K-L-6151

Conf-670905--1

MASTER

MAY 8 1967

ECONOMIC ANALYSIS OF FLUORINATION PROCESSES FOR THE RECOVERY AND RECYCLE OF VALUABLE CVD MATERIALS*

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H.C. $3.00; MN 65

This manuscript contains 23 pages, 6 tables, and 2 figures.

* This document is based on work performed at the Oak Ridge Gaseous Diffusion Plant operated by Union Carbide Corporation, Nuclear Division, for the U. S. Atomic Energy Commission.

F_2 RECOVERS CVD VALUES ECONOMICALLY

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A B S T R A C T

High purity metal fluoride feed stocks to be used directly for chemical vapor deposition of shapes and coatings or to prepare special refractory metal and alloy powders can be easily produced by a direct fluorination process. The case presented here shows a particularly attractive economic situation for this and other valuable metals. It is estimated that the cost for reconverting 400 pounds per day of tungsten-25% rhenium alloy from scrap to prealloyed powder via fluorination and flame reduction is only about $28 per pound of contained rhenium, a small fraction of the current market value of this metal.

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With the growing significance of refractory metals to our country's nuclear and space efforts, the efficient utilization of these materials could become an important economic consideration, particularly when exotic elements such as rhenium are involved.

As part of the program at the Oak Ridge Gaseous Diffusion Plant to prepare refractory metal alloy powders from the volatile fluorides by a unique flame reduction process (1), it was necessary to produce the feed materials for the pilot plant. These volatile fluorides for all of the tests described in our earlier paper (2) were prepared by reaction of elemental fluorine with the desired metal, followed by condensation of the product. For most of the tungsten-rhenium alloy powders, however, fabrication scrap alloy was fluorinated to form a mixture of the fluorides, which was condensed and then fed to the flame reactor by flash vaporization. Fluorination temperatures were generally about 180°C. It is of interest and of practical importance that purification from nonvolatile contaminants is achieved by this feed preparation step. Further purification could be obtained by distillation if desirable. Thus, the purity of the starting metal or compound may not be so critical as in other processes.

