Conf-740501--4

PROGRESS IN THE THORIUM-URANIUM 233 REPROCESSING-REFABRICATION TECHNOLOGY*

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*Research sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corporation.

GATLINBURG PAPER

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INTRODUCTION

The purpose of this paper is to present the salient features of high-temperature gas-cooled reactor (HTGR) fuel recycle technology as it stands today, and to mention some possible improvements which are being investigated.

The main elements of fuel recycle[1,2] are spent fuel shipping and storage, reprocessing operations of head-end processing followed by solvent extraction to recover the fissile and fertile fuel materials, fuel material conversion to chemical and physical forms suitable for use in fuel element fabrication, fuel element assembly, recycle plant effluent decontamination, and gaseous and solid radwaste disposal.

Shipment of HTGR spent and refabricated fuel has been studied for a number of years and has resulted in the fabrication of two truck-mounted casks for transporting spent Fort St. Vrain fuel to Idaho Chemical Processing Plant (ICPP), and in the design of truck- and rail-mounted casks for transporting spent fuel elements from large HTGRs which will be coming on-line starting 1980.

Storage facilities for spent HTGR fuel at the commercial recycle plant, due to start operations in about 1985, are at the conceptual design stage, while a 2,560 fuel element storage facility has been constructed at ICPP ready to receive spent fuel from Fort St. Vrain.

The reprocessing head-end flowsheet, chosen from numerous possible ones, is the crush-burn-leach process which has been studied since 1957.[3,4,5] Alternatives to this process may present difficulties such as materials handling, corrosion, the use of machines which are better not remotized, or too many ancillary processes required to keep the main-line processes in operation. Work on the flowsheet is being carried out at General Atomic Company (GA) and ICPP. Supporting hot

cell studies are being conducted at Oak Ridge National Laboratory (ORNL). The fissile and fertile materials will be recovered from the leach solution by the Thorex process, a modification of the Purex process.

Fabrication of the fuel form consists of three major steps: kernel preparation, coating, and rod forming, after which the fuel element, comprising the graphite block and fuel rods, can be assembled. The unit processes follow the fresh fuel manufacturing processes as closely as possible because both products are similar. The big differences between the fresh and recycle fissile fuel lie in the composition of the kernel which is all-uranium and mixed uranium-thorium, respectively, and in the necessity for shielded operations for the recycle fissile fuel. Development of fuel fabrication is being carried out at GA and ORNL.

The effect of fuel fabrication and reprocessing components of the fuel cycle on the environment is being studied at ORNL with respect to gaseous and liquid wastes, both radioactive and non-radioactive, and by the AEC[6] on the subject of solid radwaste disposal and on other components of the fuel cycle.

The development work scheduled to be carried out at GA, ORNL, and ICPP has been reported in a document published by ORNL,[7] and known as the "National Program Plan." The work scopes, schedules, and budgets for each of the participants are described. A cold reprocessing pilot plant is being constructed at GA and will be completed by 1975. Development work will continue to the late 1970s. A hot reprocessing plant will be built at ICPP for operation in 1979, when the reprocessing flowsheet will be demonstrated using Fort St. Vrain fuel initially as feed. A hot refabrication demonstration plant is being designed at ORNL for operation in 1979 when the refabrication flowsheet will be demonstrated.

HTGR FUEL

The fuel element is illustrated on Figure 1 and the fuel particles on Figure 2. Mixtures of particles are blended and formed, by hot injection of pitch/graphite flour matrix, into rods measuring about 5/8-inch diameter and 2-inches long. About 1,300 of these are loaded into one fuel element. The element is cooled with a downward flow of pressurized helium through the coolant holes.

HTGR SPENT FUEL SHIPPING SYSTEM

The HTGR spent fuel shipping system[8] provides the method and equipment required for removing and transporting spent fuel elements from a nuclear electric generating plant to a storage and/or reprocessing plant.

The system equipment is designed such that all federal regulations of the U. S. AEC and U. S. DOT and, in addition, all applicable state laws, are satisfied.

The rail shipping package consists of a cask and twelve containers. Each container holds six spent or five refabricated fuel elements. The cask is fabricated in three layers: A stainless steel inner layer, a middle layer of depleted uranium, and an outer shell of steel. The cask weight is 160 tons and it is transported in the near-horizontal position on a special railcar weighing 60 tons. The cask is finned for improving the removal of decay heat generated by the fission products. The cask is not removed from the car for loading/unloading operations but is jacked into an upright position when the lid can be removed and the fuel transferred.

Truck shipping differs from rail shipping in the size of the cask. The truck-mounted cask will accept one container which is identical to the rail container.

