~~CONFIDENTIAL~~

UNCLASSIFIED

TID-10057

FIRST ANNUAL REPORT ON THE PREPARATION
OF URANIUM HYDRIDE

~~RESTRICTED DATA~~

This document contains restricted data as defined in the Atomic Energy Act of 1954. Transmittal or the disclosure of its contents in any manner to an unauthorized person is prohibited.

This document contains Confidential-Restricted Data relating to civilian applications of atomic energy.

Technical Information Service, Oak Ridge, Tennessee

~~CONFIDENTIAL~~

DECLASSIFIED

UNCLASSIFIED

DISCLAIMER

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

DISCLAIMER

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

~~CONFIDENTIAL~~

Subject Category, METALLURGY AND CERAMICS.

This report has been reviewed under the Declassification Guide of 1955.

Work performed under Contract AF(30-1)-1350.

*Metal Hydrides, Inc.
Aug 15 1953*

The Atomic Energy Commission makes no representation or warranty as to the accuracy or usefulness of the information or statements contained in this report, or that the use of any information, apparatus, method or process disclosed in this report may not infringe privately-owned rights. The Commission assumes no liability with respect to the use of, or for damages resulting from the use of, any information, apparatus, method or process disclosed in this report.

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

Printed in USA, Charge 30 cents. Available from Technical Information Service, Industrial Reports Section, P. O. Box 1001, Springfield, Tenn. Please direct to the same address inquiries concerning the procurement of classified AEC reports.

~~CONFIDENTIAL~~

0370281030

METALLURGY AND CERAMICS

FIRST ANNUAL REPORT ON THE PREPARATION OF URANIUM HYDRIDE

By Robert W. Bragdon

CHEMICAL RESEARCH STAFF FOR PROJECT

Price \$ 0.30

M. Douglas Banus
Robert W. Bragdon
David L. Henry
Sidney Johnson
Harry O. Warren

Available from the
Office of Technical Services
Department of Commerce
Washington 25, D. C.

ANALYTICAL STAFF FOR PROJECT

J. M. Morris (Spectrographic)
A. P. Alexander
A. P. Demers
E. A. Gordon
M. B. O'Connor

CLASSIFICATION CANCELLED

DATE MAR 20 1957 *jet*

For The Atomic Energy Commission

H. F. Canale
Chief, Declassification Branch

LEGAL NOTICE

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

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

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

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

UNCLASSIFIED

SECRET

Chief Classification Branch
[Signature]
For the Atomic Energy Commission
DATE MAR 30 1981
CLASSIFICATION CANCELLED

ABSTRACT

A continuing evaluation of a laboratory-scale batch process for the preparation of uranium hydride powder is described. The reduction of uranium oxides with calcium metal and/or calcium hydride by a variety of experimental techniques has given uranium hydride which analyzes 99.5 - 99.9% pure. The methods employed are capable of 85 - 95% yields, and it is predicted that plant-scale operation will exceed 95% recovery of product. Unfortunately, existing methods of analysis are incapable of evaluating the products with a precision sufficient for A. E. C. purposes, so that it will be necessary to develop more suitable analytical techniques to satisfactorily complete this investigation. The economics of the process depend largely upon the cost of the reducing agent, and are outside the scope of this report.

DECLASSIFIED

CONFIDENTIAL

INTRODUCTION

In the early days of the Manhattan Project a considerable quantity of uranium metal was produced by the Hydrimet Process. This metal was obtained first as a fine powder, and was then processed into massive metal by a vacuum fusion at Metal Hydrides Incorporated (1), (2). The need for a rapid increase in the rate of metal production, coupled with the inadequate supply of distilled calcium metal available at that time, led to the development of the process employing magnesium metal for the reduction of uranium tetrafluoride. This latter process yielded metal in the massive form directly, and soon became the major source of supply.

Recently, the development of a powder metallurgical process for the fabrication of massive uranium, developed at Sylvania, has renewed interest in the Hydrimet Process as a source of high-purity uranium hydride powder. Solid uranium of 18.7 - 18.8 grams/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 (3). Since uranium products made by this method are processed exclusively below the α - β transformation temperature of uranium, they contain only small α -grains of random orientation. This, therefore, avoids the dimensional changes which result when metal processed by any of the usual metallurgical techniques is subjected to reactor conditions. The uranium metal powder for Sylvania's work was obtained by the low-temperature decomposition of uranium hydride powder. Recently Sylvania has found that the properties of the hydride powder itself make it ideally suited to the hot-pressing technique (4). 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 that way varies from 0.07 to 0.09%.

The original purpose of this investigation was a study of the Hydrimet Process as a potential source of uranium hydride powder of suitable purity for processing by the hot-pressing technique. The need for a critical evaluation for a process which had already produced tons of metal of satisfactory purity was twofold: First, the Hydrimet Process produced metal for the Manhattan Project which was handled and leached as the free metal, while the proposed process involves the more easily oxidized hydride; and second, the earlier material was processed by vacuum fusion, a step which has been shown capable of removing oxide impurities as a slag. (5)

The present method of producing uranium hydride powder requires the prior production of vacuum-cast massive metal, as currently practiced at the Mallinckrodt Chemical Works. This involves

several separate operations which are not easily adapted to continuous processing.

The Hydrimet Process accomplishes this same result by going directly from the oxide to the metal or the hydride. To capitalize on the directness of the Hydrimet Process, it is necessary to have available cheap, distilled calcium; probably, also, to operate on a continuous basis. With this ultimate goal of a continuous furnace in mind, these investigations have been concerned largely with the reduction of UO_2 with calcium hydride according to the equation:

While the work under this contract has also been concerned with the reduction of the oxides UO_3 and U_3O_8 , with calcium hydride and calcium metal, and to some extent magnesium metal, it will be evident that the reduction as expressed by the above equation offers certain decided advantages for continuous processing.

