RECEIVED BY DTE 11/14/70

GULF GENERAL ATOMIC

INFORMAL AEC RESEARCH
AND DEVELOPMENT REPORT

GAMD-9260
Part II

MASTER

HTGR FUEL REPROCESSING - HEAD-END TREATMENT OF EXPERIMENTAL SMALL-SCALE HTGR FUEL ELEMENTS

PART II

Work done by:

L. H. Brooks
C. L. Gray, Jr.
L. E. Jolley
D. G. Roberts

Report written by:

L. H. Brooks

This document, which was prepared primarily for internal use at Gulf General Atomic, may contain preliminary or incomplete data. It is informal and is subject to revision or correction; it does not, therefore, represent a final report.

THIS DOCUMENT CONFIRMED AS
UNCLASSIFIED
DIVISION OF CLASSIFICATION
BY JH Kahn/aml
DATE 12/10/70

Gulf General Atomic Project 317
U.S. Atomic Energy Commission
Contract AT(04-3)-167, Project Agreement 17

October 13, 1970

GULF GENERAL ATOMIC COMPANY, P.O. BOX 608, SAN DIEGO, CALIFORNIA 92112

P7701

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

Case

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

SUMMARY

Research and development work on the grind-burn-leach process has continued.

A jaw crusher has been designed and built for crushing 12-rod fuel elements. Experiments to date have indicated that a jaw crusher breaks the fuel to an acceptable size range without breaking an unacceptable fraction of fuel particles.

Tumbling and screening has been shown to be a good method of separating the crushed material into two streams: a graphite-rich and a fuel-particle-rich stream. This operation allows the utilization of two fluidized bed burners, a large one for graphite and a smaller one for fuel particles. Tumbling is fast and easy, but trials on irradiated fuels must be carried out before final conclusions can be drawn.

Burning has been carried out in fluidized beds. All types of fuel and graphite have been tested and present no insoluble difficulties.

Leaching trials have been carried out in a 1-liter leacher. Burned BISO and ground, burned TRISO fuel particles have been successfully leached. Although the rate of dissolution is acceptably high, work must be done on irradiated fuel before final conclusions can be drawn.

LEGAL NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

Carl

CONTENTS

SUMMARY	iii
INTRODUCTION	1
EXPERIMENTAL RESULTS	5
CRUSHING	5
TUMBLING AND SCREENING	5
FLUIDIZED BED BURNING	13
Two-Inch Reactor	13
Four-Inch Reactor	15
LEACHING	19
REFERENCES	26

FIGURES

1. Reprocessing block diagram for TRISO/TRISO bonded fuel	2
2. Reprocessing block diagram for TRISO/BISO bonded fuel	3
3. End view of 12-rod fuel element	6
4. Flow sheet for 12-rod fuel element	7
5. Rotating drum tumbler	9
6. Attrition of fuel rods in drum tumbler	10
7. Attrition of graphite in drum tumbler	11
8. Fraction of broken particles in each sample from drum tumbler . . .	12
9. Two-inch fluidized bed burner	14
10. Four-inch stainless steel fluidized bed burner	17
11. Leacher	20
12. Effect of HF and solution concentration on rate of dissolution of ThO ₂ in Thorex liquor	22

FIGURES (Continued)

13. ThO ₂ dissolution in Thorex liquor.	23
14. Dissolution of burned BISO fuel particles in 1100 ml Thorex liquor	25

INTRODUCTION

The economics of a 15,000-MW(e) high-temperature gas-cooled reactor (HTGR) fuel cycle strongly favor the construction of a reprocessing plant for handling only HTGR fuels (Refs. 1-3). The dissimilarities between such a plant and one for reprocessing metallic-sheathed fuel elements from water reactors lie almost exclusively in the area of preparing the fuels for chemical separation, i.e., the head-end treatment. The most favored head-end treatment method is the grind-burn-leach process (Refs. 4-8), which is the basis of the development work programmed in Section 5100 of the National HTGR Recycle Development Program Plan (Ref. 9). Initial work at Gulf General Atomic to develop the grind-burn-leach process was described in Ref. 10. Subsequent progress is described in this report.

