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FUEL ELEMENT DEVELOPMENT PROGRAM

FOR THE

PEBBLE BED REACTOR

QUARTERLY PROGRESS REPORT

November 1, 1959 to January 31, 1960.

**DO NOT
PHOTOCOPY**

Work Performed Under AEC Contract AT (30-1)-2378

SANDERSON, & PORTER

NEW YORK, N.Y.

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FUEL ELEMENT DEVELOPMENT PROGRAM
FOR THE
PEBBLE BED REACTOR

Quarterly Progress Report
Nov. 1, 1959 to Jan. 31, 1960

Summary

A variety of spherical uranium-graphite fuel elements were fabricated with the objective of meeting the requirements of the Pebble Bed Reactor. Major emphasis was on silicon-silicon carbide coatings, pyrolytic carbon coatings and alumina coated fuel particles. An exploratory program on the limits of thorium oxide loadings by the infiltration process was started. Poor results with sintered alumina coated UO_2 particles led to development work on alumina coating by vapor deposition for which the results have been most encouraging. A wide variety of sub-surface metal, metal carbide, and ceramic coatings located between an unfueled graphite shell and the fueled core of a PBR fuel element were prepared and examined. Most of the materials and processes tried showed poor results so that no further work will be done in this area. Discussions were held with numerous manufacturers on the application of various non-destructive testing techniques to PBR fuel elements. Specimens have been submitted to manufacturers on a trial basis, and to date no firm conclusions have been reached. Reprocessing studies, using the grind-leach technique, have been carried on at ORNL and excellent metal recoveries have been achieved from the metal oxide-graphite system.

Test results obtained on Si-SiC coated fuel elements during this quarter showed good fission product retention in neutron activation tests, a self-welding tendency between adjacent spheres at 2500°F surface temperature, and no evidence of failure when an internal gas pressure of 300 psi (i.e. simulating maximum PBR conditions) was applied. One type of pyrolytic carbon coating has shown good impact resistance and neutron activation tests have shown good fission product retention. Fission product release rates from one of the pyrolytic carbon coated specimens while under low level irradiation were obtained over the temperature range of 150°F to 1900°F . One capsule containing six types of specimens remained under high temperature, high flux irradiation during this quarter. These specimens will be examined during the next quarter at which time the specimen

exposure will be 5000 to 6000 KWH per sphere, which is comparable to the 125 eMW-PBR design conditions.

Design of an in-pile loop to study the behavior of fission products escaping from PBR fuel elements was continued during this quarter. This loop will furnish information on activity levels in a primary loop and methods of reducing these activity levels. The design of the loop has been established, the reactor facility (BNL) has been selected, and most of the equipment has been ordered. Loop operation is scheduled to start during the quarter beginning May 1, 1960.

1.0 Introduction

This report reviews the Pebble Bed Reactor Fuel Element Development Program for the quarterly period of November 1, 1959 to January 31, 1960. Detailed results have been given in monthly progress reports (1, 2, 3) during this quarter. Background information on the program has been given in the Phase I Summary Report (4) covering the 6 month period prior to this quarter and in a topical review issued during this quarter (5).

Section 2.0 describes the sources of PBR fuel element specimens together with results from certain allied areas such as non-destructive testing and fuel reprocessing. In general, fuel element specimens are obtained in two ways. Where commercial manufacturers have previously developed promising materials, specimens are procured on either a sample-lot-fixed-price basis or on a no-charge basis. Where fuel element concepts are not available on a commercial basis, we have sponsored research and development work in these areas.

Section 3.0 describes an evaluation program being conducted under subcontract by the Battelle Memorial Institute which covers pre-irradiation, irradiation, and post-irradiation testing of fueled specimens. A major part of this testing program involves the use of a variety of types of capsule irradiations. Section 4.0 describes an in-pile loop testing program which was carried on during this quarter under a subcontract to the Nuclear Science and Engineering Corp.

2.0 Fuel Element Development

Commercial fuel element specimens which were obtained and/or evaluated during this quarter are listed in Table I. Although the specimens are categorized in accordance with the method of fueling the graphite, the primary emphasis in selecting most of the specimen types has been on the particular feature which enhances fission product retention. Two major categories are the metal carbide surface coatings (FA-6, -8, -16; FL-2) and the pyrolytically deposited carbon coatings (FA-20, and -21). Test results obtained during this quarter on these specimens are given in Section 3.0.

2.1 Infiltration Studies

The Speer Carbon Company is studying the limits of ThO_2 loading in graphite spheres by infiltration as a function of density and available porosity. In the reference PBR design it is required to load blanket elements to 50 weight per cent ThO_2 , which is five times the loading in the fuel elements. This study is being undertaken to determine the feasibility of potentially low cost infiltration techniques for manufacturing blanket elements.

