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LOS ALAMOS SCIENTIFIC LABORATORY

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UNIVERSITY OF CALIFORNIA

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LA-1854

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SPECIFIC SURFACE AND BULK DENSITY OF U_3O_8
AND UO_2 AS FACTORS IN UF_4 PRODUCTION
ON THE 250 GRAM URANIUM SCALE

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application of atomic energy.~~

Work done by:

R. J. Bard
O. E. Fry
R. W. Kewish

Report written by:

R. J. Bard

TECHNOLOGY - FEED MATERIALS
(M-3679, 15th edition)

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ABSTRACT

Specific surface and bulk density measurements were made on samples of 22 U_3O_8 materials which had been prepared by calcination at $900^{\circ}C$ of widely differing uranium peroxide precipitates and had been evaluated as to "reactivity" by successive treatment with hydrogen and a mixture of anhydrous hydrogen fluoride and hydrogen in a production-type batch process for the preparation of UF_4 . Specific surface and bulk density measurements were also made on samples of the 22 corresponding UO_2 intermediates. The ranges of values encountered in the U_3O_8 samples and in the UO_2 samples were $0.05\ m^2/g$ to $0.37\ m^2/g$ and $0.03\ m^2/g$ to $0.33\ m^2/g$, respectively, for specific surface and $3.7\ g/cm^3$ to $1.8\ g/cm^3$ and $4.9\ g/cm^3$ to $2.7\ g/cm^3$, respectively, for packed bulk density.

Specific surface varied inversely with packed bulk density for U_3O_8 , the data showing a good correlation. A very poor correlation between specific surface and packed bulk density of UO_2 was obtained. The conversion of U_3O_8 to UF_4 in the standard process varied from 22% for the lowest specific surface, highest bulk density oxide to 98 to 99% for the high specific surface, low bulk density oxides. The observed values for properties of the U_3O_8 samples correlated better with conversion of U_3O_8 to UF_4 than did the observed values for properties of the corresponding UO_2 intermediates.

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1. Introduction

In the recovery and purification of enriched uranium at Los Alamos the following steps are employed in the production of UF_4 :

- (1) $UO_2(NO_3)_2 (aq) + H_2O_2 (aq) \longrightarrow UO_4 \cdot xH_2O (s) + 2HNO_3 (aq)$
 $HNO_3 (aq) + NH_3 (aq) \longrightarrow NH_4NO_3 (aq)$ (To control pH)
- (2) $UO_4 \cdot xH_2O (s) \xrightarrow{\Delta} UO_3 \cdot yH_2O (s) + 1/2 O_2 (g) + (x - y) H_2O (g)$
- (3) Dissolution of $UO_3 \cdot yH_2O$ in HNO_3 and repetition of step (1) to effect further purification
- (4) $3(UO_4 \cdot xH_2O) (s) \xrightarrow{\Delta} U_3O_8 (s) + 2O_2 (g) + 3xH_2O (g)$
- (5) $U_3O_8 (s) + 2H_2 (g) \xrightarrow{\Delta} 3UO_2 (s) + 2H_2O (g)$
- (6) $UO_2 (s) + 4HF (g) \xrightarrow[H_2]{\Delta} UF_4 (s) + 2H_2O (g)$

It has been the experience of the Hydrofluorination Section that different lots of U_3O_8 can vary greatly in "reactivity" with respect to conversion to UF_4 by steps (5) and (6) above. Since low-conversion lots require additional hydrofluorination time, or in some cases must be reprocessed completely to yield UF_4 suitable for reduction to uranium metal, a study of the factors affecting the "reactivity" of U_3O_8 prepared from uranium peroxide was undertaken.

In the course of the study, which was carried out using normal uranium and the same scale as used in production (250 grams of uranium), a large number of uranium peroxide precipitates, varying widely in settling and filtration characteristics, were prepared by controlled variation of the precipitation conditions. Calcination of these uranium peroxides at $900^\circ C$ in air yielded U_3O_8 samples which varied widely in "reactivity", as determined by successive reduction and hydrofluorination in a production-type batch process for the preparation of UF_4 from U_3O_8 .

