

MARVIN MAHETTA ENERGY SYSTEMS LIBRARIES



3 4456 0352756 5

ORNL-1047

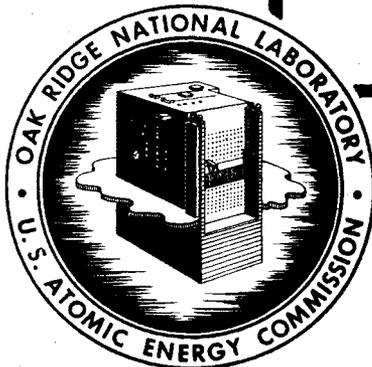
CENTRAL RESEARCH LIBRARY
DOCUMENT COLLECTION

PRODUCTION OF FISSION PRODUCT

IODINE 131

**A. F. Rupp
E. E. Beauchamp
J. R. Farmakes**

**CENTRAL RESEARCH LIBRARY
DOCUMENT COLLECTION
LIBRARY LOAN COPY
NOT TRANSFER TO**
If you wish someone else to use this document, send in name and address and the library will arrange to loan it.



OAK RIDGE NATIONAL LABORATORY
OPERATED BY
CARBIDE AND CARBON CHEMICALS COMPANY
A DIVISION OF UNION CARBIDE AND CARBON CORPORATION



POST OFFICE BOX P
OAK RIDGE, TENNESSEE



ORNL 1047

This document consists of 26 pages. Copy 8 of 195 copies. Series A.

Contract No. W-7405, eng 26

OPERATIONS DIVISION

RADIOISOTOPE DEVELOPMENT DEPARTMENT

PRODUCTION OF FISSION PRODUCT IODINE 131

A. F. Rupp, E. E. Beauchamp, J. R. Farmakes

DECLASSIFIED

Per Letter Instructions Of

AEC 7-7-55

Ms. for M.T. Bray
7/26/55

SUPERVISOR LABORATORY RECORDS

ORNL

Date Issued

DEC 18 1951

OAK RIDGE NATIONAL LABORATORY

Operated by

CARBIDE AND CARBON CHEMICALS COMPANY

A Division of Union Carbide and Carbon Corporation

Post Office Box P

Oak Ridge, Tennessee

~~RESTRICTED~~
This data as of 1940.

~~RESTRICTED~~



3 4456 0352756 5



PRODUCTION OF FISSION PRODUCT IODINE 131CONTENTS

	<u>Page No.</u>
1.0 ABSTRACT	4
2.0 INTRODUCTION	4
3.0 PROCEDURE	4
3.1 General Description	4
3.2 Dissolving	5
3.3 Steam-Air Distillation of Iodine	5
3.4 First Purification Step	8
3.5 Final Purification	8
4.0 EQUIPMENT	9
4.1 General Description	9
4.2 Slug Carrier	13
4.3 Dissolver	13
4.4 Condensers	13
4.5 Catch Tank	15
4.6 Scrubber	15
4.7 Still	15
4.8 Glass Purification Equipment	16
5.0 DISCUSSION	16
5.1 Dissolution of Uranium in HNO ₃	16
5.2 Behavior of Iodine During Dissolving	17
5.3 Condensation and Trapping of Iodine	19
5.4 Fixation of Iodine by Mercury	20
5.5 Separation of Iodine from Nitrate and Nitrite	20
5.6 Purification of Iodine	22
6.0 ACKNOWLEDGMENTS	22
7.0 REFERENCES	23
8.0 EQUIPMENT DRAWING REFERENCES	24

PRODUCTION OF FISSION PRODUCT IODINE I31

1.0 ABSTRACT

This report describes the equipment and process used for the separation and purification of fission product iodine I31 at Oak Ridge National Laboratory. The effect of process variables is discussed in detail.

2.0 INTRODUCTION

Iodine I31 is widely used for medical work and research. The demand for radioiodine exceeds that for any other radioisotope produced at ORNL. The plant described in this report has been the principal source of iodine I31 distributed under the Radioisotope Program of the AEC since September 1948.

The first iodine produced for general distribution from ORNL, in August 1946, was made from tellurium metal irradiated in the pile and separated as described in a report by Ballantine(1). It was realized at that time that the supply of iodine from this source would soon be inadequate to meet the rapidly growing demand. Distribution has increased from approximately 300 mc per month in 1946 to 30,000 mc per month in 1950. A total of about 1,000 curies of fission product iodine I31 has been produced to date by the unit described in this report. The production of fission product I31 was an obvious choice because of the fairly high fission yield (2.8%) of I31 and the economical use of pile space and neutrons.

Practically no information was available on methods of producing large quantities of pure, carrier-free, fission-product iodine. Well-established chemical principles found in many textbooks and certain special procedures used in analysis for micro amounts of iodine were used as a guide in this work.

3.0 PROCEDURE

3.1 General Description

Fission product iodine is formed within the uranium slugs during irradiation and the general problem is to release the iodine, trap it in a suitable medium, reduce the volume and purify the iodine by chemical processing. The release of iodine may be obtained by physical changes in metal or oxide produced by heating, or by dissolution in acid. The latter method is used in the process to be described. After dissolution of the metal in nitric acid, iodine is steam-air distilled out as elemental iodine, partially removed in the weak nitric acid condensate, and the balance is taken out in an alkaline scrubber. The nitric-nitrous acid distillate is treated with H₂O₂ to oxidize nitrous acid to nitric acid and iodine is distilled out, taking advantage of the fact that dilute solutions of nitric acid have a very low nitric acid vapor pressure, to obtain a small volume of distillate containing very little nitric acid and most of the iodine. The contents of the alkaline scrubber are treated in the same way after acidification with nitric acid. The crude iodine distillate is trapped in dilute sodium hydroxide solution and is then evaporated down to a volume suitable for final purification in glass equipment. Purification

is accomplished by oxidizing the iodine to iodate in 20% sulfuric acid-potassium permanganate solution after which traces of HNO_3 or other volatile substances are distilled off while the non-volatile iodate remains in the distilling flask. The permanganate and iodate are then reduced by addition of phosphorous acid catalyzed with H_2O_2 , and the iodine is distilled off as elemental iodine which is trapped in dilute sodium hydroxide. Sodium sulfite is added to the distillate as a reducing agent, the volume is adjusted, the solution is filtered and the iodine preparation is transferred to a shielded container for storage. Flow sheets for the process are shown in Fig. 1 and Fig. 2.

3.2 Dissolving

Slugs which have been in the pile approximately 60 days are delivered to the top of the cell in a shielded container and lowered through a slug chute into the dissolver. The aluminum slug carrier basket and the aluminum slug jackets (3 ORNL slugs and one basket) are removed by dissolving in 9 liters of solution of 8.2% NaOH and 16.7% NaNO_3 . The reaction can be violent and is controlled by cooling the dissolver at the start of the reaction and heating it later in the cycle; the temperature is not allowed to exceed 110°C . Ammonia gas is given off during this reaction, thus avoiding the explosive mixture of H_2 and O_2 that one might obtain in the dissolver if NaNO_3 were not used. The slugs are thoroughly washed with 4 liters of hot water, then with 10 liters of 10% HNO_3 , and finally with 20 liters of distilled water. It should be noted that the great care taken in the coating removal step is not necessarily required for the iodine separation, but is done to produce a pure UNH solution as starting material for other separations processes. The coating removal requires about 3 hours.

