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

UNION CARBIDE

ORNL-TM-1809

COPY NO. - 113

THE PROCESSING OF ThO_2 AND UO_2 SOL-GEL MATERIALS

C. F. Weaver, D. N. Hess, H. F. McDuffie,
W. T. Rainey, and B. A. Soldano

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

ORNL-TM-1809

Contract No. W-7405-eng-26

REACTOR CHEMISTRY DIVISION

THE PROCESSING OF ThO_2 AND UO_2 SOL-GEL MATERIALS

C. F. Weaver, D. N. Hess, H. F. McDuffie,
W. T. Rainey, and B. A. Soldano

JUNE 1968

OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee
operated by
UNION CARBIDE CORPORATION
for the
U.S. ATOMIC ENERGY COMMISSION

~~DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED~~

THIS PAGE

WAS INTENTIONALLY

LEFT BLANK

CONTENTS

THE PROCESSING OF ThO_2 AND UO_2 SOL-GEL MATERIALS

C. F. Weaver, D. N. Hess, H. F. McDuffie,
W. T. Rainey, and B. A. Soldano

ABSTRACT

Research in the Reactor Chemistry Division on the processing of ThO_2 and UO_2 sol-gel materials, synthesized by personnel of the Chemical Technology Division, provided part of the chemical support for programs devoted to the development and use of sol-gel reactor fuels.

The ThO_2-UO_2 (3 mole %) gels when heated gave off gases the quantity and nature of which depended strongly on particle size.

The reversible adsorption of CO_2 on finely divided gel was studied over the temperature range 250-1000^0. A method was developed to reduce the surface area of the gel and, thus, reduce the amount of gas which it could release in service.

The sol-gel ThO_2 microspheres were also found to yield gases upon heating. The largest amount of gas evolution occurred in the following centigrade temperature intervals: (240 - 260), (400 - 460), (700 - 760). Organics were essentially eliminated at 260^0, and most of the gas was either CO_2, CO, or H_2.

Attention was then turned to UO_{2+x} sol-gel microspheres. It was found that H_2O vapor carried by an inert gas (He or A) was very effective in the removal of the carbonaceous materials, that their removal was essentially complete at 550^0, and that

this removal could be monitored with a Hydrocarbon Analyser. Densification of the microspheres was achieved by sintering with H_2O + A in the temperature range 550^0 to 1000^0. Two hours at 850^0 was sufficient. Reduction of O/U ratio to two was accomplished with H_2 in the temperature range 550^0 to 1000^0. One hour at 850^0 was found to be sufficient. Typical products had the following range of analyses:

O/U = 2.000 - 2.009
C, % = <0.001 - 0.013
d, g/cc = 10.5 - 10.9
N_2, % = <0.001
S.A., m^2/g = 0.006 - 0.033

It is not yet possible to routinely obtain the best results which have occasionally occurred during these studies. The best values for the listed parameters were:

O/U = 2.000
C, % = < 0.001
N_2, % = < 0.001
d, g/cc = 10.9
S.A., m^2/g = 0.006

Although this work was brought to a close September 1, 1967, because of budget cuts, it is obvious that added studies along these lines could very well lead to significant improvement improvement in the processing and monitoring techniques.

INTRODUCTION

Research in the Reactor Chemistry Division on the processing of ThO_2 and UO_2 sol-gel materials provided part of the chemical support for programs devoted to the development and use of sol-gel reactor fuels. Such materials, as originally produced, contained large amounts of carbonaceous and nitrogenous substances. On heating, the interaction, pyrolysis and catalytic cracking of these impurities produced gases which could distort or rupture closed fuel containers and possibly weaken the container walls by chemical reaction. In addition, the density of such materials was far below the theoretical value, frequently by more than a factor of two. High density is desirable to avoid dimensional changes of the fuel as well as to retain fission products.[1] Also, when the material contained uranium, its oxygen to uranium ratio was usually higher than two. It is desirable that this ratio be as close to two as possible to provide a high thermal conductivity.[1]

The processing of uranium-thorium sol-gel oxides must then have as its goals the removal of carbonaceous and nitrogenous materials, densification of the purified product, and (in uranium containing gels) the reduction of the oxygen to uranium ratio to two. These events must occur, in the case of microspheres, without destroying the geometry of the particles.

The materials used in this work were synthesized by personnel of the Chemical Technology Division.[2] In addition, considerable processing efforts were made there with particular emphasis on scaling up the handling procedures.[3] Personnel of Metals and Ceramics Division also worked on the processing of these materials with special emphasis on differential thermal analysis, hot-stage microscopy, and sintering.[4] The relationship between shrinkage and weight loss for ThO_2 gel up to 500° was investigated by Professor M. W. Wadsworth at the University of Utah.

The efforts of the Reactor Chemistry Division involved ThO_2-UO_2 (3 mole %) Kilorod material, ThO_2 microspheres, and UO_2 microspheres. The work on the first two materials has been reported elsewhere[5-8] and is summarized here. Work on the UO_2 microspheres constitutes the major subject of this report.

ThO_2-UO_2 (3 mole %)[5-7]

The ThO_2-UO_2 (3 mole %) gels used in these studies were designated H-II, SC, and PL in the Chemical Technology Division. In addition to the materials, they supplied the information that these gels gave off gases upon heating and that the quantity of gas evolved during heating was dependent on the temperature. This factor was held constant at 1000°C in most experiments to permit exploration of other factors that affect both the nature and the amount of gas evolved from the gel.

Effects of Particle Size

A strong effect of particle size on the total gas evolved at 1000°C from SC material is indicated by Fig. 1; the results are plotted on a scale of relative surface area, derived from the arithmetic average particle diameters with an assumed value of 1.0 for surface area of spherical particles of 1.0 mil diameter. The linearity of the relationship and the extrapolation to zero gas evolution at zero surface area suggest that the evolved gas (essentially all CO_2) was being released only from the surface exposed by grinding and not from the interior of the particles.

A strong effect of particle size was also found when the H-II material was tested at 1000°C. Eight times as much gas was released from -270 mesh material as from -20 +40 mesh material. The maximum volumes of gas obtained were as high as 1.0 std cm^3/g; this was six times as much as was released from the SC material. The composition of the gas was substantially different; CO and H_2 were present as important constituents. Particle size was found to have an important effect on the gas composition as well as the total gas. Figure 2 shows the relationship between surface area (measured by the BET method) and the gas composition. Extrapolation of the relationship of Fig. 2 to the very low BET surface area of 0.1 m^2/g suggests that the gas evolved would be about 99% CO_2 - just what was observed in tests of the SC material, which had such a low surface area.

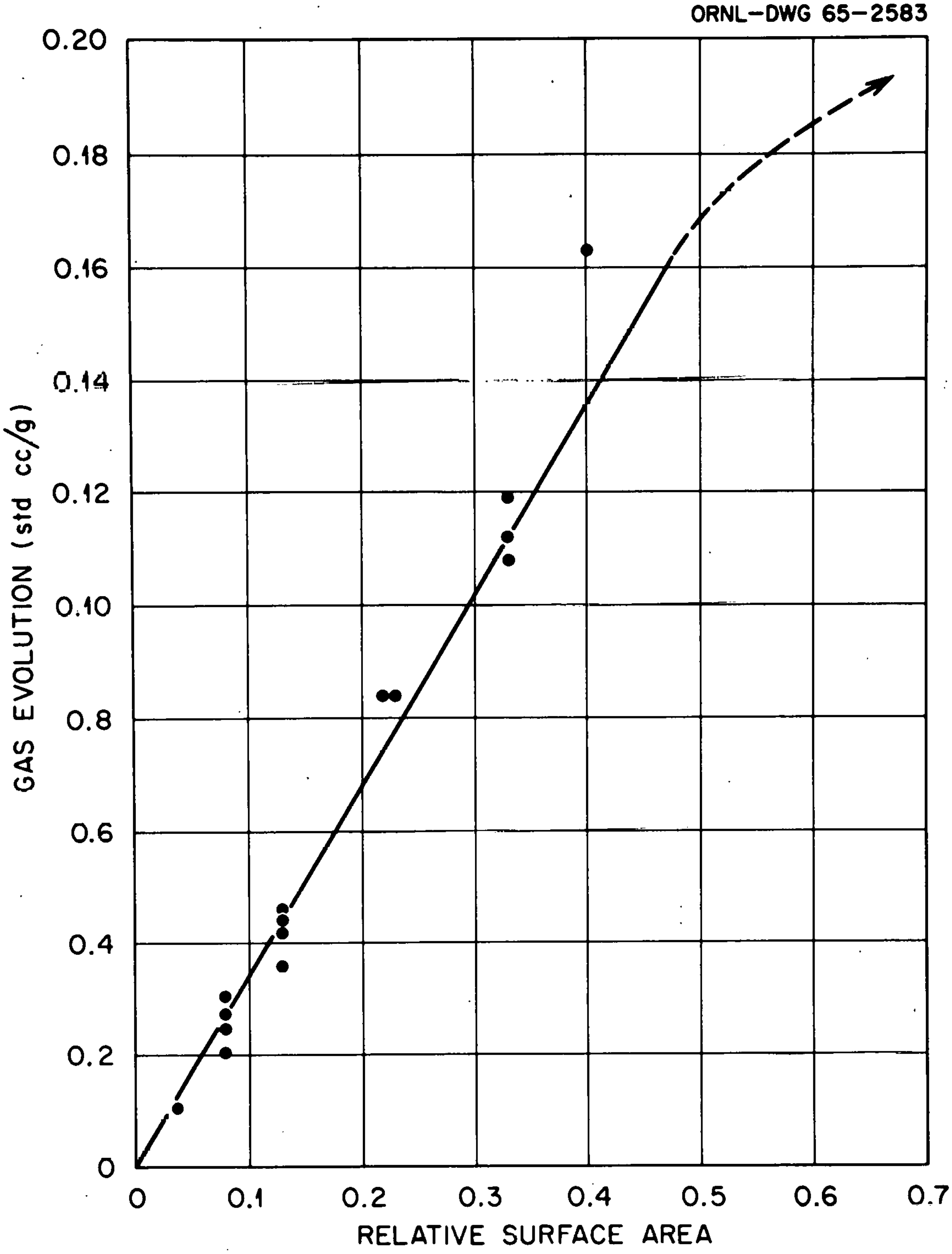


Fig. 1. Effect of Particle Size (Relative Surface Area) on Total Gas Evolution from SC Sol-Gel Material at 1000°C.