The loading technique which is being studied is the infiltration of a thorium nitrate solution into porous graphite followed by baking to convert to the oxide. Work this quarter on simple water solutions of thorium nitrate show that essentially 100% conversion to ThO_2 can be obtained. The solution was evaporated at 110°C and the residue was fired at 700°C for 4 hours. Solutions in oxalic acid and nitric acid also resulted in essentially 100% conversion. Since the simple water solution was satisfactory, future work will continue with this technique.

In the next quarter infiltration experiments will be run on a series of graphite spheres ranging in density from 1.25 to 1.75. The thorium oxide uptake as a function of solution concentration and multiple infiltrations will be established in matrix materials of six densities. All necessary glass ware and equipment has been assembled and a trial run has been made.

2.2 Coated Fuel Particles

Coated fuel particles present an extremely promising approach to the problem of fission product retention. Fission products are retained at their

TABLE I
SUMMARY OF FUEL ELEMENT TYPES

	INFILTRATED		LUMPED		UNFUELED	
Number	FI-1	FI-6	FL-1	FL-2	FX-2	FX-3
Mfgr.	Syl.	AMP	AMP	AMP	Plas.	Ray.
FUEL						
Loaded As	UNH	UNH	UC ₂	UC ₂	—	—
Final Form	UO ₂	UC ₂	UC ₂	UC ₂	—	—
Particle Size, μ	1	1	3/8"	3/8"	—	—
MATRIX						
Reimpreg.	no	yes	yes	yes	—	—
Net Density	1.65	1.85	1.85	1.85	—	—
Shell Thick.	0	0	0.35"	0.35"	—	—
Bake Temp, °F	1470	3500	3500	3500	—	—
COATING						
Material	—	ZrC	—	ZrC	ZrC	Pyro-G
Thickness	—	.001	—	.001"	.010"	.060"

Manufacturers	
AMP	- American Metal Products
BMI	- Battelle Memorial Institute
Carbo	- Carborundum
GLC	- Great Lakes Carbon
3M	- Minnesota Mining and Manufacturing
NC	- National Carbon
Plas	- Plasmakote
Ray	- Raytheon
Syl	- Sylvania-Corning Nuclear

	ADMIXTURED									
Number	FA-1	FA-2	FA-6	FA-8	FA-10	FA-16	FA-19	FA-20	FA-21	
Mfgr.	NC	BMI	3M	Carbo	GLC	3M	NC	NC	Ray	
FUEL										
Loaded As	UO ₂	UO ₂	UO ₂	UC ₂	UO ₂	UO ₂	UO ₂	UO ₂	UO ₂	
Final Form	UO ₂	UO ₂	UC	UC ₂	UO ₂	UC	UC ₂	UC ₂	UC ₂	
Particle Size, μ	100/150	67	100/200	100/200	350/420	100/200	100/150	100/150	100/150	
MATRIX										
Reimpreg.	no	no	yes	no	yes	yes	no	no	no	
Net Density	1.62	1.63	1.80	1.63	1.80	1.75	1.65	1.65	1.65	
Shell Thick	0	0	0.15"	0	0	.060"	0	0	0	
Bake Temp, °F	2560	2000	3600	3600	2000	3600	4800	4800	4800	
COATING										
Material	—	—	SiC-Si	SiC-Si	—	SiC-Si	—	Pyro-C	Pyro-G	
Thickness	—	—	.003"	.030"	—	.003"	—	.002"	.050"	

sources and the coatings are protected from external damage since they are beneath the graphite surface. In addition, fission fragments are prevented from recoiling into the graphite matrix and causing damage.

The development and testing of various types of coated particles has received considerable emphasis during this quarter. Development work continued on a sintered alumina coating and work started on a vapor deposited alumina coating. This work was done under subcontract by the Battelle Memorial Institute. A specification for a low permeability pyrolytically deposited carbon or graphite coating on uranium carbide particles was prepared and proposals for fabrication and/or development were solicited from 9 manufacturers. It is expected that work will start in this area during the next quarter.

Sintered Alumina: This process consists of preparing particles from a sinterable grade urania powder, dusting the particles with a sinterable grade alumina powder while in a pelletizing drum, isostatically pressing the coated particles and then sintering them. Further details on this process have been previously described in ref. (4). Development work during this quarter was concerned with the problems of the lower sintering shrinkage of the UO_2 compared with the alumina and with the reproducibility of the coated particles, particularly when thinner coatings (i.e. in the range of coating thickness equal to the fuel particle radius) are employed.

The primary methods of overcoming the differential sintering shrinkage are the addition of various proportions of UO_3 or alumina monohydrate to the starting UO_2 powder, since both of these materials exhibit a high degree of sintering shrinkage. Batches made with 100 w/o UO_3 starting material exhibited good reproducibility as shown a heating test in air at 1200°F. In this test, faults in the coating permit the underlying UO_2 to oxidize to U_3O_8 and weight gain is thus an indication of coating fault. However, the fuel particle shrinkage was so great in this case than an undesirably large gap between the UO_2 and the alumina resulted. Experiments with 10 w/o alumina hydrate additive to the UO_2 revealed that the gap problem could be solved but poor reproducibility was noted from batch to batch. Another series of experiments was run where the starting UO_3 content was varied from 35 to 65 w/o in UO_2 . It was found that 65 w/o was needed to produce a consistently good batch. However, when thinner coatings were tried (i.e. final UO_2 content > 25 w/o), coating reproducibility again was poor.

