OAK RIDGE NATIONAL LABORATORY LIBRARIES
3 4456 0549182 0

CENTRAL RESEARCH LIBRARY
DOCUMENT COLLECTION

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

ORNL-TM-1508
COPY NO. - 37
DATE - July 10, 1966

FORMATION OF URANIUM, ZIRCONIUM, AND THORIUM OXIDE MICROSPHERES BY HYDROLYSIS OF DROPLETS

T. A. Gens

CENTRAL RESEARCH LIBRARY
DOCUMENT COLLECTION
LIBRARY LOAN COPY
DO NOT TRANSFER TO ANOTHER PERSON
If you wish someone else to see this document, send in name with document and the library will arrange a loan.

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

LEGAL NOTICE

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

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

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

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

ABSTRACT

A new method of preparing metal oxide microspheres was investigated in the laboratory. This method involves spraying nitrate or chloride solutions or sols onto a layer of organic liquid floating on ammonium hydroxide solution. Droplets of sol or solution disperse in the organic layer and fall into the ammonium hydroxide, where they hydrolyse to hydroxide microspheres. The hydroxide microspheres are dried and fired to form oxide microspheres.

The most successful preparation involved making gels by bubbling ammonia through aqueous solutions, converting the gels to sols by warming, and adjusting the temperature of the sol so that the viscosity was that needed for forming droplets in the organic liquid. Urania and zirconia microspheres with densities up to 99% of theoretical were formed by this method.

Sols prepared from chloride salts behaved the same as those prepared from nitrate salts. However, sols prepared from uranium nitrate solution were not stable and it was necessary to use the chloride salt in making urania microspheres.

---

1. INTRODUCTION

The dispersion of a thin, aqueous sol or of an aqueous solution in an organic liquid produces spherical droplets. The purpose of this work was to form such droplets from sols or solutions of metallic salts and convert them into metal hydroxide spheres by contacting the droplets with alkaline solution. The hydroxide spheres might then be dried and fired to form useful products. For example, if the sol or solution contained salts of uranium, thorium, or plutonium, the product might be a useful reactor fuel. The main purpose of this work was not to produce microspheres having exceptional properties of high density, surface smoothness, or hardness. In fact, it is unlikely that any method of making microspheres can surpass the accomplishments of the sol-gel process[1] in respect

OAK RIDGE NATIONAL LABORATORY LIBRARIES

3 4456 0549182 0

to these qualities. However, in the new method investigated in this work some reduction in cost might be realized in the sol preparation step. An important goal of future work will be to determine if microspheres made by the new method are satisfactory for use as reactor fuels.

Only preliminary studies of a scouting nature are described in this report. Several variations in the new method for forming microspheres were tried. These involved the use of sols containing uranium, thorium, or zirconium prepared by adding ammonium molybdate solution to aqueous solutions, by raising the pH of aqueous solutions, or by adding organic thickeners to aqueous solutions, as well as the use of the aqueous solutions themselves. The only methods of characterization applied as yet to the product microspheres involved examination under the microscope and density measurements. The major effort was applied to areas of investigation not presently included in the sol-gel process, such as the formation of zirconia microspheres.

The results of these studies are sufficiently promising to indicate that further work is worthwhile. A careful measurement of interfacial tensions in the systems investigated would probably lead to improvements in this new method for forming microspheres. A theoretical model which should prove useful in future studies is presented.

Much research and development work has been done and much is still in process, in the United States and in Europe, on the preparation of microspheres for use as reactor fuels.[1-6]

2. PREPARATION OF OXIDE MICROSPHERES

Microspheres were formed by directing a stream of sol or solution containing thorium, zirconium, or uranium chloride or nitrate salts from a syringe onto a layer of organic liquid floating above 15 M NH_4OH. The sol or aqueous solution droplets fell through the organic layer into ammonium hydroxide, where the salts hydrolyzed to form hydroxide microspheres. These microspheres were then washed, dried, and fired. It is possible to make droplets having radii as small as a few microns

or as large as 1 mm by this method. The variables determining the size of the droplets are discussed in Sec 3. The droplets must be of a size which readily crosses the organic-aqueous interface.

Problems were encountered in transporting solution droplets across the organic-aqueous interface without deforming the droplets, and in drying the microspheres. Dilute solutions had to be used to avoid deformation thought to be caused by the heat of hydrolysis. These problems were less serious when using sols instead of solutions. However, additional problems were encountered when using sols. All of these problems and the solutions attempted are described below.

2.1 Preparation of Oxide Microspheres from Sols Containing Molybdenum

It was discovered that solutions of chloride or nitrate salts of thorium, zirconium, or uranium form sols when mixed with ammonium molybdate solutions. Nearly saturated solutions approximately 1 M in molybdenum were prepared by stirring a slurry of Baker and Adamson reagent grade 85% molybdic acid (chemical composition approximated that of ammonium molybdate) overnight and filtering. This molybdenum solution was then mixed with aqueous solution of the volume and concentration of thorium, uranium, or zirconium solution needed to produce a sol of the desired consistency. It is not known why these sols form. Ammonium molybdate is a highly satisfactory reagent for this use. Sols with reproducible viscosities can be prepared by simply mixing solutions. The ammonia and molybdenum volatilize during firing. Molybdic oxide volatilizes rapidly at about 1200°C. The product spheres are of low density, probably because the volatilization of molybdic acid during firing leaves the product porous.

Thorium-uranium sols were prepared by mixing either chloride or nitrate solutions of uranium and thorium with enough ammonium molybdate solution to form a sol 0.9 to 1 M in thorium with atomic ratios of molybdenum to thorium of 0.4 to 0.6. The U/Th atomic ratio was 0.02. The sol was then sprayed from a syringe equipped with a No. 25 needle (0.020 inch ID) onto a 3-inch layer of 2-ethylhexanol floating above 15 M NH_4OH. The spheres were left standing in the 15 M NH_4OH overnight to ensure

complete hydrolysis, filtered, washed in water, dried in air under a heat lamp, and fired in argon 1/2 hr at 1200°C. It appears, from the three measurements that were made, that the highest density was achieved when the Mo/Th atomic ratio was 0.45, where the density of the product was 8.75, or about 87% of theoretical (Fig. 1). Nitrate solutions were used in all experiments connected with Fig. 1. Examination of the product spheres under a microscope also showed a Mo/Th atomic ratio of 0.45 to be the best of the ratios investigated. The spheres were well formed with smooth surfaces. At lower Mo/Th atomic ratios, the sol was too soft to prevent deformation of the spheres as they crossed the aqueous-organic interface, and the product particles, while they had smooth surfaces, were elliptical in shape. At Mo/Th atomic ratios of 0.58 and higher the sol was too thick and surface irregularities did not smooth out during passage through the organic layer. The latter product particles were also hollow.

Since salts of the amphoteric element, molybdenum, are soluble in alkaline solution, studies were made to determine the rate at which the molybdenum would leach out of the spheres during the period they were in contact with ammonium hydroxide. Two extreme cases were investigated. In the first case, large spheres nearly one mm in diameter were treated with dilute (5 M) ammonium hydroxide. These spheres were formed from a thick sol, that is, a sol having a high Mo/Th atomic ratio (0.67). Very little leaching of molybdenum occurred (Fig. 2). After 3 hr, the Mo/Th atomic ratio in the spheres had decreased to 0.59 and further contact produced little additional leaching. In the second case, when small spheres, approximately 200 u in cross section, 15 M NH_4OH, and a lower

