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# CATION EXCHANGE METHOD FOR PREPARING $^{238}PuO_2$ MICROPARTICLES

MASTER

G. L. Silver

## AEC Research and Development REPORT

MONSANTO RESEARCH CORPORATION
A SUBSIDIARY OF MONSANTO COMPANY

MOUND LABORATORY
MIAMISBURG, OHIO
OPERATED FOR
UNITED STATES ATOMIC ENERGY COMMISSION
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# SUMMARY

A method has been developed for preparing metal oxide microparticles in gram quantities by ignition of metal-loaded resins. Satisfactory results were obtained only with cation exchange resins. The parameters for controlling the characteristics such as particle size, hardness and density were determined. Plutonium dioxide microparticles prepared by the method described could serve as fuel materials in isotopic heat sources. Sintering of the loaded resins in the quartz apparatus used gave satisfactory particles which were often perfect microspheres. Metal oxide microparticles of several other elements, including thorium and zirconium, were also prepared by this process.

# INTRODUCTION

In recent times much attention has been given to the preparation of plutonium or other radioelement microspheres.[1] It is the purpose of this report to summarize the ion exchange method of preparing metal oxide microparticles investigated at Mound Laboratory. Most of the work on this process was done in an attempt to devise a simple method of preparing $PuO_2$ microspheres in large quantities as an alternate to the sol-gel process for preparation of heat source fuel. Both cation and anion exchange resins were examined in this study, but only from cation exchange resins could metal oxide microspheres be prepared. The resins used in this study were obtained from Bio-Rad Laboratories of Richmond, California. The plutonium used in this study was a mixture consisting of 80% of the 238 isotope and the balance the 239 isotope. All analyses were made by alpha counting.

The loading of cation exchange resins with plutonium has been described elsewhere.[2]

# EXPERIMENTAL

## PLUTONIUM OXIDE MICROPARTICLES

The preparation of metal oxide microparticles from metal-loaded resins proved a task of some difficulty. Initially, plutonium-loaded anion exchange resin beads, loaded from 7M $HNO_3$, were ignited in small ceramic boats in a tube furnace. The oxide so prepared consisted largely of tiny fragments of $PuO_2$ with an occasional microsphere. Few attempts to prepare microparticles by loading anion exchange resins from $HNO_3$ or HCl solutions ever yielded anything but oxide fragments. After much experimentation, this method was abandoned.

Two methods of loading the resin were used. These were called "plutonium control" and "acid control". In the first, the degree to which the resin loads is controlled by limiting the quantity of plutonium available to the resin. In the second, the degree to which the resin loads is controlled by varying the acidity of the medium from which loading occurs. Better microparticles were usually obtained when resin particles loaded by the "acid control" method were ignited. This is perhaps because the "plutonium control" method favors the loading of resin surfaces at the expense of the resin interiors. Evidence for this is presented in Figure 1, which illustrates oxide fragments obtained by igniting resin loaded by the "plutonium control" method. (The enlargement for this and all of the subsequent photomicrographs is 41X.)

Early attempts to prepare oxide microparticles consisted of igniting plutonium-loaded cation resins in a small open ceramic boat placed at the bottom of a tube furnace. These experiments generally yielded but 300 mg of $PuO_2$ and no attempt to prepare larger quantities was made until studies on this scale were completed. Figure 2 shows particles of $PuO_2$ from an early experiment obtained by igniting Dowex 50W-X8, 20-50 mesh, loaded to 90% of theoretical capacity. Cracking and breakage were found to be extensive. Since the properties of crush strength and density are of particular importance for many applications of the microspheres, these parameters were among the first studied.

In Table 1 are presented data on four typical batches of $PuO_2$ prepared by igniting Dowex 50W-X8, 20-50 mesh, loaded by the "plutonium control" method.

Because experience indicated that data such as presented in Table 1 were not entirely reproducible, and because trends in such parameters as density and crush strength are perhaps more meaningful than absolute values of these parameters, much of the data of Table 1 are presented in Figures 3, 4, 5 and 6. One of the trends indicated by Table 1 is that crush strength apparently increases with ignition temperature. This was rechecked using resin loaded by the "acid control" method. Three types of resins were used: 50W-X2, 50W-X4 and 50W-X8, where X2, X4 and X8 are degrees of cross-linkage; each sample was loaded to about 90% of capacity.

Results are presented in Figure 7, where it can be seen that crush strength does indeed appear to increase with temperature.

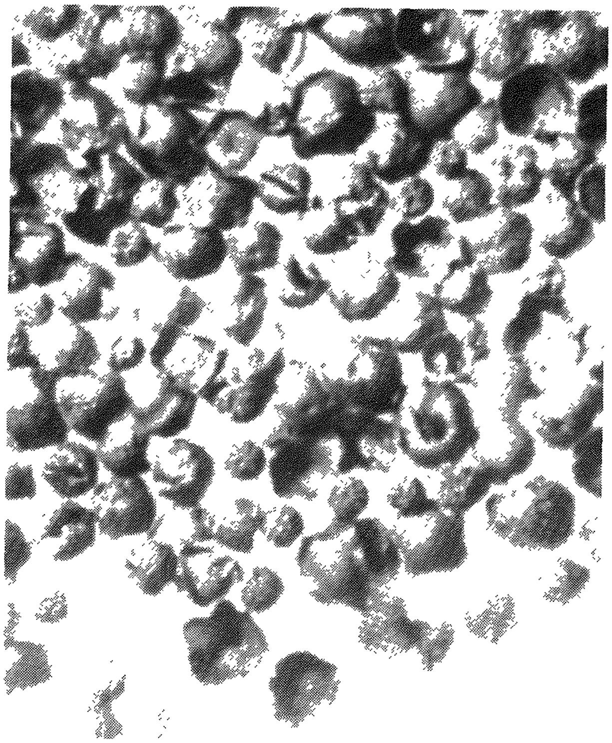

FIGURE 1 - Oxide fragments obtained by the "plutonium control" method.

Table 1

PROPERTIES OF PLUTONIUM DIOXIDE MICROPARTICLES PREPARED FROM CATION EXCHANGE RESINS

| Sample No. | Loading (%) | Ignition Temperature (°C) | Density (g/cc) | Size (mil) | Crush Strength (g) |
|---|---|---|---|---|---|
| 1 | 82 | 800 | 3.22 | 20.9 | 0 |
| | | 1000 | 6.36 | 16.7 | 3.5 |
| | | 1150 | 6.82 | 14.5 | 8.9 |
| 2 | 66 | 800 | 3.01 | 19.8 | 0 |
| | | 1000 | 5.39 | 15.8 | 6.6 |
| | | 1150 | 6.73 | 11.2 | 8.7 |
| 3 | 50 | 800 | 2.37 | 18.3 | 0 |
| | | 1000 | 4.93 | 15.8 | 3.6 |
| | | 1150 | 5.63 | 11.2 | 8.9 |
| 4 | 27 | 800 | 3.32 | 15.3 | 0 |
| | | 1000 | 2.92 | 15.9 | <1 |
| | | 1150 | 4.72 | 11.7 | 2.0 |

