V

CONF-760823-3

GENERAL ATOMIC

GA-A13807

HTGR FUEL REPROCESSING TECHNOLOGY

by
L. H. BROOKS, C. A. HEATH, and J. J. SHEFCIK

APRIL 30, 1976

DISCLAIMER

GENERAL ATOMIC

GA-A13807

HTGR FUEL REPROCESSING TECHNOLOGY

by
L. H. BROOKS, C. A. HEATH, and J. J. SHEFCIK

This is a preprint of a paper to be presented at the A.I.Ch.E. Symposium on Gas-Cooled Reactor Fuel Cycles, August 29 - September 1, 1976, Atlantic City, N. J., and to be printed in the Proceedings

Work supported by
U. S. Energy Research and Development Administration,
Contract E(04-3)-167, Project Agreement No. 53

GENERAL ATOMIC PROJECT 3225

APRIL 30, 1976

INTRODUCTION

Since nuclear fission was harnessed by man for peaceful application, the initial emphasis and success have been in the use of uranium-consuming systems which are capable of producing plutonium to extend their fuel cycle. The light water reactor (LWR), which is currently in widespread use in the U.S., was developed as an offshoot from the U.S. Navy program to develop nuclear-powered submarines. These LWR systems are fueled by uranium which is enriched to about 3% in fissile U-235. The balance is U-238 which is partially parasitic and partially converted to plutonium, providing additional fissile fuel.

It is also possible to obtain fissile material from the conversion of thorium to U-233 and thus extend what are turning out to be limited resources of uranium. Thorium is available in large deposits in several parts of the world and is reported to be 10 times more abundant than uranium. Early studies of the nuclear physics of reactor systems indicated that the optimum use of thorium in a reactor cycle could be achieved in what is now known as the High-Temperature Gas-Cooled Reactor (HTGR). The initial fissile fuel in the HTGR is uranium enriched to 93% in U-235 which is mixed with 10 to 20 times as much thorium by mass. During irradiation, a small amount of the residual U-238 is converted to plutonium, but the bulk of conversion is that of thorium to U-233.

The HTGR is different from the LWR in that cooling is performed by helium gas rather than water and the slowing down or moderation of neutron energies, which is required in these reactors to optimize the fission process, is performed by graphite rather than water. Graphite also permits the use of higher operating temperatures and, as a consequence, a more efficient use of the generated heat in producing power. The fuel form of the HTGR is therefore significantly different from that of the LWR. While both reactors employ oxides or carbides of uranium, the HTGR fuel is

retained in large graphite fuel elements whereas the LWR fuel is clad in long metallic tubes assembled into clusters. Figures 1 and 2 illustrate the fundamental difference in fuel form of these two reactor types.

In order to extend the fuel resources that are available to us in the forms of uranium and thorium, reactor fuel cycles have been designed to convert non-fissionable isotopes of uranium and thorium into fissionable isotopes. A significant amount of the plutonium formed from U-238 in the LWR and the U-233 formed from thorium in the HTGR is consumed in place. However, after extensive irradiation, the buildup of fission product elements in the reactor fuel causes an excessive parasitic consumption of neutrons and the bred plutonium or U-233 must be recovered and purified in order to be used economically as reactor fuels.

This recovery of bred fuel from irradiated fuel elements for manufacture into fuel elements for reactors is referred to as fuel recycle. That part of the process which recovers the fuel from the reactor element and separates the residual and bred fuels from the fission products is called reprocessing. The remanufacture of the recovered fuel into elements to be reinserted in the reactor is called refabrication. In this paper, selection of the reference flowsheet for reprocessing of HTGR fuels will be discussed. In a companion paper, "Flowsheet Development for HTGR Fuel Reprocessing" (Ref. 1), B. J. Baxter, G. E. Benedict and R. D. Zimmerman discuss the development of the flowsheet. The development of the refabrication technology for HTGR fuels is the subject of another paper by J. D. Sease from ORNL (Ref. 2).

