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PREPARATION OF URANIUM AND THORIUM OXIDE MICROSPHERES WITH CONTROLLED POROSITY BY A SOL-GEL PROCESS

T. A. Gens

ABSTRACT

The task of making porous nuclear fuel microspheres was undertaken in the laboratory. In certain applications, porosity should improve the performance of these fuels. Porosity was "built into" the microspheres by introducing, into the original sol, materials that volatilized during the firing. The sol was formed into gel microspheres, which were then dried and fired to produce degrees of porosity.

Urania microspheres with porosities between 1 and 44% were made by firing gel spheres containing chloride. The amount of chloride in the gel spheres, and thus the porosity of the products, was controlled by varying the volumes of ammonium hydroxide used as leachant. Urania microspheres with porosities between 19 and 34% were made by firing gel spheres containing MoO_3 (introduced as ammonium molybdate). The porosity of the product increased with increasing MoO_3 content in the gel spheres.

Also, thoria microspheres with porosities between 21 and 33% were made by firing gel spheres containing MoO_3. Mixed oxide (20% UO_2-80% ThO_2) microspheres with 43% porosity were made by the same method.

The results show that porous UO_2, ThO_2, and mixed ThO_2-UO_2 microspheres, which appear to be satisfactory for use as nuclear fuels, can be prepared by the sol-gel method. The laboratory procedures appear to be easily adaptable to larger-scale applications.

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1. INTRODUCTION

The objective of this work was to investigate, in the laboratory, methods by which porosity can be "built into" uranium and thorium oxide microspheres by introducing materials that volatilize during firing of gel microspheres. This report presents some promising methods for making gel spheres containing the volatile materials molybdenum oxide or chloride. Descriptions of the products obtained upon firing these gel microspheres are included.

Nuclear fuel microspheres having controlled porosity are desirable because the porosity may improve performance in the reactor. For example, if porous microspheres are coated with a gas-impervious material such as pyrolytic carbon, the pores can accommodate gaseous products of nuclear reactions, as well as the swelling of the fuel materials under irradiation, thereby decreasing the stress on the coat. If the pores open onto the surface of the microspheres, as do those in the products described in this report, the microspheres may be useful as emitting fuels, that is, fuels in which the volatile products of nuclear reactions are allowed to escape from the fuel, thereby preventing reactions of these products with neutrons.[1]

A recently developed method[2] for making microspheres was used in this work. Basically, four operations comprise the process: (1) sol preparation, (2) conversion of the sol into gel microspheres, (3) leaching of the gel microspheres in concentrated ammonium hydroxide to remove anions (nitrate or chloride), and (4) drying and firing. Each operation appears in the experiments described here.

The effects of incorporating two volatile materials into these gel microspheres was investigated: (1) molybdenum oxide [added as $(NH_4)_2MoO_4$], which volatilizes during the later, higher-temperature portion of the firing cycle; and (2) chloride (introduced as uranium chloride salt), most of which volatilizes during the earlier, lower temperature portion, presumably as hydrogen chloride. Both porous UO_2 and porous ThO_2 microspheres were prepared using MoO_3. Only porous UO_2 microspheres were made by volatilizing chloride during firing. Porous ThO_2 microspheres were not made by the procedure involving volatilization of

chloride because a satisfactory technique has not been developed as yet for forming them (not containing MoO_3) by the new methods used in this work. Because of the limited scope of the work described here, it was not possible to investigate the mechanism of pore formation by volatilizing molybdenum oxide or chloride.

Urania microspheres, in which the porosities amounted to as much as 44% of the microsphere volumes, were prepared by volatilizing chloride or MoO_3 during firing. The porosity was controlled by varying the amount of volatile material in the gel microspheres before firing.

Satisfactory porous ThO_2 microspheres, prepared by volatilizing MoO_3, were made with porosities only in the range of 21 to 33% of the total volume. However, a single run, made with UO_2-ThO_2 (20-80%) in which the porosity of the product was 43.4%, indicated that a greater range of porosity could be achieved with the mixed oxide spheres.

In all the porous microspheres prepared in this work, resistance to crushing decreased with increasing porosities above 5%.

2. EXPERIMENTAL

The procedures for making sols differed, depending on which volatile material, MoO_3 or chloride, was to be incorporated into the gel microspheres. The procedure for the remaining steps: conversion of the sol into gel microspheres, leaching of anions from the microspheres with ammonium hydroxide, and drying and firing, were almost the same when either volative material was incorporated into the gel microspheres. However, the volumes of ammonium hydroxide varied between runs, because the amount of chloride left in the gel microspheres was controlled by varying these volumes of leachant.

2.1 Preparation of Sols and Microspheres

2.1.1 Sol Preparation

Sols containing molybdenum were made simply by mixing solutions about 1 M in $(NH_4)_2MoO_4$ with solutions about 1 M in uranium or thorium. The resulting mixtures appeared to be sols, and, although their nature has not been investigated as yet, they will be referred to as sols in this work. Uranium sols containing between 0.1 and 0.8 atom of

of molybdenum per atom of uranium were prepared and converted into gel spheres. However, the Mo/Th atomic ratios that resulted in satisfactory sols were limited to the range of about 0.3 to 0.6. Lower ratios resulted in an elliptical, rather than spherical product, while higher ratios resulted in sols that could not be converted to gel spheres because the sols were too viscous.

Uranium (IV) chloride sols were made by bubbling NH_3-Ar into 1.0-1.7 M U^{4+} chloride solutions until the solutions gelled (pH between 3.0 and 3.3), then melting the gels at about 50°C. The solutions were prepared by dissolving UCl_3 in water. Although UCl_3 dissolves slowly at room temperature,[3] the heat of solution raises the temperature to the point that solution is complete in about 10 min. Trivalent uranium is oxidized to U^{4+} during dissolution. Presumably the dissolved compound is $U(OH)Cl_3$, which is more soluble than UCl_4. If oxygen is present, further oxidation occurs rapidly,[4] and therefore air must be kept away from the solutions and sols.

2.1.2 Formation of Microspheres

Microspheres were formed from these sols (prepared by either method) by injecting sol from a syringe onto a layer of 2-ethyl-1-hexanol floating on 15 M NH_4OH. The sol stream was dispersed in the alcohol, and the droplets that formed fell into the 15 M NH_4OH, where they were converted into gel microspheres. The variables controlling the size of the gel microspheres are discussed in ref. 2. The microspheres were then exposed further to ammonium hydroxide to complete the hydrolysis reaction and to leach entrapped or sorbed anions. The microspheres did not agglomerate or otherwise change shape during immersion in the ammonium hydroxide.

2.2 Porous Microspheres Made by Volatilizing Molybdic Oxide during Firing

2.2.1 Porous Microspheres of Uranium Dioxide

Three sols 1 M in uranium were prepared by mixing 1.6 M U^{4+} chloride solutions with ammonium molybdate solutions. The Mo/U atomic ratios were 0.11, 0.32, and 0.53. Microspheres were prepared as

described in Sect. 2.1.2 and left standing in the 15 M NH_4OH for 20 hr. Analysis showed that the respective Mo/U atomic ratios in the spheres had decreased to 0.07, 0.15, and 0.21. The respective Cl^-/U atomic ratios in the spheres had decreased to 0.02, 0.01, and 0.04, from the original ratio of 3 in the sols. The spheres were oven dried and fired in flowing argon for 1 hr at 1300°C. For comparison, spheres were prepared from sol containing no molybdenum. This sol was made by bubbling NH_3-Ar into U^{4+} chloride solution until gelation occurred, and melting the gel at 50°C.

The porosity of the products increased from 5% to 27% as the Mo/U atomic ratio in the sol increased from 0 to 0.53 (Fig. 1). Resistance to crushing for 330-μ spheres decreased from 1740 g to 100 g. The density of the UO_2 not penetrated by Hg at 8000 psi was very close to theoretical, showing that nearly all the pores had been penetrated, that is, that all pores were open to the surface.

Photomicrographs of sections of the spheres are presented in Figs. 2 and 3. The increasing porosity and pore size with Mo/U atomic ratios in the sols can be readily observed. Almost all the pore diameters fell in the range 1 to 10 μ, and most were about 1 μ in diameter. The N_2 surface areas were 0.101, 0.065, and 0.034 m^2/g for the spheres in Figs. 2B, 3A, and 3B, respectively.

Another set of experiments was performed in which the only change in procedure from that described above was that the sol was prepared in a slightly different way. A U^{4+} chloride sol was prepared by using NH_3-Ar as described above. Portions of this sol were mixed with ammonium molybdate solutions to form 1 M U sols that had Mo/U atomic ratios of 0.10, 0.29, and 0.77. This procedure differs from that described earlier in this section in that U^{4+} chloride sols, rather than solutions, were mixed with the ammonium molybdate solutions. This change in the method of sol preparation had little if any effect on the properties of the product (Fig. 4). The porosities of product from the two sols with the higher Mo/U atomic ratios are slightly higher than those obtained in the previous experiments (compare Fig. 4 with Fig. 1). For example, at the highest ratio of 0.77, the porosity

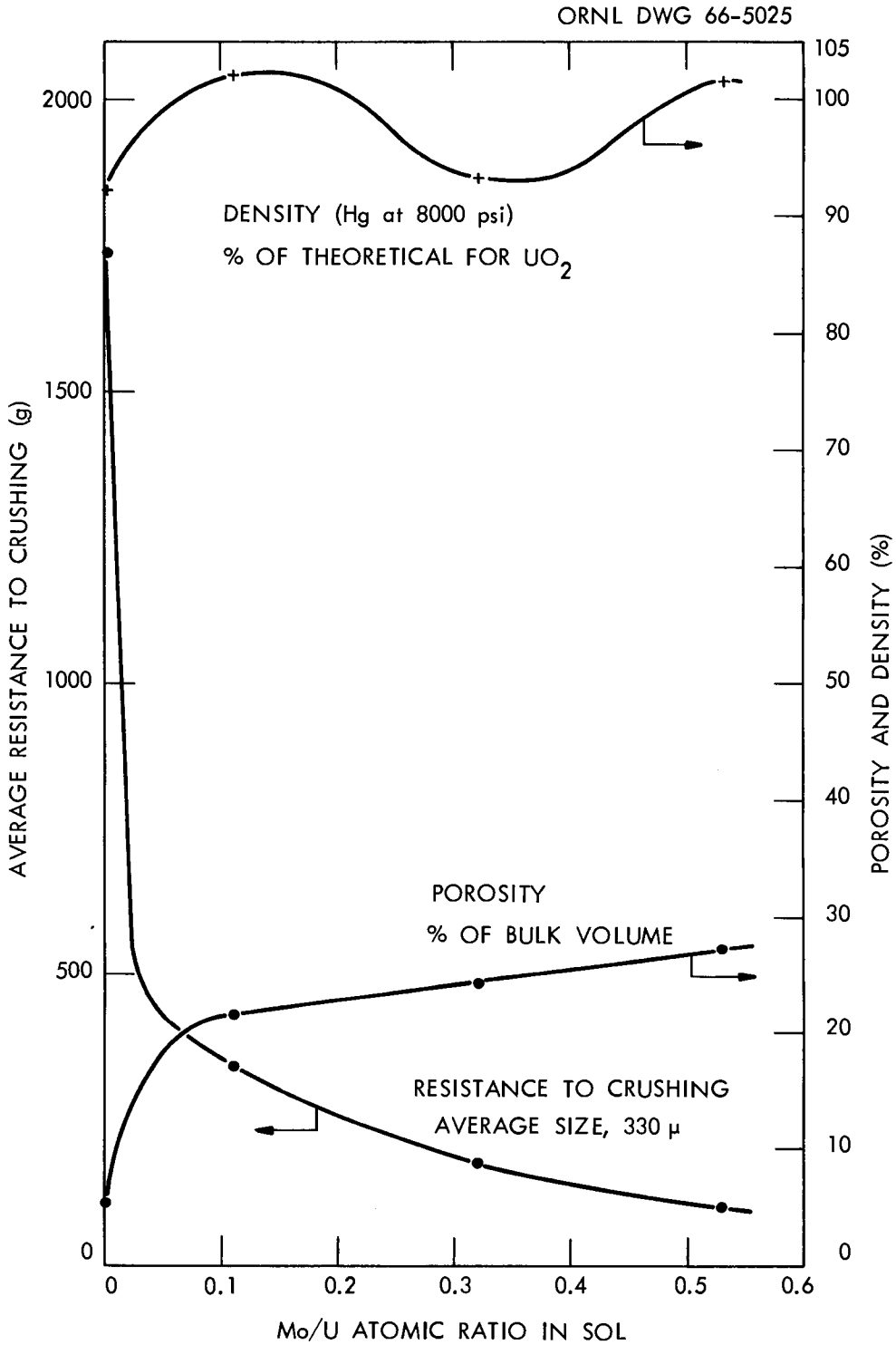

Fig. 1. Porosity of Fired UO_2 Microspheres Increases and Resistance to Crushing Decreases with Increasing Mo/U Atomic Ratio in the Sol.

