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March 12, 1982

MEMORANDUM

TIS FILE
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TO: M. H. TENNANT

FROM: W. C. MOSLEY WC Mosley

USE OF CATION EXCHANGE RESINS FOR PRODUCTION OF U_3O_8 SUITABLE FOR THE Al-U_3O_8 POWDER METALLURGY PROCESS

INTRODUCTION

The Savannah River Laboratory has developed a powder metallurgy (PM) process for making reactor fuel tubes with cores containing mixtures of U_3O_8 and aluminum powders.[1] There are incentives for improving the PM process by eliminating the recycle of SRP enriched uranium (EU) at the Oak Ridge Y-12 Plant and the grinding and sieving steps used to produce U_3O_8 powder with suitable particle size distributions. Two alternative processes with potential for onsite recycle and suitable U_3O_8 particle sizing are a uranyl formate precipitation process[2] and a cation exchange resin process.[3] This memorandum describes the production of U_3O_8 powders from three types of cation exchange resins: Dowex 50W, a strong acid, sulfonate resin; AG MP-50, a macroporous form of sulfonate resin; and Bio-Rex 70, a weak acid, carboxylic resin. Properties of U_3O_8 powders made from these three resins are described along with those of U_3O_8 powders made by the present UO_3 conversion process and the formate process. Kilogram quantities of U_3O_8 powders are being prepared from these resins to determine how U_3O_8 properties influence Al-U_3O_8 core behavior during PM fabrication of reactor fuel tubes.

SUMMARY

Macroporous sulfonate resin, AG MP-50, can be used to produce U_3O_8 powder with properties suitable for PM fabrication of reactor tubes. This strong acid resin can be loaded directly from SRP enriched uranium solution and, therefore, offers promise for use in onsite recycle. Uranyl-loaded AG MP-50 resin is converted to U_3O_8 by heating in air to above 700°C. Conversion equipment must permit adequate contact between the resin and air to prevent smothering of the decomposition reactions and to allow complete combustion of the resin to form gaseous decomposition products. Otherwise, undesirable H_2S, elemental sulfur, and tar-like deposits can form.

The particle size distribution of the U_3O_8 powder can be controlled by sizing of resin. U_3O_8 powders made from normally supplied 50-100 and 100-200 mesh granular AG MP-50 resins have narrow particle size distributions within the range used in the PM process. U_3O_8 made from 50-100 mesh granules has a low fines content with less than 5 percent of the particles being smaller than 44 µm (less than 325 mesh). Wider U_3O_8 particle size distributions, if desired, can be achieved by mixing resin sizes. If narrower distributions are needed, special order resins with closely graded sizes can be used. U_3O_8 powders prepared from AG MP-50 resins have densities of about 4.0 g/cc like those prepared by the present 800°C UO_3 conversion process.

A weak acid carboxylic resin, Bio-Rex 70, may be preferred over AG MP-50 resin for controlling U_3O_8 particle size distributions if UO_3, rather than acidic uranyl nitrate solution, is the feed material. Uranyl-loaded Bio-Rex 70 resins thermally decompose more readily than AG MP-50 resins and do not produce sulfur-bearing emissions. U_3O_8 powders produced from 50-100 and 100-200 mesh granular Bio-Rex 70 resins have narrow particle size distributions like those produced from similarly sized AG MP-50 resins but densities are lower.

DOWEX 50W resins are not recommended for preparation of U_3O_8 for the PM process since conversion is more difficult than for AG MP-50 and Bio-Rex 70 resins, and the resultant oxide particles are low-density, hollow spheres or fragments of spherical shells.

BACKGROUND

Present Powder Metallurgy Process

The PM process for reactor tube fabrication involves blending ALCOA Type-101 aluminum powder with U_3O_8 powder, isostatically compacting the blended powders into Al-U_3O_8 cores, cladding the cores in aluminum alloy to form billets, vacuum outgassing the billets, and extruding the billets to form tubes. Figure 1 shows the particle shapes of the aluminum powder.[1] The aluminum particle size distribution, as determined by analysis with the HIAC Model PA-720 System, is shown in Figure 2. The equivalent spherical particle diameter at 50 volume percent, d (50), is 24 μm and the distribution appears symmetric. U_3O_8 for the PM process is presently produced by 800°C conversion of UO_3. Grinding and sieving are used to produce powder with all particles less than 149 μm, and with no more than 40 wt % of the particles smaller than 44 μm. U_3O_8 powder produced by this process is shown in Figure 3a. The particles consist of many small oxide grains about 0.5 μm in diameter. U_3O_8 powders produced by 800°C conversion of UO_3 have densities of 3.9-4.1 g/cc as determined from measurements of the volumes of 50-150 grams of powder tapped until settling ceased.

Effects of high temperature firing on properties of U_3O_8 produced from UO_3 have been studied briefly. U_3O_8 fired at 1400°C for 5 hours in air is shown in Figure 3b. U_3O_8 particles consist of large 5-20 μm grains. The particle size distribution (Figure 4) indicates a lower d(50) = 68 μm and is considerably narrower and more symmetric than that of U_3O_8 produced by conversion of UO_3 at 800°C. U_3O_8 fired at 1400°C has a powder density of 3.5 g/cc.

Several improvements in the PM process are being considered. Presently, SRP EU solution from reprocessing is shipped in a large tank trailer to the Oak Ridge Y-12 Plant where it is concentrated and thermally denitrated to produce UO_3 for return to SRL. Adverse effects of an accident involving the tank trailer have prompted consideration of development of an onsite recycle capability at SRP to produce U_3O_8 suitable for the PM process. Also, the possibility of eliminating the grinding and sieving steps in the PM process is being investigated because of material accountability problems and environmental hazards caused by U_3O_8 fines.

Uranyl Formate Process

An alternate process for making U_3O_8 powder with a particle size distribution suitable for the PM process is based on precipitation and calcination of uranyl formate monohydrate.[2] A facility has been built by the Actinide Technology Division (ATD) for producing kilogram batches of U_3O_8 by this uranyl formate process. In concept, SRP EU solution would have to be concentrated and denitrated to provide feed for the formate process. Presently, UO_3 powder is dissolved in hot, dilute formic acid to produce a starting solution. Formic acid concentration is then increased to precipitate uranyl formate monohydrate while the slurry is agitated to prevent agglomeration of large particles. The precipitate is then filtered, washed, and calcined at 800°C to produce U_3O_8 powder. Conversion of dry uranyl formate monohydrate to U_3O_8 involves a weight loss of 26.2%.

U_3O_8 powder made from uranyl formate monohydrate by conversion at 800°C is shown in Figure 5a. The U_3O_8 particles have the shapes of the parent uranyl formate monohydrate crystals and consist of 0.5 µm grains. The particle size distribution is broad and symmetric with d(50) = 65 µm as shown in Figure 6. U_3O_8 powder density is 2.6 g/cc.

Properties of U_3O_8 made by the formate process are significantly changed by high temperature firing. Figure 5b shows formate-based U_3O_8 after firing at 1400°C for 5 hours in air. U_3O_8 particles consist of 5-30 µm grains. The particle size distribution (Figure 6) is considerably narrower than that of U_3O_8 from uranyl formate calcination at 800°C. However, d(50) = 62 µm is only slightly lower than the value of 65 µm determine for U_3O_8 from 800°C conversion. Density of the U_3O_8 powder fired at 1400°C is 3.8/cc.

Resin Process

The concept of preparing oxide powders with controlled particle size distributions from sized ion exchange resin can be applied to production of U_3O_8 suitable for the PM process. The ability to load strong acid resin directly from SRP EU solution would facilitate onsite recycle. In 1980, the Nuclear Engineering Division (NED) began to investigate the production of U_3O_8 from Dowex 50W resins. In January 1981, the Hydrogen and Ceramics Technology Division (HCTD) was asked to assist in this investigation. AG MP-50 resins were found to produce better U_3O_8 powders than the Dowex 50 resins. In January 1982, NED requested that a resin process be considered for production of U_3O_8 powder for the PM process separate from onsite recycle applications. Studies began on production of U_3O_8 from weak acid Bio-Rex 70 resins that could be loaded from feed made from UO_3 rather than from acidic SRP EU solution. The HCTD approach has been to characterize the thermal decomposition of uranyl-loaded resins and determine the properties of the resultant U_3O_8 powders. Resin decomposition was investigated using a Du Pont Model 950 Thermogravmetric Analyzer and a variety of heating tests. U_3O_8 powder characteristics such as particle shape, particle size distribution, grain size, and powder density were determined as functions of resin type, resin loading, and conversion parameters.

Kilogram quantities of U_3O_8 powders are being prepared from 50-100 mesh uranyl-loaded Dowex 50W, AG MP-50, and Bio-Rex 70 resins to determine how U_3O_8 properties influence Al-U_3O_8 core behavior during PM fabrication of reactor fuel tubes. Results of these fabricability tests will be reported later.

DISCUSSION

Production of U_3O_8 From Dowex 50W Resins

Description of Dowex 50W Resins

Dowex 50W resins are strong acid cation exchangers composed of sulfonic acid exchange groups attached to a styrene divinylbenzene polymer lattice. Commercial grade Dowex 50W resins were purchased from Bio-Rad Laboratories of Richmond, California, in the hydrogen form as sized beads. U_3O_8 was prepared from 50-100 mesh resin beads containing 2% (X2), 8% (X8), and 12% (X12) of a crosslinking agent. Resin with a low percentage of the crosslinking agent has a more open structure, imbibes more water, has a lower resistance to shrinking and swelling, and has a lower wet volume capacity than resin with a high percentage of the crosslinkage agent. Some U_3O_8 was also prepared from 20-50 mesh beads.

Resin Loading

Prior to loading, Dowex 50W resins were rinsed several times with 1 M HNO_3 and several times with H_2O to remove fines. Resins were loaded by gravity flow using two types of uranyl nitrate feed solutions. Feed No. 1 was made by dissolving uranyl nitrate in water to produce a uranium concentration of 50 grams per liter. Feed No. 2 consisted of uranyl nitrate solution with 7 grams of uranium per liter and 0.2 M nitric acid to simulate SRP EU solution. Dowex 50W-X8 resin as 50-100 mesh beads loaded with Feed No. 1 contained about 250 grams of uranium per liter of wet resin; the same resin loaded from Feed No. 2 contained about 150 grams of uranium per liter of wet resin. About 1500 grams of uranium were loaded from Feed No. 1 onto 50-100 mesh Dowex 50W-X8 resin in three two-liter batches. Smaller batches of several hundred milliliters of 20-50 mesh Dowex 50W-X8 resin and 50-100 mesh Dowex 50W-X2 and 50W-X12 resins were also loaded from Feed No. 1.

Uranyl-loaded Dowex 50W resins were dried by pulling air through the resin beds at room temperature but the resulting materials were somewhat sticky. Heating at 250°C produced freely flowing powders. Dried 50-100 mesh resins had powder densities of to 1.5 g/cc.

Thermogravimetric analysis (TGA) of 50 mg samples of uranyl-loaded Dowex 50W resins (Figure 7) showed that complete conversion to U_3O_8 required heating to above 700°C in air. Studies of conversion kinetics using TGA showed that resin had to be heated at 900°C for at least ten minutes to produce complete decomposition to U_3O_8. However, when large batches of resins were heated in air at 1000°C for ~4 hours, conversion to U_3O_8 was complete only when the resin beds were less than 1/4 inch thick. During conversion, some resin beads would ignite on heating above 500°C, become white hot, and eject from the resin bed. This behavior has been noted in other studies with Dowex 50W resin.[3]

The weight loss on conversion of uranyl-loaded Dowex 50W-X8 is a function of the uranium loaded on the resin as shown in Figure 8. TGA also shows that decomposition occurs in four stages. Heating up to 300°C produces mostly dehydration. A second stage between 300 and 450°C and a third stage between 450 and 600°C correspond to resin combustion which produce oxide with U_3O_8 structure but with some residues including sulfur. Final conversion to U_3O_8 free of residues requires heating to above 800°C. Thus, the decomposition of uranyl-loaded resin differs from that of Dowex 50W resin loaded with trivalent actinides and lanthanides which form oxysulfates when decomposed at 800-1000°C.[4] TGA was performed using 50-100 mesh beads since the ignition of 20-50 mesh beads above 350°C caused material to be ejected from the sample pan and prevented accurate weight loss measurements.

Gases evolved during decomposition of uranyl-loaded Dowex 50W-X8 have not been analyzed completely, but are expected to include H_2O, CO, CO_2, SO_2, SO_3, H_2S, and possibly, hydrocarbons. The exact composition will depend on the availability of oxygen. The H_2S component was confirmed by precipitation of CdS in an ammoniacal cadmium chloride solution in a bubbler in an off-gas line. In some tests, decomposition of H_2S causes sulfur deposits to form on cool surfaces of exhaust lines. In early conversion studies, Inconel® pans used to hold the resin were destroyed by reaction with H_2S or sulfur. Therefore, subsequent conversions were performed using Al_2O_3 dishes, platinum pans, and quartz tubes which did not react with the sulfur-bearing gases. One kilogram of U_3O_8 was prepared for PM reactor tube fabricability tests by slowly heating small batches (<1/4 in. deep in Al_2O_3 dishes) to 1000°C in air and holding for 4 hours.

U_3O_8 Made from Uranyl-Loaded Dowex 50W Resins

U_3O_8 powders produced by conversion of 50-100 mesh, uranyl-loaded Dowex 50W-X2, 50W-X8, and 50W-X12 resins at 1000°C retain the spherical resin bead shapes as shown in Figure 9a-c. However, the U_3O_8 particles are highly porous. Some have hollow centers.

Many consist of concentric spherical shells. The observation of many fragments of originally spherical particles indicates the strength of this oxide is low. Oxide grain sizes were generally 1 μm or less, although some grains in U_3O_8 produced from Dowex 50W-X8 resin were as large as 2 μm. An estimated 75% of the U_3O_8 particles made from 50-100 mesh Dowex 50W-X8 resin were larger than the 149 μm upper limit desired for the PM process (Figure 10). The powder densities of oxides made from Dowex 50W resins at 1000°C varied from 1.7 to 2.6 g/cc. Powder density of U_3O_8 from Dowex 50W resin is probably a function of several variables including uranium loading, resin properties, conversion process parameters, and particle fracturing.

When U_3O_8 made from 50-100 mesh Dowex 50W-X8 resin at 1000°C was fired at 1400°C in air for about 4 hours, sintering caused the particles to densify and oxide grains to grow as shown in Figure 9d. Most of the particles were fragments of spherical shells present in the U_3O_8 produced at 1000°C. Oxide grains were generally larger than 5 μm. The particle size distribution (Figure 10) was broad and symmetric with d (50) = 65 μm. About 6% of the oxide particles were larger than 149 μm and none were larger than 200 μm. Firing at 1400°C increased the powder density to 3.0 g/cc.

