Y-1852
Part 1

NERVA FUEL ELEMENT DEVELOPMENT PROGRAM
SUMMARY REPORT - JULY 1966 THROUGH JUNE 1972

Extrusion Studies

This document is
PUBLICLY RELEASABLE
David Hamrin, ORNL
Authorizing Official
Date 8-13-2008

**UNION
CARBIDE**

OAK RIDGE Y-12 PLANT
OAK RIDGE, TENNESSEE

prepared for the U.S. ATOMIC ENERGY COMMISSION
under U.S. GOVERNMENT Contract W-7405 eng 26

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

Reference to a company or product name does not imply approval or recommendation of the product by Union Carbide Corporation or the U.S. Atomic Energy Commission to the exclusion of others that may meet specifications.

Printed in the United States of America. Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road, Springfield, Virginia 22151
Price: Printed Copy \$5.45; Microfiche \$0.95

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.

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.

NERVA FUEL ELEMENT DEVELOPMENT PROGRAM
SUMMARY REPORT - JULY 1966 THROUGH JUNE 1972

Extrusion Studies

Compiled by
J. M. Napier

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.

Oak Ridge Y-12 Plant

P.O. Box Y, Oak Ridge, Tennessee 37830

This document is
PUBLICLY RELEASABLE

David Hamrin, ORNL

Authorizing Official

Date 8-13-2008

Date Issued - September 21, 1973

This report presents a summary of work performed on the extrusion of NERVA Fuel Elements for the Space Nuclear Systems Office, under Purchase Orders SNC-51, SNC-73, SNC-81, and SNC-95 during the period July 1966 through June 1972.

Prepared for the U.S. Atomic Energy Commission
Under U.S. Government Contract W-7405-eng-26

MASTER
DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

ABSTRACT

This part of the completion report pertaining to the NERVA graphite fuel element program covers data collected during the extrusion studies. The physical properties of the fuel element reached the following values: coefficient of thermal expansion (CTE) - $7.0 \times 10^{-6}/^{\circ}\text{C}$ (25 - $1,000^{\circ}\text{C}$); modulus of elasticity - 1.5×10^6 psi; flexural strength - $\sim 8,000$ psi; ultimate strain to failure - $5,500 \mu\text{in/in}$; good thermal stress resistance. Matrices were produced which could be vapor coated with crack-free films of zirconium carbide. The CTE of the matrix was almost equal to the CTE of the zirconium carbide coating.

CONTENTS

FOREWORD	5
SUMMARY	6
Studies Prior to Pewee 2	6
Phase I and II Programs	6
Graphitizable Binder Studies	6
Low-Fired Carbon Filler Program	7
Process Optimization	7
General Results	8
INTRODUCTION	9
EXTRUSION STUDIES	10
Development Studies Prior to Pewee 2	10
Raw Materials	10
Varcum 8251 Binder	12
Manufacturing Processes	12
Extrusion Studies Prior to the Pewee 2 Fuel Elements	14
Extrusion Pressure Effect	14
Binder Level Effect	15
Carbon Black (Thermax) Effect	16
Uranium Effect	17
Physical Properties	19
Phase I and II Programs - Increased CTE Matrix	22
Principal Problem	22
Phase I Program	23
Phase II Program	31
Properties of ITX-ACN-I Elements (POCO filler)	39
Graphitizable Binder Studies	41
Isotruxene-Acenaphthalene-Indene Binder (ITX-ACN-I)	42
Cinnamylideneindene Binder Studies	48
Grade 277-15V Pitch-Indene Binder	49
Grade 240 Ashland Pitch-Indene Binder	52
Low-Fired Carbon Filler Program	53
Program Logic	53
Grinding Carbon Powders	55
Isotruxene Elements	55
Cinnamylideneindene Elements	56
Grade 15V Coke Studies	57
Santa Maria Coke Studies	59
POCO Fillers	79
POCO PCD-0Q Studies	83
Process Optimization	92
Binder System	92

Extrusion	95
Cracks	95
Drying of Indene	97
Element Baking to 250° C	101
Curing to 850° C	101
Graphitization	102
NF-2 Element Manufacture	102
Extrusion of NF-2 Elements	102
Drying Procedure	104
Cure Procedure	105
Bake Procedure	105
Graphitization Procedure	105
Braze Process	105
Machining Procedure	107
Machined Element Inspection	108
Leach Operation	108
Leach Element Inspection	108
Zirconium Coating	112
Elements Shipped to LASL	114
CONCLUSIONS	115
REFERENCES	116
BIBLIOGRAPHY	118

FOREWORD

The NERVA graphite fuel element program, which was funded for several years by the Space Nuclear Systems office, has been terminated at the Oak Ridge Y-12 Plant.^(a) This report was abstracted from a series of progress reports which were routinely issued during the course of the fuel element studies. This part of the overall completion report covers data collected during the extrusion studies. Material development studies as well as manufacturing studies produced several types of graphite fuel element matrices.

(a) Operated by the Union Carbide Corporation's Nuclear Division for the US Atomic Energy Commission.

SUMMARY

The graphite matrix development program produced the results that are summarized in the sections that follow.

STUDIES PRIOR TO PEWEE 2

1. These studies were basically concerned with obtaining an optimum manufacturing process using a single graphite filler and a single thermosetting resin binder.
2. A typical element of this type had the following physical properties:

Longitudinal Coefficient of Thermal Expansion = $2.8 \times 10^{-6}/^{\circ}\text{C}$ (25 - 1,000 $^{\circ}\text{C}$)

Flexural Strength = 4,000 - 5,500 psi

Ultimate Strain to Failure = 2,500 - 3,000 $\mu\text{in/in}$

Modulus of Elasticity = 2×10^6 psi

Thermal Stress Resistance = good

3. The graphite filler supply was terminated due to the inability of commercial sources to supply the necessary raw materials.

PHASE I AND II PROGRAMS

1. Several graphite fillers were studied and fuel elements with a variety of physical properties were obtained.
2. Coefficient of thermal expansion (CTE) values in the extrusion direction of the fuel elements were shown to be a controllable property over a span of 3.3 to $6.5 \times 10^{-6}/^{\circ}\text{C}$ (25 - 2,000 $^{\circ}\text{C}$) by the use of selected graphite fillers.
3. Modulus of elasticity values were controllable by the use of selected fuel element fillers and binders.
4. Thermal stress resistance of the element was shown to be satisfactory when the CTE was high if the graphite matrix also had a high flexural strength, low modulus, and a high strain-to-failure value.

GRAPHITIZABLE BINDER STUDIES

1. Four thermoplastic binders were developed for the NERVA program.
2. All of the binders were modified with indene as a reactive solvent, which permitted extrusions to be made at room temperature.

3. The four binders produced a "soft" graphite phase and were successfully used in fabricating the fuel elements.

LOW-FIRED CARBON FILLER PROGRAM

1. Several low-fired carbon fillers were studied. CTE values in the extrusion direction of the elements were shown to be very sensitive to the filler firing temperature. As the filler firing temperature was decreased, the matrix CTE was increased.
2. Matrix CTE values up to $8.2 \times 10^{-6}/^{\circ}\text{C}$ (25 - 1,000 $^{\circ}\text{C}$) were obtained by the use of selected low-fired fillers.
3. Flexural strength of the elements was also shown to increase with decreasing filler firing temperatures. Flexural strengths ranged up to 8,000 psi for fueled, nonimpregnated elements; nonfueled, impregnated matrices had tensile strengths up to 10,000 psi.
4. Modulus of elasticity values were not significantly affected by the filler firing temperature. The thermoplastic binder produced matrices having a nominal modulus value of 1.5×10^6 psi.
5. Fuel element densities were shown to increase by reducing the filler firing temperature. As extruded and fired, densities of 1.75 to 1.82 gms/cc (nonfueled) were produced. Densities were increased to 1.90 to 1.92 gms/cc with pyrolytic carbon using methane in a gaseous impregnation process.
6. Thermal stress resistance was good even though the matrix CTE values were high. The high thermal stress resistance was due to the high strength and low modulus.

PROCESS OPTIMIZATION

1. A manufacturing process was developed using one low-fired filler and one graphitizable resin binder. All process parameters were not fully optimized, but a yield of 85 percent crack-free elements was produced using the process.
2. Uranium-loaded, nonimpregnated fuel elements were produced for the NF-2 reactor which had the following physical properties:

Longitudinal Coefficient of Thermal Expansion = $6.5 \times 10^{-6}/^{\circ}\text{C}$ (25 - 1,000 $^{\circ}\text{C}$)

Modulus of Elasticity = 1.5×10^6 psi

Flexural Strength = 7,785 psi

Ultimate Strain to Failure = 4,150 $\mu\text{in/in}$

Thermal Stress Resistance = good

3. Nonfueled, nonimpregnated fuel elements were produced which had the following physical properties:

Longitudinal Coefficient of Thermal Expansion = $7.0 \times 10^{-6}/^{\circ}\text{C}$ (25 - 1,000 $^{\circ}\text{C}$)

Modulus of Elasticity = 1.5×10^6 psi

Flexural Strength = 11,830 psi

Ultimate Strain to Failure = 5,500 $\mu\text{in/in}$

Thermal Stress Resistance = good

GENERAL RESULTS

1. The uranium-loaded fuel element physical properties have been improved during these studies as follows:

Coefficient of Thermal Expansion - increased from 2.8 to $7.0 \times 10^{-6}/^{\circ}\text{C}$ (25 - 1,000 $^{\circ}\text{C}$)

Modulus - lowered from 2.0 to 1.5×10^6 psi

Flexural Strength - raised from $\sim 4,500$ to $\sim 8,000$ psi

Ultimate Strain to Failure - increased from 2,500 to 5,500 $\mu\text{in/in}$

Thermal Stress Resistance - good in both types of elements

2. Fuel element matrices were produced which could be vapor coated with crack-free films of zirconium carbide. The CTE of the matrix was almost equal to the CTE of the zirconium carbide coating.

INTRODUCTION

The NERVA reactor program has had several goals during the past decade. Originally, the goal was to obtain a nuclear rocket capable of operating for less than five minutes at $\sim 4,400^{\circ}$ R exit gas temperatures. As the early program goals were achieved, new and more difficult tasks were assigned to the system. One of the last was to obtain an engine capable of operating up to 60 cycles with each run to last for ten minutes. To achieve the specified assignments, a fuel element matrix development program was conducted for the past 12 years. Some of these studies were production-support-type efforts.

The matrix development program routinely produced improved versions of the fuel elements which allowed the NERVA program goals to be achieved. During the past three years, the development efforts have produced significant improvements in the matrix quality. These improvements resulted from utilizing low-fired filler carbon in place of the standard graphitized fillers and by the use of graphitizable resins as opposed to the use of nongraphitizable resins. The complete NERVA development program included the study of organic carbon precursors, binders, and fillers, and manufacturing processes pertaining to the fuel element.

A NERVA fuel element was basically composed of a mixture of graphite or carbon filler particles, uranium fuel particles, and a resin binder which could be thermally decomposed into carbon. This mixture was extruded and heat treated to form a finished hexagonal shape having a nominal length of 52 inches and having 19 gas-passage bores. Each of the bores (~ 0.1 inch in diameter by 52 inches long) was coated with a film of metal carbide to protect the graphite matrix from chemical attack by the hydrogen propellant gas. Most reactors were bore coated with films of niobium carbide, zirconium carbide, or a mixture of these two carbides. Many separate fabrication steps were necessary to produce a fuel element having the qualities required for the NERVA program. Each operation was found to be very sensitive and the degree of process control required a continuous process development program. The evolution and studies involving the manufacture of the fuel elements are presented in this part of the overall report.

Summation reports on other phases of the NERVA program can be obtained in Documents Y-1852, Parts 2 through 5, Y-1857, and Y-1868.

EXTRUSION STUDIES

DEVELOPMENT STUDIES PRIOR TO PEWEE 2

Prior to the Pewee 2 reactor, all NERVA fuel elements were manufactured by extruding a mixture of a graphite powder, carbon black, and uranium fuel particles. The components of the mixture were bound with a thermosetting resin which produced a "glassy" carbon.⁽¹⁾ This type of fuel element was not satisfactory for several reasons. A major problem was that the fuel element had a lower coefficient of thermal expansion (CTE) than the metal carbide coatings which were applied in the gas bores to protect the graphite matrix from being attacked by the hot hydrogen propellant gas.

These development studies were basically designed to obtain an optimum manufacturing process that used a single source of raw materials. Some of the process studies performed during this phase of the program are discussed in this section of the report.

Raw Materials

Graphite Powder - The graphite filler powder for this phase of the program was specified to be Grade 1008S, manufactured by the Great Lakes Carbon Corporation. Applicable purchase specifications permitted some variations to occur in the graphite filler material. A complete manufacturing history of the powder could not be obtained from the vendor; therefore, a close control of the powder characteristics could not be effected. Upon receipt of a quantity of the graphite powder, a detailed standardization program was conducted in an endeavor to obtain a consistent material.

While the exact manufacturing history of the filler powder was unavailable, it can be assumed that the manufacturing process could have included the process steps listed in Table 1. It is apparent that powder variations did occur on a random basis.

In an endeavor to apply some type of quality control, the graphite powders were purchased in lots which were normally large enough to produce two or more reactors. When received, each drum of the powder was evaluated and then carefully cross blended to form a uniform, single-blend powder. Some of the powders purchased during the NERVA program were not the same. Some powder variations which were recognized are noted in Table 2.

Several serious manufacturing and engine design problems arose as a result of the graphite powder variations. One such problem was related to variations in the coefficient of thermal expansion (CTE) values of the fuel elements. Table 3 provides a typical list of CTE data of reactors prior to the Pewee 2 reactor. These CTE data show that most of the early reactors had about the same CTE value, while the CTE value of the XE-2 reactor was significantly lower than previous reactors.

Major powder procurement problems arose during the manufacture of the NERVA NRXA6 reactor, namely: the available powder supply was limited, and attempts to obtain additional powder having the same process history and physical characteristics were not successful. Furthermore, the vendor was not able to procure the raw materials nor manufacture the powder. As a result, a different powder was added to the available supply which produced

Table 1
TYPICAL GRAPHITE POWDER HISTORY

Process Step	Comments
Organic Source	Coal or oil deposits. Materials were not uniform and the type of material was dependent on many uncontrollable variables.
Pitch Formation	Residue from a distillation process. Materials were not uniform and since the product was considered to be a by product from the main stream, very little quality control was applied.
Coke Formation	Coking companies purchased pitch on the open market. The pitch was then heated to form the coke product. Heat-treatment temperatures of less than 1,400° C were common. Large volumes were processed and different coke materials could be easily mixed.
Primary Graphite	Calcined coke was crushed to form particles which were then mixed with a liquid binder. The binder may or may not have been the same as the precursor pitch. By molding, extrusion, or other techniques, the mixed materials were formed into bodies. The formed pieces were heated to temperatures in excess of 2,000° C. Graphitization catalysts, such as metal or inorganic compounds, may or may not have been added.
Secondary Graphite	The heated graphite body was crushed and sized into powder. Calcined coke may or may not have been added to the powder. The powder was blended with a binder and a catalyst may have been added. By extrusion or other processes, the mixed powders and binder were formed into products. The resulting body was heat treated to greater than 2,000° C.
Reject Graphite	Broken or other rejected secondary graphites were usually crushed and used as a source in place of the primary graphite.
Graphite Purification	Heat treatments in excess of 2,000° C in a flowing acid-gas atmosphere had been used.
Graphite Powder Formation	The secondary graphite was crushed and sized. Particle size distribution was controlled only by the graphite crushing properties and the crushing mill adjustments plus a screening through a single screen size. Obtaining consistent size distributions on a day-to-day operation was difficult.

Table 2
GRAPHITE POWDERS USED FOR THOSE REACTORS PRIOR TO PEWEE 2

Reactor	Graphite Powder	Comments
NRXA3, NRXA4, NRXA5, Phoebus 1B, and Phoebus 2A	GI 1008	GL 1008 was composed of isotropic, nonneedlelike particles, manufactured by the Great Lakes Carbon Company. The source and process history were not defined.
NRSA6R	75% GL 1008 and 25% Speer RL	Note previous definition of the GL 1008 powder. The Speer RL powder was predominately of nonisotropic, needlelike particles and was manufactured by the Airco Speer Carbon Products Division. This mixture was used because of the limited supply of GL 1008 powder.
XE-2	100% Speer RL	Definition for this powder is given in the preceding comment.
Pewee 1	GL 1008-B	This material was purchased by WANL (59NUB-89772). The powder had a high percentage of needlelike particles plus particles which were isotropic, but it did not have the appearance of the original GL 1008 powder. The material was obtained from the Great Lakes Carbon Company.

fuel elements having different physical properties. Thus, several manufacturing and design problems resulted because of a lack of quality control on the powder and also because the powder source was not reliable over a period of several years.

Carbon Black Powder (Thermax) - All of the reactors prior to Pewee 2 were made with a mixture of 85 percent graphite flour and 15 percent carbon black (Thermax, thermoatomic carbon, obtained from the R. T. Vanderbilt Company). Procurement of this material was not a problem. Each purchased lot of powder was evaluated and all powders were acceptable.

Varcum 8251 Binder

Varcum 8251 binder was made by a proprietary process which involved pressure polymerization of furfuryl alcohol. The polymer was normally diluted by the vendor with furfuryl alcohol to obtain a viscosity of about 250 centipoises, and the amount of furfuryl alcohol added to each blend could vary over a wide range. The material was purchased from Varcum Chemical, a Division of Reichhold Chemicals, Inc. It was a standard practice to purchase 10,000-pound quantities, each of which was cross blended in an attempt to obtain a uniform blend.

It was also a standard procedure to add 4 percent maleic acid anhydride, obtained from E. H. Sargent, to the Varcum 8251 prior to its immediate use. This anhydride served as a catalyst to the Varcum 8251 and increased its thermosetting property.

Many investigations were initiated which studied the polymerization of Varcum 8251. Bodies containing this binder could be extruded at room temperature and be thermally hardened at temperatures less than 250° C. The Varcum 8251 resin produced a nominal carbon yield of 45 to 50 percent and a carbon which was difficult to graphitize and was defined as a "glassy" carbon. The bodies produced using this binder had higher moduli of elasticity than were desired, and thermal-stress-related problems were encountered with graphites bound with this material.

Manufacturing Processes

Manufacture of a NERVA fuel element involved mixing a binder with graphite fillers and uranium fuel particles. The mixed materials were extruded, cured, and graphitized to form an element shape. The heat-treated elements were then processed through a series of machining and carbon-coating operations, then inspected after each major process step.

Some of the manufacturing processes used during the reactor studies prior to Pewee 2 are discussed in the subsections that follow.

Mixing the Binder and Powders - Many development studies were conducted in an endeavor to obtain a satisfactory resin/powder mixing procedure. The mixing procedure used in the

Table 3
COEFFICIENT OF THERMAL EXPANSION DATA ON
REACTORS MADE PRIOR TO
PEWEE 2

Reactor	Coefficient of Thermal Expansion ($\times 10^{-6}/^{\circ}\text{C}$)		
	25 - 1,000° C	25 - 1,700° C	25 - 2,000° C
Pheobus 2A	3.0	3.7	4.2
NRSA6R	3.2	3.8	4.0
XE-2(1)	3.1	3.8	4.0
	2.2	2.9	3.2
Pewee 1	3.0	3.6	3.9

(1) The majority of the XE-2 elements had the higher CTE values, but many XE-2 elements had CTE values of $2.2 \times 10^{-6}/^{\circ}\text{C}$ (25 - 1,000° C).

NERVA studies was satisfactorily optimized, but improvements in the blending procedure undoubtedly could have been made had the program been continued.

In the mixing procedure, the catalyzed Varcum 8251 binder was mixed with the fuel particles and dry graphite carbon powders. The binder and powders were normally mixed using an 8-quart liquid/solid blender, Model LB-3170, obtained from the Patterson-Kelly Company, Inc. The normal total mixing time for a blend was 25 minutes. The first five minutes were used as the blending time for the dry powders; 15 minutes were used to mix the resin and powders; and, finally, an additional five minutes to insure that the binder/powder mixing step was completed.

Chopping Operation - The mixed binder/powder materials were further blended by using a primary extruder. This machine (Hobart grinder Model 4532, obtained from the Hobart-Dayton Sales and Service Company) was basically a screw extruder in which the binder/powder blend was worked by shear forces in order to more evenly distribute the binder onto the particles. In general, two extrusion operations were conducted to obtain a uniform blend. This step would cause a large increase in the temperature of the binder/powder blend due to internal friction, but the blend temperature was limited by controlling the feed rate of the blend to the mill. In most cases, a mixing temperature of no more than 45° C was desired since the thermosetting resin binder was sensitive to heat.

Extrusion Process - The NERVA fuel elements were formed using a 120-ton extrusion press (Model 232-120-3.75, obtained from the Loomis Engineering and Manufacturing Company). This press had a total maximum ram pressure of 120 tons and was equipped with a six-inch-diameter extrusion chamber. The extrusion speed could be controlled by a valve system to the oil pump supply, but the extrusion pressure could not be controlled except by controlling the rate of extrusion.

The extrusion press was equipped with an elaborately designed extrusion die. Alterations to the die were routinely made because the fuel element designs were changed.

The mixed and chopped powder blend was placed into the press barrel without precompaction. The blend was evacuated to 1,500 torr or less in order to remove any trapped air in the powder. This evacuation step was a critical operation since volatile components of the resin binder could also be removed by too much evacuation. If parts of the binder were evacuated, a high fuel element reject rate always occurred. The evacuated blend was extruded into a hexagonal rod having a nominal cross-the-flats dimension of 0.800 inch and having 19 gas-passage holes at specified locations.

In general, the fuel element shapes were extruded, rechopped, and extruded again. Multiple extrusion was found to be desirable to obtain the maximum bulk density and element uniformity. After at least two extrusion, the elements were collected, in nominal lengths of 60 inches, on graphite plates equipped with half-hexagonal grooves. These plates were designed to closely conform to the element's outer dimensions.

Element Cure Operation - Trays containing the green, extruded elements were stacked in a manner so that all sides of the element were enclosed in a hexagonal hole in the graphite holder. The stacked arrays were placed in an air-circulating, program-controlled oven

(Model CFO, manufactured by the Cooley Electric Manufacturing Corporation). The heating program to 250° C in an air environment was determined by the offgas character of the resin binder. When Varcum 8251 resin binder was used, a 42-hour heating cycle to 250° C was used. The cycle employed a 3° C per hour rate of rise from 60 to 135° C, a 5° C per hour rate from 135 to 190° C, and a 10° C per hour rate from 190 to 250° C.

Baking Operation - After the heating cycle was completed, the cured elements were cooled to room temperature and dimensionally inspected. They were then transferred to a baking furnace (Model 855-243, manufactured by Trent, Inc) and sealed in a nitrogen or argon atmosphere. The baking cycle to temperature was usually 15° C per hour, but was again dependent on the type of resin binder. For the Varcum 8251-bound matrices, a maximum bake temperature of 450° C was used; for pitch binders, a nominal bake cycle was 15° C per hour to 450° C and 30° C per hour to 850° C.

Graphitization - The baked elements were cooled, inspected, and transferred to an induction-heated graphite susceptor furnace. A load of up to 90 fuel elements could be placed in the furnace, but the number of units processed as a single batch was limited by the amount of enriched uranium allowed under nuclear safety guidelines.

In general, the elements were heat treated at a constant rate of 125° C per hour to a predetermined maximum temperature which was dependent on the migration point of the fuel beads. Final temperatures of 2,200° C with a four-hour hold at temperature were common.

Other Process Operations - After graphitization, several other major process steps were required prior to obtaining a completed NERVA fuel element. Some of the other operations are listed in Table 4; process details of each operation can be obtained from other NERVA reports.⁽¹⁾

EXTRUSION STUDIES PRIOR TO THE PEWEE 2 FUEL ELEMENTS

During the program, many experiments were made to define the optimum process conditions for producing NERVA fuel elements which contained GL 1008 graphite-Thermax powders. Discussions of a few of the more significant experiments follow.

Extrusion Pressure Effect

A large number of experiments were conducted to define the optimum extrusion pressure using blends of 85 percent GL 1008 graphite-15 percent Thermax powders. Typical flexural and compressive strength data are indicated by the graphs of Figures 1 and 2 as functions of the extrusion pressure. These data show that high extrusion pressures produced the desired strong fuel element matrices.

For this experiment, the fuel element extrusion speed was maintained at a constant rate of 5 feet/minute. In order to change the extrusion pressure for this experiment the binder level was also varied, with a decreased binder level resulting in a higher extrusion pressure.

Table 4
FUEL ELEMENT MANUFACTURING PROCESS OPERATIONS
AFTER GRAPHITIZATION WAS COMPLETED

Process	Comment
Inspection	Physical measurements.
Semimachine	Near final dimensions.
Tip Braze	A metal carbide/carbon tip was brazed onto each element.
Inspection	Physical data.
Finish Machine	Final dimensions.
Inspection	Physical data.
NDT Inspection	Physical data.
Leach	Removal of exposed uranium particles.
Inspection	Physical data
NDT Inspection	Physical data
Metal Carbide Coat on Outer Surfaces	It was required that the elements be OD coated with a specified amount and thickness of niobium carbide, zirconium carbide, or a mixture of these.
NDT Inspection	Physical data.
Metal Carbide Bore Coat	Niobium carbide, zirconium carbide, or mixtures of these two materials were deposited in the gas passage bores at specified weights and thicknesses.
NDT Inspection	Physical data.
Final Inspection	Physical data.

Figure 1. ELEMENT STRENGTH AS A FUNCTION OF THE EXTRUSION PRESSURE ON A SIX-INCH-DIAMETER RAM.

Compressive-strength data show that, with this particular blend of 85 percent GL 1008-15 percent Thermax powders, a maximum compressive strength was obtained at a binder concentration (calculated from the binder formula) of 0.26 [weight of dry carbon

Binder Level Effect

The fuel element binder level was affected by many process variables which included the extrusion pressure, rate of extrusion, graphite powder type, and type and properties of the binder. If all other process conditions were controlled at preset conditions, a binder change produced an extrusion pressure change when the matrices were extruded at a constant speed. Because of the type of extrusion equipment used for NERVA studies, the extrusion-pressure effects could not be easily separated from the binder-change effects.

The compressive-strength data noted in Figure 3 represent an experiment in which the binder was changed.

ingredients (DCI)]. Other purchased lots of 85 percent GL 1008-15 percent Thermax powders required that the binder level be changed to a new, experimentally determined value.

It was desirable to extrude fuel elements at a fixed optimum binder level. In practice, this goal was not practical since some variations in the manufacturing processes and raw materials always existed. It was a standard practice at the Y-12 Plant to extrude fuel elements at a nominal 80 tons of pressure when using a six-inch-diameter extrusion barrel on the press. This pressure level normally required an extrusion mix which contained somewhat less than the optimum binder content. The 80-ton extrusion practice was established by several technical considerations. One argument for the practice was a statistical study of the Pheobus 1B reactor which showed that fuel elements made at or above the 80-ton pressure level performed better than elements made at lower extrusion pressures.⁽²⁾

In general it was found that the internal quality of the fuel element could be improved by extruding at less than the optimum binder level. Typical eddy-current inspection data are given in Figure 4. These data were a result of measurements taken by passing a small eddy-current gage (~0.1-inch-diameter probe) into each of the 19 gas passage holes. Eddy-current inspection detected and located all major internal defects.

Carbon Black (Thermax) Effect

Since the early days of the NERVA program, a nominal 15 weight percent^(b) Thermax was added to the fuel element matrix. The addition of Thermax served, primarily, as a means of increasing the bulk density of the fuel element.

Figure 2. FUEL ELEMENT FLEXURAL STRENGTH VERSUS THE EXTRUSION PRESSURE ON A SIX-INCH-DIAMETER RAM.

Figure 3. BINDER CONCENTRATION VARIATION.

(b) Fifteen weight percent of the total of the dry ingredients (ie, 15 wt % Thermax and 85 wt % GL 1008).

Figure 4. EDDY-CURRENT QUALITY AS A FUNCTION OF THE BINDER LEVEL. (Nominal Uranium Loading of 505 mgs U/cc)

Several experiments were made to obtain data on the effect of the Thermax addition. In Table 5, results of an experiment are reported in which Young's modulus was changed by the addition of Thermax to the fuel elements. Note that the modulus change accompanied a change in the bulk density (Figure 5). A compressive-strength change was also obtained, as noted in Figure 6.

A group of experiments were performed in which two levels of Thermax were used with varying amounts of Varcum 8251 binder. Moduli data are listed in Table 6. Note that, at a constant Thermax level of 15 percent, no significant increase in the moduli occurred when the binder level was raised. In the set which contained no Thermax, the fuel element moduli increased when the Varcum 8251 binder

level was increased. The increased moduli could be a result of an increased density (Figure 7) which also occurred with this experimental group. The compressive strengths, seen in Figure 8, also increased with this experimental group.

Uranium Effect

Most NERVA fuel element matrices, prior to the Pewee 2 reactor, contained nuclear fuel particles which were of spherical uranium dicarbide encapsulated in a pyrocarbon shell having a nominal thickness of 25 micrometers. The pyrocarbon-coated fuel particle diameters were normally less than 180 micrometers with none of the particle diameters being less than 44 micrometers.

NERVA reactor designs required that the fuel elements should contain a variable amount of uranium. Fuel loadings for a NERVA reactor could vary from 100 milligrams of uranium per cubic centimeter of element volume (mgs U/cc) to 800 mgs U/cc. Structural support elements were also required where no uranium fuel particles were added.

One of the critical graphite powder specifications was the powder particle-size range. Minor variations in the particle sizes caused fuel-element manufacturing process changes which, in

Table 5
CHANGES IN YOUNG'S MODULUS AS A
FUNCTION OF BINDER AND
THERMAX CHANGES

Percent Thermax in DCI ⁽¹⁾	Percent GL 1008	Young's Modulus (x 10 ⁻⁶ psi)	Binder Formula [x (wt DCI)]
0	100	0.3 - 1.2	0.24
5	95	1.2 - 1.4	0.24
10	90	1.4 - 1.9	0.24
15	85	2.0 - 3.3	0.24
20	80	1.8 - 2.3	0.24
30	70	2.2 - 2.7	0.24

(1) Constant binder level; variable Thermax concentration in DCI (dry carbon ingredients).

Figure 5. VARYING RATIOS OF GL 1008/THERMAX USING A CONSTANT BINDER FORMULA OF 0.24. (Wt DCI)

Figure 6. VARYING CONCENTRATIONS OF GL 1008/THERMAX POWDER AT A BINDER FORMULA OF 0.24. (Wt DCI)

turn, required binder changes. Addition of the uranium fuel particles to the powder also required a change in the powder binder ratio. Since the uranium contents of the fuel elements were not constant, it was a common practice to manufacture a series of elements during the preproduction phases of each reactor program where the uranium fuel contents were varied over a wide range. From these studies, binder levels and other process parameters were selected for each level of fuel loading.

Several experiments were conducted during the past few years to study the variable uranium loading effects. One experimental group of elements was made in which the uranium fuel content was progressively increased up to a maximum level of 1,000 mgs U/cc. All of the fuel elements contained a graphite powder blend composed of 85 percent GL 1008 and 15 percent carbon black (Thermax). Varcum 8251 was used as the element binder and a binder formula of 0.255 (weight

Table 6
CHANGES IN YOUNG'S MODULUS AS A
FUNCTION OF THE VARIABLE
BINDER LEVELS

Percent Thermax in DCI	Percent GL 1008	Young's Modulus (x 10 ⁻⁶ psi)	Binder Formula [x (wt DCI)]
15	85	1.9 - 4.1	0.22
15	85	2.0 - 3.3	0.24
15	85	2.0 - 3.0	0.245
15	85	2.3 - 2.8	0.260
15	85	2.2 - 3.2	0.270
15	85	2.0 - 2.6	0.280
15	85	1.5 - 2.5	0.300
0	100	0.3 - 1.2	0.24
0	100	1.1 - 2.5	0.26
0	100	1.1 - 1.4	0.28
0	100	1.2 - 2.2	0.30
0	100	1.3 - 1.5	0.32

Figure 7. VARYING BINDER LEVELS USING DRY CARBON INGREDIENTS COMPOSED ENTIRELY OF GRAPHITE FLOUR.

