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AQUEOUS URANIUM SLURRY STUDIES

J. O. Blomeke

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CHEMICAL TECHNOLOGY DIVISION

Chemical Development Section

AQUEOUS URANIUM SLURRY STUDIES

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1.0 ABSTRACT

A summary of the laboratory development program on aqueous uranium slurry fuels for the Homogeneous Reactor Project during the period April 1951 through March 1953 is presented. These investigations were devoted primarily to a study of the uranium oxides in aqueous suspensions. It was concluded that U(VI) was most likely to be the stable valence state in such slurry fuels and it was shown that β-$UO_3 \cdot H_2O$ platelet crystals were the stable modification at 250°C. Very pure slurries of β-$UO_3 \cdot H_2O$ platelets, uranium concentration of 250 g/liter and average particle size of about 10 μ, had favorable settling rates and could be easily redispersed. Their viscosity and corrosion rate in stainless steel were comparable with those in water. Exposure of these slurries to pile radiation disclosed that radiolytic hydrogen and oxygen gas pressures comparable in magnitude to those of uncatalyzed uranyl sulfate solutions could be expected. Fission products in the irradiated slurries were predominantly associated with the solids. Radiation also tended to promote caking of these solids on the walls of the radiation bombs.

Uranyl phosphate and the magnesium uranates were briefly investigated as alternate systems but were not found satisfactory.

The program was discontinued before the feasibility of uranium slurries for reactor fuels could be definitely established.

2.0 INTRODUCTION

The objective of the slurry development program at Oak Ridge National Laboratory has been the preparation of an aqueous uranium slurry suitable for use as a fuel in a plutonium-producing power reactor. From the standpoint of the Homogeneous Reactor Project, of which this program was a part, an ideal slurry is one containing 200-300 g of uranium per liter, present in combination with elements of low thermal-neutron cross section. The ideal slurry would be chemically inert at 250-300°C and stable in the presence of thermal neutron fluxes of 10^{14}-10^{15} n/sq cm/sec. Its physical characteristics would enable it to be economically transported within the reactor and component systems, and it would serve as an efficient heat-transfer medium. Finally, it could be easily and inexpensively prepared and be readily processed by a simple chemical scheme. Since the improbability of producing a fuel with uniformly favorable properties was acknowledged, the practical objective was to find a slurry possessing the above features to as great a degree as possible.

It was realized in the earliest days of the Manhattan Project that the choice of the most suitable uranium compound for this purpose was restricted to very few possibilities. The problems and considerations related to the development of a fuel with favorable nuclear properties and meeting the rigorous requirements of chemical stability, radiation stability, and engineering design are discussed in detail by Kirshenbaum, Murphy, and Urey.[1] The Manhattan Project group concluded that the oxides of uranium offered the best possibilities for satisfactory slurries, and their effort was devoted largely to studying the chemistry of these compounds and their physical behavior when in aqueous suspensions. Even though that program was discontinued before the feasibility of uranium oxide slurries could be established, a sizable backlog of information was acquired which has been of great value in the present work.

While advances in reactor technology since 1944 have made possible more definite concepts of homogeneous reactor design, it was found that most of the original considerations were still applicable to the development of a slurry fuel and could be applied in the present slurry program. It was concluded that the uranium oxides were still the most promising compounds for use as reactor slurry fuels, and studies were initiated with a view to establishing which of the oxides—UO_2, U_3O_8, or UO_3—was the most likely to be stable under the contemplated conditions of reactor operation. After it was determined that U(VI) was the valence state most likely to be stable, emphasis was placed on a study of $UO_3 \cdot H_2O$ preparation and crystal structure. Slurries of $UO_3 \cdot H_2O$ prepared by different procedures were inspected for physical stability after heating at 250°C, particular attention being paid to settling rates, crystal growth, caking, and dispersibility. Finally, corrosion and radiation tests were made with the more promising slurries at 250°C.

With the exception of the final section, this report is devoted to a summary of the experimental chemical work on the above subjects. The final section of the report is a discussion of the limited work done on compounds other than UO_3. None of these alternatives appeared to be competitive with UO_3.

The chemical development of uranium slurries was interrupted before their feasibility for the purpose intended could be clearly demonstrated. This report covers the work done from April 1951 through March 1953. Many of the data have been reported in the Homogeneous Reactor Project quarterly reports.

The writer wishes to express his appreciation to R. D. Ellison of the Chemistry Division, Oak Ridge National Laboratory, not only for performing the X-ray diffraction analyses, but also for his interest and many valuable suggestions pertaining to this part of the problem.

3.0 DETERMINATION OF STABLE VALENCE STATE OF URANIUM

The hydrogen and oxygen formed by radiation-induced decomposition of water, unless recombined promptly, might react with the uranium oxide in an aqueous slurry. In out-of-pile experiments, uranium trioxide was found to be the stable equilibrium form when aqueous uranium oxide slurries were heated under hydrogen-oxygen atmospheres at elevated temperatures. These observations confirmed early Manhattan Project work (reference 1, pp. 105-112). While it was recognized that reactor radiation could conceivably induce other chemical reactions and affect the physical characteristics of the slurry as well, conditions causing such effects are too complex for effective simulation outside an actual reactor. Since facilities for observation of radiation effects were not available at the beginning of this program, it was deemed advisable to check some of the older data under selected conditions of interest in the present program.

For the experiments slurries of UO_2, U_3O_8, and $UO_3 \cdot H_2O$ were put directly into stainless steel rocking-bomb autoclaves, the systems were evacuated, and hydrogen and/or oxygen gas was added to the desired pressures as measured at room temperature by a standard Bourdon gage. The autoclaves, manufactured by the American Instrument Company, had a bomb volume of 250 ml and were rocked at temperatures between 150 and 250°C, 30 degrees through the horizontal, 37 cycles/min, for varying lengths of time. The time was recorded while the autoclave was at its regulated temperature, about 90 min being required for it to reach 250°C and about 75 min for it to cool from that to 150°C, after which the bomb was generally cooled by immersion in cold water. Upon removal from the autoclave, the slurry was filtered and the solids were dried at 60°C and analyzed for U(IV) by adding ceric sulfate and back-titrating with standard ferrous sulfate solution.

<u>Uranium Dioxide</u>. Uranium dioxide was oxidized to uranium trioxide in the presence of oxygen gas, and even in the presence of excess hydrogen

gas. The extent of this oxidation depended on the oxygen pressure, and seemed to be independent of the partial pressure of hydrogen. For example, a uranium dioxide slurry under an oxygen pressure of 202 psi was 75% oxidized in 16 hr at 250°C, but, with an oxygen pressure of 378 psi, the slurry was 82% oxidized in the same time. A uranium dioxide slurry under a hydrogen pressure of 63.5 psi and an oxygen pressure of 175 psi was 91% oxidized in 16 hr (see Table 3-1).

Table 3-1

Oxidation of Uranium in Uranium Dioxide Slurries Heated under Various Partial Pressures of Hydrogen and Oxygen

Gas Pressure (psi)[a]		Heating Conditions		Uranium Oxidized (%)
Hydrogen	Oxygen	Temperature (°C)	Time (hr)	
63.5	31.8	200	48	64.9
---	202	250	16	74.5
---	378	250	16	82.2
70	61.5	250	24	78.4
70	175	250	24	91.4

(a) Measured at room temperature and corrected to the recorded temperature of the experiment.

Uranosic Oxide. The extent of oxidation of U_3O_8 to uranium trioxide depended on both temperature and oxygen pressure. The presence of a partial pressure of hydrogen did not seem to markedly inhibit the oxidation. Thus, after a U_3O_8 slurry had been heated under 51.8 psi hydrogen pressure and 25.9 psi oxygen pressure for 24 hr at 150°C, 63.2% of the uranium was oxidized. After being heated at a temperature of 225°C for the same length of time under 67 psi hydrogen pressure and

33.5 psi oxygen pressure, the uranium was 92.6% oxidized. Increasing the oxygen pressure from 17.5 to 175 psi at constant temperature increased the degree of oxidation of the uranium from 75.2 to 96.8% (Table 3-2).

Table 3-2

Oxidation of Uranium in Uranosic Oxide Slurries Heated under Various Partial Pressures of Hydrogen and Oxygen

Time of heating: 24 hr

Gas Pressure (psi)[a]		Temperature (°C)	Uranium Oxidized (%)
Hydrogen	Oxygen		
51.8	25.9	150	63.2
59.5	29.8	170	71.7
63.5	31.8	200	90.1
67	33.5	225	92.6
---	35	250	88.0
175	35	250	85.1
70	17.5	250	75.2
70	175	250	96.8

(a) Measured at room temperature and corrected to the recorded temperature of the experiment.

It is interesting to note that the uranium trioxide monohydrate formed by the oxidation of U_3O_8 in a slurry at 150 and 170°C was entirely in the form of orthorhombic rods, while at 250°C the product took the form of platelet crystals. At the intermediate temperatures of 200 and 225°C, the material was a mixture of rods and platelets, and at 250°C it was mostly platelets. U_3O_8 heated in water under an

atmosphere of air was about 85% oxidized in 3 weeks, and the product was in the form of orthorhombic rods. These $UO_3 \cdot H_2O$ crystals are discussed further in Sec. 5.0.

Uranium Trioxide Monohydrate. When a slurry of $UO_3 \cdot H_2O$ rods prepared by thermal decomposition of uranium peroxide in water was heated at 250°C under varying pressures of hydrogen and oxygen, it was unchanged in the presence of a stoichiometric mixture of hydrogen and oxygen in the ratio of water. It was only very slightly reduced by a tenfold excess of hydrogen over the stoichiometric (Table 3-3).

Table 3-3

Reduction of Uranium in Uranium Trioxide Slurries Heated under Various Partial Pressures of Hydrogen and Oxygen

Temperature: 250°C

Gas Pressure (psi)[a]		Heating Time (hr)	Uranium Reduced (%)
Hydrogen	Oxygen		
70	35	24	0.0
263	26.3	20	0.5
378	0	20	1.39
527	26.3	68	0.4

(a) Measured at room temperature and corrected to the recorded temperature of the experiment.

4.0 COPPER SULFATE CATALYSIS OF HYDROGEN AND OXYGEN RECOMBINATION

The presence of large amounts of hydrogen and oxygen in a reactor system as products of the radiation decomposition of water may be undesirable, not only because of the possibility of their chemical

reaction with the fuel, but also because of the higher reactor operating pressures that would result. In the Homogeneous Reactor Experiment very small quantities of copper added to the uranyl sulfate fuel solutions as copper sulfate effectively catalyzed the recombination of hydrogen and oxygen in the presence of radiation.[2] Results of preliminary out-of-pile experiments to evaluate the effectiveness of copper ion in catalyzing the combination of hydrogen and oxygen over uranium trioxide slurries indicated that copper sulfate is not a promising material for this purpose. While some catalytic effect was noted, most of the combination took place during the early stages of heating. It was postulated that with extended heating periods uranium trioxide reacted with copper sulfate according to the equation $2UO_3 + CuSO_4 \longrightarrow UO_2SO_4 + CuUO_4$, and that the copper was removed from solution under these conditions as insoluble $CuUO_4$. Combination of the gases was negligible when copper oxide was added to these slurries, which emphasized the importance of ionic copper in the catalysis that was observed.

Slurries containing 83.5 g of uranium trioxide rods in 0.05 M copper sulfate solution were heated at 250°C in a rocking autoclave under various pressures of hydrogen and oxygen. After one slurry had been heated for 2 hr under hydrogen and oxygen pressures of 350 psi each, combination was 50% complete, and after 17 hr of heating the combination was 80% complete. When a second slurry was heated at 250°C under a pressure of 175 psi of oxygen and 350 psi of hydrogen for 200 hr, the combination was 86% complete. Samples of these slurries were filtered, and a yellow filtrate was obtained which had a pH of 4.0 and in qualitative tests showed the presence of large amounts of uranyl and sulfate ions and gave negative tests for copper. The slurries appeared under the microscope to consist of a mixture of small, rather uniform reddish-brown plates and larger crystals resembling the truncated bipyramidal modification of $UO_3 \cdot H_2O$ to be discussed later (Sec. 5.0).

These crystals were badly mixed and grown together. In some slurries that were heated for shorter periods of time, large blue crystals formed. These were believed to be intermediate in the formation of the brown platelets.

In experiments carried out at room temperature and at 100°C there was no detectable reaction between uranium trioxide and copper sulfate after four days.

In experiments to determine the effect of copper oxide on combination, a mixture containing 5 g of uranium trioxide monohydrate and 0.5 g of copper oxide, intimately ground together, was heated for 24 hr at 250°C. The pressure in the reaction bomb decreased only from 1100 to 1000 psi. The filtrate from this slurry was colorless and had a pH of 6.0. The solids, apparently $UO_3 \cdot H_2O$ rods, were covered with a reddish-brown microcrystalline material.

Attempts to catalyze hydrogen and oxygen recombination over uranium solutions by substances other than copper have been attempted by the Radiation Chemistry Group of the Homogeneous Reactor Project.[2] Among those tried, ruthenium, platinum, titanium, and iron salts have shown some promise and might be found applicable to slurry fuels.

5.0 URANIUM TRIOXIDE CHEMICAL AND CRYSTAL STUDIES

Uranium trioxide in an aqueous slurry can exist as one of three hydrates, depending on the temperature at which it is maintained. In the earlier work (reference 1, pp. 45-49, 127-131) the monohydrate was shown to be the stable form at 200-300°C, the temperature range of interest in the present studies. Four crystalline modifications of the monohydrate were described: the α form, "large six-sided orthorhombic tablets"; β, "small six-sided orthorhombic tablets"; γ, "rhombic(?)

hexagonal rods"; and δ, "triclinic crystals with a very complicated X-ray pattern." The α and β were stable in water below 185°C and the γ and δ above 185°C (see Fig. 5-1). Zachariasen,[3] independently of the work in reference 1, reported two forms of $UO_3 \cdot H_2O$, but did not provide the chemical history of his samples.