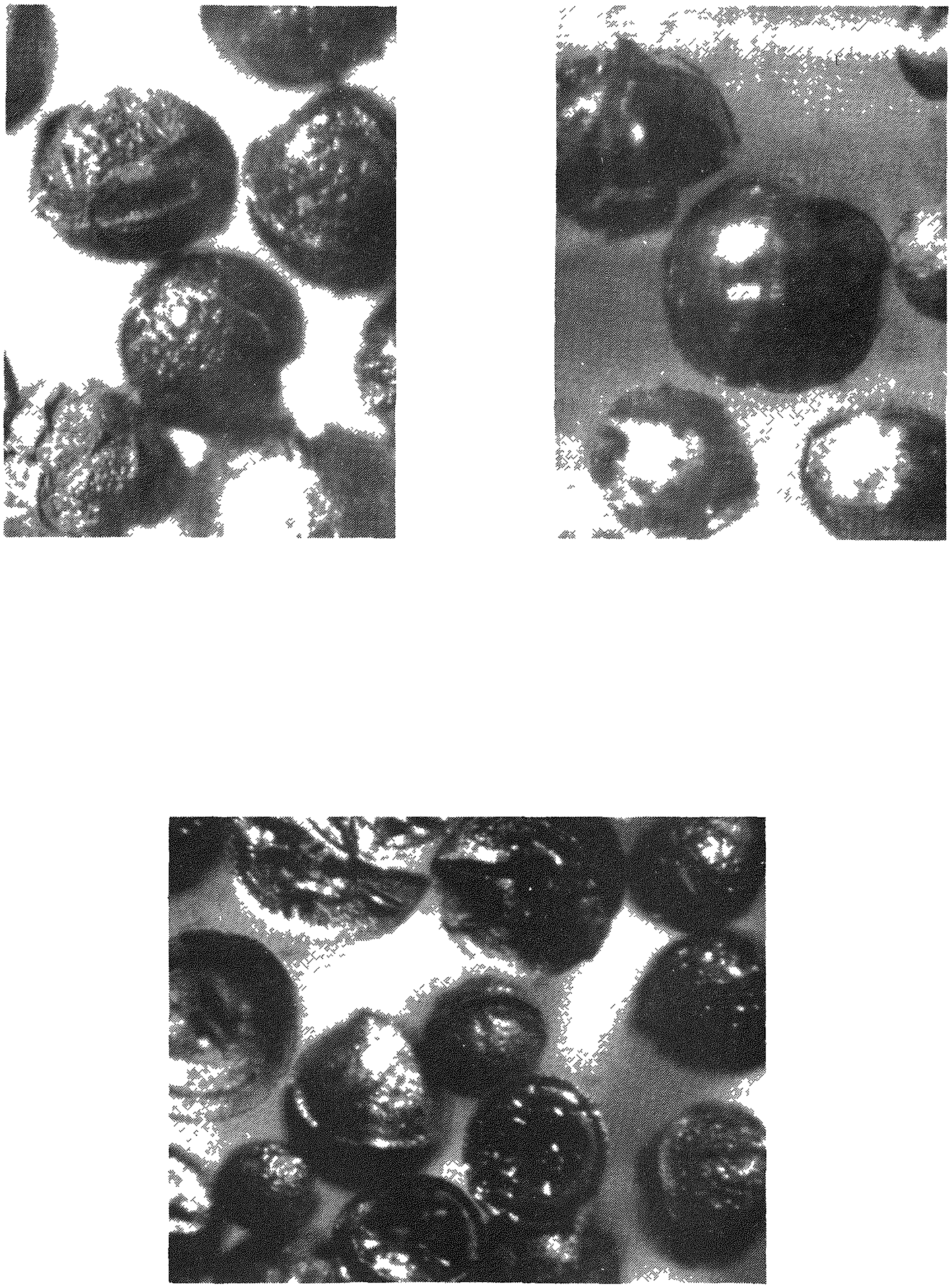

FIGURE 2 - Detail of typical cracked microparticles (20-50 mesh).

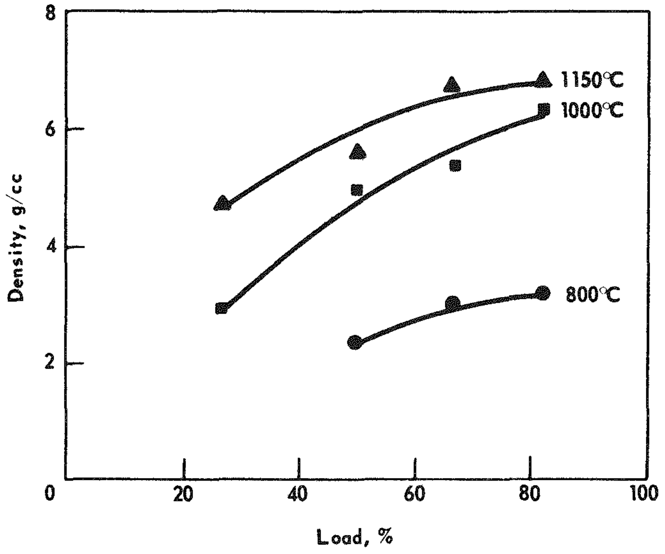

FIGURE 3 - Relationship of load and density at three ignition temperatures.

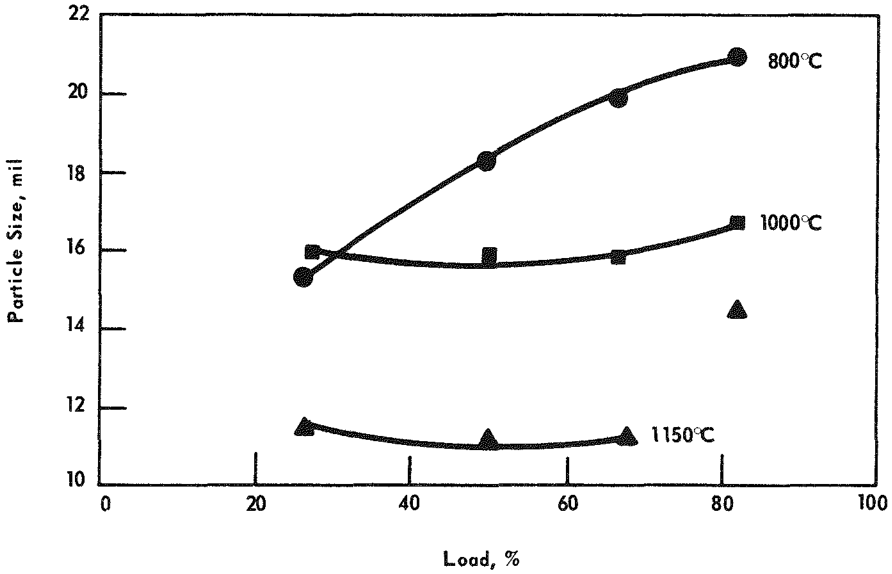

FIGURE 4 - Relationship of size and load at three ignition temperatures.

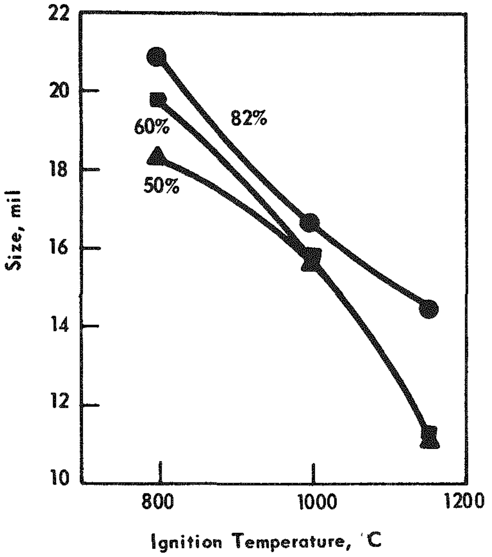

FIGURE 5 - Relationship of size and ignition temperature at three degrees of resin loading.

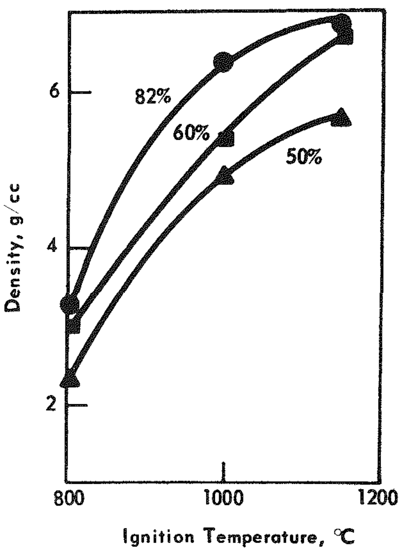

FIGURE 6 - Relationship of density and ignition temperature at three degrees of resin loading.

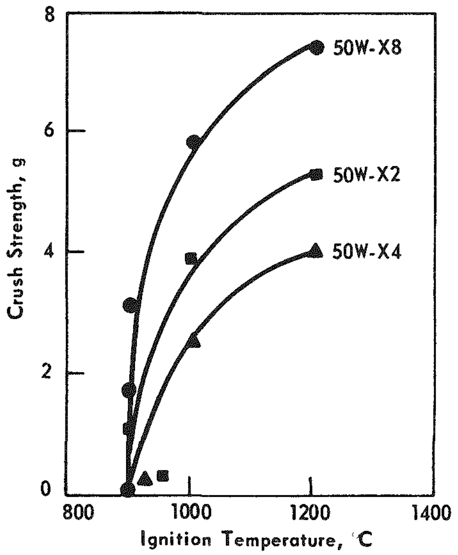

FIGURE 7 - Relationship of crush strength and ignition temperature using resins of different cross-linkages.

From Figure 7 it appears that there might be some relationship between cross-linkage and crush strength. No definite evidence for such a relationship was ever found, however. The apparent dissimilarities in crush strength for the different resin samples shown in Figure 7 probably reflect the uncertainties in the measurement of ignition temperature. The furnace used was a large tube furnace, and it was not always possible to reproduce the conditions of ignition. There was also some uncertainty in the temperature indicated by the chromel-alumel thermocouple. Hence the apparent differences in crush strength with cross-linkage shown by Figure 7 are not likely to be significant. That crush strength increases with temperature is evident, however.