The uranium (3,498 grams) is dissolved in 6 liters of 70% C.P. HNO_3 at a temperature not exceeding 110°C . A reflux condenser is used to prevent excessive loss of water and nitric acid. The progress of the metal dissolution is followed by noting the increase in specific gravity, which rises to a maximum of about 1.95. The dissolving step requires approximately 20 hours.

3.3 Steam-Air Distillation of Iodine

Some iodine is released from the dissolver during metal dissolution; however, well over 50% of the iodine remains in the dissolver and must be removed by sparging with steam and air. The reflux condenser is emptied of water and warmed slightly during sparging, which is continued for about two hours while the progress of the iodine removal is followed by means of a gamma probe on the distillate catch tank. Approximately 15 - 18 liters of distillate is obtained, which is about 20% in nitric and nitrous acid and contains about 0.2 mc/ml of I^{131} plus I^{133} . During the dissolving and sparging steps, iodine and nitrogen oxides which are not caught in the distillate pass to a scrubber which contains 10 liters of 15% NaOH solution. Practically no iodine gets past the alkaline scrubber. Xenon passes through to the off-gas system.

3.4 First Purification Step

Hydrogen peroxide solution (15%) is added to the still in an amount equal to one-half the volume of the nitric-nitrous acid solution in the catch tank. The catch tank liquid is then added very gently to the hydrogen peroxide solution, with temperature maintained as low as cooling water will permit. A 20-minute period is allowed for the reaction to go to completion and the distillation is started at a slow rate (2 liters/hour). The vapor temperature is maintained slightly above 95° C (the equipment is operated under a few inches of water negative pressure). The distillate is collected in a receiver which scrubs non-condensibles (O₂ from decomposing H₂O₂) in 250 ml of 10% NaOH. The rate of I¹³¹ distillation is followed by means of a radioactivity probe on the distillate receiver. Then the rate of I¹³¹ distillation drops off, one liter of 30% H₂O₂ is added dropwise to the still during the balance of the distillation.

3.5 Final Purification

The alkaline distillate is evaporated to approximately 400 ml volume, and transferred to a 5-liter glass distillation flask. A sample is taken for determination of alkalinity and reducing power (as referred to KMnO₄). Based upon the control analysis, a sufficient amount of 1 N KMnO₄ is added to oxidize all reducing agents, plus a 25 ml excess. A 15-minute reaction period is allowed and then sufficient 21 N H₂SO₄ is added to neutralize the alkali in the flask. If the purple color fades during acidification, 1 N KMnO₄ is added to restore the permanganate color. The temperature is not allowed to exceed 50° C. Enough 21 N H₂SO₄ is now added to make the solution in the flask 20% in H₂SO₄. Distillation is started and approximately 10% of the liquid is distilled over and discarded. Distilled water is added to the flask to restore the acid concentration to 20%. The distillate receiver is thoroughly rinsed, and before each 100 ml of product iodine is collected the following solutions are added to the receiver:

- a. 3 ml 0.4 N NaOH to distillate receiver
- b. 1 ml 0.1 N Na₂SO₃ to distillate receiver
- c. 2 ml 0.4 N NaOH to the off-gas scrubber.

Thirty ml of saturated phosphorous acid (H₃PO₃) is slowly added to the hot solution in the flask to reduce the excess permanganate and the iodate. If the permanganate color is not all discharged after two minutes, small amounts (2 - 3 ml) of H₃PO₃ are added until the solution is clear and colorless. A few drops of 30% H₂O₂ solution are added if trouble is experienced at this point. Distillation is started and the progress of the I¹³¹ distillation is followed by noting the rise in activity of the distillate receiver as measured by the monitoring chamber. Small amounts of 10% H₂O₂ are added from time to time if the rate of distillation appears sluggish. Usually from three to five 100-ml cuts are necessary for removal of most of the iodine. The distillate is drained to a collection vessel, tested for alkalinity and adjusted if necessary to a pH of 7-9. The volume is adjusted to about 500 ml; the solution is filtered through a fine fritted glass disc, and removed for packaging.

4.0 EQUIPMENT

4.1 General Description

The equipment for this process is located in two separate areas of one building; the dissolving of slugs and separation of iodine are performed in a heavily-shielded concrete cell and the product is transferred through a lead-covered line to a lead-shielded hood for final purification in glassware. The list at the end of this report gives the ORNL Engineering Department drawing numbers of prints of all equipment used except certain pieces of glassware fabricated from sketches.

The main concrete cell (Plates 1 and 2) is 4' wide by 6' long and 8' high, with walls 24" thick. A steel-clad lead door, 10" thick provides a 24" x 24" entrance to the cell at floor level. There is another smaller access door just below the ceiling of the cell, 18" x 24". This opening is shielded with 1" lead doors and extra lead brick.

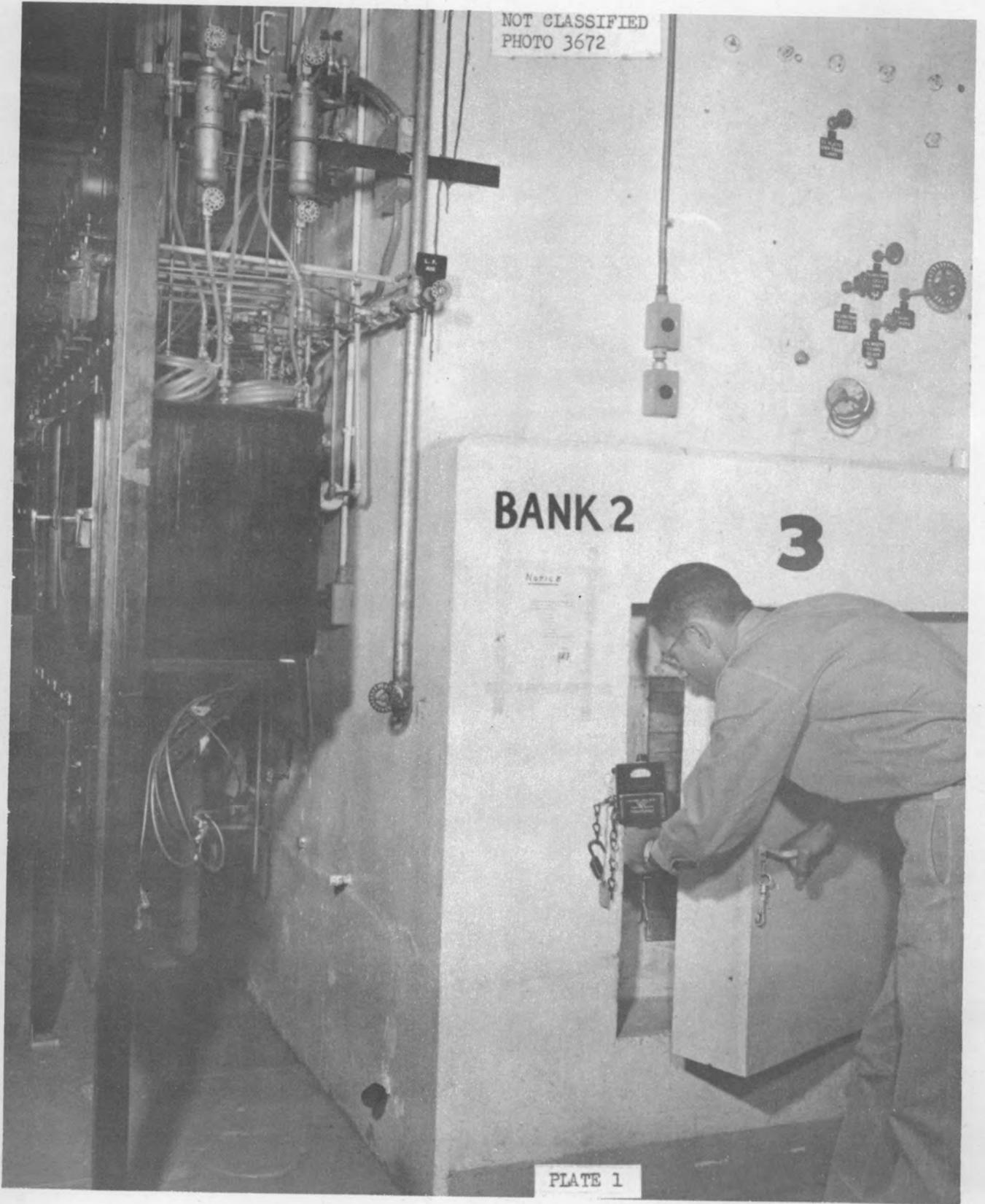
Numerous holes of various types pass through the concrete shield on two sides and the top, including five 3½"-diameter holes for periscopes and four 6"-diameter holes which may be used for zinc bromide viewing windows.