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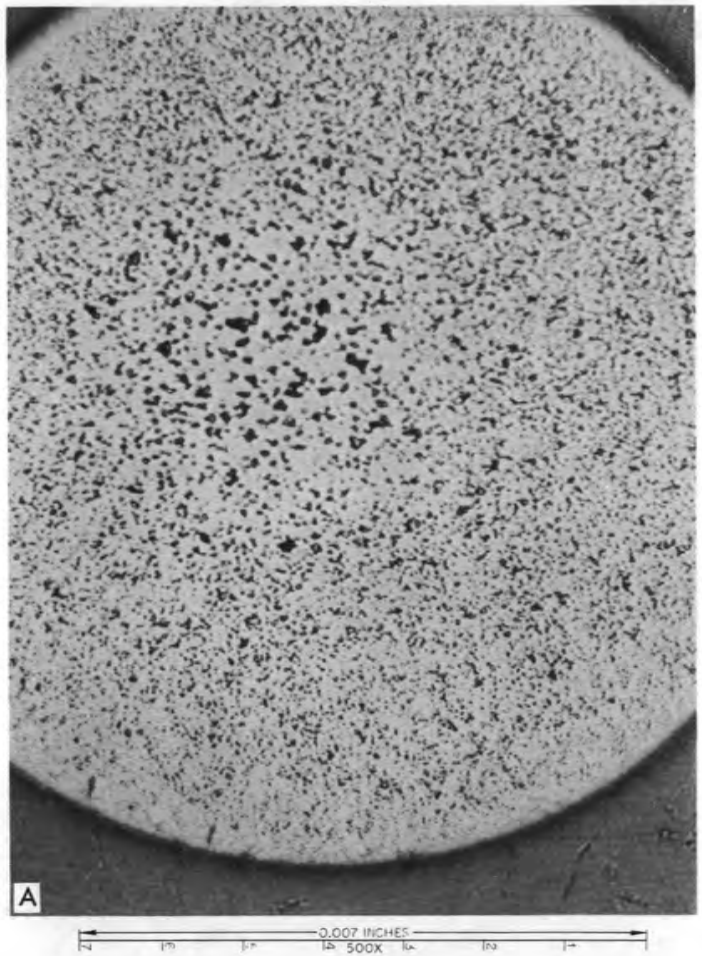

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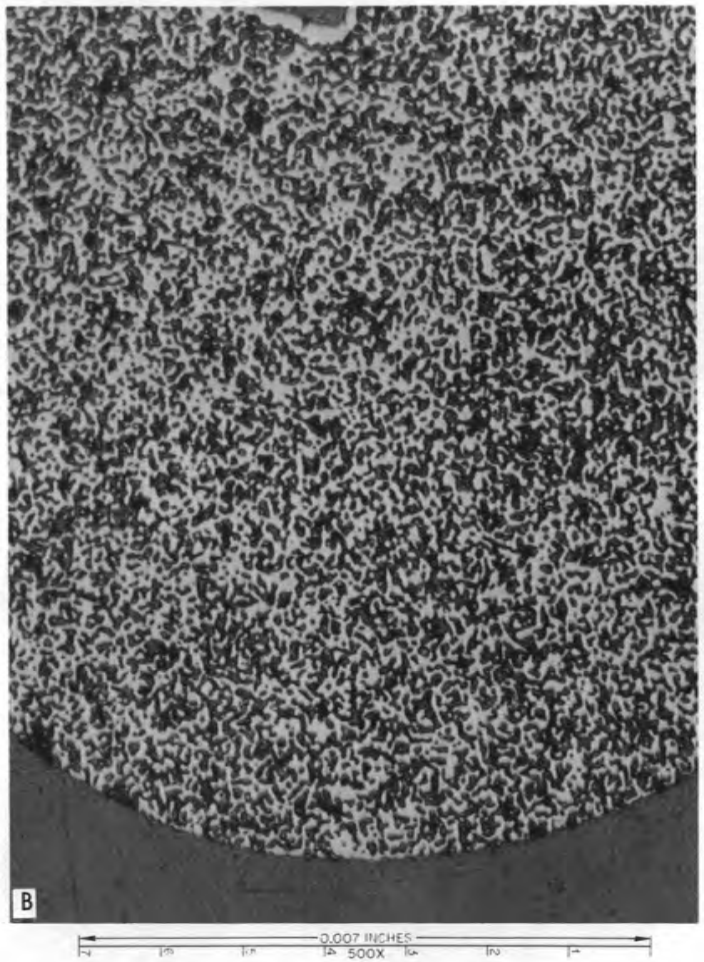

Fig. 2. Porous UO_2 Microspheres Made from U^{4+} Chloride Sols. Porosity is 5% in (a) and 21.6% in (b). The Mo/U atomic ratios in the respective sols were 0 and 0.11.

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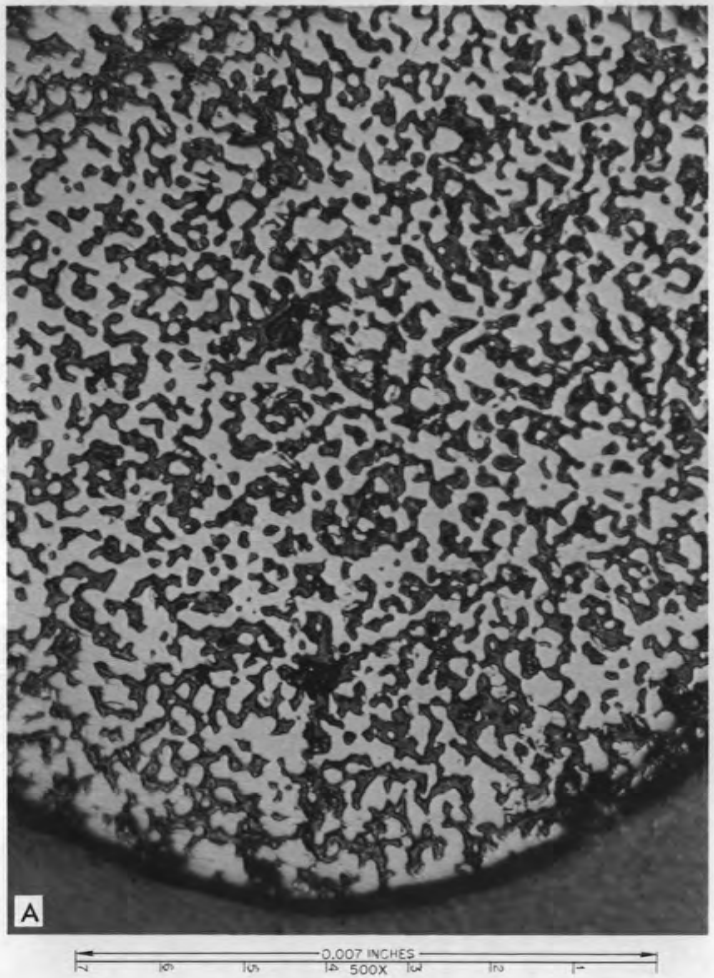

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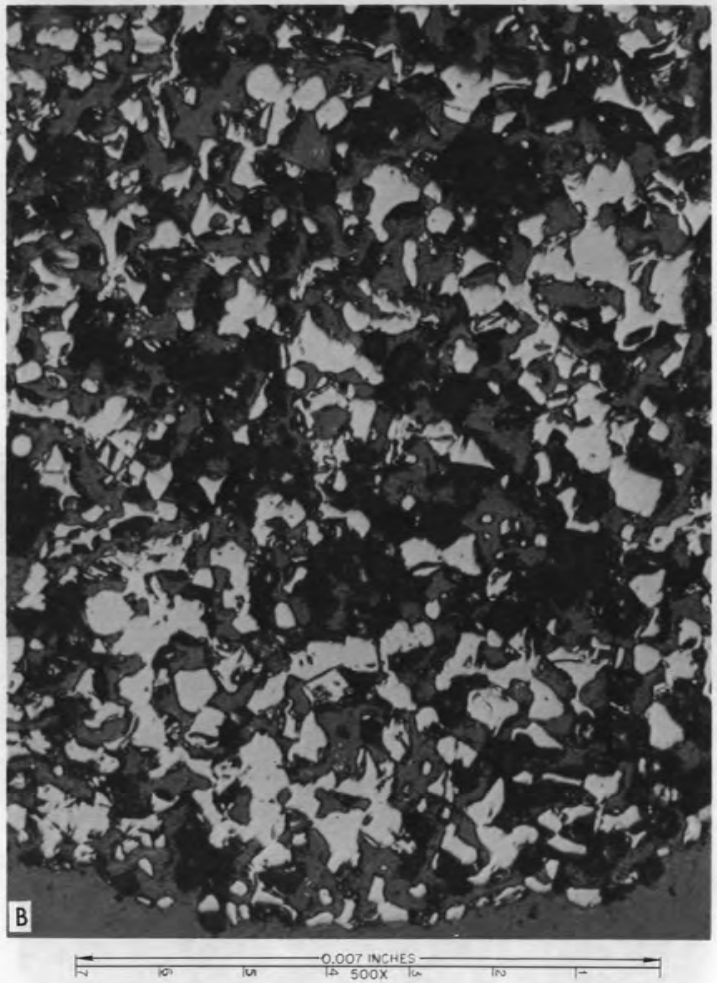

Fig. 3. Porous UO_2 Microspheres Made from U^{4+} Chloride Sols. Porosity is 23.9% in (a) and 27.2% in (b). The Mo/U atomic ratios in the respective sols were 0.32 and 0.53.

