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PROGRESS REPORT ON METAL REDUCTION,
NOVEMBER 1943

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Metallurgy – All
Uranium

ABSTRACT

The most suitable bath which has been developed contains barium fluoride and barium chloride in equimolar quantities and as little as 10% by weight of uranium tetrafluoride. The uranium is deposited in globular form in a reddish matrix. A water-cooled cathode and kerosene-dry ice quench have been found advantageous.

An initial attempt to reduce UF_4 in a fused salt medium by means of calcium was successful, but later attempts failed.

Melting of uranium and recovery of turnings under fused $BaCl_2$ have been successful in initial experiments.

Further experiments have conclusively shown that zirconia liners, in no matter what physical condition, give yields greatly inferior to those from the magnesia liners previously employed. The particle size of the calcium should be about -20, +30 mesh, for finer metal is largely oxidised before it can be used, and coarser grains do not react quickly. Copper or steel bombs with no refractory liner give yields varying between 62 and 93 percent, and warrant further study. On slow heating the standard fluoride-calcium-iodine mixture fires at 620° C, but before that time the iodine has completely reacted with the calcium, coating it with iodide, without evolving sufficient heat to trigger the main reaction. Less calcium than the customary 25 percent excess decreases the yield disproportionately.

Latest trials with 200 gram charges has given yields of over 99 percent good metal in a clean biscuit. Freshly-ground clean calcium, free from oxide, is essential. Magnesia liners, 3/8 in. thick, fired at 1750° C are used. Heating to the firing point in about 7 minutes seems best, and heat should be concentrated. so that the charge first ignites at the top.

PROGRESS REPORT ON METAL REDUCTION, NOVEMBER 1943

PART 1: ELECTROLYSIS, ALKALINE EARTH METALS IN FUSED SALTS, FLUX
MELTING

by M. Kolodney

I. ELECTROLYSIS

A. Introduction

The previous progress report (LA-35) covered work performed in the
interval of October 6 to October 28, 1943, and detailed the results of
solubility tests of uranium tetrafluoride and dioxide in various alkali and
alkaline earth fluorides as well as some electrolysis employing chiefly baths
of sodium-uranium fluorides. These baths required high concentrations of
tetrafluoride for satisfactory operation, and were quite volatile at the opera-
ting temperatures. Very small yields of uranium metal were obtained.

It was believed that considerable loss of metal resulted from oxida-
tion during the withdrawal and air cooling of the cathode, and that such
oxidation might be reduced through the use of an inert atmosphere during
electrolysis and/or during cooling after removal of the cathode from the bath.
It is obviously desirable to reduce both volatility as well as the minimum
concentration of uranium salts in the bath in order to minimize evaporation
losses.

In order to reduce air oxidation, a water-cooled steel cathode was
substituted for the previously used graphite cathode, and the electrolytic
product was quenched rapidly in kerosene which contained solid carbon dioxide.
A water-cooled cathode appears desirable because it permits deposition from a
bath above the melting point of uranium and yet produces a solid cathode
product which had been in contact only with fused salt, and should, therefore
possess a higher purity than metal deposited on the walls of a graphite crucible.

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Bath volatility can be reduced by employing fluorides or other salts of high boiling points, such as the fluorides of calcium, magnesium, barium and aluminum. Of these, the most desirable from the viewpoint of contamination are the salts of barium. Accordingly, the major effort was directed toward the development of a satisfactory barium-base electrolyte, although exploratory experiments were made with the others.

B. Experimental

The following table (Table I) summarizes the results of the electrolytic experiments. Current densities are necessarily approximate, and the voltages include line and contact drops. Temperatures were measured at the bath surface with a Leeds and Northrup optical pyrometer. Unless otherwise specified, the cathode was a water-cooled steel pipe 0.54 inches in diameter with closed end, and was quenched in kerosene containing solid carbon dioxide. The salts used were C.P. or reagent grade. The uranium deposited was almost invariably in a matrix of red-brown material and was recovered by crushing, sieving and washing.

