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STABILITY OF UO_2-NaK SLURRIES

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ARF Project C 124

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T. M. Rymarz

for

Argonne National Laboratory
Lemont, Illinois

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FOREWORD

This is the final report on ARF Project C 124, entitled "Stability of UO_2-NaK Slurries." This program which was sponsored by Argonne National Laboratory under Contract No. 31-109-eng-38-897, covered the period from March 1, 1958 to June 30, 1959.

The program was under the direct supervision of M. A. Fisher, Supervisor of Fine Particles Research. Personnel who participated in this work were S. Katz, and A. Spenney. The data reported here are recorded in ARF Logbooks C 7960, C 7974, C 7975, and C 8625.

Respectfully submitted,

Armour Research Foundation
of Illinois Institute of Technology

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STABILITY OF UO_2-NaK SLURRIES

ABSTRACT

In this project the UO_2-NaK and the UO_3-water systems were studied. The UO_2-NaK phase of the project was concerned primarily with surface phenomena, that is, wetting and flocculation. It was found that UO_2 powder of approximately 1 micron average particle diameter was wetted by NaK at approximately 400°C. No evidence of "dewetting" or flocculation was noted at temperatures up to 600°C, although it was not proved conclusively that flocculation does not occur at the higher temperatures.

Some evidence of reaction between UO_2 and NaK or impurities in the NaK was found. This was evidenced by a change in the color of the UO_2 after exposure to NaK at 600°C.

The UO_3-water system was studied with regard to application to a "filter leaf reactor", that is, a reactor core consisting of layers of granulated UO_3 cooled by water. Beds of UO_3, covered with water, were heated to 300°F. Resistance to the flow of water was measured. Heating of the beds in contact with water produced a slight change in particle size distribution but the change in flow resistance was negligible.

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STABILITY OF $U0_2$-NaK SLURRIES

I. INTRODUCTION AND SUMMARY

This is the final report for ARF Project C 124. This program was concerned primarily with a study of two systems which are of interest because of their possible applicability to nuclear reactors. These systems are:

1. uranium dioxide ($U0_2$) slurried in liquid sodium-potassium (NaK) alloy
2. uranium trioxide ($U0_3$) and water.

In addition, some preliminary and exploratory work was done in areas not directly related to the two systems already mentioned. This included work on the classification of Boehmite samples, and calculations of the characteristics of packed beds.

The $U0_2$-NaK system was studied with especial reference to the wetting of $U0_2$ by NaK and the effect of temperature on the viscosity of the $U0_2$-NaK slurry. It was found that $U0_2$ was wet by NaK at approximately 400°C even when no special precautions were taken to clean the $U0_2$. The $U0_2$-NaK slurry was heated to as high as 600°C without abrupt changes in viscosity developing.

The $U0_3$-water system was also studied by measuring the resistance of a bed of finely divided $U0_3$ to the flow of water, and the stability of the bed in contact with water at 300°F. It was found that although there was some change in the size of the $U0_3$ particles after being subjected to immersion in hot water, the system was physically stable with no detectable fracturing of particles due to thermal stresses or evidence of changes in states of hydration.

II. URANIUM DIOXIDE-NaK SYSTEM

A. Description of the System

Abraham, Flotow and Carlson[1*] have studied the properties of $U0_2$-NaK slurries in a circulating loop over a broad range of temperatures. In the course of their work it was noted that the slurry could be pumped only with difficulty at temperatures beyond 550°C.

Several explanations for this effect were advanced. These are:

1. flocculation of $U0_2$ due to interaction with sodium oxide
2. rapid settling of $U0_2$ because of decreased viscosity of NaK
3. separation or formation of a third phase
4. unexplained action by impurities in the loop or reactant materials.

Of these, some can be discounted on the basis of certain relevant facts. For example, rapid settling of the $U0_2$ in the NaK would be expected to produce plugging only if the settling velocity was of the same order of magnitude as the flow velocity. The settling velocity can be calculated readily. Thus, at 600°C, the viscosity and density of NaK are 0.168 centipoise and 0.7 g/cc, respectively. Applying Stokes law, the settling velocity, U, is given by

$$U = \frac{g D^2 (\rho_s - \rho)}{18\mu} \qquad (1)$$

where D is the mean particle diameter, ρ_s and ρ are the densities of the $U0_2$ and NaK, respectively, μ is the viscosity of NaK, and g is the gravitational constant. Substituting in (1),

$$U = 0.0529 \text{ cm/sec.}$$

This may be used to determine the Reynolds number, Re, from the

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[*] References appear in the bibliography, Appendix A.

relation

$$Re = \frac{D U \rho}{\mu} \qquad (2)$$

which yields the value

$$Re = 0.00883.$$

This indicates that Stokes law is applicable since it is generally considered valid for Reynolds numbers below 2. Because of the low settling velocity of $U0_2$ particles in the micron range it is not believed that settling could be responsible for the plugging experienced during operation of the loop at Argonne National Laboratory. If, however, some degree of agglomeration of the particles is present, that is, if the system is flocculated, much higher rates of settling would be expected.

Data published previously[1] indicate that $U0_2$ particles in NaK are flocculated to some degree. However, flocculation of the slurry should not produce a large increase in the apparent viscosity, unless actual mechanical plugging occurs. According to Abraham et al., the $U0_2$-NaK slurry becomes highly flocculated at temperatures higner than 500°C. This flocculation was reported to be so severe as to produce differences in concentration when the slurry was pumped through a loop at rates as high as 8 ft/sec. Some aspects of that work suggest that the flow discontinuities may be attributed to the presence of oxygen in the system.

B. Experimental Work

In the present program, work was directed toward the determination of the causes of the anomalous behavior of $U0_2$-NaK slurries at temperatures above 500°C. Some preliminary work was done on the determination of size distribution, analysis of impurities, and surface area of several samples of $U0_2$. These data are presented in Appendix C.

It was decided to study the UO_2-NaK system by rheological measurements. For this reason, two types of viscometers were built. These are shown in Fig. 1 and 2. The piston type of viscometer shown in Fig. 1 was employed first and, although no viscosity data resulted, the experiment did serve to prove that UO_2, even when not scrupulously cleaned and reduced with hydrogen, will be wetted by NaK at a temperature of approximately 400°C.

The experiment was performed in the following manner:

A small amount of UO_2-NaK slurry was heated in the viscometer. The dry UO_2 was placed in the viscometer first, the system was then purged out with helium gas, and enough NaK was added to make a slurry containing approximately 30% of UO_2 by volume. Under cover of the inert gas, the mixture was heated.

At a temperature of approximately 400°C, it was found that the NaK wets the UO_2. Due to the very high concentration of UO_2, the mixture was very viscous and did not flow readily. The UO_2-NaK mixture was heated to a top temperature of 600°C and then allowed to cool to room temperature.

