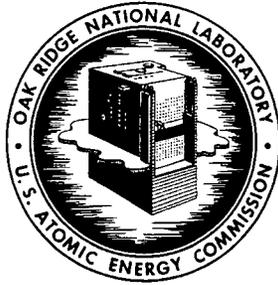




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## BURN-LEACH PROCESSES FOR GRAPHITE-BASE REACTOR FUELS CONTAINING CARBON-COATED CARBIDE OR OXIDE PARTICLES\*

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### ABSTRACT

Processing of graphite-base high-temperature gas-cooled reactor fuels containing carbon-coated carbide or oxide particles is discussed. The most promising process consists of burning of the fuel in a fluidized-bed of inert alumina followed by leaching of the product bed with Thorex reagent to recover the uranium and thorium. Decontamination and final recovery of the uranium and thorium would be achieved by conventional solvent extraction methods. A preliminary engineering evaluation and potential costs are included.

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## INTRODUCTION

High-temperature gas-cooled reactors (HTGR) that contain coated fuel particles dispersed in a graphite matrix are being developed. Eventually processes will be required for the recovery of uranium and thorium from these fuels. It is the purpose of this paper to summarize preliminary processing studies that relate to these fuels. Although materials such as pyrolytic carbon, SiC, ZrC, Al<sub>2</sub>O<sub>3</sub>, and BeO have been considered either as coatings or diluents for carbide and oxide fuel particles, this paper will be limited primarily to a discussion of processing methods for fuel that contains carbon-coated thorium-uranium carbide or oxide fuel particles. A promising processing method consists of burning the fuel in a fluidized bed of inert alumina and then leaching with fluoride-catalyzed nitric acid (Thorex reagent) to recover the uranium and thorium. Decontamination and final recovery of the uranium and thorium would be achieved by conventional solvent extraction methods. Laboratory- and engineering-scale studies of this process have been made with unirradiated prototype fuel specimens, and a few hot-cell experiments were run with irradiated material. The results of this work are summarized here; in addition, a preliminary engineering evaluation of the burn-leach process and costs as related to a conceptual fuel are included. An alternative method, burning followed by fluorination to recover the uranium as UF<sub>6</sub> is discussed briefly.

## BURN-LEACH FLOWSHEET

The burn-leach process for graphite-base fuels is shown in Fig. 1. Initially, the fuel is chopped or crushed and fed to a fluidized-bed burner. The best heat-transfer and fluidizing medium is probably a refractory grade of granular alumina. Design of the burner may be dependent on the type of fuel being burned. Burning at 700 to 750°C of fuels containing carbon-coated Th-U dicarbide particles converts the carbides to finely powdered oxides, dispersed homogeneously throughout the bed. Consequently, to recover the uranium and thorium, the entire bed must be leached. However, oxide fuel particles that have a high ThO<sub>2</sub> content might not be affected during combustion in a fluidized bed and probably can be separated from the alumina if desired before the leaching operation.

Burning is started by injecting preheated oxygen into the fluidized bed and simultaneously heating the bed by external heaters. When the fuel starts to burn, the heaters are turned off, and the heat of reaction is removed by air-cooling the bed. For efficiency, continuous operation, with feeding of fuel, fresh alumina, and oxygen to the burner, and withdrawal of ash, all at the proper rates, is preferred. Toward the end of the reaction, when the amount of carbon in the bed has been reduced to a low level, the heaters must be restarted to complete the reaction. Under normal operation, nearly quantitative consumption of the oxygen is achieved, resulting in an off-gas composed mainly of CO<sub>2</sub>. Carbon monoxide, which can form potentially explosive mixtures with oxygen, generally amounts to less than 5% of the off-gas.

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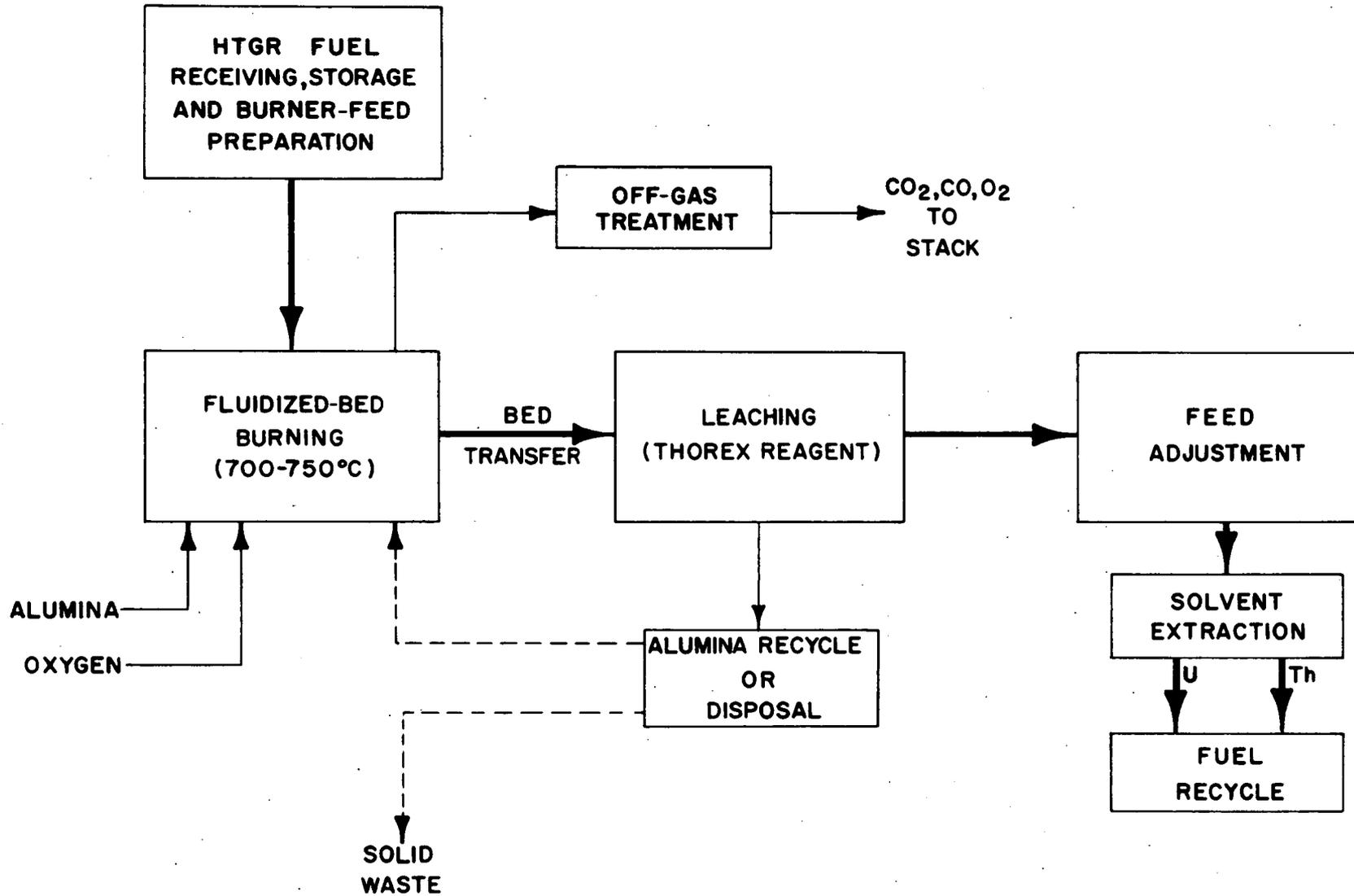


FIG. 1  
 POTENTIAL BURN-LEACH PROCESS  
 FOR GRAPHITE BASE REACTOR FUEL

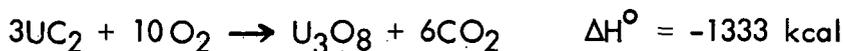
Particles in the off-gas are removed mostly by filters, and a gas-cleanup system prevents the release of all radioactivity except the noble gases.

After burning, the product bed is transferred to a leacher where the uranium and thorium are dissolved in fluoride-catalyzed nitric acid (Thorex reagent). The design of the leacher depends on the type of fuel being processed, since the product bed from carbide-bearing fuel will contain about 70%  $\text{Al}_2\text{O}_3$ , whereas the product from oxide-containing fuel can consist mostly of  $\text{ThO}_2\text{-UO}_2$  microspheres. In either case, leachates containing 0.5 to 1 M Th can be obtained. Less than 2% of the alumina is dissolved; thus, the remainder may be recycled or discharged to waste. Uranium and thorium recoveries should be greater than 99.5%.

After the concentration of the leachate is adjusted, the uranium and thorium are separated from fission products and recovered by a conventional tributyl phosphate solvent-extraction process. The product from solvent extraction can probably be used as feed for the sol-gel process for refabrication of oxide or carbide fuel particles.

