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THE REDUCTIONS OF URANIUM OXIDES

By
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THE REDUCTIONS OF URANIUM OXIDES; QUARTERLY REPORT

by Robert W. Bragdon

ABSTRACT

Progress during the third quarterly period on a program designed to evaluate methods of preparing uranium hydride from the various oxides of uranium is presented. The current portion of the investigation is concerned with the reduction of UO_2 , UO_3 , and U_3O_8 with calcium hydride and calcium metal, and twenty-three such reductions are described. The evaluation of the various products by chemical analyses has demonstrated that reductions are more quickly and completely effected in the absence of a hydrogen atmosphere. Chemical analyses of the most recent reductions have indicated uranium hydride contents greater than 99 per cent. It is concluded that the presently employed methods of evaluation of the products are inadequate for products approaching 100 per cent purity, and steps have been taken toward their evaluation after processing to massive metal by powder metallurgical techniques.

INTRODUCTION

Interest in powder-metallurgy techniques for the processing of uranium metal has been revived by the development of a hot-pressing technique at the Sylvania Bayside Laboratories. Solid uranium of 18.7 to 18.8 g./cc. density can be manufactured by hot pressing uranium powder at a compacting pressure of approximately 30 t.s.i. and a temperature of approximately 600°C .¹ Since uranium parts made by this method are processed exclusively below the alpha-beta transformation temperature of uranium, they contain only small alpha grains of random orientation. This, therefore, avoids the unusual dimensional changes which result when metal processed by any of the usual techniques of casting, hot working, heat treating, or machining is subjected to reactor conditions. The uranium metal powder for Sylvania's work was obtained by low-temperature decomposition of uranium hydride powder. Recently, Sylvania has found that the properties of uranium hydride powder itself make it ideally suited to this hot-pressing technique.² The thermal decomposition of the hydride during pressing provides a reducing atmosphere and protects the metal from oxidation. The oxide content of the final product produced in this way varies from 0.07 to 0.09 per cent.

The purpose of the current investigation is to evaluate previously known methods for the reduction of the various uranium oxides to powdered uranium or powdered uranium hydride. The scope originally included calcium, calcium hydride, and magnesium as the reducing agents. It is unlikely that magnesium will be studied very extensively because of the limitations of time and manpower. Magnesium is the least likely of the three reducing agents, mainly because of its high vapor pressure, which makes it difficult to contain in the hot zone, and the consequent explosive nature of the reaction.

The primary goal of our investigation is the direct preparation of uranium hydride powder from one of the several oxides of the metal. An economic evaluation of such a process, carried out by the Catalytic Construction Company and reported at a recent A. E. C. Symposium, indicates a decided economic advantage over the present methods for the preparation of uranium hydride which involve a number of steps to convert the oxide to the hydride. Indeed, it was pointed out by Catalytic Construction that an economic advantage would still exist if it

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were necessary to vacuum fuse such products to obtain uranium metal of sufficient purity for A. E. C. use. The production of uranium metal by the vacuum fusion of the hydride is, therefore, considered a secondary goal of our investigations.

A considerable quantity of uranium metal powder was produced at Metal Hydrides Incorporated during the last war for the Manhattan Project, employing the Hydrimet technique. In addition to the Hydrimet process, uranium metal powder has been prepared by the reduction of the oxides with calcium metal under basic patents held by Westinghouse Electric Corporation.³ In this latter case also, the metal powder was vacuum fused, and purity evaluations were conducted on the cast metal.

In addition to the application of these methods to the preparation of uranium hydride, the relation of the present investigation to this earlier work is twofold. First, it is necessary to develop methods for the precise evaluation of the metal or metal hydride powders produced by these methods; and, second, it is necessary to show that products contaminated with oxides can be substantially purified by the vacuum-fusion technique. Since, however, the ultimate criterion of acceptable material will most certainly be the density of the processed powder, it has now become evident that this same criterion is the only one suitable for the laboratory evaluation of our products.