Figure 8. COMPRESSIVE STRENGTH OF A SERIES OF ELEMENTS CONTAINING ONLY GRAPHITE FLOUR.

DCI + 0.25 weight UC_2 fuel) was used. Extrusion pressures were allowed to vary with each of the experiments. A typical extrusion pressure curve as a function of the fuel element loading is presented in Figure 9. The extrusion pressure could have been controlled by varying the binder content or the rate of extrusion.

A constant rate of extrusion was maintained at five feet per minute for all elements. As these experiments were being conducted it was apparent from the extrusion pressure that the binder formula should have been changed in order to obtain higher extrusion pressures. However, it was decided that no change in the binder equation would be made for these experiments in order to reduce the number of process variables. A second set of experiments involving preproduction-type elements were made at a reduced binder level and, therefore, a higher extrusion pressure.

Figure 9. EXTRUSION PRESSURE AS A FUNCTION OF THE URANIUM LOADING. (On a Six-Inch-Diameter Ram)

Some of the data collected during these element studies are summarized in Table 7.

Physical Properties

Carbon Density - Carbon density of the fueled NERVA elements was a function of the uranium content, among other process variables. Figure 10 provides a typical plot of carbon

density versus uranium loading which was obtained in these studies. The elements made at relatively low extrusion pressures (43 to 60 tons) and the preproduction groups made at higher pressures (75 to 90 tons) had essentially the same carbon density. In general, a linear decrease in the fuel element carbon density could be expected as the uranium content was increased.

Compressive Strength - Compressive strengths of the fuel elements appeared to decrease with an increased fuel loading (Figure 11). Since the extrusion pressure was not constant, the decreased compressive strength may have been also related to this process variable.

Flexural Strength - Flexural strength data on these elements are reported in Figure 12. These data show a linear decrease in strength with an increased fuel loading. As previously stated, the extrusion pressure also decreased with increased loading in this group of elements. The lower extrusion pressure and the decrease in flexural strength were probably related. The increased uranium loading change, therefore, may not be totally responsible for the decrease in the flexural strength.

Figure 10. URANIUM LOADING AS A FUNCTION OF THE CARBON DENSITY.

Table 7
EXPERIMENTAL AND PREPRODUCTION
ELEMENT DATA

Uranium Loading (mgs U/cc)	Average Body Leakage ⁽¹⁾ (cc/min)	Carbon Density (gms/cc)	Extrusion Pressure ⁽²⁾ (tons)
<u>Experimental Element Group</u>			
310	253	1.837	62
510	410	1.802	57
656	638	1.778	53
799	905	1.747	50.5
990	1,360	1.707	43.5
<u>Preproduction Elements</u>			
0	20	1.883	90
160	50	1.863	74
460	70	1.813	60
650	134	1.775	75

(1) As-leached elements.

(2) On a six-inch-diameter press ram.

Fuel Element Leak Rate - Total porosity of the fuel element matrix was important since, during reactor operations, the gas passage holes contain a high flow of high-pressure hydrogen gas. If the hydrogen gas could penetrate the fuel element matrix through open cracks in the metal carbide-coated gas-passage holes, the hydrogen gas would enter the graphite matrix. Under these conditions, the hydrogen gas would readily attack the hot fuel element graphite matrix. This phenomenon would also occur if the matrix had a minimum amount of open porosity, but with a lower rate of structural damage.

Most reactors have had a total-body gas-leak-rate specification on the fuel elements. Inspection was made by

applying pressurized air through the gas-passage holes of the fuel element while one end of the element was sealed and the flow of air through the matrix measured. Typical data, plotted as a function of increased uranium content, are provided in Figure 13. These data show that the elements extruded at low pressures had high body leak rates which increased when the fuel loadings were raised. The preproduction elements, formed at higher extrusion pressures, had significantly lower leak rates, but they also increased when the fuel loadings were increased.

A plot of extrusion pressure versus body leak rates is given in Figure 14.

These data indicate that high extrusion pressures were desirable in order to produce low body leak rates.

A third plot of carbon density versus body leak rates is presented in Figure 15. These data also show that increased carbon densities produced lower body leak rates. These data could also be plotted as a function of the extrusion pressure to produce a similar relationship.

Figure 12. FLEXURAL STRENGTH AS A FUNCTION OF THE URANIUM LOADING.

particles will change the powder particle size spectrum; and, if the fuel, powder blend, and binder levels are not optimized, physical-property variations as well as body-leak-rate changes can be expected to occur.

Web Reduction - Questions had been raised concerning the effect of the fuel element body leak rate as a function of the web thickness between the gas-passage holes. Normally, the outer 12 gas-passage holes had a web thickness to the outer surfaces of the element of 27 mils. It was specified that this dimension have a minimum value of 21 mils. The specified

Figure 11. COMPRESSIVE STRENGTH AS A FUNCTION OF THE URANIUM LOADING.

At the present time it is believed that several process variables can be used to control the body leak rate in NERVA fuel elements. A significant reduction can be obtained by the use of high extrusion pressures if the pressure is controlled by the binder content. Other important process variables include: (1) selection of a graphite powder-Thermax particle size blend which can be extruded into high-density fuel elements, (2) optimization of the binder and powder, (3) selection of the type of binder, and (4) others. Addition of fuel

gas-passage hole diameters ranged from a nominal 98 to 110 mils, depending on the reactor type. Since the hole diameter also influenced the outer web thickness, elements which had larger gas-passage holes than specified usually produced webs thinner than the nominal 27 mils.

A group of fuel elements were selected for this study having hole diameters of 99 and 110 mils. The outer web of all elements was progressively reduced by machining the outer dimensions of these elements. This, in effect, simulated moving the gas passage holes toward the outside diameter of the hexagonal fuel element. The body leak rate was determined after each reduction of the element outer dimension. Data, given in Figure 16, show that the fuel element body leak rate increased logarithmically with a linear decrease in web thickness. All reactors had a specified hole location plus a tolerance band on the location. Variations in the body leak rate were allowable due to the allowed variations in the outer web thickness.

Figure 13. AS-LEACHED BODY LEAK RATE AS A FUNCTION OF THE URANIUM LOADING.

PHASE I AND II PROGRAMS - INCREASED CTE MATRIX

Principal Problem

A serious mismatch of the coefficients of thermal expansion of the graphite matrix and niobium carbide bore coating existed in all NERVA fueled elements prior to the Pewee 2 reactor. This CTE difference had caused many fabrication problems over the past years with the major difficulty being open cracks in the vapor-deposited niobium carbide coatings. Methods to minimize the open cracks included patching the coating with molybdenum at low temperatures ($\sim 200^{\circ}\text{C}$) and reducing the niobium carbide deposition temperature by longer coating times or by the addition of methane gas to the coating gas mixture. However, none of these methods used to modify the coating solved the basic problem; ie, the mismatch of CTEs between the matrix and coating.

Data obtained during the production of reactors have shown that CTE changes in production elements occurred with the different purchased lots of graphite flour. It was known that three production cores (Ph2A, NRXA-6R, and XE-2) had different graphite flour sources. Such variable graphite flour characteristics required very careful evaluation of the material prior to its use. Unfortunately, careful analyses did not always guarantee that minor flour changes had not occurred. As a result, an experimental program was started to investigate the elements that were manufactured using a wide range of graphite flours. The

Figure 14. AS-LEACHED BODY LEAK RATE VERSUS THE PRESSURE PRESSURE. (On a Six-Inch-Diameter Ram)

primary goal of this program was to develop an element having a coefficient of thermal expansion more nearly equal to that of niobium carbide. A secondary goal, but equally as important as the one just noted, was to obtain a commercial source of graphite flour which guaranteed no variability for at least several years.

The element had to have the physical properties (ie, compressive and flexural strengths) which were near that of the element made before the Pewee element. Thermal stress properties of elements compounded from the material had to be determined and physical-property values established that were high enough to satisfy the reactor design.

It is generally the case that as the coefficient of thermal expansion value is increased and all other properties remain constant, any material will be more susceptible to thermal shock. If elements having an increased CTE, an increased

flexural strength, and a lowered modulus value could be produced, the thermal shock resistance of the element would probably be satisfactory.

Phase I Program

The high CTE matrix program was initially divided into separate study phases. The Phase I study was an extension of previous work in which graphite discs made from various graphite flour sources were manufactured at Y-12; while the thermal shock stability of the discs was established by the ORNL.⁽³⁾ In the Phase I program, unloaded elements were extruded from eleven different graphite flours. All elements contained 15 weight percent Thermax carbon black and were bound with the standard element binder—Varcum 8251.

Graphite Flour - For the high CTE matrix study it was decided that several types of graphite flour would be studied. Previous work at the ORNL and Y-12 had shown that pressed discs made from ground graphite of various types could have a variable coefficient of thermal expansion and thermal rupture resistance. The initial effort was simply to extend the ORNL/Y-12 work from a pressed disc shape to an extruded NERVA fuel element shape. The flour types evaluated ranged from a very needlelike material to an isotropic-type material.

Thirteen types of commercial graphites or cokes were obtained. The graphite stocks were ground to near the GL 1008 powder size distribution specifications. The carbon cokes were

prefired to 3,000° C and then ground. Due to the very limited supply of each type of flour, the particle-size spectrum of the different materials was not as well controlled as desired.

The dry graphite flours were analyzed using the standard procedures for GL 1008. The flours were dry mixed with the standard 15 percent Thermax carbon black, and catalyzed Varcum 8251 was added as a binder. Due to the variable particle-size spectrum, varying amounts of binder were used. Optimum binder levels for each graphite type were not possible. The mixes were extruded into nonfueled elements and the extrusion pressure was not controlled. Standard baking and graphitizing procedures were used for firing the elements. Only a few elements of each type were extruded and graphitized. After machining, one or more elements were sectioned for physical property determinations and one element of each type was retained for niobium carbide coating studies. The available data collected on these elements are listed in Table 8.

Figure 15. CARBON DENSITY VERSUS THE BODY LEAK RATE. (Leached Elements)

Carbon Density - As noted in the data, the final carbon density of most of the Varcum 8251-bound elements was 1.89 to 1.93 gms/cc. Exceptions to this were the elements made from Graph-i-tite "G" (1.86), POCO AXZ (1.83), and Gilsonite (1.85).

Element Resistance - The lowest electrical resistance elements were made from GL 1008 and Gilsonite coke. All other elements had higher values, particularly the fine-grain POCO elements. It is interesting to note that the low-fired (2,300° C) POCO flour elements (AXZ, AXM) had higher resistances than the same flour elements (eg, AXZ 9Q) in which the flour had been processed to higher temperatures (2,900° C).

Sonic Moduli - The moduli of all elements were measured using sonic techniques. In all cases the values were near 2×10^6 psi except for the POCO AXZ (1.3×10^6 psi). One explanation for the lowered modulus could be the low density of this element.

Compressive Strength - The compressive strength of the elements varied widely with the graphite flour source. A low of 10,400 psi was obtained on the predominately needle-coke elements (Graph-i-tite "G"); strengths of 17,000 - 18,000 psi were noted with the fine-grain POCO, Stackpole, and Speer SX5-type flours.

Table 8
PROPERTIES OF SEVERAL GRAPHITE FLOURS - PHASE I

Property	Graphite Flour Type										Gilsonite	POCO AX	Robinson
	ZTA	Graph-i-tite "G"	GL 1008	Stackpole 2033	Speer SX5	POCO AXZ9Q	POCO AXM9Q	POCO AXF9Q	POCO AXZ	POCO AXM			
Binder (pph)	26	25	25	33	26	34	36	34.5	27	31	24	49	37
Extrusion Pressure (x 10 ³ lbs)	111	162	142	80	120	160	70	120	235	230	145	162	180
Surface Area (m ² /gm)	5.54	5.65	5.16	3.26	5.47	4.95	7.73	9.65	5.76	10.26	5.15	1.95	-
Particle Size Micromerograph													
100% Less Than Size (μm)	100	180	100	125	160	180	170	120	180	180	180	180	-
90% Less Than Size (μm)	84	100	95	95	97	84	91	100	82	108	124	110	-
50% Less Than Size (μm)	47	45	52	42	41	14	36	32	11.9	46	71	14	-
25% Less Than Size (μm)	22.5	15.5	23	12.5	10.5	6.7	11.0	4.5	5.8	18	48	6	-
10% Less Than Size (μm)	7.0	6.0	8.0	4.3	4.2	4.0	5.2	2.6	3.28	7.4	31.5	4.2	-
Density, Calculated (gms/cc)													
2,200° C Bake	1.92	1.86	1.91	1.93	1.92	1.90	1.91	1.92	1.84	1.91	1.89	-	-
Lab Density (gms/cc)	1.916	1.857	1.905	1.927	1.926	1.898	1.907	1.924	1.825	1.894	1.854	-	-
Body Leak Rate (cc/min)	0	48 - 51	6	69	69	0	48 - 78	3 - 6	45	99	384	-	-
Electrical Resistance													
Milliohm/element inch	1.97	2.19	1.60	2.50	1.98	2.55	2.46	2.44	3.17	2.95	1.68	-	-
Milliohm/cm	1.55	1.72	1.26	1.97	1.57	2.01	1.94	1.92	2.49	2.32	1.32	-	-
Sonic Moduli (Young's) (x 10 ⁶ psi)													
Longitudinal	2.1	2.0	2.2	2.1	2.1	1.8	1.9	1.9	1.3	1.5	2.0	-	-
Transverse	1.6	2.0	1.7	1.6	1.6	1.4	1.7	1.9	1.4	1.9	1.5	-	-
Compressive Strength (psi)													
Maximum	12,908	10,972	14,683	19,362	16,458	20,007	19,685	19,765	19,443	18,555	12,586	-	-
Minimum	11,456	9,519	10,649	17,749	15,732	16,700	16,135	14,683	14,522	17,103	10,649	-	-
Average	12,224	10,407	12,382	18,258	16,109	17,810	17,642	17,222	17,607	17,829	11,804	-	-
Number of Samples	4	4	4	3	3	4	3	2	4	2	3	-	-
Flexural Strength (psi)													
Maximum	7,160	6,786	6,831	7,715	8,688	7,865	7,070	8,539	5,992	5,722	5,797	-	-
Minimum	6,666	6,142	5,243	5,647	4,344	4,824	4,000	3,250	4,719	5,393	5,018	-	-
Average	6,936	6,516	6,352	6,703	5,962	6,906	5,692	5,782	5,128	5,558	5,513	-	-
Number of Samples	7	7	7	6	5	6	5	3	7	2	4	-	-
Coefficient of Thermal Expansion, 25 - 2,000° C (x 10 ⁻⁶ /° C)													
Extruded Element Data	3.67	3.92	3.31	4.56	5.21	5.28	5.47	5.70	5.41	6.51	4.56	-	-

Table 8 (continued)

Property	ZTA			Graph-i-tite "G"			GL 1008			Stackpole 2033			Speer SX5			POCO AXZ9Q		
	O(1)	M(1)	I(1)	O	M	I	O	M	I	O	M	I	O	M	I	O	M	I
Mercury Porosimetry Data																		
Bulk Density (gms/cc)	1.915	1.908	1.914	1.836	1.856	1.853	1.899	1.892	1.898	1.921	1.922	1.920	1.925	1.918	1.905	1.891	1.811	1.886
Porosity (%)	3.95	5.25	4.53	7.27	7.30	5.98	5.01	4.82	4.15	2.43	2.48	2.40	2.20	2.18	2.30	3.06	3.35	3.07
Real Density (gross vol - pores/wt)	1.994	2.014	2.005	1.980	2.004	1.971	1.999	1.987	1.981	1.968	1.971	1.967	1.968	1.961	1.950	1.951	1.946	1.946
Mean Pore Size (μ)	0.032	0.025	0.028	0.090	0.12	0.06	0.041	0.040	0.032	0.035	0.037	0.035	0.035	0.028	0.028	0.068	0.057	0.044
Chemical Analysis of Elements (ppm)																		
B		2			3			4			2			12			3	
Ca		40			20			40			110			60			20	
Fe		10			15			15			12			20			30	
Mo		15			10			25			40			25			25	
Na		10			4			12			6			15			20	
Si		425			420			450			450			500			500	
Ti		18			10			10			15			25			15	
	POCO AXM9Q			POCO AXF9Q			POCO AXZ			POCO AXM			Gilsonite					
	O	M	I	O	M	I	O	M	I	O	M	I	O	M	I	O	M	I
Bulk Density (gms/cc)	1.890	1.895	1.895	1.935	1.910		1.902	1.843	1.825	1.822	1.889	1.887	1.879	1.837	1.830	1.756		
Porosity (%)	2.18	2.18	2.11	2.36	2.38		2.75	5.44	7.62	6.28	2.98	3.11	2.83	5.14	5.89	4.67		
Real Density (gross vol - pores/wt)	1.932	1.937	1.936	1.982	1.957		1.956	1.949	1.976	1.944	1.947	1.947	1.934	1.936	1.945	1.947		
Mean Pore Size (μ)	0.035	0.034	0.030	0.028	0.028		0.026	0.23	0.32	0.30	0.10	0.012	0.14	0.22	0.42	0.16		
Chemical Analysis of Elements (ppm)																		
B		20			8			1			10			3				
Ca		110			40			40			110			20				
Fe		40			25			25			25			< 10				
Mo		10			20			10			25			30				
Na		20			12			6			12			4				
Si		1,200			450			500			500			410				
Ti		45			15			20			15			10				

(1) O - outside 12-hole area; M - middle 6-hole area; I - Hole 10, bore area.

Figure 16. WEB REDUCTION STUDY.

Table 9
COEFFICIENT OF THERMAL
EXPANSION DATA FOR
THE PHASE I
ELEMENTS

Flour Type	Coefficient of Thermal Expansion, 25 - 2,000° C ($\times 10^{-6}/^{\circ}\text{C}$)
GL 1008	3.31
ZTA	3.67
Graph-i-tite "G"	3.92
Stackpole 2033	4.56
Gilsonite	4.56
Speer SX5	5.21
POCO AXZ9Q	5.28
POCO AXZ	5.41
POCO AXM9Q	5.47
POCO AXF9Q	5.70
POCO AXM	6.51

Flexural Strength - Flexural strengths varied from an averaged low of 5,130 to a high of 6,940 psi. In general, the needle-coke element strengths (ZTA, Graph-i-tite "G") were higher than GL 1008; the fine-grain elements were very nearly the same as GL 1008 (5,500 to 6,900 psi).

Coefficient of Thermal Expansion (longitudinal) - CTE values for all of the experimental elements were measured in the longitudinal direction; ie, parallel to the extrusion plane. As noted in Table 9, gross changes in the fuel element CTE were observed. The GL 1008 elements were lower than any others, while POCO AXM flour elements had the highest expansion. CTE data showed that an increased element coefficient of thermal expansion could be obtained.

Element Uniformity - Specimens were cut across the face of the elements to determine the transverse uniformity. The samples were analyzed using mercury porosimetry techniques for bulk density, percent porosity, and open pore size. The percent porosity varied from a high of 7.30 (Graph-i-tite "G") to a low of 2.11 (POCO AXM 9Q). In general, the low-percentage-porosity elements (ie, high CTE elements) had very little variation across the element face. High-porosity elements (such as GL 1008, ZTA, and Graph-i-tite "G") had a large variation across the face.

The mean pore size of the graphite matrix, important because the niobium carbide used these sites to adhere to the graphite surface, showed wide variations. In a broad sense, the high-CTE elements had a smaller pore size than the low-CTE elements. The transverse uniformity again tended to be better with the smaller-pore-size element.

Metallographic Analyses of Niobium Carbide-Coated Bores - One element, compounded of experimental flour, was bore coated with niobium carbide using the low-temperature vapor deposition process which was developed for the Pewee 1 reactor.

A representative sample from each element was analyzed metallographically for adherence and frequency of cracks in the niobium carbide coating. From this study, the number of niobium carbide cracks and crack widths was established in both the longitudinal and transverse specimens. The following general comments can be made:

1. The number of matrix cracks associated with the niobium carbide cracks significantly decreased with increased CTE values. These data are reported graphically in Figure 17. No major matrix cracks which were related to niobium carbide cracks were observed when the fuel element matrix had a CTE value of greater than $5.3 \times 10^{-6}/^{\circ}\text{C}$.
2. Frequency of the longitudinal and transverse cracks significantly decreased as the CTE parallel-to-extrusion value was increased and the perpendicular-to-extrusion value decreased. Graphically, the data are given in Figure 18.
3. Essentially, all bore coatings were adherent. No gap between the niobium carbide and matrix on any of the specimens was detected.
4. All coated specimens had cracks in the niobium carbide. The crack width of the higher CTE element samples was very small—less than 50 angstroms.

Figure 17. MATRIX CRACKS VERSUS THE COEFFICIENT OF THERMAL EXPANSION VALUES. (Parallel and Perpendicular Cracks x 19 x 52.3 Inches)

Thermal Shock Data - Three coated specimens from each element were shipped to LASL (N-7 Group) for thermal shock evaluation, and a joint report of this entire program was prepared.⁽⁴⁾ Details of the thermal shock test were reported in this document. Briefly, the test consisted of placing a 14-inch element segment into a small furnace similar to the LASL hot-gas test furnace. Hydrogen flows similar to reactor conditions were passed through the element bores and a variable amount of electrical current was passed through the specimen. The quantity of power required to break the specimen and the specimen temperature during testing were established. From these data, thermal shock calculations were made on each specimen. A summary of the thermal shock data is given in Table 10 and graphically plotted as a function of the element CTE in Figure 19. In summary, the thermal shock resistance showed a significant decrease with increasing CTE values. This relationship was expected since the sonic moduli of all specimens had essentially the same value and the flexural strengths were nearly constant. It was also consistent with the previous ORNL data on the graphite discs.

Figure 18. NIOBIUM CARBIDE CRACK DATA VERSUS THE COEFFICIENT OF THERMAL EXPANSION. (Number of Parallel and Perpendicular Cracks x 19 x 52.3 Inches)

Table 10
THERMAL STRESS DATA FOR THE PHASE I
UNLOADED ELEMENTS

Flour Type	Coefficient of Thermal Expansion, 25 - 2,000° C (x 10 ⁻⁶ /° C)	Thermal Stress (Btu/in ³ -sec)		
		Maximum	Minimum	Average
GL 1008	3.31	134	113	123
ZTA	3.67	118	106	112
Graph-i-tite "G"	3.92	117	96	106
Stackpole 2033	4.56	92	78	85
Speer SX5	5.21	87	85	86
Gilsonite	4.56	156	108	121
POCO AXZ9Q	5.28	83	61	69
POCO AXM9Q	5.47	81	66	73
POCO AXF9Q	5.70	78	75	76
POCO AXM	6.51	74	63	69
POCO AXZ	5.41	69	59	65

Electrical Resistance Measurements - Electrical resistances of the elements before and after bore coating were routinely taken by using the standard production potential drop evaluation (PDE) techniques and instrument.

A plot of the electrical resistance data, as a function of the metallographic crack count data, is presented in Figure 20. In general, most of the data points fit a straight-line curve.

Figure 19. THERMAL STRESS DATA VERSUS THE COEFFICIENT OF THERMAL EXPANSION. (LASL, Phases I and II)

Figure 20. ELECTRICAL RESISTANCE VERSUS THE NIOBIUM CARBIDE CRACK DATA. (Number of Parallel and Perpendicular Cracks x Width x 19 x 52.3 inches)

Summary - The Phase I matrix program was completed and the data analyzed. Briefly, the following statements can be made:

1. Elements having an increased coefficient of thermal expansion were successfully manufactured.
2. The elements were niobium carbide bore coated. The niobium carbide cracks decreased in size and number as the element CTE was increased.
3. The element resistance increased with increasing CTE values.
4. The thermal stress values decreased as the coefficient of thermal expansion was increased.

Phase II Program

After completing the Phase I study, the graphite flour candidates were reduced to eight; and a statistical program, designed to study these candidate materials, was developed.

The desired goal of the Phase II program was to fabricate elements having an increased coefficient of thermal expansion but with a reduced Young's modulus and/or an increased flexural strength. The variables to be evaluated were: (1) the graphite flours (eight sources); (2) the graphite flour spectrum ($< 180 \mu\text{m}$ and $< 10 \mu\text{m}$); (3) effects of Thermax (0 and 15%); and (4) binders (Varcum 8251 and a graphitizable resin system).

This study was designed to produce at least one uranium-loaded element for thermal stress analysis by the Los Alamos Scientific Laboratory N-7 Group in addition to six uranium-loaded elements for hot-gas testing at WANL. It was also desirable that additional elements be fabricated for collecting physical property data and for hot-gas test evaluation at LASL.

Graphite Procurement and Grinding - The Phase II program required a much larger quantity of graphite flours than was available. Phase I used graphite flours which were produced from billets of commercial graphite and were ground in small quantities using laboratory mills. Each of the Phase II flours had a required batch size set at 250 pounds. All POCO graphites (AXM, AXF, and AXZ) were purchased in billet form and ground to as close to the desired particle spectrum as possible using available mills.

All of the POCO graphites were very difficult to grind into the desired particle spectrum. In fact, seven grinding mills were used on a trial basis in order to determine the operating characteristics of each mill. The grinding procedure used for the graphite flours was as given in the following listings:

Minus 60 Mesh Procedure

1. The as-received graphite pieces were crushed into less than one-inch chunks using a hydraulic ram fitted with knife blades.
2. Chunks from Step 1 were fed into a nine-inch ring mill (American Pulverizer and Crusher Company) and reduced in size. The material was screened through a 60-mesh sieve with the + 60 mesh material recycled through the ring mill.
3. All of the - 60 mesh material was screened through a 200-mesh screen to establish the percentage of - 200 mesh particles. A portion of the + 200 mesh particles were put through a Micro Atomizer (Model 5, Pulverizing Machining Division, Slick Industrial Company) to reduce the particles to - 200 mesh. After the material was milled to 100 percent less than 60 mesh and 50 percent less than 200 mesh, a standard sieve analysis was made on the product. In general, the particle spectrum obtained using these two control points produced an overall particle spectrum near that of the GL 1008 flour.

Minus 200 Mesh Procedure

1. The - 60 mesh flour was split into two equal portions. Approximately 100 pounds of the 60 mesh flour was used for the extrusion of elements, the remaining 100 pounds were fed through the Micro Atomizer mill to produce a finer flour.
2. Product from the Micro Atomizer mill was screened through a 200-mesh sieve. The + 200 mesh material was recycled through the mill until all of the flour was - 200 mesh.
3. The - 200 mesh fraction was then analyzed and used for fabricating the elements.

POCO AXM 9Q flour was obtained by simply firing the ground POCO AXM to 2,900° C for one hour in an argon atmosphere.

Robinson and Gilsonite flours were obtained in the coked state (fired to a nominal 1,000° C). The cokes were prefired to 2,900° C for one hour in argon prior to grinding. Grinding the fired Gilsonite material was accomplished without difficulty, while the Robinson material exhibited a friability similar to the POCO graphite.

Stackpole 2033 flour was obtained from the Stackpole Carbon Company as a - 60 mesh powder. Analyses of each master blend of graphite flour used in the Phase II program are listed in Table 11. Variations in the particle spectrums of the flour types are clearly visible.

Binders - Phase II studies included the fabrication of elements using the standard glassy carbon resin (Varcum 8251) and a graphitizable resin system (acenaphthylene-indene-isotruxene). No effort was made to optimize each blend for all of the extrusion parameters. The Varcum binder level was set by performing a single extrusion experiment of unloaded graphite flour. To obtain an extrusion pressure greater than 40 tons, the binder level for the uranium-loaded element was adjusted.

Elements were also fabricated using a graphitizable resin developed during the NERVA binder studies. This binder was a mixture of 38 percent isotruxene, 38 percent acenaphthalene (ACN) polymer, and 26 percent indene. Neither the manufacturing process for the binder nor the fuel element manufacturing processes using the binder were optimized at the time the fuel elements were made.

Physical Properties (Varcum 8251 binder) - Each group of elements fabricated during the Phase II program was sampled in order to establish the following physical properties: (1) compressive strength; (2) flexural strength; (3) coefficient of thermal expansion; (4) electrical resistance (before and after NbC coating); (5) density, uranium loading, and carbon content; (6) mercury porosimetry of samples taken transverse to the extrusion plane; (7) sonic modulus at room temperature; (8) metallographic analysis before and after coating; and (9) scanning microscopic analyses of selected samples before and after niobium carbide coating.

Data generated during the Phase II matrix program have been compared to the Phase I matrix data and are summarized in Tables 12 and 13. Certain statements can be made about the physical property data:

Table 11
PHASE II GRAPHITE FLOUR ANALYSES

Property	GL 1008(1)	Robinson(2)	Gilsonite(2)	Stackpole 2033	POCO AXM	POCO AXF	POCO AXZ	POCO AXM9Q	POCO AXM	POCO AXF
Surface Area (m ² /gm)	4.63	9.52	16.98	2.84	7.20	6.81	4.56	5.43	9.75	7.92
Densities (gms/cc)										
Helium	2.21	2.09	2.10	2.07	2.22	2.20	2.18	2.23	2.18	2.20
Pour	0.82	0.75	0.28	0.67	0.56	0.74	0.64	0.55	0.52	0.56
Tap	1.011	1.033	0.47	0.95	0.91	0.97	0.89	0.87	0.81	0.85
X-Ray Diffraction Evaluation										
d ₁₁₀	1.2300	1.2298	1.2300	1.2296	1.2291	1.2291	1.2294	1.2294	1.2295	1.2292
d ₀₀₄	1.6814	1.6903	1.6839	(3)	1.6931	1.6928	1.6917	1.6860	1.6920	1.6931
L _a	900	327	418	297	222	229	253	245	338	297
L _c	256	125	190	-	111	107	118	138	119	110
Micromerograph Data										
100% Less Than Size (μm)	180	125	120	125	170	170	175	170	80	80
80% Less Than Size (μm)	97	100	76	77	80	80	60	80	42	51
60% Less Than Size (μm)	79	88	53	52	60	52	35	60	26	44
40% Less Than Size (μm)	64	68	33	30	31	27	15	31	13	33
20% Less Than Size (μm)	46	46	8	11	10	11	7.6	10	6	12
Ash Content (%)	0.03	0.19	0.68	0.011	0.02	0.17	0.069	0.02	0.24	0.19
Sulfur Content (%)	0.005	0.005	0.003	0.055	0.005	0.006	0.003	0.005	0.001	0.008
Loss at 100° C (%)	< 0.1	0.005	0.003	0.06	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01

(1) GL 1008 through POCO AXM9Q were at -60 mesh; POCO AXM and AXF were at -200 mesh.

(2) Coke fired to 3,000° C for one hour before grinding.

(3) Double peak indicating a mixture of materials.