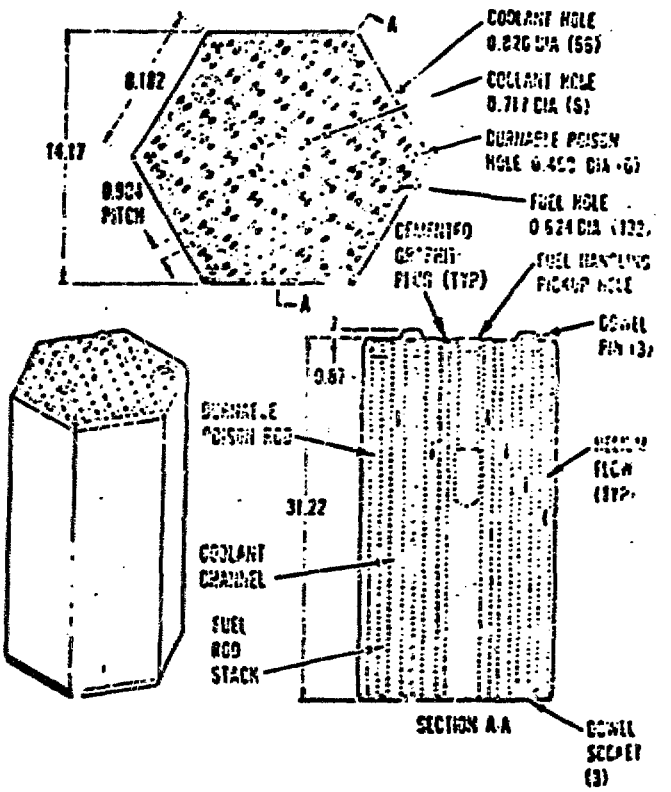

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Fig. 1 HTGR hexagonal fuel element

	FISSILE PARTICLE (TYPE 1)	FERTILE PARTICLE (TYPE 2)	RECYCLE PARTICLE (TYPE 3)
COMPOSITION	$^{235}UC_2$	ThC_2	$(Th,^{233}U)O_2$
Th:U RATIO	-	-	4.25
KERNEL DIAM. μm	200	500	400
COATING THICKNESS, μm			
BUFFER	85	85	90
INNER DENSE COATING	25	-	-
SILICON CARBIDE	25	-	-
OUTER DENSE COATING	35	75	80
TOTAL PARTICLE DIAM. μm	540	820	740

