COKING URANIUM-LOADED ION EXCHANGE MATERIALS

C. R. Schmitt

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UNION CARBIDE CORPORATION
NUCLEAR DIVISION
OAK RIDGE Y-12 PLANT

operated for the **ATOMIC ENERGY COMMISSION** *under* **U. S. GOVERNMENT Contract W-7405 eng 26**

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Material for this report has been compiled and edited from earlier Y-12 Technical Progress Reports (1962). The work is being reported at this time because of renewed interest in the general field of reactor fuel element and graphite technology.

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ABSTRACT

Uranyl compounds were adsorbed on cation and anion exchange resin spheres and cellulose materials to provide a wide range of uranium-to-resin loadings. The uranium-loaded resins and celluloses were carbonized at 950° C and high fired at 1,400, 1,700, and 2,200° C in an inert atmosphere. Chemical analyses were obtained and X-ray diffraction studies made to identify the chemical compounds of the uranium that were associated with the carbon or graphite matrix.

CONTENTS

SUMMARY	5
INTRODUCTION.	6
COKING URANIUM-LOADED ION EXCHANGE MATERIALS	7
Experimental Studies	7
Anion Resin Studies	7
Cation Resin Studies	19
Anion Exchange Cellulose Studies	21
REFERENCES.	25
ACKNOWLEDGEMENTS	26

SUMMARY

Anion and cation exchange resin spheres, representing various particle sizes, were loaded with uranium to predetermined equilibrium values from uranyl nitrate or uranyl sulfate solutions and carbonized in a flowing inert-gas atmosphere in both static and fluidized beds. After coking at 900° C, the resins retained their spherical shape, and analytical data showed that a uranium content of greater than 44 weight percent uranium and a nitrogen content of less than 200 ppm nitrogen could be obtained. The carbonized resins were high fired at 1,400, 1,700, and 2,200° C, and X-ray diffraction analyses were made to identify the chemical compound of the uranium associated with the carbon or graphite matrix. Analytical data on carbonized uranium-loaded diethylaminoethyl anion exchange cellulose showed that a uranium content of 37.7 percent uranium and a high degree of carbon purity were obtained.

INTRODUCTION

In the fabrication of uranium carbide fuel elements for certain nuclear reactors, uranium dioxide powder is blended with carbon or graphite powder and heated to approximately 2,600° C to form a graphitized carbon and uranium carbide body. Since the properties of the final fuel element depend upon the homogeneity of the dispersion of the uranium carbide throughout the fuel element, the efficiency of the initial uranium dioxide blending step is extremely important. Improved methods for achieving uniformity of the dispersion of uranium carbide throughout the graphite are, therefore, of interest. In this study, conducted at the Oak Ridge Y-12 Plant, (a) a method was developed for forming a uniform dispersion of uranium carbide in a graphite matrix by adsorbing uranium on high-purity ion exchange materials and subsequently heating the uranium-loaded resin to form uranium carbide plus carbon or graphite.

(a) Operated for the US Atomic Energy Commission by the Union Carbide Corporation's Nuclear Division.

COKING URANIUM-LOADED ION EXCHANGE MATERIALS

EXPERIMENTAL STUDIES

Anion Resin Studies

A batch of Dowex 1X1 (50 - 100 mesh) anion exchange resin was converted to the nitrate form by treatment with a 0.9 *M* ammonium nitrate-0.1 *M* nitric acid solution in a column until the column effluent was free of the chloride ion. The resin was then rinsed with distilled water. Three 100-gram portions of the resin were loaded with uranyl nitrate by equilibrating with 800 milliliters of 6.0 *M* ammonium nitrate solution containing sufficient dissolved uranyl nitrate to provide various uranium loadings of 50 to 150 gms U per gm of dry resin according to predetermined equilibrium relationships.⁽¹⁾ The resins were filtered, air dried, dried in an oven at 100° C, and pyrolyzed under flowing helium at 500, 700, and 850° C for one hour. The coke residue was ground in a mortar and pestle and screened through a 40-mesh sieve. Analytical results are summarized in Table 1. These data indicate that uranium loadings of greater than 44 percent after coking can be obtained. As shown in Table 1, the coke obtained from the 500° C pyrolysis was brown in color and indicated, as expected, that incomplete carbonization was realized at this temperature.