During the course of this contract work discussion with other A. E. C. installations and with the New York Operations Office indicated a possible economic advantage for the Hydrimet Process as applied during World War II. It was suggested by the Production Division and the Catalytic Construction Company that a re-evaluation of the process might be warranted, with a more abundant and cheap source of calcium metal. While this secondary goal was considered during the latter months of the contract period, a proportionately small amount of time was devoted to it because of its already proved success on a plant scale.

DISCUSSION OF RESULTS

The experimental approach to this evaluation problem has been generally dictated by the experimental techniques employed in the past, for similar operations⁽⁶⁾. A number of special problems unique to uranium hydride chemistry, however, have necessitated the development of more careful techniques or methods

DECLASSIFIED

of handling than have heretofore been necessary with the products of a calcium or calcium hydride reduction. To the best of our knowledge, uranium hydride has not been prepared directly by methods requiring the separation of by-products and excess reducing agent by a chemical leach. While such an operation is commonly employed in the production of other hydrides such as titanium, zirconium, etc., by the Hydrimet Process, the singular reactivity of uranium hydride has made it a much more difficult problem.

In order that oxidation of the product be minimized during the subsequent handling, techniques were developed and evaluated for handling the powders entirely in a scrupulously pure argon atmosphere. These techniques are described in the Appendix and in Reports NYO-3792, -3, -4.

There is included in the succeeding sections a discussion of the methods employed and the variables which have been studied. The methods of evaluation of the products are treated first, because the inherent limitations involved must be realized for an intelligent understanding of conclusions which may be reached.

Evaluation of Products

A suitable evaluation method must be capable of a precise indication of oxide content in the uranium hydride powders. The presence of oxide impurity is the inevitable result of an incomplete reduction, since the leach methods thus far employed are incapable of dissolving UO_2 . Oxide impurity is undesirable because it will lower the density of the metal prepared by hot pressing. The upper limit of permissible oxide content is probably about 1.0 per cent, for this amount would limit the theoretical density of a hot-pressed pellet to about 18.8 grams/cc.

The methods which have been considered for the evaluation of the purity of the uranium hydride powders prepared during this phase of the research include:

- (1) Chemical analysis for uranium and hydrogen;
- (2) Density determination of the metal powder after the removal of the hydrogen by high-temperature evacuation;
- (3) Direct oxygen determination by the vacuum-fusion method or halide-distillation method;
- (4) Mercury leach for the separation of uranium hydride from uranium dioxide;
- (5) Density determination on a hot-pressed pellet of massive metal prepared from the hydride powder.

0372291030

The limitations of Method (1) are obvious. The experimental error in the determination of the total of uranium and hydrogen content is probably ± 0.3 per cent. ± 0.3 per cent of oxygen is equivalent to ± 2.5 per cent of UO_2 . This range of error is far too great for any reasonably accurate estimation of oxygen by difference.

The analytical group has experimented with a variation of the uranium assay method, which is similar to that employed generally for the determination of tetravalent uranium in uranium dioxide. The application of this method has been described by the New Brunswick Laboratory and used on a similar type of investigation for the analysis of uranium metal powder. This method is potentially more precise than the usual assay method because the sample is treated with an excess of ceric sulfate and utilizes the change in oxidation state from 0 to +6 for the uranium metal or hydride, and +4 to +6 for the UO_2 impurity. In practice, however, this method has not yet given the desired precision, and while work is continuing with standard samples and shows some promise, it can not be relied on at this time. Both of the assay methods discussed here are described in the Appendix.

Method (2) has failed because of the difficulties encountered in obtaining an accurate density determination, both by liquid and helium displacement techniques, on the extremely reactive metal powders which are obtained by degassing uranium hydride. This work is described in more detail in Reports NYO-3792 and NYO-3794.

Method (3) is perhaps the best answer to the evaluation problem, but we have as yet been unable to locate a laboratory that is set up to carry out such an analysis.

Method (4) is based on the property of uranium hydride of forming liquid "quasi" amalgams with mercury. This technique has failed to show any promise because these "quasi" amalgams tend to wet their container and solid powders with which they make contact, thus preventing a separation.

Method (5) is particularly attractive because of the marked change in density with oxide content. It has the added advantage that the product can be evaluated for oxide content and powder metallurgical properties simultaneously. It is axiomatic that a powder which is found suitable by this method will be acceptable for A. E. C. purposes. The obvious question which must be answered, however, is whether reproducibility of this technique can be achieved, since a low density might result either from oxide content, imperfect compacting, or a combination of the two.

Dr. Hausner, at the Sylvania Bayside Laboratories, has generously offered to hot-press the hydride powder and determine the resulting densities. However, they require samples on the order of 100 to 200 grams. Since samples of this size will not be

DECLASSIFIED

available until the batch process is scaled up, it has been necessary to design and construct a drybox-size, hot-press die to prepare 10-to-30-gram pellets. As far as possible, the techniques outlined in Sylvania Reports have been followed, and much has been learned during the past two months concerning the operation of this equipment. As might be expected in the development of such a complicated technique with no first-hand experience, many difficulties have been encountered, so that this method is not yet available as an analytical tool.

For the present, therefore, it has been necessary to rely entirely on the analytical determination of uranium and hydrogen for our evaluations, and it is on this basis that we have reported 99.5 - 99.9 per cent purity. The variables discussed below can at present be evaluated only in this manner.

