CARBON AND GRAPHITE MATERIALS R&D AT THE OAK RIDGE NATIONAL LABORATORY

AN OVERVIEW

TIMOTHY D. BURCHELL
METAL & CERAMICS DIVISION
OAK RIDGE NATIONAL LABORATORY

OVERVIEW OF PRESENTATION

- HISTORICAL PERSPECTIVE
- CURRENT ACTIVITIES
  - NUCLEAR FISSION & FUSION
  - SPACE NUCLEAR POWER ACTIVITIES
  - ADSORBENT COMPOSITES FOR GAS SEPARATION (CARBON FIBER COMPOSITE MOLECULAR SIEVE)
  - ADSORBENT MONOLITHS FOR NATURAL GAS STORAGE
  - THERMAL MANAGEMENT CARBONS
    - HIGH THERMAL CONDUCTIVITY C/C COMPOSITES AND GRAPHITE FOAM
- SUMMARY & FUTURE DIRECTIONS

CARBON AND GRAPHITE MATERIALS R&D AT THE OAK RIDGE NATIONAL LABORATORY

HISTORICAL PERSPECTIVE

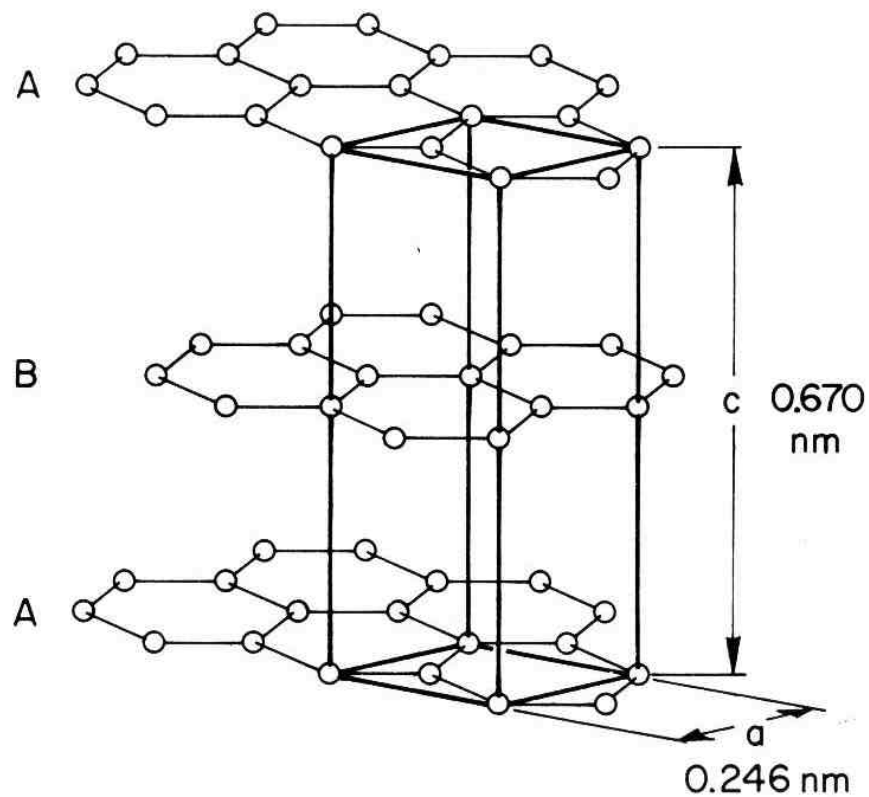
- ENRICO FERMI, THE CHICAGO PILE NO. 1, STAGG FIELD, UNIVERSITY OF CHICAGO (1942)
- WW II, THE MANHATTON PROJECT, X-10 REACTOR AT OAK RIDGE TENNESSEE (1943), AGOT GRAPHITE FROM THE NATIONAL CARBON COMPANY
- GRAPHITE MATERIALS R&D IN SUPPORT OF THE HANFORD PRODUCTION REACTORS
- GRAPHITE REACTOR DEVELOPMENT, MOLTEN SALT REACTOR, HIGH TEMPERATURE GAS COOLED REACTORS
- CARBON & GRAPHITE MATERIALS SCIENCE

CARBON AND GRAPHITE MATERIALS R&D AT THE OAK RIDGE NATIONAL LABORATORY

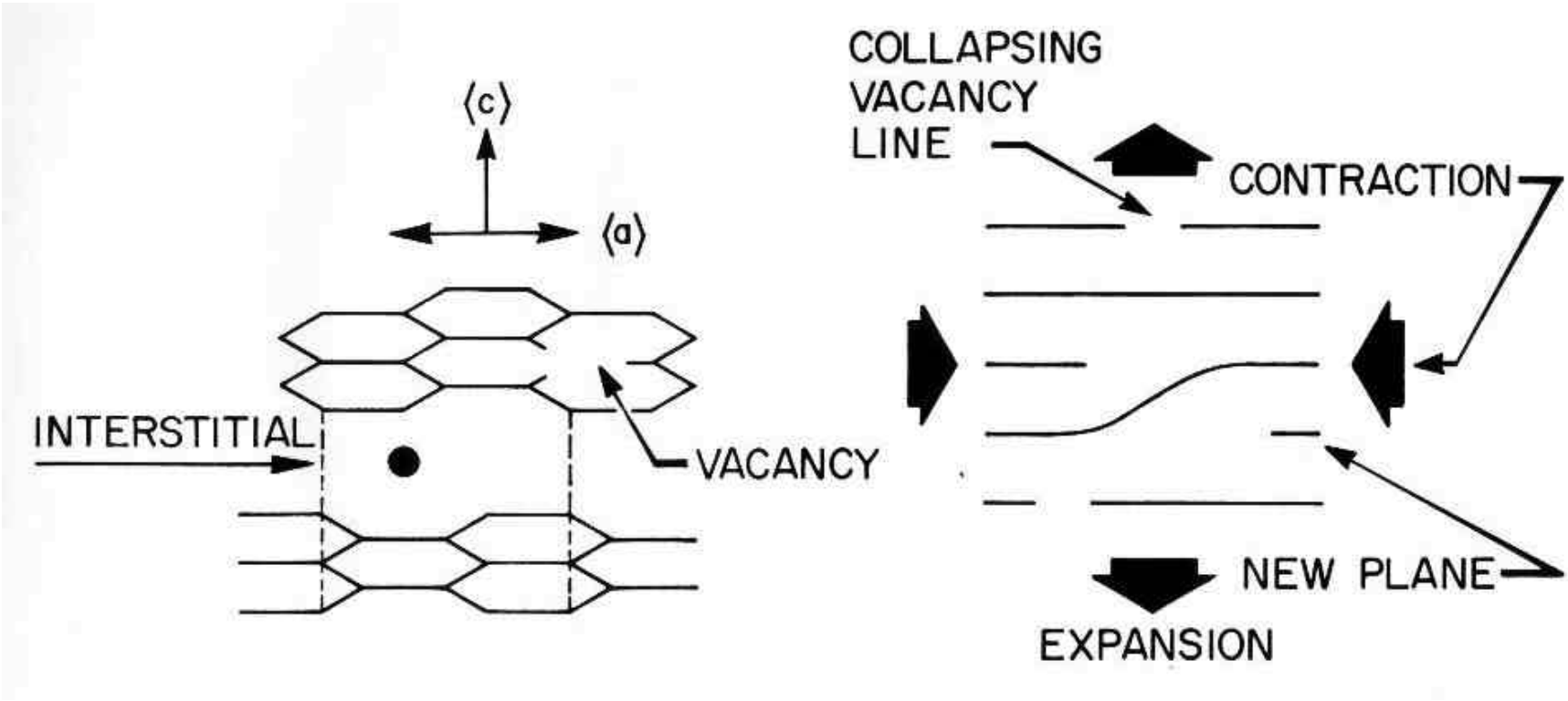
NUCLEAR FISSION & FUSION

GRAPHITE MODERATED FISSION REACTORS

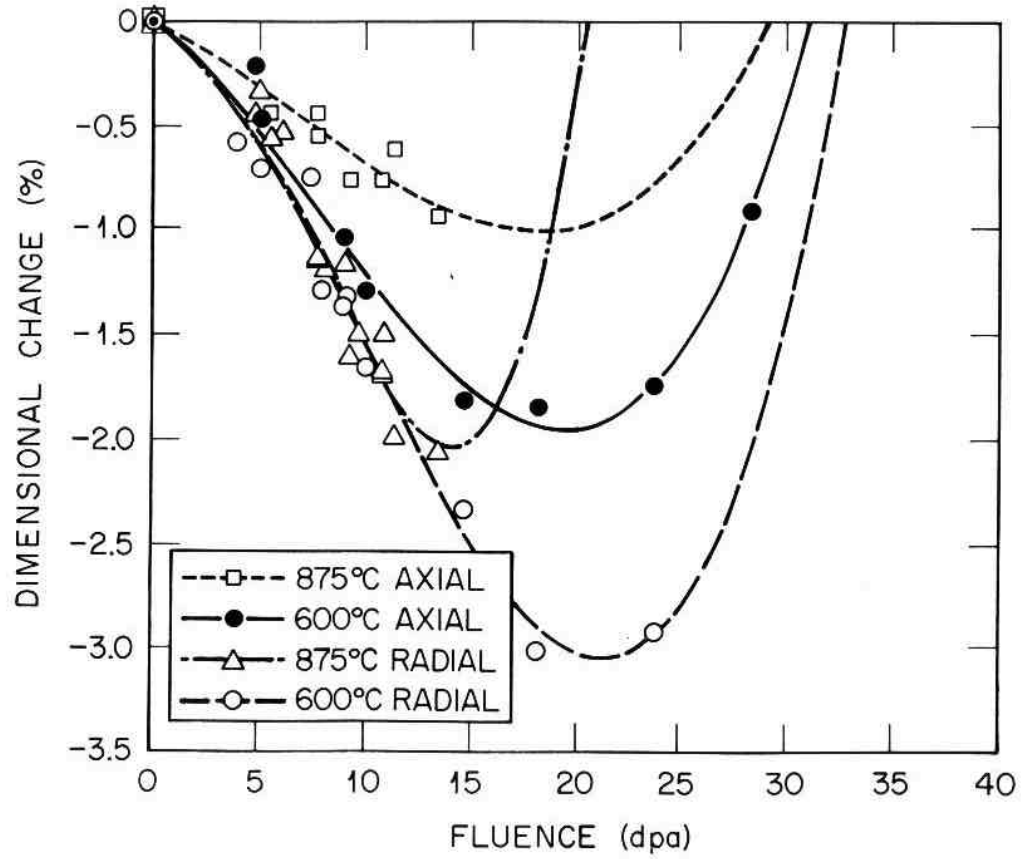
- Graphite is an excellent moderator
- neutron irradiation causes carbon atom displacement
- dimensional and physical property changes result
- elucidation of the damage mechanism
- acquisition of design data for key physical properties
- dimensional stability, thermal conductivity, strength, radiation creep behavior, fracture behavior



THE RADIATION DAMAGE MECHANISM IN GRAPHITE

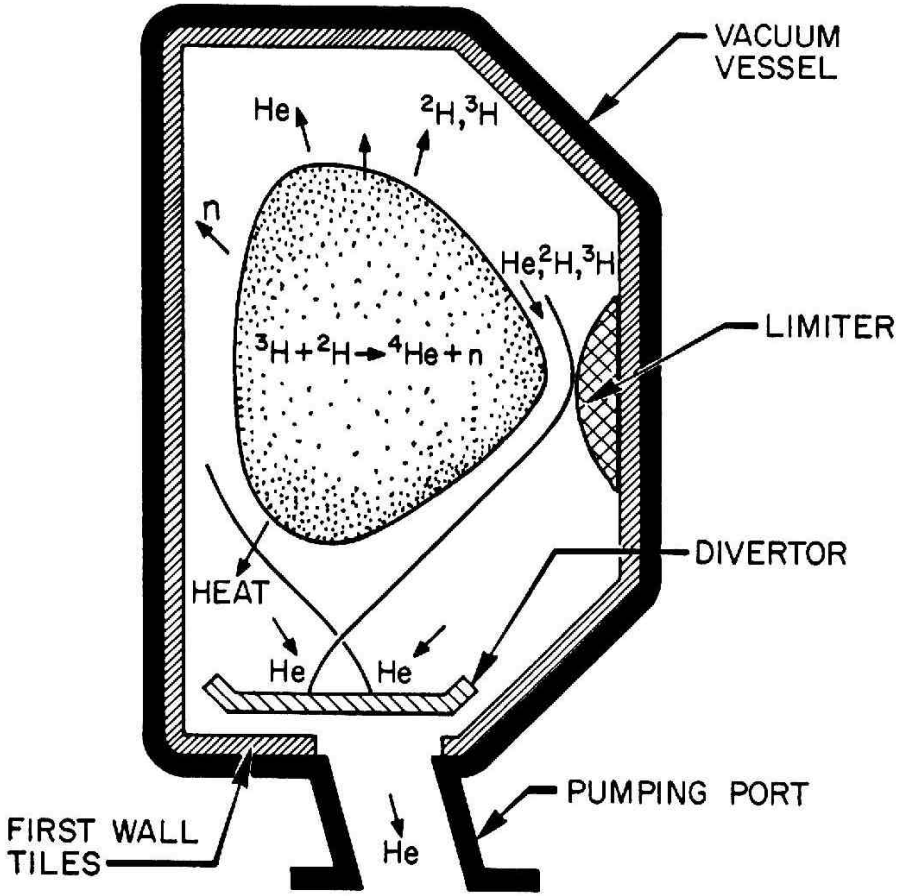


NEUTRON IRRADIATION INDUCED DIMENSIONAL CHANGES IN GRAPHNOL N3M GRAPHITE



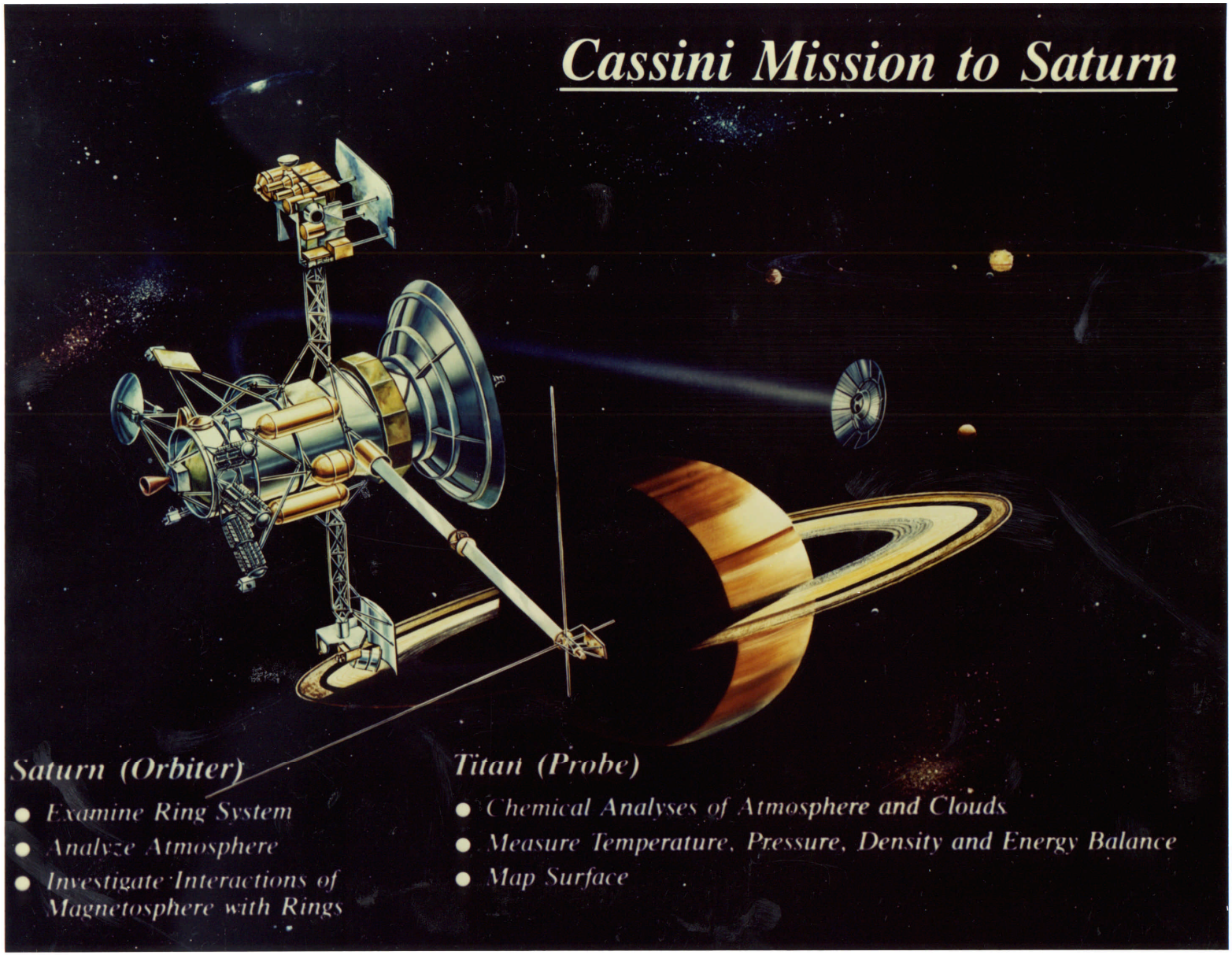
FUSION REACTOR PLASMA FACING MATERIALS

- Plasma facing carbon-carbon composite materials
- High thermal conductivity
- Low sputtering and erosion
- High thermal shock resistance
- low outgassing
- resistant to neutron irradiation damage



