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A CONTRIBUTION TO THE
STUDY OF THE REDUCTION
OF UF_4 TO URANIUM METAL

by

Jovan Milosavljevic
and Jerome Baird

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THE REDUCTION OF UF_4 TO URANIUM METAL

by

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ABSTRACT

Reduction of small charges of uranium tetrafluoride with magnesium proved to be successful. By hand-tamping of UF_4 -Mg blend, tap densities ranging between 3.1 and 3.4 g/cc were obtained, whereby the reduction yields ranged from 72.79% to 93.71%. In the case of machine-compacted UF_4 -Mg blend having tap densities from 3.58 to 3.68 g/cc, reduction yields were higher, ranging between 91.45% and 97.2%. Machine-compacted blends gave much more uniform temperature distribution curves during the preheating period, as a result of higher tap densities. The best yields were obtained by firing a machine-compacted blend containing 5% Mg excess at a furnace temperature of 650°C, giving an average crude metal yield of 96.3%. However, the high carbon content of 174 ppm in the crude uranium biscuits obtained by compacts reduction, as a result of hydrocarbon binder presence, appears to be a disadvantage. Attempts were also made to demonstrate the initiation of the reduction reaction at temperatures lower than 500°C by taking X-ray diffraction patterns of the samples of the UF_4 -Mg charges heated up to various temperatures.

I. INTRODUCTION

The production of metallic uranium by the reduction of uranium tetrafluoride with alkali earth metals has been studied for many years. In the United States,⁽¹⁾ much work was done on the use of magnesium metal as a reducing agent. At the present time, in this country, full-scale uranium metal production plants are in operation in which freshly cut magnesium metal is blended with the uranium tetrafluoride and the reduction is carried out in closed stainless steel reduction shells lined with either electrically fused dolomite or magnesium fluoride (MgF_2). A preheating period, lasting for many hours is usually required, because the lining material is a poor thermal conductor. Heat for initiating the reduction reaction is supplied by placing the container in a gas-fired or oil-fired furnace.

In Europe, the early investigation of the production of uranium metal was concentrated on the use of calcium instead of magnesium. As a result, most of the present full-scale uranium metal production plants are reducing uranium tetrafluoride with calcium metal in an open vessel using calcium fluoride (CaF_2) as a lining material. The amount of calcium necessary to produce metallic uranium is twice that of magnesium. In addition, a 15 w/o excess of calcium is required compared with the 1-6 w/o magnesium.

In 1955, in the Metallurgy Laboratory of the International School of Nuclear Science and Engineering, graphite crucibles were used as a liner in the reduction of UF_4 with Mg.⁽²⁾ This has been used for instructional purposes hundreds of times during the past five years.

The use of the graphite liner has given rise to some new technical problems. Therefore, the object of this report was to explore that new production technique and to discover the advantages and the problems involved. Much attention was concentrated on the correlation between the bulk densities of the hand-tamped and the machine-compacted UF_4 -Mg charges versus the temperature distribution during the preheating period and its influence on the production yield. The quality of the produced uranium metal was also examined, particularly with regard to its boron and carbon content.

An investigation, to determine at what temperature the initial reaction takes place, was made by heating hand-tamped UF_4 -Mg blends to a series of temperatures below 600°C . After these charges had cooled to room temperature, they were sectioned, and the samples were taken for X-ray diffraction determination.

A new full-scale production facility in Springfield, England, uses sectionalized graphite linings and UF_4 -Mg blends.⁽³⁾ Excellent thermal conductivity of the graphite, combined with its high thermal shock resistance, makes possible the use of a thin lining compared with a thick rammed lining of MgF_2 . In addition, this new production technique employs compaction of the UF_4 -Mg blend prior to its introduction to the firing crucible, which increases the tap density of charge resulting in releasing of more heat per unit volume during the reduction. The graphite liner speeds up both the heating of the charge prior to firing, and the cooling down of the metallic uranium and MgF_2 slag so that a considerable saving of time is effected in the overall cycle.

II. REDUCTION OF UF_4 TO URANIUM METAL

A. Raw Materials

The green salt which was used in all experiments, contained more than 99% of UF_4 , 0.02% of unconverted UO_2 , and 0.10% of UO_2F_2 ; there was a 0.16% loss upon ignition. Its tap density was found to be more than 3.5 g/cc. The total U content was 74.50%, and this was taken as the basis for the calculations of uranium metal yields. Sieve analysis showed that the main particle size fraction of the green salt (55.6%) was -100 +200 mesh, the remainder passing through 200 mesh. The total amount of impurities (see Appendix A, Table I) was less than 300 ppm, excluding oxygen and fluorine present in the form of unconverted UO_2 and UO_2F_2 , respectively.

Two batches of commercial atomized Mg metal of more than 99% purity, produced by Dow Chemical Company, were used in the experiments. The first batch was on hand at least one year at the Laboratory, and had a visible dark oxide layer on its surface. The second batch, purchased primarily for these series of experiments, had a shiny and bright surface. According to the spectrochemical analysis, no differences were found to exist between them. Both batches have had almost the same particle size distribution, as can be seen from Table I.

Table I

PARTICLE SIZES OF BATCHES OF MAGNESIUM

U. S. Standard Sieve Size (Mesh)	% of Mg Fraction	
	New	Old
+ 28	2.11	1.90
- 28 + 60	59.23	61.13
- 60 + 80	15.17	15.33
- 80 +100	13.92	11.23
-100 +200	8.70	9.58
-200	.26	.82

The total amount of impurities was 0.74% in both old and new Mg (see Appendix A, Table II). Oxygen content was not determined.

The first materials used as binders for making UF_4 -Mg compacts were volatile substances, such as ethyl alcohol and acetone. These compacts had very low green strength and in most cases failed even prior to complete ejecting from the die cavity. Therefore, two standard binders, polyethylene-glycol (carbowax), and polyvinyl alcohol, both water-soluble,

low-boiling point hydrocarbon polymers, were used. They were uniformly distributed in the UF_4 -Mg blend as a 3 w/o water solution. It was found that 0.1 w/o of binder in the blend yielded UF_4 -Mg compacts with very good mechanical properties.

Reaction crucibles were made from commercial coarse-grained graphite. All crucibles were baked in air at 500-600°C in a resistance-heated furnace for one to two hours prior to use. In some of the first experiments, magnesium zirconate wash was applied to the interior surface on the assumption that it helps protect the molten metal from carbon contamination. This practice was abandoned after it had been found there was no carbon pickup from the bare crucible during ignition.

B. Description of Equipment

The reduction experiments were carried out in a 10-kw vertical resistance furnace, HEVI DUTY HD818, which had a heating space of 10 in. in diameter and 20 in. deep (see Figure 1). The reduction shell rested on a brick-pedestal so that it was in a central-heating section of the furnace (see Figure 2). The furnace cover was a 3-in. thick insulation brick, and the temperature was controlled with a Wheelco controller having a thermocouple located 2 in. up from the furnace bottom.

