

**UNCLASSIFIED**

KAPL-1380(Del.)

METALLURGY AND CERAMICS

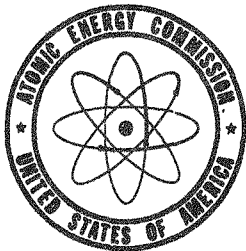
UNITED STATES ATOMIC ENERGY COMMISSION

**PREPARATION OF SPHERICAL URANIUM  
POWDER BY REDUCTION OF URANIUM  
TRIOXIDE WITH CALCIUM**

By  
A. P. Beard  
F. K. Heumann

July 22, 1955

Knolls Atomic Power Laboratory  
Schenectady, New York



Technical Information Service Extension, Oak Ridge, Tenn.

**UNCLASSIFIED**

## **DISCLAIMER**

**This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.**

## **DISCLAIMER**

**Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.**

Date Declassified: February 25, 1957.

Work performed under Contract W-31-109-eng-52.

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, express or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission to the extent that such employee or contractor prepares, handles or distributes, or provides access to, any information pursuant to his employment or contract with the Commission.

This report has been reproduced directly from the best available copy.

Issuance of this document does not constitute authority for declassification of classified material of the same or similar content and title by the same authors.

Since nontechnical and nonessential prefatory material has been deleted, the first page of the report is page 5.

Printed in USA. Price 40 cents. Available from the Office of Technical Services, Department of Commerce, Washington 25, D. C.

CONTENTS

	<u>Page</u>
ABSTRACT . . . . .	7
INTRODUCTION . . . . .	9
MATERIALS AND APPARATUS . . . . .	10
Materials . . . . .	10
Uranium Trioxide . . . . .	10
Calcium Chloride . . . . .	13
Apparatus . . . . .	13
Bombs . . . . .	13
Bomb Liners . . . . .	14
Heating Unit . . . . .	14
EXPERIMENTAL PROCEDURES AND RESULTS . . . . .	14
General . . . . .	14
Procedure . . . . .	15
Results . . . . .	17
Effect of Calcium Chloride . . . . .	17
Effect of Calcium . . . . .	21
Effect of Particle Size of Calcium Chloride . . . . .	21
Effect of Heating Rate . . . . .	22
Effect of Pressed Charges . . . . .	22
Effect of Calcium-Iodine Boosters . . . . .	22
Effect of Charge Segregation . . . . .	22
Effect of Moisture Content of Uranium Trioxide . . . . .	25
Effect of Magnesium as a Reducing Agent . . . . .	25
Effect of Uranium Fluoride as a Booster Flux . . . . .	27
Large Scale Reductions . . . . .	28
Effect of Sodium Chloride as a Flux . . . . .	28
Analysis of Uranium Metal Produced . . . . .	28
CONCLUSIONS . . . . .	29
REFERENCES . . . . .	32

GRAPHICS

	<u>Page</u>
KS-2727	Standard Free Energies of Reaction . . . . . 11
KS-2931	Typical Heating Curve . . . . . 16
KS-2921	Yields of Particles vs $\text{CaCl}_2$ + 20 mesh; -20 + 100 . . . . . 19
KS-2922	Yields of Particles vs $\text{CaCl}_2$ -100 + 325; -325 . . . . . 20
KS-2923	Yields of Particles vs Excess Ca + 20; -20 + 100 . . . . . 23
KS-2924	Yields of Particles vs Excess Ca -100 + 325; 325 . . . . . 24
KS-5360	Spherical Uranium Particles Produced by Reduction of $\text{UO}_3$ with Ca . . . . . 31

ABSTRACT

The reduction of uranium trioxide with calcium metal in a bomb, at elevated temperatures, provides an excellent method for making spherical uranium particles. The yields of metal are high (90 to 95%) and ~50% of the pellets are larger than 325 mesh (43 microns). Spherical uranium particles are of interest for use in a long-lived fuel element, consisting of such particles dispersed homogeneously in a matrix of a ductile, nonfissionable metal or alloy.

ACKNOWLEDGMENT

The authors are indebted to J. Rynaciewicz, F. P. Landis and W. D. Moak for performing the chemical analyses described in this report.



## PREPARATION OF SPHERICAL URANIUM POWDER BY REDUCTION OF URANIUM TRIOXIDE WITH CALCIUM

A. P. Beard and F. K. Heumann

### INTRODUCTION

Metallic uranium was first prepared successfully by Peligot<sup>1</sup> more than 100 years ago by the reduction of uranium tetrachloride with metallic potassium. Following this, other workers reduced uranium oxides with carbon, calcium, magnesium, or aluminum. Uranium halides were reduced with alkali or alkaline earth metals. Most of the metal produced by these reductions was in the form of powder.

At present, the uranium tetrafluoride reduction with magnesium is used on a large scale to produce massive pieces of uranium.<sup>2</sup> Uranium powder has been made in the United Kingdom by the reduction of uranium dioxide with calcium or magnesium.<sup>3,4</sup> The resultant powder is nearly spherical and ranges from 5 to 20 microns in size. Uranium dioxide is also reduced to uranium hydride by calcium hydride.<sup>5</sup> Decomposition of the uranium hydride results in finely divided metal of irregular shape. Powder produced by electrodeposition is also irregular in shape and difficult to process.

A need for spherical uranium pellets with a variety of mesh ranges has been created with the advent of a matrix or dispersion-type fuel element. Each uranium pellet would be surrounded by a matrix of magnesium, zirconium, or other suitable metal, thus confining radiation damages to a small volume and fission fragment damage in the matrix to a minimum. One possible way of making these pellets might be by atomization. In this case, an arc is struck between two uranium electrodes and a stream of inert gas blown through the arc. The resultant powder is spherical.<sup>7</sup> Another method might be the use of a shot tower.<sup>8</sup> The reduction of uranium trioxide by calcium or magnesium presents the most favorable method of making pellets with existing equipment at this Laboratory. In addition, it affords a means of studying a potential method of eliminating fluoride reductions in the production of uranium metal.

Thermodynamic calculations indicate that the uranium trioxide reduction with calcium is more feasible from the viewpoint of free energy considerations and is more exothermic than the uranium dioxide reduction with calcium or magnesium or the uranium trioxide reduction with magnesium. The uranium trioxide reduction should, therefore, result in the production of more massive uranium. The following table summarizes the data for each system that might be considered.<sup>9</sup>

TABLE I STANDARD FREE ENERGIES OF REACTIONS

<u>System</u>	<u>T<sub>max</sub> (°K)</u> (Calc)	<u>ΔH<sub>298</sub></u> Kcals	<u>ΔF<sub>298</sub></u> Kcals
UO <sub>3</sub> + 3 Ca	4055	-160.9	-157.2
UO <sub>3</sub> + 3 Mg	3722	-140.4	-135.7
UO <sub>2</sub> + 2 Ca	1888	- 42.1	- 39.9
UO <sub>2</sub> + 2 Mg	1858	- 28.4	- 25.5

The theoretical maximum temperature reached in the reaction was calculated assuming no heat losses and complete reaction of stoichiometric amounts of the reactants.<sup>10</sup> Referring to KS-2727, it is of interest to note that the ΔF° for the fourth system falls to zero at a temperature of 1600°K. Thus, care must be taken to keep the temperature below this value during the reduction. Calculations show that ΔF becomes negative at this temperature if the magnesium is at a higher pressure than the standard state of 1 atmosphere. At a magnesium pressure of 25 atmospheres, ΔF is -20,000 cal. Thus the reaction could be carried out at a higher temperature providing the magnesium could be contained. This same reasoning could be applied to reaction 2 and also to reactions 1 and 3 although perhaps to a lesser degree.

The use of a salt flux has been found to be beneficial in reactions involving a solid - liquid reaction. The use of calcium chloride in the calcium reduction of various oxides was used a number of years ago.<sup>11</sup> The calcium chloride may serve as a fluxing agent by dissolving the calcium oxide produced. This gives a fresh surface of calcium and uranium trioxide at all times and results in a faster reaction and probably a higher instantaneous temperature. It may serve also to initiate the reduction by forming liquid calcium chloride-calcium<sup>12</sup> or calcium chloride - calcium - uranium trioxide phases.