One of the main questions with alumina coated particles is compatibility with graphite. Previous tests (4) had shown no reaction at 2500°F for 168 hrs and a complete reaction between alumina and graphite at 3000°F after 6 hrs. During this quarter, a 1000 hr test at 2500°F was performed with sintered alumina incorporated in three types of graphite: (1) AGOT filler, Barrett pitch binder; (2) AGOT filler, BV 1600 resin binder; and (3) Texas 55 coke filler, Barrett pitch binder. Severe reactions were noted with graphites (2) and (3) while the particles retained their integrity with graphite (1) although a slight evidence of reaction was noted at the outer surface of the coating. These results indicate that a long time safe operating temperature should be somewhat below 2500°F and that the selection of graphite materials is quite important.

In view of the discouraging results with attempts to resolve the differential shrinkage problem and the coating reproducibility problem, development work on sintered alumina coatings was terminated during this quarter.

Vapor Deposited Alumina: During this quarter, another method of depositing an alumina coating was investigated. In this process UO_2 particles suspended in a fluid bed are coated with alumina by reducing Al_2Cl_6 vapor by hydrogen in the presence of water vapor. This method produces a uniformly tight and adherent coating of low porosity. Photomicrographs show that coatings of high integrity can be produced in thicknesses as low as 10 microns.

Two batches of vapor deposited alumina coated UO_2 particles have been prepared. In the first batch, -100 +140 mesh UO_2 shot, was coated to a 20 micron thickness. The coating was applied in three stages to reduce contamination of the coating by UO_2 dust which is present in early stages of fluidization. In the first stage, a 9 micron layer was applied. This was followed by leaching for one hour in boiling 3N HNO_3 . After the batch was rinsed and dried, and the reactor cleaned, three and eight micron coatings were applied. Chemical analysis showed that this batch contained 71 w/o UO_2 . A 38 micron batch was prepared from a portion of the 20 micron batch. Microscopic examination showed some protrusions on the coating surface. However, the coating was dense and uniform, and there was no evidence of an interface between the successively applied layers. Both batches showed good oxidation resistance on heating in 1200°F air for 5 hours. A small weight loss which was observed in the first hour of heating is believed to be caused by devolatilization of absorbed moisture. An alpha assay showed surface

contaminations of $2 \times 10^{-3}\%$ and $4 \times 10^{-4}\%$ of the total uranium for the 20 and 38 micron batches, respectively.

Further experimentation is planned for vapor deposited alumina coated particles. Portions of both the 20 micron batch and the 38 micron batches have been set aside for admixture into graphite spheres. In the next quarter neutron activation experiments will be made with normally enriched coated particles. Fully enriched coated particles will be prepared for possible irradiation in SP-5. In addition carburization tests are planned, similar to those performed on sintered Al_2O_3 coatings.

2.3 Sub-Surface Coatings

Exploratory work was continued this quarter at Battelle on various types of sub-surface coatings. The interest in this approach stems from a desire to see whether a suitable coating could be placed between an unfueled shell and a fueled core so that external loads could be taken by a graphite surface and to see whether, through suitable choice of materials, a coating operating in the plastic or molten range would seal pores and fissures in the lower temperature zone of the unfueled graphite shell. Two variations of this approach have been studied. In one, materials have melting points in the range of peak PBR operating temperatures are used. In the other, materials with a high melting point are used so that the coating can be "set" in a baking furnace prior to use in a reactor.

Two methods have been used in studying these approaches. Basic materials' compatibility has been studied using graphite crucibles filled with coating materials of interest and graphite-metal diffusion couples. Also, a number of sub-surface coated 1-1/2 inch dia. specimens fueled with normal enrichment uranium have been made and examined.

Materials' compatibility studies using the diffusion couples were completed this quarter, the previous crucible work having been described in ref. (4). In the diffusion couple studies, different materials were compressed between 1/4 inch thick graphite plates and heated at 2600°F for 8 hrs. The materials used and the results of the metallographic examinations are shown in Table II.

TABLE II

Summary of Metallographic Examination of Diffusion Couples

<u>Material</u>	<u>Wetting of Graphite</u>	<u>Depth of Penetration Into Pores in Graphite</u>	<u>Remarks</u>
Copper	None	None	Copper distributed as spherical particles after heating.
Nickel	yes	About 10 mils	Carbon dissolved in nickel and precipitated as graphite flakes on cooling.
Zirconium	Very little	Very little	Zirconium apparently was converted to either ZrC or ZrO ₂ and was present as a series of fine particles after heating.
Silicon	yes	About 5 mils	Most of the silicon metal was converted to small particles of SiC or SiO ₂ .
MoSi ₂	yes	About 10-15 mils	Two phases present in MoSi ₂ after reaction. Gray phase found in pores of graphite is probably SiC.
No. 3 glass	yes	About 2 mils	Particles of a metallic phase evident at graphite-glass interface after heating.