Figure 1

Hevi-duty 10-kw Electrical Furnace

The temperature gradient was only 10°C between the top and bottom at 700°C.

The reduction shell was made of SS-314 and was closed with an ordinary 4-in. threaded steel pipe cap (see Figure 3). Its dimensions were $3\frac{3}{4}$ in. ID, $4\frac{1}{2}$ in. OD, and $11\frac{1}{16}$ in. high. Figure 2 shows a cutaway of the reduction shell as it was located in the resistance furnace. Also shown are the six chromel-alumel thermocouples used for temperature-distribution

measurement within the charge during the preheating period. The graphite crucible had a $\frac{1}{16}$ -in. smaller OD than the ID of the reduction shell, to permit the outside thermocouple insertion. This thermocouple was used for

measuring the external crucible temperature. The temperatures were recorded on a twelve-point Bristol Dynamaster Recorder, the recorder being modified to record each of six thermocouples in a 30-sec period.

Figure 2

Hevi-duty 10-kw Furnace showing Heating Element, Furnace Pot with Charge and Seven Thermocouples

Figure 3

SS Reduction Shell Used in Experiments

For UF_4 -Mg blend pressing into the compacts, a high-pressure Hydraulic Pump D-182 (see Figure 4) was used.

Figure 4
Black Hawk High-pressure
Hydraulic Pump Used in UF_4 -Mg
Compacts Production

The press consisted of two 50-ton jacks installed on a special metal frame. Both 3-in. diameter pistons were connected to the same pump and acted simultaneously in opposite directions to give a double action pressing.

The pump developed maximum pressure of 10,000 psi. The top and bottom male dies were threaded to the jacks' pistons, while the female die was free floating. Die clearance of three mils on the diameter was found to be satisfactory, permitting easy ejection of the compacts.

C. Experimental Procedure

Two series of experiments were performed. The first series was the classical method of charge preparation in which the UF_4 -Mg blends were hand-tamped. In the second series, the UF_4 -Mg blends were machine-pressed into compacts, $\frac{1}{2}$ in. thick and 3 in. in diameter, at 10,000 psi. In both series the charges for each experiment weighed approximately 3700 grams.

In the preparation of the charges for the first series, the required amounts of UF_4 and Mg metal were carefully weighed and then blended in a porcelain ball mill, either with or without porcelain balls. At first it was thought that the balls would break the oxide layer on the surface of

the magnesium particles and thus facilitate the initial reaction. Later, it was found that there was no difference in the initial reaction temperatures whether porcelain balls were included in the blending operation or not. It was also found that one-hour blending gave enough time to produce a homogeneous UF_4 -Mg blend.

In the first few runs the blended mixture was carefully hand-tamped in the previously baked crucible by means of a $1\frac{1}{2}$ -in. diameter aluminum rod. Later on it was found that a four-pronged tamping tool made of $\frac{1}{8}$ -in. diameter SS rods yielded slightly higher tap densities.

The crucible was loaded almost to the top, leaving only enough room for the graphite cap to fit flush with the top. Figure 5 shows a top view of

Figure 5

Top View of Loaded Graphite Crucible Prior to Closing It

a loaded graphite crucible prior to closing it. The graphite cap was a snug fit and was pressed into the crucible to form the seal to prevent escape of any magnesium vapor. After being closed, the crucible was placed into the SS reduction shell. In experiments in which the temperature distribution was measured, the porcelain-insulated thermocouples with a bare tip were inserted through the graphite cap into the charge (see Figure 2). The thermocouples were sealed into the graphite cap with high-temperature cement ("Sauereissen"). The same cement was used to fasten graphite spacers to the crucible cap. After closing the SS reduction shell, thermocouples were connected to the twelve-point Dynamaster Recorder.

When ready for firing, the crucible was placed into the electric furnace which had been preheated to the desired temperature. In all experiments a thermocouple was located between the graphite crucible and the SS reduction shell, halfway down the side of the graphite crucible. It was used for recording the firing time and the maximum outside crucible wall temperature. After the ignition had taken place, the SS reduction shell was held for 20 minutes in the electric furnace, and then removed and air cooled to about 300°C , followed by a water quench.

The cold SS reduction shell was opened, the crucible slid out in a tray and then broken with a hammer. The crude uranium biscuit was easily separated from the MgF_2 slag by hand. Final cleaning of biscuits was done by wet wire brushing, to provide a clean metal surface. Hand-tamped UF_4 -Mg charges produced uranium biscuits with rough top surfaces, whereas those compacted by machine always had very smooth top surfaces.

In preparing the blend for machine compacting, UF_4 and Mg were blended dry, a binder added as a water solution, and hand mixed to give homogeneous distribution. The charge was pressed into $\frac{1}{2}$ -in. thick compacts at 10,000 psi and held for 1-2 minutes.

To reduce carbon contamination in the crude metal, and yet to obtain compacts of satisfactory strength, the concentration of binder in the aqueous solution was chosen to be 3 w/o. It was hoped that the organic binder would volatilize and escape from the charge during the preheating period.

After much experimentation, it was found that the charges with the moisture content of 3 w/o produced the best green compacts. Following pressing, compacts were air dried overnight. Approximately 9% of them developed cracks during the drying period and were rejected.

This loss was reduced to 6% by reapplying the same pressure for another 2 minutes prior to ejecting the compacts from the die. This double application of pressure gave the compacts better green strength. The individual compacts weighing 150-200 gm had the best green strength. Either smaller or larger amounts of the UF_4 -Mg mixture did not compact successfully. Figure 6 shows the dried UF_4 -Mg compacts before placing them into the graphite crucible.

Figure 6

UF_4 -Mg Compact after Drying

D. Results and Discussion

The data concerning reduction of both tamped and pressed UF_4 -Mg blend are given in Tables II and IV. The reduction yields were calculated on the basis of green salt containing 74.5% uranium.

Table II

YIELDS OF CRUDE URANIUM METAL AS A FUNCTION OF Mg METAL EXCESS,
FURNACE TEMPERATURE, AND TAP DENSITY OF HAND-TAMPED
UF₄-Mg BLEND

Expt No	Excess of Mg Metal, %	Tap Density of UF ₄ -Mg Charge, g/cc	Furnace Temperature, °C	Ignition Temperature, °C	Yield of Crude U Metal, %	Specific Gravity of U Sample, g/cc	Remarks
1	5	3 39	700	-	87 08	18 80	Crucible used as received, old Mg used
2	5	3 43	700	-	88 72	18 79	Crucible baked at 500°C for 2 hr, old Mg used
3	5	3 43	800	-	83 48	18 60	Crucible baked at 500°C for 2 hr, old Mg used
4	-	3 41	700	-	85 08	18 55	Crucible baked at 500°C for 2 hr and washed with Mg zirconate, old Mg used
5	10	3 42	600	595	78 80	18 66	Same conditions as in Expt No 4 Thermo-couples used for temp distribution measurement
6	10	3 45	700	-	72 79	18 45	Same conditions as in Expt No 4
7	5	3 47	700	-	84 96	18 70	Crucible baked at 600°C for 2 hr and washed with Mg zirconate, old Mg used
8	5	3 49	700	-	90 14	18 80	Crucible baked at 600°C for 2 hr and washed with Mg zirconate, old Mg used
9	5	3 37	600	600	82 41	18 63	Same conditions as in Expt No 4 Thermo-couples used for temp distribution measurement
10	5	3 39	700	605	88 56	18 71	Crucible baked at 600°C for 2 hr and washed with Mg zirconate, new Mg, temp distribution measured
11	6	3 48	700	-	93 71	18 78	Crucible baked at 600°C for 2 hr, new Mg used
12	6	3 38	700	-	91 64	18 82	Crucible baked at 600°C for 2 hr and washed with Mg zirconate, new Mg used