#### FLUIDIZED-BED COMBUSTION OF GRAPHITE-BASE FUEL

Fuels Containing Carbon-Coated Carbide Particles. In the fluidized-bed burning of this type of fuel, the graphite is converted to carbon oxides, and the carbides to their respective oxides. The principal reactions are:



Tests of the combustion of fuel that contained carbon-coated carbide fuel particles were conducted in 2-in.-diam and 4-in.-diam fluidized beds,<sup>1,2</sup> made of nickel. The smaller bed was used to prepare material for laboratory-scale leaching studies. The 4-in.-diam fluidized bed (Fig. 2) was used at Oak Ridge National Laboratory for pilot plant studies and had the essential features of a plant-size burner. It was divided into two sections by a perforated fuel-support grid located 2 ft above the bottom. The fluidizing gas, oxygen, was introduced through a ball-check gas distributor in the conical bottom; the ball-check also prevented plugging of the oxygen inlet line when the burner was shut down. Ash was withdrawn from the conical bottom through a cooled line by a small, 3/4-in.-diam, variable-speed screw conveyor. The bed was heated by resistance heaters and cooled by air. The enlarged disengaging space at the top was air-cooled and provided with internal fins to cool the combustion gases before filtration. Off-gas filtration was provided by two sintered stainless steel filters with an automatic blowback system. Each filter

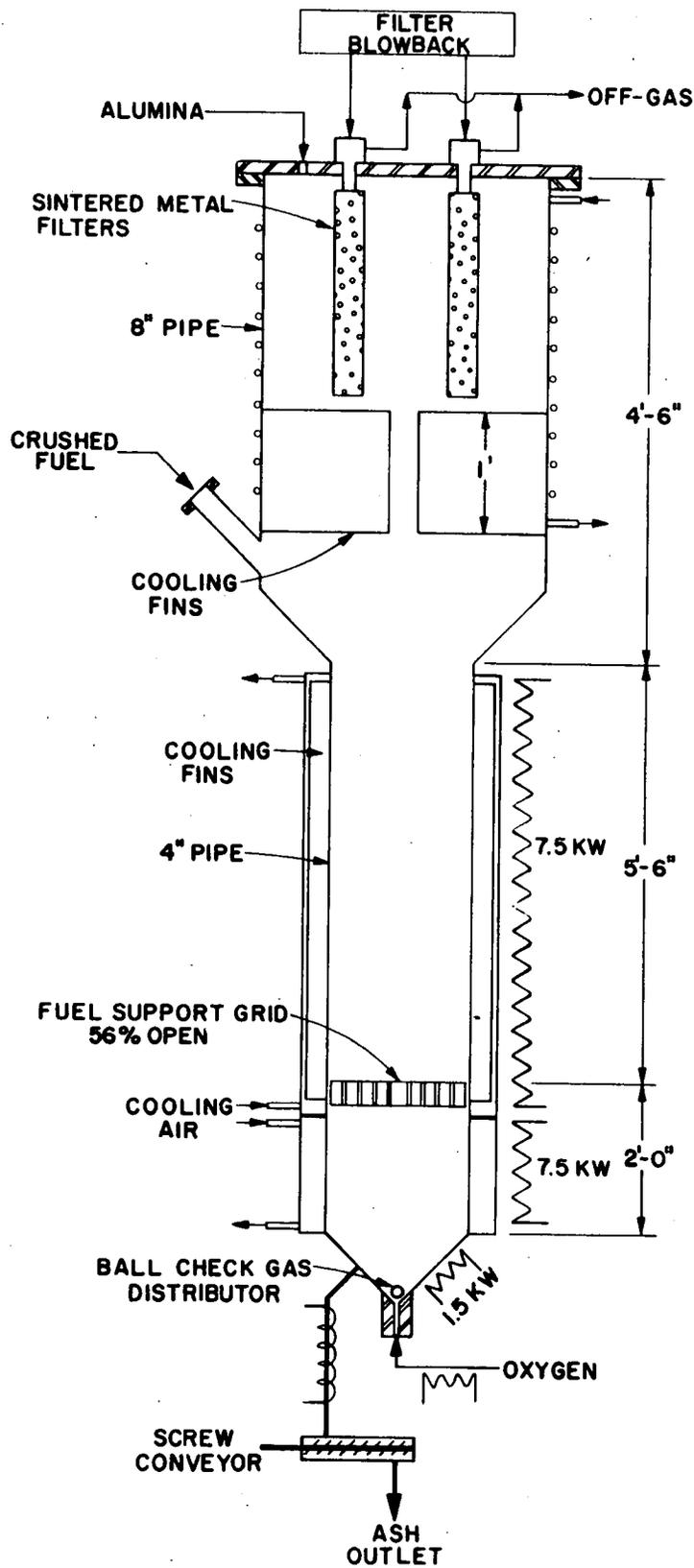


FIG. 2

FOUR-INCH-DIAMETER FLUIDIZED-BED BURNER  
 FOR PILOT PLANT STUDIES

was 2-3/4 in. in diam, 18 in. tall, and had a 20- $\mu$  mean pore size. Crushed fuel and alumina were introduced into the bed via the disengaging section. The level of the fluidized bed was determined with a thermocouple probe, and the behavior of the bed was observed through a sightglass in the center of the top flange during initial experiments with only alumina present. Other thermocouples and pressure taps were provided at various points for control purposes. The unit was made of nickel 201 so that halogens could also be used in it. Type 310 stainless steel would probably be preferred for a large-scale burner because of the better high-temperature mechanical properties of this material.

The fluidized bed of alumina was an efficient heat-transfer medium. Also, it prevented hot spots and resultant clinkering as it diluted and suspended the fuel oxides during combustion. As a result, the product was a free-flowing powder. Combustion was done at 700 to 750°C and was easily controlled. It should be pointed out that although the term "fluidized bed" is used, the entire contents of the bed were usually not fluidized by the gas stream. For instance, the larger pieces of graphite fuel formed a loosely packed bed, which rested on the fuel-support grid. Alumina fluidized in the gas passages through the bed and in the free space below and above the fuel. The best operation<sup>1</sup> was achieved when equal parts of 60- and 90-mesh Norton Abrasive Company Blue Label R.R. fused alumina was used. For example, when the initial alumina charge contained an appreciable amount of fines, as for example in a mixture of equal parts of 60-, 90-, and 120-mesh particles, the degree of fluidization decreased as additional fines were produced by the oxidation reactions, especially when the concentration of U-Th oxides approached 30 wt %. This eventually resulted in loss of fluidization, channeling, and hot spots. Satisfactory operation was restored by adding coarse alumina to regain the correct particle-size distribution for good fluidization in the presence of large amounts of fines derived from oxidation of the fuel. A one-week test showed that attrition of the fluidized alumina was negligible under normal operating conditions.<sup>2</sup>

Chopped or crushed fuel was added to approximately 20 kg of alumina, and the bed was fluidized with preheated nitrogen while additional heat was supplied by the external heaters. Since the fuel ignites at 650°C, at this temperature the nitrogen was replaced by oxygen and the heaters were turned off. Bed centerline temperatures and wall temperatures were held at about 750 and 700°C, respectively, by air-cooling the finned exterior of the fluidized bed. The concentrations of CO<sub>2</sub> and CO in the off-gas were continuously monitored by gas-chromatographic and infrared analyzers. The CO<sub>2</sub> and CO contents of the off-gas were relatively constant when there was an excess of carbon in the burner; a decrease in the CO<sub>2</sub> and CO contents showed that the carbon inventory in the bed was being depleted. Accordingly, more chopped fuel was added as needed to maintain the desired oxidation rate. Alumina was added periodically when product was continuously withdrawn. The carbon inventory in the burner was normally 2 to 4 kg during a continuous run. The major part of the reaction occurred in the bed of chopped fuel that rested on the support grid. Small particles of carbon tended to be elutriated to the region

*fluidized*

above the packed bed and reached an equilibrium concentration in the upper part of the bed. Any small particles of carbon entrained in the alumina below the grid were rapidly burned in the hot oxygen, and it was possible to continuously withdraw an almost carbon-free product stream from the bottom of the bed. Toward the end of a combustion run, when the carbon concentration in the bed was low, it was necessary to supply heat to the burner to ensure combustion of the last traces of carbon. The superficial gas velocity in the bed was about 0.76 ft/sec at the bed midpoint pressure of 17.6 psia and average temperature of 725°C.

Continuous oxidation rates<sup>1</sup> varying from 1.1 to 1.4 kg of carbon per hour were obtained in pilot plant tests with a 4-in-diam fluidized bed by varying the oxygen flow rate over the range of 1.3 to 1.6 scfm. Oxygen utilization decreased from 97 to 90% as the flow rate was increased. Other variables affecting the rate of oxidation were: carbon inventory (or perhaps more correctly, carbon surface area) in the bed, operating temperature, and oxygen content of the feed gas. The average heat flux, based on the inside area of the reactor, was about 4800 Btu hr<sup>-1</sup> ft<sup>-2</sup>, or about 2100 Btu hr<sup>-1</sup> ft<sup>-2</sup> of outside surface on the finned outer wall. The heat transfer coefficient from bed to wall was estimated at 85 Btu hr<sup>-1</sup> ft<sup>-2</sup>°F.