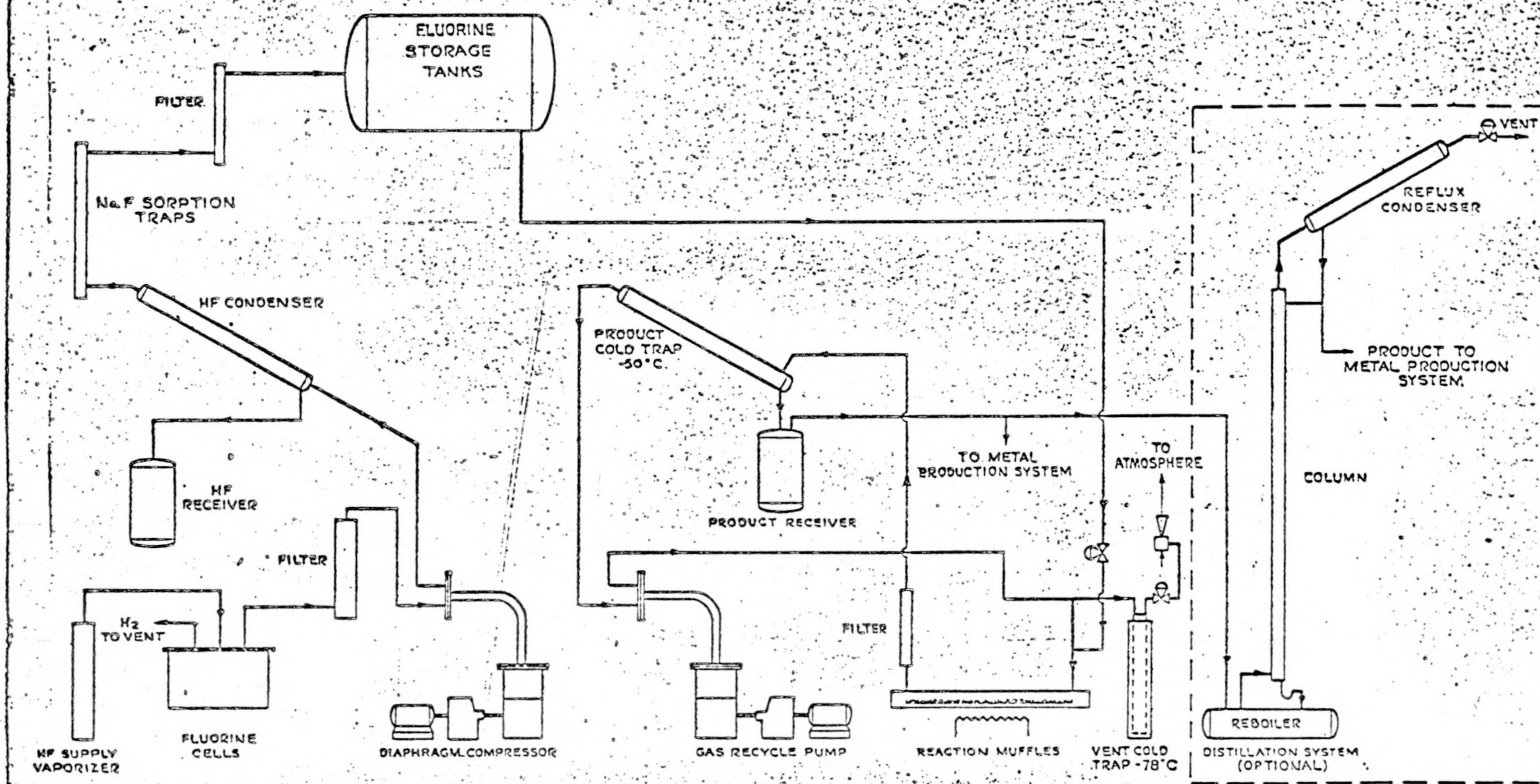
Because of the apparent ease with which all manner of tungsten, molybdenum, and rhenium containing scraps generated in materials production and fabrication programs could be converted to a usable feed as just described, it was evident that the fluorination technology might have industrial significance. Specifically, it seemed reasonable to develop capital and operating cost estimates for a system to recover rhenium values from reject streams.

For the economic analysis that follows, the assumption is made that the plant is part of an integrated chemical complex, and a daily processing rate of 400 pounds of tungsten-25% rhenium has been selected. All estimates are quite preliminary, being based on flow sheet and general background information, rather than on any detailed design effort; however, even such a cursory look presents an interesting picture in light of current industrial prices.

Although the 400-pound rate is somewhat optimistic when one considers the present national rhenium output, it is not unrealistic from at least two important standpoints. First, the rate of recycle of exotic materials, particularly for use in parts with demanding specifications, is often several times throughput. Second, the assumed rate could well be adjudged as a reasonable projection even for the intermediate term (3). Another point to contemplate is that the fluorination plant for tungsten-rhenium, probably including all major equipment, could be utilized in the recovery of other values. A large number of elements in groups V, VI, and VII of the periodic table, as well as several of the transition elements, form volatile fluorides. A particularly interesting possibility comes to mind in connection with a growing nuclear economy. Technetium is a major fission product from power reactors, and its potential for producing corrosion stability in common metals is already getting serious attention. The fact that a technetium alloy with tungsten can be readily prepared by coreducing the hexafluorides has already been noted (2).

THE RECOVERY PROCESS

Fluorination of commercially available tungsten and rhenium metal powders, reject streams from the flame reduction process, and fabrication scrap will all be possible in the same equipment. A flow sheet of the overall system is shown as figure 1. Commercial metal powder and/or fabrication scrap, reject powder streams, etc., are loaded into pans and are placed into heated muffles. Three muffles, each 10 feet long by 14 inches wide, are provided. If necessary, the powders are first treated with



FLUORIDE VOLATILITY SCRAP RECOVERY PROCESS

FIGURE 2

hydrogen to reduce the oxide content. Then, fluorine is passed over the metal to prepare the volatile fluoride. The crude product gas flows first through a sintered metal filter and then to one of two minus 50°C. cold traps, where most of the product is collected as desublimed solid. The cold trap exit gas is compressed for recycle. A small bleed flow is removed from the recycle stream through a cold trap in a dry ice slush bath to compensate for inert gases entering the system through buffer connections, filter blowbacks, etc. Fluorine is then added to maintain the desired reagent concentration. Both streams are controlled automatically and enter the system before the compressed gas is refed to the reaction muffles. The recycle gas flow is about 12 std.cfm. Valving is provided to allow operation of the muffles in series or in parallel. Product is recovered from the minus 50°C. cold traps by heating and draining as a liquid either to cylinders or to the product collection tank. Blending and batching may be accomplished in the tank and in the cylinders by thermal mixing. The cylinders can also be rolled.

