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STATUS REPORT AND PLANT PROPOSALS FOR ZIRCONIUM PURIFICATION

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CARBIDE AND CARBON CHEMICALS DIVISION
UNION CARBIDE AND CARBON CORPORATION
Y-12 Plant
Contract No. W-7405-Eng-26

Y-12 RESEARCH LABORATORY
Dr. E. D. Shipley, Director

CHEMICAL RESEARCH DIVISION
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STATUS REPORT AND PLANT PROPOSALS FOR ZIRCONIUM PURIFICATION

Abstract

This report contains a summary of the latest improvements in zirconium purification as developed by the Y-12 research, pilot plant, production, and engineering groups, all of whom have been generously cooperating in this project. Four distinct plant estimates are also proposed for the construction and operation of permanent zirconium purification facilities.

W. M. Leaders

Oak Ridge, Tennessee
January 20, 1950

STATUS REPORT ON JANUARY 17, 1950

SEPARATION OF ZIRCONIUM AND HAFNIUM

Selective Solvent Extraction of Thiocyanate Complexes

The separation of zirconium from hafnium has been achieved by the Y-12 laboratory and successfully demonstrated on a pilot plant scale during the last six months. The process involves the extraction of the metal thiocyanate complexes by a water immiscible solvent. In its present state of development, the process utilizes a solution of thiocyanic acid in a mixture of hexone and butyl acetate to extract hafnium from an aqueous phase containing zirconium, hafnium, chloride, sulfate, thiocyanate, hydrogen, and ammonium ions. The system is quite complex, containing about ten independent variables.

The research which led to the development of this process was inspired by similar work of Werner von Fischer, et al. (Zeit. fur Anorg. Chemie 1947-48) who were interested in preparing purified samples of hafnium. About the only common property of the present Y-12 process and this prior work is the thiocyanate. The research efforts in this laboratory have produced a system readily adapted to large scale production, whereas the German work was strictly for small scale laboratory application. After slightly more than three months of nearly continuous operation, most of the major and minor difficulties have become known and either solved or eliminated. Based on this operating experience, it appears that scale-up to a full sized production basis will be relatively simple.

This separation problem has been given extensive consideration since

August, 1949, by various groups in Y-12. Some of the major developments include the following:

Solvent. The original German work recommended diethyl ether as the solvent. This would have been entirely unsuited for large scale application because of the rapid rate of decomposition of the thiocyanate ions. Hexone was found to give a more favorable separation than ether and simultaneously to reduce the rate of thiocyanate decomposition. Further research established that a mixed solvent, containing about 20 percent butyl acetate in hexone, practically eliminated the difficulty due to decomposition. This mixture has been used for the last two months without difficulty.

Corrosion. The choice of equipment for this process is governed not only by cost and resistance to the corrosive action of the solutions used, but also by the purity that must be maintained in the final product. Research and experience gained in pilot plant operation indicate that glass lined equipment is very desirable from every consideration. The Hastelloys can be used at all points when necessary. In the alkaline region of the plant, ordinary 316 stainless steel is adequate. Rubber covered equipment is usable at all points except in the hexone-thiocyanic acid system. Several plastics and coating materials have been found which are acceptable for various services. Sufficient latitude has been found in acceptable materials of construction, which, combined with the mechanical simplicity of the equipment required, makes possible the design and construction of a production unit from commercially available standard equipment.

Solvent Recycle. The large quantities of solvent required in this process made the development of a suitable recycle system essential. The recycle system developed has given satisfactory service in the pilot plant thereby reducing solvent make-up costs to a small fraction of the value of solvent actually circulated.

Thiocyanate Recycle. Earlier reports on production costs included slightly more than $1.00 per pound, basis finished oxide, to cover the cost of the ammonium thiocyanate. This chemical was the largest cost item in the process. A recycle system has been developed which makes possible the recovery and reuse of practically all of the thiocyanate used. By the incorporation of this recycle system in the plants proposed herein, a saving of at least 90 percent of the cost of the thiocyanate is realized.