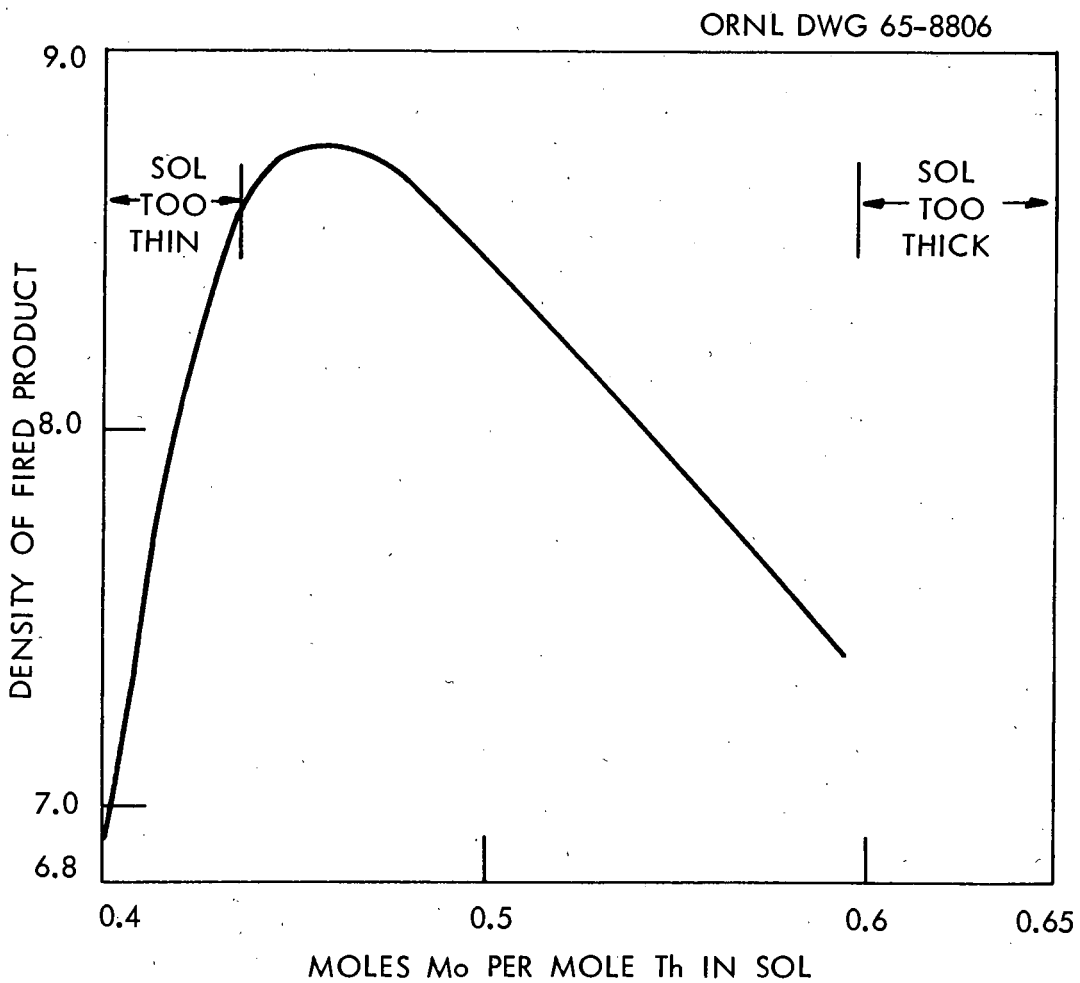


Fig. 1. The Densest Microspheres were Prepared from Sols Having 0.45 moles of Mo per mole of Th. Sols containing less molybdenum were too thin to yield a good product; those containing more than 0.6 moles of Mo per mole of Th were too thick.

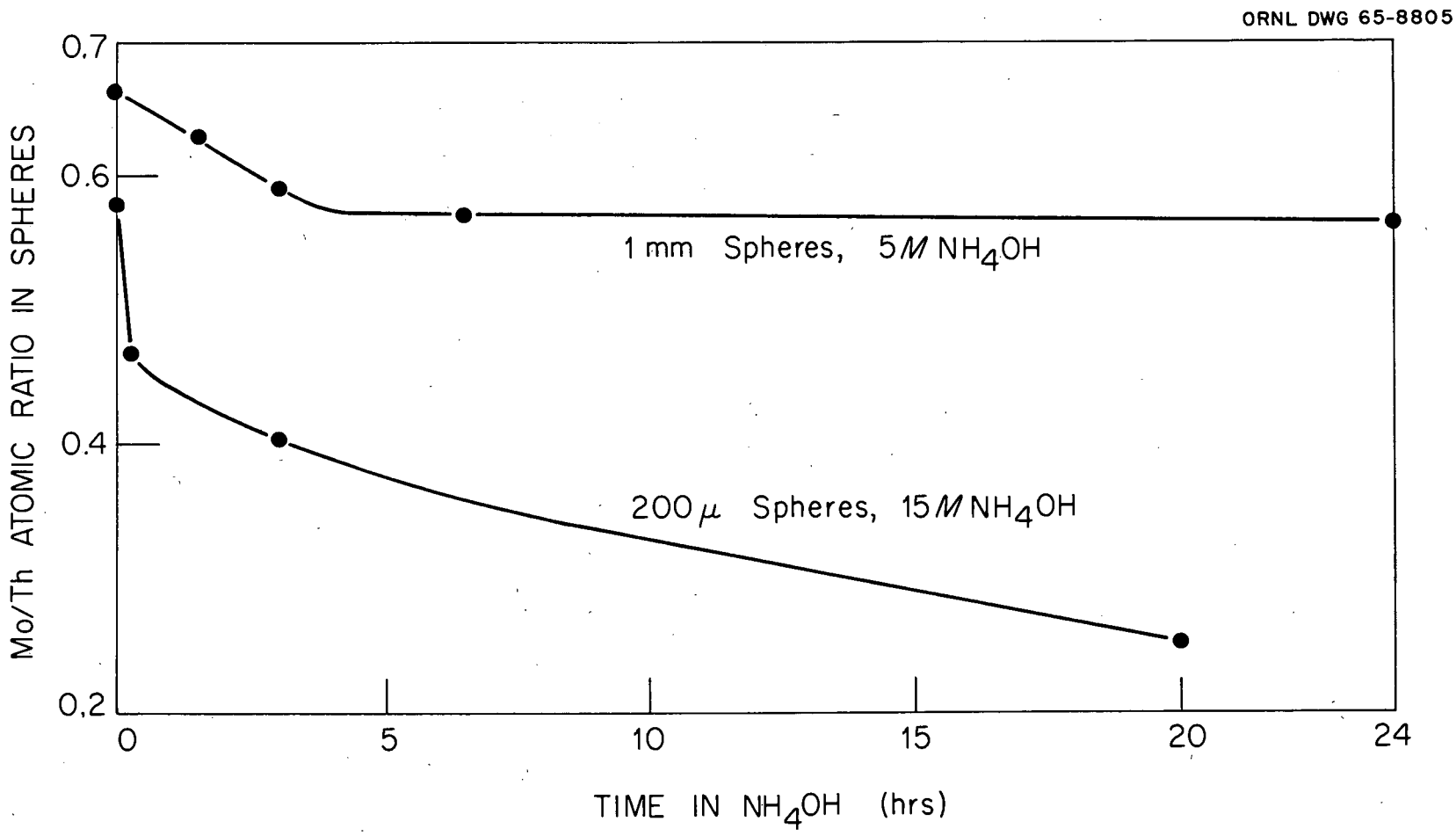


Fig. 2. Molybdenum was Leached Out of Th-Mo Hydroxide Spheres More Rapidly by 15 M NH_4OH than by 5 M NH_4OH. Even under the most favorable leaching conditions, a large fraction of the molybdenum remained in the spheres.

Mo/Th atomic ratio of 0.58 were used, the molybdenum leached out more rapidly. However, in this case, the Mo/Th atomic ratio decreased only to 0.4 and 0.3 after 3 and 14 hr, respectively.