Leach Techniques

The separation of calcium oxide from a furnace product by a chemical leach is an inherent part of the Hydrimet Process. The chemical leach solution normally consists of aqueous hydrochloric, nitric or acetic acid. While literature sources do not indicate any appreciable reaction of uranium hydride with water, it was a matter of some concern in this investigation whether an aqueous acid leach would tend to oxidize the surface of the hydride powder. Consequently, the first step in our investigation was to assess the effect of various leach solutions on a synthetic furnace product prepared from SF-grade massive metal with calcium oxide and calcium hydride. A detailed account of this study is presented in Report NYO-3793.

Two methods were established as suitable for the removal of the lime without significantly altering the chemical analysis of the uranium hydride. These methods employed a 10 per cent aqueous acetic acid solution (see Appendix for details of experimental technique), and anhydrous hydrogen chloride and methanol. The aqueous acetic acid is the preferred leach solution because of its ease of preparation, and also because the uranium hydride settles out or can be centrifuged much more rapidly in this solution than in a methanol leach solution.

The leaching method developed by this work with a synthetic furnace product was subsequently employed for the treatment of all the actual furnace products, and has worked well, as indicated by the analytical methods available. The limitations of these methods, however, preclude the detection of small amounts of surface oxidation of the uranium hydride during leach treatment.

Several unsuccessful methods of separating calcium oxide and uranium hydride are described in Reports NYO-3792, -3, -4. They include a mercury leach of uranium hydride and several prelimin-

037029.030

ary attempts at the use of flotation techniques.

Although the method developed has been suited to the small-scale operation, it is felt that extreme caution should be used in scaling up. Several explosions have been experienced during the addition of hydride to water which are believed to have been hydrogen-oxygen explosions. It is imperative that air be completely excluded from the leach apparatus, because the hydride powder sparks on contact with air and will ignite a hydrogen-oxygen explosion. The source of hydrogen in the operation is of course the hydrolysis of the excess of calcium or calcium hydride, and it is hoped that this will be greatly diminished as we are able to cut back on the excess of reducing agent, or are able to recover the excess of reducing agent by distillation during the furnace operation. Caution during scale-up is also advisable until it can be proven that the uranium hydride acid solution can be handled without danger of even isolated explosive, self-promoted reactions.

Reduction Methods

The techniques developed for the preparation of uranium hydride powder by the reduction of uranium oxide with calcium hydride and calcium metal have resulted in products analyzing in the purity range of 99.5 - 99.9 per cent. Each of the following methods have produced uranium hydride in this range of purity:

(1) The reduction of UO_2 with 50 - 100 per cent excess of calcium hydride, carried out in an atmosphere of hydrogen, at 950°C for 11 to 12 hours, according to the equation:

(2) The reduction of UO_2 employing a 100 per cent excess of calcium hydride. The initial furnacing is carried out in an atmosphere of hydrogen, which is then pumped off and replaced with argon. The furnace charge is held at a temperature of 950°C for one hour in the argon atmosphere. The argon is then pumped off and again replaced with hydrogen, and the furnace charge cooled in hydrogen, so that the final product will be uranium hydride. This method permits a shorter reaction time, probably because the vapor pressure of calcium metal in the charge is greater in an atmosphere of argon than under hydrogen. At the same time considerably more distillation of the excess reducing agent to the cold zone of the furnace occurs than when this reduction is carried out exclusively under hydrogen.

(3) The reduction of UO_2 with 10 - 100 per cent excess of calcium hydride, carried out at 950°C , under vacuum. The use of a sealed, Armco iron capsule to contain the furnace charge permits the removal of hydrogen by evacuation, but confines the calcium

DECLASSIFIED

thus formed to the reaction zone. Hydrogen is again introduced as the charge is cooled, in order that the product may be recovered as uranium hydride.

(4) The reduction of uranium dioxide with a 50 - 100 per cent excess of calcium metal in the form of small nuggets, at 950°C, in an argon atmosphere. The argon atmosphere serves to prevent excessive distillation of calcium to the cool zone of the furnace during furnacing, and at the same time permits a short reaction time. It is necessary to replace the argon atmosphere with hydrogen during the cooling step, as in the above methods. In one instance, prior to the introduction of hydrogen and while the charge was still at a temperature of 950°C, the system was evacuated and the excess of calcium permitted to distill to the cool portion of the tube. In this way the excess reducing agent was substantially recovered with no apparent reduction of purity in the product.

The tabular presentation of the results obtained with each of these methods appears in Tables I through IV. A discussion of several factors not suitably discussed as separate variables is included.

The yield data reported in these tables are apparently inconsistent and require some discussion. Many of the early leaches were carried out before the desirability of centrifuging to recover the uranium hydride was realized. Yields were low because of the loss of varying amounts of the powder as suspended fines. Even in some of the centrifuged runs, low yields were obtained occasionally because of the mechanical difficulties encountered on such a small scale. The usual procedure was to take a portion of the furnace product for the leach treatment; when the full charge was leached, yields well over 90% resulted.