After the mixture had cooled, the flow of inert gas was stopped, and the system was left closed over night. When the viscometer was opened on the following day, it appeared that enough air had diffused into the viscometer to react with a major portion of the NaK. To dissolve the alkalies and inactivate the residual sodium and potassium metals, water was slowly dripped into the system. Along with the UO_2, a bright yellow material was found which was insoluble in water. The liquid was decanted and the solid portion was treated with hydrochloric acid. The hydrochloric acid dissolved the yellow material. The mixture was then filtered to recover the

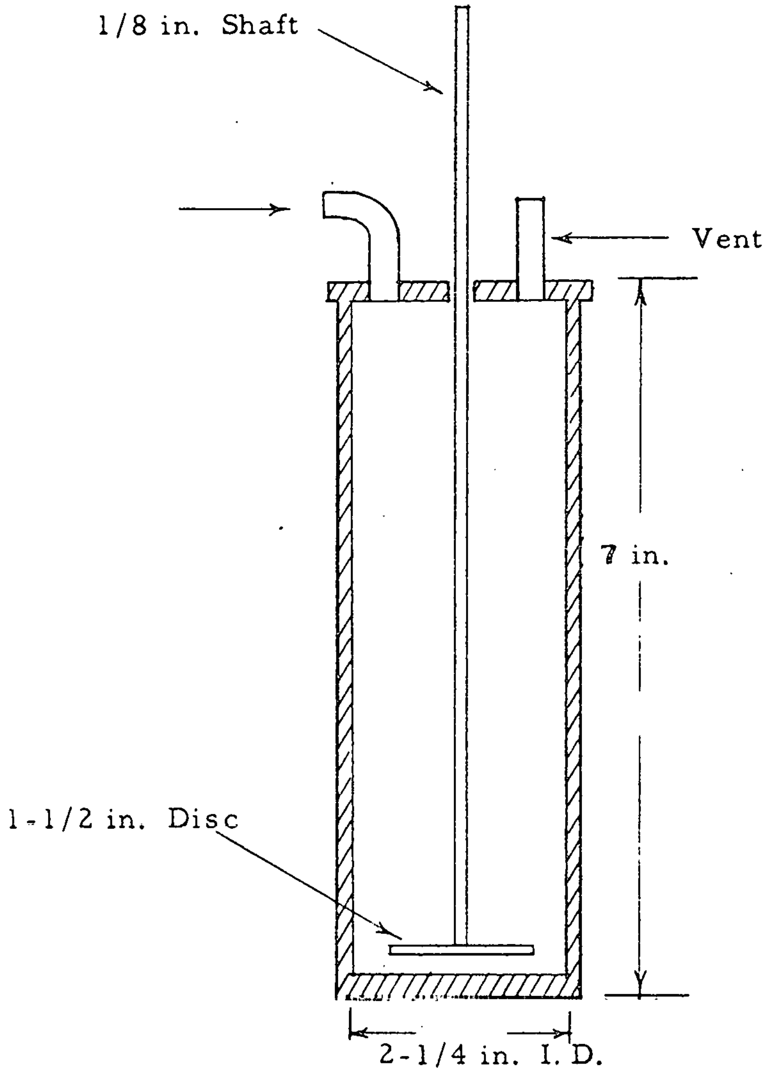

Fig. 1. PISTON VISCOMETER

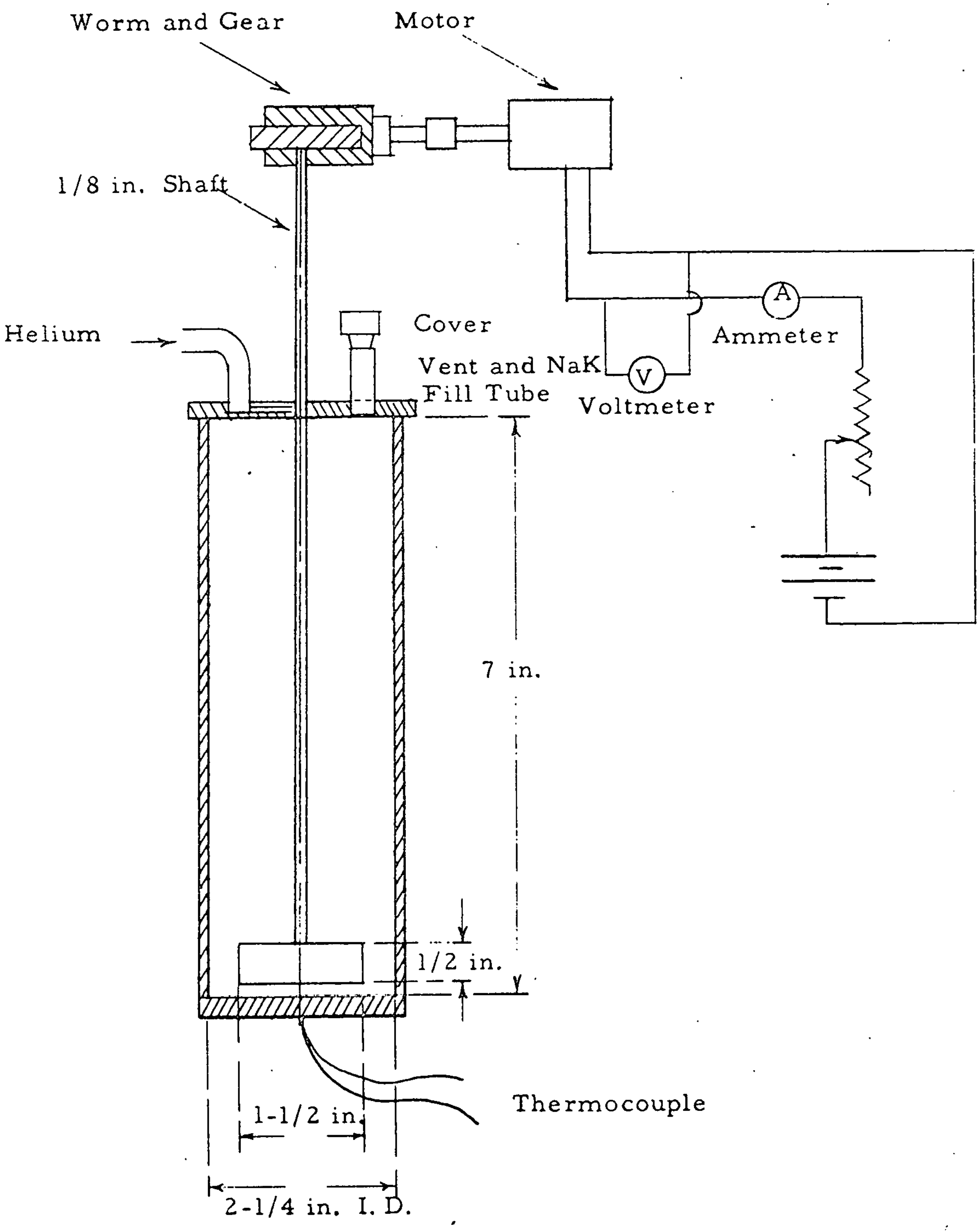

Fig. 2. PADDLE VISCOMETER

UO_2, and the filtrate was made basic with potassium hydroxide. A voluminous yellow-green precipitate formed. The precipitate was filtered, washed and dried, and an attempt was made to analyze it by x-ray diffraction. Results of the x-ray diffraction analysis were inconclusive because of the very small ultimate particle size of the material.