The present report deals with the attempted physical characterization, by means of specific surface and bulk density measurements, of a number of corresponding U_3O_8 and UO_2 samples from this study and with the relationships of these characteristics to the behavior of the oxides in a standard reduction-hydrofluorination process.

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2. Experimental Methods

2.1 Selection of Samples

Prior to the inception of the specific-surface measurements, a large number of samples of U_3O_8 had been prepared and had been treated in a standard reduction-hydrofluorination process in connection with the over-all study of the preparation of UF_4 from uranyl nitrate solutions. Corresponding samples of $UO_4 \cdot xH_2O$, U_3O_8 , UO_2 and UF_4 from each experiment had been preserved.

Of the first 44 preparations, 39 involved U_3O_8 which had been prepared by calcination of uranium peroxide in air at $900^\circ C$ for 16 hours (production conditions). In the standard process described below conversion of U_3O_8 to UF_4 for the 39 samples was distributed as follows: less than 75% for 9 samples, 75 to 95% for 25 samples, and greater than 98% for 5 samples. Eight of the nine samples in the first category and all of the samples in the third category were chosen for further study. (Sample No. 19, which had a conversion of 67.3%, was omitted because appreciable amounts of impurity had been found in the U_3O_8 .) Nine samples from the second category were selected at random, bringing the total number of samples for further study to 22.

2.2 Measurement of "Reactivity"

The criterion for "reactivity" was taken as the percent conversion of U_3O_8 to UF_4 in a standard two-step reduction and hydrofluorination process involving a total hydrofluorination time of 5-1/2 hours. The scale (250 grams of uranium), equipment, and reaction conditions were essentially the same as used in production. The standard process used in the study differed from the uninterrupted production process in that the sequence of treatment was interrupted after the reduction step, after hydrofluorination had proceeded for one hour, and after hydrofluorination had proceeded for a total of 5-1/2 hours. The sintering stage (i.e., a final two hours of hydrofluorination at $850^\circ C$) of the production process also was omitted.¹

The gas-solid reactions were carried out in a horizontal, 3-inch-diameter nickel reactor with gas inlet and outlet tubes mounted in the same end so that the inlet tube extended the length of the reactor to provide preheating of the reactant gases. A truncated semi-cylindrical platinum-rhodium boat 7 inches long, 2 inches wide and 1-1/4 inches deep was used to hold the uranium oxide charge. The temperature of the tube-type electric furnace containing the reactor was controlled by means of a Wheelco controller.

The U_3O_8 , which had been sampled, was treated with hydrogen for one hour at $700^\circ C$, at a flow rate of 2 liters of hydrogen per minute. The conversion of U_3O_8 to UO_2 was checked by weight change. Additional reduction was attempted if the conversion of U_3O_8 to UO_2 was less than 98%. The product of the reduction was sampled and was then hydrofluorinated using

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anhydrous HF and H_2 for a total of 5-1/2 hours at 550°C, at flow rates of 200 grams per hour of HF and 0.5 liter per minute of H_2 . The conversion of U_3O_8 to UF_4 was calculated from observed weight changes after 1 hour and after 5-1/2 hours of hydrofluorination. In order to avoid a chemical assay of each product, the calculation was based on the assumptions that the starting material was stoichiometric U_3O_8 and that all unconverted uranium oxide in the hydrofluorination product was present as UO_2 . Argon or helium, which had been passed over uranium turnings at 750°C, was used on all up and down heats.

2.3 Measurement of Specific Surface

The adsorption of methane at liquid nitrogen temperatures was used in the measurement of specific surface (surface area per gram) of U_3O_8 and UO_2 samples. The surface area apparatus was essentially the same as that described by Lauterbach and co-workers,² except that two additional sample tubes and mercury cut-offs were added to reduce the time per sample required to load the system and to outgas the oxides. Before adsorption measurements were started, the samples were outgassed overnight under vacuum at approximately 125°C and the rate of pressure build-up in the closed system was reduced to a permissible level by flaming the apparatus. The vapor pressure of methane at the adsorption temperature was measured directly. The calculation of specific surface from the amount of methane adsorbed at various relative pressures was carried out in accordance with the Brunauer, Emmett and Teller theory.³ A value of 15.0 square angstroms was assumed for the effective cross-sectional area of the adsorbed methane molecule.⁴