Figures 1 and 2 show the conceptual flow sheets for reprocessing TRISO/TRISO* and TRISO/BISO** pitch-bonded fuel elements, respectively. Briefly, the fuel element is crushed to liberate the fuel rods from the graphite block, and the broken pieces are then tumbled and screened. This operation divides the process stream into two parts, one containing the larger fraction of fuel particles and the other containing the larger fraction of graphite. The fuel particles are then burned in a fluid bed burner to remove the carbon, and the graphite is burned in a larger fluid bed burner. The ash from the graphite burner is fed into the particle burner so that any uranium that accompanied the graphite will be recovered. If the feed to the plant is TRISO/TRISO fuel, the product from the burner is screened to separate the fissile from the fertile particles and the fissile particles are stored. The fertile particles are ground, burned, and leached to prepare the feed for solvent extraction. If the feed to the plant is TRISO/BISO fuel, the

*TRISO/TRISO refers to the fuel containing a mixture of TRISO fissile and TRISO fertile fuel particles.

**TRISO/BISO refers to the fuel containing a mixture of TRISO fissile and BISO fertile fuel particles.

Fig. 1. Reprocessing block diagram for TRISO/TRISO bonded fuel

Fig. 2. Reprocessing block diagram for TRISO/BISO bonded fuel

product from the burner is screened to separate the fissile particles and oxide powder (from the burned BISO particles) from the incompletely burned BISO particles. The latter are recycled to the burner. The mixture of fissile particles and oxide powder is burned to reduce the carbon concentration prior to leaching. Each unit process on the flow sheets is being tested in the laboratory at a scale of about 1 kg or more per hour.

The reference fuel for the 1100-MW(e) HTGR is presently the TRISO/BISO pitch-bonded type, and most of the reprocessing development work is being done on this type of fuel. The TRISO/TRISO pitch-bonded type fuel will be used in the Fort St. Vrain HTGR and will also be used as feed for hot pilot-plant studies in the TURF facility at Oak Ridge National Laboratory. For this reason, cold development work on this fuel will continue at Gulf General Atomic.

EXPERIMENTAL RESULTS

CRUSHING

Two 12-rod fuel elements (Fig. 3) containing resin-bonded TRISO/TRISO fuel rods were crushed in a 5-in. by 6-in. jaw crusher with the minimum possible jaw gap of 1/4 in. closed and 3/4 in. open. Examination of the crushed material revealed that a large fraction of the rods had been broken into lengths which did not pass through a 1/2-in. screen. The flow sheet for the crushing and screening process and the results obtained are shown in Fig. 4. It was concluded that the jaw gap must be set at a maximum of 7/16 in. so that a fuel rod, measuring 0.492 in. in diameter, will be crushed and hence facilitate the separation of fuel particles from graphite during subsequent screening. The fraction of broken particles was acceptably low at 0.14%.

An added complication which became apparent during crushing was that the fuel elements moved up and down when the jaws closed and opened. The measured angle between the faces was 17-1/2 degrees. Experiments performed using two plates of smooth steel hinged at one end showed that to guarantee no slip when crushing graphite, the maximum angle that could be used was 11 to 13 degrees.

Based on these results, a jaw crusher was designed and built. It is large enough to handle a 12-rod fuel element, has a jaw angle of 11 degrees, and features a jaw gap that is adjustable from zero to 2 in. This machine will be operated after it has been joined to the off-gas filtration system.

