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A STUDY OF THE EFFECT OF VARIOUS FACTORS
ON THE YIELDS OBTAINED
IN THE REMELTING OF URANIUM METAL

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For The Atomic Energy Commission
W. B. Cancele
Chief, Declassification Branch

I. INTRODUCTION

One of the most important factors to be dealt with in the remelting of uranium metal is the ultimate remelt yield. This yield is defined as the ratio of the weight of metal poured from the crucible at the end of the run to the weight of metal loaded into the crucible as the charge. The object of the investigations made was to get the highest remelt yield obtainable without hurting the quality of the metal produced.

A number of things were tried in order to bring up the remelt yield. The furnace vacuum was improved. Different pouring temperatures were used until an optimum temperature was reached. The composition of the crude metal charge was studied so as to get the best usable material for the runs. Dressings were developed for graphite to give a better crucible surface. An inert gas atmosphere was used in the remelting furnace to cut down oxidation of the metal.

II. DISCUSSION

There are a number of things which affect the remelting yield of uranium metal. These things are listed below in order of their importance as nearly as possible.

The thing which has the most effect on the remelt yield is

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the quality of the crude metal used for the charge. Both the physical and chemical characteristics of the crude metal affect the remelt yield appreciably. The physical properties, being the most evident, will be taken up first.

The reduction of uranium tetrafluoride with magnesium is carried on in an upright closed cylindrical steel vessel. This vessel is lined with dolomite which is packed in very tight with the aid of a steel form and a barrel jolter. After the form is removed from the vessel, the charge of uranium tetrafluoride and magnesium is poured into the resulting space and packed down. The charge is then covered over with dolomite and a lid is bolted on the vessel to keep the contents in place. As can be seen from above, the homogeneous mass of uranium tetrafluoride and magnesium is completely surrounded with dolomite. The reduction vessel is then heated in a gas-fired furnace until the ignition temperature is reached, at which time the uranium tetrafluoride and magnesium react violently to give molten uranium metal. This reaction can be shown by the following equation.

The molten metal runs down the dolomite walls of the reaction vessel and forms a pool of crude metal at the bottom of the vessel. The slag, which consists mostly of magnesium fluoride with some dolomite mixed in, floats to the top of the pool of crude metal while it is still molten.

If the reaction is good and the liner walls withstand the im-

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part of the reduction, a crude "biscuit" is formed which is free from slag. The biscuit will have a smooth top and side walls and will separate from the by-products of the reaction easily. If the reaction is poor due to some bad firing condition or the packing technique is such that the dolomite liner gives way during the reduction, a slaggy biscuit is formed. This biscuit will be rough on top and have varying amounts of slag adhering to the upper surface of the metal. The amount of slag which adheres to these poor biscuits varies from very small amounts in pockets in the metal to a heavy layer of slag covering the whole top of the biscuit.

It is reasonable to assume that the biscuits, which are free from slag and appear to be pure metal, would give better remelt yields than the slaggy biscuits. This is true, but it has been found that, by adding one biscuit which has a very small amount of slag on it to three good biscuits (four biscuits make up a remelt charge), the remelt yield would be better than when four good biscuits were used. This is explained by the fact that four good biscuits boil violently in a crucible and leave metal adhering to the crucible walls after the pour. A mixture of one slaggy biscuit and three good biscuits boils very quietly in the remelt furnace due to the coating of slag on top of the melt. Since very little metal gets up on the side of the crucible under these conditions, the recovery is much better. Therefore, ten grams of magnesium fluoride is added to all runs of four good biscuits to take the place of slag if a slaggy biscuit is not available. Some runs

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were made using ten grams of ground slag from the reduction operation, but these were not too satisfactory due to the fact that the slag probably contains some lime.

The biscuits which are heavily coated with slag give poor remelt yields because the large amount of slag tends to mix with the metal to increase its viscosity, and the material does not flow out of the crucible well.

The chemical characteristics of the crude metal are also very important. It was discovered, during a period of low remelt yields, that the biscuits were being produced with magnesium which was very high in nitrogen content (300 to 1500 ppm). This material had no effect on the biscuit yield. The nitrogen formed uranium nitride which increased the viscosity of the metal to such an extent that the crucible walls were coated with a thin film of metal. This holdup of material caused the remelt yield to be very low. As soon as the reason for the low yields was discovered, all efforts were made to get low nitrogen content magnesium (under 75 ppm). Magnesium under 75 ppm nitrogen is acceptable and does not affect the remelt yield appreciably.

The decrease in casting yield due to the high nitrogen content of the reductant magnesium was reflected through the remelt operation in the following ways.