A second experiment was carried out with the falling piston viscometer and with a UO_2-NaK mixture containing approximately 5% of UO_2 by volume. Again, it was found that wetting occurred at approximately 400°C. However, no viscosity measurements could be made because the distilling NaK fouled the viscometer shaft. The mixture was heated to a temperature of 600°C and was then allowed to cool. A mixture of butyl and methyl alcohols was added to destroy the NaK alloy. The UO_2 suspended in the alcohol was then filtered and washed with methyl alcohol.

It was found that the UO_2 had changed in color from a dark brown to a light brown, as a result of the treatment with NaK at high temperature. To check the possibility that this change in color may have been due either to the formation of another uranium compound at the surface or to some change in the crystal structure of the UO_2, the UO_2 was washed with methyl alcohol, dried, and analyzed by x-ray diffration. The x-ray diffraction pattern was similar to that of the untreated UO_2, except for two lines which suggested the presence of a small amount of Na_2O. However, this seems doubtful, for it is difficult to see how Na_2O could be present in crystal form since no effort was made to protect the powder from atmospheric moisture. Attempts were made to resolve this problem by electron diffraction, which is sensitive to very small amounts of crystalline material on the surface of the powder, but again results were inconclusive.

The final design of the viscometer contained a paddle driven by a small, 3-volt, DC motor, as shown in Fig. 2. A voltmeter and an ammeter were connected in the motor circuit. Thus, when the voltage was kept constant, the reading of the ammeter was related to viscosity.

Approximately 20 grams of $U0_2$ were placed in the viscometer, helium was flushed through it, and approximately 45 cc of NaK were introduced. The viscometer was then heated, and the temperature, voltage, and current were noted. The data from this experiment are presented graphically in Fig. 3. It is seen that the ammeter readings generally follow the temperature curve.

The data from this experiment were somewhat obscured by the fact that condensation of NaK on the viscometer shaft produced a larger variation in the ammeter readings than any expected to occur as a result of changes in viscosity. However, definite trends can be seen in Fig. 3. During the initial heating, the ammeter readings increased rapidly in the temperature range from 300 to 475°C. This was probably due to partial wetting of the $U0_2$. After a temperature of 475°C had been reached, the wetting of the $U0_2$ appeared to be complete, and the $U0_2$ was well dispersed, so that a drop in the ammeter readings occurred. Then as the temperature dropped the current reading dropped, because of the reduced amount of vaporizing NaK depositing on the viscometer shaft. As the temperature was increased again, the ammeter readings also increased, but they did not reach the previous high readings because the $U0_2$ had already been completely wetted. No large increase in viscosity is apparent at 550°C. However, an increase may well have been obscured by the variation introduced by the accumulation of condensing NaK on the viscometer shaft. The viscosity of the slurry as a function of the increase in the ammeter reading is shown in Fig. 4.

