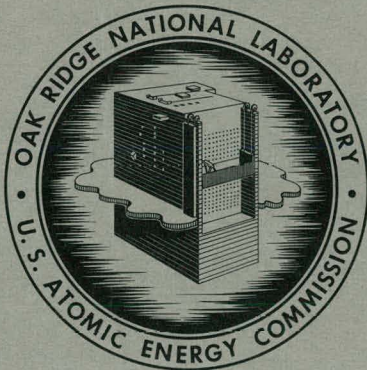ORNL-3177
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SORPTION OF URANIUM ON ZIRCONIUM OXIDE

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OAK RIDGE NATIONAL LABORATORY
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Gerald Goldstein

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ABSTRACT

The sorption of the ions of uranium, copper, and nickel on hydrous zirconium oxide was investigated at temperatures from 25° to 250°C. The work was done in connection with studies of the corrosion rates of zirconium and Zircaloy-2 in uranyl sulfate solutions. These experiments were performed by equilibrating 5 ml of the test solution with 0.5 g of zirconium oxide in a titanium autoclave, which was heated by means of a rocking furnace. The sorption of uranium was affected by characteristics of the zirconium oxide, temperature of equilibration, and concentrations of uranium and of free acid in the uranyl sulfate solutions. Conclusions are drawn concerning the relationship between each of these factors and uranium sorption.

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INTRODUCTION

In studies of the corrosion rates of zirconium and Zircaloy-2 in uranyl sulfate solutions, it has been found that the rates are appreciably greater in the presence of radiation than in the absence of radiation. Jenks[8] has proposed that heavy nuclear particles, such as fission fragments, cause the increase in corrosion by damaging the protective oxide film on the metal surface. Uranium is sorbed on the surface of the oxide, and since the range of fission fragment recoils is short, much of the damage may be caused by sorbed uranium. Studies of the sorption of uranium on zirconium oxide therefore should be helpful in understanding corrosion in irradiated aqueous media and in reducing radiation corrosion.

The results of previous work on uranium sorption[7,9] pointed out several problems. Inconsistencies in results obtained at elevated temperatures were observed and were attributed to difficulty in separating the solid and aqueous phases while they were at equilibrium temperature. However, the development of a titanium autoclave and rocking furnace apparatus[9] eliminated this difficulty. In addition, sorption of uranium on zirconium oxide was found to be critically dependent on the characteristics of the zirconium oxide. Samples of zirconium oxide obtained from different sources were shown to sorb significantly different amounts of uranium under identical conditions. More-

over, in experiments with a high-pressure chromotographic column,[8] the
properties of the oxide appeared to change during the course of the experi-
ments. Impurities in the oxide also appeared to affect its sorption character-
istics.

Some of the factors that are important in the study of uranium sorption
on zirconium oxide and that are dealt with in this work are: (1) character-
istics of zirconium oxide and changes in these characteristics with experi-
mental conditions, (2) relationship between uranium sorption and characteristics
of the oxide, and (3) relationship between uranium sorption and nature of the
solution phase.

EXPERIMENTAL DETAILS

Uranyl sulfate solutions that were 0.02 $\underline{M}$ in sulfuric acid and that
contained uranium in concentrations from 1 to 40 mg/ml were prepared and
were carefully analyzed for uranium, sulfate, and free acid.

Experiments at 25°C were performed by equilibrating 25 ml of the test
solution with 0.750 g of zirconium oxide overnight on a mechanical shaker.
Experiments at elevated temperatures were performed by equilibrating 5 ml
of the test solution with 0.500 g of zirconium oxide for 4 hours; a titanium
autoclave and rocking furnace apparatus[9] was used.

RESULTS

Characteristics of Hydrous Zirconium Oxide

The sorption of uranium on hydrous zirconium oxide was found to depend
on several factors, such as the method of preparation of the oxide, pretreatment,

surface area, water content, crystal structure, and the presence of impurities.
For example, samples of zirconium oxide from City Chemical Company, Fisher
Scientific Company, and Delta Chemical Company were all equilibrated with
uranyl sulfate solutions under identical conditions and were found to sorb
significantly different amounts of uranium. In fact, the sorptive properties
of hydrous oxides in general have been found to depend on such a variety of
conditions that, for the most part, it is not possible to prepare a hydrous
oxide of prescribed properties.[3]

The City Chemical Company zirconium oxide was chosen for characterization
and for use in uranium sorption studies because uranium sorption on this
oxide appeared to be very much like that observed in corrosion studies of
Zircaloy-2. This oxide was shown by chemical analysis to contain as major
impurities about 0.1% Ca, 0.1% Mg, 0.1% Si, and 2% sulfate.

The water content and surface area of the oxide as a function of the
temperature of calcination are given in Table 1. Water contents were determined

Table 1. Water Content and Surface Area of City Chemical Company
Hydrous Zirconium Oxide as a Function of Calcination Temperature

Temperature of Calcination, $^\circ$C[a]	H_2O, %	Surface Area, m^2/g	θ[b]
110	25	196	8.4
150	21	188	7.1
200	6.2	187	1.8
250	5.0	160	1.7
300	3.7	132	1.4
450	1.3	85.1	0.8
1000	0	13.4	0

[a] Calcined two hours at the temperature indicated.