Behavior of U_3O_8 Made From Dowex 50W-X8 During PM Tube Fabrication

One full-size reactor tube has been successfully extruded with an Al-U_3O_8 core containing U_3O_8 made by 1000°C conversion of uranyl-loaded, 50-100 mesh Dowex 50W-X8 resin. X-ray examination indicated the core contained high-density areas because of inhomogeneous U_3O_8 distribution. Metallographic examinations of tube sections are planned to characterize the core structure.

Production of U_3O_8 From AG MP-50 Resins

Description of AG MP-50 Resins

AG MP-50 resin is a macroporous form of a strong acid cation exchanger. It has a chemical composition similar to that of Dowex 50W resin. Analytical grade resins were purchased from Bio-Rad Laboratories in the hydrogen form. The 20-50 mesh resin was supplied as spherical beads while the smaller sizes were granules produced by grinding the 20-50 mesh beads.

Resin Loading

AG MP-50 resin loading procedures were similar to those used for loading Dowex 50W resins. Resins loaded with Feed No. 1

contained about 220 grams of uranium per liter of wet resin; loading with Feed No. 2 resulted in resin containing about 170 grams of uranium per liter of wet resin. About 2400 grams of uranium were loaded from Feed No. 1 onto 50-100 mesh resin in six batches. Each batch consisted of about two liters of wet resin and produced a bed depth of about ten inches. Small batches of several hundred milliliters of 20-50, 100-200 and 200-400 mesh resins were also loaded using Feed No. 1.

Uranyl-loaded AG MP-50 resins were dried by pulling air through the resin beds at room temperature to form freely flowing powders. Densities of 0.8 g/cc were determined for 50-100 mesh resin loaded with both Feed No. 1 and Feed No. 2.

Conversion of Uranyl-Loaded AG MP-50 Resins to U_3O_8

TGA (Figure 7) showed that conversion of uranyl-loaded AG MP-50 resin to U_3O_8 occurs in four stages similar to those observed during thermal decomposition of uranyl-loaded Dowex 50W resin. Heating to 300°C produced mostly dehydration. The second and third stages at about 300-350°C and 350-380°C, respectively, occurred at significantly lower tmperatures than the corresponding decomposition stages for Dowex 50W resins. The third decomposition stages was slightly exothermic. As observed for Dowex 50W resins, AG MP-50 resins had to be heated to above 700°C to produce U_3O_8 free of residues. TGA studies of resin conversion kineties showed that heating at 900°C for four minutes was sufficient to cause complete decomposition to U_3O_8. Weight loss on conversion to U_3O_8 varied with resin loading as shown in Figure 11.

During conversion of large batches of 50-100 mesh, uranyl-loaded AG MP-50 resin, resin layers had to be less than 1/2-inch thick to get complete decomposition to U_3O_8 on heating to 1000°C in air. About 1200 grams of U_3O_8 for PM fabrication tests were made by a two-step process. First, 50-60 gram batches of resin were roasted at 600-700°C for 15-20 hours to produce over 75% conversion, over nine-fold reduction in volume and material with UO_3 structure. Then, several batches were combined and heated at 1000°C for 4-5 hours to complete the conversion to U_3O_8. During these two-step conversions, no material was ejected from the resin beds as had been observed during conversion of DOWEX 50W resins. However, a thin crust of a yellow-green material, identified by x-ray diffractometry as $UO_2SO_4 \cdot 2.5\ H_2O$, formed on the tops of some batches during roasting. The uranyl sulfate probably formed by reaction between SO_3 generated by combustion of resin sulfonic acid groups and the UO_3 intermediate decomposition product. Hydration of the uranyl sulfate may have occurred by adsorption of moisture between sampling and analysis. TGA showed that $UO_2SO_4 \cdot 2.5\ H_2O$, dehydrated at 100-400°C and decomposed to U_3O_8 at 600-800°C.

Continuous conversion of 50-100 mesh, uranyl-loaded AG MP-50 resin to U_3O_8 was demonstrated using a small rotary calciner operating at 1000-1100°C. The calciner consisted of a 1-inch diameter by 24-inch long quartz tube inclined at an angle of 24° through a furnace with a 10-inch long hot zone. Loaded resin was fed into the upper end of the tube. Internal fins 1/8-inch high on the interior of the tube retained the resin in the hot zone. As the tube rotated slowly, the resin advanced through the calciner, was converted to U_3O_8, and collected at the lower end. In three hours, 96 grams of resin were converted to 23.6 grams of U_3O_8. TGA of the product showed no weight loss, indicating complete conversion to U_3O_8. During operation of the rotary calciner, a yellow flame appeared in the quartz tube when resin was fed in at too fast a rate. Also, a black, tar-like deposit from incomplete resin combustion formed on the cool ends of the tube.

In a test to determine the composition of gases evolved during combustion of AG MP-50 resin loaded from Feed No. 2, air was passed over resin heated at <10°C per minute to 950°C and the exhaust was bubbled through ammoniacal cadmium chloride solution. White fumes, possibly ammonium sulfite or sulfate, were emitted from the bubbler when the resin was heated between 325 and 700°C. Cadmium sulfide precipitated when the resin was heated between 360 and 570°C. No black, tar-like deposit formed on the cool end of the combustion tube, but a small amount of a yellow solid, probably sulfur, was noted when the resin was at 480°C. During this test, 28.8 grams of loaded resin were completely converted to 7.0 grams of U_3O_8. 1.03 grams of CdS were recovered from the bubbler corresponding to evolution of 0.24 grams of H_2S (i.e., 0.034 grams of H_2S per gram of U_3O_8 produced).

U_3O_8 Made From AG MP-50 Resins

U_3O_8 powder made from 20-50 mesh AG MP-50 resin consisted of fragments of originally spherical beads (Figure 12). Many spheres were hollow, indicating that only the outer 100 µm layers were loaded with uranium. U_3O_8 powders made from 50-100, 100-200 and 200-400 mesh resins had the granular form of the parent resins and appeared to be uniformly loaded with uranium (Figure 13). Some of the larger U_3O_8 particles made from 50-100 mesh resin showed surface fracturing similar to that observed in particles made from the larger 20-50 mesh beads. Particle size distributions of U_3O_8 powders made from 50-100, 100-200, and 200-400 mesh granular resins were narrow and symmetric as shown in Figure 14 and corresponded to d(50) sizes of 86, 58, and 35 µm, respectively. U_3O_8 particles made by conversion of uranyl-loaded AG MP-50 resin at 1000°C consisted of spherical grains <1 µm in diameter. Powder densities of different 30-100 gram batches of oxide varied from 1.8 g/cc to 4.1 g/cc as shown in Figure 15. This variability in powder density appears to be related to some subtle differences within the two-liter resin batches during loading (especially batches No. 1 and No. 3) rather than being caused by differences in the amount of uranium loaded on the resin.

When U_3O_8 made by 1000°C conversion of 50-100 mesh, uranyl-loaded, AG MP-50 resin was fired at 1400°C for 5 hours, there was very little change in the particle size distribution (Figure 16) and d(50) increased only slightly to 93 µm. Grain size of the U_3O_8 particles increased to 3-6 µm (Figure 17). However, powder density variability decreased significantly. A batch of U_3O_8 with a low powder density of 2.8 g/cc after 1000°C conversion had a density of 3.8 g/cc after firing while the high powder density of 4.1 g/cc of another batch was unchanged by firing. About 500 grams of U_3O_8 prepared from 50-100 mesh, uranyl-loaded AG MP-50 resin and fired at 1400°C for 5 hours will be used to determine how the properties U_3O_8 affect Al-U_3O_8 core behavior during PM reactor tube fabrication.

Production of U_3O_8 From BIO-REX 70 Resins

Description of Bio-Rex 70 Resins

Bio-Rex 70 resin is a weak-acid cation exchanger containing carboxylic acid exchange groups on a macroreticular acrylic polymer lattice. Analytical grade resins were purchased from Bio-Rad Laboratories in the sodium form as 50-100, 100-200, and 200-400 mesh granules.

Resin Loading

Techniques for uranium loading of Bio-Rex 70 resins were different from those used to load Dowex 50W and AG MP-50 strong acid resins. Bio-Rex 70 resins were converted to the ammonium form by rinsing with ammonium nitrate solution. Fines were removed by rinsing several times with water. Resins were loaded by gravity flow using water solutions of uranyl nitrate containing about 50 grams of uranium per liter and adjusted with NH_4OH to a pH of 2.5. About 1200 grams of uranium were loaded onto 50-100 mesh resin in three batches. Each batch consisted of about two liters of resin and formed a bed about ten inches deep. Smaller batches of 100-200 and 200-400 mesh resin were also loaded. Uranyl-loaded Bio-Rex 70 resins were dried by pulling air through the resin beds at room temperature to form freely flowing powders. Dried, 50-100 mesh resin had a powder density of 0.7 g/cc.

Conversion of Uranyl-Loaded Bio-Rex 70 Resin to U_3O_8

TGA showed that conversion of uranyl-loaded Bio-Rex 70 resin to U_3O_8 involved a significantly lower weight loss than those measured during conversion of uranyl-loaded Dowex 50W and AG MP-50 resins (Figure 7). Conversion occurred in at least five stages. Heating to 240°C produced dehydration. Between 240 and 300°C, the first stage of resin combustion produced a gradual weight loss. At 300°C, resin decomposition proceeded rapidly and became exothermic. Resin residues were burned out between 300 and 400°C and at a slower rate above 400°C. No further weight loss was detected on heating above 700°C. About 1200 grams of U_3O_8 was produced by heating 150-gram batches of 50-100 mesh, uranyl-loaded, Bio-Rex 70 resin in 1/2-inch layers up to 1000°C in air. Tests showed that complete decomposition to U_3O_8 could be achieved with resin layers up to 2 1/2-inches thick. Resin combustion between 300 and 600°C was accompanied by emission of dense, white fumes. When the heating rate between 300 and 600°C exceeded about 3°C per minute, the resin ignited and emitted a black soot that deposited on cool portions of the furnace. However, the soot burned off on heating above 700°C. Only the white fumes were emitted between 300 and 600°C when the heating rate was less than 3°C per minute. No effort was made to determine the composition of the fumes. Possible gaseous components include H_2O, CO, CO_2, and hydrocarbons. Small batches of about 50 milliliters of 100-200 and 200-400 mesh, uranyl-loaded Bio-Rex 70 resin were also converted to U_3O_8 by heating to 1000°C in air.

U_3O_8 Made From Uranyl-Loaded Bio-Rex 70 Resins

U_3O_8 powders made by 1000°C conversions of uranyl-loaded Bio-Rex 70 resins are shown in Figure 18. Particle size distributions shown in Figure 19 are almost exactly like those of U_3O_8 powders made from similarly sized AG MP-50 resins. Powders prepared from 50-100, 100-200, and 200-400 mesh granules have d(50) sizes of 86, 53, and 35 μm, respectively. However, densities of these powders of 1.9-2.1 g/cc are considerably lower than those measured for U_3O_8 powders made from AG MP-50 resins. U_3O_8 particles produced from uranyl-loaded Bio-Rex 70 resins at 1000°C consist of oxide grains <1 μm in size. Extensive micron-size porosity accounts for the low powder densities. The many particles crushed during preparation of SEM specimens indicate that these U_3O_8 particles are not very strong.

When U_3O_8 powder produced by 1000°C conversion of uranyl-loaded Bio-Rex 70 resin was fired at 1400°C for 5 hours, there was only a small change in the sizes and shapes of the oxide particles (Figure 20). As shown in Figure 21, firing shifted the particle-size distribution of U_3O_8 powder made from 50-100 mesh resin towards smaller particle sizes corresponding to a decrease in d(50) to 74 µm. Particle size distributions of U_3O_8 powders made from 100-200 and 200-400 mesh resins were essentially unaffected. During 1400°C firing, oxide grains grew to larger than 2 µm and porosity decreased resulting in powder with a density of 3.7 g/cc.

Future Development

HCTD and NED will conduct tests to determine how the properties of U_3O_8 powders made from cation exchange resins affect core behavior during PM fabrication of reactor fuel tubes. G. A. Burney of the Actinide Technology Division has assisted in loading kilogram quantities of uranium onto 50-100 mesh AG MP-50 and Bio-Rex 70 resins. HCTD has converted these uranyl-loaded resins to U_3O_8 by heating 50 gram batches at 1000°C in air. Some of the U_3O_8 powders prepared from these resins along with U_3O_8 prepared by 800°C conversion of UO_3 have been fired at 1400°C for 5 hours in air to increase particle strength. Batches of about 500 grams of these low-temperature-prepared and high-temperature-fired U_3O_8 powders were provided to NED. These quantities are sufficient for fabricating "mini"-billets with Al-U_3O_8 cores containing 62.5 wt % U_3O_8. The "mini"-billets will be extruded into thin-wall tubes in the Fabrication Development Laboratory. HCTD will assist NED in characterizing the structures of the Al-U_3O_8 cores in the tubes and correlating these results with U_3O_8 powder properties.

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TABLE I.

Properties of U_3O_8 Powders

Source	d(50) μm	$-\sigma$(1) μm	$+\sigma$(2) μm	Grain Size μm	Powder Density g/cc
AG MP-50, 50-100 Mesh, 1000°C	86	24	31	0.5-1	2.8-4.1
AG MP-50, 50-100 Mesh, 1400°C	94	25	31	3-6	3.8-4.1
AG MP-50, 100-200 Mesh, 1000°C	59	17	21	0.5-1	3.8
AG MP-50, 100-200 Mesh, 1400°C	58	14	17	3-6	4.0
AG MP-50, 200-400 Mesh, 1000°C	36	11	9	0.5-1	3.8
AG MP-50, 200-400 Mesh, 1400°C	37	10	13	3-6	3.9
Bio Rex 70, 50-100 Mesh, 1000°C	86	24	28	0.5-1	2.0-2.4
Bio Rex 70, 50-100 Mesh, 1400°C	74	22	24	2-6	3.0
Bio Rex 70, 100-200 Mesh, 1000°C	53	11	13	0.5-1	2.1
Bio Rex 70, 100-200 Mesh, 1400°C	56	14	18	2-6	—
Bio Rex 70, 200-400 Mesh, 1000°C	35	7	8	0.5-1	1.9
Bio Rex 70, 200-400 Mesh, 1400°C	35	10	14	2-6	—
Dowex 50W-X2, 50-100 Mesh, 1000°C	—	—	—	0.5	1.8
Dowex 50W-X8, 50-100 Mesh, 1000°C	>150	—	—	0.5-2	1.7-2.6
Dowex 50W-X8, 50-100 Mesh, 1400°C	65	27	49	3-15	3.0
Dowex 50W-X12, 50-100 Mesh, 1000°C	—	—	—	0.5	2.1
Uranyl Formate Monohydrate, 800°C	66	36	57	0.5	2.6
Uranyl Formate Monohydrate, 1400°C	62	27	32	5-30	3.8
UO_3, 800°C(3)	82	57	68	0.5	3.9-4.1
UO_3, 1000°C(3)	—	—	—	—	3.7
UO_3, 1400°C(3)	68	26	37	5-20	3.5
Type 101 Aluminum	24	8	9	2-40	—

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(1) $-\sigma = d(50) - d(16)$