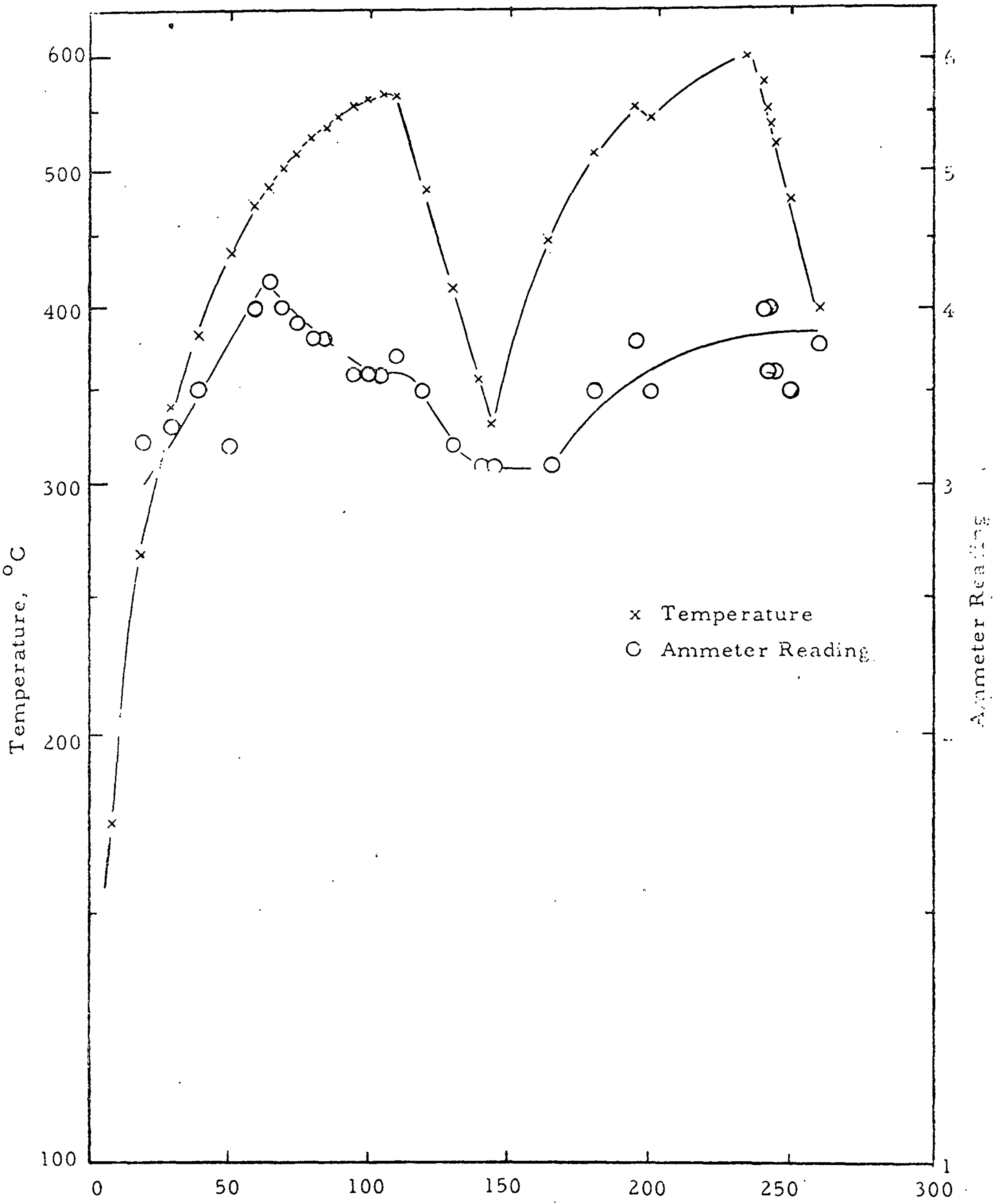

Fig. 3. EFFECT OF TEMPERATURE ON UO_2-NaK SLURRY

Table 1

URANIUM DIOXIDE-NaK SLURRY AT ELEVATED TEMPERATURES
20 grams of UO_2, 45 ml of NaK

Time, min.	Temperature, °C	Ammeter Reading
0	-	
10	174	
20	268	3.2
30	341	3.3
40	382	3.5
50	439	3.2
60	471	4.0
65	486	4.2
70	501	4.0
75	513	3.9
80	525	3.8
85	537	3.8
90	545	3.7
95	554	3.6
100	561	3.6
105	567	3.6
110	564	3.7
120	485	3.5
130	413	3.2
140	358	3.1
145	333	3.1
165	448	3.1
180	516	3.5
195	558	3.8
200	548	3.5
235	603	6.0
240	580	4.0
242	558	3.6
243	544	4.1
245	527	3.6
250	480	3.5
260	401	3.8

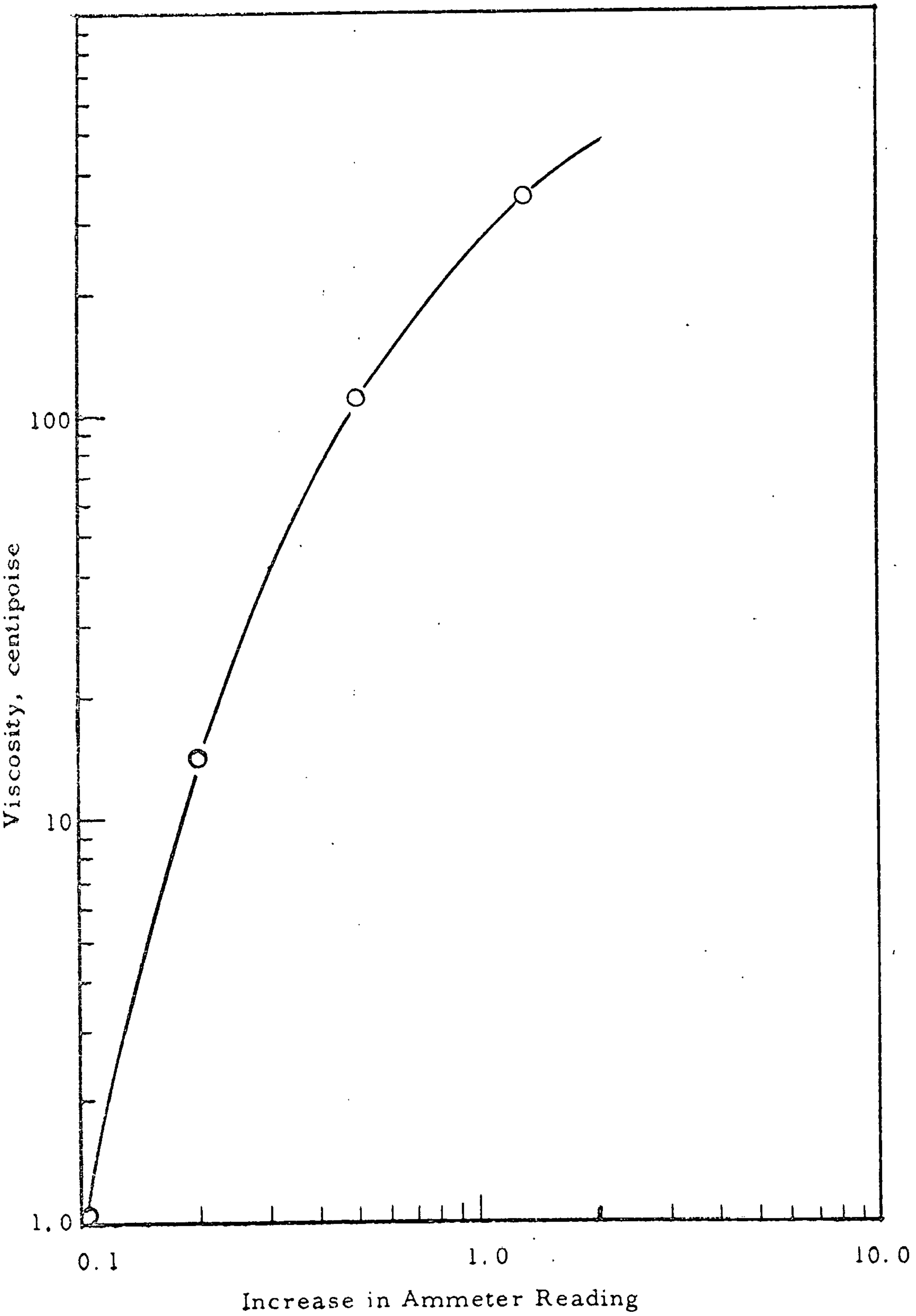

Fig. 4. CALIBRATION CURVE FOR VISCOMETER

Table 2

CALIBRATION OF VISCOMETER

Viscosity, Centipoise	Increase in Ammeter Reading I
0	0
1.0	0.1
14.0	0.2
110	0.5
350	1.3

After the UO_2-NaK slurry had cooled to approximately 300°C, a sample was withdrawn into a 4-mm I. D. Pyrex tube. The slurry wetted the tube wall and after the tube had been emptied, a film of NaK remained on the interior wall. When exposed to the air, the NaK gradually oxidized and became transparent, exposing the UO_2. The UO_2 was evenly distributed along the length of the tube.

Since several minutes had elapsed between the time that stirring had been stopped and the time that the sample had been taken, it may be concluded that the UO_2 was fairly well dispersed, otherwise the UO_2 would have settled out.

These studies do not appear to support previous observations of an abrupt change in the rheological properties of the UO_2-NaK slurry at around 550°C. Because of the uncertainty introduced into the observation by the deposition of NaK from the vapor phase, it would be of interest to repeat this measurement using an alternative method which would minimize the "background" effects of the distilling NaK.