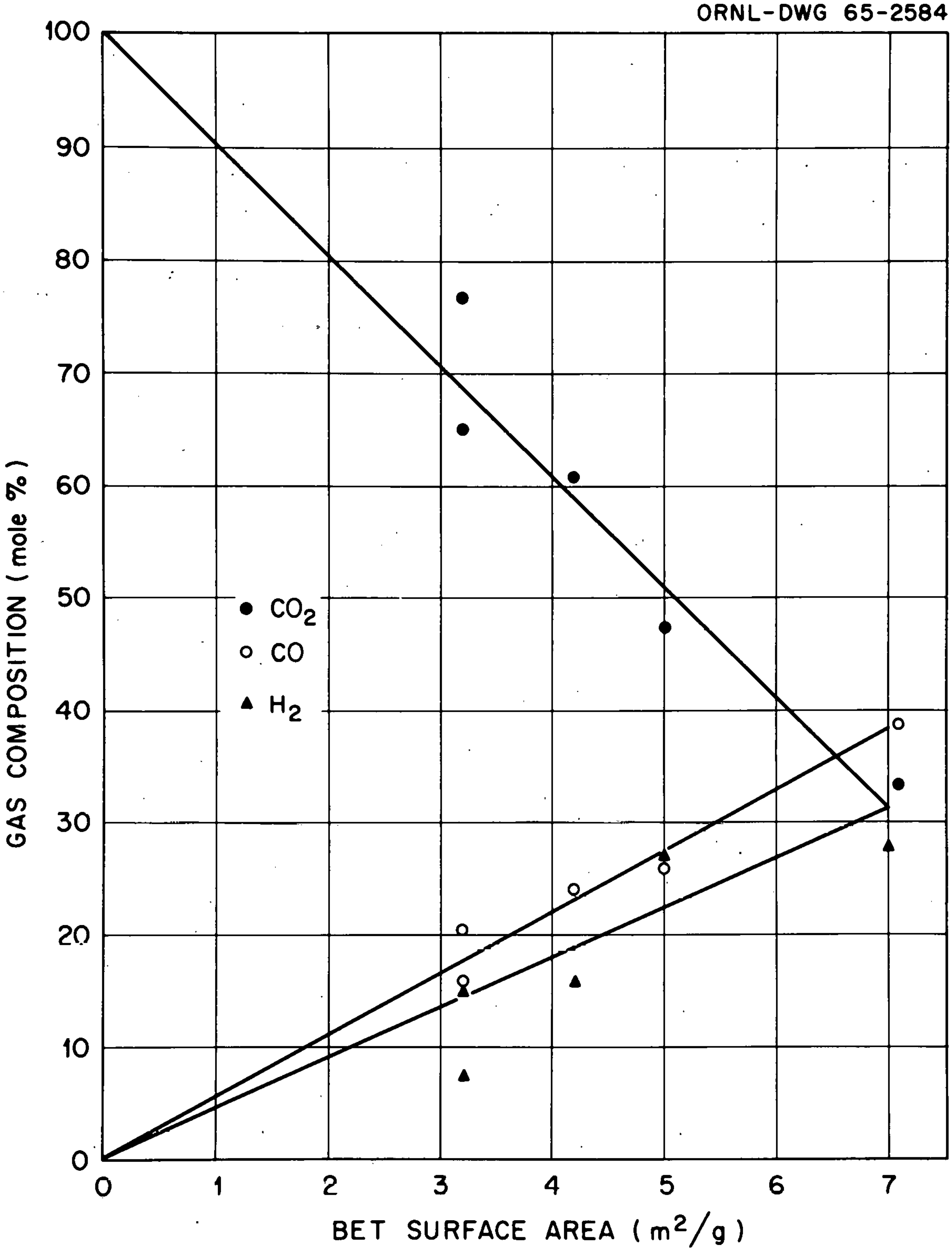


Fig. 2. Effect of BET Surface Area on Composition of Gas Evolved from H-II Sol-Gel Material at 1000°C.

Effect of Temperature

Measurements of the total gas evolved and the rate of the evolution were made on -270 mesh samples of the H-II material at temperatures of 1000 and 1200°C. More gas was consistently evolved from the samples at 1000 than at 1200°C, and there was some evidence that, at 1200°C, an initially higher gas release was being followed by a slow removal or consumption process. It is possible that the surface of the sol-gel material at 1200°C was catalyzing the water-gas reaction $H_2 + CO_2 \rightleftharpoons CO + H_2O$, for which the value of the equilibrium constant is around 2.7 at 1200°C. The gas analysis technique which was used in the experiments did not provide values for H_2O. As a consequence, the reaction of H_2 and CO_2 to form CO and H_2O could have resulted in an apparent decrease in the total gas evolved.

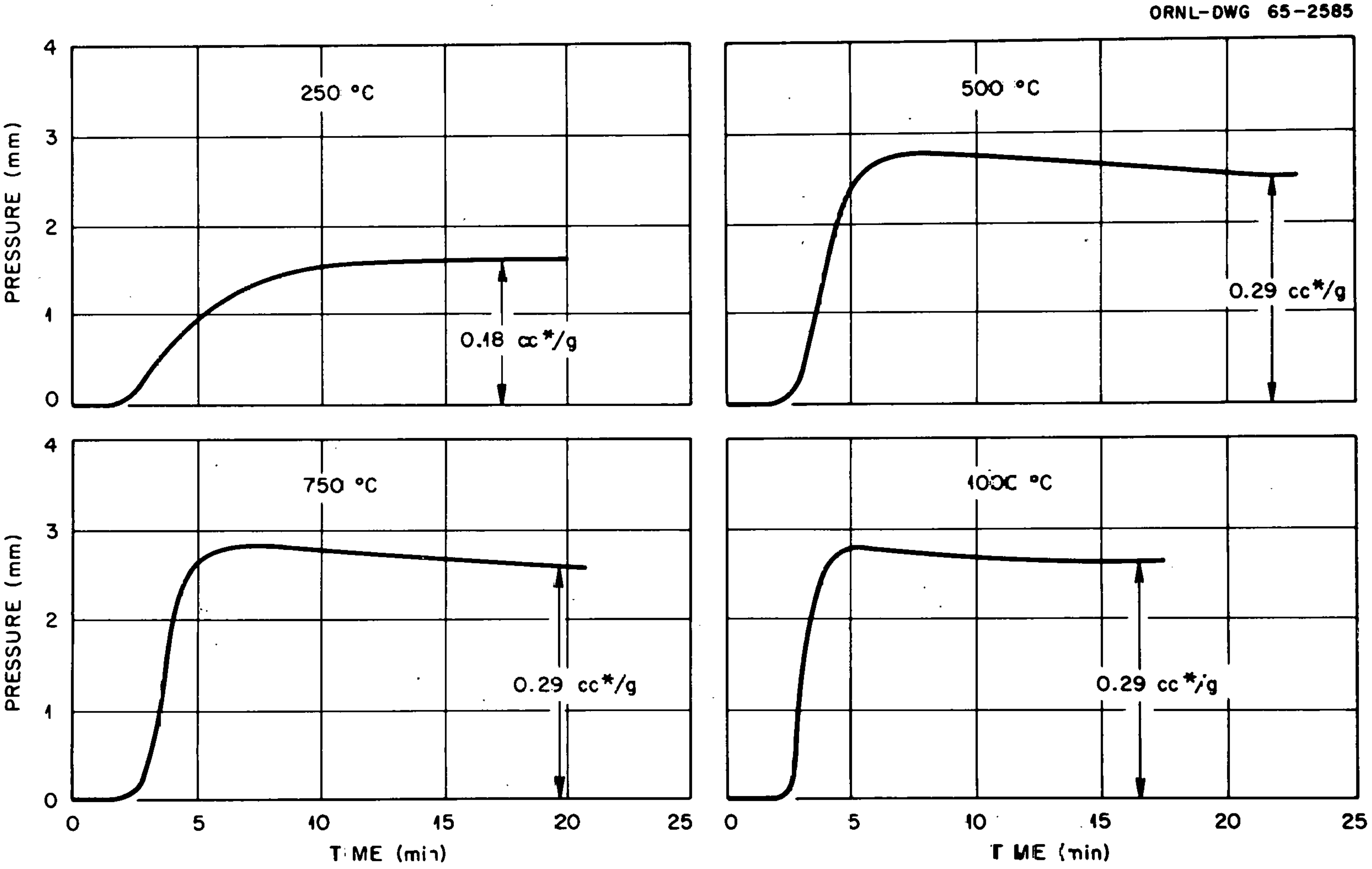
Reversible Gas Adsorption

In studies of particle size effects, the SC material had released a gas which was essentially pure CO_2. After these tests, some of the samples were exposed to air to determine whether CO_2 would be adsorbed and, if so, to what extent. Reevacuation at 1000°C was used to remove any adsorbed gas, and it was found that less than 10% of the original amount was evolved. This suggested that, for the SC material, the originally evolved CO_2 had been present in the original material and had not come from adventitious adsorption from the air during a brief exposure during weighing. The small amount of gas involved made it inadvisible to perform further studies of reversible adsorption with this material.

