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REACTIVITY STUDIES OF URANIUM OXIDES

by

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One amorphous and three crystalline polymorphic modifications of UO_3 *have been prepared by pyrolysis of uranyl nitrate hexahydrate. The hydration reactivity of* UO_3 *appears to be a function of its residual nitrogen content which is, in turn, dependent on the method, time, and temperature of denitration. Amorphous* UO_3 *is more reactive than crystalline* UO_3*.*

The initial oxidation reactivity (the oxygen sorption in 1 day at room temperature) of UO_2 *varies with the method of preparation of the* UO_3*. The average oxidation rate of* UO_2 *after the first day decreases with increasing nitrogen content of the* UO_3 *from which the* UO_2 *was made. If soluble nitrates are removed from* UO_3 *by water leaching prior to reduction, the final reoxidation reactivity of the* UO_2 *is increased by a factor of 10. Hydration and dehydration of amorphous* UO_3*, without leaching, decrease the final reoxidation reactivity of the subsequent* UO_2 *by a factor of 10.* UO_2 *made from amorphous* UO_3 *has a higher reoxidation reactivity than when made from crystalline* UO_3 *of the same nitrogen content.*

INTRODUCTION

Production of uranium metal requires several steps in processing high-purity uranium salts (pyrolysis of $UO_2(NO_3)_2 \cdot 6H_2O$ to UO_3, reduction of UO_3 to UO_2, and hydrofluorination of UO_2 to UF_4) before final reduction. The variables in each step are being investigated for their effect upon the subsequent product. This study of the structure, composition, and chemical reactivity of uranium trioxide was undertaken to determine the effects of these variables upon the reactivity of uranium dioxide made from various preparations of uranium trioxide. Chemical reactivity of UO_3 was measured by the amount of water sorption at 30 C. As a measure of the reactivity of uranium dioxide, its reoxidation rate was determined on exposure to air at room temperature. A previous Battelle report(1) describes the process of thermal decomposition of uranyl nitrate hexahydrate, the end product in the uranium-ore-purification process. It was shown, in that report, that the several polymorphic forms of UO_3, as described by Katz(2), can be produced by thermal decomposition of the nitrate. The sinterability of UO_2 made from various polymorphic forms of UO_3 was reported earlier(3). E. J. Barber(4) and workers at Mallinckrodt Chemical Works(5) have shown that there are marked differences in the rate of hydrofluorination of UO_2 made from various types of UO_3.

In view of these results and the lack of information on the relationship among structure, composition, and reactivity of uranium trioxide, it was of interest to determine how these variables affect the reactivity of the two oxides, UO_3 and UO_2.

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(1) References at end.

EXPERIMENTAL WORK

Decomposition of Uranyl Nitrate Hexahydrate

Two general methods based upon previous work(1) were employed in the pyrolytic decomposition of uranyl nitrate hexahydrate, one in which the nitrate melts during decomposition, and the other in which the nitrate decomposes without melting. The oxide obtained by the first method is crystalline, while that obtained by the latter is amorphous. Three crystalline forms of UO_3 may be produced from the nitrate. Type III UO_3*, the most common crystalline form, is produced when uranyl nitrate hexahydrate is heated in bulk quantities until the water and nitrogen oxides volatilize. Type II UO_3 is produced if a thin bed of the nitrate is heated rapidly to 450 or 500 C or if a small batch (60 to 90 g) of nitrate, to which 1 w/o acetic acid has been added, is heated to 450 C. The latter method is more reproducible. Type I UO_3 is produced by addition of ethyl alcohol to uranyl nitrate hexahydrate followed by flash denitration at 425 C.

An amorphous form of UO_3 is obtained when decomposition of uranyl nitrate hexahydrate is accomplished stepwise as described in BMI-1110.(1) The water of hydration is removed first, then the anhydrous nitrate is decomposed. Two methods of water removal were employed, one in which the nitrate was vacuum dried and further heated at increasing temperatures to 150 C and the other in which hot gas, at atmospheric pressure, dried a thin layer of nitrate as it was carried on a belt into a furnace for final denitration. Final denitration of the vacuum-dried nitrate was carried out in an open pot at various temperatures from 200 to 450 C.