In general, results of studies on preparation of uranium oxide hydrates agreed with those reported in reference 1. The most important exception was the inability to prepare a triclinic crystal resembling the δ-$UO_3 \cdot H_2O$. Attempts to prepare this modification resulted in the formation of bipyramids or platelets, depending on the conditions. The platelets appeared to be the stable form of $UO_3 \cdot H_2O$ in water at 250°C, and is the crystal most likely to be present at this temperature in a reactor fuel. Results are summarized in Table 5-1.

Although the α and β monohydrates are not stable above 185°C, they, as well as the dihydrates were of interest since they are starting or intermediate products in the preparation of the high-temperature forms.

5.1 Uranium Oxide Preparations

Uranium Peroxide. The preparation of $UO_4 \cdot xH_2O$ proved to be of special interest in this work when it was discovered that UO_3 slurries with the most desirable characteristics were best prepared by an intermediate peroxide precipitation step. The character of the $UO_4 \cdot xH_2O$ precipitate was quite sensitive to the manner in which the precipitation was performed. For example, it has been reported that $UO_4 \cdot xH_2O$ can be prepared in either of two forms, depending on its method of precipitation from $UO_2(NO_3)_2$ solution.[4] When $UO_2(NO_3)_2$ was added to excess H_2O_2 solution, microcrystalline needles were obtained, but when less than a stoichiometric amount of H_2O_2 was added to $UO_2(NO_3)_2$ solutions, the microcrystals were cubic. In similar precipitations in the present studies, with excess H_2O_2, a very viscous precipitate of $UO_4 \cdot xH_2O$ was

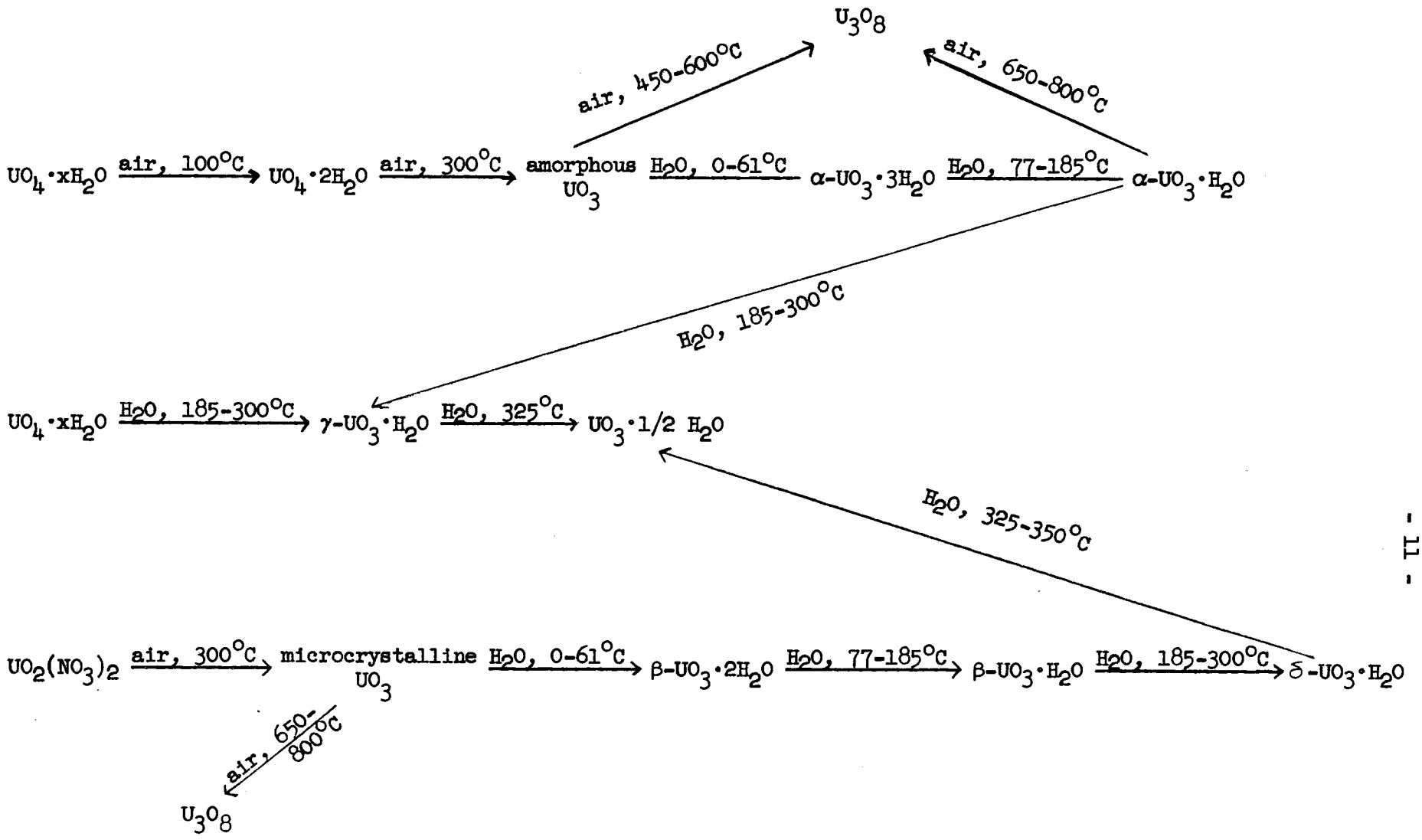

Fig. 5.1. Schematic Summary of UO_3 Stability (reference 1, pp. 45-49, 127-131).

Table 5-1. Summary of Data on Uranium Oxide Hydrates

Compound	Hydration Number,[a] n	Solubility[b] in H_2O (mg U per liter)	pH of Aqueous Slurry	Upper Limit of Thermal Stability (°C)	Crystal Data			
					Habit	Size (μ)	Structure	Color
$UO_4 \cdot nH_2O$	Unknown	0.5 (30°C) 1.4 (80°C)	---	75	Needles or cubes	< 1	---	Cream
α-$UO_3 \cdot nH_2O$	2.09	8.7 (29°C)	6.4	77	Irregular	< 1	---	Yellow
β-$UO_3 \cdot nH_2O$	2.08	9.0 (29°C)	3.6-5.8	77	Irregular	< 1	---	Yellow
α-$UO_3 \cdot nH_2O$ β-$UO_3 \cdot nH_2O$	0.81-1.06	1.5 (28°C)	6.4	185	Irregular	< 1	---	Yellow
γ-$UO_3 \cdot nH_2O$	0.83-0.90	1.4 (25°C) 1.0 (90°C)	6.3	200 (see Sec. 5.2)	Hexagonal rods	2-5 by 30	Orthorhombic	Orange-yellow
?-$UO_3 \cdot nH_2O$	1.06	2.6 (24°C) 4.5 (95°C)	6.1	325	Platelets	15-50 by 1	Orthorhombic	Cream-yellow
?-$UO_3 \cdot nH_2O$	1.03	---	4.0	325	Bipyramids	100-400	Orthorhombic	Yellow-streaked
$UO_3 \cdot nH_2O$	0.36	---	5.9	350	Imperfect rods	15-60	Monoclinic	Orange-yellow

(a) Moisture contents computed on the basis of loss in weight upon ignition to U_3O_8 at 750°C.

(b) Approximate values, determined by digesting the well-washed solids in distilled water for 2-3 days at the indicated temperature.

formed which was difficult to filter and did not settle on long standing. When $UO_2(NO_3)_2$ was present in excess, the precipitate settled rapidly and was relatively easily filtered. The primary disadvantage of the latter procedure was the large volume of low-concentration-uranium waste which resulted.

Kelchner[5] investigated $UO_4 \cdot xH_2O$ preparation from the standpoint of optimizing the most important process variables to obtain a quantitative precipitation of solids that could be easily washed and filtered. Preliminary investigations showed that the product obtained from the procedure recommended by Kelchner was satisfactory; consequently, most of the $UO_4 \cdot xH_2O$ precipitations in the present program were carried out according to that procedure.

Anhydrous UO_3. Amorphous anhydrous UO_3 was prepared by igniting uranium peroxide at 300°C for 3 hr. X-ray analysis showed it to be amorphous. When put into water, this material became hydrated readily, the process being accompanied by a very slow emission of gas, presumably oxygen.

Microcrystalline anhydrous UO_3 is prepared by calcination of uranyl nitrate. Material produced in this manner has long been made available commercially by the Mallinckrodt Chemical Company, thus providing a basis for the association of their name with any UO_3 so prepared. A quantity purchased from them for this work had picked up moisture in shipment. When dehydrated by igniting at 350°C for 4 hr, it showed a microcrystalline X-ray pattern. It became rehydrated slowly when suspended in cold water. It contained about 0.1% nitrate after exhaustive washing.

Alpha-$UO_3 \cdot 2H_2O$. Alpha-$UO_3 \cdot 2H_2O$ was prepared by shaking amorphous UO_3 with water at room temperature for 4 hr. The structure of this material was not identified, but its X-ray diffraction pattern was retained for reference.

Beta-$UO_3 \cdot 2H_2O$. Beta-$UO_3 \cdot 2H_2O$ was prepared by shaking Mallinckrodt UO_3 with water at room temperature for 24 hr. While its structure was not identified, its X-ray diffraction pattern differed from that of the α-$UO_3 \cdot 2H_2O$. It was also retained for reference purposes.

Alpha- and β-$UO_3 \cdot H_2O$. Alpha and β monohydrates were prepared by refluxing suspensions of the respective dihydrates or of the amorphous or microcrystalline anhydrous oxides, respectively, at 100°C for 24 hr. Products prepared by two different methods had the same outward appearance but gave X-ray diffraction patterns which were not always reproducible. Moisture contents varied over a range of about 20%. One explanation for this behavior was that mixtures of the two phases were being obtained.

Gamma-$UO_3 \cdot H_2O$. Gamma-$UO_3 \cdot H_2O$ was usually prepared by decomposing $UO_4 \cdot xH_2O$ in water at 250°C. It was also prepared by heating the α hydrates in water at 250°C for 8 hr or longer. The product was in the form of hexagonal rods, 2-5 μ in diameter and 10-30 μ long. The crystals were bright yellow and were of uniform size; they were shown by X-ray diffraction studies to have an orthorhombic structure corresponding to that of an α-$UO_3 \cdot H_2O$ reported by Zachariasen (see Fig. 5-2). This α-$UO_3 \cdot H_2O$ should not be confused with the α-$UO_3 \cdot H_2O$ described in reference 1 and referred to in the preceding paragraph.

Delta-$UO_3 \cdot H_2O$. Attempts to prepare the δ-$UO_3 \cdot H_2O$ described in reference 1 were unsuccessful. Triclinic crystals were never found. When β hydrates that had been exhaustively washed until the soluble uranium was less than 50 ppm in the washes were digested in water at 250°C, the product was in the form of four-sided translucent platelet crystals, about 1 μ thick and 15-50 μ along their flat edges (see Fig. 5-3). X-ray diffraction studies showed that the platelets had the same structure as a β-$UO_3 \cdot H_2O$ reported by Zachariasen, again, not to be confused with the nomenclature of reference 1. On the

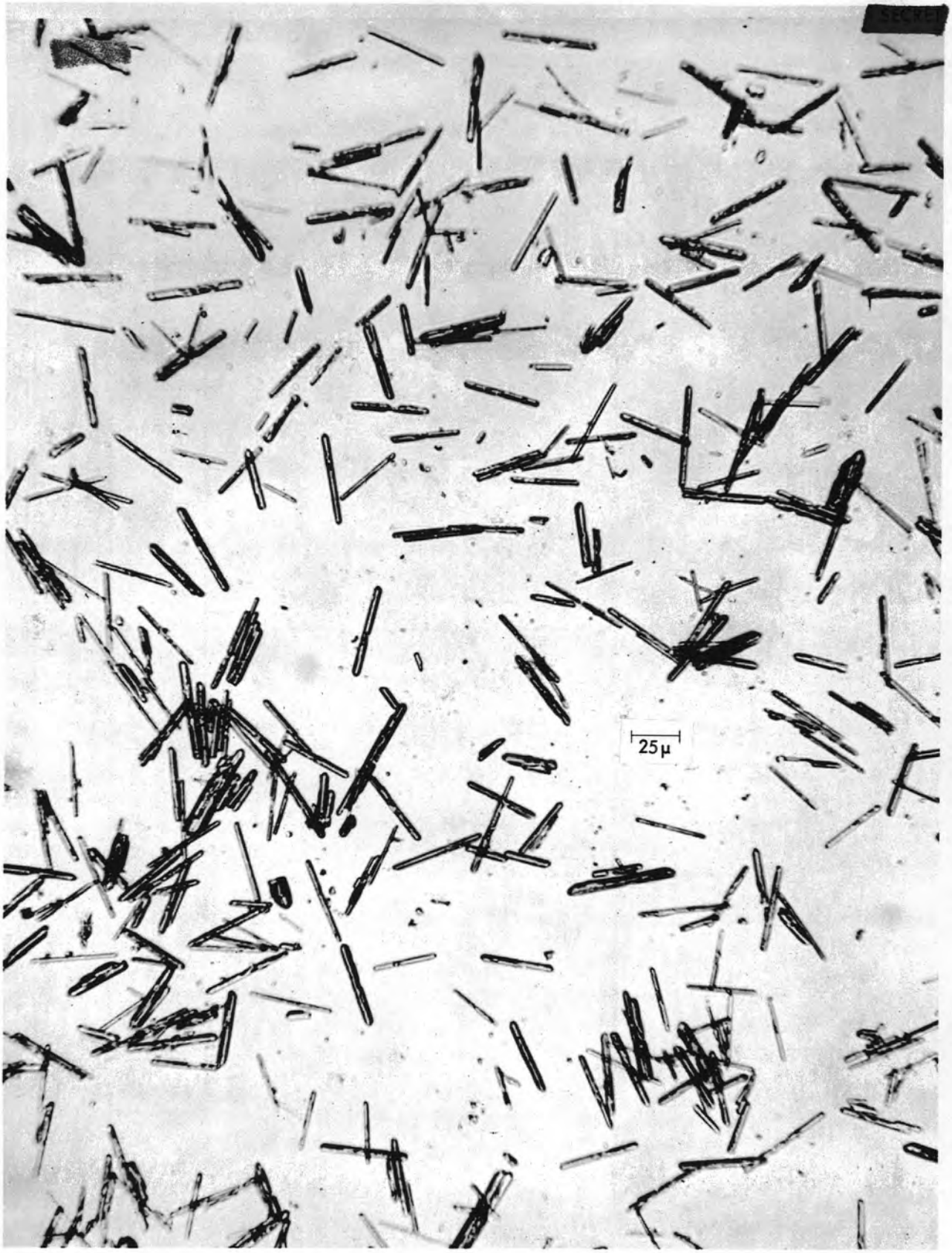

Fig. 5-2. Typical $UO_3 \cdot H_2O$ Rods, the α-$UO_3 \cdot H_2O$ of Zachariasen.[3] Prepared by decomposition of uranium peroxide in water at 250°C. 500X.