1. The crucible usage changed considerably during the high nitrogen trouble due to the fact that large amounts of metal stuck to the

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graphite walls and when the crucibles were burned out, they cracked. The crucible life dropped from an average of six runs each to four runs, or a thirty-three per cent decrease.

2. The surface of the third billet was very poor (scabby) due to the fact that the pours were very sloppy toward the end, causing splashing of the metal on to the mold walls.

One of the chemical characteristics of the crude metal which is apparent to the eye is the magnesium content of the material. Most of the biscuits which are produced are very shiny. This luster is not a surface coating of magnesium, as it will not dissolve off in acids, but seems to be an alloy of uranium and magnesium. It is most apparent on the top of the biscuit. When these shiny biscuits are remelted, the magnesium boils out of the uranium violently and deposits a coating of metal on the crucible walls above the body of the melt. When the pour is made, this material stays on the walls of the crucible and reduces the re-melt yield.

As can be seen from the above, it is very important to have the magnesium content of the crude metal as low as possible. There are two places in the reduction vessel where magnesium is used, (1) the charge and (2) the bottom of the liner. The magnesium in the charge is used to reduce the uranium tetrafluoride to metal. The magnesium in the bottom part of the liner is used to sinter the dolomite so it will take the shock of the molten metal as it collects in the bottom of the vessel. The magnesium

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in the liner also acts as a "getter" for any water which is in the dolomite.

The magnesium excess was reduced in the charge with fair success. A reduction in the magnesium in the liner, however, showed the best results. The magnesium in the liner apparently boils out into the surface of the biscuit and gives the shiny appearance. If a method could be found to pack the dolomite liner hard enough so that no magnesium was needed in it at all, much better remelt yields could be expected.

Another of the important factors in the remelting of uranium metal is the furnace atmosphere. When uranium is heated in air it oxidizes readily to U_3O_8 . Therefore, in order to melt the metal and get a decent yield, it must be done under vacuum or in an inert atmosphere. Low pressures were tried first and found to be satisfactory. The better the vacuums are, the better the remelt yields will be. An operating pressure of forty microns or below (trapped McLeod gauge) was considered satisfactory, but higher vacuums were always being strived for. If the vacuums are poor, over three hundred microns on a trapped McLeod gauge, the metal burns instead of melting. Very small amounts of U_3O_8 mixed with molten uranium increase the metal's viscosity appreciably. This makes for low remelt yields, as the metal will not run out of the crucible. Also, when the vacuums are bad, the billets get a coat of oxide on them after they are poured. This material powders off when the billets are removed from the mold.

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Argon and helium were tried as inert gas atmospheres. The remelt yields were very good from those runs because the inert gases prevented oxidation and cut boiling down to a minimum. The billets from these runs showed surface porosity and were very impure. The gases evidently dissolved in the metal and when it was poured into the graphite molds, the gases came to the surface. This caused the billets to be covered with little blowholes. This condition is unacceptable, as the extrusion operation can not handle such material.

The reason for the billets being very impure is readily seen as the inert gases cut boiling to a minimum. Therefore, the impurities did not get a chance to boil out of the metal. It was decided to pull a vacuum on a furnace containing an inert gas and a molten uranium mixture to do two things. One was to get rid of the gas so the billets would be good and the other was to allow some boiling in the crucible to get rid of the impurities. When this was tried, the metal boiled right out of the crucible, probably due to large amounts of gas dissolved in the molten material which suddenly expanded from the great decrease in pressure.

Another one of the important factors in the remelting of uranium metal is the pouring temperature. If the metal is not hot enough, three things can happen.

1. The impurities will not all be boiled out.
2. The viscosity of the metal will be too high and the material will not flow well.

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3. The billets will have cold pour marks on them such as shuts and folds.

If the metal is too hot, the following things occur.

1. Carbides and nitrides of uranium start to form very fast.
2. The metal corrodes the graphite crucible and ruins the mold when it is poured into them.
3. The yield is impaired due to the longer time the metal is in a molten state heating up to the higher temperature.

It can be seen from this that the metal must be left in the crucible long enough to boil out the regular impurities but not so long that other ones start to form. The metal must be heated hot enough to give billets free from cold pour marks but not so hot that the graphite begins to be attacked. The metal must be hot enough for it to have a proper fluidity, but must not be heated so long that the yield starts to drop off due to the excessive time that the metal is in the molten state. Carbides and oxides of uranium which increase with the length of time the metal is fluid increase the viscosity to give a poor yield.

