SEPARATION OF [illegible] SYSTEM & HAFNIUM [illegible] FOR CONSTRUCTION [illegible] DEVIRCONIZATION

[illegible]

[illegible] CARBIDE AND CARBON [illegible] COMPANY

[illegible] CORPORATION

[illegible]

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1979

#970

1-715
10-715

11735-C
A-28260

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Index No. Y-573
This document contains 12 pages.
This is copy 1 of 35, Series B.

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

W-7405-Eng-26

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.

J. M. Googin
G. A. Strasser

Oak Ridge, Tennessee
March 14, 1950

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Date Issued: October 15, 1951

[redacted]

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

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 evaluated.

Incorporation of existing extraction facilities in the permanent plant will result in an appreciable reduction in construction costs. 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 operating plant expense, utilities, and plant amortization will result if the higher rate of production is obtained as expected. A by-product analyzing [illegible] percent hafnium, zirconium basis, and containing 2,500 to 3,000 pounds hafnium per year will be produced.

[redacted]

[illegible]

DISCUSSION

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

RECOVERY OF ENRICHED HAFNIUM

With the zirconium tetrachloride [illegible] single item in the plant operations, it is essential that [illegible] to an absolute minimum. Preliminary pilot plant results [illegible] column length

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included in the proposed plant and starting [illegible] materials having two percent hafnium the yields of zirconium will be between [illegible] and [illegible] percent of that charged. The loss of hafnium in this product will be about [illegible] 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 [illegible] formed, recovery of hafnium from this would be difficult. However, if the hafnium is considered of sufficient value to be reclaimed, the substitution of [illegible] for lime for this neutralization and the installation of a filter [illegible] indicated in the flow diagram will permit the recovery of at least ninety percent of the contained hafnium as a fairly pure hydroxide with an additional cost of [illegible] per pound of zirconium produced. Since this makes the cost of the hafnium [illegible] than a few dollars a pound and this will be the worlds only large source of hafnium materials, it is felt that the collecting and storing of this [illegible] the low additional cost indicated.

ZIRCONIUM RAW MATERIALS

The only remaining cost of the proposed operation [illegible] can be significantly reduced is that spent for the zirconium [illegible] there must be either a reduction of the present price of the [illegible] substitution of another material. Since the feed to the plant must be [illegible] solution this limits one to the present tetrachloride, the zirconyl [illegible] soluble hydroxides.

Of these, none is on the market at a price more [illegible] 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 [illegible] pound of zirconium by means of sulfuric acid leaches and ammonium hydroxide precipitations under controlled conditions followed by solution in HCl. The [illegible] quite 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 [illegible] for 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 a [illegible] basis, will give a potential of 2,500 - 3,000 pounds of hafnium per year. [illegible] higher rate of production is obtained, labor, overhead, utilities, and [illegible] costs will be reduced accordingly. In view of additional operating experience, estimates relative to utilities have been increased above those [illegible] in Y-553. Other costs such as transportation, shipping containers, [illegible] have been added. Chemical costs listed in Y-553 on page 12 are in error by [illegible] pounds zirconium produced because of transposition of the incorrect [illegible] and [illegible].

OPERATING COSTS - BASIS ONE POUND ZIRCONIUM PRODUCED

OPERATING COSTS	
Chemical Costs (including transportation)	
Extraction	
Ammonium Thiocyanate	.05
Hexone	.07
Sulfuric Acid	.02
Hydrochloric Acid	.04
Ammonium Hydroxide	.04
Sub Total	
Purification	
Phthalic Anhydride	
Ammonium Hydroxide	
Lime	
Sub Total	
Total Chemical Costs (exclusive of Zirconium Tetrachloride)	$ 0.32
Zirconium Tetrachloride	$ 0.95
Total Chemical Costs (including Zirconium Tetrachloride)	$ 1.34
Miscellaneous Costs (protective [illegible], 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, the proposed [illegible] this installation be incorporated in a permanent plant. [illegible] 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 [illegible] 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 [illegible] in Report Y-553. Equipment needed for the additional processing proposed in the introduction will not have to be corrosion resistant except for [illegible] stripping columns and auxiliaries.

Chemical Reagent Storage

Tanks for ammonium hydroxide and concentrated nitric acid are available at the proposed site. The distribution system is [illegible] complete for both reagents.

Construction Time

Except for delivery of special equipment [illegible] burning furnace, construction can be completed in six months.

Plant Amortization

The cost of the plant direct [illegible] amortized on a five year basis.

[redacted]

COST ESTIMATE TO ADD NECESSARY FACILITIES TO EXISTING EXTRACTION PLANT FOR PRODUCTION OF ZIRCONIUM

	Materials To be Purchased	Labor
Preparation of Site	200.00	697.50
Chemical Supply System	600.00	2,090.00
Extraction System	850.00	1,995.00
Stripping System	00.00	285.00
Hafnium Enrichment System	1,050.00	1,330.00
Hafnium Recovery System	2,350.00	1,710.00
NH_4CNS Recovery	[illegible]	3,800.00
Purification System	[illegible]	7,030.00
Furnaces	[illegible]	3,800.00
Waste Disposal System	[illegible]	760.00
Service Piping, Fume Removal		
Lighting, Paint, etc.	2,500.00	4,275.00
Engineering		3,000.00
Totals	[illegible]	30,772.50
Contingencies		11,014.50