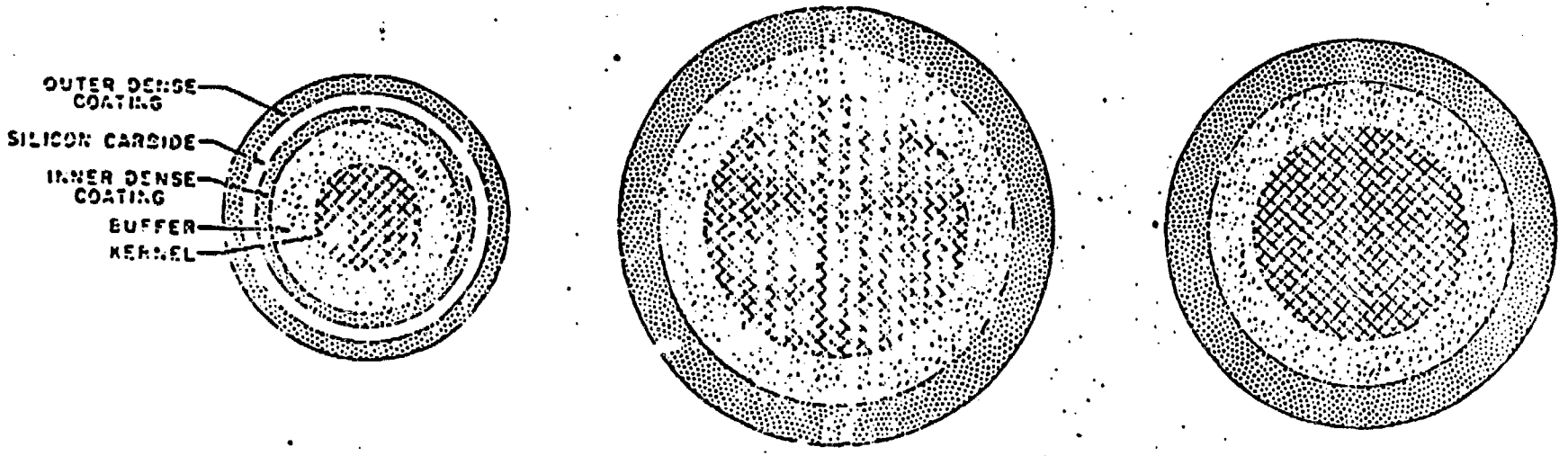

Fig. 2 DIAGRAMMATIC REPRESENTATION OF FISSILE, FERTILE, AND RECYCLE PARTICLES FOR 1150 MW(e) HTGRS

SPENT FUEL REPROCESSING

A three-stage crushing system has been adopted for the reprocessing plant, based on the experimental testing of modified commercially available equipment using full-sized fuel elements. The crushed product is -3/16-inch ring size and is suitable for feeding to a fluidized bed burner. Primary reduction is done by feeding the fuel element vertically into an overhead eccentric jaw crusher which produces 4-inch lumps. Secondary reduction is also performed in an overhead eccentric jaw crusher which produces -3/4-inch lumps. Tertiary crushing is done in either a single-roll or double-roll crusher to produce the -3/16-inch burner feed which is pneumatically conveyed to the fluidized bed burners.

The burning operation is carried out by pneumatically feeding crushed fuel to the top or base of a continuous primary fluidized bed burner. The burner is operated automatically at constant temperature by controlling the oxygen supply from the center-bed temperature signal, and the product rate is controlled from the bed-depth differential pressure signal. The feed rate is maintained as constant as possible. The primary burner product is fed to the batch-operated secondary burner where the remaining carbon is removed, the final product being oxide ash and SiC-coated particles. Secondary burner exothermic operation cannot be sustained to the low concentration of carbon required in the subsequent processing steps, so heat is supplied by means of an electrical furnace. Heat generated during the burning operation is removed by forced gas cooling in a clamshell jacket surrounding the burners. Off-gases pass through a cyclone and/or sintered metal filters for fines removal before being cooled and scrubbed for release to the atmosphere. Fines from the filter systems are recycled to the primary burner.

An alternative to crushing and fluidized bed burning is whole-block burning. The advantage of this would be the absence of the crushing stage but the disadvantage is that the technology is not sufficiently advanced for it to replace fluidized bed burning at the present time.

The off-gases from the burners are decontaminated to remove (mainly) ^{85}Kr.

Two approaches are possible in processing the carbon-free burner product. One, the reference case, is to leach the mixture with leach liquor and separate the solution from the insoluble SiC-coated particles. The other is to classify the burner product by some method, the mixed oxides reporting to the leacher. Air classification is being studied experimentally at GA and ICPP as the second approach and backup to the reference case.

The burner or classifier product is leached with nitric acid, aluminum nitrate, hydrofluoric acid (Thorex liquor) and the solution clarified by centrifugation. The clarified solution is fed to the final step in fuel reprocessing which takes the highly contaminated U-233 and thorium and separates them cleanly both from each other and from fission products. These separations are performed by solvent extraction. After adjustment of concentrations, the resultant aqueous solution is equilibrated with immiscible solutions of tributyl phosphate (TBP) in n-dodecane. The TBP solutions preferentially extract uranium and thorium nitrates, leaving fission product and other nitrates in the aqueous phase. Subsequently, concentrations are adjusted so that the thorium leaves the TBP phase to enter an aqueous phase, leaving only uranium in the TBP phase. Finally, the uranium is stripped into an aqueous phase in the form of uranyl nitrate for use in fuel particle fabrication operations.

Solvent extraction is being studied at GA as part of the cold pilot plant work and in hot cell studies at ORNL to ensure that all questions regarding fission product precipitation, product purity, equipment specifications, and process safety are answered.

FUEL REFABRICATION

The refabrication process consists of taking the 2-molar U-233 uranyl nitrate solution from solvent extraction, blending it with thorium nitrate to make 4.2:1 Th:fissile U ratio, and converting this solution into gelled microspheres by the sol-gel process. These microspheres are then dried, calcined, and pyrocarbon coated. These coated particles are blended with coated fertile particles and formed into fuel rods which are assembled into the graphite blocks to form the finished fuel element. Because of the presence of U-232 and its daughter products in the U-233, all refabrication operations are carried out remotely in a shielded facility.

The sol-gel process for forming microspheres has been developed at Oak Ridge.[12] The feed to the sol-gel process in the refabrication plant consists of a blend of the recovered U-233 uranyl nitrate solution and thorium nitrate. This nitrate solution is converted to a hydrosol by extraction of the nitrate ion into a long-chain secondary amine diluted with a normal paraffin hydrocarbon. The extraction is carried out in two stages with a digestion at elevated temperature between stages. About half the nitrate is extracted in the first stage; the digestion step releases additional nitrate, which is removed in the second extraction stage. The oxide hydrosol is introduced into the sphere-forming system. Conversion of the sol into fuel spheres is accomplished by extracting water from hydrosol drops with a countercurrent flow of an alcohol [2-ethyl-1-hexanol (2EH)]. The gelled spheres are then dried, calcined, screened, and inspected for size, shape, uranium and thorium content, density, and impurities.