Table 12
PHYSICAL PROPERTIES OF PHASE I AND PHASE II ELEMENTS
(-60 Mesh Particle Size)

Property(1)	GL 1008		POCO AXM		POCO AXZ		POCO AXF		POCO AXM9Q		Gilsonite		Robinson	
	Phase I	Phase II	Phase I	Phase II	Phase I	Phase II	Phase I	Phase II	Phase I	Phase II	Phase I	Phase II	Phase I	Phase II
Extrusion Run Number	553	581	547	575	546	577	564	576	550	571	566	570	558	569
Bulk Density (gms/cc)	1.905	2.156	1.894	2.279	1.825	2.224		2.283	1.907	2.269	1.854	2.270	-	2.189
Uranium Loading (mgs/cc)	0	418	0	425	0	419	-	427	0	417	0	414	-	415
Carbon Density (gms/cc)	1.905	1.778	1.894	1.853	1.825	1.806	-	1.854	1.907	1.847	1.854	1.851	-	1.773
Thermax Content (wt %)	15	0	15	15	15	15	15	15	15	15	15	15	15	0
Varcum Content (pph)	25	27	31	32	27	34	33	30.5	36	32.5	24	38.5	31	28
Flour Surface Area (m ² /gm)	5.16	4.63	10.26	7.2	5.76	4.56	6.81	6.81	7.73	5.43	5.15	17	9.52	9.52
Flour Particle Size														
100% Less Than Size (μm)	100	182	180	180	180	180	180	180	170	-	180	120	125	125
90% Less Than Size (μm)	95	105	108	109	82	84	104	104	91	-	124	90	105	105
50% Less Than Size (μm)	52	72	46	46	11.9	23	40	40	36	-	71	42	79	79
25% Less Than Size (μm)	23	50	18	12.5	5.8	8.2	14	14	11	-	48	11	52	52
10% Less Than Size (μm)	8	32.5	7.4	4.7	3.28	5.0	6	6	5.2	-	31.5	4	31.5	31.5
Extrusion Pressure (tons)	71	80	115	62	117	74	50	55	35	48	73	60	60	80
Compressive Strength (psi)	12,380	8,670	17,830	20,200	17,600	15,930	-	18,510	17,640	15,580	11,800	12,400	-	11,160
Flexural Strength (psi)	6,350	3,970	5,550	4,780	5,120	5,510	-	4,370	5,690	3,840	5,510	4,240	-	3,780
Sonic Modulus (psi x 10 ⁶)														
Longitudinal	2.2	1.6	1.5	1.9	1.3	1.7	-	1.9	1.9	1.8	2.0	2.3	-	1.7
Transverse	1.7	1.7	1.7	1.9	1.4	1.7	-	1.9	1.7	1.7	1.5	2.3	-	1.6
Coefficient of Thermal Expansion, 25 - 2,000° C (x 10 ⁻⁶ /° C)	3.31	3.21	6.51	5.67	5.41	5.56	6.28	6.18	5.47	5.14	3.37	3.90	4.76	5.39
Electrical Resistance, Before NbC Coat (milliohms/element inch)	1.60	-	2.95	3.25	3.17	3.06	-	3.19	2.46	2.76	1.68	1.99	-	2.14

(1) Mercury porosimeter data noted in Table 15.

Table 13
PHYSICAL PROPERTIES OF PHASE II ELEMENTS
(-200 Mesh Particle Size)

	POCO AXM		POCO AXZ		POCO AXF	
	Unloaded	Loaded	Unloaded	Loaded	Unloaded	Loaded
Extrusion Run Number	572	580	574	578	573	579
Bulk Density (gms/cc)	-	2.228	-	2.272	-	2.245
Uranium Loading (mgs/cc)	0	407	0	418	0	411
Carbon Density (gms/cc)	-	1.819	-	1.851	-	1.832
Thermax Content (wt %)	0	0	15	15	0	0
Varcum Content (pph)	45	45	40	39.5	42	42.5
Flour Surface Area (m ² /gm)	9.75	9.75	-	-	7.92	7.92
Flour Particle Size						
100% Less Than Size (μm)	82	82	80	80	82	82
90% Less Than Size (μm)	50	50	45.5	45.5	56	56
50% Less Than Size (μm)	17.5	17.5	23.5	23.5	40	40
25% Less Than Size (μm)	7.7	7.7	11.0	11.0	18	18
10% Less Than Size (μm)	2.9	2.9	5.4	5.4	5.5	5.5
Extrusion Pressure (tons)	64	60	67	50	66	48
Compressive Strength (psi)	-	19,120	-	17,900	-	18,890
Flexural Strength (psi)	-	6,100	-	4,300	-	5,510
Sonic Modulus (psi x 10 ⁶)						
Longitudinal	-	1.8	-	1.9	-	1.8
Transverse	-	1.8	-	1.8	-	1.8
Coefficient of Thermal Expansion, 25 - 2,000° C (x 10 ⁻⁶ /° C)	5.54	5.34	5.57	5.44	6.20	5.82
Electrical Resistance, Before NbC Coat (milliohms/element inch)	-	2.96	-	3.06	-	2.77

1. Minus 60 Mesh Flour Elements (< 180 μm maximum particle size)

- a. Compressive strength - Unloaded Varcum-bound elements made with Thermax in the Phase I program had essentially the same compressive strengths as the Phase II loaded Varcum-bound elements. Elements made without Thermax in the Phase II program had lower compressive strengths.
- b. Flexural strength - In general, a reduction in the element flexural strength was noted in the Phase II loaded elements when compared to the Phase I unloaded groups.
- c. Electrical resistance - Loaded Phase II elements generally had a small increase in resistance.
- d. Sonic modulus - Modulus values were equal to or slightly higher in the Phase II Varcum-bound loaded elements.
- e. Coefficient of thermal expansion - Thermal expansion values of the loaded Phase II elements were usually less than those of the Phase I elements.

- f. Thermal stress - Thermal stress data reported in Table 14 for the Phase II elements were very similar to the Phase I element data. Again, the thermal stress decreased as the coefficient of thermal expansion was increased.

2. Minus 60 Mesh Phase II Varcum-Bound Elements Versus Minus 200 Mesh Elements

- a. Carbon density - In general, no major density change was noted in the Phase II elements as the graphite filler particle sizes were reduced. Elimination of the Thermax in two of the groups of the series resulted in a slight drop in the carbon density.
- b. Compressive strength - Both the - 60 and - 200 mesh elements had essentially the same compressive strength.
- c. Flexural strength - Two groups of - 200 mesh flour (AXM and AXF) which were made without Thermax showed an increased strength with the decreased graphite filler particle size.
- d. Electrical resistance - Electrical resistance of the - 200 mesh elements made without Thermax was lower than the - 60 mesh elements made with Thermax. The - 60 mesh and - 200 mesh elements made with Thermax showed no change in electrical resistance. The data strongly suggest that the particle size reduction had no significant effect on the element resistance, but elimination of Thermax did reduce the resistance value.
- e. Sonic modulus - Sonic modulus values were essentially the same for all groups.
- f. Coefficient of thermal expansion - A slight decrease in the longitudinal thermal expansion was noted in each of the - 200 mesh groups compared to the - 60 mesh groups.
- g. Thermal stress - Thermal stress data are given in Table 14. Very little, if any, change in thermal stresses was apparent with the - 200 mesh elements compared to the - 60 mesh elements. No change was noted in the elements fabricated without Thermax.

Transverse Element Uniformity - During the Phase I and Phase II programs, an element from each test group was selected for determination of its physical characteristics. One part of this analysis included machining specimens from around the outer hole area (Holes 1, 2, 3, ...), specimens from the inner holes region (Holes 5, 6, ...), and a specimen taken around Hole 10. These specimens were submitted for mercury porosimetry analyses to obtain the bulk density, real density, percent open porosity, and pore size distribution. Data on the specimen types are listed in Tables 8 and 15.

General comments can be made concerning these data as follows:

- 1. Phase II Varcum-bound, loaded elements made from GL1008 flour without Thermax had a higher percentage of open porosity than the Phase I unloaded groups (~ 11 vs 5%).
- 2. Gilsonite Phase I and II elements had essentially the same amount of open porosity.

Table 14
THERMAL STRESS DATA FOR THE PHASE II ELEMENTS

Flour Type	Coefficient of Thermal Expansion	Thermal Stress (Btu/in ³ -sec) ⁽¹⁾		
		Maximum	Minimum	Average
<u>-60 Mesh Elements</u>				
GL 1008 (no Thermax)	3.21	171	124	148
Gilsonite	3.90	93	68	85
Robinson	5.39	81	53	67
POCO AXM9Q	5.14	80	64	70
POCO AXM	5.67	71	59	65
POCO AXF	6.18	85	79	81
POCO AXZ	5.56	83	66	74
<u>-200 Mesh Elements</u>				
POCO AXM (no Thermax)	5.34	70	63	66
POCO AXF (no Thermax)	5.87	81	68	76
POCO AXZ	5.44	83	68	74

(1) Measured at LASL.

3. All of the POCO flour groups in both the Phase I and Phase II programs (- 60 mesh), except for POCO AXZ, had very little open porosity. The AXZ group in both the Phase I and Phase II programs showed a nominal 5 to 6 percent open porosity.
4. Transverse uniformity of all of the higher-expansion elements was generally better than the lower-expansion elements.
5. The - 200 mesh Varcum-bound, POCO element groups had relatively small amounts of open porosity. The POCO AXM and AXF groups (- 200 mesh) were fabricated without the addition of Thermax carbon black. These two groups did have a slightly greater percentage of open porosity when compared to the POCO AXZ groups (- 200 mesh). The POCO AXZ group (- 200 mesh) had a lesser amount of open voids than the - 60 mesh POCO AXZ groups (3 vs 6%).

Graphitizable Binder - A binder system to replace the Varcum 8251 was developed for the NERVA program. The binder was composed of 38 percent isotruxene (ITX), 38 percent acenaphthalene (ACN), and 23 percent indene (I). For the Phase II studies, neither the binder formulation nor the manufacturing procedure was optimized. Different graphite flours were extruded into elements, graphitized, and liquid impregnated using the ITX-ACN-I binder as the impregnant. The fillers were POCO AXM (- 60 mesh), POCO AXF (- 60 mesh), POCO AXZ (- 60 mesh), and GL 1008 (- 200 mesh).

The as-extruded elements were weak after the 250⁰ C bake operation compared to the standard Varcum-bound elements. Transverse cracking of the early extruded elements in the 250⁰ C bake operation was a problem. It was found that if the baking fixtures were lightly coated with a thin film of natural flake graphite powder, the transverse cracking problem was significantly reduced.

Table 15
MERCURY POROSIMETER DATA FOR THE PHASE II ELEMENTS
(Uranium-Loaded Flour)

	GL 1008, No Thermax ⁽¹⁾			Robinson, No Thermax			Gilsonite			POCO AXM			POCO AXM90			POCO AXF			POCO AXZ			POCO AXM			POCO AXF			POCO AXZ		
	O ⁽²⁾	M ⁽²⁾	I ⁽²⁾	O	M	I	O	M	I	O	M	I	O	M	I	O	M	I	O	M	I	O	M	I	O	M	I	O	M	I
Bulk Density (gms/cc)	2.206	2.164	2.191	2.176	2.171	2.213	2.256	2.246	2.277	2.277	2.277	2.263	2.280	2.257	2.258	2.282	2.247	2.273	2.219	2.199	2.233	2.223	2.215	2.253	2.277	2.241	2.280	2.275	2.264	2.267
Porosity (%)	11.09	12.39	10.74	6.49	7.03	4.67	5.01	4.97	4.57	2.55	3.21	2.243	2.19	2.93	3.20	1.87	2.84	2.15	5.29	6.30	4.76	5.07	5.25	4.18	3.72	4.87	3.79	3.11	2.93	1.76
Real Density (gross volume-pores/weight)	2.482	2.470	2.455	2.326	2.335	2.321	2.375	2.364	2.386	2.336	2.353	2.320	2.331	2.325	2.333	2.326	2.313	2.324	2.343	2.347	2.344	2.342	2.338	2.351	2.365	2.356	2.370	2.348	2.322	2.308
Mean Pore Size (μm)	0.11	0.17	0.045	1.2	1.5	0.50	0.09	0.045	0.056	0.05	0.08	0.04	0.031	0.05	0.06	0.036	0.090	0.042	0.20	0.23	0.14	0.27	0.21	0.07	0.091	0.16	0.052	0.091	0.072	0.027

(1) Flours GL 1008 through POCO AXZ were -60 mesh; POCO AXM through AXZ were -200 mesh.
(2) O - outside 12-hole area; M - middle 6-hole area; I - Hole 10, bore area.

The available physical property data on these elements are noted in Table 16. A brief analysis of these data follows:

1. Coefficient of thermal expansion values for the POCO flour elements were high (which was expected), but about equal to Varcum-bound elements.
2. Sonic moduli of the impregnated elements were lower than equivalent Varcum-bound elements.
3. Compressive and flexural strengths significantly increased with impregnation. Values for the impregnated elements were about equal to Varcum-bound elements.

Table 16
PHYSICAL PROPERTIES OF ISOTRUXENE-ACENAPHTHALENE-INDENE-
BOUND EXTRUDED ELEMENTS

Property	POCO AXM	POCO AXF	POCO AXZ	GL 1008	Robinson
Number of Impregnations	5	5	6	5	0
Extrusion Run Number	593	597	598	599	601
Thermax Content (%)	15	15	0	15	15
Graphite Size (mesh)	-60	-60	-60	-200	-200
Binder (pph)	36	31	47	35	29
Extrusion Pressure (tons)	36	34	25	46	45 - 58
Uranium Content (mgs/cc)	376	378	328	342	-
Carbon Density (gms/cc)	1.84	1.79	1.83	1.81	-
Coefficient of Thermal Expansion, 25 - 2,000° C ($\times 10^{-6}/^{\circ}\text{C}$)	5.92	5.97	5.24	3.01	5.16
Sonic Modulus ($\text{psi} \times 10^{-6}$)					
E_1	1.4	1.4	1.6	2.0	-
E_t	1.8	1.8	1.5	2.0	-
Average Compressive Strength (psi)	18,610	18,870	15,450	10,830	-
Average Flexural Strength (psi)	5,120	4,560	4,710	5,530	-
Average Bulk Density (calculated gms/cc)	2.19	2.23	2.13	2.11	1.97
Laboratory Bulk Density (gms/cc)	2.19	2.17	2.15	2.16	-

Properties of ITX-ACN-I Elements (POCO filler)

One group of POCO AXM elements was completely processed. Available data are provided in Table 17. A similar set of data for Varcum-bound elements is shown for comparison. Electrical resistance of the ITX-ACN-I-bound elements was near that of the Varcum-bound elements. Sonic modulus values of the impregnated elements were lower than for equivalent Varcum-bound elements, and the compressive and flexural strengths were equal to or greater than the Varcum elements. Longitudinal CTE values were higher than for the elements whose binder was Varcum 8251. CTE values increased with repeated impregnations, indicating that the binder phase had a high CTE value. The LASL thermal-stress values were

Table 17
PHYSICAL PROPERTIES OF THE POCO AXM SERIES OF ELEMENTS

Property	Extrusion Batch and Binder			
	547 Varcum 8251	575 Varcum 8251	592 ITX-ACN-I	593 ITX-ACN-I
Extrusion Pressure (tons)	115	62	32	36
Binder (pph)	31	32	36	36
Flour Surface Area (m ² /gm)	10.26	7.2	7.2	7.2
Particle Size - Micromerograph Data				
100% Less Than Size (μm)	180	180	180	180
90% Less Than Size (μm)	108	109	109	109
50% Less Than Size (μm)	46	46	46	46
25% Less Than Size (μm)	18	12.5	14.5	14.5
10% Less Than Size (μm)	7.4	4.7	4.7	4.7
Density (gms/cc)				
As Graphitized	1.894	2.279	1.67	2.03
Impregnated (five times)	-	-	-	2.19
Final Leak Rate (cc/min, avg)	99	35	-	99
Final Electrical Resistance (milliohms/element inch)	2.95	3.25	-	3.16
As-Graphitized Sonic Moduli (x 10 ⁶ psi)				
E _l	1.5	1.9	-	0.90
E _t	1.7	1.9	-	1.20
Impregnated Sonic Moduli (x 10 ⁶ psi)				
E _l	1.5	1.9	-	1.4
E _t	1.7	1.9	-	1.8
As-Graphitized Compressive Strength (psi)				
Maximum	-	21,430	9,970	10,530
Minimum	-	19,230	7,920	8,360
Average	17,830	20,200	8,990	9,610
Impregnated Compressive Strength (psi)				
Maximum	-	21,430	-	19,380
Minimum	-	19,230	-	17,830
Average	17,830	20,200	-	18,610
As-Graphitized Flexural Strength (psi)				
Maximum	-	5,310	3,460	3,050
Minimum	-	4,510	1,940	2,150
Average	5,550	4,780	2,590	2,410
Impregnated Flexural Strength (psi)				
Maximum	-	5,310	-	5,620
Minimum	-	4,510	-	4,630
Average	5,550	4,780	-	5,120
Coefficient of Thermal Expansion, 25 - 2,000° C (x 10 ⁻⁶ /° C)				
As Graphitized	-	-	6.20	5.50
Final	6.51	5.67	-	5.90
Carbon Density (gms/cc)				
As Graphitized	-	-	-	1.650
Final	1.894	1.853	-	1.840
Final Uranium Loading (mgs/cc)	0	425	0	348

Table 17 (continued)

Property	Extrusion Batch and Binder			
	547 Varcum 8251	575 Varcum 8251	592 ITX-ACN-I	593 ITX-ACN-I
Thermal Stress Values (Q''' Btu/in ³ -sec)				
NbC Coated				
1	73.6	65.0	-	68.3
2	63.2	59.4	-	69.2
3	69.9	70.7	-	55.7
Thermal Stress Values (Q''' Btu/in ³ -sec)				
ZrC Coated				
1	-	60.6(1)	-	58.3
2	-	66.4(1)	-	53.4
3	-	49.0(1)	-	62.8

(1) These values were established on 630 mgs U/cg loaded POCO AXM elements which were made in the preproduction studies.

equal to the Varcum-bound elements. Both types produced a thermal-stress value lower than desired.

GRAPHITIZABLE BINDER STUDIES

During the NERVA fuel element studies, an investigation was conducted that pertained to thermoplastic-type binders which produce a carbon structure that could be converted into a crystalline, low-modulus graphite.⁽⁵⁻⁷⁾ Most thermoplastic binders, used for graphite manufacture, are commercial pitches which are still bottom fractions from refining operations using coal-tar or petroleum feedstocks. Commercial pitches vary widely in chemical composition and purity. Changes in composition occur because of changes in the precursor source and in the method of processing.

In general, pitches have a softening or melting point greater than 70° C and may range as high as 200° C. The NERVA program required that the raw materials used for binders be essentially nonvariable over a number of years and that the source not change during the life of the program. It was also desirable, but not mandatory, that the thermoplastic binder have a viscosity of about 250 centipoises at room temperature so that the existing NERVA mixing and blending equipment could be used.

Four binder systems were developed which were: (1) ITX-ACN-I, (2) CAI (cinnamylideneindene)-I, (3) Grade 277-15V^(c) pitch-indene, and (4) Grade 240^(d) pitch-indene. Extrusion studies were made using these binders where warm mixing and extrusions were performed (ie, 80° C or less). In general, the lack of adequate temperature controls on the fuel element extrusion equipment caused many problems.

(c) A coal-tar pitch made by the Allied Chemical Company, Plastics and Coal Division.

(d) A petroleum pitch made by the Ashland Oil and Refining Company.

The most successful binder system was obtained by the use of a binder which had a nominal viscosity of 250 centipoises at room temperature. The binder viscosity was controlled by the addition of indene which served as a diluent. Other organic compounds were explored for use as diluents, but none were found to be as good or better than indene.

Isotruxene-Acenaphthalene-Indene Binder (ITX-ACN-I)

A thermoplastic resin binder system was developed which utilized a mixture of ITX, ACN, and I. Considerable development time was expended in a study of the chemistry of isotruxene and acenaphthalene and a binder formulation procedure was developed. From these basic organic resins, a manufacturing process was also developed for the manufacture of a thermoplastic binder which was used in the NERVA development program.

Laboratory Development Studies - Major variables associated with the binder formulation procedure were: (1) the heat-cure conditions used in the formation of ITX pitch, (2) the composition, and (3) the temperature at which the ACN monomer was added. Of these factors, the latter appeared to be the most critical with respect to control and reproducibility. The minimum temperature at which the ACN monomer could be added to the ITX pitch was dictated by the melting properties of the ITX pitch. This restriction necessitated temperatures of $\geq 160^{\circ}\text{C}$ for the blending operation. Thermal analyses of the ACN monomer indicated a strong tendency toward polymerization as temperatures approached 160 to 170°C . Thus, resulting binder viscosities were greatly influenced by the degree of polymerization that accompanied addition of the ACN monomer to the ITX pitch.

Development data allowed a correlation between the ACN/ITX blending temperature and the degree of polymerization of ACN. These data were obtained from gel permeation chromatography (GPC) scans, which can be seen in Figure 21. Figure 21 shows the molecular distribution that is expected when no polymerization of ACN occurs; and, thus, the polymer component shown was derived from the ITX pitch. In turn, Figure 21 shows the decrease in ACN monomer content and the increase in polymer content for three formulating procedures. The ACN polymer contents in Figure 21 appear as an added response at the high-molecular-weight end of the distribution, and the response assigned to isotruxene was similar to that in the reference scan in Figure 21. Figure 21 indicates almost total polymerization of ACN. However, under the polymerization conditions, low-molecular-weight polymers were formed along with the high-molecular-weight polymers indicated previously in Figure 21. These low-molecular-weight species increased the response attributed to ITX in the reference scan (Figure 21) and probably represent a dimeric species. In summary, these data show that blending conditions significantly influenced the degree of polymerization of ACN and the molecular distribution of the resulting polymers.

An ITX-ACN-I binder that was formulated from 100 grams ITX, 100 grams ACN, and 60 grams I (ITX-ACN blended at 160°C) was allowed to stand at room temperature for several days, and the residual crystalline content that settled out was collected by filtration. The molecular distribution of the precipitate is seen in Figure 22. When compared with the GPC scans in Figure 21 it appears that the composition of this precipitate was not far removed from that of the ITX-ACN blends prior to dilution with indene.

In the interest of optimizing binder properties and reproducibility, binder formulations were evaluated by measuring viscosity as a function of: (1) the heat cure time of ITX pitch (Table 18), (2) binder composition, (3) temperatures at which the ACN monomer was blended, and (4) ACN polymer/monomer ratios. Table 18 also gives the binder viscosities (at 30° C) as a function of the ITX heat-cure time, binder composition, and ACN addition temperature. Comparison of viscosities for formulations which differed only by differences in a common variable allowed the following conclusions to be made:

1. Samples B5-1, B6-1, and B7-2 indicate that binder viscosities decreased as the ITX heat-cure times increased from 42 to 50 hours. Direct viscosity comparisons at longer heat-cure times were not made, but processing (eg, ease of blending and stability of blend) suggest that heat-cure times of 55 to 65 hours produced comparable binders and defined the time range recommended for the heat-cure conditions that were utilized (Table 18).
2. Samples B7-1 and B7-2 indicate that lower viscosities were obtained at lower ACN addition temperatures. Comparison of Samples B9-3 and B9-4 reinforced this conclusion. It appeared that ACN addition below 160° C resulted in little polymerization. Addition between 170 and 190° C did result in polymerization, and the degree of polymerization was temperature dependent. Addition at 190° C or above usually resulted in a significant exotherm.
3. Samples B9-8, B9-4, and B9-6 show viscosity variations as a function of the indene content. A reduction in the indene content from 100 grams (per 100 grams ITX pitch) to 60 grams resulted in a small viscosity increase relative to that accompanying a reduction from 60 grams (per 100 grams ITX pitch) to 30 grams.
4. Samples B9-8 and B9-9 show the viscosity changes associated with a reduction in the ACN content from 100 grams (per 100 grams ITX pitch) to 75 grams to be small.

Figure 21. GEL PERMEATION CHROMATOGRAPHY SCANS SHOWING THE MOLECULAR DISTRIBUTIONS OF ACENAPHTHALENE AND ISOTRUXENE PITCH MIXTURES (50% ACN) AS A FUNCTION OF THE BLENDING TEMPERATURE.

Figure 22. GEL PERMEATION CHROMATOGRAPHY SCAN SHOWING THE MOLECULAR DISTRIBUTION OF A RESIDUAL CRYSTALLINE PRECIPITATE COLLECTED BY FILTRATION FROM AN ISOTRUXENE/ACENAPHTHALENE/INDENE BINDER. (Binder Formulated from 100 Grams of ITX, 100 Grams of ACN, and 60 Grams of I)

Additional comparisons may be made between Samples B9-4 and B9-5, and between Samples B9-5 and B9-7.

Additional experiments were carried out in which the ACN monomer was added in two portions, each at a different temperature. Subsequently, viscosities were adjusted to approximately 1,000 centipoises by adding the appropriate quantity of indene. Data from this study are listed in Table 19. In Samples N-11-74 C1 and N-11-74 C3, small

portions of the ACN monomer (200 and 300 grams, respectively), intended to promote polymerization, were added at temperatures $\geq 180^{\circ}\text{C}$. Additional ACN monomer was added at lower temperatures. Thus, the degree of polymerization would be reflected in the viscosity of the final binder formulation and/or in the quantity of indene required to approximate a viscosity of 1,000 centipoises. Using these criteria it was deduced that the ACN polymeric content in Sample N-11-74 C3 was greater than that in Sample N-11-74 C1.

Table 18
BINDER FORMULATIONS DERIVED FROM MIXTURES OF ISOTRUXENE,
ACENAPHTHALENE, AND INDENE

Sample(1)	Heat Cure Time of ITX Pitch(2) (hrs)	Acenaphthalene Content(3) (gms)	Temperature at Which Acenaphthalene was Added ($^{\circ}\text{C}$)	Indene Content(3) (gms)	Binder Viscosity(4) (cps)
B5-1	42	100	170 - 180	100	560
B6-1	45	100	172 - 178	100	290
B7-2	50	100	170 - 180	100	150
B7-1	50	100	≤ 170	100	20
B7-3	50	100	≤ 170	60	< 200
B8-1	55	100	≤ 195	100	9,600
B8-2	55	100	≤ 160	60	210
B9-8	61	100	≤ 160	100	45
B9-4	61	100	≤ 160	60	125
B9-3	61	100	170 - 180	60	1,720
B9-6	61	100	≤ 160	30	Solid at 40°C
B9-9	61	75	≤ 160	100	65
B9-5	61	75	≤ 160	60	275
B9-7	61	50	≤ 160	60	290

- (1) Binders were formulated by blending acenaphthalene into molten isotruxene at a prescribed temperature. Indene was subsequently added at a lower temperature.
- (2) Isotruxene (20-kg batch) was heated at 300°C with air (flow rate $5\text{ ft}^3/\text{hr}$) bubbling through the molten material. Viscosity (at 300°C) of the heat-cured ITX ranged from 50 to 65 centipoises.
- (3) Per 100 grams of ITX.
- (4) Temperature at 30°C .

Table 19
BINDER FORMULATIONS DERIVED FROM MIXTURES OF ISOTRUXENE,
ACENAPHTHALENE, AND INDENE

Sample ⁽¹⁾	ITX Pitch Content ⁽²⁾ (gms)	Acenaphthalene Content ⁽²⁾ (gms)	Temperature at Which Acenaphthalene was Added (° C)	Indene Content (gms)	Binder Viscosity ⁽³⁾ (cps)
N-11-74 C1	1,000	1,000	200 gms at ~ 180; 800 gms at ≤ 160	500	870
N-11-74 C2	1,000	1,000	175 - 185	1,400	1,040
N-11-74 C3	1,000	1,000	300 gms at ≥ 180; 700 gms at ≤ 180	750	1,120

(1) ITX pitch initially heated to melt; ACN added at designated temperatures, and I subsequently added at lower temperatures.

(2) ITX Pitch was prepared by heating ITX at 300° C for 64 hours with air (flow rate 5 ft³/hr) bubbling through the molten material.

(3) Temperature at 30° C.

This deduction was in support of previous conclusions reached concerning the effect of the ACN addition temperature on binder viscosities. The two samples described may be compared with a third listed in Table 19 in which all the ACN monomer was added between 175 and 185° C. Again, the indene content suggested extensive polymerization of the ACN.

A third series of experiments was performed in which varying proportions of the prescribed ACN content were prepolymerized by autoclave treatment (Table 20), and were, thus, subsequently added to the binder formulation in polymeric form. The polymer was initially blended with the ITX pitch at approximately 200° C. Again, a certain proportion of ACN was added as the monomer and at a temperature below that required to promote polymerization of ACN (≤ 170° C). Data on these samples are given in Table 20. Variation in binder viscosity with increasing ACN polymer content is indicated in Figure 23.

In practice, high-coke-yield binders were desirable and, thus, low-coke-yield components of a binder were usually reduced to a minimum. For these formulations it was deduced that the indene content required to produce a given viscosity decreased with decreasing content of the ACN polymer. Although lowest viscosities did result from formulations in which all ACN was added in monomeric form and at low temperatures (≤ 160° C), some polymeric content seemed desirable and resulted in smoother binders having greater lubricity and, on standing, greater stability against granulation. Assuming that a given polymeric content was desirable, the use of autoclave-polymerized ACN was preferred for the following reasons: (1) prepolymerized ACN allowed better control than the polymerization of monomeric ACN as the latter required close temperature control; (2) autoclave-polymerized ACN had a lower-melting polymer (~ 50° C) than that obtained by polymerization (at 180 to 200° C) under ambient pressures; and (3) autoclave-polymerized ACN had a higher coke yield (45 to 50%) than the ACN monomer (35%) or ACN polymerized at 180 to 200° C under ambient pressures (35 to 40%).

Table 20
BINDER FORMULATIONS DERIVED FROM MIXTURES OF
ISOTRUXENE, ACENAPHTHALENE POLYMER,
ACENAPHTHALENE MONOMER,
AND INDENE

Sample(1,2)	ACN Polymer Added(3) (gms)	ACN Monomer Added(4) (gms)	Indene Content(5) (gms)	Binder Viscosities (cps)	
				At 30° C	At 60° C
N-11-74 C8	100	-	60	5,400	360
N-11-74 C6	75	25	60	1,720	
N-11-74 C4	50	50	60	860	
N-11-74 C5	50	50	60	820	
N-11-85 B2	50	50	40	1,380	110
N-11-85 B3	50	50	20	17,000	280
N-11-74 C7	25	75	60	280	

- (1) ITX pitch prepared by heating ITX at 300° C for 62 hours with air (flow rate 5 ft³/hr) bubbling through molten material.
 (2) ACN polymer prepared by heating ACN for two hours in an autoclave at 300° C and 300 psi.
 (3) Per 100 grams ITX pitch. ACN polymer added to molten ITX pitch at ~ 200° C.
 (4) Per 100 grams ITX pitch. ACN monomer added at ≤ 170° C; indene subsequently added at lower temperatures.
 (5) Per 100 grams of ITX pitch.

Figure 23. VISCOSITY (AT 30° C) OF BINDER FORMULATIONS DERIVED FROM ISOTRUXENE, ACENAPHTHALENE POLYMER, ACENAPHTHALENE MONOMER, AND INDENE AS A FUNCTION OF ACENAPHTHALENE ADDED AS THE POLYMER.

Binder Manufacturing Process - Had the NERVA development program continued, an optimum binder manufacturing process would have been completely developed. The process used for making the binder for the extrusion work was not fully developed at the time the program was terminated. Process changes were to be made to incorporate the results from the laboratory development program into full-scale manufacturing of fuel elements.

A change in the basic binder characteristic or a change in the fuel element filler carbon always generated a new set of process variables which had to be evaluated in order to establish the resulting element properties.

Manufacturing the ITX-ACN-I binder used for the extrusion studies involved several steps. Isotruxene, separately prepared, was polymerized by a high-surface-area exposure of the molten (300°C) material to recirculating air for 44 hours with an unknown amount of fresh air being admitted to the furnace. The common batch size consisted of five kilograms. Equipment was later assembled and a known amount of air bubbled through the ITX charge for 60 hours. The ITX was next cooled to room temperature, broken into chunks, and stored in closed cans.