2.4 Measurement of Bulk Density

The packed bulk densities of the uranium oxides were determined by tapping a calibrated container loaded with oxide on a hard surface until no further reduction in apparent volume was observed. Packed bulk density was calculated as the ratio of the weight of oxide to the limiting apparent volume. These determinations were made using only uranium oxide samples which had not been previously packed. (It was observed that UO_2 which was alternately packed and dispersed yielded a higher value of packed bulk density after each successive cycle until an apparent limit was reached. However, it was felt that this limiting value was of no more physical significance than the value of packed bulk density obtained from one packing since neither value could be assumed to be the "true" packed bulk density. In reaching this conclusion it was assumed that a collection of particles, irregular in shape and non-uniform in size, could exhibit a "true" packed bulk density, i.e., a true maximum in the ratio of weight to apparent volume, for only one set of relative positions and orientations of the particles in the mass of material and that this particular arrangement was very unlikely to occur in the experimental determination of packed bulk density.)

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The loose bulk densities of the uranium oxides were determined by allowing the oxide to fall freely into a calibrated container and by observing the volume occupied by a given weight of material introduced in this way. Only samples of oxide which had not been packed previously were used in these determinations. (It was observed that if a UO_2 sample was packed and then dispersed between measurements of loose bulk density, the value obtained for the loose bulk density after packing was higher than that obtained prior to packing. Presumably this was due to incomplete dispersing of the particles following the packing.)

Bulk density measurements on U_3O_8 samples were made using a 15-ml centrifuge cone. It was necessary to use a 4-ml cylindrical tube for the measurement of bulk densities of UO_2 samples because of the limited size of the UO_2 samples preserved from the chemical processing. The values of bulk density for U_3O_8 samples and for UO_2 samples were thus not measured under comparable conditions. (It has been observed that the value of packed bulk density obtained for a given oxide varies slightly with variations in the size and shape of the tube used for the determination.)

3. Precision of Measurements

3.1 "Reactivity"

The 95% confidence limits⁵ for a single determination of percent conversion of U_3O_8 to UF_4 were taken as equal to or less than $\pm 1.9\%$.

The value of $\pm 1.9\%$ was calculated from conversion data for six different samples of U_3O_8 which had been prepared in an identical manner. Since these six samples of U_3O_8 were not from a common source, the true value for the 95% confidence limits for a single determination could be less than $\pm 1.9\%$. The six samples had an average conversion of U_3O_8 to UF_4 of 92.9%. As will be discussed later, the porosity of the charge, which can vary for a given material because of variations in the manner of loading the reaction boats, has a greater effect on the rate at which conversion progresses for samples ultimately showing high conversion than for samples ultimately showing low conversion. It was therefore assumed that the above precision limits would not be exceeded for oxides showing lower conversions.

3.2 Specific Surface

The 95% confidence limits for a single measurement of surface area (employing at least five adsorption points) were determined for three values of total area of sample. The following results were obtained:

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Number of Runs Averaged	Average Value of Total Area of Sample, m ²	Standard Deviation, m ²	95% Confidence Limits, m ²
6	0.170	±0.011	±0.029
5	0.279	±0.009	±0.024
5	0.595	±0.012	±0.032

Thus the precision limits were relatively constant at about $\pm 0.03 \text{ m}^2$ throughout the range of total area investigated. The 95% confidence limits for a single determination on a specific-surface basis ($\pm 0.03 \text{ m}^2$ divided by sample weight in grams) were equal to or less than $\pm 0.02 \text{ m}^2/\text{g}$ for all U_3O_8 samples and equal to or less than $\pm 0.01 \text{ m}^2/\text{g}$ for all UO_2 samples.

3.3 Bulk Density

Duplicate determinations of loose bulk density and of packed bulk density were made for each sample of U_3O_8 . The 95% confidence limits for the average of duplicate determinations were $\pm 0.10 \text{ g/cm}^3$ for both measurements. Triplicate determinations of loose bulk density were made for each sample of UO_2 . The 95% confidence limits for the average of triplicate determinations were $\pm 0.07 \text{ g/cm}^3$. Due to the limited size of the UO_2 samples, only one measurement of packed bulk density could be made on each sample of UO_2 using material which had not been packed previously. The 95% confidence limits for a single measurement of packed bulk density of UO_2 were established at $\pm 0.18 \text{ g/cm}^3$ by running duplicate measurements on each of five samples of UO_2 not connected with the present work.

