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Report No. BMI-530

PROGRESS REPORT

on

ZIRCONIUM PILOT PLANT
RESEARCH AND DEVELOPMENT

to

ATOMIC ENERGY COMMISSION
CONTRACT NO. AT(30-1)-771B

by

O. E. Accountius, D. G. Black, C. E. Dryden,
B. C. Finney, B. A. Gruber, W. G. Jurevic,
R. McDonough, L. F. Plock, D. J. Stephan,
S. A. Woodruff, and I. E. Campbell

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BATTELLE MEMORIAL INSTITUTE

September 20, 1951

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II

TABLE OF CONTENTS

	<u>Page</u>
SUMMARY	1
INTRODUCTION.	2
PLANT OPERATION	3
Status of Repairs and Modification of Equipment.	3
Fast Vaporizer-Condenser (E V-C).	3
Four-Inch Hastelloy Valves.	4
Vacuum Pumps.	4
Iodination Run No. 3	5
Deposition Run No. 3	7
Multiple Filament	7
Single Filament	8
Inspection of Process Equipment.	8
Leak-Rate Criterion.	9
EXPERIMENTAL PROGRAM.	11
Sublimation Properties of Zirconium Iodide	11
Iodination of Zirconium Carbide.	13

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SUMMARY

The vaporizer condenser which had seven defective fin tubes was repaired and placed in operation on September 4. It was used to condense 430 pounds of zirconium iodide made in the third iodination run. No salt leakage occurred.

In preparing this iodide, Foote sponge was used. Vigorous gasification occurred during the last stages of dehydration where heat was applied. This reaction with water did not hinder subsequent iodination.

A third deposition run was made using both single and multiple filaments. With the multiple-filament configuration of four hairpins, deposition proceeded at a rate of 0.8 pound per hour for 2-1/2 hours, when a burn-out occurred. The pressure in the system was high (5 mm.),

indicating plugging. On switching to the single filament, the pressure gradually rose to 30 mm. and no metal could be deposited. By inspecting the units after shut-down, a plug was found at the entrance to each iodine condenser. The iodide condensers were in good condition. It is planned to overcome this plugging condition by modifying the coolant flows and raising the temperature of the connecting line between the iodide and iodine condensers.

Laboratory experiments on repeated sublimations of ZrI_4 are completed. When ZrI_4 is prepared "in situ" as a duplication of plant runs, the high-boiling fractions are reduced. The small quantity of greyish residue is probably an impurity in the zirconium sponge.

The iodination tower to be used in iodinating zirconium carbide and zirconium carbonitride has been completed and its electrical and temperature characteristics have been found satisfactory. The preparation of iodide in this small pilot unit will proceed immediately.

The leak-rate problem in the plant is discussed from both the ideal and practical points of view. The present leak rate of 120 micron cubic feet per minute cannot be lowered to an ideal value of below 42 micron cubic feet per minute until defective bellows in the Hastelloy valves are replaced.

INTRODUCTION

Two iodination and deposition runs were completed as of August 20. The second deposition run showed marked improvement over the first run but salt and air leakages through faulty Hastelloy welds were still hampering the testing program. A major shut-down was necessitated by

salt leakage onto one of the finned tube vaporizer-condensers. After some difficulty, small leaks around the fin spot welds were found in 7 of 24 tubes. In addition, the outside shell had cracked at the circumferential weld. A thorough repair job was done on the unit.

PLANT OPERATION

Status of Repairs and Modification of Equipment

East Vaporizer-Condenser (E V-C)

This condenser was removed for repairs because of salt leakage from the inside of the bayonet fin tubes into the vaporizing section. A careful leak test was carried out, and small leaks were discovered under spot welds in 7 of 24 tubes. It was impossible to replace these tubes in a reasonable length of time so they were blanked over at the bottom and the corresponding bayonet tubes sawed off.

On leak testing the shell, transverse cracks were found in a circumferential weld adjacent to a strip heater. Following an X-ray examination of the section, the metal around the cracks was ground out and the cracks repaired by welding. However, the localized heating caused other cracks to appear, and a large circumferential patch of Hastelloy C had to be welded over the section.