Uranium metal is melted in graphite crucibles. These crucibles become eroded and badly pitted after they have been used a few times. Most of the erosion is at the top of the melt where the metal is in constant motion from the boiling. The crucible also becomes pitted on the sides and bottom. All these pits hold up metal which reduces the remelt yield accordingly. A number of dressings were used to dry and keep the metal from attacking the

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graphite. The refractory oxide seemed to be the most promising and, after a number of trials, a mixture of magnesium oxide compounds was found to be the most suitable. This dressing not only improved the remelt yield, but it saved graphite, as the crucibles were not pitted nearly as bad as before. The dressing had to be applied each time the crucible was used. The action of the metal plus the fact that the crucibles had to be burned out after each run, destroyed most of the dressed surface.

III. EXPERIMENTAL

One of the main reasons that crude metal gives low remelt yields is because the material is high in magnesium. Different methods were tried to produce biscuits of low magnesium content. The results are shown in Table I.

TABLE I

<u>Special Features</u>	<u>Magnesium in charge</u>	<u>Magnesium in bottom liner</u>	<u>Average Biscuit Yield (X)</u>	<u>Remelt Yield (Y)</u>	<u>Overall Yield (X) (Y)</u>
Change Mg in charge	4.94% excess	2%	97.8	96.6	94.5
Change Mg in charge	4.66% excess	2%	97.7	96.8	94.6
Change Mg in charge	4.33% excess	2%	97.1	96.6	93.8
Change Mg in liner	4.94% excess	3%	97.8	96.1	94.0
Change Mg in liner	4.94% excess	1 1/2%	97.3	96.7	94.1
Change Mg in liner	4.94% excess	1%	95.5	97.1	92.7

The magnesium excess in the charge was reduced first. The amount of excess magnesium which had been used was 5.21%. This was reduced to 4.94% excess with very little drop in the reduction

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yield. With the decrease in reduction yield, an increase in the remelt yield was obtained. The highest product obtainable of the reduction yield and the remelt yield is what is desired and if one drops off more than the other one gains, the net change is a loss. When the magnesium excess was lowered to 4.34%, the reduction yield dropped off more than the remelt yield gained, so the magnesium excess was not out any more.

The magnesium in the liner was reduced next. The dolomite which was used for the bottom quarter of the liner had two per cent magnesium mixed with it. This was reduced to one and one half per cent and then one per cent. With the drop to one and one half per cent, the reduction yield dropped one half to three quarters of a per cent with a corresponding increase of two or three tenths of a per cent in the remelt yield. When the magnesium was cut to one per cent, the reduction yield dropped two per cent and the remelt yield increased a half to three quarters of a per cent. Therefore, the magnesium in the liner was at a minimum at two per cent because any reduction in it gave a lower overall yield (reduction yield times remelt yield).

Some runs were made with 4.66% excess magnesium in the charge and three per cent magnesium in the bottom liner. The reduction yield was very good, but the remelt yield went down due to the fact that the biscuits were coated with magnesium oxide and contained a large amount of magnesium metal. If some way could be found to pack the liners hard enough so that no magnesium would be needed to sinter

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the bottom, a better remelt yield could be obtained without hurting the reduction yield.

As it was found that the nitrogen content of magnesium used in reduction had a profound effect on the remelt yield, a number of biscuits were produced using magnesium with a varying nitrogen content to get an overall picture of the effect. The results are listed in Table II and shown in Figure I.

TABLE II

<u>Nitrogen Content of Magnesium in ppm</u>	<u>Remelt Yield</u>	<u>Number of Runs</u>
85	96.7	21
240	96.2	26
260	96.1	25
300	96.0	29
370	95.7	19
450	95.6	22
600	95.2	21
750	95.1	14
1000	95.0	33

As can be seen from Figure I, the correlation is practically straight line between 50 ppm nitrogen and 500 ppm nitrogen. At 500 ppm nitrogen, the curve breaks sharply and becomes asymptotic to a remelt yield of a little less than ninety five per cent. It is readily seen from this curve that magnesium of the lowest possible nitrogen content should be used in reduction.

Figure II shows the correlation between the remelt yield and the pressure at which the pour was made. As can be seen from the

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curve, the remelt yield is not affected appreciably by the pour vacuum until the pressure is forty microns (all pressures were read with trapped McLeod gauge) or lower. From 200 microns to forty microns pour pressure, the remelt yield increases three tenths of one per cent. At forty microns, however, the curve breaks sharply and between forty microns and ten microns the remelt yield increases five tenths of a per cent. Pour pressures of less than ten microns can not be reached due to equipment limitations, but by extrapolating the curve, it can be seen that very good remelt yields could be obtained at lower pressures.