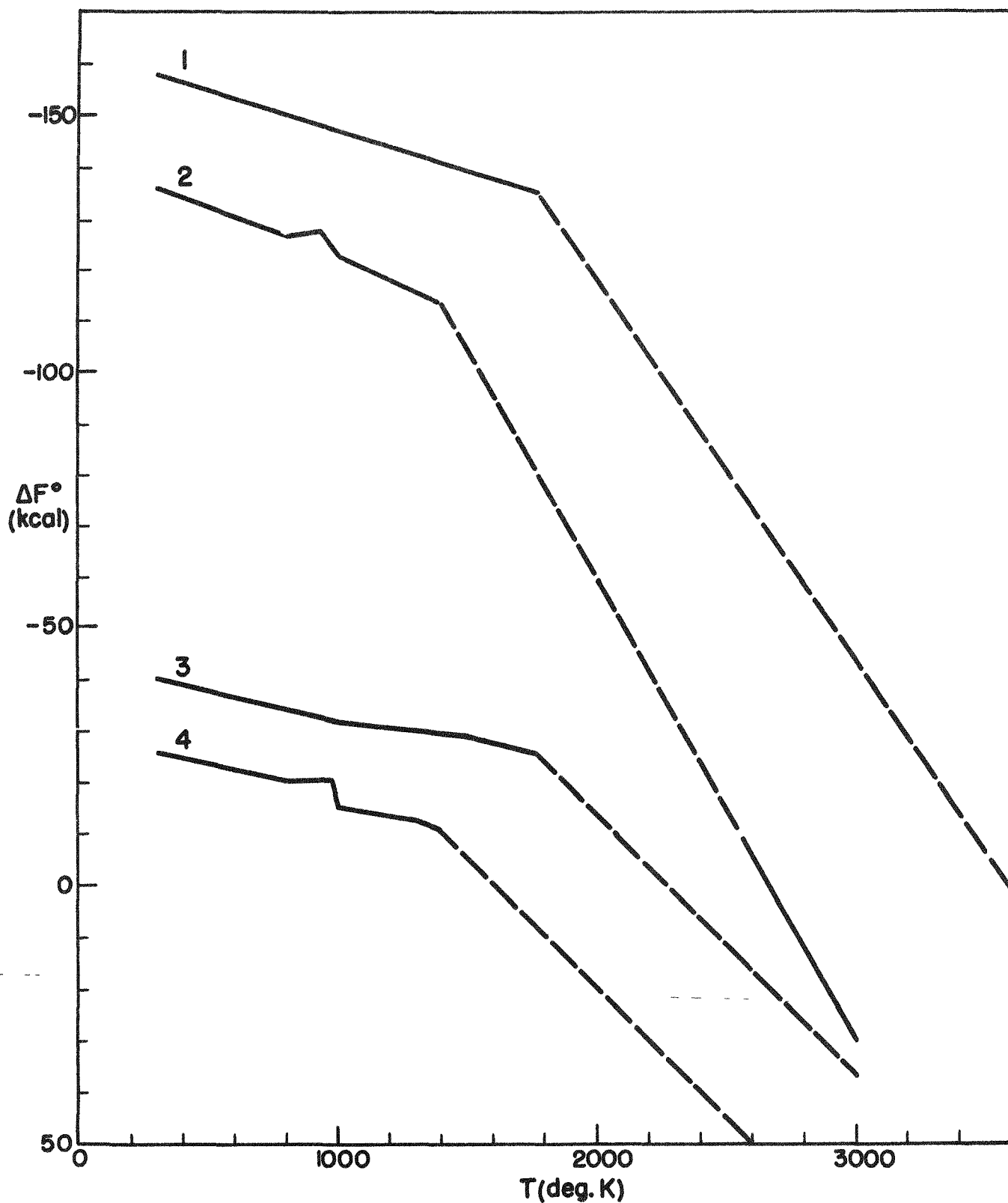
On the basis of the preceding data, the uranium trioxide reduction with calcium appears to be most satisfactory from a standpoint of producing massive pieces of uranium. A higher temperature is attained which may promote agglomeration of the uranium and at least produce larger uranium powder particles than are obtained in uranium dioxide reductions.<sup>3,4</sup>

## MATERIALS AND APPARATUS

### Materials

#### Uranium Trioxide

The uranium trioxide used in this work was obtained from the Mallinckrodt Chemical Works. A typical chemical analysis is given in Table II.



STANDARD FREE ENERGIES OF REACTIONS  
 (1)  $\text{UO}_3 + 3\text{Ca} = \text{U} + 3\text{CaO}$ ; (2)  $\text{UO}_3 + 3\text{Mg} = \text{U} + 3\text{MgO}$ ; (3)  $\text{UO}_2 + 2\text{Ca} = \text{U} + 2\text{CaO}$ ; (4)  $\text{UO}_2 + 2\text{Mg} = \text{U} + 2\text{MgO}$

KS-2727

TABLE II TYPICAL CHEMICAL ANALYSIS OF UO<sub>3</sub>

<u>Element</u>	<u>ppm</u>	<u>Element</u>	<u>ppm</u>
Al	35	Mn	NF (1)
Ag	0.1	Mo	1
As	NF (100)*	Na	NF (50)
Au	NF (10)	Ni	3
B	0.13	P	NF (500)
Bi	NF	Pb	1
Cd	NF (10)	Pd	NF (5)
Co	5	Re	NF (0.2)
Cr	NF (10)	Sb	NF (10)
Cu	3	Si	90
Fe	10	Sn	1
Ge	NF (1)	Tl	NF (5)
In	NF (2)	V	NF (20)
Mg	12	Zn	NF (50)

\*NF ( ) designates "not found" above minimum figure of sensitivity given in parentheses.

The spectrographic analyses, given in Table II, are normally accurate to approximately +50%. Thermal analyses on the uranium trioxide indicated that it contained 0.75 to 1.25 wt % water. A typical screen analysis of the oxide is given in Table III.

TABLE III TYPICAL SCREEN ANALYSIS OF UO<sub>3</sub>

<u>Mesh Range</u>	<u>Per Cent</u>	<u>Mesh Range</u>	<u>Per Cent</u>
+20	0.82	-150 + 200	5.71
-20 + 35	6.12	-200 + 270	14.69
-35 + 80	13.88	-270 + 325	3.27
-80 + 150	42.55	-325	42.86

### Calcium Chloride

The calcium chloride was Baker and Adamson, Reagent grade, obtained from the Allied Chemical and Dye Corporation, New York, New York. Various mesh sizes were used, ranging from 20 mesh to 1/2-inch lumps. A typical spectrographic analysis of the anhydrous material is given in Table V.

TABLE V TYPICAL SPECTROGRAPHIC ANALYSIS OF CaCl<sub>2</sub>

<u>Element</u>	<u>Impurity ppm</u>	<u>Element</u>	<u>Impurity ppm</u>
Al	80	Mn	4
Cr	40	Na	5000
Cu	20	Si	30
Fe	400	Ti	20
Mg	3	V	450

### Apparatus

#### Bombs

All of the reductions were made in steel bombs. The 1-kilogram bombs were 1 1/2-inches high, 5 inches outer diameter, and had a wall thickness of

3/8-inch. A 1/4-inch deep recess was machined into the flanged top of the bomb. The 1/2-inch thick lid was bolted to the flange of the bomb by means of six bolts. A copper gasket fitted into the recess of the bomb and a knife edge on the lid effected a tight seal. The lid also contained a flare fitting so that the bomb could be evacuated and filled with helium. The 4-kilogram bombs were of similar construction, about 20 inches high, 6.6 inches in outer diameter with a 7/16-inch wall thickness.

#### Bomb Liners

The material was placed in liners which fit inside the bomb. These liners, made of high-fired slip-cast magnesium oxide of low silica content, were obtained from the Norton Company, Worcester, Massachusetts. The 1-kilogram liners were 9 inches high, 3 1/4 inches outer diameter and had a wall thickness of about 1/8 inch. The 4-kilogram liners were 18 inches high, 5 1/2 inches outer diameter, and had a wall thickness of 1/4 inch. They were slightly tapered from top to bottom. Impure magnesium oxide was tamped into the space between the steel bomb and liner. This layer served as insulation and a trap for slag if the crucible broke. The layer also facilitated removal of the crucible after the reaction was completed. A lid, made of fired magnesia, was used to keep the magnesium oxide sand from contaminating the charge, as well as to contain calcium vapors.

#### Heating Unit

The bombs were heated by means of a water-cooled, 10,000-cycle high-frequency induction coil. The height of the coil was such that the lower 8 1/2 inches of the bomb were heated. A motor-generator set provided the power which was passed through a bank of capacitors. By proper selection of the capacitance, the heating could be regulated.

The temperature of the outer surface of the bomb was recorded on a Leeds and Northrup recorder with a scale from 0 to 1200°C. A chromel-alumel thermocouple was inserted into a shallow hole peened into the side of the bomb about 3 inches from the bottom and held in place with asbestos tape.

