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By
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ABSTRACT

Progress during the fifth quarterly period has been made on a continuing evaluation of the means of reduction of uranium oxides to uranium hydride powder. On the basis of previous experience, emphasis has been upon the reduction of uranium dioxide by calcium hydride, which not only has given some of the best results to date, but also is considered to be the reaction most readily adaptable to a continuous process.

A major portion of time during this quarterly period has been spent developing evaluation procedures, as no further significant progress can be made until adequate evaluation methods are available. Progress on evaluation processes has been slow and painstaking, and while it is still far too early to make definite statements about any of the procedures being studied, three methods of evaluation which are considered the most promising are being pursued. These are: (1) an uranium assay method whereby the uranium hydride powder is dissolved directly in a measured excess of ceric sulfate; (2) the density of uranium metal prepared by hot-pressing uranium hydride powder; and (3) a direct determination of oxygen by displacing this element with bromine trifluoride. In addition, the A. E. C. New Brunswick Laboratories have agreed to do a limited number of oxygen determinations by the vacuum fusion technique on uranium metal produced in this laboratory. It is certain that one or more of these methods will be suitable for a complete evaluation of uranium hydride powder.

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INTRODUCTION

The status of the problem at the conclusion of the first year of work under this contract was that uranium hydride powders were obtained, which, by three of the four experimental techniques employed, had analyses within experimental error of 100% purity. This seemingly satisfactory state of affairs is, however, quite misleading. The uranium assays up to the time of this quarterly period have been accurate to no better than $\pm 0.3\%$. While this degree of precision is entirely adequate for a great majority of chemical analyses, the very large difference between the atomic weight of uranium and of the impurities which are likely contaminants makes it imperative that a more precise method of evaluation be sought and found. Thus, if a sample is assumed to contain only uranium hydride and uranium dioxide, an analysis of $98.4 \pm 0.3\%$ uranium could have a uranium dioxide content as low as 0.43% , or as high as 6.09% . Since the maximum limit of impurities allowable by the A. E. C. is approximately 1% , it is evident that such an analysis is valueless in determining whether or not a given powder meets A. E. C. specifications. There is at present no analytical method available for analyzing uranium hydride powder per se with the required degree of accuracy. Methods involving further treatment not only are inadequately standardized, but also may be subject to changes in purity during the subsequent manipulation. A search for a more precise determination has, therefore, occupied the major portion of the past quarterly period, and while it cannot be said that a proven method has been found, progress on several promising methods has been made and is recounted in the following discussion. Thus, from necessity, the comparison of reductive processes to prepare uranium hydride has been temporarily subordinated to the development of a fully reliable evaluation method.

Since a more critical study of the effects of variables upon the reduction reactions cannot be made until a more reliable evaluation method has been found, such reductions as have been carried out were performed in order to obtain material for the purpose of studying, comparing, and correlating the various evaluation processes under consideration, rather than for evaluating the reductive processes themselves.

DISCUSSION OF RESULTS

Reductions

Nine additional reduction runs have been carried out during the last quarterly period. These have all been reductions of uranium dioxide with calcium hydride in an hydrogen atmosphere. A summary of these reductions is given in Table I, with all analytical data available at the time of writing.

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Methods of Evaluation of Reduction Product

Since further substantial progress on evaluation of preparative methods for uranium hydride and on evaluation of the variables for each individual method, is dependent on a means of product evaluation more precise than present methods of standard analyses, some time has been spent in a consideration of possible means of evaluation, and their probable precision and value in ascertaining whether or not the product meets A. E. C. specifications. Visits have been made to the A. E. C. New Brunswick Laboratory, New Brunswick, New Jersey, for discussions with Drs. Clement J. Rodden and Joseph J. Tregoning; and to the Argonne National Laboratory, Lemont, Illinois, for discussions with Drs. Joseph J. Katz and Henry R. Hoekstra; and to Massachusetts Institute of Technology, Cambridge, Massachusetts, for discussions with Mr. Edgar Read, concerning the problem. At this critical juncture the success of the program hinges upon finding a fully reliable, precise evaluation method. Because of the importance currently attached to this, opportunity is taken here to enumerate the various possible means of evaluation and to indicate the opinions of the Research Group and of the people with whom it has conferred, as to the probable value of the various evaluations as criteria for uranium hydride purity.