The cell floor is covered with lead and slopes to a sump in one corner; drainage from the cell is to a hot drain which flows to an underground storage tank. Other hot drains for chemical waste and uranium waste are provided within the cell. The cell walls are painted with a white rubber-base, acid-resistant paint. The cell is illuminated by protected incandescent lights. Ventilation is provided by an 8"-diameter duct which is attached to a general ventilation system; the exhaust air is discharged through a 250' stack. A stainless steel off-gas line, operating at 40" H₂O negative pressure, removes process gases directly from the equipment and this gas is discharged through a general system where the gases are decontaminated by passage through a wetted-wall precipitron and glass fiber filter, after which the gas is introduced into the high-volume air stream passing out the 250' stack.

The following services are provided to the cell: process water, distilled water, 125 psi steam, 25 psi steam, 90 psi air, off-gas vacuum, 110-volt A.C. electricity.

Because very little space was available, it was necessary to crowd the dissolving equipment and equipment for the first iodine purifications into this one small cell; it would have been much better if the dissolver and its auxiliaries could have been placed in a separate cell.

The lead-shielded hood for final purification work is shown in Plate 3. This hood is 2' wide, 8' long and 6' high; the sides and back are of concrete and lead equivalent to a total thickness of 3" of lead; the front is made of 3"-thick lead. Two large lead doors are provided for access, and several slots are used for viewing through internal mirrors. Originally, the 3" lead shield was only 6' high, leaving a space covered