CARBON AND GRAPHITE MATERIALS R&D AT THE OAK RIDGE NATIONAL LABORATORY

SPACE NUCLEAR POWER


Cassini Mission to Saturn
Saturn (Orbiter)
Examine Ring System
Analyze Atmosphere
Investigate Interactions of Magnetosphere with Rings
Titan (Probe)
Chemical Analyses of Atmosphere and Clouds
Measure Temperature, Pressure, Density and Energy Balance
Map Surface

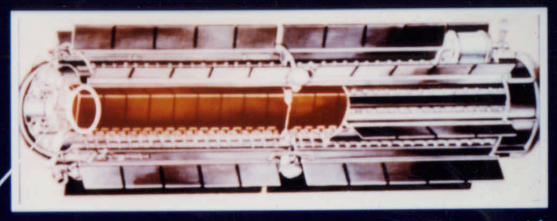
ORNL-DWG 90Z-16986

RADIOISOTOPE THERMOELECTRIC GENERATORS ARE SIMPLE, RELIABLE, AND SAFE NUCLEAR POWER SYSTEMS TO PROVIDE MULTIHUNDRED WATTS

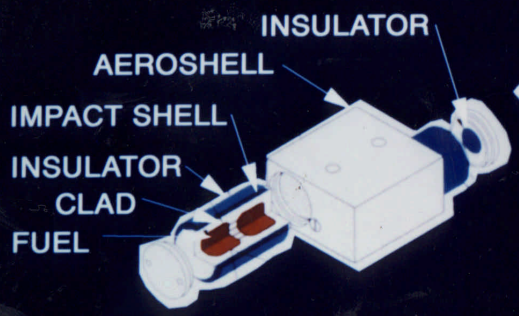
RECENT SUCCESSES

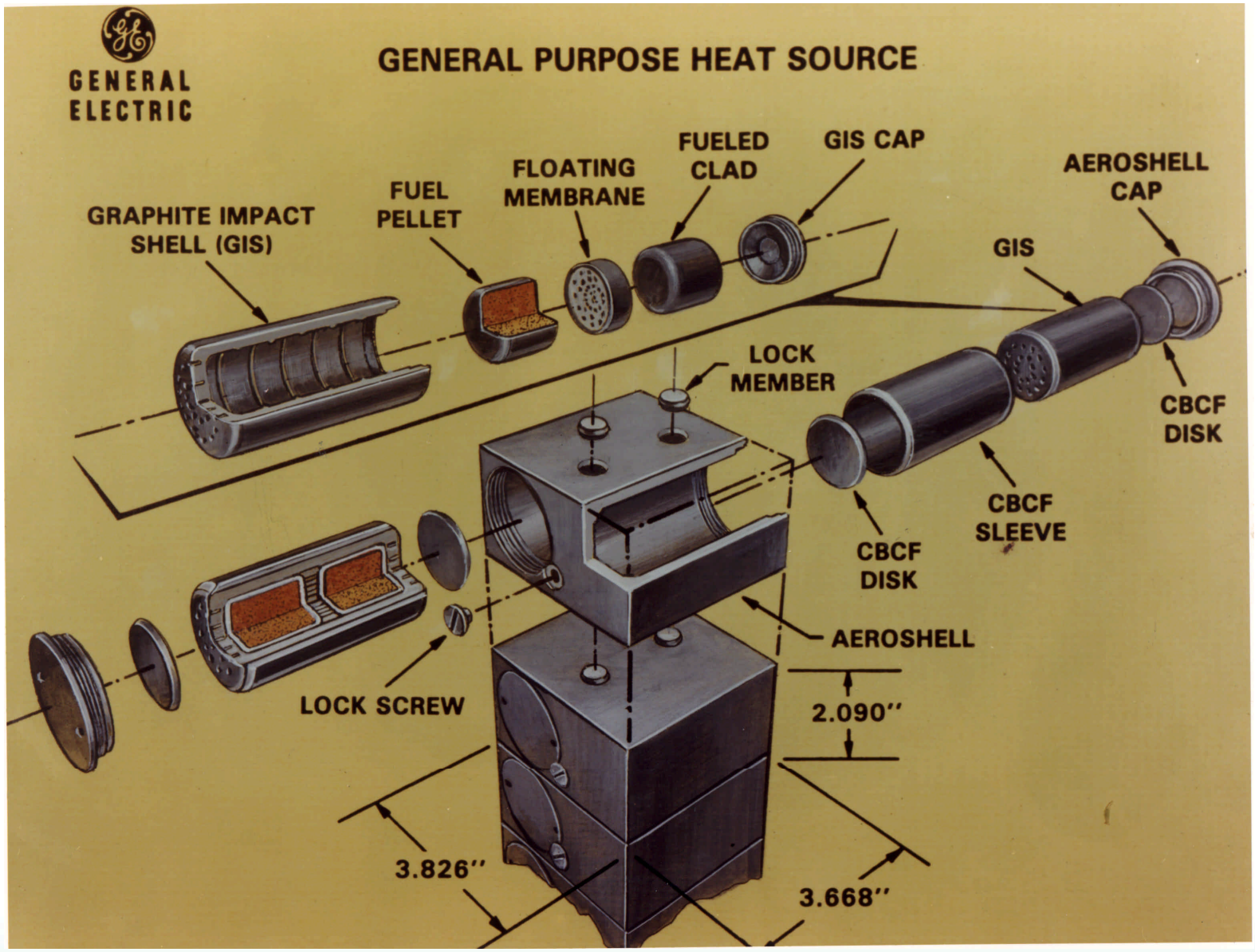
- GALILEO (OCTOBER 1989)
- ULYSSES (OCTOBER 1990)

SYSTEM DESIGN



GENERAL PURPOSE HEAT SOURCE MODULE

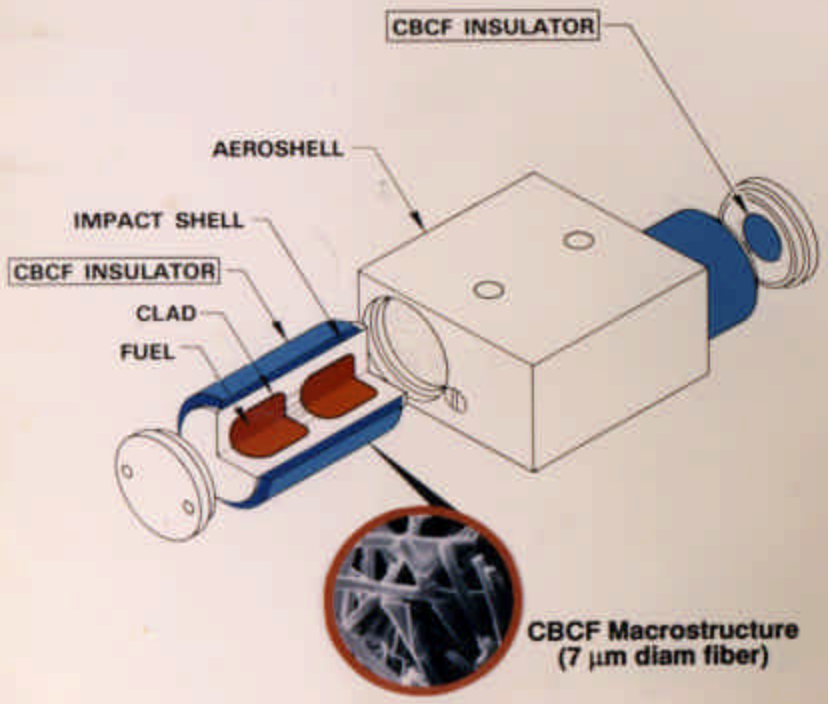



GENERAL ELECTRIC
GENERAL PURPOSE HEAT SOURCE
GRAPHITE IMPACT SHELL (GIS)
FUEL PELLET
FLOATING MEMBRANE
FUELED CLAD
GIS CAP
AEROSHELL CAP
GIS
LOCK MEMBER
CBCF DISK
CBCF SLEEVE
CBCF DISK
AEROSHELL
LOCK SCREW
2.090"
3.826"
3.668"

ORNL-DWG 88-14757

Carbon-Bonded Carbon-Fiber Set Production

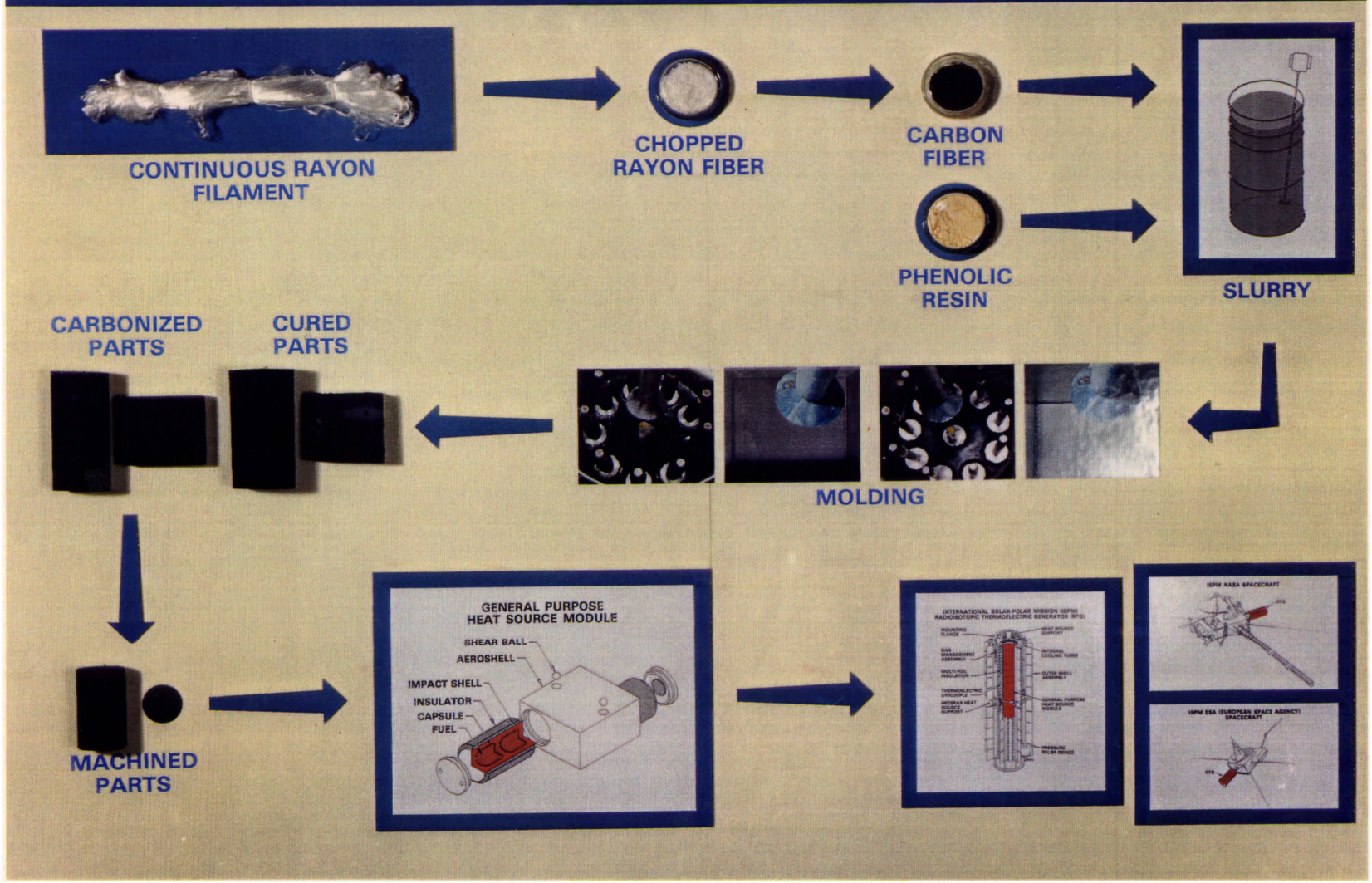
OAK RIDGE'S THERMAL INSULATION SERVES A CRITICAL PURPOSE IN THE GENERAL PURPOSE HEAT SOURCE



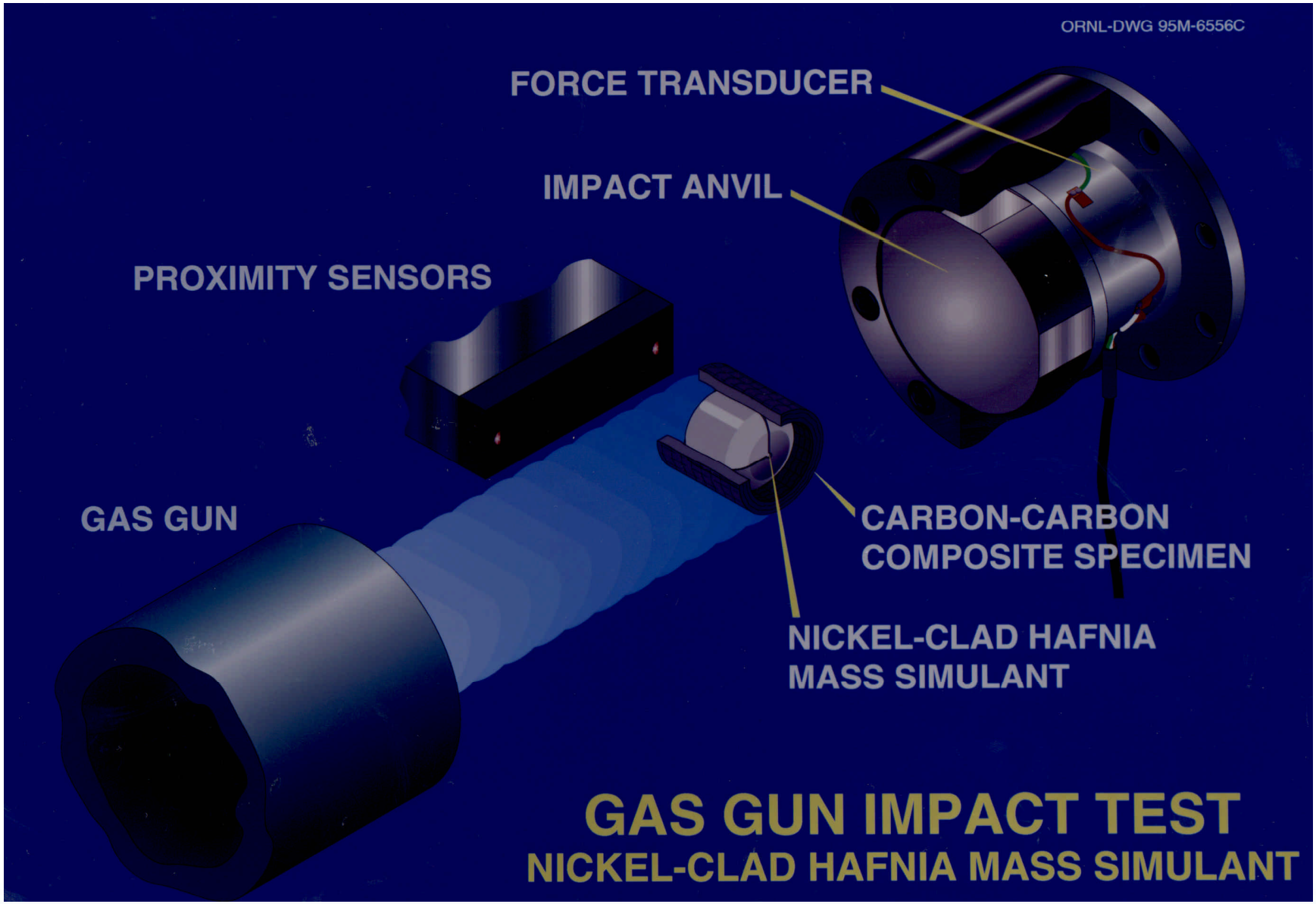
- EXHIBITS EXCELLENT HIGH-TEMPERATURE INSULATING PROPERTIES
- PREVENTS OVERHEATING OF IRIDIUM ALLOY ON HYPERSONIC REENTRY
- PREVENTS OVERCOOLING OF IRIDIUM ALLOY DURING SUBSONIC PHASE OF REENTRY