Copper and zirconium did not wet the graphite or penetrate into it. The copper apparently remained in the metallic state. The zirconium was found as a loose, powdery, non-metallic phase which is probably ZrC or ZrO₂. All of the other four materials wet the graphite and penetrated into the graphite pores. The most adherent and uniformly solid intermediate layers after reaction were those consisting of nickel and No. 3 glass. However, flakes of graphite were found in the nickel indicating solution of carbon. A

metallic phase was found in the glass next to the graphite. Cracks formed during cooling or sectioning were found between the graphite and the intermediate layer in specimens containing both silicon and MoSi_2 . Both of these latter materials wet the graphite and penetrated into the graphite pores.

Spheres were fabricated using coatings of Cu, Ni and 2 glasses (low melting materials) and also Ti, Cr, and MoSi_2 (high melting materials). The general procedure was to first form a fueled core piece, apply the coating as a powdered metal with a carbonaceous binder, and mold on an unfueled graphite shell. The specimens were then baked just above the melting point of the coating material.

A variety of results were obtained. In earlier specimens, many of the shells cracked during the bakeout. This was overcome by adjusting the shell graphite composition to minimize shrinkage. A high degree of metal (or metal carbide) penetration into the unfueled shell was noted in most cases. In the case of Cr and MoSi_2 , penetration through the outer surface could be noted. The glasses did not penetrate but there was evidence of chemical reaction with the graphite. There was only slight penetration with copper but this material tended to ball up and leave gaps near the top of the sphere due to gravitational effects.

Several attempts were made to seal two thin copper hemispheres around a fueled core. However, outgassing and chemical reactions prevented the making of a satisfactory brazed joint.

In order to overcome the penetration problems during bakeout, external pressure was applied to several specimens while they were at temperature. Incidentally, this hot-pressing technique resulted in a superior grade of graphite. By using this technique, apparently sound Ni and Cr sealed spheres were made, showing very little metal penetration into the unfueled shell and having a well-bonded metal coating.

Simple examinations of sub-surface coated specimens leaves something to be desired. The most useful information has been gained from visual examination of the external surface and sectional pieces. Radiography has been helpful in studying metal penetration of the unfueled shell. Hot oil tests have been inconclusive since degassing of the unfueled shell tends to mask leakage through the sub-surface coating. To date, no specimen has shown sufficient promise to warrant a neutron activation test.

A number of conclusions have been reached from this program. The use of materials which would melt in the range of PBR operating temperatures appears likely to result in metal penetration into the unfueled shell to an extent such that voids will form in the region of the coating, permitting fission products to leak. A pre-set coating of a high-melting material would overcome this problem but hot pressing is required to give the best results. The economics of hot pressing would require further evaluation if this concept is to prove economically feasible. No further work is contemplated in this area.

2.4 Non Destructive Testing

Fifteen manufacturers of non-destructive testing equipment were contacted regarding application of their equipment and techniques to the detection of internal flaws in the coating and matrix of PBR fuel elements. Four manufacturers showed interest and were sent fuel element specimens for testing.

Ultrasonic methods were studied by three manufacturers. One manufacturer reported that the ultrasonic beam easily penetrated all directions of a molded graphite sphere but showed a discontinuity in small areas of two spheres machined from extruded graphite. These latter spheres will be sent to Battelle for sectioning to establish whether the discontinuity was caused by a true defect. Another manufacturer advised that they had had difficulty in finding a wave frequency which would penetrate the spheres using pulse techniques. A third manufacturer found no transmission except along two axes at right angles. Further work will be necessary to explain this anomolus result.

Another manufacturer advised that their eddy-current equipment should detect cracks and voids in the region near the sphere surface, but would not detect deep seated flaws and specimens have been submitted for their experimentation.

A quantity of graphite spheres which are known to have flaws is being obtained. Evaluation of non-destructive testing techniques will continue in the next quarter.

2.5 Fuel Reprocessing

The Chemical Technology Division of the Oak Ridge National Laboratory is studying the reprocessing of various types of uranium graphite fuel elements.

In cooperation with this program, several types of PBR fuel elements were submitted to the ORNL and some results were reported during this quarter (6).

Four types of oxide fueled specimens were tested.