4. Experimental Results

The data on the conversion of U_3O_8 to UO_2 in the reduction step and to UF_4 in the combined reduction and hydrofluorination steps are given in Table 1. Table 2 contains the values of specific surface, packed bulk density and loose bulk density observed for the samples of U_3O_8 and UO_2 and a tabulation of the ratios of the values of specific surface observed for corresponding UO_2 and U_3O_8 samples.

The following empirical equations, which were fitted to the data by the method of least squares for the purpose of comparing correlations, were selected as most suitable for representing the data in Tables 1 and 2. The symbols used in the equations are defined as follows:

- σ = specific surface, m^2/g
- ρ_p = packed bulk density, g/cm^3
- ρ_l = loose bulk density, g/cm^3
- y = percent conversion of U_3O_8 to UF_4 (5-1/2 hour hydrofluorination data)

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w = percent conversion of U_3O_8 to UF_4 expressed in probability units

s = standard deviation of observed values from values calculated by means of the equation

s_σ = standard deviation in units of specific surface

s_y = standard deviation in units of percent conversion of U_3O_8 to UF_4

Relations between properties of U_3O_8 :

$$\begin{aligned} (1) \quad \sigma &= 0.629 - 0.159 \rho_p & s_\sigma &= \pm 0.028 \text{ m}^2/\text{g} \\ (2) \quad \sigma &= 0.498 - 0.126 \rho_1 & s_\sigma &= \pm 0.037 \text{ m}^2/\text{g} \end{aligned}$$

Relations between properties of UO_2 :

$$\begin{aligned} (3) \quad \sigma &= 0.461 - 0.0571 \rho_p & s_\sigma &= \pm 0.036 \text{ m}^2/\text{g} \\ (4) \quad \sigma &= 0.374 - 0.0419 \rho_1 & s_\sigma &= \pm 0.040 \text{ m}^2/\text{g} \end{aligned}$$

TABLE 1

REDUCTION AND HYDROFLUORINATION DATA

Sample No.	% Conversion of U_3O_8 to UO_2 in Reduction of U_3O_8 with H_2 at 700°C			Overall % Conversion of U_3O_8 to UF_4 after Hydrofluorination of UO_2 with HF and H_2 at 550°C	
	1 hour	2 hours	3 hours	1 hour	5-1/2 hours
1	97.4	97.4	97.4	36.2	49.8
2		64.5	65.9	17.0	22.2
4	97.0	98.6		48.0	71.4
5	98.4			50.6	90.2
6	98.3			48.4	93.6
7	98.4			24.5	29.3
12	98.1			59.9	91.2
13	98.5			45.0	99.5
14	98.4			56.7	99.2
15	98.4			53.3	99.2
16	98.4			53.2	99.5
17	94.1	98.0		54.5	98.3
20	98.2			36.7	48.8
22	98.2			50.4	91.0
27	98.3			47.8	88.7
28	98.5			39.0	59.0
30	98.5			50.4	90.6
34	98.1			47.6	86.3
35	98.0			35.9	47.0
36	97.8	98.3		42.8	63.4
38	97.9			54.1	89.1
42	98.6			54.6	90.2