[b] θ = fraction of surface covered with OH groups.

by thermogravimetric analysis (see Fig. 1), and surface areas were measured

by the nitrogen adsorption—BET method. The fraction of the surface covered

by OH groups (i.e., θ) was calculated by assuming that the OH radical of

each water molecule was adsorbed on the surface and that the area occupied

by each OH group is 15 $\mathring{A}^2$. At temperatures from 100° to $300^\circ C$, water is

lost rapidly, and the surface area diminishes. Within this temperature

range, the water content of the oxide is more than enough to form a monolayer

on the zirconium oxide surface. At about $400^\circ C$, the water content of the

oxide is equivalent to a monolayer on the surface, and a much higher temper-

ature ($\sim 800^\circ C$) is required to completely remove the monolayer. Changes in

surface area of solid oxides that contain water of constitution as a function

of temperature of calcination are interpreted by Gregg[6] as being due to two

processes. As water evaporates, an extensive internal surface made up of

the walls of fine pores is produced. At the same time, the increase in

temperature induces recrystallization of the oxide and formation of large

crystals (sintering), thereby decreasing the surface area. The net change

in surface area on heating therefore depends on the relative rates of the

two processes. However, when water is lost from a hydrous oxide that con-

tains principally adsorbed water and no water of consititution, for example,

hydrous ferric oxide, the surface area is decreased as a result of sintering.

The curve obtained by plotting surface area versus temperature for hydrous

zirconium oxide is very similar to the curve obtained from the same type

plot for hydrous ferric oxide;[4] this similarity indicates that hydrous

zirconium oxide also consists of ZrO_2 plus sorbed H_2O. Electron micrographs
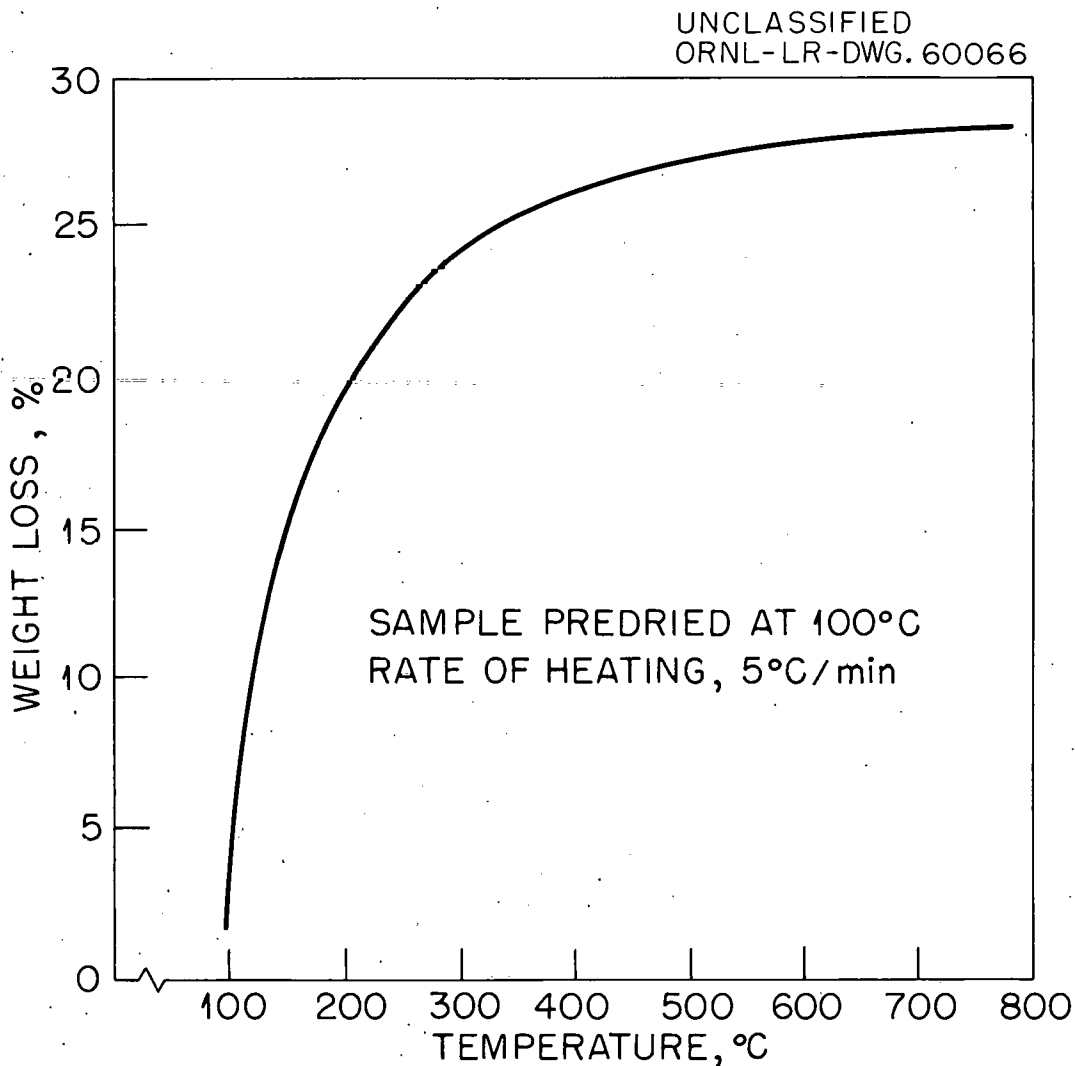
Fig. 1. Results of thermogravimetric analysis of City Chemical Company zirconium hydroxide.

