

NJ. 18

N-100

STANDARD OIL DEVELOPMENT COMPANY

LINDEN, NEW JERSEY

RESEARCH AND DEVELOPMENT DEPARTMENT

NI. 18-3

E. V. MURPHREE
VICE PRESIDENT

26 BROADWAY, NEW YORK

December 23, 1942

2170



Dr. Norman Hilberry
Metallurgical Laboratory
University of Chicago
Chicago, Illinois

Dear Dr. Hilberry:

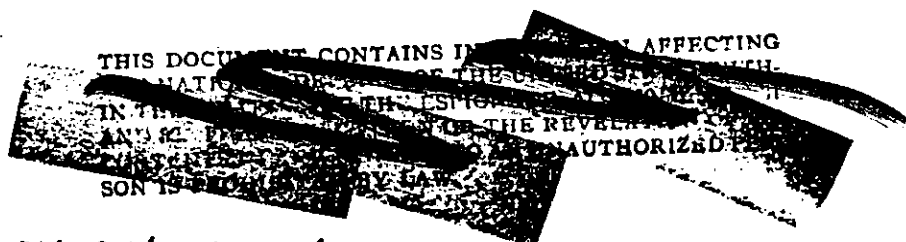
In accordance with the arrangements made with Dr. Compton, I am attaching hereto Copy No. 13 of Dr. Kraus' Progress Report dated December 15, 1942.

This report contains additional information on the preparation of metallic uranium by the reduction of UCl_3 with sodium.

Very truly yours,

RAPHAEL ROSEN

RR:GT
Attachment



With Attachment
CONFIRMED TO BE UNCLASSIFIED
DOE/OFFICE OF DECLASSIFICATION
HERBERT SCHMIDT A.D.D. DATE:
HS Schmidt, 6/10/02

DOES NOT CONTAIN
UNCLASSIFIED CONTROLLED
NUCLEAR INFORMATION

IN THE ATOMIC ENERGY ACT OF 1954
OR DISCLOSURE OF ITS CONTENTS
UNAUTHORIZED PERSON IS PROHIBITED

This document consists of
9 pages: 0 figures.,
copies 1 to 19, inc.,
Series A.

Progress Report
By Charles A. Kraus
December 15, 1942

Contract No. OEMsr-290,
Supplement 2
Contract No. OEMsr-688.

A. Preparation of UCl_5 from UO_3 and CCl_4 .

The study of the various factors which may influence the rate of reaction between UO_3 and CCl_4 has been continued and is still in progress. The procedure for carrying out the reaction, to cite a specific example, has been to allow 200 grams of UO_3 to react with a large excess of CCl_4 in a stainless steel autoclave, heated in an oil bath. When the internal temperature reaches approximately $100^\circ C$, reaction sets in and is characterized by a rapid temperature rise of 30 to 40 degrees. At the end of 10 to 15 minutes, the temperature begins to fall, indicating that the rate of conversion has slowed up considerably. The bath temperature is now elevated and the mixture continues to react until conversion is substantially complete. The end of the reaction is signaled by a leveling off of the pressure to a constant value (at constant temperature), since there is no further production of $COCl_2$. After most of the $COCl_2$ has been allowed to exhaust, the remaining $COCl_2$ and CCl_4 are distilled, and, finally, the residual volatile materials are removed under vacuum. When the products of the reaction are examined, they are frequently found to consist of two fractions; a top layer of dark red, coarsely crystalline material which has obviously been deposited from

CONFIRMED TO BE UNCLASSIFIED
DOE/OFFICE OF DECLASSIFICATION
HERBERT SCHMIDT A.D.D. DATE:

HR Schmidt 6/10/02

DOES NOT CONTAIN
UNCLASSIFIED CONTROLLED
NUCLEAR INFORMATION

solution in the excess CCl_4 , and a bottom layer which is a hard, brown cake. The two layers often differ widely in composition; the crystalline material is usually nearly pure UCl_5 , while the caked bottom layer frequently contains UOCl_2 in addition to UCl_4 and UCl_5 . Both fractions are ordinarily completely soluble in water.

In order to determine the extent of conversion to UCl_4 and UCl_5 , samples of the products have been distilled in a stream of purified N_2 at 5 mm. pressure, with the temperature reaching a final value of approximately 700°C . This process requires about 30 minutes from the time the heating furnace is turned on. If the product contains residual oxide or oxychlorides, a dark brown residue of UO_2 remains in the boat. When conversion has been substantially complete, the residue is less than 0.1%.