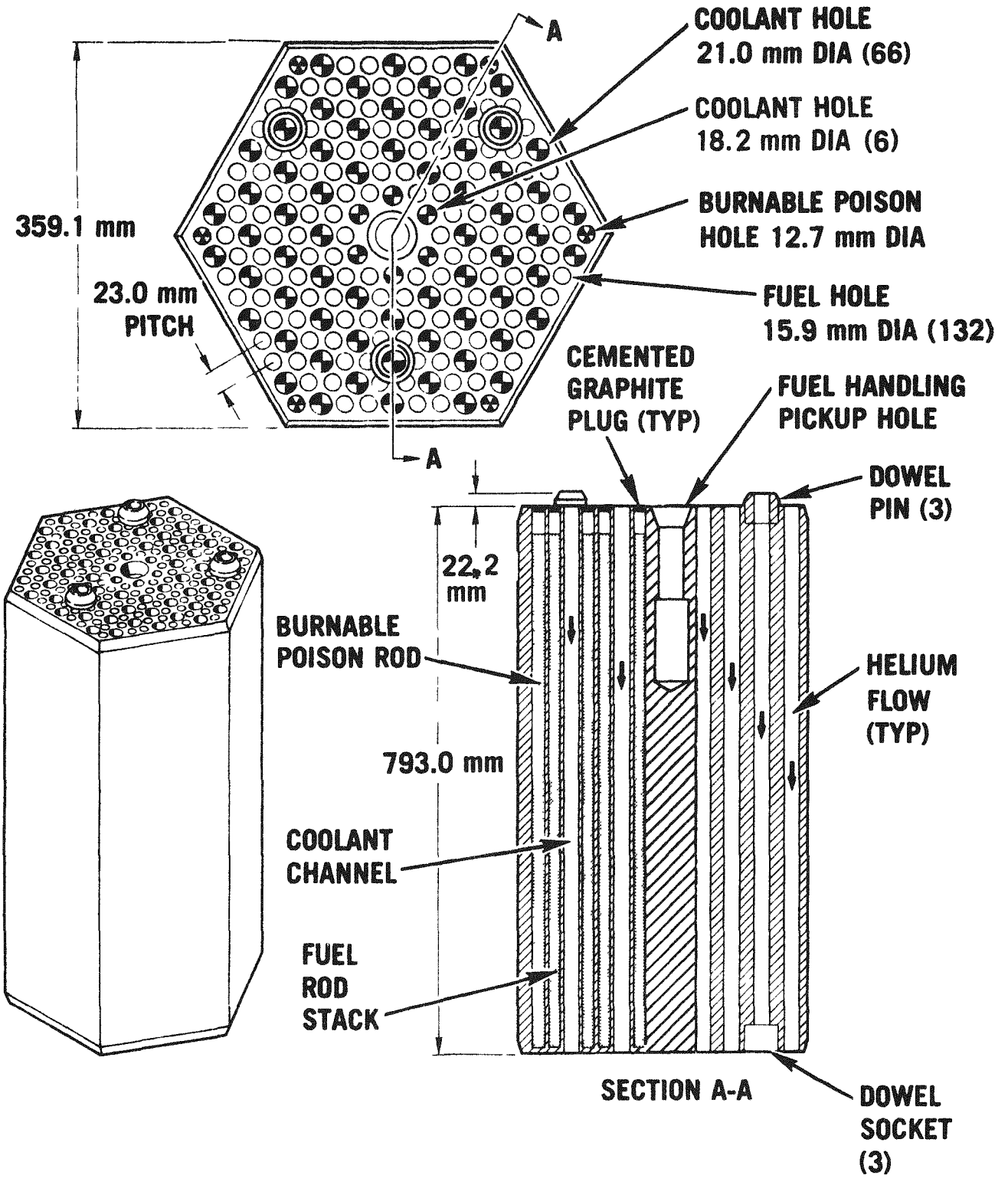
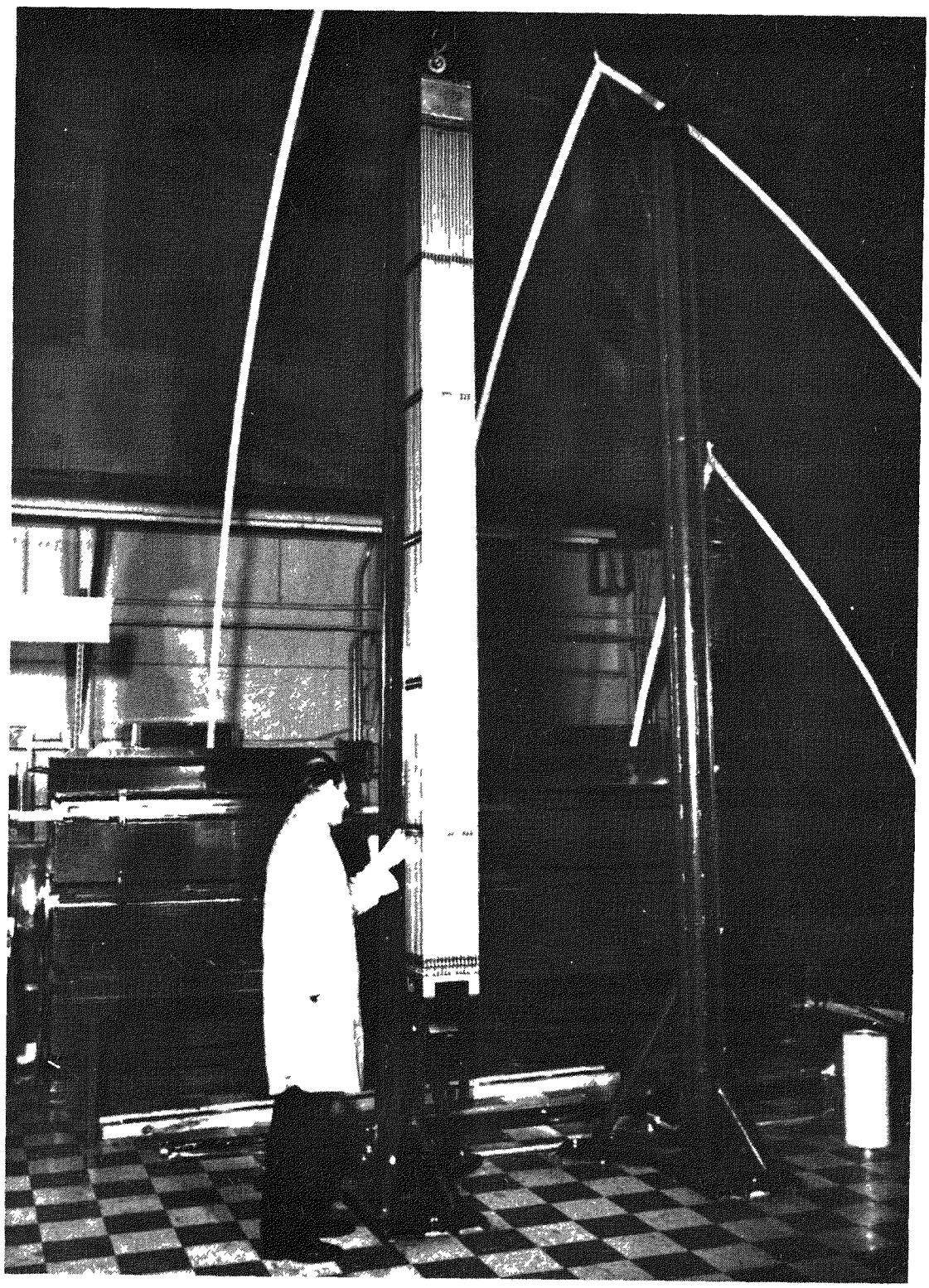