With some powder feed compositions, it may be desirable to consider purification of the product by distillation. Accordingly, a batch still is shown on the flow sheet. Although this unit is not included in the fluorination system estimate of capital expenditure, it is anticipated that the cost of such an addition would be on the order of $125,000.

COST ANALYSIS

Fluorine Generation Technology and Economics

Fluorine is generated at the rate of 17 pounds per hour in a two-cell plant, also shown schematically in figure 1. This amount is more than sufficient to provide fluorine for both the fluorination and metal reconversion systems. After filtration to remove mist carryover, the product gas from the 6,000-ampere cells is compressed to 75 psig. using a double diaphragm machine with essentially inert fluorocarbon oil in contact with the gas pumping diaphragm for safety reasons. The compressed gas is passed through a condenser to remove part of the hydrogen fluoride and then through pipes containing sodium fluoride pellets to complete the purification. The compressed purified fluorine flows into storage tanks from which it is removed as needed.

Fluorine generation technology developed by Union Carbide Corporation for the United States Atomic Energy Commission has been amply covered in unclassified literature. A 25-pound per hour plant utilizing smaller cells was described by Dykstra, et al. (4). Multiton production of fluorine, including capital and operating costs for a 40-cell plant concept, was discussed by Huber, et al. (5). Drawings (6,7) giving details of cell and plant construction are available for purchase.

The required investment for fluorine generation and supply for the two-cell plant used here is $543,000, as shown in table 1.

TABLE I

FLUORINE PLANT CAPITAL COST ESTIMATE

	Total Cost, $
Equipment, Including Fluorine Cells, Sodium Fluoride Purification Equipment, Electrolyte Makeup Equipment, Filtering Units, Gas Compressor, Hydrogen Fluoride Feed Equipment, Refrigeration, Rectifiers, Stack Exhausters, and Miscellaneous Items	100,000
Installation	40,000
	140,000
Piping	70,000
Instrumentation	28,000
Electrical	25,000
	263,000
Indirect	92,000
Engineering	39,000
	394,000
Contingency	59,000
	453,000
Building	90,000
Total	543,000

This may be compared with the $4.5 million estimated for the 40-cell plant (after escalation from 1958 to 1966). The size ratio is 20, and the cost ratio is 8.3. The cost ratio exponent is thus 0.7, which is approximately that to be expected (8).

The choice between in-house generation of fluorine or purchase becomes a matter of economics, assessment of supplier logistics, and other factors. Assuming that 15% of the investment of $543,000 must be charged each year to the fluorine generation and considering that a total of 105,000 pounds of fluorine is required per year for the fluorination system and the metal powder preparation operation, the unit capital charge in dollars is about $0.78 per pound of fluorine. The operating cost given by Huber, et al. (5), for the larger plant was $0.46 per pound. Only $0.105 of this represented labor and overhead. Although these unit costs might not be increased very much, even for the small plant, providing sufficient integration of the fluorine generation activity with other operations could be attained, it is certainly realistic to consider some increase, not only for escalation, but for differences in plant operation. It is necessary to take into account the use of compression to high pressures in the present plant and also the fact that the on-stream factor is probably not so high as for the large plant. Accordingly, we have used $1.00 per pound for the operating cost. The total cost, including amortization, would then be $1.78 per pound of fluorine.

Fluorination System Costs

The cost of the refractory metal fluorination system, table II, is estimated to be $491,000, including building space. The yearly capital charge at 15% of investment would be $74,000. Assuming 120,000 pounds of metal is processed per year, i.e., 300 days at 400 pounds per day, the capital cost per pound is then about $0.62.