Addition of the ACN was accomplished by reheating polymerized ITX (1,500-gram batches) to 300°C to ensure a complete and uniform melt. The melt temperature was then cooled to 175°C and 1,500 grams of ACN per 1,500 grams of ITX added. The ACN was at room temperature during this mixing step. The temperature of the resulting ITX-ACN blend was not controlled, but usually was not less than 160°C after the materials were mixed. Studies conducted in the laboratory binder program indicated that this was a critical operation and required close control. The ITX-ACN mixture was cooled to 130°C , or less, and 450 grams of indene per 3,000 grams of the ITX-ACN mixture added. The binder was stored in closed containers. Before use, the binder was reheated to about 90°C and additional indene was added, depending on the experiment in progress. A large number of extrusion experiments were made in which a solution of 43.5 percent ITX-43.5 percent ACN-13 percent indene was used.

Stored ITX-ACN-I, having a concentration of 43.5 percent ITX, 43.5 percent ACN, and 13 percent I, tended to gel upon storage into a semisolid-appearing material. Simple agitation restored some fluidity, but the binder appeared to be viscous. The binder was heated to 90°C with agitation and cooled. A fluid mixture was again obtained.

A limited amount of viscosity data were obtained. Figure 24 provides a plot of the measured viscosity versus the shear rate at three temperatures. The spindle rotation rates, linearly proportional to the shear rates, were plotted against the derived viscosities. These data show the expected characteristics of lowered viscosity with increased temperature. A second characteristic was the thixotropic nature indicated by the measurements (ie, decreased viscosity with an increased shear rate). This relationship is not normally associated with liquids, but is common when solids are suspended in a liquid. Molecular size and the nature of the polymers contained in the binder apparently promoted this behavior. Warm vacuum filtration of the binder showed no solid recovery.

Figure 25 gives a plot of viscosities that were measured on a more highly diluted binder (23% I) which was used in a large number of extrusion experiments. Data were taken up to

90° C at a constant shear rate at 20 rpm. These data show that small changes in viscosity occurred above 60° C. Mixing the filler and binder at or above this temperature was accomplished. The sharp decrease noted below 60° C suggested that extrusion temperature control was critical since it was performed at less than 60° C. This mix control problem required a very careful temperature control on the extrusion die.

Major process problems arose with the control of warm-temperature mixing and extrusion at about 80° C. The most successful system was obtained by using a 23 percent indene diluent and operating the mixing and extrusion processes at or near room temperature.

Cinnamylideneindene Binder Studies

Laboratory studies on organic resins indicated that a thermosetting binder could be obtained from a polymer of cinnamylideneindene (CAI). Polymers formed from this organic compound had melting points in the range of 60 to 75° C and were carbonized with carbon yields of 40 to 45 percent. The CAI polymer was also modified with potassium hydroxide to form isotropic carbon structures upon pyrolysis.

Figure 24. VISCOSITY OF ISOTRUXENE, ACENAPHTHALENE, AND 23 PERCENT INDENE VERSUS THE TEMPERATURE AT A CONSTANT SHEAR RATE.

Figure 25. VISCOSITY OF ISOTRUXENE, ACENAPHTHALENE, AND 13 PERCENT INDENE VERSUS THE SHEAR RATE.

Several attempts were made to fabricate elements at a nominal 80° C using the CAI polymer. However, because of the difficulty in controlling the mixing at extrusion temperatures, it was decided that a mixture of CAI and indene was more desirable as a binder.

Binder Formulations - Binder formulations incorporating CAI and indene were evaluated, and a single formulation selected for further studies. The early studies used CAI-indene binders which were formulated by blending indene with 300° C autoclave-polymerized CAI.

Final studies used a binder which was polymerized at 340° C, since these CAI polymers were noted to have somewhat higher coke yields than the 300° C-polymerized samples. Viscosities of formulations incorporating 40, 50, and 60 parts per hundred (phr) indene were 166, 100, and 80 centipoises, respectively, at 50° C. These binder systems appeared to be quite homogeneous and offered a range of viscosities which could be readily controlled by the indene content.

Studies of a single binder formulation consisted of an autoclave polymerization of a 10-kilogram CAI sample at 300° C for six hours. To modify the microstructure of the derived carbon, 45 grams of potassium hydroxide were dry blended with the CAI prior to polymerization, and analyses showed a potassium content of 3,850 ppm. The polymer was heated until completely molten (~ 100° C) and the indene (55 phr) added to the well-stirred fluid. On cooling to 25° C, the viscosity was determined to be approximately 1,000 centipoises, and the binder was retained for extrusion studies. Scale-up problems associated with this binder system seemed minimal.

Extrusion Studies - While only a single extrusion blend was made using the CAI-I binder, it was apparent that several manufacturing process changes were needed to adequately evaluate this binder. Elements were extruded and baked in a closed can and also in a flowing air atmosphere to 250° C. Those units baked in a closed can, when processed through graphitization, had a longitudinal crack on the numbered face of all elements, indicating that a consistent baking problem existed. The elements baked in an air atmosphere were graphitized, with the result that half of the elements were visually sound but were of a lower density (~ 0.1 gm/cc) than the equivalent ITX-ACN-bound elements. The experimental conditions which existed at the time of this experiment were:

1. Manufacture of cinnamylideneindene (ie, the polymerization/viscosity relationship) was not fully established.
2. The carbon powder which was used for this experiment had a small particle size distribution and required a high binder content.
3. The baking and graphitization time-temperature cycles that were used were not optimized for the materials under study.
4. Consistency of the matrix cracking indicated that this problem could be solved with further study. But, since no major improvements in process or element quality were apparent, studies using this binder system were stopped. The CAI polymer was later used, however, as an impregnant for the molded graphites.

Grade 277-15V Pitch-Indene Binder

Scouting experiments were made to obtain a useful binder system employing Grade 277-15V pitch,^(e) a coal-tar product. A mixture of 70 percent Grade 277-15V pitch and 30 percent

(e) Allied Chemical Corporation, Plastics Division.

indene was found to have a viscosity of 300 centipoises at 25° C, and the carbon produced from the mixture had a crystalline metallographic structure similar to the ITX-ACN-I binder.

Extrusion of experimental elements using this mixture was successful, and physically sound units were fabricated. However, the 15V pitch contained inorganic impurities that could, when carbonized, damage the coated uranium carbide NERVA fuel beads. Chemical-purity data of this material are presented in Table 21.

15V Pitch-Bound Elements - Groups of elements were extruded using a 15V pitch-indene mixture as a binder. Elements were made with and without Thermax and with fillers fired at 1,000 and 2,500° C. Physical properties of the elements are compared in Table 22 with elements bound with an ITX-ACN-I binder.

The tensile strength and ultimate strain data are presented in the graphs of Figures 26 and 27. These data show that the 15V pitch-bound elements were stronger than the ITX-ACN-bound elements.

CTE values of the 15V pitch-bound elements were equivalent to elements formulated with an ITX-ACN-I binder. The compressive, flexural, and tensile strengths of the 15V elements were slightly higher than the ITX-ACN-bound elements. However, 15V pitch contains impurities which cannot be easily removed and could be harmful to the NERVA fuel particles.

Thermal Expansion of Grade 277-15V and ITX Pitches - Some studies on the volume expansion (ΔV) of pitch materials over the temperature range from 25 to 250° C consisted of heating seven-gram samples in a 50-cubic centimeter dilatometer containing mercury.

A commercial pitch (Allied's Grade CP-277-15V) was compared with a synthetic pitch derived from ITX by oxidative polymerization. The latter softened at approximately 150° C. A volume expansion of 24 percent was measured for the 15V pitch over the temperature range from 25 to 200° C. No significant inflections in the temperature/ ΔV curves were observed. The ITX pitch had a volume expansion of 7.4 percent over the corresponding temperature range, and 17.3 percent over the temperature range from 25 to 225° C. Though apparently amorphous in the pitch form, the latter material retained

Table 21
TYPICAL GRADE 277-15V
PITCH ANALYSIS

Test	Analytical Values
Number of Samples ⁽¹⁾	4
Coking Carbon, 1,000° C (%) ⁽²⁾	41 to 58
Ash Content (%)	0.1
Molecular Weight (average)	363
Sulfur Content (%)	0.85
Oxygen Content (%)	1.66
X-Ray Diffraction, at 2,800° C	
Interlayer Spacing (Å) ⁽²⁾	3.363 to 3.3776
Lc (Å) ⁽²⁾	176 to 265
La (Å) ⁽²⁾	288 to 311
Typical Spectrographic Analysis on Ash (ppm) ⁽³⁾	
Al	3.0
B	2.3
Ca	-
Cr	< 6
Cu	< 0.3
Fe	< 3
Na	15
Ni	< 1.2
Pb	< 18
Si	3.1
V	< 0.3

(1) Number of samples represents coking carbon and X-ray diffraction data. The other analyses were normally not obtained.

(2) Low and high numbers represent the data spread.

(3) All others less than detectable limits.

Table 22
 PROPERTIES AND COMPOSITION OF 15V-PITCH AND
 ITX-ACN-I BOUND ELEMENTS

	Binder			
	15V	ITX-ACN	15V	ITX-ACN
<u>Santa Maria Coke Filler⁽¹⁾ - 2,500° C Firing Temperature</u>				
Thermax (%)	0	0	15	15
Binder Level (pph)	35	31	30	25
Extrusion Pressure (tons) ⁽²⁾	104	120	146	160
Bulk Density (gms/cc)	1.61	1.60	1.68	1.64
Electrical Resistance (milliohms/element inch)	204		232	256
Sonic Moduli ($\times 10^6$ psi)	0.8	1.0	1.0	1.0
Compressive Strength (psi)	8,950	7,280	8,340	6,610
Flexural Strength (psi)	3,550	2,900	2,760	2,210
Tensile Strength (psi)	3,065	2,050	3,725	1,925
Ultimate Tensile Strain (%)	0.33	0.18	0.30	0.18
Element Longitudinal CTE, 25 - 1,000° C ($\times 10^{-6}/^\circ$ C)	5.0	4.6	4.9	4.6
Mercury Porosimetry				
Bulk Density (gms/cc)	1.57	1.60	1.66	1.64
Real Density (gms/cc)	1.90	2.08	2.08	2.10
Mean Pore Size (μ m)	1.40	1.10	0.36	0.33
Open Porosity (%)	17.48	23.17	20.31	21.72
Thermal Stress Resistance (watts)	460 - 480	620 - 650	312 - 347	275 - 330
<u>Santa Maria Coke Filler - 1,000° C Firing Temperature</u>				
Thermax (%)	0	0	15	15
Binder Level (pph)	31.5	29	27.5	25
Extrusion Pressure (tons)	112	170	134	112
Bulk Density (gms/cc)	1.63	1.68	1.71	1.76
Electrical Resistance (milliohms/element inch)	207	182	-	210
Sonic Moduli ($\times 10^6$ psi)	1.2	1.3	1.3	1.4
Compressive Strength (psi)	13,850	13,060	15,780	12,120
Flexural Strength (psi)	6,780	5,440	6,340	3,650
Tensile Strength (psi)	3,875	3,060	3,875	-
Ultimate Tensile Strain (%)	0.37	0.30	0.38	-
Element Longitudinal CTE, 25 - 1,000° C ($\times 10^{-6}/^\circ$ C)	5.5	5.7	5.7	5.8
Mercury Porosimetry				
Bulk Density (gms/cc)	1.70	1.67	1.72	1.76
Real Density (gms/cc)	2.03	2.12	2.11	2.11
Mean Pore Size (μ m)	-	0.67	-	0.31
Open Porosity (%)	16.8	21.29	18.8	16.78
Thermal Stress Resistance (watts)	320 - 360	660 - 715	370 - 400	280 - 370

(1) Santa Maria Coke was obtained from the Collier Carbon and Chemical Corporation. The coke was further treated at the Y-12 Plant before use as a filler. The coke was ground and labeled as Blend 1. It was then heat treated to 1,000° C and 2,500° C.

(2) Reported pressure was tons on a six-inch-diameter extrusion press barrel.

considerable crystallinity and, softening at approximately 150° C, some recrystallization occurred when maximum temperatures remained below 190 to 200° C. Such a transition of amorphous to partially crystalline material was accompanied by a volume decrease. Thus, the relatively low expansion between 25 and 200° C reflects this phase transition. Further evidence of the presence of a crystalline phase was the significant volume expansion observed between 200 and 225° C. The melting point of dry ITX crystals was approximately 223° C, and the volume expansion between 200 and 225° C largely

reflected this melting transition of the dispersed crystalline phase. Temperature/ ΔV data suggested an increased value of $\Delta t/\Delta V$ over the range from 160 to 200° C, and a significant decrease in $\Delta t/\Delta V$ values between 200 and 225° C. Such data support the contention that some recrystallization occurred between 160 and 200° C, while fusion of a crystalline phase occurred between 200 and 225° C.

Viscosity of Type 15V Pitch in the Temperature Range from 125 to 300° C - The viscosity of Grade

CP 277-15V pitch was determined over the temperature range from 125 to 300° C by using a Brookfield continuous-recording viscometer. A significant decrease in viscosity was observed as the temperature approached 175° C. The viscosity at 175° C was approximately 250 centipoises. Changes with increasing temperature above 175° C were not great. The relationship between viscosity and temperature is presented in Figure 28.

Figure 27. BINDER ULTIMATE TENSILE STRAIN. (15V Pitch Versus the Isotruene-Acenaphthalene Mixture)

Grades 170 and 240 pitches are taken from a distillation process but at a controlled point along the column length. The vendor also has the ability to reduce the sulfur impurity level to values approaching 1,000 ppm or less.

It was decided to investigate the use of Grade 240 pitch as a potential binder source for the NERVA program because of the low impurity levels and the reproducibility of the pitch even though the pitch had a softening point of about 117° C which was higher than desired for NERVA applications. Previous extrusion studies had shown that it was desirable to use a binder having a viscosity of 250 centipoises or less when measured at room temperature.

Figure 26. BINDER TENSILE STRENGTHS. (15V Pitch Versus the Isotruene-Acenaphthalene Mixture)

Grade 240 Ashland Pitch-Indene Binder

During the NERVA fuel element studies, two commercial petroleum pitches (Grades 170 and 240)^(f) were investigated to determine if they could be used as raw-material sources. Typical chemical data on these materials are listed in Table 23. These two pitches are produced by a commercial process which appears to be capable of producing a reproducible product. Most commercial pitches are obtained from the bottom or waste stream of a distillation process, but the

(f) Obtained from Ashland Oil and Refining Company.

This viscosity permitted the use of standard NERVA mixing equipment. It was also decided to use indene as a diluent for the Grade 240 pitch since it had been successfully used with the ITX-ACN binder formulation.

At the time when this binder was being evaluated, a change in the extrusion mixing and blending philosophy occurred. All prior extrusions were made with binder levels which ranged from 20 to 30 percent. The optimum binder level was dependent on many process variables such as the type of filler carbon, the filler carbon surface area, and the amount of uranium loading. When a binder diluent was used in the manufacture of NERVA fuel elements, the percentage of diluent was normally added in addition to the total reported binder level.

Figure 28. VISCOSITY OF GRADE CP277-15V COAL-TAR PITCH.

Manufacturing problems arose with the use of Grade 240 pitch levels of 20 to 30 percent. Consequently, it was decided that the pitch-binder level in fuel elements had to be reduced in order to obtain a crack-free matrix. A binder system was, therefore, formulated which contained 53 percent Grade 240 pitch and 47 percent indene. This binder was made by simply melting the pitch and adding indene. When cooled to room temperature, the binder was a relatively nonviscous liquid which could be successfully used with the existing mixing equipment.

Use of this binder is further discussed in the Process Optimization section (Page 92).

LOW-FIRED CARBON FILLER PROGRAM^(5 - 12)

Program Logic

From the results of the Phase I and II matrix studies, it was apparent that the coefficient of thermal expansion of NERVA fuel elements could be raised by using selected graphite filler particles. It was also apparent that using high-fired graphite fillers would restrict the maximum CTE value to a level which was less than required for the NERVA program.

All of the NERVA fuel element studies before Pewee 2 had used a single binder and a variety of graphite fillers. The fillers had been heat treated to a high temperature in order to fully thermally stabilize them prior to final use. When these high-fired, stable graphite particles were mixed with a liquid binder and processed into fuel elements, the graphite particles were not affected by the fuel element process conditions. All of the element shrinkage was due to the action of the binder phase being converted into a carbon structure. The large volume changes associated with converting the liquid binder phase into a solid carbon phase resulted in a matrix which had very high residual internal stress regions in the binder carbon.

Table 23
ANALYSIS OF GRADES 170
AND 240 ASHLAND
PITCHES

Property	Grade 170	Grade 240
Softening Point ($^{\circ}$ C)	77	118
Molecular Weight (avg)	381	470
Ash Content (%)	0.042	0.053
Sulfur Content (%)	1.22	1.27
Oxygen Content (%)	0.25	0.18
Carbon Yield (%) ⁽¹⁾	49	60
X-Ray Diffraction Data ⁽²⁾		
Interlayer Spacing (A)	3.360	3.358
L_c (A)	520	860
L_a (A)	510	> 1,000
Spectrographic Analysis (ppm)		
Ag	< 1	< 1
Al	60	60
As	< 10	< 10
B	< 1	< 1
Ba	< 1	< 1
Be	< 1	< 1
Ca	2	20
Cd	< 1	< 1
Co	< 20	< 20
Cr	1	10
Cu	< 10	< 10
Fe	15	50
K	< 20	< 20
Li	< 10	< 10
Mg	< 10	10
Mn	< 1	< 1
Mo	< 1	< 1
Na	4	4
Ni	< 4	< 4
Pb	< 1	< 1
Si	100	200
Sn	< 1	< 1
V	< 1	< 1
W	< 10	< 10
Zn	< 60	< 60
Zr	< 2	< 2

(1) Carbonized in a closed graphite crucible using a heating time of about five days to 800° C and further heated to $2,800^{\circ}$ C in six hours.

(2) Carbon heated to $2,800^{\circ}$ C prior to this analysis.

It was postulated that a matrix could be made with fewer internal stresses being retained in the fuel element if the filler particles could also be allowed to shrink in volume. An ideal situation would be to have a filler carbon particle which would shrink at the same rate as the binder phase. In this manner, the binder carbon would not be stressed because it would be shrinking against a particle which was also shrinking in volume. It was postulated that an improved matrix could be obtained if the element carbon fillers were not fully stabilized and retained some volume shrinkage characteristics prior to the formation of a fuel element body. It was further surmised that an improved matrix would result if a thermoplastic-type resin binder was used. This type of material would retain a plastic phase up to about 450° C and, while plastic, would not be very sensitive to retained internal stresses caused by volume shrinkage during pyrolysis. A thermosetting resin such as Varcum 8251 is transformed into a rigid, nonyielding phase at temperatures of about 300° C.

A thermoplastic resin normally yields a well-ordered, low-modulus graphite phase which results in a graphite matrix with more yielding characteristics. A thermoplastic resin is converted into a glass-like carbon which cannot be easily converted into a soft graphite structure. Furthermore, it has a small crystallite size (less than 20 A) and is believed to be a carbon which could be readily attacked if exposed to a hot hydrogen gas stream.

A thermoplastic binder which produced a high carbon yield was desirable since the carbon yield and volume shrinkage were intermittently related. Further improvement could be realized by reducing the amount of binder used during the fuel element manufacture.

The development program was changed to investigate the use of matrix filler particles which had not been thermally stabilized. It was known that filler particles that were heat treated to

temperatures less than the stabilization point could be used in graphite manufacture. Crack-free graphites were expected to result in significant changes in the physical properties. Later examinations showed that the CTE values increased,^(13,14) but the change was very sensitive to the type of carbon precursor.

A variety of materials were studied in order to obtain a matrix having a CTE value equal to the carbides of niobium and zirconium.

Grinding Carbon Powders

The philosophy of the use of a broad spectrum of filler particle sizes was also changed with the studies using low-fired carbon powders. Originally it was believed that the best particle-packing density would occur by the use of a powder having particles ranging in size from a few micrometers to about 160 micrometers.

Carbon powders having this range of particle sizes were not easily obtained by conventional grinding and classification methods. Very early in the program it became apparent that the larger carbon particles could shrink in volume at a different rate than very small particles because some types of large carbon particles had internal void defects which were not readily detectable in the smaller particles (ie, less than 30 A). It was also found that smaller particles produced a more uniform and repeatable matrix when fabricated into fuel elements.

Various particle-size spectrums were studied; but, in general, a flour having a nominal 100 percent of the particles less than 80 micrometers and 90 percent less than 50 micrometers was used in most experiments. This spectrum was obtainable by conventional grinding and classification methods.

Isotruxene Elements

A quantity of 18 kilograms of isotruxene was carbonized to 900° C using a five-day coking cycle. This material was ground into extrusion powder. The powder blend was split and the fractions further heat treated to 1,000 and 1,500° C. A typical photomicrograph of the 1,000° C treated powder is presented in Figure 29, indicating that the powder had low internal porosity. The flour characterization data (Table 24) show that the surface area decreased with an increasing flour firing temperature. This trend had been observed with all other low-fired carbon flours. As expected, the carbon was free of sulfur. Iron was the major contaminant, which was added during the grinding operation. No attempt was made to remove this impurity.

Elements were extruded using the three powders. Extrusion data are presented in Table 25, and a typical extruded element matrix is provided in Figure 30. No major extrusion problems were observed. The elements, which were ITX-ACN bound, without Thermax, had higher-than-normal densities (~ 1.80 gms/cc). This trend toward higher densities, using organic resins as the carbon precursor, was also observed with cinnamylideneindene carbon.

Coefficient of thermal expansion values of the elements ranged from 6.16 to $7.16 \times 10^{-6}/^{\circ}\text{C}$ (25 to 1,000° C) and was dependent on the filler firing temperature. These

G644-1b

Figure 29. ISOTRUXENE CARBON FILLER CURED TO 1,000° C. (Sensitive Tint; 250X)

data are reported in the graph of Figure 31. All CTE values were high, but less than the primary POCO carbon elements which will be discussed in a later section (Page 83).

Cinnamylideneindene Elements

Organic resin studies had shown that isotropic and anisotropic carbon could be produced with CAI resin. A large supply of CAI powder was made and thoroughly washed to reduce the potassium level. It was later found, however, that the amount of potassium impurity had a major effect on the type of carbon produced. Low levels (< 250 ppm) produced anisotropic carbons, whereas approximately 4,000 ppm potassium produced an isotropic carbon. A 100-pound batch of CAI was calcined to 1,000° C. (The initial potassium level was about 2,300 ppm.) Later, studies revealed that this level would produce an intermediate-grade carbon precursor. The overall coke yield for the 100-pound run was 42 percent.

The CAI carbon was ground into powder for extrusion studies. A typical photomicrograph of the carbon is given in Figure 32. Anisotropic carbon particles can be readily seen. The ground powder was split into five portions and further heat treated to various temperatures.

Only the 1,000 and 2,500° C powders were fully characterized. Available data are reported in Table 26. These data show no sulfur contamination; iron was present due to the grinding operation. No effort was made to reduce any of the impurities. The 1,000° C fired powder contained some residual potassium.

Five sets of fuel elements were extruded to determine the physical properties as a function of the filler firing temperature. The available data are summarized in Table 27. Figure 33 contains a typical photomicrograph of an extruded element. Flexural strengths ranged from 3,680 to 8,320 psi, depending on the density and/or filler firing temperature.

CTE values ranged from a low of $4.63 \times 10^{-6}/^{\circ}\text{C}$ (25 to 1,000° C) with the 2,500° C fired powder to a high of $6.59 \times 10^{-6}/^{\circ}\text{C}$ (25 to 1,000° C) for the 1,000° C fired powder. These CTE data are presented graphically in Figure 31.

Grade 15V Coke Studies

Pressure-carbonized 15V pitch coke was ground and portions of the powder were heated treated at 1,000, 1,500, and 2,400° C. Elements were extruded with each of the fillers; the binder used was the ITX-ACN-I mixture. All flours had extremely poor extrusion characteristics, even when Thermax was added to the blends. Extruded elements made with the 1,000 and 1,500° C fillers produced "blistered" elements when graphitized; due, probably, to the impurities present in the fillers.

Table 24
CHARACTERIZATION OF ISOTRUXENE CARBONS

	Extrusion Number		
	666	667	668
Firing Temperature (° C)	900	1,000	1,500
Surface Area (m ² /gms)	9.4	7.2	4.44
Helium Density (gms/cc)	1.92	1.91	2.18
Pour Density (gm/cc)	0.62	0.71	0.75
Tap Density (gms/cc)	1.09	1.15	1.14
Particle Size Analysis (%)			
Screen Size (mesh)			
+60	< 0.1	0.7	0.2
-60 +100	2.8	5.2	7.0
-100 +140	4.3	2.3	4.4
-140 +200	3.8	6.2	7.0
-200 +270	1.9	4.4	5.7
-270 +325	5.4	2.5	3.7
-325	81.8	78.7	71.8
Micromerograph			
100% Less Than Size (μm)	130	195	180
90% Less Than Size (μm)	83	105	96
50% Less Than Size (μm)	15	39	39
25% Less Than Size (μm)	5	14	14
10% Less Than Size (μm)	3	5	5
Chemical Analysis (ppm)	900	1,000	1,500
Impurities (ppm)			
Ag	< 1	< 1	< 1
Al	30	30	40
B	6	12	10
Ba	2	2	2
Be	< 1	< 1	< 1
Ca	35	40	40
Cd	< 1	< 1	< 1
Co	< 20	< 20	< 20
Cr	200	250	500
Cu	10	10	10
Fe	1,000	1,000	1,000
K	20	20	20
Li	< 10	< 10	< 10
Mg	150	300	25
Mn	70	100	150
Mo	< 1	< 1	< 1
Na	25	35	20
Ni	50	50	500
P	< 100	< 100	< 100
Pb	7	4	< 1
Si	350	450	500
Sn	40	40	20
Ti	6	6	6
V	1	1	1
W	< 10	< 10	< 10
Zn	< 60	< 60	< 60
Zr	< 2	< 2	< 2
Loss at 100° C (%)	0.11	0.06	0.01
Ash Content (%)	0.56	0.40	0.49
Sulfur Content (%)	0.003	0.007	0.091

Table 25
PHYSICAL PROPERTIES OF ISOTRUXENE CARBON ELEMENTS

	Extrusion Number		
	666	667	668
Filler Firing Temperature ($^{\circ}$ C)	900	1,000	1,500
Binder Content (pph)	32.5	31	31
Extrusion Pressure (tons)	40	48	52
Bulk Density (gms/cc)			
Calculated	1.79	1.81	1.73
Laboratory	1.82	1.83	1.75
Electrical Resistance (milliohms/element inch)	223	225	232
Sonic Moduli, Longitudinal ($\times 10^6$ psi)	1.6	1.5	1.1
Compressive Strength, Average (psi)	14,500	15,200	10,100
Flexural Strength, Average (psi)	6,840	5,250	3,400
Coefficient of Thermal Expansion, 25 to 1,000 $^{\circ}$ C ($\times 10^{-6}/^{\circ}$ C)	7.16	7.11	6.16
Tensile Strength (psi)	-	-	2,520
Tensile Strain (%)	-	-	0.257

G683-7b

Figure 30. TYPICAL ISOTRUXENE CARBON EXTRUDED ELEMENT. (Flour Prefired to 1,000 $^{\circ}$ C; Sensitive Tint; 250X)

Physical Properties - Pertinent details of the manufacture and properties of the 15V coke elements are listed in Table 28. Bulk density of the extrusions from the 1,000 $^{\circ}$ C filler was comparable to the elements made from Santa Maria coke filler which will be discussed in the section to follow. Densities of the extrusions did not decrease with an increasing filler firing temperature, as was found in the Santa Maria coke groups.

CTE values decreased with an increasing filler firing temperature, as was the case with all of the low-fired coke groups. These CTE values were much lower than the Santa Maria coke elements (Figure 34), which was expected in view of the structural characteristics of the fillers. This type of carbon filler was not a NERVA candidate because of the low CTE values of the fuel elements.

Figure 31. COEFFICIENT OF THERMAL EXPANSION AS A FUNCTION OF THE FILLER FIRING TEMPERATURE.

Santa Maria Coke Studies

Coke Characteristics - An order for 225 tons of calcined Santa Maria coke (SMC) was obtained from the Collier Carbon and Chemical Corporation, a subsidiary of Union Oil Company of California. The CMF-13 group at LASL were studying this material and their analyses indicated it to be a possible candidate filler for use in the NERVA program. The LASL study had shown that the material could be ground, fired, and fabricated into graphite pieces which were fine-grained, isotropic bodies.

Figure 32. CINNAMYLIDENEINDENE EXTRUSION POWDER WITH 2,300 PPM POTASSIUM. (Sensitive Tint; 250X)

Santa Maria coke was received in a spherical granular form with a minor (< 5%) portion of included fine particles (-40 mesh). The coke had been rotary calcined to a low-volatile-content (LV) coke at about 1,100°C by the supplier. Laboratory analysis (Table 29) showed that the material contained high levels of iron, sodium, nickel, silicon, vanadium, and sulfur.

Table 26
CHARACTERIZATION OF CINNAMYLIDENEINDENE CARBONS

	Extrusion Number				
	670	671	672	673	674
Firing Temperature (° C)	1,000	1,100 ⁽¹⁾	1,200 ⁽¹⁾	1,500 ⁽¹⁾	2,500
Surface Area (m ² /gm)	15.43				2.91
Helium Density (gms/cc)	1.92				2.19
Pour Density (gms/cc)	0.51				
Tap Density (gms/cc)	0.95				
Particle Size Analysis (%)					
Screen Size (mesh)					
+60	0.28				
-60 +100	2.86				
-100 +140	2.85				
-140 +200	5.90				
-200 +270	7.36				
-270 +325	4.11				
-325	76.84				
Micromerograph					
100% Less Than Size (μm)	195				
90% Less Than Size (μm)	68				
50% Less Than Size (μm)	22				
25% Less Than Size (μm)	9				
10% Less Than Size (μm)	4				
Chemical Analysis (ppm)	1,000	1,100	1,200	1,500	2,500
Ag	2				
Al	10				
B	3				
Ba	< 1				
Be	< 1				
Ca	20				
Cd	< 1				
Co	< 20				
Cr	40				
Cu	15				
Fe	1,200				
Li	< 10				
Mg	< 10				
Mn	100				
Mo	< 1				
Na	10				
Ni	50				
P	< 100				
Pb	4				
Si	100				
Sn	10				
Ti	15				
V	< 1				
W	< 10				
Zn	< 60				
Zr	< 2				
Loss at 1000° C (%)	0.58				
Ash Content (%)	0.88				
Sulfur Content (%)	0.008				

(1) Not analyzed.