There can be but little doubt that the principal contaminant of uranium hydride powder is oxygen. Proper evaluation of the powder is then, primarily, a question of precise measurement of the oxygen content, either by direct or indirect means. The oxygen present may be a result of incomplete reduction, it may be introduced during the leaching operation, it may be a consequence of subsequent handling, or it may be a combination of any two or all three of these processes. It is hoped, therefore, that the method of oxygen determination developed can be applied at the various stages of the process, so that the actual source of oxygen contamination may be determined. Prior to this evaluation study there was no known method for determining oxygen directly on uranium hydride. The methods of analyses considered are discussed, with particular emphasis on their significance with regard to oxide content, in a subsequent section of this report.

Iron and nitrogen are other contaminants of some magnitude. While both of these are probably in excess of A. E. C. specifications in the products from a majority of the reduction runs, it has not been of undue concern, because the magnitude of the contamination is relatively small, and because fragmentary evidence seems to indicate relatively simple means of reducing the iron and nitrogen contents. Work has been initiated on this problem, but preliminary results are inconclusive.

The degassing data of Table I were compiled for the purpose of correlation with the nitrogen content of the final product, as

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TABLE I

Run	% Xs CaH ₂	Degassing Data	Time hrs.	% Yield	% X	% H	% (X+H)	% C	ppm N	ppm Fe	% O *
50 I-23	100	2 h. at 250° to 95 μ 3 h. at 250°	11	85.0	95.9	1.16	97.1	<0.1	1200	79	
51 I-24	100	15 h. at 250° to 69 μ 1.5 h. at 210°	11	75.7	96.6	1.10	97.7	0.05	870	120	
52 I-25	100	2.5 h. at 250° to 140 μ 4 h. at 200°	8	84.0		1.21	99.8 ⁺	0.07	600	71	0.21
53 I-26	10	5 h. at 250° to 190 μ 1.3 h. to 600°	11	69.0		1.02	99.3 ⁺	0.00	480	40	0.68
54 I-27	50	17 h. at 250° to 100 μ 6 h. at 270° to 800 μ 0.5 h. to 560°	11	94.5			99.3 ⁺		540	46	0.68
55 I-28	100	17 h. at 250° to 39 μ 3 h. at 180° to 500 μ 1.5 h. at 600°	11	85.0			99.2 ⁺		1000	26	0.77
56 I-29	100	20 h. at 250° to 37 μ 2.5 h. to 640°	11	87.5			99.6 ⁺		460	36	0.35
57 I-30	50	1.5 h. at 250° to 80 μ 1.5 h. at 160° to 800 μ 0.5 h. to 600°	11				99.8 ⁺				0.22
58 I-31#	25	17 h. at 250° to 46 μ 1.5 h. at 150° to 200 μ	2								

(See following page for footnotes.)

Footnotes to Table I:

- * Value calculated from an uranium assay by direct ceric sulfate method. Expressed as % 0 so that it may be compared with direct oxygen determinations by the bromine trifluoride and vacuum fusion methods when these are available.
- + Taken as difference between 100% and % 0. Included for purposes of comparison with previous runs.
- # Temperature control failed. Product colored green.

Methods of Evaluation of Reduction Product (Cont.)

it was believed that the nitrogen contamination arose in part from nitrogen which was adsorbed on the surface of the calcium hydride, which could be desorbed by thorough outgassing at an elevated temperature. Chemically combined nitrogen, of course, could not be eliminated in this way. The data are insufficient for unqualified conclusions, but indications are that degassing at elevated temperatures is only moderately effective in reducing the nitrogen content. In fact, the lowest nitrogen values, 460 and 480 ppm., were obtained in the two cases where the charge was heated rapidly up to the temperature where hydrogen was evolved. In five other cases where the temperature was held in the range 180-270°C for a considerable length of time (1-1/2 - 6 hours) while degassing, nitrogen values ranging from 540 to 1200 ppm were obtained, with a trend towards low nitrogen contents with increased degassing times. In view of the wide scattering of nitrogen values obtained in the past, it is not impossible that the coincidence between the degassing data and the nitrogen content is fortuitous. However, the data are regarded as indicating that degassing the charge does lower the nitrogen content of the final product, and that the limit to which the nitrogen content can be reduced in this way is determined by the amount of chemically combined nitrogen present in the stoichiometric charge.

