RI.01-1 3693 RI.1

MEMORANDUM

TO: FILE

DATE 9/23/87

FROM: C. YOUNG

SUBJECT:

SITE NAME: Metcalf Research Laboratory Brown University

ALTERNATE NAME: —

CITY: Providence STATE: RI

OWNER(S)
Past: Brown University Current: Brown University
Owner contacted ☐ yes ☒ no; if yes, date contacted _____

TYPE OF OPERATION

☒ Research & Development
- ☐ Production scale testing
- ☐ Pilot Scale
- ☒ Bench Scale Process
- ☒ Theoretical Studies
- ☒ Sample & Analysis

☒ Facility Type
- ☐ Manufacturing
- ☒ University
- ☒ Research Organization
- ☐ Government Sponsored Facility
- ☐ Other _____

☐ Production
☐ Disposal/Storage

TYPE OF CONTRACT

☒ Prime
☒ Subcontractor
☐ Purchase Order

☐ Other information (i.e., cost + fixed fee, unit price, time & material, etc) _____

Contract/~~Purchase Order~~ # OEMsr-290, OEMsr-688 } Office of Scientific Research & Development; W-7405-eng 73 - Manhattan Engineer District

CONTRACTING PERIOD: 1942 through 1944 and possibly later.

OWNERSHIP:

	AEC/MED OWNED	AEC/MED LEASED	GOVT OWNED	GOVT LEASED	CONTRACTOR OWNED	CONTRACTOR LEASED
LANDS	☐	☐	☐	☐	☒	☐
BUILDINGS	☐	☐	☐	☐	☒	☐
EQUIPMENT	☐	☐	☐	☐	☒	☐
ORE OR RAW MATL	☐	☐	☒	☐	☒	☐
FINAL PRODUCT	☐	☐	☒	☐	☒	☐
WASTE & RESIDUE	☐	☐	☐	☐	☐	☐

Ownership of raw materials and finished product is not completely clear, particularly during the early 1940's before controls were placed on Uranium and Thorium feed material.

AEC/MED INVOLVEMENT AT SITE

Control
- ☐ AEC/MED managed operations
- ☐ AEC/MED responsible for accountability
- ☐ AEC/MED overviewed operations
- ☒ Contractor had total control
- ☒ unknown

☐ Health Physics Protection
- ☐ Little or None
- ☐ AEC/MED responsibility
- ☒ Contractor responsibility

MATERIALS HANDLED:

Type (on basis of records reviewed)

- ☐ No Radioactive
- ☒ Natural Radioactive from Feed Materials Production
  - ☐ Ore
  - ☒ Refined Source Material
  - ☐ Residue
- ☐ Natural Radioactive Material from Non-Nuclear Activities
- ☐ Man-Made
- ☐ Other _____

Comment _____

Quantities (on the basis of records reviewed)

- ☐ None
- ☐ Production Quantities
- ☒ Small Amounts

Comment Available records suggest Kilogram or pound quantities

OTHER PERTINENT FACTS:

☐ Facility was Licensed

- ☐ During AEC/MED-Related Operations
- ☒ For Similar Activities
- ☐ For Other Activities

Comment Documents on hand indicate that the University was licensed during the period 1973 - 1984

☒ Commercial Production Involving Radioactive Material during AEC/MED Operations

☐ Facility was Decontaminated and Released

☐ Availability of Close Out Records

☒ None ☐ Some ☐ Sufficient

☒ Radioactive Status:

	YES	MAYBE	PROBABLY NOT	NOT
Contaminated	___	___	X	___
Potential for Exposure (accessible)	___	___	X	___

QUANTITY OF RECORDS AVAILABLE:

☐ Very Little ☒ Some ☐ Sufficient

PROBABILITY OF FINDING ADDITIONAL RECORDS:

☒ Low ☐ Possible ☐ High

RECOMMENDATIONS:

☒ Eliminate
☐ Consider for Remedial Action
☐ Collect More Data

Comment

REFERENCES: See attached document listing.

SUMMARY (Metallurgy Laboratory under the direction of C.A. Kraus) Brown University was under contract with OSRD apparently some time before MED was organized and was performing research in the preparation of pure halides of heavy metals. Although there were a large number of shipments of Uranium and Thorium compounds to and from the University, most were in pound or Kilogram quantities. It is also evident that the Laboratory did work for industry. The recommendation for elimination is based primarily on three factors

1) Small quantities of radioactive material were used under the supervision of experts in the field for both Government and Commercial customers.
2) There is no indication in available documentation that would give rise to concern regarding residual contamination.
3) University Officials (Dr. Kraus) apparently exercised total control over laboratory operations. Contract documents have not been found. Therefore there is some question regarding the authority to conduct remedial action, if such should be required.