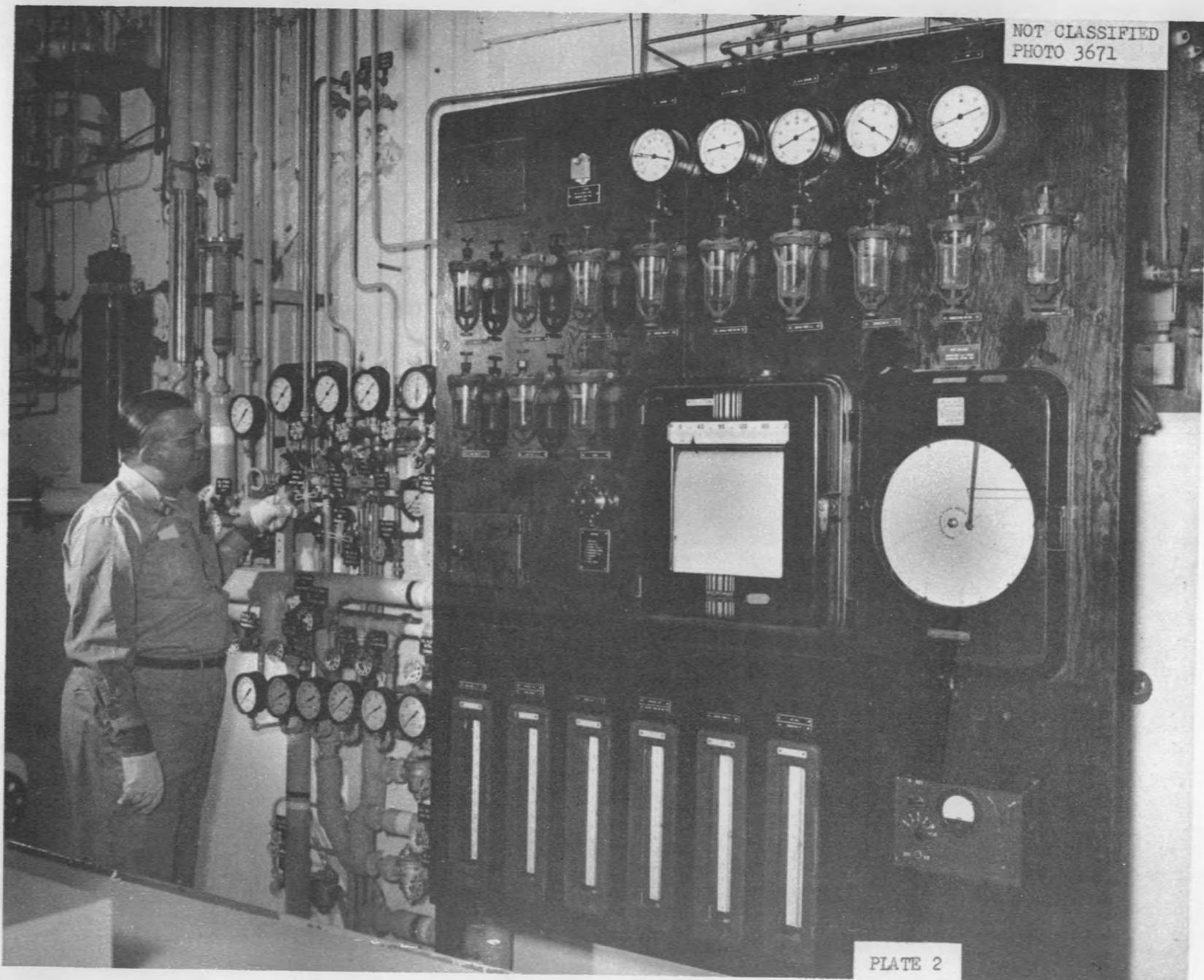


NOT CLASSIFIED
PHOTO 3672

BANK 2

3

PLATE 1



NOT CLASSIFIED
PHOTO 3671

PLATE 2

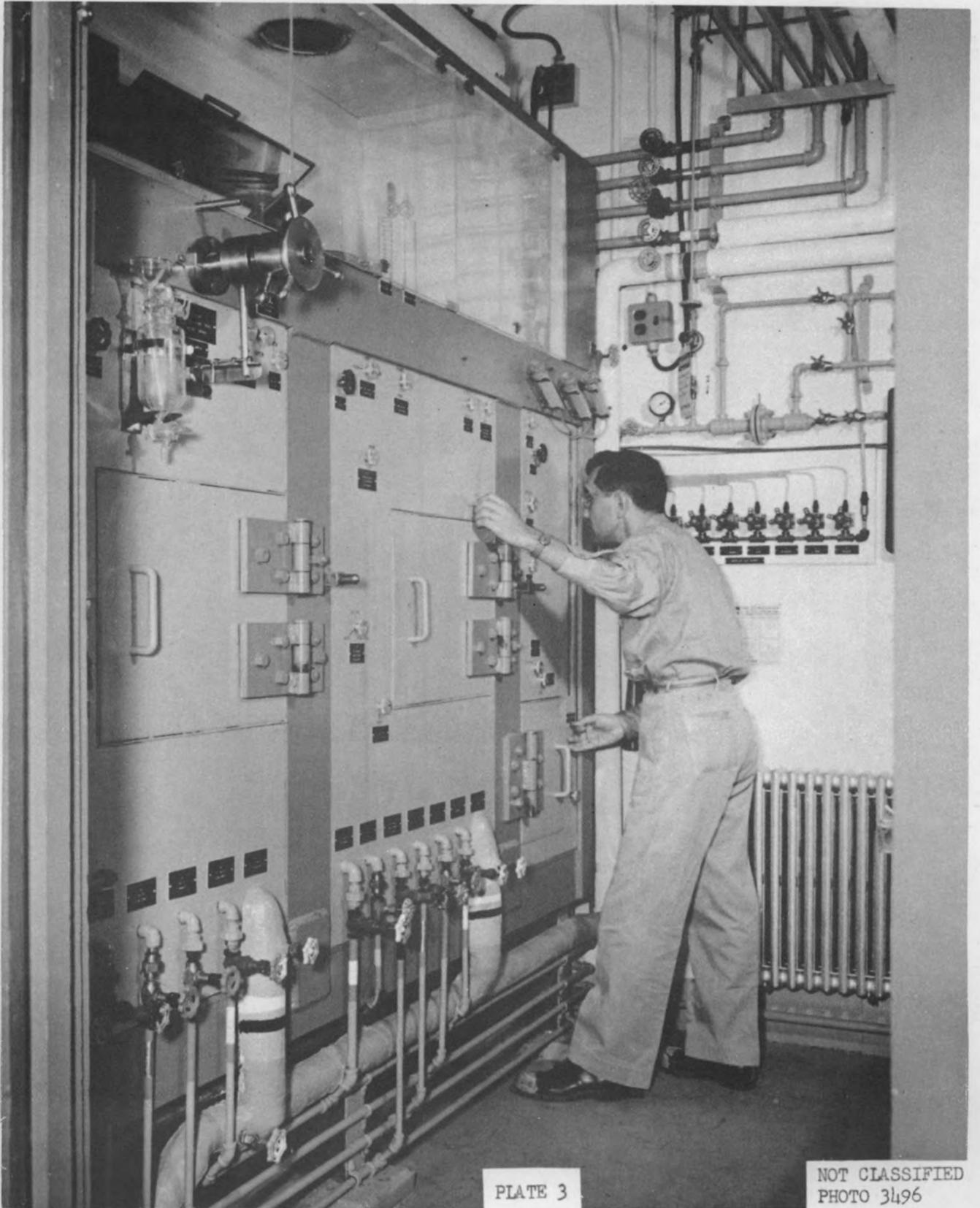


PLATE 3

NOT CLASSIFIED
PHOTO 3496

with lucite so that vision through overhead mirrors could be obtained. It was later found necessary to cover the top portion with 1" lead up to the ceiling to reduce scatter when larger amounts of iodine (up to 40 curies) were handled. The hood is provided with all services, including gas, hot off-gas lines and hot drains for waste disposal.

4.2 Slug Carrier

The slugs are loaded into a carrier (shown on top of the cell in charging position, Plate 4) in the canal at the Pile Building. This carrier is made of lead encased in steel, 18" in diameter and 28 3/4" high; the weight is 2,500 lbs. The slugs are loaded into a previously-placed basket (made of thin slotted aluminum) through which one end of a flexible braided stainless steel wire is passed; the two ends of the wire are passed out through a hole in the side of the carrier. In loading, the carrier is placed in position over the open slug chute and a movable lead drawer is pulled out at the bottom. Holding the wires, the basket containing the slugs is carefully lowered to the bottom of the dissolver by paying out the line. To retrieve the wire, one end is released and the other is reeled in until the free end is brought back to the container. The wire is wiped with a cloth as it is retrieved; very little contamination is picked up by the wire.

4.3 Dissolver

The slug dissolver is a tantalum-lined, stainless steel, cone-shaped vessel with a capacity of 30 liters. Maximum operating volume was set at 22 liters. The tantalum lining was provided to reduce metallic contamination in the UNH solution, which is sometimes used in other processes, rather than for the iodine process. It has a stainless jacket through which either steam or water may be passed and a top provided with seven tantalum-lined flanged nozzles. One nozzle is connected to a tantalum reflux condenser, the other to the slug chute. Four of the nozzles admit from one to three tantalum tubes each and the remaining nozzle is blanked off as a spare. The seven tantalum tubes are for reagent addition, steam and air sparging, sampling, liquid level, specific gravity, vacuum, and a thermowell.

4.4 Condensers

The tantalum-lined reflux condenser was salvaged from a single effect acid evaporator used on another part of the Project. It is 4' long and the cooling water flows through an outer steel jacket and through a tantalum bayonet inside the 3"-diameter tantalum main tube condenser. This unit is mounted on top of the dissolver in a vertical position.

A curved tantalum-lined stainless steel pipe connects the reflux condenser to a stainless-steel multitube condenser mounted at an angle of 45 degrees off the horizontal. Stainless steel is used from the top connection of this condenser throughout the rest of the equipment in the cell. The condenser is constructed of type 18-8 S-Cb SS; it is 3 1/2' long, made up of a nest of seven type 304 SS 3/4" o.d. tubes. The lower end has two