(2) $+\sigma = d(84) - d(50)$

(3) Ground and sieved after 800°C conversion

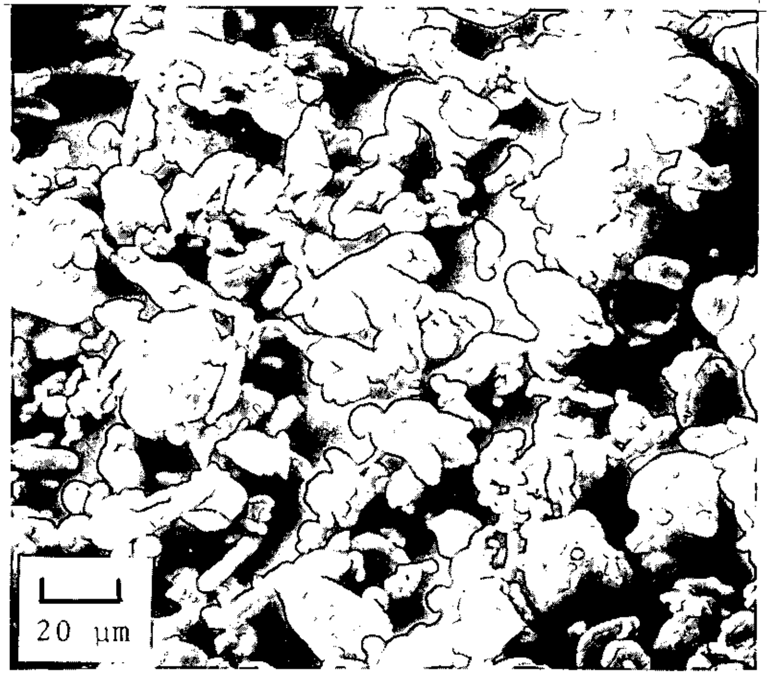


Figure 1. ALCOA Type 101 Aluminum Powder Used in PM Process

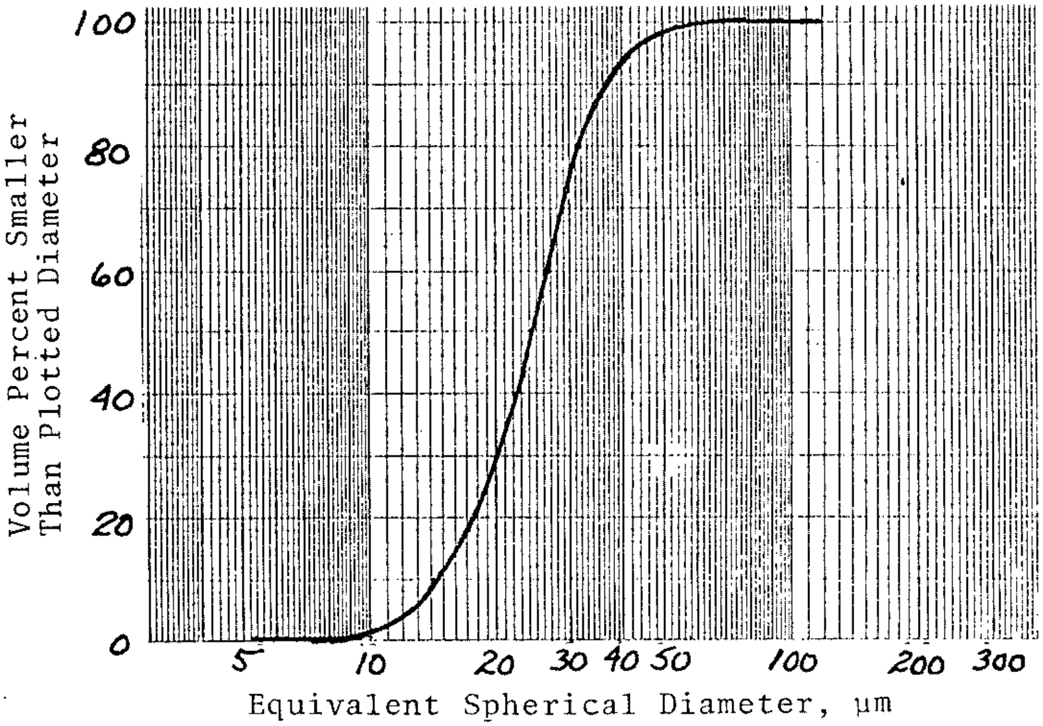
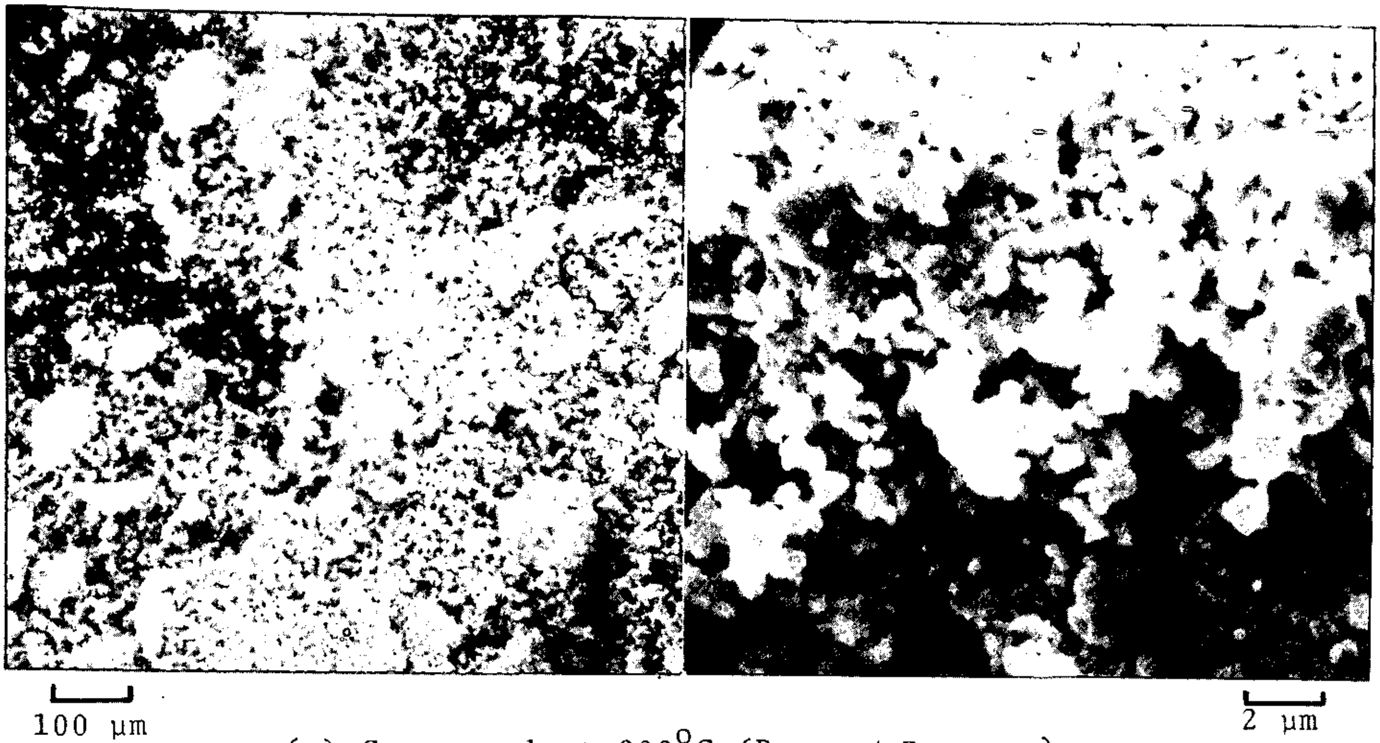


Figure 2. Particle Size Distribution of ALCOA Type 101 Aluminum Powder



(a) Converted at 800°C (Present Process)

(b) Fired at 1400°C

Figure 3. U_3O_8 Powder Produced From UO_3

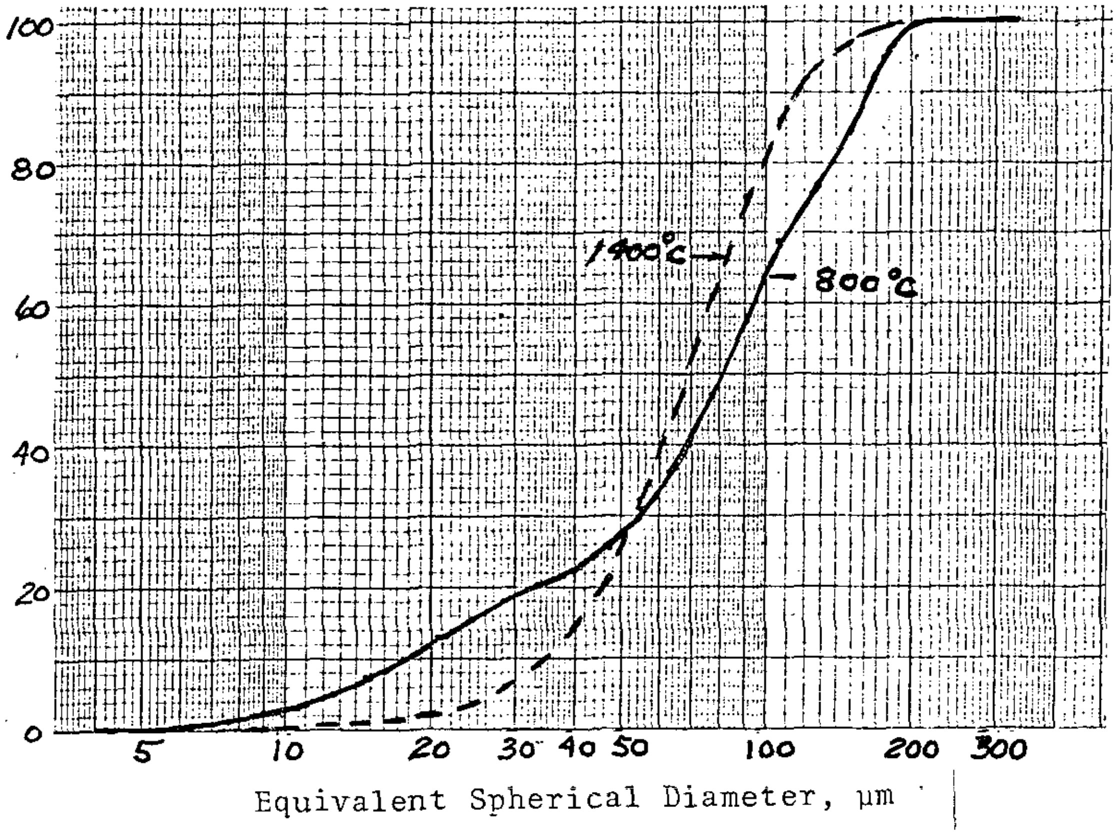
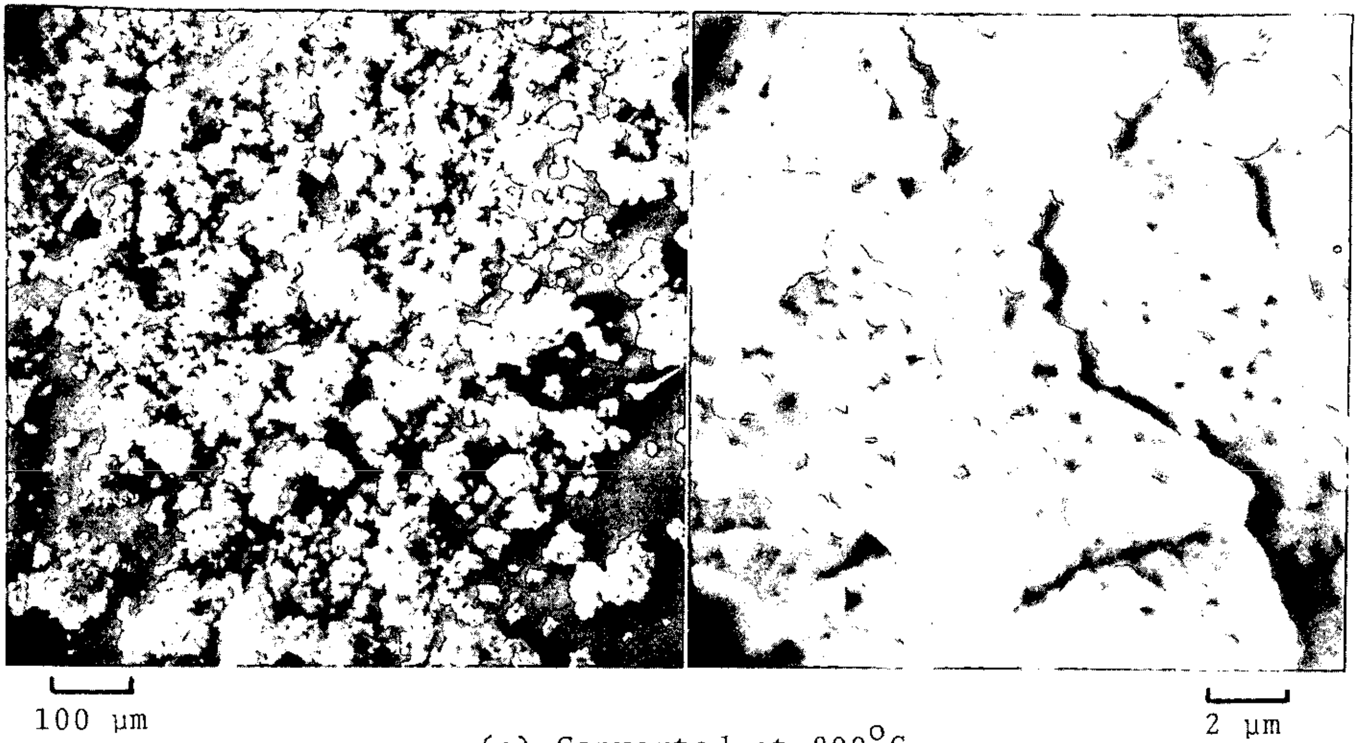
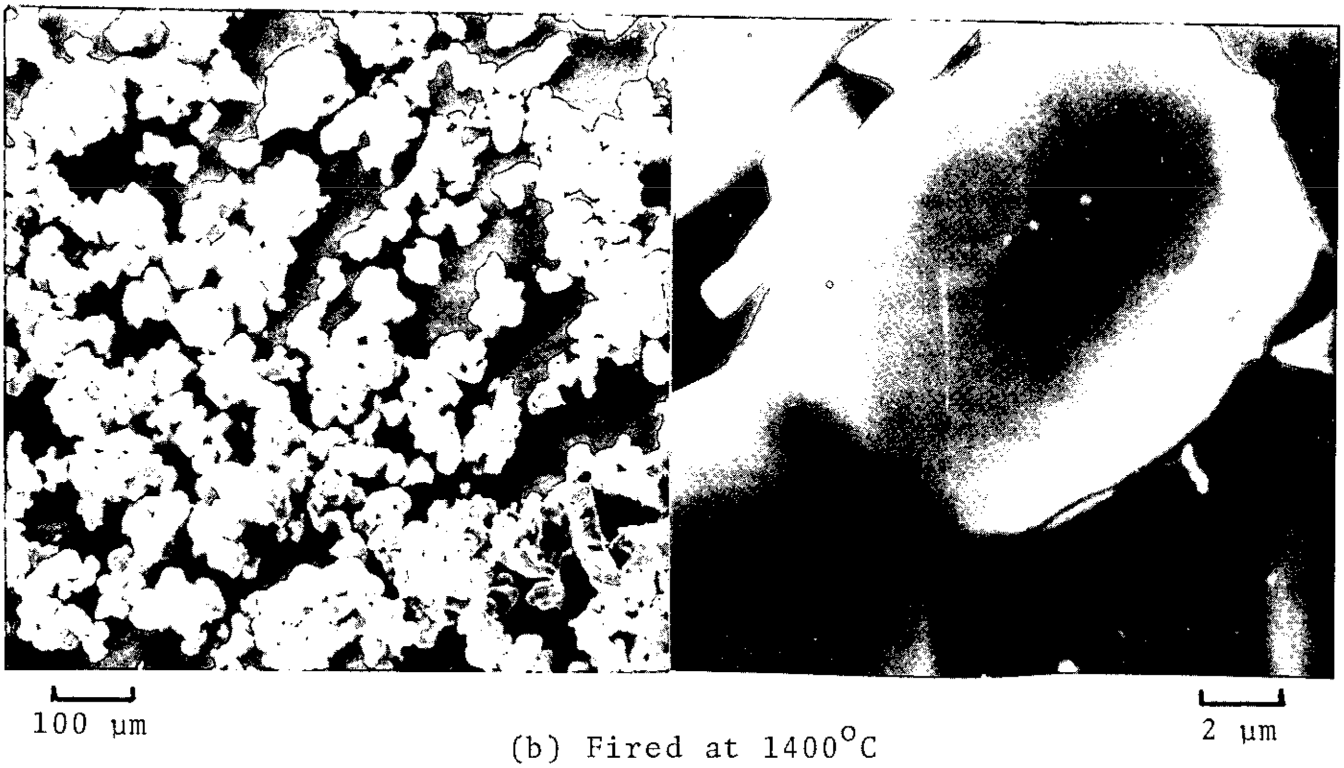