UO_3 Analysis and Reactivity Measurement

Since the final denitration temperature used in the production of UO_3 may not yield completely decomposed nitrate, analyses were made for retention of nitrogen in the UO_3 structure. Water may also be retained in the UO_3 structure. Analysis for water may be obtained by difference, assuming the nitrogen to be present as nitrate. For all UO_3 preparations, the structure type was determined by powder X-ray diffraction, using filtered iron radiation. The per cent conversion of the nitrate to UO_3 was determined by weight change on ignition to U_3O_8 at 750 C. Residual nitrogen content of UO_3 was obtained by the Kjeldahl method. The results of these analyses are given in Table 1. The last column in Table 1 gives the hydration reactivity in terms of equilibrium water content of the various preparations on exposure to water-saturated air at 30 C. Type I UO_3 has not been prepared in sufficient quantity for hydration-reactivity studies or for nitrogen analyses.

The results on Type III and amorphous UO_3 indicate two systematic trends. The nitrogen content of UO_3 decreases with increasing temperature of denitration, as shown in Figure 1, while the hydration reactivity of UO_3, presented graphically in Figure 2, increases with nitrogen content. The reactivity of amorphous oxide is significantly greater than that of Type III oxide at corresponding low nitrogen contents, 0.1 w/o. X-ray diffraction analyses of the hydrated samples show that amorphous UO_3 hydrates to the dihydrate structure, while Type III UO_3 hydrates to the monohydrate structure.

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* The structure types of UO_3 correspond to those described by Katz, Reference (2).

TABLE 1. COMPARISON OF PERCENTAGE CONVERSION AND NITROGEN CONTENT OF UO_3 WITH FINAL DENITRATION TEMPERATURE AND HYDRATION REACTIVITY

Starting Material	Type of UO_3	Denitration		Conversion, per cent UO_3	Nitrogen, w/o	Hydration, w/o H_2O
		Temperature, C	Time, hr			
UNH	III	200	4	98.98	.24	15.84
UNH	III	250	4	94.50	.12	-
UNH	III	300	4	99.59	.104	8.89
UNH	III	325	4	99.35	-	-
UNH	III	350	4	99.58	.101	-
UNH	III	400	4	99.65	.098	8.28
UNH	III	425	2	99.36	.075	-
UNH	III	425	4	99.60	-	-
UNH	III	450	4	99.66	.058	8.38
UNH, moving-belt method	Amorphous	350	-	97.87	.24	16.30
UNH, moving-belt method	Amorphous	400	-	98.97	.064	13.44
UNH, moving-belt method	Amorphous	425	-	98.88	.032	12.44
UNH, moving-belt method	Amorphous	450	-	99.08	.02	12.50
UNH, vacuum dried at 125 C	Amorphous	250	2	96.56	-	22.65
UNH, vacuum dried at 125 C	Amorphous	350	2	99.62	-	-
UNH, vacuum dried at 125 C	Amorphous	450	2	99.92	.002	-
UNH, vacuum dried at 150 C	Amorphous	300	2	97.20	.57	22.18
UNH, vacuum dried at 150 C	Amorphous	300	4	99.27	.13	15.21
UNH, vacuum dried at 150 C	Amorphous	300	8	99.38	-	-
UNH, vacuum dried at 150 C	Amorphous	400	4	99.72	.01	13.16
UNH,+ ethyl alcohol	I	425	1/30	96.55	-	-
UNH + 0.6 w/o acetic acid	II	425	4	99.32	-	10.85
UNH + 1.0 w/o acetic acid	II	450	4	99.56	-	11.00