No chloride was found by analysis of microspheres prepared by the same method as described above, except that the sols were prepared from a solution 1 M in Th and 7 M in Cl instead of from $Th(NO_3)_4$ solution. The absence of chloride in the product spheres was not surprising, since any chloride present would be expected to form chlorides of molybdenum, uranium, or thorium which would volatilize rapidly during firing at about 400, 600, and 800°C, respectively. However, it was necessary to determine if any chloride was left in the spheres after the treatment with ammonium hydroxide, because any chloride present during firing on a larger scale might cause excessive corrosion in metallic parts of the equipment. After contacting 15 M NH_4OH for only 0.5 hr, no chloride was found in spheres about 200 u in diameter, prepared from a sol having a Mo/Th atomic ratio of 0.5 (Fig. 3, curve B). The method of analysis used could have detected chloride if present at a Cl/Th atomic ratio of 0.01 or greater. In order to obtain hydrolysis rates slow enough to measure, it was necessary to prepare large spheres nearly 1 mm in diameter from a thick sol (Mo/Th atomic ratio of 0.66) and use dilute ammonium hydroxide (5 M NH_4OH). Under these conditions, the Cl/Th atomic ratio decreased to 0.4 in about 3 hr and was affected very little by further contact with the 5 M NH_4OH (curve A, Fig. 3). In practice the spheres would be prepared as were

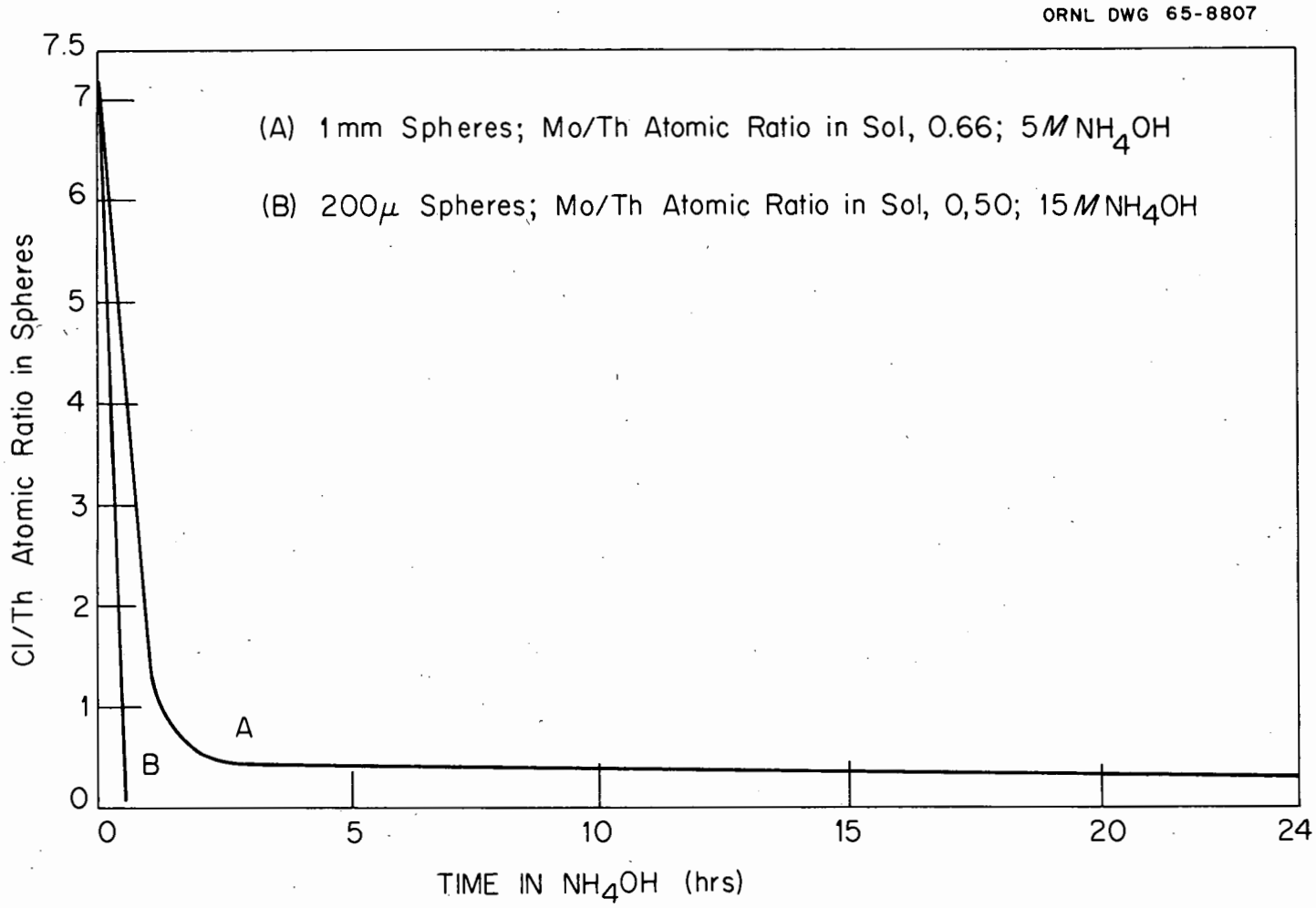


Fig. 3. Chloride was Almost Completely Removed from 200 u Microspheres Within 0.5 hr by 15 M NH_4OH. The use of less concentrated ammonium hydroxide, larger spheres, or thicker sols caused less rapid removal of chloride.

those for curve B, and the use of 15 M NH_4OH would ensure that little chloride remained in the spheres at the beginning of the firing step. The rates of hydrolysis of nitrate salts was not investigated because small amounts of nitrate should not cause serious corrosion problems during firing. The thoria microspheres can be prepared equally well by the method described here using as starting material either chloride or nitrate solutions of thorium.

2.2 Preparation of Oxide Microspheres from Sols Formed by Raising the pH

Sols prepared by methods other than by using molybdenum solution, as described in previous section, should have properties of viscosity and surface tension which would cause them to behave similarly to the molybdenum-containing sols if subjected to the same sphere-forming procedure. Another method of making sols involves raising the pH of a solution containing soluble salts of metals such as uranium, thorium, or zirconium, until formation of the insoluble hydroxide begins. Such sols can be prepared in several ways: by slow addition, with rapid stirring, of dilute alkaline solution, by hydrolysis of urea, by mixing precipitated hydroxide with acidic solution in the proper ratio, or by introducing ammonia gas. These methods usually require careful control of such variables as pH and temperature to prevent precipitation while yielding desirable micelle diameters and sol viscosity.[2,4]

A thin sol was prepared by very slowly adding ammonium hydroxide to 2.81 M $ZrO(NO_3)_2$ with rapid stirring. Microspheres were formed from this sol by the method described in Sec 2.1, except that benzene was used in place of 2-ethylhexanol. The spheres would not cross the aqueous-organic interface when 2-ethylhexanol was used. After firing for one-half hr at 1200°C in Argon, the surfaces of the spheres appeared rough under the microscope. Despite this surface roughness, the density of the spheres was greater than 99% of theoretical, measured in either toluene or water. The theoretical density of ZrO_2 was assumed to be 5.68 g per cc, the literature value for the monoclinic form.[8]

Microspheres of thoria were prepared in a similar manner using a 2.68 M Th solution (3.5 moles of NO_3^- per mole of Th) and 2-ethylhexanol as the organic liquid. The product was spherical, translucent, and glass-like in appearance. Most of the spheres cracked upon firing at 1200°C in Argon.

2.2.1 Use of Sols Formed by Liquifying Gels

A simpler method of forming sols which requires less careful control of such parameters as pH, temperature, and rate of micelle formation, was investigated. Ammonia, diluted with air or Argon was bubbled at room temperature into nitrate or chloride solutions approximately one molar in zirconium or uranium until the solutions solidified into gels. The gels were melted in a water bath at about 60°C and filtered to remove small particles of insoluble hydroxide. The viscosity of the resultant sol was adjusted by varying the sol temperature until the point was reached where droplets formed easily when the sol was injected into the organic liquid.