A sample of -270 mesh H-II material was used for a series of studies of the reversible adsorption of CO_2; the desorption was followed as a function of time at various temperatures, while the adsorption was always achieved by exposing the sample to 15 mm of dry CO_2 and permitting it to cool to room temperature in this environment. The samples were then evacuated at room temperature before the test boat was re-inserted into the preestablished temperature region of the furnace. Figure 3 shows the results of successive tests at 250, 500, 750, and 1000°C; the desorption was quite rapid, and temperatures of 500°C or higher were apparently adequate to remove all the adsorbed gas in these tests. The reversibility of the CO_2 sorption-desorption is illustrated by Figure 4, showing how the pressure in the apparatus (originally evacuated at room temperature after exposing the sample to 15 mm of CO_2) changed as the H-II sample was heated to 1000°C and then allowed to cool down. A similar reversibility was found for SC material, but the amounts of gas and pressures were negligible.

Reduction of Surface Area

These studies were directed toward the development of treatments which would reduce the surface area of the prepared sol-gel and, thus, reduce the amount of gas which it could release in service. Batch exposures at temperatures of 1000°C to CO_2 or H_2O alone did not give substantial changes in the



* TOTAL GAS, MEASURED AT ROOM TEMPERATURE

Fig. 3. Desorption of CO_2 from H-II Sol-Gel Material at Various Temperatures.

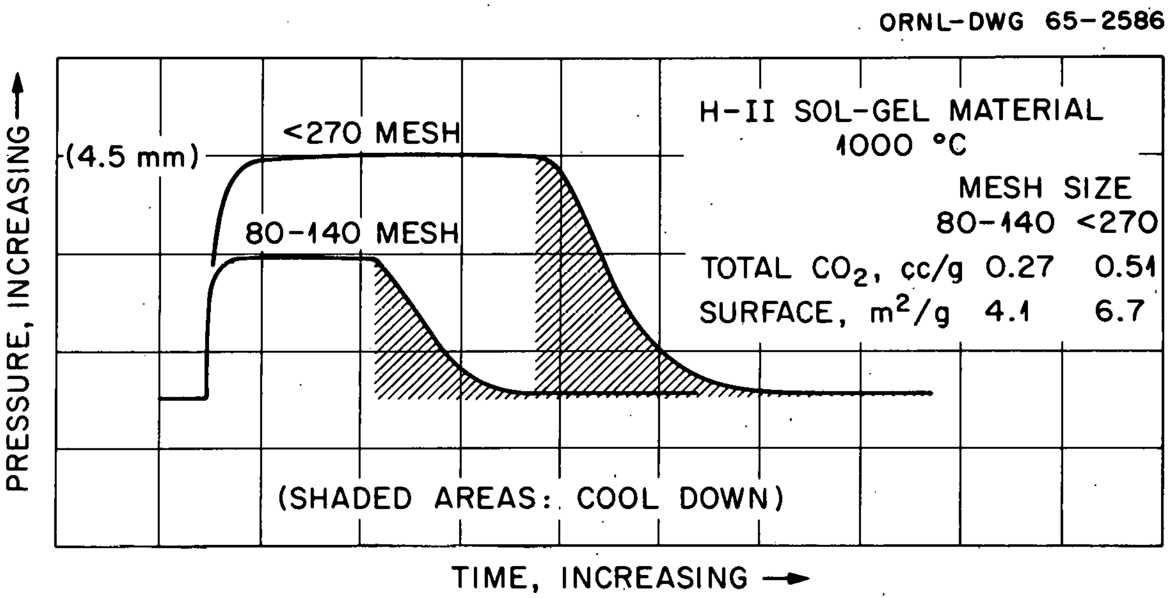


Fig. 4. Reversibility of CO_2 Desorption from H-II Sol-Gel Material at 1000°C.

surface area of the sol-gel or in its capacity for reversible adsorption of CO_2. Mixtures of the two gases, CO_2 and H_2O, at 1000°C, on the other hand, were found to give approximately 50% decreases in the surface and adsorption capacity of the sol-gel for each treatment, although the duration of the treatment did not appear to be important. Thus, two treatments would reduce the surface area to 25% of the original -- three to 12.5% of the original. Tests in which the sol-gel pellets were ground to successively smaller particle sizes between successive batch treatments with mixtures of H_2O and CO_2 at 1000°C suggested that the effect of the treatment permeated the entire material and was not localized at the surface exposed by grinding. Table I illustrates these results; a three-fold reduction in BET surface area was accompanied by a four-fold reduction in CO_2 adsorption capacity, although the particle size reduction would have, in an untreated sol-gel, caused a several-fold <u>increase</u> in both surface area and gas evolution with an accompanying increase in CO_2 adsorption capacity.

Since batch treatments are not convenient for larger scale concepts and since single batch treatments, however extended in time, did not give more than 50% reduction in area, the effect of treatment in a flowing stream of $H_2O + CO_2$ at 1000°C was studied. As shown in Figure 5, the flowing stream technique was much more effective; the capacity of the sol-gel for gas adsorption appeared to be a predictable function of treatment time, regardless of whether the treatments were continuous or

Table I. Effect of Treatment with H_2O-CO_2 on Sol-Gel Properties

Particle Size Mesh	Sequence of Tests and Treatment	BET Surface Area m^2/gm	Reversible CO_2 Absorptive Capacity std. cc/gm
40-80	Original material: degassed 1000^0C	2.57	0.20
40-80	After first surface area reduction		0.10
<140	Ground and sized to 80-140 mesh (otherwise untreated)	1.58	0.10
80-140	After second surface area reduction		0.08
<270	Ground and sized to 200-270 mesh (otherwise untreated)	1.67	0.06
200-270	After third surface area reduction	0.78	0.05

