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Summarizing Report
By Charles A. Kraus
Brown University
Providence, Rhode Island
June 1, 1943

Contract OEMsr-290,
Supplement 3
Contract OEMsr-688
Supplement 1

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SUMMARIZING REPORT OF INVESTIGATIONS RELATING TO
URANIUM COVERING THE PERIOD SEPTEMBER 1, 1942 to
APRIL 15, 1943

Work under contract OEMsr-290 and Supplement 1 was initiated about March 1, 1942 and continued into September, 1942. These investigations were concerned with the properties of solutions of uranyl salts. The results of these investigations have been fully presented in a report from Brown University under date of October 26, 1942.

The present investigation, which is concerned with the production of metallic uranium by reduction of uranium salts with metallic sodium, was initiated in September, 1942, under contract OEMsr-688 and was continued to April 15, 1943 under contract OEMsr-688 and its Supplement 1. Subsequent to October 1, 1942, the work on the two contracts, OEMsr-290 and OEMsr-688 and their supplements, was merged. The results of these investigations have been presented up to April 15, 1943. The present report is intended to summarize the results of these investigations in brief form.

In the production of metallic uranium by reduction with sodium, various halides of uranium may be employed, particularly the chlorides and fluorides. When the present investigation was initiated, some studies had been made elsewhere on the reduction of the fluoride by means of sodium as well as by means of other metals. However, no systematic investigation had been made of the reduction of chlorides by means of metallic sodium. Accordingly, the investigation was directed toward the production of chlorides and their reduction by means of sodium. Incidentally, the reduction of uranium tetrafluoride by means of sodium has likewise been investigated.

I. THE CHLORIDES OF URANIUM

Uranium forms four chlorides: UCl_6 , UCl_5 , UCl_4 and UCl_3 . Normally, either UCl_4 or UCl_5 is produced directly by the action of suitable chlorinating agents on oxides of uranium.

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either UO_2 or UO_3 . When UO_2 is employed, the product is necessarily UCl_4 while, when UO_3 is employed, UCl_5 is obtained under suitable conditions and, in some instances, UCl_6 .

Uranium Pentachloride, UCl_5 . The most convenient starting material for the preparation of the various chlorides of uranium is UCl_5 , which is best prepared by the reaction of liquid CCl_4 with UO_3 at temperatures ranging from 100° to 160° C. The temperatures employed are somewhat dependent upon the nature and state of the oxide. UO_3 prepared from the nitrate, when ground to proper particle size, may be reacted ~~with~~ carbon tetrachloride at 160° in one hour. UO_3 which has been prepared by calcining UO_4 at 350° , reacts with CCl_4 at 100°C in the course of approximately two hours. Conversion in either case is practically complete; the residual non-volatile material obtained on evaporating the product in a vacuum in the neighborhood of 600° may be reduced to as low as 0.02%.

In carrying out the reaction between UO_3 and CCl_4 , it is necessary to provide suitable controls since, under certain conditions, the temperature of the reaction mixture may increase rapidly as a result of the heat generated by the reaction. If reaction proceeds too rapidly, it may become uncontrollable. At the proper temperature, reaction may be controlled readily by evaporating a portion of the solvent.

Uranium Tetrachloride. While uranium tetrachloride may be prepared by passing carbon tetrachloride or sulfur monochloride over UO_2 or UO_3 at suitable higher temperatures, it is most readily prepared by the decomposition of UCl_5 at temperatures ranging from 250° to 500°C . Chlorine is evolved copiously at 250°C and the last traces of excess chlorine are quickly removed at the higher temperatures. In the dechlorination of UCl_5 by this means, such impurities as iron are removed to a large extent in the form of ferric chloride which is volatilized.