Operating Personnel. The operation of the pilot plant equipment during the past three months has made possible the training of a group of operators who are thoroughly grounded in the techniques involved in the zirconium-hafnium separation process. Several of these operators would be immediately available for service on a large plant if installed.

Production Costs

Chemical Costs. Improvements in operating technique combined with research advances have reduced the over-all chemical cost from $5.04 per pound of zirconium metal equivalent, which was the average cost during the first month's operation, to $2.54 per pound of zirconium in the purified oxide form. A detailed breakdown of these costs is listed below.

Item	Cost Per Pound of Zirconium Charged to the Plant: First Month	Cost Per Pound of Zirconium Charged to the Plant: Final Pilot Plant Cost
Sulfuric Acid	\$0.288	\$0.288
Hexone	0.463	0.338
Zirconium Tetrachloride	0.878	0.878
Ammonium Sulfate	0.158	0.158
Ammonium Thiocyanate	1.364	0.099
Ammonium Hydroxide	0.281	0.216
Hydrochloric Acid	0.194	0.148
	\$3.63	\$2.125
	Yield $\approx$ 72%	Yield $\approx$ 84%
	Cost of zirconium produced \$5.04 per pound	Cost of zirconium produced \$2.54 per pound

This marked reduction in chemical costs is the direct consequence of the research program which was conducted concurrently with the pilot plant operations. Initial operation of the pilot plant was undertaken with only a limited amount of completed research. Continued research and operation should also yield further reductions, although possibly not as spectacular as the period just mentioned. These figures are based on actual operating experience on a semi production scale and as such are very realistic.

Separation from Other Impurities. The figures quoted above are for the separation of hafnium from zirconium. It became apparent during the last few weeks of 1949 that after the removal of hafnium, it would be necessary to separate the other impurities from the zirconium oxide. Once the tentative specifications were available, a method was developed based on the precipitation of zirconium salicylate which would produce a material meeting these specifications. The method was given a thorough test on pilot plant scale and found to be entirely satisfactory. Several improvements were made during these pilot plant operations which made the method even more desirable from a production standpoint.

The chemical cost of this operation are as follows:

Basis one pound Zirconium	
Salicylic Acid	\$0.945
Other chemicals and supplies	0.07
	\$1.015

Yield 98% = \$1.04 cost per pound produced

Labor Costs. Because this process of separation of hafnium from zirconium is applicable to continuous processing methods, the labor cost is practically a fixed charge. Therefore, the cost per pound of product varies almost inversely with the quantity produced. The pilot plant installation operated with a direct labor cost of approximately \$700.00 per week. This is probably a minimum labor cost for safe operation on a 24 hour per day, seven day week basis. It is estimated that the maximum labor cost for a plant of 200,000 to 300,000 pounds per year capacity would be \$2,200.00 per week. These labor figures include the operation of the three units which make up the integrated zirconium purification system, viz., extraction of hafnium, separation from other impurities, and ignition to oxide. The variation in labor cost per pound of product with the size of the plant is estimated to be the following:

Plant Capacity	Labor Cost Per Pound of Zirconium
Production Unit	
1,000#/week	$1.50
2,000#/week	0.80
3,000#/week	0.60
6,000#/week	0.37

Thus, it becomes exceedingly clear that the thiocyanate process contributes its maximum benefit at the higher production capacities. Further increases in production as future needs demand would lead to even lower unit labor cost.

Recent Developments

During the first week of 1950, the Commission office in New York requested that Y-12 undertake the production of 25,000 pounds of zirconium oxide with less than 0.1 percent hafnium. Through the joint effort of the Chemical Research Division and the Production Division, major revisions were made on the previously existing pilot plant to accomodate these increases in throughput. A two section series fed column of total length equal to 60 feet was erected with its auxiliaries. A completely new purification plant was built and a furnace to burn the salicyate precipitate to the oxide was designed and built. All of this equipment has been operated successfully on a production basis.

The remarkable success achieved with these new production units greatly affects the over-all desirability of the thiocyanate process.