Examination of the results indicates that while uranium may be electrodeposited from simple mixtures of sodium and uranium fluorides, the proportion of tetrafluoride is high and evaporation is excessive. The metal can also be successfully deposited from similar mixtures with calcium fluoride but there is a marked tendency for current fluctuation, and the tetrafluoride content was high in order to reduce the melting point. It is likely that lower UF_4 concentrations would result in more unsteady conditions. A simple mixture of barium and uranium fluorides behaved in similar fashion. However, mixtures of barium fluoride, barium chloride, uranium dioxide and uranium

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fluoride appeared promising because lower concentrations of uranium salts seemed successful, and a portion of the undesirable fluoride could be replaced by chloride. These baths, however, appeared subject to vexatious peculiarities seemingly dependent upon the method of addition of materials. For this reason, the use of UO_2 (which seemed to be the cause of the difficulty) was temporarily abandoned, and in the baths listed last in Table I (37-40) only the barium salts and the tetrafluoride were present. The barium compounds are in molecular ratio because in this proportion the melting point is approximately 1000 C, higher than that of any other $BaCl_2$-rich mixture. It will be noted that when the total electrolyte weight is about 800 grams, it is possible to operate satisfactorily with a UF_4 concentration of 10 weight percent, a decided advantage from the viewpoint of vaporization losses.

In addition to the experiments listed in Table I, two others were performed with submerged cathodes in the hope of eliminating air oxidation. In the first (41), a graphite cathode projecting from the base of a graphite crucible was in close proximity to a graphite anode, in the expectation of reducing current passage to the crucible walls. The bath was substantially similar to those of runs 37-40. Only a bronze powder was obtained at the cathode. In the second (42), a porcelain crucible was employed with a bottom graphite cathode and a similar bath. Some particles of uranium were obtained at the cathode, but were in a reddish matrix, resembling the cathode products of top-cathode runs.

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TABLE I   SUMMARY OF ELECTROLYTIC EXPERIMENTS

Run	Bath Composition Weight Percent	Operating Conditions	Result	Remarks
14	12 NaF; 88 UF_4	Graphite crucible cathode; 4 amp 1 sq in; 30 amp hrs; 5-6 volts; 1100C	Faint traces of uranium detected by grinding	Bath melts at about 650 C; Excellent conductivity. Evaporation considerable
15	12 NaF; 88 UF_4	70 amp/sq in; 7 amp hr; 6 volts; 1150 C; air-cooled	Uranium deposited in globular form. Recovered 2 globules 2-3 mm diam.	Considerable bath volatilization
17	11 NaF; 9 BaF_2; 80 UF_4	70 amp/sq in; 5 amp hr; 6 volts; 1130-1150 C	Considerable uranium as small globules 1 mm diam.	
18	Same as run 17	1225-1275 C	Considerable uranium. Particle size increased over run 17	Considerable bath evaporatic
19	11 NaF; 9 BaF_2; 80 UF_4	23 amp/sq in; 11 amp hr; 6 volts; approx 1000 C	Thick heavy deposit of fine uranium. Deposit pyrophoric when crushed	
20	36 BaF_2; 64 UF_4	0-110 amp/sq in; 9 volts; 1125-1150 C	Fine spheroids of uranium	Bath fumed. Current fluctuat widely apparently because of failure of salt to wet cath
21	85 Tech grade cryolite; 15 UF_4		Non-conducting film formed cathode. Current zero	

TABLE I   SUMMARY OF ELECTROLYTIC EXPERIMENTS (cont)

Run	Bath Composition Weight Percent	Operating Conditions	Result	Remarks
22	20 CaF_2; 80 UF_4	110 amp/sq in; 15 amp hr; 7.5 volts; 1135-1150 C	Much metal deposited in rod-like growths about $\frac{1}{2}$-1 mm diam.	
23	20 CaF_2; 80 UF_4	70 amp/sq in; 15 amp hr; 8 volts; 1200 C	Deposit in rod-like growths. One piece 3x5 mm	
24	20 CaF_2; 80 UF_4	32 amp/sq in; 33 amp hr; 1210-1225 C	Layer 1/8" thick consisting almost entirely of fine uranium	Current unsteady
25	36 BaF_2; 10 $BaCl_2.2H_2O$ 12 UO_2; 42 UF_4 or 36.6 BaF_2; 8.6 $BaCl_2$ 12.2 UO_2; 42.5 UF_4	110 amp/sq in; 7 amp hr; 7 volts; 1060 C	No metal. Deposit reddish	Current steady. Bath prepared by melting UO_2 and UF_4 and adding BaF_2 and $BaCl_2 \cdot 2H_2O$ in succession
26	36 BaF_2; 10 $BaCl_2 \cdot 2H_2O$ 12 UO_2; 42 UF_4 or 36.6 BaF_2; 8.6 $BaCl_2$ 12.2 UO_2; 42.5 UF_4	110 amp/sq in; 11 amp hr; 1225 C	Uranium deposited in the form of pieces 1-3 mm diam.	
27	Same as run 26	110 amp/sq in; 22 amp hr; 7 volts; 1285-1300 C	Layer 1/16" thick, mostly uranium in fine form	