The first twelve experiments (see Table II) were carried out by firing tamped UF_4 -Mg blend. The reduction yields ranged widely, from 72.79 to 93.71%, depending upon the charge composition, its tap density, and the furnace temperature. The highest yields were obtained in Experiments 11 and 12, for which 93.71 and 91.64% uranium recovery were achieved. These experiments were carried out at a furnace temperature of 700°C , using the new Mg metal in 6% excess.

Although the chemical analyses showed no significant difference in the oxygen content between crude uranium biscuits obtained by using different quality Mg, it is apparent that under the same working conditions the new batch of Mg metal gave better yield than the old one when a hand-tamped charge was fired.

Using the stoichiometric ratio of magnesium, a crude yield of 85.08% was obtained (Experiment No. 4). By increasing the Mg excess to 5%, the crude yield increased to an average of 88.61% (Experiments 1, 2, and 8). However, further increase of the amount of magnesium to an excess of 10% resulted in a very low yield, 72.79% (Experiment No. 6). A very low yield of 78.80% was also obtained in Experiment No. 5 when using 10% Mg excess and firing the UF_4 -Mg charge at a furnace temperature of 600°C instead of at 700°C . It appears that a too large excess of magnesium is a severe depressive factor on the reduction reaction, acting as a heat absorbent because of its low boiling point of 1107°C .

Consider variation of the furnace temperature with other conditions remaining unchanged. A decrease of 5% in crude yield was noticed as the temperature increased from 700°C (Experiments 1 and 2) to 800°C (Experiment No. 3). Almost the same decrease in crude yield occurred in Experiment No. 9 in which the furnace temperature was 600°C . According to some published data, the optimal furnace temperature is 676°C (1250°F) for a MgF_2 -lined reduction shell. However, higher temperatures do not affect significantly the uranium metal yield.⁽⁴⁾ Apparently, high variation in the crude yields occurs with variation of the furnace temperature because of the different physical properties of graphite. Figure 7 shows the crude uranium biscuits obtained by firing the hand-tamped UF_4 -Mg blends, after being cleaned by wet wire brushing.

Figure 7
U Metal Biscuits
after Sampling

There was an heterogeneous distribution of minute uranium metal particles and uranium compounds (mostly in the oxide form) in the MgF_2 slag. As shown in Table III, the highest uranium concentrations were found in the $\frac{1}{8}$ -in. thick slag layer next to the crucible wall, whereas the central part of the MgF_2 slag had a much lower uranium content.

Table III

U DISTRIBUTION IN THE MgF_2 SLAG

Expt. No.	Central Part of MgF_2 Slag, w/o	Part of MgF_2 Slag Close to the Crucible Wall, w/o
1	10.28	21.81
2	8.93	24.38
3	2.96	10.73
4	1.50	35.35
5	9.23	21.85
6	0.67	34.02
7	8.27	34.23
8	4.07	35.10
9	4.53	19.28

The entrapped uranium metal particles were present only in this outer layer, due to the fact that the released heat of reaction was not high enough to

Figure 8

Cutaway of the MgF_2 Slag Obtained by Firing Hand-tamped UF_4 -Mg Blend

balance the heat dissipation through the crucible wall. This dissipation was always very fast, causing solidification of a thin MgF_2 layer before the whole reduced uranium metal had separated and collected on the bottom of crucible. In addition, there was always a small amount of entrapped uranium metal in the form of small balls in the MgF_2 slag, just above the crude biscuit (see Figure 8).

In the case of machine-compacted UF_4 -Mg blend, as Table IV shows, the reduction yields were higher, ranging from 91.45 to 97.20%. Such high yields were due to the very uniform temperature distribution

throughout the whole charge, as a result of higher tap densities. The highest reduction yields of 97.20% and 95.48% were achieved in Experiments 21 and 25, which were carried out at a furnace temperature of 650°C , using new Mg in 6% excess.

Table IV

YIELDS OF CRUDE URANIUM METAL AS A FUNCTION OF Mg METAL EXCESS,
FURNACE TEMPERATURE, AND TAP DENSITY OF UF_4 -Mg BLEND
COMPACTED AT 10,000 psi

Expt No	Excess of Mg Metal, %	Tap Density of UF_4 -Mg Charge, g/cc	Furnace Temperature, °C	Ignition Temperature, °C	Yield of Crude U Metal, %	Specific Gravity of U Sample, g/cc	Remarks
13	5	3 58	700	-	91 99	18 72	Crucible baked for 2 hr at 500°C, PVA used as a binder, old Mg used
14	5	3 61	700	-	91 45	18 81	Crucible baked for 2 hr at 600°C, PVA used as a binder, old Mg used
15	5	3 59	700	610	-	16 25	Same conditions as in Expt No 13, thermocouples used for temp distribution measurement
16	5	3 58	650	-	94 97	18 79	Crucible baked for 2 hr at 500°C, CW used as binder, old Mg used
17	5	3 63	650	-	94 30	18 88	Crucible baked for 2 hr at 500°C, CW used as binder, old Mg used
18	5	3 61	700	580	82 96	18 68	Same conditions as in Expt No 16, thermocouples used for temp distribution measurement
19	6	3 66	700	-	86 88	18 69	Crucible baked for 2 hr at 500°C, CW used as binder, new Mg used, temp distribution measured
20	6	3 63	700	588	95 40	18 90	Crucible baked for 2 hr at 500°C, CW used as binder, new Mg used
21	6	3 64	650	-	97 20	18 92	Crucible baked for 2 hr at 500°C, CW used as binder, new Mg used
22	5	3 66	650	-	93 35	18 62	Crucible baked for 2 hr at 500°C, CW used as binder, new Mg used
23	5	3 68	650	-	94 68	18 56	Crucible baked for 2 hr at 500°C, CW used as binder, new Mg used
24	6	3 65	700	-	92 95	18 73	Crucible baked for 2 hr at 500°C, CW used as binder, new Mg used
25	6	3 67	650	-	95 48	18 59	Crucible baked for 2 hr at 500°C, CW used as binder, new Mg used

By decreasing the Mg excess to 5%, for the same temperature (Experiments 22 and 23), the reduction yield dropped from 96.34% to 94.15%. Further decrease in yield to 92.95% was noticed using the same 5% Mg excess, but firing the charge at 700°C instead of at 650°C (Experiment No. 24).