ORNL-DWG 66-977

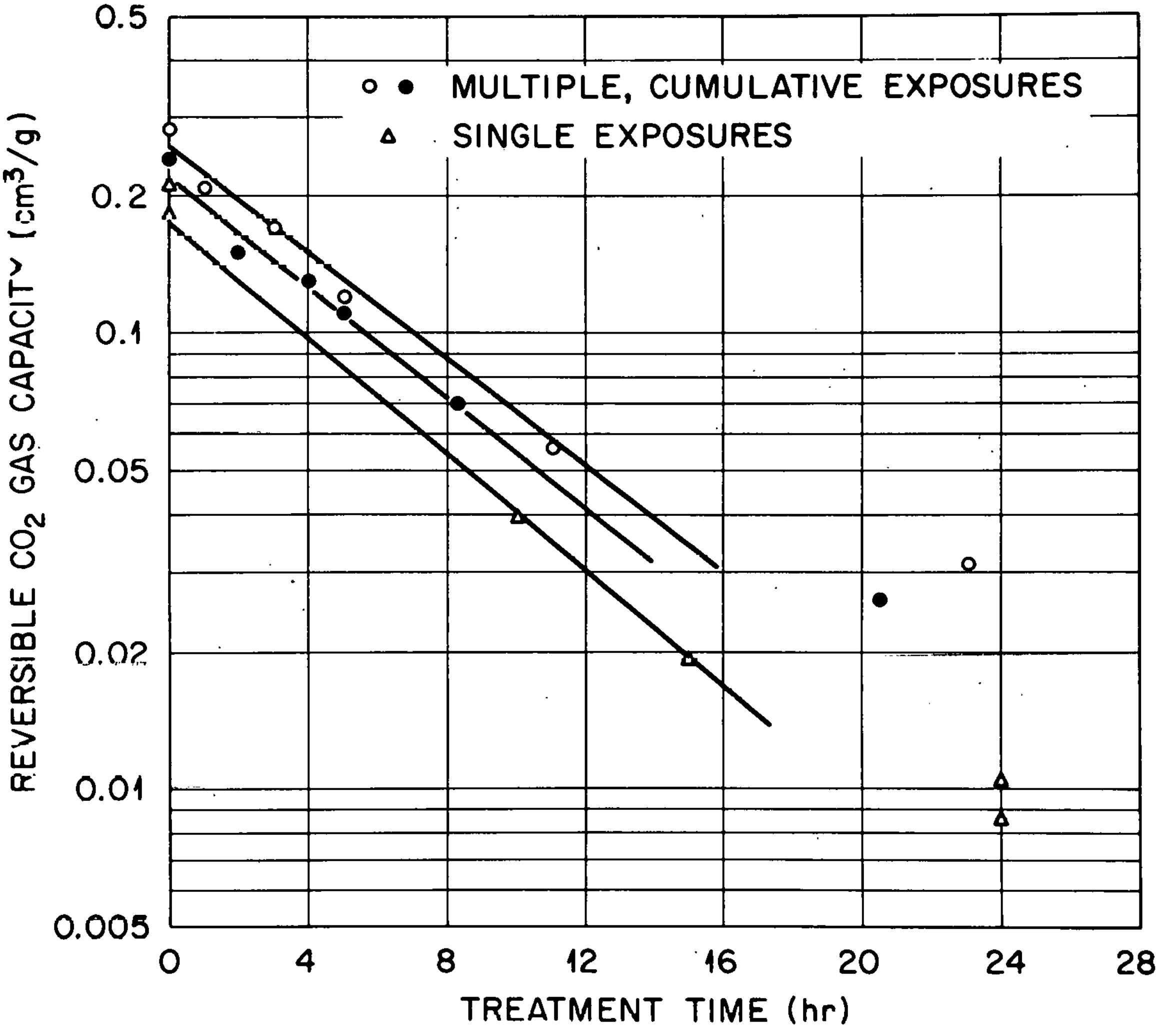


Fig. 5. The Effect of a Flowing Mixture of CO_3 and H_2O at 1000°C on the Reversible CO_2 Capacity of ThO_2-3% UO_2 Sol-Gel.

interrupted. A 16-hour treatment appeared appropriate for a 90% reduction in the original gas-adsorption capacity of the material. Corresponding reductions in the BET surface area of the material were obtained. The linearity of the semi-logarithmic plot in Figure 5 suggests that there may be a first order process which is responsible for the surface area reduction.

A different series of laboratory samples of sol-gel material, prepared with various furnace atmospheres during heating, calcination, and cooling, and designated the PL series, was evaluated with respect to gas evolution and reversible gas adsorption. (Table II). All PL samples gave much less gas evolution upon being ground in the as-received condition and heated to 1000^{0}C in vacuo; about 0.30 std cc/gm gas was evolved compared with 1.30 for the H-II samples previously studied. An even more striking reduction was noted in the capacity of the PL series for reversible CO_2 adsorption; values of 0.02 std cc/gm were obtained compared with 0.27 for the H-II material.

ThO_2 MICROSPHERES

The ThO_2 microspheres (designated PL-12-6-1600 in the Chemical Technology Division) possessed a uniquely defined spherical particle size distribution, in contrast with the randomly crushed sol-gel material previously studied. Since the sol-gel microspheres as received from Chemical Technology Division had not as yet been calcined, they were expected to contain an excessive amount of gas. The study, therefore, was

Table II. Gas Evolution Results on PL Series Oxides

Sample	Amount of Gas Evolved, cc/gm As-received	Reversible
Haw's #2	1.30	0.27
PL-1	0.28	0.01
PL-2	0.30	0.02
PL-3	0.28	0.02
PL-4	0.32	0.02

directed toward a definition of the composition and the amount of gas evolved from the sol-gel microspheres, as a function of temperature.

Experimentally, 4.04 grams of "as received" air-dried microspheres were evacuated to 1μ at room temperature. The sample was then heated through arbitrarily selected temperature ranges, and the gases were collected. The results are listed in Table III from which several observations can be made. The amount of gas evolved from air-dried sol-gel microspheres was greater than $\sim\frac{20\text{ccs}}{\text{gram}}$. This estimate can be contrasted with the value of $\sim\frac{.05\text{ccs}}{\text{gram}}$ of gas evolved from the previously studied PL series. However, it must be emphasized that the microspheres had not, as yet, been calcinated at 1150°C. The largest amount of gas evolution occurred in the following centigrade temperature intervals (240-260), (400-460), (700-760). Above 760°C, only a small amount of gas remained and the volatile organics were essentially eliminated at ~260°C. Most of the gas evolved was either CO_2, CO, or H_2. This gas composition was similar to that previously found in ThO_2-UO_2 Kilorod material.

Since this material was obtained in a wet,* unfired condition, the amount of gas present far exceeded that associated with the previous sol-gel material. The objectives of this study, therefore, were:

*that is, saturated with the organic mixture used for dehydration of the sol.

Table III.

Gas Evolution Data on Air-Dried ThO_2 Microspheres Over 25-1000°C Temperature Range

Temperature Interval °C	ΔT °C	Quantity of Gas cc/g	Principal Gases Collected under Increasingly Intensive Trapping Conditions		
			Room Temperature	Dry Ice	Liquid Nitrogen
120-150					
150-190*	70	1.2	Organic	CO_2	NO, N_2
190-240					
240-260*	70	>3.7	Organic	CO_2, NO	CO, N_2, H_2
260-360	100	~3.7	None	CO_2	CO, H_2
360-400					
400-460*	100	>3.7	Organic	CO_2; organic	CO, H_2, CH_4
460-520					
520-580*	120	~3.0	CO_2, organic	CO_2	CO, H_2
580-600					
600-760*	180	>3.7	CO_2		CO, H_2
760-1000	240	0.27	CO_2, CO		CO, H_2, N_2

*In this range the macro-portion of the gas was evolved.

(1) Investigation of the factors that facilitate gas removal from the wet, uncalcined sol-gel microspheres without impairing their structural integrity.

(2) Assessment of the factors affecting the subsequent readsorption of gas by the sol-gel microspheres after intial degassing.

Relative to the first, studies were undertaken to determine whether or not any carbonaceous material remained in the microspheres after initially heating to 1000°C in the presence of O_2 and H_2O. Previously, it had been noted that firing gave rise to a blackening of the sol-gel beads, suggesting that the discoloration might be due to the presence of embedded carbon. To test for carbon, the microspheres were then ground up to less than 270 mesh and reheated to 1000°C, and the residual gases were removed. One cc/g of gas was released; this contrasted with 0.27 cc/g previously released at 1000°C from microspheres. The composition of the gas was as follows:

Gas	Volume %
CO_2	50.1
CO	13.2
H_2	32.2
N_2	4.5

Pure oxygen was then introduced at 1000°C for the purpose of burning any carbonaceous material; the appearance of CO_2 in the collected gas would indicate the presence of contained carbon. Analysis of the residual oxygen showed CO_2 to the extent of 0.01 cc/g. The material was subsequently treated at

1000^{0}C four times more with oxygen and once with water. In view of the lack of generation of additional CO_2, it was assumed that no further carbon remained in the material. The black color of the calcined sol-gel microspheres should, therefore be attributed to structure defects in the material. It was concluded that color changes do not serve as good indicators for carbon.

At this time, the amount of CO_2 readsorbed after the sol-gel had been cleared of entrapped gas was determined. The clean sol-gel material was treated with O_2 and fired at 1000^{0}C four times, followed by evacuation. An excess of CO_2 was then contacted with the sample at room temperature. After equilibration, the excess CO_2 was pumped off. The sample was then fired to 1000^{0}C, and the amount of CO_2 evolved was measured. The magnitude of the "reversible" CO_2 adsorption, 0.14 cc/gram can be contrasted (see Table II) with those of the Haw's II and PL 1-4 series. One notes that the "reversible" gas adsorption of PL 12-6-1600 microspheres was considerably closer in magnitude to that of Haw's #II, than to that of the PL 1-4 sereis.

UO_{2+x} MICROSPHERES

The chemistry of UO_{2+x} microspheres is clearly more complex than that of ThO_2 microspheres. This, however, may be turned to use. For example increasing the value of x in UO_{2+x} strongly enhanced the rate of low temperature sintering and made it unnecessary to exceed 1000^{0}C, a distinct engineering advantage. Our approach to the processing problem was first to make a series of probing experiments. The results along with information from the literature, were used to design a processing scheme which, while overly complex and time consuming, did work well. Finally, emphasis was placed on monitoring the removal of carbonaceous material, simplifying the sequence, shortening the time, and reducing the maximum temperature.