TABLE I

REDUCTIONS OF URANIUM OXIDES WITH CaH_2 IN HYDROGEN

No.	% xs CaH_2	T °C	Time Hrs.	% Yield	% X	% H	% X+H	% C	PPM N	PPM Fe	Remarks
I-1	100	ca 900	1	61.9	94.0	0.80	94.8	<0.1	346	--)	Temperature measured external to furnace tube
I-2	100	ca 900	1	72.6	94.1	0.76	94.9	<0.1	1156	--)	
I-3	100	ca 900	1	63.5	93.7	0.64	94.3	<0.1	479	--)	
I-4	100	ca 900	3	--	92.2	0.76	93.0	0.24	859	132)	
I-5	100	ca 900	3	56.8	95.7	0.86	96.6	0.12	464	--)	
I-6	100	ca 900	3	72.1	96.8	0.89	97.7	0.13	752	203)	
I-7	100	ca 900	3	84.6	97.4	0.93	98.3	0.17	1395	106)	
I-8	100	950	11.5	63.7	96.7	1.11	97.8	0.07	--	--	-325 mesh UO_2 -10 +40 mesh UO_2 -200 +325 mesh UO_2 -40 +100 mesh UO_2 Total furnace charge leached Unsieved UO_2 $\text{CaH}_2 \cdot \text{MgO}$ used
I-9	100	950	11.5	96.1	97.4	1.11	98.5	0.04	--	--	
I-10	100	1050	--	--	96.2	--	--	--	1476	--	
I-11	100	1050	19.0	78.4	96.8	1.08	97.9	0.16	1108	226	
I-12	100	950	11.0	57.3	98.7	1.09	99.8	0.08	913	79	
I-13	100	950	11.5	87.8	97.2	1.21	98.4	N.D.	846	252	
I-14	100	1000	17.0	92.9	97.4	1.11	98.5	N.D.	971	888	
I-15	100	950	11.0	79.8	98.4	1.16	99.6	0.04	896	<1	
I-16	100	950	11.0	89.0	99.3	1.18	100.5	<0.1	274	179	
I-17	100	1050	11.0	93.0	97.1	1.20	98.3	N.D.	632	108	
I-18	50	950	12.0	95.0	98.2	1.24	99.4	N.D.	556	136	
I-19	100	950	11.0	87.5	98.7	1.16	99.9	<0.1	594	106	
I-20	100	950	11.0	76.5	96.1	1.17	97.3	N.D.	705	10	
I-21	100	950	11.0	90.4	96.8	1.19	98.0	<0.1	591	95	
I-22	100	950	11.0	56.2	93.5	0.86	94.4	0.30	123	1169	

12

TABLE II
REDUCTIONS WITH CaH_2 IN ARGON ATMOSPHERE AT 950°C

No.	% xs CaH_2	Time Hrs.	% Yield	% U	% H	% U+H	% C	PPM N	PPM Fe	Remarks
IV-1	100	3	86.8	96.9	1.10	98.0	0.1	2200	149	
IV-2	100	4	90.1	97.3	1.17	98.5	N.D.	--	--	
IV-3	50	3.5	76.6	97.1	1.00	98.1	<0.1	713	306	
IV-4	100	3	84.7	97.1	1.16	98.3	0.11	1429	264	
IV-5	100	4	79.2	96.8	1.18	98.0	0.14	--	193	
IV-6	50	3.5	84.6	96.8	1.13	97.9	0.07	902	--	
IV-7	100	1	89.5	97.7	1.06	98.8	N.D.	--	--	H_2 removed by single expansion into 35-liter vacuum before argon admitted.
IV-8	100	2	87.6	97.3	1.15	98.5	<0.1	--	--	H_2 removed by six separate expansions as above.

TABLE III

REDUCTION OF UO_2 WITH CALCIUM HYDRIDE IN SEALED IRON TUBES UNDER VACUUM

No.	% xs Ca	T °C	% Yield	% U	% H	% U+H	% C	PPM N	PPM Fe	Remarks
III-1	50	950	93.5	98.6	0.18	98.8	0.06	1078	544	
III-2	100	950	92.7	98.1	0.16	98.3	0.03	708	456	
III-3	50	950	--	98.5	1.20	99.7	N.D.	526	572	
III-4	100	950	--	97.9	1.15	99.1	--	1327	430	
III-5	50	950	78.8	98.5	1.19	99.7	N.D.	217	387	III-1 hydrided and re-leached.
III-6	100	950	83.3	98.3	1.21	99.5	N.D.	631	341	III-2 hydrided and re-leached.
III-7	50	950	33.5	98.5	1.20	99.7	N.D.	985	360	
III-8	10	950	71.5	98.1	1.14	99.2	N.D.	1456	162	

TABLE IV

REDUCTIONS OF UO_2 WITH CALCIUM METAL IN ARGON

No.	% xs Ca	T °C	Time Hrs.	% Yield	% U	% H	% U+H	% C	PPM N	PPM Fe	Remarks
II-1	100	950		74.6	98.6	1.18	99.8	0.14	795	329	
II-2	100	950		80.0	98.9	1.23	100.1	N.D.	418	357	
II-3	100	950		59.6	--	0.09	--	0.17	186	414	Ethyl Ca Sand distilled from UO_2 with incomplete reaction.
II-4	100	950		87.3	96.5	1.09	97.6	N.D.	930	88	
II-5	100	950	3.0	79.4	98.6	1.14	99.7	N.D.	523	1479	Excess Ca distilled from charge.
II-6	100	1050	3.0	--	95.0	0.13	95.1	N.D.	283	184	E.F.D. liner used.

The nitrogen contents of the products are directly related to the purity of the reducing agent employed. This conclusion is emphasized by Runs I-22 and IV-3, in which low nitrogen values were obtained by employing reducing agents relatively pure in nitrogen content. Unfortunately, the selection of various grades of reducing agents, either calcium or calcium hydride, has been severely limited by the availability of materials pure enough for our consideration. We have been limited to three separate batches of calcium hydride and one of calcium nuggets for our investigation, other than the two runs just mentioned, in which one was made with a calcium hydride - magnesium oxide mixture, and the other with Ethyl Corporation calcium sand. Neither of these latter two reducing agents have proved suitable during this investigation, the first for reasons mentioned later, the latter because its finely-divided state causes a fast reaction, producing a dense slug which cannot be easily hydrided or leached. Nevertheless, the point is clear that the nitrogen content is introduced by the reducing agent either in the form of calcium nitride or as nitrogen adsorbed on finely-divided reducing agents. Nitrogen in this latter form can be controlled to some extent by careful outgassing techniques prior to the furnacing cycle. This being the case, it is certain that nitrogen content can be minimized by the use of a high-purity, freshly-distilled calcium or calcium hydride.