The furnace temperature was also an influence on the crude uranium metal yield when old Mg was used. By firing machine-compacted UF₄-Mg charge at a furnace temperature of 650°C, using 5% Mg excess, the crude yield was 94.63% (Experiments 16 and 17). However, for the same Mg excess and a furnace temperature of 700°C, the crude yield dropped to 91.72% (Experiments 13 and 14).

The crude U metal separation was much better for machine-compacted charge than for the hand-tamped one, even though there were still some uranium particles captured by the $\frac{1}{8}$ -in. thick brown MgF₂ slag layer next to the crucible wall. These particles were smaller in size and much fewer, but yet confirmed very fast heat dissipation through the graphite. The MgF₂ slag, in almost all experiments, was pure white, except in the $\frac{1}{8}$ -in. thick outer layer, and had insignificant uranium content. Only in Experiments 18 and 19, where the crucibles cracked during the initial reaction, all of MgF₂ slag was light brown.

According to chemical analyses (see Appendix A, Table VI), the carbon content in the crude metal ranged widely, from 6 to 225 ppm. The reduction of hand-tamped UF₄-Mg blend yielded crude metal with carbon content varying from 6 to 102 ppm, with an average value of 43 ppm. However, in the crude uranium metal obtained by reducing machine-compacted UF₄-Mg charges, the carbon content ranged from 133 to 225 ppm, with an average value of 173 ppm. Undoubtedly the use of a hydrocarbon binder caused higher carbon content in the crude metal. It is expected that the amount of carbon pickup could be reduced either by decreasing the amount of hydrocarbon, followed by higher compacting pressures, or by vaporizing the binder during the preheating period. It is hoped that additional work on the method of machine compaction of UF₄-Mg blends will yield crude derbies of higher quality containing considerably less carbon.

There was a considerable difference in contents of oxygen, nitrogen, and hydrogen between derbies obtained from the same type of charge (see Appendix A, Tables VII and VIII). It is well known that these impurities are not uniformly distributed, and it is difficult to get samples for accurate chemical analysis. However, these impurities can be drastically reduced by vacuum melting of the crude uranium biscuit, and therefore do not represent serious problems.

There was no boron pickup from the graphite crucible by the molten uranium. Although the reduction took place adjacent to the crucible wall, the fast solidification of a thin MgF₂ layer next to the wall was very beneficial, acting as protection for the molten metal.

The amount of other impurities present in the crude metal, as determined by spectrochemical analyses, ranged between <500 and <800 ppm, as shown in Appendix A, Table III. All results are given with an accuracy determined by a factor of 2.

Temperature distribution in the UF_4 -Mg charge during the preheating period was recorded in Experiments 5, 9, 10, 15, 18, and 19, and is presented in Figures 9 through 14 for both hand-tamped and machine-compacted blend. The temperature was measured with six thermocouples located at the different charge heights (see Figure 2). Three of them were used for measuring the temperature of the charge next to the crucible wall, while the other three were employed for measuring the temperature of the central charge portion. In addition, a thermocouple located 3.5 in. above the reduction shell bottom was used for measuring the temperature between the graphite crucible and the reduction shell.

The temperature-distribution diagrams for the hand-tamped UF_4 -Mg blend (see Figures 9, 10, and 11) show lack of uniformity of heat distribution. Heat transfer across the hand-tamped charge was the best in the lowest part, where the highest tap densities are to be expected, and in addition the electric furnace was at the bottom. As the tap density decreased, going from the bottom to the top of crucible, the temperature difference became greater, thus decreasing the average temperature of charge. By the time ignition occurred, this accumulated heat plus heat released in the reaction did not ensure complete uranium metal separation. This, particularly, became an important fact when graphite was used as a lining material. In the case of the MgF_2 lining, whose thermal conductivity is much lower, nonuniform heat distribution was not as important a problem as when graphite was used as a lining material.

The uniform heating of the charge in the case of machine-compacted UF_4 -Mg blend (see Figures 12, 13, and 14) was a result of more uniform and higher tap density. Increase of the average temperature of the UF_4 -Mg blend and the heat created per unit volume during ignition raised the peak temperature of the molten reduction products. Therefore, the amount of entrapped uranium in the $\frac{1}{8}$ -in. thick dark slag layer adjacent to the crucible wall was much less.

Finally, Figure 15 shows the temperature difference between the part of UF_4 -Mg charge along the crucible central line and that next to the crucible wall versus preheating time.

Figure 9

Temperature-distribution Curves in the Case when UF_4 -Mg Blend Is Tamped. Two Thermocouples Are Located in the Charge 0.5 in. (1.27 cm) above the Graphite Crucible Bottom. (3,700-gm Charge with 5% Mg Excess)

Figure 10

Temperature-distribution Curves in the Case when UF_4 -Mg Blend Is Tamped. Two Thermocouples Are Located in the Charge 3.5 in. (8.9 cm) above the Graphite Crucible Bottom. (3,700-gm Charge with 5% Mg Excess)

Figure 11

Temperature-distribution Curves in the Case when UF_4 -Mg Blend Is Tamped. Two Thermocouples Are Located in the Charge 7 in. (17.8 cm) above the Graphite Crucible Bottom (3,700-gm Charge with 5% Mg Excess)

Figure 12

Temperature-distribution Curves in the Case when UF_4 -Mg Compacts Are Used. Two Thermocouples Are Located in the Charge 0.5 in. (1.27 cm) above the Graphite Crucible Bottom. (3,700-gm Charge with 5% Mg Excess)

Figure 13

Temperature-distribution Curves in the Case when UF_4 -Mg Compacts Are Used. Two Thermocouples Are Located in the Charge 3.5 in. (8.9 cm) above the Graphite Crucible Bottom. (3,700-gm Charge with 5% Mg Excess)

Figure 14

Temperature-distribution Curves in the Case when UF_4 -Mg Compacts Are Used. Two Thermocouples Are Located in the Charge 7 in. (17.8 cm) above the Graphite Crucible Bottom. (3,700-gm Charge with 5% Mg Excess)

Figure 15

Temperature Differences between the Center Line
through a Charge and the Crucible Wall

When the results are considered, it seems logical to perform the reduction in a graphite crucible with a machine-compacted UF_4 -Mg blend instead of a hand-tamped one. Higher yields in crude uranium metal justify the cost of compact production, especially if the green salt is fluffy, as when prepared by wet methods. Therefore, compaction appears to be very attractive as a method which could be used, not only with UF_4 , but also with any other important fluorides, as ThF_4 . Also, the greater thermal conductivity of the graphite liner makes faster heating of UF_4 -Mg blend possible, which results in the shorter preheating period.