The operating cost for the fluorination step is given in table III. Note that fluorine is charged off at $1.00 per pound operating cost as a worked material and that amortization for the fluorine plant is added separately. The unit operating cost is $2.09 per pound of metal, while the total unit cost, including amortization, is $3.24 per pound of metal. On a rhenium basis, this figure becomes $12.95 per pound of rhenium.

Cost of Conversion of Refractory Metal Fluorides to Metal Powders

Although the fluorination system product can be used for other applications, e.g., gas plating of particles and shape formation using vapometallurgy techniques for deposition, reconversion to pure single component and alloy metal powder will probably be the fate of much of the recovered scrap. Accordingly, cost estimates are presented below for a plant operating to produce 96,000 pounds of tungsten-25% rhenium alloy powder per year. This figure represents 80% of the reduction system throughput, since it is expected that, for many fabrication requirements, it will be necessary to

TABLE II

REFRACTORY METAL FLUORINATION SYSTEM
CAPITAL COST ESTIMATE

	Total Cost, $
Equipment, Including Muffles and Furnaces, Recycle Compressor, Cold Traps, Refrigeration, Purge System, Gas Scrubber, Hydrogen Supply, Gas Preheater, and Product Collection Tank	89,000
Installation	36,000
	125,000
Piping	62,000
Instrumentation	15,000
Electrical	15,000
Special Analyzer	8,000
	225,000
Indirect	79,000
Engineering	45,000
	349,000
Contingency	52,000
	401,000
Building	90,000
Total	491,000

TABLE III

REFRACTORY METAL FLUORINATION
OPERATING COST ESTIMATE

		$/Year
Operating Labor	25,000	
Maintenance Labor	30,000	
Supervision	8,000	
Basic Labor		63,000
Maintenance Materials	20,000	
Other Materials	5,000	
Total Materials		25,000
Basic Cost		88,000
Fluorine, 82,000 Pounds at $1.00 Per Pound		82,000
Overhead, 100% of Basic Labor		63,000
Utilities		18,000
Total Operating Cost		251,000
Unit Operating Cost, $/lb. of Metal		2.09
Amortization Metal Plant, $/year		74,000
Unit Amortization Metal Plant, $/lb. of Metal		0.62
Amortization Fluorine Plant, $/year		64,000
Unit Amortization Fluorine Plant, $/lb. of Metal		0.53
Total Unit Cost, $/lb. of Metal		3.24
Total Unit Cost, $/lb. of Rhenium Metal		12.96

recycle to the fluorination system that fraction of the product appearing in the receiver below the reduction reactor leg.

The capital cost estimate for the powder production system is shown in table IV. As shown in figure 2, the plant provides for a flame reduction reactor, plus filter, hydrogen supply and purification equipment, feed vaporizers, dry boxes, off-gas scrubber, furnaces and muffles operating in hydrogen up to 1150°C. for reduction of fluorine content of the powder and for tailoring physical properties, and rod mill to be used if necessary for breaking up agglomerates. Overall, the loss of material is essentially zero, since as noted above, any off-specification powder is recycled to the fluorinators. The cost of the refractory metal powder production system is estimated to be $382,000, including building space. The yearly capital charge at 15% of investment would thus be $57,000. Assuming 96,000 pounds per year of satisfactory product is made, i.e., 300 days at 400 pounds per day throughput with an 80% yield, the contribution of these capital charges to the unit cost is $0.59 per pound.

The operating cost estimate for the reconversion to metal is given in table V. Fluorine, used to initiate and sustain the reduction reaction, is charged off at $1.00 per pound in the operating cost as a worked material; however, the amortization for the fluorine plant is added separately. The unit operating cost is $2.09 per pound of metal product; amortizing the capital

TABLE IV

REFRACTORY METAL POWDER PRODUCTION SYSTEM
CAPITAL COST ESTIMATE

	Total Cost, $
Equipment, Including Hydrogen Purification Equipment, Flame Reactor, Filter, Backup Filter, Furnacing Equipment (1150°C.), Rod Mill, Off-Gas Scrubber, Feed Flash Vaporizer, and Hydrogen Supply	58,000
Installation	23,000
	81,000
Dry Boxes	12,000
Piping	41,000
Instrumentation	20,000
Electrical	10,000
	164,000
Indirect	57,000
Engineering	33,000
	254,000
Contingency	38,000
	292,000
Building	90,000
Total	382,000