Fig. 1. HTGR standard fuel element



73K1399

Fig. 2. LWR fuel element

CHARACTERISTICS OF HTGR FUELS

The basic fuel element in the HTGR is a graphite block 793 mm (31.4 in.) high with a hexagonal cross section 359 mm (14.2 in.) across the flats, as illustrated in Figure 1. The graphite block is drilled lengthwise with two sets of holes; one allows the passage of helium coolant and the second contains the fuel rods. Fuel rods are formed by the molding of selected blends of fuel particles with a graphite pitch; each fuel rod is 51 mm (2 in.) in length and has a diameter of 15.8 mm (0.625 in.). The fuel particles used in the HTGR fuel are schematically shown in Figure 3. These fuel particles contain either uranium dicarbide (highly enriched in U-235 or recycle U-233) or ThO_2. The particles shown in Figure 3 typically have diameters of 500 to 800 μm.

Two particle types are used in the HTGR fuel; they are categorized by the coatings that have been applied to them. As can be seen in Figure 3, they are classified as BISO or TRISO coated particles. BISO particles are coated with a relatively porous buffer layer of carbon and then with a dense coating of pyrolytic carbon. TRISO coatings, in addition, have a silicon carbide coating placed between two layers of pyrolytic carbon. The SiC layer provides a means of separating these particles from the BISO particles in head-end reprocessing operations; it also enhances fission product retention in the fissile particles. BISO coatings are used for particles initially loaded only with thorium oxide, while TRISO coatings are used for particles loaded with uranium.

During irradiation in the reactor, the fissile and fertile materials undergo one or more of the processes illustrated in Figure 4.

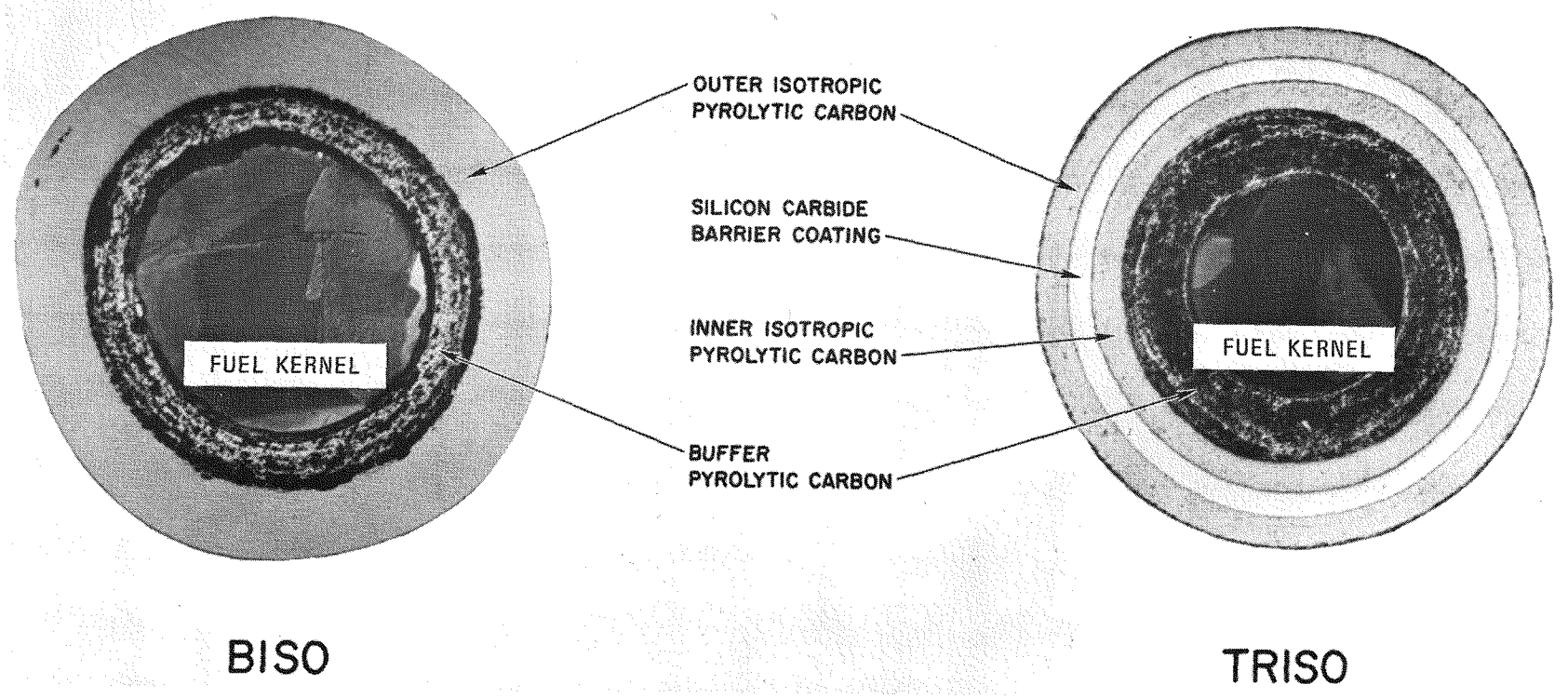
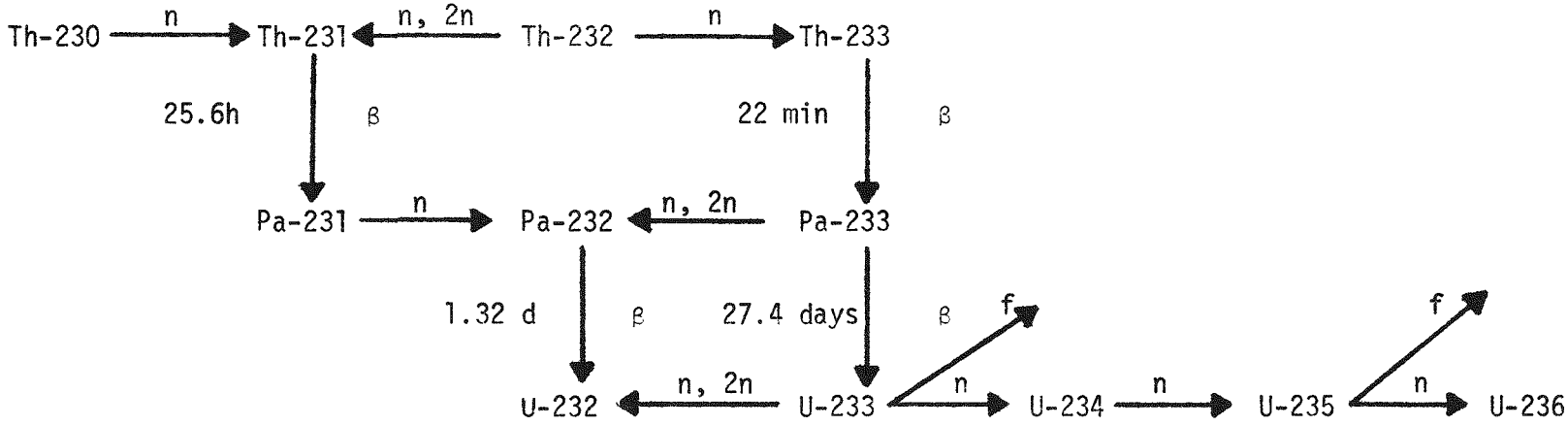