The preheating time necessary to bring the charge to the firing temperature ranged in all experiments between 28 and 30 minutes, regardless of the ignition temperature. In Experiments 10, 15, 18, and 19, where the temperature-distribution measurements were performed, crude metal yields were lower than those obtained under the same conditions but without thermocouples. The reason for this is attributed to the holes drilled for thermocouples insertion through the graphite cap, which, even though carefully sealed, failed during the ignition, permitting Mg vapor to leak.

E. Study of the Chemical Changes Occurring in the UF_4 -Mg Blend prior to Ignition

This study was undertaken to investigate the accumulation of the magnesium metal in the lower part of the UF_4 -Mg charge during the preheating period, which had been discovered by early investigators.

Small charges ranging between 400 and 420 gm of UF_4 -Mg blend, containing a 5% Mg excess over the stoichiometrical ratio, were hand-tamped into the graphite crucibles and subjected to thermal treatment. This treatment consisted of heating each hand-tamped charge for two hours at a selected temperature below the ignition temperature. The experimental temperature was recorded by means of a thermocouple placed between the graphite crucible and the reduction shell. After heating, the system was air cooled to room temperature. In order to obtain the clear picture of the heated charge, the graphite crucible with its entire charge was sectioned vertically with the dry abrasive cut-off wheel. The cutaways are shown on Figure 16.

Figure 16
Cutaways of Hand-tamped
 UF_4 -Mg Charges after Being
Heated to Various
Temperatures

The blend heated at 320°C showed no apparent change in the green color. The charge heated at 350°C had a small, light brown, $\frac{3}{16}$ -in. diameter core, which was visible 1 in. above the crucible bottom. At 400°C , this core had an oblong shape, $\frac{3}{8}$ in. wide by $\frac{3}{4}$ in. long, extending almost to the

crucible bottom. At 450°C, the brownish core had grown tremendously, but was limited to the bottom half. Its dimensions were $1\frac{1}{8}$ in. in diameter by $1\frac{3}{4}$ in. long, and had a darker shade. Further increase in temperature to 550°C yielded a still darker brown core, covering about 75% of the cross section and extending throughout the entire lower half of the charge.

To prove that the change in the color was due to the reaction between UF_4 and Mg rather than a result of the UF_4 crystal growth,* a series of charges of hand-tamped UF_4 without Mg were heated at temperatures corresponding to the previous series. As Figure 17 shows, there was no change in its color even though the charges were heated to 550° and 575°C.

Figure 17
Cutaways of Hand-tamped
 UF_4 Heated to 550°C
and 575°C

In order to eliminate oxygen and moisture as factors influencing reaction during the preheating period, a third series of experiments were performed. Loading procedure was the same, but this time hand-tamped UF_4 -Mg charge was dried at room temperature in an uncovered crucible in a vacuum of better than $1\ \mu$ for 12 hours. The vacuum chamber was then back filled with argon to atmospheric pressure and the graphite cap quickly impressed on the top of the crucible.

Two chromel-alumel thermocouples were inserted into the UF_4 -Mg charge to about $\frac{1}{2}$ in. above the crucible bottom. This operation was done in the protective argon atmosphere. One thermocouple was located in the center line of charge, while the other was located close to the inside crucible wall. A third thermocouple was placed, as usual, between the crucible and the SS reduction shell. Heating of each charge and subsequent cooling were done while there was a continuous flow of argon into the space between the crucible and the reduction shell.

In Figures 18 and 19 are shown typical temperature-distribution curves selected from 25 runs during which ignition took place after 21-22 minutes of preheating.

*It is well known that large UF_4 crystals have dark greenish color.

Figure 18

Temperature-distribution Curves in the Case when UF_4 -Mg Blend Is Tamped. Two Thermocouples Are Located in the Charge 1 in. (2.54 cm) above the Graphite Crucible Bottom (400-gm Charge with 5% Mg Excess; Furnace Temperature Was 700°C)

Figure 19

Temperature-distribution Curves in the Case when UF_4 -Mg Blend Is Tamped. Two Thermocouples Are Located in the Charge 1 in. above the Graphite Crucible Bottom. (400-gm Charge with 5% Mg Excess; Furnace Temperature Was 700°C)

Figure 20 presents thermal conditions in those experiments where ignition has taken place after an exceptionally long preheating period of over 30 minutes. Finally, Figure 21 shows the thermal condition when ignition failed to take place even after 40 minutes of charge preheating. The most important part in all these diagrams is the intersection point occurring during the preheating period. This point lies between 350°C and 475°C, and undoubtedly represents the point at which a localized exothermic reaction takes place. This reaction raises the temperature of the middle part of the UF_4 -Mg charge above that at the periphery, thus reversing the temperature gradient. This phenomenon has been noticed and recorded in over thirty experiments performed in the small charges, but it was not detected with 3700-gram charges.

A fourth series of experiments was also performed in an argon atmosphere for the same purpose as the first, i.e., to observe the chemical and physical changes occurring during the preheating period. The loading procedure was the same as in the third series of experiments, except that the thermocouples inside the tamped charge were not used. The charges were heated to the various temperatures and then immediately removed from the electric furnace and air cooled. In all experiments the furnace was held at 700°C. The control thermocouple was located between the graphite crucible and SS reduction shell. Since the temperature of charge within the crucible was the basis for experimental data, centerline temperatures were estimated according to the calibration curves obtained in Figures 18 and 19. The experience gained in the third series showed that those temperatures can be predicted with an accuracy of $\pm 30^\circ\text{C}$.

In Figure 22 are shown the cutaways of some of these samples. It took only 14 minutes to reach the centerline temperature of 475°C. This resulted in the formation of a small, light brown core which was similar in appearance and location to that obtained in the first series when the charge was held at 350°C for two hours. As the temperature rose, this core grew larger, and its color kept changing until the whole charge was dark greenish-brown at 580°C. Higher temperatures caused no further change in color. This change in color was accompanied with a sintering phenomenon which became especially vivid at 580°C, when the whole charge looked like fused solid mass. The magnesium particles were not visible because of the brown layer formed on their surfaces. The samples heated to 570°C and 630°C showed the magnesium separation. Since the magnesium melts at 651°C, its segregation at lower temperatures proves the existence of a local exothermic reaction creating local hot spots in the lower part of charge, whose temperatures exceed the melting point of Mg.

Figure 20

Temperature-distribution Curves in the Case when UF_4 -Mg Blend Is Tamped. Two Thermocouples Are Located in the Charge 1 in. above the Graphite Crucible Bottom.
(400-gm Charge with 5% Mg Excess;
Furnace Temperature Was 700°C)

Figure 21

Temperature-distribution Curves in the Case when UF_4 -Mg Blend Is Tamped. Two Thermocouples Are Located in the Charge 1 in. above the Graphite Crucible Bottom.
(400-gm Charge with 5% Mg Excess;
Furnace Temperature Was 700°C)

Figure 22

Cutaways of Hand-tamped UF_4 -Mg Charges
Heated in a 700°C Furnace and Removed
when Center Part Reached the Desired
Temperature

The X-ray diffraction patterns of the reaction samples showed, in almost all cases, the presence of UF_4 , UF_3 , and UO_2F_2 , while the presence of MgF_2 and uranium oxides could not be proven satisfactorily. However, it is to be pointed out that the X-ray patterns of a given compound can be taken only if its concentration exceeds 5 w/o. In addition, a multicomponent sample always causes difficulties in distinguishing the lines of one compound from those corresponding to another having nearly the same lattice parameters.