TUMBLING AND SCREENING

The objective of the tumbling and screening step is to separate the product from the crusher into two parts: a graphite-rich stream containing

Fig. 3. End view of 12-rod fuel element

Fig. 4. Flow sheet for 12-rod fuel element

as few fuel particles as possible, and a fuel-particle-rich stream containing as little graphite as possible. A diagram of the tumbling machine is shown in Fig. 5. The drum, covered with 1/4-in.-mesh woven cloth, is rotated at 24 rpm. Flights inside the drum lift the feed and allow it to fall, thus causing attrition. The -1/4-in. pieces fall through the mesh into the fines product hopper, whereas the +1/4-in. pieces are retained in the drum until the disk is withdrawn from the drum end. The coarse material then falls into the coarse product hopper. When a mixture of crushed graphite and bonded rods is used as fuel, some of the graphite is recovered free of particles, and the rods, which convert more readily to single particles and particle agglomerates through attrition, are recovered containing some graphite. Dust created during operation is removed through the exhaust duct.

The results of tumbling and screening some crushed resin-bonded TRISO/TRISO fuel elements are given in Fig. 6. It can be seen that virtually all the fuel particles had passed through the screen in 35 min. After tumbling for 65 min, all the fuel particles were collected in the -1/4-in. fraction and were accompanied by 18% of the graphite. The remaining 82% of the graphite was recovered as the +1/4-in. fraction. Of the total weight of burnable carbon (i.e., graphite, outer pyrolytic carbon, and matrix), 29% accompanied the particle stream and 71% the graphite stream. This result indicates that the graphite and particle fluidized bed burners shown on the flow sheet in Fig. 1 would have to have throughputs of 75 and 30 kg/hr, respectively. The attrition rate of graphite during tumbling, shown in Fig. 7, settles down to an average value of 6%/hr. Particle breakage during tumbling, shown in Fig. 8, averages 1.2%. Analysis of the broken particle residue indicated that the ratio of the number of broken fertile to fissile particles was 2.8.

A noteworthy point during all four runs was that blinding of the screen was virtually zero. Two lumps of graphite had to be pressed out from the screen at the end of the four runs. Vibration of the drum appeared to shake lumps out of the holes during rotation.

Fig. 5. Rotating drum tumbler (sectional view)

Fig. 6. Attrition of fuel rods in drum tumbler. Feed composition: graphite, 1662 g; fuel rods, 941 g

Fig. 7. Attrition of graphite in drum tumbler. Feed composition: graphite, 1662 g; fuel rods, 941 g. Product size: $-1/4$ in.

Fig. 8. Fraction of broken particles in each sample from drum tumbler

The applicability of tumbling and screening as a unit process in the head-end flow sheet depends on the difference in attrition rate between graphite and fuel rods after irradiation. If trials on irradiated material at a later date (i.e., when this material becomes available) show that separation cannot be achieved or cannot be achieved without unacceptably high particle breakage, it may be necessary to eliminate the tumbling step and burn the whole of the product from the crusher in a large particle burner.

FLUIDIZED BED BURNING

Two-Inch Reactor

The 2-in. reactor (Fig. 9) was constructed in order to gain experience in fluidized bed burning. All experiments have been carried out using a mixture of -1/8-in. graphite and -90/+120 mesh alumina. Start-up was achieved by electrically heating the bed to about 700°C and then starting the oxygen flow. When combustion commenced, the electrical heater automatically switched off and heat was radiated from the reactor wall. After 20 runs it was concluded that:

1. Burning was fairly uniform up to the maximum bed height of 20 in., judging by the red-hot reactor wall.
2. The middle bed temperature could be maintained at 650° to 850°C.
3. Combustion was difficult to reinitiate if the temperature dropped below 600°C.
4. The carbon concentration will burn down to 0.5% in the alumina before the temperature falls below 750°C owing to lack of fuel.
5. Batch addition of feed causes the bed temperature to slump; continuous addition enables a more constant bed temperature to be maintained.

Fig. 9. Two-inch fluidized bed burner

6. Smoothest operation was obtained with a bed depth between 12 and 20 in.
7. Oxygen utilization exceeds 90% under optimum operating conditions of temperature and carbon concentration.
8. A burning rate of 3.5 g/min was achieved without difficulty.