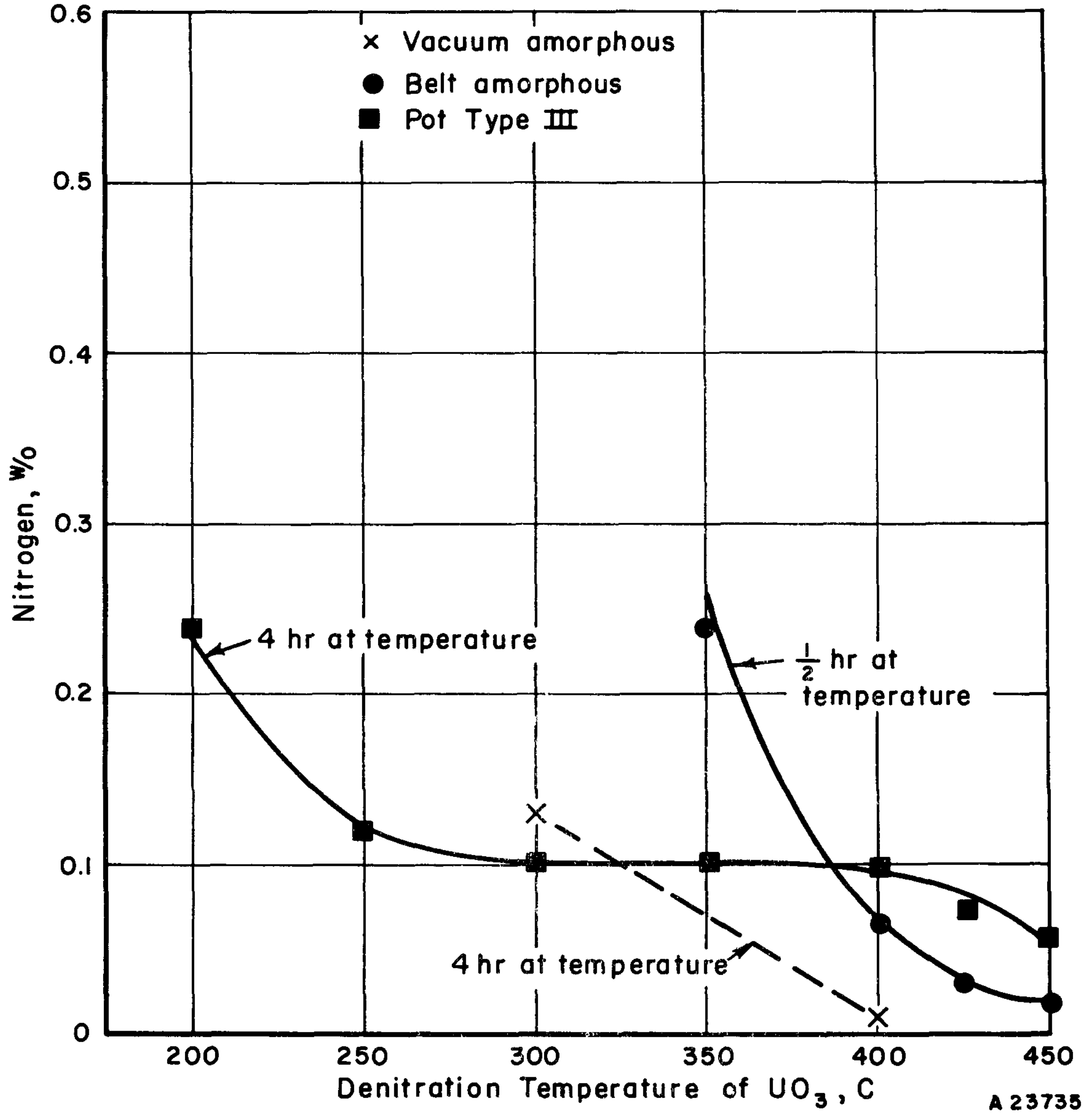

FIGURE 1. NITROGEN CONTENT OF UO_3 VERSUS TEMPERATURE OF DENITRATION

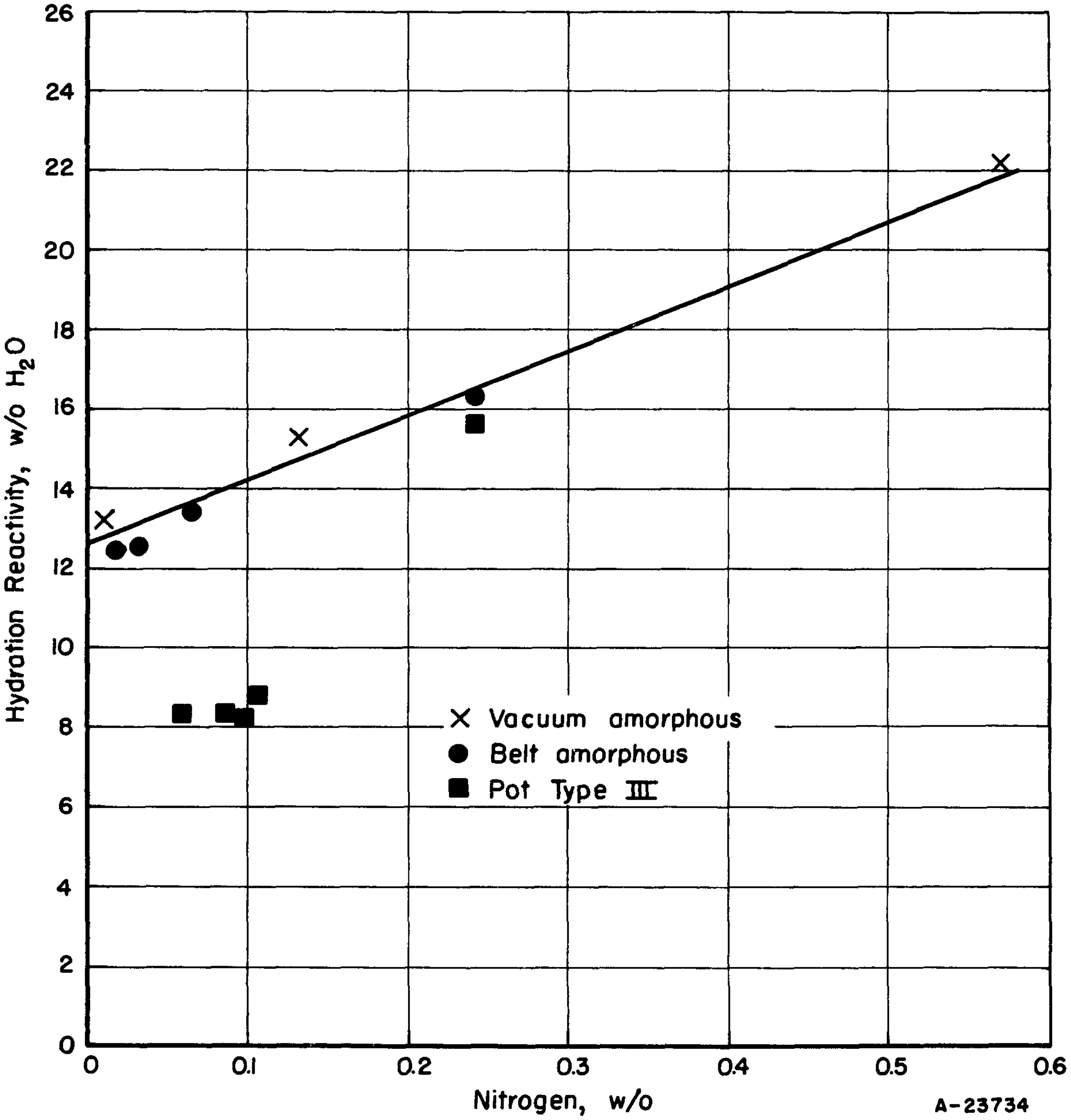

FIGURE 2. HYDRATION REACTIVITY VERSUS NITROGEN CONTENT

These differences in the amount of hydration and in the structure of the hydrate phases suggest a difference in the free energy of the two forms of UO_3.

Since the hydration reactivity is directly related to the nitrogen content for a given UO_3 structure, removal of the residual nitrate nitrogen by water leaching was studied. Several UO_3 preparations were leached with water until the filtrate was no longer colored. The insoluble portion was dried at 300 C and analyzed in the same manner as the original preparation. The change in nitrogen content as a result of leaching is presented in Table 2. In order to differentiate between the effects of hydration and leaching, several samples were hydrated in such a way as to minimize removal of the soluble salts, dried at 300 C, and then analyzed for nitrogen content. The last column of Table 2 indicates that a significant amount of nitrogen remained in these samples. X-ray analyses showed that only amorphous UO_3 was obtained from leached and dried UO_3. High-nitrogen UO_3, hydrated and dried, gave diffraction patterns of crystalline UO_3, while the structure of low-nitrogen UO_3 (whether crystalline or amorphous) was not changed by hydration and drying.