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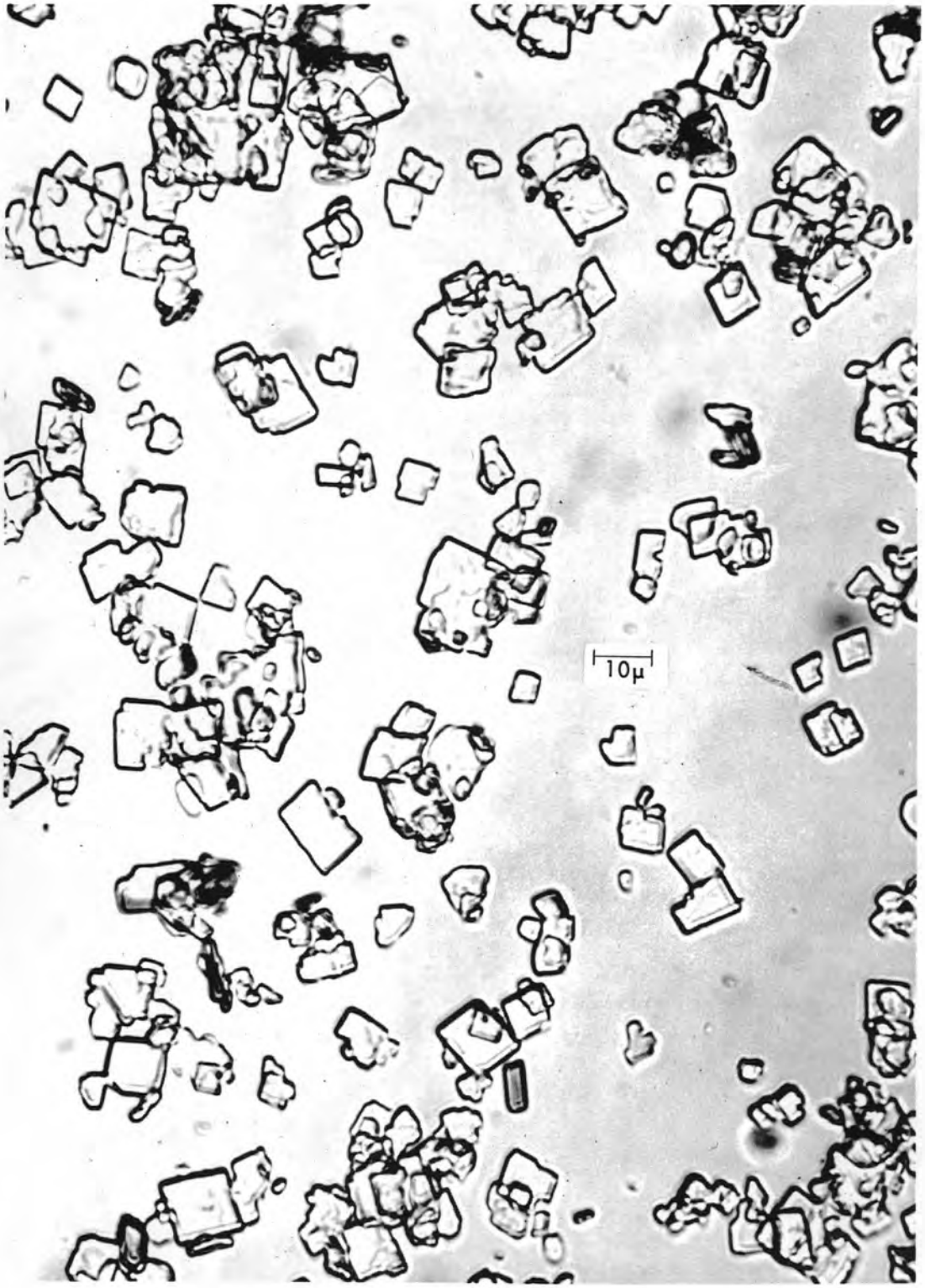

Fig. 5-3. Typical $UO_3 \cdot H_2O$ Platelets, the β-$UO_3 \cdot H_2O$ of Zachariasen.[3] Prepared by digestion of fragmented $UO_3 \cdot H_2O$ rods in water at 250°C. 1500X.

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other hand, if the β hydrates were incompletely washed free of soluble uranium, digestion at 250°C, in what amounted to dilute uranyl nitrate solution, gave a product of very large crystals resembling bipyramids, several hundred microns on edge (see Fig. 5-4). Single-crystal X-ray diffraction studies made with a precession camera indicated that the cell sizes and intensities of reflections of the bipyramid crystals were also those of the β-$UO_3 \cdot H_2O$ reported by Zachariasen. It was concluded that the platelets and the bipyramids were actually the same crystal at different stages of growth. Their structure was orthorhombic.

Uranium Trioxide Hemihydrate. This compound, $UO_3 \cdot 1/2\ H_2O$, was prepared by digesting γ-$UO_3 \cdot H_2O$ (rods) in water at 250°C for 50 hr. The product, a solid closely resembling the $UO_3 \cdot 1/2\ H_2O$ reported in reference 1, was found to have a monoclinic structure.

Uranium Trioxide Deuterates. A preliminary study of the deuterates of uranium trioxide indicated that this oxide gives identical reactions with deuterium oxide and with water, and that no significant difference exists between the deuterates and the hydrates. Anhydrous uranium trioxide was mixed with deuterium oxide to form uranium trioxide dideuterate. This slurry was filtered, transferred to a vacuum desiccator, and dried for 2 hr. The product was then ignited to U_3O_8 and the formula for the original compound was computed on the basis of weight loss as $UO_3 \cdot 1.9D_2O$. Uranium trioxide monodeuterate prepared by digestion of uranium trioxide in deuterium oxide at 100°C for 2 days had the composition $UO_3 \cdot 1.01D_2O$, corresponding to a monohydrate. Uranium trioxide monodeuterate was also prepared by heating uranium trioxide dideuterate at 250°C for 20 hr. This material had the composition $UO_3 \cdot 0.82D_2O$, which compares in moisture content to the rods in a natural water system.

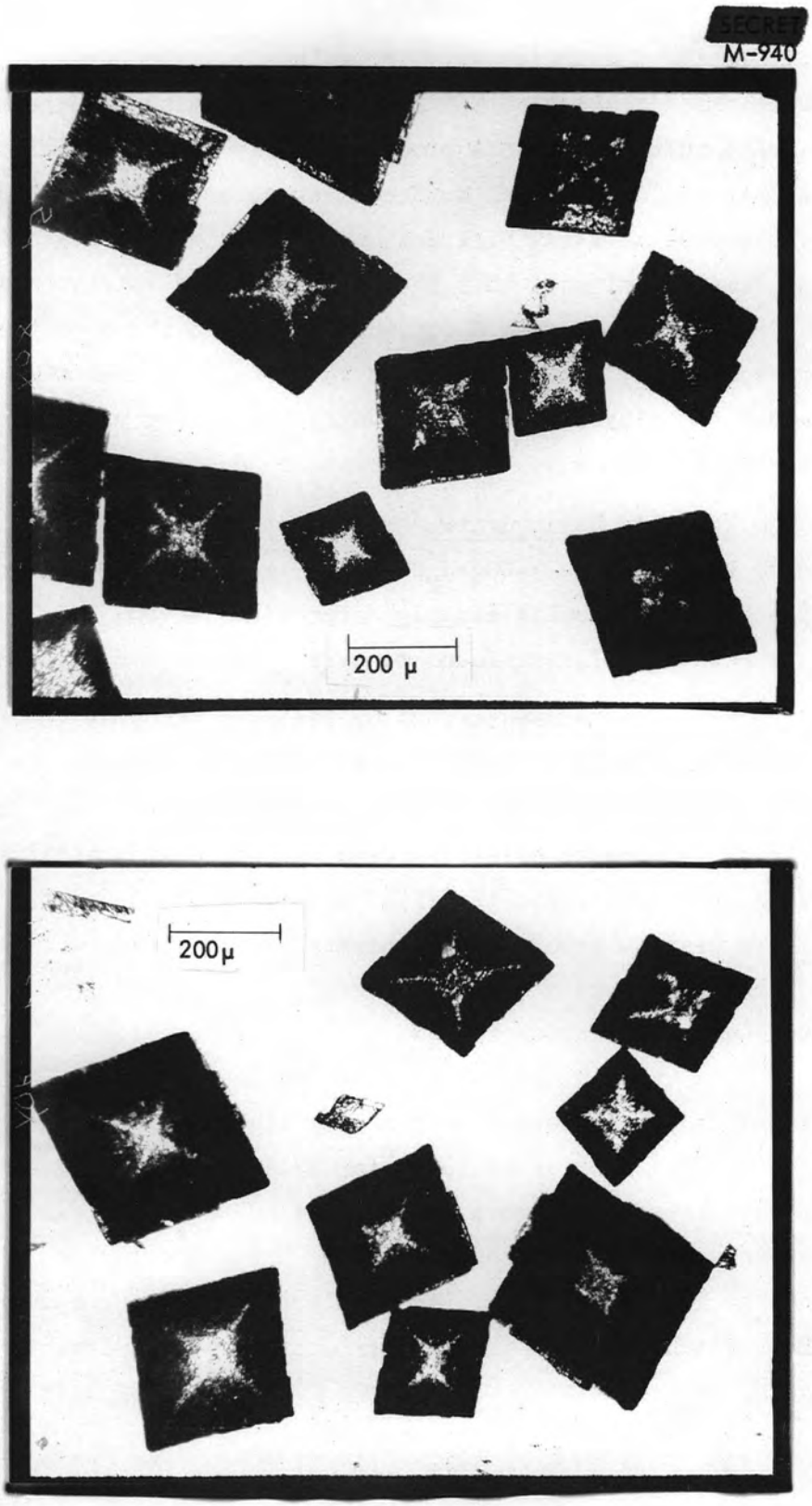

Fig. 5-4. Typical $UO_3 \cdot H_2O$ Bipyramids, the β-$UO_3 \cdot H_2O$ of Zachariasen.[3] Prepared by digestion of amorphous UO_3 in dilute uranyl nitrate solution at 250°C. 80X.

5.2 Stability of $UO_3 \cdot H_2O$ Rods and Platelets

While the above studies gave convincing evidence that UO_3 was stable in water between 220 and 300°C as the monohydrate, the question remained as to the relation between the two crystalline modifications, rods and platelets, that exist in this temperature region. It was important from the standpoint of slurry stability to establish which was more likely to be stable under the proposed conditions of reactor operation. Results of the valence state studies (see Sec. 3.1) indicated that rods were stable at temperatures below 200°C and platelets above that temperature. Pumping tests carried out in the Reactor Experimental Engineering Division of the Oak Ridge National Laboratory indicated that conversion from rods to platelets would occur after only a few hours of turbulent circulation at 250°C. And, in static radiation tests carried out at 250°C in the ORNL graphite reactor with slurries of rods, there was a marked tendency for platelets to be formed as the rods were fractured by fission recoils.

$UO_3 \cdot H_2O$ Rods. This material, presumably identical with the γ-$UO_3 \cdot H_2O$ described in reference 1, was formed by decomposition of $UO_4 \cdot xH_2O$. The crystals were normally bright yellowish-orange and of a very uniform size. They had a pronounced tendency to grow upon digestion at 250°C until they were about 5 μ in diameter and 30 μ long. At this point, attained after about 70 hr digestion, their rate of growth decreased rapidly. Their solubility in water was 1-2 ppm at room temperature (see Table 5-1), and did not greatly increase after digestion at 250°C for several hundred hours. On the other hand, if the rods were broken down by grinding or other types of attrition, such as might be expected to occur in the course of reactor operation, platelets were formed at 250°C, and the soluble uranium increased to 40-50 ppm. This figure was greatly in excess of the solubility of platelets, which was 2-5 ppm (Table 5-1). It was concluded that the

increase of soluble uranium was due to $UO_2(NO_3)_2$ that had been carried down by occlusion in the rods during preparation and released when the rods were fragmented.