### EXPERIMENTAL PROCEDURE AND RESULTS

#### General

A number of bomb reductions were made on the 1-kilogram scale to determine the conditions which would give the least amount of -325 mesh powder. The reductions were made under a variety of conditions and the following variables were considered:

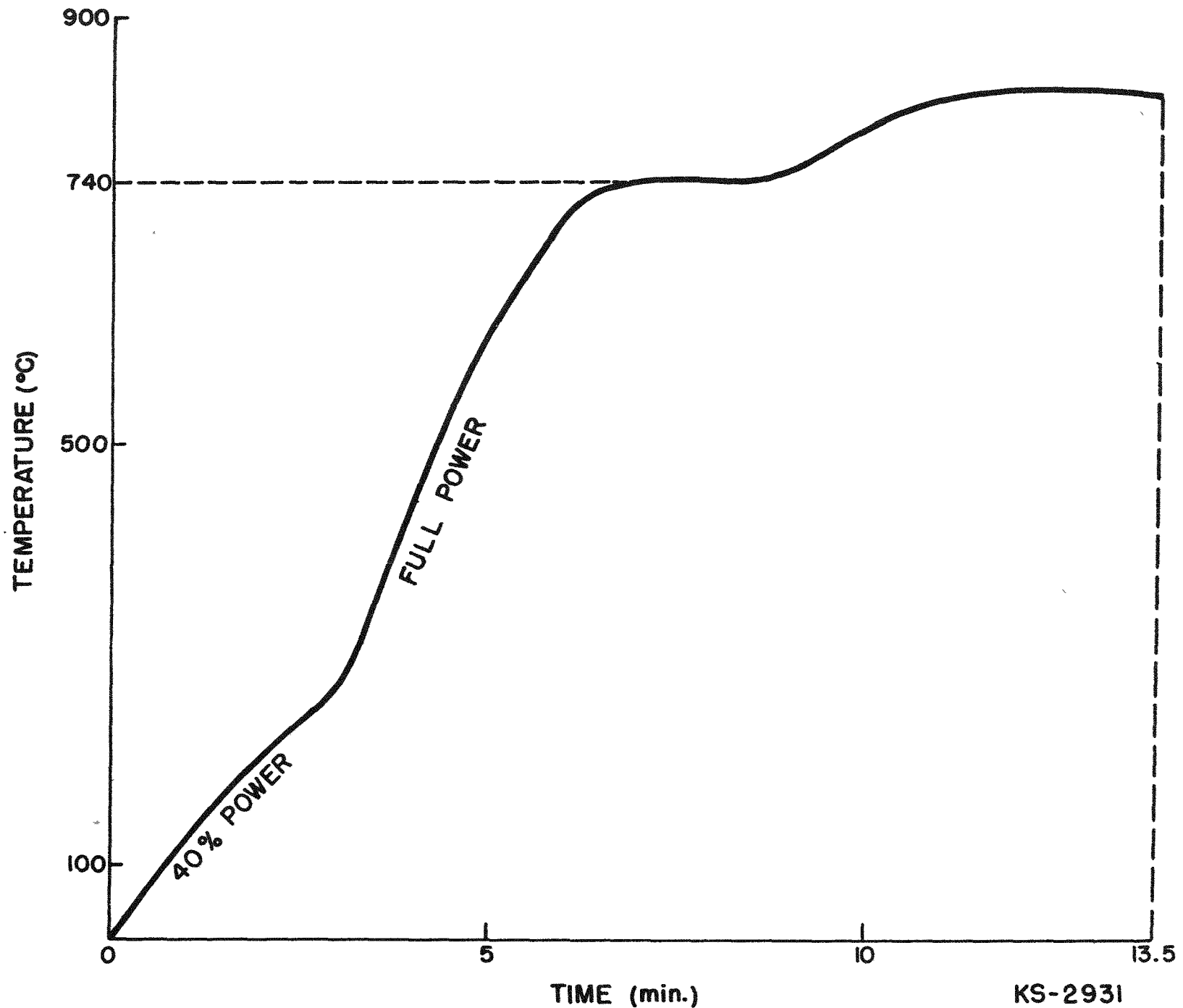
1. Calcium chloride, with uranium trioxide and 50% excess calcium.
2. Excess calcium, with uranium trioxide and a mole ratio of calcium chloride per uranium trioxide of 0.84 moles.

3. Mesh size of calcium chloride.
4. Heating rates.
5. Pressed charges.
6. Calcium-iodine boosters.
7. Charge segregation.
8. Moisture content of uranium trioxide.
9. Magnesium reductant.
10. Uranium tetrafluoride booster-flux.
11. Reduction bomb size.

### Procedure

A standard procedure was adopted with regard to making a reduction. In the first 24 runs the uranium trioxide, calcium chloride, magnesia sand, liner, and bomb were dried in an oven at about 180°C for a period of 15 hours. The uranium trioxide, calcium chloride, and calcium were intimately mixed (by rolling) in a large jar. The liner was placed in the bomb with magnesia sand on the bottom and around the sides. The charge was poured in the liner, the cover put in place, and sand poured on top to fill the bomb. The bomb lid was bolted on with the copper gasket in its recess. The bomb was evacuated and flushed with helium three times and sealed with an atmosphere of helium inside. The bomb was heated, usually at a rate of 100°C per minute. A plateau generally occurred in the temperature - time curve around 740°C before the reaction took place. After the reaction started, an increase in temperature occurred. The external heating was maintained throughout the entire reaction and was discontinued when the temperature started to drop. A typical heating curve is shown in KS-2931.

After the crucible was removed from the bomb it was separated from the melt, usually quite easily, by chipping with a hammer. The crucible was difficult to remove when calcium chloride was not present in the slag. The melt was nonpyrophoric and usually was yellow or green in color. It was dissolved in a 10% acetic acid solution. Ice was added to keep the temperature below 25°C. The calcium oxide, calcium, and calcium chloride went into solution quite readily in most cases. The leaching time of the massive reaction product was about 4 hours. After leaching, the uranium was screened into four fractions, +20 mesh, -20 to +100 mesh, -100 to +325 mesh, and -325 mesh. The -325 mesh uranium powder was recovered by filtering the solution that passed through the 325 screen. It was washed, dried with acetone, and stored. The other mesh sizes were washed, cleaned in nitric acid, dried with acetone, and stored. It was found that surface oxidation was reduced if the uranium was stored dry in closed bottles rather than under acetone or benzene. Even the -325 material was generally nonpyrophoric.



TYPICAL HEATING CURVE OF SMALL SCALE REDUCTION



## Results

### Effect of Calcium Chloride

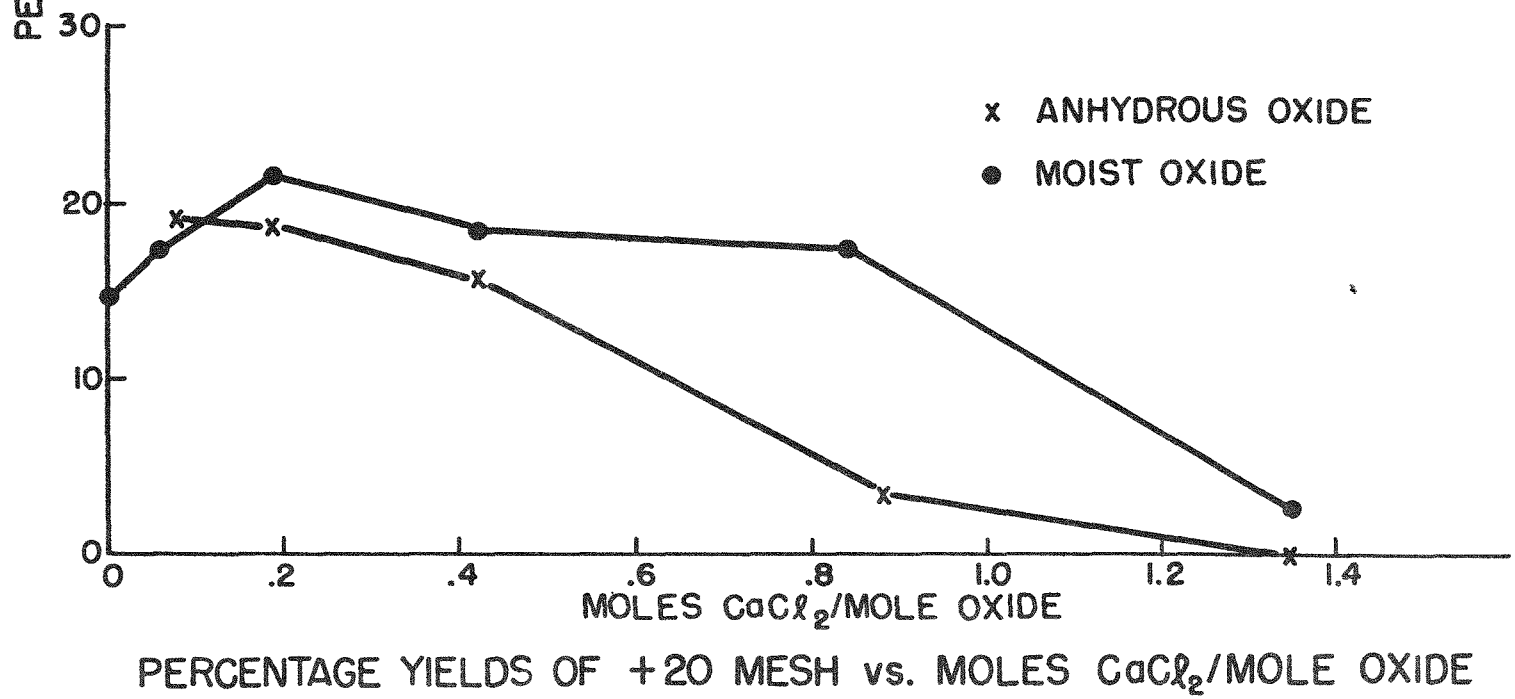
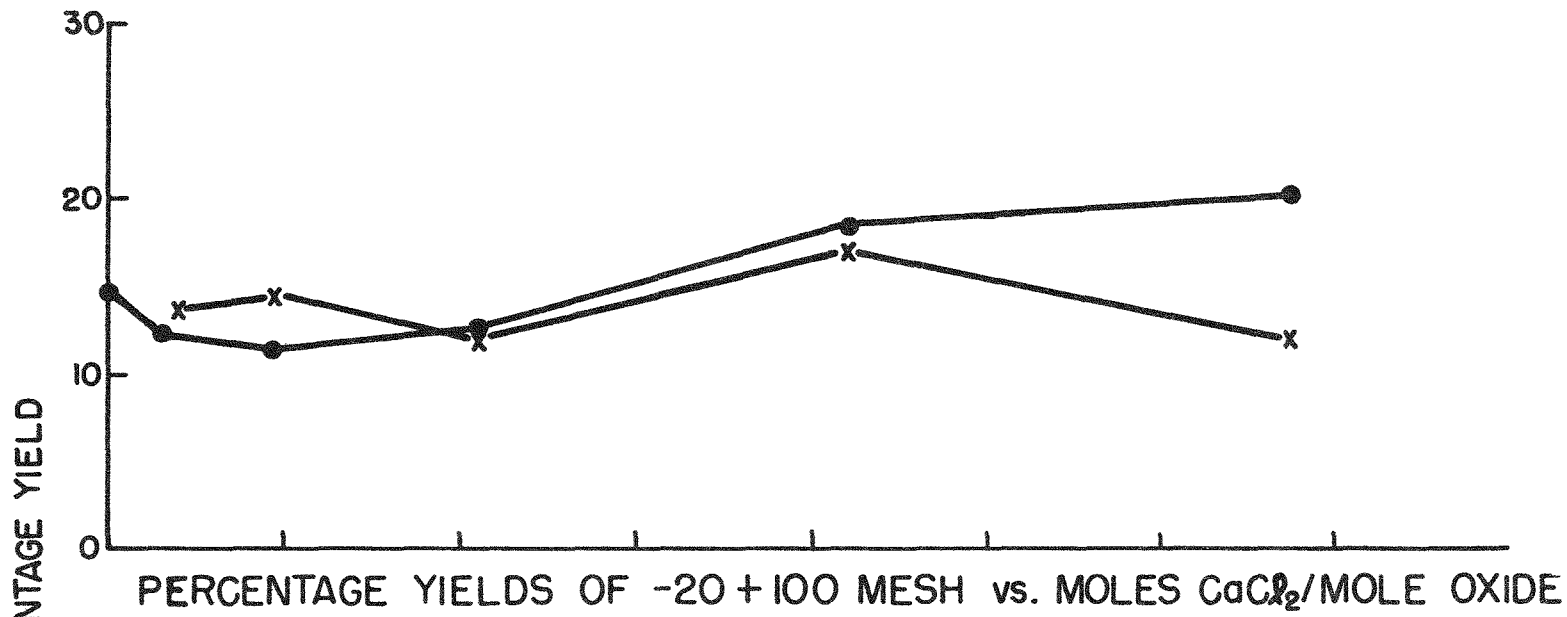
A series of runs was made to determine the effect of the amount of calcium chloride used on the particle size distribution. The calcium chloride should act as a flux by removing the calcium oxide from the surface of the calcium and uranium and thus help to promote complete reaction. Each run was made with 15 moles of calcium, 3.32 moles of uranium trioxide, (dried at 180°C) and variable amounts of calcium chloride. Run 7 was an exception, since only 2.92 moles of uranium trioxide and 13.2 moles of calcium could be loaded into the crucible. The calcium chloride used was crushed 1/2-inch lumps. A heating rate of 100°C per minute was used in all of the runs except Run 1 where the rate was 77°C per minute.