MARTIN MARIETTA

CARBON-BONDED CARBON FIBER INSULATION FOR RADIOISOTOPE SOURCE POWER



Filament Wound Impact Shell With Integral Closure


ORNL-DWG 95M-6556C
FORCE TRANSDUCER
IMPACT ANVIL
PROXIMITY SENSORS
GAS GUN
CARBON-CARBON
COMPOSITE SPECIMEN
NICKEL-CLAD HAFNIA
MASS SIMULANT
GAS GUN IMPACT TEST
NICKEL-CLAD HAFNIA MASS SIMULANT

CARBON AND GRAPHITE MATERIALS R&D AT THE OAK RIDGE NATIONAL LABORATORY

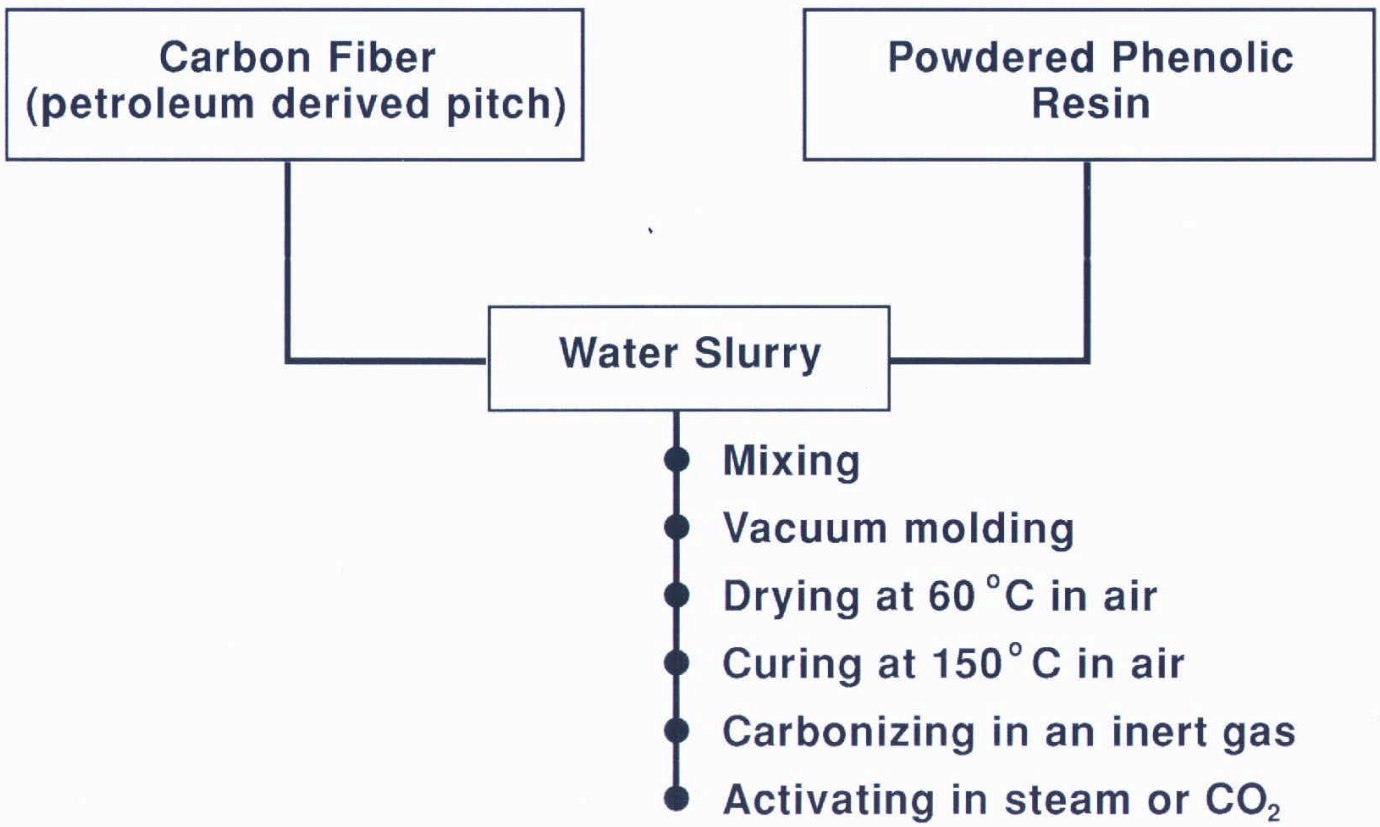
ADSORBENT COMPOSITES FOR GAS SEPARATION

CARBON FIBER COMPOSITE MOLECULAR SIEVE

ATTRIBUTES

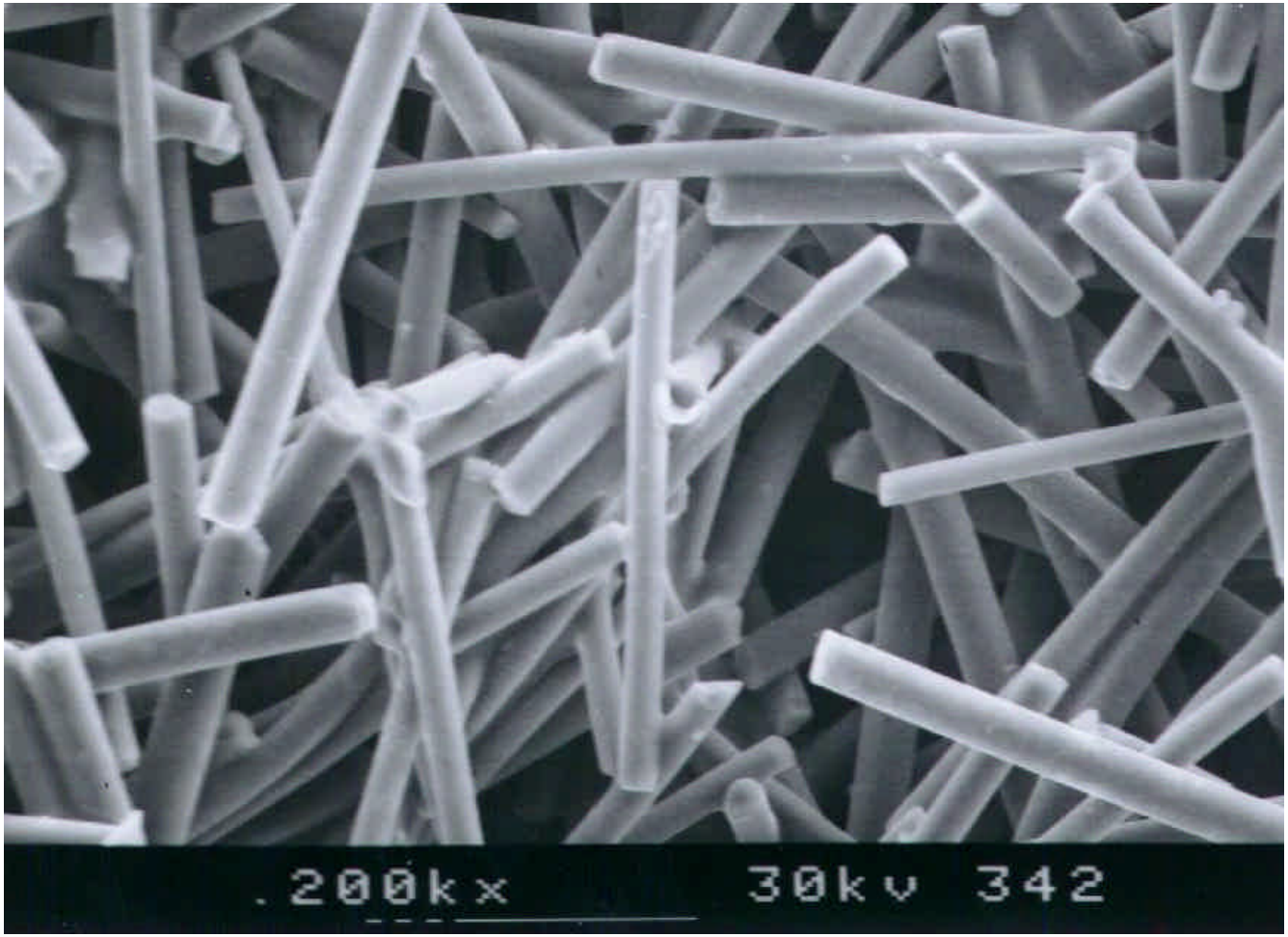
- OPEN STRUCTURE, BUT HIGHLY MICROPOROUS
- RIGID, STRONG, MONOLITHIC
- KINETIC ADVANTAGE DUE TO SMALL FIBER DIAMETER (8-16 mm)
- OVERCOMES PROBLEMS OF GRANULAR ADSORBENTS
- ELECTRICALLY CONDUCTIVE