NOT CLASSIFIED
PHOTO 3673

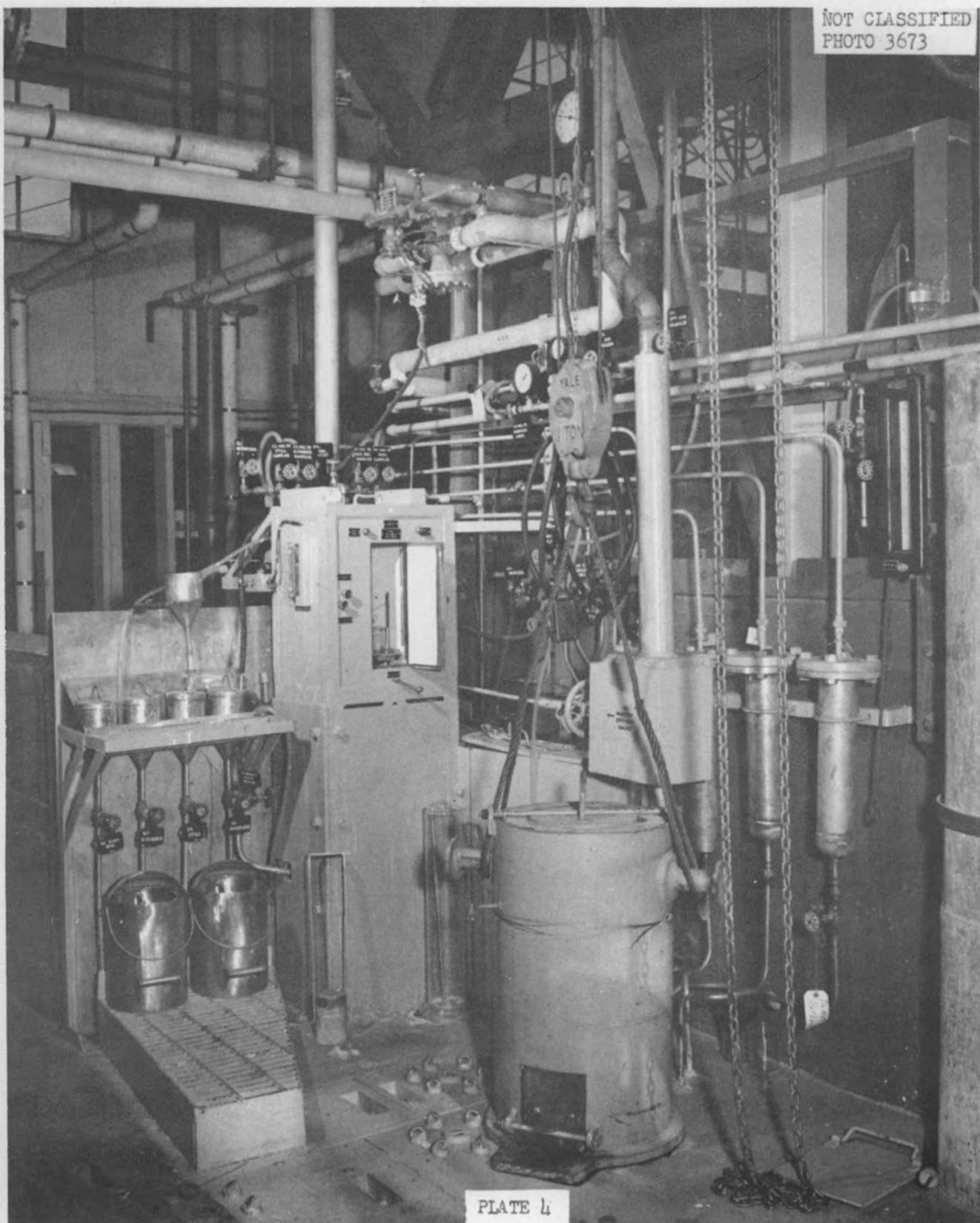


PLATE 4

outlets, one at the bottom for condensate, which is attached to the catch tank, and the other on the opposite side to pass non-condensibles to the scrubber. A thermocouple at the inlet end is used to measure the temperature of the incoming vapor.

4.5 Catch Tank

The catch tank is a type 316 SS cylindrical vessel of 29 liters' capacity; maximum operating volume is 25 liters. Seven nipples placed along the top provide for liquid level and specific gravity measurements, vacuum, off-gas, reagent addition, and spare lines. The tank is mounted on its side and is sloped slightly toward a valved drain which connects to the still.

4.6 Scrubber

The scrubber is of fixed volume type, which is filled with sufficient alkaline solution to neutralize all acid vapors passing through it. The capacity is 25 liters and the operating volume is 16 liters. It is a cylindrical vessel made of type 316 SS, 11" in diameter by 43" high. It is divided into two chambers of approximately equal volume, the upper one being an expansion chamber in which the entire contents of the lower scrubbing chamber may be contained in case of a suck-back. After pressure conditions return to normal, the scrubbing liquor returns by gravity to the scrubbing chamber. The gases from the condenser enter the top of the scrubber, pass through the expansion chamber, and then into a dip leg which extends to the bottom of the scrubber. The gas is passed out through small holes in a cross-shaped distributor and bubbles up through the liquid, where it encounters two perforated plates, which re-form the bubbles to some extent. The gas leaves the scrubber through a baffled line at the top and side of the scrubbing chamber. The vessel is provided with a reagent addition line, valved transfer line to the catch tank, sampler line, and a thermocouple.

4.7 Still

The still is a simple one composed of a cylindrical boiling pot, entrainment separator, vapor line, condenser, and distillate receiver. It is constructed of type 309 SS throughout with the exception of the heating coils which are made of type 316 SS, 7/16"-diameter tubing, 0.065" wall thickness. The entire still was heat-treated after fabrication. The boiling pot has a capacity of 35 liters and operating volume of 24 liters. The entrainment separator is an enlarged section of vapor pipe containing a series of baffles. The condenser is made of three worm coils in parallel enclosed in a stainless steel shell. The distillate receiver has an operating volume of 3 liters. It is constructed so that any non-condensibles are scrubbed through a heel of alkaline liquid; the dip-leg is attached to an expansion chamber similar to that described for the scrubber to avoid the danger of suck-back. The still is provided with the following lines: liquid level and specific gravity, vapor line, reagent addition, product inlet, sampler, product outlet from distillate receiver.

4.8 Glass Purification Equipment

The final purification still is composed of a five-liter round flask connected through a double entrainment trap to a spiral condenser. The distillate receiver is a 350-ml pear-shaped vessel in which the distillate leg dips below the surface of the distillate so that non-condensibles are scrubbed to remove iodine. The still is operated under a slight negative pressure and the non-condensibles pass through a small column packed with glass beads which are constantly wetted with dilute sodium hydroxide; the gases then pass to the off-gas system.

The still is heated by means of a remote control Fisher-type gas burner which can be moved in and out of position under the still by a system of gears; the burner is lighted electrically by a spark which is passed from a platinum point to the top of the burner. The still is cooled by water sprays while the burner is moved out of position. The flask is protected from localized heating by stainless steel gauze. This arrangement has been in constant use for four years with no difficulties or flask breakage.

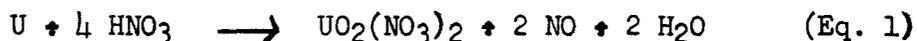
The product is transferred to an evaporator which is simply a Pyrex beaker heated by infra-red lamps. A sample is checked for pH at this point (using pH paper), the volume adjusted and passed through a 3" diameter fine sintered glass filter to product storage.

The performance of this equipment has been good. Regular attention to greasing stopcocks and joints (with silicone grease) has resulted in relatively trouble-free routine operation.

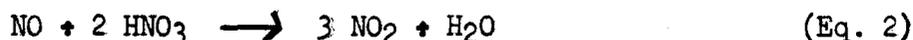
5.0 DISCUSSION

5.1 Dissolution of Uranium in HNO₃

Uranium metal is dissolved in nitric acid according to the following equation.



When the nitric acid is concentrated, during the first part of the dissolving operation, some of the NO is oxidized to NO₂ by the boiling concentrated HNO₃.



NO is also oxidized to NO₂ by oxygen coming into the system (i.e., instrument manometer bubblers).

The reaction is autocatalytic to some extent and after slight induction period rises to a peak in about one hour; this maximum rate continues for 2-3 hours, after which it begins to fall gradually during the next 16 hours. During this time, the UO₂(NO₃)₂ · 6 H₂O (uranyl nitrate hexahydrate, UNH) concentration rises to approximately 80% by weight. One must avoid cooling at this point, for such a solution freezes at about 40° C.

5.2 Behavior of Iodine During Dissolving

In the particular dissolving equipment described in this report, it was found that approximately 30% of the total iodine was given off during the metal dissolving step. It is necessary to resort to sparging with steam and air to remove 50% more of the iodine. The remaining 20% of the iodine is removed at a very slow rate so that it is usually sent to waste with the metal solution. Sparging with steam is used only as a means of keeping the temperature up, since not enough heat can be supplied by the steam jacket alone.