The rods appeared to have some very desirable characteristics for slurry use. At a uranium concentration of 250 g per liter of aqueous slurry, they formed a very flocculent precipitate and could be easily redispersed by mild agitation after standing for as long as 30 days at room temperature.

$UO_3 \cdot H_2O$ Platelets. The platelet form of $UO_3 \cdot H_2O$ was normally obtained upon digestion at 250°C of microcrystalline UO_3 as well as from digestion of fragmented rods, as discussed above. The platelets upon digestion at 250°C grew at a rate comparable to that of the rods, eventually approaching a size of 50-60 μ along their edges and 1-3 μ in thickness. They were not so bright a yellow as the rods, and, when formed directly from microcrystalline UO_3, their slurries packed to a higher bulk density and were not so easily redispersed after settling. When they were broken down mechanically, they assumed their original form on further digestion and gave a similar increase in the soluble uranium concentration as did the rods.

Crystal Structure Studies. The importance of crystal structure studies in the development of an aqueous fuel is emphasized by the fact that a definite relation can exist between the crystal structure and other properties of the solids, such as crystal habit, density, heat capacity, and hardness. In the present case, crystal structure studies were used primarily to determine the relative stability of rods and platelets at 250°C. In the course of this work, the existence of a temperature—crystal structure relation was demonstrated.

As was discussed previously (Sec. 5.1), the rods appear to be the same material as a γ-$UO_3 \cdot H_2O$ reported in reference 1 as having an orthorhombic structure. Unfortunately, cell dimensions were not

given in this reference, and it was impossible to establish the identity without question. Zachariasen[3] reported the cell dimensions of two different $UO_3 \cdot H_2O$ crystals but gave no information concerning the chemical history of his samples. He indexed both of these structures as orthorhombic and called them α- and β-$UO_3 \cdot H_2O$, independently of the nomenclature of reference 1. From the cell dimensions given by Zachariasen, the positions of all possible lines in the X-ray diffraction patterns were calculated, thus permitting a comparison to be made with material prepared in the present studies. It was established from this that the rods gave the same X-ray diffraction pattern as Zachariasen's α-$UO_3 \cdot H_2O$ and that the platelets had the structure of his β-$UO_3 \cdot H_2O$.

The experiments performed to clarify the relation between the rods and platelets are presented schematically in Fig. 5-5. It was found, initially, that a transition from β- to α-$UO_3 \cdot H_2O$ occurred when platelets were ground in air at room temperature. While such a transition from a "frozen in" high temperature to a low-temperature form is not rare among inorganic salts, it has been known to occur much less frequently with hydrates.

The micronized platelets were then divided into four parts and heated in water for 16 hr at 150, 180, 215, and 250°C, respectively. Those samples heated at 150 and 180°C retained the α-$UO_3 \cdot H_2O$ structure, with the fragments growing in size and assuming a rodlike habit. The samples heated at 215 and 250°C were converted to platelets and had the β-$UO_3 \cdot H_2O$ structure, with the fragments growing in size and assuming a rodlike habit. The samples heated at 215 and 250°C were converted to platelets and had the β-$UO_3 \cdot H_2O$ structure after having been cooled to room temperature at the rate of about 2°C per minute. These experiments indicate that the transition temperature from α to β must lie in the neighborhood of 200°C.

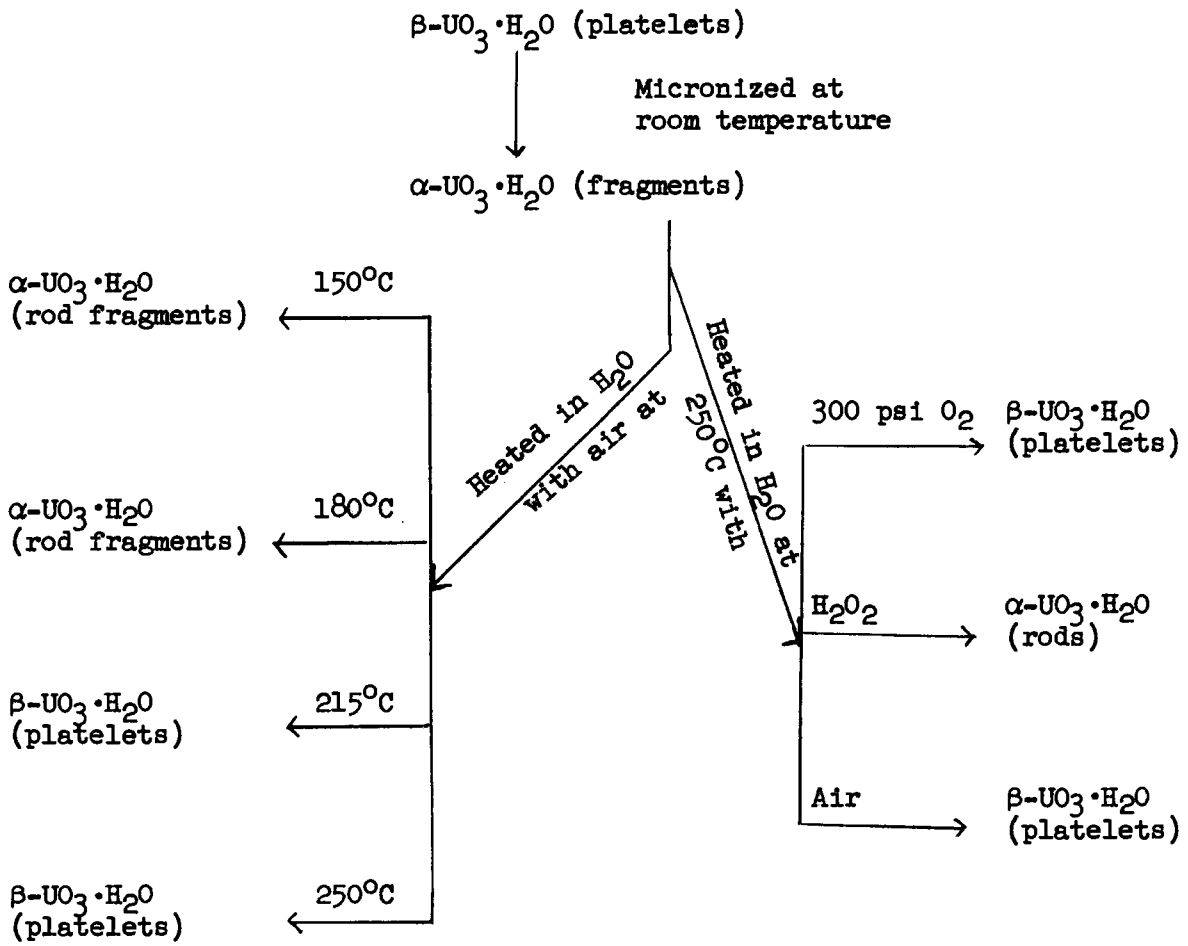

Fig. 5-5. Stability of Forms of $UO_3 \cdot H_2O$

The question of what induces the formation of rods from $UO_4 \cdot xH_2O$ at 250°C seems to be partially answered by the remaining three experiments noted in Fig. 5-5. Samples of micronized platelets were heated in water at 250°C under atmospheres of oxygen introduced in two different ways. In one case the oxygen was introduced as the gas to a pressure of 300 psi at 250°C. In the second case, 30% H_2O_2 was added in such quantity as to produce the same oxygen pressure upon decomposition at 250°C. After being heated for 15 hr, the micronized rods had been converted to platelets in the first case, but had retained their α structure and regained the rod crystal habit where the H_2O_2 solution had been added. As discussed above, when only air was present above the slurry at 250°C, the customary conversion to platelets occurred. These experiments indicate that the presence of peroxidic oxygen intimately associated with the fragmented crystals promoted the formation of α-$UO_3 \cdot H_2O$ even at temperatures above the transition point.

5.3 Slurry Stability Calculations

Very rough calculations were made with a view to estimating the temperature a solid particle of $UO_3 \cdot H_2O$ suspended as part of a slurry fuel in a homogeneous reactor would likely attain if the water of suspension was maintained at 250°C. This question has a direct bearing on the chemical form of the slurry under reactor operating conditions. It was found that under such circumstances essentially no temperature gradient existed within the particle itself and that a temperature difference of only 10.5°C would exist between the solid and an enveloping steam film at 250°C. Such a difference would fall well within the limits of $UO_3 \cdot H_2O$ stability.

The calculations assumed a reactor power level of 15 kw/liter, a uranium concentration of 250 g/liter, and spherical $UO_3 \cdot H_2O$ particles, 2 μ in diameter. The heat flux under these conditions would be 38

Btu/hr/ft^2 or 3.61 x 10^{-8} cal/sec/particle. The temperature distribution equations of Carter[6] were used. The temperature gradient across a steam film around such a particle is dependent on the thermal resistance of the film. No applicable film coefficient expressing the resistance across a UO_3-steam interface was available, but a value of h = 200 Btu/hr/ft^2/^{o}F was assumed.

6.0 PREPARATION OF PURE URANIUM TRIOXIDE MONOHYDRATE

Impurities, even in small amounts, influence the type and size of crystal formed by many compounds. In the case of uranium trioxide monohydrate, the most significant impurities are UO_2^{++} and NO_3^- ions originating in the uranyl nitrate solutions from which the oxide is prepared and liberated when the oxide crystals are fragmented. Uranyl nitrate in concentrations as low as several hundred parts per million promotes caking of the slurry, making redispersion of settled solids more difficult and increasing corrosion. The uranyl nitrate content of the product oxide may be as high as 0.01 to 0.1%.

The criteria adopted for a suitable large-scale preparation of uranium trioxide monohydrate platelet were that the starting material be either commercially available or easily prepared from commercial material, that the method of preparation be short and simple, and that the resulting product be both of a suitable particle size for use in a slurry and of such purity that its slurry properties would remain unimpaired during use as a fuel. Observations of a large number of slurry preparations indicated that a satisfactory product would be one containing uniform platelets averaging 3 μ or less on a dimension and yielding less than 10 ppm of soluble uranium on being heated in water at 250°C at a uranium concentration of 250 g/liter.

Results of preparation studies indicated that the most satisfactory method of preparing uranium trioxide monohydrate platelets is repeated

calcination and hydration of $UO_3 \cdot H_2O$ rods, formed from uranium peroxide. A satisfactory product was also obtained from ammonium uranyl carbonate, and a good product directly from uranium peroxide. Commercially available UO_3, uranyl acetate, and U_3O_8 were not suitable starting materials. Spray calcination, grinding, and leaching were not promising methods.

6.1 By Calcination and Hydration of Various Starting Materials

Under some conditions repeated hydration and dehydration of UO_3 was found to degrade the particles and liberate entrapped ions. The efficiency of this process and the quality of the product depended on the starting material as well as on the operating conditions.

Uranium Trioxide Monohydrate Rods. Breakdown of $UO_3 \cdot H_2O$ rods by the calcination-hydration procedure was difficult, but the product was excellent. When the rods were calcined at 375°C and hydrated at 250°C for two cycles, long thin platelets were formed. A total of five cycles resulted in platelets about 4 μ on an edge. The soluble uranium concentration of the product was 4 ppm.

The rods were prepared by thermally decomposing uranium peroxide in water at 250°C.

Uranium Peroxide. The uranium peroxide prepared by the procedure of Kelchner [5] was more easily processed than the rods, but the product was less pure. Calcination of the $UO_4 \cdot xH_2O$ at 350°C for 16 hr and hydration at 250°C for 16 hr yielded $UO_3 \cdot H_2O$ platelets about 10 μ on an edge and several microns thick after the first cycle. After five cycles, the platelets had an average size of about 5 μ on an edge, but the soluble uranium concentration was 23 ppm.

Mallinckrodt and Harshaw Uranium Trioxide. The most obvious method of preparing $UO_3 \cdot H_2O$ platelets by calcination and hydration

is to start with commercially available Mallinckrodt or Harshaw trioxide, both of which are prepared by thermal decomposition of uranyl nitrate and contain 1.4-1.5 wt % soluble uranium as uranyl nitrate. The Harshaw product is subjected to a size-reduction step. However, a satisfactory product was not obtained with these materials.

Exhaustive washing of the Mallinckrodt material reduced the soluble uranium to 0.3 to 0.5%. Hydration of the washed oxide at 100°C and calcination at 400°C gave a product composed of very hard lumps which were difficult to break and slow to hydrate. Autoclaving of this product at 250°C gave platelets 25-30 μ on an edge. After five cycles of calcination at 400°C and hydration at 250°C, the average particle size was about 7 μ, too large for use as a slurry and indicative of a substantial uranium content in the supernatant.

The Harshaw oxide, after being washed at 85°C and treated further by three cycles of alternate calcination at 250°C and hydration at 250°C, yielded a product consisting of large and very irregular platelets. The supernatant contained 38 ppm of soluble uranium calculated on the basis of 250 g of uranium per liter (see Table 6-1).

Table 6-1

Removal of Uranyl Nitrate Impurity from Harshaw UO_3 by Calcination and Hydration

Operation	Temperature (°C)	Time (hr)	Soluble Uranium in Supernatant[a]
Water wash	85	0.5	1.4 wt %
Hydration	250	16	540 ppm
Calcination and hydration, I	350 250	16 16	154 ppm
Calcination and hydration, II	350 250	16 16	95 ppm
Calcination and hydration, III	350 250	16 16	38 ppm

(a) Solubility values given in parts per million were calculated on the basis of a slurry containing 250 g of uranium per liter as $UO_3 \cdot H_2O$.