Uranium (IV) oxide microspheres were made from a 1.3 M uranium (IV) chloride solution. This solution was made by dissolving UCl_3 in water. Sols prepared from $U(NO_3)_4$ were not stable. The uranium (IV) chloride sol was injected at 25°C into 2 ethylhexanol floating above 15 M NH_4OH. The microspheres were removed from the 15 M NH_4OH after 5 hr, dried 1 hr in a stream of Argon at 100°C and fired 1/2 hr in 5% H_2-Ar. Air was carefully excluded during firing to prevent oxidation of U(IV) to U(VI). Spheres fired at 800°C were 95% of theoretical density; those fired at 1250°C had densities as high as 99% of theoretical. The product microspheres were well shaped and had smooth surfaces (Fig. 4).

The size distribution obtained among the product spheres can be observed in Fig. 4. The largest spheres are about 500 μ in diameter; the smallest, 60 microns. The sizes can be controlled within this range to produce a narrower distribution of sizes by carefully controlling the velocity with which the sol is injected into 2 ethylhexanol (see Sec 3). The spheres were dark colored, with smooth, glossy surfaces. The surface of each sphere contains a lighter colored section.

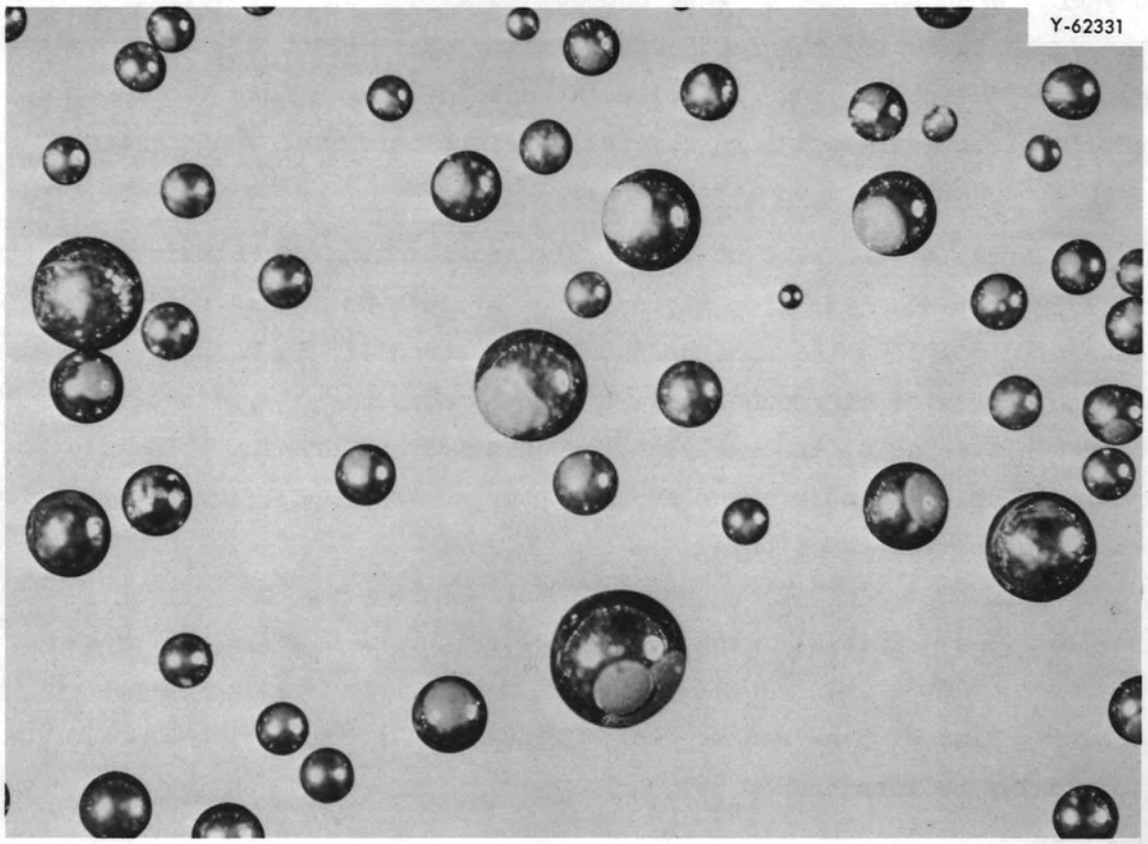


Fig. 4. Microspheres Formed from 1.3 M U(IV) Chloride Sol. Density is 96% of theoretical.

It was necessary to allow some oxidation of the tetravalent uranium oxide to occur in these microspheres before firing to obtain a product such as shown in Fig. 4. When air was carefully excluded from all steps in the process, the product spheres, after firing 1/2 hr at 1250° in 5% H_2-Ar, had chipped surfaces and large grains were visible within the spheres. Such spheres were only about 93% of theoretical density. The spheres shown in Fig. 4 were dried at 100°C in Argon containing 10 ppm oxygen. When the spheres were exposed to higher concentrations of oxygen, many cracked during the 100°C drying step. The effect of oxygen and methods for introducing controlled amounts of oxygen into the spheres should be investigated more carefully before this method of making UO_2 microspheres is used on larger scale.

A study of the rate of hydrolysis and leaching of chloride from the freshly prepared hydroxide microspheres by 15 M NH_4OH was needed to determine how long the spheres should be "cured" in 15 M NH_4OH. Samples of the hydroxide microspheres were removed periodically, dissolved in dilute nitric acid, and analysed for chloride and uranium. The atomic ratio of chloride to uranium in the spheres was found (Fig. 5) to decrease according to the equation

$$\log\left(\frac{Cl}{U}\right) = \text{initial } \left[\log\left(\frac{Cl}{U}\right)\right] - 0.76 \text{ (curing time in hours)} .$$

A curing time of 5 hr was needed to reduce the atomic ratio of chloride to uranium to less than 0.001.

Zirconia microspheres were formed from 1 M zirconyl nitrate solutions by a process very similar to that described above for urania microspheres. Argon rather than mixed Ar-H_2 was used during firing for 1/2 hr at 1250°C. The microsphere product was only 95% of theoretical density. By heating the sol to 80°C and using heptane instead of 2 ethyhexanol, a product was obtained which measured 99% of theoretical density in water and 100% of theoretical density in toluene. Unfortunately, the microspheres were not perfectly round but had small tails which formed when the droplets crossed the organic-aqueous interface.