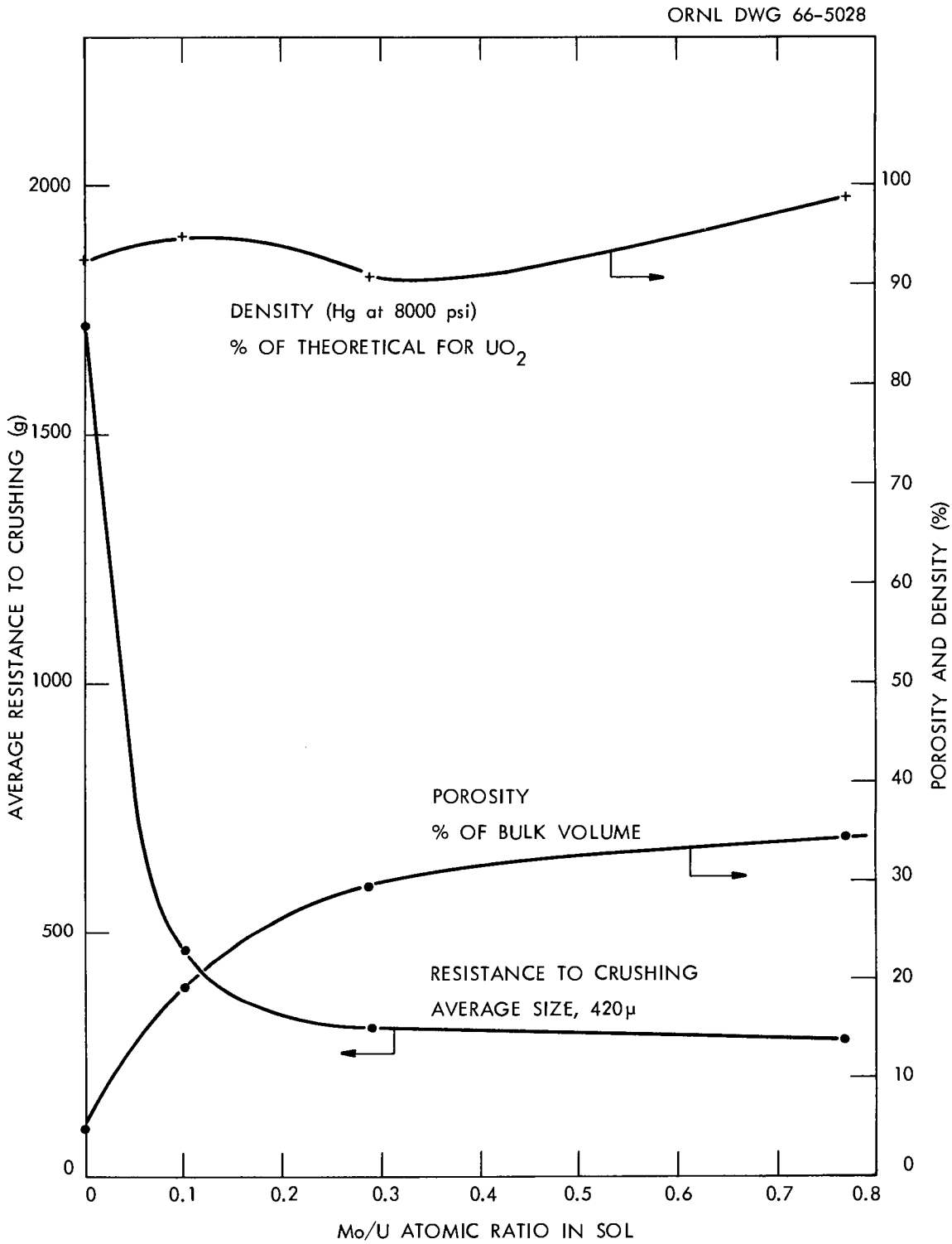

Fig. 4. Porosity of Fired UO_2 Microspheres Increases and Resistance to Crushing Decreases with Increasing Mo/U Atomic Ratio in the Sol.

of the product was 34.4% (see photomicrographs, Figs. 5 and 6). It can be seen that these products are quite similar to those in Figs. 2 and 3. The N_2 surface areas were 0.067, 0.065, and 0.055 for the spheres in Figs. 5A, 5B, and 6, respectively. Nearly all of the pore diameters in these products fell in the range 1 to 10 μ, and most were about 1 μ in diameter.

2.2.2 Porous Microspheres of Thorium Oxide

As already discussed in the introduction to Sect. 2, satisfactory ThO_2-MoO_3 spheres could be prepared only from sols having a Mo/Th ratio in the range 0.3 to 0.6. The thorium concentration in the sol could not exceed about 0.7 M. At higher concentration, the spheres burst as they dried, apparently because of variation in the crystal structure or orientation with depth in the spheres. Microscopic examination of the ruptured spheres revealed that they had chalk-like interiors, which were surrounded by a glassy exterior layer. Moreover, the properties of the product spheres, such as porosity and strength, appeared to be only partly dependent on the Mo/Th atomic ratio. The technique used in mixing the thorium and molybdenum solutions to prepare the sols also affected the properties of the product. Therefore, to obtain reproducible porosity in ThO_2 microspheres prepared by this method, it will be necessary to investigate further the sol-preparation step.

In all the products described in this section, the pore diameters were narrowly distributed in the vicinity of 1 μ.

Sols Made by Stirring Ammonium Molybdate Solution into Thorium Nitrate Solution. — Sols were made by stirring, into 1 M $Th(NO_3)_4$ solutions, ammonium molybdate solutions of the proper concentration to yield Mo/Th atomic ratios in the sols of 0.4, 0.5, or 0.6. Spheres were made as described in Sect. 2.1.2, dried, and fired 1 hr at 1300°C in argon purified by passage over hot copper.

The porosity of the product was about 40% for all three Mo/Th atomic ratios (Figs. 7 and 8). Denser areas mixed with pores (Fig. 7a) and poorly shaped product with nonuniform porosity (Fig. 8) were observed. It was concluded that sol prepared in this way did not yield

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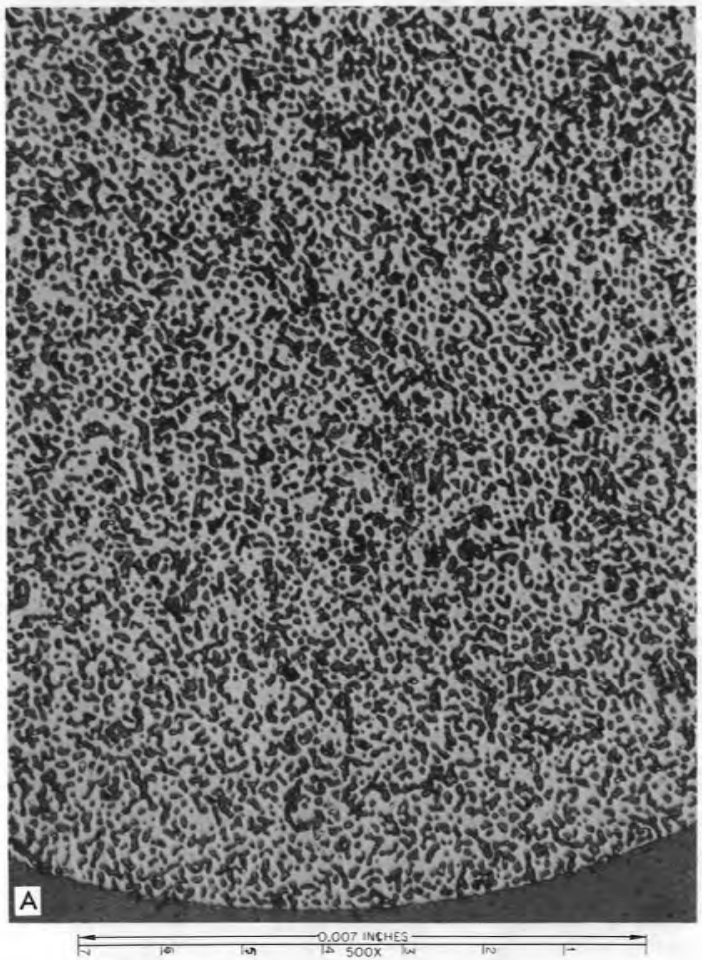

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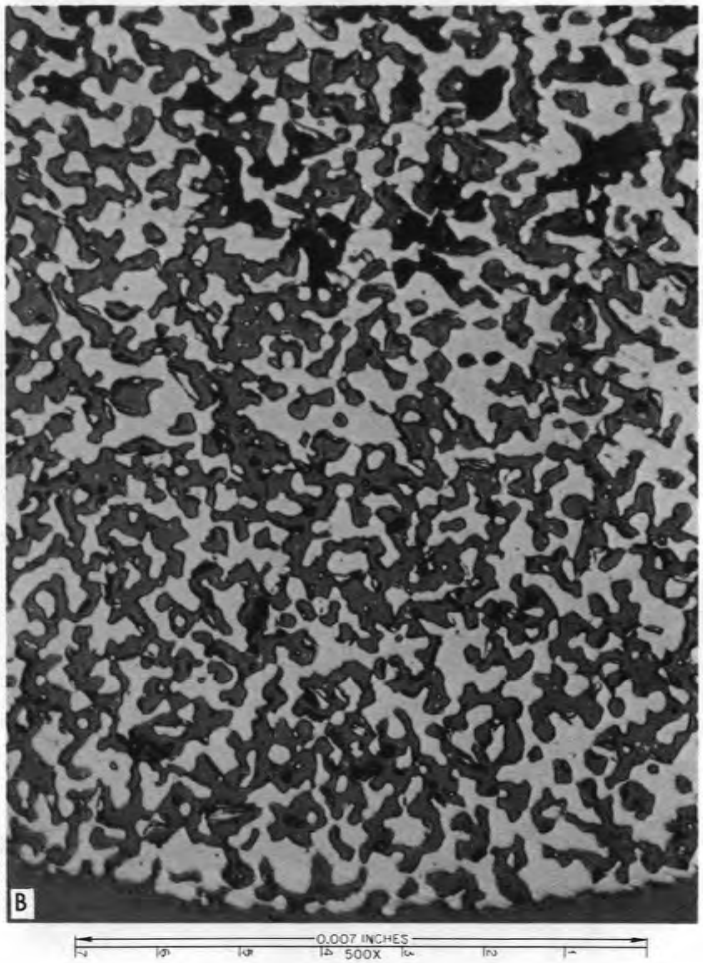

Fig. 5. Porous UO_2 Microspheres Made from U^{4+} Chloride Sols. Porosity is 19.2% in (a) and 29.7% in (b). The Mo/U atomic ratios in the respective sols were 0.10 and 0.29.

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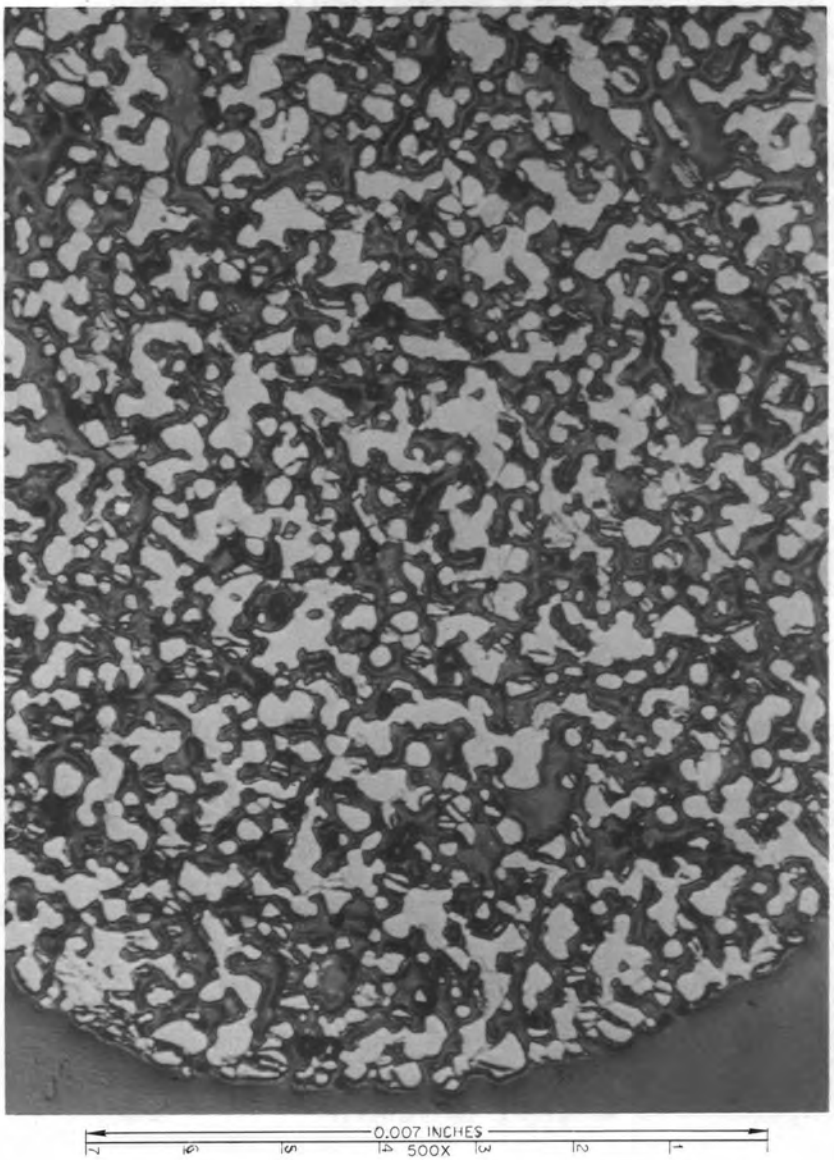

Fig. 6. Porous UO_2 Microsphere Made from U^{4+} Chloride Sol. Porosity is 34.4%. The Mo/U atomic ratio in the sol was 0.77.