This trouble warned that the placement of strip heaters next to Hastelloy metal, particularly in the vicinity of welds, should be avoided. A high-conductivity metal sheath should be spot-welded over the Hastelloy before attaching the strip heaters. Since the plant was found to operate without the use of strip heaters, except in

emergencies such as salt leakage through the bayonet tubes, the use of strip heaters on vaporizing cycles has been temporarily discontinued.

The failure of some of the fin tubes was discussed with the supplier, the Brown Fintube Company. They stated that this was the first Hastelloy they had ever fabricated. There may have been faulty welding, but they were not aware of it. Nothing further could be done about the matter.

Four-Inch Hastelloy Valves

The trouble with leaking Hastelloy bellows continues. A report received this month from the Cook Electric Company states that inclusions in the Hastelloy metal received from the Haines-Stellite Company were to blame for the crack in the particular bellows they inspected. Chemical corrosion had occurred in the area around the inclusion, thus starting the crack. Negotiations are being made to secure an Inconel or 347 stainless steel bellows for the spare valve so that an actual plant service test can be carried out.

Meanwhile, the plant is being operated by pumping on the exhaust ports of all the valve bellows. While this reduces the air leakage into the system, only a tight bellows will insure leak rates well under the specified maximum.

Vacuum Pumps

To avoid the nuisance of frequent oil changes, sticking and corrosion of valves, and to maintain steady vacuum operation, a Hilco Oil Reclaim Unit, Model EM-1, is being purchased. It will be delivered at Battelle on October 15, barring material shortages.

Iodination Run No. 3

In preparation for the third deposition run, more iodide was required since not more than 150 pounds remained from the last deposition run, D2.

The starting crude zirconium for the run was taken from the first shipment of the Foote Mineral Company. The two previous batches had been largely TAM material. The Foote material had a larger percentage of fines than that of TAM. However, material smaller than 12 mesh was rejected. The lot also contained old filament ends which were not charged to the tower.

A summary of iodination Run No. 3 is found in Table 1. Dehydration at low temperatures proceeded smoothly. To remove the last traces of water, heat was applied gradually by pulsing salt in the zirconium tower jacket. After 8 minutes the tower temperature rose rapidly to 800°C. and a gas evolution started. This subsided quickly, but the behavior at this stage was different from the last two runs. Since Foote sponge appears quite reactive, it was thought that the observed reaction was that with residual water vapor. The tower contents were inspected before iodination and found to be covered with greyish-white dust, probably zirconia.

Iodination proceeded at a pressure greater than 5 mm. since a simultaneous degassing occurred. The tower temperatures were, on the average, lower than previously experienced. However, very little residual iodine was recovered from the iodine condenser and the discharged tower residue did not burn in air. The zirconium tetraiodide yield should be quite good. The tetraiodide was transferred to the deposition system within 8 hours.

TABLE 1. SUMMARY OF DATA FOR IODINATION

	Run No. 3
Type of zirconium	Footc
Weight of crude zirconium charged, pounds	92
Weight of water removed, pounds	9
Weight of iodine used, pounds	416
Cycle time	
Charging time, hours	1
Dewatering and degassing (including week end), hours	65
Iodination, hours	17
Cooling and discharging, hours	8
Average iodine flow rate, pounds per hour	24.5
Weight of unreacted residue, pounds	17
Per cent unreacted residue	20.8
Range of tower temperatures observed during iodination	350-670°C.
Estimated weight of ZrI_4 produced, pounds	430

Since no NO_2 fumes were observed during operation, it was concluded that the E V-C had been satisfactorily repaired.

The tower has been reloaded with TAM sponge and the fourth iodination run is under way. The goal is to produce about 1000 pounds of ZrI_4 for the deposition cycle to test the original design capacities of the condensers.

Deposition Run No. 3

Multiple Filament

A filament, 41 feet, 8-3/4 inches in length and 0.203 inch in diameter, weighing 3.7 pounds, was made by welding together the ends of two similar pieces. This was bent into four hairpins and attached to the multiple-filament assembly. Three 20-mil molybdenum wire supports were attached to each insulator. Vaporization of the iodide from S V-C to N V-C was started. After one hour, the filament was heated rapidly to a K per cm. value of 0.6. Deposition immediately started and continued at a steady rate for 2-1/2 hours before a burn-out occurred. The flow of vapor was from top to bottom and the total bulb pressure was steady at 5 mm. pressure. The production rate during this period was 0.8 pound per hour.