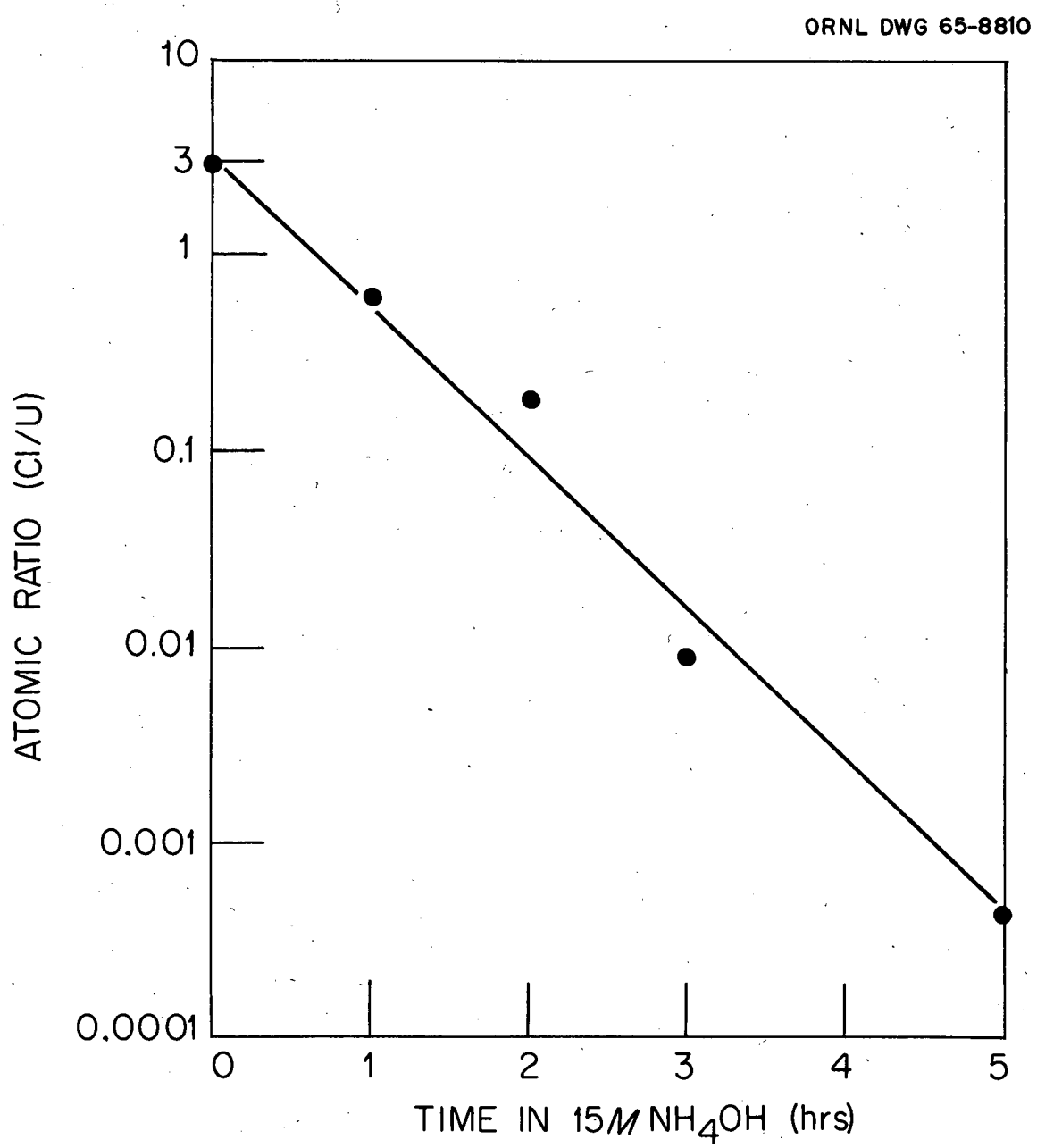


Fig. 5. Microspheres Formed from 1.3 M U(IV) Chloride Sol Must be Cured in 15 M NH_4OH for 5 hr to Reduce the Atomic Ratio of Cl/U to Less Than 0.001.

2.3 Preparation of Oxide Microspheres Directly from Aqueous Solutions

Attempts to prepare microspheres by the new method from sols are described above. Aqueous solutions can be dispersed in the organic layer to form droplets at least as easily as can sols. The droplets hydrolyze rapidly upon falling into the alkaline solution to form hydroxide microspheres similar to those formed from sols. Therefore, efforts were directed toward finding systems in which aqueous solutions could be sprayed onto an organic layer to form droplets which would fall freely through the organic-aqueous interface.

The transport of the droplets across the interface is a major problem in this approach. The droplets must cross the interface rapidly; otherwise they will collect and coalesce into larger droplets before falling through the interface. The physical chemistry of the organic-aqueous systems strongly favors such coalescence (see Sec 3). Because the solution droplets are very fluid, the forces acting upon the droplets at the interface tend to deform them, resulting in a product of non-spherical shape. These two problems are probably different manifestations of a single problem, the drastic change in surface tensions occurring at the phase boundaries during passage through the interface. Thus, both problems are greatly alleviated by use of surfactants which causes the surface tension changes to be less drastic. In addition, the surfactant probably serves to "insulate" the solution droplets against the alkaline solution, thereby slowing the hydrolysis reaction and permitting the heat of hydrolysis to dissipate more slowly. It was necessary to use solutions of not more than 1 M in thorium or zirconium in order to obtain a spherical product, presumably because at higher concentrations the heat of hydrolysis caused expansion and deformation as the droplets were converted to hydroxide in 15 M NH_4OH.

Thoria microspheres were prepared by the method described in Sec 2.1, using 0.6 M $Th(NO_3)_4$ solution. One vol % Triton 100 (a water-soluble surfactant, an alkyl phenoxy polyethoxy ethanol made by Rohm and Haas Co.) added to the 15 M NH_4OH surfactant made it possible to form well shaped spheres less than about 200 μ in diameter. Droplets larger than 200 μ developed tails upon passage through the aqueous-organic interface.

The spheres were dried by two methods, by freezing at dry ice temperature and evacuating with a mechanical vacuum pump, and by extracting water with dry 2-ethylhexanol. These partially dried products were then dried in air at 50 to 100°C and fired in air for 1/2 hr at 1200°C. Product spheres up to 250 u diameter which had been subjected to freeze-drying were only 84% of theoretical density; those with diameters less than 100 μ were 94% of theoretical density. Product spheres, 100 to 200 μ in diameter, dried by contacting with 2-ethylhexanol, were 96% of theoretical density.

Zirconia spheres were prepared by a similar procedure from 1 M $ZrO(NO_3)_2$ solutions. Heptane or hexane was used instead of the 2-ethylhexanol used in making thoria spheres. The droplets would not cross the organic-aqueous interface when 2 ethylhexanol was used. This procedure yielded well-shaped spheres up to 600 μ in diameter.

The major problem encountered with the zirconia spheres was that they tended to crack during the early stages of drying. It was necessary to wash the spheres, before air drying, with a water or ammonia solution containing Triton-100 surfactant. The spheres apparently sorb heptane during formation and the heptane causes cracking during drying. In one case the spheres exploded during firing in air, due to the ignition of the sorbed heptane. Washing with surfactant solution removes part of the sorbed heptane. In some cases, good yields of uncracked spheres were obtained, but these yields were not reproducible every time. The spheres were also dried by contacting with dry 2 ethylhexanol, but up to 50% of the spheres cracked. All of the spheres cracked when removed from the 2-ethylhexanol and spread out in air at room temperature unless the sorbed 2-ethylhexanol was first extracted by washing with hexane or heptane. Then no further breakage occurred at room temperature. Cracking also occurred during firing in air. This cracking also appeared to be caused by a small amount of sorbed organic material which caused the spheres to change from colorless to tan at about 350°C. The color disappeared upon heating to 400-600°C and many spheres cracked.

Spheres dried in 2-ethylhexanol, washed with heptane, and fired one-half hour at 600°C measured 93% of theoretical density, despite the presence of many cracked spheres. These spheres were 100 to 300 μ in diameter.

The problem of cracking during drying and firing appears to be connected with sorbed organic liquid. This problem does not appear to be caused by residual nitrate because nearly all nitrate is removed by hydrolysis in the 15 M NH_4OH. In samples removed after one hr at 15 M NH_4OH, dissolved in cool hydrochloric acid, and analysed, there were only 0.004 moles of nitrate per mole of zirconium.

2.3.1 Use of Organic Thickeners

To overcome the difficulties caused by cracking of zirconia spheres during drying, a small amount of organic thickener was blended into zirconyl nitrate solutions before the solution was sprayed onto the layer of heptane. The carbon from the thickener was removed by firing in air. It was found that firing in air to burn out the thickener caused the spheres to crack. The other steps in the process worked very well.

The organic thickeners used were cellulose derivatives. In the work described below, Burtonite V37E, a natural product, was used. Some work was also done using synthetic Dow Methocel thickeners. The latter thickeners offer the advantage of a wide range of viscosities; therefore, the desired viscosity can be achieved over a wide range of thickener concentration.

The problem of cracking observed above (Sec 2.3) was completely overcome by using 0.9 M $ZrO(NO_3)_2$ solution containing 2 wt % Burtonite thickener. The procedure was the same as that of Sec 2.3. The addition of 1 vol % Triton 100 surfactant to the 15 M NH_4OH was necessary to permit the droplets to cross the aqueous-organic interface, just as it was when no organic thickener was used. Thus, the thickened solutions closely resembled the unthickened solutions, rather than sols (Secs. 2.1 and 2.2), with which no surfactant was needed. The spheres could be

dried at 100°C immediately after removal from the 15 M NH_4OH, without any breakage. Upon firing in air, the spheres became brown at 350 to 400°C due to pyrolysis of the thickener. At about 400°C, cracks developed as the thickener began to burn out. Long treatment at 400°C or 1 hr at 500°C caused the spheres to become colorless, showing that the thickener was all burned out, and also produced small surface cracks on the spheres. Despite the surface cracks the density of these spheres was measured as 91% and 95% of theoretical, respectively.