Table 1
PYROLYSIS OF URANIUM-LOADED ION EXCHANGE RESIN

Sample Number	Initial Uranium Loading (gms U/kg dry resin)	Pyrolysis Temperature (1) (° C)	Coke Analyses			
			Color	gms U/gm	Carbon (%)	Nitrogen (ppm)
IEC-1	56.5	500	Brown	0.2244	55.16	360
IEC-2	92.1	700	Black	0.3582	47.48	243
IEC-3	135.6	850	Black	0.4486	38.79	189

(1) 1.0 hour soak time in flowing helium.

X-ray diffraction studies of the carbonized residues showed weak and diffuse lines in a heavy background which indicate a very small crystallite size. The lines were not defined well enough to definitely identify the uranium compound, but they were in the general vicinity of where some of the uranium dioxide lines would be. These X-ray diffraction results suggest that higher carbonizing temperatures would be required to produce any extensive uranium carbide formation or graphitization.

Spectrographic analyses of the pulverized coke (minus 40 mesh), as shown in Table 2, indicate that a high degree of uranium and carbon purity can be attained by this method. Although iron and copper are shown to be the principal impurities present

Table 2
SPECTROGRAPHIC ANALYSIS OF PYROLYZED
URANIUM-LOADED RESIN
(All Values in ppm, U_3O_8 Basis)

Element	Pyrolysis Temperature ($^{\circ}C$) Coke Number $\rightarrow$ IEC-1	500 IEC-2	700 IEC-3	850
Al	< 40(1)	< 40	< 40	
As	< 10	< 10	< 10	
Au	< 1	< 1	< 1	
B	18	2	1.5	
Ba	12	8	2	
Be	< 0.01	< 0.01	< 0.01	
Bi	< 1	< 1	< 1	
Ca	< 400	< 400	< 400	
Cd	0.8	0.2	0.2	
Co	5	< 1	< 1	
Cr	15	12	10	
Cu	400	100	200	
Fe	400	200	175	
In	< 2	< 2	< 2	
Li	30	1.8	0.8	
Mg	100	100	40	
Mn	4	1	1	
Mo	< 100	< 100	< 100	
Na	50	40	35	
Ni	30	20	20	
P	< 100	< 100	< 100	
Pb	6	2	< 1	
Sb	< 2	< 2	-	
Si	< 400	< 400	< 400	
Sn	30	35	30	
Sr	< 20	< 20	< 20	
Ti	15	10	< 4	
V	3	3	3	
Zn	75	20	20	

(1) Precision for all values is approximately -40 to $+80$ percent of the value reported.

(ranging from 100 to 400 ppm on a U_3O_8 basis), the iron and copper contents range from only 85 to 93 ppm when calculated on a sample weight basis.

Uranium adsorption from uranyl nitrate in the presence of 6.0 M ammonium nitrate solution resulted in the retention of some residual ammonium nitrate solution after equilibrating, filtering, and air drying the resin. The nitrogen content of the coked resins, as shown in Table 1, indicates that thermal decomposition of this ammonium nitrate was fairly complete, and that the residual nitrogen content decreased with increasing pyrolysis temperature. Although the possibility of spontaneous ignition or violent decomposition of the anion exchange resins in the nitrate form was known and had occurred elsewhere, (2) no abnormal thermal decomposition occurred.