Figure 8 presents another aspect of the relationship of crush strength to firing conditions. This plot demonstrates the increase in crush strength with period of ignition at 1200°C. The point at time zero on this plot means that the temperature of the furnace was brought to 1200°C

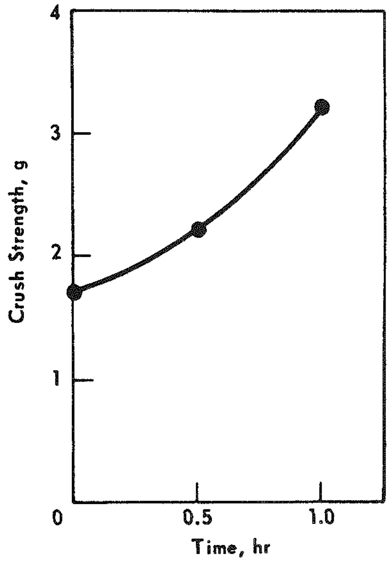

FIGURE 8 - Relationship of crush strength to period of ignition at 1200° C.

and the furnace was immediately allowed to cool. The temperature profile of the furnace for this firing is shown in Figure 9. Evidently both temperature and exposure time affect crush strength. Since crush strength increases both with temperature and period of ignition, it would appear that increasing crush strength results from the gradual sintering of the particles. Further evidence for this was provided by an interesting experiment in which a small sample of loaded resin beads was heated to 1200° C in the absence of air. At this temperature, hot air was suddenly drawn through the particles, causing them to incandesece. The particles were momentarily at white heat. These particles had a crush strength in excess of 500 g. Figure 10 shows another result of extending the period of ignition: particles apparently decrease in size as heating is prolonged.

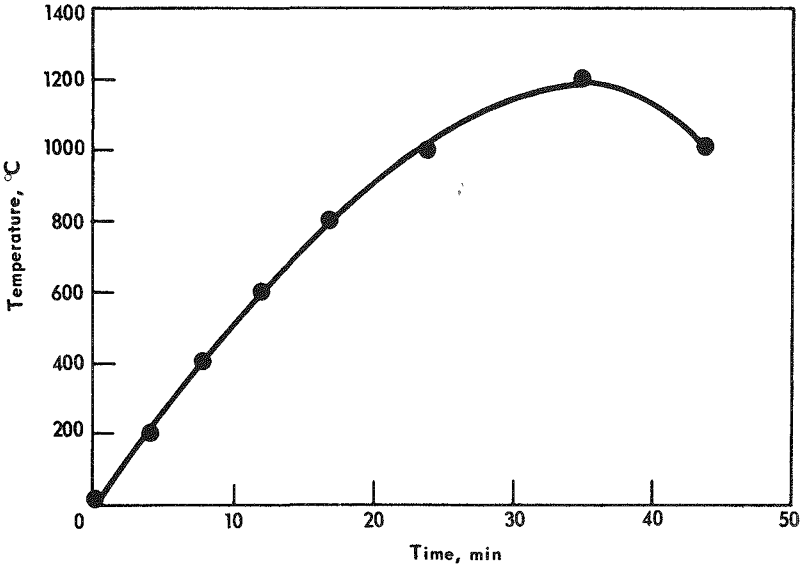

FIGURE 9 - Time-temperature profile of tube furnace.

From these observations on the properties of particles prepared by igniting plutonium-loaded cation exchange resins in open ceramic boats a number of generalizations appear possible:

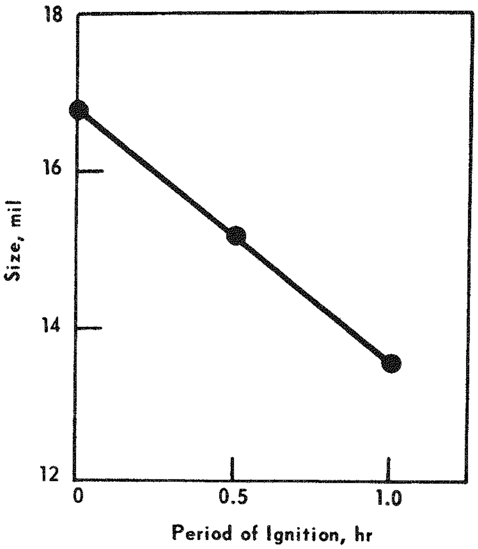

FIGURE 10 - Relationship of size to period of ignition at 1200°C.

a. At constant loading, density increases with ignition temperature.

b. At constant loading, size decreases with ignition temperature.

c. At constant ignition temperature, size increases with loading, but this increase need not be large.

d. At constant ignition temperature, density increases with loading.

e. Crush strength increases with ignition temperature and with period of ignition at a given temperature.

f. Crush strength and density do not seem to be related.

g. As loading of the resin beads decreases below 50% of theoretical, it is increasingly difficult to prepare good oxide microspheres.

Upon completion of a cursory study of the behavior of the parameters of interest, an attempt was made to improve the quality of the particles. By "quality" is meant such characteristics as smoothness of surface, absense of cracking and breakage, and uniformity of the particles. These attempts to improve the "quality" of the particles are best described by photographs. Figures 11, 12 and 13 show various resins of the Dowex 50W type, 50-70 mesh, after being loaded with plutonium and ignited. The size of these particles is typically 5-7 mil, at a density of 2-4 g/cc, and with a crush strength of 0-5 g. These figures indicate that, while good microspheres of $PuO_2$ can be made by this process, the process is not always dependable. These photographs are typical of the material obtained by firing small amounts of resin in an open ceramic boat.

Experience in burning metal-loaded resin particles demonstrated the need to dry the particles thoroughly prior to ignition. If particles of resin are not dried prior to use, extensive decrepitation of the resin beads occurs and the metal oxide microspheres remaining after ignition of the beads will appear cracked and broken. This is perhaps due to the explosive escape of internally generated steam in the resin beads. Plutonium-loaded resin beads which are air dried only will lose considerable moisture if allowed to stand for a few weeks. It is interesting that, in these studies, decrepitation was most severe in particles of high

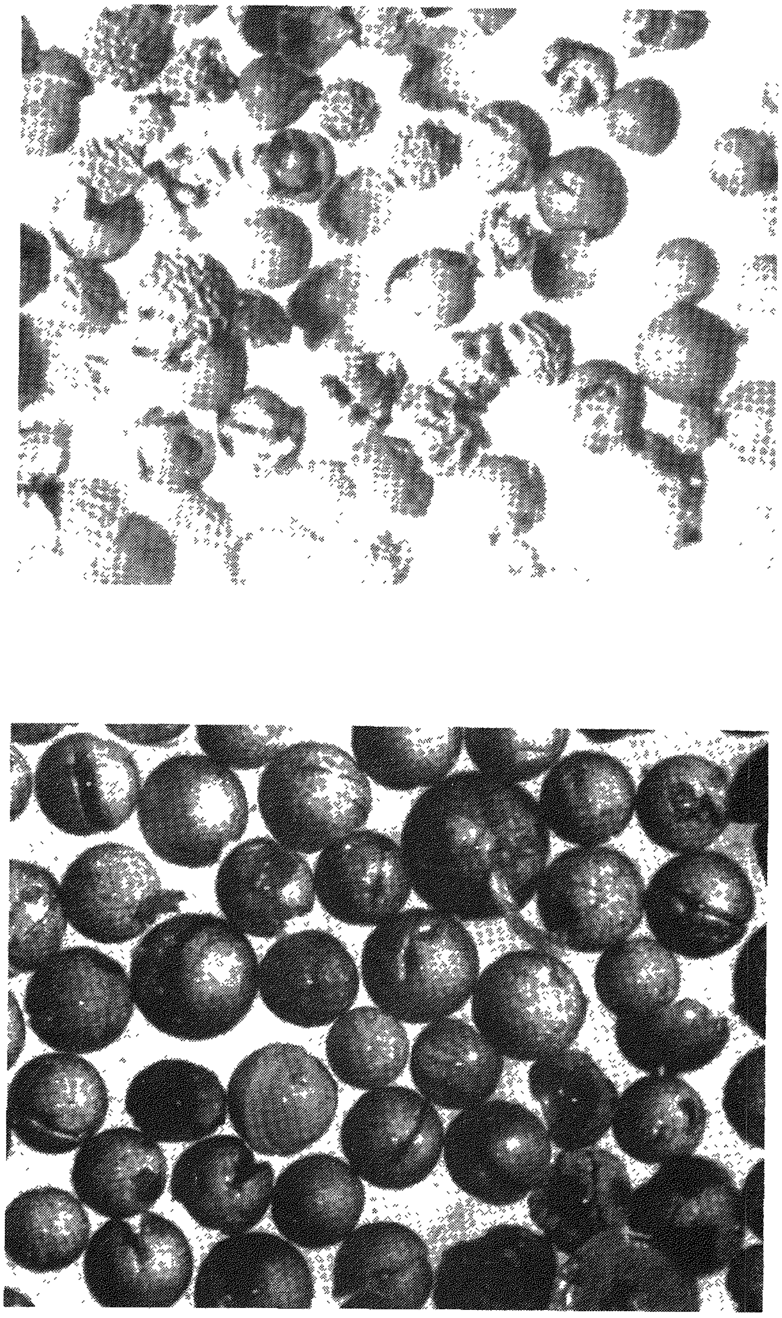

FIGURE 11 - Microparticles obtained from 50-70 mesh cation exchange resin.