III. URANIUM TRIOXIDE - WATER SYSTEM

The object of this phase of the program was to obtain preliminary data on the properties and physical characteristics of uranium trioxide in water to permit evaluation of the feasibility of a filter-leaf reactor concept. The filter leaf reactor is visualized as consisting of a series of trays or screens on which would be deposited a layer of granular uranium trioxide. Heat would be removed from the fuel by water flowing through the granular layer.

Data have been obtained on the size distribution of the $U0_3$, bulk density of the coarse fractions, resistance to flow of water, and the physical stability of the $U0_3$ particles at elevated temperatures and pressures in contact with water. Table 3 presents the size distribution of the $U0_3$ used.

Table 3

SIZE DISTRIBUTION OF URANIUM TRIOXIDE
(By Sieve Analysis)

Size		
Mesh	Particle Diameter, microns	Percent by Weight
30	590	2.4
30-70	590-210	73.0
70-100	210-149	18.2
100-140	149-105	4.3
140-200	105-74	1.7
200-325	74-44	0.1
325	44	0.3

Since in this reactor concept interest lies in the larger size fractions, only the 30 to 70 and the 70 to 100-mesh fractions were studied in detail. Table 4 shows the resistance to flow of water for the two $U0_3$ size fractions. The physical stability of the $U0_3$ particles in contact with water at 300°F was studied in the Dowtherm-heated autoclave shown in Fig. 5. The $U0_3$ was screened and then washed to remove any fine particles which had not been separated in the screening operation. The $U0_3$ slurry was then poured

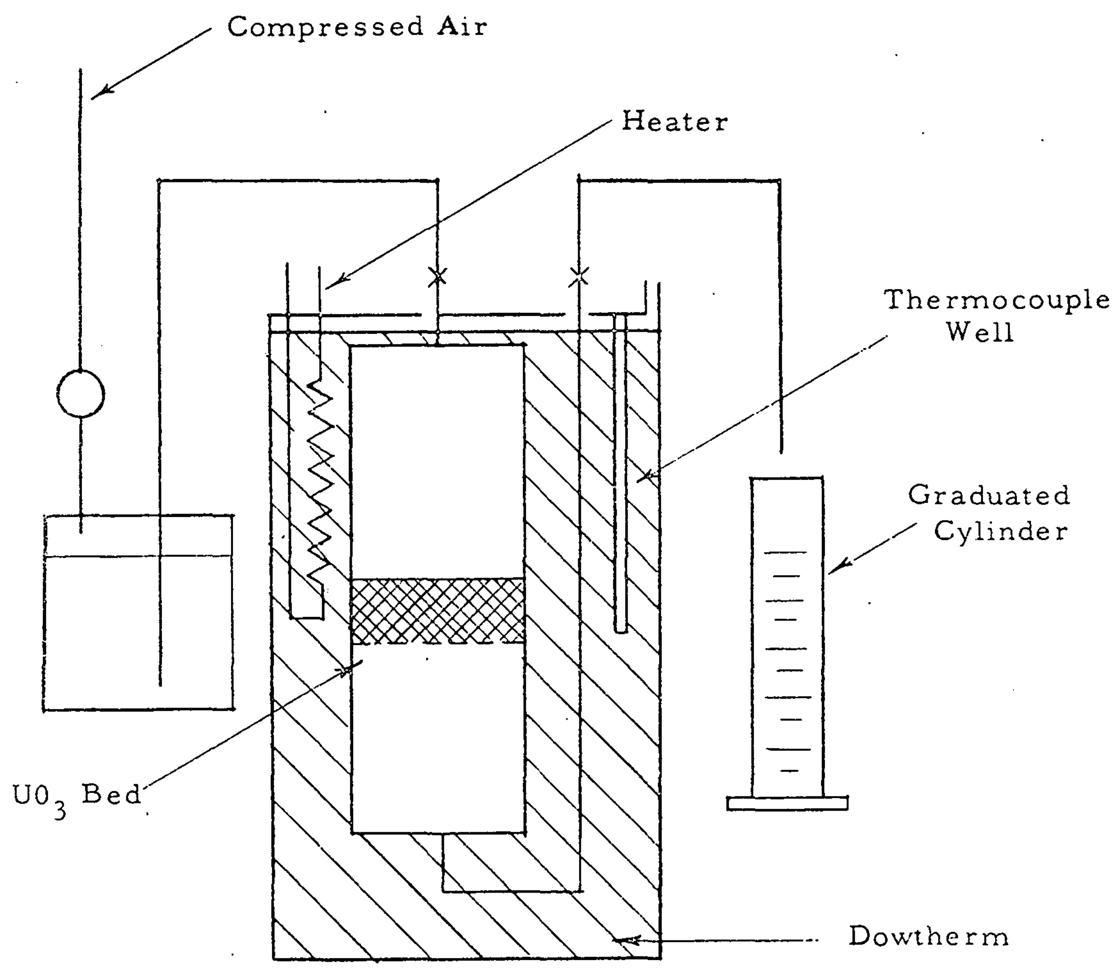

Fig. 5. DOWTHERM-HEATED AUTOCLAVE

into the autoclave and suspended on a 200-mesh stainless steel screen. The autoclave was sealed and heated to 300°F. Periodically the autoclave was cooled down and the permeability of the UO_3 bed was measured.

The 30 to 70 mesh fraction was heated for a total of 123.8 hr and the 70 to 100 mesh fraction was heated for a total of 307.6 hr. In neither case was any significant differences in flow properties found.

Table 4

FLOW RESISTANCE OF URANIUM TRIOXIDE AT 20°C

Flow Rate, lb water/(sq ft)(min)	Pressure Drop, in. of water/in. of bed 30-70 mesh	70-100 mesh
20	1.0	3.5
30	1.6	6.7
40	2.2	10.4
50	2.9	14.7
60	3.5	18.8
80	5.0	29.0
100	6.4	40.0

However, some changes in particle size were noticed after the UO_3 had been heated in contact with water. After the 30 to 70 mesh fraction had been removed from the autoclave and rescreened, it was found that 0.7% of the UO_3 was larger than 30 mesh, 95.2% was still in the 30 to 70 mesh range, and 4.3% was smaller than 70 mesh.

The 70 to 100 mesh fraction showed a much greater change in particle size. Thus, after the autoclaving and rescreening, it was found that 30.2% of the UO_3 would not pass the 70 mesh screen, 69.1% was still in the 70 to 100 mesh range, and 0.7% was smaller than 100 mesh.

The seemingly large difference in the particle growth of the two fractions can probably be explained by the fact that the 30 to 70 mesh fraction contains relatively few particles which are very close to 30 mesh in size.

Thus, the particles can grow considerably and still pass through the 30 mesh screen.