- Type A: Admixture; nominal 3 w/o UO_2 + 27 w/o ThO_2 , added separately to the graphite.
- Type B: Admixture; nominal 50 w/o ThO_2 only.
- Type C: Admixture; 10 w/o coprecipitated oxides;
 $\text{ThO}_2:\text{UO}_2 = 11:1$ (Type FA-14).
- Type D: Admixture; 10 w/o coprecipitated oxides;
 $\text{ThO}_2:\text{UO}_2 = 6.4:1$

A grind-leach technique was used to recover the U and Th from these samples. Two types of leaching solutions were tried:

- (1) 13 M HNO_3 - 0.04 M NaF - 0.1 M $\text{Al}(\text{NO}_3)_3$.
- (2) 15.8 M HNO_3

The fluoride catalyzed nitric acid solution was tried because of previous experience which showed that it dissolved high fired ThO_2 more readily than HNO_3 . The recovery of U and Th as a function of the degree of grinding, the leachant, and the number of washes are summarized in Table III. The excellent Th recovery using the fluoride catalyzed acid can be noted. In the case of Type A, where the UO_2 particles were physically separate from the ThO_2 particles, the U recovery using nitric acid was independent of the Th recovery although this was not the case where the coprecipitated Th and U oxides were used. The metal recovery from Type A increased with finer grinding from -10 +20 mesh to -200 mesh. For Types C and D, the acid leachants chemically disintegrated the -10 mesh powders to -100 mesh causing excellent metal recoveries (>99.9%). This is the highest recovery yet obtained in the ORNL studies.

TABLE III
Recovery of Th and U from PBR Samples

Sample ^(a)	Mesh Size	Acid, ^(a) 1st Leach	Metal Recovered, %							
			1st Acid Leach + 2 Water Washes		3rd Water Wash		2nd HNO ₃ Leach + 1 Water		Graphite Residue	
			U	Th	U	Th	U	Th	U	Th
A	-10+20	(1)	93.0	97.1	0.5	0.6	5.7	1.5	0.67	0.80
A	-10+20	(2)	93.4	1.6	0.6	0.004	5.2	0.2	0.78	98.2
A	-200	(1)	96.0	98.8	0.3	0.1	3.5	1.0	0.33	0.09
A	-200	(2)	97.4	0.6	0.3	0.002	2.0	0.33	0.33	99.0
B	-10+20	(1)		99.5		0.06		0.37		0.02
B	-10+20	(2)		1.75		0.003		0.46		97.8
B	-200	(2)		1.62		0.004		0.92		97.5
C	-10	(1)	99.8	99.4	0.005	<0.01	0.2	0.6	0.02	0.004
C	-10	(2)	3.1	0.5	<0.005	<0.02	0.2	<0.03	96.7	99.5
D	-10+20	(1)	99.8	99.5	<0.02	0.1	0.2	0.5	0.01	0.02
D	-10+20	(2)	0.6	0.4	<0.04	0.03	0.4	0.1	99.0	99.5
D	-200	(1)	99.7	98.9	<0.03	0.02	0.2	1.1	0.08	0.02
D	-200	(2)	4.0	2.9	<0.2	0.1	3.8	4.0	92.3	93.1

(a) See page 12 for legend.

3.0 Fuel Element Testing & Evaluation

Various fuel element types are screened by simple mechanical and physical tests prior to extensive additional testing. Promising specimens are graduated to neutron activation experiments where fission product retention ability is evaluated. Capsule tests are used for evaluation of both fission product retention ability and the effects of irradiation on mechanical properties. The testing methods and apparatus have previously been described in detail in reference (4). The results of testing during the quarter are summarized below.

3.1 Silicon-Silicon Carbide Coatings

Type FA-6, Type FA-16: These fuel element types, made by the Minnesota Mining and Manufacturing Co. have siliconized silicon carbide coatings applied to a thickness of about 0.003 in on an isotropic graphite matrix consisting of an unfueled shell surrounding a fueled core. The coatings are the same on both types. Type FA-16 has an improved graphite matrix developed to avoid incipient cracking observed in Type FA-6 specimens.

Two FA-6 spheres showed a tendency to self-weld when tested for 66 hours in helium at 2500°F under a load of 50 pounds. The self-welding may have been accentuated by oxygen contamination in the helium stream since a white film was observed on the surface of the spheres. The apparatus is being modified to insure the elimination of oxygen and the self-welding test will be repeated.

An alpha assay on a Type FA-16 specimen showed a surface uranium contamination of the order of 0.001% of the total uranium. Neutron activation experiments will be irradiated in Furnace Capsule SPF-2 which will be inserted in the BRR in mid-February. An FA-16 specimen will also be irradiated in one of the two sweep compartments in SP-5.

Type FA-8: This specimen type is manufactured by the Carborundum Co. The coating thickness is about 0.03 in applied directly to a fueled graphite core. The previously measured high uranium contamination was confirmed by a surface count at 18 different locations, each with an area of 1/36 of the total sphere surface. This local count showed that the uranium contamination was essentially uniform over the surface of the sphere. The averaged effective surface contamination was 0.3 per cent of the total uranium in the sphere, considerably greater than desired for fuel elements. The Carborundum Co. is presently working to reduce this contamination and new specimens for testing are expected next quarter.