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TABLE 2

PROPERTIES OF THE URANIUM OXIDES

Sample No.	Specific Surface of U_3O_8 , m^2/g	Packed Bulk Density of U_3O_8 , g/cm^3	Loose Bulk Density of U_3O_8 , g/cm^3	Specific Surface of UO_2 , m^2/g	Packed Bulk Density of UO_2 , g/cm^3	Loose Bulk Density of UO_2 , g/cm^3	Ratio of Specific Surface of UO_2 to Specific Surface of U_3O_8
1	0.18	3.14	2.87	0.29	4.71	4.15	1.63
2	0.05	3.71	3.46	0.03	4.90	4.45	
4	0.20	2.77	2.60	0.22	4.25	3.78	1.12
5	0.29	2.17	1.77	0.28	3.55	2.69	0.98
6	0.27	2.33	1.97	0.24	3.83	3.00	0.91
7	0.11	2.98	2.66	0.19	4.38	3.76	1.80
12	0.25	2.38	1.88	0.24	3.53	2.77	0.94
13	0.32	1.89	1.63	0.31	2.96	2.49	0.96
14	0.32	1.97	1.70	0.31	3.21	2.64	0.97
15	0.33	2.04	1.82	0.29	3.24	2.85	0.89
16	0.35	1.76	1.51	0.33	3.24	2.48	0.96
17	0.37	2.02	1.15	0.32	2.70	1.85	0.86
20	0.14	3.14	2.85	0.20	4.79	4.10	1.41
22	0.25	2.45	1.93	0.25	3.75	2.72	1.02
27	0.23	2.29	1.83	0.23	3.51	2.69	1.01
28	0.15	3.04	2.85	0.20	4.53	3.97	1.28
30	0.26	2.08	1.72	0.22	3.58	2.64	0.88
34	0.20	2.62	2.36	0.21	4.07	3.55	1.05
35	0.13	2.92	2.65	0.17	4.36	3.72	1.32
36	0.15	2.80	2.47	0.19	4.27	3.63	1.26
38	0.25	2.30	1.54	0.20	3.48	2.38	0.80
42	0.29	2.22	1.51	0.26	3.42	2.27	0.89

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Relations between percent conversion of U_3O_8 to UF_4 and properties of U_3O_8 :

$$\begin{array}{ll} (5) & w = 3.451 + 11.34 \sigma & s_y = \pm 5.63\% \\ (6) & w = 10.759 - 1.877 \rho_p & s_y = \pm 8.04\% \\ (7) & w = 9.091 - 1.431 \rho_l & s_y = \pm 9.21\% \end{array}$$

Relations between percent conversion of U_3O_8 to UF_4 and properties of UO_2 :

$$\begin{array}{ll} (8) & w = 3.217 + 12.07 \sigma & s_y = \pm 16.82\% \\ (9) & w = 11.127 - 1.334 \rho_p & s_y = \pm 9.20\% \\ (10) & w = 9.341 - 1.062 \rho_l & s_y = \pm 10.47\% \end{array}$$

The above equations in w are the linear forms of normal distribution functions in y . The fitting of these functions to experimental data is discussed in Appendix A.

A number of pairs of the equations were compared as to "goodness of fit" by means of the "z test".^{6,7} The difference in variance which would occur by chance less than 5 times in 100 was taken as the criterion of a statistically significant difference in "goodness of fit". The results of these comparisons are given in Table 3.

TABLE 3
COMPARISON OF "GOODNESS OF FIT" AMONG PAIRS OF EMPIRICAL EQUATIONS*

Equation No.	1	2	3	4	5	6	7	8	9	10
1		nd	nd							
2				nd						
3				nd						
4										
5						nd	D	D		
6							nd		nd	
7										nd
8									D	D
9										nd
10										

* "D" indicates a statistically significant difference in "goodness of fit".

"nd" indicates no statistically significant difference in "goodness of fit".

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5. Discussion and Conclusions

5.1 Properties of U_3O_8

Corresponding values for specific surface and packed bulk density of U_3O_8 samples are plotted in Fig. 1. The straight line shown was derived from Eq. (1). The data can be correlated equally well by means of a logarithmic function or by means of a hyperbolic function, as shown by the following equations in which σ , ρ_p and s_σ have the definitions given previously:

$$\begin{aligned} (1) \quad \sigma &= 0.629 - 0.159 \rho_p & s_\sigma &= \pm 0.028 \text{ m}^2/\text{g} \\ \sigma &= 0.598 - 0.942 \log \rho_p & s_\sigma &= \pm 0.028 \text{ m}^2/\text{g} \\ \sigma &= -0.185 + 1.002 (1/\rho_p) & s_\sigma &= \pm 0.030 \text{ m}^2/\text{g} \end{aligned}$$

The lack of statistically significant differences in the "goodness of fit" among these three equations (demonstrable by means of the "z test") indicates that the range of properties in the series of samples is too small to yield the general empirical relationship between specific surface of U_3O_8 and packed bulk density of U_3O_8 . None of the above equations yields a reasonable value for packed bulk density of U_3O_8 for zero specific surface, corresponding to a hypothetical infinite solid with bulk density equal to the true density. The X-ray crystal-lite density of 8.39 g/cm^3 for U_3O_8 (Ref. 8) is considerably higher than the limiting values obtainable from the above equations.