Table 27
PHYSICAL PROPERTIES OF CINNAMYLIDENEINDENE CARBON ELEMENTS

	Extrusion Number				
	670	671	672	673	674
Filler Firing Temperature ($^{\circ}$ C)	1,000	1,100	1,200	1,500	2,500
Binder Content (pph)	35	34	34	34	34
Extrusion Pressure (tons)	60	86	80	86	50
Bulk Density (gms/cc)					
Calculated	1.82	1.73	1.70	1.72	1.66
Laboratory	1.77	1.74	1.69	1.72	1.70
Compressive Strength, Average (psi)	16,650	11,300	11,510	5,585	7,800
Flexural Strength, Average (psi)	8,320	7,000	5,980	5,290	3,680
Sonic Moduli, Longitudinal ($\times 10^6$ psi)	1.5	1.4	1.3	1.3	1.0
Coefficient of Thermal Expansion, 25 to 1,000 $^{\circ}$ C ($\times 10^{-6}/^{\circ}$ C)	6.59	5.82	5.83	6.04	4.63

G766-1

Figure 33. TYPICAL CINNAMYLIDENEINDENE EXTRUDED ELEMENT. (Flour Prefired to 1,000 $^{\circ}$ C; CAI Contained 2,300 ppm Potassium; Sensitive Tint; 250X)

Grinding Studies - The LASL CMF-13 program included a study to determine the grinding properties of the coke. In order to obtain NERVA element data it was jointly agreed by LASL and Y-12 to grind the initial test lots in the as-received, calcined state. It was recognized that grinding in this state may not be optimum, but the CMF-13 data suggested that some degree of particle size control could be obtained when ground in the calcined state.

Initial grinding tests were essentially a duplication of the LASL efforts except that larger test lots were ground. The full fuel element development program required quantities of material that were sufficiently large for manufacturing the elements. The initial studies required that three particle spectrums be produced. These spectrums were loosely defined as Blends 1, 2, and 3, as listed in Table 30. Blend 1 had a maximum particle size of 60 mesh, and more than 50 percent of the particles were to be less than 325 mesh ($-44 \mu\text{m}$). Blend 2 was a near duplication of the GL 1008 flour spectrum which has a maximum particle size of

Table 28
ELEMENT DATA FOR GRADE 15V COKE
(ITX-ACN-I Binder)

	Extrusion Number(1)			
	656	655	657	654
Filler Firing Temperature ($^{\circ}$ C)	1,000	1,500	2,400	2,400
Thermax (%)	15	15	15	0
Binder Content (%)	26	26	28	34
Extrusion Pressure ($\times 10^3$ lbs)	120	94	120	120
Bulk Density (gms/cc)	1.72	1.72	1.73	1.66
Longitudinal CTE, 25 - 1,000 $^{\circ}$ C ($\times 10^{-6}/^{\circ}$ C)	4.9	4.7	4.2	4.2
Flexural Strength (psi)				
Maximum	3,290	3,370	3,770	4,650
Minimum	2,920	2,850	3,010	4,210
Average	3,240	3,120	3,290	4,430
Compressive Strength (psi)				
Maximum	9,380	8,210	9,260	9,460
Minimum	5,180	5,410	5,230	7,290
Average	6,940	7,400	7,070	8,780
Mercury Porosimetry				
Bulk Density (gms/cc)	1.72	1.73	1.74	1.69
Real Density (gms/cc)	2.14	2.15	2.08	2.04
Open Porosity (%)	19.89	19.54	16.37	17.4

(1) Elements graphitized at 2,200 $^{\circ}$ C.

Figure 34. COEFFICIENT OF THERMAL EXPANSION AS A FUNCTION OF THE FILLER FIRING TEMPERATURE.

60 mesh and a nominal 30 percent of the particles less than -325 mesh. Blend 3 was a blend having a maximum particle size of 60 mesh, and about ten percent of the particles were expected to be less than -325 mesh. These three blends were extruded into elements and also die pressed into thermal shock discs. Physical properties of each type were determined.

During the grinding studies, the coke was ground using three mills at various feed rates and settings—a hammer mill, a roller mill, and a Micro Atomizer mill. The coke was passed through the hammer mill one time which produced about a 30 weight percent yield of -60 mesh powder, and about 4 weight percent of the material was -325 mesh. Several passes through the mill increased the overall -60 mesh yield to about 50 percent. The coke, when passed through the roller mill, had about the same yield as through the hammer mill, and the spectrum was similar to the hammer-mill product.

For experimental studies, 200 to 300 pounds of coke were ground in each mill. The coke was subsequently screened through a 60-mesh sieve and used in element fabrication studies.

Coke had been ground in the Micro Atomizer at a variety of motor speeds. Spectrums from each speed were determined. In general, low speeds (400 to 1,200 rpm) produced the same

particle-size spectrum after the ground coke was sieved through a 60-mesh screen. The +60 mesh fraction decreased with increasing motor speeds. At a speed of 1,750 rpm, a test portion of flour (~50 lbs) was ground which had 80 percent of the particles less than 60 mesh in size. The -60 mesh fraction contained a nominal 20 percent of -325 mesh particles.

Impurities - Damage to the pyrolytic fuel bead containment shells by various metallic impurities in graphite matrices has been documented. In particular, the iron, nickel, silicon, and vanadium contents in the Santa Maria coke were objectionable in the presence of fuel beads.

Boron was originally reported at two to eight ppm from a significant number of Santa Maria coke samples. Three attempts to reduce this impurity by gaseous purification treatments did not lower the measured boron content. Finally, very careful analytical and sample-preparation techniques in an isolated laboratory established the absolute boron level at one ppm in the as-received coke. The original boron measurements were shown to be biased by a high laboratory background level resulting from prior analyses of high-boron-content samples.

Sulfur was present at a markedly high level. However, no interaction between pyrolytic bead shells and sulfur was recognized. Although unknown, sulfur and the thermoplastic binder interaction was not believed to be detrimental at this time. Evolution of appreciable quantities of gaseous sulfur from elements during graphitization could pose a problem. Therefore, reduction of the sulfur content was advisable prior to incorporating the flour into elements.

Removal of the principal metallic impurities and significant reduction of the sulfur was warranted for the use of Santa Maria coke as an element filler carbon. The prime process goal was to establish a gaseous purification process that was effective at the lowest practical temperature consistent with retaining the desired low-fired filler carbon properties.

In an effort to purify this material, a blend of ground Santa Maria coke was heat treated in a chlorine atmosphere for several hours at 1,000° C. As noted in Table 31, the chlorine-treated powder had essentially the same purity level as the raw Santa Maria coke. In addition, the treated coke did have a high level of chlorine remaining in the powder. Because the powder was tightly packed into graphite crucibles for processing, it is thought that the poor contact between the gas and powder limited the ability to remove significant amounts of impurities.

Several trial purification runs were made using various blends of Santa Maria coke powders. It was thought that the less densely packed granular coke particles would be easier to purify than the ground powders. A production purification process was derived from a series of experimental furnace runs. The process treated 120-kilogram quantities of dried, screened

Table 29
SANTA MARIC LOW-
VOLATILE COKE
ANALYSIS

Element	ppm ^(1,2)
Ag	< 1
Al	40
B	5
Ba	6
Be	< 1
Ca	60
Cd	< 1
Co	< 20
Cr	6
Cu	< 10
Fe	400
Mg	40
Mn	5
Mo	10
Na	500
Ni	500
P	< 100
Si	400
V	800
Zn	< 60

- (1) Average values of several samples taken from the as-received coke.
- (2) Weight loss at 1100° C, 0.31 to 4.56 percent; ash, 0.56 to 0.84 percent; sulfur, 4.20 to 5.35 percent.

Table 30
SANTA MARIA FLOUR EVALUATION

Property	Blend 1 Mikro-Atomizer (fast speed)	Blend 2 Mikro-Atomizer (1,750 rpm)	Blend 3	
			Hammer	Roller
Density (gms/cc)				
Pour	0.22	0.94	0.908	0.833
Tap	0.42	1.12	1.081	1.006
Helium	2.04	1.98	2.00	1.98
Particle Size Data				
Screen Size (mesh)				
+60	1.2	0.9	0.5	0.3
-60 +100	9.6	21.8	31.2	36.6
-100 +140	11.2	19.3	24.3	29.0
-140 +200	13.7	20.5	18.0	10.6
-200 +270	14.1	1.1	8.3	5.7
-270 +325	4.2	15.3	5.4	3.8
-325	46.0	21.1	12.2	13.9
Micromerograph				
100% Less Than Size (μm)	180	190	190	190
90% Less Than Size (μm)	93	115	125	125
80% Less Than Size (μm)	73	105	103	115
70% Less Than Size (μm)	59	95	90	105
60% Less Than Size (μm)	46	84	80	93
50% Less Than Size (μm)	33	73	70	80
40% Less Than Size (μm)	17	60	60	70
30% Less Than Size (μm)	9	44	49	56
20% Less Than Size (μm)	5	22	37	42
10% Less Than Size (μm)	2.8	8	20	22
X-Ray Diffraction (heated to 2,800° C)				
L_c (Å)	148	130	168	116
L_a (Å)	326	534	422	453
d_{004} (Å)	1.6874	1.6879	1.6848	1.6882
d_{110} (Å)	1.2298	1.2302	1.2298	1.2298

granules at 1,300° C by using chlorine and argon as the treatment gases. Granules after purification were milled into a flour which was then screened, magnetically treated for iron removal, and blended. Table 32 provides a listing of Purification Batches 13-1 through 13-4. These data show that metallic impurities and sulfur were effectively reduced to low levels.

Nonfueled Extrusion Studies - A series of unloaded elements was extruded to study several parameters. The SMC filler was ground in the as-received, 1,100° C fired state into three basic particle-size spectrums. These spectrums were labeled as fine (SM-1), medium (SM-2), and coarse (Williams mill). A representative quantity of the fine ground material (SM-1) was heat treated at various temperatures up to 2,500° C. The medium (SM-2) and coarse (Williams mill) powders were heated to 2,500° C prior to extrusion. Analyses of the powders used in these experiments are reported in Table 33. Of interest in these data is the reduction of impurities with an increased firing temperature, which was expected. The percent ash after firing to 1,200° C was 0.725 percent, whereas the 2,500° C powder had a reported ash value of 0.058 to 0.40 percent.

The basic goals of this study were to establish the physical properties of elements as a function of: (1) the filler-firing temperature, (2) particle size distribution, (3) nongraphitizing and graphitizing binders, and (4) Thermax content.

1. Filler-firing temperature. The SM-1 blend was selected as the filler starting material for these studies. Elements were made using Varcum 8251 and ITX-ACN-I binders, and with fillers which had been pre-fired at several temperatures. The units were extruded with and without the addition of Thermax.

The primary effect of the filler-firing temperature series was expected to be related to the CTE of the elements. Changes made in the element CTE values are graphically indicated in Figure 35.

The experiments produced the following information:

- a. Element CTEs were very sensitive to the filler-firing temperature. High values were always obtained with low-fired fillers.
- b. Graphitizable resin-bound elements produced CTE values slightly higher than the Varcum-bound elements.

- c. Thermax addition did not significantly change the element's CTE.

- d. The filler particle size spectrum did not greatly change the element's CTE, but did change the bulk density.

- e. Flexural strengths of the graphitizable resin groups increased with decreased filler-firing temperatures.

2. Particle-size distribution. Santa Maria coke, heated to 2,500° C, was ground into three particle-size distributions and used for this study. All elements were bound with the

Table 31
CHARACTERISTICS OF LOW-FIRED
SANTA MARIA COKE POWDER

Property	Cl ₂ Leached (1,000° C)	As Ground
Sulfur Content (%)	2.74	3.17
Chlorine Content (%)	1.54	0.07
Ash Content (%)	-	0.513
Spectrographic Analysis ⁽¹⁾ (ppm)		
Al	10	50
B	1	1
Ba	3	2
Ca	125	150
Cr	6	6
Cu	10	10
Fe	275	600
Mg	20	60
Mn	2	4
Mo	10	6
Na	10	400
Ni	600	800
Si	200	650
Ti	10	10
V	900	700
Surface Area (m ² /gm)	7.54	13.45
Helium Density (gms/cc)	1.93	1.95
Pour Density (gm/cc)	0.56	0.47
Tap Density (gm/cc)	0.84	0.96
Wet Screen Mesh (%)		
+60	0.32	0.60
-60 +100	3.40	3.40
-100 +140	7.48	6.20
-140 +200	11.34	10.45
-200 +270	3.95	7.92
-270 +325	4.01	3.42
-325	69.49	68.53
Micromerograph		
100% Less Than Size (μm)	130	107
90% Less Than Size (μm)	81	73
50% Less Than Size (μm)	38	17
25% Less Than Size (μm)	17.5	4.6
10% Less Than Size (μm)	4.0	3.0

(1) All others less than the detectable limits.

Table 32
CHARACTERISTICS OF SANTA MARIA
COKE PURIFIED FLOUR

Chemical Analysis							
Element	ppm	Element	ppm	Element	ppm	Element	ppm
Batch 13-1 (175-pound portion) ⁽¹⁾							
Ag	< 1	Ca	2	Fe	40	Ni	< 4
Al	15	Cd	< 1	Mg	< 10	P	< 100
B	1	Co	< 20	Mn	< 1	Si	40
Ba	2	Cr	< 10	Mo	< 1	V	35
Be	< 1	Cu	< 10	Na	< 1	Zn	< 60
Batches 13-2, 13-3, and 13-4 (500-pound portions) ⁽²⁾							
Ag	< 1	Ca	2	Fe	< 10	Ni	< 4
Al	10	Cd	< 1	Mg	< 10	P	< 100
B	1	Co	< 20	Mn	< 1	Si	13
Ba	< 1	Cr	< 1	Mo	< 1	V	2
Be	< 1	Cu	< 10	Na	< 1	Zn	< 60
Physical Properties							
Mesh Size Screen		Batch 13-1 (% retained)		Batches 13-2, 13-3, and 13-4 (% retained)			
60		0.1		0.1			
70		0.7		1.3			
100		3.4		4.0			
140		6.7		5.4			
200		13.0		12.2			
270		16.1		8.1			
325		8.6		2.9			
<325		51.4		67.0			
Helium Density (gms/cc)		2.13		2.22			
Surface Area (m ² /gm)		21.25		18.80			
Micromerograph							
90% Less Than Size (μm)		85.0		74.3			
50% Less Than Size (μm)		37.5		27.4			
10% Less Than Size (μm)		3.5		2.8			

(1) Drying loss at 110° C, 2,630 ppm; ash, 170 ppm; sulfur, 3,200 ppm.

(2) Drying weight loss at 110° C, 2,100 ppm; ash, 165 ppm; sulfur, 2,800 ppm.

nongraphitizing binder (Varcum 8251), and some of the elements contained Thermax. The blends were identified as "fine", "medium", and "coarse". Particle-size distributions are reported in Table 33.

These element data (Table 34) show that the fine and medium grinds produced the same CTE element, but an increase in CTE was noted with the coarse grind. Flexural strengths decreased as the filler size distribution increased. Bulk densities also decreased as the filler size distribution increased.

Table 33
CHARACTERIZATION OF SEVERAL SANTA MARIA FLOURS

	Blend Number					
	SM-1	SM-1	SM-1	SM-1	SM-2	Williams Mill
Firing Temperature ($^{\circ}$ C)	1,100	1,200	1,500	2,500	2,500	2,500
Surface Area (m^2/gm)	11.52	5.56	5.19	4.86	2.68	1.35
Helium Density (gms/cc)	1.87	2.05	2.05	2.10	2.15	1.96
Pour Density (gm/cc)	0.562	0.676	0.661	0.608	-	-
Tap Density (gms/cc)	0.993	1.070	1.108	0.987	-	-
Particle Distribution (wt %)						
Wet Screen Size (mesh)						
+60	0.01	1.91	0.94	2.27	0.30	0.50
-60 +100	7.09	5.45	7.40	8.73	9.50	30.80
-100 +140	8.75	10.29	7.61	-	14.70	23.50
-140 +200	12.58	13.86	14.45	14.57	20.20	17.80
-200 +270	8.63	8.90	10.89	10.70	14.10	8.40
-270 +325	5.26	3.05	3.22	6.79	9.00	6.10
-325	57.61	56.53	55.50	41.46	31.50	12.80
Micromerograph						
100% Less Than Size (μm)	108.0	125.0	125.0	186.0	186.0	195.0
90% Less Than Size (μm)	87.6	85.0	85.0	91.0	83.0	119.0
50% Less Than Size (μm)	43.8	32.5	33.6	33.5	42.0	72.0
25% Less Than Size (μm)	7.2	7.8	9.0	8.4	9.6	38.0
10% Less Than Size (μm)	3.4	3.6	3.6	3.9	3.0	9.0
X-Ray Diffraction Analysis						
d ₀₀₄ (A)	-	-	-	1.6860	-	-
d ₁₁₀ (A)	-	-	-	1.2300	-	-
L _a (A)	-	-	-	367	-	-
L _c (A)	-	-	-	156	-	-
Chemical Analysis						
Loss at 100 $^{\circ}$ C (%)	0.190	0.037	0.023	0.10	0.01	-
Ash Content (%)	1.728	0.725	0.682	0.40	0.058	-
Impurities (ppm)						
Ag	1	1	1	< 1	< 1	-
Al	100	150	130	< 10	< 10	-
B	1	1	1	< 1	1	-
Ba	< 1	< 1	< 1	6	2	-
Be	< 1	< 1	< 1	< 1	< 1	-
Ca	200	200	200	100	40	-
Cd	< 1	< 1	< 1	< 1	< 1	-
Co	< 20	< 20	< 20	< 20	< 20	-
Cr	6	15	10	4	3	-
Cu	10	40	15	< 10	< 10	-
Fe	1,000	1,100	1,000	400	80	-
K	< 20	40	20	< 20	< 20	-
Li	< 10	< 10	< 10	< 10	< 10	-
Mg	60	70	60	< 10	< 10	-
Mn	6	8	7	< 1	< 1	-
Mo	8	10	12	10	8	-
Na	50	100	60	< 1	< 1	-
Ni	500	700	600	125	35	-
P	< 100	< 100	< 100	< 100	< 100	-
Pb	1	< 1	< 1	< 1	< 1	-
Si	300	100	100	< 10	< 10	-
Sn	< 1	< 1	< 1	< 1	< 1	-
Ti	15	15	15	20	15	-
V	600	650	700	1,000	800	-
W	< 10	< 10	< 10	< 10	< 10	-
Zn	< 60	< 60	< 60	< 60	< 60	-
Zr	< 2	< 2	< 2	< 2	< 2	-

3. Nongraphitizable and graphitizable binder. Santa Maria coke powder, pre-fired to both 1,100 and 2,500° C, was selected for this study. Elements were extruded with Varcum 8251 (nongraphitizing) and ITX-ACN-I (graphitizing) binders. Thermax was also used in some of the experiments.

4. Thermax content.

Varcum with Thermax elements. Physical properties of this group made with Varcum, Thermax, and fillers fired to variable temperatures are listed in Table 35. Of interest in these data is the reduction in flexural strength noted with a reduction in the filler-firing temperature. CTE values increased with a decreasing filler-firing temperature. Past studies have shown that, with Varcum binder, the flexural strength decreased with increasing CTE values.

Varcum without Thermax elements. Physical properties for these elements are listed in Table 36. Again, the flexural strength decreased with a decreasing filler-firing temperature. CTE values increased with a decreasing filler-firing temperature.

Figure 35. COEFFICIENT OF THERMAL EXPANSION VARIATION AS A FUNCTION OF THE COKE FIRING TEMPERATURE.

Table 34
VARIABLE PARTICLE SIZE SPECTRUMS FOR SANTA MARIA COKE

	Blend Number				
	SM-1	SM-1	SM-2	SM-2	Williams Mill
Flour Grind(1)	Fine	Fine	Medium	Medium	Coarse
Thermax Content (%)	0	15	0	15	15
Extrusion Number	629	628	633	632	630
Binder Content (pph)	29	25	24	24	25
Extrusion Pressure (x 10 ³ lbs)	132	142	120	120	178
Bulk Density (gms/cc)	1.80	1.87	1.82	1.86	1.78
Electrical Resistance (milliohms/element inch)	163	185	146	175	183
Sonic Moduli (x 10 ⁶ psi)	1.5	1.9	1.7	1.8	1.5
Compressive Strength (psi)	13,830	18,300	14,630	16,710	13,710
Flexural Strength (psi)	5,280	6,050	5,650	5,950	4,830
Element Longitudinal CTE, 30 to 1,000° C (x 10 ⁻⁶ /° C)	4.8	4.8	5.0	4.8	5.2
Mercury Porosimetry					
Bulk Density (gms/cc)	1.80	1.88	1.82	1.86	1.78
Real Density (gms/cc)	1.96	1.93	1.94	1.92	1.92
Mean Pore Size (μm)	0.16	0.031	0.12	0.043	0.43
Open Porosity (%)	8.19	2.51	5.83	3.22	7.39

(1) All fillers graphitized to 2,500° C prior to extrusion. All elements were bound with Varcum 8251.

Table 35
 VARCUM-BOUND SANTA MARIA COKE
 ELEMENTS CONTAINING THERMAX

	Extrusion Number	
	626	628
Flour Firing Temperature ($^{\circ}$ C)(1)	1,100(2)	2,500
Binder Content (pph)	25	25
Extrusion Pressure ($\times 10^3$ lbs)	180	142
Bulk Density (gms/cc)	1.83	1.87
Electrical Resistance (milliohms/element inch)	-	185
Sonic Moduli ($\times 10^6$ psi)	1.7	1.9
Compressive Strength (psi)	16,420	18,300
Flexural Strength (psi)	4,110	6,050
Element Longitudinal CTE, 30 to 1,000 $^{\circ}$ C ($\times 10^{-6}/^{\circ}$ C)	5.5	4.8
Mercury Porosimetry		
Bulk Density (gms/cc)	-	1.88
Real Density (gms/cc)	-	1.93
Mean Pore Size (μ m)	-	0.031
Open Porosity (%)	-	2.51

- (1) Santa Maria Blend SM-1 was fired at the stated temperatures. Thermax (15%) was added prior to mixing and extrusion. All elements were fired to 2,500 $^{\circ}$ C prior to testing and evaluation.
 (2) Nominal value; material was the as-received coke from the vendor. All others fired at Y-12.

The CTE value was not affected by the Thermax content (Table 35 versus Table 36). Varcum binder demand was increased four percent by eliminating the Thermax.

ITX-ACN-I mixture with Thermax. Physical property data for these elements are noted in Table 37. CTE values for the elements were sensitive to the filler-firing temperature, and the values were generally higher than the Varcum-bound pieces. Bulk densities and sonic moduli values were expected to be lower than the Varcum-bound elements. Flexural strengths increased with decreasing filler-firing temperatures, which was not the case with the Varcum-bound elements. The flexural strength was considered to be high when related to the low bulk density and modulus.

ITX-ACN-I mixture without Thermax. Physical properties for these elements are given in Table 38. Again, a four percent binder increase was noted, due to the elimination of the Thermax particles. CTE data again showed a significant variation and were related to the filler-firing temperature. Flexural strengths increased with decreasing filler-firing temperatures. The group made with filler, fired to 1,100 $^{\circ}$ C, had an average flexural strength of 5,440 psi, which was very good when related to the low density and modulus. Bulk densities were low, but increased with decreasing filler-firing temperatures.

These data (Table 38) when compared to the ITX-ACN-I mixture with the Thermax group (Table 37) showed no major change except that a reduction occurred in the electrical resistance of the element. The group without Thermax had lower electrical

Table 36
 VARCUM-BOUND SANTA MARIA COKE
 ELEMENTS WITHOUT THERMAX

	Extrusion Number		
	627	631	629
Flour Firing Temperature ($^{\circ}$ C)(1)	1,100	1,500	2,500
Binder Content (pph)	29	29	29
Extrusion Pressure ($\times 10^3$ lbs)	166	158	132
Bulk Density (gms/cc)	1.82	1.87	1.80
Electrical Resistance (milliohms/element inch)	-	188	-
Sonic Moduli ($\times 10^6$ psi)	1.6	1.8	1.5
Compressive Strength (psi)	18,250	17,930	13,830
Flexural Strength (psi)	3,890	5,140	5,280
Element Longitudinal CTE, 30 to 1,000 $^{\circ}$ C ($\times 10^{-3}/^{\circ}$ C)	5.5	5.5	4.8
Mercury Porosimetry			
Bulk Density (gms/cc)	1.83	1.87	1.80
Real Density (gms/cc)	1.98	1.98	1.96
Mean Pore Size (μ m)	0.024	0.028	0.16
Open Porosity (%)	7.70	5.37	8.19

(1) Santa Maria Filler Blend SM-1 was fired to the stated temperature except for the 1,100 $^{\circ}$ C group which was the nominal temperature stated by the vendor. All elements were fired to 2,500 $^{\circ}$ C prior to testing and evaluation.

resistances than the group with Thermax. Thermal conductivities of the elements have not been measured. However, a decreased electrical resistance normally indicates a decreased thermal conductivity.

Thermal Stress, Tensile, and Strain Results - Thermal-stress evaluations were completed on extruded Santa Maria coke elements. These elements were part of an evaluation of the effects caused by changes in the filler-firing temperature, binder type, Thermax addition, and filler particle size distribution. Prior to the thermal stress measurements, all elements received a final heat treatment at 2,200 $^{\circ}$ C.

The thermal-stress specimens were machined from extruded elements and consisted of wafers that were 100 ± 1 mils thick. Twenty wafers per extrusion batch were examined. The thermal-stress test consisted of striking an arc (using a welding machine) onto the center hole of the wafer. The power to the machine was preset prior to striking the arc. Data on the energy, in watts, which was impressed on the wafer were recorded. The power was progressively raised until the wafer ruptured. In no case was a wafer struck with the arc more than one time. The reference material used in these tests was a Pewee 2 element made with POCO AXF-Thermax filler, bound with Varcum.

Relative values are tabulated in Table 39 along with other physical properties. The thermal stress data are also graphically reported in Figure 36. The Pewee 2 base-line element had a threshold value of 250 watts; the ITX-ACN-bound SMC pieces, made without Thermax, had

Table 37
ISOTRUXENE-ACENAPHTHALENE-INDENE
BOUND SANTA MARIA COKE
ELEMENTS WITH THERMAX

	Extrusion Number			
	636	642	639	634
Flour Firing Temperature ($^{\circ}$ C)(1)	1,100	1,200	1,500	2,500
Binder Content (pph)	25	25	25	25
Extrusion Pressure ($\times 10^3$ lbs)	112	124	178	160
Bulk Density (gms/cc)	1.76	1.70	1.70	1.64
Electrical Resistance (milliohms/element inch)	210	257	267	256
Sonic Moduli ($\times 10^6$ psi)	1.4	1.1	1.1	1.0
Compressive Strength (psi)	12,120	10,070	9,750	6,610
Flexural Strength (psi)	3,650	4,190	3,650	2,210
Element Longitudinal CTE, 30 to 1,000 $^{\circ}$ C ($\times 10^{-6}/^{\circ}$ C)	5.8	5.7	5.7	4.6
Mercury Porosimetry				
Bulk Density (gms/cc)	1.76	-	-	1.64
Real Density (gms/cc)	2.11	-	-	2.10
Mean Pore Size (μ m)	0.31	-	-	0.33
Open Porosity (%)	16.78	-	-	21.72

(1) Santa Maria Filler Blend SM-1 was fired to the stated temperature except for the 1,100 $^{\circ}$ C group which was the nominal temperature stated by the vendor. All elements were fired to 2,500 $^{\circ}$ C prior to testing and evaluation.

values of 590 to 715 watts. Elements made with fillers prefired to 1,100 $^{\circ}$ C (which was the lowest in this test group) produced the highest threshold levels (660 to 715 watts). Thermax addition reduced the threshold values by about a factor of two. Filler particle size distribution changes did not significantly change the thermal stress resistance values. All of these specimens were bound with Varcum and the flour distribution changes were not great except for the -325 mesh portions. Flour distributions for the samples were previously reported (Table 33). Varcum binder, in general, produced low thermal stress values.

Ultimate Tensile Strength and Strain (percent) - Several sections of each of the Santa Maria coke (SMC) elements were broken in flexure using four-point loading. These data are reported in Table 40. A six-inch piece of each element type was tested in tension by the ORNL to establish the ultimate tensile strength. Strain gages were also placed on the piece to monitor the strain-to-failure percentage. These element data are also noted in Table 40, plus comparative data on the Pewee 2 base-line element and as-purchased POCO AXM graphite.

Filler-Firing Temperature Series - The tensile and strain data of ITX-ACN and Varcum-bound elements have been graphically reported in Figures 37 and 38. These data show that the Varcum-bound element strengths were not significantly changed by changes in the filler-firing temperatures. The Varcum-bound elements had a tensile strength of about 3,000 psi and an ultimate tensile strain ranging from 0.21 to 0.32. The ITX-ACN-bound elements had strengths which increased with decreasing filler-firing temperatures. Tensile strain values also increased with decreasing filler-firing temperatures. These same trends were

Table 38
ISOTRUXENE-ACENAPHTHALENE-INDENE
BOUND SANTA MARIA COKE ELEMENTS
WITHOUT THERMAX

	Extrusion Number			
	637	643	640	635
Flour Firing Temperature ($^{\circ}$ C)(1)	1,100	1,200	1,500	2,500
Binder Content (pph)	29	28.5	29	31
Extrusion Pressure ($\times 10^3$ lbs)	170	186	176	120
Bulk Density (gms/cc)	1.68	1.63	1.63	1.60
Electrical Resistance (milliohms/element inch)	182	213	207	-
Sonic Moduli ($\times 10^6$ psi)	1.3	1.1	1.1	1.0
Compressive Strength (psi)	13,060	8,100	8,620	7,280
Flexural Strength (psi)	5,440	2,240	3,770	2,900
Element Longitudinal CTE, 30 to 1,000 $^{\circ}$ C ($\times 10^{-6}/^{\circ}$ C)	5.7	5.5	5.5	5.1
Mercury Porosimetry				
Bulk Density (gms/cc)	1.67	-	-	1.60
Real Density (gms/cc)	2.12	-	-	2.08
Mean Pore Size (μ m)	0.67	-	-	1.10
Open Porosity (%)	21.29	-	-	23.17

(1) Santa Maria Filler Blend SM-1 was fired to the stated temperature except for the 1,100 $^{\circ}$ C group which was the nominal temperature stated by the vendor. All elements were fired to 2,500 $^{\circ}$ C prior to testing and evaluation.

also observed with the bulk densities. The elements made at the lowest filler-firing temperature had tensile strengths that were greater than the Varcum-bound pieces, even though the bulk density was only 1.68 gms/cc; whereas, the Varcum-bound pieces had densities up to 1.87 gms/cc. An abnormal data point was observed with one element (628) compounded with Thermax and Varcum. This specimen had a high tensile strength of 4,125 psi, but a strain-to-failure percentage of only 0.32.

Variable Filler Particle Size Spectrum - These series were all made with Santa Maria flours prefired to 2,500 $^{\circ}$ C and were Varcum bound. Pertinent data are given in Figures 39 and 40. There were no apparent differences in the tensile or strain-to-failure values of the elements which could be attributed to the filler particle size changes. The tensile strengths ranged from 3,230 to 4,125 psi and the strain ranged from 0.25 to 0.30 percent.

Impregnation of Santa Maria Coke Elements - Elements made with SMC filler (1,100 $^{\circ}$ C) without Thermax and bound with an ITX-ACN mixture were gaseous impregnated with pyrocarbon to variable densities. Some of the elements were impregnated after baking to 2,200 $^{\circ}$ C and were called Type 1; others impregnated after baking to 850 $^{\circ}$ C were called Type 2. The elements which were heat treated to only 850 $^{\circ}$ C were impregnated at 700 and 750 $^{\circ}$ C. The 2,200 $^{\circ}$ C fired elements were gaseous impregnated at 750 $^{\circ}$ C. All elements were impregnated using 1,3-butadiene gas and were given a final heat treatment of 2,200 $^{\circ}$ C prior to testing.