of hydrous zirconium oxide obtained by Banter[9] confirm the increase in crystallite size of hydrous zirconium oxide when it is treated at elevated temperatures.

Impurities in zirconium oxide, both cationic and anionic, can affect significantly the change in surface area of the oxide with temperature. Cationic impurities generally accelerate sintering by increasing the attractive forces between crystallites and by surface diffusion to fill up cracks and pores in the surface.[6] It is well known that small percentages of calcium and magnesium, which are present as impurities in zirconium oxide obtained from City Chemical Company, stabilize the cubic modification of the zirconium oxide structure at temperatures below 1000°C, which structure in pure zirconium oxide is stable only at temperatures greater than 1000°C.[2] X-ray diffraction patterns of City Chemical Company zirconium oxide show the presence of cubic structure in both material that was calcined at 450°C and material that was acid treated at 250°C. Anionic impurities, such as sulfate, also affect the surface area.[4]

The effect of treatments with water and with 0.02 $\underline{M}$ sulfuric acid at various temperatures on the surface area of hydrous zirconium oxide was studied; the data are given in Table 2. Water-treated zirconium oxide has a larger surface area per unit weight of oxide than does acid-treated zirconium oxide. Both water treatment and acid treatment at 25 and 100°C increase the surface area of a fixed weight of zirconium oxide, the increase being greater at 100°C that at 25°C. Although part of the change in surface

Table 2. Effect of Water and Sulfuric Acid Treatments at Various
Temperatures on Surface Area of 110°C-Calcined Zirconium Oxide

| Treatment | | Surface Area, |
Temperature, °C	Reagent	m²/g
--	--	196
25	H_2O	213
25	0.02 M H_2SO_4	201
100	H_2O	270
100	0.02 M H_2SO_4	239
250	0.02 M H_2SO_4	97

area of the original oxide is due to the change in the weight of ZrO_2 per

gram of hydrous zirconium oxide when H_2O or H_2SO_4 are sorbed or desorbed, a

possible explanation for the increases in surface area is that water and

acid leach impurities from the oxide leaving voids in the crystal lattice.

The concentrations of magnesium found in the solutions following acid treat-

ment were: at 25°C, 0.0030 meq/ml; at 100°C, 0.0044 meq/ml; and at 250°C,

0.0079 meq/ml. Since the zirconium oxide used in these experiments had been

calcined at 110°C, it is not likely that subsequent treatment at 25° or 100°C

would decrease its surface area by sintering, and the leaching of the impurities

might then account for the increase in surface area. Acid treatment at 250°C

decreases the surface area to an area smaller than that of 250°C air-fired

zirconium oxide. Similar results have been found previously.[7] It would

be expected that if an oxide that had been calcined in air at 110°C were

heated to 250°C, the surface area would be decreased. In addition, the surface area of zirconium oxide treated with acid at 250°C may be smaller than that of a zirconium oxide calcined at 250°C because of rapid dissolution and recrystallization of the zirconium oxide surface in sulfuric acid solution at the elevated temperature.

Sorption of Uranium on Zirconium Oxide after Various Pretreatments

The sorption of uranium from 0.02 $\underline{M}$ sulfuric acid solutions of about 20-mg/ml uranium concentration on zirconium oxide that had been pretreated in various ways was determined at 25° and 250°C. The results are presented in Table 3; the complete data are tabulated in Apx. I.

At 25°C, zirconium oxide that was calcined at 110°C sorbed 50.3 mg of uranium per gram of solid. Sorption of uranium on zirconium oxides calcined at 150° to 450°C was constant at 11.0 mg per gram of oxide. Since the surface area of zirconium oxide calcined at 110°C (196 m²/g) was approximately the same as that of zirconium oxide that had been equilibrated with acid at 25°C (201 m²/g), the final surface areas of the oxides used in sorption experiments at 150° to 450°C were probably also approximately the same as their initial surface areas shown in Table 1. It is then apparent that the sorption of uranium at 25°C is due, at least in part, to some mechanism that is independent of the surface area of the oxide because the uranium sorption is constant even when the surface area decreases. One possibility is that uranium is sorbed by ion exchange with calcium and magnesium in the zirconium oxide. The amount of uranium sorbed from the solution at 25°C was