An attempt was made to remove the nitrate impurity from the Harshaw oxide by passing superheated steam through a bed of the material maintained at 230°C. Tests of the effluent steam indicated the presence of an acid component. When the apparatus was disassembled, a partial decomposition of the UO_3 to U_3O_8 was noted, which is an indication of overheating. Channeling had also occurred within the oxide bed. The product oxide yielded 0.2% soluble uranium on extraction with hot water. Experimental difficulties with the high-temperature autoclave prevented a study of the behavior of this material on hydration at 250°C.

Ammonium Uranyl Carbonate. It has been noted that many metallic oxides, when prepared by the thermal decomposition of the carbonate or an organic salt of the metal, are obtained as powders of low bulk density and high surface area, from which soluble materials should be more easily removed by calcination and hydration. Results of preliminary experiments indicated that pure $UO_3 \cdot H_2O$ platelets could be obtained more easily by starting with ammonium uranyl carbonate than from those materials mentioned above. When $UO_3 \cdot H_2O$ that had been prepared from $(NH_4)_4UO_2(CO_3)_3$ was calcined and hydrated through two cycles, the supernatants contained not more than 10 ppm of uranium, indicating the oxide to be of the desired purity (see Table 6-2). The average particle size was less than 10 μ.

Two methods were used to prepare the ammonium uranyl carbonate. In the first method, ammonium diuranate was precipitated from a uranyl nitrate solution and then metathesized to ammonium uranyl carbonate in a concentrated solution of ammonium carbonate. In the second method, uranyl ion was sorbed from a nitrate solution onto Dowex-50 resin. The resin was washed free of nitrate, and the uranium was eluted with ammonium carbonate. The ammonium uranyl carbonate products were decomposed to UO_3 at 350°C. The oxides were washed for 1 hr at 90 to 100°C, and then recalcined at 350°C, and hydrated to platelets at 250°C.

Table 6-2

Conversion of $2(NH_4)_2CO_3 \cdot UO_2CO_3$ to Slurry-Grade $UO_3 \cdot H_2O$

Operation	Temperature (°C)	Time (hr)	Soluble Uranium in Supernatant (ppm)[a]		
			AUC-1[b]	AUC-2[c]	AUC-3[c]
Conversion of $(NH_4)_4UO_2(CO_3)_3$ to UO_3	350	16	---	---	---
Water wash	90-100	1	100	130	100
Calcination and hydration, I	350 250	16 16	10	88	10
Calcination and hydration, II	350 250	16 16	9	10	--

(a) Calculated on the basis of a slurry containing 250 g of uranium per liter as $UO_3 \cdot H_2O$.

(b) Ammonium uranyl carbonate prepared by metathesizing ammonium diuranate with concentrated ammonium carbonate solution.

(c) Ammonium uranyl carbonate prepared by ion exchange method.

Uranyl Acetate. Uranyl acetate is a water-soluble salt with low thermal stability. Results of experiments indicated that a complete separation of acetate radical from the $UO_3 \cdot H_2O$ product would be difficult to achieve without causing some reduction of the uranium. It was concluded that uranyl acetate had no significant advantages over uranyl nitrate as starting material for the preparation of pure $UO_3 \cdot H_2O$ platelets. Direct calcination of uranyl nitrate in air at 360 and 270°C resulted in the formation of U_3O_8. Hydrolysis at 100°C in an open beaker produced $UO_3 \cdot H_2O$, which showed a tendency to reduction when heated at 250°C in water. Precipitation of $UO_4 \cdot xH_2O$ from $UO_2(C_2H_3O_2)_2$ and subsequent conversion to $UO_3 \cdot H_2O$ yielded a product identical to that obtained from $UO_4 \cdot xH_2O$ precipitated from $UO_2(NO_3)_2$. The precipitation of $UO_4 \cdot xH_2O$ from $UO_2(C_2H_3O_2)_2$ solution was somewhat simpler than the corresponding precipitation from $UO_2(NO_3)_2$ since no pH adjustment was required in the former; however the peroxide precipitate was equally difficult to process in the two cases.

U_3O_8. A potential method for preparation of UO_3 free from NO_3^- ion is the high-temperature oxidation of U_3O_8 by oxygen as described by Sheft and Fried,[7] but on the basis of laboratory-scale work it did not appear promising for large-scale preparation of pure UO_3 platelets.

As investigated in the laboratory, the preparation consisted in first precipitating ammonium diuranate and igniting this to U_3O_8 by heating at 450°C in air. The U_3O_8 was then heated at 750°C at an oxygen pressure of 850 psi. After 3 days' heating, only partial conversion of the black U_3O_8 to the yellow microcrystalline UO_3 was indicated. The oxide was returned to the autoclave and heated at 750°C and 400 psi oxygen pressure for 3 more days. X-ray analysis showed this oxide to be somewhat similar to that obtained by heating microcrystalline amorphous UO_3 at 600°C in air for 100 hr. The uranium

Table 6-3

Preparation of $UO_3 \cdot H_2O$ from $UO_2(C_2H_3O_2)_2$

Experiment and Conditions	Results
Calcination in air at 360°C for 16 hr	U_3O_8 product
Calcination in air at 270°C for 4 hr	U_3O_8 product
Hydrolysis at 100°C for 15 hr in open beaker	Yellow, irregular $UO_3 \cdot H_2O$ crystals; after being autoclaved for 16 hr at 200°C, acquired a greenish tint; analysis showed 0.034% U(IV)
Hydrolysis in autoclave at 250°C for 16 hr	Yellow bipyramidal crystals of $UO_3 \cdot H_2O$; analysis showed 0.13% U(IV)
Hydrolysis in autoclave at 250°C for 64 hr	Greenish bipyramidal crystals of $UO_3 \cdot H_2O$; analysis showed 0.16% U(IV)
Precipitation of $UO_4 \cdot xH_2O$ followed by digestion at 250°C	$UO_3 \cdot H_2O$ rods; no U(IV) detected

trioxide prepared by the oxidation of U_3O_8 still contained 0.16% NO_3^- ion by weight, and water slurries of this oxide heated at 250°C for 60 hr did not appear to be substantially different from a control prepared from Mallinckrodt oxide.

6.2 By Spray Calcination

An experimental spray calciner similar to one described by Silverman et al.[8] was constructed and operated in an attempt to produce uniform micron-sized particles of UO_3 from uranyl nitrate solutions. It was concluded that the apparatus as constructed was not adequate for the preparation of UO_3 of suitable quality for this program. Four preliminary runs were made in this calciner and conversions to UO_3 of 26, 82, 53, and 79% were obtained. No correlation was found between operating conditions and the fraction of the uranyl nitrate converted to the trioxide. A microscopic examination of the product indicated that it was neither uniform nor did it lie in the desired size range.

6.3 By Grinding and Leaching

Purification by this procedure was accomplished by a mechanism similar to the calcination-hydration technique described above. The essential difference lay in the use of a fluid energy mill to break down the $UO_3 \cdot H_2O$ crystals and liberate entrapped ions which could be leached with water. The desired purification was obtained by grinding the $UO_3 \cdot H_2O$ rods or platelets, leaching the UO_2^{++} and NO_3^-, and autoclaving the solids with water at 250°C; however, the difficulties of operating the mill and the resultant contamination of the product with iron made this procedure less attractive than the calcination-hydration technique.

6.4 By NO_2 and HNO_3 Vapor Oxidation of U_3O_8

NO_2 (gas) passed over U_3O_8 at 300 to 325°C slowly oxidizes the material to form a brick-red UO_3.[9] Similarly, HNO_3 vapor, obtained by bubbling N_2 or air through nitric acid at 70°C, yields a bright red UO_3. For slurry purposes, these compounds showed no advantage over other forms of UO_3 and the plates formed at 250°C seemed to be identical to those obtained from Mallinckrodt UO_3. Both the red forms when prepared in the laboratory hydrated more slowly in cold water than the usual UO_3 to form $UO_3 \cdot 2H_2O$. With water at 100°C, $UO_3 \cdot H_2O$ was formed, and with water at 250°C, $UO_3 \cdot H_2O$ platelets were produced. All these hydrates had a greenish tinge, indicating traces of U_3O_8 to be present.

7.0 SLURRY CHARACTERISTICS

A true chemical solution can be completely characterized by specifying the composition, concentration, and temperature. In a solid-liquid system, such as a slurry, still another property must be considered, namely, that pertaining to particle size and the solid-liquid interfacial area. Because of the extremely large interfacial area present in slurries of micron-sized particles, a relatively small variation in particle size could have considerable effect on such properties as settling rate, viscosity, dispersability, and erosion rates.

As a means of effectively characterizing slurries, studies were made of methods of particle size and surface area measurement of $UO_3 \cdot H_2O$-water systems. Limited work was done on crystal growth in and viscosity of these slurries.

7.1 Particle Size Measurements

Particle diameters and surface areas of $UO_3 \cdot H_2O$ powders in

slurries containing 100 and 250 g of uranium per liter were determined by a variety of methods. Values obtained with all methods (see Table 7-1) except the stearic acid adsorption agreed fairly well with those obtained by nitrogen adsorption, which is generally accepted as the best means of measurement. The other methods are shorter and require less elaborate equipment.

The surface area per gram, S_w, and the platelet particle diameter, D_{sv}, were related by the equation

$$S_w = 6/\rho D_{sv} \qquad (1)$$

where S_w = specific surface area, per unit weight, m^2/g

ρ = density of solids, g/cc (5.72 g/cc for $UO_3 \cdot H_2O$ platelets)

D_{sv} = particle diameter, μ

For rods the equation is $S_w = 4/\rho D_{sv}$.

Table 7-1

Particle Diameters and Surface Areas of $UO_3 \cdot H_2O$ Platelets by Various Methods

Sample	Method	Specific Surface Area, S_w (m^2/g)	Particle Diameter, D_{sv} (μ)
1	N_2 adsorption isotherm	0.45	2.4
	Stearic acid adsorption		
	Conductimetric titration	0.89	1.2
	Hydrophil balance	0.08	13.1
	n-Heptoic acid adsorption	0.41	2.6
2	N_2 adsorption isotherm	0.60	1.8
	Sedimentation rate		
	U, 100 g/liter	0.41	2.6
	U, 200-500 g/liter	---	1.5 to 2.7
	Microscopic	0.25	4.3

Surface Area by Stearic Acid Adsorption. In determining the surface area by the stearic acid adsorption technique described by Russell and Cochran,[10] changes in stearic acid concentration due to adsorption on the surfaces of the solid were determined by conductimetric titration and by a hydrophil balance. With $UO_3 \cdot H_2O$ platelets agreement was very poor between the stearic acid and nitrogen adsorption methods (see Table 7-1).

Surface Area by n-Heptoic Acid Adsorption. This method, adapted from one described by Saunders,[11] consisted in shaking a weighed sample of $UO_3 \cdot H_2O$ powder (4-5 g) with 50 ml of n-heptoic acid--isopropyl alcohol solution (0.3 mg of n-heptoic acid per milliliter of solution) for 1 hr. An aliquot of the supernatant was run into an equal volume of 0.01 M sodium hydroxide and the excess alkali was back-titrated with 0.01 M hydrochloric acid to a phenolphthalein endpoint. The change in concentration of acid due to adsorption is related to the surface area of the powder by assuming that the cross-sectional area of the n-heptoic acid molecule is 25×10^{-16} cm^2. Agreement between values obtained by this method and the nitrogen adsorption technique was good (see Table 7-1).

Surface Area by Microscopic Method. Photomicrographs of $UO_3 \cdot H_2O$ powders were made and particle diameters and surface area were measured by methods described by DallaValle.[12] The values given in Table 7-1 were calculated from Eq. 1 and the equation

$$\log D_{sv} = \log D_g + 5.757 \log 2\sigma_g \qquad (2)$$

where D_g = geometric mean particle diameter = 3.4 μ

σ_g = standard deviation of D_g = 2.7 μ

D_{sv} as defined above contains a statistical correction for a spread in particle-size distribution.

It is believed that the explanation for the larger values obtained for particle diameters by the microscopic method compared

to nitrogen adsorption (see Table 7-1) lies in a subconscious tendency to bias results in favor of the larger particles since they are easier to see.

Particle Diameters by Sedimentation Rates. Sedimentation rates in concentrated suspensions differ from those in dilute suspensions, in which Stokes' law is applicable. The values given in Table 7-1 for particles in slurries with uranium concentrations of 100 g/liter were obtained by a method adapted from one proposed by Allison and Murray[13] for use with concentrated suspensions. This method is based on an analogy between the movement of a mass of particles through a stagnant column of fluid and the flow of a fluid through a porous bed of particles. Their equations relating to the flow of fluids through porous media were applied to the settling of particles in a stagnant fluid, resulting in the relation

$$\frac{dV_s}{dt} = \frac{60gAe^3\rho_s}{5\eta S_v^2(1-e)^2} \qquad (3)$$

where dV_s/dt = change in volume of sediment with time

g = acceleration due to gravity = 980 cm/sec^2

A = area of cross-section of sediment bed, cm^2

e = porosity of sediment = V_l/V_s

V_l = volume of liquid in sediment, cc

V_s = volume of sediment, cc

ρ_s = bulk density of sediment, g/cc, at time t

η = viscosity of liquid, centipoises

S_v = specific surface area of particles, per unit volume, cm^2/cc

If dV_s/dt is plotted against $e^3\rho_s/(1-e)^2$, a straight line passing through the origin is obtained with a slope of $60gA/5\eta S_v^2$. Since S_v is the only unknown, it can be calculated. The particle diameter can then be obtained by applying Eq. 1 and the obvious relation $S_w = S_v/\rho$.

