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ABSTRACT

An economic evaluation has been made of the silica gel adsorption process for the separation of hafnium and zirconium. It is estimated that hafnium-free zirconium can be prepared at a cost of $7.10 per pound in the form of $ZrOCl_2 \cdot 8H_2O$. This salt is satisfactory for the preparation of ZrF_4 by the Ames wet process.

While the adsorption process does not appear competitive with the Y-12 thiocyanate extraction process, it is pointed out that there are several revisions of the adsorption process which should reduce the overall cost. These economies have not as yet been demonstrated, however, on a pilot-plant scale.

INTRODUCTION

A process for the separation of hafnium from zirconium based on the preferential adsorption of hafnium tetrachloride from a solution of hafnium and zirconium tetrachlorides in methanol has been described by Hansen et. al. (3,4,5). Giffen (2) and Beyer and Giffen (1) have described a continuous process for obtaining high purity zirconyl chloride by the adsorption method followed by recrystallization of the zirconium salt. Giffen also presented the design of a pilot plant for the production of 1000 pounds per month of zirconium in the form of purified zirconyl chloride octahydrate; the cost of producing the salt by this method was also estimated.

Since the completion of Giffen's work, some additional studies on the process indicate the need for revision of the original cost estimates. Further development of the thiocyanate extraction process at Y-12 (6,7) also requires a re-evaluation of the adsorption process to determine if further work on the adsoprtion process may prove profitable.

CURRENT STATUS OF THE SILICA GEL ADSORPTION PROCESS

Since the conclusion of the work of Giffen, there have been no further performance studies made on the small-scale plant. There has been a critical study of the behavior of silica gel which indicates that the gel may be recycled after treatment, thus reducing the gel cost. The treatment involves stripping the gel with sulfuric acid, washing the sulfuric acid from the gel, and reactivating the gel by drying it to about 3.5 per cent moisture. Studies show that gel may be satisfactorily reused four or more times using this treatment.

The chief advantage of the adsorption process lies in the ease with which the product salt may be converted to zirconium tetrafluoride by the Ames wet process, which consists of precipitating $ZrF_4 \cdot H_2O$ by treatment of an aqueous solution of zirconyl chloride with aqueous hydrofluoric acid, followed by drying the precipitate in an HF atmosphere to give anhydrous ZrF_4. The tetrafluoride may be reduced by bomb reduction using calcium as a reductant to give zirconium metal of good purity and a hardness only slightly greater than that of crystal bar zirconium.

Among the disadvantages of the adsorption process at present are the following:

1. Lack of pilot-plant experience on the production of the purified salt, including lack of information on
   - (a) Use of recycle gel to give a satisfactory product
   - (b) Labor required for continuous production
   - (c) Difficulty of control of a continuous process involving a solid-liquid system
   - (d) Maintenance requirements and the life of materials of construction.
2. Lack of present demand for the product of this process. It is believed, however, that the conversion of zirconyl chloride to zirconium tetrachloride would be relatively simple.

3. The process does not produce a hafnium concentrate directly, and it appears that any production of a hafnium concentrate from this process would be expensive.

The overall zirconium yield for the adsorption process appears to be in the neighborhood of 83 per cent. The anticipated yield of the thiocyanate extraction process is about 94 per cent (6), but pilot-plant yields for a ten-month period appear to be about 80 per cent (7).

COST OF SILICA GEL RECLAMATION

The cost of chemicals and utilities required to strip and reactivate the silica gel are summarized in Table I. It should be noted that reclamation costs are approximately

Table I

Cost of Silica Gel Reclamation
(Basis: 1 lb. silica gel)

Item	Amount required	Unit Cost	Cost/lb. gel
Sulfuric acid	1.02 lb.	$0.02	$0.020
Caustic soda	0.84 lb.	.03	.025
Fuel (natural gas)	.0048 MCF	.75	.004
Electric power	.120 KWH	.04	.005
			$0.054

$0.05 per pound of gel compared to $0.44 per pound for new gel. As a result, the total gel cost for purification of one pound of zirconium is only $0.25 if the gel is cycled five times compared to $0.85 if the gel is used only once.

The cost of silica gel plus reclamation costs per pound of zirconium processed for varying numbers of gel cycles is shown in Table II.

Table II

Economy of Gel Reuse
(Based on silica gel cost of $0.44/lb.)