Initial Experiments

The gases H_2, H_2O, CO and CO_2 may be used[9-11] to control the value of x in UO_{2+x} by reactions (1) and (2).

$$[O]_{UO_{2+x}} + H_2 \rightleftharpoons H_2O \qquad (1)$$

$$[O]\ UO_{2+x} + CO \rightleftharpoons CO_2 \qquad (2)$$

Stronger oxidants, like O_2, would tend to cause phase changes and, hence, endanger the geometric integrity of the microspheres. We have observed that UO_2-ThO_2 ss (Kilorod material) as well as UO_{2+x} microspheres frequently, but not always, reacted with H_2O vapor to produce H_2. This reaction has been reported in the literature, and its thermodynamics well described.[11] From this paper it is clear that whether or not reaction (1) proceeds to a measurable extent depends on the value of x. This explains why on occasion the UO_{2+x} microspheres will not reduce H_2O or CO_2. To confirm that UO_{2+x} from a sol-gel source behaves as the UO_2 described in the literature, a sample from Batch P-6-3-1600, F-10 was ground to <270 mesh and reduced with CO at 1200°C until no further reaction occurred. This product was readily oxidized by either

H_2O or CO_2 producing H_2 or CO respectively. Once the oxidizing reaction had proceeded to its limit the solid product could again be easily reduced with CO, producing CO_2. These reactions occured without changing the total pressure in the system. This is consistent with equations (1) and (2) above and indicates that higher oxides were not produced in the oxidation, a result consistent with the literature.[11]

Since CO was one of the products formed during the outgassing of UO_{2+x} microspheres, the possibility of the reaction $2CO \rightarrow CO_2 + C$ was of interest. This reaction has been shown[12] to be kinetically inhibited by small amounts of CO_2 which also occur during outgassing. Thus carbon deposits, formed by this mechanism, were not expected. This is consistent with our experience in applying the processing scheme recommended later.

The reactions of water with carbon to form CO, CO_2, and H_2 occur in the temperature range of the proposed UO_2 microsphere processing scheme. The reaction of H_2O at 1000°C with charcoal produced CO_2, CO, and H_2 at rates comparable to those observed during UO_2 microsphere processing and was therefore definitely part of carbon removal chemistry providing part of the explanation for the favorable effect of excess H_2O vapor in carbon removal.

The wet UO_2 microspheres yielded CO_2, CO, H_2, N_2, O_3, NO and organics when heated with steam and evacuated. The temperature intervals of maximum gas evolution were 150 to 250°C and

400 to 650°C. The principal organic gas evolved (primarily in the 300 to 350°C range) was CH_4. This was in direct contrast with the production of higher molecular weight organic products previously noted in the case of dry ThO_2 microspheres. A possible explanation[13] for the difference is that steam changes the cracking pattern, yielding almost exclusively methane with a trace of ethane, in contrast to the yield of larger organic fragments when these materials are simply heated under vacuum. These would be more easily removed from the microspheres, thus, providing another part of the reason why water vapor enhances the removal of carbonaceous materials. Previous work on "as received" ThO_2 microspheres indicated that direct heating of the unfired sol-gel beads resulted in the entrapment of the organic impurities in the sol-gel thereby precluding further removal of this potential source of gas in the reactor fuel. If, on the other hand, the unfired sol-gel was first treated with an excess of water vapor at room temperature prior to heating, a significant amount of the organic contaminants could be removed with a commensurate reduction in the possibility of carbon entrapment.

Consequently, the technique first applied to UO_2 microspheres was to subject them to an excess of water vapor at room temperature. Upon completion of water sorption, the excess water vapor was removed by vacuum pumping. The sample was then heated to the particular temperature under investigation. At this temperature, both the total volume of gas as well as those gases which were uncondensible in liquid nitrogen, were collected. The temperature range from 500 to 600°C was the most effective with respect to removal of gases by this method.

Next an attempt was made to combine the effects of steam, continuous flow, and mixtures of H_2O and CO_2, treatments previously found useful in the reduction of the surface area of Kilorod material.

A 1:1 mixture of CO_2 and H_2O was passed over UO_{2+x} microspheres at 550° for several hours. This treatment reduced the reversible sorptive capacities to 0.18 cc/g and 0.05 cc/g for H_2O and CO_2 respectively.

Two additional experiments with flowing CO_2 and H_2O mixtures were made to determine the change in O/U ratio and the reduction of carbon content. In both cases the H_2O to CO_2 ratio was 3:1 and the flow rate was 8 cc/min. The samples were treated as shown in Table IV.

After the 500°C flow treatment, each sample was inserted in a vacuum line for evaluation which consisted of heating the sample at 500°C and determining the amount and composition of the gases remaining in the sample (or sorbed by the sample in the process of transfer from flow to vacuum system). Then, the sample was heated above 500°C in 100°C intervals with intermediate pump-downs at temperature, and similar determinations made as shown in Table V.

The second procedure gave a product with less residual gas. Nevertheless, the final products (after the gas removal at

Table IV. Gas Flow Treatment of UO_{2+x} Microspheres

First Sample

Temperature, °C	Time, hr.	Sweep Gas
125	16	CO_2, H_2O
250	2	CO_2, H_2O
350	1	CO_2, H_2O
450	3	CO_2, H_2O
500	2	CO_2, H_2O
Cooled and flushed	16	N_2

Second Sample

Temperature, °C	Time, hr.	Sweep Gas
125	16	CO_2, H_2O
250	1/2	CO_2, H_2O
250 - 500	1-1/2	CO_2, H_2O
500	6	CO_2, H_2O
Cooled and flushed	16	CO_2, H_2O

Table V. Analysis of Product Gases

Temperature °C	Total Gas Not Condensible at $-78^\circ C$ cc gas/gm sample	Composition, Volume %				
		CO_2	CO	H_2	N_2	O_2
Sample 1:						
500	0.51	93.7			5.4	0.9
600	0.26	93.5			5.6	0.9
700	0.01	89.3			9.8	0.9
800	0.03					
800-1000	0.03	43.6	14.1	2.1	36.1	3.7
Sample 2:						
500	0.09	89.5	2.7	0.2	4.9	
600	0.00					
600-1000	0.07	92.7			6.5	

1000°C) were identical in carbon content (0.013%) and almost identical in oxygen:uranium ratio (2.124 vs 2.153). It is clear that flowing mixtures of CO_2 and H_2O will reduce considerably the reversible sorptive capacities, the residual gases, the carbon content and the O/U ratio of the UO_{2+x} microspheres.

Next, the combination of steam stripping with continuous flow in the absence of CO_2 was applied to the microspheres. The sweep rate and gas ratio were 8 cc/min and 1:3 He:H_2O. The time-temperature cycle was 20 hours at 125°C, 4 hours at 300°C, and 4 hours at 500°C. After this treament, the reversible CO_2 adsorption of the sample between room temperature and 500° was found to be 0.03 cc/g. After the reversible CO_2 test, the sample was heated to 1000°C in vacuo and alternatively treated with water vapor and evacuated at 1000°C. The release of gas was negligible, and there was no evidence for CO_2 readsorption. Finally, the sample was analyzed for O/U ratio and percent carbon. An O/U ratio of 2.071 and a carbon content of 0.006% were found.

Additional tests were performed on the microspheres with mixtures of H_2O and He. The treatment schedules are indicated in Table VI. The ratio of H_2O to He was 3:1 with a flow rate of 8 cc/min. When He alone was used, the flow rate was 2 cc/min. After the intermediate treatment at 400 or 500°, each material was calcined in He at 1000° for one hour and subsequently cooled in He.

Table VI. Gas Flow Treatment of UO_{2+x} Microspheres

	125°C		400°C		500°C		Product		
	Time hrs.	Sweep Gas	Time hrs.	Sweep Gas	Time hrs.	Sweep Gas	O/U	Carbon %	Physical Appearance
1.	4	H_2O-He							
	15	He							
	2	H_2O-He	4	H_2O-He			2.022	0.014	good
2.	16	H_2O-He	2	H_2O-He			2.026	0.017	good
3.	16	H_2O-He	6	H_2O-He			2.025	0.012	good
4.	16	H_2O-He			2	H_2O-He	2.027	0.014	good
5.	16	H_2O-He			6	H_2O-He	2.034	0.014	good
6.	16	H_2O-He	6	He			2.003	0.017	Partially disintegrated
7.	16	He	6	He			2.018	0.273	Partially disintegrated

The carbon content of sample 7 was very high, emphatically demonstrating the necessity of H_2O for satisfactory carbon removal. The O/U ratio of sample 6 was anomalously low for a sample processed without H_2 reduction and is probably erroneous. Thus, the flowing mixture of He and H_2O reduced the carbon content to about the same extent found with CO_2 and H_2O mixtures. The O/U ratio, however, was considerably lower in the absence of CO_2. This seems to explain the observation that mixtures of CO_2 and H_2O cause faster sintering than H_2O alone, since it is generally accepted[1] that higher O/U ratios result in faster sintering.

The previous studies were made with batch P-1-24-1226, UF-2. As received, it had an O/U ratio of 2.265 and a carbon content of about 8%. The processing experiments with flowing H_2O with an inert carrier gas (A or He) were continued with a new batch, P-6-15-1607, F-19. As received it had a O/U ratio of 2.571 and a carbon content of greater than 6%. The effect of H_2 on the O/U ratio was also investigated. Tables VII and VIII summarize the treatment schedules and results.