In washing the UO_3 fractions preparatory to their introduction into the autoclave, it was found that a considerable amount of UO_3 could be washed off as slime. For example, 18.8 g of the 70 to 100 mesh UO_3 fraction was washed 15 times with 50-cc portions of distilled water. These washings were dried and weighed to determine the amount of suspended UO_3. A total of 2.4% of the UO_3 was washed off in this manner.

The bulk densities of the 30 to 70 and 70 to 100 mesh fractions were also determined when the fractions were deposited from the water slurry. These were 3.34 and 3.74 g/cc, respectively.

IV. CONCLUSIONS

1. Uranium dioxide powder* as commercially prepared is wet by NaK at approximately 400°C.

2. Once wetted, the UO_2 does not "de-wet" when cooled below 300°C.

3. Although flocculation may occur at higher temperatures, the system does not become rigid, and it can still be pumped and redispersed under the conditions of this investigation.

4. Hydrated uranium trioxide in sizes ranging from 30 to 100 mesh can be treated in contact with water to 300°F for long periods of time without the physical dimensions of the particles being materially affected.

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*Micronized UO_2 - Malincrodt Chemical Co.

APPENDIX A

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APPENDIX B

PHYSICAL PROPERTIES OF BOEHMITE

As a supplement to the work performed at the Foundation for the Argonne National Laboratory under Project C 124, a study was made of some physical properties of two samples of Boehmite. These are classified as Boehmite No. 2, a high purity sample, and Boehmite No. 1, of somewhat lesser purity. The following discussion refers to Boehmite No. 2 unless otherwise noted.

Initial attempts to separate a narrow size fraction in the 1-micron range failed when examination showed that there was very little material in this range. While it was not clearly established whether the larger sizes were due to agglomeration, superficial treatment produced negligible attrition. The material was therefore ball-milled in a porcelain mill with agate balls in an aqueous medium. The milled powder was washed with CP hydrochloric acid and then allowed to settle in water. The various settled fractions were separated and examined for size. The size range corresponding to about 1 micron was collected, about 10 grams were submitted to the Argonne Laboratory, and a fraction was reserved for surface area and particle size study.

Figure 1B shows the size distribution of the original sample on a weight basis, determined with the Sharples micromerograph. Figure 2B is the distribution of the sized fraction supplied to Argonne, on a count basis.

Surface area measurements were made on a portion of the sized fraction using the method of Brunauer, Emmett and Teller.* The Boehmite was desiccated and heated to 180°C under vacuum prior to the measurement.

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*Bugge, P. E. and Kerlogue, R. H. J.S.C.I. 66, 377, 1947.

A 2.22-g sample was used, and five points were determined in the adsorption isotherm. A density of 3.01 was used.

The surface area obtained was 28 sq m/g. The superficial surface area of 1 g of 1-micron spheres is calculated to be about 2 sq m. Thus, a high internal surface must be present in the Boehmite unless a large number of fines are present.