Before retiring the 2-in. fluid bed burner, the last few runs were directed toward perfecting an in-bed CO/O₂ burner for bed ignition. CO was chosen so as to obviate the formation of water vapor during combustion. The start-up procedure is as follows. CO and O₂ are introduced into a mixing chamber, where two spark plugs cause ignition. Combustion takes place in the mixing chamber and the flame enters the fluid bed. It heats the bed to ignition temperature and is then made progressively richer in oxygen until the bed ignites. The CO is turned off when fluid bed burning is under way. Since quick ignition is facilitated by a small initial bed, feed addition begins just after ignition, and the bed is readily built up to the desired height.

Four-Inch Reactor

A 4-in. reactor has been installed and is being used to attain the following primary objectives:

1. To determine the throughput of carbon, with and without an inert fluidizing medium
2. To determine the fraction of broken fuel particles caused by burning
3. To determine the minimum concentration of carbon that can be achieved in the burner product
4. To define the best type of gas distributor for use at the base of the reactor

5. To decide whether it is better to feed the solids on top of or into the base of the fluidized bed
6. To determine whether to dump blowback fines on top of or feed them into the base of the fluidized bed
7. To determine the heat balance
8. To observe any difference in operation when feeding TRISO/TRISO pitch-bonded fuel, TRISO/BISO pitch-bonded fuel, and graphite
9. To decide on batch or continuous operation

The less important objectives pertain to methods of solids feeding, off-gas analysis, oxygen utilization, temperature of operation, materials of construction, heat removal, methods of automatic control, etc.

A diagram of the burner is shown in Fig. 10. The heat exchanger, reactor, clam-shell jacket, and cone base are made of stainless steel. All other parts are made of carbon steel. A ball in the cone prevents grains of bed material from blocking the gas inlet pipe. Solids are presently fed to and taken from the reactor by means of variable-speed screw transporters. Start-up is achieved by igniting a 450-g bed of -20/+100 mesh coke with the CO/O₂ flame; and when the center bed temperature reaches 800°C, the oxygen rate is increased and the CO rate gradually decreased to zero. The solids feed is then started and the bed built up to operating weight. The advantage of this start-up method is that the reactor wall is not covered by an electric heater and can be observed, thus giving an indication of the uniformity of red-heat distribution. Another advantage is that the reactor can be brought up to operating temperature in 20 min, as compared with about 2 hr with the electrically heated 2-in. burner.

The work done using the 4-in. reactor can be divided into four fuel feed categories: TRISO/TRISO, TRISO/BISO, crushed graphite only, and miscellaneous.

Fig. 10. Four-inch stainless steel fluidized bed burner

Experiments have been carried out using a feed of crushed TRISO/TRISO fuel rods mixed with graphite. No major difficulties were encountered. It was found that combustion proceeds smoothly provided that the bed is fluidized. If the bed defluidizes because of insufficient gas flow rate, local high temperatures arise in the space of a few seconds and melt the stainless steel reactor wall or thermowell. Loose TRISO/TRISO fuel particle mixtures have also been burned, with and without an inert fluidizing medium. Again, no difficulties were encountered. It was found that because SiC-coated particles behave as an inert fluidizing medium, no advantage was gained by adding alumina to the bed. In these experiments, burning rates of ~ 27 g carbon/min were achieved, but this does not represent an upper limit. During continuous operation, the carbon concentration in the product varies between 0.5% and 2%.

Experiments with TRISO/BISO crushed fuel rods mixed with graphite showed that the release of thorium powder to the bed had a profound effect on the burning operation. It was found that the accumulation of -420 -micron material up to about 30% of bed weight caused combustion to cease even though an adequate supply of carbon was available. Close examination of this effect showed that a solution to the problem was to screen out the -420 -micron material and return the $+420$ -micron material to the bed. Under these conditions, operation could be maintained. Removal of carbon from the -420 fraction was then achieved by batch burning it in a fluidized bed using an inert fluidizing medium. This step required heat input to the reactor and was carried out in the 2-in. burner. The final concentration of carbon in the product was 0.22%.