Only a limited investigation was made of the UO_3 hydration reactivity after prior hydration and drying. It was observed that, if a structural change developed during the first cycle of hydrating and drying, the second hydration reactivity was different from the first, otherwise the hydration reactivity was not significantly different. No hydration-reactivity data were obtained on leached samples of UO_3.

UO_2 Analysis and Reactivity Measurement

The UO_3 preparations discussed in the previous section were reduced to UO_2, and the effects of the prior UO_3 structure and composition upon the reactivity of the UO_2 were investigated. Uranium trioxide, when exposed to hydrogen for 2 hr at 600 C, is reduced to red UO_2. In the present study, dry hydrogen was used to carry out reduction, and the UO_2 was cooled to room temperature in hydrogen. Analysis of the oxygen content of the UO_2 was obtained by weight change on ignition in air at 750 C. The as-reduced oxide gave an oxygen-to-uranium ratio of nearly 2.00 before exposure to air. However, upon exposure to air, the oxide changed color, evolved heat, and the oxygen-to-uranium ratio increased. The amount of this increase in 1 day is presented in Table 3 for UO_2 made from various preparations of UO_3. The last two columns in Table 3 give the oxygen-to-uranium ratio of these UO_2 preparations after storing at atmospheric temperature for more than 3 weeks. The average rate of change in the oxygen-to-uranium ratio during storage increases with decreasing nitrogen content for all methods of UO_3 preparation, as shown in Figure 3. However, the magnitude of the change in oxygen-to-uranium ratio is greater for UO_2 made from amorphous UO_3 than for UO_2 made from crystalline UO_3 of the same nitrogen content. Thus, it seems that the reactivity of UO_2 during storage is affected by both structure and composition of the UO_3.

Since the reactivity of UO_2 is influenced to a great extent by the nitrogen content for a given UO_3 structure, the effect of nitrogen removal from UO_3 on the reactivity of UO_2 was investigated. The water-soluble nitrates in UO_3 were leached out, as described in the previous section, before reduction to UO_2. The UO_2 reactivities for leached and unleached UO_3 samples are given in Table 4. Except for two samples, the

TABLE 2. COMPARISON OF NITROGEN CONTENT OF UO_3 PREPARATIONS BEFORE AND AFTER WATER LEACHING AND HYDRATING

	Nitrogen Content, w/o		
Type of UO_3	Original Preparation	After Leaching[a]	After Hydrating[a]
Amorphous	0.24	.005	--
Amorphous	0.032	.005	--
Amorphous	0.13	.005	--
Amorphous	0.01	.005	--
III	0.24	--	.048
III	0.104	.005	.038
III	0.101	.005	--
III	0.098	.005	.037
III	0.058	.005	.027
III	0.111	--	.030
III	0.085	--	.037
III	0.103	--	.041
III	0.093	--	.039

(a) The water of hydration was removed by drying at 300 C. This second heating of the samples reduces the nitrogen as shown in the last column.

TABLE 3. CHANGE IN OXYGEN-TO-URANIUM RATIO OF UO_2 COMPARED WITH THE METHOD OF PREPARATION AND NITROGEN CONTENT OF UO_3

	UO_3			Oxygen-to-Uranium Ratio of UO_2			Rate of
Preparation Method	Denitration Temperature, C	Type	Nitrogen Content, w/o	In 1 Day	After X Days	Storage Time, days	Reoxidation in O/U Per Day 10^3
Belt amorphous	350	Amorphous	0.24	2.259	2.341	21	3.8
Belt amorphous	400	Amorphous	0.064	2.108	2.137	21	1.4
Belt amorphous	425	Amorphous	0.032	2.128	2.254	47	2.7
Belt amorphous	450	Amorphous	0.02	2.093	2.185	21	4.2
Vacuum amorphous	250	Amorphous	--	2.166	2.323	23	6.2
Vacuum amorphous	350	Amorphous	--	2.181	2.327	22	8.6
Vacuum amorphous	450	Amorphous	0.002	2.203	2.357	20	7.7
Vacuum amorphous	300	Amorphous	0.57	2.155	2.175	19	1.1
Vacuum amorphous	300	Amorphous	0.13	2.166	2.263	21	4.6
Vacuum amorphous	400	Amorphous	0.01	2.183	2.335	21	7.2
Pot	200	III	0.24	2.037	2.047	28	0.36
Pot	250	III	0.12	2.036	2.047	28	0.39
Pot	300	III	0.104	2.039	2.044	28	0.18
Pot	350	III	0.101	2.031	2.047	27	0.59
Pot	400	III	0.098	2.041	2.048	27	0.26
Pot	450	III	0.058	2.049	2.072	27	0.85
Pot	250	III	0.111	2.045	2.050	22	0.23
Pot	300	III	0.085	2.054	2.076	22	1.0
Pot	350	III	0.103	2.037	2.055	21	0.85
Pot	400	III	0.093	2.036	2.050	21	0.67
Pot	425	II	--	2.069	2.125	21	2.7
Pot	425	I	--	2.146	--	--	--