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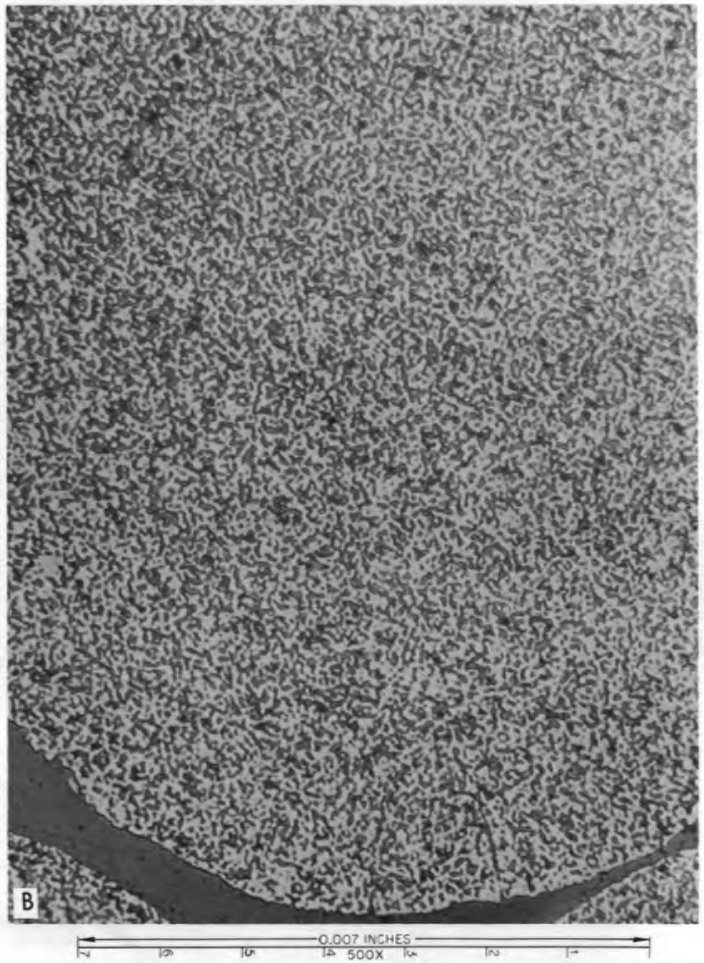

Fig. 7. Porous ThO_2 Microspheres. Mo/Th atomic ratios in sols: (a) 0.3, (b) 0.4. Porosities: (a) 40.1%, (b) 38.8%.

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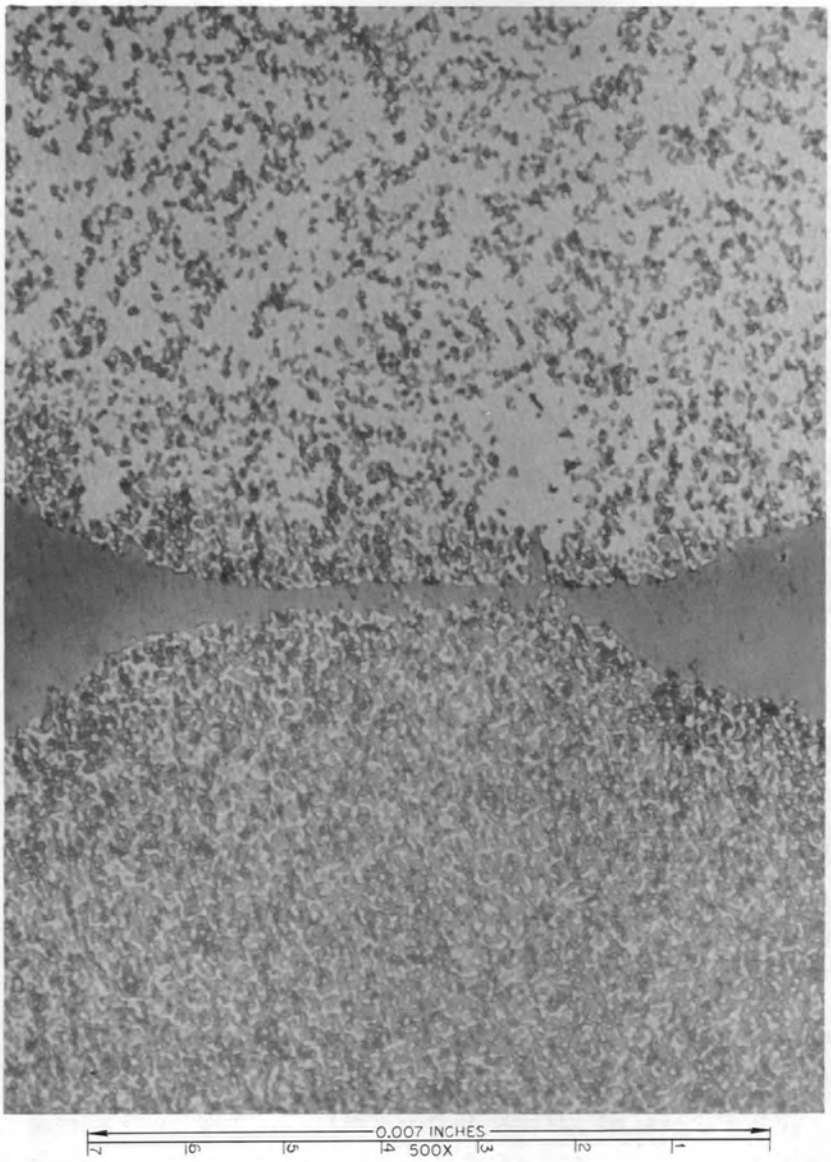

Fig. 8. Porous ThO_2 Microspheres. Mo/Th atomic ratio in sol, 0.6. Porosity, 41.1%.

a very satisfactory product. Therefore, a slightly different mixing procedure was tried; the procedure and results are given in the following section.

Sols Made by Mixing Thorium Nitrate Solutions into Ammonium Molybdate Solutions. — The solutions used to make these sols were the same as those described in the preceding section, but the order of mixing was reversed. The 1 M $Th(NO_3)_4$ solutions were injected rapidly from a syringe into the ammonium molybdate solutions. These sols were more viscous than those described in the previous section. They were also translucent, while those in the previous section were opaque.

Again, the porosity did not appear to be a function of the Mo/Th atomic ratio over the range 0.4 to 0.6. Porosities varied between 21 and 33% (Figs. 9, 10, and 11). In contrast to products described in the previous section, these microspheres were well shaped, although nonuniform porosity and small nonporous areas were observed (see Figs. 9B, 10A, and 11A, for example).

It is thought the procedure used for these sols has a major influence on the quality of the product. The reason for this is that the sols form very rapidly upon mixing the molybdenum and thorium solutions. Thus, to obtain a uniform sol, it is necessary that the rate of mixing be even faster than the rate at which the sols form. A promising approach in future work would be to attempt to decelerate the sol-forming process, perhaps by cooling.

Leaching Experiments and Comparison of Product Properties. — To gain some insight into the effect on the product of such variables as the different orders of mixing of the thorium and molybdenum solutions during sol preparation, analyses were made of wet spheres

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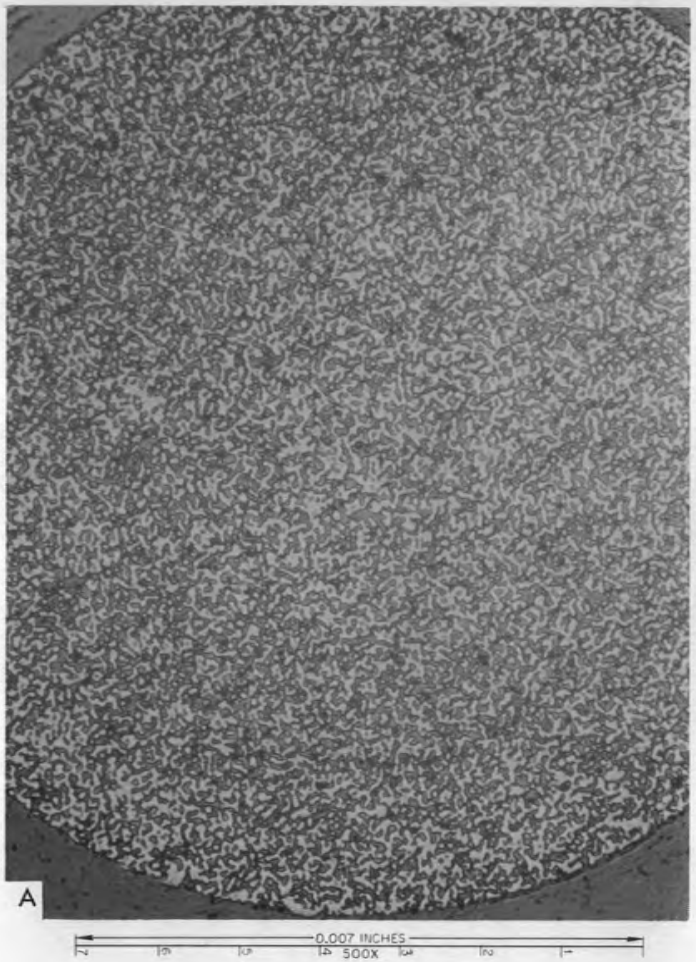

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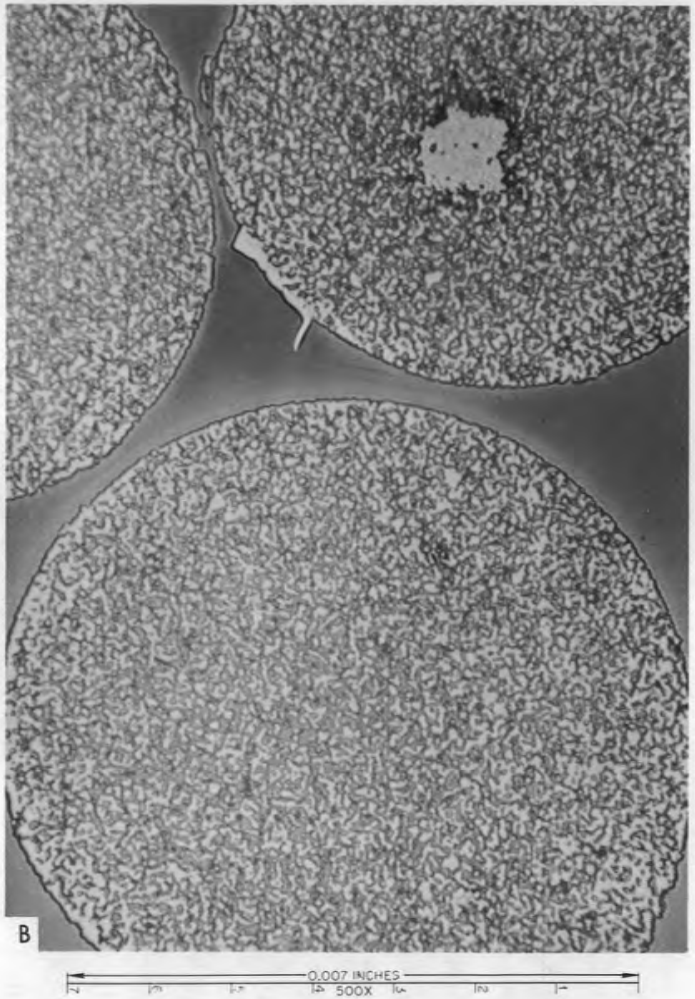

Fig. 9. Porous ThO_2 Microspheres. Mo/Th atomic ratio in sols, 0.5
Porosities: (a) 24.0%, (b) 33.3%.