1. Influence of Excess CCl_4 on the Rate of Conversion. As has been pointed out in earlier progress reports, when the reaction is first initiated, it proceeds very rapidly. There is a possibility that it would continue to progress rapidly if the reactants remained continuously in contact with each other, but as the products accumulate and the CCl_4 layer becomes saturated with UCl_5 , the remaining oxide becomes coated with products of reaction and as a result, further reaction is very seriously inhibited. This view is supported by the improvement obtained in the conversion when the amount of excess CCl_4 is increased to large values, as summarized in Table I. The results of four experiments are given in which the amount

Progress Report
December 15, 1942

of excess CCl_4 varied from 100% to 300%. This does not change the temperature at which reaction sets in nor the time, t_1 , for the completion of the initial rapid phase but use of larger amounts of CCl_4 shortens the time, t_2 , required for completion of the conversion and reduces the maximum temperature which is reached in the initial phase. The amount of crystalline product is likewise increased and the quality of the material found in the bottom layer is improved. The maximum pressure reached is also reduced, due to the solubility of COCl_2 in CCl_4 . It may be concluded that the preparation of UCl_5 (and UCl_4) is facilitated by the use of CCl_4 in large excess.

TABLE I

Influence of Excess CCl_4 on the Rate of Chlorination of UO_3

Exp. No.	Materials Used			Initial Reaction Temp.	t_1^* Min.	Temp. of Maximum	t_2^{**} hrs.	Final Temp. °C
	UO_3 g.	UCl_5 g.	CCl_4 % excess					
89	200	30	100	103	10	159	2.5	154
90	200	30	200	105	17	145	1.3	164
91	330	30	200	104	16	143	2.0	165
92	250	20	300	104	13	128	1.0	160

* t_1 = time of initial reaction phase

** t_2 = time from end of initial reaction phase until reaction appears to be complete

Analysis of Products

Exp. No.	% Product		Ratio Cl/U		Non-volatile residue, %	
	Top	Bottom	Top	Bottom	Top	Bottom
89	50	50	4.78	4.86	0.3	26.1
90	52	48	4.91	4.78	0.1	12.3
91	48	52	4.95	4.51	0.1	1.5
92	61	39	4.96	4.93	0.1	0.6

Progress Report
December 15, 1942

2. Effect of the State of Subdivision of UO_3 . It was observed in earlier experiments that when U_3O_8 was not ground to a fine powder, but was used in the lumpy condition in which it was produced by decomposition of UO_4 , the rate of conversion to UCl_5 and the extent of the reaction were unsatisfactory. On the other hand, with finely ground U_3O_8 , a satisfactory rate of the conversion to UCl_5 was obtained. UO_3 is more reactive than U_3O_8 , and it was of interest to test the effect of its state of subdivision upon the rate of reaction and, particularly, to learn whether the rapid initial phase of the reaction could be eliminated by use of coarser UO_3 . In one experiment, the UO_3 was sifted to remove the fines; the oxide used passed a 20 mesh but was retained by a 60 mesh sieve. In Table II, the results are compared with those obtained with ground and unground UO_3 . It will be noted that there were no significant differences.

TABLE II

Exp. No.	Materials used			Initial Temp. °C	t_1^* Min.	Max. Temp. °C	t_2^* Min.	Final Temp. °C	Cl/U Ratio	Non-volatile oxide %
	UO_3 g.	UCl_5 g.	CCl_4 % excess							
80 Not ground	200	15	75	96	37	137	100	128	4.91	--
79 Ground	200	15	75	102	25	147	120	118	3.91	--
88 Fines removed	200	30	75	101	10	164	120	148	4.71	0.32

*The symbols t_1 and t_2 have the same significance as in Table I.

Progress Report
December 15, 1942

3. Effect of Addition of CCl_4 in Small Increments. In an attempt to control the initial rapid reaction between UO_3 and CCl_4 , the CCl_4 was injected by means of a pump in increments of approximately 25 cc. After the oxide and UCl_5 (catalyst) had been placed in the autoclave, the lid was clamped on and 40 cc. of CCl_4 were introduced, and the temperature of the external oil-bath was raised slowly. Reaction set in at approximately the same temperature as usual, but the temperature rise was very much greater. In one experiment, the internal temperature reached 305°C in 10 minutes. When the mixture had cooled somewhat, additional CCl_4 was introduced, but the rate of the subsequent reaction was slow. Reaction was not complete; analysis of the product showed that it contained unconverted oxides or oxychlorides. The injection method of controlling the reaction fails because there is no excess CCl_4 for removing the heat generated in the reaction as it proceeds.