Several miscellaneous data were obtained on FA-8 specimens during this quarter. An internal pressure of 300 psi argon was applied to a specimen immersed in 380°F silicon oil. No leakage was observed. Hot cell examination of a FA-8 specimen which had been irradiated in SP-3 showed no cracks in the coating and that a good bond continued to exist between the coating and the matrix. An FA-8 specimen is being irradiated in SP-4 and should provide data on the effects of high level irradiation on physical properties.

3.2 Pyrolytic Carbon Coatings

Type FA-20: This specimen type has been prepared by the National Carbon Co. Carbon coatings have been deposited on the surface of uranium carbide fueled spheres by the pyrolysis of a hydrocarbon gas. Coating thicknesses have ranged from .002 to .005 inch. This type of coating has shown promise because impact loads of 3.6 ft lbs have been required to damage the coating and 7.8 ft lbs to break the graphite matrix. Both of these values are well above the design objective of 2 ft lbs. Uranium contamination of the coating is no problem, even though the coating is applied directly to the fueled graphite sphere. The average surface contamination of this type specimen has been found to be $3 \times 10^{-4}\%$ of the total uranium in the sphere.

The irradiation of an FA-20 specimen in furnace capsule SPF-1 was completed during this quarter. In this type of experiment, a helium stream is swept over the surface of the specimen while it is under low level irradiation. The helium stream is monitored for fission product leakage and specimen temperature is adjusted by means of an electrical heater. Data at 1500°F from SPF-1 had been previously reported and correlated with neutron activation data at 1500°F on the same specimen (4). During this quarter, data at 150°F, 1000°F, and 1500°F was obtained. Table IV is a summary of the data at each temperature where the average leakage factor, R/B' (i.e. rate of leakage/rate of production), is listed for each of the 5 isotopes detected in the gas stream

TABLE IV
Summary of SPF-1 Data on FA-20 Specimen

Specimen Temp.	Kr 85m	Kr 87	Kr 88	Xe 133	Xe 135
150°F	.00038	.00016	(a)	.0046	.0015
1000°F	.0043	.0023	.0038	.0057	.0039
1500°F	.016	.013	.016	.041	.009
1900°F	.026	.0107	.0224	.067	.019

(a) No detectable release.

A number of methods of analyzing this data are being studied. One method had been previously outlined (4) in which the surface coated sphere is treated as a balloon. This mathematical model accounts for diffusion through the coating material and allows for decay during diffusion. No retention by the graphite matrix is postulated. Using this method, a diffusion coefficient was calculated for each isotope at each temperature. Results are plotted versus reciprocal temperature in Figure 1. As can be noted, a fair degree of agreement is seen between isotopes of the same species in the 1000°F to 1900°F temperature range. The significance of the relatively high values at the lowest temperature is not known, although it may indicate that diffusion coefficients are relatively insensitive to temperature below 1000°F. Diffusion coefficients for Kr are generally seen to be about one order of magnitude higher than for Xe, reflecting the smaller molecular size of Kr.

An FA-20 specimen has been included in Static Capsule SP-4 (see Section 3.5). It is expected that the rather high burnup achieved in this capsule when it is examined during the next quarter should give some excellent information on the effect of irradiation on pyrolytic carbon coatings.

During this quarter, a batch of FA-20 specimens were received on which the coating had been deposited at a temperature of 1800°C, about 100°C higher than the deposition temperature for the FA-20 specimen tested in furnace capsule SPF-1. Neutron activation data for this 1800°C material showed no detectable fission product release during 70 minutes at 1700°F and 100 minutes at 2200°F. This data shows that there is at least an order of magnitude reduction in fission product release for the 1800°C coating as compared with previous data (4) on the 1700°C coating. Specimens of this type fueled with enriched uranium are being procured for possible use in Sweep Capsule SP-5 starting in March.

Type FA-21, FX-3: Another type of pyrolytically deposited carbon coated specimen has been made by Raytheon who have applied their "Pyrographite" material to fueled spheres (FA-20) and unfueled spheres (FX-3) which are otherwise similar to fueled spheres used in the FA-20 specimens. "Pyrographite", as used in non-nuclear applications, is deposited at about 2100°C. Densities closely approaching theoretical carbon density and very low permeabilities are achieved at this deposition temperature, however a high degree of anisotropy also results. This leads to a low thermal contraction of the coating which can cause poor bonding to the graphite sphere upon cooling from the fabrication temperature.

FISSION PRODUCT DIFFUSION COEFFICIENTS
FOR PYROLYTIC CARBON COATING (TYPE FA-20)
CAPSULE SPF-1

FIG. 1

A few specimens of this type having a .050 in thick shell were examined during this quarter. In several of the specimens, the graphite sphere could be felt to rattle inside the coating shell indicating poor bonding. In this case, impact failure was noted at 1.0 ft lbs. On other specimens having tight coatings, impact failures at 2.5 ft lbs were noted. This latter batch was fabricated at 1700°C, indicating that the thermal contraction of the coating was sufficiently increased at this temperature to resolve the shrinkage problem. In all cases, the as-received specimens passed the hot-oil leakage test. Surface uranium contamination was found to be $10^{-4}\%$.