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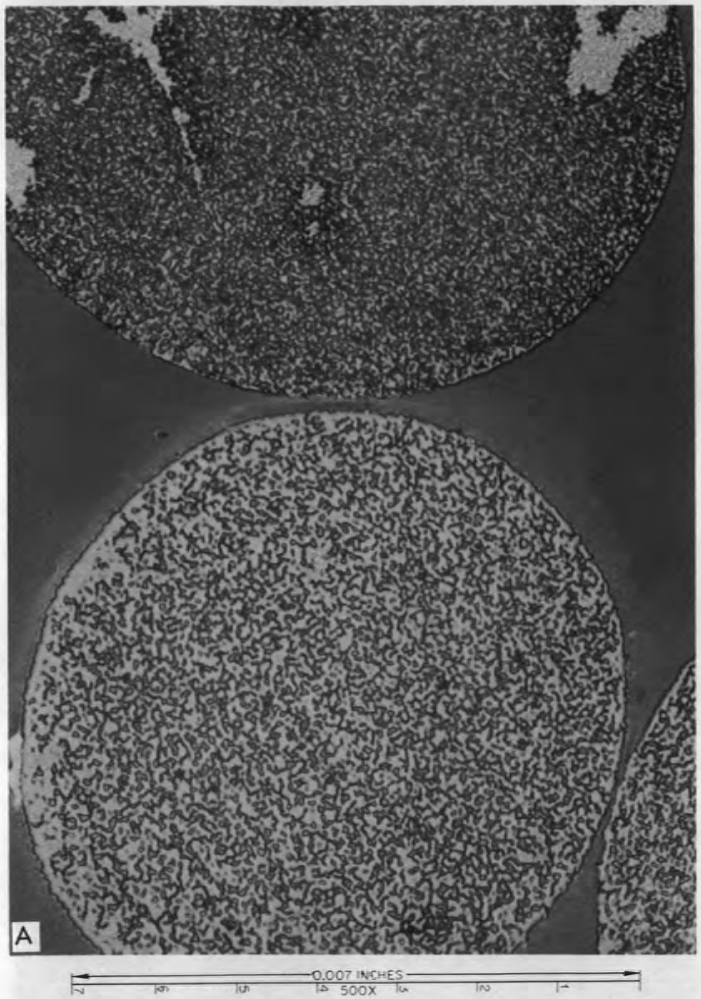

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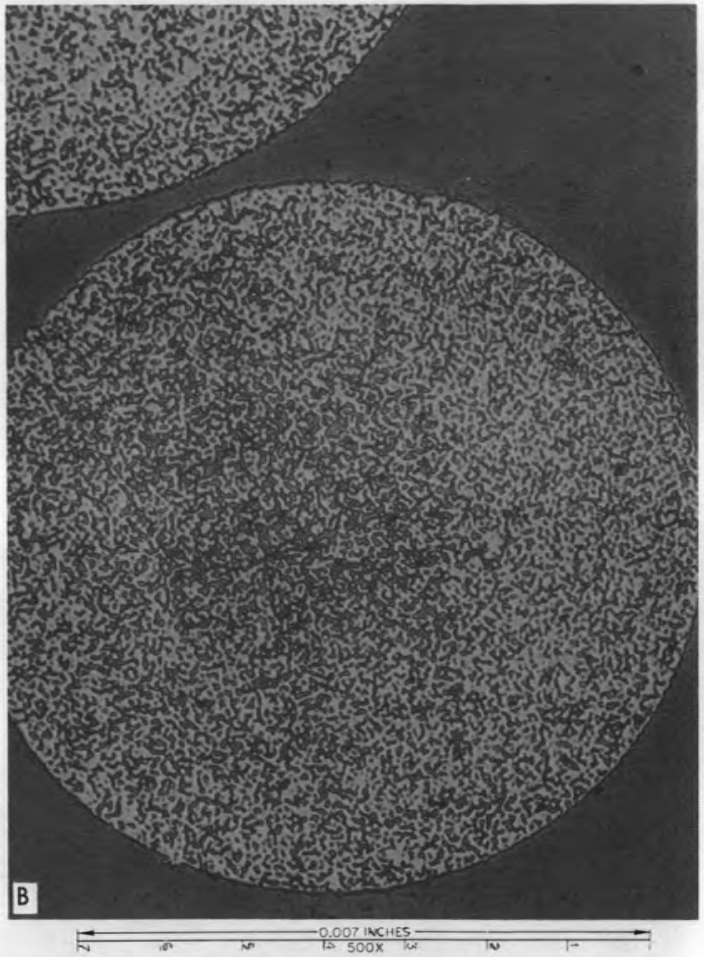

Fig. 10. Porous ThO_2 Microspheres. Mo/Th atomic ratio in sols: (a) 0.4, (b) 0.6. Porosities: (a) 32.1%, (b) 33.1%.

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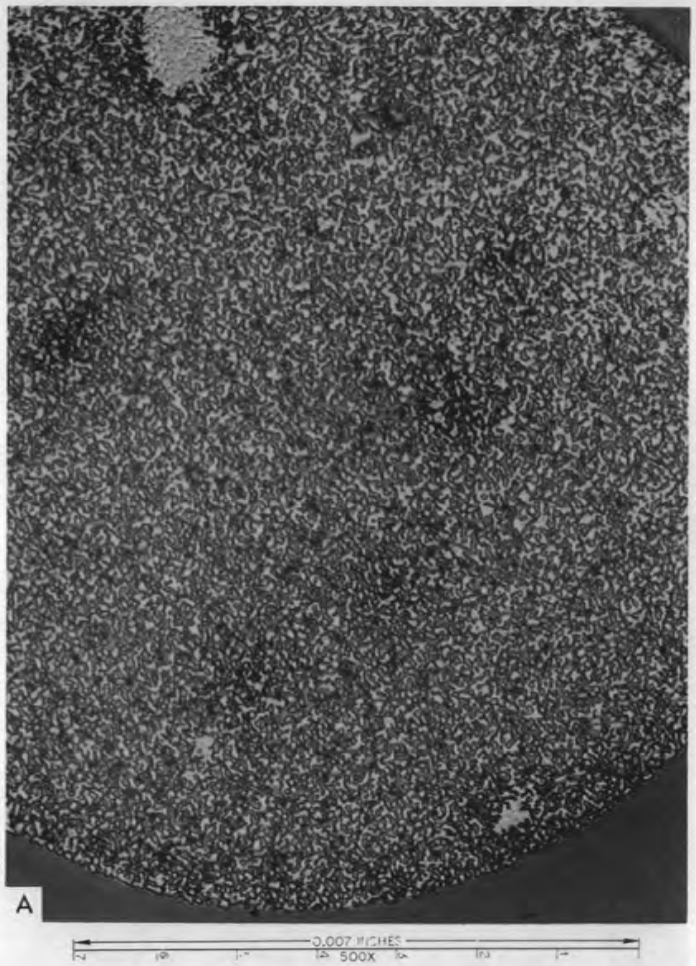

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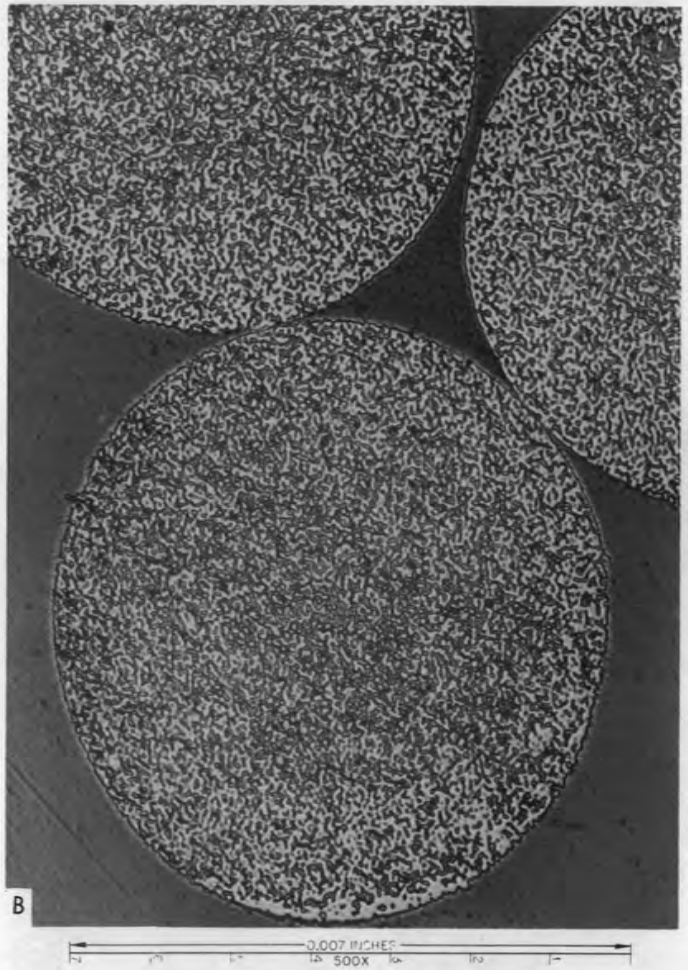

Fig. 11. Porous ThO_2 Microspheres. Mo/Th atomic ratio in sols, 0.6. Porosities: (a) 21.4%, (b) 27.0%.

prepared both ways. In both cases, a series of sols having atomic ratios of Mo/Th of 0.4, 0.5, and 0.6 were prepared, and 0.01 mole of thorium was used in each sol. The spheres were all made by using 100 ml of 15 M NH_4OH. Immediately after the spheres were formed, NH_4OH was drained off and replaced with 200 ml of fresh 15 M NH_4OH, which was left on the spheres overnight. This forming and leaching procedure was the same for all six preparations. When the spheres were removed from the 15 M NH_4OH, they were washed with dilute NH_4OH, and a sample was removed and dissolved in 4 N HCl. This solution was analyzed for Th, Mo, and NO_3^-.

These tests disclosed no differences in the leachability of spheres from sols prepared by either method (Table 1). Very little molybdenum leached out, while the NO_3^-/Th ratio decreased from 4 in the original sol to 0.01 to 0.02 in the leached spheres. The leaching procedure appeared to reduce the nitrate content of the spheres to a satisfactory level.

Spheres made from sols prepared by adding thorium solution to molybdenum solution (procedure B, Table 2) were significantly stronger than those prepared by the reversed mixing procedure (procedure A, Table 2). This difference in resistance to crushing corresponds to differences in porosity. The spheres from procedure A all had porosities of about 40% (Figs. 7 and 8); those from (B) had porosities between 20 and 30% (similar to products in Figs. 9, 10, and 11). Microscopy revealed many misshapen particles among the product from procedure A, while no distorted particles were among the product from procedure B.

An experiment was performed to determine the effect of extensive washing of the wet spheres. Sols were prepared (molybdenum solution added to thorium solution), and spheres were formed as in the above experiments. After they were left for 1 hr in 200 ml of 15 M NH_4OH, the spheres were placed on a porous Pyrex frit through which flowing tap water was passed (upward through the bed of spheres) for 20 hr. The wet products were analyzed as before. The analyses (Table 3) showed that about half the molybdenum had been removed by the flowing water. All the spheres, when fired, had crush

Table 1. Gel Spheres from Sols Prepared by Procedure A (Molybdenum Solution Added to Thorium Solution) are Leached with the Same Efficiency as those Prepared by Procedure B (Thorium Solution Added to Molybdenum Solution)

Mo/Th Atomic Ratio in Sol	Atomic or Ion Ratios after Leaching			
	Mo/Th		NO_3^-/Th	
	A	B	A	B
0.4	0.38	0.40	0.010	0.009
0.5	0.47	0.49	0.009	0.021
0.6	0.58	0.61	0.013	0.018

Table 2. Crush Resistance of Fired ThO_2 Microspheres (A and B have same meanings as in Table 1)

Mo/Th Atomic Ratios in Sols from A

0.4	0.5		0.6	
	Size μ	Wt Required to Crush (g)	Size μ	Wt Required to Crush (g)
<100 g, all sizes	420	400	420	150
	420	650	420	100
	420	570	390	150
	360	450	360	300
	360	360	360	175

From B

Size μ	Wt Required to Crush (g)	Size μ	Wt Required to Crush (g)	Size μ	Wt Required to Crush (g)
720	350	300	380	600	1800
600	220	300	360	540	440
450	350	270	390	480	250
360	250	270	300	360	300
360	270	270	440	330	140

Table 3. Extensive Water Washing of the Wet Gel Spheres Removes Molybdenum

Mo/Th Atomic Ratio in Sol	Atomic or Ionic Ratios: After Removal from 15 M NH_4OH		Atomic or Ionic Ratios: After Washing in Flowing Water 20 hr	
	Mo/Th	NO_3^-/Th	Mo/Th	NO_3^-/Th
0.4	0.35	< 0.001	0.19	< 0.002
0.5	0.40	0.005	0.23	< 0.002
0.6	0.43	0.006	0.27	< 0.002

resistance of less than 100 g. It was concluded that water washing not only was unnecessary but that it also weakened the product.