The use of inert gases, both argon and helium, increased the remelt yield from 96.5 per cent to between 97 and 98 per cent, but, as was mentioned before, the billet surfaces were very poor and the practice had to be abandoned.

Figure III shows the result of varying the pouring temperature on the remelt yield. All temperatures were read with an optical pyrometer and are probably lower than the actual temperature of the melt. The reading is made through a sight glass in the top of the furnace and is taken on the top of the melt. The metal is covered with a coating of slag which is probably not as hot as the metal beneath it. The true temperature is not actually needed as long as each melt is poured at the same pyrometer reading.

As can be seen from the figure, a reading of 2350° F. gave a low yield. The billets from these heats showed cold pour marks

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also. The heats poured at 2400° F. gave the best yield and the billet surfaces were good. With a fifty-degree higher reading, the yield dropped off a little and the billets showed an oxide coating. The carbon and nitrogen content of the metal was higher at this elevated temperature. Evidently the carbides and nitrides of uranium begin to form very fast at a temperature of around 2450° F.

In order to improve the graphite crucible surface, a number of dressings were tried.

It was thought that the dressing should have the following characteristics.

1. It should make a good suspension.
2. It should wet the graphite easily.
3. It should dry quickly and not tend to powder off the graphite when dry.
4. It should not contaminate the metal.

A number of refractories were then dried. They had the following approximate bulk densities.

Zirconium oxide	10 fluid ounces per pound
Titanium oxide	45 fluid ounces per pound
Magnesium oxide	80 fluid ounces per pound

The zirconium oxide was tried first and found to be unsatisfactory. Due to its high density, the material would not stay in suspension in an aerosol solution and it was impossible to paint it on the graphite. A thick slurry was made up of ZrO_2 and CCl_4 and the material was rubbed into the graphite. The carbon tetrachloride

evaporated too fast and left an easily removed, uneven coat of dressing. This material was discarded in favor of a lighter refractory.

A mixture of ten grams titanium oxide and fifty cc. of aerosol was prepared and found to make a suitable suspension. When painted on the graphite, it dried to a powdery coat which came off very easily. This dressing was considered too sensitive and was discarded in favor of a harder material.

A number of grades of magnesium oxide were available and they were all tried. Magnesium Oxide U.S.P. XII Heavy Powdered was tested first and found to be too heavy. The Analytical Reagent grade of magnesium oxide worked all right but was too expensive to use. Magnesium Oxide U.S.P. XII Light Powdered made a good suspension and stayed on the graphite well but had poor covering power. The Standard Luminescent grade of magnesium oxide showed very good covering power but tended to powder when dry. Different mixtures of Magnesium Oxide U.S.P. XII Light Powdered and Magnesium Oxide Standard Luminescent (SL) grade were tried until a very good dressing was obtained.

A mixture of three parts of Magnesium Oxide SL and four parts Magnesium Oxide U.S.P. XII Light had a bulk of 120 fluid ounces per pound. This was mixed with 150 cc. of one tenth per cent aerosol solution and stirred to a smooth paint. This dressing was then painted on the crucible walls and allowed to air dry for two or three hours. The crucibles were then heated in gas-fired pit heater for eight hours, bottom up. This last heating in the pit

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heater drove all remaining traces of water from the graphite. The crucibles were then cooled down and used immediately. The dressing had to be applied after each run.

IV. SUMMARY

1. In order to get the best remelt yield from crude metal, the biscuits should be free from slag and should be made from magnesium which is low in nitrogen content. The biscuits should also be as free from magnesium as possible.
2. The pressure in the remelt furnaces should be kept as low as possible to keep the metal from oxidizing to U_3O_8 . A vacuum of forty microns or less (trapped McLeod gauge) should be strived for at all times.
3. Inert gas atmospheres cannot be used in a remelting furnace as the gases dissolve in the metal and are given off when the metal is poured into the molds. This degassing causes the billets to have porous surfaces which are unacceptable in the extrusion operation.
4. Remelted uranium metal must be poured at the correct temperature to insure the highest yield and purity. This temperature is 2400° F. read at the top of the melt with an optical pyrometer.
5. The graphite crucibles which contain the uranium melt should be coated with a dressing. This dressing improves the remelt yield by cutting down pitting of the crucible which in turn lessens metal hold up. This dressing also lengthens crucible

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life because the metal does not erode the graphite as bad
as it does when no coating is used.

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Figure I

Relationship between the nitrogen content
of the reductant magnesium and the
remelt yield

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Figure II

Relationship between the pressure at
the time of pouring and the
remelt yield

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Figure III

Relationship between the pouring temperature and the remelt yield