TABLE I   SUMMARY OF ELECTROLYTIC EXPERIMENTS (cont)

Run	Bath Composition Weight Percent	Operating Conditions	Result	Remarks
28	Same as run 26	Graphite rod cathode; 110 amp/sq in; 7 amp hr; 1200 C approx	Considerable metal in form of spheres ranging from powder to several mm diam.	
29	Same as run 26	Graphite rod cathode; 90 amp/sq in; 11 amp hr; 1150-1180	Considerable uranium similar to run 28	Bath prepared by premixing all salts
30	Same as run 26	Same as run 29, but 1225-1250 C; 6 amp hr	3 fairly large pieces of uranium, larges 9 mm long x 3 mm wide	
33	26 BaF_2; 36 $BaCl_2 \cdot 2H_2O$ 19 UO_2; 19 UF_4 or 27.5 BaF_2; 32.5 $BaCl_2$; 20 UO_2; 20 UF_4	70 amp/sq in; 23 amp hr; 9 volts; 1290-1300 C	Considerable uranium in particles ranging from powder to about 3 mm. Recovered material represents current efficiency of 13%	Bath is result of additi of UF_4 to BaF_2, $BaCl_2$, UO_2 mixture
35	Same as run 33 Fresh bath			Bath prepared from pre-mixed materials; melt viscous. Severe anode effect which was elimina by addition of UF_4

TABLE I   SUMMARY OF ELECTROLYTIC EXPERIMENTS (cont)

Run	Bath Composition Weight Percent	Operating Conditions	Result	Remarks
37	38 BaF_2; 53 $BaCl_2 \cdot 2H_2O$ 9 UF_4 or 41.3 BaF_2; 49 $BaCl_2$ 9.8 UF_4	Approx 4 amp hr; 6.5 volts; 1210 C	Considerable metal in particles 1 mm diam.	Current not perfectly steady. Total electrolyt 200 g.
38	30 BaF_2; 41.5 $BaCl_2 \cdot 2H_2O$ 28.5 UF_4 or 32 BaF_2; 37.6 $BaCl_2$; 30.4 UF_4	15 amp hr; 6.5 volts 1175 C	Much uranium in form of small particles	Current steady. Total electrolyte 200 g.
39	Same as run 37	40 amp/sq. in; 12 amp hr; 6 volts; 1125 C	Great deal of uranium in form of small spheres	Bath prepared by melting $BaCl_2 \cdot 2H_2O$; adding BaF_2 a UF_4 in succession. Total electrolyte 880 grams. Current very steady. Evaporation slight.
40	Same as 39. Replenished with UF_4	23 amp/sq in; 25 amp hr; 6 volt; 1190 C	Great deal of uranium; larger pieces 5 mm long	

C. Plans for Future Work

It is planned to determine the effect of operation in inert atmosphere in order to determine whether the non-metallic material codeposited with the uranium is a product of an oxidation. In any case, an inert atmosphere would be essential if the solidified uranium is to be withdrawn from the bath continuously.

There has been some indication in the experiments that higher current densities may result in a less contaminated product, but such work awaits removal to new quarters.

Much work remains to be done on the proper selection of bath materials and proportions. The proportions of barium fluoride and chloride, the effect of UO_2, and additions of other fluorides require investigation. In addition, the field of alkaline baths containing oxides has not been explored.

Plans are at present being made for work directed toward the plating of uranium from fused salts and organic solvents in the hope of obtaining uniform deposits at low temperatures. This work, too, must await removal to new quarters.