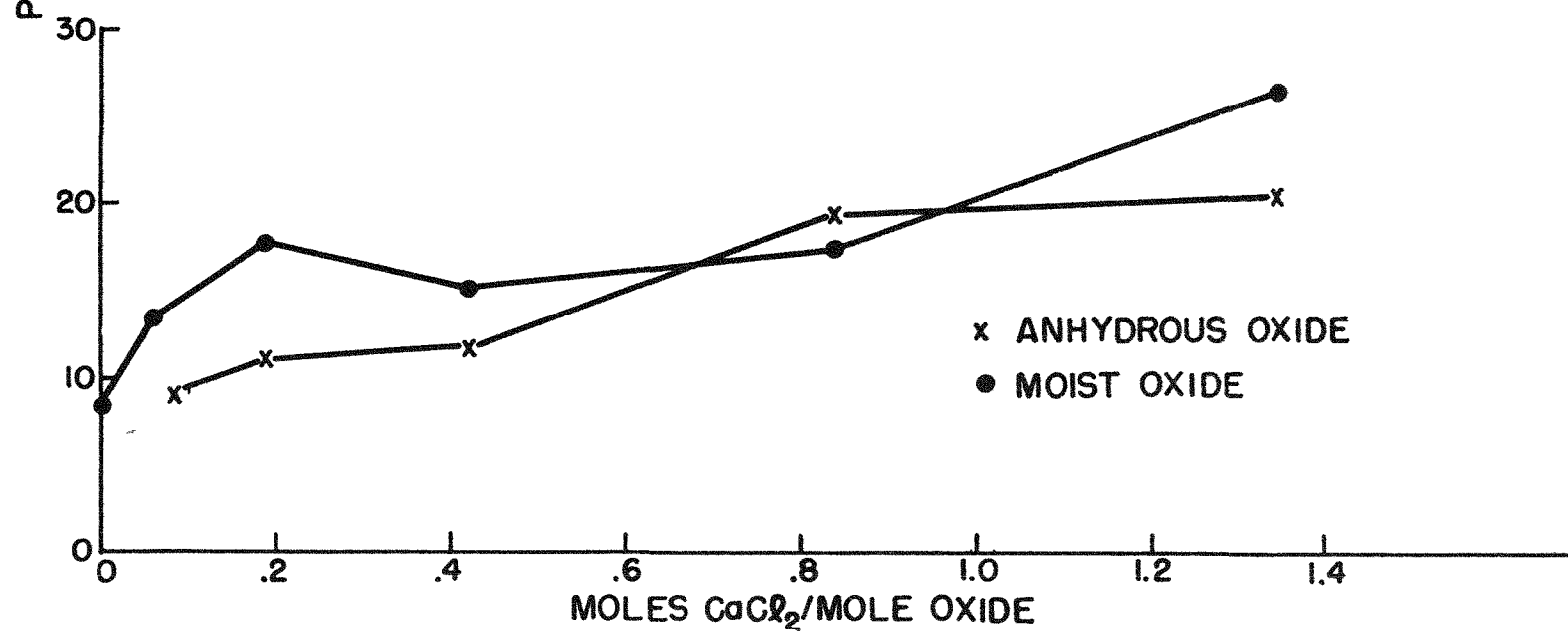
Six different amounts of calcium chloride were investigated ranging from 0 to 1.36 moles of chloride per mole of oxide. The results are given in Table VI, Runs 1 to 8. The +20 mesh material had a general tendency to decrease with an increasing amount of calcium chloride. This relationship illustrated by the lower curve in KS-2921, where the moles calcium chloride per mole uranium trioxide is plotted versus per cent of yield of +20 mesh metal. Conversely, the -20 to +100 and -100 to 325 mesh material shows a slight tendency to increase with increasing calcium chloride. The upper curve in KS-2921 and lower curve in KS-2922 illustrate this effect. There was a definite downward trend in the amount of -325 mesh material with increasing calcium chloride when moist oxide was used. This trend is shown by the upper curve in KS-2922. Reductions containing a mole ratio of calcium chloride per uranium trioxide of 0.84 appear to give the best over-all results for all four of the mesh ranges, and also appear to allow satisfactory processing after reduction. Run 4 was a duplication of Run 1, and the results are in excellent agreement. However, Run 19, a duplication of Run 7, gives much higher yields of the -325 mesh material and lower yields of the other mesh ranges than Run 7. This result indicates that the reductions are not completely reproducible. The average recovery for all of these runs was ~90%, which the authors considered to be fairly good since some of the -325 mesh material was so small it passed through the filter.