Table 39
THERMAL STRESS RESISTANCE OF ELEMENTS MADE FROM SANTA MARIA COKE

Batch	Filler Firing Temperature (° C)	Density (gms/cc)	Flexural Strength (psi)	Modulus (x 10 ⁻⁶ psi)	Coefficient of Thermal Expansion ⁽¹⁾ (x 10 ⁶ /° C)	Approximate Thermal Stress (watts)
<u>Without Thermax, ITX-ACN-I Binder</u>						
637	1,100	1.68	5,440	1.3	5.7	660 - 715
643	1,200	1.63	2,240	1.1	5.5	640 - 660
640	1,500	1.63	3,770	1.1	5.5	590 - 615
635	2,500	1.60	2,900	1.0	5.1	620 - 650
<u>With Thermax, ITX-ACN-I Binder</u>						
636	1,100	1.76	3,650	1.4	5.5	280 - 370
642	1,200	1.70	4,190	1.1	5.5	295 - 399
639	1,500	1.70	3,650	1.1	5.4	315 - 380
634	2,500	1.64	2,210	1.0	4.6	275 - 330
<u>Without Thermax, Varcum Binder</u>						
627	1,100	1.82	3,890	1.6	5.5	315 - 340
631	1,500	1.87	5,140	1.8	5.5	275 - 300
629	2,500	1.80	5,280	1.5	4.8	560 - 580
<u>With Thermax, Varcum Binder</u>						
626	1,100	1.83	4,110	1.7	5.5	140 - 150
628	2,500	1.87	6,050	1.9	4.8	290 - 300

Table 39 (continued)

Batch	Thermax (%)	Flour Grind	Density (gms/cc)	Flexural Strength (psi)	Modulus (x 10 ⁻⁶ psi)	Coefficient of Thermal Expansion ⁽¹⁾ (x 10 ⁶ /° C)	Approximate Thermal Stress (watts)		
With Thermax, Varcum, Graphitized Powder									
629	0	Fine	1.80	5,280	1.5	4.8	560 - 580		
628	15	Fine	1.87	6,050	1.9	4.8	290 - 300		
633	0	Medium	1.82	5,650	1.7	5.0	617 - 636		
632	15	Medium	1.86	5,950	1.8	4.8	561 - 572		
630	15	Coarse	1.76	4,830	1.5	5.2	415 - 540		
Batch	Thermax (%)	Binder	Filler Firing Temperature (° C)	Flour Grind	Density (gms/cc)	Flexural Strength (psi)	Modulus (x 10 ⁻⁶ psi)	Coefficient of Thermal Expansion ⁽¹⁾ (x 10 ⁶ /° C)	Approximate Thermal Stress (watts)
15V Pitch Binder Versus ITX-ACN-I Binder									
644	15	15V	2,500	Fine	1.68	2,760	1.0	4.9	312 - 347
645	0	15V	2,500	Fine	1.51	3,550	0.8	5.0	460 - 480
634	15	ITX	2,500	Fine	1.64	2,210	1.0	4.6	275 - 330
635	0	ITX	2,500	Fine	1.60	2,900	1.0	5.1	630 - 650
641	15	ITX	2,500	Coarse	1.58	2,190	1.1	4.9	300 - 325
646	15	15V	1,100	Fine	1.74	6,340	1.3	5.7	370 - 400
647	0	15V	1,100	Fine	1.62 - 1.76	6,780	1.2	5.5	320 - 360 250 - 300
Pewee II AXM, Varcum - Base line As-Bought Graphites									
Tensile Strength (psi)					Strain (%)				
AXM					~ 7,000				
ATJ					3,500				
					~ 0.50				
					0.36				

(1) Temperature, 25 to 1,000 $^{\circ}$ C.

Figure 36. THERMAL STRESS STUDIES FOR SANTA MARIA COKE ELEMENTS.

Table 40
TENSILE STRAIN DATA ON SANTA MARIA COKE ELEMENTS

Batch	Binder	Thermax (%)	Flour Grind	Filler	Flexure Strength (psi)		Tensile Strength (psi)	Tensile Strain (%)
				Firing Temperature (° C)	Average	Range		
<u>Without Thermax, ITX-ACN-I</u>								
637				1,100	5,440	6,240 - 4,370	3,060	0.30
643				1,200	2,240	2,560 - 1,900	2,250	0.29
640				1,500	3,770	3,910 - 3,640	2,290	0.28
635				2,500	2,900	3,010 - 2,770	2,050	0.18
<u>With Thermax, ITX-ACN-I</u>								
636				1,100	3,650	4,040 - 3,170	-	-
642				1,200	4,190	4,240 - 4,100	2,475	0.26
639				1,500	3,650	3,740 - 3,470	2,075	0.24
634				2,500	2,210	2,540 - 1,990	1,925	0.18
<u>Without Thermax, Varcum</u>								
627				1,100	3,890	4,430 - 3,510	-	-
631				1,500	5,140	5,800 - 4,660	2,770	0.21
629				2,500	5,280	5,540 - 4,890	3,230	0.30
<u>With Thermax, Varcum</u>								
626				1,100	4,110	4,430 - 3,640	-	-
628				2,500	6,050	6,300 - 6,010	4,125	0.32
<u>With Thermax, Varcum</u>								
629	Varcum	0	Fine	2,500	5,280	5,540 - 4,890	3,230	0.30
628	Varcum	15	Fine	2,500	6,050	6,300 - 6,010	4,125	0.32
633	Varcum	0	Medium	2,500	5,650	5,840 - 5,510	3,490	0.32
632	Varcum	15	Medium	2,500	5,950	6,400 - 5,100	3,270	0.24
630	Varcum	15	Coarse	2,500	4,830	5,080 - 4,630	3,275	0.30
<u>15V Pitch Binder Versus ITX-ACN-I</u>								
644	15V	15	Fine	2,500	2,760	3,230 - 2,030	3,725	0.30
645	15V	0	Fine	2,500	3,550	5,410 - 3,230	3,065	0.33
634	ITX	15	Fine	2,500	2,210	2,540 - 1,990	1,925	0.18
635	ITX	0	Fine	2,500	2,900	3,010 - 2,770	2,050	0.18
641	ITX	15	Coarse	2,500	2,190	2,360 - 2,020	2,115	0.28
646	ITX	15	Fine	1,100	6,340	7,400 - 5,620	3,875	0.38
647	15V	0	Fine	1,100	6,780	8,060 - 5,740	3,875	0.38
<u>Pewee 2 POCO AXM-Thermax Base Line</u>								
-	Varcum	15	Coarse	2,500	~ 4,800	-	3,300	0.20
<u>As-Purchased Graphites</u>								
Poco AXM	-	-	-	-	-	-	~ 7,000	~ 0.50

Thermal Stress Resistance of Impregnated Elements - Thermal stress resistance and other physical property data are reported in Table 41. As noted in Figure 41, the flexural strength and density are linearly related. These data were obtained on the elements fired to 2,200° C (Type 1) prior to impregnations. Flexural strengths of more than 9,000 psi at densities near 1.90 gms/cc appeared feasible. The Type 2 elements were not tested in flexure. It is quite possible that the flexural values of these matrices would have been equal to or greater than the values obtained on the 2,200° C fired pieces.

Figure 37. TENSILE STRENGTH FOR VARCUM VERSUS THE ISOTRUXENE-ACENAPHTHALENE MIXTURE.

Figure 38. TENSILE STRAIN FOR VARCUM VERSUS THE ISOTRUXENE-ACENAPHTHALENE MIXTURE.

Figure 42 is a graph of the thermal stress resistance of element wafers plotted as a function of density. These data show that the Type 1 matrices were less resistant to thermal stress than the Type 2 elements. The thermal stress resistance increased significantly with bulk density. For comparative purposes, simulated 19-hole element cross sections were machined as wafers from a block of ATJS graphite in the with-grain direction.^(g) ATJS graphite is con-

sidered to have excellent thermal stress properties and a low coefficient of thermal expansion. As noted in Figure 42, the ATJS data appear to fit the 850° C bake element data. These data show that very high thermal stress values can be obtained on fuel elements which possess high coefficient of thermal expansion (CTE) properties. When the SMC matrices are densified to satisfactory densities (~ 1.85 gms/cc), thermal stress resistance values in excess of 1,800 watts can be expected. These levels would be an improvement of about a factor of five or more when compared to the Pewee 2 element type.

Figure 43 provides a plot of thermal stress resistance versus flexural strength on Type 1 elements. These data show that thermal stress resistances and flexural strengths are closely related. Similar data for Type 2 elements which were impregnated in the 850° C bake state are not available.

Tensile and Tensile Strain-to-Failure Data of Impregnated SMC Elements - In addition to the thermal stress resistance, impregnated elements were tested in tensile by the ORNL and

(g) Union Carbide Corporation-Carbon Products Division.

Figure 39. TENSILE STRENGTH OF FUEL ELEMENTS MADE FROM SANTA MARIA COKE POWDER. (Effects of the Filler Particle Size Spectrum)

were also measured for tensile strain. The available data are listed in Table 42. These data show that gaseous impregnation increases the density, tensile strength, and ultimate strain. The matrices used for this series were SMC (1,100° C) fired filler, bound with ITX-ACN, and did not contain Thermax.

of SMC elements was made so that nonfueled and fueled matrices could be compared. Two types of SMC powder were used: (1) as-received, impure material, and (2) a chlorine-leached blend. No manufacturing difficulties were encountered with either of the element groups. All elements were made without Thermax addition to the fillers.

Physical Properties - Physical properties of the as-graphitized elements are listed in Table 43. Note that the bulk densities of the elements made with the as-received Santa Maria coke were higher than the chlorine-treated coke. CTE values for the elements were 5.9 to $6.1 \times 10^{-6}/^{\circ}\text{C}$ (25 to 1,000° C), but with no appreciable drop noted by the addition of the uranium carbide fuel particles.

Figure 40. TENSILE STRAIN OF FUEL ELEMENTS MADE FROM SANTA MARIA COKE POWDER. (Effects of the Particle Size Spectrum)

Flexural strengths of the as-received coke elements were higher than the chlorine-treated elements (~2,000 psi). The increased strength may be due to the increased bulk density. Flexural strengths of the loaded and unloaded elements were about equal and were high (~6,000 psi) at densities of 1.67 gms/cc for unloaded elements.

Fuel Particle Damage - An element from each group was graphitized to 2,200° C in order to conduct studies on physical properties, bead damage, and metallography. After this heat treatment it was found that 10 to 15 percent of the fueled particles were migrated. The beads appeared to have been attacked from the outside, which was probably due to the impurities in the filler carbon. The remaining elements were graphitized to 2,200° C in an anhydrous hydrogen chloride atmosphere in an attempt to reduce the bead damage by removing the impurities before they attacked the beads. These leached, graphitized elements showed that none of the fuel beads were damaged. The leach-graphitize sequence was used routinely after this experiment.

Uranium-Loaded SMC Elements - The nonfueled SMC element studies had shown that an increased CTE matrix could be obtained. An experimental group

Metallographic Structure - Views of the structures of the bead-loaded elements made in this study are provided in Figure 44. For comparison, a typical photograph of a Varcum-bound matrix made from the same Santa Maria coke blend, but fired to 2,500° C prior to extrusion, is also shown. The latter photograph shows grainy regions and appears to be similar to the Pewee 2-type matrices. The low-fired Santa Maria coke bound with ITX-ACN-I shows a fine-grained isotropic structure.

POCO Fillers

Studies were made using commercial POCO graphite fired to a minimum of 2,300° C in the search for a filler which could be extruded into elements which would produce isotropic, improved CTE matrices. During this program, the POCO Graphite Company agreed to supply materials which had been heat treated to lower temperatures. Billet Form POCO ACF-4Q was purchased, a material that was POCO AXF processed only to 1,400° C. A powder labeled POCO PCD-0Q, which had been processed to 1,000° C, was also received. A third type of powder, labeled POCO PCD-9Q, which had been processed to 900° C, was later obtained. All of these materials (ACF-4Q, PCD-0Q, and PCD-9Q) were stated to be the starting material for the manufacture of standard-grade POCO AXF-5Q.

Figure 41. DENSITY VERSUS FLEXURAL STRENGTH. (Type 1 Elements; Impregnated after a 2,200° C Bake; Element + Impregnant Reheated to 2,200° C)

Table 41
THERMAL STRESS RESISTANCE OF
IMPREGNATED ELEMENTS

Batch	Impregnation Temperature (° C)	Density (gms/cc)	Flexural Strength (psi)	Thermal Stress (watts)
Type 1(1)				
637	As Graphitized	1.68	5,440	660 - 715
637	750	1.78	6,640	683 - 814
637	750	1.81	7,720	1,250 - 1,346
637	750	1.84	8,110	1,470 - 1,560
Type 2(2)				
659	As Graphitized	1.62	4,190	560 - 570
658	As Graphitized	1.72	5,670	750 - 760
659	750	1.73	-	1,240 - 1,350
658	700	1.78	-	1,560 - 1,670
Commercial ATJS(3)				
-	As Received	1.81	-	1,750 - 1,960

- (1) Element impregnated after a 2,200° C bake; graphitized element and impregnant reheated to 2,200° C.
 (2) Elements impregnated after baking to 850° C; impregnant plus element graphitized at 2,200° C.
 (3) Fuel element shape, with-grain direction.

ACF-4Q and PCD-0Q Scouting Studies - The as-received billets of POCO ACF-4Q were sampled. Typical chemical analyses of the billets and a typical photomicrograph are given in Table 44 and Figure 45. A chemical analysis showed that the billet contained very few metallic impurities; X-ray diffraction data revealed that the material had not been high fired. When fired to 2,800° C, the material appeared to be the same as POCO AXF-9Q.

The POCO ACF-4Q billet was ground into an extrusion flour blend. POCO ACF-4Q and POCO PCD-0Q powders were sampled. Metallographic analyses of both flours are reported in Table 45 and photomicrographs provided in Figure 46. A typical photograph

Figure 42. DENSITY VERSUS THERMAL STRESS RESISTANCE FOR THE THREE TYPES OF ELEMENTS LISTED IN TABLE 41.

Analyses of each of the primary POCO flours used in this extrusion series are reported in Table 45. Analysis of the as-received material showed it to contain a high sulfur content ($> 1\%$) and high iron and silicon levels. The metallic impurities could have been a result of the grinding operation. Several large pieces ($\sim 1/2$ inch in diameter) were found in the PCD-0Q as-received batch. Photomicrographs of these few chunks showed the particles to have the same structure as the as-received PCD-0Q powder. The PCD-0Q powder and large, unground pieces were chemically analyzed. Chunks of the PCD-0Q had an iron level of 250 ppm, and the as-received PCD-0Q flour had an iron level of 800 to 1,000 ppm. The silicon level in the chunks was 110 ppm versus 500 ppm in the as-received powder. These data indicate that iron and silicon are being added by the grinding operation. Chemical data on the PCD-0Q powder are presented in Table 46. These impurity levels were brought to the attention of the vendor.

Extrusion Studies - As previously stated, elements were made from flours prefired to 1,000, 1,400, 1,800, and 2,500° C. Table 47 reports the available extrusion data. A typical photomicrograph of an extruded element is presented in Figure 47. Physical property data of these elements are discussed in the sections that follow.

Coefficient of Thermal Expansion - The most significant finding of this experimental study was to determine the coefficients of thermal expansion. The CTE data again were related to the filler-firing temperature and were high in all cases. The 1,000° C flour produced a CTE value of $8.15 \times 10^{-6}/^{\circ}\text{C}$ (25 to 1,000° C), which is higher than any other flours tried to date. CTE data, with other element data, are given by the graph of Figure 31. The high values obtained on these elements match or slightly exceed the CTE of the metal carbide bore coating.

of POCO AXF flour is also presented in Figure 46 for comparison purposes. The photographs show that the POCO ACF-4Q flour had high internal porosity in the particles, while POCO PCD-0Q flour had noticeably less internal porosity.

POCO ACF-4Q flour was split and portions fired to 1,800 and 2,500° C. Elements were extruded using the four POCO fillers (1,000, 1,400, 1,800, and 2,500° C fired powders). It is recognized that the 1,000° C fired powder had a different history than the other three powders. However, except for the particle size spectrum, POCO Graphite Company has stated that this material was identical in history to the POCO ACF-4Q powder.

Analyses of each of the primary POCO flours used in this extrusion series are reported in Table 45. Analysis of the as-received material showed it to contain a

Other Physical Properties - Several other properties are also noted in Table 47. Densities of the as-extruded element were satisfactory and could be raised by impregnation. Flexural strengths were high, especially with the 1,000° C fired flour elements. Tensile and strain-to-failure results on the elements were also satisfactory.

Thermal stress resistances ranged from 550 to 1,120 watts, and were about the same for all of the element types (Table 48). These ranges were high in relation to the Pewee 2-type matrices which had values of about 250 watts. In view of the high coefficient of thermal expansion values, the thermal stress resistance is considered to be very good.

Gaseous Impregnated POCO AXF Graphite

Studies - The experimental elements were pulse-vacuum gaseous impregnated with 1,3-butadiene gas and the physical properties further defined.

Table 42

TENSILE STRENGTH AND TENSILE STRAIN OF IMPREGNATED ELEMENTS

Sample	Density (gms/cc)		Average Flexural Strength (psi)	Tensile Strength (psi)	Tensile Strain (%)
	Original	Impregnated			
637	1.68	No Data	5,440	3,060	0.30
659	1.62	No Data	4,190	No Data	No Data
658	1.70	No Data	5,670	No Data	No Data
659	1.64	1.73	-	3,240	0.28
658	1.72	1.78	-	6,060	0.47

Thermal Stress Resistance of Impregnated Elements - The primary POCO element matrices were gaseous impregnated with 1,3-butadiene gas to varying densities while the matrices were in the 850° C bake state. Samples were periodically taken from the elements as the densities were increased, and were graphitized to 2,200° C prior to the test.

Wafers were cut from the graphitized elements for thermal stress, strain to failure, density, mercury porosimetry, and metallographic examination. Thermal stress resistance data on each of the filler types are provided by the graphs of Figures 49 through 51. These curves show resistances as functions of density, and indicate that the thermal stress resistance increased as a function of density.

Figure 43. FLEXURAL STRENGTH VERSUS THERMAL STRESS RESISTANCE FOR TYPE 1 ELEMENTS.

A metallographic examination was performed on each of the elements. In general, all of the matrices were fine-grained structures and had uniform pore distributions. Typical data of an impregnated element are compared in Figure 48. No apparent surface sealing was observed and the impregnant apparently filled the pores in a uniform manner and decreased the pore opening size.

Thermal Stress Resistance of Impreg-

Table 43
PHYSICAL PROPERTIES OF SANTA MARIA
COKE ELEMENTS

	Extrusion Number ⁽¹⁾			
	658	659	661	660
Filler Number ⁽²⁾	SM As Ground	SM, Cl ₂ Leached	SM As Ground	SM, Cl ₂ Leached
Binder Level (pph)	30	30	29	29
Extrusion Pressure ($\times 10^3$ lbs)	120	130	124	90
Bulk Density (gms/cc)	1.69	1.60	2.19	2.13
Uranium Content (mgs/cc)	0	0	499	493
Carbon Density (gms/cc)	1.69	1.60	1.68	1.63
Longitudinal CTE, 25 - 1,000° C ($\times 10^{-6}/^\circ\text{C}$)	6.0	6.2	6.0	5.9
Flexural Strength (psi)				
Maximum	7,250	4,680	8,210	4,330
Minimum	3,670	3,380	5,150	3,210
Average	5,670	4,190	6,170	3,760
Compressive Strength (psi)				
Maximum	17,670	11,560	15,870	10,000
Minimum	14,750	9,720	14,050	8,530
Average	16,300	10,610	15,050	9,360
Mercury Porosimetry Data				
Bulk Density (gms/cc)	1.72	1.64	2.17	2.14
Real Density (gms/cc)	1.92	2.07	2.59	2.60
Open Porosity (%)	12.19	20.61	16.23	17.77

(1) All elements were graphitized at 2,200° C.

(2) Filler firing temperature, 1,100° C; no Thermax added; binder, ITX-ACN-I mixture.

Physical Properties of Impregnated Elements - Physical properties examined included tensile strength, tensile strain to failure, and tensile modulus. These data are summarized in Table 49 for the 1,400, 1,800, and 2,500° C fired filler elements. A brief summary of the physical properties exhibited by the impregnated elements, which used 1,400° C fired fillers, is given in the paragraphs that follow.

Density - As expected, density increased as a function of the impregnation time. A maximum density of 1.92 gms/cc was obtained on the nonfueled elements. Due to a temperature gradient in the impregnation furnace, the 74-hour sample showed a slight density decrease compared to the 37-hour sample. This sample was located in a slightly cooler region of the furnace ($\sim 20^\circ\text{C}$) than the other samples.

Tensile Strength - A significant increase in tensile strength was noted on the impregnated samples (Figure 52).

Tensile Strain - The tensile strain to failure and tensile strength increased linearly as a function of density (Figures 53 and 54). A nominal 0.07 percent strain per 1,000-psi tensile strength was observed on this element group.

Density and Tensile Modulus - It was expected that a density increase would cause a change in the tensile modulus of the specimens. Presented in Figure 55 are the data on the test groups which show that an increased modulus change occurred on the densified samples.

MS-70-0042-3

(a) Low-Fired Coke; ITX-ACN-I Binder.

F699-2a

(b) High-Fired Santa Maria Filler, Varcum Binder.

Figure 44. TYPICAL PHOTOMICROGRAPHS OF SANTA MARIA ELEMENTS. (Sensitive Tint; 100X)

POCO PCD-0Q Studies

Because of the high CTE values obtained with the PCD-0Q powder, additional lots of this powder were obtained as a prime candidate for the filler for NERVA reactor graphite fuel elements.

Powder Preparation and Purification - POCO low-fired carbon (POCO LF) was received in four shipments. The four shipments consisted of one 10-pound, one 50-pound, and two 500-pound batches. The four shipments were believed to represent a distinct sampling of the production line. Table 50 lists the significant chemical impurities found in the four shipments. It is believed that most of the impurities originated during the time the raw feed was processed to the coked state. The iron content was probably variable due to the raw feed supply and difficulties the vendor experienced during the grinding operation.

Impurities, normally, are of little concern in the manufacture of commercial graphite. Some impurities are known to be added during the manufacture of some types of graphites to produce alterations to the binder and/or filler. Effective and fairly rapid impurity removal from commercial graphites is obtained by high-temperature processing and/or gaseous leaching at high temperatures. In a bead-loaded element matrix, however, many impurities cannot be tolerated. Iron, silicon, and vanadium are particularly objectionable since graphite

Table 44
ANALYSIS OF AS-RECEIVED POCO
ACF4Q FLOUR

Element	Concentration (ppm)	Element	Concentration (ppm)
<u>Chemical Analyses</u>			
Ag	< 1	Mn	3
Al	60	Mo	< 1
B	< 1	Na	10
Ba	4	Ni	40
Be	< 1	P	< 100
Ca	20	Pb	< 1
Cd	< 1	Si	60
Co	< 20	Sn	< 1
Cr	1	Ti	< 6
Cu	10	V	80
Fe(1)	250	W	< 10
K	25	Zn	< 60
Li	< 10	Zr	< 2
Mg	18		

X-Ray Diffraction

	Interlayer Spacing (A)	L _c (A)	L _a (A)
As Received	3.400	-	-
Heat Treated to 2,800° C	3.378	108	330

(1) Contaminated during sample preparation.

G563

Figure 45. PHOTOMICROGRAPHIC VIEW OF POCO ACF-4Q FLOUR. (As Received; Sensitive Tint; 250X)

Table 45
 PROPERTIES OF PRIMARY POCO
 CARBON POWDERS

	Extrusion Number			
	668	663	664	665
Filler Firing Temperature (° C)	1,000	1,400	1,800	2,500
Filler Type	PCD-0Q	ACF-4Q	ACF-4Q	ACF-4Q
Surface Area (m ² /gm)	12.73	23.9	9.47	5.10
Helium Density (gms/cc)	1.95	1.99	1.89	2.20
Particle Size Analysis (%)				
Screen Size (mesh)				
+60	0.17	0.25	0.10	< 0.10
-60 +100	0.31	3.99	3.77	0.10
-100 +140	0.48	5.54	6.43	2.50
-140 +200	5.66	7.02	7.48	2.60
-200 +270	9.79	5.27	6.46	6.00
-270 +325	6.90	3.61	4.85	3.80
-325	76.68	74.32	70.92	85.00
Micromerograph				
100% Less Than Size (μm)	86	190	180	180
90% Less Than Size (μm)	52	77	87	87
50% Less Than Size (μm)	24	10.8	13.6	11.2
25% Less Than Size (μm)	9.3	4.4	3.9	3.5
10% Less Than Size (μm)	4.3	3.0	2.2	2.2
Loss at 100° C (%)	0.38	0.22	0.024	0.06
Ash Content (%)	0.42	0.22	0.12	0.41
Sulfur Content (%)	1.05	0.74	0.43	< 0.01
Impurities (ppm)				
Ag	< 1	< 1	< 1	< 1
Al	70	20	12	< 10
B	1	< 1	< 1	< 1
Ba	5	4	4	1
Be	< 1	< 1	< 1	< 1
Ca	60	60	40	15
Cd	< 1	< 1	< 1	< 1
Co	< 20	< 20	< 20	< 20
Cr	10	4	6	2
Cu	10	10	< 10	< 10
Fe	800	1,000	700	150
K	50	< 20	< 1	< 1
Li	< 10	< 10	< 10	< 10
Mg	20	30	15	1
Mn	15	10	6	1
Mo	< 1	< 1	< 1	< 1
Na	35	20	6	< 1
Ni	50	60	60	10
P	< 100	< 100	< 100	< 100
Pb	175	6	< 1	< 1
Si	500	125	10	< 10
Sn	150	< 1	< 1	< 1
Ti	6	15	< 6	6
V	70	125	80	50
Zn	< 60	< 60	< 60	< 60
Zr	< 2	< 2	< 2	< 2

(a) PCD-0Q. (1,000° C)

G644-26

(b) ACF-4Q. (1,400° C)

G503-5

(c) AXF. (2,500° C)

G436-3

Figure 46. PHOTOMICROGRAPHS OF TYPICAL POCO CARBONS. (Sensitive Tint; 250X)

Table 46
PROPERTIES OF POCO PCD-0Q CARBON
(50-Pound Lot)

Material	Impurities (ppm)																			
	Al	B	Be	Ca	Cr	Fe	K	Li	Mg	Mn	Mo	Na	Ni	Pb	Si	Sn	Ti	V	W	Zr
PCD-0Q (as received)	60	3	4	60	6	800	60	< 10	30	20	< 1	15	30	50	500	60	6	70	30	< 2
PCD-0Q (lumps)	60	2	4	60	6	250	40	< 10	20	4	< 1	15	45	2	110	> 1	6	70	10	< 2
PCD-0Q (screened) (1)	70	2	4	60	8	900	60	< 10	30	20	< 1	12	40	70	500	70	< 6	70	20	< 2
PCD-0Q (magnet fraction)	70	2	4	60	10	1,000	60	< 10	30	25	1	12	35	70	500	50	6	70	30	< 2

Results of Powder After Screening

Density	Wet Screen Analysis (%)		
Helium (gms/cc)	1.98	+60	0.1
Pour (gm/cc)	0.49	-60 +100	0.1
Tap (gm/cc)	0.93	-100 +140	0.3
		-140 +200	3.5
Particle Size		-200 +270	9.0
Micromerograph		-270 +325	6.3
100% Less Than Size (μ m)	72	-325	80.6
90% Less Than Size (μ m)	52		
50% Less Than Size (μ m)	7.8	Surface Area (m^2/gm)	13.9
25% Less Than Size (μ m)	4.4		
10% Less Than Size (μ m)	2.8		

(1) 1.72 percent sulfur.

Table 47
PHYSICAL PROPERTIES OF PRIMARY POCO ELEMENTS

	Extrusion Number			
	669	663	664	665
Filler Type	PCD-0Q	ACF	ACF	ACF
Filler Firing Temperature ($^{\circ}$ C)	1,000	1,400	1,800	2,500
Binder Content (pph)	31	44	44	44
Extrusion Pressure (tons)	57	40	40	34
Bulk Density (gms/cc)				
Calculated	1.74	1.78	1.73	1.67
Laboratory	1.70	1.80	1.74	1.70
Electrical Resistance (milliohms/element inch)	-	284	283	234
Sonic Modulus, Longitudinal ($\times 10^6$ psi)	1.2	1.6	1.2	1.0
Compressive Strength, Average (psi)	18,400	20,200	16,500	12,200
Flexural Strength, Average (psi)	8,920	6,150	5,620	4,100
Coefficient of Thermal Expansion, 25 to 1,000 $^{\circ}$ C ($\times 10^{-6}/^{\circ}$ C)	8.15	7.83	7.01	6.28
Ultimate Tensile Strength (psi)	3,200	2,770	3,440	2,520
Ultimate Tensile Strain (%)	0.2625	0.165	0.2975	0.3175

recrystallization and fuel-bead migration have both been attributed to these impurities. The pyrocarbon coating on the fuel beads had been observed to be degraded by these impurities at modest temperatures ($\sim 1,500^{\circ}$ C). Therefore, it was decided that a reduction in the impurities in the POCO LF flour was required.

G683-3a

Figure 47. TYPICAL EXTRUDED ELEMENT MATRIX; PRIMARY POCO ACF POWDER. (1,800° C Filler Firing Temperature; Sensitive Tint; 100X)

Table 48

THERMAL STRESS RESISTANCE OF LOW-FIRED POCO ELEMENTS

Extrusion(1)	Flour Firing Temperature (° C)	Density (gms/cc)	Flexural Strength (psi)	Coefficient of Thermal Expansion(2) ($\times 10^{-6}/^{\circ}\text{C}$)	Thermal Stress Range (watts)	Tensile Strength (psi)	Tensile Strain (%)	Tensile Modulus ($\times 10^6$ psi)
669(3)	1,000	1.74	8,920	8.15	630 - 680	3,200	0.2625	1.375
663	1,400	1.78	6,150	7.80	720 - 1,120	2,770	0.165	1.925
664	1,800	1.73	5,620	7.00	630 - 710	3,400	0.2975	1.375
665	2,500	1.67	4,100	6.30	550 - 620	2,520	0.3175	1.02

(1) This series was made without Thermax and bound with ITX-ACN.

(2) Temperature, 25 to 1,000° C.

(3) Batch 669 was extruded at a high pressure of 100 tons. Because of a lack of raw material, the pressure could not be adjusted.

A three-stage, cross-belt magnetic separator was previously used to successfully reduce the iron content in the SMC-ground flour. The same equipment, however, was not successful using the POCO LF-type flour. During studies with the SMC-ground flour, two gaseous purification runs were attempted to purify the flour. The results showed a variability in the impurities within the furnace load, which indicated a problem of uniform exposure of the powder to the reactants. Based on these unsuccessful attempts, no gaseous leaching runs were made to purify the as-received POCO LF powder.

A purification process was established in which the element was extruded, baked to 1,200 to 1,500° C, and then leached with chlorine. Purification of the extruded, impure matrix reduced the impurities to an acceptable level (<100 ppm), and no bead damage was observed even when elements were processed to a temperature of 2,225° C (observed), which is 100° C higher than the Pewee 2 elements.

The as-received POCO LF powder was blended and screened through a 70-mesh screen prior to its use. Approximately 0.5 gram of unknown fibers per 5,000 grams of flour were removed from all lots of POCO LF carbon. Chemical analysis of the fibers indicated high magnesium and silicon levels. It is presumed that this fibrous material originated in the vendor's powder manufacturing operation, and that the vendor could eliminate these contaminants.

Physical characteristics of the POCO LF carbons are listed in Table 51. Figure 56 shows photomicrographs of the two most dissimilar powder distributions (LF-2 and LF-3). The

carbon particles exhibited surface-connected porosity, rather uniformly distributed, which appeared spherical or "bubble-like" within the particle. Variation in pore size within a single lot was very small, but the average size varied considerably on a lot-to-lot basis.