Following is a summary of possible methods of evaluation, with a brief indication as to the present status of each method, and comments on what action is contemplated in the future.

1. Present Methods of Analysis

These have been described fully in the last Yearly Report (NYO-3795). The uranium, hydrogen, carbon, nitrogen, and iron analyses are the basis for the conclusions drawn and recommendations made thus far. The accuracy of the uranium analyses by the "nitrate" method is no better than $\pm 0.3\%$. Superficially, this does not appear to be too unsatisfactory; however, as al-

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ready pointed out, a sample analyzing 98.4% uranium could have an uranium dioxide content as low as 0.43%, or as high as 6.09% (calculations made assuming uranium hydride and uranium dioxide are the only constituents present in sample). As it is understood that in order for the uranium hydride powder to be acceptable for A. E. C. purposes, the uranium dioxide content should not exceed approximately 1%, it is obvious that such an analysis cannot be relied upon for final evaluation of the reduction product. Even if the accuracy of the analysis could be improved to $\pm 0.1\%$, which is believed to be approximately the limit of accuracy which could be achieved, an uranium assay of 98.6% would indicate an uranium dioxide content of from 0.43 to 2.32%. Thus, even at the limit of accuracy of the method, one could not obtain analyses suitable for determining whether or not the material meets A. E. C. specifications.

While it has been clear for some time that the uranium assays carried out by this method could not possibly determine the ultimate suitability of uranium hydride powder, it was necessary to continue the assays because they were the only method of evaluation available. Recently, however, an uranium assay method wherein the uranium hydride powder is dissolved directly in a measured excess of ceric sulfate and back titrated with ferrous sulfate has been developed to the point where it gives greater precision and reliability than the "nitrate" method. It has, accordingly, now been adopted as the standard uranium assay method.

2. Uranium Assay by Direct Solution in Ceric Sulfate

This method, which was first employed by Mr. Petretic, of the A. E. C. New Brunswick Laboratories, has been under study for some time by the Metal Hydrides research and analytical groups, and through their combined efforts has been developed sufficiently so that the precision and accuracy attained is now greater than that which was realized by the former uranium assay method. For a given sample of uranium hydride, the stoichiometry of the reaction in the new method is such that, for a given error in the titration value, it has a precision nearly five times as great as that of the old method. This is perhaps best illustrated by considering the error in oxygen content to be associated with an absolute error of one equivalent of ceric sulfate during the titration. In the "nitrate" method oxygen can only be estimated by difference, and therefore an absolute error of one equivalent of ceric sulfate indicates an error in oxygen content equal to the equivalent weight of uranium in going from the tetravalent to the hexavalent state, i.e., 119.04 grams. In the "direct" method, however, the difference between the maximum titer (which would be ob-

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tained if the sample were pure uranium hydride) and the actual titer is a measure of the uranium dioxide present. The uranium in the uranium dioxide is oxidized from +4 to +6 (a change of two valence units), while the uranium hydride may be considered to undergo a valence change equivalent to six units according to the equation:

Thus, one mole of uranium hydride requires four more equivalents of ceric sulfate than does a mole of uranium dioxide, and where uranium dioxide is a minor constituent only, we may consider that an absolute error of one equivalent will introduce an error of approximately one-fourth of the oxygen content of a mole of uranium dioxide, i.e., 8.00 grams. This is, approximately, only one-fifteenth of the error present in the "nitrate" method. Since, however, the error has been taken in terms of equivalents of titrant used, it is necessary to consider that, for a given sample weight, about three times as much ceric sulfate is required by the "direct" method as is required by the "nitrate" method, and if the error is considered to be in the titrant, the favorable precision ratio of the "direct" method is reduced by a factor of three, or from fifteen to five.