Table 3. Sorption of Uranium from Uranyl Sulfate Solutions on Zirconium Oxide Pretreated in Various Ways

Zirconium Oxide Pretreatment	Uranium Sorbed, mg/g		Equilibrium pH[a]		Excess Sulfate, meq/ml[b]		Ca + Mg, meq/ml	
	25°C	250°C	25°C	250°C	25°C	250°C	25°C	250°C
110°C calcined	50.3	101	2.85	1.50	0.0055	0.0151	0.0050	0.0109
150°C "	11.0	81.3	2.00	1.50	0.0137	0.0955	0.0036	0.0150
200°C "	11.0	84.3	1.85	1.52	0.0055	0.0188	0.0031	0.0132
250°C "	11.0	----	1.69	----	0.0099	------	0.0036	------
300°C "	11.0	67.2	1.58	1.44	0.0039	0.0310	0.0032	0.0145
450°C "	11.0	15.3	1.43	1.39	0.0033	0.0219	0.0033	0.0092
1000°C "	----	3.8	----	1.83	------	0.0216	------	0.0119
250°C water-treated	----	1.3	----	1.29	------	0.0210	------	0.0084
250°C acid-treated	4.3	9.1	1.42	1.30	0.0173	0.0202	------	0.0072

(a) Initial pH, 1.40.
(b) $[SO_4^=] - ([U^{?+}] + [H^+])$ = excess sulfate,

about 0.0025 meq/ml, whereas the concentration of calcium plus magnesium in the solutions after equilibration was approximately 0.003 meq/ml.

In all the experimental work at 25°C, the sorption of sulfuric acid was measured. Loss of sulfuric acid from the solution decreased as the temperature at which the zirconium oxide was calcined increased (decreasing surface area). Sulfate ion concentration in the equilibrium solution was only slightly in

excess of that required to ionically balance the uranyl and hydrogen ions found to be present. The excess could be accounted for as calcium sulfate and magnesium sulfate.

At 250°C sorption of uranium was greater than at 25°C and decreased as the temperature at which the oxide had been calcined increased. In general, the uranium sorption followed the same trend as the surface area. Little sorption of hydrogen ion was observed at 250°C, and at this temperature the total sulfate concentration in the solution generally either did not change or increased slightly. Solutions equilibrated at 250°C with oxides that had been pretreated with water or sulfuric acid at 250°C showed an increase in both hydrogen ion and sulfate concentrations. The concentration of excess sulfate in the equilibrated solutions was greater at 250° than at 25°C. Concentrations of calcium and magnesium in the equilibrium solutions were also greater at 250° than at 25°C but did not account for all the excess sulfate, thus indicating that cations other than calcium and magnesium may also be present in the solutions. However, the concentration of excess sulfate is a relatively small value that is calculated from the difference between two large numbers and therefore may be in error.

Sorption Isotherms of Uranium and Copper on Hydrous Zirconium Oxide

In Fig. 2 isotherms are shown for the sorption of uranium on hydrous zirconium oxide from 0.02 $\underline{M}$ sulfuric acid solutions at 25°, 100°, and 250°C, and from 0.04 $\underline{M}$ sulfuric acid solutions at 25°C. The sorption data at 250° are taken from reference 9. In addition, the isotherm for the sorption of

copper on hydrous zirconium oxide from 0.02 $\underline{M}$ sulfuric acid solutions is presented. The data are tabulated in Apx. II. Final surface areas of the oxides treated with acid at 25°, 100°, and 250°C are 201, 239, and 70 m²/g, respectively. These areas were used to calculate the sorption data for uranium that are plotted in Fig. 2.

The sorption of uranium per unit surface area increases with temperature, and the shape of the isotherm also changes. At 25° and 100°C, a maximum sorption is reached, as would be expected from adsorption theory for the formation of a monolayer. However, the 250°C isotherm does not level off in the range of uranium concentration studied, possibly because of the formation of several sorbed layers at elevated temperature. Similar isotherms were obtained[7] in studies of a different zirconium oxide. If the sorption process is considered to be similar to the process of crystallization of uranyl sulfate from solution, a positive entropy of sorption is indicated since $\Delta S°$ of crystallization of uranyl sulfate is about +26 entropy units. The heat of sorption is estimated to be about +2.5 kcal/mole, and increasing sorption with increasing temperature would be expected since the entropy of sorption is probably also positive.