One specimen was tested for fission product retention in a neutron activation test. At 1650°F for 75 minutes, Xe 133 release was less than the detectable amount of .004%. At 2300°F for 80 minutes, the barely detectable amount of .004% of the Xe 133 was found. Further evaluation of this type of coating is planned during the next quarter.

3.3 Metal Carbide Coatings

Relatively little work was done this quarter on metal carbide coatings. Zirconium carbide coated specimens manufactured by American Metal Products, (Type FL-2) and by Plasmakote (Type FX-2) were tested for load-deflection characteristics in the low-load region. Load moduli of 21,400 pounds per inch and 18,500 pounds per inch were measured for Type FL-2 and FX-2, respectively. Metallographic examination of FL-2 showed a very fine intergranular porosity in the coating which accounts for the fine stream of bubbles when this specimen was hot-oil tested. Because of the generally unfavorable test results of metal carbide coatings, which were reported in reference (4), and the fact that no promising information was obtained in this quarter, this type of metal carbide coating will receive little emphasis in future work.

3.4 Uncoated Spheres

Type FX-4: A statistical compression and impact study was made on unfueled spheres which were made by machining Speer Moderator Grade B graphite. Twenty-five specimens tested for compressive strength had a mean fracture load of 2932 ± 113 (1) lbs. Deflection was $0.130 \pm .003$ (1) inch and load modulus (2) was 25,000 lb per in. Twenty spheres tested for impact had an average energy at failure of $16.4 \pm .4$ foot-pounds (1). Testing of additional specimens showed that higher starting impact energies resulted in slightly high impact energies at failure.

(1) Based on 95% confidence range.

(2) Based on the best straight-line portion of the load deflection curve.

3.5 UO₂ Stability

The stability of four types of UO₂ particles in graphite under high temperature irradiation is being determined in Capsule SP-4. Irradiation of this capsule commenced on August 25, 1959. Typical operating conditions are summarized in Table V.

TABLE V

<u>Specimen</u>	<u>Operating Conditions for Capsule SP-4</u>			
	<u>Measured Graphite Block Temp. °F</u>	<u>Ht. Gen Rate, KW</u>	<u>Calculated Surface Temp.</u>	<u>Central Temp., °F</u>
FA-1	1290	1.95	1620	1780 (a)
FA-8	1410	2.24	1770	1830
FI-1	1400	2.37	1760	1850
FA-2	1410	2.27	1770	1910
FA-20	1250	1.96	1560	1770
FA-10	1300	1.75	1630	1730

(a) Measured temperature. One thermocouple is imbedded in the center of this specimen only. All other center temperatures are calculated.

The distinguishing characteristics of the four uncoated specimens contained in this capsule are given below.

1. Type FI-1: 1 μ UO₂, by infiltration
2. Type FA-2: 67 μ UO₂, by admixture
3. Type FA-1: 100 μ UO₂, by admixture
4. Type FA-10: 400 μ UO₂, by admixture

In addition, one FA-20 specimen and one FA-8 specimen are being irradiated in SP-4. Duplicates of all the specimens in SP-4 are contained in an out-of-pile thermal history apparatus in which the specimens are in a thermal environment maintained similar to that in the capsule. The heater for the thermal history apparatus is programmed from temperature recorded for the capsule specimens so that the out-of-pile duplicates receive thermal cycles identical to the capsule specimens. In this way changes in the irradiated specimens caused by temperature or thermal cycling can be distinguished from changes caused by irradiation.

Present plans are to terminate this irradiation in March 1960 at which time the exposure will be 5000 to 6000 KWH per sphere. This is comparable to the design exposure of the 125 eMW-PBR.

4.0 In-Pile Loop

The design of an in-pile loop to study the behavior of fission products escaping from a PBR fuel element was continued during this quarter under a subcontract to the Nuclear Science and Engineering Corp. The purposes of this loop are to study the equilibrium activity levels in a recycle helium stream; methods of lowering gas stream activity level; the amount, location, and nature of the deposited fission products; and methods of decontaminating equipment surfaces. The program will include deliberately violated PBR specimens in addition to good PBR specimens.

The loop will be operated in one of the 4 in experimental holes in the West face of the Brookhaven Graphite Reactor. Design characteristics of the loop are as follows:

Circulating Fluid	Helium
Operating Pressure	14 psia
Flow Rate	8 scfm
Max. Helium Temp.	1250°F
Min. Helium Temp.	250°F
Max. Specimen Temp.	1800°F
Max. Specimen Power	0.25 KW

Two major variables, the system pressure and the specimen power, have been selected with view to minimizing the cost of the loop. The use of subatmospheric pressure eliminates the need for double containment while the modest power level in the specimen will provide measurable activity yet minimize the gas flow requirements and shielding costs.