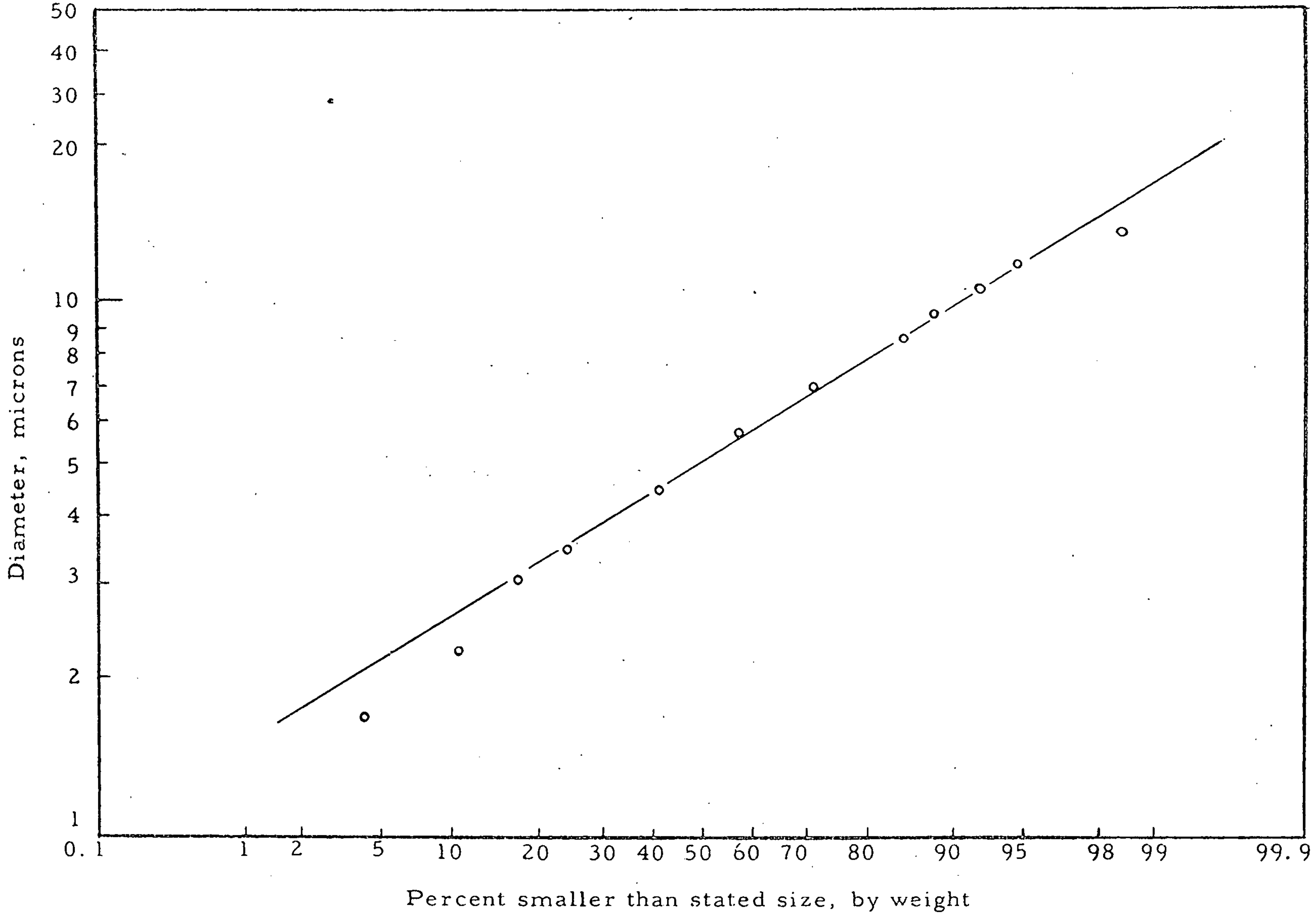

Fig. 1B. SIZE DISTRIBUTION OF ORIGINAL BOEHMITE

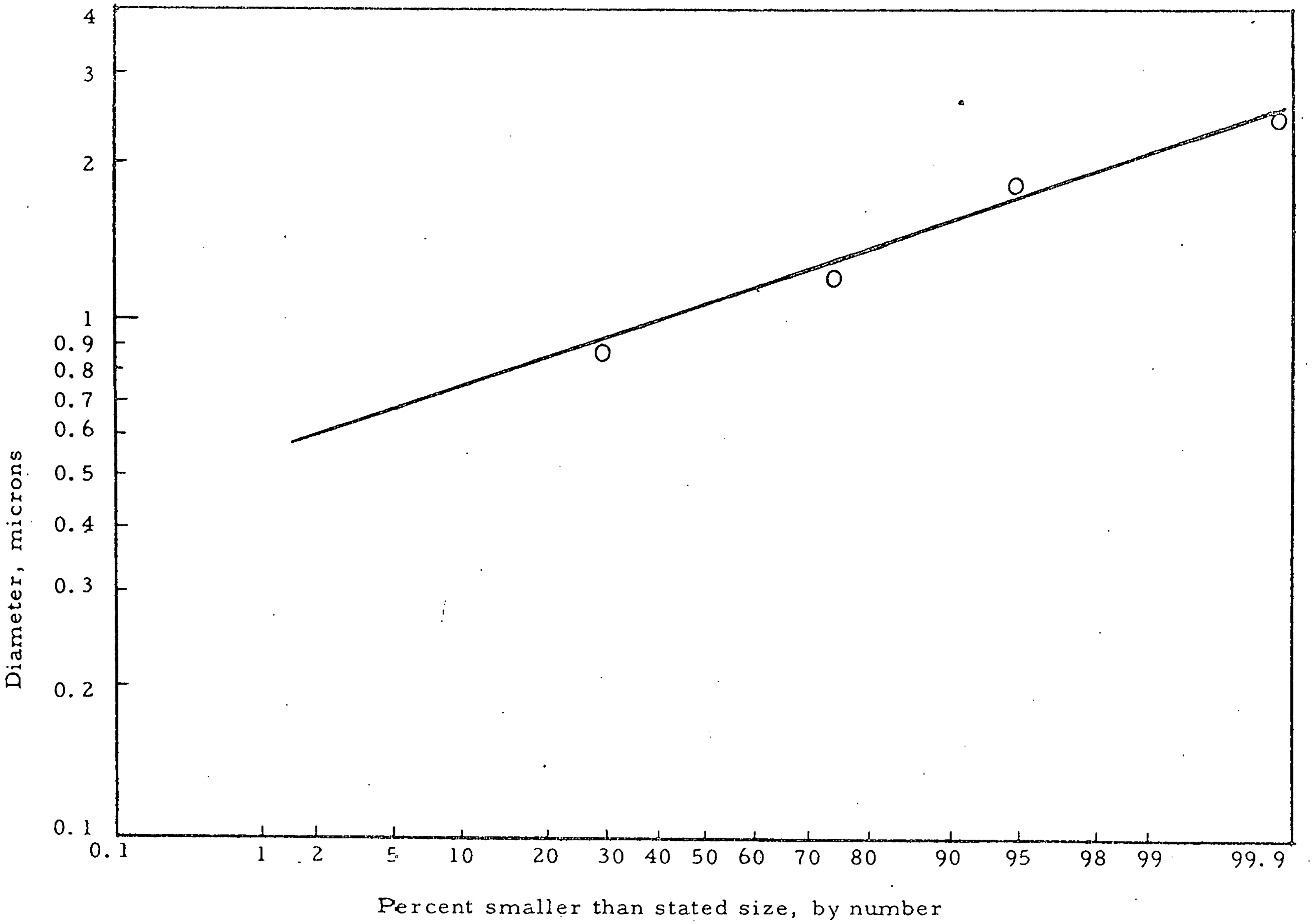

Fig. 2B. SIZE DISTRIBUTION OF CLASSIFIED BOEHMITE

APPENDIX C

SIZE DISTRIBUTION AND ANALYSIS OF IMPURITIES OF URANIUM DIOXIDE

The size distribution of four samples of $U0_2$, received from Argonne National Laboratory was measured by optical microscopy. The samples consist of:

1. micronized $U0_2$ - as received from Malinckrodt Chemical Company,
2. production work $U0_2$ - as received from Malinckrodt Chemical Company,
3. toluene-ground $U0_2$ - ball-milled in toluene at Argonne National Laboratory,
4. high-fired $U0_2$ - fused and ground $U0_2$.

The size distributions are shown graphically in Fig. 1C and 2C.

The toluene-ground sample was also analyzed for impurities by mass spectrometry of the gases evolved during heating. The results are shown in Table 1C.