Sorption of copper at 25°C is much greater than sorption of uranium under the same conditions on the basis of the number of milliequivalents sorbed. Nickel, however, is not sorbed at 25°C from 0.02 $\underline{M}$ sulfuric acid solutions that contain nickel in concentrations as high as 30 mg/ml.
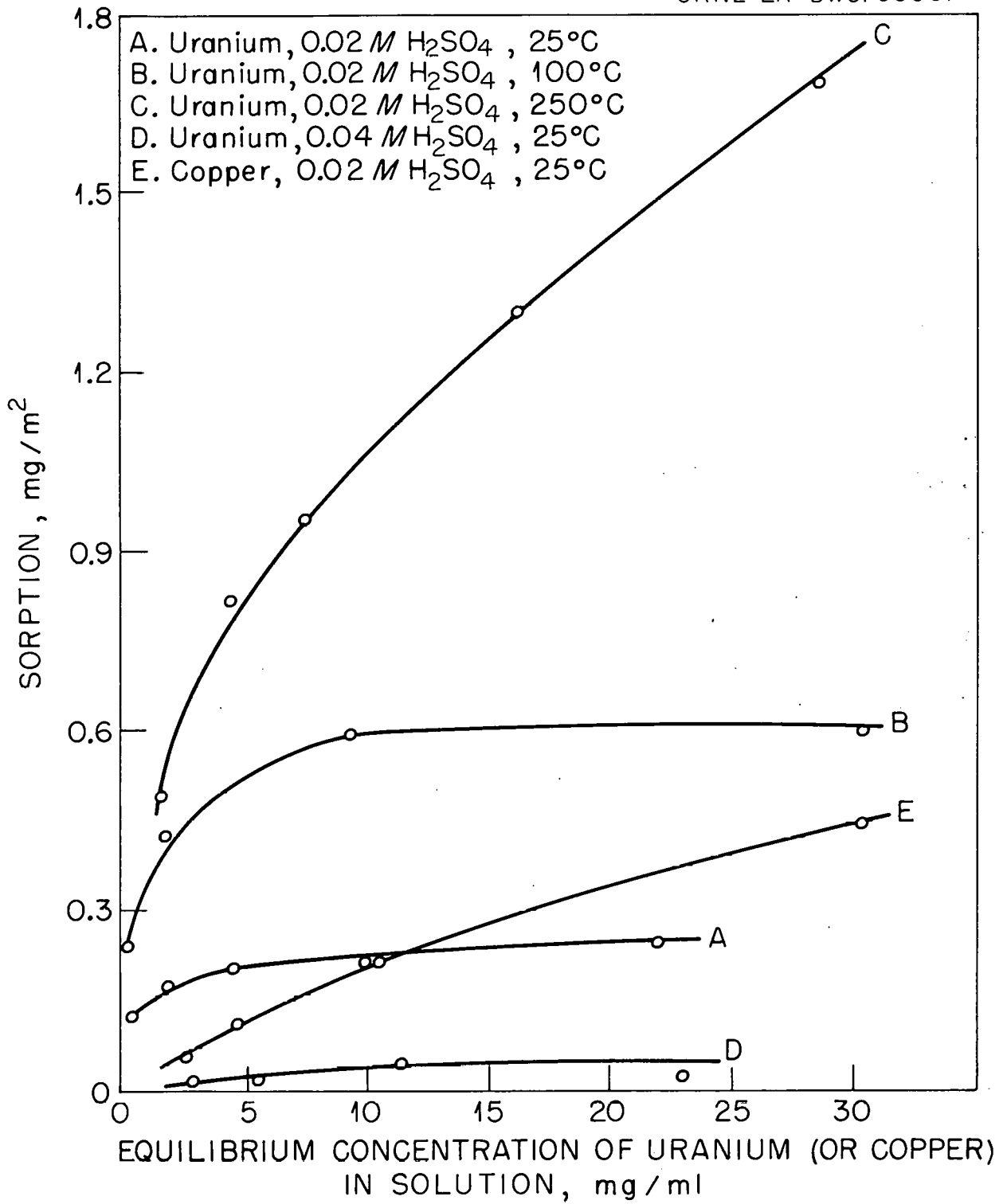
Fig. 2. Sorption isotherms for uranium and copper on hydrous zirconium oxide.

From the initial and equilibrium pH values of the solutions, sorption

of hydrogen ion can be determined. It can be shown[11] that when the mechanisms

of sorption of two substances, in this case uranium and hydrogen ion, are

the same, the relationship of the equilibrium concentrations of the ions is

defined by the equation

$$D = \frac{[U]_s}{[U]_a} = \left(\frac{[H^+]_s^2}{[H^+]_a^2}\right)\left(\frac{(\gamma_{H^+})_s^2 \, (\gamma_U)_a}{(\gamma_{H^+})_a^2 \, (\gamma_U)_s}\right) \tag{1}$$

where the subscripts s and a refer to the solid and aqueous phases, respec-

tively, and γ refers to the activity coefficient. Therefore, if the activity

coefficients do not change over the concentration range studied and if the

concentration of hydrogen ion sorbed on the solid is constant, then

$$\log D = \log K + 2 \, pH \tag{2}$$

At 25° and 100°C hydrogen ion is almost quantitatively sorbed from the

solution on the zirconium oxide and consequently the concentration of

hydrogen ion in the solid is essentially constant. A plot of $\frac{U \text{ sorbed, mg/m}^2}{U \text{ in solution, mg/ml}}$

vs pH is shown in Fig. 3. The slope is 2.2 at 25°C and 1.9 at 100°C; the

theoretical value of the slope is 2. For a given amount of uranium sorbed,

slightly more hydrogen ion is sorbed at 100° than at 25°C, probably because

of the different heats of sorption of uranium and hydrogen ion.