Fig. 3. HTGR coated fuel particles

FERTILE PARTICLES



FISSILE PARTICLES

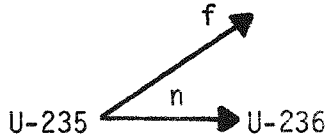


Fig. 4. Nuclear reactions in the fuel

An initial core loading of fissile and fertile particles will be irradiated to spent fuel with fissile particles containing mostly U-235, U-236 and fission products, and fertile particles containing mostly thorium, U-233 and fission products. The main objective of reprocessing the spent fuel is to recover the bred fissile U-233 in a form suitable for use in recycle fuel elements. Secondary objectives are to recover thorium and unused U-235 for later possible reuse in recycle fuel and to separate fission products for subsequent waste processing. A successful reprocessing technique must recover the bred U-233 from the fertile particle with minimal contamination by the U-236 now contained in the spent fissile particles. U-236 acts as a neutron absorber or posion in the HTGR core and significant contamination of bred fuel with U-236 reduces its value in the reactor.

The fuel design described here is different from the fuel in the Fort St. Vrain HTGR. Both fissile and fertile particles in Fort St. Vrain are TRISO coated, and the fissile particle contains a 4.25:1 ratio of Th to U in a $(U/Th)C_2$ form. Since fuel from Fort St. Vrain will be the only irradiated HTGR fuel available in large quantities during the reprocessing development program, process demonstration will be performed with TRISO-TRISO fuel. However, as will be shown, reprocessing of TRISO-TRISO fuel is considered more difficult than reprocessing TRISO-BISO fuel.

CRITERIA FOR A FUEL REPROCESSING FLOWSHEET

As discussed in the paper by L. L. Bennett and R. F. Turner (Ref. 3), the value of the bred U-233 in the HTGR system provides a considerable economic incentive to recycle this material in the reactor. However, it is recognized that the cost of reprocessing and refabrication of the fuel and of converting the waste fission products into an

acceptable form for ultimate disposal or terminal storage must be minimized, or at least kept to a reasonable level, to obtain the benefit of the value of the bred fuel.

It is important, therefore, that the recycle technology be developed for application in commercial facilities which can reduce the unit cost through large throughput and efficient operation. General criteria of any flowsheet will therefore include requirements that:

1. The process and the process equipment must

   - be suitable for large volume throughput;
   - utilize proven technology to the maximum extent practical and therefore require the minimum amount of R&D to permit the design and operation of a plant with reasonable assurance of success;
   - be amenable to accountability of the value of fuels received from multiple customers as well as the overall accountability of special nuclear material for safeguards purposes as required by the Federal government.

2. The process selected must be capable of

   - remote operation;
   - producing a product suitable as feed to a fuel fabrication facility;
   - accommodating anticipated variations in feed composition;
   - yielding wastes convertible to forms acceptable for shipment to terminal storage at a Federal repository;
   - separate recovery of the bred U-233 and the U-235;
   - creating only the minimum amount of material to be reworked.

3. The process equipment must

   - be capable of sustained operation with a minimum of maintenance;
   - be adaptable to a remotely maintained facility.

4. Any reprocessing facility constructed must

   - have reasonable capital and operating costs;
   - be licensable by the Nuclear Regulatory Commission; comply with applicable federal, state and local regulations.