The measurement of specific surface has a decided advantage over particle size determination, because the former is relatively independent of the effects of agglomeration of the ultimate particles. Apparently the measurement of packed bulk density also possesses this desirable feature to some extent. For example, Samples 2 and 16 of U_3O_8 , which yielded widely different values of packed bulk density consistent with the specific surface values, both were composed of aggregates of roughly the same size. Also, Sample 16 of U_3O_8 , which consisted of relatively large agglomerates, and Sample 17 of U_3O_8 , which consisted of fine powder, both yielded values in the same range for specific surface and for packed bulk density.

The correlations between loose bulk density and all other variables considered in this report are poorer than the correlations between packed bulk density and corresponding variables, although in no case to a statistically significant degree, according to comparisons made by the "z test". Consequently, the discussion will usually be limited to packed bulk density where bulk-density considerations are involved.

5.2 Properties of UO_2

As can be seen in Fig. 2, the correlation between corresponding values observed for specific surface of UO_2 and for packed bulk density of UO_2 is poor. The scatter of the data exceeds that which might be expected on the basis of the precision of measurements. The

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Fig. 1

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Fig. 2

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properties of Sample 2 were not included in this correlation because the reduction product was not chemically comparable to the reduction products of the remaining samples (see Table 1).

5.3 Comparison of Properties of U_3O_8 and UO_2

If one assumes that during the conversion of a collection of irregular U_3O_8 particles to UO_2 the form factors for the particles remain unchanged and the particles do not develop new surface or sinter, it is possible to compute a value for the change in specific surface during the process. Such a calculation, given in detail in Appendix B, yields a value 0.847 for the ratio of specific surface of UO_2 to specific surface of U_3O_8 . Inspection of Table 2 reveals that for some of the samples the observed ratio has a value significantly greater than 0.85. If one assumes further that the effective cross-sectional area of a methane molecule adsorbed at liquid nitrogen temperature (i.e., the number of adsorbed molecules necessary to form a mono-molecular layer divided by the true area of the surface) is the same for both U_3O_8 and UO_2 , the formation of new surface during reduction is indicated for those samples.

A comparison of the values of packed bulk density for U_3O_8 and UO_2 was not made because the values are not comparable. (See Sec. 3.)

5.4 "Reactivity" and Properties of U_3O_8

Figures 3 and 4 contain plots of percent conversion of U_3O_8 to UF_4 versus specific surface of U_3O_8 and versus packed bulk density of U_3O_8 , respectively. Data for both 1 hour and 5-1/2 hours of hydrofluorination are shown. The curves drawn through the 5-1/2 hour hydrofluorination points were derived from Eqs. (5) and (6).

Visual and microscopic examination of the hydrofluorination products revealed a striking lack of homogeneity in color within given samples of product. This situation was most evident in the cases of the samples which underwent less than 70% conversion to UF_4 in 5-1/2 hours of hydrofluorination. In general, the lack of homogeneity in color was apparent on the surfaces of individual particles, with colors varying from black or brown, characteristic of uranium oxides in the U_3O_8 to UO_2 range, to green, characteristic of UF_4 . The proportion of apparently unreacted surface on the individual particles decreased as the value of specific surface for the collection of particles increased.

In the cases of the low specific surface, high packed bulk density oxides (for example, Samples 2, 7, 35 and 20), 4-1/2 hours of hydrofluorination beyond the initial 1-hour treatment did not result in greatly improved conversion to UF_4 . These samples, which consisted of relatively large particles, formed fairly porous beds in the reaction boats. The limiting process, with respect to the hydrofluorination of these samples, would thus appear to be the reaction of HF with the uranium oxide rather than the diffusion of HF through the charge.