HISTORICAL LISTING

FILE #	DATE	FROM	TO	SUBJECT	SITES
IL.6	07/12/43	DOAN, R.,	RUHOFF, J.,	REQUEST FOR MATERIAL FROM AMES AND BROWN TO MET LAB	AMES, BROWN UNIVERSITY
3.1MG A	01/14/46	KELLEY, W.,COE	NICHOLS, K.,	SPECIAL SHIPMENTS OF X-CONTAINING MATERIALS	MULTIPLE, MCW, HARSHAW, LINDE, DUPONT, MIDDLESEX, ELECTROMET, BROWN UNIVERSITY, IOWA STATE, CALEXICO ENGINEER WORKS
RI.1	05/23/44	CHAPMAN, T.,CHO ✓	KRAUS, C.,	USE OF CODE SYMBOLS "T" AND "R" BY BROWN	BROWN UNIVERSITY
RI.1	07/30/43	RUSSELL, C.,COE ✓	HUNTER, J.,	SHIPMENT OF TEGRACHLORIDE TO KODAK FROM BROWN UNIVERSITY	BROWN UNIVERSITY, EASTMAN KODAK ROCHESTER
RI.1	09/08/43	CHIPMAN, J.,ML ✓	COMPTON, A.,	METALLURGICAL RESEARCH AT BROWN UNIVERSITY	BROWN UNIVERSITY
RI.1	10/13/43	CHIPMAN, J.,ML ✓	KRAUS, C.,	PREPARATION OF A NUMBER OF HALIDES	BROWN UNIVERSITY
RI.1	12/06/43	HUGHES, D.,ML ✓	PETERSON, A.,	SAMPLES FROM BROWN UNIVERSITY	BROWN UNIVERSITY
RI.1	01/12/44	CHIPMAN, J.,ML ✓	HILBERRY, N.,	PROGRAM FOR BROWN UNIVERSITY LAB UNDER DIRECTION OF C. KRAUS - DEVELOPMENT OF METHODS FOR PRUDUCTION OF PURE URANIUM AND PLUTONIUM METAL	BROWN UNIVERSITY
RI.1	12/01/42	KRAUS, C.,BROWN UNIV ✓	PROGRESS REPORT,	PROGRESS REPORT FOR DECEMBER 1, 1942	BROWN UNIVERSITY
RI.1	12/23/42	ROSEN, R.,STANDARD ✓	HILBERRY, N.,	PROGRESS REPORT BY DR. KRAUS DATED DECEMBER 15, 1942	BROWN UNIVERSITY, STANDARD OIL DEVELOPMENT CO
RI.1	~~08/18/44~~	~~BELCHER, P.,CIC~~	~~OFFICER IN CHARGE,~~	~~LOSS OF "S" SALTS IN SHIPMENT ORIGINATING AT BROWN~~ UNIVERSITY ON 30 JUNE 1944.	~~BROWN UNIVERSITY~~

Document could not be located

RJ 1 CC-402 1A

[redacted] document contains [redacted] the national [redacted] United States [redacted] of the Espio[redacted] C. 50; 31 and 32. [redacted] or the reve[redacted] contents in any ma[redacted] unauthorized pers[redacted] by law.

[redacted]
ARGONNE RECORD COP
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CLASSIFICATION CHANGED
TO: NOT CLASSIFIED
List #7/725

PROGRESS REPORT FOR DECEMBER 1, 1942

Brown University-Charles A. Kraus

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Preparation of Metallic Uranium in Massive Form.

Metallic uranium in massive form has been prepared by reacting sodium with UCl_4 and UCl_3, respectively. Up to the present, the work has been handicapped by lack of suitable resistant refractory crucibles in which to carry out the reduction. Recently, a few small zirconium oxide crucibles were received and, pending the shipment of larger crucibles, two experimental reductions have been carried out. The crucibles were charged with about 45 grams of UCl_4 or UCl_3, placed in alternate layers with an equivalent amount of sodium, and heated in an atmosphere of helium. The highest temperature reached in each instance was 1125°C and the crucibles were above 1100°C for 35 minutes. With UCl_4, reaction set in at 407° and with UCl_3, at 640°. Considerable heat was evolved in both cases, the heat effect appearing to be somewhat greater in the case of UCl_4.

The product of the UCl_3 reduction was washed out with water and filtered. Pellets of metallic uranium, some as large as buckshot, were found, showing that the temperature had been raised high enough to fuse the metal. The pellets were fairly soft and when filed, exhibited a white metallic luster. On the other hand, some of the product was so finely divided that it was pyrophoric when dry. The extent to which fusion and coagulation had been attained is illustrated by the amount of product recovered, classified according to the state subdivision:

Fused pellets	10 grams
Sintered masses	6 "
Fine powder	3.5 "
	19.5 grams (Theory = 34.6 grams)

The zirconium oxide crucible used in the reduction of UCl_3 was attacked only superficially and could have been re-used. The one used with UCl_4 was cracked and broken,

evidently due to the thermal shock when the reaction occurred. In other respects, the results with UCl_4 were similar to those with UCl_3. However, only 8.4 grams of metal were obtained as pellets and sintered material, due to the breaking of the crucible.