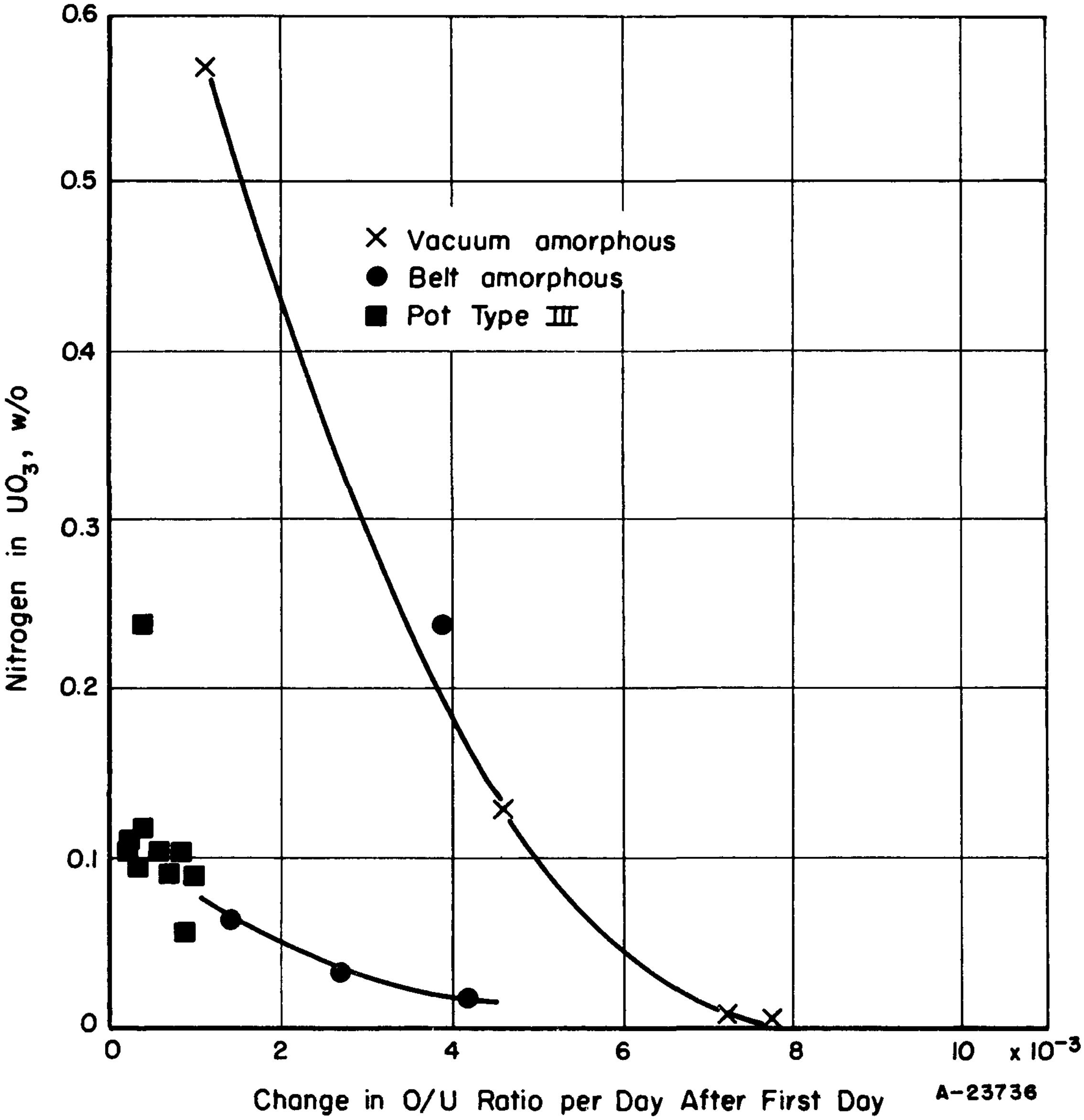

FIGURE 3. REACTIVITY OF UO_2 WITH TIME VERSUS NITROGEN CONTENT OF UO_3

TABLE 4. EFFECT OF WATER LEACHING OF UO_3 ON REACTIVITY OF UO_2

		UO_2 Made From Original UO_3				UO_2 Made From Leached UO_3[(a)]			
		Oxygen-to-Uranium Ratio				Oxygen-to-Uranium Ratio			
Original UO_3 Type	Denitration Temperature, C	In 1 Day	After X Days	Storage Time, days	Rate of Reoxidation, O/U per day x 10^3	In 1 Day	After X Days	Storage Time, days	Rate of Reoxidation, O/U per day x 10^3
Vacuum amorphous	250	2.166	2.323	23	6.8	2.116	2.230	21	5.4
Vacuum amorphous	300	2.155	2.175	18	1.1	2.089	2.179	45	2.0
Vacuum amorphous	300	2.166	2.263	21	4.6	2.091	2.210	21	5.7
Vacuum amorphous	400	2.183	2.335	21	7.2	2.081	2.166	21	4.0
Belt amorphous	350	2.259	2.341	21	3.9	2.113	2.221	21	5.6
Belt amorphous	425	2.128	2.254	47	2.7	2.104	2.238	21	6.4
MCW, III(b)	--	2.047	2.072	58	0.43	2.048	2.085	48	0.77
MCW, III(b)	--	2.037	2.059	58	0.38	2.070	2.105	48	0.73
MCW, III(b)	--	2.056	2.075	56	0.34	2.051	2.094	21	2.0
MCW, III(b)	--	2.042	2.080	56	0.68	2.051	2.077	21	1.2
MCW, III(b)	--	2.047	2.074	28	0.96	2.047	2.086	28	1.45
III	300	2.039	2.044	28	0.18	2.043	2.109	21	3.1
III	350	2.031	2.047	27	0.59	2.061	2.091	21	1.5
III	400	2.041	2.048	27	0.26	2.057	2.073	21	1.7
III	450	2.049	2.072	27	0.85	2.084	2.123	21	1.9

(a) The leached samples of UO_3 were dried at 300 C before reduction to UO_2.

(b) Mallinckrodt Chemical Works produced UO_3.

rate of change in the oxygen-to-uranium ratio of the UO_2 increased as a result of leaching. However, leaching hydrates the UO_3. Table 5 presents corresponding data on the reactivity of UO_2 made from hydrated UO_3 samples, in which leaching was not carried out. The UO_2 reactivity decreased in all cases of UO_2 made from amorphous UO_3 but is increased for the UO_2 made from Type III UO_3.

Analyses for residual nitrogen by the Kjeldahl method were made on UO_2 samples prepared from UO_3 containing high and low nitrogen contents. These analyses revealed that less than 0.002 w/o nitrogen was retained through the reduction step.

DISCUSSION OF RESULTS

The results of this investigation on the reactivity of uranium oxides show that structural and compositional differences, resulting from methods of production, may be inherited and may influence the activity of materials in subsequent processing steps. Only a limited amount of study of this phenomenon in relation to the hydrofluorination and magnesium-reduction steps of uranium production has been done. However, studies carried out by Barber(4) and at Mallinckrodt Chemical Works(5) through the hydrofluorination step show a marked effect of UO_3 structure upon the hydrofluorination reactivity of the UO_2.