DISCUSSION OF RESULTS

Methods of Evaluation of Products

Apparently, no precise method is reported in the literature for the evaluation of metal powders of these types. It was the consensus of opinion at the recent A. E. C. Symposium that such evaluation could best be done on the massive metal prepared in a variety of ways. It was, in fact, stated at that time that chemical analysis of the powders, in this case zirconium, bore little or no relation to the purity of metal compacts prepared from the powder. After somewhat extensive investigations of various methods of analysis of our uranium hydride powder, we have come to the same conclusion: namely, that the only truly reliable, precise evaluation must be done on the massive metal prepared from the uranium hydride powder. There is included here a discussion of each of the methods of evaluation which we have employed or plan to employ in the near future.

Chemical Analyses

The chemical analyses upon which we have relied to date include the uranium assay by ceric sulfate titration and the hydrogen analysis by micro combustion technique. When each of these analytical methods are applied to the analysis of more stable materials, such as, for example, U_3O_8 in the uranium assay and titanium hydride in the microcombustion technique, the precision and accuracy realized is on the order of $\pm$ one part per thousand for the assay, and $\pm$ two parts per hundred for the hydrogen analysis. It has been observed during our studies that, when these same analytical methods are applied to our uranium hydride powder, extreme difficulty is encountered in obtaining the same precision. At the present time, it is not believed that an accuracy of greater than $\pm$ three parts per thousand can be claimed for the uranium assay, nor greater than $\pm$ five parts per hundred for the hydrogen analysis, although, in some cases in the latter analysis, considerably greater variation has been encountered. The exact causes of these inaccuracies are not known, but it seems likely that they are due to the extreme reactivity of the powders and the very rigorous handling techniques which must be employed. Nevertheless, for the want of a better method, it has been necessary to rely entirely on chemical analyses to interpret the results of our studies of the variables thus far in the program. A study of the tables presented later in this report will show a gradual trend toward higher analyses, and it is felt that chemical analyses have served the purpose thus far. The purity of the products now, however, is so closely approaching 100 per cent that it will no longer be advisable to rely upon uranium and hydrogen analyses as an indication of the oxide content present, since small differences between large percentages are seldom a suitable analytical measure of trace impurities.

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Density of Degassed Powders

The large difference in density between the oxides of uranium and the metal itself offers an almost unique method for the measurement of oxide content of the otherwise pure material. For example, if one makes the assumption that density decreases linearly with oxide content and that the oxide is present as UO_2 , then for each tenth of a per cent oxygen, there is a lowering in density of approximately 0.07 g./cc., an amount which it would appear could easily be determined by conventional methods for density determination of powdered metals. Repeated attempts have been made to apply two such methods of density determination to the uranium metal powder obtained by the careful degassing of pure uranium hydride powder with completely unsatisfactory results.

The helium densitometer described in Report NYO-3793 has not proved as satisfactory for density determinations on uranium powder as had been expected. One reason for its failure to meet our requirements is the unfavorable ratio of bulk to true density of this particular powder. Schumb and Rittner⁴ state that a ratio of bulk to true density of about 0.5 is necessary to realize the maximum accuracy of the instrument. The ratio of bulk to true density for the powders with which we are working is approximately 0.25 to 0.30. Another possible source of error in the density determination by this technique is the adsorption of the helium gas on the powdered metal. While we have not previously observed any adsorption on many of the other samples of metal and metal hydride powders investigated in our laboratories, we do not exclude the possibility of adsorption on such an active metallic surface as is encountered with freshly degassed uranium hydride. The problem of the ratio of bulk to true density is not one that can be overcome merely by changing the relation of the sizes of the sample bulbs and the remainder of the apparatus. When the above-mentioned density ratio is as poor as is encountered here, the free volume or the void space within the powdered sample is too great to permit the required pressure increase which is necessary for accurate determinations.

In addition, a wet pycnometric method employing toluene as the displacement liquid in a vacuum-jacketed pycnometer fitted with a thermometer has been investigated. We have been unable to obtain density values on degassed SF-grade uranium hydride samples which are at all consistent with the chemical analyses of these materials. We are well aware of the extreme reactivity of uranium powder prepared in this manner; yet do not feel that the unsatisfactory results are due either to contamination of the sample during handling in the dry box or to reaction with the toluene during the measurement. It seems more likely, at this time, that the low density values obtained are due to incomplete wetting of the uranium metal powder by the toluene. It is a well-known fact that metal powders prepared by the low-temperature degassing of the hydrides are produced in an extremely distorted form, full of rifts and jagged edges. It is not considered at all unlikely that incomplete wetting of the powder would result under these conditions.