CFCMS IS MANUFACTURED VIA A SLURRY MOLDING PROCESS

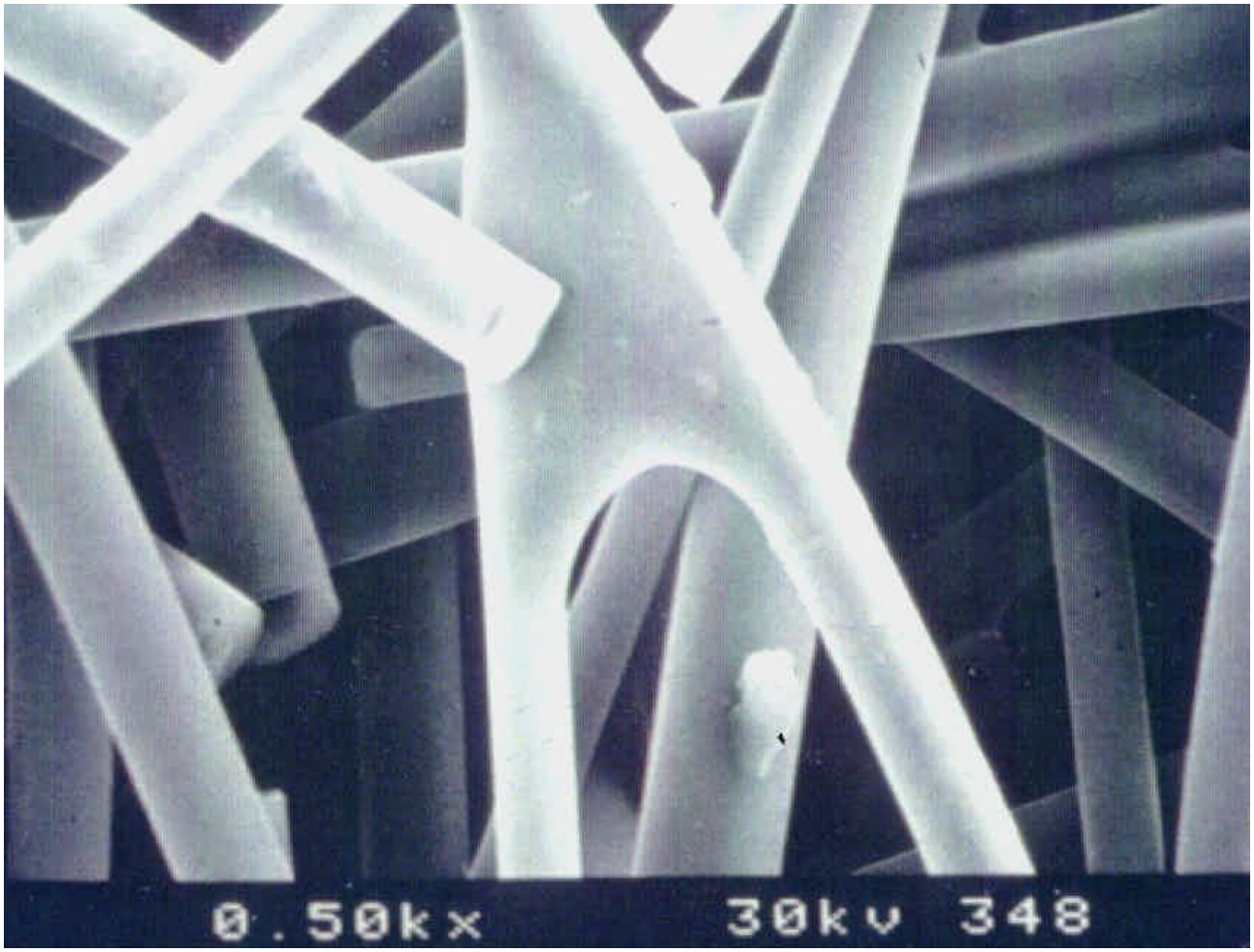


CFCMS SLURRY MOLDING APPARATUS

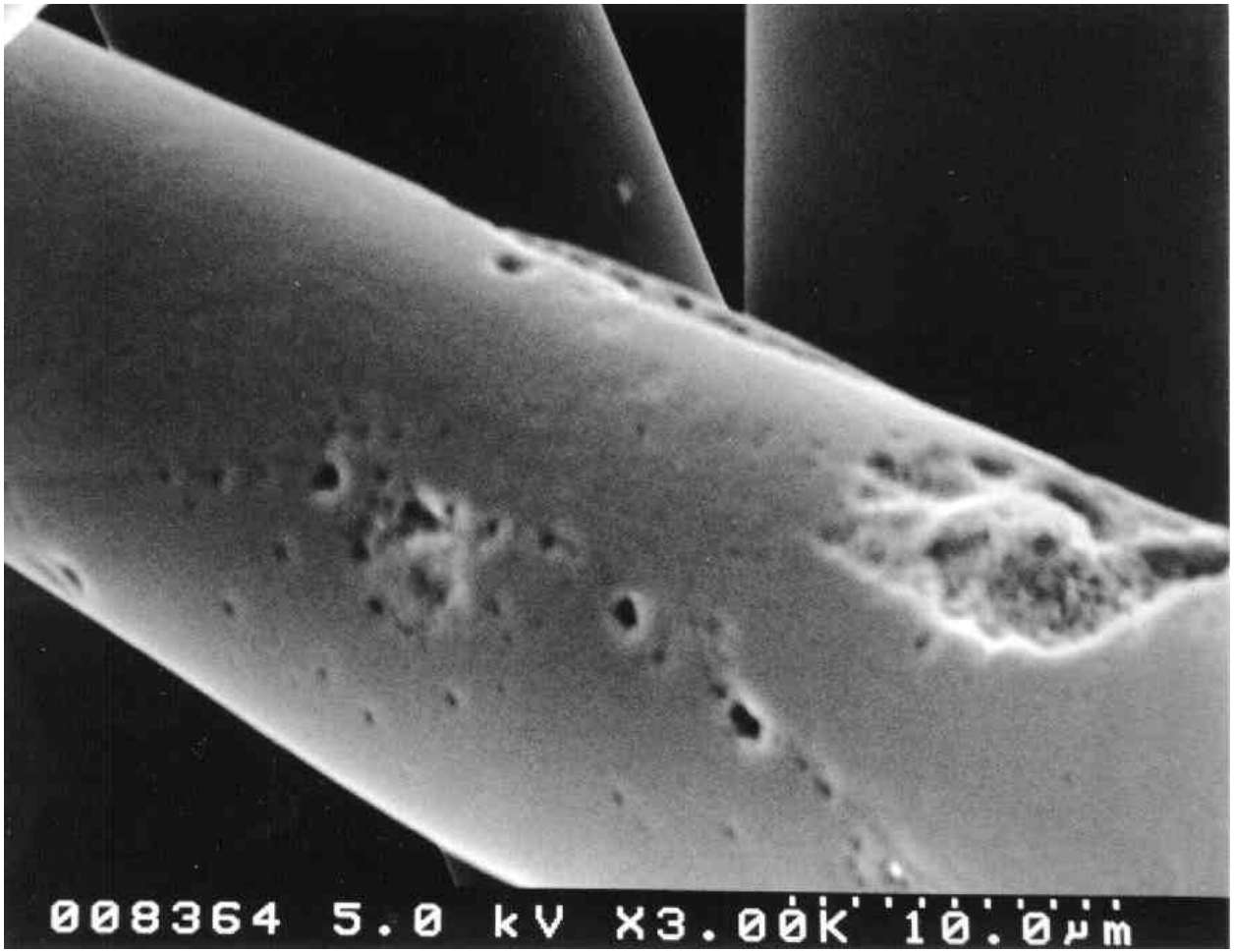
CFCMS MICROSTRUCTURE



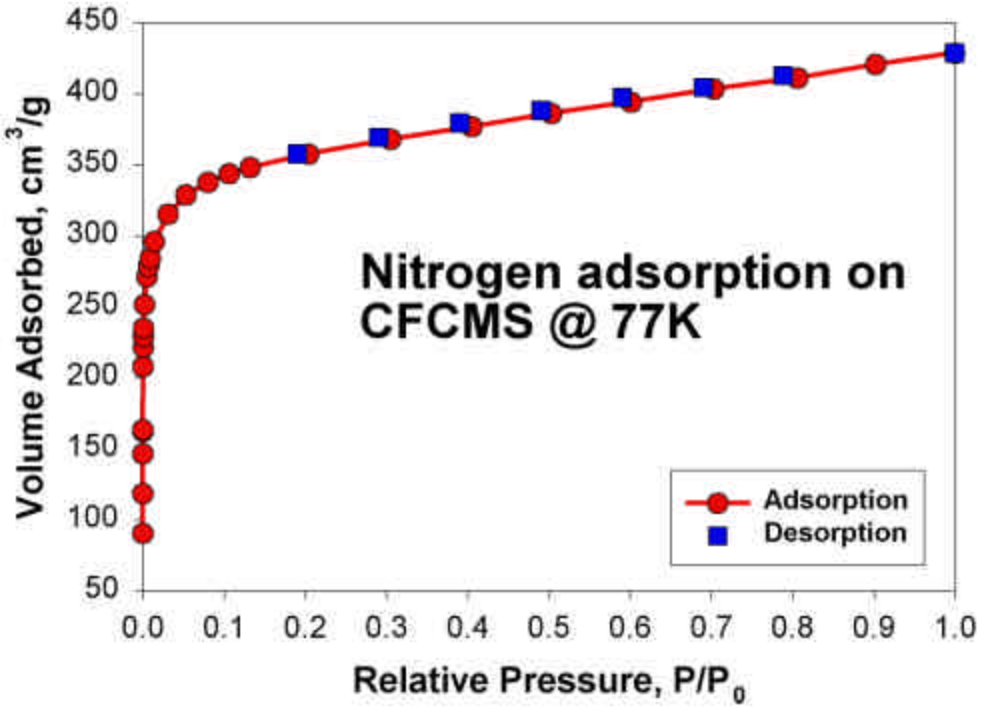
CFCMS MICROSTRUCTURE



CFCMS MICROSTRUCTURE



CFCMS IS HIGHLY MICROPOROUS



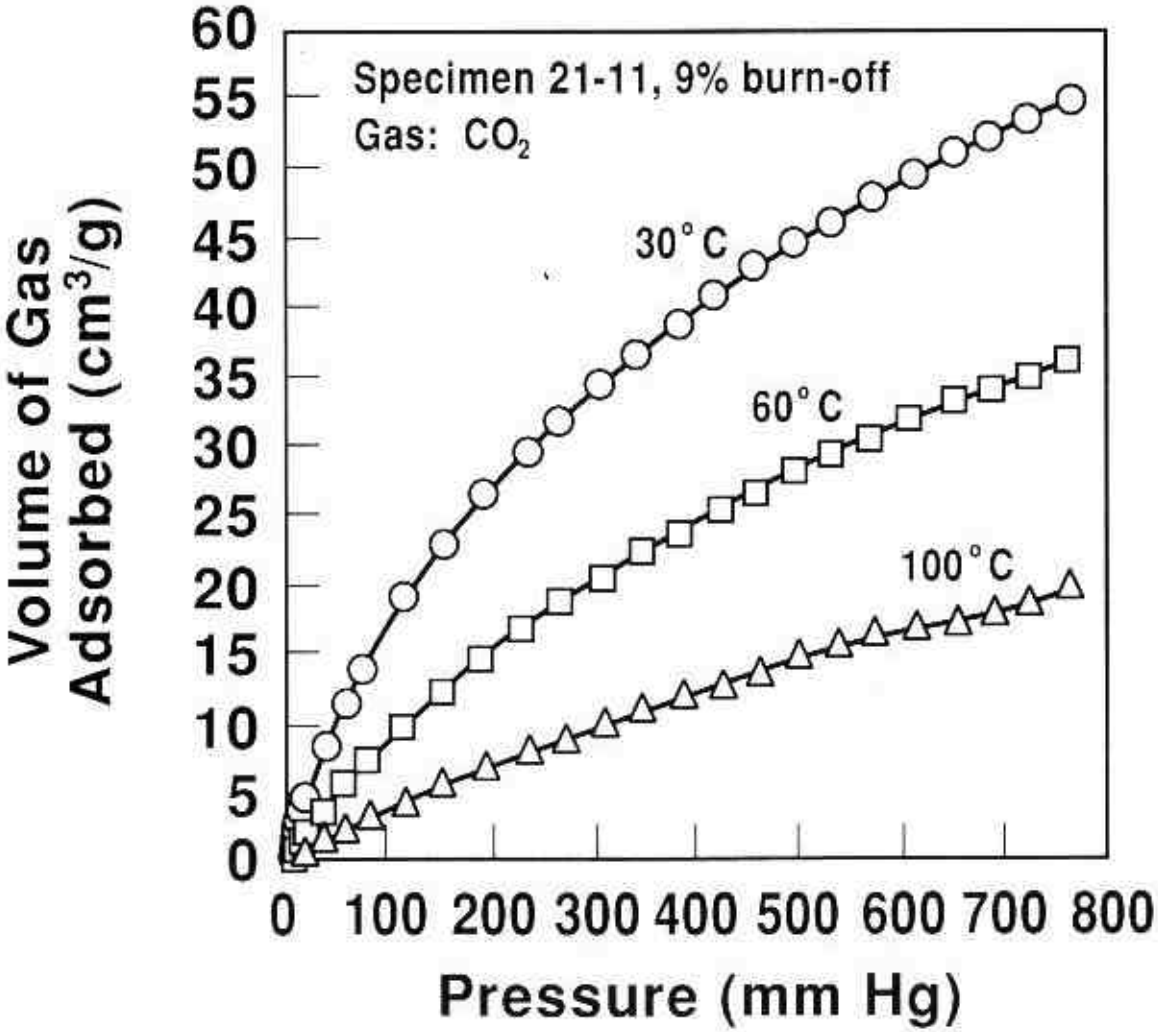
- TYPE I ISOTHERM INDICATIVE OF A MICROPOROUS CARBON
- LARGE BET SURFACE AREA, CAN BE >2500 m^2/g.
- LARGE MICROPORE VOLUME, 0.1 - 1.0 cm^3/g
- MEAN MICROPORE SIZE, BET AREA, & MPV CONTROLLED THROUGH DEGREE OF ACTIVATION

CARBON FIBER COMPOSITE MOLECULAR SIEVE

RECENT SEPARATIONS ACTIVITIES

- ALKALINE FUEL CELL GAS CLEAN-UP (WITH ZETEK)
- TURBINE EXHAUST GAS CO_2 REMOVAL (WITH CCP)
- NATURAL GAS CLEAN-UP (CO_2 REMOVAL)
- CHEMICAL WEAPONS COLLECTIVE PROTECTION

CFCMS HAS A STRONG AFFINITY FOR CO_2



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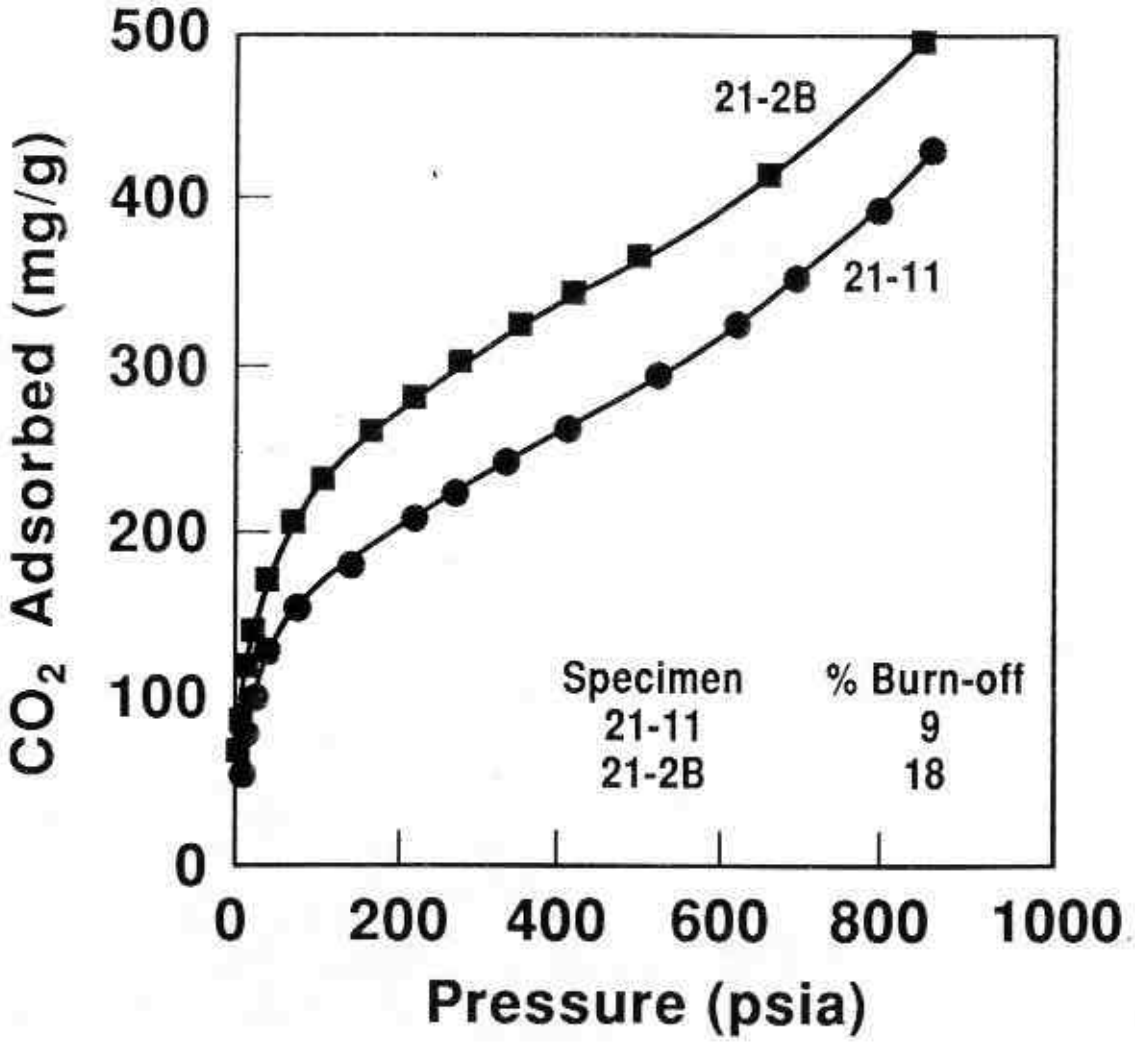
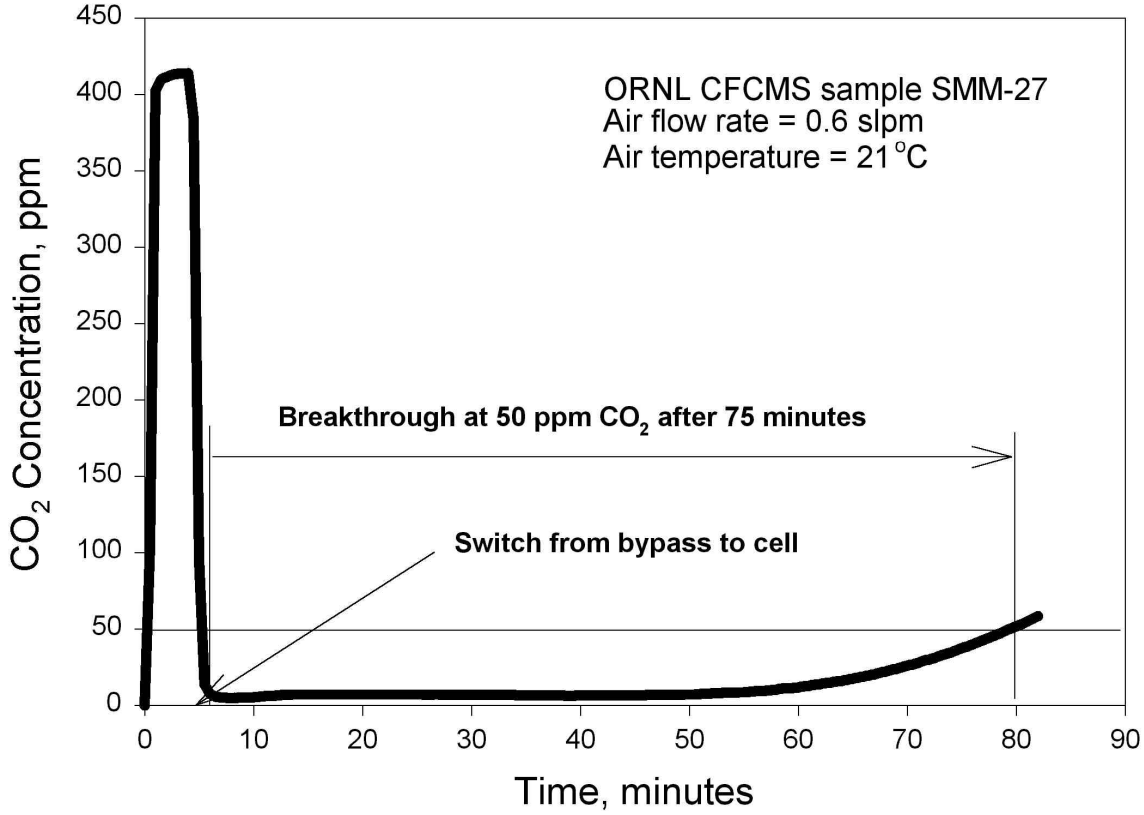