The iron content has varied greatly in each of the four general methods successfully employed. The extremely low values obtained in certain isolated cases, as for example, Runs I-15 and I-20, suggest that while considerable portions of iron may be picked up by a furnace charge, the iron thus picked up is in a form which is more or less easily removed during the leach operation. Run I-15, for example, was subjected to an unusually long leach period. The results, though inconclusive, indicate that while this extended leach did not apparently have any deleterious effect on the quality of the uranium hydride powder, it nevertheless lowered the iron content to considerably less than that contained in the uranium dioxide from which the powder was prepared.

The following variable factors were given individual consideration, and are discussed separately.

Uranium Oxide

Although uranium trioxide is the first compound obtained by modern ore purification methods which is suitable for reduction and preparation of the hydride powder, the dioxide is easily prepared from the trioxide by hydrogen reduction, and is more suitable for this reduction for a number of reasons. Most important of these is that it requires only two-thirds the amount of reducing agent necessary to convert the trioxide to the hydride. This, in turn, results in the formation of only two-thirds the amount of calcium oxide by-product, and consequently requires less acid during the

007029.030

leach operation. Furthermore, the trioxide as presently prepared always contains small amounts of nitrates, which contaminate the final product with nitride; and it is hygroscopic, thus causing difficulties during the mixing operation with the reducing agent. While some of the preliminary reductions employed U_3O_8 and UO_3 , the bulk of our investigations have been concerned with the reduction of UO_2 . It has been demonstrated in Report NYO-3794 that the furnacing operation in an atmosphere of hydrogen results in the reduction of UO_3 or U_3O_8 to UO_2 in a temperature range of 600 - 650°C, while the charge is being raised to reaction temperature and before the secondary reduction, which results in metal, commences. The water formed by this first step, of course, reacts with calcium hydride as it is liberated. The course of the reaction has been clearly demonstrated in a graph, plotting per cent of hydrogen evolution versus temperature. Thus, it is believed that any effect that different oxides as starting materials might cause would not be the result of any fundamental difference in the reduction, but rather to some other variable, such as particle size and ease of mixing of the reactants. Therefore, it was felt that the confinement of our later studies to the reduction of UO_2 facilitated the more rapid study of other variables, whose effect on the reduction of UO_2 would apply equally well to the reduction of UO_3 or U_3O_8 .

Reducing Agents

Calcium hydride and calcium metal have been employed in all but one of our reductions. One attempt was made to take advantage of the low cost of magnesium metal as a reducing agent in a novel manner. There seems to be little difference in calcium or calcium hydride in so far as completeness of reduction of uranium oxide is concerned. The chief difference between these two reductants as observed in our small, laboratory-scale furnaces is the speed with which the reduction can be completed. The factor which is important in determining the speed of reaction, as well as the completeness of reaction, is the vapor pressure of calcium in the furnace charge. This is true even in a calcium hydride reduction in which, it is believed, the hydride is chemically inert and the reduction mechanism depends upon liberation of free calcium metal by the dissociation of the hydride to effect the reduction of the uranium oxide. It would be predicted that the vapor pressure of calcium in an inert atmosphere would be considerably greater than the vapor pressure of calcium in a hydrogen atmosphere. Confirmation of this point can be found in the experimental observation that considerably more distillation of excess reducing agent occurs when calcium metal is used in argon than when calcium hydride is used in an atmosphere of hydrogen. There is apparently little difference between calcium metal and calcium hydride in so far as purity and physical characteristics of the product are concerned, at least on our present scale of operations. However, there are differences between the two re-

DECLASSIFIED

ducing agents more than those which necessitate slightly different furnacing techniques. For example, calcium hydride can be ground into a fine powder more easily, and thus mixed more intimately with the uranium oxide. Calcium hydride reduces uranium oxide endothermically, so that the furnace charge never rises above the temperature of the furnace. On the other hand, the reductions can apparently be effected more quickly with calcium metal (probably violently with the higher oxides). The added heat of reaction employing calcium metal might prove an advantage in power supply requirements, if it can be adequately controlled. This same heat of reaction may form particles which are less susceptible to surface contamination because of improved surface characteristics. Using calcium metal, no provision has to be made for the gas evolution which occurs during the reduction with calcium hydride. It is felt that a satisfactory choice between these two reducing agents cannot be made relying upon the inadequate means of evaluation employed thus far, and that a final elimination of either one must await the perfection of a density determination of the hot-pressed pellets and a study of the powder characteristics.

While magnesium metal is thermodynamically capable of reducing the oxides of uranium, there are a number of factors which have discouraged any extensive study of this reduction during these investigations. The chief objection to its use is the vigor of the reaction. Once it is initiated, it is reported to be difficult to control, because of the volatility of the magnesium and the high heat of the reaction. This theory is not altogether consistent with the heat of reaction data presented in the literature, which indicate that the reduction of the fluoride is hotter than the reduction of the dioxide. The higher oxides, however, should result in much more violent reactions, and this may have been the cause of earlier troubles with the magnesium reduction. A second obstacle in the use of magnesium is the difficulty to be expected in leaching the ignited magnesium present as a by-product in the furnace charge.