Inspection of the filament assembly showed that the wire had been corroded through at the point of attachment of the molybdenum wire at one of the four bottom supports. The other three were also badly attacked. There was no noticeable corroding at the top supports. These results are not unreasonable, since the bottom region would have a higher iodine concentration in downward flow.

In preparing the next multiple-filament assembly, only a single strand of 20-mil molybdenum wire will be used and the operating K will be increased. To duplicate the Westinghouse assembly, 30-mil molybdenum wire was ordered several months ago from Fansteel Metallurgical Company, but the shipment has not yet been received.

The zirconium deposited was quite bright and showed no evidence of a nitride coating. Traces of NO_2 gas were exhausted for several minutes when the vaporization was first started.

The lower rate of deposition, compared with Run No. 2 (0.8 versus 1.05 pounds per hour), could be the result of the high deposition bulb pressure in the latter run. Since this high-pressure condition was further exaggerated on shifting to the single filament assembly, a more complete discussion of pressure build-up follows.

Single Filament

The operation was shifted to the bulb containing the single filament with the vaporizing flow maintained in the same direction. No deposition occurred during a two-hour interval so the cycle was reversed. The bulb pressure rose gradually from 5 to over 30 millimeters with no deposition even at a K/cm. of 1.6. This condition was maintained for 24 hours while attempts were made to locate the pressure block with argon gas. Nothing definite could be established, so that the system had to be shut down for inspection.

Inspection of Process Equipment

All of the condensing units for both iodide and iodine were opened for inspection. There was an excessive quantity of iodine vapor

in the iodide condensers, indicating the presence of a plug, either in the iodide condenser or in the connecting piping between the iodide and iodine condensers. When the south system acted as a condensing unit, the pressure build-up occurred. On removal of the valve between the two condensers, a solid plug was found at the entrance to the iodine condenser. The solid material in the plug consisted of iodine, zirconium iodide, and zirconium oxide. Since the bellows on this valve, I-6, leak badly, it was not surprising to discover oxide present. This condition will be remedied by running the valve box temperature higher, and controlling the coolant flows to the two condensers. It is planned to run the iodide condensing salt at a lower temperature and lower flow rate in order to keep the bottom section colder while maintaining the top section hotter. This should give a better distribution of iodide over the entire length of the condenser. The brine flow to the iodine condensers will be reversed to keep the fin tubes at the vapor entrance warmer than at the exit.

The fin tubes in all of the iodide condensers are in good shape, and have no oxide scale. The system seems capable of handling 1000 pounds of iodide so that present plans are to clean out plugs in the iodine condensers. Another 500 pounds of iodide will be added to the deposition system by completing iodination Run No. 4. Deposition will then proceed with a rated capacity of iodide.

Leak-Rate Criterion

There has been some question about the criterion picked for calculating the maximum allowable air-leak rate into the deposition

process equipment. As a first practical operating goal, an allowable leak rate was chosen such that the crystal bar would contain 50 parts per million of nitrogen, if all of the air which leaked into the system reacted with the zirconium crystal bar. This in it self provides a safety factor since a portion of the air may leak around flanges and valves which are located between the deposition bulb and the vacuum pump.

To establish a figure for the permissible air leakage as micron cubic feet per minute, a formula was derived from ideal gas laws on the basis of the assumption stated above.

Let L = pressure rise, microns per minute,

V = volume of the system, cubic feet,

T = temperature of the system, °K.,

Z = zirconium production, pounds per hour. Then the maximum allowable leak rate is

$LV = 0.0364ZT$ micron cubic feet per minute. Using this formula, the following table gives some working values for cold and hot leak rate tests based on production rates of 1 and 4 pounds of zirconium per hour.