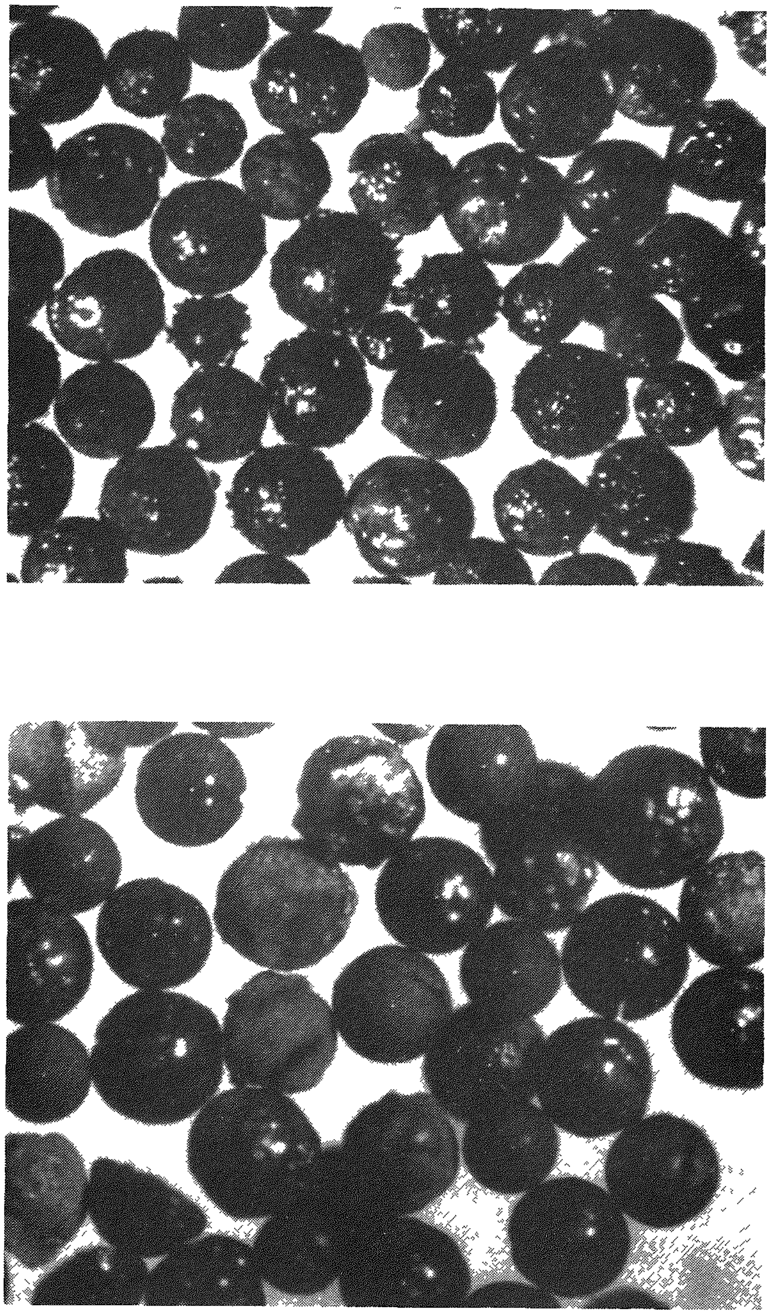

FIGURE 12 - Microparticles obtained from 50-70 mesh cation exchange resin.

FIGURE 13 - Microparticles obtained from 50-70 mesh cation exchange resin.

cross-linkage (e.g., 12% and 16%). These resins are probably less elastic and less permeable than the lower cross-linked resins.

When plutonium-loaded resins are slowly heated in vacuum to 300°C before ignition, extensive denitration occurs in addition to dehydration, as indicated by the evolution of dark brown fumes from the resin beads. The brown fumes are probably oxides of nitrogen originating from the nitrate ions held as counter ions by the plutonium in the resin.[3] It is not likely that the evolution of these gases is beneficial to the preparation of good microspheres. Therefore, it is possible that loading from some other medium, for example plutonium chloride in dilute hydrochloric acid, would produce a metal-loaded resin which would produce better oxide particles upon ignition.

## PREPARATION OF GRAM QUANTITIES OF MICROPARTICLES

Since the possibility of preparing $PuO_2$ microparticles by experiments with small quantities of plutonium-loaded resin was demonstrated, an attempt was made to produce gram quantities of oxide microspheres. It was apparent that simple ignition in an open crucible would not work since, in large batches, only those particles on the surface of the sample to be ignited would completely burn to yield a carbon-free oxide. Two possible solutions to the problem of burning large quantities were proposed.

The first attempt to prepare gram quantities of microspheres involved placing a quartz tube threaded as a screw into a tube furnace inclined at approximately 30° to the horizontal. Particles were slowly fed into the top of the screw and, as the screw turned, the particles were passed through the hot interior of the furnace. The particles were collected in a beaker at the lower end of this "worm" furnace, which was maintained at a temperature of 1000°C for these experiments. Particles which had passed through the furnace were examined under a microscope.

The microscopic view of such particles, a yellow and black mosaic of spheres and fragments, suggested that all of the carbon in the resin beads had not been oxidized. Passing the particles through the furnace a second time converted the samples to the familiar yellow-green of $PuO_2$, but the material was fragmented and ground to such an extent that few $PuO_2$ particles remained intact. It was surprising that an initial residence time of 6 min within a furnace at 1000°C was insufficient to remove all of the carbon from the particles. Changes in the speed of rotation of the "worm" (and hence, residence time in the furnace) and the introduction of a continuous air flow through the "worm" did not prevent fragmentation of the oxide particles. One of the reasons for the failure of this approach could be thermal shock, which is particularly severe since a temperature interval of 1000°C is traversed twice within a period of a few minutes. Typical "worm" furnace material is shown in Figure 14.

A second attempt to prepare gram quantities of $PuO_2$ microparticles involved the quartz apparatus shown in Figure 15. Resin particles were

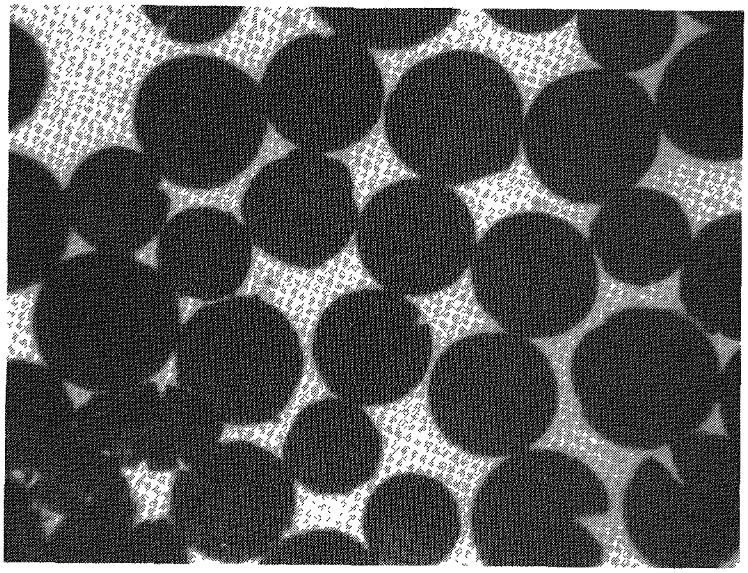

FIGURE 14 - Microparticles obtained from a "worm" furnace.

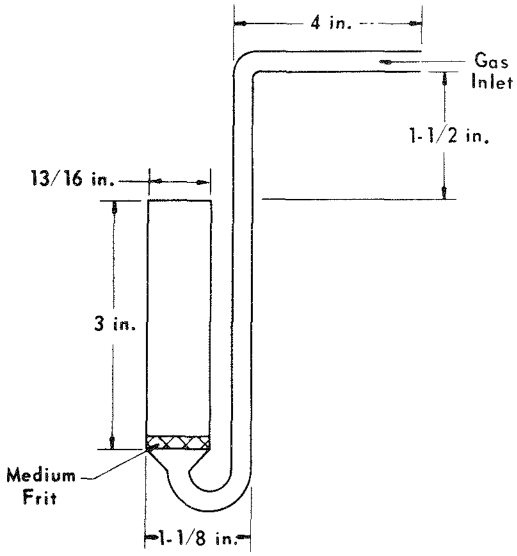

FIGURE 15 - Quartz sintering tube for preparing metal oxide microspheres.

placed in the tubular receptacle and the vertical section of the vessel was placed in the core of a vertical tube furnace. Several small samples of resin (yielding about 0.5 g of $PuO_2$) were ignited in this apparatus.