2.2.3 Porous Microspheres of 20% UO_2--80% ThO_2

The procedure used to prepare porous, mixed thoria-urania spheres differed in only one respect from procedures used to make the products described in Sect. 2.2.2. The difference is that 0.8 M $Th(NO_3)_4$--0.2 M $UO_2(NO_3)_2$, rather than 1 M $Th(NO_3)_4$, was added to ammonium molybdate solution. The resultant sol was 0.54 M in Th, 0.13 M in U, and the Mo/(Th + U) atomic ratio was 0.6.

The porosity of the fired product was 43.4%, and 98% of the pore diameters were in the range 0.56 to 1.57 μ (Fig. 12). Microscopy showed that the product particles were all spherical. Crush resistances of 300-μ spheres fell in the range 200 to 300 g, slightly higher than that observed for pure ThO_2 microspheres (Sect. 2.2.2) and pure UO_2 microspheres (Fig. 1, Sect. 2.2.1) of comparable size and porosity.

2.3 Porous Microspheres of Uranium Dioxide Made by Volatilizing Chloride During Firing

The preparation of U^{4+} chloride sols and the method used to convert sols to microspheres was described in Sect. 2. It was discovered that pores comprising up to 44% of the volume of the product could be

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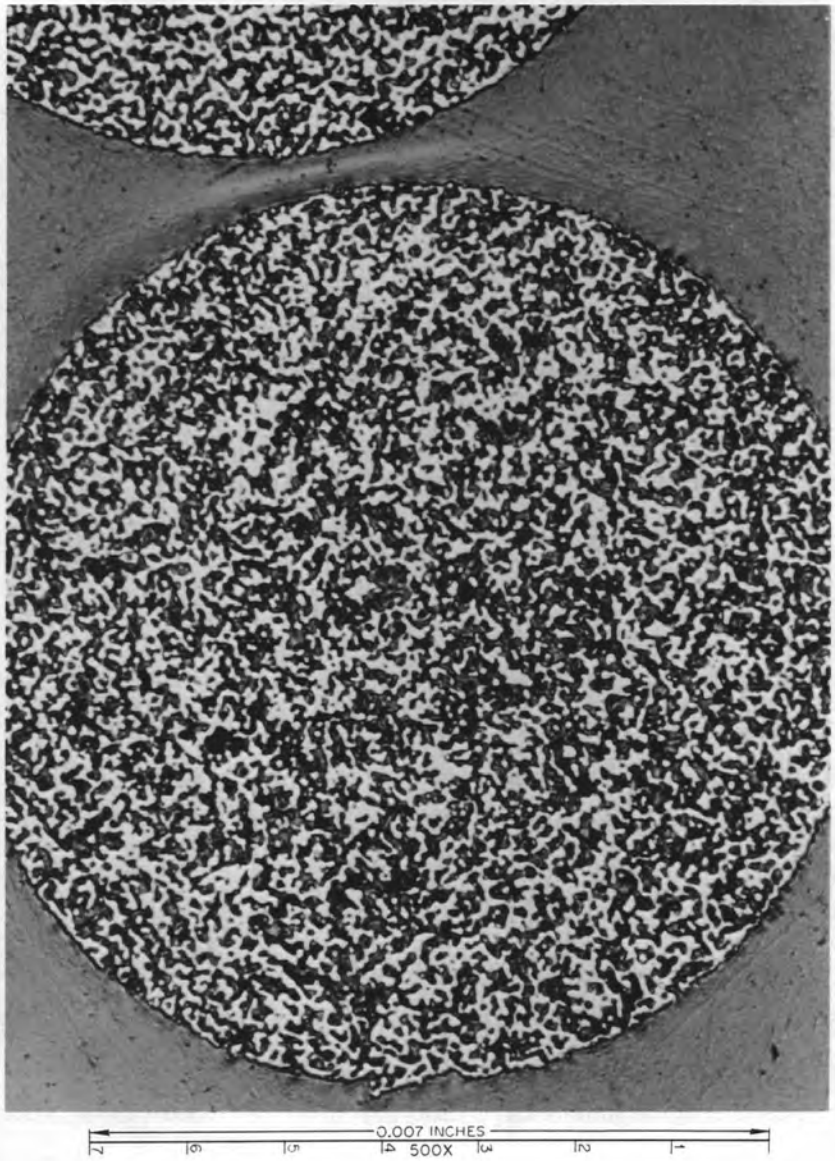

Fig. 12. Porous 80% ThO_2-20% UO_2 Microspheres Made from a $Th(NO_3)_4$-$UO_2(NO_3)_2$-$(NH_4)_2MoO_3$ Sol. Mo/(Th + U) atomic ratio in sol, 0.6. Porosity, 43.4%.

introduced if the chloride was incompletely leached from the gel spheres. At porosities above 25%, at least 95% of the pores were about 1 μ in diameter. At lower porosities, the pore diameters had a much wider distribution—0.01 to 10 μ. In this section, the effect that the volume of leachant (15 M NH_4OH) has upon the amount of residual chloride in gel spheres, and the effect that the amount of chloride has upon porosity and crush resistance in the fired product will be described. Photomicrographs of fired spheres having porosities up to 44% of the sphere volume are shown.

As would be expected, the amount of chloride left in the gel spheres decreased as the volume of 15 M NH_4OH used for leaching increased (Fig. 13 and Table 4). For example, after leaching overnight with 60 moles of NH_4OH per mole of uranium, the spheres still contained 0.43 atom of chloride per atom of uranium, as contrasted to a ratio of 3 in the sol. This ratio decreased to less than 3×10^{-4} when 900 moles of NH_4OH were used per mole of uranium. The increase in steepness of the slope of the leaching curve in Fig. 13 with increasing NH_4OH/U ratio is probably due to multiple leachings at NH_4OH/U ratios greater than 100. Multiple leachings were necessary when using ratios higher than 100 because the beakers used were not large enough to hold larger volumes of 15 M NH_4OH. In all cases the leachant was left in contact with the spheres at least 2 hr before it was replaced by fresh leachant.

The porosity of the product decreased from a maximum of 44% to 7% as the atomic ratio of Cl/U in the leached spheres decreased from about 0.2 to less than 10^{-4} (Fig. 13). A porosity of only 1% was achieved in one case, but this low porosity may have resulted from firing in a reducing atmosphere. A porosity of 1.6% was produced in an argon-fired product (not listed in Table 4) by leaching with ammonium hydroxide circulated through a still to remove chloride. Evidently, quantities of chloride too small to be detected by the analytical methods used (that is, less 10 ppm or at atomic ratio of Cl/U of about 10^{-4}) were still responsible for porosities amounting to several percent of the volume of the product. The maximum porosity which could be introduced into the UO_2 spheres was 44%, which corresponds to an atomic ratio of

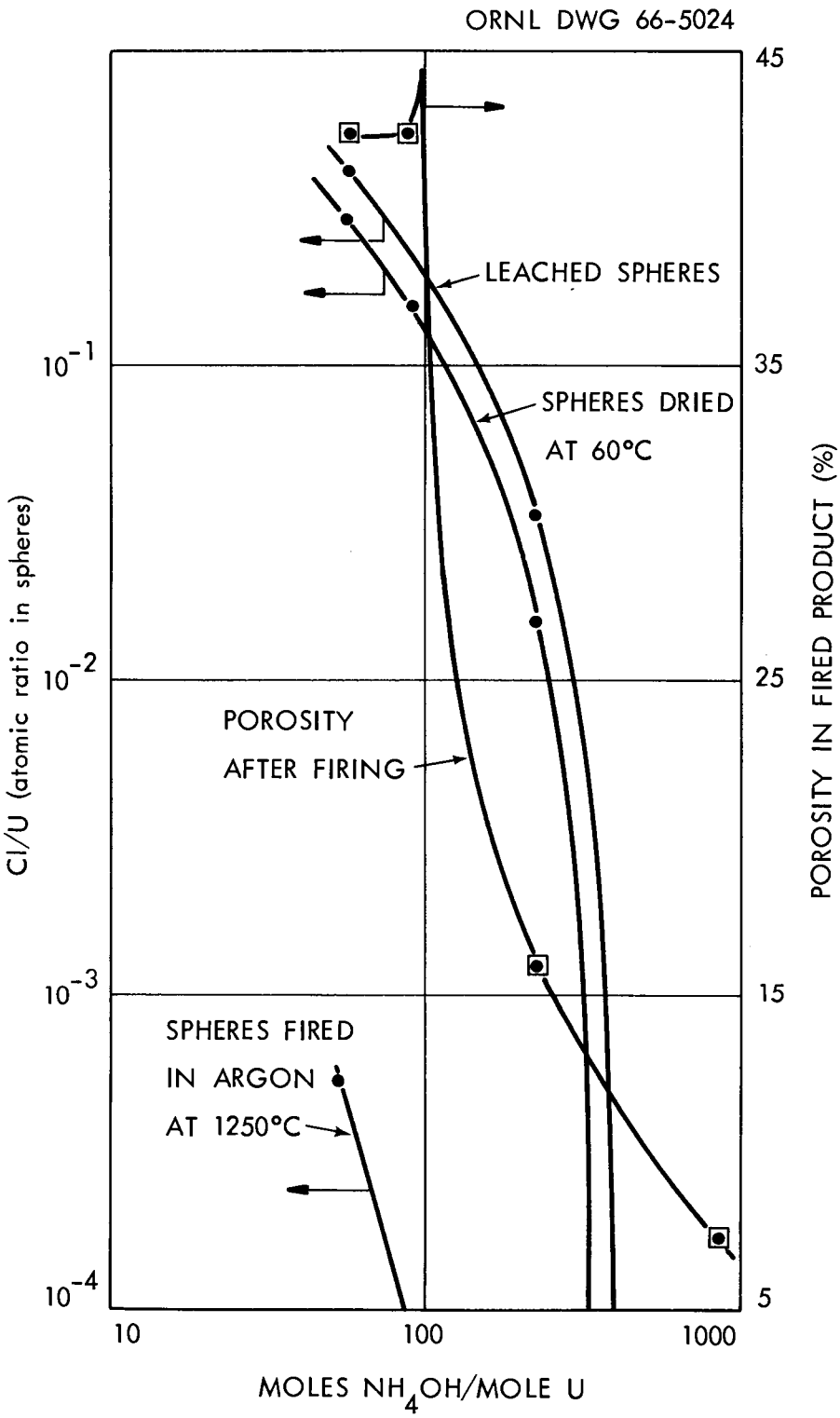

Fig. 13. Porosity of the Fired UO_2 Microspheres Decreases with the Amount of Chloride Left in the Gel Spheres. The amount of chloride left decreases as the amount of 15 M NH_4OH used as leachant increases.

Table 4. Effect of Amounts of Leachant Used on Porosities of Fired UO_2 Microspheres

Leachant Used, Moles NH_4OH per mole U	Atomic Ratio, Cl/U			Porosity by Mercury Porosimetry (% total volume)		Product	
	After Leaching	After Drying at 60°C	After Firing	Dried at 60%	Fired	UO_3/UO_2	Surface Area (m^2/g)
60	0.43	0.30	5.4×10^{-4}	5.1	42.5	0.003	-
90	-	0.15	$< 9 \times 10^{-5}$	3.0	41.6	0.019	-
92	-	-	-	-	44.0	0.089	-
100	-	-	-	-	27.1	0.034	-
225	0.034	0.016	$< 1 \times 10^{-4}$	1.7	16.1	0.023	-
800	$< 8 \times 10^{-4}$	$< 2 \times 10^{-4}$	$< 2 \times 10^{-4}$[a]	1.2	1.3[a]	0.018[a]	-
900	$< 3 \times 10^{-4}$	$< 1 \times 10^{-4}$	$< 1 \times 10^{-4}$	7.1	1.9	0.042	0.008

[a]Fired 1 hr in 4% H_2-Ar at 1150°C. All other firings in pure argon, 1 hr at 1250°C.