II. REDUCTION BY ALKALINE EARTH METALS IN FUSED SALTS

A. Introduction

In the course of conversation with Mr. Kinzel, the probable importance of complete dehydration of fused salts was mentioned, and subsequently, Mr. Jette suggested that dehydration might be assured by the addition of a metal such as calcium to the fused salt. It occurred to the writer that such a process might yield uranium in a manner analogous to the bomb reaction.

B. Experimental

The first fused salt mixture selected for a trial of calcium addition was the bath which had been employed in run 41 and which had been subsequently electrolyzed. Approximately 4 grams of lump distilled calcium from Electrometallurgical Sales Corporation were added to the bath at about 1100 C, after which the bath was again electrolyzed for a short time. Upon removal of the solidified salt, 11 grams of uranium were obtained in the form of 4 pellets, 3 large and 1 small.

Since the process appeared relatively simple, further experiments were performed using calcium, barium and magnesium as reductants in various calcium and barium salt mixtures. In all, 7 reductions with calcium, 3 with barium, and 1 with magnesium were attempted. Only minute particles of uranium were obtained at best.

C. Conclusions

It is believed that the reaction in the presence of fused salts of the types described is not simple, but is probably complicated by the reduction of the bivalent salts to well-established monovalent compounds such as BaCl, BaF, CaF, CaCl, etc. The same process presumably occurs in electrolysis, and may account for the success of the initial attempt. The obvious suggestion is the use of salts of monovalent metals such as sodium, but unfortunately, while calcium and barium enter melts of their respective salts in well-behaved fashion, their introduction into sodium fluoride is accompanied by pyrotechnical display occasioned by volcano-like eruptions of the fused salt.

A few additional experiments are planned, but it appears likely that adequate solution of the problem would require a lengthy research program.

III. FLUX MELTING

In further investigation of the presence of water in $BaCl_2$ melts, their effect on metallic uranium was studied. The barium chloride was melted in graphite without any previous dehydration, heated to 1350 C and 28 grams of extruded Tuballoy introduced. After cooling, approximately 28 grams of cast uranium were recovered. The experiment was repeated with more careful weighing, the salt heated to 1425 C, and the metal introduced at 1350 C. Some carbide appeared to form on the surface of the cast product. After cleaning, the recovery on a 40 gram charge was 97-98%.

In cooperation with R. Kamm, approximately 800 grams of Tuballoy were melted under very little $BaCl_2$ (much of the fused salt was lost by splashing resulting from introduction of the metal) at 1300 C and the whole poured by tipping into a graphite mold. The resultant casting appeared visibly sound after sectioning, but contained numerous microscopic rosettes of some unidentified material.

Uranium turnings contaminated with carbon and oil were cleaned with water, dilute alkali and nitric acid, and 50 grams of these added to 100 grams of a $BaCl_2$ melt at 1275 C. Recovery after cleaning the ingot was 94.6%. Similarly, 10 grams of the same turnings were compressed into a pellet and added to $BaCl_2$ melt at 1200 C. The resultant button just failed of complete fusion, a portion being only sintered, probably because of low temperature. After removal of carbide with dilute acetic acid, recovery was 99.5%.

The barium chloride melts appeared little affected by the uranium, but were not crystalline and were slightly yellow. On the other hand, $BaCl_2$-BaF_2 melts had been observed to turn brown during calcium reductions.

It was thought that this might be the result of solution of UO_2. A molar proportion mixture of BaF_2-$BaCl_2$ was melted and 50 grams of uranium turnings added at 1300 C. The salt turned brown, was crystalline, but only 69% recovery was obtained in the form of a coherent ingot after cleaning.

The experiments are too few for decisive conclusions.

PART 2: SMALL-SCALE BOMB PRODUCTION

by R. D. Baker

I. ZIRCONIA LINERS

In LA-35 it was stated that zirconia liners fired to 1800° C gave an average yield of 73.0% as compared with 95.5% when using fired magnesia liners. Further work has been done using zirconia liners. The charge consisted of 10 grams UF_4, 3.42 grams - 20 + 30 mesh Ca and 1.15 grams iodine. These weights 1/7 mole I_2/mole UF_4 and 25% excess calcium. The bombs were heated in a 3 KW induction furnace. The data obtained are given in the following table.