A batch of Dowex 21K (16 - 20 mesh) anion resin was loaded with uranyl nitrate by equilibrating with 6.0 M ammonium nitrate solution containing sufficient uranyl

nitrate to provide an initial uranium loading of 29 gms U per kg of dry resin. The resin was filtered, air dried, and pyrolyzed under flowing helium for one hour at 950° C using a vertical quartz-tube pyrolysis unit. A heating cycle of approximately six hours was used to attain the target carbonization temperature of 950° C, and considerable volatile material was expelled from the resin throughout this period.

It was observed that the carbonized resin beads remained as individual particles and appeared somewhat elliptical in shape when viewed under a microscope. Photomicrographs of the spherically shaped, uranium-loaded Dowex 21K resin beads before carbonization and the elliptically shaped resin beads obtained after pyrolysis treatment at 950° C are presented in Figure 1.

It was estimated that the resin beads had shrunk approximately 33 percent (by linear dimensions) after pyrolysis treatment. It was learned, subsequently, that the elongated shape of the carbonized beads resulted from physical deformation during pyrolysis in the vertical quartz tube used to contain the batch of resin beads. The weight of the resin charge in the tube caused lateral distortion of the beads at the middle and lower regions of the tube while they were being heated in their semi-plastic and softened condition. This conclusion was also borne out by the fact that some of the beads retained their original spherical shape after pyrolysis, and these beads corresponded to those that were located at the top portion of the resin bed during pyrolysis treatment.

Portions of the batch of carbonized resin beads were then high fired in flowing helium for three hours at 1,400 and 2,200° C in a carbon induction furnace, but no significant further shrinkage was evident, as Figure 2 indicates.

Photomicrographs of cross sections of the carbonized uranium-loaded beads after a 950 and 2,200° C heat treatment are given in Figures 3 and 4. From these figures it may be seen that the elongated carbonized beads show internal porosity or fissures that run parallel to the axis of deformation, as would be expected from gas-flow conditions in the vertical quartz tubes, and that the spherical carbonized beads sampled from the top of the pyrolysis tube exhibit a more heterogeneous type of internal porosity. The spherical carbonized resin bead shown in Figure 3(a) also shows a distinct coating of pyrolytic carbon which had been deposited on its external surface. A pyrolytic carbon deposit is also evident for the high-fired spherical beads shown in Figure 2, which show the spherical beads as dull and unreflective in contrast to the shiny and elongated resin beads.

Additional photomicrographs of spherical and elongated resin beads after firing at 2,200° C for three hours in flowing helium are seen in Figure 5. These views indicate that the pyrolytic carbon deposit resulting from the 950° C carbonization treatment of the spherical beads is retained at high temperatures.

(a) Before Carbonization

16692

(b) Carbonized at 950° C

16693

Figure 1. URANIUM-LOADED DOWEX 21K ANION RESIN BEADS. (16-20 Mesh; Bright Field Illumination; 10X)

(a) At 1,400° C

16862

(b) At 2,200° C

16863

Figure 2. URANIUM-LOADED DOWEX 21K ANION RESIN BEADS AFTER FIRING AT TWO DIFFERENT TEMPERATURES UNDER HELIUM. (Bright Field Illumination; 10X)

(a) At 950° C

16494

(b) At 2,200° C

16863

Figure 3. CROSS SECTIONS OF CARBONIZED URANIUM-LOADED DOWEX 21K ANION RESIN BEADS AFTER THEY HAD BEEN HEAT TREATED AT TWO DIFFERENT TEMPERATURES UNDER HELIUM. (Bright Field Illumination; 75X)

Figure 4. PERIPHERAL CROSS SECTION OF A URANIUM-LOADED DOWEX 21K ANION RESIN BEAD AFTER HEAT TREATMENT TO 950°C UNDER HELIUM. (Spherical Bead from the Top of the Bed; Bright Field Illumination; 1,000X)

Since some of the uranium-loaded resin beads retained their original spherical shape after pyrolysis treatment at 950°C , it was indicated that deformation and elongation of the bulk of the resin batch can be avoided by conducting the pyrolysis treatment by fluidizing the resin bed with an inert gas such as helium or argon.