Calcium chloride effects the reduction simultaneously as a flux and heat diluent. The fluxing is considered desirable in aiding reaction of uranium trioxide with calcium, and in aiding formation of -325 mesh spherical metal instead of sintered aggregates of this size material. It also promotes separation of the reaction mass from the high-fired magnesia crucible and leaching of this reactor mass to obtain the uranium. As a heat diluent, the calcium chloride is desirable as far as yields of the three size ranges greater than 325 mesh uranium are concerned. For both moist and dry uranium trioxide, the amount of +20 mesh uranium decreases, in general, with increasing calcium chloride, thus indicating that the heat diluent effect has greater influence in this size range, of particles than the fluxing effect does. In the two ranges of particle size, -20 +100 mesh and -100 +325 mesh metal, there is a

TABLE VI. SUMMARY OF REDUCTIONS USING MOIST  $UO_3$ 

Run No.	$UO_3$		$CaCl_2$		Ca		External Temp °C		Percentage Yields in Mesh Ranges				Total Recovery	Heating Rate °C/min	$CaCl_2$ Size	Other Conditions
	g	moles	g	moles	g	moles	Initial	Final	+20	+100	-100	+325				
3	950	3.32	0	0	600	15.0	745	860	15	14.7	8.2	62.1	88	100	Crushed 1/2-in. lump	
8	950	3.32	22	0.20	600	15.0	712	797	17.2	12.2	13.5	57.0	81.2	100	Crushed 1/2-in. lump	
6	950	3.32	70	0.63	600	15.0	730	840	21.7	11.4	17.8	49.1	88.0	100	Crushed 1/2-in. lump	
1	950	3.32	155	1.4	600	15.0	680	780	21.1	12.3	14.9	51.6	62.0	77	Crushed 1/2-in. lump	
4	950	3.32	155	1.4	600	15.0	740	790	18.5	12.5	15.2	53.8	92.0	100	Crushed 1/2-in. lump	
2	950	3.32	310	2.79	600	15.0	730	835	17.7	18.6	17.3	46.3	91.4	100	Crushed 1/2-in. lump	
20	950	3.32	310	2.79	600	15.0	740	865	6.7	19.1	31.3	42.9	87.9	100	20 mesh	7 layers $UO_3$ - $CaCl_2$ between layers of Ca
22	850	2.98	277	2.50	536	13.4	748	835	3.6	16.2	25.1	55.1	89.2	100	20 mesh	7 layers $UO_3$ - $CaCl_2$ between layers of Ca
21	850	2.98	277	2.50	536	13.4	740	825	3.4	14.2	19.4	63.0	87.4	100	20 mesh	3 layers $UO_3$ - $CaCl_2$ between layers of Ca
14	1332	4.66	435	3.92	842	21.1	690	880	5.2	18.1	22.2	55.3	100.0	100	20 mesh	Charge pressed using 5.7 tsi
15	1332	4.66	435	3.92	842	21.1	700	785	2.6	16.2	23.2	57.1	84.	100	20 mesh	Charge pressed using 5.7 tsi
16	950	3.32	310	2.79	600	15.0	680	750	12.4	21.5	14.0	51.1	91.	50	20 mesh	
17	950	3.32	310	2.79	600	15.0	680	835	14.5	15.3	19.5	50.7	91.7	50	4 mesh	
13	795	2.78	260	2.34	520	13.0	670	800	9.2	20.1	29.3	83.3	96.0	100	20 mesh	1/2 mole $I_2$
23	795	2.78	260	2.34	520	13.0	740	795	3.8	12.2	18.5	65.5	92.5	100	20 mesh	1/2 mole $I_2$
24	795	2.78	260	2.34	540	13.5	750	925	9.4	12.1	12.2	66.3	82.0	100	20 mesh	1 mole $I_2$
7	836	2.92	440	3.96	528	13.2	720	790	2.7	20.1	33.5	43.7	96.5	100	Crushed 1/2-in. lump	
19	836	2.92	438	3.94	585	13.1	745	875	1.4	13.2	26.4	59.3	94.5	100	20 mesh	
9	950	3.32	310	2.79	460	11.5	722	800	1.7	15.6	23.5	63.3	104	100	28 mesh	
10	950	3.32	310	2.79	520	13.0	720	790	2.2	17.6	21.1	60.2	86	100	20 mesh	
12	892	3.12	291	2.61	602	15.0	680	820	3.2	17.3	35.9	44.4	101	100	20 mesh	
18	892	3.12	291	2.61	600	15.0	750	850	9.7	16.5	18.8	55.0	93.3	100	20 mesh	
11	837	2.93	273	2.46	600	15.0	720	790	3.5	16.1	16.5	63.9	95.2	100	20 mesh	





PERCENTAGE YIELDS OF -100 + 325 MESH vs. MOLES  $\text{CaCl}_2$ /MOLE OXIDE

KS-2922

slight trend toward greater amounts of each range with increasing calcium chloride. This is considered as an indication that the fluxing effect influences the formation of these particles more than the heat diluent effect. In the -325 mesh particles it appears that in the reduction of moist uranium trioxide the percentage yields decrease with increasing calcium chloride, while just the opposite occurs with dry uranium trioxide. This indicates that the presence of moisture influences the fluxing action of calcium chloride in a favorable manner.

#### Effect of Calcium

A second series of runs was made to determine the effect of the amount of excess calcium used on the particle size distribution. The mole ratio of calcium chloride to uranium trioxide was held constant at 0.84 moles on all of these runs since this value gave the best composite results in the previous series of runs. The calcium chloride flux was 20 mesh material. The results of four Runs, 9, 10, 11, and 12 are given in Table VI. There was only a slight effect on the amount of +20 mesh material produced. The lower curve in KS-2923 increases slightly with increasing calcium, but the total amount of +20 mesh metal produced is relatively small. The amount of -20 to +100 mesh material again shown in KS-2923, remains relatively constant over the range of excess calcium investigated. There is a general tendency for the amount of -100 to +325 mesh metal to decrease in the reduction of moist oxide with an increasing amount of excess calcium. This effect is illustrated by the lower curve in KS-2924. The results for the -325 mesh are somewhat irregular, as can be seen from the upper curve in KS-2924. There is a minimum in the curve at 50% excess calcium and a sharp increase going either to a higher or lower amount of calcium. Run 18 was a duplication of Run 12, made with 60% excess calcium. There is, as can be seen from Table VI, a great difference between the two runs. The -325 mesh metal has increased and the other ranges decreased correspondingly.

In general, the variations in yields of the various mesh sizes of spherical uranium with percentage of excess calcium are not pronounced. Some type of unknown, and unreproducible effect on yields of -325 mesh metal does occur in reduction of moist uranium trioxide with about 50% excess calcium.

#### Effect of Particle Size of Calcium Chloride

Two reductions, 16 and 17, were made with calcium chloride of different particle size +4 mesh and +20 mesh, respectively. A heating rate of 50°C per minute was used. The results given in Table VI show that the -325 mesh yield is essentially the same for each run. The only real difference was in the yields of the two middle mesh ranges where the difference between runs was 5 to 6%. If Run 2, made with 1/2-inch lump calcium chloride, which had been crushed, and a heating rate of 100°C per minute, is compared with Runs 16 and 17, one finds little difference between them except for a slightly lower amount of -325 mesh and a corresponding increase in the +20 mesh. Thus, the conclusion drawn from these results is that the particle size of calcium chloride has little or no effect on the particle size distribution of the uranium product.

### Effect of Heating Rate

Several runs were made to determine the effect on particle size distribution if different heating rates were used. Runs 2, 16, and 17 were identical runs except for heating rate. The first was heated at 100°C per minute while the latter two were heated at 50°C per minute. These runs were discussed in the previous paragraph and were in agreement with each other within 4%. Runs 1 and 4 were also identical except for the heating rate. Run 1 was heated at 77°C per minute and Run 4 at 100°C per minute. Again the results were almost identical, agreeing to within 3%. It is apparent, on the basis of these results, that heating rate has little effect on the particle size distribution.