Despite these obstacles, the low cost of magnesium metal prompted us to undertake an exploratory run employing a calcium hydride - magnesium oxide mixture as the reducing agent. This material is a patented product of Metal Hydrides Incorporated, and is prepared by the action of magnesium metal on calcium oxide in a hydrogen atmosphere, in the neighborhood of 500°C. It has not found extensive use in the Hydrimet Process because of the tendency to reverse at high temperatures to liberate magnesium metal. For the particular case of uranium dioxide reduction, however, such a reversal did not seem deleterious, since magnesium metal was also considered a good reducing agent[†]. It was hoped that an easily controllable reaction might be obtained, even in the event of such a reversal, by striking a good heat balance between the mixing magnesium, calcium oxide and uranium dioxide and heating

0311291030

in hydrogen to cause a preliminary reaction, $\text{CaO} + \text{Mg} + \text{H}_2 \longrightarrow \text{CaH}_2 + \text{MgO}$, to occur, and then to raise the temperature to 1000°C to initiate the secondary reaction, $2\text{CaH}_2 + \text{UO}_2 \longrightarrow 2\text{CaO} + \text{U} + 2\text{H}_2$.

The results of the single reduction attempted are designated as Run No. I-22 in Table I. The expected difficulty in leaching out the magnesium oxide was encountered. The reversal of the reaction, to yield magnesium metal, was confirmed by the recovery of large crystals of the metal in the cool portion of the furnace tube. Examination of the furnace tube after the run was completed revealed that it was belled outward at the end of the tube. Although it is not certain whether this was caused by vigorous magnesium reduction, or whether it resulted from an inadvertent increase to three atmospheres of hydrogen pressure which occurred during the reaction, further reductions of this type are not contemplated, since this group has been requested to concentrate on calcium and calcium hydride reductions. The nature of the result in this experiment should serve as a caution, should a magnesium reduction be attempted elsewhere.

Excess of Reducing Agent

The effect of the excess of reducing agent has not been extensively studied for any of the varied techniques employed. Most of the reductions were made with either 50 or 100 per cent excess, and little difference in results is evident from a study of the analyses. The comprehensive study of this aspect of the situation has been postponed, pending development of the density evaluation method, since it is apparently impossible to detect the small variations in results caused by different proportions of reducing agents.

In one case, employing the Armco iron capsule technique, only a 10 per cent excess of reducing agent was employed, and in this case the purity exceeded 99 per cent, and was almost within experimental error of the range of 99.5 - 99.9 per cent. In another single experiment (Run II-5), the excess of reducing agent (100 per cent) was distilled from the charge and collected as calcium metal by a short vacuum treatment, following completion of the reduction cycle. The furnace product from this run was completely inactive (no hydrogen evolution) during the leach treatment, and the final product analyzed 99.8 per cent pure. It may be possible, therefore, to recover whatever excess of reducing agent is used by the simple expedient of vacuum distillation prior to the leach step; but the possibility of a reversal of the reduction reaction must be considered. Although the results in Run No. II-5 seem to be favorable, we have had indications that the reaction may reverse under vacuum treatment. For example, a measurable amount of free calcium metal was detected after heating a mixture of calcium oxide and uranium hydride powder at 950°C for six hours under vacuum.

DECLASSIFIED

Temperature of Reduction

The furnace temperature employed in the Hydrimet Process for the production of uranium metal for the Manhattan Project during World War II was 950°C ⁽⁵⁾. This temperature has worked satisfactorily in the present studies.

It has been demonstrated that reductions can be successfully carried out in this temperature range under hydrogen, argon, or in vacuum. The operational techniques involved are necessarily different, depending on the atmosphere employed. The experimental results indicate that these operational differences are largely concerned with preventing the loss of reducing agent by distillation. For example, in a run carried out under vacuum, in the vicinity of 1000°C calcium is very rapidly distilled from the furnace charge, in a small-batch operation. This loss can be prevented to a large extent by carrying out the reduction under an inert atmosphere, such as argon or helium.

Operation in a hydrogen atmosphere at 950°C gives a slow reaction because the vapor pressure of calcium is lowered by the formation of solid solutions of calcium and calcium hydride in one another. It has already been mentioned that considerably longer reduction periods were necessary in the presence of hydrogen.

Attempts to employ higher temperatures resulted in poor reductions, evidently caused by interaction with the stainless steel crucible. Large amounts of chromium and nickel were picked up in runs conducted at $1000 - 1050^{\circ}\text{C}$. This source of contamination is more troublesome when calcium metal is present in the liquid phase in unlined, stainless steel crucibles. The use of electrically fused Dolomite liners to protect against this contamination in the high-temperature region has given inconclusive results in preliminary runs.

It will be desirable to continue this phase of our studies to determine whether the rate of reaction can be substantially increased at the slightly higher temperatures. Furnacing temperatures of less than 950°C have been used only in the early runs, when the temperature was controlled by a thermocouple external to the furnace tube. While a more extensive study will be made of the low-temperature region when the hot-press density evaluation is available, it is not likely that any advantage will be discovered, since the rate of reaction is probably slower.

RECOMMENDATIONS

The urgent need for a suitable method for evaluating the purity of uranium hydride powder requires that the great majority of emphasis in the immediate future be directed toward the study of the preparation of hot-pressed pellets and/or the search for a direct

037229.030

method for the determination of oxygen content. Until this problem is solved, no further progress in the study of furnace and leach operations is possible.