3. DISCUSSION OF THE VARIABLES AFFECTING DROPLET SIZE AND INTERFACIAL PROBLEMS

It was apparent from the experimental work that droplets of aqueous solution, or thin sol, of very small diameter could be formed in an organic liquid if the solution or sol was sprayed rapidly from the syringe into the organic liquid. The greater the force applied to the syringe, the smaller were the dispersed droplets.

A simple model, based on conservation of energy, can be derived to explain this observation. This model also explains, at least in part, the difficulties experienced in achieving the transfer of solution droplets across the organic-aqueous interface.

The kinetic energy of a volume (CC) of solution leaving the syringe is:

$$\frac{KE}{CC} = \frac{MV^2}{2(CC)} = \frac{V^2D}{2} \qquad (1)$$

where M/(CC) is the density, D, of the solution, and V is the velocity. In this discussion, the velocity upon leaving the syringe is assumed to be the velocity with which the solution enters the organic liquid. The excess pressure, P_E, required to prevent the collapse of a droplet is:[9]

$$P_E = \frac{2\gamma}{r}, \qquad (2)$$

where γ is the interfacial tension between the droplet and the organic liquid. Since energy can have the dimensions pressure times volume,

Eq. 1 is dimensionally the same as Eq. 2. By making the simplifying assumption that all the kinetic energy is used in forming droplets, the two equations can be set equal,

$$\frac{2\gamma}{r} = \frac{V^2 D}{2} . \tag{3}$$

Rearranging yields the interesting result that the radius of a droplet is proportional to the interfacial tension and inversely proportional to the square of the velocity with which the solution or sol enters the organic liquid,

$$r = \frac{4\gamma}{V^2 D} . \tag{4}$$

By assuming likely values for V, γ, and D, some useful conclusions can be drawn using this model. Consider the system in Table 1,

Table 1.

Property	Liquids		
	1 M $ZrO(NO_3)_2$	Heptane	15 M NH_4OH
D, g/cc	1.1	0.7	0.9
γ (sphere or droplet vs liquid), dynes/cm	---	50	>100

where values of D and estimations of γ are listed. Although these values for γ are estimations, they serve very well for illustrating the relation between velocity and droplet size, as well as the problems involved in transporting droplets across the aqueous-organic interface (Fig. 6). The value of the interfacial tension between the hydroxide sphere and 15 M NH_4OH (>100 dynes/cm listed in Table 1, 100 dynes/cm used in calculating curve in Fig. 4) in particular, is not known, but is thought to be much larger than that between the aqueous droplets and heptane. Careful measurements of these interfacial tensions, as recommended in Sec 4, would lead to a better understanding of this sphere-forming process.

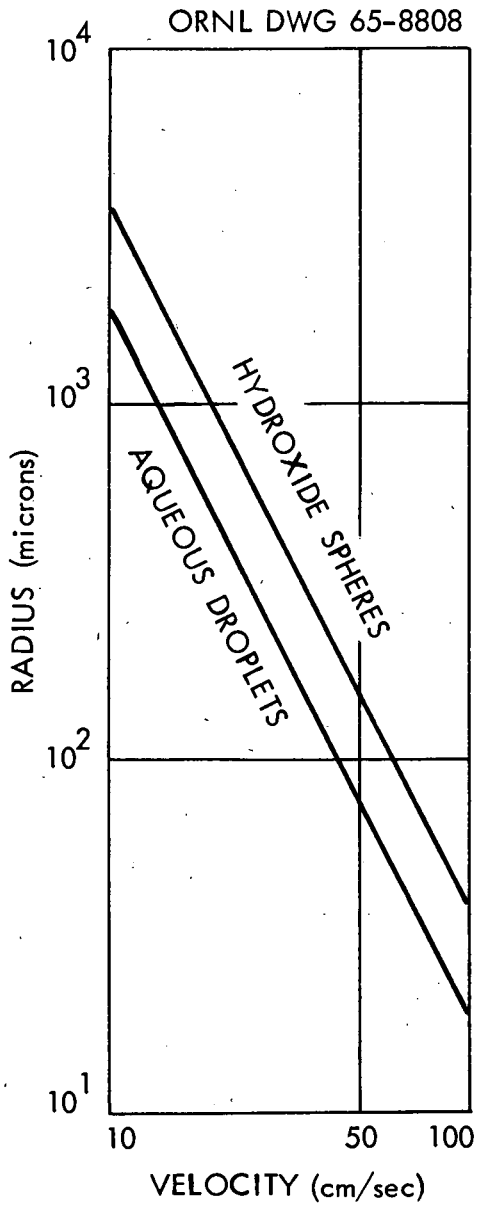


Fig. 6. The Radius of Stable Aqueous Droplets and Hydroxide Spheres Can Be Related, by Eq. (4), to the Velocity with Which the Solution or Droplets Enter the Organic or Aqueous Phases, Respectively.

The radius of the droplets of solution, calculated from Eq. 4, decreases from greater than 10^3 to about 20 microns as the velocity with which the solution is sprayed onto the heptane increases from 10 to 100 cm/sec (lower cruve, Fig. 4).

In contrast to the droplet-forming step, there is little that the experimenter can do to control the velocity of the droplets as they enter the 15 M NH_4OH layer. The droplets must be allowed to fall freely through the organic layer since application of any force (other than gravitational) to increase their velocity would produce turbulence. Turbulence at the interface deforms the droplets and causes an unsatisfactory product.

Figure 6 can be used to predict the velocity that the droplets should have to match the two systems, droplet-heptane, and $Zr(OH)_4$--15 M NH_4OH. For example, if the 1 M $ZrO(NO_3)_2$ solution is sprayed onto the heptane with a velocity of 50 cm/sec, the bottom curve in Fig. 4 indicates that the droplets dispersed in the heptane would have a radius of about 175 μ. The upper curve shows that, to obtain stable hydroxide spheres having a radius of 175 μ, the droplets should have a velocity of 60 cm/sec upon entering the 15 M NH_4OH. Experiments described below in Sec 3.1 indicate that the droplets have a velocity somewhat less than 50 cm/sec upon entering the 15 M NH_4OH. Thus, the droplets will tend to expand as they pass through the heptane--15 M NH_4OH interface and convert to hydroxide. This is exactly what is observed to occur using solutions and no surfactant in the 15 M NH_4OH. Large perfectly-formed spheres are obtained which, upon drying, prove to be hollow shells. The use of surfactant, which apparently decreases the difference in surface tensions between the systems droplet-hexane and $Zr(OH)_4$-NH_4OH (or perhaps only the rate of change from one system to the other), results in solid spheres.