Radical innovations in the chemical make up of the feed solutions to the extraction unit, combined with an unexpected efficiency of the 60 foot extraction column have both contributed to marked decreases in the total cost of producing low hafnium zirconium oxide.

These new methods have completely eliminated one operation which was essential previously. The operation thus eliminated was an ammonia precipitation and filtration. This improvement further reduces the labor and chemical cost of the process.

Based on present production experience, the chemical cost for the extraction process of separating hafnium from zirconium are as follows:

Basis One Pound Zirconium Charged to Plant		
Zirconium Tetrachloride		$0.878
Sulfuric Acid		0.071
Hexone		0.085
Ammonium Thiocyanate		0.027
Ammonium Hydroxide	eliminated	
Hydrochloric Acid	eliminated	
Ammonium Sulfate	eliminated	
		$1.061

Yield 85%

Cost per pound of zirconium produced $1.25

Note: These costs are not being realized at the present time because recycle equipment for recovery and reuse of all of the hexone and thiocyanate could not be incorporated in the present plant both from lack of space and time. The permanent production units proposed herein incorporate all of these refinements for reducing operating expenses.

PROPOSAL FOR CONSTRUCTION AND OPERATION OF ZIRCONIUM PURIFICATION PLANT

In preparing the detailed estimates and general summary sheets attached hereto, the following factors have been taken into consideration.

Location of Proposed Plant

It is planned to house all of the facilities presented in this proposal in a building now in operation at Y-12, namely 9206. This eliminates considerable expense which would otherwise be incurred in structural facilities. It also provides ready accessibility to water, power, and sewage mains.

Materials of Construction

Most of the equipment required for this processing operation is glass or glass lined. Most of the tanks are now available in Y-12 and represent the major portion of the equipment included in this category in the detailed breakdown.

Some considerable portion of the equipment, especially the filters, must be rubber lined and will have to be purchased. All of the chemical piping proposed will be standard pyrex industrial pipe and fittings. A major portion will have to be purchased.

The gas fired furnaces required to reduce the final product to a dry oxide powder suitable for further processing represent a new type of operation to the Y-12 area and practically all material for these will have to be purchased.

Chemical and Interstage Storage

A rather extensive glass lined tank farm is now available at the building site. This will be available with moderate additions to the proposed plants. The large quantities of feed materials required for these operations require rather extensive revisions and additions as indicated in the detailed estimate for storage, handling, and solution make up.

Labor

By locating the three units, extraction, purification, and ignition in one area a considerable reduction in the over-all labor requirement is achieved. This is the basis upon which these estimates were made.

Plant Amortization and Maintenance

In order to present as nearly an accurate total cost of the product from these plants as possible, the cost of the plants has been amortized on a five year basis. This includes the estimated maintenance over this period and is believed to be realistic.

Construction Time

It is estimated that a construction time of five months will be required to have one of these plants ready for initial operation following the final approval.

Flow Sheet

The flow sheet attached is a schematic representation of the complete plants as proposed in this report. It is divided into logical sections, each of which includes a nearly complete operation in the over-all process.

GENERAL SUMMARY SHEET

	Unit Costs per Pound of Zirconium Produced in Each of Four Proposed Plants			
	50,000 lb. Plant	100,000 lb. Plant	150,000 lb. Plant	300,000 lb. Plant
Plant Amortization From page 11 and detailed estimate sheets	$0.58	$0.36	$0.285	$0.171
Chemical Cost for Extraction of Hafnium From page 9	1.061	1.061	1.061	1.061
Chemical Cost for Removal of other Impurities From page 7	1.015	1.015	1.015	1.015
Over-all Labor From page 8	1.50	0.80	0.60	0.37
Power and other Utilities (estimated)	0.10	0.07	0.05	0.05
Direct Cost per Pound of Zirconium Produced	$4.256	$3.306	$3.011	$2.667
Overhead on Labor	1.50	0.80	0.60	0.37
TOTAL COST	$5.756	$4.106	$3.611	$3.037