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Fig. 3

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Fig. 4

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On the other hand, in the cases of high specific surface, low packed bulk density oxides (such as Samples 13, 14, 15, 16 and 17) the percent conversion increased from about 50% at 1 hour to almost 100% at 5-1/2 hours. Apparently this behavior was due to layer thickness of the charge in that the lower porosity of the bed limited the access of HF to particles below the surface of the bed. It was observed that after 1 hour of hydrofluorination of this type of oxide, the top layers of particles appeared to be highly reacted, whereas the bottom layers of particles showed little visible evidence of reaction.

5.5 "Reactivity" and Properties of UO_2

Figures 5 and 6 contain plots of percent conversion of U_3O_8 to UF_4 versus specific surface of UO_2 and versus packed bulk density of UO_2 , respectively. The curves were derived from Eqs. (8) and (9). A normal distribution function was fitted to the data plotted in Fig. 5, for which the correlation is very poor, solely for purposes of comparison.

It can be seen in Fig. 5 that a number of samples of UO_2 with approximately the same specific surface were converted to UF_4 to different extents. The possibility was considered that in such sets the samples which underwent the least conversion may have contained a few large particles which only partially reacted. In this event, such samples should have higher bulk densities than the more completely reacted samples.

Inspection of the data shows that this explanation applies quite well to such sets of samples as 1, 5, 15 and 4, 30. The percent conversion of $1 < 5 < 15$, whereas the packed bulk density of $1 > 5 > 15$. Likewise, the percent conversion of $4 < 30$, whereas the packed bulk density of $4 > 30$. Moreover, this explanation could apply to the set of Samples 7, 35, 20, 28, 36, 38. The percent of conversion of $7 < 35 < 20 < 28 < 36 < 38$, whereas the packed bulk density of 38 is significantly greater than that of any of the other samples in the set, the observed values of packed bulk density for which do not differ significantly.

The strictly empirical nature of the correlations between percent conversion of U_3O_8 to UF_4 and properties of the oxides is emphasized by the fact that correlations involving properties of U_3O_8 are in general better than correlations involving corresponding properties of UO_2 . Since the percent conversion of U_3O_8 to UF_4 is essentially a measure of the success of the hydrofluorination step, it would seem to be more reasonable for the magnitude of this quantity to be more closely related to the properties of UO_2 , the material subjected to the action of HF, than to the properties of the U_3O_8 from which the UO_2 was produced. Moreover, it is surprising that the percent conversion of U_3O_8 to UF_4 should correlate fairly well with both packed bulk density of UO_2 and loose bulk density of UO_2 since the condition of the UO_2 charge at the beginning of hydrofluorination is essentially the same as the condition of UO_2 after loose bulk density measurements and is quite different from the condition of UO_2 after packed bulk density measurements.

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Fig. 5

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Fig. 6

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6. Summary

Values of specific surface ranging from $0.05 \text{ m}^2/\text{g}$ to $0.37 \text{ m}^2/\text{g}$ and values of packed bulk density ranging from 3.7 g/cm^3 to 1.8 g/cm^3 were encountered in the study of samples of 22 U_3O_8 materials which had been prepared by calcination at 900°C of widely differing uranium peroxide precipitates and which had been evaluated as to "reactivity" by successive treatment with hydrogen and a mixture of anhydrous hydrogen fluoride and hydrogen in a production-type batch process for the preparation of UF_4 . The values of specific surface and packed bulk density for the 22 corresponding UO_2 intermediates varied from $0.03 \text{ m}^2/\text{g}$ to $0.33 \text{ m}^2/\text{g}$ and from 4.9 g/cm^3 to 2.7 g/cm^3 , respectively. Comparison of the ratios of observed specific surface of UO_2 to that of U_3O_8 with a calculated ratio indicated that formation of new surface took place in the reduction of some of the U_3O_8 samples to UO_2 .

A good correlation was obtained between the values for specific surface of U_3O_8 and packed bulk density of U_3O_8 , the data showing an inverse relationship. A very poor correlation between specific surface of UO_2 and packed bulk density of UO_2 was obtained. The percent conversion of U_3O_8 to UF_4 in the standard two-step process varied from 22% for the lowest specific surface, highest bulk density oxide to 98 to 99% for the high specific surface, low bulk density oxides. Values of percent conversion of U_3O_8 to UF_4 correlated better with the observed values for properties of the U_3O_8 samples than with the observed values for properties of the corresponding UO_2 intermediates.