Values of D_{sv} obtained by the sedimentation method were somewhat higher than those obtained by nitrogen adsorption. This is expected since the formation of a fluid film about the particles would effectively increase the particle-size diameter.

When the uranium concentration was increased to 250 g/liter, this method could not be used. The explanation appeared to be that, at a uranium concentration of 100 g/liter, flocculation did not occur during sedimentation while at higher concentrations it did. Sedimentation rate--time curves (Fig. 7-1) show that at a uranium concentration of 100 g/liter, the settling rate decreased with time but at 250 g/liter it remained constant. This indicates that in the more concentrated slurry larger particles form at such a rate that the decrease in sedimentation rate is opposed by the more rapid settling rate. Since the method is based on the flow of fluids through a porous bed of unchanging particles, the occurrence of flocculation renders it invalid.

The values given in Table 7-1 for slurries with uranium concentrations of 200-500 g/liter were obtained from equations of Hatch and Isakoff.[14] Proceeding from the consideration that sedimentation in concentrated suspensions of solid particles is one aspect of the flow of fluids through porous media, they presented the equation

$$\frac{dH}{dt} = \frac{g(\rho - \rho_1)D_{sv}^2 e^3}{k\eta(1-e)} \qquad (4)$$

where dH/dt = rate of subsidence of solid phase boundary

ρ = density of solid, g/cc

ρ_1 = density of liquid, g/cc

k = numerical constant = 12.7 for this system

If dH/dt is determined for slurries of several different concentrations and plotted against $e^3/(1-e)$ for each slurry, the resultant curve should be a straight line passing through the origin, with a

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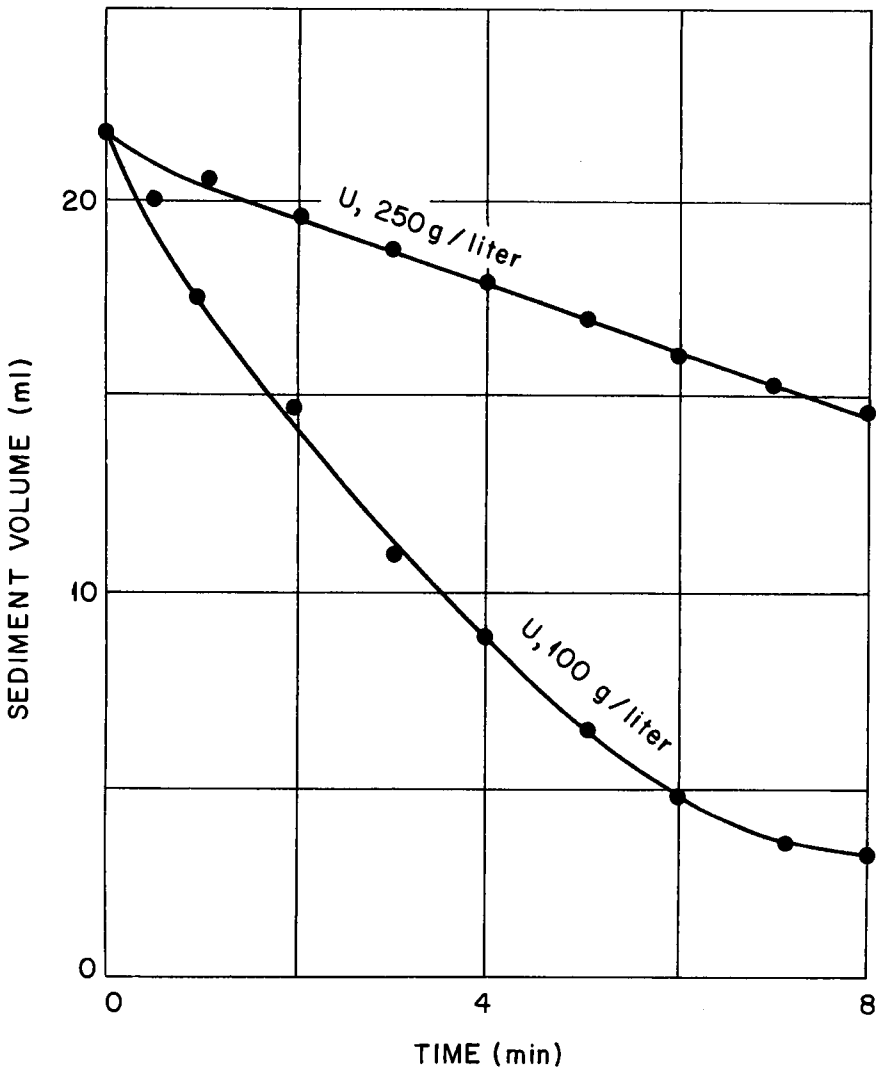

Fig. 7-1. Sedimentation Curves for Uranium Trioxide Monohydrate Slurries. Temperature = 20°C.

slope of $g(\rho-\rho_1)D_{sv}^2/k\eta$, the value of $e^3/(1-e)$ being obtained from the average of the initial and final values of e in each sedimentation experiment. Presuming the equation to hold, it should be possible to calculate D_{sv} from the slope since all other terms in the expression are known.

The value of k is very close to 5 when the ratio of the volume of solids to the total system volume is high. When this ratio is low, as in the case of a slurry containing 250 g of uranium per liter, there is some evidence that the value of k is about 12.7. This is borne out by a comparison of the results obtained using the two different values of k with the nitrogen adsorption results. In the nitrogen adsorption determination, it is assumed that the surface of the solid is covered by a monolayer of nitrogen gas, making it possible to calculate a surface area. Analogously, it is generally held that a film is formed about a particle on its immersion in a liquid. This film, which moves with the particle through the fluid, should increase the effective particle size of the solid. Since the particle diameters calculated with k = 5 are nearly the same as those obtained from the nitrogen adsorption data while those obtained with k = 12.7 are larger, the higher value for k appears to be more reasonable for these systems.

Two platelet preparations were investigated, both prepared from uranium peroxide by alternate calcinations and hydrations. One was also micronized between cycles of calcination and hydration, but there was no detectable difference in particle size.

The values obtained for the particle diameter by sedimentation are independent of the sedimentation tube diameter (see Table 7-2). This points up the utility of the method in that a measurement can be made on as small a sample as 0.2 ml.

Table 7-2

Particle Size Measurements in $UO_3 \cdot H_2O$ Slurries by Sedimentation Methods

Type	Uranium Concentration (g/liter)	Diameter of Sedimentation Tube (cm)	Particle Size, D_{sv} (μ)		
			Sedimentation		N_2 Adsorption
			k = 5	k = 12.7	
Platelets	200-500	2.10	1.5	2.4	1.8
	250	0.95	1.7	2.7	1.8
	250	0.12[a]	1.6	2.6	1.8
Rods	250	0.95	1.7	2.7	1.8

(a) 0.2-ml serological pipet.

7.2 Crystal Growth in $UO_3 \cdot H_2O$ Slurries

Since particle size is such an important factor in determining the physical properties of slurries, a study of crystal growth in $UO_3 \cdot H_2O$ slurries was initiated. Rods and platelets prepared from uranium peroxide and platelets prepared from calcined uranyl nitrate were used in the study. The rate of growth in all cases was rapid during the first 2 hr of heating but decreased markedly as the heating was extended to 24 hr. In the case of rods and platelets prepared from uranium peroxide, the stable particle size was 3.9 and 7.8 μ, respectively, expressed as equivalent spherical diameters.

The starting material for the crystal growth measurements on rods was $UO_3 \cdot 2H_2O$ prepared by calcination of well-washed uranium peroxide and subsequent hydration in hot water. $UO_3 \cdot H_2O$ rods were formed from the dihydrate during crystal growth at 250°C.

The starting material for platelet growth studies was prepared in one case by micronizing a sample of rods and in the other by calcining $UO_2(NO_3)_2$, washing, and hydrating to $UO_3 \cdot 2H_2O$. Platelets of $UO_3 \cdot H_2O$ were formed from both samples during heating at 250°C.

Samples of the slurries were held at 250°C, in sealed quartz tubes, in a rocking autoclave for the desired length of time. Particle sizes were determined by gravitational and centrifugal sedimentation from glycerin-water suspensions of suitable viscosity containing a deflocculent to break up aggregates. A weight percentage distribution of particles in terms of equivalent spherical diameter was thus obtained. The average particle size was calculated from the weight distribution by the relation

$$S_w = 6\ W/100\ \rho\ \bar{D}$$

or, for spherical particles,

$$S_w = 6/\rho\ D_{avg}$$

where W = weight percentage of solids between D_1 and D_2

$\bar{D}$ = arithmetical average = $(D_1 + D_2)/2$, microns

D_{avg} = average diameter defined as $100\ \bar{D}/W$, microns

These calculations are quite reliable when D_1 and D_2 are taken over a sufficiently small size interval and the particle diameters are greater than 0.1 μ. While this method probably does not measure true particle sizes, it does yield values that are closely related to the property of interest, that is, the behavior of particles on settling from a fluid medium. Moreover, since the data were obtained under consistent conditions, changes in particle size were a measure of rate of growth.

The data (see Table 7-3) indicate that small $UO_3 \cdot H_2O$ particles increased in size on being heated at 250°C in water until a relatively stable particle size was reached after a few hours. The observed

equilibrium particle size for nonmicronized rods was 3.9 μ; for platelets prepared from micronized rods it was 7.8 μ; and the platelets prepared from $UO_2(NO_3)_2$ appeared to have an equilibrium particle size considerably larger than that of the other two.

The observed growth rates may be explained by the various factors governing particle size increase. It is well known that growth by coalescence of small particles is a very rapid process since two small particles tend to adhere as a result of the decrease in the surface energy of the particles caused by the collision. This type of process may explain rapid growth in the early stages of the experiment when small particles predominate. However, as the particle size increases, there is less tendency toward this type of process since the surface energy of the larger particles is much lower. The growth is then controlled by other factors such as solubility, which also decreases with increasing particle size, and rates of diffusion and deposition of the soluble uranium. These factors result in slower growth rates.

In this work soluble uranium, varying from 130 to 625 ppm, was present and this may have increased both the rate of particle size growth and the equilibrium particle size.

7.3 Viscosities of $UO_3 \cdot H_2O$ Slurries

The viscosity of slurries is of interest mainly from an engineering point of view. It plays an important role in both heat transfer and material-handling considerations. The viscosities of suspensions of $UO_3 \cdot H_2O$ rods and platelets with uranium concentrations of 250 g/liter were so close to the viscosity of water that the difference could not be measured by a Stormer or Brookfield viscosimeter. A capillary tube viscosimeter was therefore used.* A Saybolt viscosi-

*Measurements were made at the micromeretics laboratory of Prof. J. M. DallaValle, Georgia Institute of Technology, Atlanta.

Table 7-3

Particle Size Growth in Slurries of $UO_3 \cdot H_2O$ on Heating

Uranium concentration 250 g/liter; slurry heated in sealed quartz tubes

Heating Conditions	Particle Size[a] (μ) Avg	2.5% by Wt under Stated Size	10% by Wt above Stated Size	Soluble Uranium in Supernatant (g/liter)
Rods				
Unheated	0.5	0.3	1.3	---
Heated to 160°C and allowed to cool	2.6	1.0	3.9	0.134
Heated to 250°C and allowed to cool	2.3	1.6	2.7	0.096
Heated at 250°C for				
1 hr	3.0	1.6	6.1	0.135
2 hr	3.1	1.9	4.9	0.210
4 hr	3.2	1.5	5.3	0.240
24 hr	3.9	1.8	5.5	0.200
Platelets Prepared from Micronized Rods				
Unheated	1.8	0.4	---	---
Heated to 160°C and allowed to cool	2.8	0.7	7.4	0.250
Heated to 250°C and allowed to cool	4.2	1.6	10.3	0.310
Heated at 250°C for				
1 hr	4.8	1.3	10.4	0.280
2 hr	6.0	2.5	13.3	0.468
24 hr	7.8	5.0	14.6	0.625
Platelets Prepared from $UO_3(NO_3)_2$				
Heated to 250°C and allowed to cool	2.9	1.1	9.9	
Heated at 250°C for				
1 hr	5.9	3.1	8.3	
2 hr	7.2	3.2	13.3	

(a) Particle sizes expressed as equivalent spherical diameters.

meter was adapted for this purpose by sealing a vertical tube of the proper dimensions to the exit nozzle. In this apparatus, only the temperature and concentration could be varied for a given tube. T[redacted]re was fixed by the head of the suspension within the viscosimeter.

Viscosities were determined by measuring the time required for a known volume of slurry to flow through the tube. The viscosity of the slurry increased with increasing solids concentration and decreased with increasing temperature for a given concentration (see Fig. 7-2). The viscosity of a slurry containing 250 g of uranium per liter as $UO_3 \cdot H_2O$ was greater by 40-50% than that of water at the corresponding temperatures. There was no detectable difference in viscosity between the slurries of rods and those of platelets at this uranium concentration. Isotherms obtained by plotting the fluidity, which is the reciprocal of viscosity, against concentration converge at a uranium concentration of 890 g/liter when extrapolated to zero fluidity (see Fig. 7-3). This result is of interest since it appears to be related to the concentration of a settled slurry that has been heated over 24 hr at 250°C. The settled solid after such treatment occupied 20 to 30% of the total volume, which is equivalent to a uranium concentration of 1250 to 830 g/liter in the settled solids volume.