The off-gases were cooled in the top of the reactor, passed through the filters at the top of the burner to remove entrained carbon dust and oxides, and sent to an off-gas system. Plugging of the filters was not a problem, and the filter blowback system was not used during routine operations. Micropore filtration<sup>2,3</sup> of the off-gas for various periods showed that practically no particles escaped through the primary sintered-metal filters, thus demonstrating that the dust-coated filters were extremely efficient. Previous work<sup>4</sup> had shown that 99% of the particles in fixed bed combustion off-gas were less than 0.3 μ in diameter. Oxygen utilization in the burner was high, as noted above, and a typical off-gas consisted of about 90% CO<sub>2</sub>, 5% CO, and 5% O<sub>2</sub>. The CO concentration in the off-gas was below the flammability limit. Corrosion of the burner was negligible,<sup>1</sup> about 4 mils/year.

The carbon content of the discharged bed was generally less than 0.1%. Beds containing up to about 30% oxides (ThO<sub>2</sub> + U<sub>3</sub>O<sub>8</sub>) were produced,<sup>2</sup> with no noticeable difference in operating efficiency.

Fuels Containing Carbon-Coated Oxide Particles. To date, no fuel containing carbon-coated ThO<sub>2</sub>-UO<sub>2</sub> microspheres has been burned in a fluidized bed. A problem with this fuel arises from the uncertainties concerning the integrity of the microspheres after irradiation to projected burnups of 50,000 to 80,000 Mwd/metric ton of thorium plus uranium. If the microspheres retain their shape, it might be possible to separate them from most of the alumina after burning the carbon. This might result in a simpler leaching system. However, if the particles are broken during irradiation or combustion, they will be dispersed thoroughly in

the alumina, requiring that an excess of alumina be fed to the leaching system. In either case, the same fluidized-bed burner probably could be used. A conceptual drawing of a large burner is shown in Fig. 3; it is a scaleup of the pilot plant burner and would be operated similarly. Provisions for removing heat from more central portions of large fluidized beds must be made to avoid excessive centerline temperatures. This additional heat transfer surface is provided by air-cooled bayonets immersed in the bed.

For this study, it was assumed that the microspheres would not be broken and that a classifying operation after burning would permit leaching a product that is practically all microspheres with very little, if any, alumina. Eventually, the alumina will have to be discarded through the classifier and the leacher because of degradation of the alumina by attrition. However, as noted previously, the attrition seems to be very slow and the useful lifetime of the alumina is expected to be long.

Fission Product Behavior During Combustion. The behavior of the fission products was not studied during actual fluidized-bed combustion but was examined cursorily in laboratory-scale tube-furnace experiments. In one series of experiments,<sup>5</sup> in which a large excess of oxygen was used to burn prototype Peach Bottom fuel irradiated to about 10,000 Mwd/metric ton (U + Th), up to 35% of the cesium and 96% of the ruthenium were volatilized from the high-temperature zone during 6-hr combustions at 800°C. Experiments<sup>6</sup> in the same equipment with a slightly irradiated fuel at 700°C showed that up to 1.1% of the cesium and 65% of the ruthenium were volatilized in 6 hr. In each case, practically all the fission products were trapped in the cool end of the reaction tube and nearly all remaining activity was removed by filtering the off-gas through a clean, sintered, 40- $\mu$ -porosity metal filter in a manner similar to the method proposed for a plant-scale fluidized-bed burner. The overall decontamination factor was greater than  $10^4$  in all experiments. In other studies<sup>7</sup> only a small amount of cesium and ruthenium were volatilized from the hot zone when the fuel was burned in a deficiency of oxygen at 800°C. Waste calcination experiments<sup>8</sup> demonstrated the beneficial effect of a reducing gas (CO or NO) and elevated temperatures in decreasing ruthenium volatility by reducing higher oxides to the less volatile RuO<sub>2</sub>. The preceding data suggest that volatilization of fission products, other than the noble gases, will not occur to a significant extent in a fluidized bed if the oxygen consumption is nearly quantitative and if the off-gases are cooled before filtration. Furthermore, if the ThO<sub>2</sub>-UO<sub>2</sub> microspheres retain their integrity during irradiation and combustion, little release of activity to the fluidized bed is expected during combustion.

Final Off-Gas Treatment. Initial cleanup of the off-gas is achieved by cooling and then filtering it through sintered-metal filters in the burner. The gas passing through the filters (CO<sub>2</sub>, CO, O<sub>2</sub>, noble-gas fission products) should be nearly free of particles, as noted above. Iodine will not be present in significant amounts if the decay period is sufficiently long before it is processed. Supplemental treatment

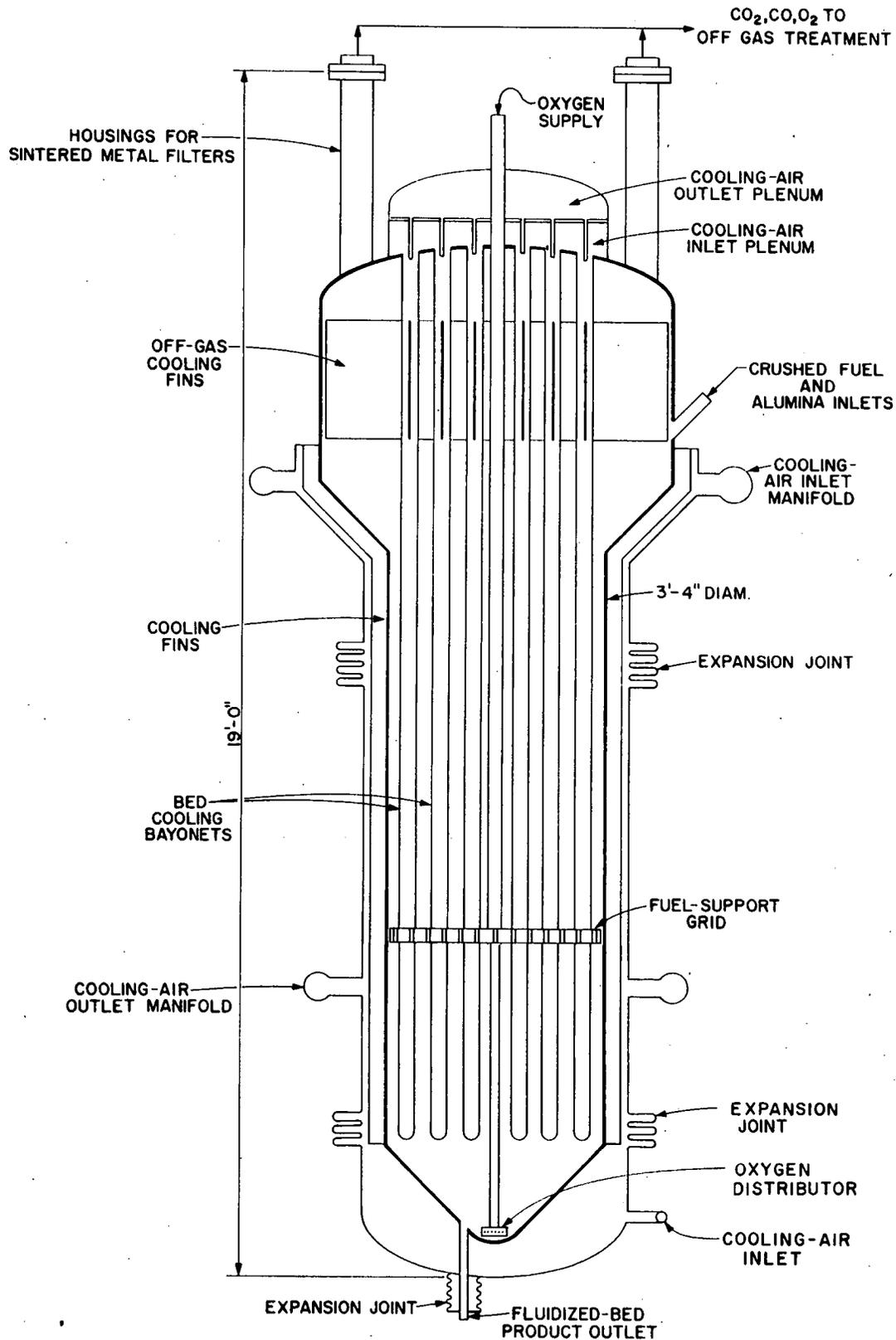


FIG. 3

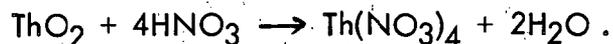
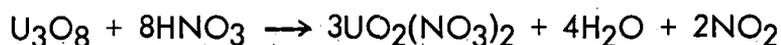
CONCEPTUAL DESIGN FOR A LARGE, FLUIDIZED-BED  
BURNER FOR GRAPHITE-BASE FUELS