The inspected uranium-thorium oxide kernels are conveyed to fluidized bed coaters. In these coaters a low-density carbon layer, called a buffer coat, is deposited on the kernels by high-temperature vapor-phase deposition from hydrocarbon gas diluted with an inert gas such as argon or nitrogen. By changing the coating conditions, the low-density coating is followed by a high-density isotropic carbon coating. The fuel particle is now called a fissile BISO particle. This coating step is followed by a thorough inspection of coating thickness and density.

The fissile particles produced in the refabrication plant are blended with coated fertile particles in a mold and hot injected with a viscous mixture of pitch and graphite flow which on cooling solidifies to form the green fuel rod measuring 5/8-inch diameter by 2 inches long. The rod is pressed out of the mold and is inspected to ensure conformance with specifications of diameter, length, and uniformity of fissile particle loading.

Fifteen fuel rods selected to give the correct combined length are loaded into each fuel hole in the graphite block and graphite plugs cemented into place. The green fuel element is then heated at about 1,800°C in an inert atmosphere to carbonize the pitch and form a strong rod of high thermal conductivity. Conditions are so arranged that there is a gap between the rod and the fuel-hole wall such that radiation-induced swelling does not create pressure on the fuel-hole wall.

The fuel element is inspected for damage and stored in the refabricated fuel vault.

RADWASTE

A great deal of effort goes into reducing the quantity of radioactive materials being discharged to the environment.

Gaseous effluents from the reprocessing plant will be treated to remove radioactive and non-radioactive pollutants. A major component of gaseous radioactive waste is the carbon dioxide from the burners. This gaseous waste will contain ^{85}Kr, ^{129}I, ^{3}H, non-radioactive gases, and suspended particulates. A combination of filtration and the KALC process will be used to clean up this gaseous waste. The KALC process, being developed at ORNL, is based on the relative volatilities of Kr (and other gaseous products of the burner) and carbon dioxide under conditions of temperature and pressure at which the CO_2 is partially liquefied. By use of vapor-liquid distribution of CO_2 and contaminants in packed columns, Kr and other gases, e.g. O_2, N_2 and CO, will be removed from the CO_2. Additional stages in the KALC process may remove I and ^{3}H.

Liquid effluents will be concentrated by evaporation and added to the high-level liquid waste stream for calcination to a solid.

Solids from the calciner will eventually be canned and sent to a federal repository.

ACKNOWLEDGMENT

A portion of this work was supported by the U. S. Atomic Energy Commission under Contract AT(04-3)-167, Project Agreement No. 17.

REFERENCES

1. L. H. Brooks et al, Spent Fuel Shipping, Reprocessing, and Recycle Fabrication in the HTGR Fuel Cycle, ASME Publication 73-PWR-2, Sept. 1973.
2. R. G. Wymer, Elements of HTGR Fuel Recycle. Presentation at Tennessee Industries Week, Sept. 1973, Copies available from author, ORNL.
3. L. M. Ferris, Head-end Processes for Graphite-base and Carbide Reactor Fuels. Process Chemistry, Vol. 4, 121. Progress in Nuclear Energy Series III, Pergammon Press, 1969.
4. L. H. Brooks, Survey & Evaluation of Methods for Reprocessing Spent HTGR Fuel, GA-A12853, January 1974.
5. E. L. Nicholson, et al. Burn-Leach Processes for Graphite-base Reactor Fuels Containing Carbon Coated or Oxide Particles. ORNL-TM-1196. 1965.
6. F. Pitman. Statement by the Director of the Division of Waste Management and Transportation before the Joint Committee on Atomic Energy, March, 1973. USAEC.
7. National HTGR Fuel Recycle Development Program Plan. ORNL-4702, Rev. 1, August, 1973.
8. H. G. Reeser. GA document. (In preparation)
9. R. S. Lowrie, Study of the Waste Handling Requirements for the HTGR Fuel Recycle Development Program. ORNL-TM-3597, March 1972.
10. R. W. Glass et al. HTGR Head-end Reprocessing: A Preliminary Evaluation of Processes for Decontaminating Burner Off-gas. ORNL-TM-3527. July 1972.
11. M. E. Whatley, Calculations on the Performance of the KALC Process, ORNL-4859, April 19[illegible]
12. C. C. Haws, B. C. Finney, W. D. Bond, Engineering Scale Demonstration of the Sol-Gel Process, ORNL-4544, May 1971.