Although a linear relationship has been used to obtain the fluidity intercept, there is no theoretical basis for assuming this to be the correct extrapolation. Moreover, variation in the particle-size distribution could also affect the results.

8.0 CORROSION STUDIES

The problem of corrosion in a reactor slurry fuel is undoubtedly closely related to other phenomena such as erosion, metastable flow

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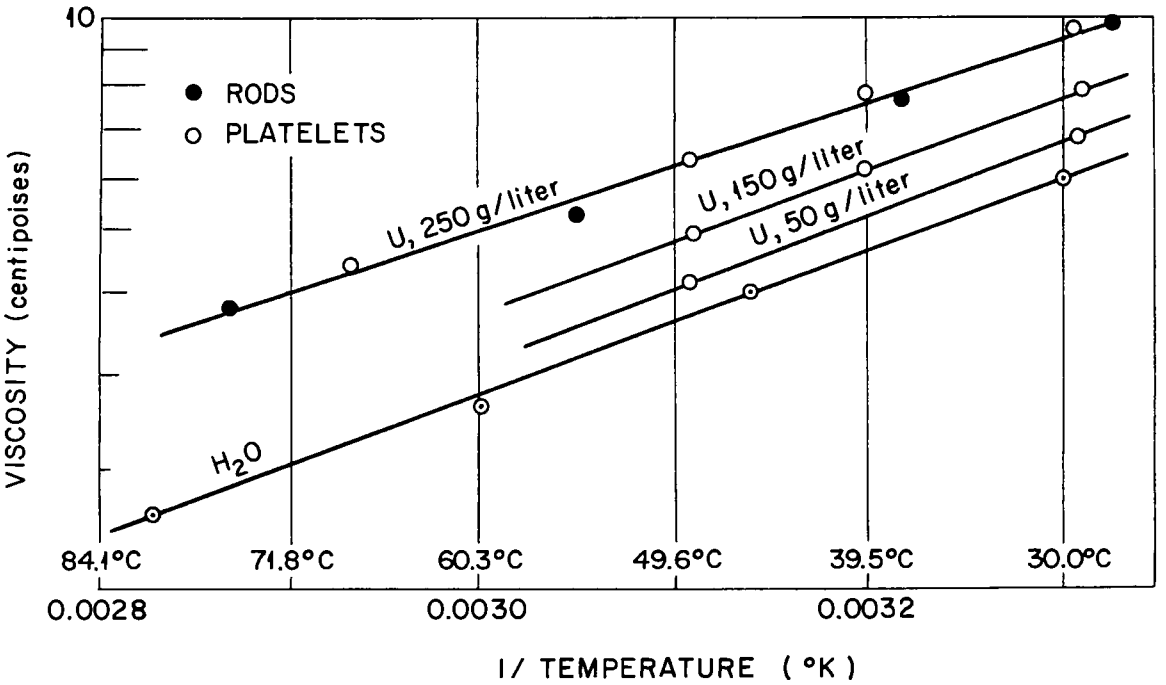

Fig. 7-2. Viscosity of Uranium Trioxide Monohydrate Slurries as a Function of Temperature.

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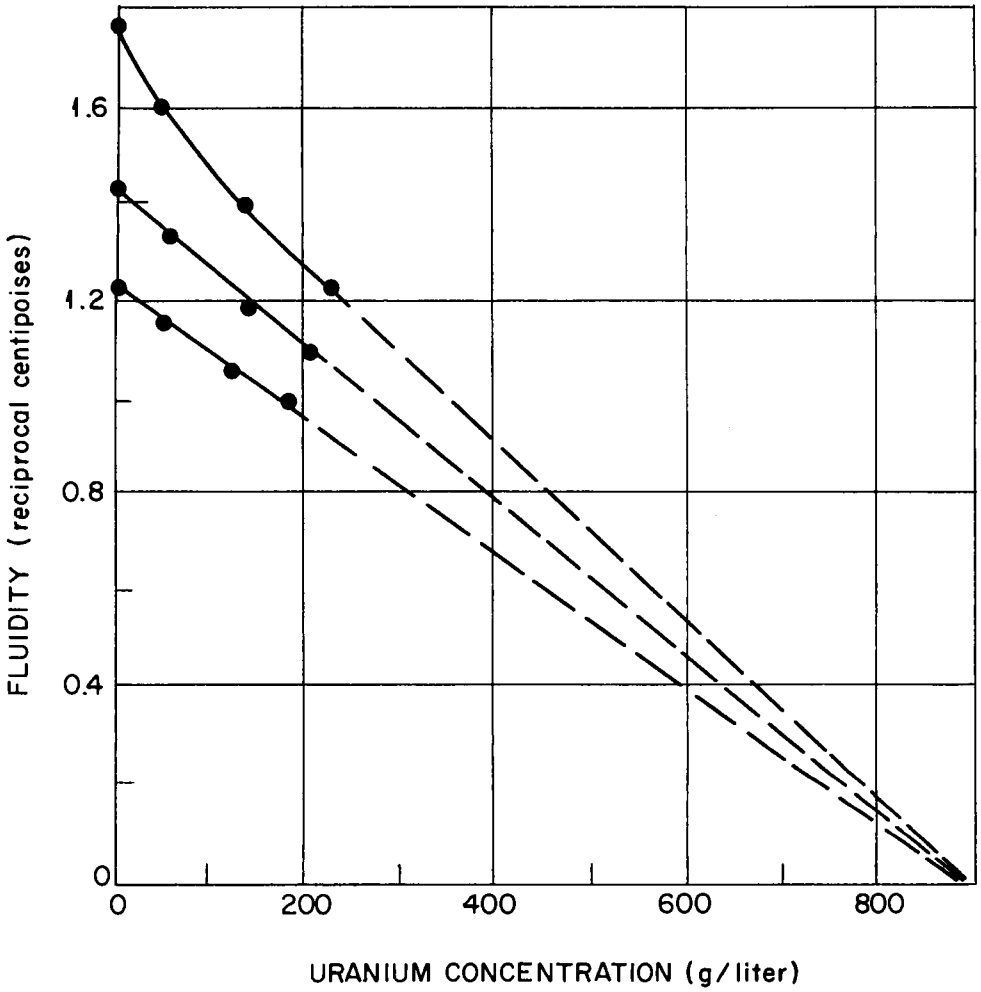

Fig. 7-3. Fluidity of Uranium Trioxide Monohydrate (Platelet) Slurries as a Function of Concentration.

conditions, and the build-up of products of the radiation process. These factors cannot all be investigated simultaneously without resort to a circulating in-pile loop. However, indications of their relative importance can be gained by less pretentious experiments designed to study these effects separately.

Under quasi-static conditions pure $UO_3 \cdot H_2O$ slurries under an atmosphere of hydrogen and oxygen corroded type 347 stainless steel at a rate of 0.6 mil/yr. In distilled water and uranyl sulfate the corrosion rates were 0.4 and 45 mils/yr, respectively (see Table 8-1). Dissolved salts such as sodium nitrate and potassium sulfate accelerated the corrosion rate slightly, increased the concentration of soluble uranium, and promoted caking. Fission product ions in the same concentrations as would be expected after about 30 hr irradiation did not change the corrosion rate appreciably.

For this work, test specimens of type 347 stainless steel were held in rocking autoclaves by type 347 stainless steel wires. Two hundred milliliters of water or $UO_3 \cdot H_2O$ slurry containing various additives was placed in the 320-ml autoclave which was rocked, at 250°C, 30 degrees through the horizontal, at 37 cycles/min for 16-20 hr. The corrosion films on the specimens were removed by electrolytic stripping in a 5% sulfuric acid bath containing rodine, an organic corrosion inhibitor.

Table 8-1

Corrosion Rates of $UO_3 \cdot H_2O$ Slurries on Type 347 Stainless Steel at 250°C

Duration of tests: 20 hr

Uranium concentration: 250 g/liter

Slurry	Corrosion Rate (mils/yr)
Distilled H_2O (evacuated)	0.4
Distilled H_2O plus 0.25% K_2SO_4 and air	0.9
$UO_3 \cdot H_2O$ platelets (evacuated)	0.6
$UO_3 \cdot H_2O$ platelets plus air and 10 psi O_2	0.9
$UO_3 \cdot H_2O$ platelets plus air and 0.5% $NaNO_3$	0.5
$UO_3 \cdot H_2O$ platelets plus air and 0.25% K_2SO_4	0.7
$UO_3 \cdot H_2O$ platelets plus 60 psi O_2 and 120 psi H_2	0.6
$UO_3 \cdot H_2O$ platelets plus air and 0.25% $NaNO_3$	0.8
Washed Mallinckrodt $UO_3 \cdot H_2O$ plus air	1.1
$UO_3 \cdot H_2O$ rods used in loop studies	0.3
UO_2SO_4 (uranium concentration 270 g/liter, pH 1.65)	45
$UO_3 \cdot H_2O$ rods plus air and 0.012 g of KI per liter	1.1
$UO_3 \cdot H_2O$ platelets plus air and 0.026 g of $BaSO_4$ per liter	0.2
$UO_3 \cdot H_2O$ platelets plus air, 0.052 g of $BaSO_4$ per liter and 0.024 g of KI per liter	0.9
$UO_3 \cdot H_2O$ platelets plus air, 0.052 g of $BaSO_4$ per liter, 0.024 g of KI per liter, and 0.062 g of $Zr(OH)_4$ per liter	0.3

9.0 RADIATION STUDIES

Five radiation experiments with uranium oxide slurries were performed in the ORNL graphite reactor (see Table 9-1 for conditions). Effects directly attributable to radiation were difficult to determine with such a small number of experiments, and results were further beclouded by variations in chemical purity of the starting material. In all but one of the experiments the slurries caked on the sides of their containers, resulting in very low recovery of irradiated solids and rendering quantitative chemical observations unreliable. The caking appeared to be more pronounced at higher fission densities and in those slurries of highest nitrate impurity. The rate of radiolytic gas production was about half that of uranyl sulfate solutions of the same concentration, but this was offset by a slower rate of recombination, resulting in steady-state gas pressures comparable in magnitude to those of solutions. Crystallographically, the irradiated solids could be characterized mainly by their lack of uniformity in both size and shape although the starting material had been uniform. In every case there was some crystal growth as well as degradation to fragments and fines. In four of the experiments, 2 to 10% of the uranium in the irradiated slurries was found in the reduced, or U(IV), state. In the fifth experiment, no reduction was observed. More than 90% of the fission product activity was associated with the solids, and attempts at leaching the fission products by partial dissolution of the UO_3 in nitric acid indicated that many were adsorbed on the surface of the solids. Iodine was the major constituent in the supernatant activity.

Ten- to thirty-milliliter portions of the slurries were sealed in stainless steel bombs of the type shown in Fig. 9-1. The bombs, approximately 1 in. in diameter by 5 in. long, overall, were equipped with a thermocouple well (1) for measuring the temperature and a 35-mil stainless steel capillary tubing (2), permitting a continuous

Table 9-1

Summary of Experimental Conditions for $UO_3 \cdot H_2O$ Slurry Irradiations

Expt.	Uranium Conc. (g/liter)	Enrich-ment	Approx. NO_3^- Impurity (%)	Physical State before Irradiation	Thermal Neutron Flux ($n/cm^2/sec$)	Temp. (°C)	Duration of Expt. (hr)
1	250	Normal	0.1	Rods, 20-30 μ long	4×10^{11}	250	136
2	250	93.4%	0.1	Rods, 15-20 μ long	4×10^{11}	250-300	250
3	250	93.4%	0.1	Rods, 15-20 μ long	4×10^{11}	280-300	144
4	250	Normal	0.01	Platelets, ~3 μ	7×10^{11}	250	504
5	40	93.1%	0.01	Platelets, ~10 μ	7×10^{11}	250-295	585

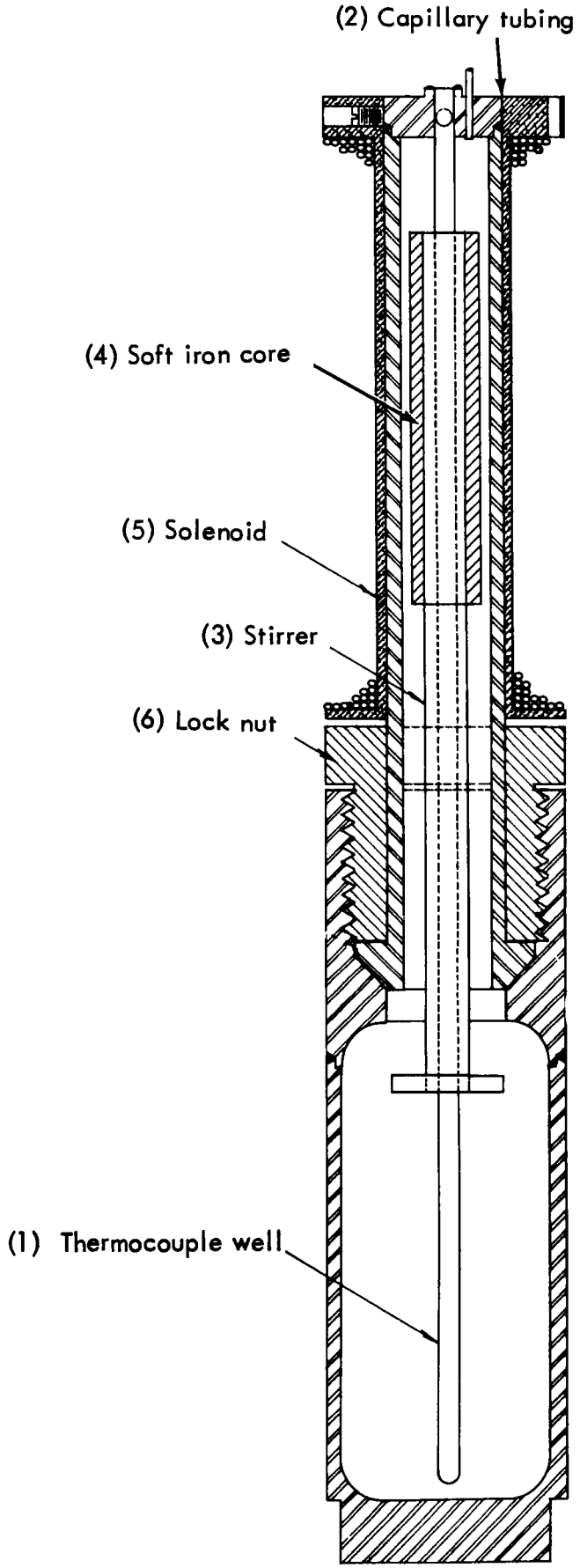

Fig. 9-1. Bomb Used in Slurry Irradiation Studies.

record of the pressure. The slurries were agitated with a stirrer (3) containing a soft iron core (4) which fitted concentrically around the thermocouple well. Stirring was accomplished by activating a solenoid (5) at 10-sec intervals. The stirrer was raised when the solenoid was activated and fell, under gravity, when the current was off. Improper performance of the stirrer could be readily detected since its position relative to the activating solenoid determined the voltage induced in an induction coil (not shown) on the solenoid. The top assembly was sealed to the bomb by a locknut (6). The temperature of the slurry was generally maintained near 250°C and could be controlled by either an electric resistance heater adjacent to the bomb or by cooling air.