The results are expressed as "per cent oxygen", so that this method can be compared directly to the direct oxygen determinations by the bromine trifluoride or vacuum fusion methods as they become available. The per cent oxygen is calculated from the equation,

$$16.87 - \frac{0.6778 \text{ NV}}{\text{S}},$$

where N and V signify the normality and volume (in milliliters), respectively, of the ceric sulfate titrant, and S, the sample weight. This equation was derived from considerations similar to those mentioned in discussing the error of the method. Results obtained by this method are tabulated in Table I.

Before this can be regarded as a proven method, it is necessary to confirm the oxygen values by a direct method. The fact that the results are of the expected magnitude, based on the direct oxygen assays obtained by the bromine trifluoride method is encouraging. Determinations on uranium hydride prepared from SF₆ uranium metal have given values of 0.20, 0.08, 0.31, 0.22, 0.40, and 0.45 per cent oxygen. This averages 0.28 ± 0.11%, and is perhaps indicative of the precision at present. (A sample of this uranium hydride powder has just recently been hot-pressed to a density of 18.80 gms./cm.³.) By slight modifications of technique and equipment, it is hoped that the precision will be materially improved in the near future. The results to date are sufficiently encouraging to warrant continued application of the method.

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3. Density of Hot-Pressed Uranium

Until recently, the density of a hot-pressed pellet was regarded as about the only suitable criterion available for final evaluation of an uranium hydride powder. However, after conversations with other groups and a detailed consideration of probable errors, it appears ill-advised to rely solely upon a density determination for process evaluation purposes. Dr. Tregoning has reported that with a 50-gram wafer of massive SF uranium metal, the density could be experimentally determined with a reproducibility of ± 0.2 mole per cent of uranium dioxide. While this is not discouraging in itself, it must be realized that this variation is only in the density determination, and does not include any of the variables of the actual hot-pressing process.

If one takes the densities of uranium metal and uranium dioxide to be 19.05 and 10.97, respectively, and assumes that the density of the mixture is equal to the weighted average of the densities of these component parts, the contribution of each constituent being determined by the fraction of the total volume which it occupies, one finds that the density of a mixture composed of 99 mole per cent uranium metal and one mole per cent uranium dioxide is 18.89. Thus, material of this density might be assumed to barely meet the minimum requirements of the A. E. C., yet it compares not unfavorably with most densities reported from hot-pressing uranium or uranium hydride powders. (Dr. Kells of the New York A. E. C. Office has reported verbally that the Sylvania Bayside Laboratories have obtained densities as high as 18.94 gms./cm.³--which correspond to 99.3 mole per cent uranium metal.) A density obtained by a hot-pressing technique can, of course, only approach the theoretical density as a limit, but until some correlation is determined between the actual density and the theoretical density, with due consideration for oxide and other impurity contents, density determinations can have but little value as an analytical tool. Further work on the reproducibility of densities by hot-pressing a number of pellets from the same starting material must be done if the method is to be considered in evaluating the variables of the reduction process. The density of a hot-pressed pellet does serve to determine very nicely a maximum limit to which impurities may be present, and has the advantage over all other methods that it is also an evaluation of the suitability of the product for powder metallurgical applications, for which it is intended to be used.

Particularly because of the last-mentioned consideration, considerable time has been spent developing a small-scale hot-pressing technique; but results to date have not been encouraging due to the very small scale which was first tried. The original hot-press die unit has been described in detail in the last yearly report (NYO-3795). It was not possible to use Rexalloy or a weld deposit of Hayes Stellite for a die unit of this design because the difficulties in fabrication were such as to cause a prohibi-

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tive time delay. Accordingly, the die body, plunger, and bottom plate were made of Haldi #2 tool steel supplied by Hawkrige Bros. Co. of Boston, Massachusetts; but this material possessed insufficient structural strength at 600°C for satisfactory performance. Only two hot-pressed pellets were produced in this die unit, and neither gave a satisfactory density.

