlinburg, Tennessee, May 3-6, 1966, USAEC, Division of Technical Information.

9. G. Cogliati et al., "The Preparation of Dense Particles of Thorium and Uranium Oxide," A/Conf. 28/P/555, Proc. Intern. Conf. Peaceful Uses At. Energy, 3rd, Geneva, 1964 (1965).

10. John G. Moore, Preparation of Thorium-Uranium Oxide Sols Through Solvent Extraction by the Amine Denitration Process, ORNL-4095 (in press).

11. H. A. Green, W. J. Savournin, A. H. Weiss, and J. J. Donovan, Final Report, Jan. 1956-June 1958, Preparation of Thoria Sols and Micro-beads, Subcontract 904 under W-7405 eng-26, 58-OCR-15, Houdry Process Corporation, Linwood, Pa. (Dec. 30, 1958).

12. K. H. McCorkle, Surface Chemistry and Viscosity of Thoria Sols (Thesis), ORNL-TM-1536 (July 1966).

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