CFCMS/ESA CELL

WE HAVE DEMONSTRATED THE REMOVAL OF CO_2 FROM AIR USING CFCMS



CARBON AND GRAPHITE MATERIALS R&D AT THE OAK RIDGE NATIONAL LABORATORY

ADSORBENT MONOLITHS FOR NATURAL GAS STORAGE

NATURAL GAS STORAGE MONOLITHS BASED ON CARBON FIBER COMPOSITES

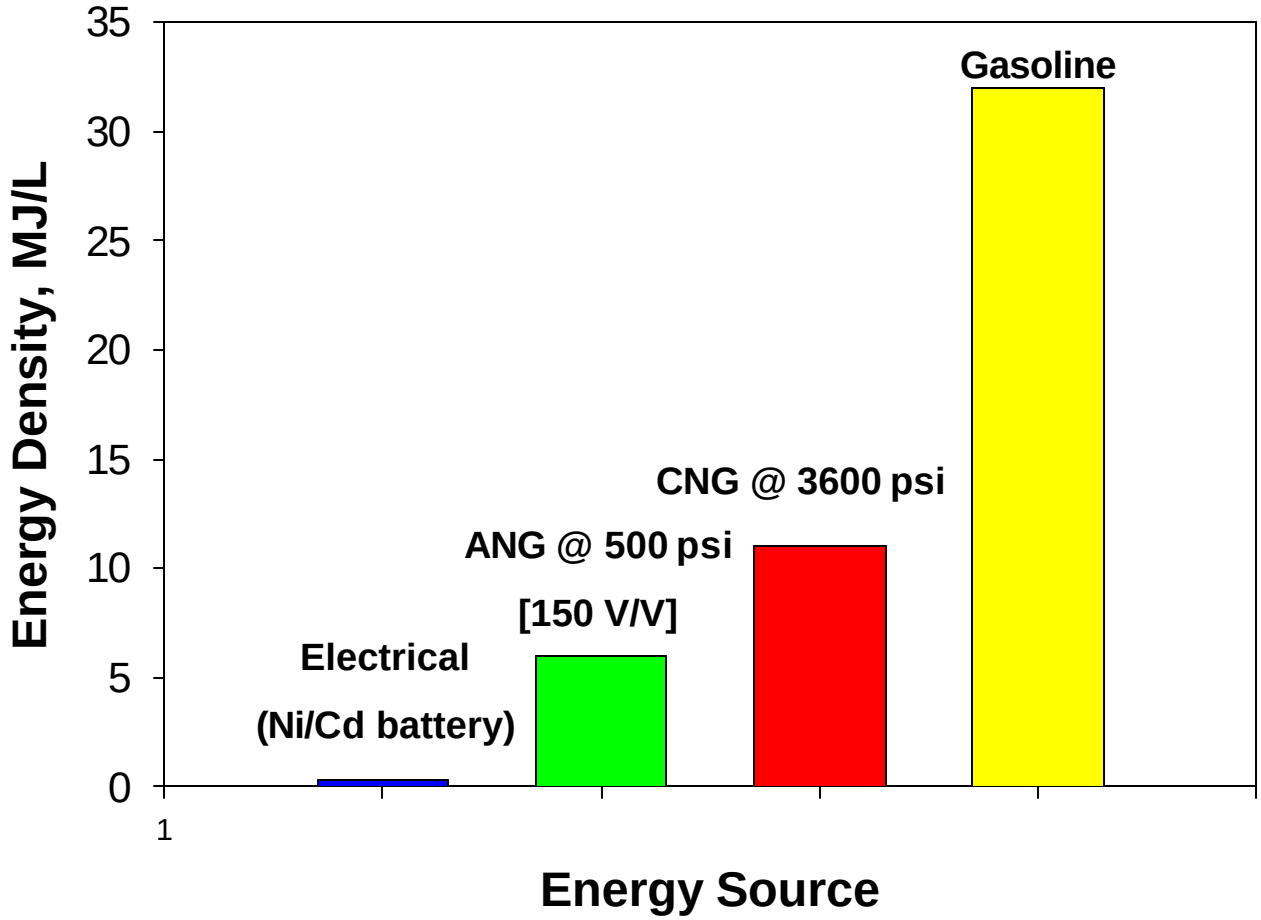
GAS STORAGE OPTIONS

- **Compressed Natural Gas (*CNG*) @ 24 MPa (3600 psi)**
- **Adsorbed Natural Gas (*ANG*) @ 3.4 MPa (500 psi)**

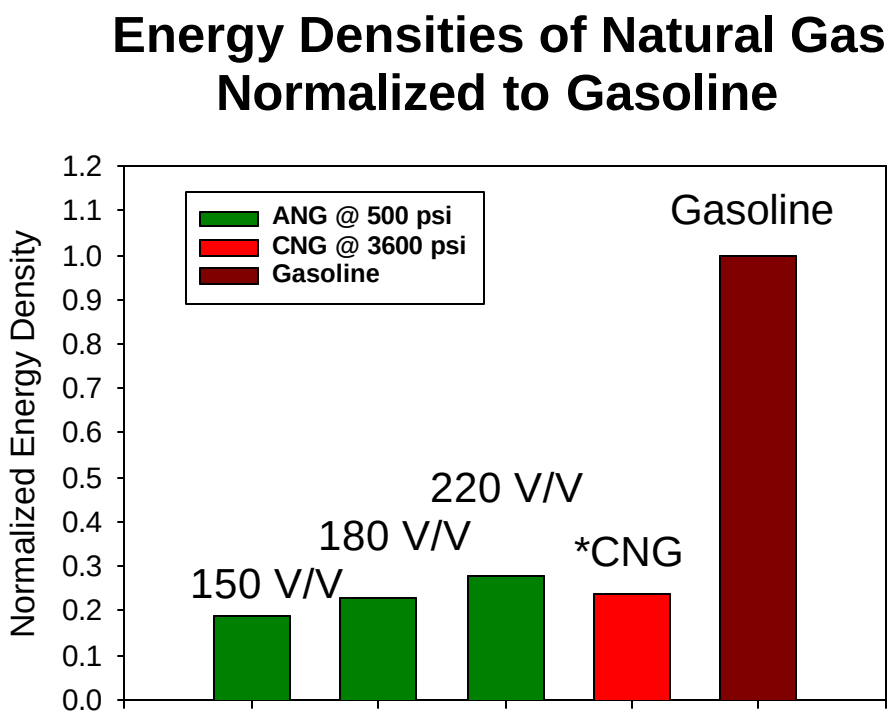
ADVANTAGES OF ADSORBED NATURAL GAS STORAGE

- Low pressure storage (500 psi)
- Lower cost, conformable tanks
- Fewer barriers to infrastructure development (single stage vs. multistage compression)
- Controlled release of gas in event of tank rupture

ENERGY DENSITY OF FUELS



LOW PRESSURE STORAGE OF NATURAL GAS FOR VEHICLES



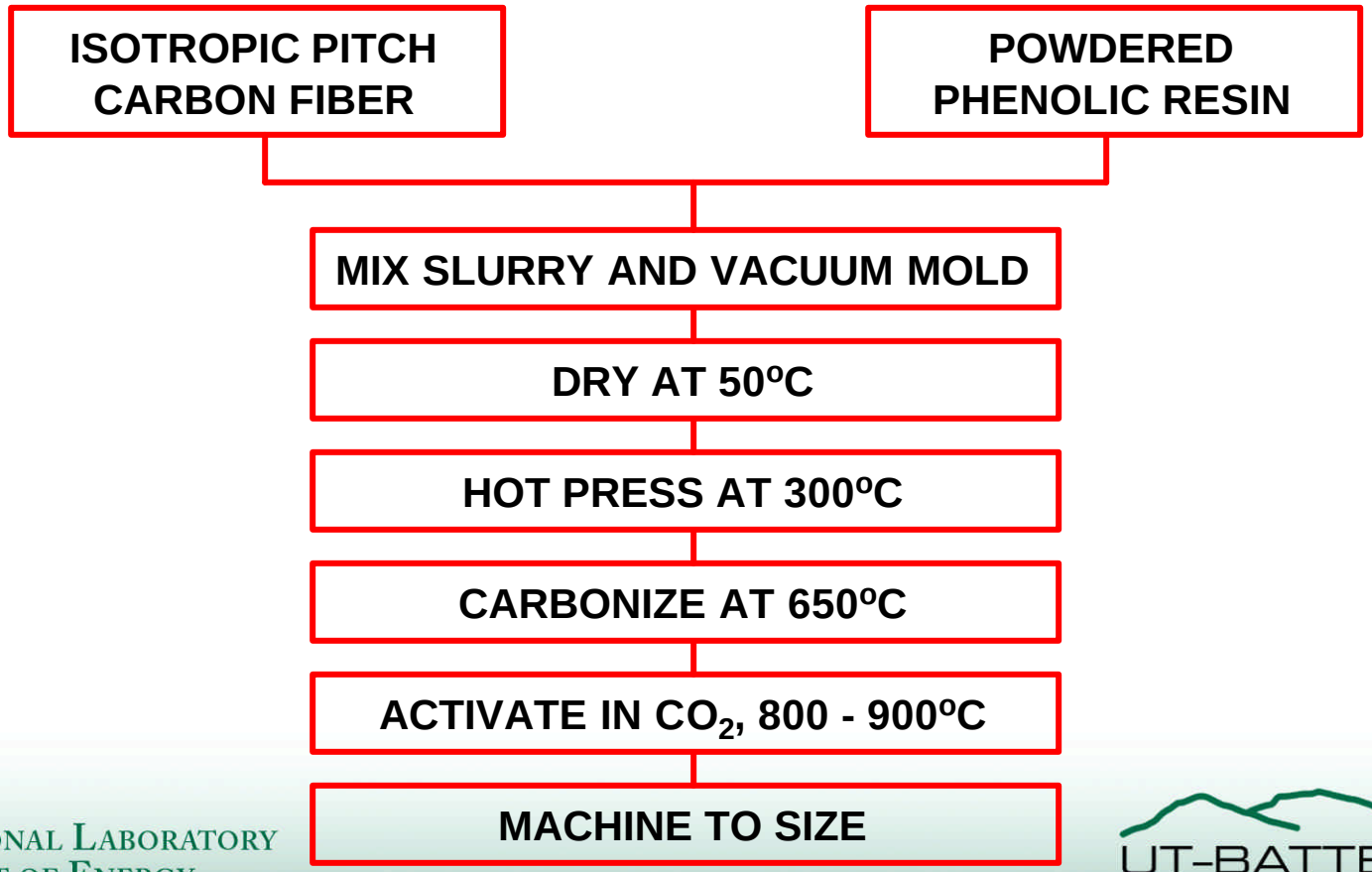
*CNG energy density estimated on the basis of tank external volume envelope

- **Natural gas can be stored in the physically adsorbed state (ANG) at low pressure (500 psi) and at useful energy densities.**
- **The low storage pressure of ANG allows for more efficient packing than for CNG**

ADVANTAGES OF ORNL's STORAGE MONOLITH

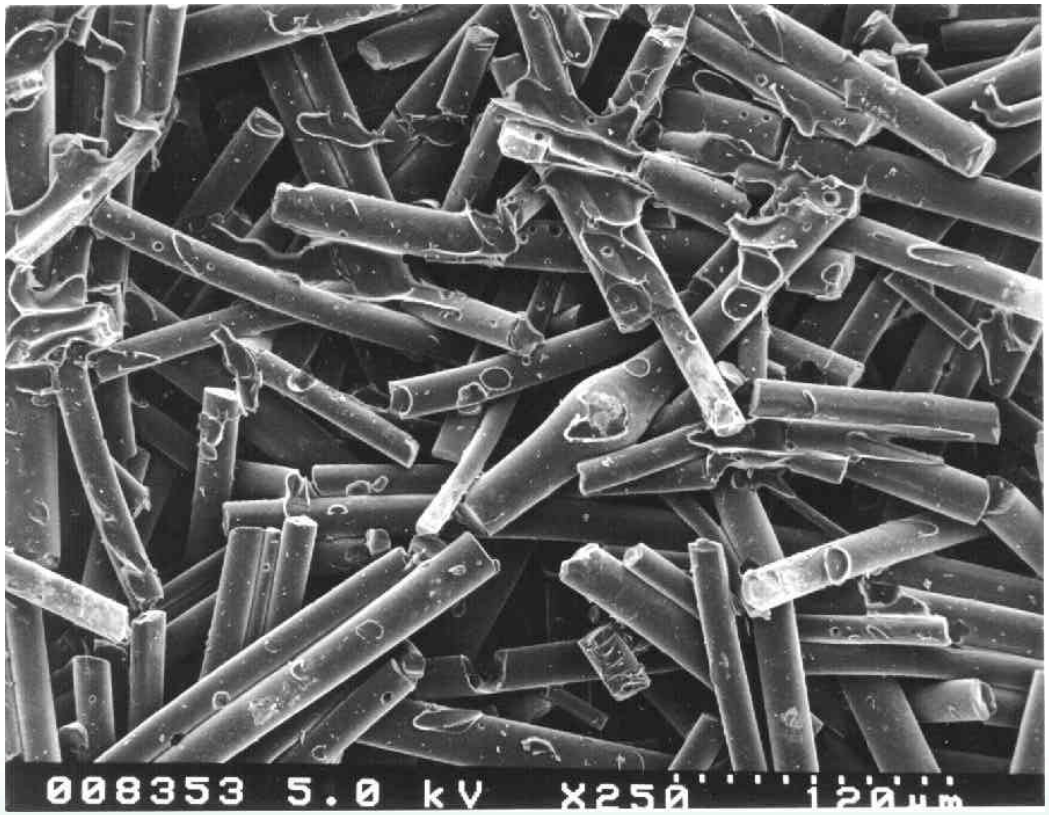
- Conformable - more efficient packing
- No attrition, unlike carbon granules & pellets
- Greater thermal conductivity
- Electrically conductive - allowing self heating

THE MANUFACTURING PROCESS FOR CARBON FIBER BASED GAS STORAGE MONOLITHS



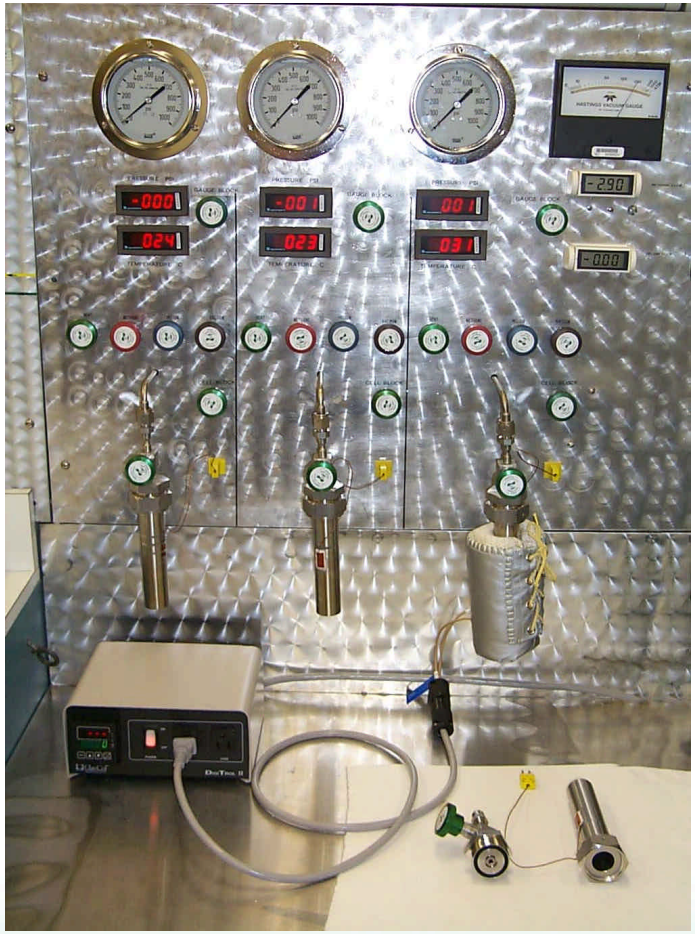
NOVEL CARBON NATURAL GAS STORAGE MONOLITHS

