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FIRST QUARTERLY REPORT ON THE REDUCTIONS OF URANIUM OXIDES

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For The Atomic Energy Commission

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Chief, Declassification Branch *tc*

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ABSTRACT

The preliminary results of a program designed to evaluate methods for preparing uranium hydride from the various oxides of uranium are presented. The apparatus has been designed and constructed for the purpose of carrying out batch reductions under a variety of conditions employing calcium hydride, calcium metal and magnesium metal as the reducing agents. Since the separation of the alkaline earth oxides, present as by-products in the furnace products, promises to be the most difficult problem encountered in this investigation, a major portion of the time during this past quarterly period has been directed toward the development of a suitable leach method. No investigation of the reduction methods has been possible to date because of the inability to obtain SF materials. A brief outline of the future work is included.

FIRST QUARTERLY REPORT ON THE REDUCTIONS OF URANIUM OXIDES

By Robert W. Bragdon

A. INTRODUCTION

Uranium metal has been processed almost exclusively by vacuum fusion methods since the early days of the Manhattan Project, even though the metal was first prepared commercially as a powder. This was not because of any inherent superiority of vacuum fusion methods over powder metallurgy techniques, but rather was a policy dictated by the urgency of the situation.

Interest in powder metallurgy techniques has been revived by the development of a hot pressing technique at the Sylvania Bayside Laboratories. Solid uranium of 18.7 to 18.8 grams per cc. density can be manufactured by hot pressing uranium powder at a compacting pressure of approximately 30 tsi. 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 the 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 .07 to .09%.

The present method of producing uranium hydride is expensive and involves many steps. Starting with purified uranium trioxide (UO_3), it is necessary to reduce with hydrogen to the dioxide, fluorinate with hydrogen fluoride to uranium tetrafluoride, reduce to the metal with magnesium and finally hydride the recast metal.

The purpose of the current research program is to decrease the cost of production of the hydride with the elimination of some of these steps by the direct reduction of the oxide. The most obvious method, of course, is a "Hydrimet" reduction of yellow oxide with calcium hydride.

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(2) SEP-39

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Calcium, calcium hydride and magnesium are all thermodynamically capable of reducing the oxides of uranium and presumably they all may be employed to produce the hydride by carrying out the reduction in a hydrogen atmosphere, or cooling the furnace product in hydrogen. The literature is somewhat contradictory concerning the results to be obtained with these reducing agents, but it is very likely that the presence of oxide in the final product was a result of the leach methods employed rather than incomplete reduction of the oxide. Uranium metal powder was produced at Metal Hydrides Incorporated during the last war for the Manhattan Project employing the "Hydrimet" technique. Most of the difficulties in obtaining oxide-free metal at that time were the result of attempts to get production from the plant while it was still being constructed.⁽³⁾ It is the consensus of opinion that oxide was introduced during the leaching and drying steps and did not result from incomplete reduction with calcium hydride.

Since U_3O_8 and UO_2 can be easily prepared from the trioxide by thermal decomposition or hydrogen reduction, all three must be evaluated as starting materials.

Uranium trioxide would seem to be the most desirable starting point for the reductions because it is obtained early in the production line and is therefore less expensive. There are a number of reasons, however, why it may become expedient to use one of the other oxides of uranium, even though they require more processing. The yellow oxide usually contains variable amounts of water and nitrates and is very hygroscopic. The presence of water in the oxides will, of course, add to the vigor of the reactions and consume some of the excess reducing agent. It must be determined whether the nitrate present in the yellow oxide will be converted to uranium nitride and thus contaminate the final product. Since UO_3 contains the greatest amount of oxygen for those oxides under consideration, the heat of reduction with the various reducing agents is considerable. See Table I. U_3O_8 , which can be prepared easily from UO_3 by furnacing in air at $800-900^\circ C$., is substantially free from water and nitrates and because it contains less oxygen, a smaller heat of reduction is encountered. Brown oxide (UO_2), which is prepared by the reduction of UO_3 in hydrogen at around $800^\circ C$. is also free from nitrates and water and while it is the most stable of the oxides of uranium, nevertheless the heat of reduction with the above reducing agents is the least.