As has already been found,^(5,6) UF_3 seems to be the only stable intermediate compound leading to the formation of uranium metal. The reaction

takes place in the graphite crucible at the temperatures well below that necessary for the ignition of the whole charge. Since it leads to a partial distortion of the UF_4 crystal lattice, it can be explained as a gas-solid surface reaction. Its rate depends on the pressure of magnesium vapor and therefore is highly affected by the charge temperature and the size of the magnesium particles. The observed sintering phenomenon is very probably the result of solidification of magnesium vapor occurring during the cooling of partially reacted UF_4 -Mg blend, as well as a result of the formation of MgF_2 on the UF_4 particles.

The second possible interpretation of the UF_4 reduction is based on the possible diffusion of magnesium into the UF_4 crystal lattice.⁽⁷⁾ Although this type of reaction is not exclusive, it is less acceptable, at least in the case of the UF_3 formation. It appears that such reaction may occur in the last step as a consequence of interaction between UF_4 and molten Mg, resulting in the complete destruction of the UF_4 crystal.

According to the experimental results obtained, the melting of magnesium can occur only in those parts of the hand-tamped UF_4 -Mg blend where the temperature is above its melting point. Therefore, following such reasoning, it seems logical that the ignition of whole charge can take place only in the dark brown core when sufficient molten magnesium has been formed. The formation of the brown core, as was proven by the X-ray diffraction patterns, is a result of a surface reaction creating UF_3 and a small amount of heat, causing local overheating of the charge. Once started, reduction proceeds upward through the charge leading to its complete ignition.

III. VACUUM MELTING AND CASTING OF CRUDE URANIUM BISCUITS

A. Description of Equipment

For the purpose of vacuum melting and casting of the crude uranium metal biscuits, a small-scale, high-frequency, vacuum induction melting furnace was employed. This furnace had a manifold made of SS with the flange supporting the furnace shell. The shell was made of $\frac{1}{8}$ -in. thick Vycor tube, 6 in. in diameter by 21 in. high, with ends ground flat and parallel. The vacuum seal between the Vycor tube and the furnace manifold flange was achieved by means of a flat silicon rubber gasket, 1 in. wide by $\frac{1}{8}$ in. thick. The manifold also served as a mold and crucible supporter, and was attached to the vacuum-producing system. The water-cooled copper tubing induction coil surrounded the furnace shell at the height where the melting crucible was located. The source of heat was a 30-kw, 9600-cycle motor-generator set. The upper furnace cover, made of brass, also had a silicon rubber gasket to provide a vacuum seal. The cover had a viewing tube with a sight glass and two vacuum seals for $\frac{1}{4}$ -in. rods. One of them was used for the vacuum seal thermocouple, and the other one for the vacuum seal pull rod. The pull rod was made of Type 304 SS and was connected to the stopper rod by means of a saddle and connecting pin, the last two being made of molybdenum and tantalum respectively.

Figure 23

Cutaway of the Vacuum
Melting Furnace

Melting crucibles were made of graphite and had dimensions of $2\frac{1}{2}$ in. ID by 3 in. OD by 4 in. high, with a $\frac{1}{4}$ -in. pouring hole in the bottom. Their capacity was about 2,000 gm of crude uranium metal in the form of irregular chunks. The graphite stopper rod was $\frac{1}{2}$ in. in diameter with the tip machined to a $\frac{1}{4}$ -in. diameter to plug the pouring hole in the crucible. Casting molds were also made of graphite and had dimensions of $1\frac{1}{2}$ in. ID by $2\frac{1}{2}$ in. OD by $3\frac{1}{2}$ in. high.

Figure 23 shows a cutaway of the vacuum melting furnace setup. The graphite mold rested on an open framework in the interior of the furnace manifold, while the insulation and the graphite crucible rested on the top of the mold. The insulation was made of porous Al_2O_3 bricks and had a dual purpose. First, it

helped to protect the Vycor tube against very high heat radiation, and secondly, by surrounding the melting crucible, it conserved the induced heat.

The vacuum system consisted of the 6-in. Booster Type Diffusion pump, Model MB-200, and a fore pump, Model Welch 1397B. This system provided a vacuum better than 1μ within 30 min after closing up the melting furnace. A thermocouple gauge made by National Research Corporation, capable of reading vacuum down to 1μ , was used for vacuum measurements. It was attached to the side of the furnace manifold.

B. General Procedure of Melting and Casting

Crude uranium biscuits, cut in the form of small chunks, were placed in the graphite crucible around the graphite stopper rod. In order to protect the molten metal from carbon pickup, both melting crucible and stopper rod were coated with ZrO_2 . This coating was done by means of a "Plasma Flame" torch, capable of realizing temperatures up to $30,000^\circ F$. At such high temperatures it was possible to spray ZrO_2 in the liquid form, which, after hitting relatively cold graphite surface, solidified, forming a protective layer. It was believed that such a layer would be capable of withstanding high temperatures and would not be attacked by molten uranium. To prevent this layer from cracking due to thermal shock, the metallic charge was heated at a slow rate in all experiments, taking about 40 min to reach $800^\circ C$. The rate of heating was increased gradually until charge melted.

After the crucible had been loaded and furnace closed, the whole system was evacuated by means of mechanical rotary pump. Further pumping down to 1μ , or even less, was achieved with the Booster Type Diffusion pump. In all experiments, a vacuum better than 1μ was obtained in about 30 min. The melting of uranium metal was always accompanied with the release of gases, causing a vacuum drop, and with bubbling due to the vaporization of the magnesium metal present in the crude uranium metal.

The casting temperature was $1,350^\circ C$ in all experiments, as measured by an optical pyrometer through the sight glass in the furnace cover. The use of optical pyrometer was justified by the fact that the sight glass remained clean throughout the whole experiment. Its accuracy was proven, because it always indicated the melting point of uranium at $1,130$ - $1,140^\circ C$. Casting of molten metal was usually accompanied with a slight pressure drop because of rapid outgassing of the relatively cold graphite mold.

There was no significant shrinkage on the top of the castings. All had a very smooth surface and needed only a light brushing to remove the mold coating. Each casting, $1\frac{1}{2}$ in. diameter by 3 in. high, was sectioned horizontally 1 in. from the bottom. Microscopic observations of the casting cross sections at 75X showed them to be sound.