of the off-gas could be made in several ways, and several useful high-efficiency methods have been demonstrated in the waste calcination programs at Idaho<sup>8</sup> and Hanford.<sup>9</sup> One method might consist in passing the off-gases through a silica-gel trap, which would adsorb ruthenium (if present) and act as a deep-bed filter, then through absolute filters, and finally to a stack. However, this may not give sufficient decontamination. Scrubbing with acidic or caustic solutions could also be done, but this is not very efficient for trapping small particles.<sup>10</sup> Furthermore, scrubbing with caustic would result in the absorption of CO<sub>2</sub> and the generation of a large amount of aqueous waste. Significantly, scrubbing with caustic was not very effective in cleaning the off-gas from a waste-calcination process.<sup>9</sup> A more attractive method might be to mix steam with the off-gas, condense the vapor, and then filter through absolute filters. Waste-calcination work<sup>9</sup> indicated that a system combining sintered-metal filters, condensation of vapor, and finally absolute filtration can yield decontamination factors  $\geq 10^8$  for the off-gas. When fluidized-bed burning tests are made with irradiated fuel, we will be able to define the off-gas cleanup problems more clearly and specify the cleanup system in more detail. However, at this point it does seem probable that a high-efficiency cleanup system which contributes a negligible amount to radioactive liquid and solid wastes can be devised for the fluidized-bed burning of graphite fuel.

## LEACHING OF FLUIDIZED-BED PRODUCTS

Products from Fuels That Contain Carbon-Coated Carbide Particles. Since the product from the combustion of this type of fuel is a homogeneous dispersion of thorium and uranium oxides in alumina, the entire bed must be leached. In the first leaching tests,<sup>1,2</sup> a simple cylindrical vessel in which the bed was supported on a sieve plate was used. With this leacher, preheated leachant was circulated either upflow or downflow through the bed. A more efficient bench-scale batch leacher was devised<sup>2</sup> (Fig. 4); the leaching acid was recirculated upflow through the bed, fluidizing the bed. Excellent contact was obtained, and gas evolution and boiling in the bed did not interfere with the leaching. Then, the product solution was drained from the bed, and the bed was washed with water. In practice, the washed alumina would then be slurried with water and transferred to an alumina recovery system where it would be dried and then either discarded or returned to the burner.

Leaching resulted in uranium and thorium recoveries of greater than 99.5%, while less than 2% of the alumina was dissolved. The main reactions are:



Very little heat is evolved by either reaction; this requires that the leachant be heated - to boiling if maximum efficiency is desired.

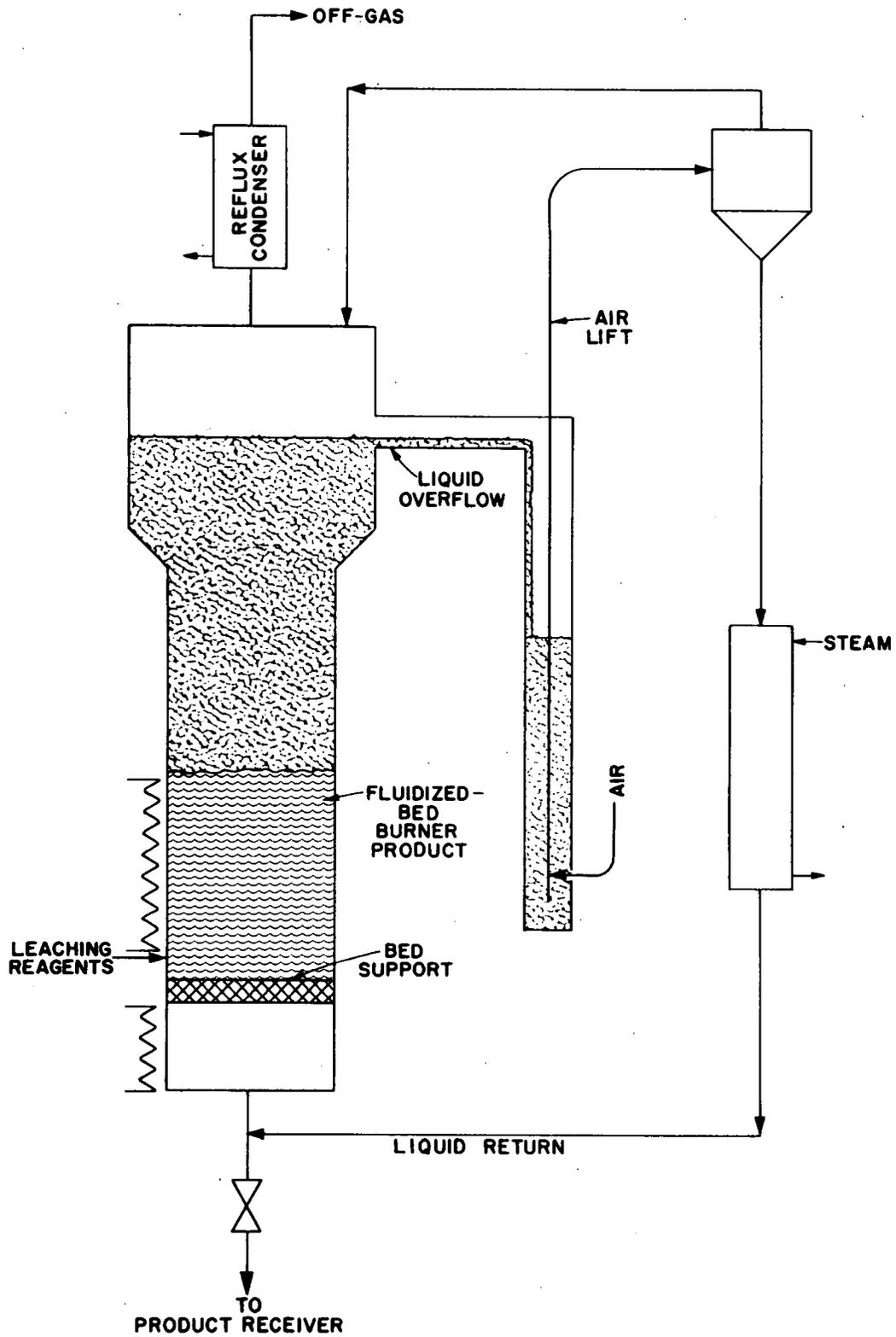


FIG. 4  
BENCH-SCALE BATCH LEACHER

In cold bench-scale tests<sup>3</sup> with a bed consisting of 3%  $U_3O_8$ , 17%  $ThO_2$ , and 80% Norton R.R. alumina, more than 99.9% of both the uranium and thorium were recovered by leaching with 12  $M$   $HNO_3$ —0.04  $M$   $HF$  at 110°C. Laboratory-scale leaching studies at Oak Ridge National Laboratory showed that excellent recoveries of uranium and thorium can be achieved with a variety of Thorex-type leachants. The bed material for these studies was produced by burning unirradiated Peach Bottom fuel compacts (carbon-coated Th-U dicarbide particles dispersed in a graphite matrix) in a fluidized bed of Norton R.R. alumina at 700 to 750°C. The product bed consisted of 6%  $U_3O_8$ , 25%  $ThO_2$ , and 69%  $Al_2O_3$ . In 5-hr leaches, more than 99.5% of the uranium and thorium were recovered when the  $HNO_3$  concentration was 4  $M$  or higher, and when the  $HF$  concentration was 0.02 to 0.05  $M$  (Table 1). Aluminum nitrate, up to 0.1  $M$  in the leachant, had no adverse effect on the recoveries. In no case was more than 2% of the alumina dissolved. Uranium and thorium recoveries were inadequate with 13  $M$   $HNO_3$  and with 2  $M$   $HNO_3$ —0.05  $M$   $HF$  (Table 1). The effect of lower leaching temperatures is being investigated.

Products from Fuels Containing Carbon-Coated Oxide Particles. As mentioned previously, there has been no experimentation with fuels that contain carbon-coated oxide particles. However, if this fuel burns as predicted, leaching of uranium and thorium may simply involve dissolution of  $ThO_2$ - $UO_2$  microspheres in the presence of a small amount of alumina. For criticality control, use of two geometrically safe slab leachers in series is envisaged for dissolving practically all the fuel particles before the solution and alumina slurry flow into large-diameter feed adjustment vessels. A schematic drawing of the leacher system is shown as Fig. 5. The leachers would be equipped with thermosiphon heating loops and would operate continuously in series. Solids (mainly fuel particles still being dissolved and the insoluble alumina) that settle out on the sloping trays in each leacher would be partially recirculated within that leacher. Eventually the insoluble alumina would be transported through the system with the leachant to the feed adjustment vessels. Leachant would be pumped into the first slab-shaped tank and maintained at its boiling point throughout the leaching system. Holdup time in each leacher would be about 3 hr. Solids and solution from the first leacher would overflow continuously into the second one. Alumina would be transported through the system without being attacked appreciably by the dissolvent. Solution from the second leacher would be transferred semicontinuously by intermittent air lift to a feed adjustment system where any small fuel particles still remaining in the leacher overflow would be dissolved rapidly.