Solubility in Mercury

The property of uranium hydride of forming psuedo liquid amalgams with mercury has been considered as a possible means of purification of uranium hydride powder, as well as a method of qualitatively evaluating the purity of the powder. It has been shown in earlier work (see Report NYO-3792), that mercury can be completely removed from its psuedo amalgams with uranium hydride powder by vacuum distillation. It has also been shown that, while this would seem to offer a suitable method for leaching uranium hydride powder from its furnace products with calcium oxide and calcium hydride, the wetting power of these psuedo amalgams is so great that a separation from finely divided powders is impossible. Nevertheless, it was felt that such a technique might be successfully applied to uranium hydride powder contaminated with small amounts of uranium oxide and that, in effect, this would be similar to, but much more convenient laboratory-wise, than a vacuum-fusion technique for the purification of such materials. An attempt to leach a sample from Run No. 12 with a large excess of mercury was completely unsuccessful. The phases (8 grams of UH_3 and 150 grams of mercury) remained wholly immiscible after thorough shaking. When hydrogen was bubbled through the mixture, a brownish-gray mirror formed on parts of the glass wall, but the phases remained mostly un-

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changed. A similar attempt to mix 85 grams of mercury with a 15-gram sample from Run No. 9 produced the same results; and when pure hydrogen was bubbled through the tube at 200°C, some wetting occurred, as indicated by agglomeration of the powder. When 77 grams more of mercury were added, the mass gave the bumpy appearance of very dirty mercury. Further work is in progress.

The failure of mercury to wet samples from Runs No. 9 and No. 12 is taken to indicate the presence of oxides, probably in the form of surface coating in these particular samples. The analyses of the same materials, reported in Table II later in this report, would certainly suggest the presence of sufficient oxide to account for such behavior toward mercury. This somewhat qualitative method will be further studied with some of the purer materials prepared later.

Vacuum Fusion

The solubility of oxygen, whether as gas or oxide, in uranium metal is reported⁵ to be on the order of 0.003 weight per cent at its melting point. This fact, coupled with the large difference in density between the oxide phases and the metal, suggests that vacuum-fusion techniques should be admirably suited to the separation of residual oxide content from uranium metal. It is now believed, in the light of these facts, that the notable success reported by earlier workers employing calcium and calcium hydride for the reduction of uranium oxides can perhaps be accounted for by the fact that their evaluations were, without exception, made on the vacuum-fused products. It is our intention, therefore, to investigate the vacuum-fusion technique for two purposes. First, it would be desirable to clear up one question by establishing whether or not a vacuum-fusion technique is indeed a purification step for metal powders of uranium. This information is considered necessary, since no previous evaluation of the metal powders themselves appears in the literature. Second, the decided possibility that uranium powder containing small amounts of oxide and prepared by a calcium or calcium hydride reduction of uranium oxide could be purified by vacuum fusion to yield a less expensive product of suitable purity is worthy of investigation. The analysis of these powders for oxygen and nitrogen by the vacuum-fusion method should also be investigated, but facilities for such work are not available at Metal Hydrides.

Hot-Pressed Density

The vacuum-fusion technique mentioned in the previous paragraph will, of course, not be a suitable method for the evaluations of the powders if, in effect, it is a purification step in itself. Furthermore, the other methods of evaluation discussed above are not considered adequate as the purity of our products approaches 100 per cent. It is felt that the only suitable method for evaluation of our products must be the density of the metal processed in a manner in which it is intended to be used. For this reason, we have designed and are having built a small dry-box-size hot-press die. It is our intention to process a sample from each of our most promising products into pellets of approximately 0.5 cc. and to determine subsequently the density of these pellets by a water-displacement method. Only in this manner it is felt that a fair evaluation of our products can be carried out.