(3) CA-278

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Table I

Thermochemical Calculations for the Reductions of Uranium Oxides (4)

<u>Reaction</u>	$\Delta H_{298^\circ K.}$ <u>K-cal/mol U</u>	$\Delta H_{1100^\circ K.}$ <u>K-cal/mol U</u>
$2CaH_2 + UO_2 \longrightarrow U + 2CaO + 2H_2$	+56.4	+77.8
$3CaH_2 + UO_3 \longrightarrow U + 3CaO + 3H_2$	-18.4	+13.9
$\frac{8}{3}CaH_2 + \frac{1}{3}U_3O_8 \longrightarrow U + \frac{8}{3}CaO + \frac{8}{3}H_2$	+14.5	+44.5
$2Ca + UO_2 \longrightarrow U + 2CaO$	-33.8	-33.0
$3Ca + UO_3 \longrightarrow U + 3CaO$	-153.7	-152.4
$\frac{8}{3}Ca + \frac{1}{3}U_3O_8 \longrightarrow U + \frac{8}{3}CaO$	-105.8	-103.3
$2Mg + UO_2 \longrightarrow U + 2MgO$	-17.6	-21.8
$3Mg + UO_3 \longrightarrow U + 3MgO$	-129.4	-135.6
$\frac{8}{3}Mg + \frac{1}{3}U_3O_8 \longrightarrow U + \frac{8}{3}MgO$	-84.2	-88.4

Calcium hydride was used for the preparation of large amounts of uranium powder at this plant during the last war. The source of uranium was U_3O_8 and later UO_2 . Calcium hydride offers a number of advantages over calcium metal for this type of reaction. First, the hydride is far more brittle than the metal and can thus be ground to a fine powder which can be intimately mixed with the oxide to be reduced. Second, the reduction of uranium oxides by calcium hydride is endothermic (with the exception of UO_3). Because of this, the temperature of the charge never rises above the temperature of the furnace and the furnace product may be easily ground to a fine powder whether the uranium metal or uranium hydride is the desired product. Third, hydrogen gas is released during the reaction and offers a convenient method for following the course of the reaction. This hydrogen can be stored in a uranium hydride reservoir and later used to hydride the uranium metal in the furnace product as the charge cools to room temperature.

(4) Values for $\Delta H_{298^\circ K}$ were taken from NBS Circular 500. Values for $H_{1100^\circ K} - H_{298^\circ K}$ for U, UO_2 , Ca, CaO , Mg, and MgO were obtained from Bureau of Mines Bulletin 476. UO_3 value was extrapolated from the same data. Value for CaH_2 was taken from dissociation pressure work by Bronsted, Z. Elektrochem. 20, 81-3 (1914). The value for U_3O_8 was taken from "The Chemistry of Uranium," National Nuclear Energy Series VIII-5.

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Magnesium metal has not been so widely used to reduce uranium oxide. Owing to its high vapor pressure, it tends to distill from the reaction mass and, therefore, must be used under pressure. Once initiated, the reaction is evidently violent and difficult to control. This method will probably prove to be competitive only if the by-product of magnesium oxide can be more easily removed by leach methods than can calcium oxide, and this does not seem likely.

Calcium metal has been employed by a number of workers ⁽⁵⁾ to prepare uranium metal of a high degree of purity. The usual method employs a flux such as calcium chloride to aid in producing a fluid mass. The exothermic nature of these reductions contributes to the production of more or less large pellets of metal, although careful governing of the reaction temperature has permitted the production of a fine powder. The use of an inert atmosphere serves to minimize the distillation of the calcium metal from the reaction zone. It is probable that if the furnace product were cooled from its reaction temperature in an atmosphere of hydrogen that a fine powder of uranium hydride could be obtained.

The excess alkaline earth reducing agent and alkaline earth oxide by-product are generally separated from uranium by an aqueous acid leach. The possibility that this operation may introduce oxygen into the product has prompted us to start an investigation of nonaqueous leach solutions. One such method would employ a solution of anhydrous HCl in absolute alcohols. Solutions of anhydrous acids in inert solvents react with calcium metal and calcium oxide slowly but the calcium salts formed must be soluble in the leach solution to be effective. An example is a hexane solution of glacial acetic acid which reacts quite readily with furnace products converting calcium metal and calcium oxide to calcium acetate. The latter salt, however, is insoluble in the leach solution and cannot be separated from the furnace product without washing with an hydroxylic solvent or the use of a flotation technique. Similarly, calcium acetate is sufficiently insoluble in methyl, ethyl and butyl alcohols to discourage their use for leaching.

An alternative and nonoxidative leach method suggested by a study of the literature is the use of mercury ⁽⁶⁾ to form a UH₃-mercury amalgam-like composition as reported by Spedding's group. It would be expected that treating a furnace product mixture of uranium hydride and calcium oxide would result in such an "amalgam" and that the calcium oxide would separate as a scum on the surface of a more dense "amalgam." While such a method appears costly, because of the expense of mercury, it would certainly prove useful as a standard leach method for the evaluation of the various reductions to be studied. It might even be developed into an industrial method because the mercury should be able to be recovered completely.