Unlike the oxide product from the combustion of Th-U dicarbide particles, unirradiated  $ThO_2$ - $UO_2$  microspheres probably cannot be dissolved readily in a dilute Thorex solution (Table 2). However, almost theoretically dense, 300- to 600- $\mu$ -diam  $ThO_2$  microspheres were dissolved in 3 to 6 hr in boiling 13  $M$   $HNO_3$ —0.05  $M$   $HF$ , even in the presence of a large excess of alumina. In other studies,<sup>11-13</sup> irradiated  $ThO_2$ - $UO_2$  appeared to dissolve faster than unirradiated oxide. Thus, the 6-hr dissolution period estimated for fuels containing  $ThO_2$ - $UO_2$  microspheres should be adequate.

Table 1. Results of Laboratory-Scale Leaching Experiments

Leachant: Boiling  $\text{HNO}_3$ -HF- $\text{Al}(\text{NO}_3)_3$

Fluidized-bed product from combustion of Peach Bottom fuel:  
6%  $\text{U}_3\text{O}_8$ , 25%  $\text{ThO}_2$ , 69% Norton R.R. alumina

Leaching time: 5 to 7 hr

Final solutions were about 0.6 *M* in Th

Leachant Composition ( <i>M</i> )			Amounts Leached (%)		
$\text{HNO}_3$	HF	$\text{Al}(\text{NO}_3)_3$	U	Th	Al
2	0.05	0	83.6	83.0	0.2
4	0.05	0	99.9	99.9	1.9
4	0.05	0.1	99.7	99.5	-
13	0.0	0	27.7	14.8	-
13	0.02	0	99.9	99.6	-
13	0.05	0	99.9	99.9	1.9
13	0.05	0.1	99.9	99.9	-

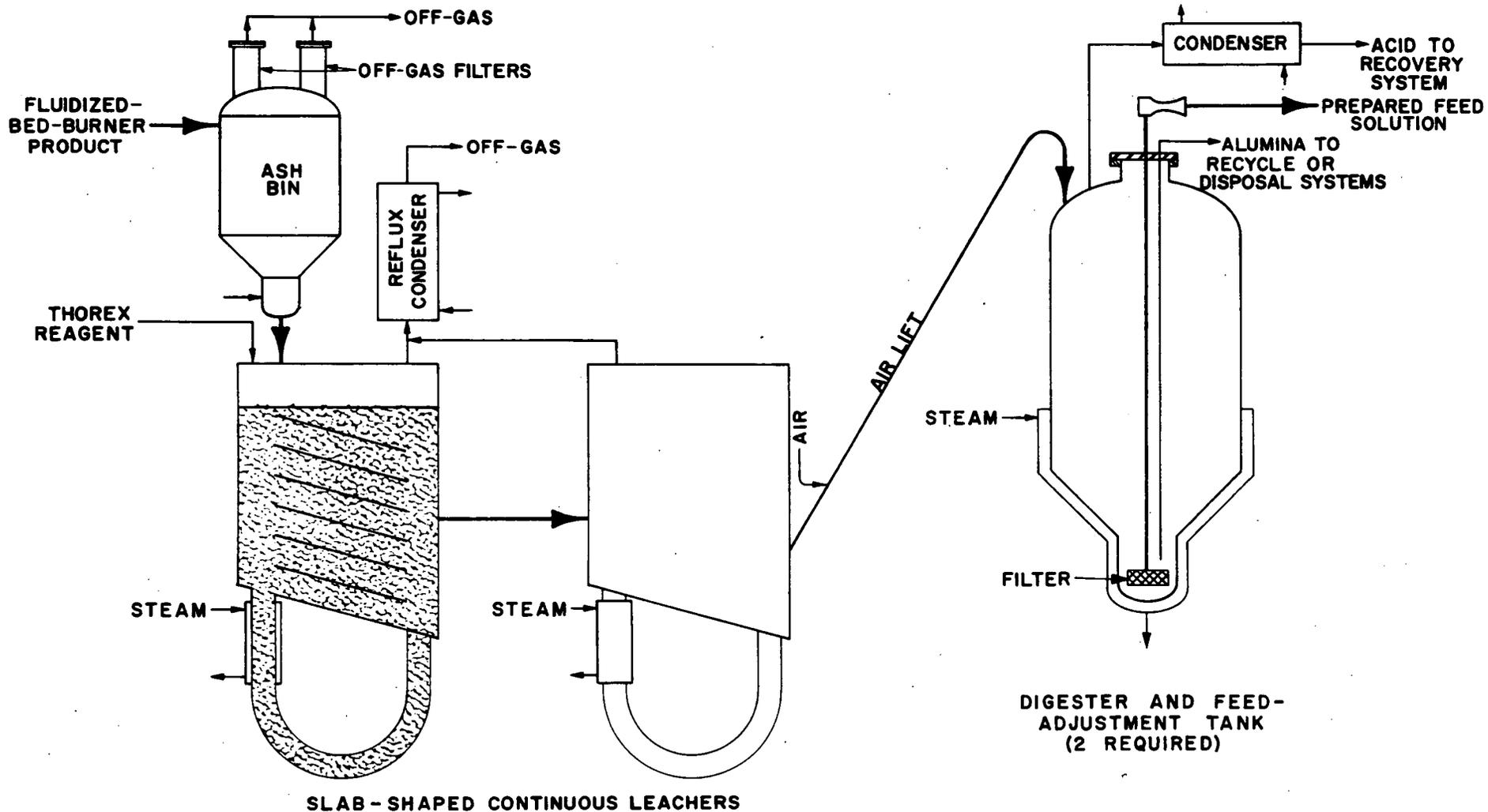


FIG. 5

CONCEPTUAL LEACHING AND FEED-ADJUSTMENT SYSTEM FOR GRAPHITE-BASE FUELS THAT CONTAIN  $\text{ThO}_2\text{-UO}_2$  MICROSPHERES

Table 2. Dissolution of Sol-Gel ThO<sub>2</sub> Microspheres in Boiling Thorex Reagents

Reaction time = 6 hr

Diameter of Microspheres ( $\mu$ )	Reagent Composition ( <i>M</i> )		Amount Dissolved (%)
	HNO <sub>3</sub>	HF	
250-300	2	0.05	20
420-600	2	0.05	33
250-300	4	0.05	57
420-600	4	0.05	73
250-300	13	0.05	100
420-600	13	0.05	100

## SOLVENT EXTRACTION

The solvent extraction system for recovering the uranium and thorium is based on the newer processes,<sup>14</sup> in which an acid-deficient feed is used for maximum fission product decontamination. Nitric acid is used as the salting agent instead of  $\text{Al}(\text{NO}_3)_3$ . This reduces the amount of  $\text{Al}(\text{NO}_3)_3$  in the stored waste. If thorium recovery is desired, a process similar to the Acid Thorex Extraction process (Fig. 6) could be used. The organic product has a low acid content; consequently, the thorium and uranium can be co-stripped with a minimum aqueous volume and number of stages. Uranium and thorium may also be recovered separately in partitioning and stripping columns if desired. If thorium recovery is not desired, the Acid-Interim-23 process<sup>14</sup> could be used. The irradiated thorium will probably contain enough  $^{228}\text{Th}$  to interfere with fuel manufacture in lightly shielded fuel-refabrication facilities. Consequently, until such time as heavily shielded facilities are available, it may be desirable to concentrate the thorium product and store it for about ten years to permit decay of  $^{228}\text{Th}$  before recycle of the thorium.

## PRELIMINARY ECONOMIC EVALUATION

A preliminary plant design and capital- and operating-cost estimates were made for a head-end facility that would provide for irradiated fuel-element receipt and storage, crushing, burning, leaching, feed adjustment to acid-deficient conditions suitable for solvent extraction, adjusted feed-storage surge capacity, and tank storage of the recovered thorium for  $^{228}\text{Th}$  decay. This head-end facility is assumed to be located at a conventional fuel-processing plant, such as the one built by Nuclear Fuel Services, Inc. (NFS). At this plant, the uranium and thorium would be recovered separately by solvent extraction, the thorium returned to the head-end facility for decay storage, and the fission product waste concentrated for disposal.