During each ignition, air was forced upward through the sample, providing a uniform atmosphere for the entire mass of particles. The air flow caused gentle agitation of the resin beads. With this apparatus the resin beads are agitated with preheated air, and the entire apparatus, along with the resin particles, can be heated slowly. Examples of the material obtained in this apparatus are shown in Figure 16.

The combustion of the organic resin in this apparatus proceeds smoothly. At some temperature below red heat a blue flame appears at the lip of the ignition tube. After several minutes the flame disappears and combustion is nearly complete. In all of the samples ignited by this method, however, some "sparking" or "fiery decrepitation" was observed. Some of the particles seemed to explode upon burning, caused perhaps by the excessive rate of heating of the material. For the most part, however, ignition of the samples proceeded smoothly and quietly. Other samples prepared by ignition in the quartz sintering tube are shown in Figures 17 and 18. This material was ignited at 1000-1200°C for 30 min. The size of the particles is 6-7 mil and the density is about 1.5 g/cc.

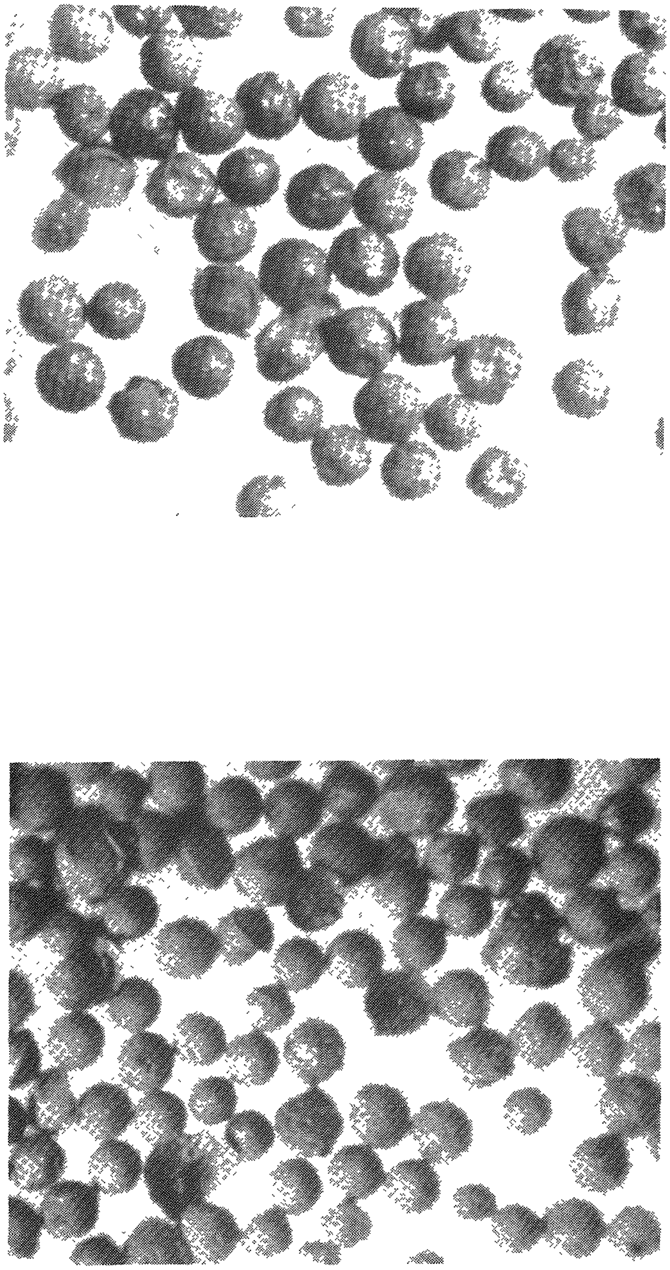

FIGURE 16 - Microparticles obtained from the quartz apparatus.

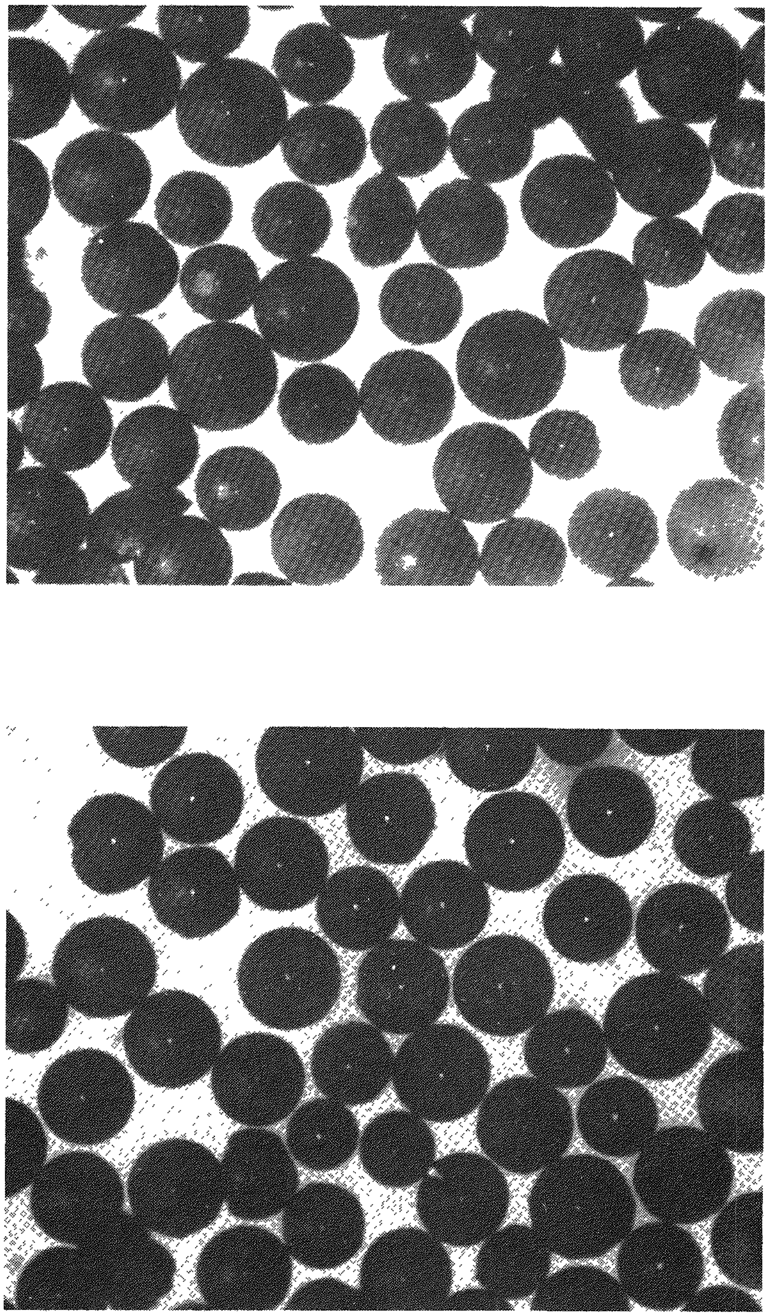

FIGURE 17 - Microparticles obtained from the quartz apparatus.