DETAILED COST ESTIMATE OF ZIRCONIUM

PRODUCTION PLANT

Capacity - 50,000# zirconium per year

	Material	Labor
Preparation of site	$ 200.00	$ 1,500.00
Chemical Supply System	2,200.00	1,480.00
Feed System	14,600.00	1,572.00
Extraction System	6,000.00	1,850.00
Thiocyanate Recovery	6,000.00	1,295.00
Purification System	12,000.00	1,295.00
Waste Disposal	2,000.00	1,850.00
Service Piping	1,800.00	2,775.00
Ventilation	2,700.00	2,775.00
Storage, Lighting, Handling Devices, etc.	4,000.00	7,215.00
Furnaces	15,000.00	4,995.00
Engineering	-	3,600.00
	$66,500.00	$32,202.00

Estimated equipment available on Y-12 area - $15,000.00

SUMMARY OF COSTS

Direct Cost to Government Including Contingencies -	$96,793.00
Overhead on Labor -	32,202.00
Y-12 Equipment -	15,000.00
Total	$143,995.00

DETAILED COST ESTIMATE OF ZIRCONIUM

PRODUCTION PLANT

Capacity - 100,000# Zirconium per year

	Material	Labor
Preparation of Site	$ 200.00	$ 1,500.00
Chemical Supply System	3,200.00	2,220.00
Feed System	16,600.00	2,127.50
Extraction System	6,500.00	2,220.00
Thiocyanate Recovery	6,500.00	1,572.50
Purification System	20,000.00	2,127.50
Waste Disposal	2,500.00	2,405.00
Service Piping	2,000.00	3,300.00
Ventilation	3,000.00	3,300.00
Storage, Lighting Handling Devices, etc.	5,000.00	8,695.00
Furnaces	20,000.00	5,550.00
Engineering	-	4,000.00
	$85,500.00	$39,017.50

Estimated equipment available on Y-12 area - $23,000.00

SUMMARY OF COSTS

Direct Cost to Government Including Contingencies -	$117,871.00
Overhead on Labor -	39,017.50
Y-12 Equipment -	23,000.00
Total	$179,888.50

DETAILED COST ESTIMATE OF ZIRCONIUM

PRODUCTION PLANT

Capacity - 150,000# zirconium per year

	Material	Labor
Preparation of Site	$ 300.00	$ 1,500.00
Chemical Supply System	3,500.00	2,405.00
Feed System	17,800.00	2,867.50
Extraction System	8,500.00	3,977.50
Thiocyanate Recovery	7,300.00	2,127.50
Purification System	23,000.00	3,977.50
Waste Disposal	2,900.00	2,590.00
Service Piping	2,400.00	3,700.00
Ventilation	3,600.00	3,885.00
Storage, Lighting, Handling Devices, etc.	6,000.00	9,435.00
Furnaces	24,000.00	6,475.00
Engineering	-	4,000.00
	$99,300.00	$46,940.00

Estimated equipment available on Y-12 area - $27,000.00

SUMMARY OF COST

Direct Cost to Government including Contingencies -	$138,558.00
Overhead on Labor -	46,940.00
Y-12 Equipment -	27,000.00
Total	$212,498.00

DETAILED COST ESTIMATE OF ZIRCONIUM

PRODUCTION PLANT

Capacity - 300,000# Zirconium per year

	Material	Labor
Preparation of Site	$ 500.00	$ 2,250.00
Chemical Supply System	3,900.00	3,145.00
Feed System	18,600.00	3,607.50
Extraction System	10,500.00	5,457.50
Thiocyanate Recovery	8,500.00	2,867.50
Waste Disposal	3,200.00	2,775.00
Purification System	28,000.00	5,457.50
Service Piping	3,000.00	4,255.00
Ventilation	4,000.00	4,440.00
Storage, Lighting, Handling Devices, etc.	6,500.00	9,805.00
Furnaces	32,000.00	9,250.00
Engineering	-	4,600.00
	$118,700.00	$57,910.00