The study was made for a fuel that contains sol-gel oxide microspheres coated with pyrolytic carbon, which may be the favored HTGR fuel of the future. Although the processing of carbide-particle fuels may be somewhat different, the resulting differences in estimated costs would probably be small and within the margin of error of the estimate. The fuel element is assumed to be a 4.5-in.-diam, 20-ft-long, graphite "log" from which the fueled particles are not easily separable; thus, provisions are made for crushing and burning the entire element. Each element contains 107 kg of carbon and about 10.9 kg of thorium plus uranium, before irradiation. After an assumed burnup of 50,000 to 80,000 Mwd/metric ton in about 6 years of irradiation, and 6 months or more postirradiation time for fission product heat reduction and protactinium decay, the element contains about 10 kg of thorium plus uranium, the balance having been converted to fission products.

The conceptual design of the head-end facility is shown as Figs. 7, 8, and 9. The processing capacity is 40 elements per day for up to 225 days a year, with

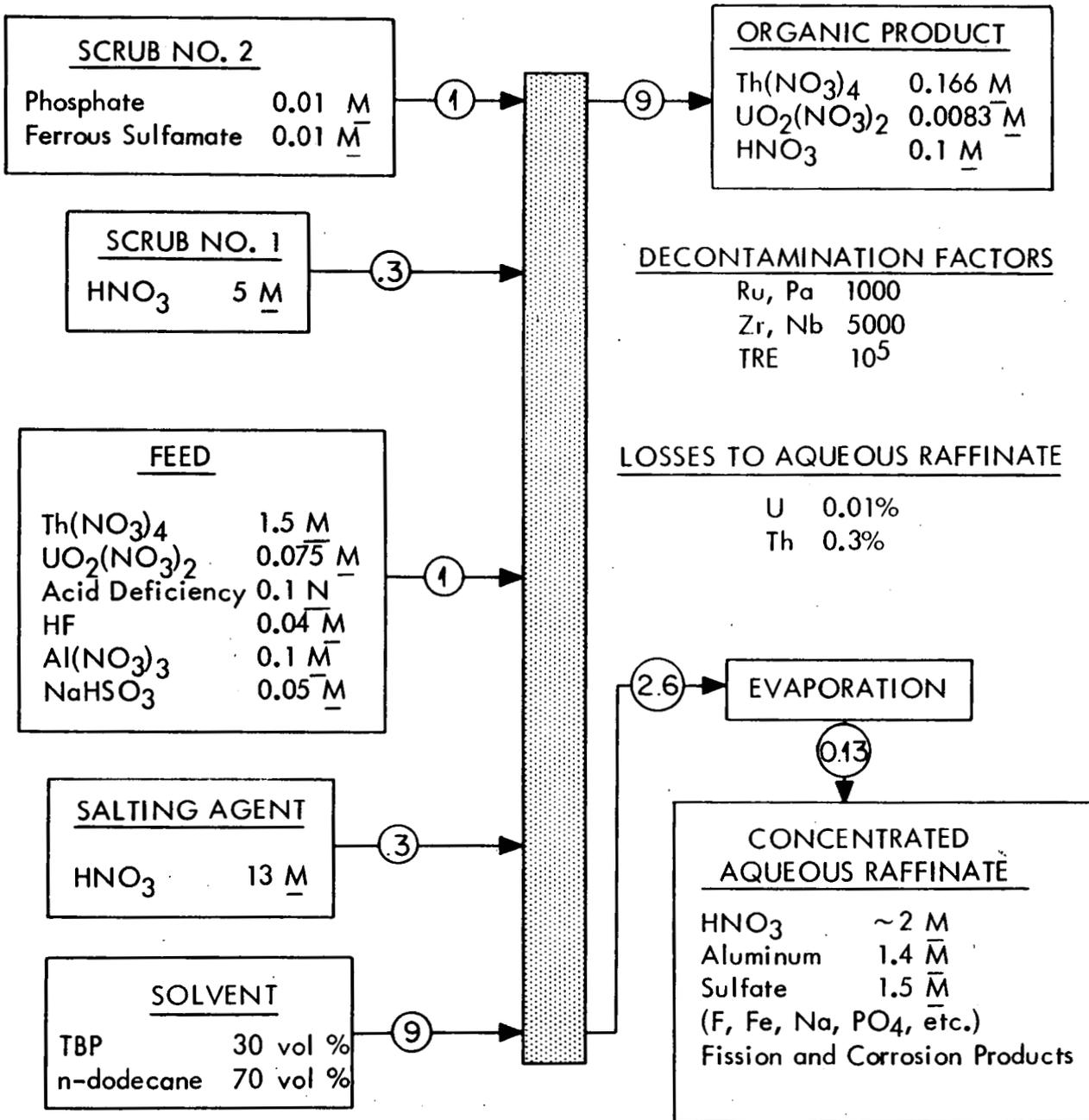


Fig. 6

ACID THOREX PROCESS FOR CO-EXTRACTION OF URANIUM AND THORIUM

- KEY
- 1 Railroad car shed
  - 2 Fuel-cask unloading cell
  - 3 Fuel-storage and burner-feed-preparation cells
  - 4 Burner cells
  - 5 Leaching and feed-preparation cells
  - 6 Off-gas treatment cell
  - 7 Feed-storage cell (below)
  - 8 Thorium-evaporation and acid-waste cell
  - 9 Vessel off-gas filter cells

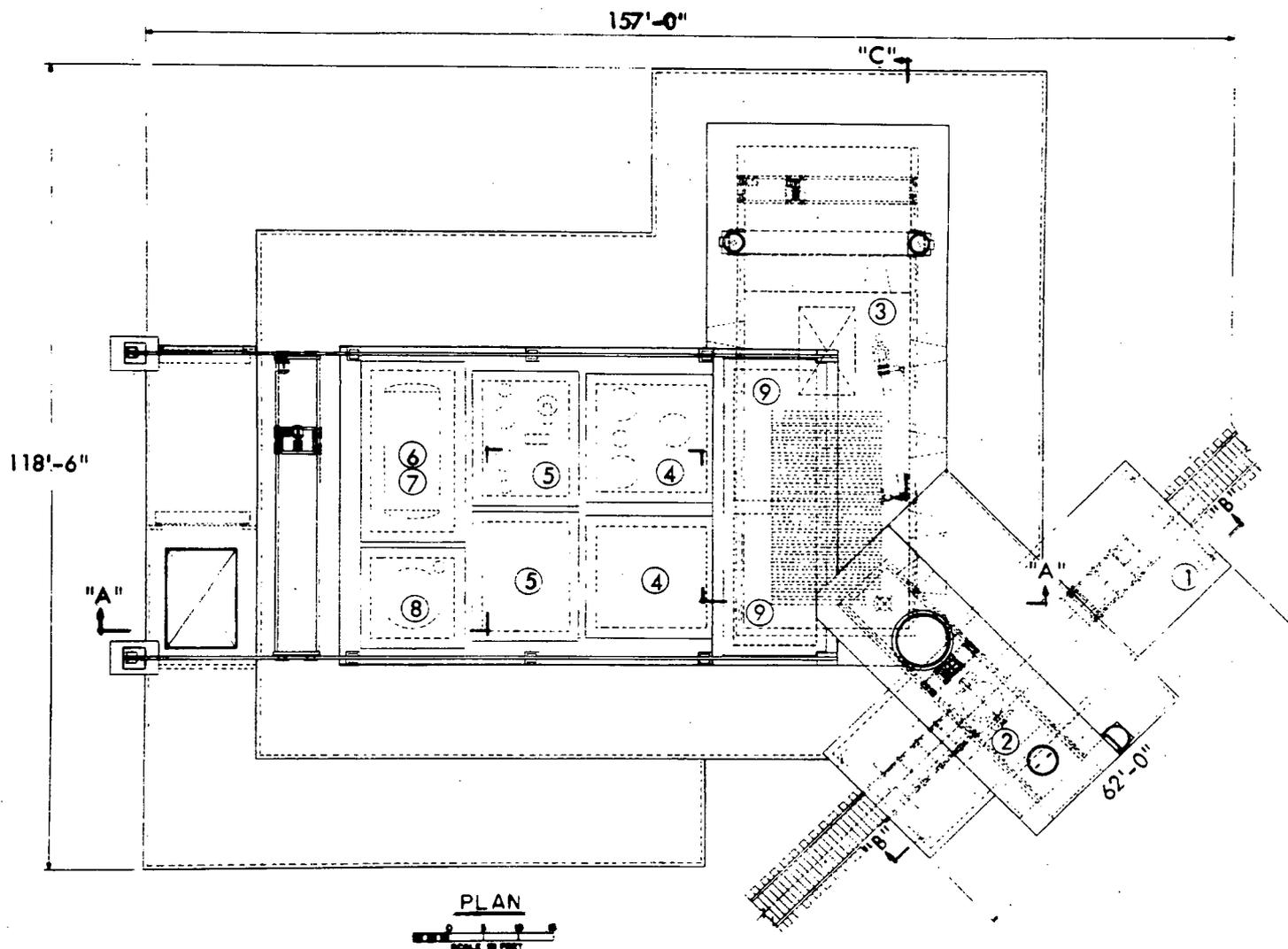
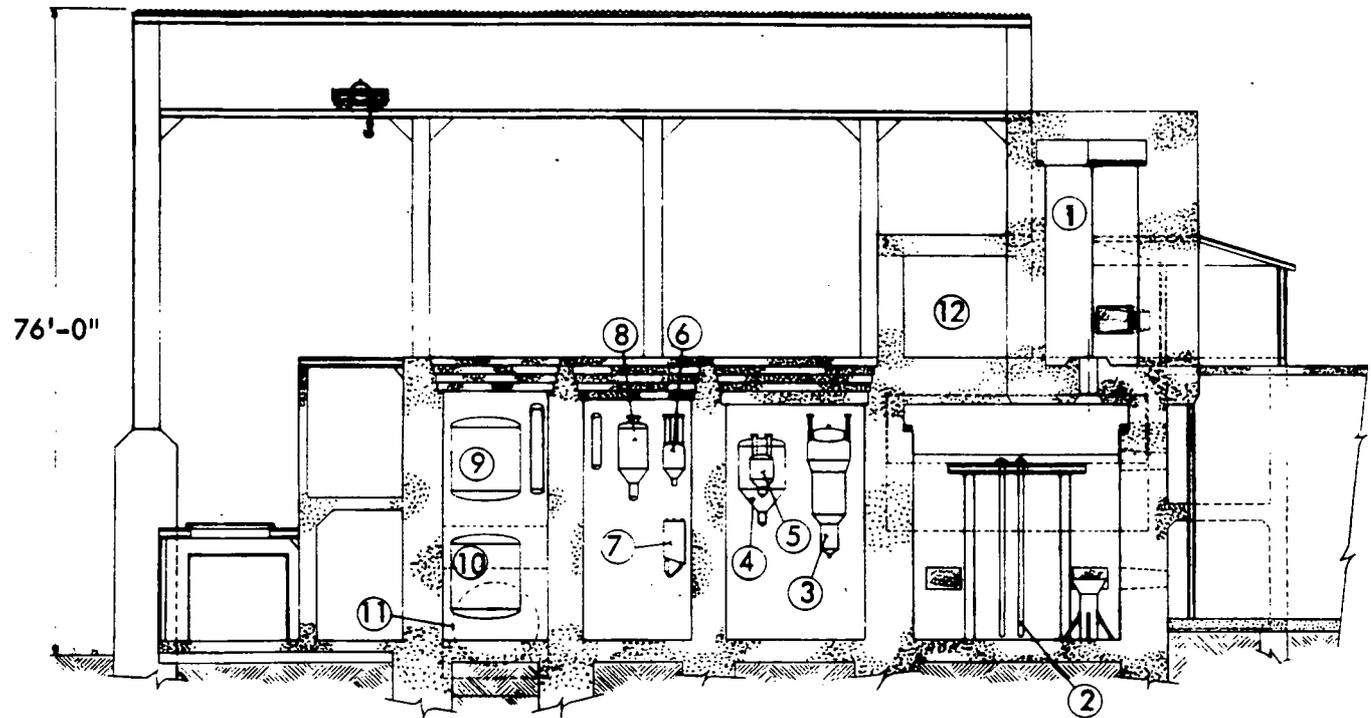