TABLE I

Reductions in Zirconia Liner
(10 gram charge, throughout)

Liner	Heating Time To Fire (Min.)	Yield, %	Remarks
1. ZrO_2 fired to 1800 C 3/16" wall	4	73.0 (av)	Poorly formed buttons, beads of metal entrapped in slag.
2. ZrO_2 fired to 1700 C 3/16" wall	4	53.0	Same as 1.
3. ZrO_2 fired to 1600 C 3/16" wall	4	80.0	Poorly formed button of metal, some beads held in slag layer.
4. Same as 3	4	50.9	Same as 3.
5. ZrO_2 fired to 1500 C 3/16" wall	4	0	Only powdered metal obtained.
6. ZrO_2 fired to 1400 C 3/16" wall	4	0	Same as 5.
7. ZrO_2 + 4% sawdust fired to 1800 C 3/16" wall	4	70.5	Beads of metal, no coherent piece.
8. Dry packed ZrO_2 3/16" wall	4	63.0	Poorly formed button of metal.

TABLE I (cont)

	Liner	Heating Time (Min)	Yield	Remarks
9.	ZrO$_2$ fired to 1800 C 1/16" wall	3.5	81.0	Poorly formed button, beads of metal entrapped in slag.
10.	Same as 9	3.5	80.9	Same as 9.
11.	ZrO$_2$ fired to 1800 C 1/8" wall	4	69.7	Poorly formed button, beads of metal entrapped in slag.
12.	Same as 11	4	36.8	Same as 11.
13.	ZrO$_2$ fired to 1800 C 1/4" wall	4	24.3	Same as 11.
14.	Same as 13	4	62.3	Same as 11.
15.	ZrO$_2$ fired to 1800 C 1/16" wall	8	72.3	Poorly formed button, beads of metal in slag.
16.	ZrO$_2$ fired to 1800 C 1/8" wall	9	62.3	Same as 15.
17.	ZrO$_2$ fired to 1800 C 1/4" wall	10	81.0	Poorly formed button, beads of metal in slag.
18.	ZrO$_2$ fired to 1800 C 3/16" wall	16	77.7	Same as 17.

Entries 1 through 6 are for liners fired to different temperatures. The liners fired to 1800°, 1700° and 1600° C appeared to be the same. They were very hard and had smooth walls. In all cases the slag formed a layer on the walls of the liner in which small beads of metal were entrapped. The buttons of metal were all poorly formed and were covered with slag. Because of the low and erratic yields no definite conclusions can be drawn concerning the liners fired to 1800°, 1700°, or 1600° C. The liners fired to 1500° and 1400° C were soft but the walls were as smooth as on liners fired at higher temperatures. These low fired liners gave

only powdered metal. The liner which was made from a mixture of ZrO_2 and sawdust (7) was hard but had rough porous walls. The dry packed but unfired ZrO_2 liner (8) gave results comparable with the fired liners.

Entries 9 through 14 in Table I give the results of experiments on wall thickness of liners. The dimensions of the charge were the same as in all runs reported, the size of the bomb being different to accommodate the different wall thickness of the liner. These data on wall thickness indicate that the 1/16" wall liner is the best, however, the yields are low in all cases. Entries 15 through 18 show the results obtained by slow heating of the charges in zirconia liners of various wall thickness. The slow firing had no definite effect on the yields or character of the metal obtained.

The results presented in Table I indicate that the poor yields may be due to a change in the composition of the slag as compared with magnesia liners rather than to differences in heat conductivity or porosity. A charge consisting of 5 grams of the ZrO_2 used for liners, 4.13 grams of - 20 + 30 calcium and 0.96 grams of I_2 was placed in a bomb with a ZrO_2 liner, heated for 4 minutes under the same conditions as in a reduction of UF_4. A black sintered powder was formed. This powder was treated with water to remove the calcium and leached until no longer alkaline. The black powder which remained burned vigorously to a white oxide when heated to a low temperature. It contained approximately 13% zirconium metal as calculated from the gain on ignition. An analysis of uranium metal produced in a zirconia liner which had been fired to 1800° C gave 0.18% zirconium metal. This further indicates that the zirconia liner is reduced by the calcium metal.