Additional resin pyrolysis studies were made by fluidizing the uranium-loaded resin spheres in an atmosphere of flowing argon or helium using the vertical-tube pyrolysis apparatus shown in Figure 6. It was found that the resin spheres retained their spherical shape after slow carbonization treatment, and particle agglomeration and elongation was prevented. The same apparatus shown in Figure 6 was also used to coat the coked resin spheres with pyrolytic carbon using methane gas as the source of carbon. Typical particle sphericity shown by some uranium-loaded ion exchange spheres after carbonization in a fluidized bed at 950°C is indicated in Figure 7.

X-ray diffraction studies of the uranium-loaded resin after carbonizing at 950°C , and firing at 1,400, 1,700, and $2,200^{\circ}\text{C}$ under flowing helium, were made in an attempt to identify the chemical form of the uranium associated with the carbon resin matrix at these various firing temperatures. A comparison of the X-ray diffraction patterns obtained with uranium dioxide, uranium monocarbide, graphite, and uranium octoxide standards is given by the diffractographs in Figure 8. These studies show that at $1,400^{\circ}\text{C}$ the uranium was almost all present as the dioxide.

(a) Spherical Bead from the Top of the Bed

16863

(b) Elongated Bead from the Bottom of the Bed

16863

Figure 5. PERIPHERAL CROSS SECTION OF A URANIUM-LOADED DOWEX 21K ANION RESIN BEAD AFTER HEATING TO 2,200° C UNDER HELIUM. (Bright Field Illumination; 1,000X)

Figure 6. FLUIDIZED BED APPARATUS FOR COKING RESIN MICROSPHERES AND COATING THEM WITH PYROLYTIC CARBON.

Figure 7. URANIUM-LOADED RESIN MICROSPHERES AFTER CARBONIZING IN A FLUIDIZED-BED APPARATUS. (Bright Field Illumination; 40X)

Only a few weak lines did not correspond with the standard uranium dioxide pattern, and these were suspected as part of the carbon pattern. At $1,700^{\circ}\text{C}$, the diffraction pattern of the coked resin showed the presence of the dioxide and monocarbide, probably some carbon, and possibly some of the octoxide. A comparison of the X-ray diffraction patterns of the resin high fired at $2,200^{\circ}\text{C}$ with standard patterns of uranium monocarbide and uranium dicarbide, as shown in Figure 9, shows the presence of both carbides. The extra lines shown by the resin pattern are probably due to graphite.

A summary of the uranium content, carbon content, and mercury displacement density of uranium-loaded Dowex 21K resin beads after heating under flowing helium at 950 , $1,700$, and $2,200^{\circ}\text{C}$ is given in Table 3. These data again indicate that carbonization is rather incomplete at 950°C , as shown by the large increase in carbon content upon firing at $2,200^{\circ}\text{C}$.

Table 3
PROPERTIES OF A COKED, URANIUM-LOADED
ION EXCHANGE RESIN

Heat Treatment ⁽¹⁾ ($^{\circ}\text{C}$)	Coke Content (gms U/gm Coke)	Carbon Content (% C)	Density (gm/l)
950	0.03977	86.16	0.933
1,400	0.04313	-	0.930
2,200	0.04318	95.14	0.980

(1) In an inert gas atmosphere.

Cross-sectional examination at $1,000\times$ of elongated and spherical beads after high firing at $2,200^{\circ}\text{C}$, as shown in Figure 5, indicates that the uranium carbide is dispersed in the solid portion of the carbonized bead as pepper-like grains. An attempt was made to bring out this pepper-like structure in more detail by etching the bead with an equal-volume solution of nitric acid, acetic acid, and water, but no improvement resulted from this treatment. Since no pepper-like structure was discernible in cross sections of the 950°C -coked resin beads at $1,000\times$, as seen in Figure 4, it is assumed that the pepper-like structure was attributable to uranium carbide or dicarbide and was not a result of any polishing defects.