SUMMARY OF COSTS

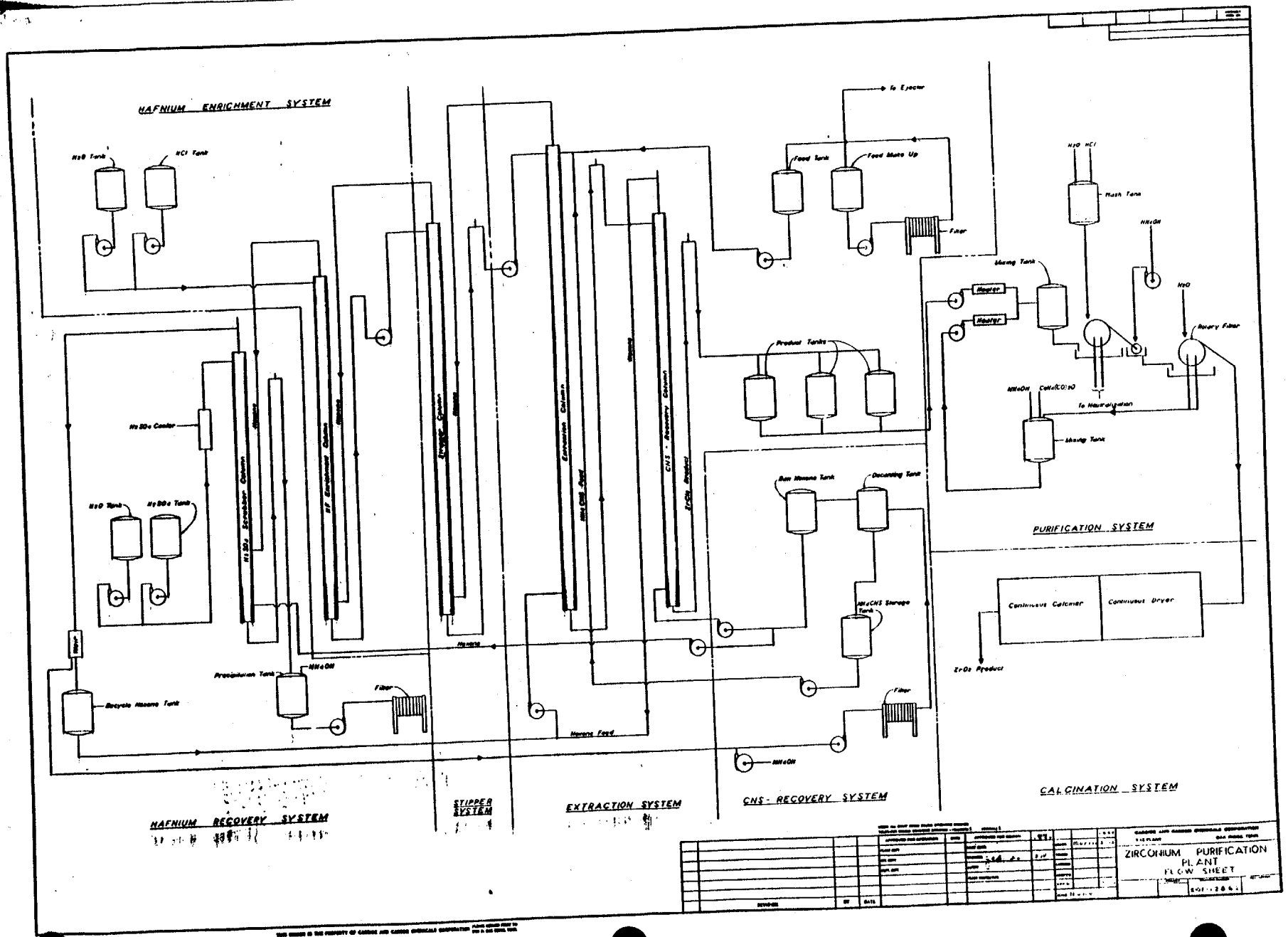
Direct Cost to Government, Including Contingencies	190,386.50
Allocated Plant Expense	30,772.50
Y-12 Equipment to be Used	34,000.00
Estimated Value of Existing Zirconium Plant in Building 9211	60,000.00
TOTAL	215,159.00

[redacted]

GENERAL SUMMARY SHEET

Unit Cost Per Pound of Zirconium Produced

OPERATING COSTS	
Chemical Costs	.39
Zirconium Tetrachloride	.95
Labor	.55
Analytical Labor & Material	.07
Maintenance	.08
Miscellaneous	.02
Utilities	0.16
TOTAL OPERATING COSTS	2
PLANT AMORTIZATION (based on direct cost to Government)	.12
ALLOCATED PLANT EXPENSE	
Labor	.61
Utilities	0.20
TOTAL COST	.15


HAFNIUM ENRICHMENT SYSTEM
HAFNIUM RECOVERY SYSTEM
STIPPER SYSTEM
EXTRACTION SYSTEM
CNS - RECOVERY SYSTEM
CALCINATION SYSTEM
PURIFICATION SYSTEM
To Ejector
Feed Tank
Feed Make Up
Filter
Wash Tank
Mixing Tank
Heater
Rotary Filter
To Neutralization
Product Tanks
Decanting Tank
Continuous Calciner
Continuous Dryer
Precipitation Tank
Recycle Hexone Tank
Hexone Feed
ZrO2 Product
ZIRCONIUM PURIFICATION PLANT FLOW SHEET