II. PARTICLE SIZE OF CALCIUM METAL

The calcium metal used in all reductions reported above and in LA-35 was redistilled calcium as received from Electro-Metallurgical Company. This metal was ground in a Wiley mill and the - 20 + 30 mesh fraction used. Some experiments on particle size of calcium metal were run; the data being reported below. The charge consisted of 10 grams UF_4, 3.42 grams Ca and 1.15 grams I_2. The liners used were of magnesia fired at 2200° C. The wall thickness was 3/16". The bombs were heated in an induction furnace at 3 KW for the times stated.

TABLE II

	Size of Ca Used	Heating Time (min)	Yield	Remarks
1.	Pieces 2x2x1 mm	4	44.8	Poorly formed button covered with slag.
2.	Same as 1	4	76.5	Same as 1.
3.	-30 mesh as taken from Wiley mill	4	65.0	Poorly formed button covered with slag.
4.	Same as 3	4	76.2	Same as 3.
5.	-30 +80 mesh	4	95.5	Well formed button, free of slag.
6.	Same as 5	4	96.5	Same as 5.
7.	-100 +270 mesh	4	0	Only powdered metal formed.
8.	Same as 7	4	0 0	Same as 7.

The large pieces of calcium metal (entries 1 and 2) gave low yields and poor checks. The slag layers on the walls of the liners were uneven, most of the slag having run down on top of the metal. Entries 3 and 4 show the results obtained by using the - 30 mesh material as taken from the Wiley mill. This material had

the following screen analysis: - 30 + 80, 90%; - 80 + 100 mesh, 5%; - 100 + 270,

5%. The results obtained with this Ca were similar to those obtained using the

large pieces of Ca. The - 30 + 80 mesh calcium used in entries 5 and 6 was the

same as in 3 and 4 except that the - 80 mesh material was removed. The results

were very similar to those reported using - 20 + 30 mesh calcium. The buttons of

metal were compact and were free of slag. The - 100 + 270 mesh material used in

7 and 8 gave only powdered metal. These fine particles become covered with a

layer of oxide during milling, the presence of which probably accounts for the poor

results. This is also brought out by comparing entries 3 and 4 with entries 5 and

6. With the exception of the large pieces, it is believed that the above data does

not show the effect of particle size of the calcium but the effect of the amount

of oxide on the calcium particles. It is believed that the lower yields obtained

with the large pieces of calcium are due to poor mixing of the calcium and UF_4.

Some experiments were also run using - 20 + 30 mesh Baker reagent grade

calcium. It was received in the form of turnings and ground in the Wiley mill.

All conditions were the same as used for the reductions given in Table II. The

yields on two runs were 94.2 and 93.7%. The results were comparable with those

obtained using the - 20 + 30 mesh calcium prepared from the Electro-Metallurgical

calcium.

III. METAL BOMBS WITHOUT LINERS

Only preliminary work has been done on the use of metal bombs without

liners. The bombs used had the same internal dimensions as the liners used in

previous reductions. The steel bombs used were of two wall thicknesses, namely

1/8" and 1/4". The copper bombs used had a wall thickness of 1/4". The covers

were of the same material and were held on by a clamp. A thin layer of magnesia

was placed on the bottom before the standard 10 gram charge was poured in. The

data obtained are given in Table III. The yields are probably low because the bombs leaked iodine during heating, which was done in a 3 KW induction furnace. There was a slag layer formed on the sides of the bombs very similar to that formed in a magnesia liner. There was some slag on the button of metal. The walls of the steel bombs showed no attack but the Cu bombs were attacked slightly. Further work using metal bombs is now in progress.

TABLE III

Reduction in unlined metal bombs

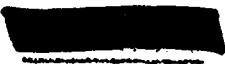|	Bomb	Heating Time (Min)	Yield	Remarks
1.	Steel, 1/8" wall	1.5	61.7	Poorly formed button. Bad I_2 leak.
2.	Same as 1	1.5	85.6	Same as 1.
3.	Steel, 1/4" wall	2	82.5	Same as 1.
4.	Copper, 1/4" wall	4	92.5	Well formed button, yellow color on slag.
5.	Same as 4	4	72.4	Poorly formed button, yellow color on button and slag. I_2 leak.
6.	Same as 4	4	79.4	Same as 5.