Cross sections of Dowex 21K resin beads before and after uranyl nitrate adsorption were also examined to show that the internal voids and fissures resulting from pyrolysis treatment at 950°C were not inherent in the anion exchange resin structure before carbonization. A typical cross section of a uranyl nitrate-loaded Dowex 21K resin bead is given in Figure 10. The large, black areas are defects resulting from embedding the resin bead in the plastic molding compound. The soft resin bead was extremely sensitive to the mechanical polishing treatment, and numerous polishing defects are visible. The large diagonal scratch across the resin bead, however, readily attests to the solidarity of the resin prior to carbonization.

Figure 8. IDENTIFICATION OF CARBONIZED URANIUM-LOADED DOWEX 21K RESIN BY X-RAY DIFFRACTION.

UC

Coked
Resin
(2,200° C) UC₂

Figure 9. COMPARISON OF X-RAY DIFFRACTION PATTERNS OF URANIUM-LOADED DOWEX 21K RESIN WITH URANIUM CARBIDES.
(Resin Fired at 2,200° C)

1/120

Figure 10. CROSS SECTION OF A URANYL NITRATE-LOADED DOWEX 21X RESIN BEAD. (Bright Field Illumination; 100X)

Cation Resin Studies

A batch of Dowex 50-X12 cation exchange resin (100 - 200 mesh spheres) in the hydrogen form was contacted with uranyl sulfate solution (approximately 200 gms U/l) for 48 hours using magnetic stirring. The resin was filtered, rinsed rapidly with distilled water to remove any residual mother liquor, and oven dried at 110° C. This treatment provided a resin uranium loading at 7.32 grams uranium per kilogram of dry resin. A photomicrograph showing a cross section of the Dowex 50-X12 cation resin beads after loading with uranyl sulfate is given in Figure 11.

19014

Figure 11. CROSS SECTION OF URANYL SULFATE-LOADED DOWEX 50-X12 CATION EXCHANGE RESIN. (Bright Field Illumination; 500X)

The uranium-loaded resin was pyrolyzed under flowing helium using a vertical quartz pyrolysis tube. A heating cycle of approximately six hours was used to attain the target carbonization temperature of 900°C . Considerable volatile material, with a prevalent odor of sulfur dioxide, was expelled from the resin throughout the heating period. Upon removing the coked resin product from the pyrolysis unit after cooling, it exhibited a pyrophoric tendency upon exposure to air. It was subsequently found that the use of a slower heating cycle (ie, 2 or 3 days) to attain the carbonization temperature of 900°C gave coked resin spheres having superior qualities.

A cross section of the uranium-loaded Dowex 50-X12 cation resin beads after carbonization at 900°C is shown in Figure 12. The uranium, carbon, and sulfur contents of these beads were 1.85, 79.18, and 6.08 percent, respectively.

As shown in Figure 12, the uranyl sulfate-loaded cation resin beads retained their physical integrity after pyrolysis treatment, and they exhibited fewer fissures and pores than had uranyl nitrate-loaded anion resin beads after pyrolysis under equivalent conditions in previous tests. It is believed that the smaller-sized cation beads and/or the relatively high residual sulfur content of the carbonized resin at 900°C may account for this difference. Although much sulfur was expelled from the resin during the pyrolysis treatment, as evidenced by the prevalent odor of sulfur dioxide,

19015

Figure 12. CROSS SECTION OF URANIUM-LOADED DOWEX 50-X12 CATION RESIN BEADS CARBONIZED AT 900° C. (Bright Field Illumination; 500X)

it was found in subsequent tests that temperatures of approximately 1,800° C would be required to volatilize the sulfur more completely.