The initial test of the hot-press technique was made with a synthetic uranium hydride of high purity prepared by hydriding SF uranium metal at 225-275°C and cooling under hydrogen. A portion of this hydride (11.4 grams) was loaded into the die, which was placed in the vacuum jacket. The plunger was placed in the die so as to make direct contact with the ram contained in the bellows, and the thermocouple and heating unit were positioned and connected to their external leads. The entire unit was sealed, removed from the dry box, and evacuated. On this run the glass manifold was inadvertently broken during the heating, and the vacuum lost temporarily. After re-attainment of a vacuum, the temperature was raised to 600°C, and a pressure of 30 t.s.i. applied for one-half hour. The unit was then allowed to cool overnight under vacuum.

The die and plunger were removed and were found to have "frozen" together during use. The metal of the plunger had pressed out against the die wall under the duress of the operation. The numerous slow coolings on testing the equipment prior to the first pressing had caused soft annealing. An attempt to remove the pellet by applying pressure to the plunger caused the soft metal of that portion of the plunger which was not yet in the die to mushroom, and it was necessary to drill out the plunger in order to obtain the pellet. The pellet itself was not "frozen". The density of this pellet, determined by water displacement, was 18.6 gms./cm.³.

The second pellet was produced from uranium hydride powder obtained from Run #43, and having the following analysis:

U (by "nitrate" method)	98.1%
H	1.23%
C	0.00%
N	556 ppm
Fe	79 ppm

This material was hot-pressed in the same fashion, except that it was subjected to a pressure of only 20 t.s.i. for 25 minutes. It was hoped that these slightly less drastic conditions would be sufficient, and that the life of the die would be prolonged. However, the die and plunger were again "frozen", and it was necessary to drill out the plunger in order to obtain the pellet. The pellet was visibly nonhomogeneous, and had smooth-surfaced voids, where it did not conform to the shape of the die. The hot-pressing was obviously unsatisfactory, and the over-all density was only 16.6 gms./cm.³.

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Many of the difficulties encountered in the first experiences with the hot-pressing technique have been a consequence of limitations imposed on the design of the die unit by the stipulation that it was required to be manipulated and hot-pressed in the dry box. When it was found to be unnecessary to carry out the actual hot-pressing in the dry box, a new, improved die unit was designed. The parts are being fabricated from RexM-2, which is readily available, and hot-pressing operations will be resumed upon receipt of these parts. As yet, no local machine shop is able to fabricate the parts from Rexalloy, which must be cast and ground, rather than machined. Other machine shops are being consulted, as it is felt that an alternative material must be on hand in the event that Rex M-2 should prove to be unsatisfactory.

4. Analysis by Reduction with Zirconium

Mr. Edgar Read of the A. E. C. Metallurgical Project at Massachusetts Institute of Technology has suggested that it may be possible to determine the oxygen in uranium by reducing it with zirconium and then analyzing for zirconium oxide by the method which he has developed. This, of course, is contingent upon zirconium being a sufficiently good reducing agent to remove the oxygen quantitatively from uranium dioxide, which is highly problematical. If feasible, the determination would be made by mixing zirconium with a known oxygen content (preferably extremely low), with the uranium or uranium hydride to be analyzed. These would then be fused together by induction heating in vacuum in a carbon crucible, taking care not to maintain it above the melting point longer than necessary to cause solution of the two metals. The resulting uranium-zirconium alloy with zirconium oxide would then be analyzed for zirconium oxide by the method developed by Mr. Read. He believes that uranium itself would be untouched and that the unvolatized zirconium would remain behind as zirconium oxide and could be determined as such.

The thermodynamic values listed in Table II, taken from a compilation of thermodynamic properties ("Selected Values of Chemical Thermodynamic Properties", F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine, and I. Jaffe, Natl. Bur. Standards Circ. 500, U. S. Government Printing Office, Washington, 1950, p. 308, 358) and giving the heat, free energy and equilibrium constant of formation and entropy at 25°C, indicate the quantitative removal of oxygen from uranium by zirconium is far from certain. Of course at the elevated temperatures to which Mr. Read was referring, the possibility of complete removal cannot be ruled out. However, no attempt will be made to try to prove out this method since, at best, it would be difficult to perform without adding oxygen contamination during the determination.