Because of the high radiation levels associated with spent nuclear fuel, massive concrete structures are required to shield the public and operating personnel from the radiation sources, namely the process equipment. Consequently, the process must be remotely operated. Equipment clean-out to the extent necessary to permit contact maintenance without undue radiation exposure to personnel is difficult and time consuming. This dictates the need for specifying a process operable in equipment having a very high degree of reliability and amenable to repair and/or replacement by remote techniques.

The high cost of the shielding structure places a premium on using small-sized equipment to minimize building costs. Equipment size can be best minimized by using continuous rather than batch operation wherever possible. Continuous operation also minimizes the number of operating personnel required and thus the operating cost. Batching points, however, are required for accountability purposes. The need to ship the process wastes to a Federal repository cannot be overlooked. The process specified must yield

wastes - solids, liquid and gaseous - that are suitable for conversion to forms acceptable for terminal storage in the most economical manner.

SELECTION OF A REFERENCE REPROCESSING FLOWSHEET

Large-scale chemical separation of thorium, uranium and fission products has been performed in government and private facilities using the process of solvent extraction. The process steps required to convert the fuel elements discharged from the reactor to the feed solutions for the solvent extraction process are collectively referred to as the head-end of the flowsheet.

The reprocessing of LWR fuels to this time has been performed by chopping up the metal-clad fuel elements and dissolving, or leaching, the fuel in acid solutions. The solvent extraction process for uranium-plutonium fuels is the Purex process (Ref. 4). A variation of the Purex process for the handling of uranium-thorium fuels, known as the Acid-Thorex process, was developed at the Oak Ridge National Laboratory in the late 1950s (Ref. 5) and has been used to process some uranium-thorium fuels in government facilities.

Both the Purex and the Acid-Thorex processes meet the requirements listed in the previous section and would be suitable for commercial application if acceptable head-end techniques are developed. For HTGR fuel, Acid-Thorex would be used for the separation of the bred uranium in the fertile particles from thorium and fission prodcuts. The Purex process would be used for processing the uranium in the fissile particles.

The development of reprocessing technology for HTGR fuel has, therefore, concentrated primarily on a head-end process to reduce the fuel to a form compatible with solvent extraction. Although other processes have not been arbitrarily excluded, the experience available with solvent extraction has been considered a very considerable advantage over any other technique. Furthermore, investigation of head-end methods for HTGR fuel has centered around the oxidation or burning of the graphite and the carbon-coated fuel to produce an oxide ash which could be dissolved in nitric acid to produce an acid-feed compatible with the solvent extraction process.

Head-end methods that have been explored (Ref. 6) are summarized in Figure 5. There are two approaches for consideration - to separate the fuel from the block or not. The objective of separating the fuel from the block was to reduce the volume of material which had to be handled to recover the bred uranium. It was considered that the block, freed from fuel, could be broken into chunks and burned in a large water-cooled burner, the technology of which is well known. An alternative is to bury the block as radioactive waste without further processing.

Table I summarizes processes explored which might separate the individual fuel rods from the fuel elements. For those techniques that appeared the most promising, experimental tests were performed as a preliminary evaluation. As can be seen from the table, in each case the process has disadvantages which disqualify it against the criteria discussed. In general, the mechanical complexity of the systems required make remote operation and disassembly for maintenance impractical.

