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**SEPARATION OF ZIRCONIUM AND HAFNIUM.
PROPOSAL FOR CONSTRUCTION AND
OPERATION OF ZIRCONIUM PRODUCTION
PLANT**

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March 14, 1950

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2

Y-573

CARBIDE AND CARBON CHEMICALS DIVISION
UNION CARBIDE AND CARBON CORPORATION
Y-12 PLANT

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CHEMICAL DIVISION
Mr. J. M. Herndon, Superintendent

SEPARATION OF ZIRCONIUM & HAFNIUM - PROPOSAL FOR
CONSTRUCTION & OPERATION OF ZIRCONIUM PRODUCTION
PLANT

Abstract

A re-evaluation of the cost of producing essentially hafnium-free zirconium as zirconium oxide at a rate of 150,000 - 200,000 pounds zirconium per year by solvent extraction of the metal thiocyanates in a permanent plant has been made. Using part of the present temporary facilities, the cost, with five year amortization of the plant, will be \$3.15 per pound zirconium. A by-product of the mixed oxides of hafnium and zirconium, having at least fifty percent hafnium and perhaps as high as ninety percent hafnium, can be made available with little additional cost.

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INTRODUCTION

Because of recent developments made in the zirconium purification process, a revised cost estimate for the construction and operation of facilities for this production is submitted. Chemical costs will be reduced substantially by increases in process efficiency, substitution of less expensive reagent chemicals, and decreases in chemical consumption by recycling. Since approximately seventy percent of the estimated chemicals cost is zirconium tetrachloride feed, substitution of some other material may result in additional savings. A complete report on these developments will be submitted when the data is tabulated.

Incorporation of existing extraction facilities in a permanent plant will result in an appreciable reduction in construction cost. The proposed plant will produce from 150,000 to 200,000 pounds zirconium per year at an operational cost of \$2.22 per pound of zirconium produced, based on the lower production rate. Total costs of \$3.15 per pound zirconium produced include plant amortization and all allocated plant expense. Appreciable savings in labor, allocated plant expense, utilities, and plant amortization will result if the higher rate of production is obtained as expected. A by-product analyzing 50 - 90 percent hafnium, zirconium basis, and containing 2,500 to 3,000 pounds hafnium per year will be produced.

DISCUSSION

As outlined in Report Y-553 the separation of zirconium from hafnium by solvent extraction of the metal thiocyanate complex has been achieved in the laboratory, demonstrated on a pilot plant scale, and the process has been operating on a production scale since early January. Because of developments made by the Production and Research Divisions during the production period, substantial cost reductions can be realized by modification of the original process. These modifications involve an increase in the percentage zirconium recovery in extraction by the addition of stripping columns and the substitution of phthalic anhydride for salicylic acid in the purification of zirconium oxide. The ease of metathesis of the phthalate precipitate to the hydrous oxide greatly reduces the difficulty of the drying and calcining operation, and the major portion of the phthalate is available for re-use. Experience in operating the temporary four-inch glass column extraction plant indicates that production can be substantially higher than was originally postulated. This will permit incorporation of the existing temporary extraction facilities into a permanent plant with a capacity of 150,000 to 200,000 pounds per year of essentially hafnium free zirconium as purified oxide. Increasing extraction yields to reduce the cost will result in a by-product of highly enriched hafnium; depending on the feed materials obtained, this will be between 50 - 90 percent hafnium in the proposed plant.

RECOVERY OF ENRICHED HAFNIUM

With the zirconium tetrachloride as the most expensive single item in the plant operations, it is essential that the zirconium loss be kept to an absolute minimum. Preliminary pilot plant results indicate that with the column length

included in the proposed plant and starting with feed materials having two percent hafnium the yields of zirconium will be between 97 and 99 percent of that charged. The loss of hafnium in this product will be about two percent of the element charged. Under these operational conditions the hafnium content of the hafnium-zirconium waste will be at least fifty percent, and will probably be much higher as more experience is gained with the plant. For the most economical operations as a zirconium producer the sulfuric acid waste containing the hafnium would be neutralized with lime and discarded. Because of the large amount of calcium sulfate formed, recovery of hafnium from this would be difficult. However, if the hafnium is considered of sufficient value to be reclaimed, the substitution of ammonia for lime for this neutralization and the installation of a filter press as indicated in the flow diagram will permit the recovery of at least ninety percent of the enriched hafnium as a fairly pure hydroxide with an additional cost of about \$0.03 per pound of zirconium produced. Since this makes the cost of the hafnium no more than a few dollars a pound, and this will be the worlds only large source of high hafnium materials, it is felt that the collecting and storing of this waste is justified at the low additional cost indicated.

ZIRCONIUM RAW MATERIALS

The only remaining cost of the proposed operation which can be significantly reduced is that spent for the zirconium feed. To do this there must be either a reduction of the present price of the chloride or the substitution of another material. Since the feed to the plant must be in hydrochloric solution this limits one to the present tetrachloride, the zirconyl chloride or the HCl soluble hydroxides.