The chemical changes which iodine undergoes during the dissolving process are probably quite complex. Some work has been done on this subject by workers who were interested in the behavior of iodine during metal dissolution only as related to other problems.

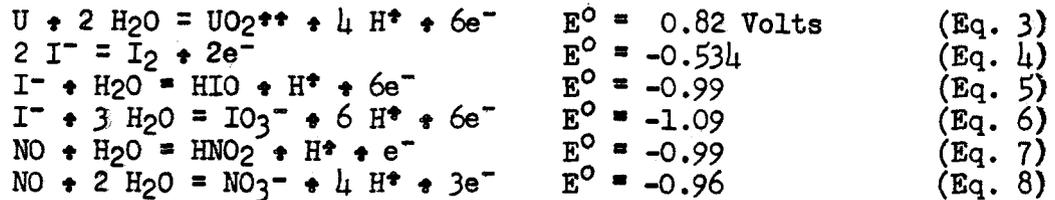
Dreher, Kamack and Thompson⁽²⁾ found that the evolution of iodine from uranyl nitrate solution is principally influenced by the concentration of iodine and is substantially independent of the concentration of nitric acid or uranyl nitrate. The reaction involved in the evolution of iodine appears to be approximately a second order reaction with respect to the concentration of iodine. Since added iodide or iodate is quickly liberated without exchange from dissolver solution, they conclude that the fission iodine exists in a complex ion, and in an oxidation state higher than I_2 .

Glendenin⁽³⁾ has pointed out that the interchange between freshly formed radioiodine atoms and carrier is slow and incomplete. In order to get rapid and complete interchange, it is necessary to pass the iodine plus carrier through several oxidation states together.

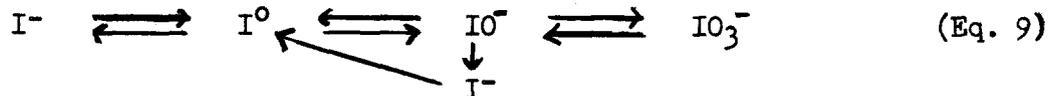
Freed, et al.,⁽⁴⁾ dissolved uranium in HCl for the production of iodine and showed that precise control of the oxidation-reduction potential during oxidation of U^{+4} to UO_2^{+2} is necessary in order to get good iodine yields. They found that iodine could be distilled out at a rate proportional to the amount of iodine present until the total iodine concentration reached about 500 μ g/liter, when the rate decreased more rapidly.

While an exhaustive laboratory study was not made by us, certain conclusions may be reached by using some of our observations, supplemented by other data. The percentage of the total radioiodine released from a dissolver depends upon a number of factors, including size and shape of the dissolving vessel, use of refluxing scrubbing towers, size of the charge, rate of dissolution, chemical conditions during dissolving, and age of the slugs. The release of iodine depends primarily upon three conditions: (a) iodine must be present as elemental iodine, for the iodide and iodate are practically non-volatile when present in small amount in aqueous solutions; (b) iodine atoms must combine to form I_2 molecules and diffuse either to the surface of the liquid or into a bubble of gas which will carry it to the surface; (c) after escape in a gas, it must not be scrubbed out within the environs of the dissolver, either by purely solution scrubbing or because of chemical changes.

Iodine probably occurs within the uranium metal entrapped either as iodine atoms of zero valence or as molecular I_2 . Upon dissolving, the immediate surroundings can be both oxidizing and reducing in character; i.e., the nitric-nitrous acid solution and the surface of the uranium metal. Any reduction to iodide would tend to be of very short duration during the first stages of dissolving. Some of the couples of interest in this system are listed below⁽⁵⁾:



Equilibrium can be set up which varies throughout the dissolving cycle, as indicated below:



As elemental iodine atoms are formed, two atoms must unite to form volatile molecular I_2 , which is then removed from the system. Conditions early in the dissolving period (boiling 70% HNO_3) are conducive to oxidation of iodine to iodate⁽²⁾⁽⁶⁾. The energy available for the oxidation of iodine to iodate is corrected for concentrations other than one molar, as follows:

$$E = E^{\circ} - \frac{0.059}{3} \log \left[\frac{(NO_3) (H^+)^4}{(NO) (H_2O)^2} \right] \quad (\text{Eq. 10})$$

It is apparent that conditions which favor the oxidation of iodine to iodate are high nitric acid concentration and low nitric oxide pressure. There is sufficient energy for nitric acid to oxidize iodide directly to iodate; however, the intermediate reaction indicated in Eq. 5 is probably favored. The hypoiodite formed then decomposes:



Iodate and iodide react to form elemental iodine in acid solution. Therefore, the dissolver should not contain both iodate and iodide at the end of the processing cycle unless the reaction rate becomes very small at extreme dilution. However, the presence of NO even during the latter stages of dissolving would preclude the existence of iodide for NO is a very efficient agent for oxidizing iodide to elemental iodine (Eqs. 4, 7). Iodate may also be reduced by NO , although the rate of reduction is very slow at high hydrogen ion concentrations. It is possible that iodate formed early in the dissolving cycle survives the balance of operations on the dissolver solution. However, we were not able to positively identify iodate in the 10-20% iodine which remained in the dissolver after sparging.

The effect of the size of the dissolving vessel is the same as that of a scrubber. The smaller the dissolver, the larger will be the relative size of walls, top, and other surfaces in which the vapor is condensed and refluxed back to the liquid. Iodine is scrubbed out in all these liquid films. Observations have been made over a period of years of various sizes of dissolvers ranging from one-slug capacity to those taking several tons of slugs. A stainless steel one-slug dissolver, with no special reflux equipment except a long gas exhaust pipe, discharged less than 1% of the iodine during metal dissolving. A quarter-ton dissolver with a reflux scrubber discharged only about 5% of the iodine. Dissolvers, with scrubbing equipment, which dissolve one-ton batches of metal, discharge up to 45% of the iodine. The dissolver described in this report handles up to six ORNL slugs and discharges about 30% of the iodine during the metal dissolving step. In some dissolving operations, it is the practice to leave large heels of metal from one batch to the next. The accumulated heels present a very large uranium metal surface which will tend to enhance reducing conditions and thus may inhibit iodate production.

Slugs used for I^{131} production are usually from 30- to 60-day slugs. They are transferred to the dissolver as soon as possible after discharge from the pile. The radioisotopes of iodine which are present are 2.4-hour I^{132} , 22-hour I^{133} , and 8-day I^{131} ; small amounts of very long-lived I^{129} and stable I^{127} are also present. After all the metal is dissolved, the concentration of I^{131} (if the iodine is all considered to remain in the solution) is about 0.01 mg/liter; the I^{133} concentration is about 0.003 mg/liter; I^{132} is of too short half-life to be considered. However, long-lived I^{129} and stable I^{127} are formed, in a ratio of about 10 to 1, in such amount to give a concentration of 0.01 mg/liter, with 30-day slugs. Since this iodine is stable, or practically stable, the build-up is linear with time. For this reason, the total amount of iodine present is about one-third more for 60-day slugs than for 30-day slugs. This increase is reflected in the better yields of I^{131} experienced with older slugs.