Figure 2 is a schematic diagram of the in-pile loop. Gas leaves the in-pile section at 1250°F and enters the shell side of a coiled tube heat exchanger where it is cooled to 550°F. The exchanger is designed for easy replacement of the tube coil so that deposition on the tube surface as a function of temperature can be studied. An intermediate Dowtherm loop, which transports heat from this exchanger to a water-cooled sink, has been included to permit adequate control of the helium outlet temperature. The helium next passes through a removable 550°F test section and a precooler to lower the temperature to 250°F which enables the use of an economical low temperature blower. Before entering the blower, provision is made for in-line or bypass operation of an analytical train which will gather data on fission product release rate and activity levels in the gas stream.

REVISIONS					
REV	MADE BY	DATE	CHKD	APPVD	DESCRIPTION

PRINTS ISSUED					
REV	DATE	FIELD			

DATE PRINTED		
IN PILE LOOP SCHEMATIC		
PEBBLE BED REACTOR FUEL ELEMENT PROGRAM AEC CONTRACT AT(30-1)-2378 SANDERSON & PORTER, INC. NEW YORK, N. Y.		
DESIGN DRAWN <i>A. Baker</i> DATE 3-22-60	ENGINEERING APPV'D <i>J.P.</i> DATE 3-22-60	SCALE <i>1/2"</i>
CHECKED DATE APPV'D	DATE APPV'D	DRAWING NO. 1964-A-100

Two Dexter-Conde positive displacement blowers are provided, although only one is required for normal operation. Each blower and its drive motor are mounted in a canned enclosure to provide a zero leakage system. Flow variation is achieved by powering the drive motors from a variable frequency motor generator set. A bypass charcoal trap is provided from the blower discharge back to the blower inlet so that the effect of continuous gas decontamination can be studied. After leaving the blower, the helium temperature is raised to 1200°F by an electrical resistance heater and then enters the in-pile section.

The in-pile section is designed for accommodation in a four inch square experimental hole. Co-axial flow is used in the in-pile region, while separated pipes are possible in most of the shield plug. A flange near the point where the inlet and outlet pipes become co-axial permits removal of the test specimen and high temperature plate-out coupons. A vacuum jacket insulates the co-axial section while fibrous insulation is used for the inlet and outlet pipes. The test specimen, a fueled 1-1/2 inch graphite sphere, is surrounded with portions of dummy spheres to simulate the flow pattern in a ball bed.

Purchase orders for all major components except the heat exchangers and the heater have been placed. Final design of the coolers will be completed early next month so that components can be procured. Approval of the heater purchase order is expected early next month. However, since this is the item having the longest delivery, final assembly and shakedown at Brookhaven is scheduled for May 1st.

5.0 Conclusions

Current emphasis in the PBR Fuel Element Development Program is on the retention of fission products in high temperature ceramic fuel elements. Three methods of retaining fission products which show the most promise and are being extensively investigated include surface coatings of silicon-silicon carbide and pyrolytic carbon, and fuel particle coatings of alumina.

Si-SiC coatings have previously shown the best ability to retain fission products at high temperature due primarily to the presence of free phase silicon. This is based on both neutron activation data and one data point from Sweep Capsule SP-3 (4). The subsequent failure of this Si-SiC specimen in Capsule SP-3 was attributed to incipient faults in the graphite, rather than in the coating itself. During this quarter, most of the time has been spent in obtaining improved graphites for the Si-SiC coated fuel elements. One limitation of this coating was discovered, however. In self-welding tests, no effects were noted at 2000°F but at 2500°F, a tendency to self-weld was observed due to the free phase silicon exuding from the coating. Since the maximum surface temperature in the PBR is 1800°F, this presents a slight margin of safety.

Pyrolytically deposited carbon coatings are of interest because they have essentially no temperature limitation and can be made to have a very low permeability and density closely approaching theoretical carbon density. Acceptable mechanical properties have been found for one type (FA-20). Neutron activation data has shown low fission product leakage rates, however, there is some evidence that fission product leakage will be influenced by the type of pyrolytic carbon (i. e. deposition temperature). A complete survey of fission product diffusion from a .002 mil, 1700°C pyrolytic carbon coating was completed this quarter. Although the release rates of the long-lived fission product gases were significant, there is the expectation that short-lived gaseous fission products can be held up by decay so that the maintenance problems in the primary loop, from their non-volatile daughters, will be alleviated.

UO₂ particles coated with alumina by the vapor deposition process have been shown to be superior to particles coated by the sintering process with regard to reproducibility, lower coating thickness, and minimum gap. One limitation with this material is the graphite-alumina reaction. By the proper selection of graphite materials, this limit can be as high as 2500°F. Major effort will be placed on the further evaluation of the fission product retention characteristics of alumina during the next quarter.

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