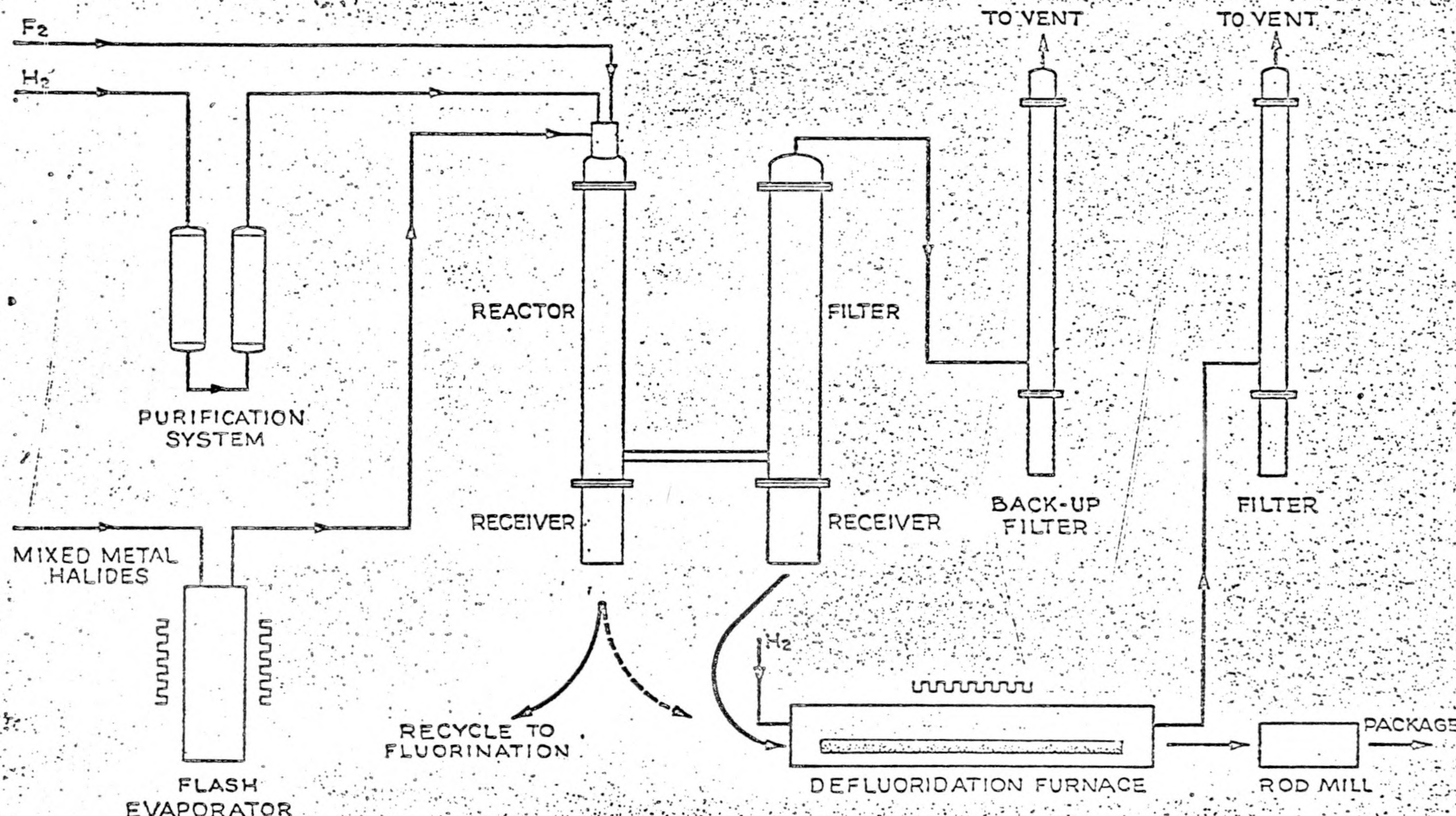
TABLE V

REFRACTORY METAL POWDER PREPARATION
OPERATING COST ESTIMATE

Basis: 96,000 Pounds of Product Per Year at 80% Process Yield

		$/Year
Operating Labor	25,000	
Maintenance Labor	23,000	
Supervision	8,000	
Basic Labor		56,000
Maintenance Materials	23,000	
Other Materials	10,000	
Total Materials		33,000
Basic Cost		89,000
Fluorine, 23,000 Pounds* at $1.00 Per Pound		23,000
Hydrogen, 3,000,000 scf. at $5/1,000 scf.		15,000
Overhead, 100% of Basic Labor		56,000
Utilities		18,000
Total Operating Cost		201,000
Operating Cost, $/lb. of Metal		2.09
Amortization Metal Plant, $/year		57,000
Unit Amortization Metal Plant, $/lb. of Metal		0.59
Amortization Fluorine Plant, $/year		18,000
Unit Amortization Fluorine Plant, $/lb. of Metal		0.19
Total Unit Cost, $/lb. of Metal		2.87

* 0.12 pound of fluorine per pound of hexafluoride used in flame reactor.



REFRACTORY METAL POWDER PREPARATION SYSTEM

FIGURE 3

cost for both fluorine and powder production as already described places the overall unit cost at $2.87 per pound. On a rhenium basis, the value becomes $11.48 per pound of contained rhenium.

The total annual cost, table VI, for scrap fluorination and reconversion to metal powder, including handling of all internal recycle streams, to produce 96,000 pounds per year of pure alloy powder thus becomes $665,000 using the appropriate capital charges shown in preceding tables. The unit cost per pound of acceptable alloy metal powder produced is therefore $6.92. On a rhenium basis, this figure becomes $27.68 per pound of contained rhenium.

CRITIQUE

The cost analysis just presented certainly indicates an attractive economic situation for recovering pure feed stock which can be used either directly for chemical vapor deposition of shapes, etc., or to prepare powders having controlled chemical compositions and unusual physical properties. In the case of the powders, both the pure and alloyed products are obtained for a small fraction of the cost of the commercially available materials.