Figure 4. Particle Size Distributions of U_3O_8 Powders Prepared by 800°C Conversion of UO_3 (Present Process) and After Firing at 1400°C.



(a) Converted at 800°C



(b) Fired at 1400°C

Figure 5. U_3O_8 Powders Prepared From Uranyl Formate Monohydrate

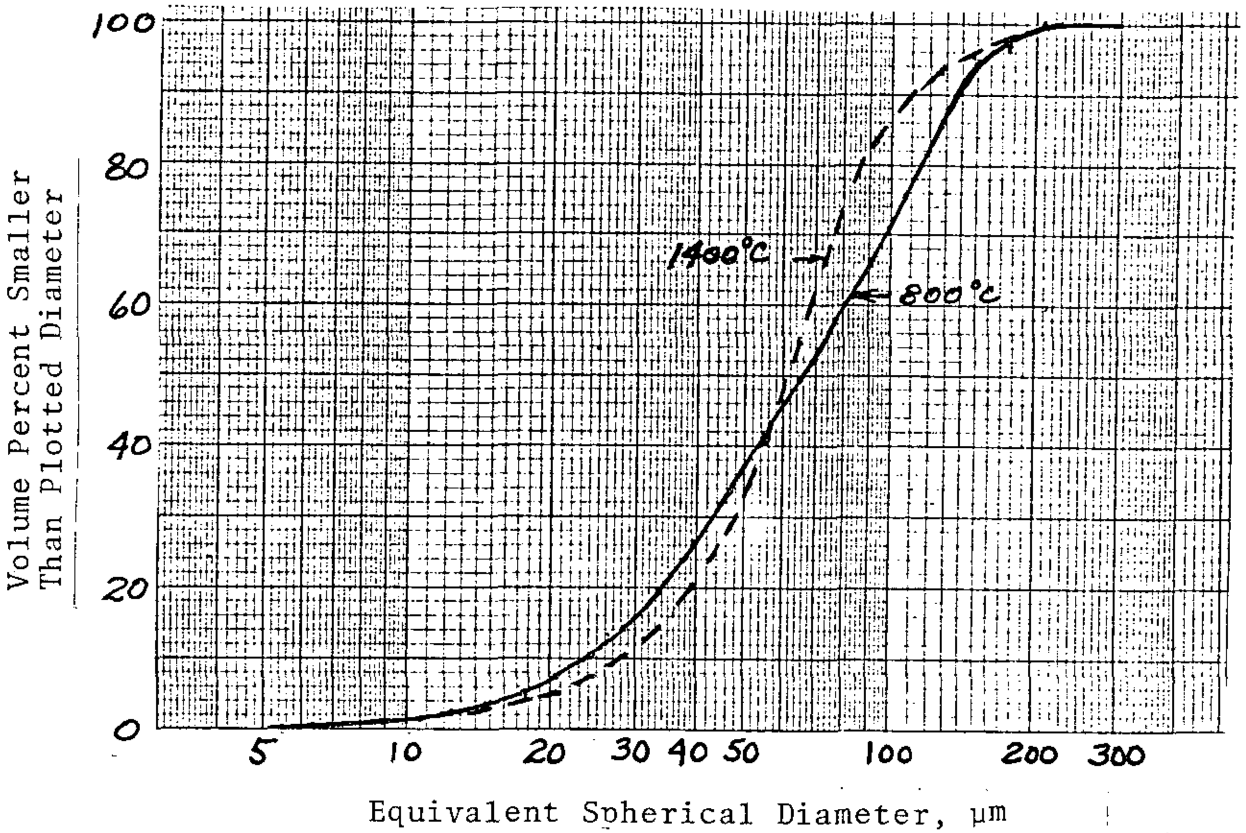


Figure 6. Particle Size Distribution of U_3O_8 Powders Produced by 800°C Conversion of Uranyl Formate Monohydrate and After Firing at 1400°C.

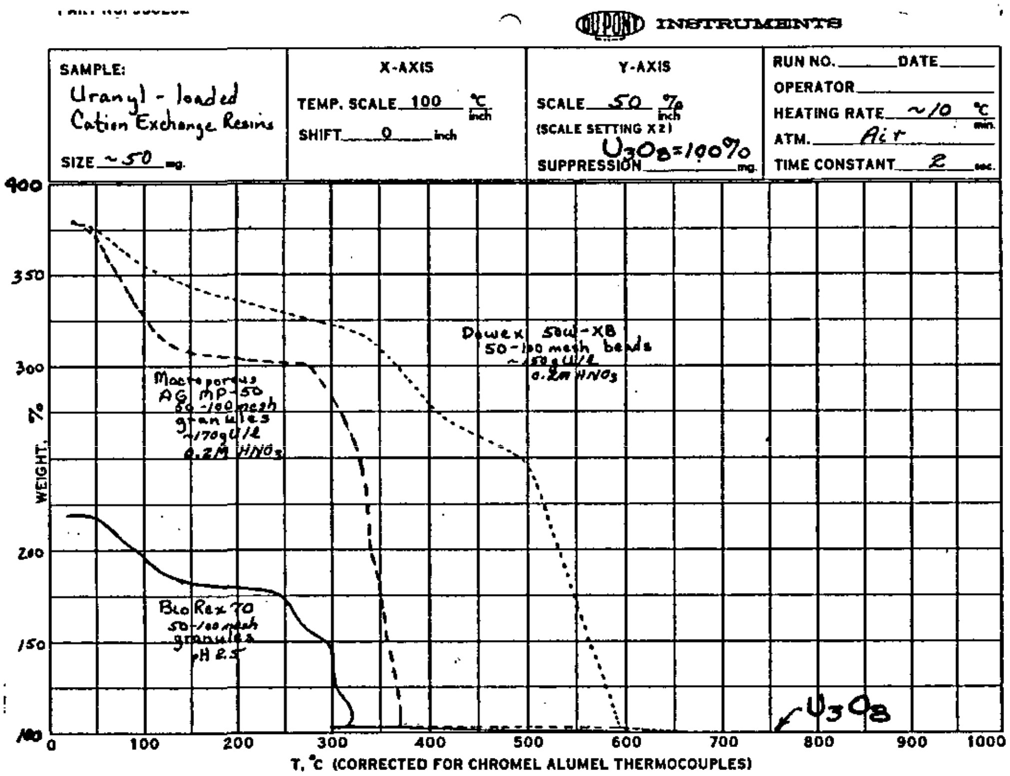


Figure 7. Thermogravimetric Analyses of 50-100 Mesh, Uranyl-Loaded DOWEX 50W-X8, AG MP-50 and Bio-Rex 70 Resins

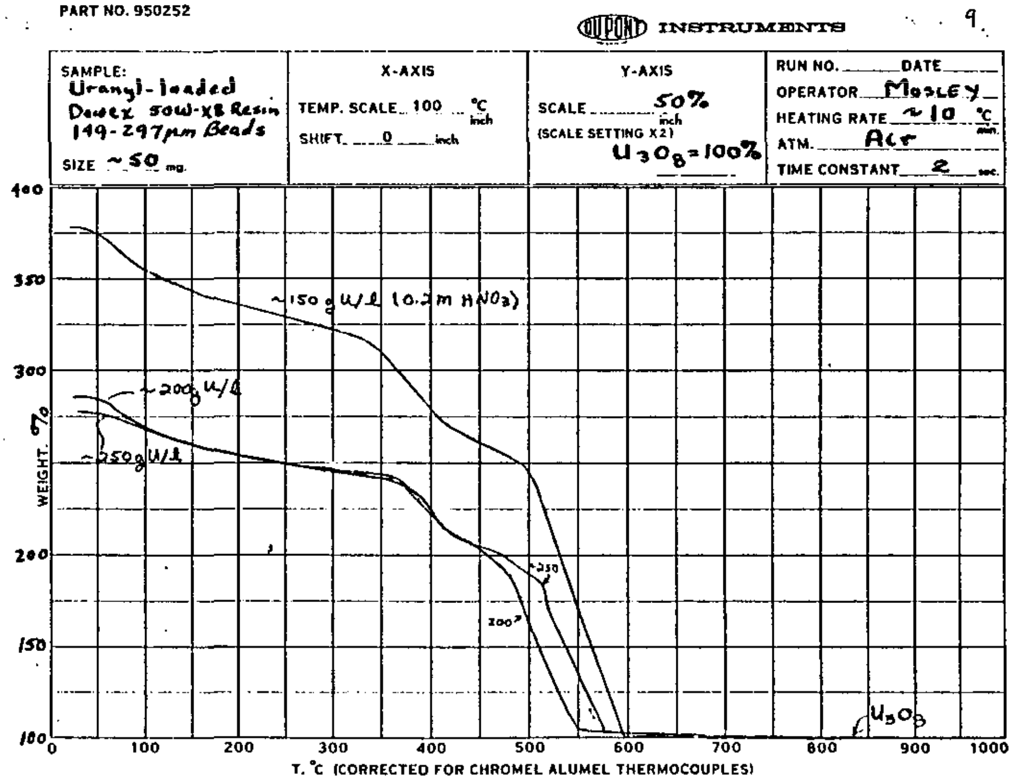
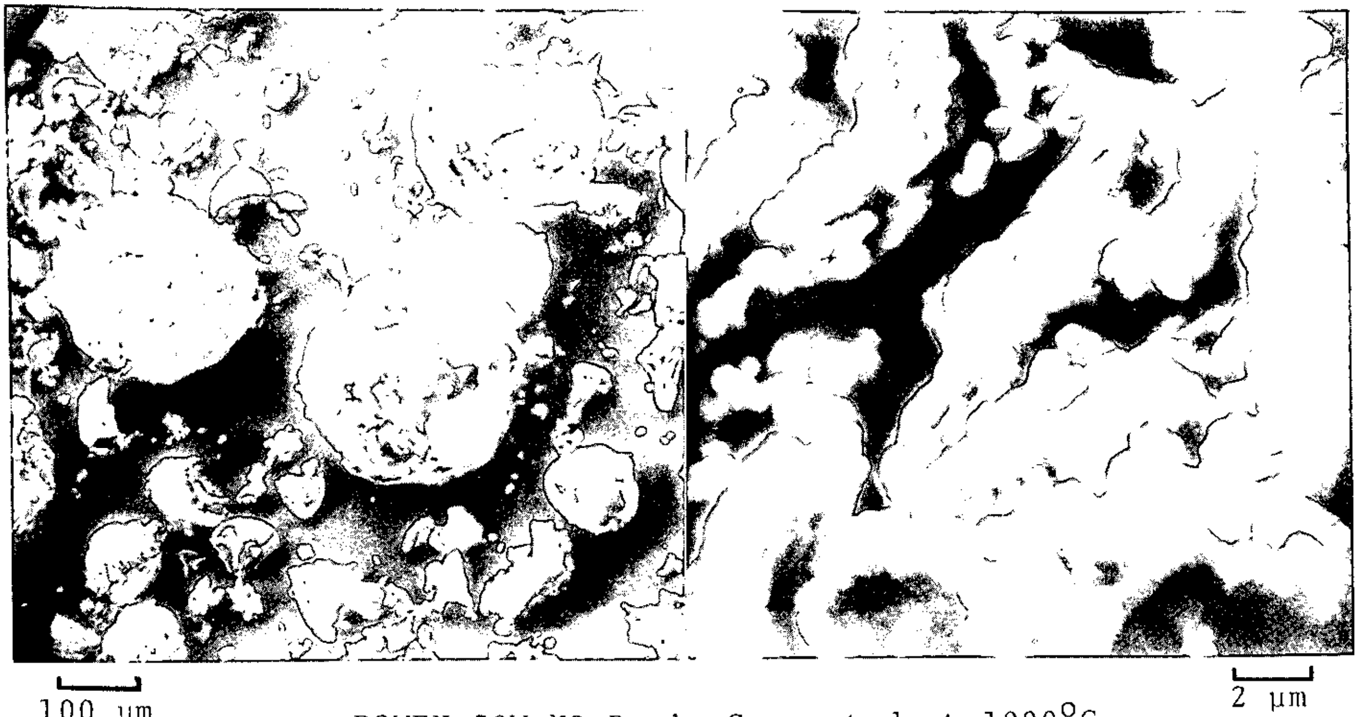
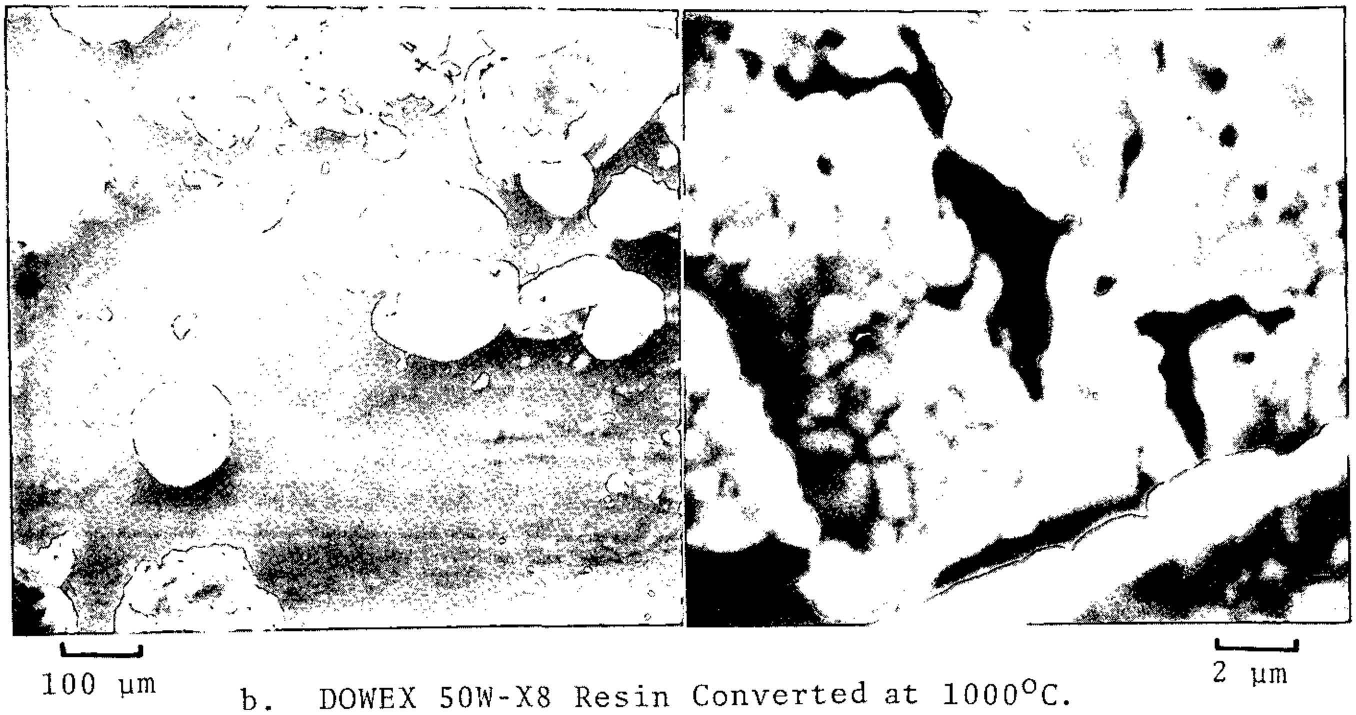