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TABLE II

Formula	State	ΔH_f^0 kcal./mole	ΔF_f^0 kcal./mole	$\log_{10} K_f$	S^0 cal./deg. mole
ZrO ₂	c,III	-258.2	-244.4	179.14	12.03
UO ₂	c	-270	-257	188.4	18.6

5. Analysis by Ignition to U₃O₈

Dr. Rodden of the New Brunswick group has suggested that analysis of uranium hydride powder by ignition might give more meaningful results than a standard titration for uranium assay. Calculations show, however, that a difference in oxide content of 1% (by weight) causes a difference of only 12.6 milligrams of U₃O₈ on ignition of a 10-gram sample of uranium hydride powder. Hence the method cannot be regarded as particularly sensitive to oxide content. If direct oxygen determinations using bromine trifluoride are successful, the use of ignition analyses is not contemplated.

6. Direct Oxygen Determination by Vacuum Fusion

The A. E. C. New Brunswick Laboratory will be set up for a direct oxygen analysis on or about the first of October. They have agreed to make a small number of determinations on either hot-pressed uranium pellets or sintered uranium metal prepared from uranium hydride powder. This would serve to correlate the density of the hot-pressed pellet with the oxygen content, and also would be a check on the direct oxygen determination using bromine trifluoride as a reagent.

7. Direct Oxygen Determination by Bromine Trifluoride Method

After a conference at the Argonne National Laboratory with Drs. Katz and Hoekstra, it is believed the method of direct oxygen determination utilizing bromine trifluoride, which has been developed at Argonne, offers the most positive and convenient method for a routine oxygen analysis. A total of five determinations were made at Argonne; three on uranium hydride produced by the calcium hydride reduction of uranium dioxide, and two on uranium hydride produced from SF₆ uranium metal and hydrogen gas of highest purity. The latter two analyses gave values of 0.27 and 0.23 per cent oxygen, which represent primarily oxygen pick-up in handling for analysis. The analysis of uranium hydride powder from a reduction run gave values of 0.87, 0.63, and 0.98 per cent noncondensable gases calculated as oxygen. To obtain a true oxygen value, the experimental figure should be corrected

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for the nitrogen content (0.10 per cent for the sample used) and possibly there should be a correction for the carbon content, part of which may appear as CF_4 . The higher values for the uranium hydride prepared from the calcium hydride reduction of uranium dioxide as compared to that synthesized from the elements is, in part, a result of the more extensive handling and exposure to which the sample was subjected. Thus the reduction product, besides the exposure necessitated by the furnace tube unloading and leaching operations, was exposed for the purpose of taking the various analytical samples, and in preparing the sample for transporting to Argonne, as well as the exposure in the dry box at Argonne. The uranium hydride prepared from the elements, on the other hand, was prepared and sealed off in situ, and was never exposed prior to being handled in the dry box at Argonne.

While the oxygen values obtained for the uranium hydride powder prepared from SF_6 uranium metal and hydrogen represent oxygen pick-up in handling, it should be emphasized that no blank value is inherently necessary in the analysis. The oxygen pick-up in these particular samples can be readily attributed to two causes: (1) the dry-box atmosphere at the Argonne National Laboratory was tank nitrogen, which is inadequate for handling uranium hydride powder without contamination; and (2) being unfamiliar with the method, the samples were delivered to Argonne in such a form as to necessitate more exposure within the dry box than would otherwise be necessary.

An apparatus similar to that used at Argonne for the direct determination of oxygen utilizing bromine trifluoride as a reagent will be set up at Metal Hydrides. The glass portion of the line has been constructed, but procurement of the necessary nickel parts to construct that portion of the line which is in contact with the bromine trifluoride is slow.

Dry-Box Purification

A completely new dry-box purification train has been set up, similar to that used at the National Bureau of Standards. Activated alumina and hot copper wool are used for the removal of water and oxygen, respectively. The circulating pump has been entirely enclosed in a gas-tight, flanged steel cylinder. The system has given the best prolonged satisfactory service experienced to date.

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