UCl_3 . UCl_3 is prepared by passing hydrogen over UCl_4 at a temperature of 575° until most of the tetrachloride has been converted to the trichloride. Thereafter, the material is heated as high as 640° , or higher, to convert the residual tetrachloride. Carried out at atmospheric pressure, this reaction requires about five hours but it has been shown that the reaction may be carried out under higher pressures of hydrogen and that the rate of reduction is approximately proportional to the pressure of hydrogen. At a pressure of 100 lbs., with the temperature initially at 575° , the reaction may be completed in the course of about one hour.

UCl_6 . UCl_6 is related to UCl_5 by the following reactions:

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Reaction (a). When UCl_5 is heated in a high vacuum, UCl_6 may be condensed and UCl_4 remains behind. When UCl_6 passes over UCl_4 at higher temperatures, UCl_5 results. At higher temperatures, UCl_5 also decomposes with the formation of UCl_4 and chlorine, thus:

The production of UCl_6 from UCl_5 by vacuum distillation at temperatures between 100° and 200° is practicable and is now being used at the Radiation Laboratory with a fair degree of success. The theoretical yield is, of course, 50% and the residual UCl_4 must be reconverted to UCl_5 in order to produce further UCl_6 .

This reaction is one which has been developed at the Radiation Laboratory and is mentioned here for the sake of completeness in connection with the UCl_6 problem which will be discussed from the standpoint of reaction (b) in the next paragraph.

Reaction (b). Observations made in connection with various preparations of UCl_5 indicated the presence of small quantities of UCl_6 . In the case of one reaction carried out over a 72-hour period, at 78°C , as much as 15% of UCl_6 was present in the product. Studies carried out since April 15th, which may be briefly summarized here, have shown clearly that reaction (b) is reversible and that UCl_5 may be converted to UCl_6 by heating it in CCl_4 to which has been added a considerable amount of chlorine. In one experiment, for example, 80%, or more, of the pentachloride was converted to the hexachloride by heating for six hours at 100° in a mixture containing approximately 20% chlorine and 80% CCl_4 . It has been shown that the reaction takes place in the homogeneous phase. On the basis of this experiment, it has been found that at 100°C , UCl_6 is produced from UCl_5 at the rate of 15 grams per 1000 g. of CCl_4 per hour. This is for a solvent containing 18% of chlorine. Further study of this reaction may provide a means of producing UCl_6 from UCl_5 in 100% yields at temperatures in the neighborhood of 100°C .

II. PRODUCTION OF METALLIC URANIUM BY REDUCTION WITH SODIUM

The reduction problems fall into two main groups, namely: (1) the provision of a suitable crucible material in which the reaction may be carried out and the metal melted after reduction, and (2) the production of a salt which will react with sodium as nearly quantitatively as possible.

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Method of Carrying out the Reduction Reaction. In carrying out a reaction in which large quantities of uranium are reduced, 50 to 100 pounds, for example, the heat of reaction, once it is initiated, is sufficient to carry the reaction to completion and to raise the temperature of the reaction mass to a point sufficiently high to permit the fine particles of reduced metal to coalesce and form either droplets or a large mass of metal. In such cases, external heat is required only to the extent of initiating the reaction. When, however, it becomes necessary to carry out a reduction with small quantities of material, then, although the heat of the reaction may carry the reaction mass to a temperature above the melting point of uranium, the mass cools so rapidly that the particles do not have time to coalesce properly. If the particles do not so coalesce, the material obtained is pyrophoric. Accordingly, if the metal is to be obtained in massive form with small quantities of uranium salt, it is necessary to heat the mass externally to a temperature sufficiently high to permit the particles of metal to coalesce and to form either droplets or a larger homogeneous mass of metal.

In the investigations carried out thus far, the charges have run from 150 to 1000 g. of uranium salt. The crucible in which the reaction was to be carried out was placed in a No. 309 or No. 310 stainless steel tube which was, in turn, placed in a rhodium-platinum wound alundum furnace and the temperature carried to from 1225° to 1250°C. The air was carefully removed from the reaction tube and an atmosphere of helium was introduced.