GENERAL DISCUSSION

From the experimental data, the following conclusions may be drawn about

the nature of the zirconium oxide sorbant. "Zirconium hydroxide" consists

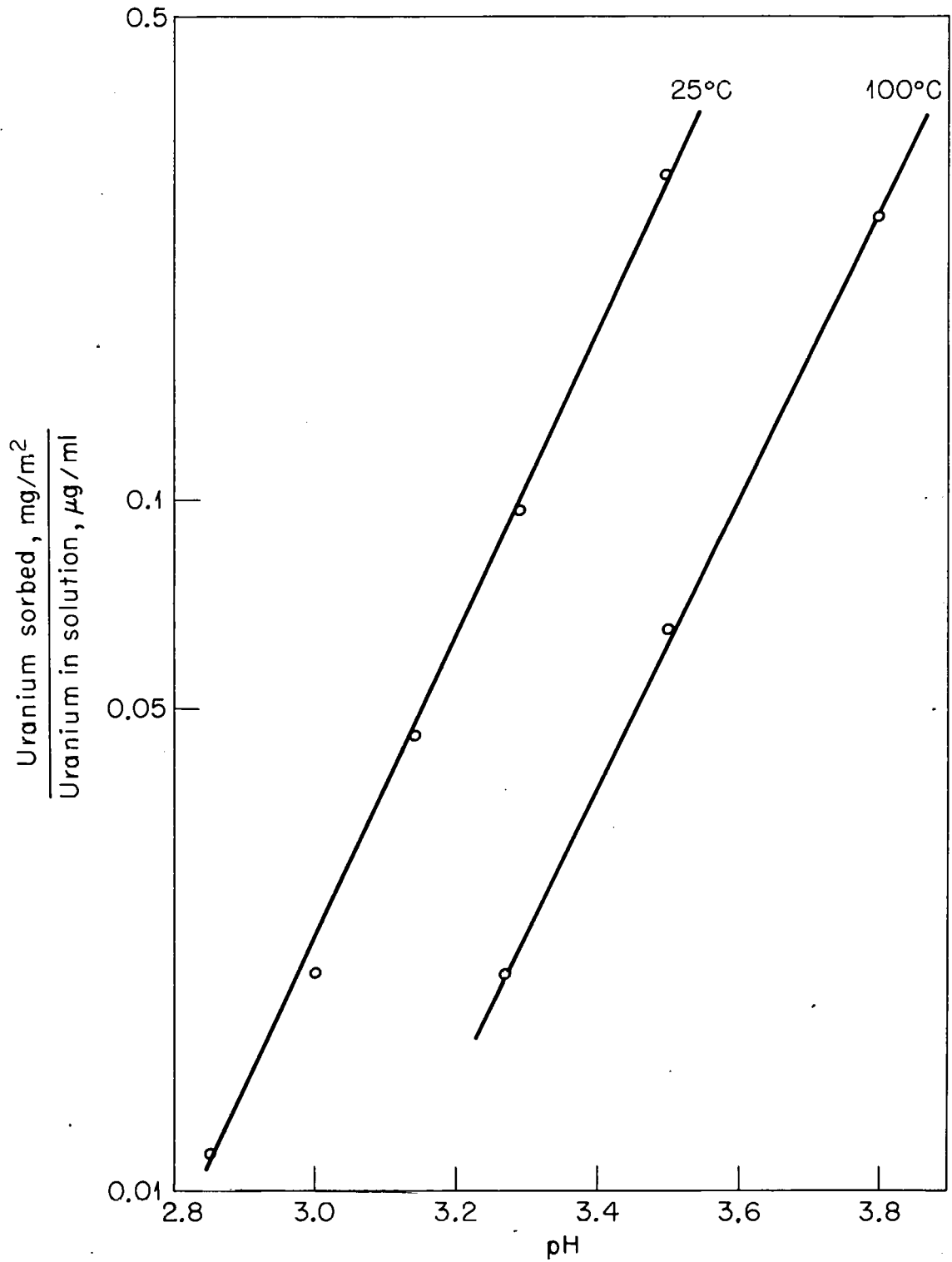of a zirconium oxide lattice with water sorbed on the surface of the particles.

Fig. 3. Sorption of uranium on hydrous zirconium oxide as a function of pH.