This model explains why greater interface problems were encountered when solutions, rather than sols, were used. The interfacial tension at the sol-organic liquid interface is greater than at the solution droplet-organic liquid interface. Therefore, only a small change in

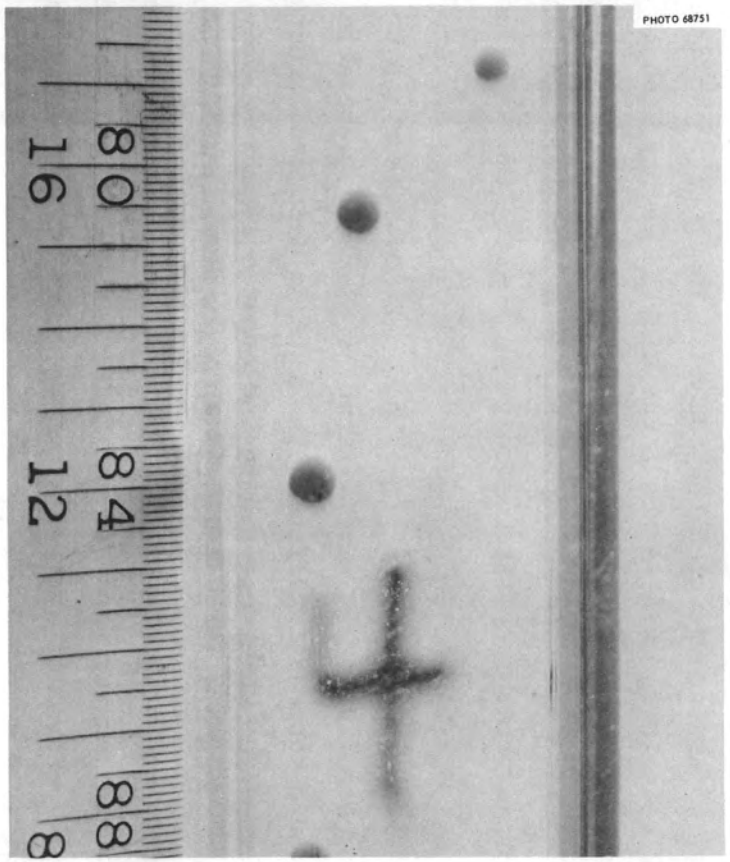
interfacial tension occurs as a sol droplet leaves the organic layer and forms an hydroxide sphere in the ammonium hydroxide layer. For this case, a set of two curves corresponding to those of Fig. 4 would be close together and the small change in radius necessary to form stable hydroxide spheres could be accomplished without seriously deforming the spheres.

The surface tension at the heptane-aqueous solution interface (about 50 dynes/cm) is about six times that at the 2-ethylhexanol-aqueous solution interface. Thus, the use of heptane with aqueous solutions should lead to a better product than does the use of 2-ethylhexanol. This was found experimentally to be true. Well-shaped ZrO_2 spheres up to 600 μ in diameter were prepared using heptane. Droplets of $Th(NO_3)_4$ would not cross the heptane-NH_4OH plus surfactant interface and it was necessary to use 2-ethylhexanol in place of the heptane. Thoria spheres over 200 u in diameter were poorly shaped. It is not known why the $Th(NO_3)_4$ droplets would not cross the interface when heptane was used.

3.1 Experimental Verification of Droplet Size Equation

An experimental check of Eq. (4) was desired to determine the range of velocities, if any, over which the equation is useful. No correction terms are included in Eq. 4 to account for kinetic energy used in processes other than droplet formation. Therefore, the equation should not predict droplet size accurately under conditions in which much kinetic energy is lost in other processes, such as in heating the solution.

It was not possible to check Eq. 4 over a wide range of velocities by measuring the size of spheres produced by methods described above, because only spheres having a narrow range of diameters were able to cross the organic-aqueous interface without being deformed. Therefore, aqueous droplet sizes were measured in the organic liquid (2-ethylhexanol) by photographing the droplets as they formed and enlarging the photographs so that accurate measurement was possible. Water colored with Sheaffers washable #44 blue ink was used for the aqueous phase (Fig. 7). Injection velocities were controlled by a constant-velocity syringe drive manufacturer by Harvard Co.



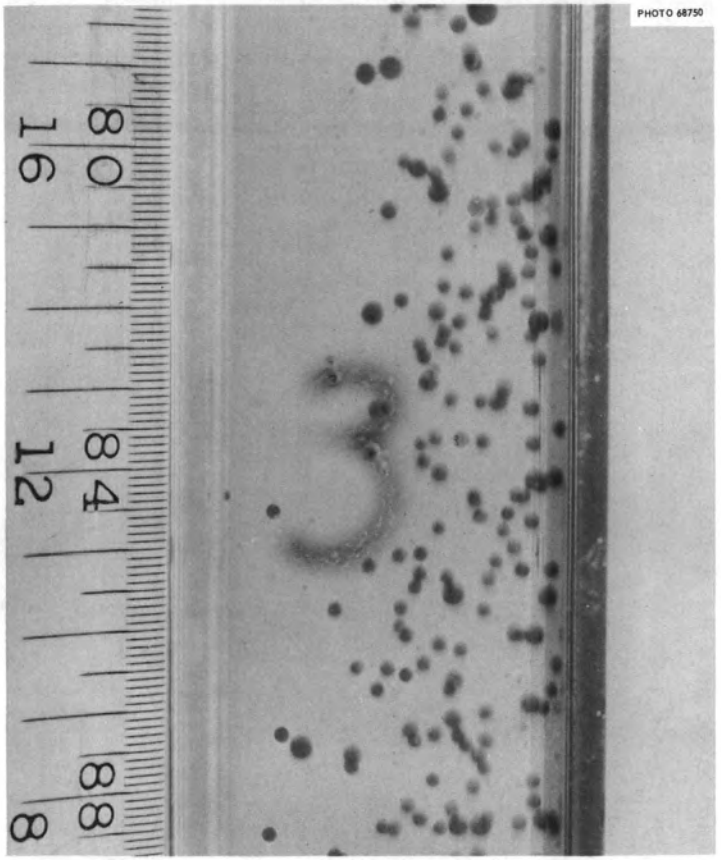


Fig. 7. As the Velocity with Which Colored Water was Injected into 2-Ethylhexanol Increased from 81 cm per sec (Left) to 162 cm per sec (Right), the Average Radius of the Water Droplets Decreased from 0.015 cm to 0.0073 cm. The smallest scale division is 0.04 in.

Equation 4 can be rearranged to:

$$\log r = \log \left(\frac{4\gamma}{D}\right) - 2 \log V \ . \qquad (5)$$

The slope of a plot of log r vs log V should be (-2) over the range in which Eq. 4 is useful.

The radii of droplets measured at controlled injection velocities from photos like those of Fig. 7, substituted in Eq. (5), resulted in a curve with a slope of -2 when the velocity was about 80 cm per sec (Fig. 8). At lower velocities, the radii approached a constant value of about 0.03 cm. This value apparently corresponds to the velocity produced by gravity. At velocities above 80 cm per sec, the deviation from a slope of -2 is thought to be due to the loss of kinetic energy to processes other than formation of droplets. At 800 cm per sec, great numbers of droplets formed and the individual droplets could not be seen clearly. Thus, the value shown in Fig. 8 at 800 cm per sec does not represent an accurate measurement.

Equation 4 can also be used to calculate interfacial surface tension by taking values of velocity and radius at a point where the slope of the log r vs log V curve is (-2). The calculation for the colored water droplets, using values of 0.015 and 81.3 cm per sec for r and V, respectively (taken from Fig. 8) yields a value of 25 dynes per cm for the interfacial surface tension. This value can be compared to the handbook value of 8.5 dynes per cm between n-octanol, which has the same number of carbon atoms per molecule as 2-ethylhexanol, and water. The suspended ink used to make the water droplets visible probably increased the interfacial surface tension above that of pure water in 2-ethylhexanol.