Fig. 7  
 FUEL-REPROCESSING HEAD-END BUILDING FOR HTGR FUEL

KEY

- 1 Fuel-cask unloading cell
- 2 Fuel cans on storage rack
- 3 Fluidized-bed burner
- 4 Silica-gel adsorber for ruthenium
- 5 Waste-alumina bin
- 6 Ash bin
- 7 Continuous leacher
- 8 Digester and feed-adjustment tank
- 9 Thorium evaporator
- 10 Acid-waste-collection tank
- 11 Feed-storage tank
- 12 Vessel off-gas filter cell



SECTION "A-A"

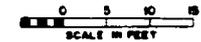
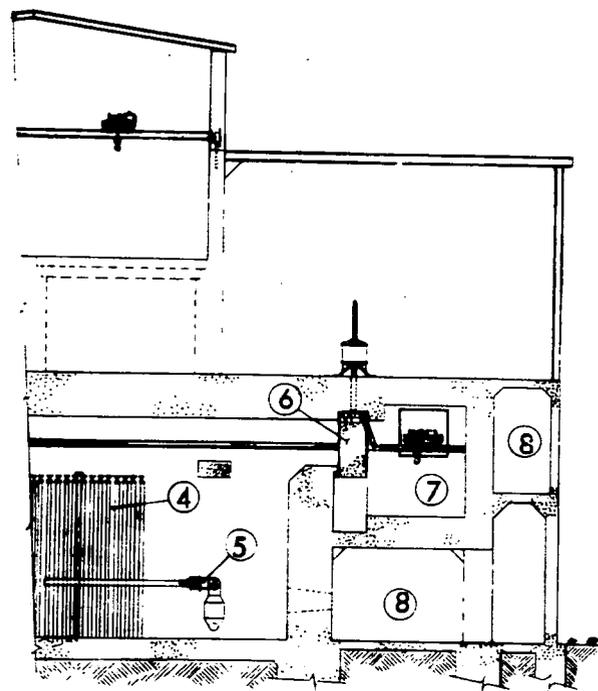


Fig. 8

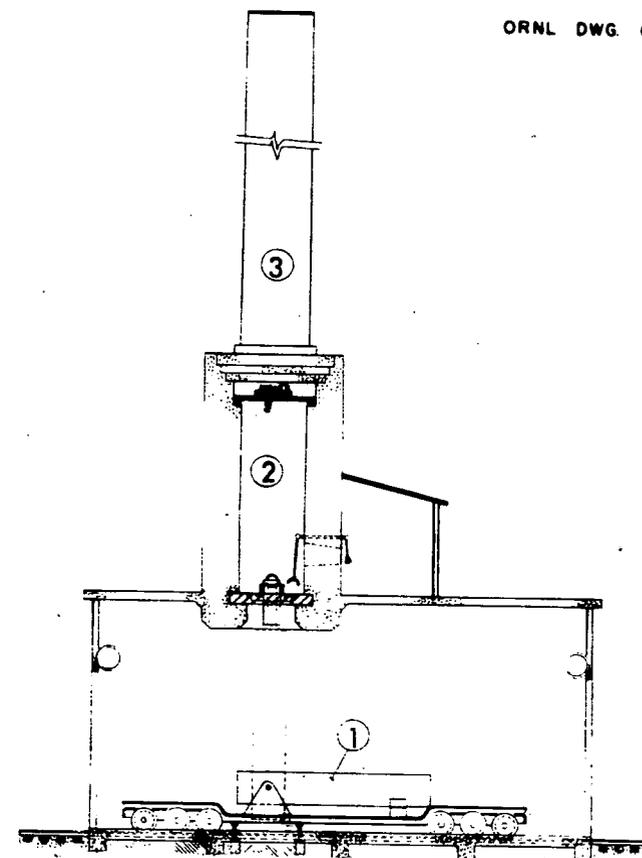
FUEL-REPROCESSING HEAD-END BUILDING FOR HTGR FUEL

KEY

- 1 Fuel-shipping cask
- 2 Fuel-cask unloading cell
- 3 Plant stack
- 4 Fuel-storage rack
- 5 Fuel-can dumper and burner-feeding system
- 6 Vertical-lift shielding door
- 7 Remote crane repair room
- 8 Viewing and operating areas



SECTION "C-C"



SECTION "B-B"

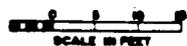


Fig. 9

FUEL-REPROCESSING HEAD-END BUILDING FOR HTGR FUEL

two parallel lines of crushing-burning-leaching-adjustment equipment (Figs. 3 and 5). At maximum throughput rate, such a facility could handle the fuel from reactors having up to 10,000 Mw (electrical) of installed capacity; however, as discussed below, the cost of the plant might have to be borne by a smaller industry than this. Fuel unloading and storage cells are designed for remote operation and limited remote maintenance, and the chemical process cells are designed for direct maintenance. Analytical, administrative, chemical supply, waste disposal, and plant utility services are assumed to be provided by the associated solvent extraction plant, with appropriate enlargements where necessary. A complete, independent, radioactive off-gas and cell-ventilation system, plus disposal stack, are included. Limited office and change-room facilities are provided in the building. An 11,500-gal surge tank is included to hold up about 16 metric tons of thorium plus uranium as adjusted feed, permitting some scheduling leeway between the head-end and solvent-extraction facilities. An evaporator for the partially decontaminated thorium second-cycle raffinate is included, as is a 12,400-gal storage tank which holds about 33 metric tons of thorium as the hydrated nitrate. Additional thorium storage tanks would be built as needed, and these are assumed to be paid for by the value of the thorium when it is recycled after the  $^{228}\text{Th}$  decays.