The mole ratio of H_2O to ZrO_2 is about 2 when the solid is dried at $100^{\circ}C$. Heating the hydrated oxide in air evaporates the sorbed water and, at the same time, induces adhesion between the crystallites; therefore the surface area of the solid decreases. The last trace of water is retained on the surface of the solid as a monolayer. In order to remove the monolayer completely, it is necessary to heat the oxide to about $800^{\circ}C$. When the hydrated oxide is heated at $250^{\circ}C$ in water or in sulfuric acid, the water content and surface area of the oxide are reduced. The decrease in area is due partly to sintering and partly to recrystallization on the surface of the oxide. When the oxide that had been calcined in air at $100^{\circ}C$ was treated with acid or water at 25° or $100^{\circ}C$, an increase in the surface area was observed which was attributed to the leaching of impurities from the oxide. Structurally, the ZrO_2 crystallites are very small when the oxide is heat treated at temperatures up to $100^{\circ}C$ and are probably in the monoclinic form. When the oxide is heat treated at elevated temperatures, the crystallite size increases, and the cubic modification of the ZrO_2 lattice becomes evident. Impurities in the oxide can affect its properties by accelerating the sintering process and by stabilizing the cubic crystal structure. In addition, impurities on the surface of the oxide may leach out of the solid and either change the composition of the equilibrium solution or enter into an ion-exchange process with ions in solution.

The relationship between uranium sorption and the characteristics of zirconium oxide is not clear. Sorption experiments at $250^{\circ}C$ on oxides that

had been pretreated in various ways show a fair correlation between sorption and surface area; however, at 25°C uranium sorption apparently does not depend on surface area. Likewise, the concentration of the impurities leached from the oxide by the solution does not show any consistent relationship to the amount of uranium sorbed. It is possible that the sorption of uranium depends on more than one process and that at different temperatures different properties of the oxide are important. For example, a chemisorption process having a positive heat of sorption would not occur to any great extent at room temperature but would account for an increase in sorption at elevated temperature. On the other hand, an ion-exchange process would be essentially unaffected by temperature.

Although it is well known that the concentrations of the species in acid aqueous solutions of uranyl sulfate are a function of temperature, no attempt has been made to correlate uranium sorption with the concentrations of the various species. At elevated temperature, undissociated uranyl sulfate and the $[UO_2(SO_4)_2]^=$ ion are the dominant species, whereas the uranyl ion concentration is negligible.[5] However, in the experiments at 250°C (Table 3), the ratio of sorbed uranium to sorbed sulfate varied with the pretreatment given to the oxide, probably because of the sulfate impurity in the oxide. Consequently, it is not possible to deduce from these experiments which uranium species are sorbed. At 25° and 100°C an equilibrium exists between the sorption of uranium and the sorption of hydrogen ions from acid solutions of uranyl sulfate. At 250°C hydrogen ion is not sorbed to any

extent. If the validity of equation 1 (page 14) is assumed, uranium sorption can, in principle, be related to the sorption of any other species.

In his studies of the ion-exchange properties of columns of hydrous zirconium oxide, Kraus[10] proposed that in an acid solution the oxide coordinated hydrogen ions at the surface, giving the surface a positive charge. Anions that were present in the solution would then tend to become incorporated into the solid; it therefore appears that, in an acid solution, zirconium oxide is an anion exchanger. When a basic solution was equilibrated with the oxide, hydroxyl ions were coordinated on the surface, and the oxide became a cation exchanger. However, it was pointed out by Amphlett[1] that some ions, such as ferric, uranyl, and cupric, tend to be sorbed on the oxide even from acid solutions. Amphlett proposes that the zirconium oxide surface consists of -Zr-OH groups and the sorption reaction is

$$n \, (-Zr-OH) + M^{n+} \rightarrow (-Zr-O)_n M^{n+} + n \, H^+$$
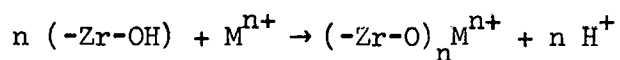
so that sorption of cations depends on the ionization of -Zr-OH to $(-Zr-O)^- + H^+$ and on the affinity of the $(-Zr-O)^-$ group for the metal ion. It is clear from the data shown by Amphlett and from the data for uranium, copper, and nickel sorption presented in this work that the sorption of cations from solution cannot be explained by a simple electrostatic attraction between a charged surface and an oppositely charged ion. It is equally uncertain that such species as $(-Zr-O)^-$ can exist in contact with an acid solution and why the affinity of cupric ion for this group should be greater

than that of uranyl or nickelous ions. Moreover, in batch-type experiments with uranium, it is not even certain that the uranyl ion is the species that is sorbed. Further work on the sorption of uranium and other cations will be required to determine the mechanism of sorption.

REFERENCES

1. C. B. Amphlett and J. Kennedy, "The Absorption of Polyvalent Cations on Ion Exchangers Through Ion-Pair or Complex Formation," Chem. and Ind. (London), 1200 (1958).

2. W. B. Blumenthal, The Chemical Behavior of Zirconium, p 161, Van Nostrand, Princeton, New Jersey, 1958.

3. J. F. Danielli, K. G. A. Pankhurst, and A. C. Riddiford, Ed., Surface Phenomena in Chemistry and Biology, p 209, Pergamon Press, New York, 1958.

4. J. F. Goodman and S. J. Gregg, "The Preparation of Active Solids by Thermal Decomposition. Part IX.* The Calcination of Hydrous Ferric Oxide and of Lepidocrocite," J. Chem. Soc., 3612 (1956).