Handling Techniques

A brief description of our dry-box technique was included in Report NYO-3793. The purification method for the argon atmosphere employed is substantially as outlined in that report. This purification method employs titanium metal in the form of small, sintered, irregular chunks heated to 800-900°C in a stainless steel furnace tube. Originally, a small blower, operated by a $\frac{1}{4}$ -H.P. motor, was employed to circulate the argon through the purifier both as it was introduced originally into the box and continuously from the box through the purifier while the box was in use. It has since been necessary to substitute a Pressovac pump for the purposes of circulating the argon because of the extreme difficulty in completely sealing the blower. Furthermore, with the incorporation of an oil pump in the line, it was necessary to in-

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clude a filter to prevent the contamination of the getter tube and the dry box with a fine mist of oil. A photograph of this piece of equipment, together with a flow sheet describing its operation, is included. (See Figures I and II.) Time and manpower requirements have not permitted a thorough evaluation of this method of purification; yet our experience in using NaK as an indicator makes us confident that our dry-box conditions in actual operation more than meet the requirements necessary for the handling of uranium hydride powder. We are not as yet satisfied, however, that the atmosphere is of sufficient purity to permit handling of very small samples of freshly degassed uranium hydride without some contamination with hydrogen and perhaps very small quantities of oxygen and nitrogen. Not visible in the illustration, but depicted on the flow sheet, are two inlets for electrical power which will serve to heat the hot-press die described above.

Reductions Under Hydrogen

A series of ten reductions of various uranium oxides employing calcium hydride as the reducing agent in an atmosphere of hydrogen has now been completed. The results of all these reductions are tabulated in Table I. This table includes data previously reported, where it is necessary to emphasize the effect of the variables.

Table I—Calcium Hydride (100% Excess) Reduction of Uranium Oxides
In A Hydrogen Atmosphere

Run No.	T, °C*	Hours at T, °C	% Yield	% U	% H	% U + H
1	<950	1	61.9	94.0	0.80	95.2
2	<950	1	72.6	94.1	0.76	94.9
3	<950	1	63.5	93.7	0.64	94.3
4	<950	1	--	92.2	0.76	93.0
5	<950	3	56.8	95.7	0.86	96.6
6	<950	3	72.1	96.8	0.89	97.7
7	<950	3	84.6	96.9	0.95	97.9
14	950	17	63.7	96.7	1.11	97.8
15	950	17	96.1	97.4	1.11	98.5
20	1050	13	>100	96.5	0.92	97.4

*The temperatures reported as <950° were recorded as 950°C external to the furnace tube.

It is evident that reductions carried out in the hydrogen atmosphere require extended reaction periods to approach completion in the temperature ranges thus far studied. It is also evident from the almost negligible amount of distillation of the excess calcium hydride from the reaction zone that the vapor pressure of calcium over calcium hydride in an atmosphere of hydrogen must be considerably less than the normal equilibrium vapor pressure of calcium metal. This in itself offers a valid reason for the increased length of time required, or perhaps for the unfavorable equilibrium encountered. This lowered vapor pressure can affect our results in two manners. First, it can cause reaction to take place very slowly; and, second, it can cause the equilibrium reaction to be unfavorable for the desired results. Our experiments have shown that increasing the length of time of the reduction, even by substantial amounts, did not materially reduce the oxide content of the products. In the one case (Run No. 20) in which a higher temperature range was investigated, the results were negated by the vigorous attack of the stainless steel boat by the furnace charge. Considerable quantities of chromium, iron, and nickel were found in the furnace product by a qualitative spectrographic analysis. Most of these impurities were successfully removed during the aqueous acetic acid leach. Nevertheless, the effect of this corrosion and contamination on the purity of the final product is not known. The decided advantage of carrying out a reaction in a hydrogen atmosphere when one considers

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the possibilities of developing a continuous process prompt us to continue our investigations at higher temperatures, and, to this end, we are investigating the preparation of calcium oxide liners for our crucibles.