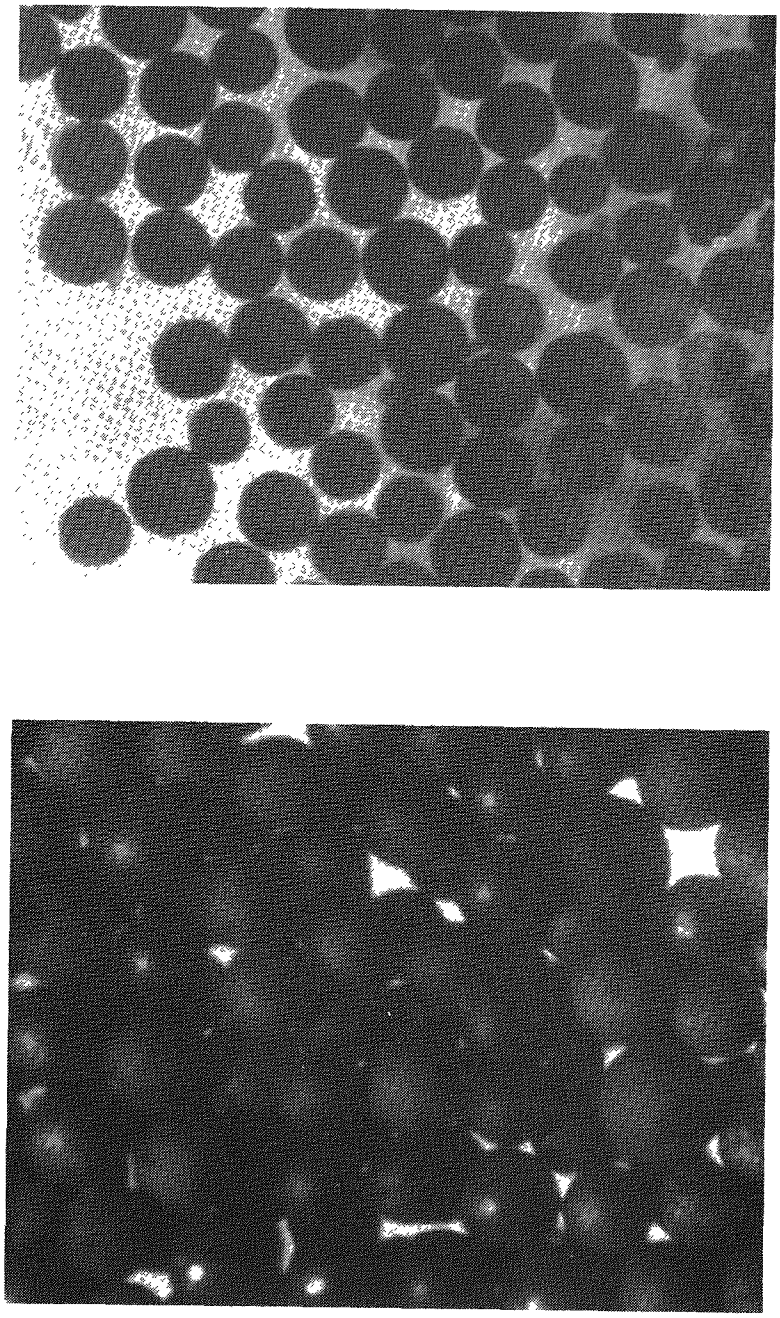

FIGURE 18 - Microparticles obtained from the quartz apparatus.

## METAL OXIDE MICROPARTICLES

In order to learn more about the ion exchange method of preparing oxide microparticles, attempts were made to prepare oxide microparticles of several other elements. Some of these attempts were successful, and some did not appear at all promising. Elements which display chemistry even slightly analogous to that of plutonium(VI) were selected as being the best candidates to yield microparticles similar to those obtained with plutonium. Two elements chosen for testing on this basis were thorium and zirconium.

Figure 19 shows representative samples of three batches of zirconium dioxide microparticles obtained from Dowex 50W-X12, 20-50 mesh, loaded by allowing the resin to equilibrate in a solution of zirconium sulfate dissolved in water. The resin beads were loaded from an excess of zirconium; the particles were prepared by the quartz tube process. Examination of these particles indicated that they are very porous. They are easily prepared in lots of 5 g and do not appear to be particularly fragile. Figure 20 shows, for comparison, zirconium dioxide microparticles which are available commercially.

Figures 21 and 22 illustrate microparticles of thorium dioxide prepared by igniting Dowex 50W-X8 loaded by equilibrating for several hours in a solution of thorium nitrate in water. The particles of Figure 21 were prepared from resin of 20-50 mesh, while particles of Figure 22 were prepared from resin of 50-100 mesh. Cracking is evident in these particles, and in many respects they appeared similar to $PuO_2$ microparticles. Both the $ZrO_2$ and the $ThO_2$ microparticles prepared by the ion exchange technique are pure white.

Figure 23 shows microparticles of magnesium oxide. Both these particles and those of aluminum oxide shown in Figure 24 appear somewhat translucent or "glassy". There was much fragmentation and dust formation during the ignition of resin loaded with these metals. Figure 25 shows particles of cerium oxide prepared by igniting resin loaded with trivalent cerium. Fragmentation and cracking were extensive. Figures 26 and 27 show microparticles of lanthanum and uranium oxides, respectively. Several attempts to prepare oxide microparticles of other elements were not successful. Among those which did not yield microparticles at all were iron, copper and nickel.

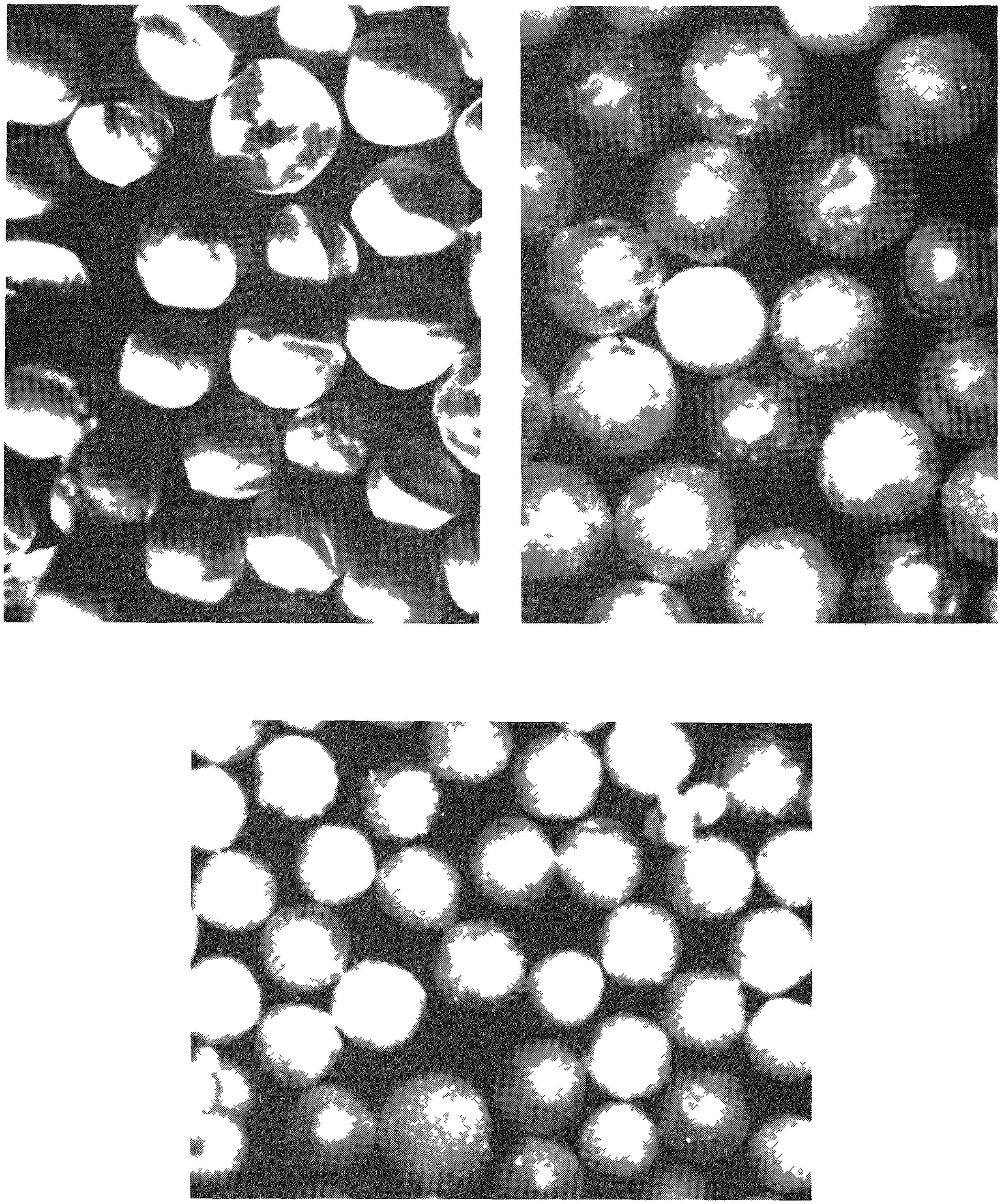

FIGURE 19 - Zirconium dioxide microparticles obtained by the cation exchange process.