Upon removal from the pile, the bombs were opened remotely in a shielded cell equipped with a lead-glass window which permitted direct observation of the working area. The slurries were transferred by vacuum into glass equipment where they could be observed and sampled.

9.1 Gas Production

The rate of radiolytic gas production (oxygen and hydrogen) was very dependent on the fission density in the slurry. The steady-state gas pressure was generally unpredictable for the first two or three days of each experiment, rising as high as 2000 psi with natural uranium slurries and 6000 psi with the enriched slurries. The steady-state pressure decreased, however, as the irradiation progressed, and near the end of the experiments pressures were near 200 psi for natural uranium slurries and 3000 psi for enriched.

In experiment 5, performed with 40 g of enriched uranium per liter as $UO_3 \cdot H_2O$ platelets, a G value (molecules of water decomposed per 100 ev of energy absorbed) of 0.4 at 250°C was obtained. The G

value found for uranyl sulfate solutions of the same concentration is approximately 1. With the exception of the first 3 days of irradiation, the gas pressure could be correlated with temperature by the use of the kinetic expression developed for solutions,[15] and the steady-state pressure decreased by at least a factor of 2 as the slurry temperature was increased from 250 to 295°C.

The out-of-pile rate of combination of hydrogen and oxygen in a slurry of $UO_3 \cdot H_2O$ platelets, uranium concentration of 250 g/liter, at 250°C was determined* to be approximately half that of a uranyl sulfate solution of 40 g of uranium per liter. It gave a first order solution rate constant of 2 $hr^{-1.5}$. The slurry studies were carried out in new stainless steel bombs simultaneously with similar studies on uranyl sulfate solutions containing 40 g of uranium per liter.

9.2 Physical Effects

When the irradiated bombs were opened, it was found that a large fraction of the solids could not be readily removed. The percentage recoveries in experiments 1 through 5 were 34, 18, 20, 97, and 30, respectively. Visual examination of the bomb interiors showed that material had plated out on the walls. It could be recovered by adding 1/4-in. steel balls to the bombs, closing, and shaking them vigorously for several hours. The solids so recovered were dark brown in color and were insoluble in 8 M nitric acid. An adequate explanation for this phenomenon was not developed. Only in experiment 4, carried out at both low fission density (about 0.2 watt per gram of oxide) and with very low nitrate contamination (0.01%), could this be considered a minor problem. Later out-of-pile tests with $UO_3 \cdot H_2O$ slurries in radiation bombs showed that the slurries caked after having been heated at 250-275°C for 16 or more hours, and that consequently this effect was not solely a result of pile radiation.

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*By E. L. Compere and H. H. Stone, Chemistry Division, ORNL.

If there is an inverse solubility of $UO_3 \cdot H_2O$ in water at these temperatures, this could be a contributing factor since it could result in scale formation on the container walls, normally at a higher temperature than the slurry.

The fraction of the slurries which was readily transferable---usually greenish brown in color---showed no obvious impairment of slurry properties. Photomicrographs of the irradiated solids showed that appreciable degradation to fragments and fines had occurred. Regardless of whether rods or platelets had been used as the starting material, a small fraction of the solids appeared in the form of recognizable platelets after irradiation. In addition, many larger particles (50-100 μ in cross section) of irregular shape were always present.

Nearly all the fission product activity in the irradiated slurries was associated with the solids. Based on the assumption that the activity per unit weight of the unrecovered solids is the same as that in the recovered, the percentage of the total activity in the supernatants was 3, 6, 1, and 1 for experiments 1, 2, 3, and 5, respectively. Radiochemical analyses (see Table 9-2) for those products of highest fission yields showed that iodine was the major constituent in the supernatants.

The high G value of 0.4 indicates that many of the recoiling fission fragments were being released into the aqueous phase. The preponderance of activity associated with the solids, however, could only mean that most of these had subsequently been adsorbed on or near the surface of the particles. To determine the feasibility of removing this surface activity without destroying the slurry, irradiated $UO_3 \cdot H_2O$ solids were extracted with water and very dilute nitric acid. The results (Table 9-3) indicated that water alone was not effective but that water with 800 ppm of nitric acid did remove sizable amounts of activity with relatively little dissolution of the uranium oxide.

Table 9-2

Distribution of Activity in Irradiated Uranium Oxide Slurries

Fission Product Activity	Percentage of Activity in Aqueous Phase			
	Expt. 1	Expt. 2	Expt. 3	Expt. 5
Gross β	3	6	1	1
	Percentage of Gross β			
Total rare earth β	0.2	2	0.3	0.4
Ru β	0.3	4	0.5	0.1
Zr β	1	2	0.3	0.05
Nb β	0.3	0.3	0.4	0.07
Cs β	0.6	0.2	0.1	2
Sr β	---	0.08	0.04	1
Ba β	---	0.06	0.02	0.5
Np β	---	2	2	---
I β	---	61	31	19
Te β	---	1	0.2	0.2
Mo β	---	---	0.7	0.2

Table 9-3

Extraction of Activity from Irradiated $UO_3 \cdot H_2O$

Expt.	Original Slurry Irradiated	Supernatant	U Conc. (g/liter)	Soluble U (g/liter)	Temp. (°C)	Reaction Time (hr)	Percentage of Activity					
							In original Solid		In Original Supernatant		In Residue[b] after Dissolution	
							α[a]	β	α[a]	β	α[a]	β
1	$UO_3 \cdot H_2O$ platelets	Water	33	---	100	3	98.8	99.5	1.2	0.5	---	---
2	$UO_3 \cdot H_2O$ platelets	Water	17	---	250	66	62	98.6	0.2	0.06	37.8	1.3
3	$UO_3 \cdot H_2O$ platelets calcined at 400°C and reslurried	Water	26	0.01	150	16	99.7	98	0.3	2	---	---
4	$UO_3 \cdot H_2O$ platelets	HNO_3 (aq), 800 ppm	51	2.2	250	16	73.5	68.9	26.5	31.1	---	---
5	Product from Expt. 4	HNO_3 (aq), 800 ppm	48	2.4	250	16	88.0	73.0	11.9	19.7	0.1	7.3
6	$UO_3 \cdot H_2O$ platelets	Water + 900 psi CO_2	46	0.01	100	16	98.1	97.2	0.6	0.2	1.3	2.6

(a) Corrected for uranium α.

(b) Insoluble in 4 M HNO_3.

The fact that $UO_3 \cdot H_2O$ slurries may be readily converted to carbonate by reaction with CO_2 prompted experiment 6 in Table 9-3. It was expected that conversion to carbonate might release activity to the solution but this was not observed.

9.3 Chemical Effects

The irradiated slurries were analyzed chemically for reduced uranium [U(IV)], soluble uranium, and the corrosion products iron, nickel, and chromium. Owing to the low recovery of the oxide, quantitative interpretations were impossible. Reduction of the uranium occurred in the first four experiments and appeared to be influenced by the amount of nitrate present in the original solids. The extent of reduction varied from near 10% in experiments 1-3 to 2% in experiment 4. In the fifth experiment, no reduction of the uranium was observed.

Corrosion of the radiation bombs appeared to be greater in experiments 1-3 where soluble impurities were highest, although the corrosion occurred at a very insignificant rate even in these runs. Based on chemical analyses for iron, nickel, and chromium in the irradiated slurries, the corrosion rates in experiments 4 and 5 were of the order of magnitude of 0.2 mil/year, which was in the same range as in previous out-of-pile experiments.

10.0 ALTERNATE SYSTEMS

Limited investigations were carried out on magnesium uranate and uranyl phosphate as alternate slurry fuels. While these compounds have more complicated molecules than the uranium oxides, which could result in stability problems under radiation conditions, it was felt that they might possess certain other characteristics which would make them desirable for use. Magnesium uranate suspensions could be

expected to have higher pH's than the oxides, and this could be advantageous from the standpoint of corrosion. Uranyl phosphate had been observed to possess very favorable settling characteristics and crystal stability at elevated temperatures. However, results did not indicate that these compounds had any advantage over UO_3.

Magnesium Uranate. This compound was prepared by adding ammonia to a solution of the chlorides. While uranium analysis of this product gave 72.6% uranium (theoretical for $MgUO_4$, 72.9%), a magnesium determination indicated the presence of only 1.6% magnesium (theoretical, 7.5). In slurry form, this material had a pH of about 7. The color and the pH changed when it was heated at 250°C. The slurry caked when settled.

Magnesium Diuranate. MgU_2O_7 was prepared from $Mg(UO_2)_2(OC_2H_3O_2)_6 \cdot 6H_2O$ by the procedure recommended by Hockstra and Katz.[16] The product showed, upon analysis, 77.0% uranium (theoretical, 77.7%). When heated in a sealed pyrex tube at 250°C for 20 hr, a suspension of this solid in water changed from the original brownish yellow to lemon yellow, indicating thermal instability.

Studies of $UO_3 \cdot H_2O$-MgO Mixtures. Slurries were prepared by adding known weights of MgO to a $UO_3 \cdot H_2O$ slurry of known uranium concentration and boiling on a hot plate. The original $UO_3 \cdot H_2O$ slurry had a pH of 5.8. With a MgO/UO_3 mole ratio of 1/20 the pH was 10.0, but after the suspension had boiled for an hour the pH dropped to 6.6. Successive additions of MgO raised the initial pH, but it gradually decreased again on boiling. At a mole ratio of 1/5, the pH dropped to near the original; at higher concentrations of MgO the pH dropped more slowly on boiling and leveled off at about 8.5. When slurries of higher MgO concentrations were heated to 250°C in a sealed tube, the pH dropped to 7.5 with considerable caking of the solid.

Uranyl Phosphate. The solids in slurries containing 250 g of uranium per liter as uranyl phosphate, $(UO_2)_3(PO_4)_2 \cdot 5H_2O$, occupy about 80% of the

total volume, presumably as a result of the needlelike structure of the crystals which, on settling, form a brush-pile type of structure. Uranyl phosphate was prepared from uranyl ammonium phosphate by heating in 1 M nitric acid at 98°C until conversion was complete:

$$3UO_2NH_4PO_4 \underset{}{\overset{HNO_3}{\rightleftharpoons}} (UO_2)_3(PO_4)_2 + (NH_4)_3PO_4$$

The uranyl phosphate, being less soluble at 98°C, precipitates out, shifting this equilibrium to the right.

Particle size determinations were made on the uranyl phosphate slurries both before and after heating for various periods of time at 250°C (Tables 10-1 and 10-2). With slurries of uranyl phosphate both as prepared and micronized, no appreciable change in the volume of settled solids was brought about by the heating even though there was some particle growth and some reduction of hexavalent to tetravalent uranium. The pH of the uranyl phosphate slurry was originally 3.95 and decreased to 3.0 during the heating, suggesting that more thorough washing would be required to remove the acid carried over from the conversion step.

Table 10-1

Thermal Stability of Uranyl Phosphate Slurries

250 g of $(UO_2)_3(PO_4)_2 \cdot 5H_2O$, 250 g of uranium per liter; heated at 250°C in sealed quartz tubes in a rocking autoclave; settled at room temperature for 24 hr

Heating Time (days)	Ratio of Settled Solids Vol. to Total Vol.
0	0.80
3	0.79
7	0.80
14	0.81

Table 10-2

Thermal Stability of Micronized Uranyl Phosphate Slurries

Slurry of micronized $(UO_2)_3(PO_4)_2 \cdot 5H_2O$, 250 g of uranium per liter, heated at 250°C in sealed quartz tubes in a rocking autoclave

Heating Time (days)	Particle Size, D (μ)				Ratio of Settled Solids Vol. to Total Vol.
	10 wt % of particles between 0 and D μ	25 wt % of particles between 0 and D μ	50 wt % of particles between 0 and D μ	62.5 wt % of particles between 0 and D μ	
0	1.64	2.41	4.29	4.95	0.76
4	3.84	5.28	6.73	---	0.74
11	3.72	6.26	10.5	---	0.73
15	3.05	5.6	11.2	---	0.73

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