MONOLITH MICROSTRUCTURE



NOVEL CARBON NATURAL GAS STORAGE MONOLITHS

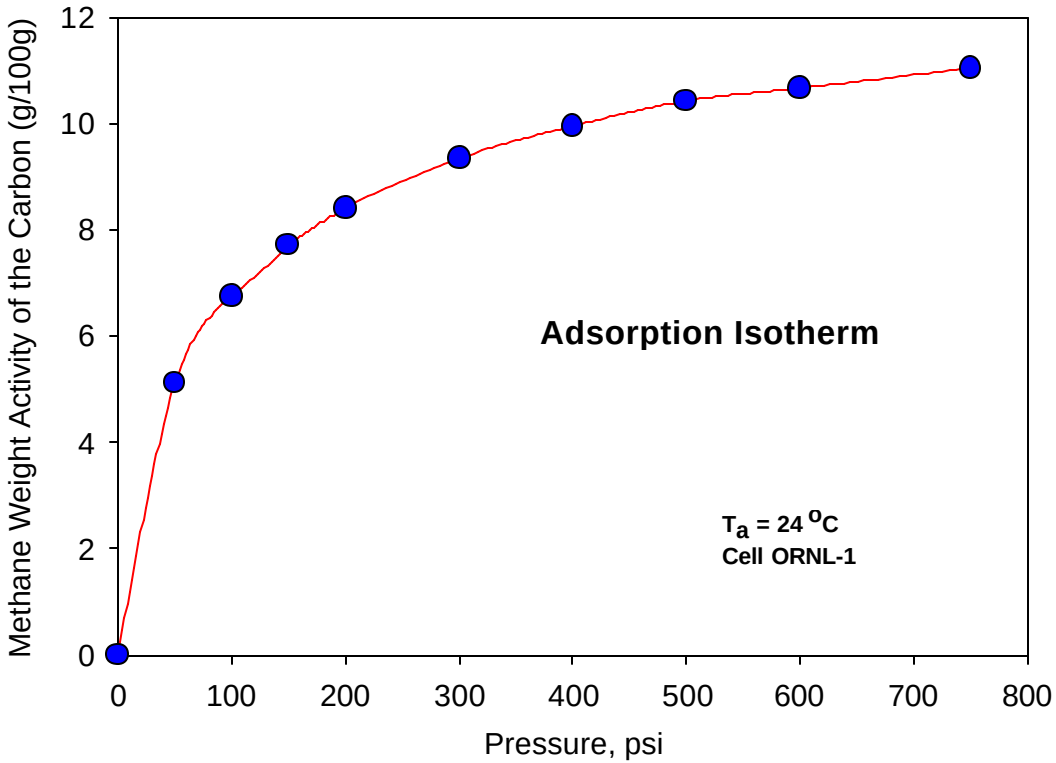
Methane Adsorption Capacity Test Rig



- **Maximum pressure 1000 psi.**
- **Outgas capability (200°C and < 100 mTorr).**
- **Digital and analog instrumentation**
- **Three test stations**

NOVEL CARBON NATURAL GAS STORAGE MONOLITHS

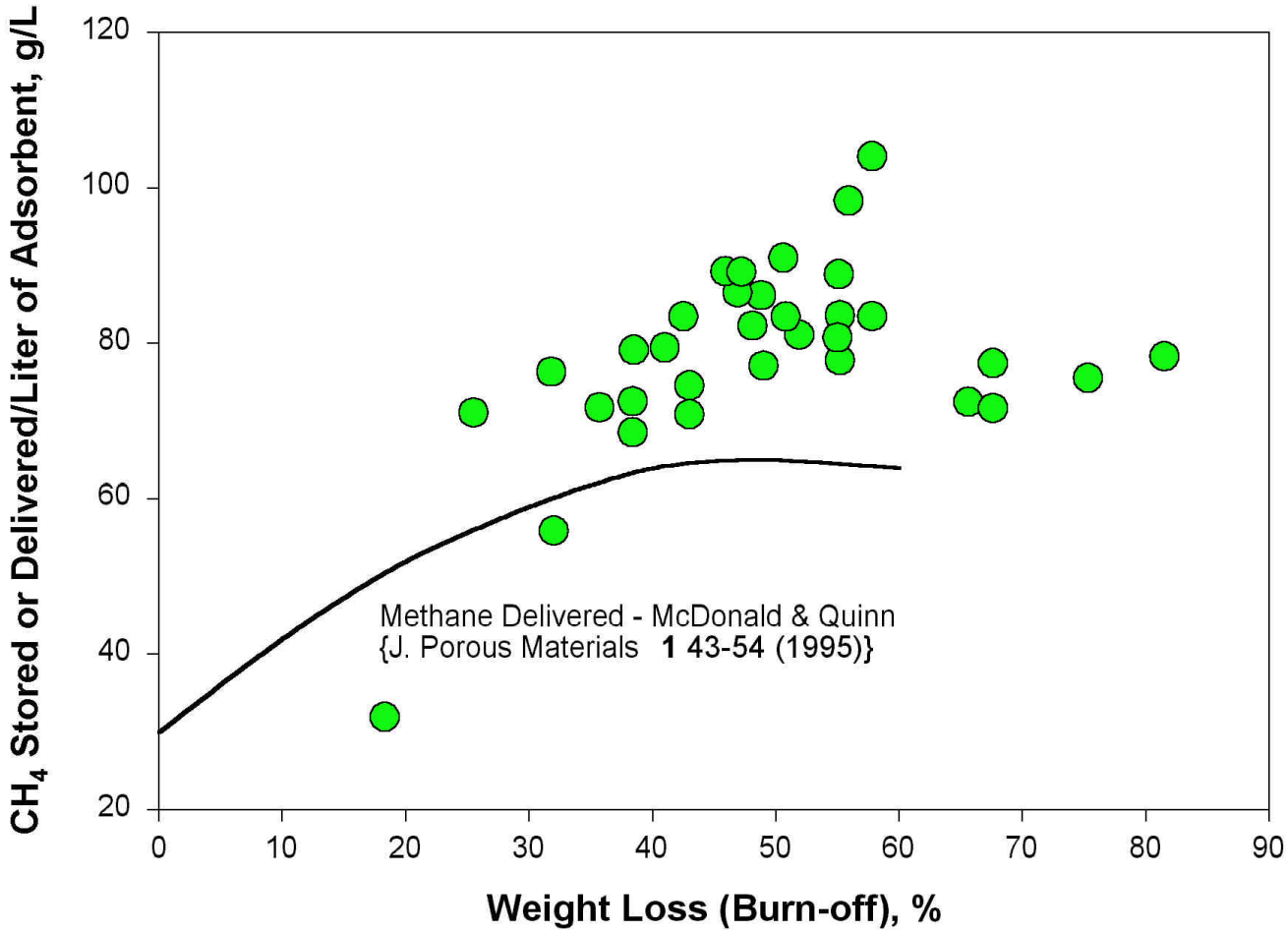
Methane Weight Activity of Carbon (wt%)



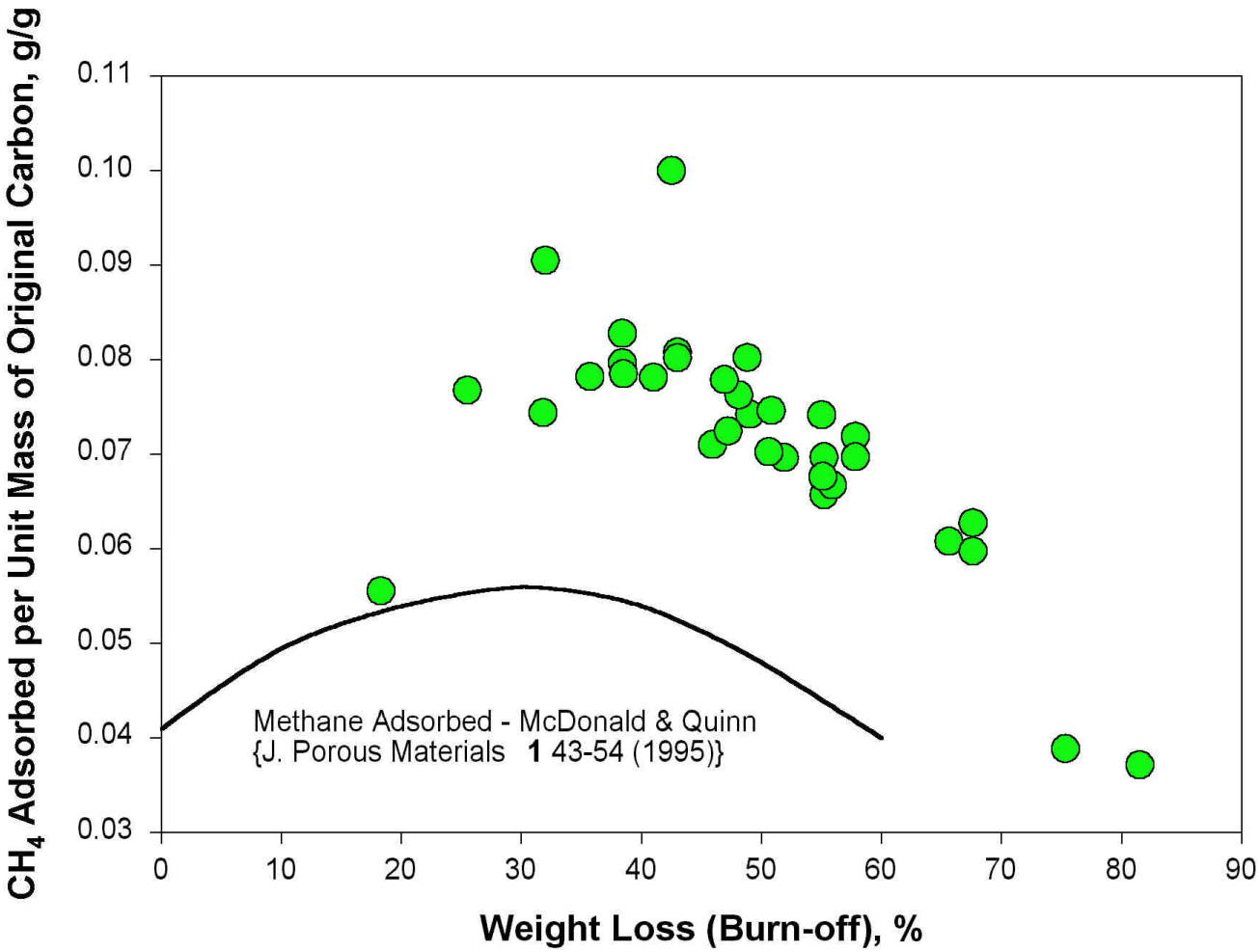
PHYSICAL ADSORPTION OCCURS IN MICROPORES

- Micropores have widths < 2 nm.
- The methane gas density in the micropores at 3.4 MPa (500 psi) is 4 to 8 times greater than in the gas phase at the same pressure.
- Control of micropore size and volume is critical to maximizing gas storage density.

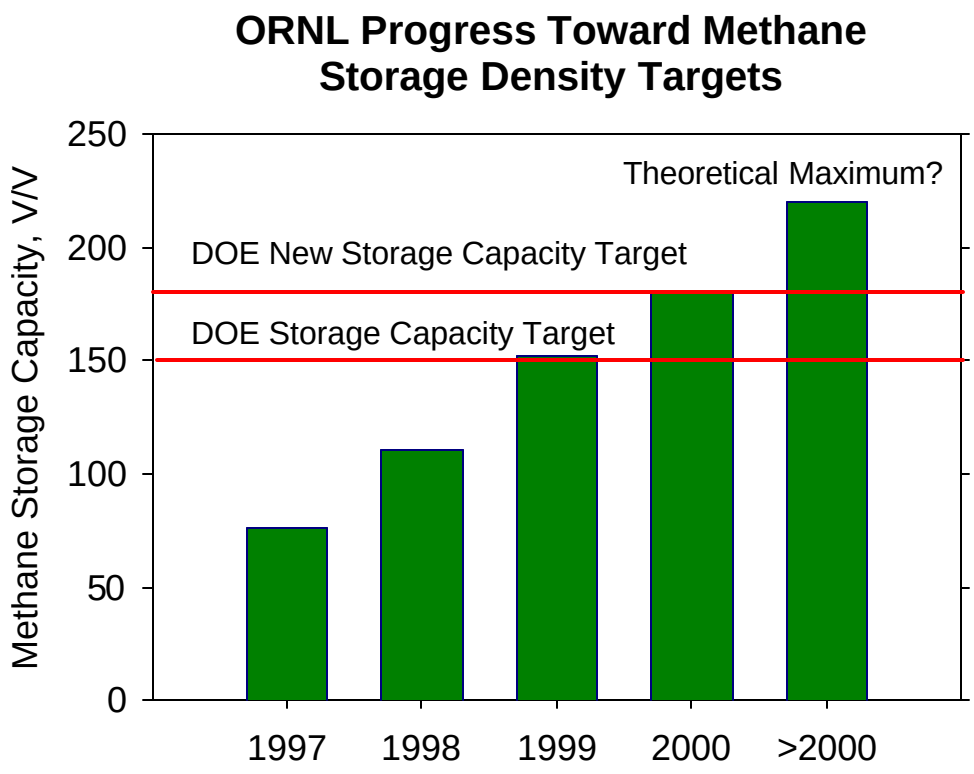
COMPARISON OF ORNL AND MACDONALD & QUINN DATA FOR METHANE CAPACITY (STORED OR DEL.)



COMPARISON OF ORNL AND MACDONALD & QUINN ADSORPTION CAPACITY (per g of original carbon)