Cl/U of about 0.2 in the wet gel spheres before firing. When this ratio was increased to between 0.2 and 0.4, the porosity decreased rather than increased. Although the products were still spheres, photomicrographs revealed that the pore structure had begun to break down. At ratios higher than 0.43, the product was a powder.

Very little chloride was removed during drying in argon at 60°C. Chloride was detected in the fired product in only one case when the Cl/U atomic ratio in the leached spheres was very high (0.4), and in this case the ratio was only 5×10^{-4} (less than 100 ppm) after firing. When the ratio in the gel spheres was lowered to 0.15 or less by more extensive leaching, the fired product contained less than 10 ppm of chloride.

Resistance to crushing decreased from over 1700 g (300-μ-diam-spheres) at 5% porosity to 100 g at 44% porosity (Fig. 14). Surprisingly, resistance to crushing decreased as the porosity decreased from 5%, and approached a value of 800 g as the porosity approached zero. The two circled points at 42% in Fig. 14 represent product from gel spheres in which the Cl/U atomic ratio was greater than 0.2 before firing. The onset of deterioration into powder had lowered both the resistance to crushing and the porosities of these products.

Photomicrographs of the UO_2 microspheres, arranged in order of increasing porosity, are displayed in Figs. 15-18. The partial breakdown of the pore structure that occurred in the product from spheres in which the atomic ratio of Cl/U in the gel was greater than 0.2 is apparent in Fig. 17. Spheres having the highest porosity attained, 44%, are shown in Fig. 18. From the photograph taken at lower magnification, it is apparent that the porosity is uniformly distributed.

3. CONCLUSIONS

The results show that porous UO_2, ThO_2, and mixed ThO_2-UO_2 microspheres can be prepared by the sol-gel method. The laboratory procedures developed to make porous microspheres involved simple operations which should be easily scaled up.

Porosity amounting to as much as 44% of the product can be introduced into fired UO_2 microspheres prepared from U^{4+} chloride sol.

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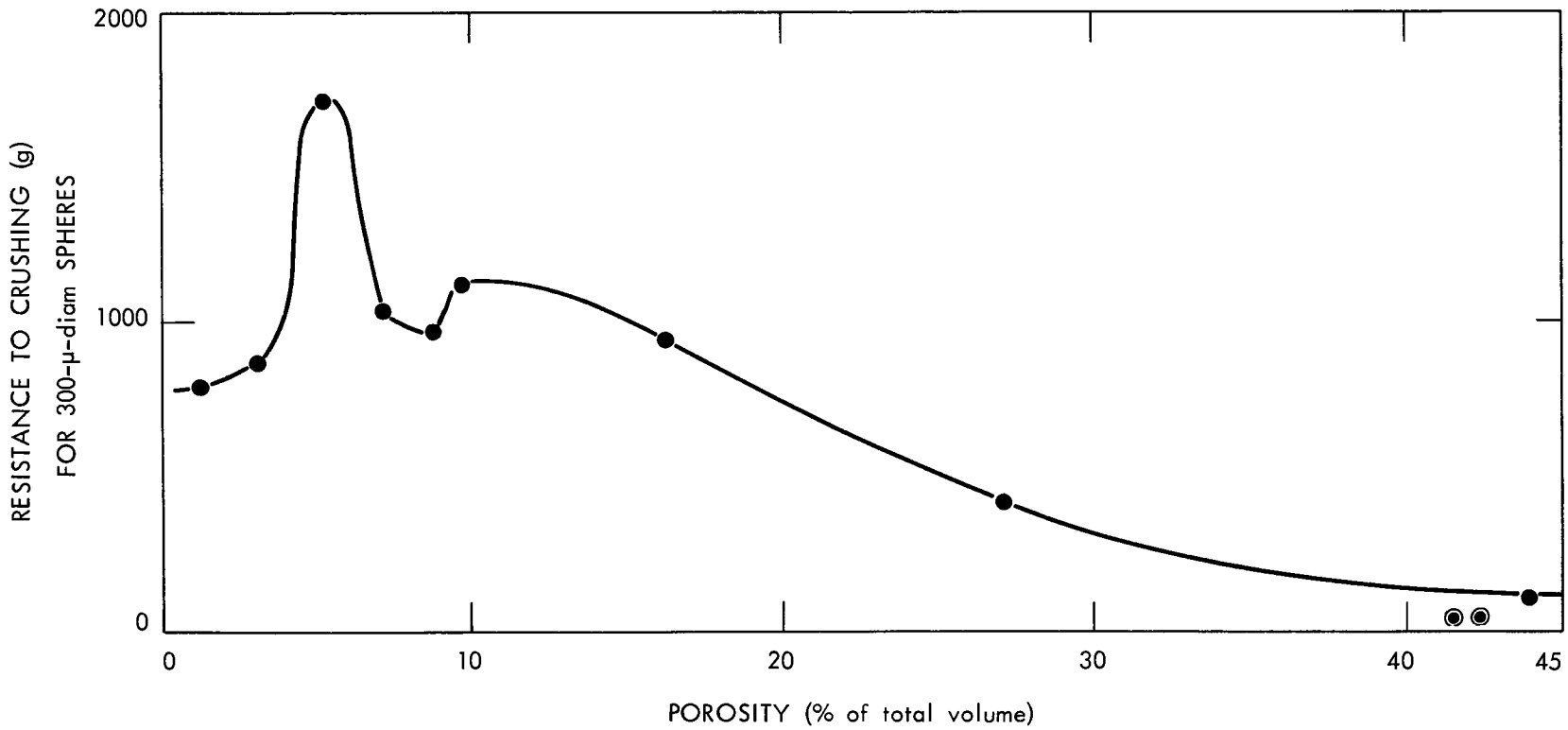

Fig. 14. Resistance of UO_2 Microspheres to Crushing Increases as the Porosity Increases to 5%, then Generally Decreases with Increasing Porosity.

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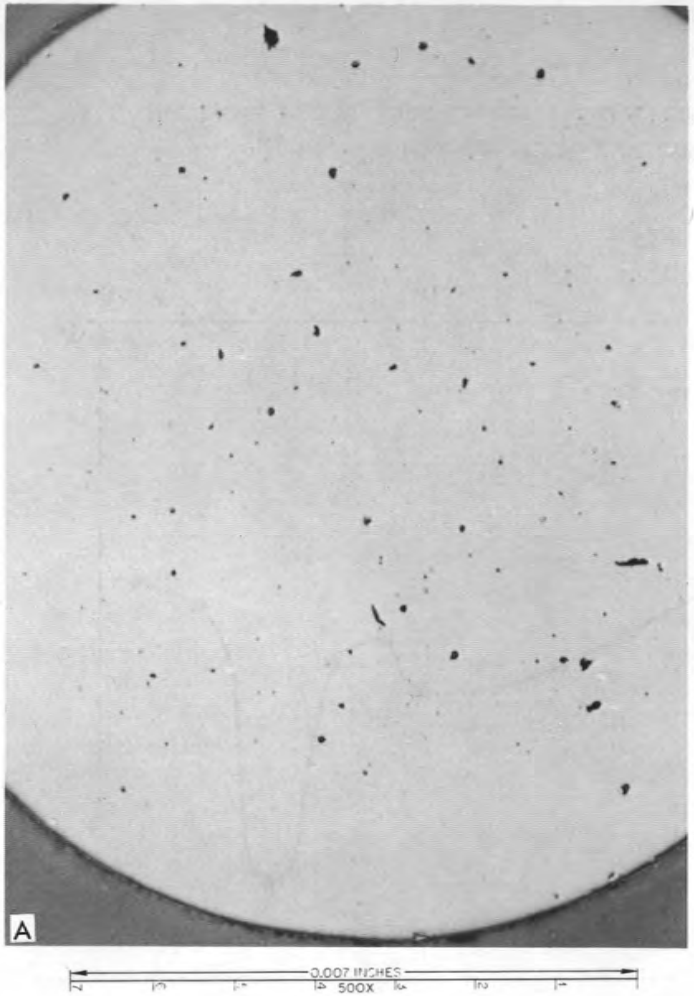

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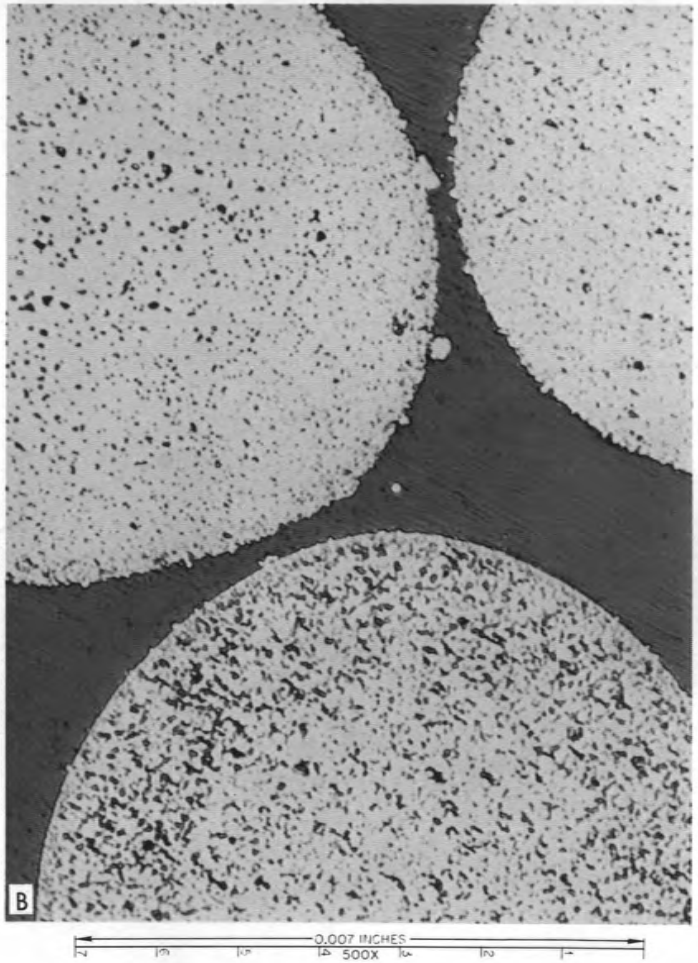

Fig. 15. UO_2 Microspheres with Lower Porosities: (a) 1.2%, (b) 7.1%. The gel spheres contained less than 10 ppm of chloride before firing.

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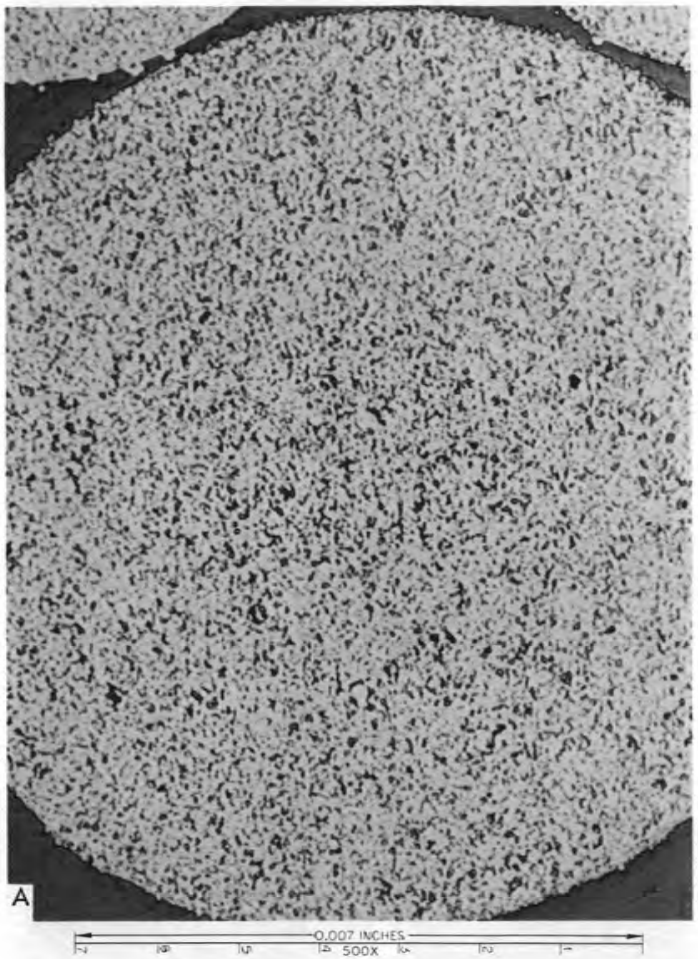

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Fig. 16. UO_2 Microspheres with Intermediate Porosities: (a) 16.1%, (b) 27.1%. Atomic ratios of Cl/U before firing: (a) 0.034, (b) not measured.