Figure 8. Thermogravimetric Analyses of 50-100 Mesh, Uranyl-Loaded DOWEX 50W-X8 Resins With Different Uranium Loadings.

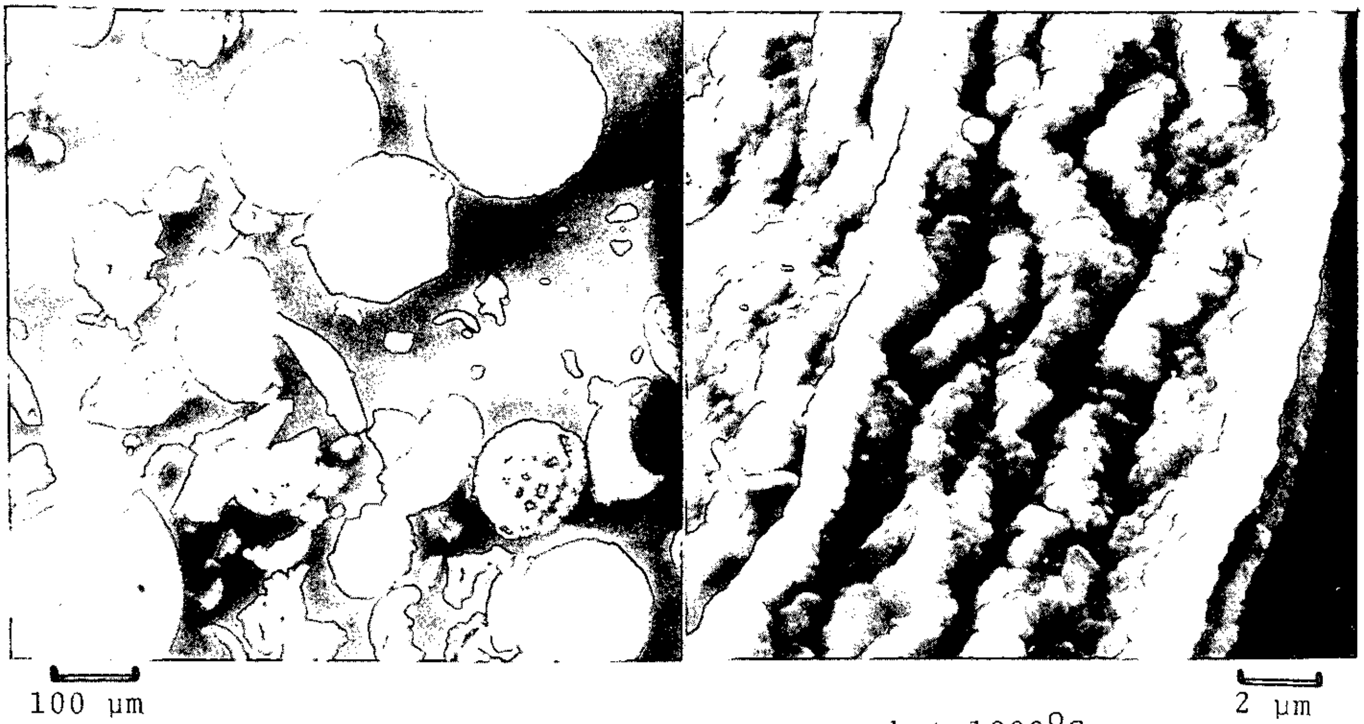


a. DOWEX 50W-X2 Resin Converted at 1000°C.

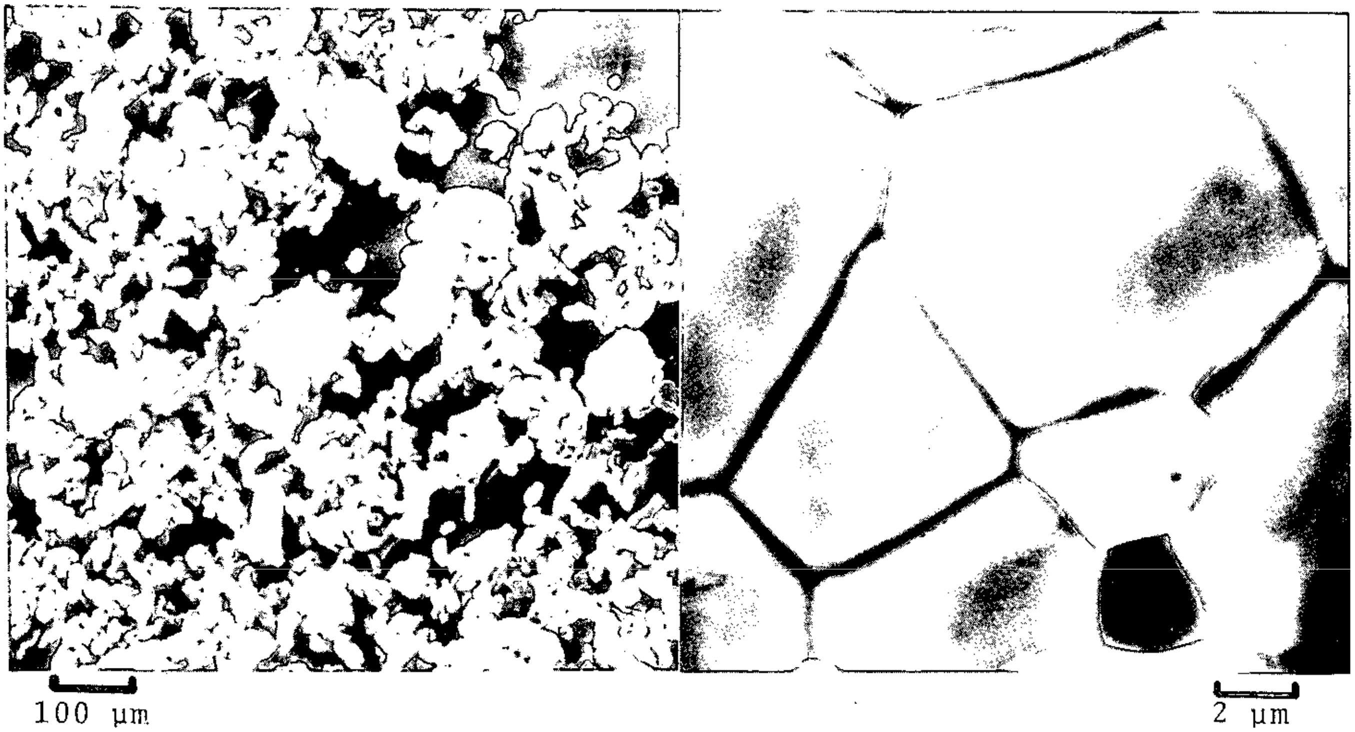


b. DOWEX 50W-X8 Resin Converted at 1000°C.

Figure 9. U_3O_8 Powders Produced From 50-100 Mesh, Uranyl-Loaded DOWEX 50W Resins.



c. DOWEX 50W-X12 Resin Converted at 1000°C



d. U_3O_8 From DOWEX 50W-X8 Resin Fired at 1400°C

Figure 9 (Continued).

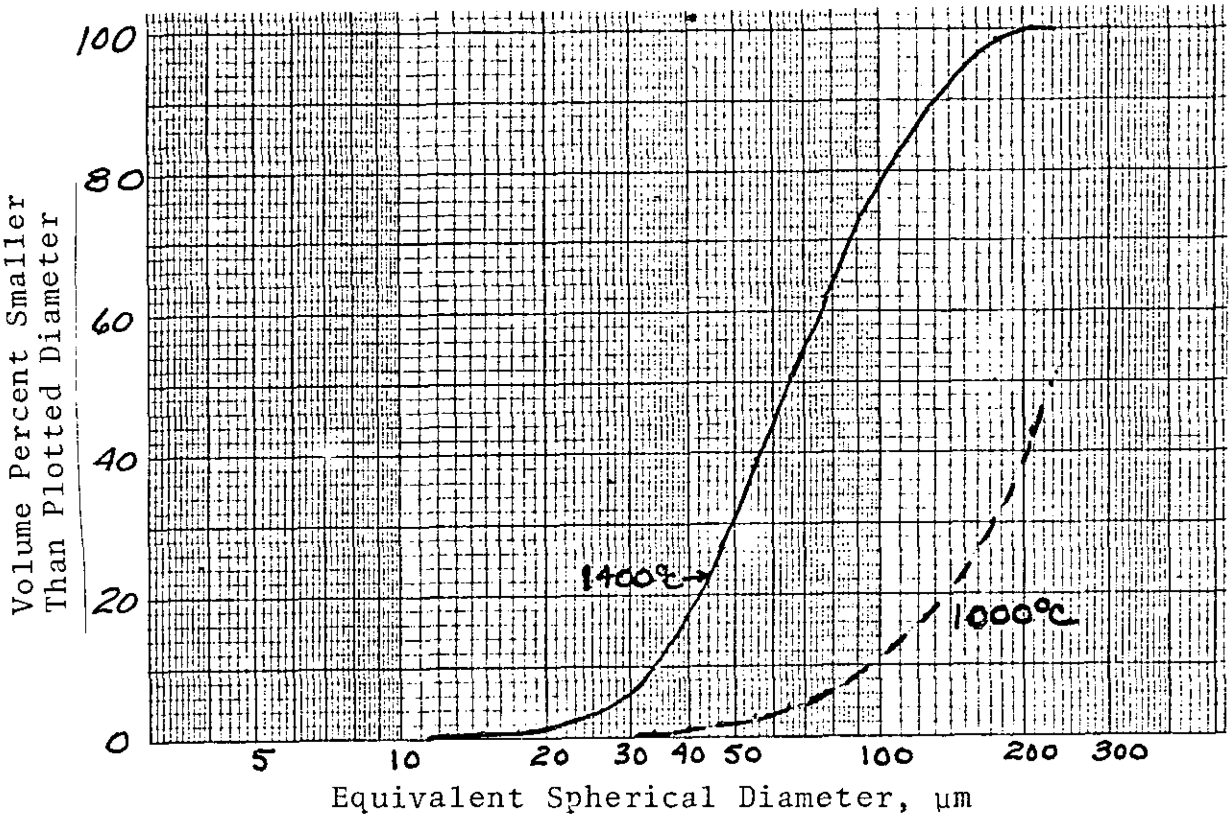
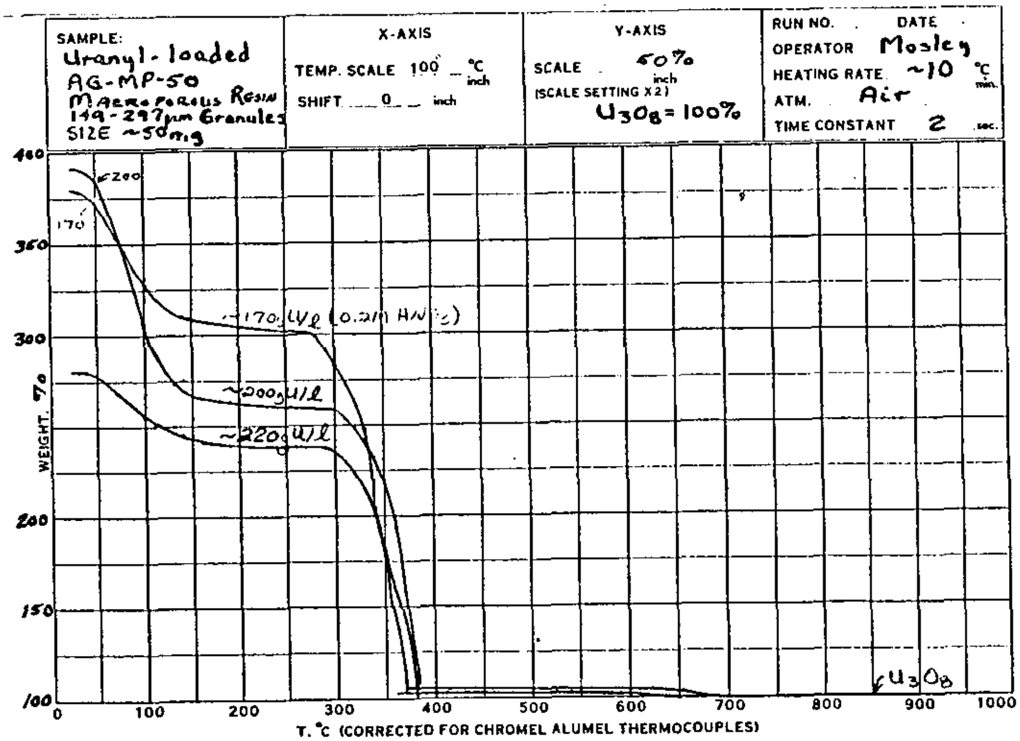


Figure 10. Particle Size Distributions of U_3O_8 Powders Produced by 1000°C Conversion of 50-100 Mesh, Uranyl-Loaded DOWEX 50W-X8 Resin and After Firing at 1400°C



SAMPLE: Uranyl-loaded AG-MP-50 Macroporous Resin 149-297μm Granules

SIZE ~50 mg

X-AXIS

TEMP. SCALE 100 °C/inch

SHIFT 0 inch

Y-AXIS

SCALE 50 %/inch (SCALE SETTING X2)

U_3O_8 = 100%

RUN NO.