IV. PREHEAT EXPERIMENTS

It is planned to carry out experiments in which the loaded bomb is heated at a temperature below the ignition temperature before it is fired in the induction furnace. Work has been carried out to determine the temperature at

which the reaction starts. These experiments were done with the standard 10 gram charge in an unlined steel bomb with a thermocouple attached to the side. The bomb was placed in a cold electric muffle furnace and heated at such a rate that it took 1 hour 20 minutes to reach 620° C, at which temperature the reaction started and the temperature suddenly increased.

The standard charge was held at 500° C for 1 hour and examined. The UF_4 remained unchanged. No iodine was visible and the Ca particles were covered with a brown material, probably CaI_2. The same results were obtained at 300° C. It therefore seems unlikely that the iodine "booster" helps by its heat of reaction, and its effect is probably entirely due to the fluxing action of the iodide.

V. VARIATION OF THE AMOUNT OF CALCIUM

Experiments using less Ca that the standard 25 percent have been run. Reductions using a charge of 10 grams of UF_4, 2.87 grams (5 percent excess) -20 +30 Ca, 1.15 grams I_2, fired in MgO liners by the standard method gave a yield of 59.5 percent in one trial, and only powdered metal in another.

Charges consisting of 10 grams of UF_4, 2.7 grams of Ca and 1.15 grams of I_2 were also studied with standard liner and firing technique. This charge contains Ca for all the UF_4 and 90 percent of the I_2. Yields of 30.3 and 45.6 percent were obtained. There was evidence of unreacted UF_4 in the slag.

PART 3:   BOMB REDUCTION ON 200-GRAM SCALE

by R. H. Dunlap

INTRODUCTION

This report relates to the results thus far obtained in the production of tuballoy on a 200-gram scale by the bomb reduction method. The ultimate object of the investigation is the development of a method suitable for the production of 25.

To obtain optimum conditions for this type of reduction a standard charge was adopted and a series of variables were investigated. The experiments were designed to determine the effect of:

1. liner thickness

2. fired vs tamped liners

3. top vs bottom firing of charge

4. fast vs slow firing (effect of preheat)

5. particle size of calcium on yield

6. oxide content of calcium

Experiments, wherein the optimum conditions so far determined have been employed, have resulted in yields of uranium in excess of 99 percent of the theoretical.

METHOD

Briefly the method comprises reacting a charge consisting of uranium tetrafluoride plus 1/7 of a mole of iodine per mole of tetrafluoride with calcium metal in an amount 25 percent in excess of the theoretical requirements for reaction with the tetrafluoride and iodine. The charge is fired in a suitable refractory crucible within a sealed metal container, heated by high frequency induction.

APPARATUS AND MATERIALS

Three steel (SAE 1020) reaction chambers, or bombs, of 3/16" wall thickness were made. Each bomb had an inside height of 6 1/2" and had a detachable cover at one end. The inside diameters of the three bombs were 2", 2 1/4", and 2 1/2" respectively. This variation in the I.D. of the bombs enabled the use of fired liners having a constant I.D. of 1.75" but wall thicknesses of 1/8", 1/4" and 3/8" respectively. A fourth bomb was made of 1/4" thick steel (SAE 1020) provided with detachable covers at both ends. This bomb was designed for 3/8" liners and was one inch greater in inside height than the single cover 3/8" liner bomb previously described. This extra height enabled the use of shaped bottoms in the crucibles, if desired.

All liners, or crucibles, were made by tamping dry (200 mesh) periclase in a graphite mold and firing at 1750° C by induction heating. The 1/8" and 1/4" thick liners can be satisfactorily fired in 20 minutes. The 3/8" liners require 30 minutes, preferably 35, to avoid internal breakdown due to the initial shrinkage of the outside of the liner. The shrinkage factor lies between 6 and 7 percent. Tops for crucibles are made by firing a cylinder of the desired diameter and cutting slices of the required thickness.

The bomb firing was done in a 6" high frequency coil. Power input was obtained from either a 50 KW 3000 cycle motor generator set or a 20 KW spark gap high frequency outfit as indicated in the tables.

The tetrafluoride used was batch M 4215 LR 64. The iodine was regular Baker reagent. The calcium was cut in a Wiley mill to various grain sizes as will be discussed under the individual experiments.