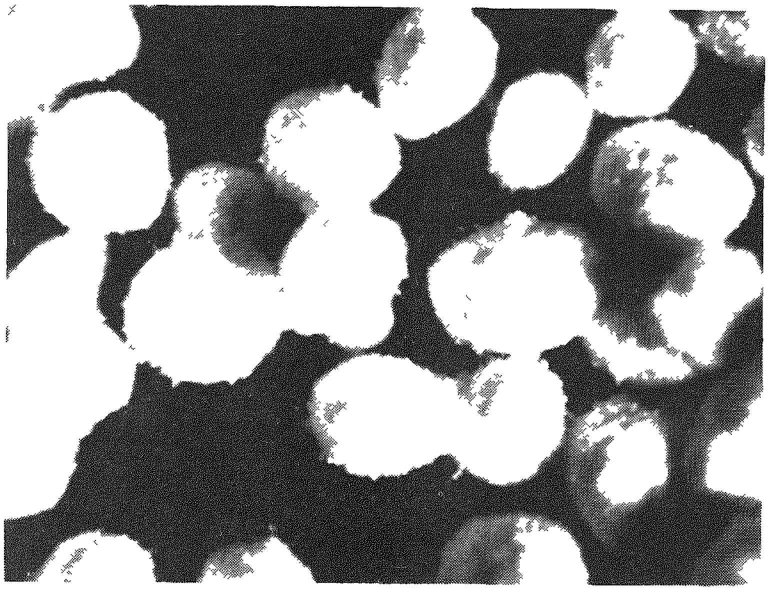

FIGURE 20 - Commercial zirconium dioxide microparticles.

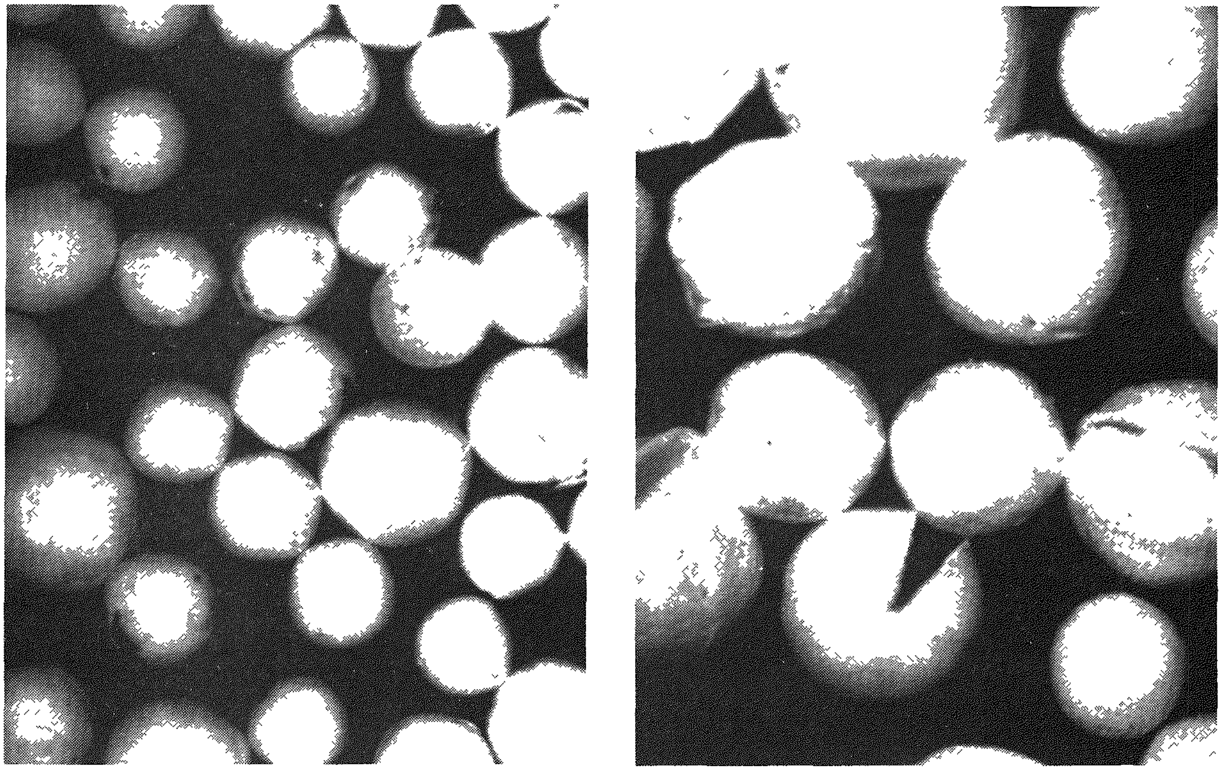

FIGURE 21 - Thorium dioxide obtained from 20-50 mesh cation exchange resins.

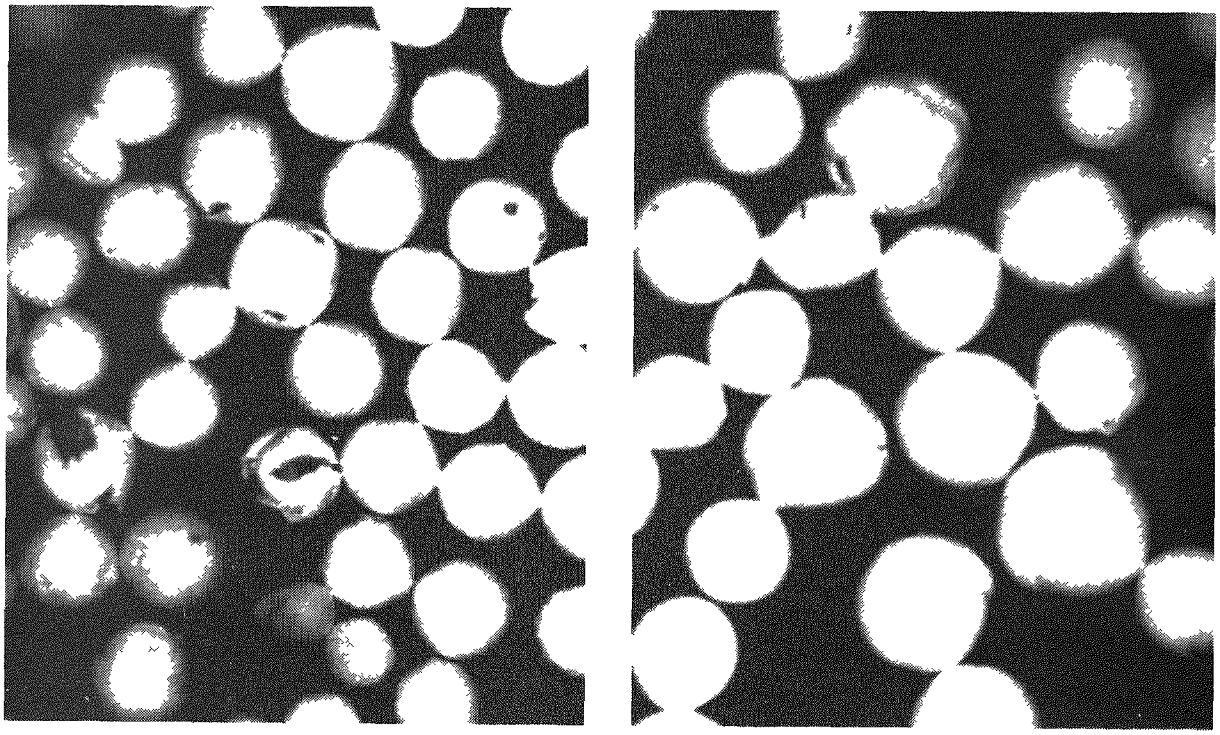

FIGURE 22 - Thorium dioxide obtained from 50-100 mesh cation exchange resins.

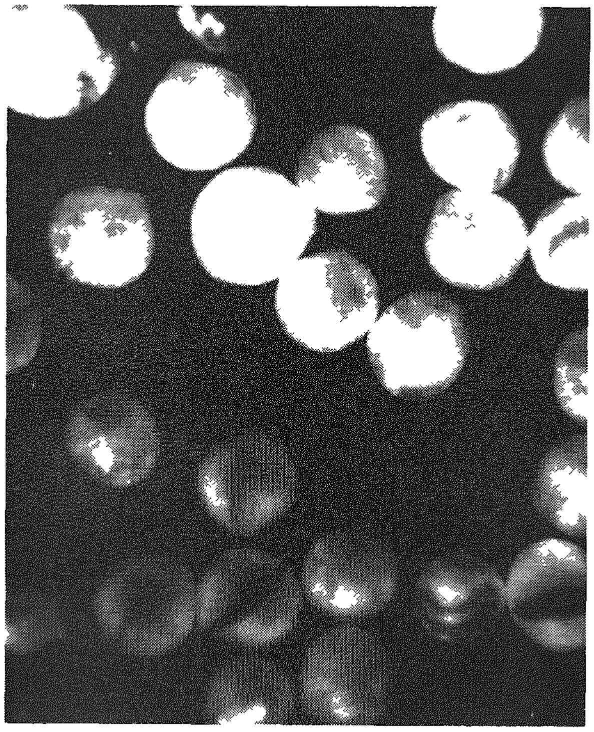

FIGURE 23 - Microparticles of magnesium oxide.