Experiments 1-6 and 9 were made with a constant pre-treatment time and temperature (16 hrs at 125°C) and a constant calcination (1 hr at 1000°C in helium). The variations studied were in the temperature and duration of exposure to a helium-water mixture at intermediate temperatures. All seven of the treatment combinations gave products with low carbon content. Experiments 7, 8, and 10-18 involved H_2 as well as

Table VIIa. Conditioning of UO_2 Microspheres

Time (hrs) and Atmosphere at Temperature

No.	125°C	200°	250°	300°	350°	400°	450°	550°	1000°
1	16; $He-H_2O$	6 $He-H_2O$							1 - He
2	16; $He-H_2O$	2 $He-H_2O$							1 - He
3	16; $He-H_2O$			6; $He-H_2O$					1 - He
4	16; $He-H_2O$					2; $He-H_2O$			1 - He
5	16; $He-H_2O$	(run interrupted and cooled to room temperature)				2; $He-H_2O$			1 - He
6	16; He		2.5; $He-H_2O$		3; $He-H_2O$		1.25; $He-H_2O$	1 - He	1 - He
7	2; $A-H_2O$		2; $A-H_2O$		2; $A-H_2O$		2; $A-H_2O$	2 - H_2	1 - H_2
8	1.25 He		1.5 H_2-H_2O		1.5 H_2-H_2O		1.5 H_2-H_2O	1 - H_2	1 - H_2

Table VIIb. Conditioning of UO_2 Microspheres

	Product Quality		
No.	O/U	% C	Physical Characteristics
1	2.040	0.002	much broken
2	2.039	0.003	perfect
3	2.168	<0.001	(~10%) broken
4	2.036	<0.002	(~10%) fragments
5	2.050	0.004	(~30%) fragments
6	2.109	0.002	many broken
7	2.001	<0.002	perfect
8	<2.000	0.008	perfect

Table VIIIa. Conditioning of UO_2 Microspheres

		Experimental Conditions			
		Temperature			
No.	Time (hrs)	125°C	300°C	400°C	1000°C
9	16	$He-H_2O$			
	2		$He-H_2O$		
	1				He
10	16	$He-H_2O$			
	6		$A-H_2-H_2O$		
	1				$A-H_2$
11	16	$He-H_2O$			
	6			$He-H_2O$	
	1				$A-H_2$
12	16	$He-H_2O$			
	2		$A-H_2-H_2O$		
	1				$A-H_2$
13	16	$He-H_2O$			
	6			$A-H_2-H_2O$	
	1				$A-H_2$
14	16	$He-H_2O$			
	6		$He-H_2O$		
	1				$A-H_2$
15	16	$He-H_2O$			
	6			$A-H_2-H_2O$	
	1				$A-H_2$
16	13	$He-H_2O$			
	4		$He-H_2O$		
	1				$A-H_2$
17	16	$He-H_2O$			
	2		$A-H_2-H_2O$		
	1				$A-H_2$
18	16	$He-H_2O$			
	6		$A-H_2-H_2O$		
	1				$A-H_2$

Table VIIIb. Conditioning of UO_2 Microspheres

	Product Quality		
No.	O/U	% C	Physical Characteristics
9	2.035	<0.002	Perfect
10	<2.001	0.003	Very good
11	2.001	0.003	Many chips
12	<2.001	<0.002	Many chips
13	2.002	<0.002	Very few chips
14	<2.001	<0.002	Perfect
15	2.001	<0.002	Considerable yellow powder and thin shells
16	2.001	<0.002	Very few chips
17	<2.001	<0.002	Perfect, except for gold sheen on spheres
18	2.002	<0.002	Many chips Yellow dust and gold sheen on spheres

the previous H_2O-inert gas mixtures. The O/U ratio was reduced to very nearly 2, and the carbon content remained low (<10 to 80 ppm).

Attention was now turned to the production of high density without adversely effecting the final O/U ratio and carbon content. Experiments were performed on the UO_{2+x} microspheres from batches P-6-3-1600, F-10; P-9-12-1153, SG-11 and P-6-2-1445, F-9. These were received in a steam dried condition[3] and were poorly formed.

Tables IX and X show the processing treaments and the results. In three of the four cases the final densities were undesirably low. These results suggested as does the literature[1] that a longer sintering time in the temperature range 450 - 1000^0 was necessary. Subsequent experiments (Tables XI - XVIII) confirm this conclusion.

Process Development

Having recognized the importance of sintering at higher temperatures, we tested two procedures designed to produce a material satisfactory with respect to O/U ratio, carbon content and density. Tables XI and XII show the processing schemes and the very acceptable results. The product shown in Table XII was a slightly better one, and this scheme was selected at this point in the research as our standard procedure.

The lower temperature portion of the processing scheme removed copious amounts of hydrocarbons and nitrogenous material. Since it was very difficult, if not impossible, to remove

Table IX. Flow Treatment of Steam-Dried UO_2 Microspheres

Material	Weight (g)	Time (hr)	Temperature (°C)	Sweep Gas
F-10	7.21	16	125	$He-H_2O$
		2	300	$A-4\%\ H_2-H_2O$
		1	1000	$A-4\%\ H_2$
			cool	$A-4\%\ H_2$
F-10	9.64	16	150	$He-H_2O$
		2	250	$A-4\%\ H_2-H_2O$
		2	350	$A-4\%\ H_2-H_2O$
		2	450	$A-4\%\ H_2-H_2O$
		1	1000	$A-4\%\ H_2$
			cool	$A-4\%\ H_2$
SG-11	7.22	16	150	$A-H_2O$
		2	250	$(A-4\%\ H_2)-H_2O$
		1.25	350	$(A-4\%\ H_2)-H_2O$
		2	450	$(A-4\%\ H_2)-H_2O$
		1	1000	$(A-4\%\ H_2)-H_2O$
			cool	$(A-4\%\ H_2)-H_2O$
F-9	9.33	16	150	$He-H_2O$
		2	250	$(A-4\%\ H_2)-H_2O$
		2	350	$(A-4\%\ H_2)-H_2O$
		2	450	$(A-4\%\ H_2)-H_2O$
		1	1000	$(A-4\%\ H_2)-H_2O$
			cool	$(A-4\%\ H_2)-H_2O$

Table X. Product Quality After Flow Treatment of UO_2 Microspheres

Material	O/U	% C	Density	Appearance
F-10	2.006	0.006	9.6	No fines No chips Twins Conglomerates
F-10	2.004	0.006	9.14	Same as above
SG-11	2.001	0.017	10.54	Nonuniform size
F-9	2.020	0.006	9.20	Nonuniform size Conglomerates Nonspherical Some dull black

Table XIa. Flow Treatment of UO_2 Microspheres

Material	Weight (g)	Time (hr)	Temperature (°C)	Sweep Gas
SG-11	11.20	16	170	$A-H_2O$
		1	250	$A-H_2O$
		1	350	CO_2-H_2O
		1	450	CO_2-H_2O
		1	550	CO_2-H_2O
		1	650	CO_2-H_2O
		1	750	CO_2-H_2O
		0.67	850	CO_2-H_2O
			cool	CO_2
		1.17	25 - 850	CO_2-H_2O
		3.50	850	H_2
		1.67	1000	H_2
			cool	H_2

Table XIb. Product Quality After Flow Treatment of UO_2 Microspheres

Material	SG-11
O/U	2.006
% C	0.012
Density	10.82
Appearance	Nonuniform size

Table XII. Gas Flow[a] Conditioning Scheme for Sol-Gel UO_2 Microspheres

Batch P-9-12-1153, SG-11

A. Treatment Schedule:	16 hr	170°C	$A-H_2O$[b]
	2	250	A-4% H_2-H_2O
	2	350	A-4% H_2-H_2O
	2	450	A-4% H_2-H_2O
		cool	A-4% H_2-H_2O
	16 hr	store	He
		25 → 550	A-4% H_2-H_2O
	2	550	A-4% H_2-H_2O
	2	650	A-4% H_2-H_2O
	2	750	A-4% H_2-H_2O
		cool	A-4% H_2-H_2O
	16 hr	store	He
		25 → 850	A-4% H_2-H_2O
	1 2/3	850	A-4% H_2-H_2O
	2	850	$CO_2-75\%\ H_2O$
	1/2	850	H_2
	3/4	1000	H_2

B. Physical Data; Analytical Data

O/U	% C	Density with 210 psi Hg	Appearance
2.001	0.008	10.82	Shiny black No fines Nonuniform size

---

[a] Total pressure = 1 atmosphere.

[b] A = Argon.

[c] 3 to 1 mixture of H_2O with A - 4% H_2.

these materials after the sintering step and since the samples varied considerably, it was thought desirable to have an immediate monitor of the off gas in addition to the final analyses to assure that their removal was complete before processing with the sintering step. For this purpose a Beckman Hydrocarbon Analyser was added to the system. The suppliers of this instrument claimed that it was sensitive to all organic compounds, but insensitive to CO_2, CO, H_2O, H_2, N_2, He and A. We also found the equipment insensitive to the gases which we tested which were CO_2, CO, H_2O and H_2.

During the processing tests it was assumed that the removal of carbonaceous material could always be followed by observing the production of hydrocarbons. This is not necessarily true, since carbon can also be removed by the formation of CO and CO_2 which cause no response in the hydrocarbon analyser. Consequently, a sample of charcoal was oxidized with A-H_2O at 1000^0C and the off gases passed through the hydrocarbon analyser. While the products were primarily CO and H_2, sufficient quantities of hydrocarbons were always produced to cause a response in the hydrocarbon analyser. Thus, the assumed correspondence between the cessation of response of the hydrocarbon analyser and the completion of carbon removal was apparently justified. Of course, the carbon analysis of the fully processed UO_2 microspheres provided an additional and independent check of satisfactory carbon removal. This instrument was particularly useful in determining the minimum time required for the removal of organic materials and considerably shortened the treatment time as shown in the following sections.