Anion Exchange Cellulose Studies

A batch of DEAE (diethylaminoethyl) anion exchange cellulose was contacted with 6.0 M ammonium nitrate solution containing uranyl nitrate (approximately 50 gms U/l) for 48 hours with magnetic stirring. The uranium-loaded cellulose was filtered and oven dried at 110° C, and showed a uranium content of 5.9 percent uranium. It was then pyrolyzed by heating to 900° C over a six-hour heating period in flowing helium. The carbonized product (irregular fused pieces) showed a pyrophoric tendency upon exposure to air. After crushing to powder in an iron mortar and pestle, the material had a helium displacement density of 3.1 gms/cc and a uranium content of 34.72 percent.

Photomicrographs of the DEAE anion exchange cellulose, the cellulose after loading with uranyl nitrate, and the loaded cellulose after carbonizing at 900° C are presented in Figure 13. Spectrochemical analysis of the carbonized uranium-loaded DEAE cellulose, as reported in Table 4, indicates that a high degree of uranium and carbon purity can be obtained.

Table 4
SPECTROGRAPHIC ANALYSIS OF CARBONIZED URANIUM-LOADED
ION EXCHANGE DIETHYLAMINOETHYL CELLULOSE

Element	Concentration (%)	Element	Concentration (%)
Ag	< 0.005	Mn	< 0.005
Al	< 0.01	Mo	< 0.002
Au	< 0.02	Na	0.01
B	0.08	Nb	< 0.02
Ba	< 0.002	Ni	< 0.01
Be	< 0.001	P	< 1
Bi	0.15	Pb	< 0.01
Ca	< 0.005	Pt	0.02
Cd	< 0.04	Sb	< 0.04
Co	< 0.005	Si	< 0.01
Cr	< 0.002	Sn	< 0.005
Cu	< 0.005	Ta	< 0.15
Fe	< 0.02	Ti	< 0.005
Hf	< 0.02	V	< 0.002
K	< 0.04	Zn	< 0.08
Li	< 0.002	Zr	< 0.002
Mg	< 0.01		

As seen in Figure 13, Views (a) and (c), ion exchange cellulose, Type DEAE, has a fibrous structure; but, when the fibers became loaded with uranyl nitrate, Figure 13(b), the fibers became matted together, probably during the vacuum filtration operation. However, individual cellulose fibers are still evident.

An ion exchange process that uses powdered resins instead of conventional beads and granules has also been reported.⁽³⁾ It is expected that the method of adsorbing uranium on cation, anion, or cellulose-type materials of this type would also have considerable versatility for fuel element fabrication.

Most of the experimental work at Y-12 on uranium loading and coking of ion exchange materials was conducted using a commercial variety of spherical ion exchange resin particle. This type of particle represented the general anion type, because related studies at Y-12 involving the anion exchange behavior of hexavalent uranium from various nitrate solutions enabled uranium adsorption equilibrium values to be controlled within desired limits. The uranium loading and coking studies were then extended to a commercial variety of spherical ion exchange resin particles representing the general cation type, and to a fibrous cellulose ion exchange material only, to show the general feasibility of the method. Thus, a preponderance of experimental information was obtained on coked uranium-loaded anion resins; although, in some respects, the coked uranium-loaded cation resins showed some superior characteristics such as greater structural strength and less internal porosity.

The general method of coking uranium or metal-loaded resin microspheres is particularly attractive from the standpoint that the uranium content and the uranium-to-carbon ratio can be varied and controlled over a wide range by using predetermined and accurately known equilibrium adsorption data. Since a wide variety of

(a) Untreated Fibers

19018

(b) Fibers Loaded with Uranyl Nitrate

19016

(c) Loaded Fibers that were Carbonized at 900° C

19019

Figure 13. ANION EXCHANGE CELLULOSE-TYPE DIETHYLAMINOETHYL (DEAE). (Polarized Light; 100X)

carbonaceous ion exchange resin materials are commercially available in spherical form, ranging in diameter from less than 40 microns to greater than 1,000 microns⁽⁴⁾ and with wide variations in coking characteristics (eg, divinylbenzene copolymer content), carbonized uranium-loaded fuel element particles can also be made with various amounts of controlled internal porosity.

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