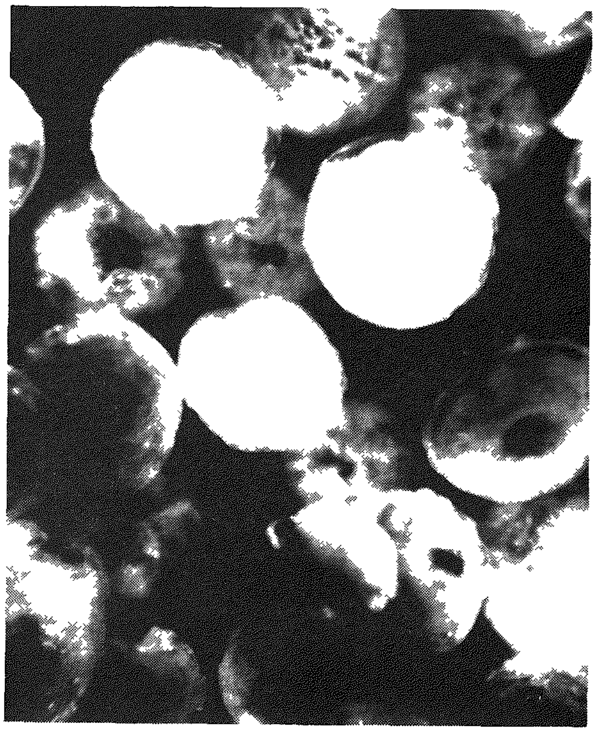

FIGURE 24 - Microparticles of aluminum oxide.

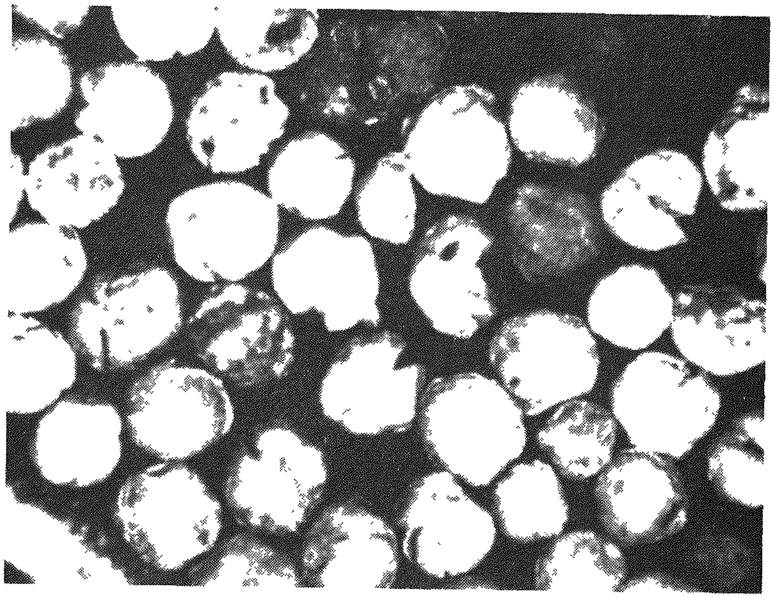

FIGURE 25 - Microparticles of cerium oxide.

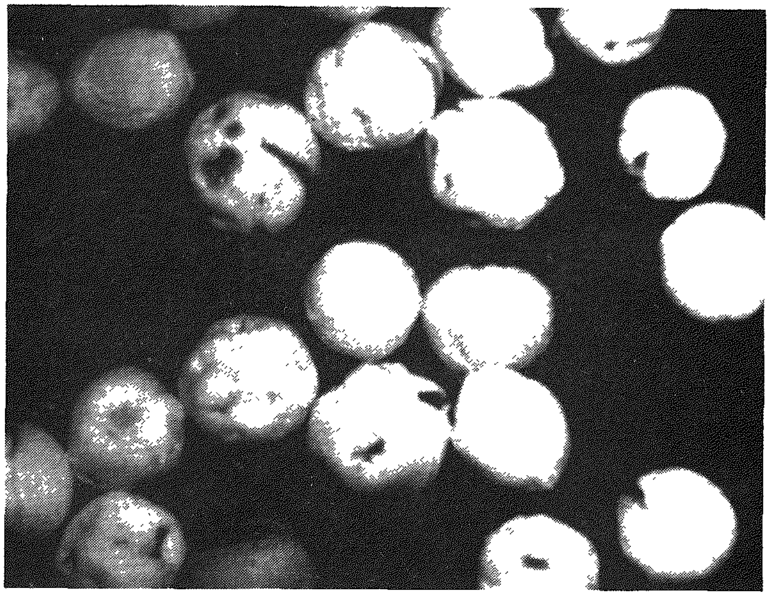

FIGURE 26 - Microparticles of lanthanum oxide.

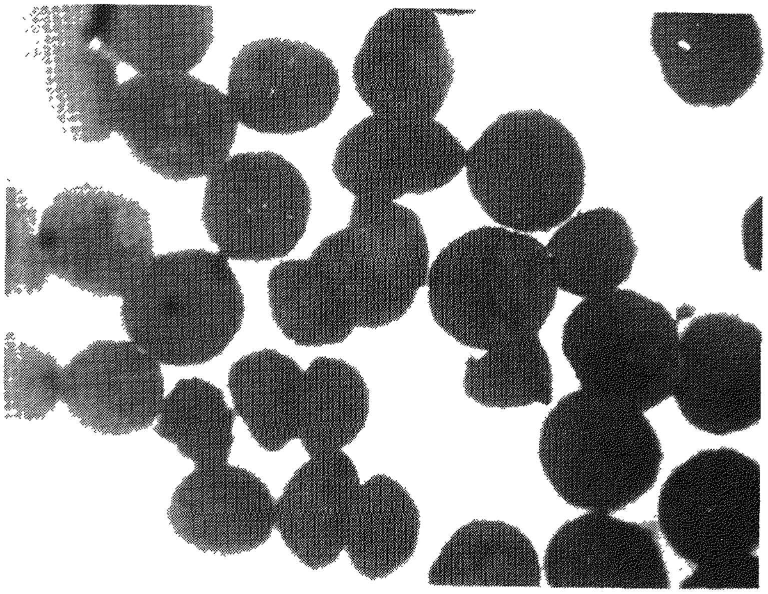

FIGURE 27 - Microparticles of uranium oxide.

# DISCUSSION

From such cursory examinations, as well as from knowledge of certain aspects of the chemistry of various elements, it would appear that certain generalizations concerning microparticle preparation might be possible. These might include: metals which might be good candidates for the production of oxide microparticles from loaded resins should not have low-melting carbonates or sulfates (when sulfonated resins are used), should not be easily reduced to the metallic state by carbon or carbon monoxide, and should not produce different oxides or allotropic forms under the preliminary reducing and later oxidizing conditions of the hot sintering tube.

The study of the preparation of oxide microparticles by ignition of metal-loaded cation exchange resins suggests possibilities for other preparations by this technique. One possibility is the preparation of oxide microparticles from metal-loaded anion exchange resins. As mentioned earlier, this technique was not successful when applied to the preparation of $PuO_2$ microparticles from anion exchange resins loaded with hexanitratoplutonate(IV). In this study there was no further experimentation with plutonium and anion exchange resins. A variety of possibilities remain unexplored, however.

The reason for the failure of the anion exchange technique to yield $PuO_2$ microparticles is not known. Possibly the presence of large amounts of nitrate in the resin prevents the smooth burning of the beads. Were this the case, anionic complexes of plutonium formed by carbonaceous radicals, such as citrate or tartrate, might yield better microparticles. Perhaps the diffusion rates of large plutonium anions are so slow that it is not possible to obtain an even distribution of plutonium in the resin in a reasonable time. This might result in structural abnormalities and weaknesses as the oxide microparticles are formed from the burning resin beads.

It would appear possible to produce certain carbonate and perhaps sulfate particles by the ion exchange procedure. It might also be possible to prepare fluoride microparticles, since fluorine is often capable of replacing oxygen in even the most stable oxides. It is possible, however, that oxygen could displace fluorine from metal fluorides under the hot reducing conditions of the burning organic resin. With these considerations in mind, an attempt was made to prepare $BeF_2$ microparticles by ignition of anion exchange resin beads loaded with the tetrafluoroberyllate anion.

A sample of AG1-X4, 50-100 mesh, was allowed to equilibrate for 24 hr in a solution containing a slight excess of beryllium chloride and a large excess of ammonium fluoride. When the resin was ignited, a white fluffy material resulted in which only fragments of microspheres were discernible. The material contained less than 1.5% fluorine.

# CONCLUSIONS

In conclusion, it appears that the method of preparing metal oxide microparticles by burning metal-loaded cation exchange resin beads can be made to yield gram quantities of material. Many factors are important in this process: degree of loading of the resin beads, sintering time and sintering temperature, among them. It is also important to use materials free from impurities, specifically transition metals such as iron and copper, if round and unbroken particles are desired.

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