The present investigation revealed a marked difference in reoxidation reactivity of UO_2 which could be related to the prior UO_3 structure, as was exhibited in the hydrofluorination reactivity tests. In addition to the effect of prior structure, the higher the nitrogen content of the UO_3 the lower was the reoxidation reactivity of the subsequent UO_2, even though there was no evidence for retention of nitrogen in the UO_2 structure. Assuming the Kjeldahl method of analysis is sensitive to all the nitrogen retained in the UO_2 structure, the effect of nitrogen in UO_3 on the reoxidation reactivity of UO_2 must be related to the method of nitrogen removal during the reduction step. Fundamental investigations on the nature of bonding of impurity atoms in the oxides and on the pore structure of UO_2 made from high- and low-nitrogen UO_3 are necessary for a better understanding of uranium oxide chemistry. However, based upon the results of the present investigation, the following conclusions can be drawn concerning nitrogen retention in UO_3 and the reoxidation reactivity of subsequent UO_2.

(1) The residual nitrogen content of UO_3 depends upon the time and temperature of denitration and the uranyl nitrate hexahydrate pyrolysis method.

(2) For open-pot pyrolysis methods, which result in Type III UO_3, the residual nitrogen content of the oxide decreases rapidly from 200 to 250 C, does not change appreciably with temperature from 250 to 400 C, and decreases slowly with temperature above 400 C.

(3) For stepwise (water, then nitrogen oxide) pyrolysis methods which result in amorphous UO_3, the residual nitrogen content decreases rapidly with temperature from 300 to 425 C.

(4) The nitrogen content of amorphous UO_3 is higher than that of Type III UO_3 for comparable times of denitration at 300 C, but less at 400 C and above.

TABLE 5. EFFECT OF HYDRATION OF UO_3 ON REACTIVITY OF UO_2

		UO_2 Made From Original UO_3				UO_2 Made From Hydrated UO_3[(a)]			
		Oxygen-to-Uranium Ratio				Oxygen-to-Uranium Ratio			
Original UO_3 Type	Denitration Temperature, C	In 1 Day	After X Days	Storage Time, days	Rate of Reoxidation, O/U per day x 10^3	In 1 Day	After X Days	Storage Time, days	Rate of Reoxidation, O/U per day x 10^3
125-vacuum amorphous	250	2.166	2.323	23	6.8	2.088	2.147	56	1.05
150-vacuum amorphous	300	2.155	2.175	18	1.1	2.072	2.116	56	0.79
150-vacuum amorphous	300	2.166	2.263	21	4.6	2.102	2.118	57	0.28
150-vacuum amorphous	400	2.183	2.335	21	7.2	2.083	2.115	57	0.56
Belt amorphous	350	2.259	2.341	21	3.9	2.098	2.133	57	0.61
Belt amorphous	400	2.108	2.137	21	1.4	2.090	2.105	57	0.26
Belt amorphous	425	2.128	2.254	47	2.7	2.094	2.121	58	0.46
Belt amorphous	450	2.093	2.185	22	4.2	2.081	2.098	57	0.30
III	200	2.037	2.047	28	0.36	2.048	2.086	21	1.8
III	250	2.045	2.052	30	0.23	2.053	2.101	21	2.3
III	300	2.039	2.044	28	0.18	2.048	2.065	21	0.8
III	300	2.054	2.076	22	1.0	2.049	2.080	21	1.5
III	350	2.037	2.055	21	0.85	2.053	2.081	21	1.3
III	400	2.041	2.048	27	0.26	2.052	2.090	21	1.8
III	400	2.036	2.050	21	0.66	2.046	2.101	21	2.6
III	450	2.049	2.072	27	0.85	2.039	2.080	21	1.9

(a) The hydrated UO_3 samples were dried at 300 C before reduction to UO_2.

(5) The reactivity of UO_3 towards hydration increases with increasing nitrogen content. For a given nitrogen content, amorphous UO_3 has a higher hydration reactivity than crystalline Type III UO_3.

(6) The change in the oxygen-to-uranium ratio of UO_2 on exposure to air (measured after the first day) varies inversely with nitrogen content of UO_3.

(7) The activity of UO_2 may be increased by leaching or hydrating crystalline Type III UO_3 or by leaching amorphous UO_3, but is decreased by hydration and dehydration of amorphous UO_3 prior to reduction.

ACKNOWLEDGMENT

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