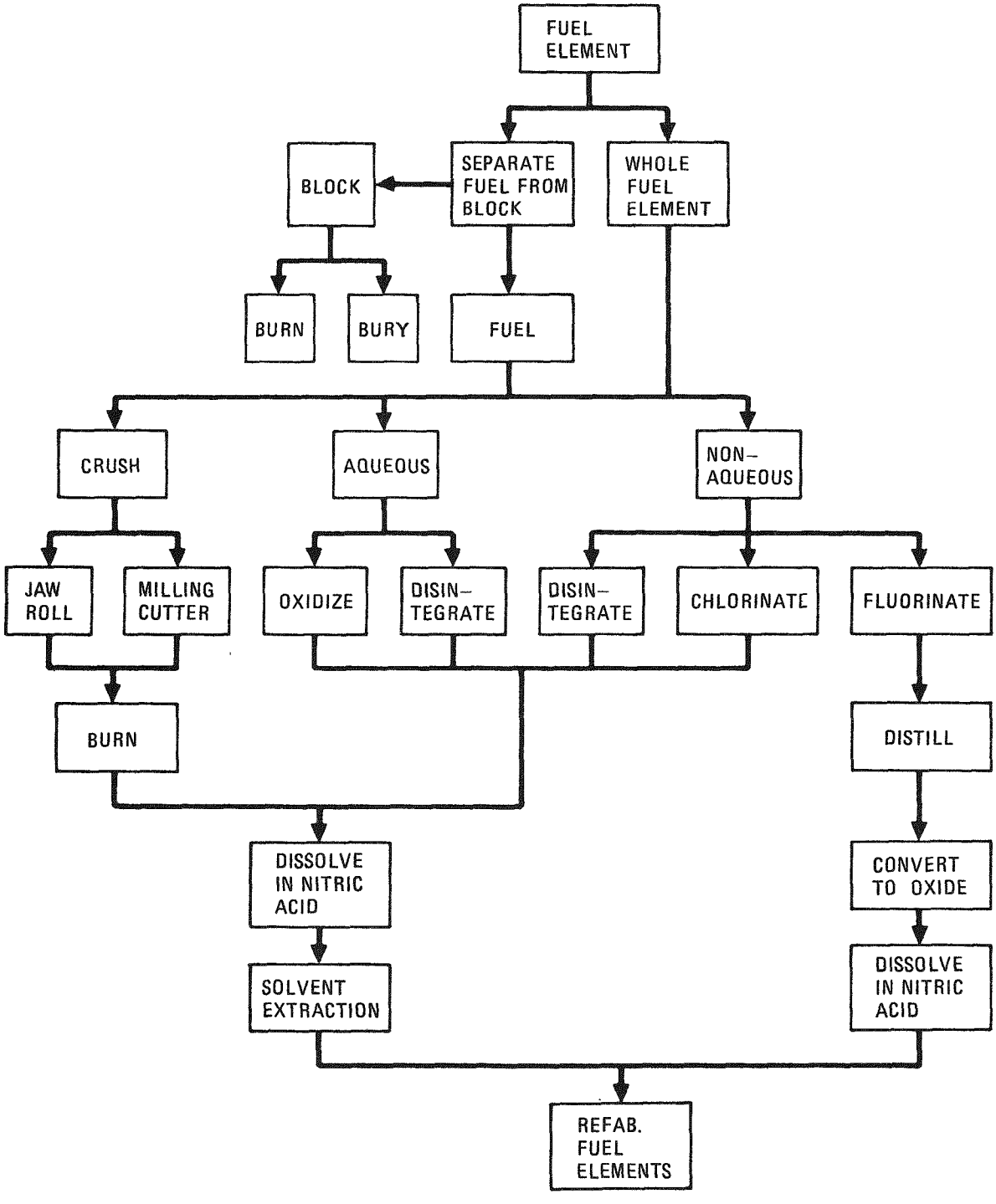


Fig. 5. Head-end methods prior to nitric acid dissolution

TABLE I

HEAD-END PROCESSES FOR SEPARATING THE FUEL FROM THE GRAPHITE ELEMENT

Process	Key Characteristics	Advantages	Disadvantages
Gaseous Debonding	Preheat to 750°C. Individual oxygen lances for each fuel rod hole.	Final product suitable for leaching.	Low process rate requires multiple machines. Each machine requires 132 lances. Complex mechanism not amenable to remote operation.
Shock Depressurization	Pressurization with gas or water suddenly released.		Porosity of fuel block eliminates desired effect.
High Velocity Water or Steam Jet	Debonding with water at 5000 psi.		High particle breakage. Water purification requirements. Criticality problems.
Abrasive Jet	High velocity water jet containing abrasives.		The use of water jet plus scoring of nozzle and added decontamination problems arise.
Wire Brushing	Cylindrical wire brush rotated in fuel holes to debond material.		Compaction of brush wires or clogging with matrix material.
Trepanning	A battery of cylindrical tubes equipped with cutters to ream out fuel holes.		Drift of cutting tubes. Fuel elements are slightly but non-uniformly bowed by irradiation. Short cutter life. Additional processing still required.

TABLE I (continued)

Process	Key Characteristics	Advantages	Disadvantages
Punching	Cylinder pushed through end cap to push rods out of block.	Simple and effective if fuel rods are unbonded to graphite after irradiation.	Uncertainty of final condition of irradiated fuel blocks. Tests simulating bonding of rods caused bending of punch head.
Broach and Split	Cutting into interstitial web from coolant holes. Insert tapered bars to force breakage. Screening or tumbling to separate fuel rods.		Element breakage is irregular; fuel rods do not always separate. Fuel and graphite sizes intermixed makes separation difficult.

A significant disadvantage inherent in the development of all these separation techniques is that the behavior of irradiated material could be significantly different than unirradiated so that development testing with unirradiated fuels would be insufficient. For example, if a high percentage of fuel rods shattered or crumbled in these operations, subsequent fuel graphite separation would be extremely difficult except by burning the entire product.

In view of these results, fuel/block separation was regarded as non-viable because the incentive of developing a head-end process with a reduced throughput was outweighed by the complexity of the equipment and uncertainty that it would work effectively with irradiated fuel.

Table II summarizes the processes examined for recovering the U-233. These processes include aqueous solution techniques, the use of halogens and their compounds, and combustion processes. As is seen from the comments in the table, all methods suffer disadvantages. The main problems with those processes not involving burning is that either extensive development is required because of lack of technological expertise, or the ancillary processes accompanying the main line are complex.

After detailed consideration of flowsheets involving each process, it was concluded that burning the carbon and dissolution of the ash in nitric acid was the closest approach to proven technology. It appeared that combustion could be operated without fail to produce an ash which could be dissolved in acid and fed to a solvent extraction facility. No unusual chemicals would be introduced such as bromine and potassium, and no aqueous systems containing finely divided solids such as carbon-containing sludges would have to be handled.

TABLE II

HEAD-END PROCESSES NOT REQUIRING SEPARATION OF FUEL FROM THE GRAPHITE ELEMENT

Process	Key Characteristics	Advantages	Disadvantages
Aqueous Solution Methods	Low-temperature (300°C) high-pressure (1500 psi) combustion with excess oxygen. Oxidizing media: HNO_3-O_2/H_2O/basic chromate solution/2M $NaNO_3$/ 1M NaOH.	Low temperature. Low corrosion potential.	High pressure. Slow reaction rate. Dilute high volume solutions. Criticality problems.
Dissolution in Concentrated Acids	Low-temperature (300°C) dissolution in H_2SO_4 or chromic acid.	Low temperature. Low pressure. Low corrosion potential.	SO_2 evolved and sludges formed. Complex ancillary processes required.
Disintegration of Graphite	With bromine or potassium which breaks the fuel element down to fuel particles and powdered graphite. Reagents recycled and purified by distillation.	Low temperature. Low pressure.	High corrosion potential. Purification of reagent from fission products likely to be very difficult. Carbon has to be removed by some process such as burning.
Complete Combustion by Fluorination Using BrF_3, BrF_5, BlF_3, or F_2	Convert all the materials to fluorides and separate by distillation.	Few process steps. U recovered as UF_6 for possible enrichment.	Fairly high temperatures with violent reactions a possible risk. No highly active experience available. Many ancillary processes. Entirely new waste treatment system required.