Two sizes of charge were used as below:

	150-gram theoretical yield.	200-gram theoretical yield
UF_4	197.85 grams	263.80 grams
I_2	22.85 "	30.46 "
Ca	67.50 "	90.01 "

Both of these charges represent 1/7 mole of I_2 per mole of UF_4 and 25 percent excess of calcium metal over that required for complete reaction with the UF_4 and I_2. These charges, hereinafter referred to as standard 150-gram and 200-gram charges, respectively, were used in all experiments.

EXPERIMENTAL RESULTS

1. Effect of liner thickness and point of firing

Table A, below, indicates the effect of increasing liner thickness and method of firing the charge on the percentage yield.

TABLE A

	Liner Wall Thickness		
	1/8"	1/4"	3/8"
Run No.	2098	2099	2100
Yield, top fired (percent)	93.14	95.3	96.66
Run No.	2101	2102	2103
Yield, bottom fired (percent)	86.07	91.7	93.0

All runs used the standard 150 gram charge with redistilled calcium ground to -20 +30 mesh size and were fired in 7 minutes by the use of 5KW in the 50 KW outfit. The improvement in percentage yield with increased liner thickness, with top firing is evident. There was a very definite improvement in the condition of the reduced button with top firing. It is believed that the higher yield and better button from top firing result from the fact that the reaction proceeds downward with a constantly increasing pool of metal collecting on the lowering surface of the reacting mass.

2. Effect of tampered V fired liners

The standard 200 gram charge was employed with -20 +30 mesh redistilled calcium. The bombs were fired as between 4 and 5 KW in the 50 KW outfit. Time to fire was approximately 6 1/2 to 7 minutes. A tampered MgO liner resulted in a yield of 93.7 percent (Run no. 2107) as against 96.8 percent (Run no. 2135) for the run employing a fired MgO liner.

3. Effect of rate of firing

The standard 200 gram charge was employed with redistilled calcium of a -20 +30 mesh size. The runs were made in 3/8" fired MgO liners, top fired. Table B indicates the results of this work.

TABLE B

Run No	Time to Fire	Power Source	KW Input	Percent Yield
2120	3 min	generator	10 KW	92.8
2135	7 min	"	4 to 5 KW	96.8
2143	" "	"	"	95.5
2154	25 min to 600 C 10 Min at 950 C	spark gap	4 KW 25 min 8 to 10 KW 10 min	93.5
2155	as above	"	as above	94.3

4. Effect of particle size and condition of calcium

Excessively large particle size as well as the use of oxidized calcium has been found detrimental to high yields. Table C indicates the results obtained. The first two runs indicate the effect of particle size and are particularly significant inasmuch as the turnings were cleaner metal than the fines, thus indicating that particle size is of even more consequence than the condition of the calcium. The last five runs indicate the effect of oxidation when particle size is uniform. All runs in the table are 200 gram standard charge, 3/8" fired MgO liners, top fired.

TABLE C

Run No	Time to Fire	Power Source	KW Input	Type of Calcium	Percent Yield
2143	7 minutes	generator	4 to 5 KW	-30 mesh & down, redistilled, somewhat oxidized	95.5
2144	" "	"		Turnings (Merck) Lot no 9232	87.6
2147	(25 min to 600 C (10 " at 950 C	Spark gap generator	(4 KW 25 min (8 to 10 KW 10 min	As above, ground 20 mesh and down	98.1
2156	As above	"	as above	As above	99.15
2154	" "	"	" "	Redistilled, somewhat oxidized, 20 mesh and down	93.5
2155	" "	"	" "	As above but -30 mesh removed and remainder reground	84.3
2165	" "	"	" "	Redistilled, new can, as ground, 20 mesh and down	99.3

CONCLUSIONS

Experimental work to date on improving the percentage yield of uranium in the reduction of UF_4 by calcium in the presence of iodine indicates that liners of $3/8$" wall thickness (MgC fired 1750° C) are superior to liners of $1/4$" or $1/8$" wall thickness. Fired liners are superior to tamped liners. Top firing of the charge is superior to bottom firing. Slow firing (long preheating) is superior to fast firing. Small particle size in calcium (20 mesh and down) is superior to machine turnings. Oxidized calcium is very detrimental to high yields.

By the use of $3/8$" fired MgC liners; slow preheat; top firing; clean, small particle size calcium; the standard 200 gram charge can be expected to result in yields in the range 98 percent and 99 percent.