### Effect of Pressed Charges

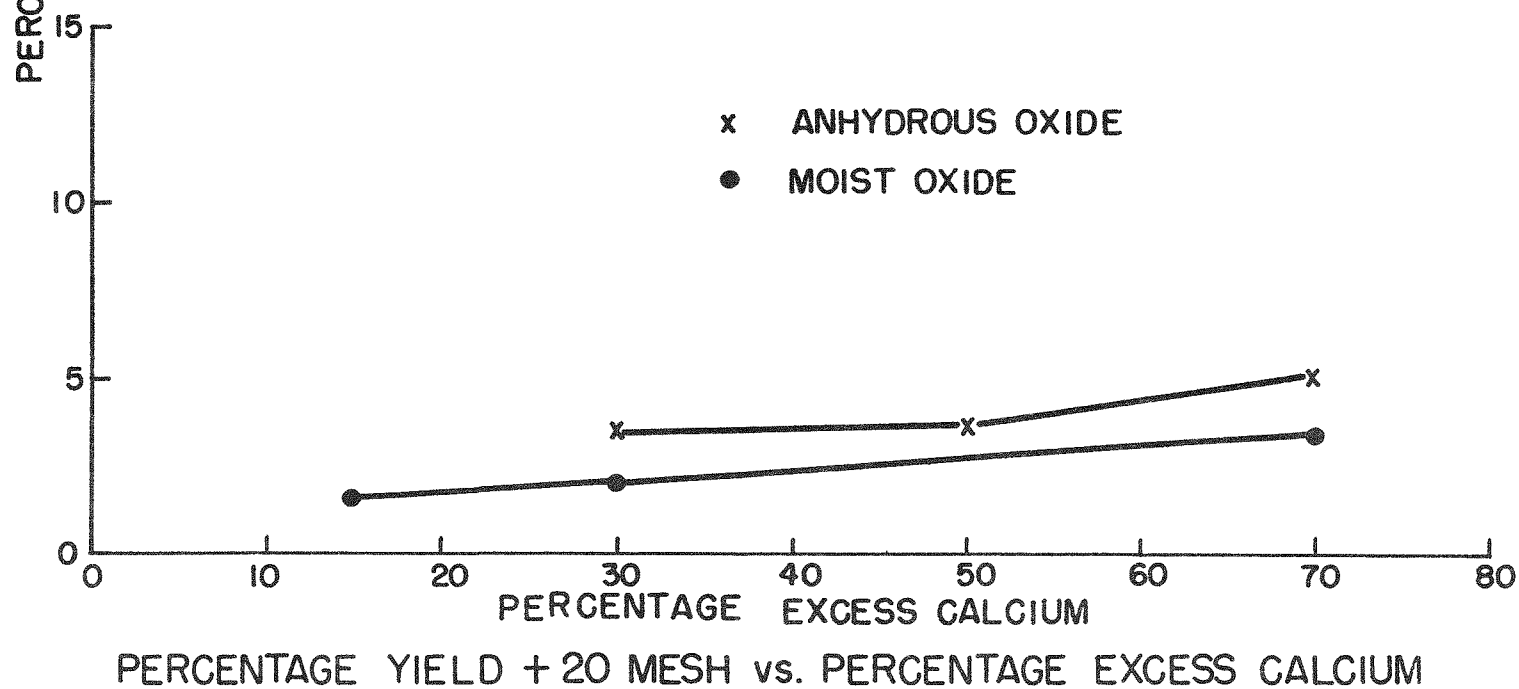
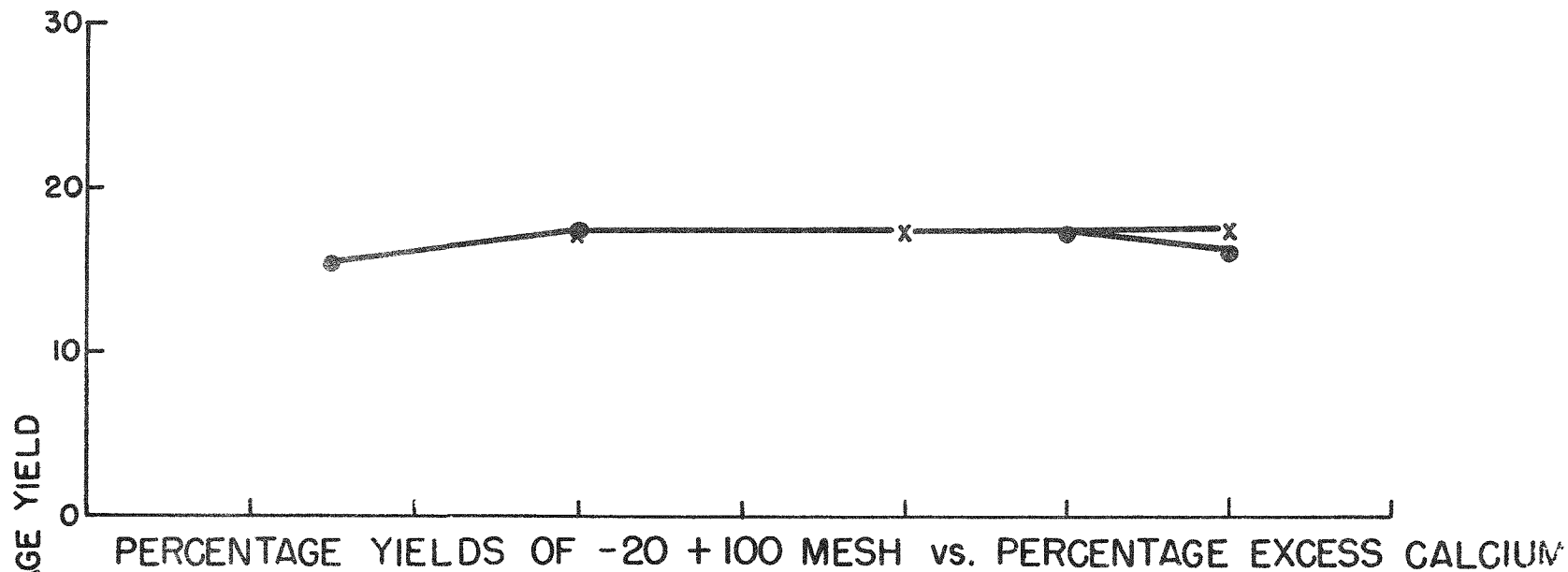
Two reductions were made to determine if compressing the charge would have any effect on the yield. Each charge contained 0.84 moles of calcium chloride per mole uranium trioxide and 50% excess calcium and was pressed into four cakes under 40-ton pressure. This procedure resulted in a charge 33% more dense than the normal charge and thus should give 33% more heat liberated in the reaction. Runs 14 and 15 were made as described above. The amount of -325 material increased noticeably as compared to a normal run (Run 2). There was also a slight increase in the amount of -100 to +325 mesh material but a substantial decrease in the +20 mesh yield. Pressing the charge does not, apparently, increase the over-all yields of the first three mesh ranges, but does increase the amount of -325 mesh. Thus, this method does not appear to be of any value and was not considered useful.

### Effect of Calcium-Iodine Boosters

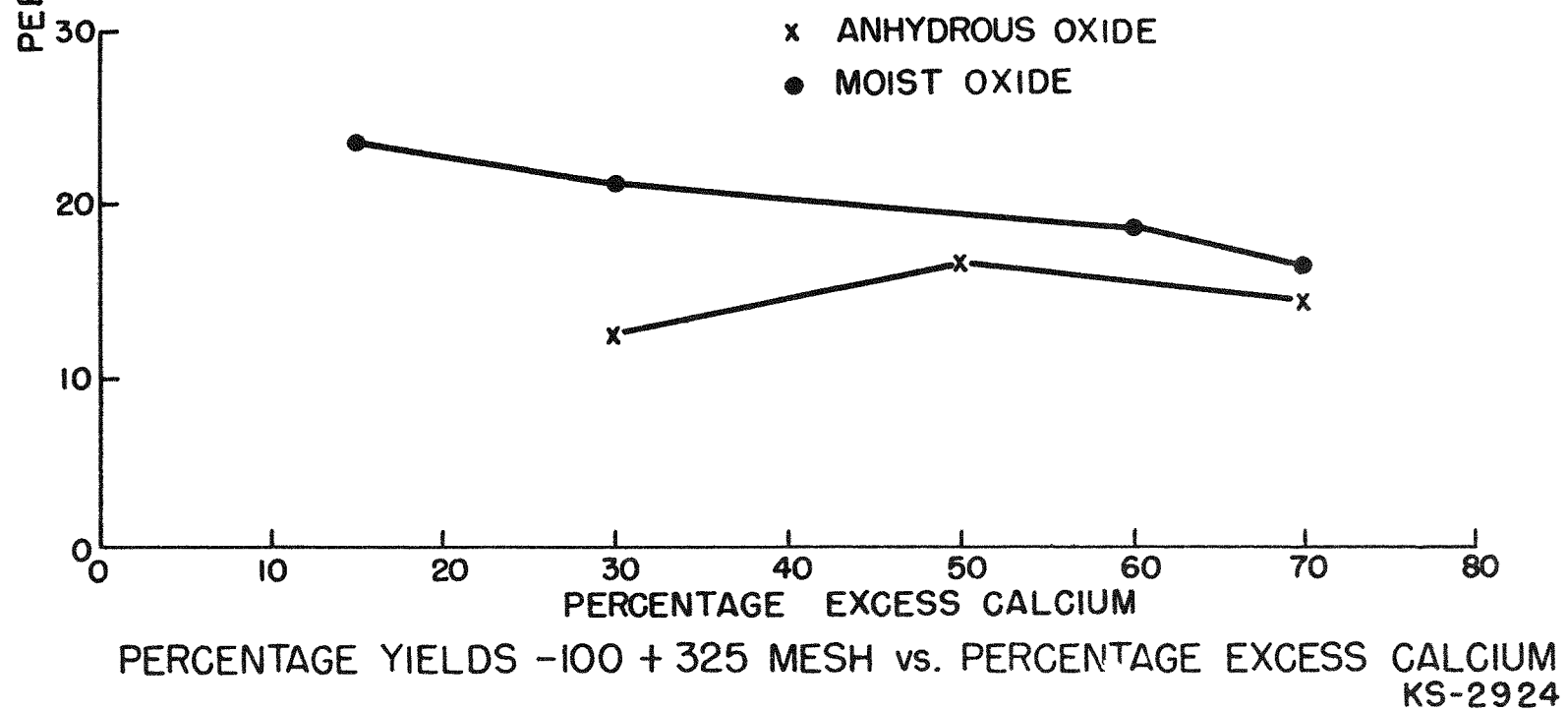
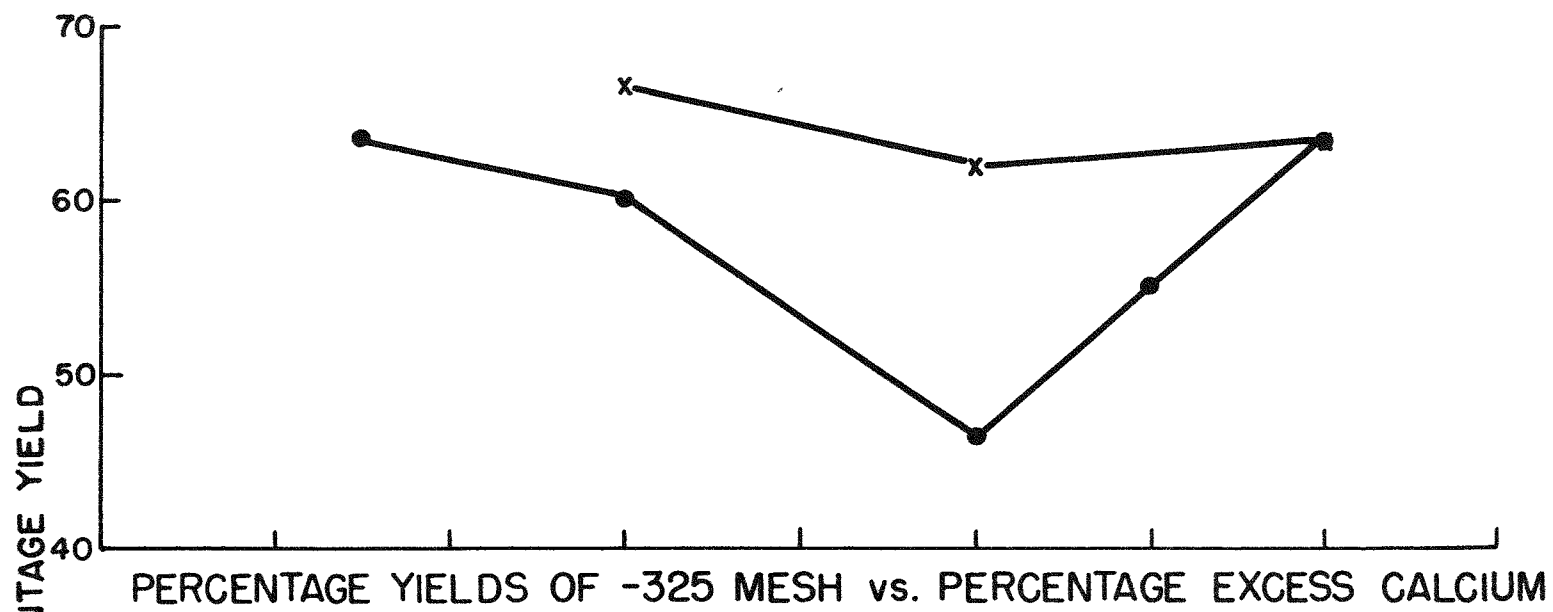
Three runs were made using the calcium and iodine reaction to add more heat to the charge. Each run contained 50% excess calcium and 0.84 moles calcium chloride per mole uranium trioxide. Two Runs, 13 and 23, were made with 0.5 moles iodine added and Run 24 contained 1 mole iodine. Additional calcium was added in each case to react with the iodine. The results, given in Table II, have a great deal of scatter. The -325 mesh is relatively low in Run 13 while in Run 23, which is a duplicate run, it is 50% higher. Similarly, the -100 to +325 mesh material has a fairly high percentage in Run 13 and is considerably lower in Run 23. The reduction made with 1 mole of iodine, Run 24, had the highest yield of -325 mesh and the lowest yields for the middle two mesh ranges. These results indicate that the addition of a booster is not feasible if it is done in this manner. Since the amount of uranium trioxide had to be cut down to make room for the iodine, some heat was lost and the addition of iodine did not make up for it. The reductions do not appear to be reproducible in this case, as was also true in the preceding cases.