Crucible Materials. The possibility of using crucibles made of beryllium oxide or zirconium oxide was investigated. Neither material was found satisfactory. Both materials are somewhat fragile, are highly absorbent and they cannot be reheated after initial use. Moreover, they are relatively expensive.

It was found that rather satisfactory crucibles could be produced by lining an iron or stainless steel tube with magnesium oxide. Fused magnesium oxide which had been ground to approximately 200 mesh is moistened with approximately 10% by weight of water and this moistened material is pressed into an iron shell by means of a properly shaped mandrel. After forming the lining in the iron or stainless steel shell, it is dried by heating slowly to 600°C and thereafter to about 1200° to sinter the magnesium oxide coating. The magnesium oxide contains a small amount of silica which serves as binding agent.

After sintering, the lining is reasonably strong and the uranium compounds and sodium may be introduced into the crucible and reaction and fusion carried out without injury to the lining. The crucibles may be used several times, and, perhaps oftener, without difficulty.

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The magnesium oxide lining is porous and, once reaction occurs, the salt resulting from the reaction is, in large measure, absorbed in the lining. Unless the reaction mixture reaches a sufficiently high temperature to cause the particles of metal to coalesce, the finer particles are absorbed into the magnesium oxide lining along with the salt. When larger quantities of uranium salt are employed, from 500 to 1000 g., the heat generated is sufficient to cause the greater portion of the uranium particles to coalesce into droplets sufficiently large so that they do not enter the pores of the liner. Thus, in one reaction with 750 g. of UCl_3 in which the furnace temperature reached a maximum value of only $1000^{\circ}C$, the yield of usable metal was 77%. The melting point of uranium is a little below $1100^{\circ}C$. In working with small quantities of material, however, the temperature is not sufficiently high to effect the agglomeration of the metal and, consequently, much of the metal is lost into the liner. It has been found that the difficulty may be overcome, in a large measure, by introducing a melted salt, such as sodium chloride, prior to carrying out the reaction; in this way, the pores of the magnesium oxide liner are filled with salt and the particles of metal are not lost.

Reduction of UF_4 . While UF_4 has been reduced by means of metallic sodium with fair yields, the results, on the whole, are less favorable than are those with UCl_3 . For example, in one reaction, 600 g. of UF_4 were reduced with an equivalent amount of sodium. The yield obtained was 86.6%, 95% of which was in one piece. In another reaction, 830 g. of UF_4 were reacted with an equivalent amount of sodium; the yield obtained was 79%, of which 62% was in one piece. In both cases, when reaction was completed, considerable sodium remained unreacted, and a considerable amount of UF_4 remained behind. The solid lumps of metal contained intrusions of sodium fluoride which were not readily removable because of the solubility of NaF in water.

The incompleteness of the reduction of UF_4 is doubtless due to the fact that the sodium does not disperse itself uniformly throughout the mass of crystals. The reason for this probably is that sodium does not properly wet the surface of the UF_4 crystals.

Reduction of UCl_4 . Uranium tetrachloride does not lend itself to reduction with metallic sodium, partly because of its low melting point and high volatility and partly because sodium does not properly wet the surface of the UCl_4 crystals. Reactions with UCl_4 are initiated in the neighborhood of 500° and are quite violent. Reaction, however, is not complete and much unreacted sodium remains on completion of the reduction process. In two such reactions, using 400 g. of UCl_4 , the yields obtained were 69.5% and 48.8%, respectively, with, respectively, 57% and 83% of the recovered metal in the form of a solid mass.

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Reduction of UCl_3 . Uranium trichloride has yielded much the best results on reduction with sodium. Using 1000 g. of UCl_3 , the yield of recovered metal was 91.5% and 94.1% in two reactions. In the first case, 96% of the metal was in one lump and 70% in the second. All the recovered metal not in one lump was in the form of droplets which were not pyrophoric. In one case, using 750 g. of UCl_3 , a yield of 98.5% was obtained, of which 89% was in one lump.