The estimated capital cost of this facility is \$9,040,000 (Table 3). This includes \$1,260,000 for the second processing line, an expenditure that could be postponed until required if the plant were started on a fraction of its design load. The "standby" operating cost, that is, the minimum labor, utility, and overhead cost of maintaining the facility when fuel is not being processed, is estimated to be \$115,000 a year. Additional labor and overhead costs when fuel is being processed are estimated at \$350 a day. The cost of oxygen and alumina is estimated at \$846 a day for one burner line, or \$1,020 for two burner lines. The lower unit cost for two lines is the result of lower oxygen costs at the high usage rates. The costs of nitric acid, other chemicals, waste disposal, etc., were not estimated separately since they were considered to be a part of the normal solvent extraction costs, since the costs should be nearly the same as those for standard, metal-clad oxide fuel on an equivalent throughput basis.

The translation of these cost estimates into unit costs, per kilogram of thorium plus uranium, or per kwhr (electrical), depends critically on the actual fuel load (compared with the nominal capacity) and on the limitations imposed by the associated solvent extraction plant. The head-end facility might be built at a large multipurpose processing plant of the future, with a solvent extraction processing rate of several metric tons a day. Thus, the burn-leach lines might operate full-time, accumulating adjusted feed in the surge tank for a few solvent extraction campaigns per year. It might be built as a part of an integrated single-purpose HTGR fuel-processing plant with solvent-extraction capacity matched to the burn-leach capacity. If such a head-end facility were built in the next several years, it might be located at a relatively small multipurpose plant, such as the NFS plant, where the fraction of solvent extraction capacity that could be allocated to HTGR elements would limit the HTGR head-end facility to part-time operation. In any of these three instances,

Table 3. Capital-Cost Estimate for HTGR Head-End Facility

Item	Cost <sup>a</sup>
Building and services	\$ 550,000
Building equipment	130,000
Cell structure	1,295,000
Cell services	565,000
Cell equipment	247,000
Process equipment	1,098,000
Process piping	906,000
Process and radiation instrumentation	350,000
Outside equipment	346,000
Site improvements	50,000
Utilities	85,000
Subtotal	\$5,622,000
Engineering and inspection (20%)	\$1,124,000
Subtotal	\$6,746,000
Contingency (25%)	\$1,687,000
Subtotal	\$8,433,000
Interest during construction, startup costs, and working capital	\$ 607,000
Total	\$9,040,000

<sup>a</sup> Installed cost, including contractor's overhead and profit.

if this head-end facility were built in time to process the first fuel discharged from the first HTGR, the processing load initially would represent only a fraction of nominal capacity, and it would be several years before capacity was reached, depending on the growth rate of the HTGR industry. The same problems in calculating processing costs were originally faced for estimating the cost of processing elements from the first commercial power reactors. Costs were determined on an interim basis by a USAEC-guaranteed reprocessing charge,<sup>15</sup> based on cost estimates for a conceptual<sup>16</sup> "Reference Fuel-Processing Plant," and then by the NFS-USAEC contract.<sup>17</sup> This contract provided for charges based on a fully loaded plant, with the government providing a base load to partially make up for the lack of adequate private load during the early growth period of the power reactor industry. There is at present no equivalent accepted basis for determining charges for HTGR fuels; so the discussion which follows is highly speculative.

The NFS plant has a nominal capacity of 1000 kg of uranium per day for 225 days a year. This is for standard uranium fuels of up to 3% enrichment and burnups of 20,000 Mwd/metric ton. For higher enrichments and burnups, and for small fuel batch sizes, the effective processing rate may have to be reduced. For thorium fuels, the nominal capacity is 500 kg of thorium plus uranium per day. The reported capital cost is about \$30,000,000, including site, fuel receipt and storage, chop-leach head-end, solvent extraction, waste disposal, engineering and interest, working capital and startup. The nominal annual charges are \$7,050,000, including both capital and operating costs; this corresponds to about 0.20 mill/kwhr (electrical) if all the fuel were from typical, large, pressurized- or boiling-water reactors.

Based on a superficial comparison of building and equipment sizes, and on the HTGR head-end facility cost estimate described above, we see no reason why an integrated, single-purpose processing plant for HTGR fuel, consisting of our conceptual head-end facility plus matching solvent extraction and other facilities, should have capital or operating costs significantly greater than those for the NFS plant, except that the costs for oxygen and alumina would be extra. Assuming NFS-type financing, such a reference plant could charge \$75 to \$80 per kg of uranium plus thorium, equivalent to a power-cost component of 0.11 to 0.15 mill/kwhr (electrical), depending on burnup and thermal efficiency. This is an attractively low prospective cost, but there may not be enough HTGR's to fully load such a plant until 1980 to 1985.

A much more conservative approach would be to assume that our conceptual HTGR head-end facility would be built at NFS in 1973, that it would have a load increasing from 3 metric tons a year in 1973 to 51 in 1980, that the HTGR head-end capital investment must be recovered, with interest, profit, and taxes by 1980 (the end of the nominal 15-year plant life for the NFS facilities), and that HTGR fuel processing costs must pay the full, regular, NFS charges in addition to the special head-end charges. A present-worth economic analysis,<sup>18</sup> using a discount factor of 8 to 10% and a corporation income tax rate of 50%, of such a hypothetical case indicated the following:

Special head-end capital and operating charges	\$107-134/kg (Th + U)
Regular NFS charges for thorium fuels	\$56-79
	<hr/>
Total	\$163-213/kg (Th + U)

This total corresponds to 0.2 to 0.4 mill/kwhr (electrical) and is high enough to be a barrier to consideration of this approach to commercial HTGR fuel processing. On the other hand, since the total is based on a fairly pessimistic set of assumptions, extending the economic plant life plus providing some kind of base-load guarantee would permit substantially lower charges.

A significant technical assumption that would permit lower charges in a small HTGR fuel processing plant would be to specify a fuel element from which the fuel particles can be poured into a shipping container at the reactor. This would reduce shipping costs and permit cheaper fuel receipt and storage facilities at a processing site or the use of existing facilities at the NFS plant. In addition, the burner could be much smaller, with a single burner line possibly fitted into present cell space in the NFS plant.

### COMBUSTION-FLUORINATION PROCESS

Burning of graphite fuels in fluidized beds of inert alumina, followed by fluorination of the ash, is a potential nonaqueous alternative to the burn-leach method. Preliminary experiments<sup>3</sup> at Brookhaven National Laboratory indicate that it might be possible to achieve acceptable uranium recoveries from fuel that contains carbide particles. Pilot plant oxidation-fluorination experiments with prototype Peach Bottom fuel were conducted in a 4-in.-diam fluidized bed. The fuel was burned at 725 to 800°C in fluidized Norton R.R. alumina (equal parts of 60-, 90-, and 120-mesh). The product bed contained about 14% ThO<sub>2</sub>, 3% U<sub>3</sub>O<sub>8</sub>, and 83% Al<sub>2</sub>O<sub>3</sub>. After combustion, the bed was fluorinated at 450 to 550°C with F<sub>2</sub>-N<sub>2</sub> mixtures containing between 25 and 50 vol % F<sub>2</sub>. Uranium recoveries (as UF<sub>6</sub>) were 92.1 and 98.8% after fluorination times of 2.4 and 3.8 hr. A very exothermic reaction occurring above 500°C was controlled only by reducing the fluorine concentration in the fluidizing gas. However, since little UF<sub>6</sub> evolved at temperatures below 500°C, operation in the range 500 to 550°C appears mandatory if acceptable uranium recoveries are to be achieved. One other limitation of the combustion-fluorination process was noted in the preliminary tests. The thorium fluoride concentration in the bed must be held below about 38 wt % to keep the bed from caking. More experiments will be required to determine whether or not acceptable uranium recoveries from fuel that contains carbide particles can be achieved by the combustion-fluorination process. Even if such conditions are found, loss of thorium to the bed seems inevitable because of the extremely low volatility of ThF<sub>4</sub>.

Preliminary experiments<sup>19</sup> indicate that the combustion-fluorination method will not be applicable to fuels that contain high-density  $\text{ThO}_2\text{-UO}_2$  microspheres, especially if the microspheres do not crack or break during irradiation and combustion. The reactivity of 150- to 180- $\mu$ -diam 96%  $\text{ThO}_2$ -4%  $\text{UO}_2$  sol-gel microspheres in fluorine was tested on a laboratory scale. In a 4-hr experiment at 480°C, the microspheres were unaffected. Also, at 650°C, only 15% of the uranium was volatilized as  $\text{UF}_6$  in 4 hr; this was equivalent to a radial penetration of only 6  $\mu$ .

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