According to the chemical analyses presented in Appendix B, Table II, most of the remelted ingots had carbon content several times as high as the crude uranium biscuits. The carbon content appeared to be dependent upon the thickness of the ZrO_2 coating on the melting crucible. In the case of the thin translucent coating, when it was possible to see the crucible color as a grayish background, carbon pickup was about 500 ppm. When the coating was thick enough to obliterate the color of graphite, the average carbon pickup was 92 ppm. Almost the same results were observed by others⁽⁸⁾ who have experimented with the wide variety of the coating materials applied to the graphite crucible in different ways. The best coating that had been evaluated was oxy-acetylene flame-sprayed magnesium-zirconate, which rather limited carbon pickup to an average value of 73 ppm. The use of ZrO_2 coating applied with "Plasma-Flame" torch appears to be a promising method of crucible preparation. It makes possible spraying of refractory oxides in the liquid form, thus forming an adherent carbide layer which protects the graphite from being dissolved in molten uranium metal. It would be a worthwhile study to evaluate such a coating procedure which will yield an ideal ZrO_2 coating thin enough to resist thermal shock, but yet thick enough to prevent the carbon pickup in molten uranium metal.

IV. CONCLUSION

It is possible to reduce uranium tetrafluoride with magnesium metal in a graphite-lined SS reduction shell. By firing hand-tamped charges of 3700 gm containing 6% excess of magnesium at a furnace temperature of 700°C, the maximum crude yield obtained was 93.71%. By compacting the same amount of UF_4 -Mg blend at 10,000 psi and firing it at 650°C, the crude yield increased to 97.2%, and there was an excellent separation from the MgF_2 slag. These yields were obtained using atomized magnesium metal, only a few months old, having bright and shiny surface.

The crude biscuits had a satisfactory purity, the total amount of impurities ranging from 500 to 800 ppm. The uranium metal obtained from hand-tamped blends had a very low carbon content (an average value of 42 ppm), which indicated that the molten uranium metal did not come in contact with the graphite lining. In the case of compacted UF_4 -Mg blend, the average carbon content was 173 ppm, which exceeded the maximum tolerance for reactor-grade uranium. All hydrocarbon binders used in making UF_4 -Mg compacts caused an increase in the carbon content of the crude uranium metal of 130 ppm compared with that in crude ones obtained by reducing the hand-tamped charges.

The X-ray diffraction patterns of the samples taken from the hand-tamped UF_4 -Mg charges during the preheating period showed that the initial reduction takes place far below 600°C. The reduction proceeds through an intermediate step characterized by formation of UF_3 , and could be interpreted as a gas-solid reaction.

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VI. APPENDIX A

Table A-I

CONTENT OF IMPURITIES (in ppm) PRESENT IN UF₄ USED
IN EXPERIMENTAL WORK

Ag	<1	Be	<0.5	Cr	1	Li	<1	Ni	<5	Sn	<5
Al	<5	Bi	<1	Cu	2	Mg	1	P	<50	Sr	-
As	<10	Ca	<20	Fe	<2	Mn	<1	Pb	<1	Ti	<50
B	<0.1	Cd		Hg	-	Mo	<20	Sb	<1	V	-
Ba	-	Co	<5	K	<50	Na	<5	Si	15	Zn	<50
										Zr	-

Table A-II

CONTENT OF IMPURITIES PRESENT IN MAGNESIUM USED IN (OR FOR)
REDUCTION OF UF₄

Name of Element	Magnesium (in %)		Name of Element	Magnesium (in %)		Name of Element	Magnesium (in %)	
	Old	New		Old	New		Old	New
Ag	<0.01	<0.01	Fe	<0.01	<0.01	Si	<0.01	<0.01
Al	<0.01	<0.01	Hg	-	-	Sn	<0.01	<0.01
As	<0.1	<0.1	K	-	-	Sr	<0.1	<0.1
B	<0.01	<0.01	Li	<0.01	<0.01	Ti	<0.01	<0.01
Ba	<0.1	<0.1	Mn	0.008	0.008	V	-	-
Be	<0.01	<0.01	Mo	-	-	Zn	0.08	0.08
Bi	<0.01	<0.01	Na	<0.01	<0.01	Zr	0.08	0.08
Ca	<0.01	<0.01	Ni	<0.01	<0.01	C	125-135*	110-138*
Co	<0.01	<0.01	P	<0.1	<0.1			
Cr	<0.01	<0.01	Pb	<0.01	<0.01	O ₂	-	-
Cu	<0.01	<0.01	Sb	<0.01	<0.01			

* ppm

Table A-III

CONTENT OF IMPURITIES (in ppm) PRESENT IN THE GRAPHITE
USED FOR CRUCIBLE MAKING

Ag	<0.1	Be	<0.5	Cu	<5	Mg	200	P	<200	Sr	-
Al	300	Bi	<1	Fe	1000	Mn	0.7	Pb	1	Ti	200
As	<20	Ca	700	Hg	-	Mo	-	Sb	<2	V	200
B	1.35	Co	<2	K	10	Na	-	Si	100	Zn	<20
Ba	4	Cr	5	Li	0.4	Ni	20	Sn	<1	Zr	<1

Table A-IV

CONTENT OF THE IMPURITIES PRESENT IN THE CRUDE URANIUM DERBIES
OBTAINED BY FIRING HAND-TAMPED UF₄ Mg BLEND

NAME OF ELEMENT	EXPERIMENT NO (Amounts in ppm)											
	1	2	3	4	5	6	7	8	9	10	11	12
Ag	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
Al	15	15	15	15	15	15	15	15	5	< 5	< 5	< 5
As	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10
B	0.3	0.3	0.3	0.3	0.4	0.2	0.2	0.2	< 0.1	< 0.1	< 0.1	< 0.1
Be	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
Bi	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
Ca	< 50	< 50	< 50	< 50	< 50	< 50	< 50	< 50	< 20	< 20	< 20	< 20
Cd	< 20	< 20	< 20	< 20	< 20	< 20	< 20	< 20	< 20	< 20	< 20	< 20
Co	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5
Cr	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	75	< 1	< 1	< 1
Cu	5	10	7	5	10	3	5	5	2	1	2	2
Fe	50	60	50	50	60	50	50	50	20	8	10	50
K	< 50	< 50	< 50	< 50	< 50	< 50	< 50	< 50	< 50	< 50	< 50	< 50
Li	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
Mg	40	50	40	50	700	160	30	50	30	30	>1000	60
Mn	40	40	40	40	40	40	30	40	150	100	100	10
Mo	< 20	< 20	< 20	< 20	< 20	< 20	< 20	< 20	< 20	< 20	< 20	< 20
Na	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 5	< 5	< 5	< 5
Ni	5	6	5	5	6	5	5	5	300	< 5	< 5	15
P	< 50	< 50	< 50	< 50	< 50	< 50	< 50	< 50	< 50	< 50	< 50	< 50
Pb	3	1	2	2	1	1	2	2	5	< 1	< 1	1
Sb	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
Si	< 10	10	10	< 10	20	15	15	20	15	15	15	15
Sn	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5
Ti	< 50	< 50	< 50	< 50	< 50	< 50	< 50	< 50	< 50	< 50	< 50	< 50
Zn	50	50	50	50	50	50	50	50	100	50	75	50