In addition to temperature ranges, there are several other variables which may play an important part in the completeness of reduction under these conditions. Among these variables is the particle size of the oxide to be reduced. While these oxides are, in general, very fine powders, they do contain small percentages of larger agglomerates which may be quite resistant to attack by low vapor pressures of calcium. The investigation of this variable will be twofold: first, the reduction of oxides from which the larger agglomerates have been screened out; and, second, the ball milling of the calcium hydride - uranium oxide mixture prior to furnacing. Another variable which may be of importance is the composition of the calcium - calcium hydride mixture which is in contact with the uranium at equilibrium. The calcium-hydrogen system, similar to most of the other hydride systems, demonstrates a composition-dependent dissociation pressure. When calcium hydride is heated to a given temperature, as, for example, 950°C, and the equilibrium pressure of hydrogen is fixed at one atmosphere, the composition of the condensed phases (i.e., calcium metal and calcium hydride) is also fixed, as can be demonstrated by the phase rule. It seems likely that the vapor pressure of calcium over such a mixture would be lower, the lower the concentration of free calcium metal in the mixture. This line of reasoning would predict a direct dependence of calcium vapor pressure on the pressure of hydrogen maintained during the furnacing operations.

Reductions Under Argon or in Vacuum

In Table II can be found the results of fifteen reductions of uranium oxides in which the reductions were carried out in an argon atmosphere or in vacuum. Some of the variables studied in this series are the effect of the oxide starting material, the effect of changing the reaction temperature, and the effect of excess of reducing agent. Temperatures denoted as less than 950°C represent experiments in which the temperature was controlled by a thermocouple external to the furnace tube. We have recently incorporated a thermowell in the furnace tube to permit us to measure internal temperatures, and this was the temperature which controlled Experiments 16 through 23. In Runs 8 through 13, the furnace charges were heated to 950°C external temperature in an atmosphere of hydrogen and held there until evolution of hydrogen had ceased. The hydrogen atmosphere was then removed by evacuation and was replaced with an atmosphere of argon in which the charge was heated for an additional hour at temperature. In Run 16, the hydrogen was partially removed after measurable amounts of hydrogen had ceased to be evolved, by permitting the atmosphere present in the furnace tube proper to expand into some 35 liters of volume in the rest of the evacuated system. After one such expansion, the pressure in the furnace tube was brought to atmospheric pressure by the introduction of pure argon and the furnacing continued for one hour. In Run 17, hydrogen was removed from the furnace tube proper by a series of expansions (six) of the gas into the evacuated volume. In this manner, considerably more hydrogen was removed from the charge prior to admission of argon than in Run 16. These latter two runs were carried out in this manner in an attempt to remove the inhibiting effect of the hydrogen gas without causing excessive distillation of the reducing agent. The previous procedure employed was to remove the hydrogen atmosphere by evacuation until the pressure was reduced to about 5 mm. of mercury. The selection of limiting pressure or evacuation time was necessarily empirical and was not entirely satisfactory, since excessive distillation of calcium resulted. It was felt that the loss of reducing agent could be substantially reduced by the adoption of the expansion technique, since the gas pressure would not fall below the vapor pressure of calcium at any time.

In Runs 18-5, 18-10, 19-5, and 19-10, advantage was taken of a technique commonly used in the determination of dissociation pressures of hydrides of volatile metals. This technique employs a sealed Armco iron capsule which is permeable to hydrogen at the reaction temperature but serves to contain the calcium. The particular capsules used in this work were cylinders of 37 mm. diameter and 45 mm. height with a small 6 mm. O. D. tubing extending from one end. In Runs 18-5 and 18-10, the furnace charge was loaded into the capsules through this

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Table II—Reduction of Uranium Oxides in Vacuum or Under Argon

Run No.	T, °C	Oxide	Reducing Agent*	% Yield	% U	% H	% U + H
8	950	UO ₂	100 CaH ₂	86.8	96.9	1.10	98.0
9	950	U ₃ O ₈	100 CaH ₂	90.1	97.3	1.09	98.4
10	950	U ₃ O ₈	50 CaH ₂	76.6	97.1	1.08	98.2
11	950	UO ₂	100 CaH ₂	84.7	97.1	1.09	98.2
12	950	U ₃ O ₈	100 CaH ₂	79.2	96.8	1.18	98.0
13	950	U ₃ O ₈	50 CaH ₂	84.6	96.8	1.13	97.9
16	950	UO ₂	100 CaH ₂	89.5	97.7	1.15	98.9
17	950	UO ₂	100 CaH ₂	87.6	97.3	1.15	98.5
18-5	950	UO ₂	50 CaH ₂	93.5	98.6	0.18	98.8
18-10	950	UO ₂	100 CaH ₂	92.7	98.1	0.16	98.3
19-5	950	UO ₂	50 CaH ₂	--	98.5	1.20	99.7
19-10	950	UO ₂	100 CaH ₂	--	97.9	1.15	99.0
21	950	UO ₂	100 Ca	74.6	97.6	1.18	98.8
22	950	Run 15	100 Ca	82.2	96.1	1.07	97.2
23	950	Run 17	100 Ca	100.0	--	0.74	--