No. of gel cycles	Lb. gel req'd lb. Zr	Lb. gel reclaimed lb. Zr.	Cost of gel	Cost of reclamation	Gel Cost lb. Zr
1	1.920	0	$0.845	0	$0.845
2	0.960	0.960	.422	$0.052	.474
3	.640	1.280	.282	.069	.351
4	.480	1.440	.211	.079	.290
5	.384	1.536	.169	.083	.252
6	.320	1.600	.140	.086	.226

COST OF SILICA GEL ADSORPTION PROCESS

The cost of chemicals and raw materials have been recalculated on the basis of an 83 per cent overall zirconium yield and a five-cycle silica gel life. These costs are presented in Table III. The total chemical cost is $1.88 per pound of zirconium.

The overall processing costs for the adsorption process are given in Table IV. These are compared with the costs for pilot-plant operation at Y-12 (7). The overall cost by the adsorption process is $7.10 per pound of zirconium in the form of $ZrOCl_2 \cdot 8H_2O$, which compares unfavorably with $5.37 per pound of zirconium in the oxide form from the thiocyanate extraction process. It is believed that the process costs for the thiocyanate extraction process

Table III

Chemical Costs for the Adsorption Process

(Basis: 1 lb. Zr as product salt)

Item	Quantity	Unit cost	Total cost	Remarks
Zirconium tetrachloride	2.95 lb.	$0.34	$1.05	83% recovery
Methanol	1.42 gal.	.35	.50	No recovery
Silica gel	0.384 lb.	.44	.17	5 gel cycles
Sulfuric acid	1.97 lb.	.02	.04	5 gel cycles
Caustic soda	1.61 lb.	.03	.05	5 gel cycles
Hydrochloric acid	a		.05	
Acetone	a		.02	
			$1.88/lb. Zr	

[a]Giffen estimate (2).

Table IV

Comparative Cost of Producing Purified Zirconium Compounds

(Basis: 1 lb. of Zr as product salt)

Item	Y-12 Oxide[a]	Ames $ZrOCl_2 \cdot 8H_2O$
Raw materials and Chemicals	$2.85[b]	$1.88
Plant amortization (5-year)	0.40	1.17[c]
Power and utilities	.09	0.25[c]
Direct Labor ans Supervision	.44	1.90[c]
Overhead	1.59	1.90[c,d]

[a]From Y-817 (6) based on period July, 1950 through April, 1951.

[b]$1.12 to $1.25 of this cost is salicylic acid. Replacement of this precipitant by ammonium phthalate, which is largely recoverable, should reduce this cost.

[c]Beyer and Giffen estimate (1).

[d]Taken as 100 per cent of direct labor on the usual Ames Laboratory basis.

have been lowered by approximately $1 per pound of zirconium by the substitution of ammonium phthalate for salicylic acid as a zirconium precipitant.

POSSIBLE REDUCTIONS IN COST OF THE SILICA GEL ADSORPTION PROCESS

The cost figures presented in Table IV indicate the silica gel adsorption process is not competitive with the thiocyanate extraction process developed at Y-12. There are, however, a number of possible cost reductions which should be considered. Among these are:

1. The possibility of recovering and recycling methanol. Giffen estimated an 80 per cent recovery was possible; this would lower the cost of zirconium by approximately $0.40 per pound.

2. Some of the pilot-plant equipment has a capacity considerably above that required for 1000 pounds of zirconium per month. For example, the silica gel dryer can process enough gel in 77 operating hours or less to supply the gel columns for a 540-hour month. It is not realistic to amortize the gel dryer on the basis of the pilot-plant capacity only because the dryer was the smallest available.

3. The labor requirements are largely unknown, and should be determined by pilot-plant operation. It is quite possible that the labor required for pilot-plant operation could equally well handle a plant having several times the capacity of the plant designed by Giffen.

CONCLUSIONS

The apparent high cost of the silica gel adsorption process compared to that of the thiocyanate extraction process makes further development work on the silica gel process somewhat attractive. This factor, together with the present low demand for the zirconium product in the form of $ZrOCl_2.8H_2O$, would seem to preclude further studies. It was pointed out in the previous section, however, that there is an excellent probability that pilot-plant experience with the process would prove that additional economies are possible. At present, the Ames Laboratory experience with the adsorption process is insufficient to determine the practicality of the proposed changes.

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