TABLE II (continued)

Process	Key Characteristics	Advantages	Disadvantages
Chlorination with Cl_2	Crush the block and fuel and distill the volatile chlorides out.	Few process steps.	Graphite apparatus. Problems of condensation. Residual graphite to be removed in some way. High temperature. Entirely new waste treatment system required. Corrosion problems.
Fixed Bed Combustion (Shaft Kiln)	Crush the fuel elements to 4-in. chunks and burn in downdraft mode. The ash falls to the bottom.	Fine crushing not required.	Local hot spots cause melting. Shaking grate is required. Solid product must be milled to smaller size and burned in a fluidized bed because carbon content is high. A fluidized bed burner is required.
Whole Block Burning	Place the fuel elements end to end and oxidize. The fuel particles are carried out in the off-gas.	No crushing required.	Local hot spots cause sintering. Uniformity of combustion has not been proven. Bypassing gas is a problem. Experience is with blocks only--not fuel. Fluidized bed burner is required.
Fluidized Bed Combustion	Reduce the fuel element to fluidizable size and burn in a fluidized bed.	Crushing or milling are well known processes. Fluidized bed combustion has been studied extensively. No rework required.	Crushing and milling in these circumstances require full-size testing. Fluidized bed combustion has to be proved reliable and operable.

The choice between the three combustion methods was decided by a detailed study of each system. The fixed bed burner has the particular disadvantage that as the fuel burns and moves downward, pieces as large as the grate spacing tend to collect above the grate and prevent solids flow. This problem could be solved by having a shaking grate which causes the lumps to drop through unburned. Because the lumps contained unburned fuel particles, grinding and a second burning step would be necessary. The latter would be done in a fluidized bed. This situation requires the development of both the fixed bed burner and the fluidized bed burner.

The whole block burner concept suffers from a similar disadvantage. As the block burns away, pieces which contain unburned fuel particles are carried away from the burning zone and have to be subsequently burned. Hence, a fluidized bed burner would have to be developed in addition to the whole block burner.

The main disadvantages of the fluidized bed burner were fines recycle and materials of construction. Both these problems appear to have been solved after extensive development work which will be described in a subsequent paper (Ref. 7).

The fluidized bed burner demands a feed which is fluidizable, i.e., 4 mm (3/16 in.) ring size. The methods for comminuting a fuel element to this small size are by crushing with jaw and roll, or by cutting in a milling machine. Both routes are not without difficulty. The principles involved in the choice were that there must be no rework, the system must work with irradiated material, although testing would only be done with unirradiated materials; broken and pieces of fuel elements must be processable in main line equipment; and the equipment must be robust. It was concluded that since the throughput of a large processing plant will be several fuel elements every hour, numerous milling machines would be required with milling

heads requiring frequent replacement. On the other hand, jaw crushers followed by rolls have been used in the ore processing industries where the feed is very large lumps of hard rock with throughputs up to 100 tons per hour not unusual. On account of the impressive record of reliability exhibited by this kind of heavy crushing machinery, jaw crushers followed by roll crushers were chosen to prepare the feed for the fluidized bed burners.

THE HTGR CONCEPTUAL FLOWSHEET

The crush-burn-leach flowsheet adopted by GA for reprocessing spent HTGR fuel has been developed with ERDA and GA funding since 1968. Improvements in equipment operation and awareness of the technological and regulatory requirements have resulted in the flowsheet illustrated in Figure 6.

WASTE TREATMENT

The bulk of the fission products report to the liquid waste arising from the solvent extraction processing steps. Since these waste streams are chemically similar to those from LWR fuel reprocessing, the technology being developed for LWR liquid waste treatment should be directly applicable. A small amount of development work is required to demonstrate their applicability and, if necessary, determine the modifications needed because of the small chemical differences. Solid process wastes - the SiC hulls - may require some development work to convert them to a yet-to-be defined form acceptable for terminal storage at a Federal repository. Gaseous effluents from the aqueous processing steps are also similar to those of LWR fuel reprocessing. This technology has been demonstrated. An exception is radon which is unique to HTGR spent fuel. The development of adsorption beds to selectively retain radon,