When this is accomplished to a degree which will permit a precise study of these operations, a more thorough review of the variables already investigated is recommended. Information gained in this study will be useful in the planned scale-up to a 2-5-pound operation. It is as yet not known which of the following causes oxygen contamination: (1) incomplete reduction of uranium dioxide, which is not then removed by the leach; (2) oxidation of the pure uranium hydride powder by the leach solution; and (3) oxidation of the pure, dry uranium hydride by traces of oxygen in the dry box during subsequent handling for analysis, hot pressing, etc. The major sources of this contamination must be discovered when accurate oxygen analyses are available, so that the correct variables can be studied.

Larger-scale operations should permit a successful evaluation of the feasibility of the process during the next contract year.

APPENDIX

Furnacing Procedure

Procedure A

A sample of uranium oxide containing 71.4 grams (0.3 mole) of the metal is weighed into an 8-ounce bottle. The desired excess of calcium hydride is added and the reactants mixed thoroughly by shaking in the capped bottle for five minutes. The charge is loaded in a stainless steel boat, placed in a furnace tube, and attached to the metal vacuum line by means of a vacuum coupling. The charge is degassed at room temperature for one hour, at 200°C for one hour, and is then heated to 950°C in an initial static vacuum. As the pressure of evolved hydrogen rises above one atmosphere (usually at about 800°C), it is released into an evacuated storage system. The charge is held at 950°C under one atmosphere of hydrogen for 11 hours, and then cooled slowly to room temperature, with hydrogen supplied to keep a pressure of greater than one atmosphere over it. The closed furnace tube is disconnected from the vacuum line and transferred to the dry box, where it is opened, the boat withdrawn, and the powder poured into a half-pint mason jar. A 40-gram portion, to be leached, is weighed into a 100-milliliter, round-bottom flask which is then capped with a clamped, rubber connecting hose.

Procedure B

Procedure B employs calcium hydride as in Procedure A, and the operation is identical until the charge has been heated to 950°C. At this temperature the hydrogen is evacuated until a pressure of one millimeter remains (about 15 minutes). Argon is then admitted to one atmosphere of pressure, and the charge held at temperature for one hour. The tube is then re-evacuated, purified hydrogen is admitted, and the furnace charge is cooled slowly to room temperature. Subsequent handling is similar to Procedure A.

Procedure C

The mixed charge, as prepared in Procedure A, is loaded into an Armco iron capsule which is then sealed by crimping off the stem with pliers. The capsule is placed in the furnace tube attached to the vacuum line, and the furnace temperature raised to 950°C with continued evacuation, and held at temperature for 3.5 hours. The furnace is cooled, the furnace tube opened in the dry box, and the Armco shell broken open. The capsule is then returned to the furnace tube, reattached to the metal line, and hydrided by heating to 225°C in hydrogen for 3 hours. This step is necessary because of the impermeability of the iron at hydriding temperatures. The furnace tube is then returned to the dry box, and the powder prepared for the leach operation as in Procedure A.

0371229.030

Procedure D

Calcium metal in the form of small nuggets is used in place of calcium hydride powder, as in Procedure A. The operations are identical for mixing, loading and degassing. Pumping is continued until the temperature in the furnace is raised to 600°C. Three atmospheres of argon are then admitted, and the temperature raised to 950°C, held there for 3 hours, and then lowered to 600°C. The argon is then evacuated, and hydrogen admitted to 2 atmospheres' pressure, and the charge permitted to cool to room temperature. Subsequent handling of the product is similar to that described in Procedure A.

Fig. 1 — Metal reduction line.

Leach Operation

The powder addition bulb containing a sample of furnace product as described above is attached to a 2-liter, round-bottom, three-neck flask by means of rubber tubing. The 2-liter flask is fitted with a "Tru-Bore", vacuum-tight stirrer and a water-cooled bulb condenser. Under a blanket of argon the powder is added slowly, with stirring, to 550 cc. of 10 per cent acetic acid solution which is chilled in an ice bath. After being stirred in this solution for 15 minutes, the product is allowed to settle for 30 minutes, and the supernatant liquid is decanted and centrifuged to collect the slow-settling "fines". To the product which settles rapidly is added 300 cc. of 10 per cent

acetic acid leach solution, and these are held in contact for about 30 minutes. The second leach is used as a carrier to aid in the transfer of the entire yield to the centrifuge bottles. The product is then washed twice with 300-cc. portions of deaerated, distilled water. These are followed by three anhydrous methanol washes, the final one being used to transfer the product to tared bottles. The bottles are then placed in a resin reaction kettle on a vacuum line and dried for 20 hours by evacuation at room temperature. The kettle is then filled with gettered argon, and the bottles capped, weighed and removed to the dry box, where the analytical samples are taken.

Fig. 2—Leach apparatus.

Hot-Press Technique

Approximately 11.3 grams of hydride are loaded, with tamping, into the die unit. This must be done after the die body, with bottom plug inserted, is in position in the vacuum unit. The plunger is then positioned and the thermocouple put in place. The heater is lowered around the die, and the top of the vacuum pot put in place. The ram must be centered, and seated flush on the top of the plunger. The unit is then sealed, removed from the dry box, and placed on a vacuum line. The entire system is connected to the various leads--that is, current for the heater, thermocouple, and the water-cooling coil. The unit is evacuated until a 5 - 10 μ vacuum is obtained, and the heat is turned on

Fig. 3—Vacuum hot-press die disassembled.