DATE

OPERATOR Mosley

HEATING RATE ~10 °C/min.

ATM. Air

TIME CONSTANT 2 sec.

Figure 11. Thermogravimetric Analyses of 50-100 Mesh, Uranyl-Loaded AG MP-50 Resins With Different Uranium Loadings

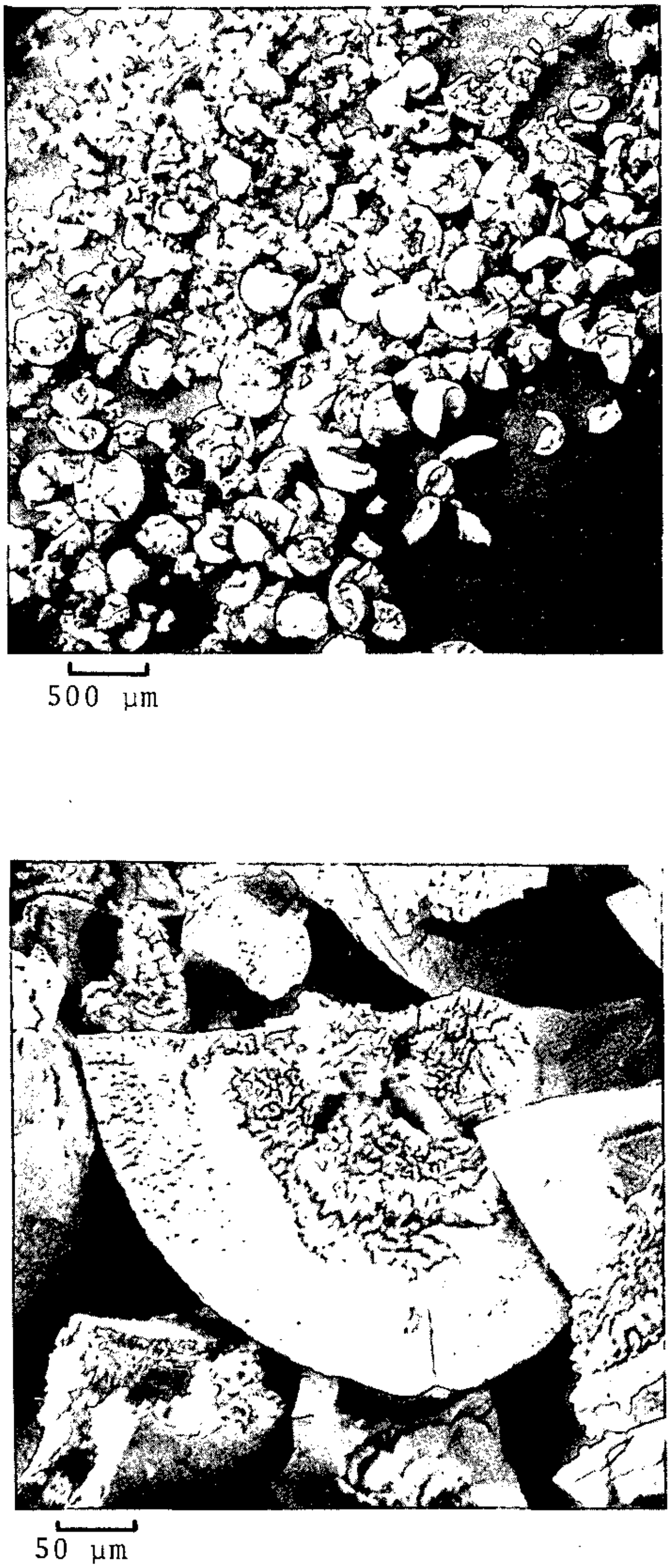
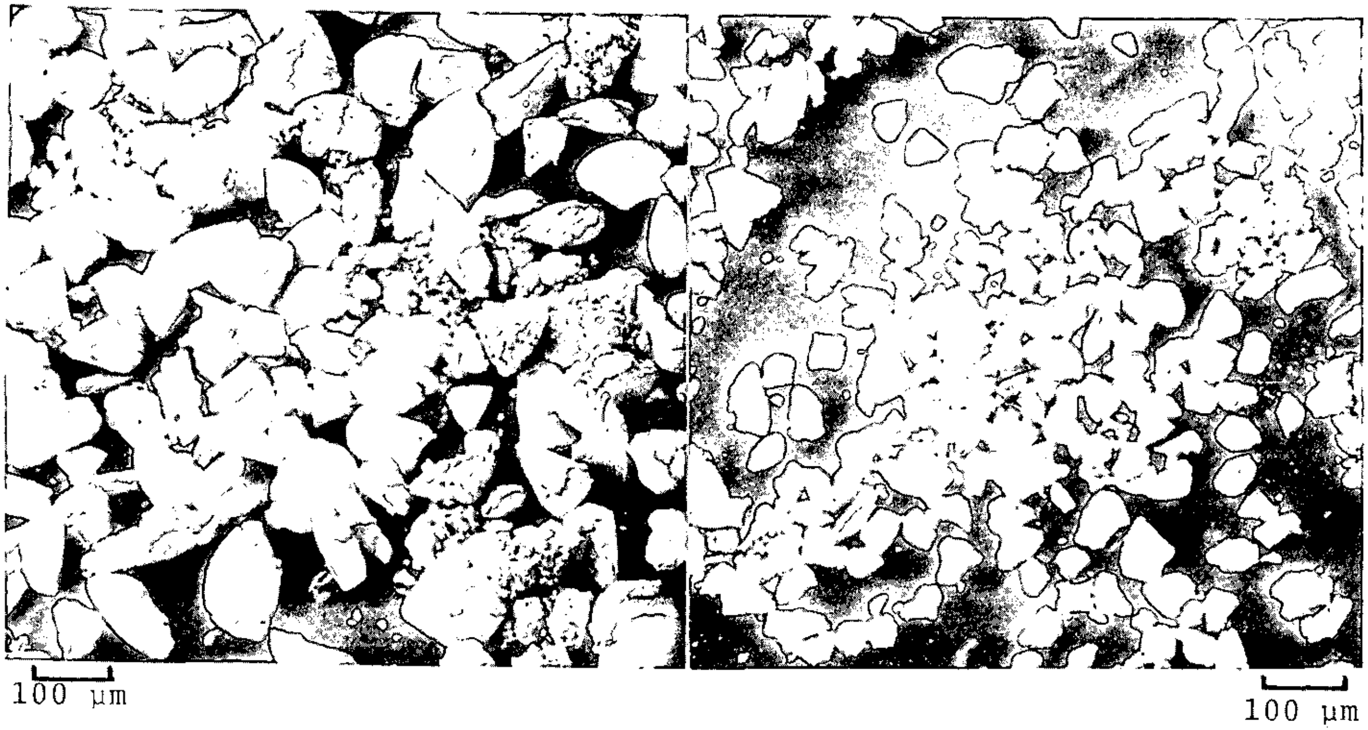
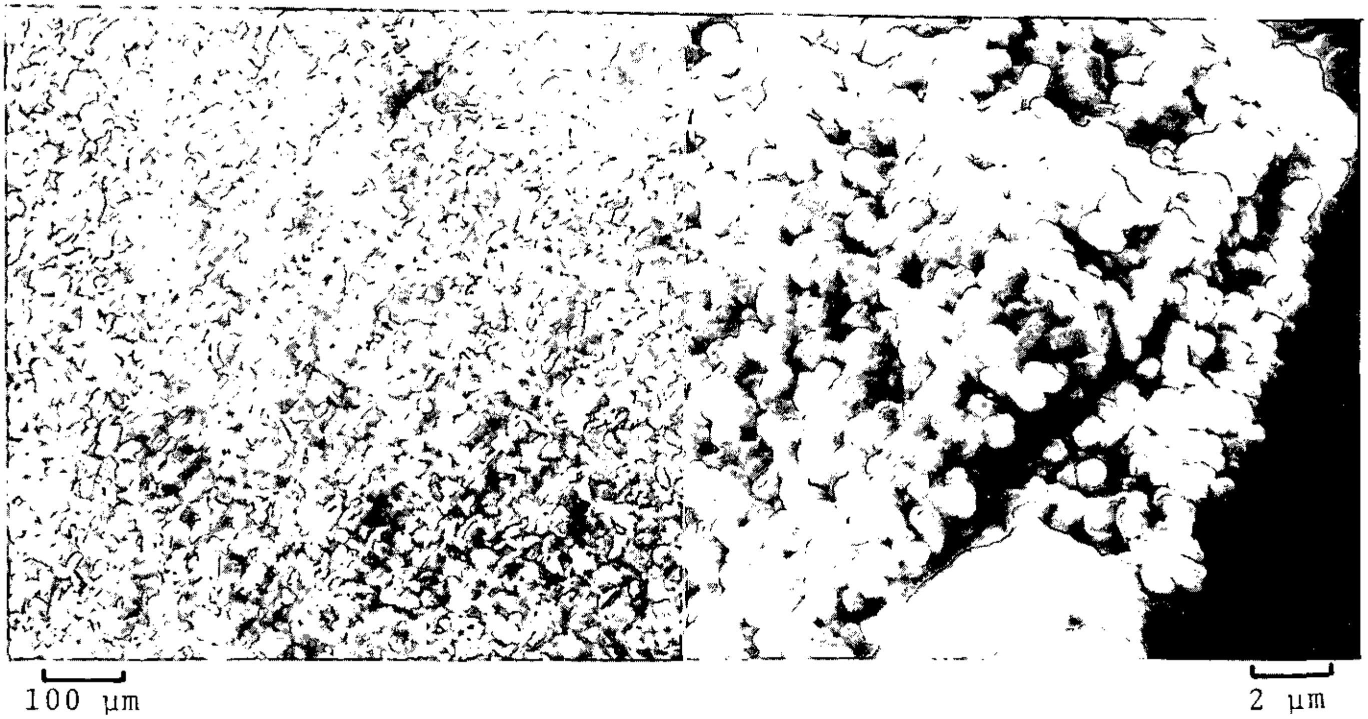


Figure 12. U_3O_8 Powder Produced by 1000°C Conversion of 20-50 Mesh, Uranyl-Loaded AG-MP-50 Resin (Bead Form)



a. From 50-100 Mesh Resin b. From 100-200 Mesh Resin



c. From 200-400 Mesh Resin d. Typical Grain Structure

Figure 13. U_3O_8 Powders Produced by 1000°C Conversion of Uranyl-Loaded AG MP-50 Resins (Granular Forms)

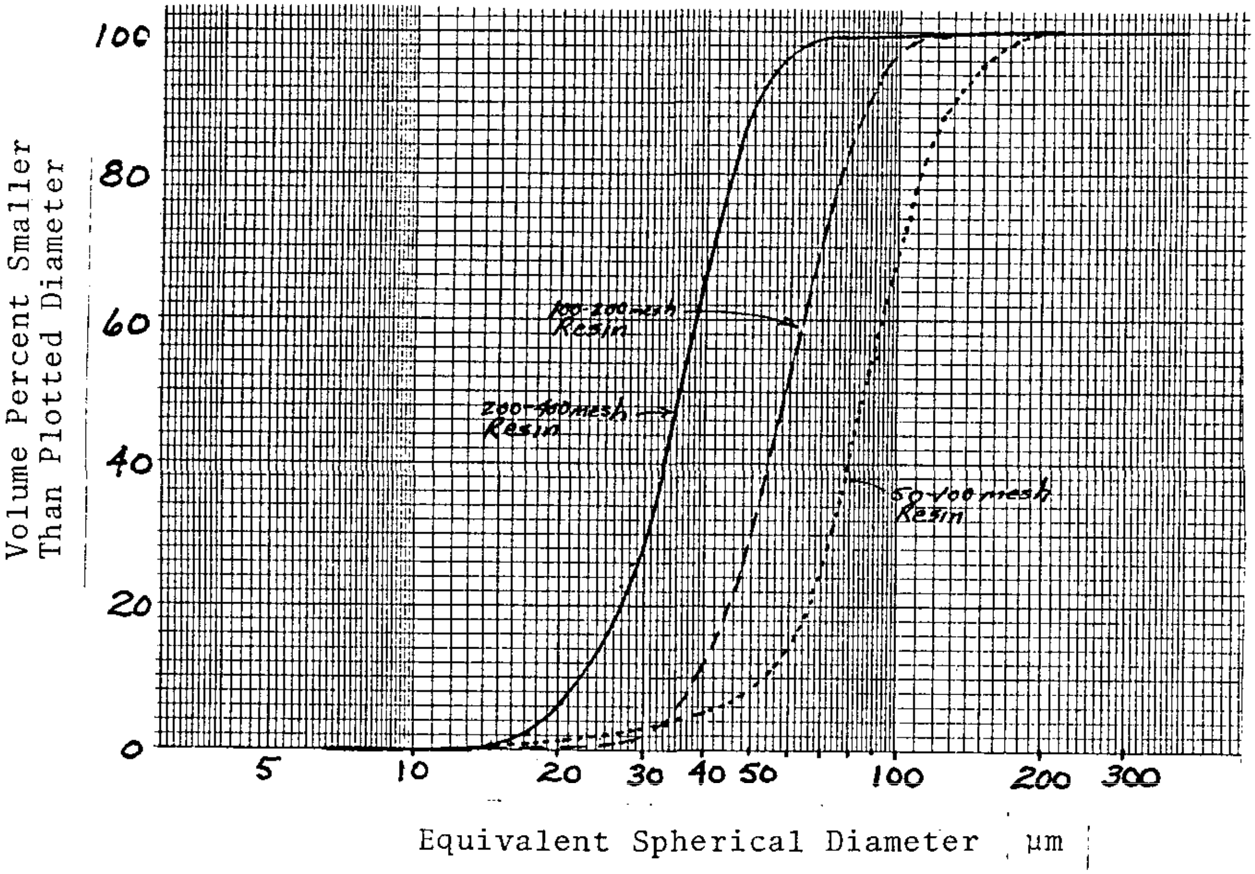
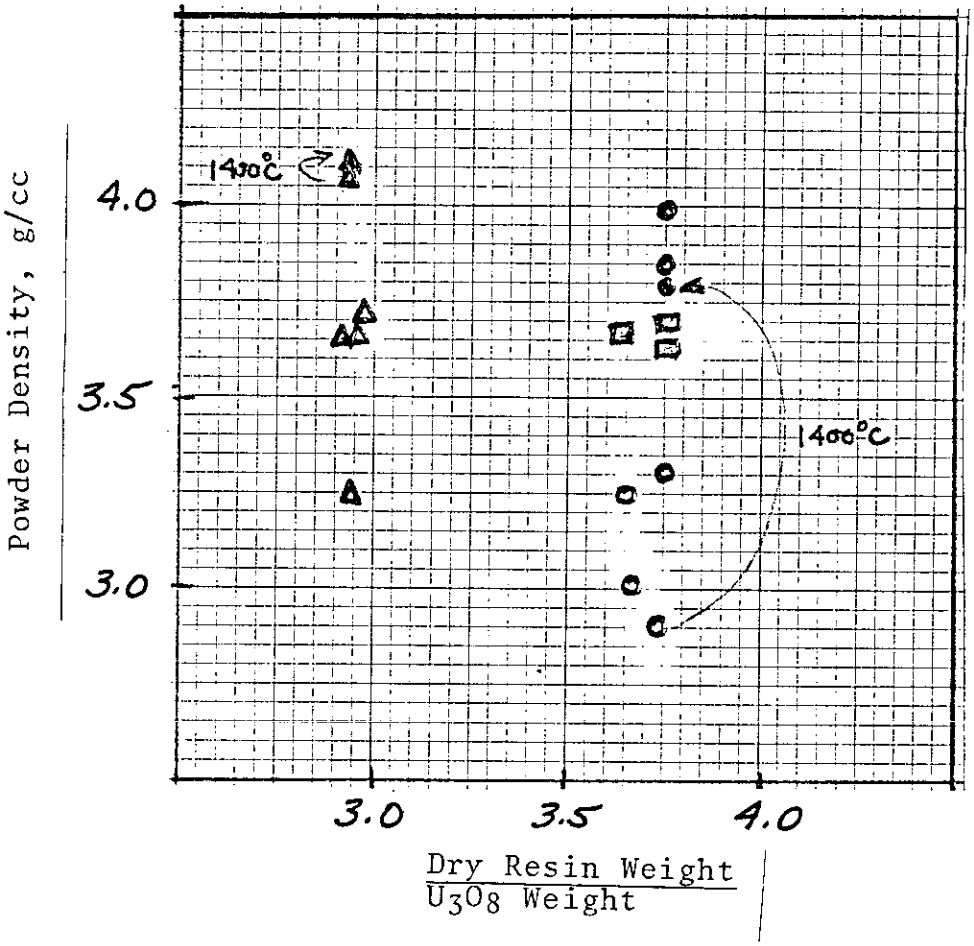