Of these, none is on the market at a price more favorable than the present feed. However, if some oxide ore like baddeleyite can be obtained for less than one hundred dollars per ton, preliminary experiments indicate that a saturated solution of zirconyl chloride can be prepared for less than \$0.50 per pound of zirconium by means of sulfuric acid leaches and ammonium hydroxide precipitations under controlled conditions followed by solution in HCl. Whether or not an equally cheap process for the zircon type ores can be devised has not been investigated. Perhaps the availability of such a process would influence the present cost of the tetrachloride.

COST ESTIMATES

A revised cost estimate taking advantage of the improvements outlined is submitted. This cost estimate is based on a production rate of 150,000 pounds of zirconium per year which, if two percent hafnium on zirconium basis, will give a potential of 2,500 - 3,000 pounds of hafnium per year. If a higher rate of production is obtained, labor, overhead, utilities, and amortization costs will be reduced accordingly. In view of additional operating experience, estimates relative to utilities have been increased above costs listed in Y-553. Other costs such as transportation, shipping containers, etc., have been added. Chemical costs listed in Y-553 on page 12 are in error by \$0.21 per pound zirconium produced because of transposition of the incorrect figures from pages 7 and 9.

OPERATING COSTS - BASIS ONE POUND ZIRCONIUM PRODUCEDOPERATING COSTSChemical Costs (Including transportation)Extraction

Ammonium Thiocyanate	\$ 0.05
Hexone	0.07
Sulfuric Acid	0.02
Hydrochloric Acid	0.04
Ammonium Hydroxide	0.04

Sub Total \$ 0.22

Purification

Phthalic Anhydride	\$ 0.11
Ammonium Hydroxide	0.05
Lime	0.01

Sub Total \$ 0.17

Total Chemical Costs (exclusive of zirconium tetrachloride) \$ 0.39

Zirconium Tetrachloride \$ 0.95

Total Chemical Costs (including zirconium tetrachloride) \$ 1.34

Miscellaneous Costs (protective clothing, shipping containers, etc.) \$ 0.02

Labor Costs \$ 0.55

Analytical Costs \$ 0.07

Maintenance (labor and materials) \$ 0.08

Utilities \$ 0.16

TOTAL OPERATING COSTS \$ 2.22

CONSTRUCTION COSTS

Detailed estimates are based on the following factors:

Location

Because of the high rate of production obtained in the temporary extraction plant located in Building 9211, Y-12, it is proposed that this installation be incorporated in a permanent plant. Existing extraction and scrubbing columns and related service piping will be essentially unchanged; stripping columns, precipitation vessels and filters will be provided for recovery of chemicals on a semi-continuous basis. Space is available for installation of purification and burning facilities in this building. These operations will be on a continuous basis.

Materials of Construction

Materials of construction will be essentially as outlined in Report Y-553. Equipment needed for the additional processing proposed in the introduction will not have to be corrosion resistant except for the stripping columns and auxiliaries.

Chemical Reagent Storage

Tanks for ammonium hydroxide and concentrated sulfuric acid are available at the proposed site. The distribution system is partially complete for both reagents.

Construction Time

Except for delivery of special equipment such as the calcining furnace, construction can be completed in six months.

Plant Amortization

The cost of the plant (direct cost to the government) has been amortized on a five year basis.

COST ESTIMATE TO ADD NECESSARY FACILITIES TO EXISTINGEXTRACTION PLANT FOR PRODUCTION OF ZIRCONIUM

	<u>Materials</u> <u>To be Purchased</u>	<u>Labor</u>
Preparation of Site	\$ 200.00	\$ 697.50
Chemical Supply System	1,000.00	2,090.00
Extraction System	1,950.00	1,995.00
Stripping System	200.00	285.00
Hafnium Enrichment System	2,050.00	1,330.00
Hafnium Recovery System	2,350.00	1,710.00
NH ₄ CNS Recovery	5,100.00	3,800.00
Purification System	11,950.00	7,030.00
Furnaces	21,000.00	3,800.00
Waste Disposal System	300.00	760.00
Service Piping, Fume Removal, Lighting, Paint, etc.	2,500.00	4,275.00
Engineering		3,000.00
Totals	\$ 48,600.00	\$ 30,772.50
Contingencies		\$ 11,014.50

SUMMARY OF COSTS

Direct Cost to Government, Including Contingencies	\$ 90,386.50
Allocated Plant Expense	30,772.50
Y-12 Equipment to be Used	34,000.00
Estimated Value of Existing Zirconium Extraction Plant in Building 9211	60,000.00
TOTAL	\$215,159.00

GENERAL SUMMARY SHEET

Unit Cost Per Pound of Zirconium Produced

OPERATING COSTS

Chemical Costs	\$ 0.39
Zirconium Tetrachloride	0.95
Labor	0.55
Analytical Labor & Material	0.07
Maintenance	0.08
Miscellaneous	0.02
Utilities	<u>0.16</u>

<u>TOTAL OPERATING COSTS</u>	\$ 2.22
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<u>PLANT AMORTIZATION</u> (based on direct cost to Government)	0.12
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ALLOCATED PLANT EXPENSE

Labor	0.61
Utilities	<u>0.20</u>

TOTAL COST	\$ 3.15
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Fig. 1 Zirconium Purification Plant Flow Sheet.

0-12