Fig. 4—Vacuum hot-press die assembled for operation.

to supply 85 watts, to continue the degassing of the apparatus. The temperature is allowed to rise gradually to 200°C, with a good vacuum. The power is then increased to 275 watts. The temperature then rises rapidly to a plateau of 385 - 400°C, which seems to be the point at which a major portion of the hydrogen is evolved. After taking one-half hour to go from 385°C to 400°C, the temperature takes a sharp rise and reaches 600°C quickly. With the temperature at 600°C, the vacuum is tested, and when it returns to the micron range, pressure is applied. The pressure has to be applied gradually to prevent lowering of the temperature. After one-half hour under pressure, the heat is turned off and the die allowed to cool in vacuum for 15 hours. The apparatus is then removed from the vacuum, and opened to obtain the pellet. The density of the pellet is then determined by the standard water-displacement technique.

Fig. 5—Argon dry box.

Procedure for Vacuum-Fusion of Uranium

A 25-to-35-gram sample of uranium hydride powder is weighed out in the argon dry box, and introduced into a round-bottom Vycor flask fitted with a ground-glass stopcock adaptor. The stopcock is closed, and the flask and adaptor removed from the argon box and attached to a high-vacuum line. The argon is slowly pulled out of the flask; and after a good vacuum is attained, the flask is slowly heated to about 275°C under vacuum until hydrogen evolution ceases, as evidenced by re-attainment of a good vacuum. The temperature is then raised to 800°C and held at this point

Fig. 6—Vacuum fusion crucible and shield.

Fig. 7—Vacuum fusion apparatus.

for approximately one hour, to loosely sinter the powder, and then allowed to cool under vacuum. The flask is removed from the vacuum line and taken into the argon box. The uranium metal is a gray, porous lump, which is removed by breaking the flask. A small sample of the sintered uranium metal is removed from the dry box to test the pyrophoricity. Approximately 20 grams of the sintered uranium metal is loaded into a carbon crucible which was previously degassed by induction heating to about 1500°C. This is removed from the argon box and immediately fitted with an inner Alundum sleeve and an outer Alundum sleeve on which a molybdenum radiation shield is mounted. The entire set-up is then placed in a quartz tube with a 71/60 standard taper, ground inner joint, and supported in the proper position by Alundum tubing. This is placed through the induction coil and attached to a vacuum source through a corresponding 71/60 outer condenser joint. The system is evacuated and heated with low power to assure complete outgassing. The temperature is then raised to approximately 1350°C, until the charge becomes molten. One to five minutes are required. The charge is then cooled under vacuum, removed from the quartz tube, and the crucible cut open and the contents removed. The cylindrical portion is cut off, and the outer surface removed with a grinding wheel. The density of the pellet is determined by displacement of water by the standard technique.

Uranium Assay

Procedure A

A sample of uranium hydride powder of approximately 2 grams, which has been weighed analytically in the dry box, in a 1-1/2-ounce, plug-cap vial, is just covered with distilled water and then washed into a 250-milliliter beaker. 20 milliliters of concentrated HNO_3 and 40 milliliters of 1:1 H_2SO_4 are added. When solution is complete, it is evaporated on the hot plate for 15 minutes after the appearance of dense, white fumes. It is then cautiously diluted with 15 cc. distilled water and fumed once more for 15 minutes. The sample is diluted, cooled, and transferred to a 100-milliliter volumetric flask and made up to volume. 25-milliliter aliquots are reduced in the Jones reductor, aerated and titrated with approximately 0.1 N ceric sulfate, using Ferroin as the indicator. The ceric sulfate is standardized against MS-ST U_3O_8 (?).

Procedure B

A sample of approximately 0.35 grams, which has been weighed in the dry box into a 1-1/2-ounce, plastic cap vial, is covered with deaerated, distilled water introduced by means of a hypodermic syringe through the plastic cap. The material is transferred under water to a 500-cc. round-bottom flask and 100 milliliters of 0.1 N ceric sulfate is added. The flask is connec-

0370281030

ted to a condenser by means of a 24/40 standard taper joint, and the mixture is gently refluxed until solution of the sample is complete. The flask is cooled, the condenser washed down with distilled water and the excess of ceric sulfate back-titrated with 0.1 N ferrous sulfate, using Ferroin as the indicator. The uranium hydride content is calculated by the formula:

$$\% \text{UH}_3 = 5.718 \frac{VN}{S} - 42.355$$

V = volume of ceric sulfate reduced by uranium, in milliliters

N = normality of ceric sulfate

S = sample weight in grams

Carbon and Hydrogen Analysis

Carbon and hydrogen analyses are carried out by a standard micro-combustion procedure⁽⁸⁾, in which the sample of approximately 0.2 grams is heated by a blast burner in a stream of oxygen. Water formed by the combustion is trapped by anhydrous, and the carbon dioxide by Ascarite. The only deviation from standard technique is that the samples are weighed onto aluminum foil and carefully wrapped in the foil in the dry box, so that no air may have access to the hydride while loading the sample into the combustion line.

BIBLIOGRAPHY OF REFERENCES

- (1) P. P. Alexander, "The Production of Uranium Metal by Metal Hydrides Inc.", in National Nuclear Energy Series, Division VII, Volume 2B
- (2) R. J. Anicetti, "Development of a Furnace for Melting and Casting Uranium Metal", in National Nuclear Energy Series, Division VII, Volume 2B
- (3) NYO-1129
- (4) SEP-39
- (5) Uranium Technology, National Nuclear Energy Series, Division VII, Volume 2A, p. 145
- (6) P. P. Alexander, "The Hydride Process. Commercial Production of Uranium", Metals and Alloys, 9:270 (1938)
- (7) MDDC-1134
- (8) Niederl and Niederl, "Micromethods of Quantitative Organic Analysis", 2nd. edition, 1942, pp. 101-150

0371228.030