*Figures denote the per cent excess of reducing agent

small tube extension in the dry box, and the tubes were sealed by crimping the tubing extension with wire-cutting pliers. The crimped edges were then arc-welded. The reductions were carried out with continuous evacuation to remove hydrogen as it was generated, but to retain all of the calcium vapor in the hot zone. By the use of this technique, a new problem was encountered, that of rehydriding the product after the completion of the reduction. Because of the excessively high dissociation pressure of uranium hydride, it was necessary to cool the tubes to approximately 500°C in order that a hydrogen pressure greater than the dissociation pressure of uranium hydride could be maintained over the furnace product. At this temperature, the diffusion of hydrogen through the Armco iron was so slow that very low hydrogen content of the final products resulted. (See Table II.) In Runs 19-5 and 19-10, the experimental procedure was similar, with the exception that the crimped Armco iron tubing extension was not welded. It was felt that a seal of sufficient tightness would be obtained so that calcium vapor would not escape, yet hydrogen gas would diffuse easily through the crimped portion during the rehydriding step. This was not found to be the case, and it was necessary to remove the Armco iron liners from the furnace tube to the dry box, where they were broken open and later returned to the furnace tube for hydriding. It will be seen in Table II that the results of these two runs are easily the best obtained to date, and it is felt that these results emphasize again the steps which are necessary in achieving complete reduction of uranium oxides with calcium or calcium hydride: namely, that the hydrogen must be removed while simultaneously retaining the calcium vapor in the hot zone.

The results of these four experiments dictated the immediate undertakings of reductions by calcium metal in the absence of hydrogen or hydride. Run 21 employed a 100 per cent excess of calcium pellets loosely mixed with uranium dioxide but with the bulk of the calcium at the bottom of the boat so that the distilling calcium vapor must pass through the charge. The reaction was carried out in an argon atmosphere, held at 950°C for three hours. Unfortunately, this system was evacuated prior to the admission of the argon at 800°C, during which operation considerable of the calcium distilled. It is for this reason that this experiment must be repeated, avoiding any evacuation at high temperature, for, while the apparently desirable absence of hydrogen was achieved, we cannot be sure that the calcium vapor was held in contact with the uranium oxide for a sufficient length of time to ensure reduction. Runs 22 and 23 are calcium metal reductions in argon of previously prepared products. Run 22 was an unleached sample from Run 15, while Run 23 was a leached sample from Run 17.

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Yields

It will be apparent from the accompanying tables, particularly Table II, that the yields obtained are particularly good for this type of reaction. We have consistently obtained on this very small laboratory scale 85 to 90 per cent yields when the leach solutions are centrifuged for the complete recovery of the product. Because of the inherent difficulties in obtaining high yields on a small laboratory scale, it is felt that, on a plant scale, the percentage yields obtained by this type of procedure, whether batch or continuing, will be entirely satisfactory.