5. R. S. Greeley, Comment on Calculations by Lietzke and Stoughton on Concentrations of Species in Aqueous UO_2SO_4 Solutions as a Function of Temperature, ORNL CF-60-3-139 (Mar. 31, 1960).

6. S. J. Gregg, "The Production of Active Solids by Thermal Decomposition. Part I. Introduction," J. Chem. Soc., 3940 (1953).

7. G. H. Jenks et al., Homogeneous Reactor Project Quarterly Progress Report, October 31, 1958, ORNL-2654, p 179 (Feb. 9, 1959).

8. G. H. Jenks et al., Homogeneous Reactor Project Quarterly Progress Report, April 30, 1959, ORNL-2743, pp 158, 163 (July 30, 1959).

9. G. H. Jenks et al., Homogeneous Reactor Project Quarterly Progress Report, January 31, 1960, ORNL-2920, p 78 (Apr. 25, 1960).

10.   K. H. Kraus, H. O. Phillips, T. A. Carlson, and J. S. Johnson, "Ion Exchange Properties of Hydrous Oxides," Second United Nation Conf. on the Peaceful Uses of Atomic Energy, June, 1958, Paper 1832 (USA).

11.   J. H. Yoe and H. J. Koch, Jr., Trace Analysis, p 65, Wiley, New York, 1957.

APPENDIX I

Sorption of Uranium on Zirconium Oxide after Various Pretreatments

Initial Composition of Solution:

[U], 23.5 mg/ml

$[SO_4^{2-}]$, 11.4 mg/ml

$[Ca^{2+}]$, absent

$[Mg^{2+}]$, absent

pH, 1.40

Zirconium Oxide Pretreatment	Equilibrium Concentrations				
	Uranium, mg/ml	Sulfate, mg/ml	pH	Calcium, mg/ml	Magnesium, mg/ml
At 25°C					
110°C calcined	22.0	9.15	2.85	0.050	0.030
150°C "	23.2	10.5	2.00	0.012	0.036
200°C "	23.2	10.3	1.85	0.008	0.033
250°C "	23.2	10.8	1.69	0.008	0.039
300°C "	23.2	10.8	1.58	0.005	0.036
450°C "	23.2	11.3	1.43	0.007	0.036
At 250°C					
110°C calcined	16.9	9.1	1.50	0.060	0.096
150°C "	15.4	12.3	1.50	0.042	0.157
200°C "	15.1	11.8	1.52	0.047	0.133
300°C "	16.8	10.0	1.44	0.058	0.141
450°C "	22.0	11.9	1.39	0.066	0.072
1000°C "	23.1	11.1	1.83	0.040	0.120
250°C water-treated	23.4	12.9	1.29	0.055	0.069
250°C 0.02 M H_2SO_4-treated	22.6	12.5	1.30	0.080	0.039

APPENDIX II

Sorption of Uranium, Copper, and Nickel from Sulfuric Acid Solutions on Hydrous Zirconium Oxide[a]

Temperature, °C	pH Initial	pH Equil.	Uranium Initial	Uranium Equil.	Sulfate Initial	Sulfate Equil.
25	1.40	4.4	-----	----	1.90	1.09
		3.50	1.17	0.42	2.46	1.48
		3.29	2.88	1.82	3.23	1.32
		3.14	5.70	4.47	4.44	2.52
		3.00	11.90	10.57	6.80	4.52
		2.85	23.53	22.02	11.35	9.15
25	1.09	1.80	-----	----	3.89	1.29
			1.15	1.11	4.35	1.80
			2.82	2.76	5.03	2.39
			5.59	5.49	6.15	4.10
			11.67	11.40	8.60	5.90
			23.07	22.90	13.2	10.6
100	1.40	----	-----	----	1.90	0.46
		5.86	1.17	0.005	2.46	0.35
		6.06	2.88	0.005	3.23	0.52
		4.86	5.70	0.012	4.44	0.63
		3.80	11.90	1.67	6.80	1.26
		3.50	23.53	9.22	11.35	4.57
		3.27	45.00	30.3	20.15	11.9

Temperature, °C	pH Initial	pH Equil.	Copper Initial	Copper Equil.	Sulfate Initial	Sulfate Equil.
25	1.50	3.47	2.90	2.55	6.0	3.90
	1.51	3.38	5.30	4.64	9.8	7.60
	1.55	3.30	11.30	10.0	17.3	15.1
	1.55	3.23	22.50	19.8	32.6	30.2
	1.59	3.17	33.0	30.3	47.5	44.4

Temperature, °C	pH Initial	pH Equil.	Nickel Initial	Nickel Equil.	Sulfate Initial	Sulfate Equil.
25	1.50	4.68	2.45	2.46	6.0	4.40
	1.60	4.59	5.00	4.80	10.5	8.50
	1.65	4.52	9.60	9.60	18.4	16.6
	1.70	4.31	19.5	19.5	33.3	33.2
	1.73	4.48	29.7	29.7	52.0	51.0

[a] Extent of sorption is indicated by the decrease in the concentration of the substance in solution.

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