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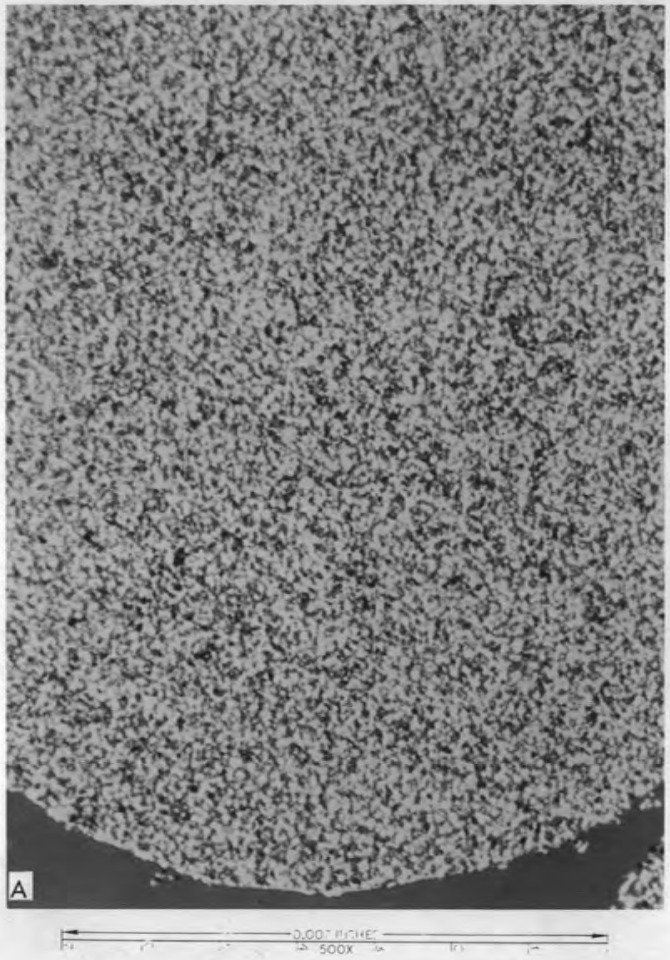

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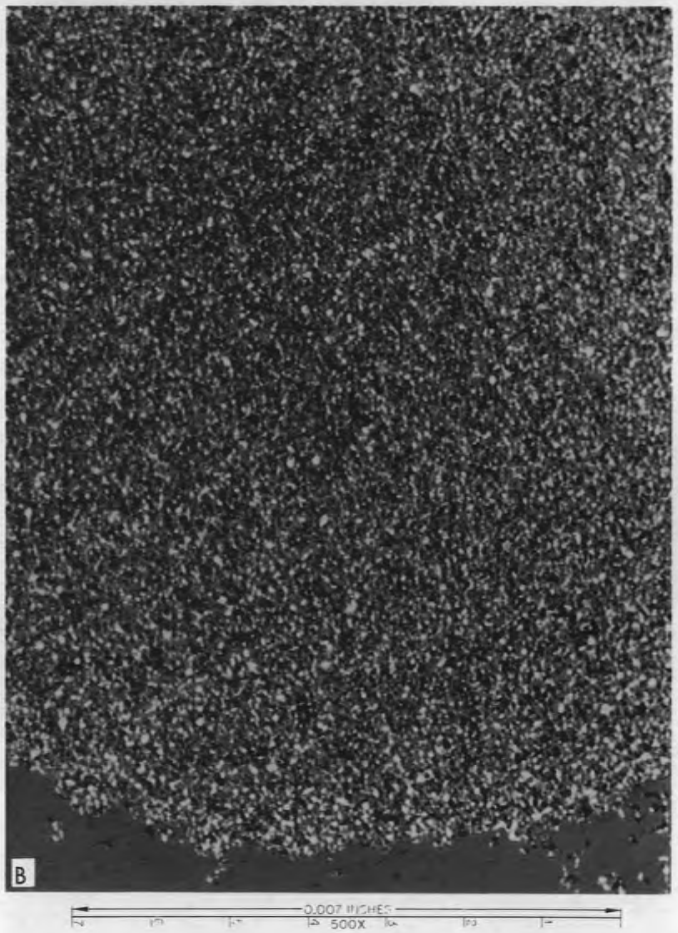

Fig. 17. Very Porous UO_2 Microspheres in Which the Pore Structure has begun to Break Up. Porosity: (a) 41.6%, (b) 42.5%. Atomic ratios of Cl/U before firing: (a) 0.22, (b) 0.43.

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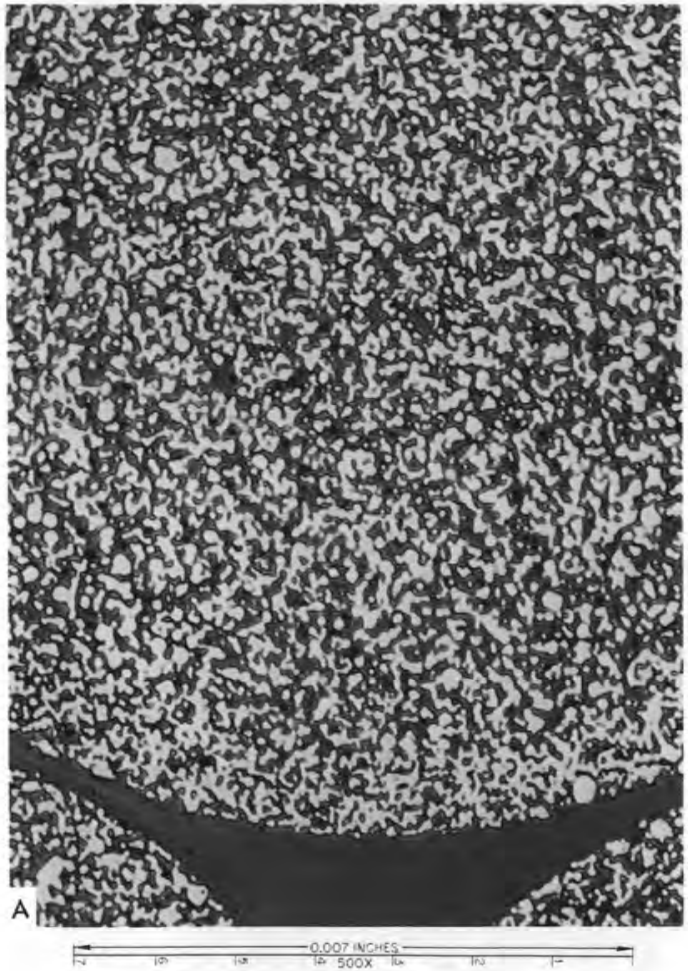

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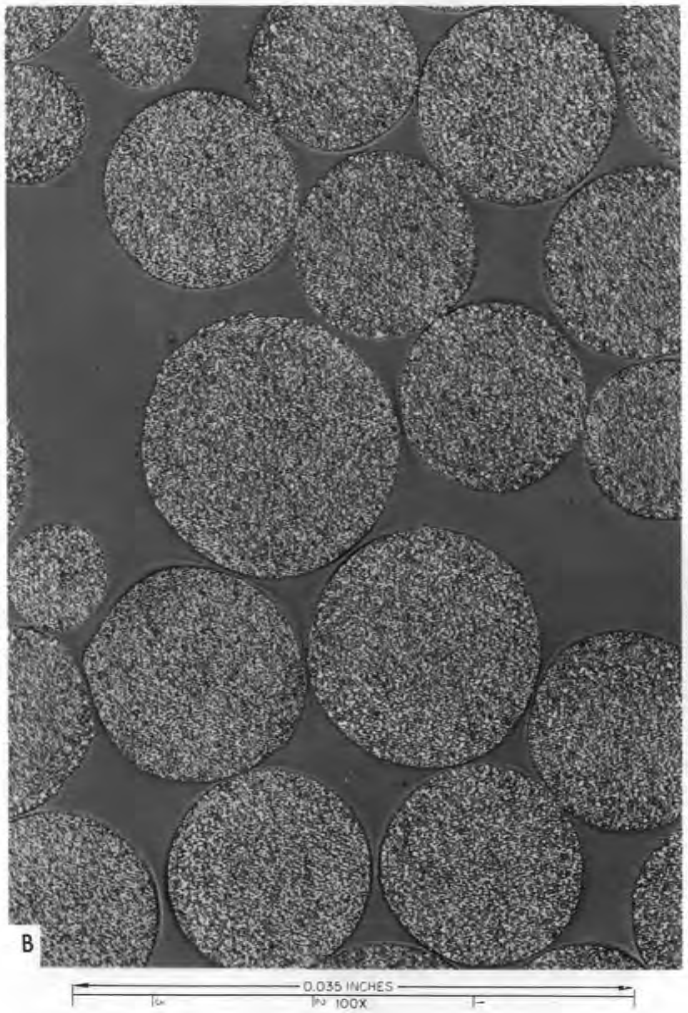

Fig. 18. UO_2 Microspheres with 44% Porosity. The pores are uniformly distributed throughout the microspheres.

The porosity can be controlled by varying the amount of 15 M NH_4OH used to leach chloride from the wet gel spheres, in other words, by controlling the amount of chloride in the gel spheres before firing. Reproducible relationships were found between the volume of leachant and the porosity of the product. Most pores were about 1μ in diameter, particularly at porosities above 25%. At lower porosities, the pore sizes were distributed over the range 0.01 to 10 μ.

Porosities in the range of 20 to 35% of the product can be introduced into fired UO_2 microspheres prepared from sols made by mixing U^{4+} chloride solution with ammonium molybdate solution. The porosity can be controlled by varying the atomic ratio of Mo/U in the sols over the range 0.1 to 0.8. Porosity of the fired products increases with increasing atomic ratios of Mo/U in the sols. The products closely resemble those described in the preceding paragraph, the only difference being that the pores introducted by using the molybdenum-containing sol tended to be larger (1 to 10 μ) and increased in size with increasing porosity. At a porosity of only about 20%, the products made by either method have an almost identical pore-size distribution.

Porosities in the range of 21 to 33% can be introduced into fired ThO_2 microspheres prepared from sols made by mixing $Th(NO_3)_4$ solution with ammonium molybdate solution. Attempts to control this porosity by varying the atomic ratio of Mo/Th in the sols over the range 0.4 to 0.6 did not yield reproducible results, and some unknown variable appears to cause fluctuation of the porosities within the range quoted above. Spheres with porosities of up to 40% were made using a slightly different sol preparation, but the products often were poorly shaped and had low resistance to crushing. In all the ThO_2 spheres, the pore sizes were narrowly distributed in the vicinity of 1μ.

Urania-thoria (20%-80%) microspheres of 43% porosity were prepared by a method very similar to that for the pure ThO_2 microspheres described in the preceding paragraph. The atomic ration of Mo/(Th + U) in the sol was 0.6. Although only one run was made, it indicated that

the mixed UO_2-ThO_2 microspheres can be prepared with a greater range of porosity than can the pure ThO_2 microspheres.

4. ACKNOWLEDGMENTS

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