Experiments with graphite have shown that it is not necessary to add an inert fluidizing medium. Provided that the gas flow rate is sufficient to give good fluidization, combustion is uniform throughout the bed. The highest burning rate achieved to date is 72 g/min for 37 min. The gas flow rate was 200 liter/min, and the solids feed size was $-3/16$ -in. mesh.

When the results of this work with the 4-in. fluidized bed are compared with those of others (Refs. 11,12,13), it is seen that our bed temperature of

950° to 1040°C is higher than their 750°C bed temperature. If the bed center temperature drops below 850°, it is very difficult to retrieve combustion. This disagreement will have to be resolved.

Some miscellaneous runs have been performed:

1. Secondary oxygen was introduced just above the bed to reduce the fines carry-over to the cyclone. The results showed very clearly that this step made no measurable difference.
2. Fines fed into the bottom of the bed were completely burned.
3. Measurement of the heat balance in a run showed that 324 kcal/min out of a total of 460 kcal/min were removed by the cooling air passing through the clam-shell cooler. The calculated heat transfer coefficient from the outer wall to the gas was $34 \text{ Btu/hr-ft}^2\text{-}^\circ\text{F}$.

LEACHING

After TRISO fertile fuel particles have been burned and screened to separate them from the fissile particles, as shown in Fig. 1, they are ground to rupture the SiC layer, burned to convert the carbide kernel to oxide, and leached in Thorex* liquor to obtain a nitrate solution. As shown in Fig. 2, BISO fuel particles do not require the grinding step because the kernel is exposed after the first burn.

Both of these particle systems have been subjected to leaching trials in the leacher shown in Fig. 11. This leacher can be operated either "batchwise" or continuously. When operated "batchwise," stage 1 is charged with 1 liter of Thorex liquor and heated to 115°C. The airlift is started, and the batch of solids feed is introduced down the airlift return line. After the whole batch has been drained and stirred, a solution sample is taken. The batch is then replaced and dissolution is continued. Continuous operation is carried out by charging stage 1 with 1 liter of Thorex

*Thorex liquor consists of 37.5 g $\text{Al}(\text{NO}_3)_3 \cdot 9 \text{H}_2\text{O}$, 1.0 ml of 48% HF, 70% nitric acid added to make 1 liter of solution.

Fig. 11. Leacher

liquor and stage 2 with water. Both stages are then raised to operating temperature. Solids feed is metered into the airlift return line, and hot Thorex liquor is metered in below the bed of solids. Samples of product are taken from stage 2.

Numerous leaching experiments were performed, but the following four are of particular interest:

1. A 240-g batch of ground, burned TRISO fertile particles was leached; 96% of the thorium dissolved in 30 min, and 98.6% in 150 min.
2. Many small batches of burned BISO particles were added sequentially to 1 liter of Thorex liquor, a new batch being added when the previous batch was on the point of complete dissolution. The result is shown in Fig. 12. The effect of the HF in the liquor is observed as a dramatic increase in the reaction rate. It is also apparent that the dissolution rate does not decrease markedly as the solution concentration increases. The crystallization data show that the design thorium concentration of 264 g ThO_2 /liter is well below that at which crystals form at room temperature.
3. A continuous experiment was performed using ThO_2 calcined from oxalate, with an average particle size of 1 micron. This material was used instead of burned BISO particles because of the short supply of the latter. The results are shown in Fig. 13. The liquor rate was maintained at 25 ml/min, and the solids rate was varied to give three different dissolution rates. No difficulties were encountered, but the 9.9 g/min rate was regarded as being close to the maximum that this leacher would take. It is believed that any increase above this rate would have resulted in a cloudy product solution containing undissolved ThO_2 .
4. A mixture of TRISO and BISO fuel particles was burned in the 4-in. reactor and the -420 micron material was collected. The latter was then burned in the 2-in. reactor until virtually all the carbon