Degassing Procedure and Nitrogen Contents of Products

It was noted in the early runs (see Report NYO-3793) that the nitrogen content of the products was in some cases higher than could be accounted for by the Kjeldahl nitrogen determinations on the calcium hydride employed. It was also noticed that these high nitrogens occurred in runs in which the degassing technique was not particularly rigorous. A sample of the calcium hydride was analyzed for nitrogen content by the Dumas method. This analytical method will determine any nitrogen present as adsorbed gas in addition to nitride nitrogen. A value of 0.21 per cent nitrogen was obtained by the Dumas method as opposed to 0.04 per cent nitrogen by the Kjeldahl method. Similar comparative analyses on the calcium metal which is being employed in our reductions display no such discrepancy, both analyses being within experimental error of 0.03 per cent nitrogen. These results are consistent with the theory that the finely-ground calcium hydride which we are employing has adsorbed on its surface quantities of air and that the nitrogen component of this adsorbed gas layer, while not detected by the Kjeldahl technique, is nevertheless present in the calcium hydride and is completely taken up by the uranium during the reductions unless it is first removed by a very careful degassing technique. The calcium metal, on the other hand, consists of small, irregular pellets of approximately 4 to 10 mm. in diameter and, therefore, has a much smaller area of surface upon which a gas layer can be adsorbed. It has been our intention to obtain a fresh batch of calcium hydride which is low in nitride nitrogen and also which has not been exposed during any step in its processing to atmospheric conditions but handled only under argon in the dry box. In this manner, the danger of nitrogen contamination of the products due to adsorbed air would be eliminated. Unfortunately, the only commercial grade of calcium which is available to us at the present time and is low enough in nitrogen content for consideration for our uses is a particularly difficult form to hydride, so that we have not yet succeeded in obtaining another suitable sample of low-nitrogen calcium hydride for this investigation.

Other Impurities

Table III contains a tabulation of the nitrogen and iron content found in our products thus far. The source of nitrogen contamination has been discussed in some detail already. Suffice it to say that we consider the nitrogen contents we are now obtaining excessive; yet we are not particularly concerned, since we feel that this problem is merely one of preparing calcium metal or calcium hydride of a higher purity. The iron contents of our products we also consider excessive, but this is felt merely to be a container-material problem which will be solved after the problem of obtaining complete reduction has been achieved.

Effect of the Starting Oxide

The courses of the reductions in Runs 7, 8, 9, and 10 were followed by observing the rate of hydrogen evolution versus the time and temperature as the external furnace temperature was raised to 950°C. These data are presented in the form of graphs which accompany this report. They indicate the UO_3 and U_3O_8 are reduced to UO_2 at 600-650°C while the charge is being raised to reaction temperature in an atmosphere of hydrogen. Apparently, hydrogen reacts with the higher oxide, producing water, which in turn reacts with the calcium hydride to liberate still more hydrogen. The net effect is an increase in pressure, as observed on the graph. It will be noted that the break in the U_3O_8 curve takes place at approximately 25 per cent hydrogen evolved, which would be theoretical for the reduction of U_3O_8 to UO_2 according to the equations:

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Other than this difference—namely, the initial reduction of the higher oxides to UO_2 in a hydrogen atmosphere as the temperature is raised—we have found no significant difference between the various oxides reduced, with the exception of the noticeably higher nitrogen content which results when UO_3 is employed because of the attendant impurity of uranyl nitrate hexahydrate. For this reason, and also because UO_2 requires considerably less reducing agent, we have concentrated our investigations on the study of the reduction of UO_2 , feeling that, should it be desirable at a later date to turn to some other oxide for economic reasons or other means of convenience, the variables which we are now studying would apply equally well, since UO_2 has been shown to be an intermediate in all reductions.

Table III—Nitrogen and Iron Contents of Leached Products

Run No.	P. P. M., N	P. P. M., Fe
1	346	--
2	1156	--
3	479	--
4	859	132
5	464	--
6	752	203
7	748	82
8	2203	149
10	713	306
11	1429	264
12	1566	--
13	902	193
18-5	1078	544
18-10	708	456
19-5	526	572
19-10	1327	430
20	1434	659
21	795	375

PLANS FOR THE FUTURE

1. A thorough investigation of the reduction of UO_2 with calcium metal in an atmosphere of argon;
2. An investigation of the effect of the particle size of both reactants on the completeness of reduction;
3. High-temperature (1050°C) reductions both with calcium and calcium hydride in suitable atmospheres and in suitable container materials;
4. The effect of a vacuum fusion on the purity of our products, in particular with regard to oxide content;
5. The use of a dry-box-size hot-press die for the processing of our uranium-hydride products to obtain massive metal suitable for accurate density determinations;
6. The utilization of the maximum capacity of our reduction apparatus both as a preliminary study of scale-up operations and as a source of products for evaluation of powder metallurgical properties.

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Fig. I—Drybox and Purification System

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Fig. II — Flow Sheet for Drybox Purification System

Fig. III — Reduction System

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Fig. IV —Apparatus for Leaching Furnace Products

Fig. V — CaH_2 Reduction of X Oxides

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