### Effect of Charge Segregation

Three runs were made in which the uranium trioxide-calcium chloride mixture was segregated from the calcium. This was done to investigate the



KS-2923





influence of local concentrations of uranium trioxide on the particle size distribution. All of the runs were made using 50% excess calcium, 0.84 moles calcium chloride per mole uranium trioxide, and either 2.98 or 3.32 moles of uranium trioxide. The results of the reductions, 20, 21, and 22, are given in Table II. The -325 mesh is fairly low and the -100 to +325 mesh relatively high in Run 20 made with 7 layers of uranium trioxide-calcium chloride sandwiched between layers of calcium. A repeat run, Run 22, although made with less uranium trioxide, resulted in a substantially greater amount of -325 mesh and a slightly lower amount of -100 to +325 mesh. A third run, Run 21, was made with 3 layers of uranium trioxide-calcium chloride. In this case there was a large amount of -325 mesh material and a corresponding decrease in the other mesh ranges. It should be noted that the recoveries are somewhat lower than normal in all cases.

It appears that segregation of uranium trioxide-calcium chloride and calcium in 7 alternate layers does not affect the reduction yields of +325 mesh metal unfavorably. However, the reduction of a charge composed of 3 alternate layers definitely increased the yield of -325 mesh metal. All 3 reductions of segregated charges resulted in lower total yields than reductions of well-mixed reactants under similar conditions.

#### Effect of Moisture Content of the Uranium Trioxide

The uranium trioxide used in reductions listed in Table VI was assumed to be anhydrous and was dried at 180°C. It was later found to contain from 0.75 to 1.25% by weight water. A thermal analysis indicated that it was necessary to heat this material to 450°C to remove all the water. A number of runs made with uranium trioxide dried at 450°C is given in Table VII.

Comparisons of the effects of calcium chloride and calcium respectively on the yields of various mesh sizes of uranium from moist and dry uranium trioxide have been given in detail in previous discussions (see pp. 19-23). In summary, however, a definite advantage of using moist oxide is indicated in the decrease of -325 mesh uranium with increasing calcium chloride as shown in KS-2922. The effect of calcium on the yields of -325 mesh metal is not as clear cut (KS-2924) as the effect of calcium chloride.

#### Effect of Magnesium as a Reducing Agent

Several reductions were attempted using magnesium instead of calcium as the reducing agent. Each run contained 0.84 moles calcium chloride per mole uranium trioxide and 50% excess magnesium. The first run was made by the usual method, and a large amount of the magnesium vaporized and condensed on the lid and upper walls of the crucible. The melt was coke-like in appearance and was apparently composed of uranium dioxide and metal. In the second run a smaller charge was used and the void volume of the crucible was filled with a thick layer of magnesium oxide and a layer of tamped magnesia. A lid placed immediately on top of the charge prevented contamination from magnesium oxide.

TABLE VII SUMMARY OF REDUCTIONS USING MOIST UO<sub>3</sub>

Run No.	UO <sub>3</sub>		CaCl <sub>2</sub>		Ca		External Temp °C		Percentage Yields in Mesh Ranges					Total Recovery
	g	moles	g	moles	g	moles	Initial	Final	+20	-20 + 100	-100 + 325	-325		
25	950	3.32	310	2.19	600	15	735	800	3.8	17.1	19.5	59.8	87	
26	836	2.92	438	3.94	525	13.1	740	795	0	12.1	20.4	67.8	92	
27	950	3.32	155	1.40	600	15	740	875	15.9	12.0	11.9	60.2	80.5	
28	950	3.32	310	2.79	600	15	765	840	4.8	17.6	16.6	59.8	88.6	
29	950	3.32	70	0.63	600	15	770	905	18.8	14.7	11.3	55.2	94.3	
30	950	3.32	30	0.27	600	15	745	895	19.0	13.9	9.1	57.9	94.5	
32	950	3.32	310	2.79	520	13	740	830	3.5	17.2	12.7	66.6	89	
33	837	2.92	273	2.46	600	15	750	820	5.2	17.2	14.4	63.2	91.7	
37	3952	13.82	1290	11.62	2496	62.4	800	950	16.31	21.8	20.9	40.9	90.7	
38	3952	13.82	1290	11.62	2496	62.4	790	990	14.9	20.2	16.6	48.2	92.7	
39	3952	13.82	645 340	5.81 5.81*	2496	62.40	710	890	7.6	8.4	16.2	67.8	70.9	
40	3952	13.82	1290	11.62	2496	62.40	660	810	11.1	19.3	23.1	46.5	86.7	
41	3952	13.82	1290	11.62	2496	62.40	710	840	11.8	17.6	23.5	47.2	90.6	

\*340 g or 5.81 moles of NaCl also used.

After reduction it was found that the melt was almost completely encased in magnesium metal. The melt was again coke-like in appearance. Practically all of the product, which was probably uranium and uranium dioxide, was -325 mesh material.

It appears that magnesium will not reduce uranium trioxide satisfactorily under the conditions that have been tried. Experiments designed to perform reductions at elevated temperatures and at higher pressures than are considered safe with present equipment deserve further investigation.

#### Effect of Uranium Tetrafluoride as a Booster-Flux

Three reductions were made in which varying amounts of uranium tetrafluoride were used in the charge along with the uranium trioxide. The uranium tetrafluoride is reduced to the metal by calcium, liberating 134 Kcals of heat per mole uranium tetrafluoride. The resulting calcium fluoride should also serve as a flux so that the amount of calcium chloride required could be cut substantially. Thus, more heat should be liberated in the over-all reaction and there is less diluent present to take the heat away. It was hoped that agglomeration of the uranium formed would be improved under these conditions.

The total amount of flux, calcium chloride and calcium fluoride, was held constant at 2.78 moles in all of the runs. Each run contained 950 grams of uranium trioxide dried at 450°C and 50% excess calcium. The stoichiometric amount of calcium to react with the uranium tetrafluoride used in the reduction was also added. The results of the runs are shown below in the following tabulation.