Figure 14. Particle Size Distributions of U_3O_8 Powders Produced by 1000°C Conversion of Uranyl-Loaded AG-MP-50 Resins.



	1000°C Conversion	1400°C Firing
Resin Batch 1	○	●
Resin Batch 2	▭	▬
Resin Batch 3	△	▲

Figure 15. Variations in Density of Small Batches of U_3O_8 Powder Produced From Three Large Batches of 50-100 Mesh, Uranyl-Loaded AG-MP-50 Resin.

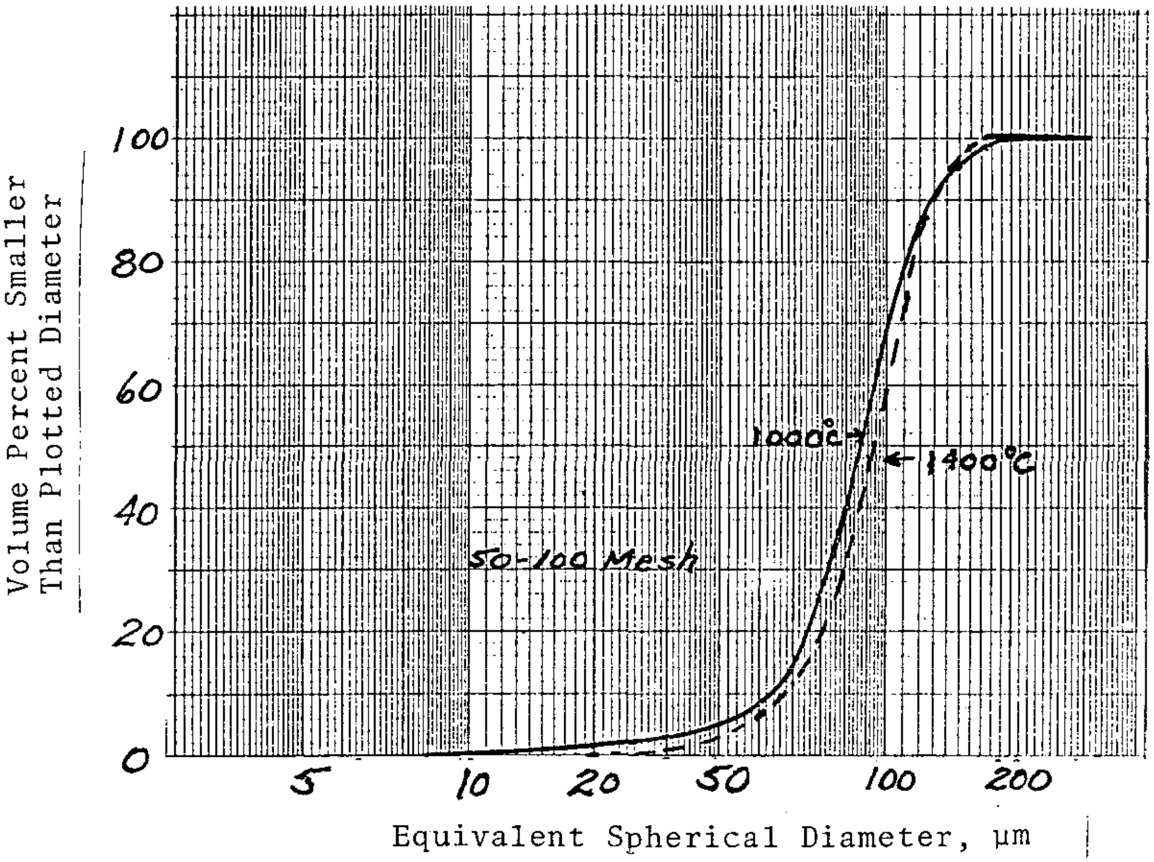
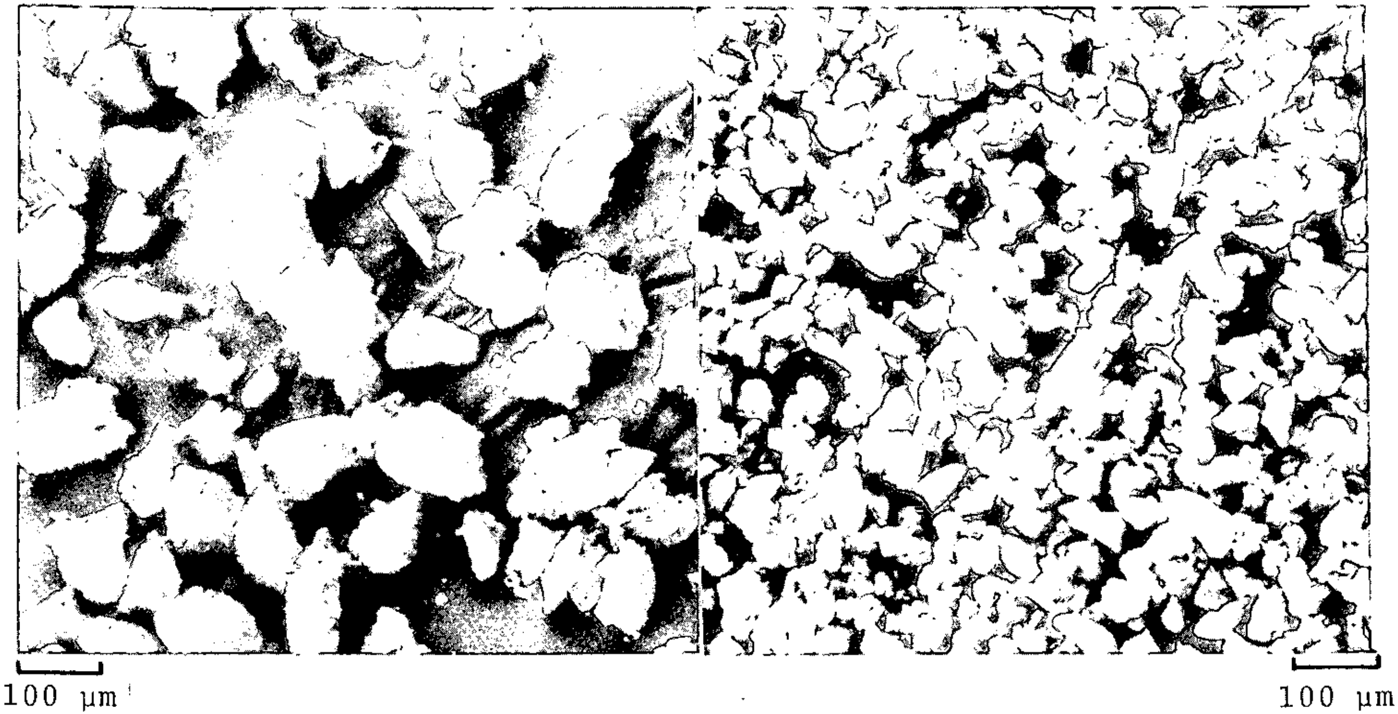
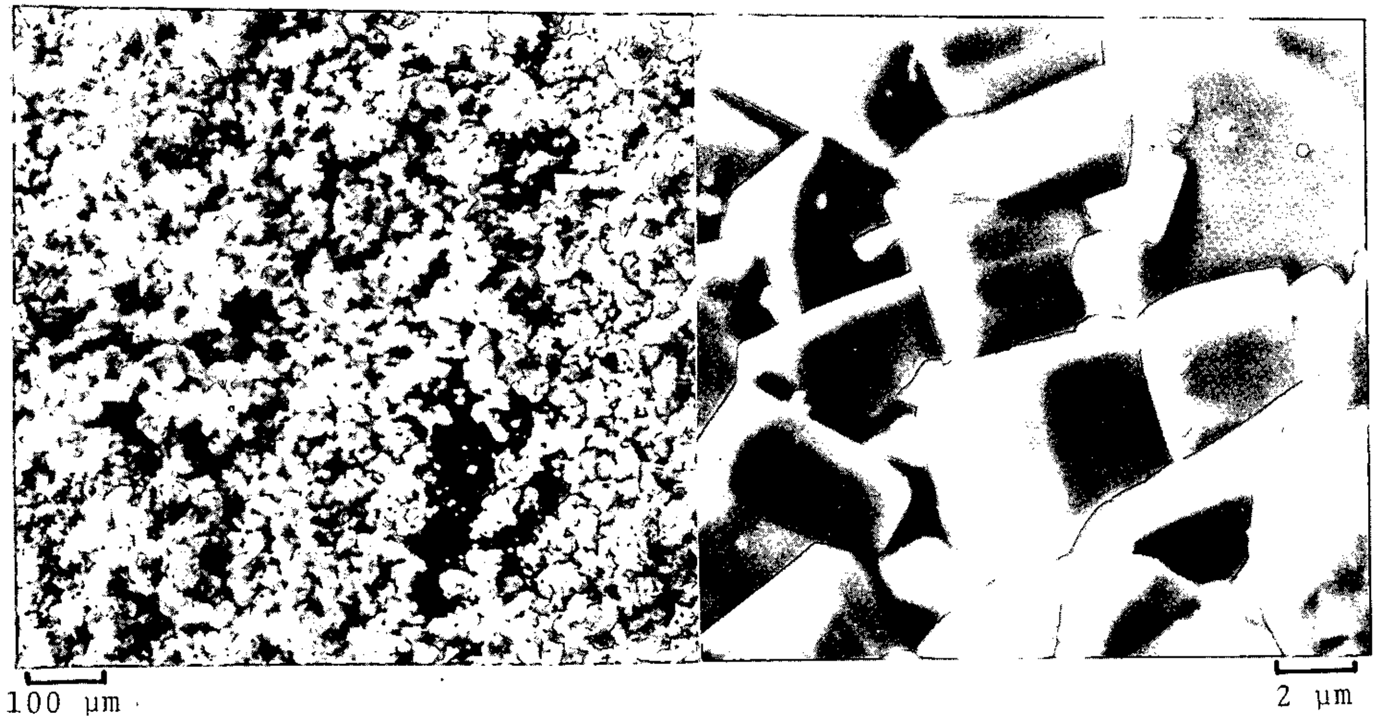


Figure 16. Particle Size Distributions of U_3O_8 Powders Produced by 1000°C Conversion of 50-100 Mesh, Uranyl-Loaded AG-MP-50 Resin and After Firing at 1400°C.