Examination of the finer particles indicated that the preferred fracture mode during the grinding step was through pores. The lot having the finest particle distribution (LF-2) exhibited the lowest surface area. When extruded, the binder demand for this powder was 43 pph, whereas the LF-3 batch required 39 pph. Process changes were made between the extrusion of the LF-2 flour and LF-3 four, which may or may not have accounted for the change in binder demand.

Fuel Element Studies - A large amount of development time was spent in an attempt to obtain a satisfactory manufacturing process for the routine extrusion of fuel elements made with POCO PCD-0Q powder and bound with ITX-ACN-I binder. The POCO flour was different from other flours which had been used in that it responded differently in the manufacturing process. Amount of binder, wetting effect of the binder with the flour, extrusion pressures, tendency of the matrix to crack, and various other process steps were

Figure 48. PORE DISTRIBUTION OF PRIMARY POCO MATRICES.

Figure 49. THERMAL RESISTANCE DATA FOR BATCH 663. (1,400° C; Primary POCO Flour)

bulk and carbon densities increased to 2.19 and 1.74 gms/cc, respectively. In the latter batches (Generations 3 and 4), less impregnant was added because the as-made densities had increased to reasonably acceptable levels of 2.23 and 1.79 gms/cc, respectively. By this time, testing of the earlier batches indicated that the impregnated elements did not test as well as the nonimpregnated elements. It appeared that after impregnation and subsequent graphitization at 2,225° C, the matrix quality deteriorated. The latter elements (Generations 3 and 4) were impregnated after graphitization.

Flexural and Compressive Strengths - Only a few Generation 1 elements were produced that appeared worthy of testing, and none were available for flexural tests. However, the uranium-loaded Generation 2 elements had an average flexural strength of about 4,340 psi without impregnation and was increased to 5,435 psi with impregnation. Flexural strengths of the loaded elements reached a maximum with the Generation 3 elements at an average of 6,200 to 6,250 psi. The values actually varied from 5,300 to 7,200 psi due to the temperature gradients in the various graphitization furnaces. With the double graphitization step, the high values were obtained at the ends of the element and the lower values in the middle. The flexural strength for the Generation 4 elements dropped off to an average of 5,235 psi. This decrease was not due to graphitization but to the extrusion process changes where the binder level was lowered to increase the extrusion pressure to the 70 to 80-ton range. This pressure in the past had produced a matrix containing few flaws. However, with the low-fired flour, the flexural strengths reached a maximum and then dropped off as the extrusion pressure continued to increase (Figure 57).

different for this powder, and all had to be resolved. As a result, only a few elements were produced from the 50-pound lot of POCO LF-1 flour. The 500-pound lot (LF-2) was different from the 50-pound lot (LF-1), and the process steps and effects had to be redetermined. This variation was also true of the third lot of powder (500 lbs of LF-3).

Several manufacturing steps were changed during the course of the studies. As a result of these changes, several types of uranium-loaded elements were made. Each type has been defined as Generations 1 through 4.

Carbon Density - Bulk and carbon densities of uranium-loaded Generation 1 elements (LF-1) were ~ 2.10 and 1.65 gms/cc, respectively. After the elements were purified at 1,500° C with hydrogen chloride and pulsed-vacuum gaseous impregnated with 1,3-butadiene gas, the

A compressive strength of 14,900 psi was obtained for Generation 3 elements and 15,500 psi for Generation 4.

Thermal Stress - Thermal-stress values (as obtained on the ORNL apparatus) gave an average of 370 watts for Generation 1 and 400 watts for Generation 3. These values can be compared to a Pewee 2-type element which had break values of 250 watts.

Coefficient of Thermal Expansion - A prime reason for switching to POCO low-fired flour was the fact that the coefficient of thermal expansion (CTE) was substantially higher than for the SMC elements. At 1,000° C, the comparable values were: SMC-loaded elements, $5.2 \times 10^{-6}/^{\circ}\text{C}$; POCO LF-loaded elements, $7.0 \times 10^{-6}/^{\circ}\text{C}$ (25 to 1,000° C). Initial hot-gas testing of the SMC elements indicated a reactor life of about two hours instead of the desired five hours.

Figure 50. THERMAL RESISTANCE DATA FOR BATCH 664. (1,800° C; Primary POCO Flour)

Loaded elements made from the first lot of powder (50 lbs of LF-1) had a CTE at 1,000° C of $7.1 \times 10^{-6}/^{\circ}\text{C}$, which was in agreement with the values obtained with the original experimental lot of flour. Fueled elements were run in the LASL high-temperature CTE furnace and produced comparable values of about $7.0 \times 10^{-6}/^{\circ}\text{C}$ at 1,000° C and about $7.7 \times 10^{-6}/^{\circ}\text{C}$ at 2,000° C. A summary of the values is presented in Tables 52 and 53. As indicated, there was little difference between the impregnated, nonimpregnated, and coated samples.

Upon receipt of the larger (500-lb) preproduction lot of flour (LF-2), attention was focused upon the many problems of defining an acceptable manufacturing process. CTEs of the elements from LF-2 flour were found to vary from 6.2 to $6.7 \times 10^{-6}/^{\circ}\text{C}$ and not the $7.0 \times 10^{-6}/^{\circ}\text{C}$ value of the LF-1 flour (25 to 1,000° C). As noted in Table 52, there was no apparent correlation between the CTE values and the extrusion conditions.

Once the third lot of preproduction flour (LF-3) was put in use, it was obvious that its characteristics were different from the previous flours. The binder level had to be lowered significantly to produce a visually sound element matrix. CTE values were measured and were determined to have a wide variation. However, by this time the extrusion process was somewhat better understood and it was possible to correlate the decline in CTE to the extrusion process, as reflected by the increase in extrusion pressure (Table 54 and Figure 58). In addition to changes in the amount of binder, other process variables included: (1) temperature of the heated die, (2) changes in the die design, (3) number of passes through the "hamburger" mill, (4) number of days the mix was held before extrusion, and (5) number of preextrusions from the extrusion press.

Figure 51. THERMAL RESISTANCE DATA FOR BATCH 665. (2,500° C; Primary POCO Flour)

PROCESS OPTIMIZATION (6, 15)

A major problem was encountered in the extrusion of fuel elements containing low-fired carbon fillers and a graphitizable resin binder which resulted in cracking of the matrix during processing. Evaluation of the extrusion data from previous experiments indicated that the matrix cracking problem was of basically two types, namely: internal web cracks and gross transverse cracks. Both types of cracks appeared to be related to three stages of fabrication: (1) binder level, (2) binder mixing, and (3) flour compatibility with the binder. A large number of experiments were conducted in order to define and eliminate the matrix cracking problem.

In order to solve the cracking problems, some major process changes were made: (1) the type of binder was changed from an ITX-ACN-I binder to an Ashland 240 pitch-indene binder, (2) the matrix filler carbon was changed from POCO PCD-0Q (1,000° C) to POCO PCD-9Q (900° C), and (3) the binder content was significantly reduced from the 22-percent level to 16 percent.

The cracking problem was successfully eliminated by reducing the binder content of the extrusion mix and by multiple extrusion of the mix, which aided in the production of a uniform blend. Use of these mixing practices increased the element yields from nominal 10 percent crack-free elements to greater than 75 percent crack-free elements.

Binder System

Two major problem areas were found to be the blending and extrusion operations. Because of the high viscosity of the graphitizable resins, free indene was used as a binder solvent. Other organic compounds were used, but were not as effective an agent as indene. Free indene in the binder served as a flour wetting agent, plasticizer, and binder solvent. It was believed that the indene diluent and resin binder were not adequately distributed by the use of the standard Patterson-Kelly Vee-type blender.

Binder Content - Successful extrusion experience had consistently shown that the total binder content of most mixes ranged from 20 to 30 percent. The level was dependent on many process variables such as the type of flour and surface area. If a diluent was used in the binder, the percentage of diluent was normally computed separately from the total reported binder level. The binder was defined as the material which contributed to the matrix structure; therefore, the diluent was not considered to be a binder.

Table 49
PHYSICAL PROPERTIES OF IMPREGNATED LOW-FIRED POCO FILLERS

Batch	Impregnation ⁽¹⁾ Time (hrs)	Density ⁽¹⁾ (gms/cc)	Tensile Strength (psi)	Ultimate Tensile Strain (%)	Tensile Moduli (x 10 ⁶ psi)	Coefficient of Thermal Expansion ⁽²⁾ (x 10 ⁻⁶ /° C)
663 ⁽³⁾	0	1.774	2,770	0.165	1.925 ⁽⁴⁾	7.8
	8	1.720	5,850	0.400	1.52	
	8	-	5,250	0.405	1.47	
	18	1.81	7,150	0.476	1.73	
	27	-	7,550	0.512	1.74	
	27	1.895	8,880	0.517	2.05	
	35	1.92	7,400	0.478	2.055	
	74	1.90	8,480	0.566	2.05	
	74	1.90	8,480	0.566	2.05	
664 ⁽⁵⁾	0	1.757	3,400	0.2975	1.375	7.0
	8	1.778	5,200	0.390	1.51	
	8	-	6,340	0.491	1.55	
	18	1.833	8,000	0.573	1.75	
	18	-	7,000	0.501	1.67	
	27	1.908	9,050	0.613	1.85	
	27	-	9,520	0.649	1.87	
	35	1.920	7,560	0.526	1.91	
	74	1.910	6,900	0.511	1.82	
665 ⁽⁶⁾	0	1.656	2,520	0.3175	1.02	6.3
	8	1.744	4,420	0.389	1.37	
	8	-	4,700	0.416	1.40	
	18	1.805	6,270	0.497	1.63	
	27	1.870	7,550	0.512	1.81	
	27	-	6,960	0.505	1.74	
	35	1.880	4,325	0.315	1.73	
	74	1.860	5,480	0.437	1.68	
	74	1.860	5,480	0.437	1.68	

(1) Densities did not always increase with increased plating time because of a nonuniform temperature in the gas inlet and of the impregnation furnace. The temperature at the "0" region was approximately 30° C colder than other points. The samples were taken from the element hot-end region and replaced in the impregnation furnace; the cold-end section remained at a constant location in the furnace.

(2) Temperature, 25 to 1,000° C.

(3) Batch contained POCO filler prefired to 1,400° C and gas impregnated in the 850° C element bake state and varying densities. The final graphitization temperature was 2,200° C.

(4) Value believed to be in error.

(5) Batch contained POCO filler prefired to 1,800° C and gas impregnated in the 850° C element bake state. The final graphitization temperature was 2,200° C.

(6) Batch contained POCO filler prefired to 2,500° C and gas impregnated in the 850° C element bake state. The final graphitization temperature was 2,200° C.

As a matter of practice, the binder level was routinely adjusted to produce a blend which could be extruded at 60 to 85 tons of pressure (6-inch-diameter ram with an extrusion speed of 5 ft/min). From this process, crack-free elements were extruded and processed using standard NERVA heat-treatment cycles.

Those experiments that used low-fired carbon fillers specified a binder level of 22 weight percent of the dry carbon ingredients, or higher. Cracks in the extruded matrices indicated, however, that the elements contained an excessive amount of binder. Past efforts to reduce the binder level below 22 weight percent were not successful.

It was decided that additional studies would be made in which decreased binder levels would again be studied. It was also decided that the free indene diluent would be increased as the binder content was decreased, and the total binder and diluent system would be held at a viscosity of about 250 centipoises or less when measured at room temperature. This viscosity would permit using the standard mixing equipment.

Several scouting experiments were made from which it appeared that a binder level of 16 weight percent would be desirable. A nonfueled extrusion mix that was typical of these tests contained 3,500 grams of POCO PCD(-9)Q flour (900°C), 667 grams of Ashland-240 pitch, and 590 grams of indene diluent. This binder-flour composition was significantly different from past mixes in which a typical nonfueled extrusion blend would be composed of 3,500 grams of POCO PCD(-9)Q flour, 1,200 grams of Ashland-240 pitch, and 180 grams of indene.

Only Ashland-240 pitch was investigated in the new binder composition. In earlier studies, an ITX-ACN-I binder system was extensively investigated in which the binder level was greater than 22 percent. With the reduced binder system under study, it was believed that the ITX-ACN-I binder would produce the same results as the Ashland-240 pitch-indene system. If the ITX-ACN-I binder was to be used, it would be desirable to use the same binder-diluent combination as was used with the Ashland-240 pitch-indene binder. Substitution of the ITX-ACN-I binder did not appear to be a major problem since both binders produce a similar type of crystalline carbon structure when heated to graphitizing temperatures.

Binder Carbon Yield - Carbon yields obtained from graphitizable resins were dependent on a number of variables, namely: (1) the type of resin, (2) the heating cycle employed, and (3) the heating crucible design. Using one coking method common to most of the resin studies at the Y-12 Plant, Ashland-240 pitch showed a carbon yield of 60 percent. This method employed heating the pitch in a crucible using the standard NERVA fuel-element cycles.

Carbon yield, obtained on the resin, was generally useful in the selection of binder materials. In practice, the binder carbon yield which was obtained in fuel elements was more important than the original resin-carbon yield. The binder carbon yield obtained in a fuel element manufacturing process was generally higher than that obtained on the original resin.

Figure 52. TENSILE STRENGTH AS A FUNCTION OF DENSITY FOR BATCH 663 ELEMENTS. (1,400°C Filler Firing Temperature)

Figure 53. TENSILE STRAIN AS A FUNCTION OF DENSITY FOR BATCH 663 ELEMENTS. (1,400° C Filler Firing Temperature)

Figure 54. TENSILE STRENGTH VERSUS TENSILE STRAIN FOR BATCH 663 ELEMENTS.

Several experiments were made in which fuel-element weights were determined during the extrusion and heat-treatment operations. These data showed that a nominal 50 to 58 percent of the indene diluent was lost during the mixing, chopping, and extrusion operations; the remaining 42 to 50 percent was vaporized during a heating treatment at 80 to 100° C for several hours. Weight loss from 100 to 250° C was essentially zero.

Fuel-element carbon yield from the pitch binder was generally 65 to 70 percent. Major gas losses from the pitch occurred over the temperature range from 250 to 800° C. Fuel-element carbon-yield calculations were based on the assumption that the indene diluent did not produce binder carbon since it was vaporized at less than 100° C.

Extrusion

The new binder-flour composition was processed through the mixing operation with no apparent major problems. When the mixture was chopped by the hamburger-mill operation, some of the free indene was lost by evaporation. Several extrusions were required in order to obtain crack-free matrices. It was thus indicated that the early-stage mixing processes were insufficient, and final mixing was being obtained by the use of the high-pressure extrusion process.

The first time the material was extruded, a high extrusion pressure of about 90 tons always occurred; but, as the material was repeatedly extruded, the extrusion pressure would decrease and ultimately increase. After the point where the minimum pressure occurred (which was normally four

extrusions), the elements were collected for baking.

Cracks

Matrix Cracks - Transverse element cracks were common with elements which were extruded one or two times. An occasional transverse crack was noted during the third and

fourth extrusions. After the extrusion pressure reached the minimum point, transverse cracks were normally eliminated.

Web Cracks - Cracks within the element matrix normally increased in number until the minimum extrusion pressure was obtained. The fifth extrusion usually was higher in pressure than the fourth extrusion, and a nominal 45 to 50-ton pressure was typical. At this stage, the element mix was plastic enough for sound matrix knitting to occur, but dry enough to prevent the binder phase from concentrating in the "knit" or flow lines as the matrix moved through the die chamber. Elements collected after the extrusion pressure turned upward; and, up to a maximum of 80 tons, could be baked without cracks. From the standpoint of both the transverse and matrix cracks, an optimum extrusion pressure after the normal fifth extrusion appeared to lie between 45 and 70 tons (total force on a 6-inch-diameter ram).

Figure 55. TENSILE MODULUS AS A FUNCTION OF DENSITY FOR THREE BATCHES OF ELEMENTS.

Table 50
IMPURITIES IN THREE LOTS OF
POCO (PCD-0Q) FLOUR

Impurity (ppm)	Development(1)	Proproduction		
		LF-1(2)	LF-2(3)	LF-3(3)
Al	70	100	40	25
Ba	5	4	4	40
Ca	60	50	50	60
Cr	10	10	6	10
Fe	800	2,560	980	2,500
Mg	20	30	20	30
Ni	50	60	60	60
Pb	175	90	8	2
Si	500	500	100	90
Sn	150	80	8	< 1
V	70	90	104	100
Sulfur Content (%)	1.72	1.70	0.93	0.97
Ash Content (%)		0.40	0.256	0.380

(1) Ten-pound lot.

(2) Fifty-pound lot.

(3) Five-hundred-pound lot.

Table 51
SELECTED PHYSICAL PROPERTIES OF
POCO (PCD-00) FLOUR

	Development ⁽¹⁾	Preproduction		
		LF-1 ⁽²⁾	LF-2 ⁽³⁾	LF-3 ⁽³⁾
Helium Density (gms/cc)	1.98	1.81	1.90	1.91 ⁽⁴⁾
Surface Area (m ² /gm)	12.73	13.31	10.39	13.09 ⁽⁴⁾
Micromerograph				
100% Less Than Size (μm)	86	90	63	108 ⁽⁴⁾
90% Less Than Size (μm)	52	53.5	43.5	61
75% Less Than Size (μm)	-	40	34	45
50% Less Than Size (μm)	24	20.5	18	14.6
25% Less Than Size (μm)	9.3	8.2	8.8	6.0
10% Less Than Size (μm)	4.3	3.7	5.0	3.2

(1) Ten-pound lot.

(2) Fifty-pound lot.

(3) Five-hundred-pound lot.

(4) Average of four measurements.

Drying of Indene

A problem area which had a major effect on both types of cracks was the drying of the indene from the mixture. This drying problem occurred during the mixing, chopping, and extrusion processes as well as during the element baking process. If the amount of indene lost during mixing was large, a nonuniform blend was produced. The indene loss rate during mixing was controlled by maintaining the mix at or near room temperature. If the mix temperature rose to greater than 50° C, an excessive amount of indene was always evaporated.

During chopping of the mix, the indene was also evaporated. Again, the mix temperature was not permitted to rise greater than 50° C.

During extrusion, the mix was evacuated to remove the entrained air. It was found that a vacuum level of about 1,000 to 2,000 micrometers was sufficient. If a vacuum less than 1,000 micrometers was used, an excessive amount of indene was removed which resulted in a dry, nonextrudable mix. The mix temperature was also critical and had to be less than 50° C during the evacuation process.

As the mix was repeatedly extruded, the extrusion pressure decreased, indicating that a uniform mixture had not been achieved. The pressure became stable and then rose with further extrusion cycles. This pattern also indicated that some evaporation of the indene was possibly occurring which, if not controlled, would ultimately result in a nonextrudable mix. If the program had continued, a constant temperature of about 40° C on all of the processes would have been applied to these operations.

After extrusion, the element matrix contained about 42 to 50 percent of the original indene which had to be removed. It was decided that if the indene could be slowly evaporated, at a low temperature, the matrix would still be plastic enough to seal the voids created by the vaporized indene.

(a) LF-2. (50-lb lot)

(b) LF-3.(500-lb lot)

Figure 56. PHOTOMICROGRAPHS OF TWO SHIPMENTS OF POCO CARBON. (100X)

Table 52
PROPERTIES OF ELEMENTS MADE USING POCO LOW-FIRED FLOUR

Generation	Flour Batch	Coating Run	Impregnation?	Density (gms/cc)		Flexure Strength (psi)	Compressive Load (psi)	Thermal Stress (watts)	Coefficient of Thermal Expansion ($\times 10^{-6}/^{\circ}\text{C}$)		
				Bulk	Carbon				1,000° C	1,500° C	2,000° C
1a	LF-1	-	No	2.10	1.65	-	-	-	7.0	7.5	7.8
1b	LF-1	83016	Yes	2.09	1.74	-	-	370 ⁽¹⁾	6.9	7.3	7.6
2a	LF-2	83017	No	2.17	1.72	4,340	-	Cracked	(2)	-	-
2b	LF-2	83017	Yes	2.23	1.79	5,435	-	-	(2)	-	-
3a	LF-3	83018	No	2.22	1.77	6,240	14,900	400	6.7 - 7.0	-	-
3b	LF-3	83020	Yes	2.23	1.78	6,200	-	-	-	-	-
4a	LF-3	83020	No	2.23	1.76	5,235	15,500	-	6.1 ⁽³⁾	6.4 ⁽³⁾	6.9 ⁽³⁾
4b	LF-3	-	Yes	-	-	-	-	-	-	-	-

(1) Not coated.

(2) Values range from 6.2 to 6.7.

(3) Not coated nor impregnated.

Experiments determined the time and temperature range over which the free indene diluent was completely removed. For example, at 100° C the free indene was removed within 10 hours in a flowing-air-atmosphere furnace. A nominal element shrinkage of 0.8 linear percent occurred and was dependent on the amount of free indene and in the fuel element. An additional linear shrinkage of 0.1 percent occurred between the temperature range of 100 and 230° C.

During the cure to 250° C, the elements were flexible and plastic. Transverse cracks could occur due to the shrinkage, frictional drag of the extruded element in the graphite setter, and to the inherent weak internal strength of the uncured matrix. If internal web cracks were present, they occurred after this operation.

Figure 57. EFFECT OF THE BINDER LEVEL ON THE ELEMENT FLEXURE STRENGTH OF POCO LOW-FIRED FLOUR. (LF-3)

Table 53
LONGITUDINAL THERMAL EXPANSION
MEASUREMENTS ON POCO PCD-0Q
LF-1 FLOUR ELEMENTS

Temperature (° C)	Impregnated Element 500-300149		Nonimpregnated Element 500-300151	
	$\Delta L/L_0$ (%)	CTE $\times 10^6/\text{° C}$	$\Delta L/L_0$ (%)	CTE $\times 10^6/\text{° C}$
100	0.045	5.57	0.044	5.45
200	0.099	5.51	0.098	5.46
300	0.157	5.62	0.156	5.55
400	0.221	5.81	0.217	5.71
500	0.291	6.05	0.283	5.90
600	0.366	6.30	0.355	6.12
700	0.445	6.54	0.432	6.35
800	0.526	6.75	0.513	6.58
900	0.609	6.92	0.598	6.79
1,000	0.691	7.06	0.684	6.98
1,100	0.773	7.16	0.772	7.15
1,200	0.854	7.23	0.859	7.28
1,300	0.934	7.29	0.945	7.38
1,400	1.014	7.35	1.029	7.46
1,500	1.095	7.40	1.111	7.51
1,600	1.177	7.45	1.192	7.54
1,700	1.261	7.51	1.271	7.57
1,800	1.346	7.56	1.353	7.60
1,900	1.428	7.60 ⁽¹⁾	1.440	7.66
2,000	1.503	7.59 ⁽¹⁾	1.537	7.76

(1) Uranium effect. The element was not leached and free uranium was present in the matrix.

Table 54
COEFFICIENT OF THERMAL EXPANSION OF ELEMENTS
MADE WITH POCO LOW-FIRED FLOUR

Generation	Flour	ZrC Coated	Gas Impregnated	Binder Level (%)	Extrusion Pressure (tons)	Coefficient of Thermal Expansion ($\times 10^{-6}/^{\circ}\text{C}$)		
						1,000° C	1,500° C	2,000° C
1	LF-1	No	No	41 1/2	67	7.0	7.5	7.8
1	LF-1	No	Yes	41 1/2	67	7.1	7.4	7.7
1	LF-1	Yes	Yes	41	58	6.9	7.3	7.6
2	LF-2	No	No	43	56	6.7	-	-
2	LF-2	No	Yes	43	63	6.2	-	-
2	LF-2	Yes	Yes	42	68	6.3	-	-
3	LF-3	Yes	No	42	35	7.0	-	-
3	LF-3	Yes	No	40 1/2	45	6.7	-	-
4	LF-3	No	No	39	57 1/2	6.3	-	-
4	LF-3	No	No	39	66 1/2	6.1	6.4	6.9
For Comparison	SMC	Yes	Yes	47	83	5.6	5.8	6.1

Figure 58. EFFECT OF THE EXTRUSION PRESSURE ON THE COEFFICIENT OF THERMAL EXPANSION OF POCO LOW-FIRED FLOUR. (LF-3)

heating cycle. The heating time was increased up to 84 hours, but with no apparent improvement in the overall element quality. After baking, the matrices were hard, brittle, and could be easily broken. All matrix cracks could be observed after this bake. Subsequent baking operations to 850° C did not produce matrix cracks.

Curing to 850° C

The 250° C elements were transferred to a standard NERVA curing furnace in which they were further heated to 850° C in a nitrogen or argon atmosphere under ambient pressure conditions. The standard heating cycle employed a nominal 72 hours to maximum temperature. The cooldown rate was not controlled. Several cycles were tested including one in which the elements were heated in less than 16 hours to temperature. If the matrices were crack free before this heating cycle, they remained crack free. The standard NERVA cycle appeared to be satisfactory; but, if thicker web elements are needed, this operation should be investigated in more depth.

The indene drying cycle was not fully optimized, but a nominal 36-hour bake at 50° C in a flowing-air furnace was found to be satisfactory. If thicker web matrices were needed, such as for central support elements, a longer bake time would be desirable. The main point of this operation was to dry the indene slowly but completely.

Element Baking to 250° C

After the indene drying step, the elements were heated to 250° C in the standard NERVA oven using a 42-hour

Graphitization

The standard cycle employed a heating rate, in argon, of about four hours to reach $1,000^{\circ}\text{C}$, followed by a rate of 125°C per hour to an observed $2,225^{\circ}\text{C}$ ($2,300^{\circ}\text{C}$, corrected) in a hydrogen chloride-argon atmosphere which was used to remove the metallic impurities. The furnace was the standard NERVA graphitization furnace. Due to a temperature gradient in the furnace, the elements were graphitized, cooled, inverted in the furnace, and regraphitized. The heating cycle was not studied since the one just described appeared to be satisfactory.

NF-2 ELEMENT MANUFACTURE

It was desirable to produce uranium-loaded graphite elements for the nuclear furnace test reactor (NF-2 reactor). Basic specifications for these elements required a uranium fuel loading equivalent to 385 milligrams of uranium per cubic centimeter of element. The fuel was to be added as pyrocarbon-coated uranium dicarbide particles and was to use the same particles which had been used in the previous graphite reactors. The standard reactor fuel element specifications were applied to these elements. The element matrices were to contain the most recent manufacturing developments which had occurred during the investigations on the use of the low-fired carbon fillers and graphitizable resin binder.

It was decided that these matrices would be extruded using POCO PCD(-9)Q carbon filler (900°C) and bound with the Ashland-240 pitch. Typical chemical analyses of these materials are reported in Tables 23 and 55. The manufacturing process conditions were not fully established prior to the extrusion of these elements. For example, the shrinkage data on fueled elements were not fully defined. These data are critical in the selection of the die design and also in determining the amount of fuel particles required in the extrusion blend.

Extrusion of NF-2 Elements

It was decided that the NF-2 elements would be extruded in four basic extrusion groups. The first group would be processed through the graphitization cycle prior to the start of the second group. As the inspection data were collected, minor process changes would be made to the remaining extrusion batches. It was also decided that two of the four extrusion groups would be made using the development equipment, and the other two groups would be made using the standard fuel element manufacturing plant equipment. The basic equipment in both of these areas was essentially identical, but small differences in the equipment did exist.

An NF-2 element extrusion batch consisted of 3,000 grams of POCO PCD(-9)Q filler carbon, 1,521 grams of fuel beads, 644 grams of Ashland-240 pitch, and 486 grams of indene diluent. The extrusion plan required mixing in the standard Vee-type blender, multiple chopping, and multiple extrusion. The number of chopping steps was not specified, but the number of extrusions were to be set by the extrusion pressure curve.

NF-2 Extrusion, Group 1 - It was expected that the first element group would produce problems which had not previously been encountered. Since the elements were made in the development facility, the extrusion press was operated in a "stop-go" manner. The stop-go

operation is defined as a situation in which an element is extruded, the extrusion press is stopped by releasing the pressure, the element is withdrawn, and the press restarted. On restart, the pressure is slowly increased until the extrusion starts. This operation resulted in an extruded element in which the initial part of the element is made at a lower-than-normal pressure. Part of the low-pressure-extruded region of the element was recycled in an effort to minimize this effect. It was later found that the stop-go operation was not satisfactory because of the large number of matrix cracks which were found in the first 20-inch region of these elements.

Altogether, 28 elements were made in the Group 1 extrusion. Seven of the as-extruded matrices had visible cracks and would have normally been recycled. After each of the process heat treatments, the elements were inspected. A large number of the elements had a longitudinal crack in the end of the element which was first extruded from the press. This consistent type of crack emphasized the need for a continuous extrusion as opposed to the stop-go method. An overall crack-free element yield of 21 percent was obtained. It was decided that the next group would be processed using a continuous extrusion method.

Table 55
PROPERTIES OF POCO PCD(-9)Q
POWDER

Property	Y-12 Powder ⁽¹⁾	WNCO Powder ⁽²⁾
Surface Area (m ² /gm)	7.7	12.0
Density (gms/cc)		
Pour	0.56	0.55
Tap	1.02	1.12
Helium	1.92	1.86
Ash Content (%)	0.65	-
Loss at 100° C (%)	0.37	-
Sulfur Content (%)	1.18	0.80
Screen Analysis (% retained on mesh fraction)		
+60	< 0.1	0.07
-60 +100	0.2	0.03
-100 +140	0.8	0.04
-140 +200	5.2	1.28
-200 +270	0.2	8.45
-270 +325	1.1	9.04
-325	92.6	81.10
Spectrographic Analysis (ppm)		
Al	65	100
B	< 1	< 1
Ba	12	< 1
Ca	90	40
Co	< 20	< 20
Cr	85	250
Cu	15	10
Fe	4,500	1,200
K	20	70
Li	< 10	< 10
Mg	100	50
Mn	40	35
Mo	1	< 1
Na	30	30
Ni	100	65
P	< 100	< 100
Pb	6	5
Si	225	375
Sn	10	< 1
Ti	20	8
V	125	100
W	< 10	< 10
Zn	< 60	< 60
Zr	4	4

(1) Y-12 powder was used in the NF-2 element studies.

(2) WNCO powder data are reported for reference purposes.

NF-2 Extrusion, Group 2 - This set of elements was to be made in the same manner as those of Group 1 except that production equipment was to be used. Most of the production equipment was identical to the development equipment, but minor differences existed which presented some problems.

The first problem encountered was the rapid drying of the extrusion mix during the processing operations. It was very important that the free indene diluent not be removed from the mixture until the mix had been thoroughly wetted by multiple extrusions. If rapid drying occurred during the first few extrusions, a nonuniform mix was always obtained.

The production ventilation hoods were built to permit a large volume of air to pass through the hoods. This rapid air movement caused some early drying of the mix during the chopping operations. Since several chopping steps were required, large fractions of indene were removed.

A second step which removed large amounts of indene was the extrusion press evacuation. The press had an excellent vacuum system, and a pressure of less than 1,000 micrometers could easily be obtained in less than two minutes. This low vacuum level was able to evaporate indene at a high rate and also prevent the formation of a uniformly wetted blend.

A third step which caused some difficulty was the use of an extrusion die assembly which was different from the Group 1 elements. This problem was corrected before the Group 3 elements were made, but the Group 2 elements had a displaced hole pattern. The two drying problems were corrected when they were recognized as problem areas. An overall crack-free element yield of 52 percent was noted with this group.

NF-2 Extrusion, Group 3 - This set of elements was also made in the production equipment, but modification to the vented hood air flow was made and also the press evacuation procedure was controlled at evacuation pressures of 1,000 to 2,000 micrometers. The developmental die assembly was also used for these elements. No major problems were experienced during manufacture, and an overall crack-free element yield of 85 percent was obtained.