#### Percentage Yields of Uranium Powder Using UF<sub>4</sub> Booster-Flux

Run No.	Moles, UF <sub>4</sub>	Temp Rise, °C	Percentage Yields in Mesh Ranges					Percentage Recovery
			+20	-20	+100	-100	+325	
25	0.00	65	3.8	17.1	19.5	59.8	87.0	
35	0.28	70	10.5	18.8	17.1	53.6	91.8	
34	0.69	-	21.3	19.4	14.2	45.1	89.9	
36	1.00	90	33.2	13.8	12.1	40.9	88.3	

The amount of +20 mesh increases with an increasing amount of uranium tetrafluoride and is, in all cases, much greater than in the runs made with no uranium tetrafluoride and dry uranium trioxide. The amount of -325 mesh is correspondingly lower, being 20% less in Run 36 as compared with the runs containing no uranium tetrafluoride. If one assumes that all the uranium from the uranium tetrafluoride ends up as +20 mesh and subtracts this from the results, the yields on the basis of only uranium trioxide are obtained. These corrected values are given on the following page.

Percentage Yields of Uranium Powder on Basis of UO<sub>3</sub>

Run No.	Moles, UF <sub>4</sub>	Percentage Yields in Mesh Ranges			
		+20	-20 + 100	-100 + 325	-325
25	0.00	3.8	17.1	19.5	59.8
35	0.28	3.0	20.4	18.5	58.1
34	0.69	5.1	23.4	17.9	54.4
36	1.00	13.0	17.9	15.7	53.3

It would thus appear that the addition of uranium tetrafluoride decreased the amount of -325 mesh material by only about 6 to 7% in the most favorable case, the run containing 1 mole of uranium tetrafluoride. The recoveries are slightly lower than normal, probably because the calcium fluoride was insoluble in acetic acid and had to be separated by washing of the -325 mesh uranium. It is apparent from these runs that the use of uranium tetrafluoride as a booster-flux does not affect the results enough to warrant its use.

Large-Scale Reductions

Four reductions have been performed on a 4-kilogram scale using 3952 grams of anhydrous uranium trioxide, 1290 grams calcium chloride and 2496 grams of calcium. These reductions resulted in a noticeable decrease in the percentage yields of -325 mesh uranium as shown in Table VII, Runs 37 and 38, 40 and 41. Subsequent work on a high temperature (1000 to 1200°C) post-heat of the reaction mass may result in further increase of the yields of +325 mesh spherical uranium.

Effect of Sodium Chloride as a Flux

The use of a flux other than calcium chloride was investigated briefly. Sodium chloride was used in conjunction with calcium chloride in one large reduction. The sodium chloride has a melting point at 801°C not far different from calcium chloride, which melts at 772°C. The results of this experiment are given in Table VII, Run 39. The amount of -325 mesh material increased to about 160% of that obtained in the runs using only calcium chloride while the other mesh ranges decreased, except for the -100 to +325 mesh, which remained about the same as in the other runs. It appears, on the basis of this one reduction, that sodium chloride is of no value as a flux in the reduction of uranium trioxide with calcium.

Analysis of Uranium Metal Produced

Samples of uranium from several runs were analyzed spectrographically for impurity elements. The analysis is semiquantitative, and the probable

error to be expected is +50% of the value given. The samples were also analyzed for carbon by the High Frequency Induction-Volumetric Method.<sup>13</sup> A typical analysis is given in Table VIII.

TABLE VIII TYPICAL ANALYSIS OF URANIUM FROM REDUCTION OF UO<sub>3</sub>

<u>Element</u>	<u>ppm</u>	<u>Element</u>	<u>ppm</u>
Mg	300	Ca	50
Si	85	Ni	20
Fe	80	B	2
Al	35	Cu	1
Mn	25	Ag	0.5
		C	500

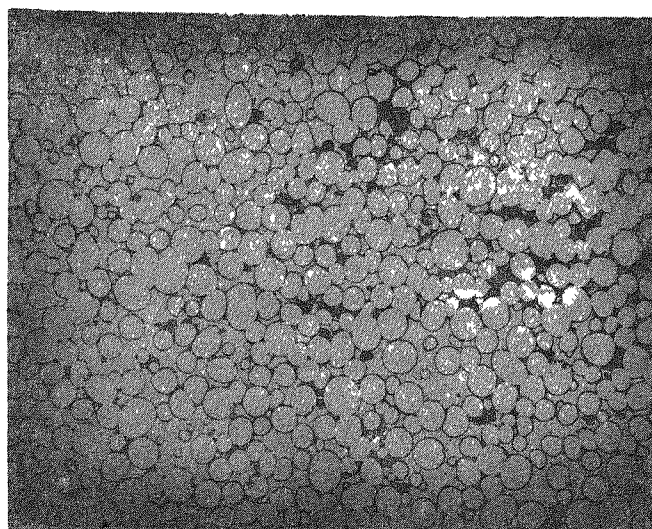
### CONCLUSIONS

The preceding data show that spherical uranium particles (KS-5360) a large portion greater than 325 mesh size, can be produced by the direct reduction of uranium trioxide with calcium. The percentage yields of -325 mesh uranium are about 57% in 1-kilogram scale reductions and about 46% in 4-kilogram scale experiments. It should be noted also that the percentage of -325 mesh uranium from the anhydrous uranium trioxide (dried at 450°C) ran about 7% higher than from runs made with uranium trioxide dried at 180°C. There was also a general trend for the quantities of other mesh ranges to be somewhat higher for reductions made with moist uranium trioxide than those made with anhydrous uranium trioxide.

Calcium chloride is desirable in the reductions for fluxing purposes and to promote ease of processing. About 50% excess calcium appears desirable. The mesh size of calcium chloride up to 1/4-inch particles did not affect the reductions. Similarly, heating rate variations had a very small effect. The segregation of the charge and pressing of the charge appear undesirable. The use of calcium-iodine boosters did not improve the results, but further work could be done on this. A booster-flux of uranium fluoride helps slightly in reducing the amount of -325 mesh uranium but the calcium fluoride produced is difficult to separate. Reductions employing magnesium in place of calcium were unsuccessful. However, heating the bombs to high temperatures under pressure and using larger bombs should be investigated. The use of sodium chloride as a fluxing reduction of uranium trioxide with calcium does not appear desirable.

Reductions on a 4-kilogram scale resulted in about 10% increase in the yields of spherical uranium larger than 325 mesh size, thus substantiating the belief that less heat losses from the reduction mass are desirable and can be obtained on large scale reductions.

The reduction of uranium trioxide with calcium is a feasible technique or producing spherical uranium particles (see KS-5360) which are of interest in development of long-lived fuel elements, consisting of these particles dispersed in a ductile, nonfissionable metal or alloy.



Spherical Uranium Particles  
From Reduction of  $\text{UO}_3$  with Calcium, 7 X

REFERENCES

1. Katz, J. J. and Rabinowitch, E., "The Chemistry of Uranium", New York, McGraw-Hill Book Co., Inc., 1951, p. 122.
2. Spedding, F. H., Wilhelm, H. A., Keller, W. H., "The Production of Uranium by the Reduction of  $UF_4$  by Mg", CT2712, June 26, 1945.  
Spedding, F. H., Wilhelm, H. A., Keller, W. H., "The Production of Uranium by the Reduction of  $UF_4$  by Ca", CT2711, July 13, 1945.
3. Myers, R. H., Mayo, R. G. P., and Bellamy, R. G., "The Production of Uranium Powder by the Uranium Dioxide-Calcium Route", AERE M/R-862, February 1952.
4. Bellamy, R. G. and Buddery, J. H., "The Production of Uranium Powder by the Uranium Dioxide-Magnesium Route", AERE M/R-1049, October 28, 1952.
5. WASH-171, USAEC-UK Metallurgy Progress Letter No. 1, February-April 1954, June 15, 1954.
6. Lilliendahl, W. C., Wroughton, D., Nagy, R., Marden, J. W., "Electrolytic Production of Uranium Powder", U. S. Patent 2,690,421, September 28, 1954.
7. Hausner, H. H. and Mansfield, H., "Atomization Method of Making Uranium Powder", NYO-1133, August 7, 1950.
8. HW 34455 - Metallurgy Unit Quarterly Progress Report, October-November-December 1954, Hanford.
9. Coughlin, J. P. "Contributions to the Data on Theoretical Metallurgy, XII. Heats and Free Energies of Formation of Inorganic Oxides", Bureau of Mines Bull. 542, (1954).
10. Glasstone, S., "Textbook of Physical Chemistry", D. Van Nostrand Co., Inc., New York, 1946, p. 214.
11. Marden, J. W. and Rentschler, H. C., "Metallic Thorium", Industrial and Engr. Chem., 19, 97-103 (1927).
12. Quill, L. L. (editor), "The Chemistry and Metallurgy of Miscellaneous Materials: Thermodynamics", New York, McGraw-Hill Book Co., Inc., 1950, p. 10.
13. Pepkowitz, L. P. and Chebniak, P., "Precision Determination of Carbon in Metals", Analytical Chem. 24, 889-890 (1952).
14. Mantell, C. L. and Hardy, C., "Calcium Metallurgy and Technology", New York, Reinhold Publishing Co., 1945, p. 24.