Fig. 12. Effect of HF and solution concentration on rate of dissolution of ThO₂ in Thorex liquor (ThO₂ obtained by burning BISO fertile particles at 850°C)

Fig. 13. ThO₂ dissolution in Thorex liquor. ThO₂ prepared by calcination of thorium oxalate.

had been burned out. This product was then leached by dividing it into 11 batches and boiling each batch for 40 min in the same Thorex solution. The weight loss of each batch was measured to determine the quantity of material dissolved. The results are given in Fig. 14. Because each batch was seen to dissolve within 10 min, the batch size was increased toward the end of the experiment. The combined residue from all the batches was dried and burned in a tray to determine the concentration of carbon, which was 0.22%. The residue, after burning, was leached again to recover any traces of thorium; 1.26 g of thorium was found. It was concluded that ThO_2 prepared from the oxidation of BISO fuel particles dissolves rapidly in boiling Thorex liquor, even up to a concentration of 540 g ThO_2 . The carbon did not interfere with dissolution. A very fine powder suspended in the final solution was found to contain mostly iron, nickel, and chromium. It is assumed that this material is produced by the corrosion of the stainless steel reactor during burning operations.

Fig. 14. Dissolution of burned BISO fuel particles in 1100 ml Thorex liquor

REFERENCES

1. Reese, S. L., et al., "Feasibility Study for Reprocessing HTGR Fuels Based on Using the Nuclear Fuel Services, Inc. Reprocessing Plant," USAEC Informal Report GAMD-6360, General Dynamics, General Atomic Division, December 15, 1964.
2. Shefcik, J. J., "Reprocessing HTGR Hex Block Fuels at the Nuclear Fuel Services Plant," USAEC Informal Report GAMD-7657, General Dynamics, General Atomic Division, January 23, 1967.
3. Private communication from Nuclear Fuel Services, Inc. to General Dynamics, General Atomic Division, December 15, 1964.
4. Ferguson, D. E., et al., "Chemical Technology Division Annual Progress Report for Period Ending May 31, 1968," Section 3, USAEC Report ORNL-4272, Oak Ridge National Laboratory, September 1968.
5. Lowrie, R. S., Oak Ridge National Laboratory, "Fuel Cycle Studies Monthly Report," unpublished data.
6. Shefcik, J. J., "HTGR Fuel Reprocessing. Effects of Including a Silicon Carbide Coating on Fertile Fuel Particles," USAEC Informal Report GAMD-8661, Gulf General Atomic Incorporated, May 10, 1968.
7. Shefcik, J. J., H. E. Stelling, and K. G. Steyer, "HTGR Fuel Reprocessing," Gulf General Atomic, unpublished data.
8. Stelling, H. E., and K. G. Steyer, "Design Study and Economic Evaluation of a Head-End Reprocessing Facility Integral with an HTGR Power Plant," USAEC Informal Report GAMD-7294, General Dynamics, General Atomic Division, August 18, 1966.
9. "National HTGR Recycle Development Program Plan Subtask 5100: Reprocessing Development," Oak Ridge National Laboratory, unpublished data.
10. Brooks, L. H., "HTGR Fuel Reprocessing - Head-end Treatment of Experimental Small Scale HTGR Fuel Elements," USAEC Informal Report GAMD-9260, Gulf General Atomic Incorporated, September 9, 1969.

11. Reilly, J. J., et al., "Fluidized Bed Reprocessing of Graphite Matrix Nuclear Fuel," Ind. Eng. Chem. Process Design Develop. 5 (1), 51 (1966).
12. Nicholson, E. L., et al., "Burn-leach Processes for Graphite-base Reactor Fuels Containing Carbon-coated or Oxide Particles," USAEC Report ORNL-TM-1096, Oak Ridge National Laboratory, April 1965.
13. McLaren, J., and D. F. Williams, "Combustion Efficiency, Sulphur Retention and Heat Transfer in Pilot Plant Fluidized Bed Combustors," Combustion 41 (11), 21 (1970).