These droplet size measurements, in general, support Eq. 4, although they show that the equation is useful over only a limited range of velocities Unfortunately, a range of sizes was observed at 81 and 163 cm per sec (Fig. 8). The measurement of droplet sizes at other velocities in the vicinity of 80 cm per sec and statistical analysis of the distribution of radii observed would be necessary to accurately establish the point or section of the curve at which the slope is -2. The useful range of Eq. 4

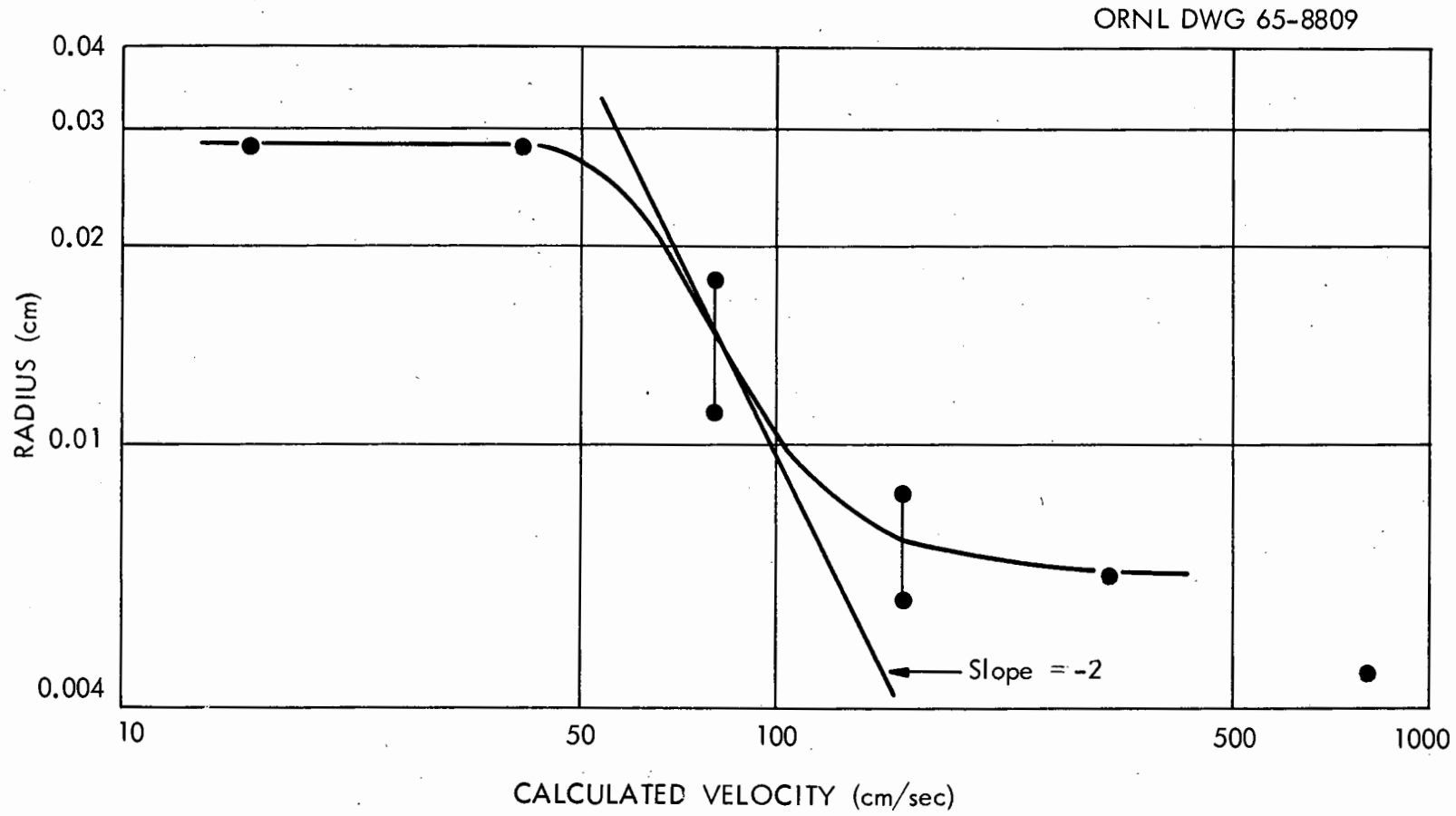


Fig. 8. The Slope of the Log-Log Plot of Radius vs Velocity Equals (-2) when the Velocity is About 80 cm per sec.

could be extended by adding a term to account for the kinetic energy lost to processes other than formation of droplets.

4. CONCLUSIONS

The most promising variation of the new method for preparing oxide microspheres described above involved the preparation of gels with ammonia and melting these gels to form sols which are sprayed into organic liquid floating above 15 M NH_4OH. This procedure yielded urania microspheres which appear to have excellent qualities of density, roundness, and surface smoothness. The same procedure also looks promising for making zirconia microspheres. Because of the simplicity of this method, further development might result in an economical process for making microspheres which are useful as reactor fuels.

Sols prepared from chloride salts behaved the same as those prepared from nitrate salts. However, sols prepared from $U(NO_3)_4$ were not stable and it was necessary to use uranium chloride salt to make urania microspheres.

The preparation of thoria microspheres from sols formed by adding ammonium molybdate solution to thorium nitrate or chloride solutions also worked well. However, this method yielded microspheres of less than 90% of theoretical density.

Attempts to form microspheres directly from solutions rather than from sols were not successful. This work, however, did indicate areas in which the physical chemistry of the systems involved should be investigated before useful processes could be developed. For example, measurements of the surface tensions between organic liquids and aqueous solutions and between hydroxide gels and ammonium hydroxide solution, both in the presence of, and in the absence of, surfactants, would supply information needed to make use of the droplet size equation derived in Sec 3. Such information would also be useful in further development of the methods involving sols rather than solutions.

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," 3rd U.N. Int'l. Conf. on the Peaceful Uses of Atomic Energy, May 1964, A/CONF. 28/P/237.

2. Preparation of Thoria Sols, final Houndry subcontract report, 58-OCR-15 (December 1958).

3. E. C. Martin, Encapsulation of Sols to Produce Rounded Particles, Final Southwest Research Institute Summary Report prepared for Oak Ridge National Laboratory records (October 1964).

4. C. Cogliati, et al., "The Preparation of Dense Particles of Thorium and Uranium Oxide," 3rd U.N. Int'l. Conf. on the Peaceful Uses of Atomic Energy, May 1964, A/CONF. 28/P/555.

5. M. E. A. Hermans, H. S. G. Slooten, and N. V. Kenra, "Preparation of UO_2 and ThO_2 Powders in the Subsieve Range," 3rd U.N. Int'l. Conf. on the Peaceful Uses of Atomic Energy, May 1964, A/CONF. 28/P/634.

6. D. M. Helton, A Survey of the Literature on Hydrated Actinide Oxide Sols and U(IV) and U(VI) Hydrolysis Reactions, ORNL-TM-1052 (February 1964).

7. R. G. Wymer and D. A. Douglas, Jr., Thorium Fuel Cycle Program and Related Studies Status Report of February 1965, ORNL-CF-64-6-12 (April 1964) p. 9.

8. W. B. Blumenthal, "The Chemical Behavior of Zirconium," D. Van Nostrand Co., Inc., New York, 1958; p. 159.

9. S. Glasstone, "Testbook of Physical Chemistry," D. Van Nostrand Co., New York, 1964, p. 486.

INTERNAL DISTRIBUTION

1. R. E. Blanco
2. W. D. Bond
3. R. E. Brooksbank
4. K. B. Brown
5. F. R. Bruce
6. J. M. Chandler
7. F. L. Culler, Jr.
8. D. E. Ferguson
9. L. M. Ferris
10. H. E. Goeller
11-12. T. A. Gens
13. A. T. Gresky
14. P. A. Haas
15. R. G. Haire
16. C. J. Hardy
17. C. C. Haws
18. F. E. Harrington
19. D. M. Helton
20. A. R. Irvine
21. R. E. Leuze
22. M. H. Lloyd
23. A. B. Meservey
24. L. E. Morse
25. K. J. Notz
26. J. R. Parrott
27. W. L. Pattison
28. J. J. Perona
29. J. W. Prados
30. J. T. Roberts
31. J. L. Scott
32. F. J. Smith
33. J. W. Snider
34. J. W. Ullmann
35. R. G. Wymer
36. ORNL Patent Office
37-38. Central Research Library
39. Document Reference Section
40-41. Laboratory Records
42. Laboratory Records (RC)
43. R&D Division, ORO

EXTERNAL DISTRIBUTION

44. W. H. McVey, Atomic Energy Commission, Washington
45. R. E. Pahler, Atomic Energy Commission, Washington
46. M. J. Whitman, Atomic Energy Commission, Washington
47. C. B. Deering, Atomic Energy Commission, Oak Ridge
48-63. DTIE