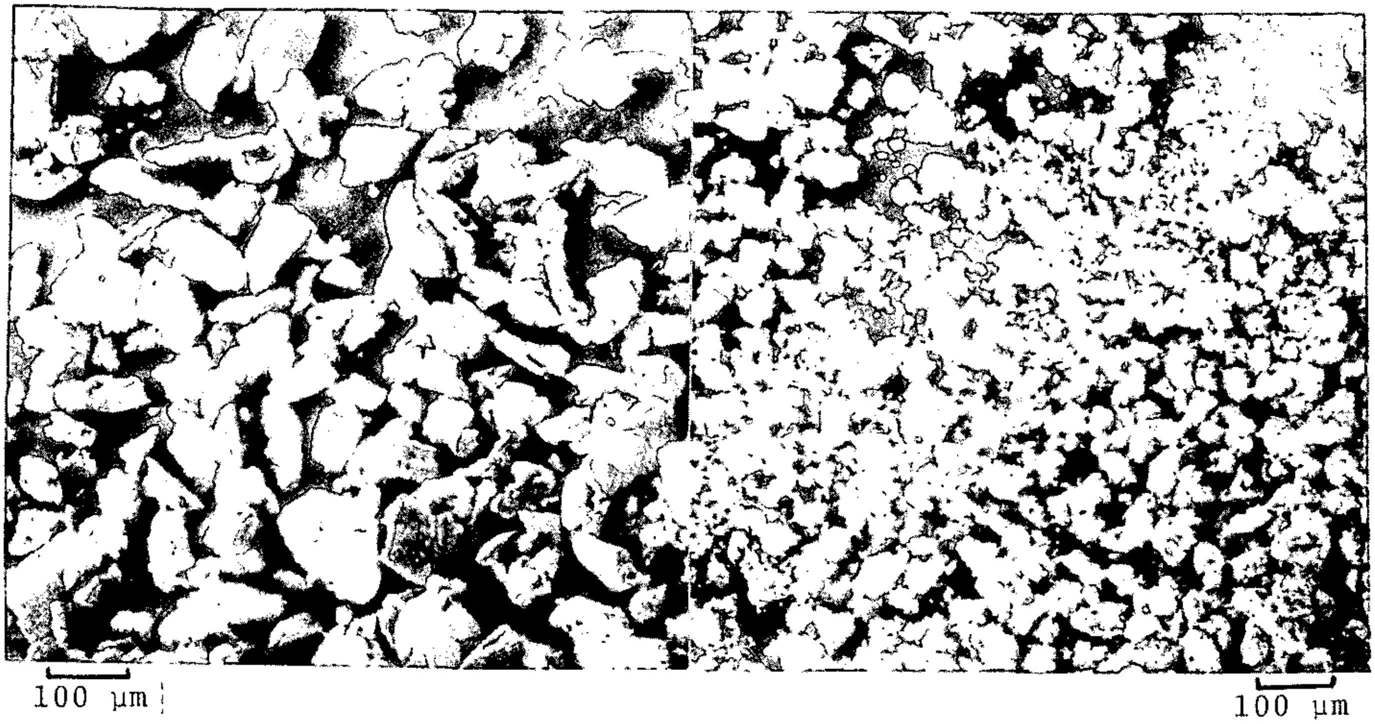


a. From 50-100 Mesh Resin b. From 100-200 Mesh Resin



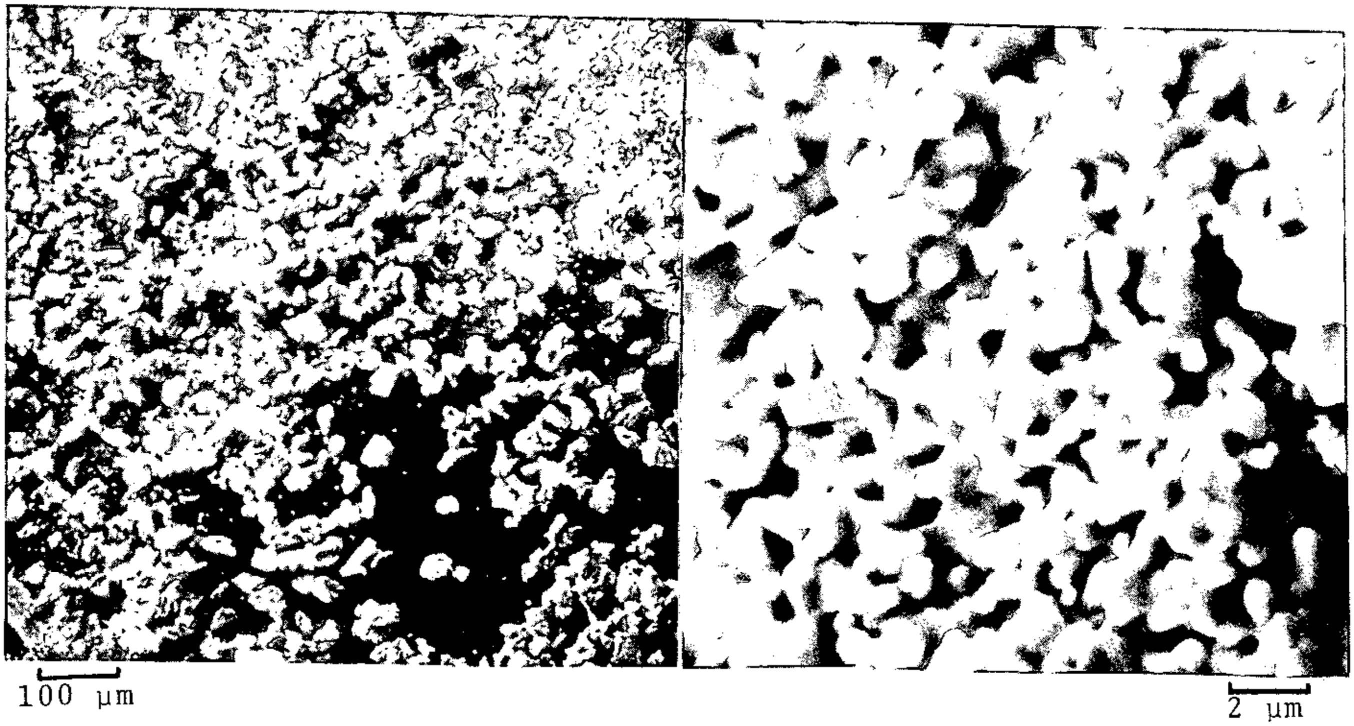
c. From 200-400 Mesh Resin d. Typical Grain Structure

Figure 17. U_3O_8 Powders Produced From Uranyl-Loaded AG MP-50 Resins After Firing at 1400°C.



a. From 50-100 Mesh Resin

b. From 100-200 Mesh



c. From 200-400 Mesh Resin

d. Typical Grain Structure

Figure 18. U_3O_8 Powders Produced by 1000°C Conversion of Uranyl-Loaded Bio-Rex 70 Resins (Granular Form).

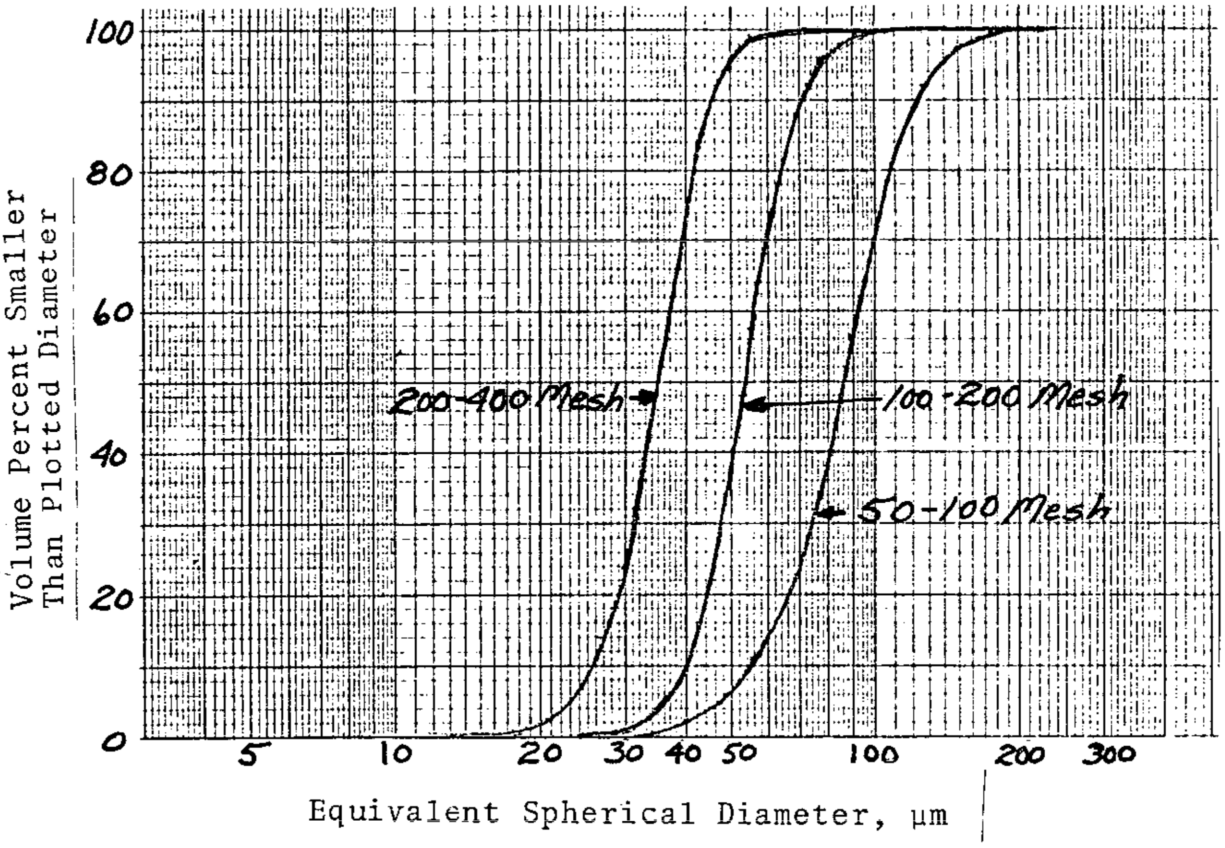
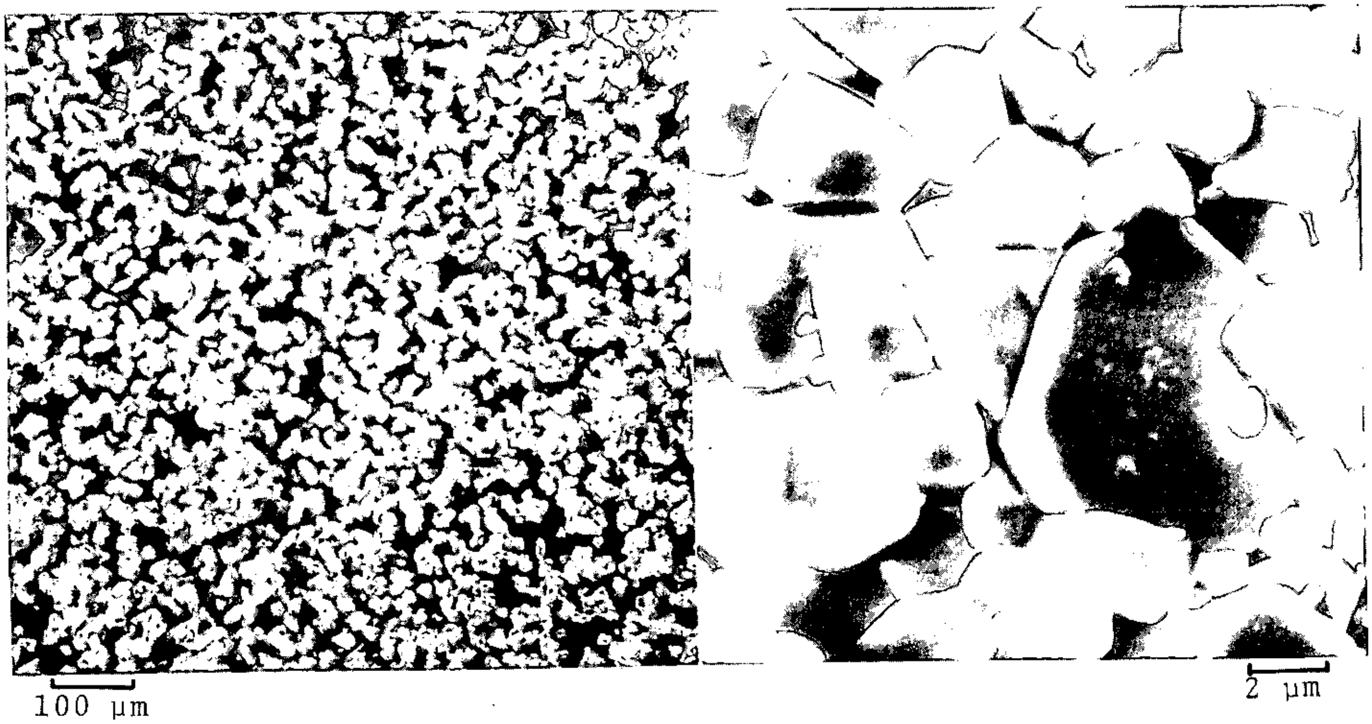


Figure 19. Particle Size Distributions of U_3O_8 Powders Produced by 1000°C Conversion of Uranyl-Loaded Bio-Rex 70 Resins

a. From 50-100 Mesh Resin b. From 100-200 Mesh Resin



c. From 200-400 Mesh Resin d. Typical Grain Structure

Figure 20. U_3O_8 Powders Produced From Uranyl-Loaded Bio-Rex 70 Resins After Firing at 1400°C.

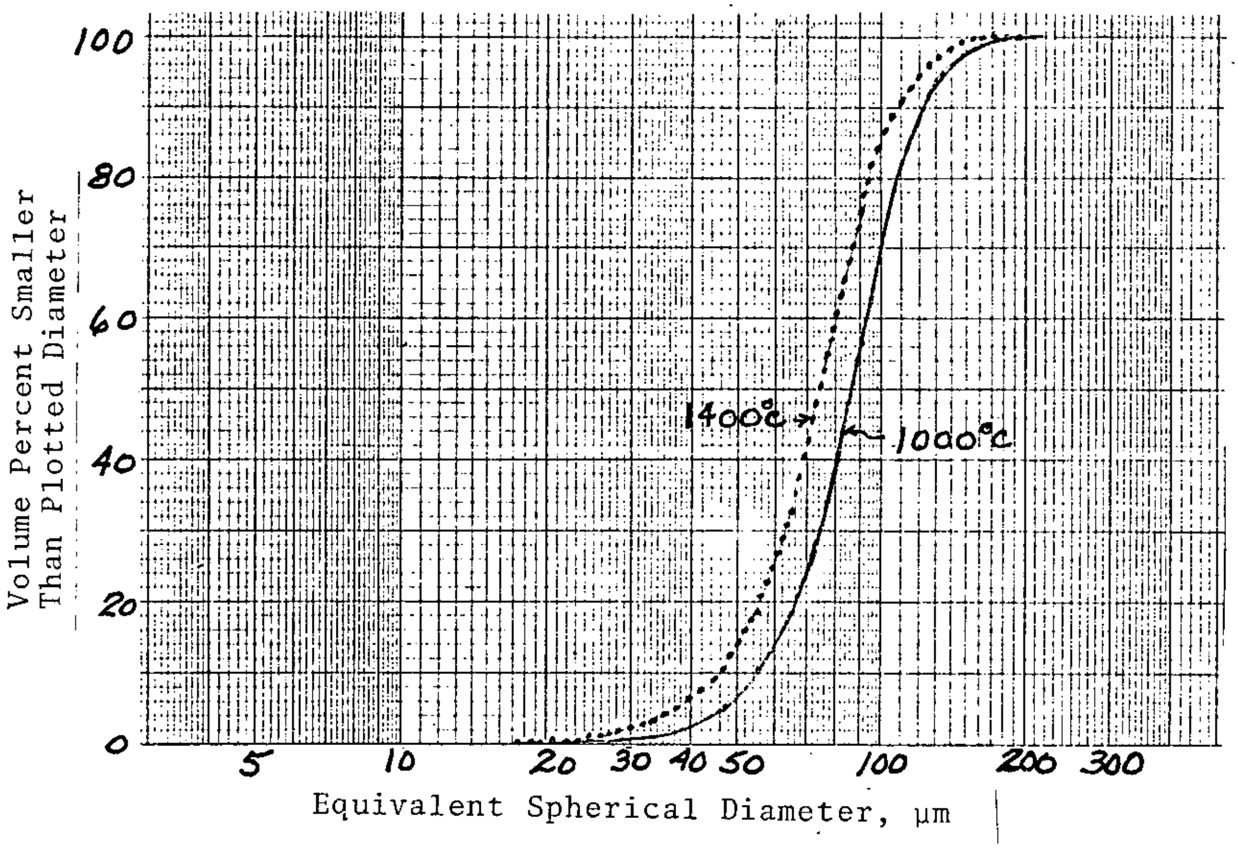


Figure 21. Particle Size Distributions of U_3O_8 Powder Produced by 1000°C Conversion of 50-100 Mesh, Uranyl-Loaded Bio-Rex 70 Resin and After Firing at 1400°C