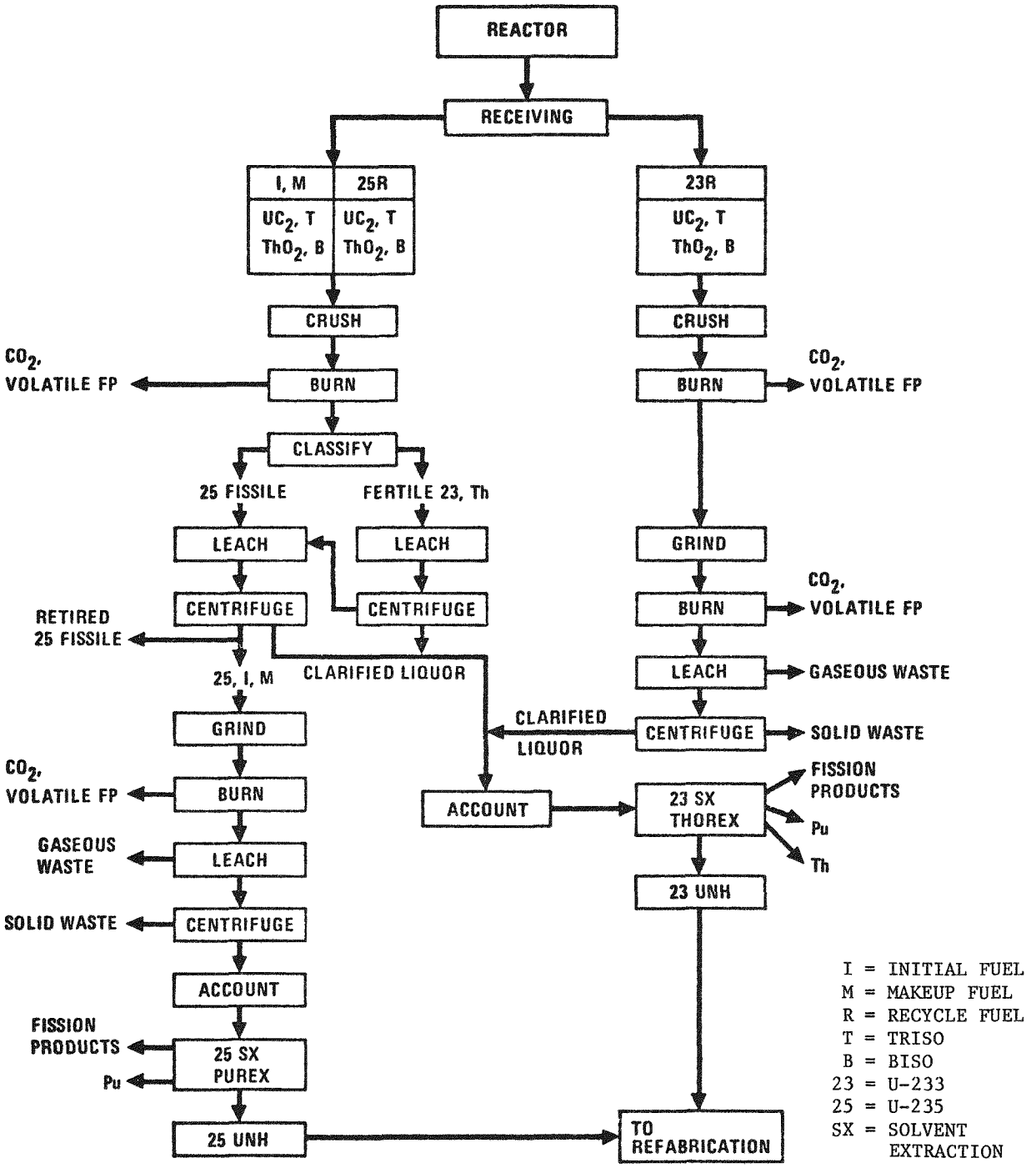


Fig. 6. Reprocessing flow diagram

however, is well advanced. New technology is being developed for the treatment of the gaseous effluents from the fluidized bed burners. The details of this treatment will be discussed in a later paper (Ref. 8).

DISCUSSION

It is recognized that full-scale commercial reprocessing is one of the most difficult processes to undertake. The relatively simple processes of chop, leach, and solvent extraction for spent LWR fuel required extensive development with many unexpected problems cropping up.

Reprocessing HTGR fuel is of similar complexity in that crushing and burning replaces the chop step for the LWR. In addition, the moderator has to be disposed of.

With these factors in mind, it is believed that the flowsheet chosen is the simplest available and uses well-known technology where possible.

REFERENCES

1. Baxter, B. J., G. E. Benedict, and R. D. Zimmerman, "Flowsheet Development for HTGR Processing," in Proceedings of the A.I.Ch.E. Symposium on Gas-Cooled Reactor Fuel Cycles, August 29 - September 1, 1976, Atlantic City, N.J., to be published.
2. Sease, J. D., "Development of Processes and Equipment for the Refabrication of HTGR Fuels," in Proceedings of the A.I.Ch.E. Symposium on Gas-Cooled Reactor Fuel Cycles, August 29 - September 1, 1976, Atlantic City, N.J., to be published.
3. Bennett, L. L., and R. F. Turner, "Economic Performance of HTGR Fuel Cycles Under Various Recycling and Economic Conditions," in Proceedings of the A.I.Ch.E. Symposium on Gas-Cooled Reactor Fuel Cycles, August 29 - September 1, 1976, Atlantic City, N. J., to be published.
4. Richards, R. B., and S. Stoller, Reactor Handbook, Volume 2, Fuel Reprocessing Edition, Interscience Publishers, 1961, p. 146.
5. Moore, J. G., and Rainey, R. H., "Laboratory Development of the Acid-Thorex Process for Recovery of Thorium Reactor Fuel," Nucl. Sci. Energy 10, 367 (1961).
6. Brooks, L. H., "Survey and Evaluation of Methods for Reprocessing Spent HTGR Fuel," General Atomic Report GA-A12853, December 1974.
7. Palmer, W. B., "HTGR Fuel Reprocessing - Fluidized-Bed Burner Development at Allied Chemical Company," in Proceedings of the A.I.Ch.E. Symposium on Gas-Cooled Reactor Fuel Cycles, August 29 - September 1, 1976, Atlantic City, N. J., to be published.
8. Meyer, H., "HTGR Fuel Reprocessing Off-Gas Treatment," in Proceedings of the A.I.Ch.E. Symposium on Gas-Cooled Reactor Fuel Cycles, August 29 - September 1, 1976, Atlantic City, N. J., to be published.