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Appendix A

Curve Fitting by Means of Normal Distribution Functions

The technique used in evaluating the normal distribution function to represent a given set of data is illustrated in Fig. 7. The data were first plotted on probability paper. A straight line on probability paper indicated that a normal distribution function could be used to relate the data. The values of the variable on the probability axis were then expressed in probability units by means of the table of Bliss,¹ and the least squares equation for the line was determined.

It can be seen in Fig. 7 that a straight line on probability paper is equivalent to a straight line on rectangular coordinate paper when the variable on the probability axis is expressed in probability units.

The value of s_y was calculated by first computing values of w from the least squares equation in w and then converting these values to percent units (by means of the table of Bliss) for comparison with observed values of percent conversion of U_3O_8 to UF_4 . The curves in Figures 3 to 6 were obtained by converting values of w calculated from the least squares equations to percent units.

(1) C. I. Bliss, Ann. Appl. Biol., 22, 134 (1935).

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PERCENT CONVERSION OF UO_3 TO UF_4 (IN PROBABILITY UNITS)

Fig. 7

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Appendix B

Calculation of Changes in Specific Surface

The calculation of the specific surface of a sample of UO_2 from that of the original U_3O_8 can be attempted with the following method of calculation, suggested by R. W. Kewish:

Consider a single particle of U_3O_8 of volume V . The surface area, $A_{\text{U}_3\text{O}_8}$, will be:

$$A_{\text{U}_3\text{O}_8} = K(V)^{2/3},$$

where K is a form factor related to the shape of the particle. (K has a value of 6 for cubes, $(36\pi)^{1/3}$ for spheres, etc.) When the particle of U_3O_8 is converted to UO_2 , a loss in weight and a gain in density occur. The volume of the UO_2 product, V_{UO_2} , will be:

$$V_{\text{UO}_2} = V \left(\frac{8.39}{10.96} \right) \left(\frac{3\text{UO}_2}{\text{U}_3\text{O}_8} \right) = V \left(\frac{8.39}{10.96} \right) (0.9620) = 0.736V,$$

where 8.39 and 10.96 are taken as the densities of U_3O_8 and UO_2 , respectively. If the form factor does not change and if the particle does not develop new surface or sinter during the course of the reaction, the surface area of the product particle, A_{UO_2} , will be:

$$A_{\text{UO}_2} = K(V_{\text{UO}_2})^{2/3} = K(0.736V)^{2/3} = 0.815K(V)^{2/3}$$

(Observations of single U_3O_8 particles weighing about 7 mg show that the particles retain their shapes but decrease in size during reduction to UO_2 .)

Consider now a 1-gram sample of U_3O_8 containing N_{11} particles of volume V_1 and form factor K_1 , N_{ij} particles of volume V_i and form factor K_j , etc. The total surface area, $A_{\text{U}_3\text{O}_8}$, will be:

$$A_{\text{U}_3\text{O}_8} = N_{11}K_1(V_1)^{2/3} + \dots + N_{ij}K_j(V_i)^{2/3} + \dots$$

$A_{\text{U}_3\text{O}_8}$ is also the specific surface since 1 gram of sample is being considered.

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If the form factors do not change and if the particles do not develop new surface or sinter during the course of the reaction, the total surface area of the product, A_{UO_2} , will be:

$$\begin{aligned} A_{\text{UO}_2} &= N_{11} 0.815 K_1 (V_1)^{2/3} + \dots + N_{ij} 0.815 K_j (V_i)^{2/3} + \dots \\ &= 0.815 (N_{11} K_1 (V_1)^{2/3} + \dots + N_{ij} K_j (V_i)^{2/3} + \dots) \\ &= 0.815 A_{\text{U}_3\text{O}_8} \end{aligned}$$

Since weight is lost during the reaction, the calculated specific surface of UO_2 equals $A_{\text{U}_3\text{O}_8} \times 0.815/0.9620$. Thus the calculated ratio of specific surface of UO_2 to specific surface of U_3O_8 is 0.847.

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