4. Effect of Prolonged Preheating of the UO_3 - CCl_4 Mixture at its Boiling Point. The rapid initial phase of the reaction is moderated by prolonged refluxing of the UO_3 - CCl_4 mixture at atmospheric pressure. In Table III, the results of two experiments, No. 96 and No. 97, are summarized. Experiment No. 83 has also been included for comparison but, in this case, the mixture was heated for five hours in a sealed autoclave, where it presumably did not boil. In Experiments Nos. 96 and 97, the reactor was provided with a reflux condenser and the carbonyl chloride was allowed to escape at atmospheric pressure. Boiling for 6 hours with 100% excess CCl_4 (No. 96) had little effect on

Progress Report
December 15, 1942

the course of the reaction, although the amount of caking was unusually small, and the product was chiefly UCl_4 . Boiling for 12 hours with 150% excess CCl_4 (No.97), had the effect of practically eliminating the rapid phase of the reaction; no sharp increase in temperature was observed. The product was nearly pure UCl_5 . When a sample was distilled, less than 0.2% non-volatile oxide remained in the container.

TABLE III

Effect of Preheating the UO_3 - CCl_4 Mixture

Exp. No.	Materials Used			Time of Reflux hrs.	Initial Reaction Temp. °C.	Max. Temp. °C.	Final Temp. °C.
	UO_3 g.	UCl_5 g.	CCl_4 %excess				
83	200	30	75	5	109	120	135
96	200	30	100	6	101	170	158
97	200	30	150	12	94	96	158

Analysis of Products

Exp. No.	Cl/U Ratio	Non-volatile Residue %
83	4.917	--
96	4.323	0.52
97 Top layer	4.975	--
Bottom layer	4.960	0.2

B. Reaction of UO_3 and CCl_4 at the Boiling Point.

To ascertain the nature of the products of the low temperature reaction between UO_3 and CCl_4 , several 50-gram lots of UO_3 were refluxed in glass vessels with 75%, or greater, excess of CCl_4 at atmospheric pressure for periods varying from 6 to 72 hours. The results are tabulated in Table IV in the order of increasing time of reflux. In cases where the time of reflux was the same, the data are arranged

according to increasing amounts of UCl_5 added to the reaction mixtures. The ratios Cl/U , which are given in column 5, have been corrected for the UCl_5 added originally. The percentage of material which did not volatilize when the products were heated in a stream of nitrogen at 5 mm. pressure, are given in column 7. They have also been corrected for the amount of UCl_5 added to the reaction mixture.

From the appearance of the product, its behavior in solution and its analysis after 6 hours of reflux, more than 50% of the UO_3 was converted to UO_2Cl_2 . With longer boiling, the Cl/U ratio increased steadily and after 72 hours, nearly all the UO_3 had been converted to UCl_5 . The content of non-volatile material in this product was reduced to 1.64%.

TABLE IV.

Results of Refluxing 50 grams UO_3 with Excess CCl_4

Exp. No.	Hours of Reflux	% excess CCl_4	Grams UCl_5	Cl/U Ratio	% In-soluble Residue	% Non-volatile Residue
4	6	75	7.5	1.26	5.4	--
7	6	75	20.0	2.02	0.25	--
3	12	75	7.5	2.82	0.52	--
2	18	75	7.5	3.0	0.17	--
10	24	75	0.0	4.21	0.2	--
1	24	75	7.5	3.94	0.12	32.0
8	24	100	30.0	3.88	0.28	20.1
9	24	100	60.0	4.24	0.37	15.4
6	72	75	7.5	4.80	0.2	1.6

C. Solubility of UCl_5 in CCl_4 .

The only mention of the solubility of UCl_5 in CCl_4 in Gmelin is the qualitative statement that it is "somewhat soluble". Solubilities were determined at 25° and 70°C and

Progress Report
December 15, 1942

estimated at 160°C from the weight of crystals precipitated from reactions carried out at 160°C. The results are as follows:

Temperature	25°C	70°C	160°C
Solubility g. UCl ₅ /100 g. CCl ₄	1.04	5.3	20

The value given for 160° is a very rough one, since the precise weight of CCl₄ liquid could not be determined and an unknown quantity of COCl₂ was dissolved in the CCl₄.

D. Preparation of Metallic Uranium by Reduction of UCl₃ with Sodium.

Additional experiments have been carried out in the study of the reduction of UCl₃ by means of sodium. The reduction is accomplished without difficulty and if the temperature is maintained above 1100°C sufficiently long, the fused particles of the metal agglomerate into a regulus. At present, the chief problem is the development of suitable containers in which to carry out the reduction.

Crucibles of zirconium oxide are fairly satisfactory, but expensive. It is not possible to use them more than two or three times, since they are porous to fused sodium chloride and they begin to disintegrate on long use. A zircon crucible was found to be wholly unsatisfactory.

A steel tube, lined with partially sintered magnesium oxide, gave satisfactory results. Such containers are easy to construct and can be re-used. Reaction containers of this type are being studied further.

As may be seen from Table V, the yield in later experiments