Larger Scale Preparations of UCl_5 from UO_3 and CCl_4.

A larger stainless steel autoclave (2.5 liters capacity) having been constructed, reactions were carried out using larger quantities of reactants. The autoclave was provided with a thermocouple well for the determination of the temperature of the reacting mixture. With larger charges, once the reaction was initiated, there was a very rapid rise in the internal temperature, above that of the surrounding oil bath; if the rate of reaction was not controlled, the pressure and temperature rose to very high values. However, if the rate of the initial reaction was controlled, the conversion then proceeded smoothly to completion. When the temperature was kept low, the product was fairly pure UCl_5, but when higher temperatures were reached in the initial reaction, a mixture of UCl_5 and UCl_4 was obtained and in some cases, $UOCl_2$ was present.

A study of the varous factors which might influence the rate of the initial rapid reaction has been in progress for some times. The following factors have been considered.

1. Proportion of Excess CCl_4. In the earlier experiments previously reported, in which a small steel autoclave was charged with 25 to 50 grams of UO_3, the initial reaction with CCl_4 proceeded rapidly after it had once set in, but it never became uncontrollable no matter what the ratio of CCl_4 to UO_3 happened to be. No provision was made for the determination of the internal temperature, so it is not known to what levels it rose; the course of the reaction was followed by the pressure increase only, and this was never excessive. With larger amounts of UO_3 (200 grams and up), charged into the new autoclave, it has been found that after the initial reaction has set in, the rate of conversion is extremely rapid and very difficult to control unless the amount of CCl_4 is considerably greater than the theoretical quantity. The greater the amount of UO_3, the greater is the excess of CCl_4 required. With 200 grams of UO_3, the reaction is readily controlled when 75% excess CCl_4 is introduced with the charge; the reaction usually starts when the internal temperature reaches about 100°C and is marked by a rapid temperature rise of 30 to 40 degrees. The excess CCl_4 serves to remove the heat evolved by distilling to the cooler top portion of the autoclave. It also reduces the pressure by dissolving the $COCl_2$ formed in the reaction.

The effect of adding the CCl_4 in small increments is now being studied.

SECRET

This document contains information affecting the national defense [redacted] within the meaning of the [redacted] Its transmission or the revelation [redacted] in any manner to an unauthorized person is prohibited by [redacted]

2. Effect of Moisture. Using 75% excess of CCl_4, a reaction was carried out with 200 grams of UO_3 which had been allowed to absorb moisture (5.2 grams) by standing in moist air. The only effect of the water was to defer the initial reaction but, once reaction had started, it was just as rapid as though dry material had been used.

3. Effect of Longer Heating at Lower Temperatures. A reaction mixture containing 200 grams of UO_3, 30 grams of UCl_5 (catalyst) and CCl_4 in 75% excess, was heated at 80°-90° for 5 hours. There was evidently a very slow reaction as a small temperature increase and rise in pressure were noted. When the temperature was raised to 104°, at the end of the 5-hour period, the rate of reaction increased, but not as rapidly as usual. The effect of a long preliminary heating is being studied further.

4. Substitution of UO_2 for UO_3. With 200 grams of UO_2 in place of UO_3, only about 22% conversion was obtained in 3 hours, with the internal temperature reaching a final value of 164°C. No rapid phase of the reaction was detected. In addition to UCl_4, the product contained an oxychloride, probably $UOCl_2$.

Thermal Decomposition of UCl_5 to UCl_4.

The preparation of UCl_4 from UCl_5 was discussed in the progress report of November 17th (page 4, OEMsr-290 and 688). As a result of further work, it may be stated that the conversion is substantially complete when UCl_5 is heated to 450°, and held there for one-half hour, in a stream of an inert gas at atmospheric pressure.

Conversion of UCl_5 to UCl_4 by Refluxing with S_2Cl_2.

Samples of UCl_5, weighing about 50 grams, were refluxed with 500 grams of purified S_2Cl_2 for two hours. UCl_4 was formed as a pale green, insoluble powder. The greenish gases evolved (perhaps containing free chlorine) were condensed in a trap cooled in "dry-ice"; about 5cc. of a pale yellow solid were obtained. The solid was probably SCl_4, since it decomposed into Cl_2 and S_2Cl_2 on being warmed up to room temperature.