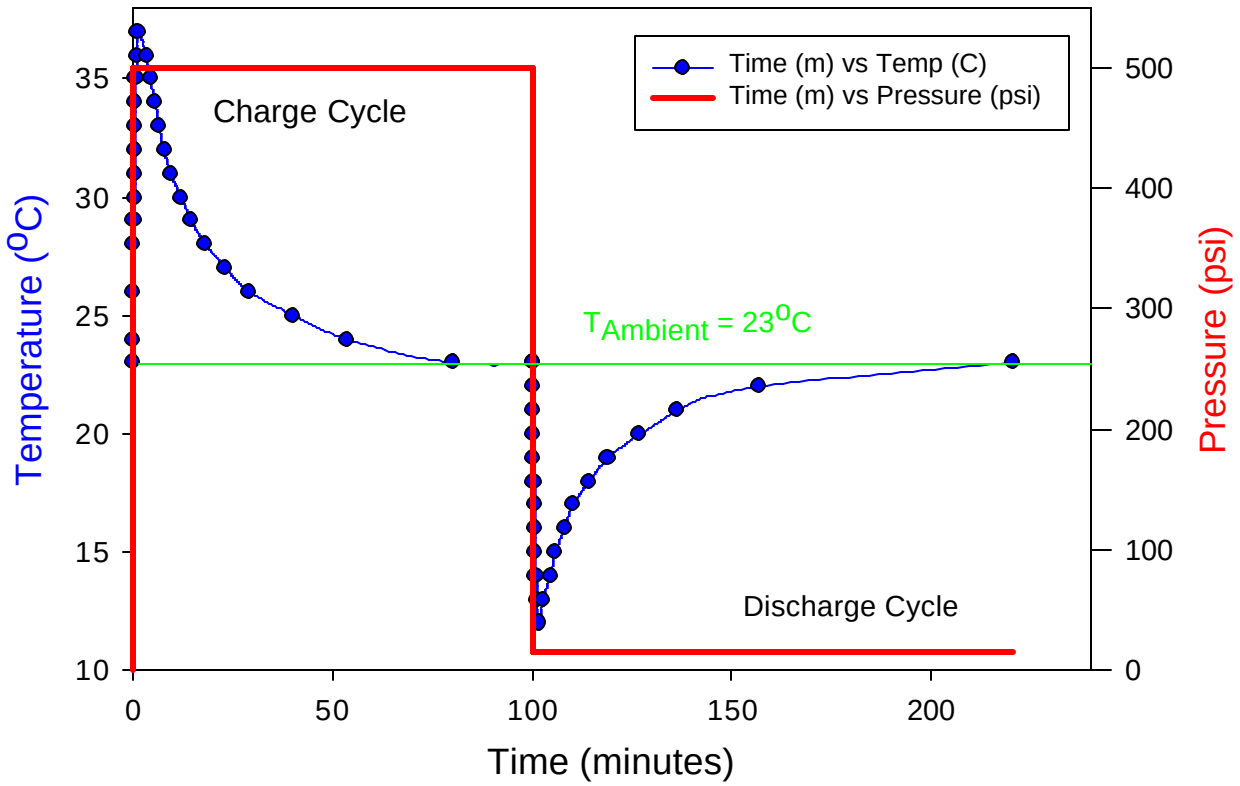


ORNL HAS EXCEEDED THE DOE METHANE STORAGE TARGET

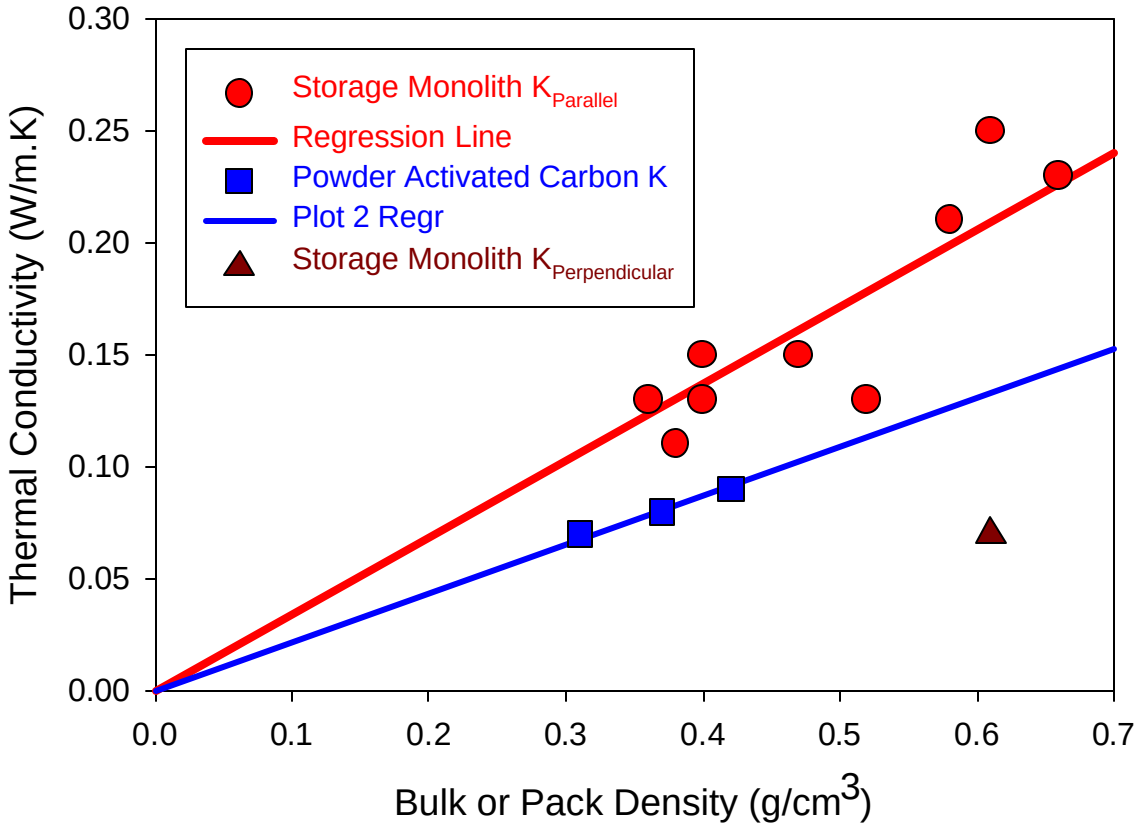


- **ORNL's novel carbon fiber based adsorbent monoliths can store > 150 V/V methane at 500 psi**
- **Current work directed toward achieving the revised target of 180 V/V**

TEMPERATURE VARIATION OF A METHANE TEST CYLINDER (50 cc VOLUME) DURING THE INITIAL FILL & DISCHARGE CYCLE



VARIATION OF THERMAL CONDUCTIVITY (AT 25 ^{O}C) WITH DENSITY FOR PAC & STORAGE MONOLITHS



CARBON AND GRAPHITE MATERIALS R&D AT THE OAK RIDGE NATIONAL LABORATORY

THERMAL MANAGEMENT CARBONS

ORNL MESOPHASE-DERIVED GRAPHITIC FOAM

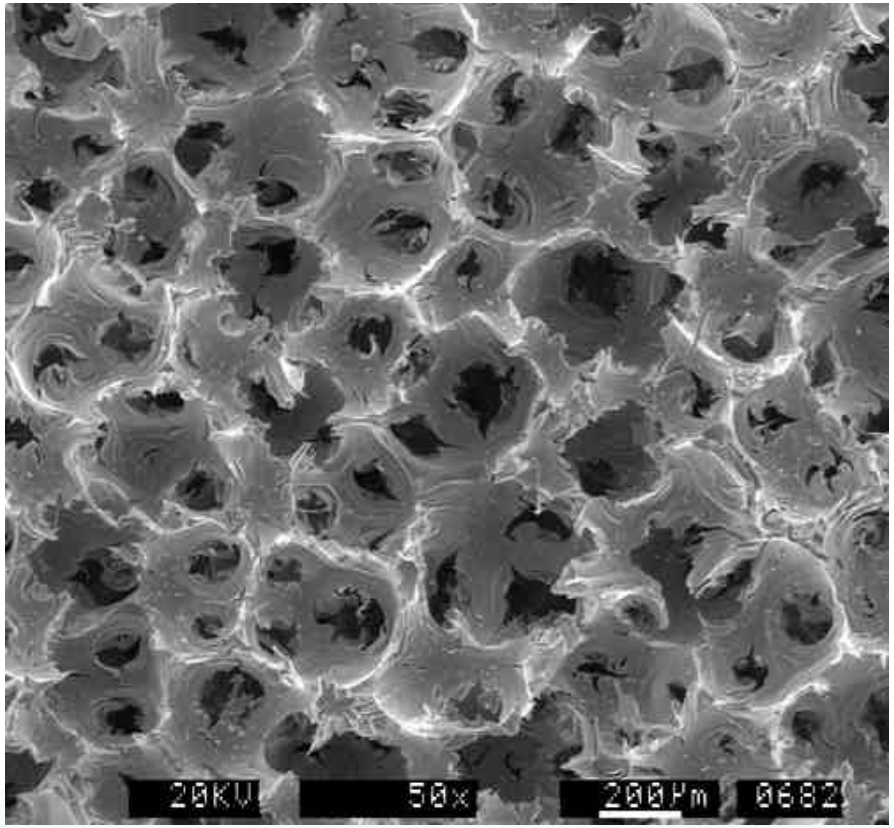
- **2 patents, 11 pending, 2000 R&D 100 Award Winner**
- **Novel Process and Novel Material**

➢ Highly Ordered Graphitic ligaments
  - Graphitic-like properties

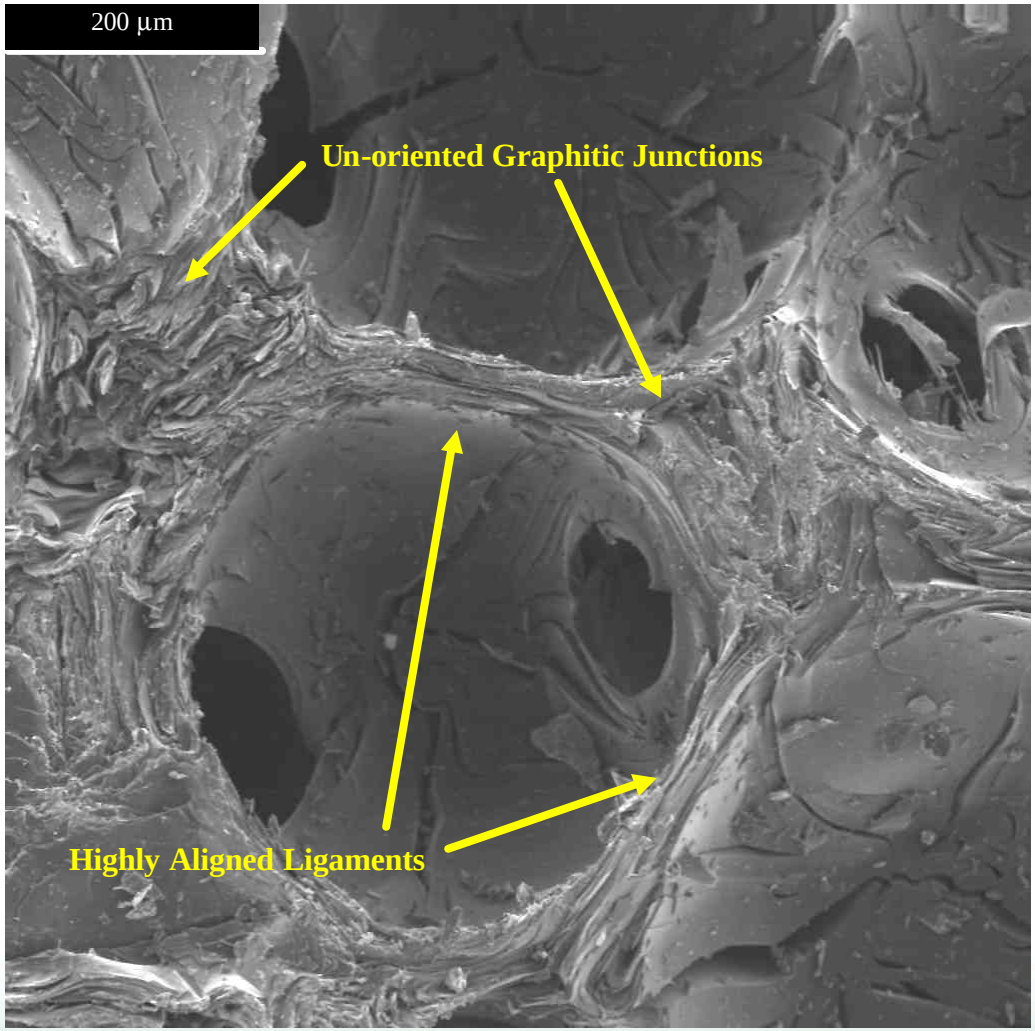
➢ Dimensionally stable
  - low CTE - ~2 - 4 in/in/°C

➢ Open Porosity
  - fluid permeable

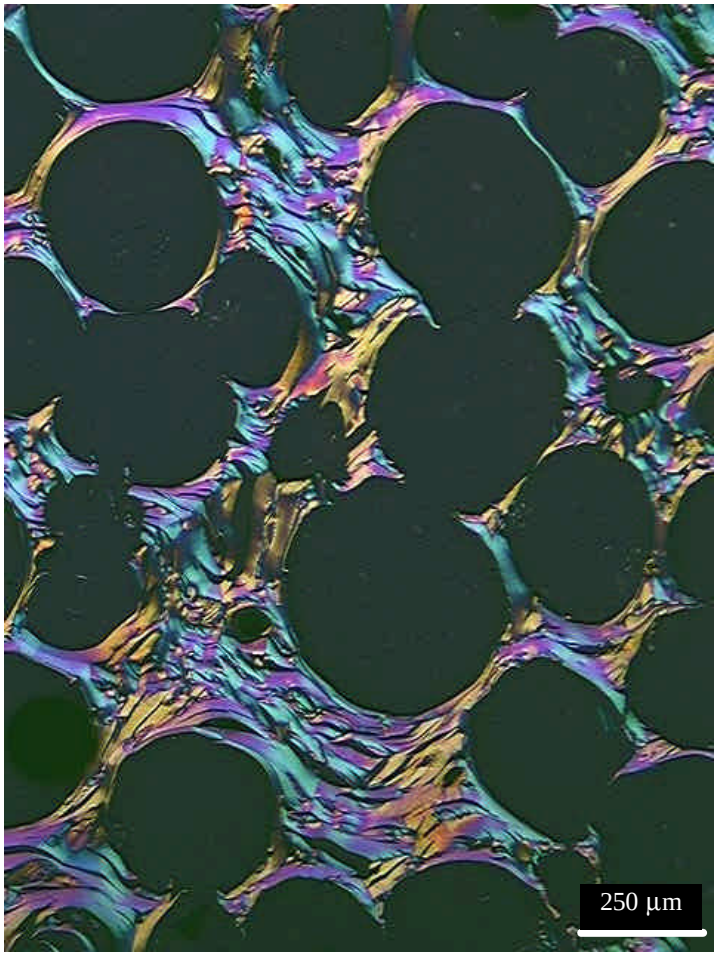
➢ Excellent thermal management material



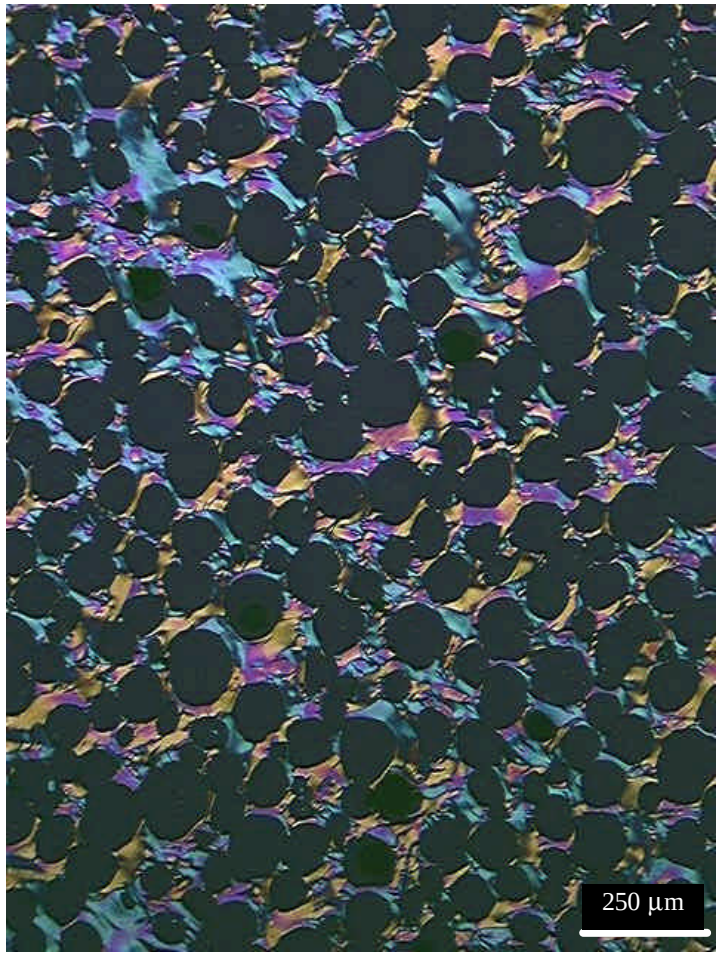
GRAPHITIC STRUCTURE - AR PITCH -D



GRAPHITE FOAM MICROSTRUCTURES

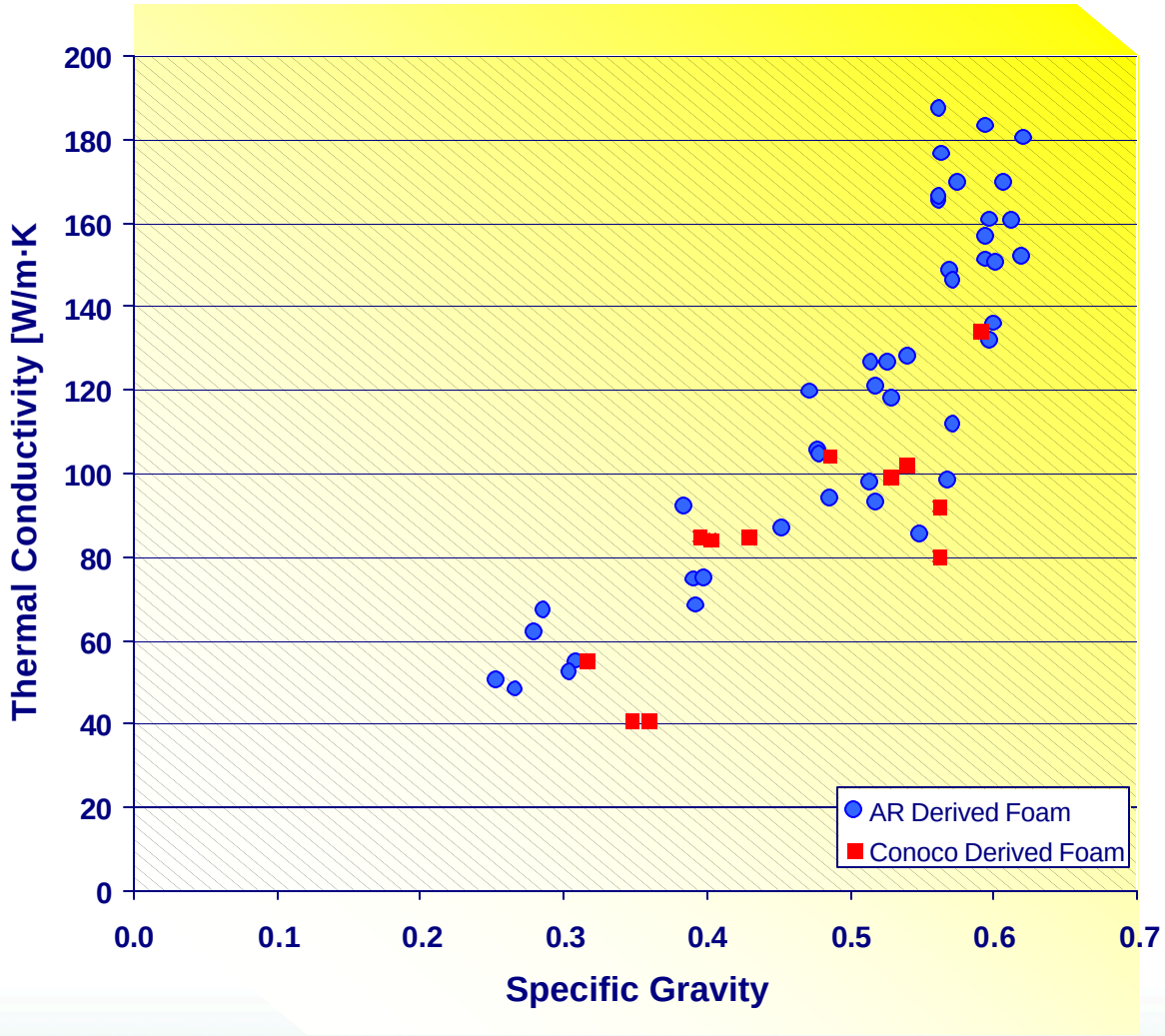


AR Derived Foam (D)