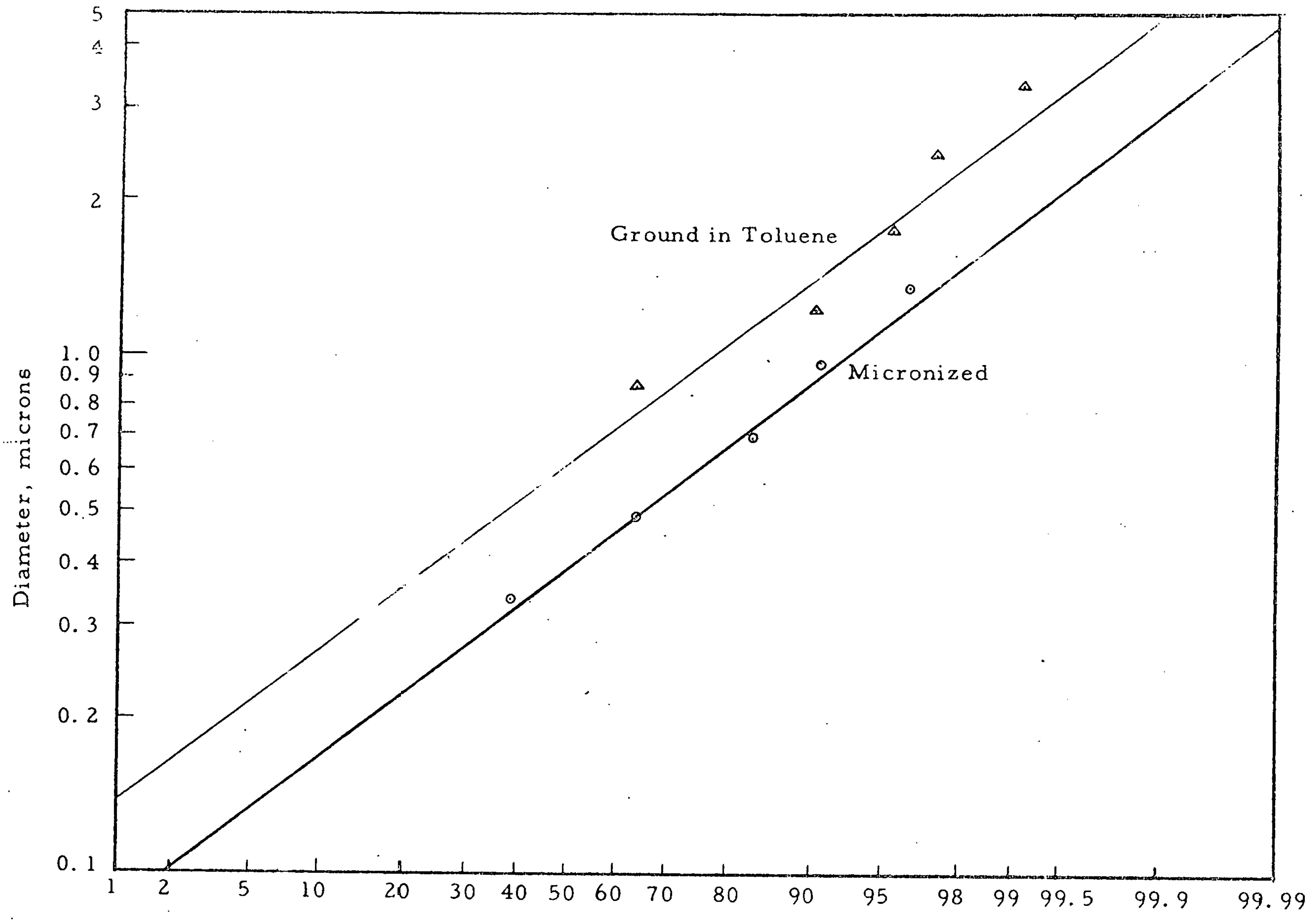

Fig. 1C. SIZE DISTRIBUTION OF FINE UO_2

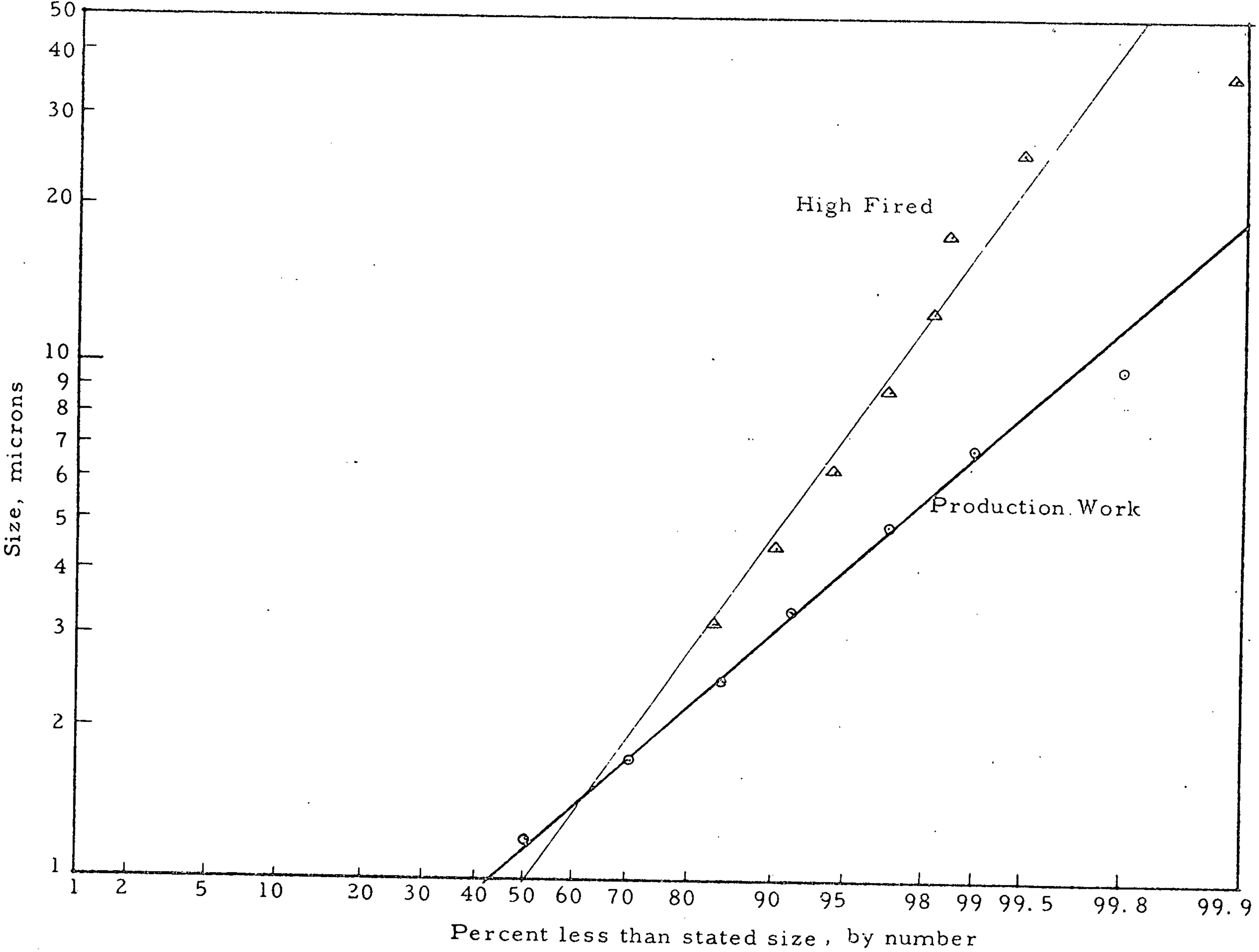

Fig. 2C. SIZE DISTRIBUTION OF COARSE UO_2

Table 1C

IMPURITIES PRESENT IN TOLUENE-GROUND URANIUM DIOXIDE
(By Mass Spectrometry)

Temperature Range	20-110°C	110-300°C	300-500°C	500-800°C
N_2	-	0.0	1.0	0.8
CO	-	3.8	6.7	0.5
CO_2	-	93.1	89.3	97.7
H_2	-	0.5	2.7	0.0
CH_4	-	0.2	0.0	0.0
Toluene	-	0.7	0.3	0.1
Nitrogen Oxide	-	1.7	0.0	0.9
		100.0	100.0	100.0
Total evolved gas, cc/g, dry		0.32	0.22	0.50
Free water, %		20.1	0.6	16.6