(5) "The Chemistry of Uranium," National Nuclear Series VIII-5.

(6) MDDC-1586.

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B. DISCUSSION OF RESULTS

1. Apparatus

The all-metal vacuum line which has been designed and constructed for carrying out the various reductions is illustrated in Figure 1. It consists of an oil diffusion pump (A) backed by a Cenco pressovac fore pump and connected to a 1" copper tube by Bellows valve (B). A second Bellows valve (B) connects to a flexible metal tube leading to the reduction furnace. A rough indication of the pressure within the apparatus can be observed on pressure gauges (C) which indicate the vacuum in inches and the pressure in psi. A 9 gallon stainless steel hydrogen reservoir (D) can be used for the storage of hydrogen and serves as a buffer for pressure surges. Hydrogen can be admitted to the apparatus by valve (E) (All needle valves are Hoke miniature Bellows valves.) and absorbed in the uranium metal in furnace (F). By regenerating the hydrogen from the uranium hydride thus formed, extremely pure hydrogen can be obtained for hydriding the furnace product. A water-cooled copper condenser (G) prevents conduction of heat from furnace (F) to the vacuum line. Valve (H) can be used to introduce argon or other inert gas and to connect to a manometer or to release sudden pressure surges. Thermocouple gauges (I) serve to read the pressure in the range 0 to 500 microns both in the vacuum line and in the reduction furnace. Water-cooled copper tubing at (K) prevents the heat of the furnace tube from decomposing the silicone rubber gasket. The furnace charges are contained in boat (M) which for the present, at least, will be constructed of stainless steel. (N) and (O) are Wheelco capacitrols for controlling the temperatures of the furnaces to $\pm 5^{\circ}\text{C}$. The furnace tube connection to flexible tube (J) will be so constructed that it can be disconnected after each run and the entire furnace tube transferred to an argon-filled dry box. In this manner the furnace product can be unloaded with the complete exclusion of air. It will be noted that hydrogen evolved during reduction of oxides with calcium hydride can be absorbed by the uranium in furnace tube (F) and later regenerated during the cooling of the charge to hydride the uranium formed by the reduction. In this manner it will be possible to avoid the troublesome and sometimes ineffective gettering methods for purification of tank hydrogen.

2. Leach Methods

It has been necessary to devote the major portion of our time during this quarterly period to the study of various leach methods, since it is not possible to evaluate a reduction until the problem of oxygen contamination by the leach is solved. We therefore prepared a synthetic furnace product by grinding uranium hydride with calcium hydride and calcium oxide. In the interests of speed, it was necessary to prepare the uranium hydride from a sample of AR grade Mallinckrodt uranium which had been in our laboratory for some time. This particular sample did not absorb hydrogen in anywhere near the usual amount and resulted in a product with a hydrogen to uranium ratio of 2.02 (0.82% hydrogen). It could not be determined whether this low absorption of hydrogen was due to the presence of oxygen in the particular sample of uranium metal that we employed or whether it was oxygen or

some other impurity introduced during subsequent handling of the uranium hydride. Nevertheless, in the interests of obtaining some preliminary information, a synthetic furnace product was made up of 241 parts by weight of this uranium hydride, 84 parts of calcium and 112 parts of calcium oxide. (This is equivalent to the products from the reaction,

when 100% excess of calcium hydride is employed.) This mixture was then ball milled for several hours to insure thorough mixing and was stored under argon in a sealed glass bottle. Approximately 45 gram samples of this mix were then subjected to a variety of leach methods. These methods included:

- (1) anhydrous HCl in methanol;
- (2) glacial acetic acid;
- (3) glacial acetic acid in methanol;
- (4) aqueous acetic acid;
- (5) air flotation techniques in combination with the above leaches;
- (6) glacial acetic acid in hexane and flotation of the calcium acetate;
- (7) "amalgam" technique.

While preliminary tests had shown that the complexing agent "Versene" was insoluble in organic solvents, an additional leach method using an alkaline aqueous solution of this reagent is being studied. "Versene" is an organic chelating agent which forms stable water-soluble complexes with calcium at a pH greater than 6.5 and with magnesium at a pH greater than 8.6. Most divalent and trivalent metals are also complexed under similar conditions. Preliminary tests show that the rate of solution of CaO in "Versene" is low, but the latter is claimed to be a solvent for CaC_2O_4 whose solubility in water is much less than the oxide. While no definite conclusions can be drawn from these experiments because of the indefinite purity and nature of the uranium hydride employed, nevertheless it was possible to obtain some information that will serve as a guide to later leach studies.