Table A V

CONTENT OF THE IMPURITIES PRESENT IN THE CRUDE URANIUM DERBIES
OBTAINED BY FIRING UF₄ Mg BLEND COMPACTED AT 10 000 psi

NAME OF ELEMENT	EXPERIMENT NO (Amounts in ppm)											
	13	14	16	17	18	19	20	21	22	23	24	25
Ag	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
Al	< 50	5	< 5	< 5	5	8	< 5	30	< 5	< 5	< 5	< 5
As	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10
B	< 0.1	< 0.1	< 0.1	< 0.1	< 0.2	< 0.1	< 0.8	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Be	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
Bi	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
Ca	< 20	< 20	< 20	< 20	< 20	< 20	< 20	< 20	< 20	< 20	< 20	< 20
Cd	< 20	< 20	< 20	< 20	< 20	< 20	< 20	< 20	< 20	< 20	< 20	< 20
Co	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5
Cr	< 1	< 1	< 1	< 1	15	< 1	30	< 1	< 1	< 1	< 1	< 1
Cu	2	2	2	2	2	1	1	5	1	2	1	1
Fe	20	20	20	10	15	10	15	50	10	10	15	10
K	< 50	< 50	< 50	< 50	< 50	< 50	< 50	< 50	< 50	< 50	< 50	< 50
Li	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
Mg	15	20	60	100	70	300	20	200	100	600	400	60
Mn	100	100	100	100	100	100	20	5	2	2	5	40
Mo	< 20	< 20	< 20	< 20	< 20	< 20	< 20	< 20	< 20	< 20	< 20	< 20
Na	< 5	< 5	< 5	< 5	20	< 5	< 5	< 5	< 5	< 5	< 5	< 50
Ni	5	15	15	< 5	< 50	< 5	200	15	< 5	< 5	< 5	< 5
P	< 50	< 50	< 50	< 50	< 50	< 50	< 50	< 50	< 50	< 50	< 50	< 50
Pb	3	3	3	3	1	2	1	1	< 1	< 1	< 1	< 1
Sb	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
Si	15	15	15	15	15	15	15	10	10	10	10	10
Sn	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5
Ti	< 50	< 50	< 50	< 50	< 50	< 50	< 50	< 50	< 50	< 50	< 50	< 50
Zn	< 50	< 50	75	75	75	100	< 50	< 50	< 50	< 50	< 50	< 50

Table A-VI

CARBON CONTENT IN THE CRUDE URANIUM METAL DERBIES

Carbon Content (ppm)			
Expt. No.	Derbies Obtained by Firing Hand-tamped UF ₄ -Mg Mixture	Expt. No.	Derbies Obtained by Firing UF ₄ -Mg Mixture, Compacted at 10,000 psi
1.	67.0; 94.0	13.	134.0; 133.0
2.	80.0; 102.0	14.	135.0; 147.0
3.	43.0; 39.0	16.	196.0; 193.0
4.	37.0; 33.0	17.	202; 225.0
5.	37.0; 35.0	18.	163.0; 161.0
6.	16.0; 10.0	19.	206.0; 180.0
7.	12.0; 6.0	20.	213.0; 225.0
8.	15.0; 23.0	21.	190.0; 188.0
9.	28.0; 52.0	22.	148.0; 156.0
10.	64.0; 43.0	23.	157.0; 198.0
11.	28.0; 48.0	24.	144.0; 197.0
12.	61.0; 62.0	25.	224.0; 205.0

Table A-VII

CONTENT OF THE GASES PRESENT IN THE CRUDE URANIUM DERBIES
OBTAINED BY FIRING HAND-TAMPED UF₄-Mg BLEND

Name of Element	Experiment No. (Amounts in ppm)											
	1	2	3	4	5	6	7	8	9	10	11	12
O ₂	17.0	19.0	7.0	3.0	16.0	4.0	5.0	11.0	91.0	-	7.0	-
	30.0	8.0	3.0	3.0	7.0	8.0	6.0	29.0	149.0	-	6.0	-
N ₂	21.0	54.0	43.0	26.0	14.0	19.5	29.0	15.0	<10	-	<10	-
H ₂	9.0	6.6	3.1	2.5	6.0	1.5	4.2	7.5	11.0	-	3.0	-
	10.0	3.7	1.5	1.7	8.0	2.4	3.6	8.6	15.0	-	1.8	-

Table A-VIII

----- CONTENT OF THE GASES PRESENT IN THE CRUDE URANIUM DERBIES -----

OBTAINED BY FIRING UF₄-Mg COMPACTED AT 10,000 psi

Name of Element	Experiment No. (Amounts in ppm)											
	13	14	16	17	18	19	20	21	22	23	24	25
O ₂	14.0	10.0	34.0	11.0	179.0	-	-	10.0	-	7.0	6.0	14.0
	11.0	7.7	47.0	2.3	343.0	-	-	15.0	-	18.0	6.0	12.0
N ₂	90.0	35.0	10.0	<10.0	48.0	-	-	23.0	-	<10.0	28.0	25.0
H ₂	7.0	4.0	6.0	7.0	10.0	-	-	7.0	-	5.0	5.5	7.0
	8.0	4.5	11.0	8.0	6.0	-	-	8.0	-	5.0	7.0	11.0

VII. APPENDIX B

Table B-I

IMPURITIES (in ppm) PRESENT IN REMELTED URANIUM INGOTS

Name of Element	Experiment				Name of Element	Experiment			
	A	B	C	D		A	B	C	D
Ag	<1	<1	<1	<1	Mn	40	20	15	40
Al	10	<5	<5	<5	Mo	<20	<20	<20	<20
As	<10	<10	<10	<10	Na	<10	<10	<10	<10
B	0.1	0.6	0.3	0.3	Ni	50	60	5	5
Be	<0.5	<0.5	<0.5	<0.5	P	<50	<50	<50	<50
Bi	<1	<1	<1	<1	Pb	<1	<1	<1	<1
Ca	<20	<20	<20	<20	Sb	<1	<1	<1	<1
Cd					Si	15	15	15	15
Co	<5	<5	<5	<5	Sn	<5	<5	<5	<5
Cr	3	3	3	<1	Ti	<50	<50	<50	<50
Cu	2	2	2	2	Zn	<50	<50	<50	<50
Fe	10	10	40	30	O ₂	5	7	3	13
K	<50	<50	<50	<50	H ₂	1.0	1.5	1.8	.7
Li	<1	<1	<1	<1	N ₂	30	18	10	10
Mg	5	7	5	10	C ₂	295	661	462	107
						292	669	547	116

Table B-II

CARBON CONTENT IN SAME TYPICAL URANIUM SAMPLES
BEFORE AND AFTER VACUUM MELTING AND CASTING

Expt. No.	Carbon Content in Uranium Metal (ppm)		Thickness of ZrO ₂ Coating
	Before Melting	After Melting	
A	173	290	Thick coating; graphite invisible
B	173	665	Thin coating; graphite visible
C	43	111	Thick coating; graphite invisible
D	43	546	Thin coating; graphite visible