Estimated equipment available on Y-12 area - $34,000.00

SUMMARY OF COSTS

Direct Cost to Government including Contingencies -	$166,062.00
Overhead on Labor -	57,910.00
Y-12 Equipment -	34,000.00
Total	$257,972.00

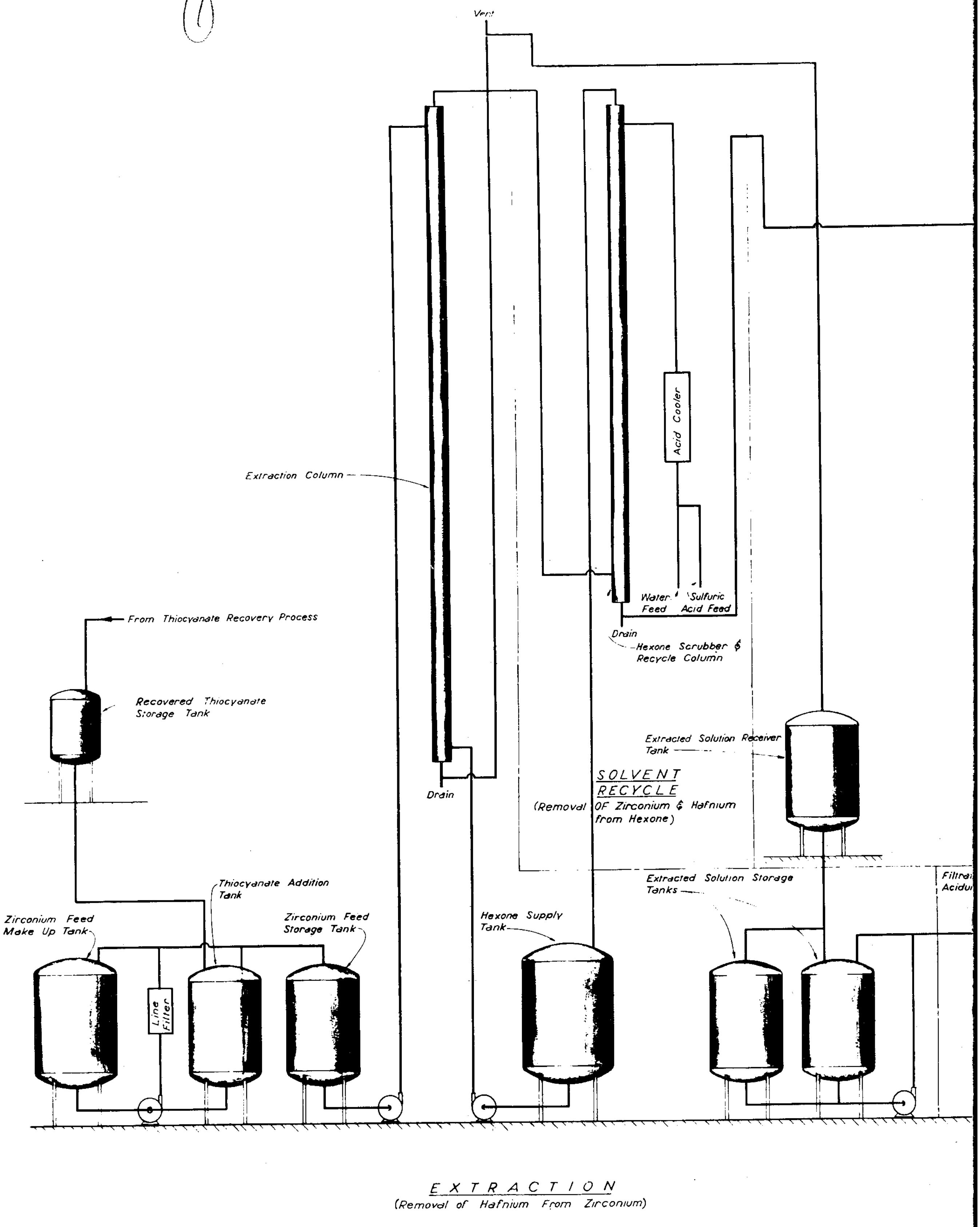
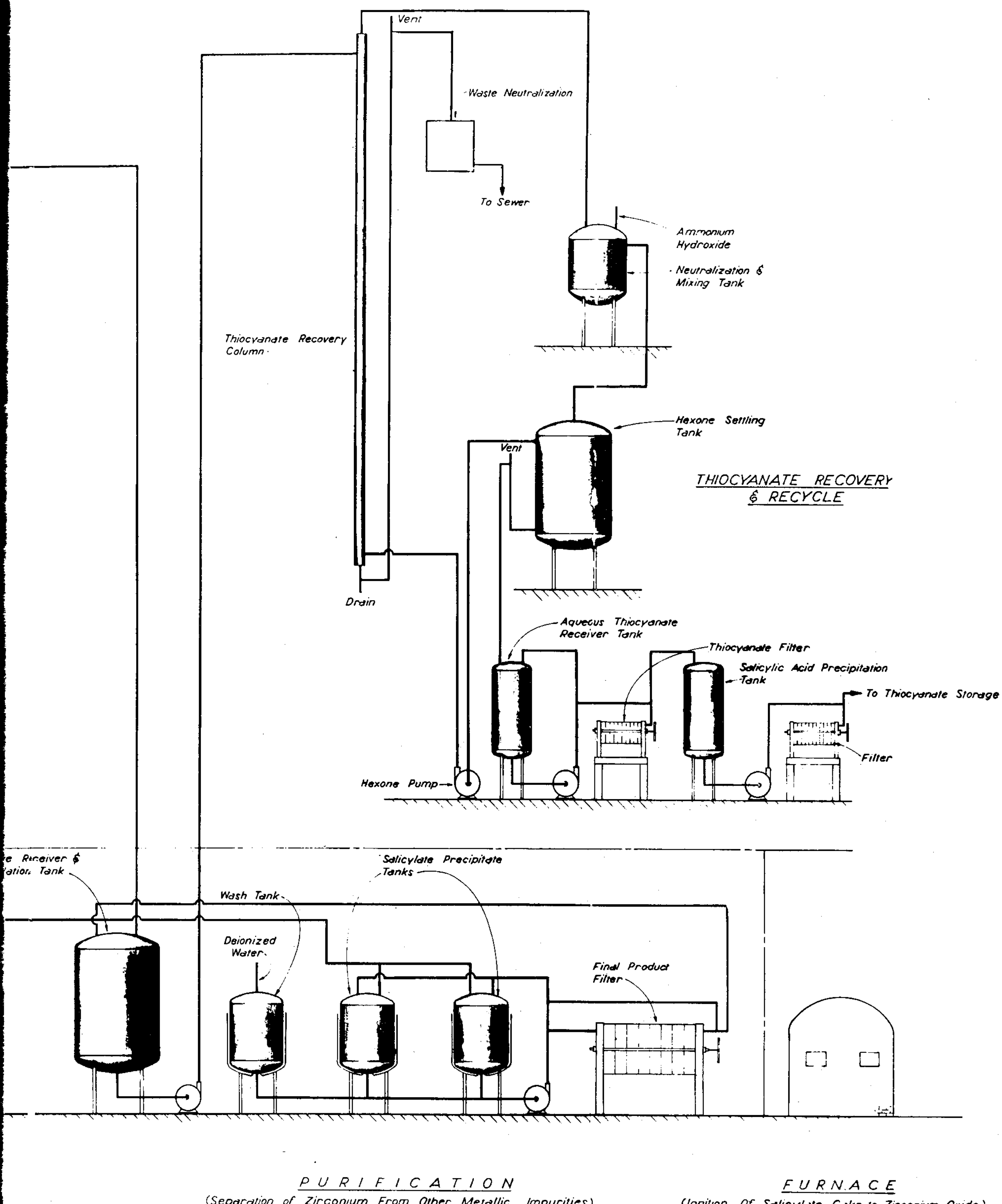


Fig. 1 Zirconium Purificatic



n Plant. Proposed Layout.