Table II

Uranium Hydride Recovered from Synthetic Furnace Product Mix ($\text{UH}_{2.02}$)

<u>Leach Method</u>	<u>%X</u>	<u>%H</u>	<u>$\frac{H}{Y}$</u>	<u>% Yield</u>
HCl in methanol	95.7	0.86	2.12	44.8
HCl in methanol at -78°C .	93.7	0.81	2.02	--
HAC in deairedated H_2O at 0°C .	--	0.82	--	86.1
HAC in methanol	93.4	0.24	0.6	79.7

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The results of these leach studies in the above table indicate no serious introduction of impurities by the leach solution with the exception of the glacial acetic acid in methanol. In this particular treatment considerable acid was added in an attempt to break an acetate gel. The low yields obtained with methanolic hydrogen chloride are somewhat surprising. They are caused by solution of uranium as evidenced by the formation of green solutions. To date the most satisfactory leach solution has been dilute aqueous acetic acid. This is certainly encouraging and yet it must be kept in mind that the low purity of the uranium hydride used in these experiments does not preclude the possibility that a surface coating of oxide serves to protect the uranium from the action of the leach.

Upon receipt of a fresh sample of AR grade Mallinckrodt uranium, this investigation was repeated. The purity of this fresh sample of uranium was checked by both uranium assay and density measurements. The density varied from 18.5 to 18.55 grams per cc. and the uranium assays all exceeded 99%. The uranium hydride prepared from this material had a hydrogen to uranium ratio of 2.92, which is considered good for AR grade metal. Complete analytical results have not been received. The leach experiments currently in process using uranium hydride with a ratio of hydrogen to uranium of 2.92 should settle the question of whether or not these leach solutions attack uranium hydride to too great an extent. We are certainly aware, however, that the action of these leach solutions on a synthetic furnace product is not the same situation as is to be encountered with an actual furnace product where some of the alkaline earth oxide to be leached may be protected from the action of the leach by a coating of uranium hydride or uranium metal.

The best criterion of high purity oxide-free metal is the density. We feel that a density determination on the dehydrided powder after leaching and drying will be the ultimate proof of the effectiveness of the leach method. Therefore, samples of the UH_3 powder as prepared will be degassed and the density checked (by the method of Schumb and Rittner⁽⁷⁾ as well as liquid displacement). A comparison of the density of the degassed-leached powder will show the extent of oxygen contamination by a given leach method.

3. Uranium Hydride "Amalgam" Leach

The fluid amalgam-like composition formed by uranium hydride and mercury reported by Spedding's group at first seemed to offer an ideal nonoxidative leach method for the extraction of uranium hydride from furnace products containing calcium oxide as a by-product. Interest in this method was heightened when it was discovered in our laboratories that the mercury could be completely removed from these "amalgams" by vacuum distillation at 225-250°C. Although this process results in the loss of hydrogen as well, this is of little significance, since the residue can

(7) Schumb and Rittner, J. Am. Chem. Soc. 65, 1692(1943).

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be rehydrided at the end of the vacuum distillation. The easy removal of mercury prompted us to undertake the extraction of uranium hydride from the synthetic furnace product, especially since neither CaO nor CaH_2 are wet by the pure mercury. It was felt that a nonoxidative leach method of this type would be ideal as a standard laboratory leach method for the evaluation of the various reductions which we plan to study. Unfortunately, the uranium hydride "amalgam" compositions have the undesirable property of wetting their container as well as the calcium oxide powder. Small amounts of mercury when added to synthetic furnace product are completely absorbed by the powder. As more and more mercury is added, this powder changes slowly to a muddy slurry with no indication of CaO separating as a slag. Our attempts to separate pure uranium hydride "amalgam" from this mixture by various filtration methods and centrifugation have so far met with no success whatsoever. While we are still searching for some refinement which will permit us to take advantage of this uranium hydride "amalgam" technique, it must be admitted that this method no longer shows much promise.

C. OUTLINE OF FUTURE PROGRAM

While it is certainly not possible to outline in detail the program of reduction investigations which we will carry out, nevertheless there are certain variables which it can be anticipated it will be necessary to investigate. The program is presented in outline form.

I. Oxide

- A. UO_2
- B. U_3O_8
- C. UO_3

II. Reducing Agents

- A. Calcium
- B. Calcium Hydride
- C. Magnesium

III. Variables*

- A. Temperature
- B. Time
- C. Excess of reducing agents
- D. Atmosphere
- E. Use of a flux
- F. Compacting of reactants*

*It is hoped to completely eliminate leach methods as a variable by being able to settle on some satisfactory standard leach technique.

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Metal Line for Reduction of Uranium Oxides

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