Conoco Derived Foam (D)

THERMAL CONDUCTIVITY VS. DENSITY



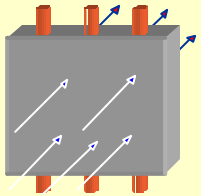
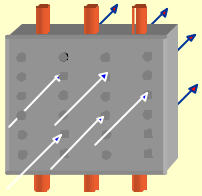
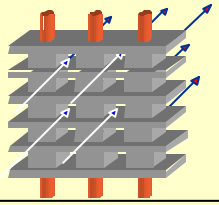
APPLICATIONS CURRENTLY BEING FUNDED

- **>$6.5 M in funding over 3 years**
  - **Composite Materials**
  - **Power Electronics Cooling**
  - **Fuel Cell Inlet Air Humidification**
  - **Radiators**
    - **Heavy vehicles, fuel celled vehicles, racing vehicles**
  - **Nuclear Reactor Core –Inherently safe design**
  - **Basic Research**
    - ***DESIGN AND CONTROL OF STRUCTURE***

HEAT EXCHANGER NEEDS FOR HEAVY VEHICLES

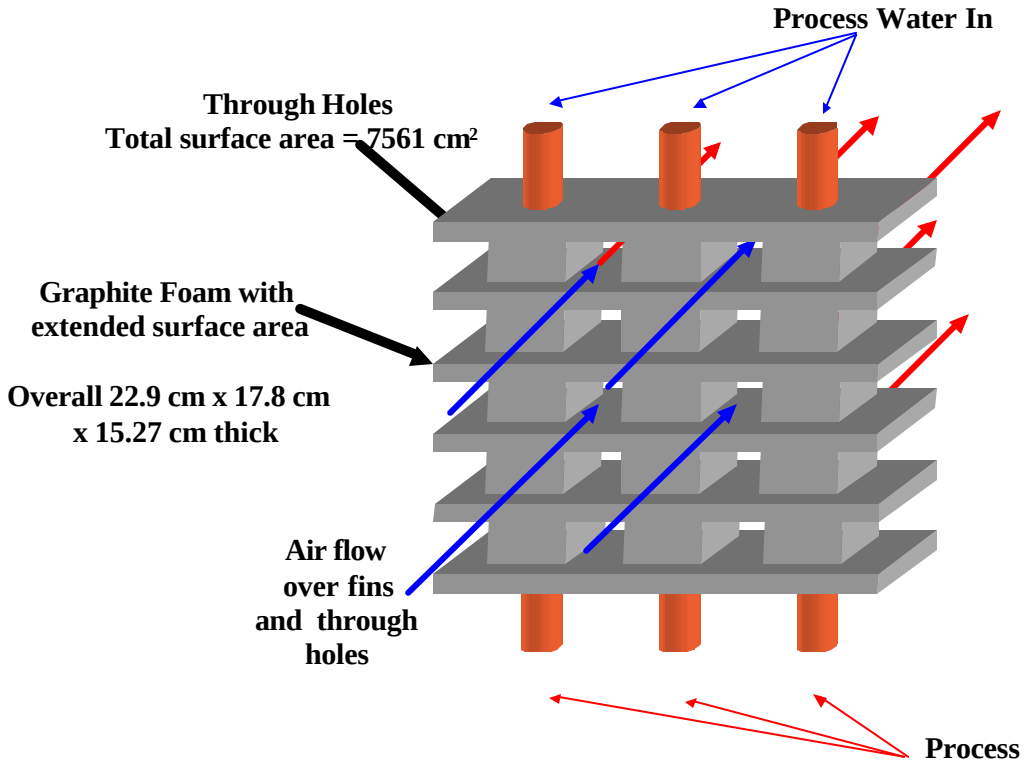
- **The large size and up-front location of radiators greatly increases the aerodynamic drag of most vehicles.**
- **Drag can account for nearly 25% of the fuel use in a heavy vehicle at 60 mph.**
- **The need for exhaust gas recirculation (EGR) cooling is expected to increase radiator size by up to 30-40% in some cases.**
- **Thus, development of smaller, lighter, and more efficient radiators and EGR coolers will impact the styling, driver visibility, and the fuel economy of a wide variety of trucks.**

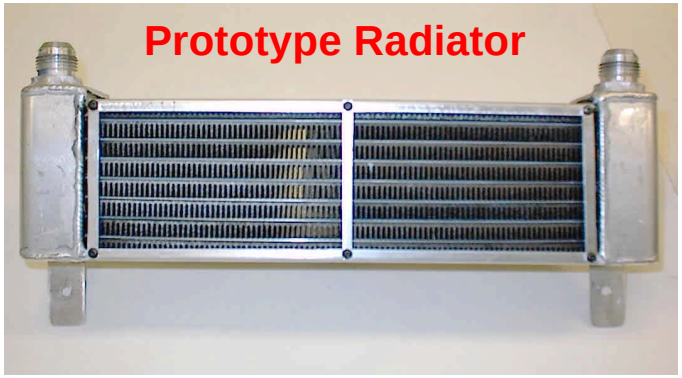
VEHICLE RADIATOR APPLICATION OF FOAM

		Heat Transfer Coefficient h, (W/m²·K)	DP/L (psi/in)
Solid Foam		**10,000***	**2**
Through-holes		**1,000***	**0.1**
Finned		**1,000***	**0.05**
Current Radiator		**30**	**<0.05**

* Preliminary Data

PROTOTYPE RADIATOR DEMONSTRATED



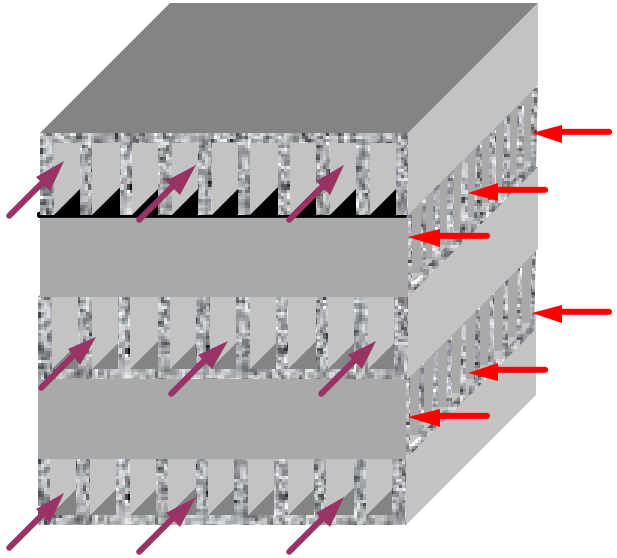


Measured U_o **= 1000 W/m^2 ·K depending on air humidity**

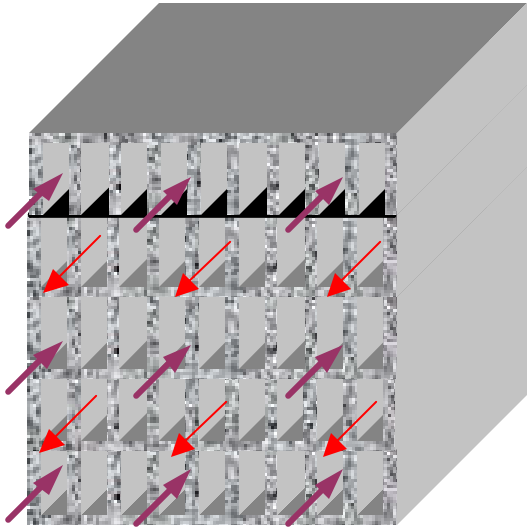
Similar design tested successfully for 800 hp Winston Cup racing engine

CROSS FLOW HEAT EXCHANGERS (EGR)

- Foam rigidized with SiC CVI for dramatic improvement in durability
- Test samples survived operation in air at 1200°C for more than 6 hours!

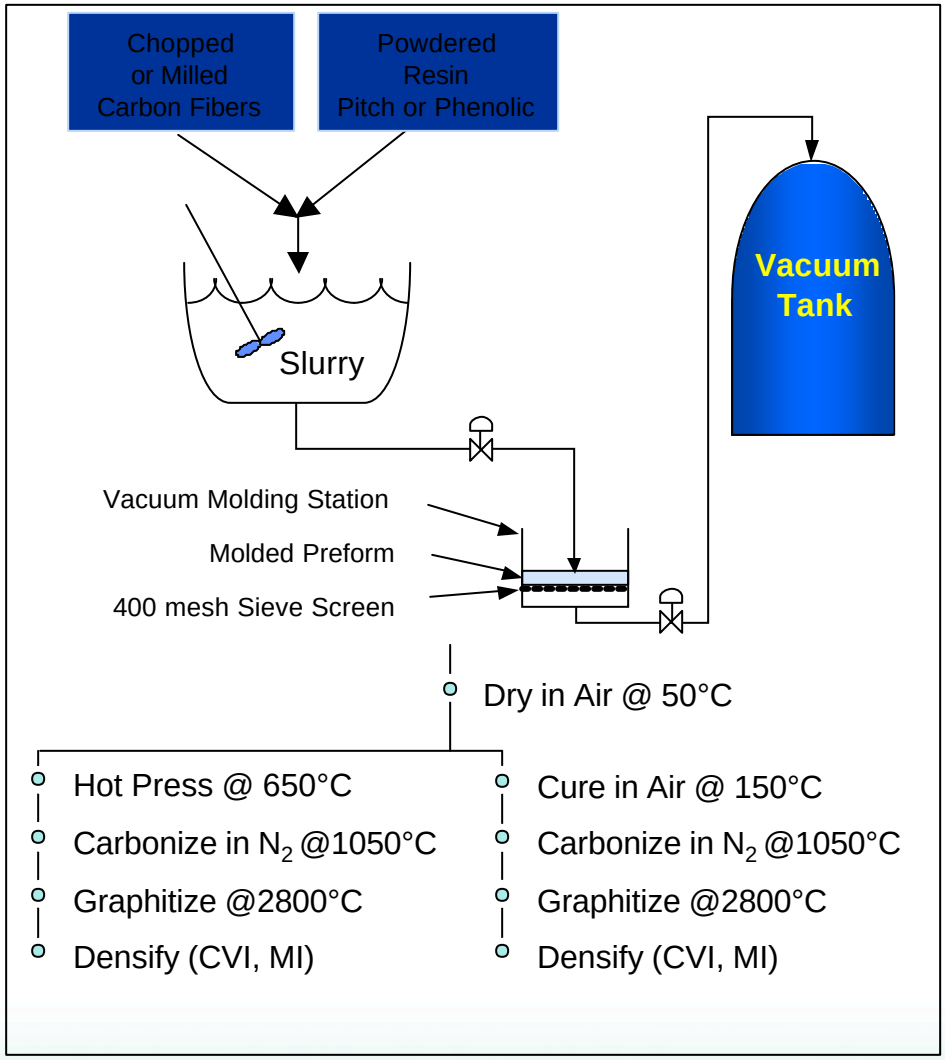


Cross Flow
Easiest to Manifold



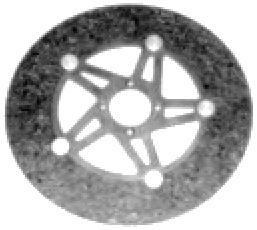
Counter-Current Flow
Most Efficient

ORNL SLURRY MOLDING PROCESS



Advantages

- Tailorability
  - Milled Fibers to 1” fibers
  - Pitch to Phenolic Resin
  - Use different fibers to tailor properties
- Easily Automated
- Scalable to large parts
  - 28 20-in. dia. parts fabricated



8” Bicycle Brake

20” Brake Rotors

Properties that can be tailored

- Thermal Conductivity
- Tensile and Shear Strength
- Modulus
- CTE
- Impact Resistance

CARBON-CARBON BRAKE PREFORMS

PROPERTIES OF SLURRY MOLDED COMPOSITES

Shuttle Orbiter Carbon-Carbon

Composite	Density [g/cm³]	Flexural Strength [MPa]	Flexural Modulus [GPa]	Thermal Conductivity [W/m•K]	
				xy-	z-
RCC - 19 ply	1.6	100	17	8	6
ACC K652 - 19 ply	1.8	280	82	15	3

Slurry Molded Carbon-Carbon - Hot Pressed

SMCC	1.3 - 1.5	50-100	10 - 20	50-160	9-25
SMCC - Densified	1.6 - 1.7	100-170	30-50	120-205	14 - 44

Slurry Molded Carbon-Carbon - As Molded - CVI Densified

SMCC	1.3 - 1.5	40 - 48	21	12-15	12-15

ESTIMATED MANUFACTURING TIMES [HOURS]

Step	Traditional Pitch Impregnation	Traditional CVI	Slurry Molded [As-Molded] CVI	Slurry Molded [As-Molded] Pitch	Slurry Molded [Hot-Pressed] CVI	Slurry Molded [Hot-Pressed] Pitch
Preform Manufacture	10	10	1-2	1-2	10	10
Impregnation/Densification/Carb.	200	200-300	100	48	100	48
Machining	2	2	2	2	2	2
Re-Impregnation/Carbonization	up to 1000 (5 cycles)	up to 1000 (5 cycles)	100	48	--	--

- After capital is amortized, costs are directly related to manufacturing times
- Slurry molded processing is significantly quicker
- Therefore, slurry molding ultimately will be lower cost

SUMMARY & FUTURE DIRECTIONS

- CARBON & GRAPHITE MATERIALS R&D HAS BEEN ONGOING AT ORNL SINCE THE 1940's
- THE CARBON RESEARCH GROUP HAS AN ANNUAL RESEARCH BUDGET OF $3 - 4 MILLION
- SUPPORT FOR NEW SPACE MISSIONS (INCREASED SAFETY MARGINS)
- NUCLEAR REACTOR TECHNOLOGY - HTR'S (GT-MHRS & PEBBLE BED REACTOR)
- EXPANDED ACTIVITIES IN SUPPORT OF DOE FUEL CELLS PROGRAMS AND GREENHOUSE GAS SEPARATION AND CAPTURE
- THERMAL MANAGEMENT MATERIALS FOR ELECTRONIC SYSTEMS
- INCREASED EMPHASIS OF FUNDAMENTAL CARBON MATERIALS SCIENCE