5.3 Condensation and Trapping of Iodine

Elemental iodine is carried from the dissolver either in a stream of NO and NO₂ or air. The vapors are saturated with water and nitric acid as they enter the condenser. During condensation of the water and nitric acid, a large portion of the iodine is scrubbed out in the condensate. It was shown that the concentration of iodine is too low to permit condensation of iodine itself to take place by passing I^{131} in dry nitric oxide through an efficient condenser at -20° C. Although some of the nitrogen oxide was frozen out, a large part of the iodine passed through the condenser. The cooling of saturated vapors provides a very efficient scrubbing action, and approximately 90% of the iodine which leaves the dissolver is taken out at this point. The condensate is collected in the catch tank, where it is kept cool until the next operation. The condenser operates with regular plant system water at about 15-20° C.

The amount of nitric acid carried over in the vapors is quite small, but a considerable amount of nitric and nitrous acid is formed by absorption of nitrogen oxides in water. Iodine, nitrogen oxides, and non-condensibles are passed to the alkaline scrubber where the balance of the

iodine is removed; less than 0.1% of the iodine passes the scrubber. NO and NO₂ in equimolar quantities are absorbed in NaOH to produce NaNO₂. If NO₂ or extra oxygen is absent, NO will pass through the scrubber.

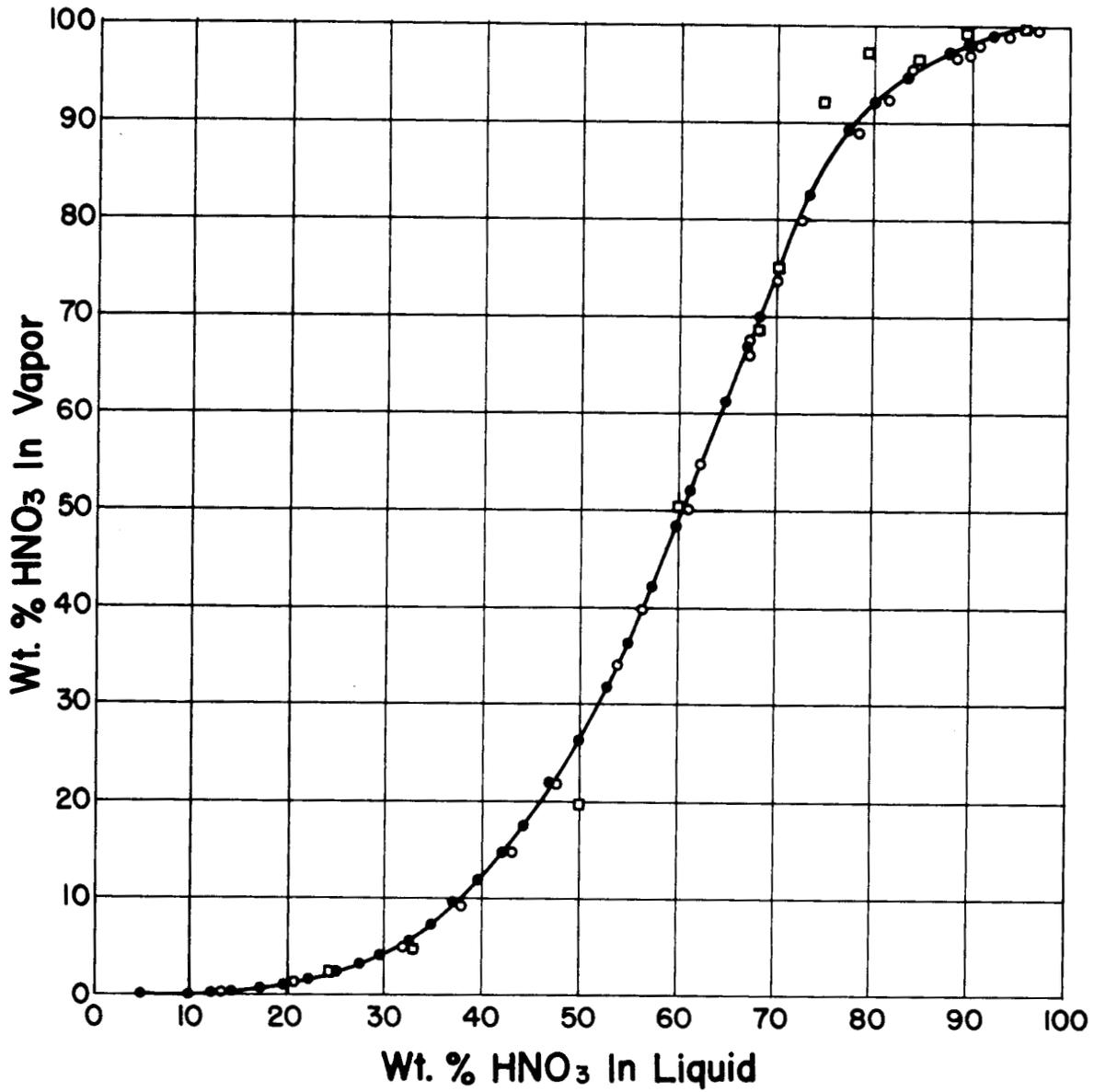
5.4 Fixation of Iodine by Mercury

The first process considered for removing the aluminum jackets from slugs was dissolution of the aluminum in nitric acid with mercuric nitrate catalyst. However, it was learned that the mercury contamination left behind from the coating removal step completely inhibited the release of iodine from the dissolver. Indeed, many chemical runs using boiling nitric acid in the dissolver were necessary to decontaminate the equipment from mercury before satisfactory iodine yields could be obtained. The action of mercury is due to the formation of the stable HgI₂ or the extremely stable complex ion HgI₄²⁻. It is very important to exclude even the slightest traces of mercury from any part of the iodine processing equipment. Interference is probably caused by other heavy metals, such as silver, but this has not been investigated. It is also important to exclude greases and oils from iodine processing equipment.

5.5 Separation of Iodine from Nitrate and Nitrite

In distilling iodine from acidified scrub liquor and condensate containing large amounts of nitrate, advantage is taken of the fact that the nitric acid vapor pressure over moderately concentrated solution is low, as shown in Fig. 3. It is necessary to oxidize any nitrite to nitrate to avoid decomposition of nitrite and contamination of the distillate with nitrous acid. Hydrogen peroxide was found to be most suitable for this oxidation. The technique used for combining the nitrite liquor and acidified hydrogen peroxide is important. The required amount of diluted hydrogen peroxide and nitric acid (in the case of the alkaline scrub liquor) is cooled to as low a temperature as possible. The cold nitrite liquor is allowed to run slowly into the hydrogen peroxide. After the nitrite is oxidized to nitrate, the mixture is heated slowly and the iodine is distilled over and trapped in dilute sodium hydroxide. The multitude of minute bubbles formed in the distilling mixture are effective in sweeping iodine out of the distilling kettle. After the distillation rate slows down and most of the hydrogen peroxide has been used, small amounts of hydrogen peroxide are added to the kettle beneath the surface of the liquid to promote the distillation of iodine.

The action of hydrogen peroxide on the system iodide-iodine-iodate is complex(7) (8) (9). Both oxidation and reduction of various components can take place, but the equilibrium that would be established with microgram quantities of iodine is very much in doubt. Most of the iodine distills over in the first 10% of the distillate, followed by a very slow, relatively constant rate of distillation of the remainder. Possibly significant is the fact that the rate of iodine distillation is momentarily increased when hydrogen peroxide is added; whether this is a chemical effect, or physical (increase in bubbles) is debatable.