The next several experiments (Tables XIII - XVI) were made to investigate the usefulness of the Hydrocarbon Analyser and to determine if a chemically simpler, shorter, and lower temperature procedure could be found. A sample from batch P-11-9-1301, F-22 was treated according to the process shown in Table XIII. The results were:

$O/U = <2.001$

$\% C = 0.007$

^{d}Hg at 210 psi* = 11.01, 10.3

$\% N_2 = 0.003$

*Two measurements on apparently identical samples.

Consequently, the use of H_2 in the processing scheme shown in Table XII prior to the CO_2-H_2O step may be avoided as well as the 16-hour step at 125°. In addition the maximum temperature may be reduced to at least 850°C. Another sample of batch P-11-9-1301, F-22 was subjected to the treatment shown in Table XIV. Analysis of the final product yielded:

O/U	2.0085
% C	0.004
% N_2	<0.01
^{d}Hg at 210 psi	10.8

Earlier work had shown that the combination, $CO_2 + H_2O$, enchanced the rate of sintering of UO_2 more than either gas

Table XIII. Gas Flow Conditioning Scheme for Sol-Gel UO_2 Microspheres

2 hr	250°C	$A-H_2O$
"	350	"
"	450	"
"	550	"
"	650	"
"	750	"
"	850	"
"	850	CO_2-H_2O
"	850	H_2

Table XIV. Gas Flow Conditioning Scheme for UO_{2+x} Microspheres

Time, hr	Temp., °C	Gas*
2	250	$A-H_2O$
2	350	"
2	450	"
2	550	"
2	650	"
2	750	"
3 2/3	850	"
2	850	H_2

*Gas flow rate was ca. 2 ml/sec. A water bath at ca. 94°C was aspirated to provide the H_2O.

separately. However, the treatment with H_2O in argon has produced densification to at least 10.8. Thus, a chemically simplified process using only H_2O, H_2, and A seems satisfactory.

The hydrocarbon analyser was used to follow the evolution of carbonaceous material qualitatively during several processing runs. The results indicated that:

(1) Details of the pattern of hydrocarbon generation varied from run to run, even though the samples were selected from the same batch of microspheres. Generally bursts of hydrocarbons occurred near 250, 350, 450, and 550°C with a maximum at 450°C.

(2) Very little, if any, hydrocarbon was evolved at 170, 650, 750, or 850°C. This reconfirmed the belief that the 16 hour treatment of Table XII was unnecessary and indicated that the H_2O-A treatment at 650, 750, and 850°C did not trap carbon in the process of sintering.

The capability of the hydrocarbon analyser to monitor the removal of carbonaceous material, the absence of hydrocarbon production above 550°C, and the results obtained by applying the treatments in Tables XIII and XIV suggested the use of a drastically shortened treatment. Therefore a sample of batch P-11-9-1301, F-22 was treated according to Table XV.

In the course of heating the sample from 100 to 550°C a number of bursts of hydrocarbons were observed as follows:

a. At ~190°C evolution commenced at a rapid rate.

b. Peaks were observed at ~300°, ~340°, and 450°C.

Table XV. Gas Flow Conditioning Scheme for UO_{2+x} Microspheres

Time, hrs	Temp., ^0C	Gas*
1 1/2	100 - 550	$A-H_2O$
2**	550	"
3/4	550 - 850	"
2	850	"
2	850	H_2

*The argon and hydrogen flow rates were ca. 2 ml/sec. The argon was aspirated through a water bath at ca. 93-97^{0}C.

**This was the time required for complete loss of hydrocarbons, as indicated by Analyzer.

Table XVI. Gas Flow Conditioning Scheme for UO_{2+x} Microspheres

Time, hrs	Temp., ^0C	Gas
1 1/2	100 - 550	$A-H_2O$
2	550	"
3/4	550 - 850	"
2	850	"
1	850	H_2

c. No hydrocarbons were observed above 550°C. Thus, the continuous temperature increase to 550° produced essentially the same hydrocarbon removal pattern observed with the stepwise temperature profile. Analysis of the product yielded:

O/U	2.0091
% C	0.005
% N_2	<0.01
d_{Hg} at 210 psi	10.8
S.A., m^2/g	0.013

These results suggested that the processing of UO_2 microspheres may be satisfactorily completed in about eight hours.

An additional sample of Batch P-11-9-1301, F-22 was processed according to the shortened scheme, except that the time of H_2 treatment at 850° was reduced to one hour. The results were:

O/U = <2.001
% C = 0.004
% N_2 = <0.001
S.A., m^2/g = 0.007
d_{Hg} at 210 psi = 10.9

Thus, a processing time as shown in Table XVI of approximately seven hours seems satisfactory.

Several processing attempts were unintentionally terminated by equipment failure. Analyses of samples from these runs provide some information on the characteristics of the UO_{2+x} microspheres at different stages of the processing scheme. Table XVII gives typical ranges for these results. Numbers for which no range is given represent one datum only.

The usefulness of water vapor in the processing scheme has been indicated earlier (see Table VI, experiment 7). This was investigated again, since the procedure had been considerably altered. A series of samples from batch P-11-9-1301, F-22 were processed according to the shortened scheme (Table XVI, control sample) except that H_2O was added at the end of the 550^0 period (run 1), at the beginning of 850^0 period (run 2), and not at all (run 3). The results are shown in Table XVIII. It can be seen that the carbon content progressively increases as the H_2O is applied at higher temperatures and for shorter times. The maximum carbon content, however, was only 150 ppm. The complete removal of water appears (one experiment only, run 3) to increase the final N_2 content by a factor of greater than thirty and to double the final surface area per unit weight without noticeably affecting the density. The results should be contrasted with those of Table VI, experiment 7, a dry run that retained 0.273% carbon. Note that a 16 hour exposure to dry He at 125^0 was applied in that case, and H_2 reduction, a water producing step, was not applied. Thus experiment 7 of Table VI was a far dryer procedure than experiment 3 of Table XVIII. We concluded that with the shortened procedure, as with earlier ones, the H_2O vapor was essential for the production

Table XVII. Properties at Various Stages of Processing

	O/U	C, %	Density g/cc	Nitrogen %	Surface area m^2/g
Starting Material	2.25-2.49	1.8-8.0	4.70	0.09-0.19	50.8
End Stripping 550°C	2.11-2.21	0.012-0.017	8.78		
End Sintering 850°C	2.092	0.002	10.8		
End Reduction 850°C	2.000-2.009	<0.001-0.013	10.5-10.9	<0.001	0.006-0.033

Table XVIII. Analyses of Processed UO_2 Sol-Gel Microspheres

Run No.	Control	1	2	3	Starting Material
O/U	2.009	2.001	2.001	2.001	2.486
% C	0.005	0.008	0.015	0.014	1.83
% N_2	<0.001	<0.001	<0.001	0.036	0.090
S.A., m^2/g	0.013	0.008	0.008	0.019	50.8
d_{Hg} at 210 psi	10.8	10.7	10.7	10.7	4.70

of the highest purity UO_2 microspheres. A variety of additional batches of UO_2 microspheres were subjected to the shortened procedure. The results in Table XIX show variation from sample to sample, but the products in general were satisfactory.

Product Stability

It was of interest to learn whether processed samples were inert to the constituents of the atmosphere, since sorption of gases could cause spurious O/U ratios or carbon contents in the analytical results. A freshly processed sample of batch P-11-9-1301, F-22 was divided into three portions. One was sent for analysis immediately. One of the remaining samples was exposed to oxygen and one to carbon dioxide. The pressure and time were one atmosphere and two weeks. The results were:

	% C	O/U
Initial	0.004	<2.001
Exposed to O_2		2.001
Exposed to CO_2	0.001	

Apparently neither gas caused a significant change in composition of the processed microspheres. This stability must be due to low surface area since UO_2 does oxidize in air at room temperature and the extent depends on surface area.[14]

It was reported[15] that "Dried gel microspheres prepared from ThO_2 (20 to 25%) UO_3 sols . . . exhibited an unexpected heating effect when exposed to air." This phenomenon may

Table XIX. Properties of Processed Batches

Properties	P-6-12-1153	P-6-19-1408	P-6-16-1545	P-6-14-1550
O/U	2.001	2.007	<2.002	2.005
C, %	0.013	<0.001	0.018	0.002
Surface area m^2/g	0.013	0.033	0.006	0.011
d_{Hg} at 210 psi	10.5	10.36	10.78	10.52
N_2, %	0.001			

result from the heat of adsorption of moisture on UO_2-ThO_2 samples possessing large surface areas. We have observed that UO_2 microspheres outgassed with H_2O vapor to 450°C, evacuated, cooled to ambient temperatures, and exposed to moisture caused the manifold containing the sample to become extremely hot. It was also noticed that ThO_2 powder out-gassed by heating to 1000° in a vacuum, cooled to room temperature, and exposed to H_2O vapor exhibited a large exothermic effect. Three batches of UO_2 gel (P-6-19-1408, P-6-16-1545, and P-6-14-1550) were conglomerations consisting of microspheres and finer material. These batches also displayed heat effects when exposed to air. These materials were sieved before processing to obtain a sample of microspheres free of fine particles. During the sieving procedure, the samples became hot. Batch P-6-14-1550 displayed the most intense heat effect, produced fumes, and continued to break up during the initial part of the screening. C. H. Secoy, et al[16-18] and others[19] have reported a very high initial heat of adsorption of H_2O vapor on ThO_2. Data for the heats of immersion of ThO_2 are given[16-19] and may be converted to heats of adsorption of H_2O gas by adding the heat of condensation of water. These data depend on both the surface area and the temperature of out-gassing of the samples. Kinetically the heat is released in an initial burst followed by two, one or no slow processes depending on the temperature at which the samples have been calcined. Fully processed sol-gel microspheres with their very low surface area, have not shown this heat effect on exposure to moist air. These reports and observations suggest that excessive heat effects are to be expected with UO_2, UO_2-ThO_2ss and ThO_2 microspheres out-gassed at elevated temperatures without densification to reduce their surface area. Densification to near theoretical density and the consequent reduction in surface area to the $10^{-2} m^2/g$ range before exposure to H_2O gas or moist air seems to avoid this difficulty.