In one experiment, the amount of UCl_4 recovered was 45.46 grams, or 95% of the predicted amount; the product contained 62.50% U, 36.49% Cl, 0.56% residue (after ignition to U_3O_8) and 0.45% unaccounted for. The atom-ratio of Cl to U was 3.920. The material in the product which is listed as "unaccounted for" was probably sulfur, as there was some evidence of sulfur when a sample of the material was dissolved in water.

Distillation of the UCl_4 from the product in a stream of oxygen- and moisture-free nitrogen, at 5 mm. pressure, showed the presence of some sulfur and left a residue in the boat amounting to 1.20% of the weight of the sample. This appeared to be UO_2.

NAME AND ADDRESS		DOCKET NUMBER	LICENSE NUMBER	PROGRAM CODE	EXPIRATION DATE	STATUS
BRISTOL METAL CO. INC. 58 BROAD COMMON RD. BRISTOL	RI 02809	030-17102	38-19184-01	03120	12/31/84	4
BROWN UNIVERSITY PROVIDENCE	RI 02912	030-01016	38-00169-08	01200	02/28/79	4
BROWN UNIVERSITY PROVIDENCE	RI 02912	030-01017	38-00169-09	01200	11/30/78	4
BROWN UNIVERSITY PROVIDENCE	RI 02912	030-01018	38-00169-14	01200	04/30/74	4
BROWN UNIVERSITY PROVIDENCE	RI 02912	030-01019	38-00169-15	01200	06/30/77	4
BROWN UNIVERSITY PROVIDENCE	RI 02912	030-01020	38-00169-16	01200	01/31/74	4
BROWN UNIVERSITY PROVIDENCE	RI 02912	030-01021	38-00169-17	01200	01/31/75	4
BROWN UNIVERSITY PROVIDENCE	RI 02912	030-01022	38-00169-18	01200	11/30/73	4
BROWN UNIVERSITY PROVIDENCE	RI 02912	030-01023	38-00169-19	01200	01/31/75	4

1200 = ACADEMIC OTHER

NAME AND ADDRESS	DOCKET NUMBER	LICENSE NUMBER	PROGRAM CODE	EXPIRATION DATE	STATUS
OWN UNIVERSITY SCIENCER PROVIDENCE RI 02912	030-01024	38-00169-20	01200	06/30/81	4
OWN UNIVERSITY PROVIDENCE RI 02912	030-01025	38-00169-21	01200	11/30/75	4
OWN UNIVERSITY PROVIDENCE RI 02914	030-01026	38-00169-22	01200	04/30/76	4
OWN UNIVERSITY PROVIDENCE RI 02912	030-08201	38-00169-24	01200	11/30/76	4
OWN UNIVERSITY PROVIDENCE RI 02912	030-08428	38-00169-25	01200	02/28/77	4
OWN UNIVERSITY PROVIDENCE RI 02912	030-08436	38-00169-26	01200	02/28/77	4
WN UNIVERSITY PROVIDENCE RI 02912	030-08780	38-00169-27	01200	07/31/77	4
WN UNIVERSITY PROVIDENCE RI 02912	030-09093	38-00169-28	01200	12/31/77	4
WN UNIVERSITY PROVIDENCE RI 02912	030-09143	38-00169-29	01200	06/30/78	4

NAME AND ADDRESS	DOCKET NUMBER	LICENSE NUMBER	PROGRAM CODE	EXPIRATION DATE	STATU
BROWN UNIVERSITY PROVIDENCE RI 02912	030-09210	38-00169-30	01200	07/31/78	4
BROWN UNIVERSITY PROVIDENCE RI 02912	030-09878	38-00169-31	01200	11/30/78	4
BROWN UNIVERSITY PROVIDENCE RI 02912	030-11776	38-00169-32	01100	05/31/81	4
BROWN UNIVERSITY DIVISION OF BIOLOG PROVIDENCE RI 02912	030-00835	38-00169-23	01200	05/31/76	4
CABLE ELECTRIC PRODUCTS INC. P.O. BOX 6767 PROVIDENCE RI 02940	030-19542	09786	03120	/ /	4
CABLE ELECTRIC PRODUCTS, INC. 234 DABOLL ST. PROVIDENCE RI 02940	030-21054	17486	03255	/ /	3
CIBA-GEIGY CORPORATION 180 MILL STREET CRANSTON RI 02905	030-09346	38-15559-01	03120	05/31/83	4
COLEMAN MD., LEO 126 PROSPECT STREET PAWTUCKET RI 02860	030-10846	38-16340-01	02200	12/31/79	4
CONKLIN MD., FRANCES P. 54 HYBRID DRIVE CRANSTON RI 02920	030-08402	38-15008-01	02300	05/31/83	4