If it is known that fabrication scrap can be easily fluorinated and subsequently recovered as a pure feed material, then the fabrication methods themselves can be selected and optimized for use on the basis of a more liberal materials allowance.

TABLE VI

SUMMARY OF ANNUAL COSTS FOR
RECOVERY AND RECONVERSION

Refractory Metal Fluorination (120,000 lb./yr.)	
Operating Cost	$251,000
Metal Fluorination Capital Charge	74,000
Fluorine Plant Capital Charge	64,000
Total	$389,000
Metal Powder Production (96,000 lb./hr.)	
Operating Cost	$201,000
Metal Powder Plant Capital Charge	57,000
Fluorine Plant Capital Charge	18,000
Total	$276,000
Grand Total	$665,000
Unit Cost Per Pound of Metal Powder	6.92
Unit Cost Per Pound of Rhenium	27.68

Furthermore, it should be important to have such a recovery technology because of the potentially strategic nature of a metal like rhenium; i.e., the supply of rhenium could suddenly become very limited, thus causing an even higher premium to be placed on its efficient use.

The particular study of a fluorination recovery scheme covered by this paper was made because of the current interest in rhenium and because of the applicability of the process to technetium (2). It should be noted, however, that the same basic chemical engineering technology could also apply to chlorination and bromination processes; chlorides and bromides of refractory metals are also employed in significant vapor deposition programs. Of course, each case would have to be examined independently to determine economic potential.

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(6) CAPE 55, Paducah Fluorine Plant, 34 drawings, price about $10. This set of drawings may be purchased from Clearinghouse for Federal Scientific and Technical Information, U. S. Department of Commerce, 5285 Port Royal Road, Springfield, Virginia 22151.

(7) CAPE 486, 6,000 Amp ORGDP Fluorine Cell, 33 drawings, price about $10. This set of drawings may be purchased from the same address listed in reference (6) above.

(8) Schuman, S. C., "How Plant Size Affects Unit Costs", Chem. Eng., 173-6 (May, 1955).