RECOMMENDATIONS AND CONCLUSIONS

Experience has shown that the hydrocarbon analyser will be most useful in the monitoring and control of processing plants. This is especially so since the samples vary somewhat from each other and no fixed set of processing conditions can handle them all without wasting time on batches that are relatively easy to process.

Quantitative kinetic studies providing rate expressions and activation energies for the sintering and reducing steps of the processing scheme are badly needed. This information would allow prediction of the effects of altering the processing procedure and might indicate the nature of the rate limiting steps.

There was considerable scatter in results for most of the final analyses. While the processed material was apparently satisfactory as a reactor fuel, it should be noted that the products of the short schemes, Tables XV, XVI and XIX, are not quite as good as those from the longer procedures, Tables

XI and XII. Further, it is not yet possible to routinely obtain the best results which have occasionally occured during these studies. The best values obtained for the listed parameters are shown in Table XX.

Although this work was brought to a close September 1, 1967, because of budget cuts, it is obvious that added studies along these lines could very well lead to significant improvement in the processing and monitoring techniques.

Table XX. Best Results Obtained

O/U	2.000
C, %	<0.001
N_2, %	<0.001
d_{Hg} at 210 psi	10.9
Surface Area m^2/g	0.006

ACKNOWLEDGEMENTS

The analytical services of Hershel Davis, Bill Laing and Charles Boyd of the Analytical Chemistry Division, of the Oak Ridge National Laboratory and of Jake Horton at the Oak Ridge Gaseous Diffusion Plant are gratefully acknowledged. Two summer participants, David Keeton and David Worley, also contributed to the early experimental portion of this work.

REFERENCES

1. W. E. Bailey et al, "Steam Sintering of Uranium Dioxide," Am. Ceram. Soc. Bulletin, 41, 768 (1962).
2. R. G. Wymer and D. A. Doughlas, Jr. (compilers), "Status and Progress Report for Thorium Fuel Cycle Development," Dec. 31, 1965, ORNL-4001, pp. 41-68.
3. Inquiries concerning this work should be directed to R. G. Wymer and W. D. Bond, Chemical Technology Division, Oak Ridge National Laboratory. See also: P. A. Haas, W. D. Bond, M. H. Lloyd, and J. P. McBride, "Sol-Gel Process Development and Microsphere Preparation," in Proceedings of Second International Thorium Fuel Cycle Symposium, Gatlinburg, Tennessee, May 3-6, 1966, USAEC Technical Information Division, February 1968, pp. 391-416.
4. Inquiries concerning this work should be directed to H. Beutler and R. L. Hamner, Metals and Ceramics Division, Oak Ridge National Laboratory.
5. D. N. Hess, W. T. Rainey, and B. A. Soldano, Reactor Chem. Div. Ann. Progr. Rept. Jan. 31, 1965, ORNL-3789, pp. 177-180.
6. D. N. Hess and B. A. Soldano, Reactor Chem. Div. Ann. Progr. Rept. Dec. 31, 1965, ORNL-3913, pp. 72-73.

7. R. G. Wymer and D. A. Douglas, Jr. (compilers), "Status and Progress Report for Thorium Fuel Cycle Development," Dec. 31, 1965, ORNL-4001, pp. 117-120.
8. D. N. Hess, H. F. McDuffie, B. A. Soldano, and C. F. Weaver, *Reactor Chem. Div. Ann. Progr. Rept., Dec. 31, 1966*, ORNL-4076, pp. 78-79.
9. E. Aukrust, T. Forland, and K. Hagemark, "Equilibrium Measurements and Interpretation of Non-Stoichiometry in UO_{2+x}" in Proceedings of the Symposium on Thermodynamics of Nuclear Materials, Vienna, May 1962, IAEA, September 1962, pp. 713-22.
10. Charles Holley, ed., Thermodynamic and Transport Properties of Uranium Dioxide and Related Phases, IAEA, Vienna, 1965, pp. 29-38.
11. R. E. Wilson, C. Barnes, and L. Baker, Jr., *Studies of the UO_2-Steam Reaction*, ANL-7125 (1966), pp. 159-163.
12. L. E. J. Roberts, A. J. Walter, and V. J. Wheeler, "The Oxides of Uranium. Part IX. The Decomposition of Carbon Monoxide on Uranium and Thorium Dioxides," *J. Chem. Soc.*, 2472-81 (1958).
13. P. H. Emmett, consultant, personal communication (1966).
14. J. S. Anderson, L. E. J. Roberts, and E. A. Harper, "The Oxides of Uranium. Part VII. The Oxidation of Uranium Dioxide," *J. Chem. Soc.*, 3946-59 (1955).
15. ORNL Status and Progress Report, ORNL-4158 (June 1967), p. 3.

16. H. F. Holmes and C. H. Secoy, "Heats of Immersion in the Thorium Oxide-Water System," J. Phys. Chem., 69, 151 (1965).

17. H. F. Holmes, E. L. Fuller, Jr. and C. H. Secoy, "Heats of Immersions in the Thorium Oxide-Water System. II," J. Phys. Chem., 70, 436 (1966).

18. C. H. Secoy, E. L. Fuller, Jr., H. F. Holmes and S. A. Taylor, "Surface Chemistry of Thoria," Reactor Chem. Div. Ann. Progr. Rept. Dec. 31, 1966, ORNL-4076, pp. 74-77.

19. M. E. Winfield, Australian J. Sci., Res. 3A, 290 (1950).

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

INTERNAL DISTRIBUTION

ORNL-TM-1809

1. L. G. Alexander
2. J. W. Anderson
3. H. Beutler
4. R. E. Blanco
5. W. D. Bond
6. G. E. Boyd
7. R. B. Briggs
8. R. E. Brooksbank
9. K. B. Brown
10. F. R. Bruce
11. J. M. Chandler
12. S. D. Clinton
13. F. L. Culler
14. J. E. Cunningham
15. P. H. Emmett (Consultant)
16. D. E. Ferguson
17. L. M. Ferris
18. R. B. Fitts
19. J. H. Frye, Jr.
20. E. L. Fuller, Jr.
21. R. B. Gammage
22. H. E. Goeller
23. A. T. Gresky
24. W. R. Grimes
25. P. A. Haas
26. J. P. Hammond
27. R. L. Hamner
28. W. O. Harms
29. C. C. Haws, Jr.
30-34. D. N. Hess
35. M. R. Hill
36. H. F. Holmes
37. A. R. Irvine
38. P. R. Kasten
39. C. E. Larson
40. R. E. Levye
41. A. L. Lotts
42. H. G. MacPherson
43. J. P. McBride
44-48. H. F. McDuffie
49. A. B. Meservey
50. E. L. Nicholson
51. A. R. Olsen
52. J. R. Parrott
53. P. Patriarca
54. R. B. Pratt
55-59. W. T. Rainey
60. J. T. Roberts
61. M. W. Rosenthal
62. J. L. Scott
63. J. D. Sease
64. D. M. Shepard
65. J. W. Snider
66-70. B. A. Soldano
71. D. B. Trauger
72. M. W. Wadsworth (Univ. Utah)
73. G. M. Watson
74-78. C. F. Weaver
79. A. M. Weinberg
80. M. E. Whatley
81. R. G. Wymer
82. ORNL Patent Office
83-84. Central Research Library
85-86. Document Reference Section
87-96. Laboratory Records (LRD)
97. Laboratory Records - Record Copy (LRD-RC)

EXTERNAL DISTRIBUTION

98-99. D. F. Cope, AEC-ORNL R.D.T. Site Office
100. J. W. Crawford, AEC-RDT, Washington
101. C. B. Deering, AEC-ORO
102. A. Giambusso, AEC-Washington
103. W. J. Larkin, AEC-ORO
104. C. L. Matthews, AEC-ORO
105-106. T. W. McIntosh, AEC, Washington
107. C. E. Miller, Jr., AEC, Washington
108. B. T. Resnich, AEC, Washington
109. H. M. Roth, AEC ORO
110. Milton Shaw, AEC, Washington
111. W. L. Smalley, AEC-ORO
112. R. F. Sweek, AEC-Washington
113-127. Division of Technical Information Extension (DTIE)