Using only 150 g. of UCl_3 , yields of usable metal have been obtained that range, in general, between 78% and 85%. In one case, for example, the yield was 85.5% of usable metal, 89% of which was in one lump. In another case, the yield was 78% of usable metal, with 92.5% in one lump.

The problem of reducing small charges of uranium trichloride effectively resolves itself into that of producing a suitable lining material for the crucibles in which the reaction is carried out and the metal is subsequently melted and agglomerated. This study is taking the direction of filling the magnesium oxide liner with resistant salts such as sodium, magnesium, calcium or barium fluorides. It is reasonable to assume that yields of 80%, or more, of usable metal may be obtained. The remaining metal, of course, is not lost; it may be recovered but it must be put through a recovery process. It is believed, however, that with improved crucible liners and by operating at higher temperatures, which may be readily done, it will be possible to raise the yields considerably above the present values.

While uranium trichloride would seem to offer the best solution of the problem of producing metal in smaller quantities, it seems not unlikely that the method which has been employed in the case of small charges may also be advantageously employed in the case of larger charges. Using charges of 750 g. and heating the crucible only to a point where reaction is initiated, metal was obtained in rather good yields, but little of it had coalesced into a large, coherent mass. The temperature had, obviously, been carried well above the melting point of uranium by the heat of the reaction but with the small amount of material employed, radiation losses were so high that the particles solidified before they were properly agglomerated. If larger charges were employed, radiation losses would be greatly diminished and one might reasonably expect that the metal would be obtained in massive form.

The technique employed in the case of the smaller charges could readily be employed in that of large charges. An iron tube could be lined with magnesium oxide and this tube, in turn, could be placed in a stainless steel cylinder having a removable closure at the top. Such a cylinder could be evacuated and filled with helium and the lower portion could then be introduced into a suitable furnace and heated with gas to a temperature at which reaction was initiated. Once

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reaction was initiated, the temperature would rise well above the melting point of uranium and would be maintained there for a sufficient length of time to permit the particles of metal to coalesce. With this arrangement, no oxidation of the crucible itself would occur, while the outer, stainless steel tube would never reach a temperature sufficiently high for oxidation to become a serious problem.

III. SOME OTHER RESULTS GROWING OUT OF THIS INVESTIGATION

While these investigations were, in the main, directed toward the problem of producing metallic uranium by reduction with sodium, there have been a number of by-products which have been useful to other groups interested in uranium.

Samples of metallic uranium have been supplied to Dr. Rosen and to Dr. Howe, of the Metallurgical Laboratory.

Ten pounds of UCl_4 were supplied to the Westinghouse Company for an examination of its possible use in the production of metal by electrolysis. Samples of UCl_4 were also supplied to Dr. Gilman, Dr. Smyth, of Princeton, and Dr. Rosen. Samples of UCl_3 , UCl_4 and UCl_5 have been supplied to the Eastman Company and ninety pounds of UCl_5 have been supplied to the Radiation Laboratory for their use in the production of UCl_6 .

Recently, a reactor has been constructed, capable of producing approximately 4 kg. of UCl_5 per operation and this reactor has been shipped to the Radiation Laboratory for their use in the production of UCl_5 from which to produce UCl_6 . Mr. George C. DeCroes, who has been associated with the development of the process of producing UCl_5 , has been sent to California, for the time being, to put the reactor into service. On June 21st, he joins the Eastman Company in connection with their development for the production of UCl_4 and UCl_5 .

One other contribution of this laboratory may be mentioned. It has provided training for something like fifteen men in the chemistry of uranium. Several of these men are now in the industry in connection with uranium projects. Whatever may be the outcome of the investigations in which this laboratory has been immediately engaged, there can be no question but that, should the uranium problem develop along any one of several lines, men will be needed who are familiar with the chemistry of uranium. Such men will, ultimately, have to be drawn from those laboratories that have, up to now, been engaged in the study of this element.