**HNO₃ Content Of The Liquid And
Vapor At The Boiling Point**

-
- Data From Carpenter, Babor
 - Data From Pascal
 - ◻ Data From Berl, Samtleben
-

FIG. 3

NOT CLASSIFIED

5.6 Purification of Iodine

The first distillation from nitric acid solution is relatively pure, except for nitrate and excess sodium hydroxide. Metallic impurities from the corrosion of stainless steel vessels are also present. Radiochemical purity of I¹³¹ plus I¹³³ is greater than 99%. Even the condensate collected from the dissolver contains only a very slight amount of entrained dissolver solution; no evidence of the distillation of ruthenium or other fission products has been noted. Potassium permanganate is used to oxidize to iodate⁽¹⁰⁾ since the oxidation may be started in alkaline solution and finished in acid solution. Phosphorous acid, catalyzed with hydrogen peroxide, has been studied by Chaney⁽¹¹⁾ as a reducing agent for the micro-determination of iodine. This reagent has proved very effective for reducing permanganate and iodate, although it is possible to add too much phosphorous acid and reduce the iodine to iodide, which is relatively non-volatile.

The distillation is conducted under a slight vacuum and air is drawn through the distilling liquid to increase the efficiency of the distillation⁽¹²⁾.

The iodine is distilled into sodium hydroxide-sodium sulfite solution and tends to be reduced to the iodide. However, upon standing, oxygen of the air and hydrogen peroxide formed by beta irradiation of water tend to produce iodate. This will be the subject of further study. Iodine preparations have been found to be radiochemically pure, within the limits of existing analytical methods. Chemical impurities, except for a trace of nitrate, are only those added with the sodium hydroxide, sodium sulfite, and distilled water.

6.0 ACKNOWLEDGMENTS

We wish to acknowledge particularly the assistance of E. E. Pierce in this project. Assistance and suggestions were also contributed by R. P. Shields, E. G. Richardson, P. B. Orr, E. M. King, and R. B. Waters.

7.0 REFERENCES

- (1) D. S. Ballantine and W. Cohn, MDDC-1600, (1947)
- (2) J. Dreher, H. Karmack and S. Thompson, (H)(CN-3285), (1945)
- (3) L. Glendenin, CC-2218, (1945)
- (4) S. Freed, G. Hebert, J. Dial, A. Bogard and A. Brosi, Memorandum No. 47-9-538, (1947)
- (5) Latimer, The Oxidation States of the Elements, Prentice-Hall, Inc., (1938)
- (6) E. Moles and A. Perez-Vitoria, Bol. Acad. ciencia exactas fis-quim, 1, 5-6, (1936)
- (7) H. Liebhafsky, J. Am. Chem. Soc., 56, 2369, (1934)
- (8) W. Bray, J. Am. Chem. Soc., 43, 1262, (1921)
- (9) R. Luther and G. Sammet, Z. Electrochemie, 11, 293, (1905)
- (10) N. L. Matthews, G. M. Curtis, and W. R. Brode, Ind. & Eng. Chem., 10, 612, (1938)
- (11) A. L. Chaney, Ind. & Eng. Chem., 12, 179, (1940)
- (12) A. G. Bratton and J. F. McClendon, Ind. & Eng. Chem., 10, 600, (1938)

8.0 EQUIPMENT DRAWING REFERENCES

<u>Drawing No.</u>	<u>Title</u>
C-956	Fission I131 Drawing List
D-970	Dissolver
C-977	I131 Vacuum Pot
D-984	I131 Condenser and Connecting Pipe
D-985	Piping Inside Dissolver
C-989	Slug Carrier Tube
D-990	3-Slug Carrier
D-1574	Dissolver Support
D-1575	Dissolver Shield Support
D-1576	Sampler Elevator
D-1577	I131 Hood Revision - Room 10
D-1578	Front Wall Assembly
D-1579	Doors and Door Support - Room 10 Hood
C-1580	Hood Floor - Room 10
C-1601	Sampler - Pyrex Glass
B-1602	Sampler Carrier (Lead)
C-1603	Probe Shield and Support
C-1605	Manometer Line Expansion Chamber
D-1606	Slug Carrier Yoke
A-1607	Remote Control Yoke for Sampler
B-1608	Glass Sampler Bracket
B-1609	Sampler Outside Mirror Frame and Bracket
B-1610	Sampler Inside Mirror Frame and Bracket
D-2327	Vacuum Pot Support
B-2328	Reflux Condenser Support
B-2329	Condenser Support
C-2330	Jet Discharge Condenser and Support
D-2331	Gas Scrubber
C-2332	Primary Still Condenser
C-2333	Entrainment Separator
C-2334	Distillate Receiver
C-2335	Solution Addition Funnel Rack
C-2336	Catch Tank and Bracket
D-2337	Ammonia Piping
C-2338	Still
D-2340	Sampler Shield and Rack
C-3688	Room 10, Product Transfer Pot Shield
A-3689	Remote Control Knob and Rod for Room 10 Hood
C-3690	Glassware Support for Hood in Room 10
C-3691	Bracket and Shield for Burner
C-3692	Bracket and Extension Arm Burner Support
C-3693	Shield for Burner
C-3694	Transfer Vessel - Liquid Depth Indicator - Room 10
D-3695	Bending Jig - Assembly
D-3696	Bending Jig - Details No. 1
C-3697	Bending Jig - Details No. 2
D-3698	Probe Shield Details 2, 3, 8 and 11
C-3699	Probe Shield Support

<u>Drawing No.</u>	<u>Title</u>
C-4005	Bevel Gear Drive for Burner Bracket
D-4677	Probe Shield Assembly
A-4678	Probe Shield Details 6 and 7 - Clamps
A-4679	Probe Shield Details 9 - Body
D-4718	I131 Distilling Flask and Head
A-4719	Modified Flexaframe Type "C" Clamp
C-4720	Fission I131 Drawing List
A-4721	Modified Flexaframe
B-4722	Stack Extension
A-4723	Concrete Plug
D-4724	Panel Board
D-4725	I131 Flowsheet - Room 10
A-4742	Room 10 Hood - PH Vessel
C-4745	I131 Reel and Box
B-4746	Lead Brick Support
C-4747	I131 Miscellaneous Sampler Fittings
C-4748	Ta to Steel Connector
C-4749	Room 10 Hood - Off Gas Bubblers
C-4751	Receiver for Hood - Room 10
E-4752	I131 Equipment Flowsheet
C-4753	I131 Fission Process Off-Gas System
B-4754	Plug for Vent Duct, Cell 3, Bank 2
C-4755	Expansion Chamber for Sampler
C-4756	Mix Pot, Lid and Coil
C-4757	Waste Hold Up Tank
D-4768	Pre-Evaporator Assembly
D-4769	Pre-Evaporator Details
C-4770	Calibration Curve - Dissolver
C-4771	Calibration Curve - Catch Tank
C-4772	Calibration Curve - Still
C-4773	Calibration Curve - Distillate Receiver
E-4774	I131 Fission Flow Diagram
E-4775	External Piping and Instrumentation Cell 3, Bank 2
Q-583-A*	Gamma Ionization Chamber, Assembly
Q-583-B*	Gamma Ionization Chamber, Details
Q-826-B*	Low Drift A.C. Electrometer
H-9-26-46**	Ta Connecting Pipe
D-4479-1**	Reflux Condenser
D-4533-3**	Ta Lined S.S. Dissolver

* ORNL Instrument Department Drawings.

** Fansteel Metallurgical Corporation Drawings.