TABLE 2. MAXIMUM ALLOWABLE LEAK
RATES CALCULATIONS

Zirconium Production, lbs./hour, Z	System Temperature, T, °K.	Leak Rate, micron cu. ft./minute, LV
1	300	10.6
1	573	20.3
4	300	42.4
4	573	81.2

Only cold leak rate test results have been reported so far. Since the outgassing rate of the system at higher temperatures is

excessive, it requires a great deal more time to establish a valid hot leak rate under these conditions. The lowest value reported thus far (see BMI-529, p. 5) for the system is a cold leak rate value of 120 micron cubic feet per minute. This cannot be lowered until the valve bellows situation is remedied and the plant is operating with vacuum-tight valves.

EXPERIMENTAL PROGRAM

Sublimation Properties of Zirconium Iodide

In previous reports (BMI-528 and 529), repeated sublimation of zirconium iodide always yielded higher boiling residues, the chemical composition of which could not be reliably established. The zirconium iodide used as starting material was that made in the NRC unit while studying the iodination of zirconium machine turnings. It is quite possible that this material contained excess zirconium and combined oxygen. A chemical assay of 17 per cent zirconium showed that either or both were possibilities.

Because of the uncertainty of the starting material in the experiments reported last month, zirconium iodide, formed directly in the vacuum train by passing iodine through a heated tube containing dehydrated zirconium sponge, was used to simulate actual plant operation.

Two experiments were carried out using this technique. In Run No. 6 there was an excess of iodine over the stoichiometric requirement if all of the zirconium present were reactive. In Run No. 8, there was an excess of zirconium present. However, since the iodination

was a flow process with gaseous iodine reacting with zirconium packed in a tube, there was an excess of zirconium present at all times. The Vycor reaction tube was maintained at a dull red heat, but not all of the zirconium reacted. However, sufficient iodide was prepared to carry out repeated sublimations. Results of both runs are listed in Table 3.

TABLE 3. REPEATED SUBLIMATION
OF ZrI_4 PREPARED IN SITU

Temperature Range of Subliming Zone, °C.	Vacuum at Pump, microns	Weight of High-Boiling Residue, grams	Per Cent of Residue Based on Initial ZrI_4 Used
<u>Run No. 6</u>			
300-500	33	0.3	4.3
250-300	28	0.2	2.9
220-250	30	1.5	21.4
180-220	30	5.0	71.4
<u>Run No. 8</u>			
>500	45	0.0	0.0
300-500	100	0.0	0.0
250-300	90	1.4	8.5
180-250	90	15.0	91.5

All of the high-boiling residues had a greyish appearance and gave off iodine vapors on ignition with a loss of about one-third the initial weight.

In Run No. 8 it was shown that no residue existed after sublimation above 300°C. and a pressure of noncondensibles of less than 100 microns. This is the first experiment in which no residue was found. The 8.5 per cent nonvolatile fraction from the sublimation between 250° and 300°C. possessed the characteristic grey color. From the nature of these experiments, one can speculate as to the possible

6146-14

chemical constituents of these residues. Because there is excess zirconium present in the heated tube at all times, it is possible to form di- and tri-iodides which are boiled or entrained into the condenser. A second possibility would be impurities in the zirconium sponge which form high boiling iodides and distill over per se. The third possibility would be an oxyiodide, the oxygen being supplied by an initial chemisorption on the zirconium sponge which can only be freed by a high-temperature reaction on the surface. In any event, it seems possible to recover pure ZrI_4 from the plant iodination tower if the gas velocity is maintained low enough to prevent entrainment and if excessive iodination temperatures are avoided. The grayish residues observed in the laboratory experiments are also found after each iodination run in the bottom of the zirconium tower and no residues have been observed on the finned tube condenser. An effective fractionation of ZrI_4 from the high-boiling constituents is thus being carried out in the plant.

Iodination of Zirconium Carbide

The apparatus has been assembled. The split graphite electrode was tested at a rated power of 10 kw. and the furnace temperature reached 1050°C. with no difficulty. The copper electrodes overheated so that it was necessary to provide water cooling. Iodination of carbide should start the week of September 17.

OEA: DGB: CED: BCF: BAG: WGJ: RM: LFP: DJS: SAW: IEC: jer
September 24, 1951