NF-2 Extrusion, Group 4 - The last group of elements was made in the development equipment, but the first seven inches of each element that came out of the press were recycled. No fabrication problems were experienced with this set of elements.

NF-2 Extrusion Summary - Extrusion problems associated with the manufacture of these elements emphasized the need for close control on the mixing, drying, and extrusion operations. The overall yield of crack-free elements progressively increased with each successive extrusion group. This increased yield was primarily due to recognizing and eliminating problems. It is believed that if a controlled mix/drying step had been employed, a high yield of crack-free matrices would have been consistently produced.

Drying Procedure

The as-extruded elements were air dried to remove the free indene at 50 to 60° C for 24 to 48 hours. For this drying step, the elements were placed in the standard NERVA extrusion and baking setters. The ends of the fixtures were open to permit warm furnace air to pass through and around the elements. After drying, the elements were not inspected prior to further processing.

Cure Procedure

The elements were baked to 250° C in flowing air using the standard NERVA bake cycle. This cycle is a programmed cycle that extends about 42 hours. The elements then were cooled and inspected for cracks, weighed, and measured for length. The data were recorded.

Bake Procedure

Next, the elements were placed in the standard NERVA bake setters and heated to 850° C in flowing argon using the NERVA heating cycle (~ 72 hours to 850° C). After cooling, the elements were again inspected, weighed, and the lengths recorded.

Graphitization Procedure

Finally, the elements were placed in the standard NERVA graphitization furnace using the regular graphite holders.

There was a possibility that the multiple extrusion practice may have damaged some fuel particles. Also, the POCO PCD(-9)Q powder used in these elements contained an iron impurity level of 4,500 ppm (Table 55). In view of these facts it was decided to use the graphitization heating cycle used previously in the NERVA fabrication studies, but the furnace temperature would be increased slightly and the furnace atmosphere would be a hydrogen chloride-argon mixture. This gas mixture was put in the furnace at a temperature of about 1,000° C and would be passed through the furnace while heating to 2,225° C (the observed temperature). The intent of the hydrogen chloride-argon mixture was to remove any metallic impurities prior to the temperature in which they would induce recrystallization of the graphite element structure. This recrystallization tended to undesirably reduce the coefficient of thermal expansion of the fuel element.

Due to a temperature gradient in the graphitization furnace it was also decided that the elements would be graphitized two times; and, between these runs, the elements would be inverted in the furnace to reduce the effect of the temperature gradients.

All of the NF-2 elements were graphitized as a single batch except for Group 4 which was processed in subsequent runs. Uranium loss during the graphitization-leach runs was low, indicating that no major bead-breakage problem had occurred during extrusion.

The hydrogen chloride-argon mixture thoroughly removed the metallic impurities without any matrix recrystallization. A typical double-graphitized matrix structure is indicated in Figure 59.

Braze Process

It was required that a metal carbide-carbon composite tip, having a nominal thickness of 0.4 inch, be brazed on one end of the element. These loaded graphite elements had a coefficient of thermal expansion which was higher ($6.5 \times 10^{-6}/^{\circ}\text{C}$, 25 - 1,000° C) than any elements previously made. Because of the increased thermal expansion it was believed that the standard Pewee 2 composite tip material would not be compatible with these matrices due

MS-71-1133-2

Figure 59. TYPICAL PHOTOMICROGRAPH OF AN NF-2 ELEMENT. (Element 385-300630; 52-Inch Region; 100X)

to a mismatch of CTE values. The standard composite material was a hot-pressed mixture of 65 percent niobium carbide and 35 percent graphite. A new composite material was supplied by LASL and machined into tip stock at the Y-12 Plant for use on the NF-2 element matrices. The new material was a hot-pressed mixture of tantalum carbide, niobium carbide, and graphite. This material had a high coefficient of thermal expansion ($\sim 7.0 \times 10^{-6}/^{\circ}\text{C}$, 25 - 1,000 $^{\circ}\text{C}$) which was approximately equal to the CTE value of the fueled elements.

A braze procedure was previously established for the Pewee 2 reactor. In general, if the matrix structure or the composite tip material was changed, modifications to the braze process were required. Since both the matrix structure and tip stock were new materials, it was not known if the Pewee 2 reactor procedure would be applicable.

Due to the limited program time available it was not possible to do a thorough investigation of the braze process. A few specimens were brazed, with the new matrix and tip stock, and the Pewee 2 procedure was followed. Basically, this procedure required that the matrix and composite tip-joint area be coated with a thin film of molybdenum powder. The joint region was rapidly heated to a nominal 2,285 $^{\circ}\text{C}$ and a compressive load was applied to the element joint. After brazing, the joints were tested to determine the flexural strength; also, the brazed joint region was metallographically inspected for fuel bead damage and degree of graphite precipitation in the joint. If damage had occurred, the braze temperature was normally reduced; if the joint strength was less than 2,000 psi in flexure, the braze temperature was modified by either raising or lowering the temperature.

As previously stated, the Pewee 2 braze procedure was performed on test joints. The average flexural strength of the as-brazed joints was 2,710 psi. It was decided that the braze temperature should be raised to 2,335° C (which was 50° C higher than the Pewee 2 cycle). Test joints made at this temperature had an average strength of 3,360 psi (Table 56).

Table 56
SUMMARY DATA FROM THE INSPECTION OF AN
NF-2 ELEMENT

Property	Extrusion Group Number			
	1	2	3	4
Uranium Loading (mgs U/cc)	368	400	387	398
Eddy Current Data				
Number of Elements with Visual Flaws	17	6	1	2
Number of Elements with NDT Flaws	5	4	2	5
Number of Acceptable Elements	6	11	10	3
Electrical Resistance, PDE (milliohm/element inch)				
As Leached	290 to 330	295 to 340	300 to 335	330 to 370
As Coated	20 to 180	23 to 190	20 to 200	22 to 195
Flexure Strength ⁽¹⁾ (psi)				
Uranium Loaded (avg)	7,785			
Nonfueled (avg)	11,830			
Braze Joint Strength (psi)				
Braze Temperature (° C)				
2,285	2,710			
2,335	3,360			

(1) Flexure and braze-joint-strength data are for all four element groups.

In previous reactors it was required that the joint also be cyclic heated to a preset temperature and again tested for strength and metallographically examined. However, due to the limited program time there were no cyclic heating tests performed on the element joints; but, a few element brazed joints were retained to perform this test if problems should arise later.

A deviation from the Pewee 2 braze procedure was made in the acid-leach step before the braze. Prior to the braze, the end of the element was machined to obtain a flat surface. As a result of the machining step, some of the coated uranium dicarbide fuel particles were cut. Normally, the machined element end was acid leached at about 80° C in a 20 percent nitric acid solution which removed the exposed uranium dicarbide particles. For the NF-2 elements it was decided that the end face would be machined after the first leach-graphitization step. The exposed fuel particles were removed during the second leach-graphitization operation. The leach-graphitization cycle employed a gaseous mixture of argon and hydrogen chloride at temperatures up to 2,225° C (observed).

Machining Procedure

All NF-2 elements were machined using standard graphite fuel element techniques.

Machined Element Inspection

Physical Inspection - All elements were inspected after machining, using the standard Pewee 2 procedures, and the dimensional data recorded. The element body leak was not measured except to note that the body leak rate was greater than 480 cc/min. The matrix structure had an open porosity of from 15 to 18 percent because of the graphitizable resin binder. A pore entrance diameter of less than two micrometers was also typical. These data were not collected on the NF-2 elements, but previous development elements had consistently shown these data.

NDT Inspection - After machining, the elements were eddy-current inspected to determine flaws, and the electrical resistance was measured by applying potential drop evaluation (PDE) techniques. These data were primarily taken for record purposes. The elements were also dimensionally reinspected after the leach operation.

Leach Operation

After machining and inspection, the elements were processed through a high-temperature leach operation. The Pewee 1 reactor leach cycle was used which was basically a single heating to 2,125° C (observed) in a flowing hydrogen chloride-argon atmosphere.

Leach Element Inspection

The leached elements were examined using standard inspection procedures (Pewee 2) and the data made a matter of record. The observations that were noted are discussed in the sections that follow.

Hole Pattern - Groups 1, 3, and 4 elements had Grade 1 or 2 hole patterns. The outside 12 holes were uniformly inwardly displaced, but were within the specification band. An inward displacement of six to nine mils was common. The Group 2 elements had Grade 3 hole patterns. The outside 12 holes were inwardly displaced 12 to 20 mils. Such displacement was a result of the die used and could be corrected by a proper die selection. Since the element shrinkage data were not known at the time of manufacture, a die was selected that was based on the estimated shrinkage data.

Uranium Loading - Before the extrusion of standard NERVA elements, a calibrated uranium loading curve was always generated. This curve was obtained by extruding elements which contained variable amounts of uranium. The elements were processed through all of the manufacturing steps using procedures identical to the ones to be used for production operations. After processing, they were analyzed for their uranium content. Process variables which affected the loading included: element shrinkage, number of beads broken during manufacture, loss of uranium during the leaching processes, and other process variables. There was not sufficient development time remaining in the program to generate a loading curve for the NF-2 elements. The amount of uranium added to the extrusion mix was an estimation, based on prior extrusion experience.

The NF-2 desired uranium level was 385 milligrams of uranium per cubic centimeter (mgs U/cc). After processing the elements, the uranium loading for the four groups of elements

ranged from 368 to 398 mgs U/cc (Table 56). A typical plot of the uranium distribution along an element length is presented in Figure 60.

Coefficient of Thermal Expansion - One of the major goals of the graphite fuel element program was to develop a uranium-loaded matrix having a CTE approximately equal to the thermal expansion of zirconium carbide ($7.0 \times 10^{-6}/^{\circ}\text{C}$, 25 - 1,000 $^{\circ}\text{C}$). A large number of NF-2 elements was measured to determine their expansivity values. For these tests, the CTE unit at the Y-12 Plant was used. This instrument required a two-inch specimen which was heated to a nominal 1,000 $^{\circ}\text{C}$ using a linear heating rate. The temperature and expansivity data were automatically recorded on tape at two-minute intervals. About 100 data points were taken on each CTE sample. These data were processed through a computer code which corrected the data to compensate for the expansivity of the quartz specimen holder. The CTE printout contained the raw data, as taken, as well as the normalized data.

Figure 60. URANIUM DISTRIBUTION OF NF-2-TYPE ELEMENTS.

Table 57
COEFFICIENT OF THERMAL
EXPANSION REFERENCE
GRAPHITE DATA

Date	Value(1) ($\times 10^{-6}/^{\circ}\text{C}$)
1-27-72	6.93
1-27-72	6.93
2-2-72	7.05
2-3-72	6.88
2-7-72	6.79
2-14-72	7.03
2-22-72	7.08
2-28-72	6.94
3-6-72	6.98
3-9-72	6.99
3-16-72	6.98
3-20-72	6.94
Average	6.96
Range	6.79 to 7.08
Percent from Average	2.4 to 1.7

(1) Temperature 25 to 1,000 $^{\circ}\text{C}$.

Two reference graphites were originally obtained from LASL and were defined to be the CTE standard graphites. These graphites were repeatedly run in the LASL 30-inch CTE furnace to establish the expansivity values. One of the reference graphites was routinely run in the Y-12 Plant equipment. The data were used to verify that the equipment was operating satisfactorily. Table 57 gives a listing of 12 runs on this reference graphite which were made on different dates. These data show that the repeatability of the Y-12 instrument is -2.4 to +1.7 percent. A larger listing of the data is available, if needed.

Table 58 lists the CTE values of the NF-2 elements. The CTE data show that the loaded NF-2 elements had an average CTE value of $6.5 \times 10^{-6}/^{\circ}\text{C}$ (25 to 1,000 $^{\circ}\text{C}$) which was almost equal to the expansion of

zirconium carbide ($6.9 \times 10^{-6}/^{\circ}\text{C}$, 25 to 1,000 $^{\circ}\text{C}$).

An element section was also shipped to LASL for CTE measurements up to 2,000 $^{\circ}\text{C}$. A plot of the element and zirconium carbide expansion data is seen in Figure 61. The element section, when heated to obtain the high-temperature CTE data, had essentially no measurable permanent dimension change.

Table 58
COEFFICIENT OF THERMAL EXPANSION
FOR ELEMENTS OF GROUPS
1 THROUGH 4

Specimen Number	Values at the Indicated Location ($\times 10^{-6}/^{\circ}\text{C}$, 25 to 1,000 $^{\circ}\text{C}$)		
	0 Inch	26 Inches	54 Inches
<u>Group 1 Elements</u>			
385-300629	6.4	6.2	6.8
385-300630	6.8	6.2	6.3(1)
385-300630	6.8	-	6.4(1)
385-300637	6.9	6.8	6.5
385-300641	6.6	6.6	6.4
385-300645	6.4	7.0	6.2
385-300650	-	-	6.9
385-300650	-	-	6.4
<u>Group 2 Elements</u>			
385-300658	-	-	6.4
385-300659	6.7	-	-
385-300662	-	-	6.5
385-300663	6.5	-	-
385-300668	-	-	6.5
385-300669	6.3	-	-
<u>Group 3 Elements</u>			
385-300675	6.4	-	-
385-300676	-	-	6.5
385-300678	-	-	6.3
385-300681	6.5	-	-
385-300684	-	-	6.5
385-300685	6.5	-	-
<u>Group 4 Elements</u>			
385-300688	-	-	6.7
385-300689	6.6	-	-
385-300690	-	-	6.7
385-300691	6.5	-	-
Average CTE Value ⁽¹⁾	$6.5 \times 10^{-6}/^{\circ}\text{C}$ (25 to 1,000 $^{\circ}\text{C}$)		
CTE Range	$6.2 - 7.0 \times 10^{-6}/^{\circ}\text{C}$ (25 to 1,000 $^{\circ}\text{C}$)		
Number of Data Locations	35		

(1) This sample was also measured by LASL. The first LASL run had CTE values of 6.4 (25 to 1,000 $^{\circ}\text{C}$) and 7.4 (25 to 2,000 $^{\circ}\text{C}$). The second LASL run had CTE values of 6.1 (25 to 1,000 $^{\circ}\text{C}$) and 7.2 (25 to 2,000 $^{\circ}\text{C}$)

strength values for Pewee 2-type elements were 3,500 to 4,500 psi.)

Strain to Failure - Some of the flexural samples were equipped with a strain gage to monitor the flexural strain to failure. A typical strain-to-failure curve is given in Figure 62 for a

A nonfueled NERVA graphite element, made identical to the NF-2 elements, was also measured to determine the CTE values. Three samples, taken along the element length, had an average value of $6.95 \times 10^{-6}/^{\circ}\text{C}$ (25 to 1,000 $^{\circ}\text{C}$) with a range of 6.78 to $7.12 \times 10^{-6}/^{\circ}\text{C}$.

A nonfueled, central support element was fabricated using the same manufacturing techniques as those used on fuel elements. This element had a single gas hole instead of the 19 gas holes. The extrusion blend was mixed and wetted using the 19-hole extrusion die. However, the die was changed to make the central element. The extruded element had an average CTE value of $7.6 \times 10^{-6}/^{\circ}\text{C}$ (25 to 1,000 $^{\circ}\text{C}$) with a range from a low of 7.58 to a high of $7.62 \times 10^{-6}/^{\circ}\text{C}$. These CTE values were significantly higher than the 19-hole, nonfueled element which was $6.95 \times 10^{-6}/^{\circ}\text{C}$.

A variation in the fuel element CTE data was observed when the elements were extruded using stop-go practices. The data, reported in Table 58, show that some of the Group 1 elements had small variations in the longitudinal CTE.

Flexural Strength - Flexural strengths of the graphite nonfueled elements averaged 11,830 psi, with a range of 11,000 to 13,000 psi. The NF-2-loaded elements had an average flexural strength of 7,785 psi with a range of 7,200 to 8,300 psi (Table 56). These element strengths are significantly higher than previous graphite fuel elements. (Typical

fueled NF-2 element. A strain-to-failure value of 4,150 $\mu\text{in/in}$ was typical. The nonfueled elements had a typical strain-to-failure value of 5,500 $\mu\text{in/in}$. The strain-to-failure values are higher than Pewee 2-type elements which had a typical strain value of 3,000 $\mu\text{in/in}$.

Internal Matrix Quality - All of the NF-2 elements were inspected using standard eddy-current techniques. Table 56 provides a brief summary of these inspection data. The internal quality of the acceptable elements was excellent, and the eddy-current inspection data indicated that a very uniform matrix was present.

Electrical Resistance Data (PDE) - Electrical resistance data of "as-leached" elements are also tabulated in Table 56. Figure 63 contains a typical PDE plot of an element. Elements of Groups 1, 2, and 3 had PDE values ranging from 290 to 340 milliohms/element inch; Group 4 elements had PDE values ranging from 330 to 370 milliohms/element inch.

Figure 62. STRESS-STRAIN CURVE FOR ELEMENT 385-300629.

thermal stress break values (Q^{111}) of 80 to 85 Btu/in³-sec were obtained; the minimum NF-2-design break value was 60 to 65 Btu/in³-sec.

Figure 61. EXPANSION OF ZIRCONIUM CARBIDE VERSUS THE NF-2 FUEL ELEMENT. (Data Collected by LASL on Y-12 Material)

Thermal Stress Test - Thermal-stress-resistance data were determined using the welder test unit. Wafers having a thickness of 0.100 inch were machined from the 19-hole fuel elements. The average power fracture level was 385 watts with a range of 350 to 450 watts. Nonfueled element wafers were also tested and fractured at an average of 545 watts (500 to 600-watt range). A typical fracture value for Pewee 2-type elements was 250 watts. The higher wattage level for the NF-2 elements indicates an improved thermal stress resistance.

Three fueled elements, which were not zirconium carbide coated, were shipped to LASL for measurement of the thermal stress resistance using the standard LASL test equipment. LASL test data showed the matrices to be significantly higher than the required minimum level. Typical

Zirconium Coating

The NF-2 elements were zirconium carbide coated using the low-temperature methane process. Outer surfaces as well as the gas passage bores were coated.

Outer Surface Coating - Process parameters used for coating the outer surface and the zirconium carbide thickness distribution are listed in Figure 64. Run 81028Q was made to coat five loaded graphite elements, four LASL composite elements, and one LASL graphite element. This run was also considered to be the pilot run for the NF-2 elements.

Figure 63. ELECTRICAL RESISTANCE OF AN NF-2 ELEMENT.

NF-2 elements (10 elements) were given an outer-surface coating in Run 81029Q. The same process was used for both of these runs. Distribution of the zirconium carbide thickness was not measured on the NF-2 elements because of an NDT equipment problem. However, it was assumed that the profiles for the two runs were the same since the weight-gain data were equal and the measured dimensions of the elements were the same. Basically, the outer surface coating was uniformly distributed along the element length to a thickness of 1.4 mils. Plating temperatures ranged from 1,090° C at the three-inch point to 1,210° C at the 55-inch point.

Date	Run	Type	Run Time (hrs)	Weight Gain (%)				Pre-Heater Time (hrs)	Number and Type Elements	Gas Flow (l/min/element)					Salt (gm/min/element)
				High	Low	Average	Gms/Hr			Ar	HCl	H ₂	CH ₄	Salt	
2-10-72	81028Q	OD GEM-ZrC	20	20.7	17.0	18.0	0.90	109	28 LASL Y-12	2.0	-	0.59	0.038	0.058	0.56

Figure 64. ESTIMATED THICKNESS FOR GEM-ZIRCONIUM CARBIDE OUTSIDE-DIAMETER COATING. (GEM - Process Where the "G" End of the Element was the Entrance - "E" - End for the Coating Gases and Carbon Supplied by Methane - "M" - Gas)

Bore Coating - Two bore-coating runs were made. Run 81028Q was considered to be a pilot run for the NF-2 elements and Run 82019Q contained the NF-2 elements. The coating chemistries and zirconium carbide distribution in the element bores are noted in Figures 65 and 66. The coating gas mixtures for both runs were of the same composition.

Date	Run	Type	Run Time (hrs)	Weight Gain (%)				Pre-Heater Time (hrs)	Number and Type Elements	Gas Flow (l/min/element)					Salt (gm/min/element)
				High	Low	Average	Gms/Hr			Ar	HCl	H ₂	CH ₄	Salt	
2-15-72	83028Q	ID GEM-ZrC	33	150	134	140.7	4.26	40	14 LASL Y-12	2.5	-	0.33	0.020	0.062	0.60

Figure 65. GEM-ZIRCONIUM CARBIDE BORE COATING. (Preliminary Run for Element NF-2; for Definition of "GEM", See Title to Figure 64)

Date	Run	Type	Run Time (hrs)	Weight Gain (%)				Pre-Heater Time (hrs)	Number and Type Elements	Gas Flow (l/min/element)					Salt (gm/min/element)
				High	Low	Average	Gms/Hr			Ar	HCl	H ₂	CH ₄	Salt	
2-23-72	83029Q	ID GEM-ZrC	37	164	155	158.8	4.29	47	14 POCO 900°	2.50	-	0.33	0.020	0.062	0.60

Figure 66. GEM-ZIRCONIUM CARBIDE BORE COATING FOR ELEMENT NF-2. (For Definition of "GEM", See Title to Figure 64)

Plating temperatures ranged from 1,120° C at the three-inch point to 1,400° C at the 55-inch point. These temperatures deposited a zirconium carbide film which should contain very few gaseous impurities. The pilot run (Run 83028Q) was terminated after 33 hours, and a nominal 141 grams of zirconium carbide were deposited in the element bores. The NF-2 run (Run 83029Q) was terminated after 37 hours, and a nominal 159 grams of zirconium carbide were deposited in the bores.

High-Resolution Eddy-Current Data - Coated bores were inspected using the high-resolution eddy-current instrument (HREC) to determine the number of cracks in the zirconium

carbide. Data on each element showed that some elements had no detectable cracks, but a few elements had small, detectable cracks. The number of cracks were significantly less than had been found in previous studies. A typical HREC curve is given in Figure 67 and represents a crack-free coated element.

PDE Data - Electrical resistance data on coated elements are noted in Table 56. The resistance varied from a nominal 190 milliohms/element inch (at the 0 element-inch point) to 20 milliohms/element inch (at the 52 element-inch point). The PDE variation was due to the coat-thickness profile distributed in the element bores.

Air-Flow Data - Coated bores had a nominal 92-mil diameter. The before-coating diameters were nominally 102 mils. No obvious module deposits of carbide were noted in the coated bores.

Elements Shipped to LASL

Tables 59 and 60 list the elements shipped to LASL for evaluation.

Table 59
DATA FOR NF-2 ELEMENT,
RUN 82019Q

Element Number	ZrC Coating		Extrusion Group	Element Weight (gms)
	Outside Diameter	Inside Diameter		
385-300626	17.3	160.2	1	782.3
385-300634	18.0	156.9	1	774.4
385-300635	18.7	158.8	1	777.5
385-300636	18.9	161.5	1	773.3
385-300639	20.7	163.8	1	788.1
385-300675	17.5	156.4	3	787.0
385-300678	18.3	159.0	3	781.2
385-300680	17.3	161.3	3	787.0
385-300685	17.9	155.4	3	782.7
385-300686	17.4	164.2	3	789.9

Figure 67. COATING RUN 83029Q FOR HIGH-RESOLUTION
EDDY-CURRENT GROUP 1 ELEMENT. (Element 385-
300635; Bore 9; 85-Mil Probe)

Table 60
DATA LIST FOR PILOT
RUN 81028Q

Element Number	ZrC Coating		Extrusion Group	Element Weight (gms)
	Outside Diameter	Inside Diameter		
<u>Graphite-Loaded Elements</u>				
385-300633	17.8	149.9	1	767.9
385-300679	19.3	144.6	3	769.5
385-300687	17.9	146.9	4	766.5
385-300690	18.5	143.2	4	768.6
385-300692	19.5	143.9	4	773.9
<u>LASL Composite Elements</u>				
298-93447	17.0	136.0	-	1,169.0
298-93449	18.0	137.0	-	1,170.0
298-93450	17.0	134.0	-	1,166.0
298-93451	17.0	139.0	-	1,172.0
<u>LASL Nonfueled Element</u>				
009-04699	17.7	137.5	-	699.2
<u>Y-12 Loaded, Noncoated Elements(1)</u>				
385-300632	-	-	1	604.4
385-300689	-	-	4	607.1
385-300677	-	-	3	590.9

(1) Elements submitted for physical property measurements.

CONCLUSIONS

These fuel-element studies have demonstrated that the physical properties can be changed over a wide range. With the use of low-fired fillers and a graphitizable resin binder, fuel elements were produced which had a high CTE, high strength, low modulus, and high strain to failure. These fuel elements also had good thermal-shock-resistance properties.

Matrix studies were not completed at the end of the program. However, a manufacturing process produced a yield of 85 percent crack-free elements. When optimized it is believed that a higher yield of crack-free elements should be produced.

The filler-firing temperature was reduced to only 900° C during these studies. Future studies should be made of mesophase carbon fillers fired to 450 to 500° C. Extremely low binder contents should be possible if the volatile content of the mesophase carbon is controlled at or near 7 percent. The remaining organic volatile matter would serve as the binder phase. Use of organic precursors to form the carbon filler should be continued. Organic resin studies produced several candidate fillers which would be a reliable source of carbon over an extended period of time. Since a NERVA fuel element contains only about one pound of carbon per element (and the development, fabrication, and certifying costs of the fuel element are very expensive) it should be logical to obtain carbon raw materials from demonstrably reliable and consistent sources.

REFERENCES

- (1) *Rover Fuel Element Development Activities*, Union Carbide Corporation-Nuclear Division, Oak Ridge Y-12 Plant, Oak Ridge, Tennessee (1962-1968).
- (2) VanHull, A. K. and Smith, R. D.; *Phoebus 1B Studies Interim Report*, Y-EB-36; Union Carbide Corporation-Nuclear Division, Oak Ridge Y-12 Plant, Oak Ridge, Tennessee; September 6, 1967.
- (3) Greenstreet, B. L. et al; *Fracture of Graphite*, Quarterly Progress Reports; Union Carbide Corporation-Nuclear Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee; July 1969 through 1971.
- (4) *Status Report on Development and Evaluation of NERVA Fuel Element Matrices*, Y-DA-2763; Union Carbide Corporation-Nuclear Division, Oak Ridge Y-12 Plant, Oak Ridge, Tennessee; May 9, 1969.
- (5) *Rover Fuel Element Development Activities*, Y-DA-4601; Union Carbide Corporation-Nuclear Division, Oak Ridge Y-12 Plant, Oak Ridge, Tennessee; February 29, 1972.
- (6) *Rover Fuel Element Development Activities*, Y-DA-4316; Union Carbide Corporation-Nuclear Division, Oak Ridge Y-12 Plant, Oak Ridge, Tennessee; August 16, 1971.
- (7) *Rover Fuel Element Development Activities*, Y-DA-4184; Union Carbide Corporation-Nuclear Division, Oak Ridge Y-12 Plant, Oak Ridge, Tennessee; May 14, 1971.
- (8) *Rover Fuel Element Development Activities*, Y-DA-3940; Union Carbide Corporation-Nuclear Division, Oak Ridge Y-12 Plant, Oak Ridge, Tennessee; November 25, 1970.
- (9) *Rover Fuel Element Development Activities*, Y-DA-4093; Union Carbide Corporation-Nuclear Division, Oak Ridge Y-12 Plant, Oak Ridge, Tennessee; February 12, 1971.
- (10) *Rover Fuel Element Development Activities*, Y-DA-3811; Union Carbide Corporation-Nuclear Division, Oak Ridge Y-12 Plant, Oak Ridge, Tennessee; August 26, 1970.
- (11) *Rover Fuel Element Development Activities*, Y-DA-3238; Union Carbide Corporation-Nuclear Division, Oak Ridge Y-12 Plant, Oak Ridge, Tennessee; October 30, 1969.
- (12) *Rover Fuel Element Development Activities*, Y-DA-3618; Union Carbide Corporation-Nuclear Division, Oak Ridge Y-12 Plant, Oak Ridge, Tennessee; May 11, 1970.
- (13) Collins, F. M.; "Dimensional Changes during Heat Treatment and Thermal Expansion of Polycrystalline Carbons and Graphites", *First and Second Carbon Conference*, pp 177-178; American Carbon Committee, McMillan Company, New York, New York (1953-1955).

- (14) Collins, F. M.; "Thermal Expansion of Polycrystalline Carbons and Graphites", *Third Carbon Conference*, pp 659-674; American Carbon Committee, McMillan Company, New York, New York (1957).
- (15) *Rover Fuel Element Development Activities*, Y-DA-4729; Union Carbide Corporation-Nuclear Division, Oak Ridge Y-12 Plant, Oak Ridge, Tennessee; May 4, 1972.

BIBLIOGRAPHY

Routine Y-12 quarterly reports issued during the course of the NERVA fuel element development studies include the following:

Rover Fuel Element Development Activities Report, Y-DA-3097, August 8, 1969.

Rover Fuel Element Development Activities Report, Y-DA-3238, October 30, 1969.

Rover Fuel Element Development Activities Report, Y-DA-3432, February 4, 1970.

Rover Fuel Element Development Activities Report, Y-DA-3618, May 11, 1970.

Rover Fuel Element Development Activities Report, Y-DA-3811, August 26, 1970.

Rover Fuel Element Development Activities Report, Y-DA-3940, November 25, 1970.

Rover Fuel Element Development Activities Report, Y-DA-4093, February 12, 1971.

Rover Fuel Element Development Activities Report, Y-DA-4184, May 14, 1971.

Rover Fuel Element Development Activities Report, Y-DA-4316, August 16, 1971.

Rover Fuel Element Development Activities Report, Y-DA-4494, November 30, 1971.

Rover Fuel Element Development Activities Report, Y-DA-4601, February 29, 1972.

Rover Fuel Element Development Activities Report, Y-DA-4729, May 4, 1972.

DISTRIBUTION**Atomic Energy Commission - ORO**

Hickman, H. D. (2)
Zachry, D. S., Jr

Battelle Memorial Institute

Blocher, J. M.

Los Alamos Scientific Laboratory

Baker, R. D.
Bowman, M. G.
Elliott, D. E.
Hessing, H.
Lyon, L. L.
MacMillan, D. P.
Rowley, J. C.
Smith, M. C.
Spence, R. W.
Taub, J. M.

Oak Ridge Gaseous Diffusion Plant

Wilcox, W. J., Jr
Winkel, R. A.

Oak Ridge National Laboratory

Eatherly, W. P.
Greenstreet, W. L.
Grimes, W. R.
Overholser, L. G.
Scott, J. L.

Oak Ridge Y-12 Plant

Burditt, R. B.
Burkhart, L. E.
Denny, A.
Keith, Alvin
Kite, H. T.
Lundin, M. I.

Marrow, G. B.
McLendon, J. D.
Mitchel, G. W.
Napier, J. M. (10)
Schreyer, J. M.
Smith, J. H.
Smith, R. D.
Tench, F. M.
Weathersby, W. E.
Whitson, W. H.
Williams, R. D.
Yaggi, W. J./Googin, J. M.
Y-12 Central Files (5)
Y-12 Central Files (master copy)
Y-12 Central Files (route)
Y-12 Central Files (Y-12RC)

Paducah Gaseous Diffusion Plant

Levin, R. W.

Sandia - Albuquerque

Auerbach, I.

Space Nuclear Systems Office

Dix, G. P.
Gabriel, D. S.
Gavingan, F. X.
Lombardo, J.
Scheib, W. S.
Schwenk, F. C.
Thielke, N. R.

In addition, this report is distributed in accordance with the category UC-80, **Reactor Technology**, as given in the *USAEC Standard Distribution Lists for Unclassified Scientific and Technical Reports*, TID-4500.