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3-D Woven, Mullite Matrix, Composite Filter

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PB.6 3-D Woven, Mullite Matrix, Composite Filter

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Period of Performance September 30, 1994 to December 30, 1995 (Phase I)

Schedule and Milestones

FY95 Program Schedule

	O	N	D	J	F	M	A	M	J	J	A	S
NEPA Report	—	—										
Test Plan	—	—										
Develop 3D Preform			—	—	—	—	—	—				
Develop Mat'l Process			—	—	—	—	—	—				
Evaluate Best Material									—	—	—	—

OBJECTIVES

Westinghouse, with Techniweave as a major subcontractor, is conducting a three-phase program aimed at providing advanced candle filters for a 1996 pilot scale demonstration in one of the two hot gas filter systems at Southern Company Service's Wilsonville PSD Facility. The Base Program (Phases I and II) objective is to develop and demonstrate the suitability of the Westinghouse/Techniweave next generation composite candle filter for use in Pressurized Fluidized Bed Combustion (PFBC) and/or Integrated Gasification Combined Cycle (IGCC) power generation systems. The Optional Task (Phase III, Task 5) objective is to fabricate, inspect and ship to Wilsonville

50 advanced candle filters for pilot scale testing.

BACKGROUND INFORMATION

Hot gas particulate filters are key components for the successful commercializaion of advanced coal-based power-generation systems such as Pressurized Fluidized-bed Combustion (PFBC), including second-generation PFBC, and Integrated Gasification Combined Cycles (IGCC). Current generation monolithic ceramic filters are subject to catastrophic failure because they have very low resistance to crack propagation. To overcome this problem, a damage-tolerant ceramic filter element is needed.

PROJECT DESCRIPTION

Westinghouse and Techniweave have undertaken a three-phase progam to develop an advanced filter with damage tolerance, increased durability, increased resistance to crack propagation, and non-catastrophic metal-like failure characteristics through the use of:

- A 3D continuous fiber preform for reinforcement;
- Oxide materials, which are inherently stable in oxidizing environments and have been shown by Westinghouse under DOE Contract #DE-AC21-88MC25034, Thermal/Chemical Degradation of Ceramic Cross-Flow Filter Materials, to be more resistant to corrosive alkali species than nonoxides, such as SiC and Si_3N_4; and,
- Low cost sol-gel processing.

Phase I, Filter Material Development and Evaluation, activities include the laboratory-scale development, characterization, and testing of a mullite matrix 3D fiber-reinforced (Nextel 550) ceramic composite filter material. This effort focuses on meeting filter material requirements. Phase II, Prototype Filter Fabrication and Evaluation, activities include the development of a prototype filter and filter qualification testing in a simulated pressurized-bed combustion environment in the Westinghouse High-Temperature High-Pressure (HTHP) filter test facility. Phase III, Optional Pilot-Scale Filter Manufacturing, activities include the manufacture of 50 full size candle filters for pilot scale testing at Wilsonville and to implement quality assurance/quality control and non-destructive evaluation procedures developed in Phase II.

At present, only Phase I has been funded. A breakdown of the experimental activity for Phase I, Task 3 (Tasks 1 and 2 were the NEPA Report and Test Plan, respectively) follows:

Phase I

Task 3 - Development, Qualification, and Testing of Hot Gas Filter
- 3.1.1 - Develop 3D Fiber Architecture
- 3.1.2 - Develop Composite Filter Material Fabrication Process
- 3.1.3 - Fabricate and Evaluate Best Filter Material

RESULTS

During the first half of FY95, after completing Tasks 1 and 2, efforts have been focused on experimental subtasks 3.1.1 and 3.1.2 in Task 3. A description of objectives in each subtask and a discussion of the status or resulting data in each area follows.

3D Fiber Architecture Development

A low cost, three-dimensional (3D) fiber architecture, that is both easy-to-manufacture and automatable, is required to produce an economical 3D preform suitable for candle filter use. Toughness in all directions, good shear properties, homogeneously distributed porosity, and surface smoothness are desirable features for selecting a preform for fabricating a ceramic matrix composite (CMC) candle filter fiber preform. A 3D fiber architecture can be designed to fulfill these requirements. Techniweave's fiber architecture design philosophy has been guided by the selection of automatic net shape weaving techniques, the generation of thin wall structures, the achievement of fiber continuity through highly stressed regions and the tailoring of the preform to the mode of matrix introduction.

Over the past five years, Techniweave has developed equipment and process technology for weaving seamless, tubular filter preforms with ceramic fibers. During an IRAD program, the use of a multilayer fabric was demonstrated for fabricating a porous mullite/mullite CMC. This technology provides the basis for the fiber architecture variations being evaluated in this program for the economical production of a fiber preform for candle filters. A generic sketch of the multi-layer fabric is presented in Figure 1.

From this baseline weave, Fig. 1, twelve fiber architectures were designed to examine the effect of fiber volume, wall thickness, fiber architecture and yarn construction on the CMC filtration characteristics and mechanical properties. The fiber orientation and yarn construction were varied to modify the sizes and distributions of porosity in the preform. The amount of fiber at the preform surface was varied to control the filtering surface smoothness and porosity.

A low cost woven preform is required. The best solution is one that will provide adequate filtration and mechanical performance while using the least amount of fiber. Thus, wall thickness was limited to 0.1 in. thick to control fiber cost and permit ease of manufacture and automation.

Initial weaving trials were conducted to establish what maximum level of fiber volume could be achieved in the warp (axial direction along the length of the filter) and fill (circumferential direction) directions without damaging the fibers. It was determined that a balanced weave could be woven with a maximum total fiber volume of 35%. The axial and circumferential loading on a candle filter in use are expected to be different. In order to be able to optimize the fiber volume in both directions, some preforms were woven with different amounts of fiber volume in the warp and fill directions.

From these initial weaving trials, eleven candidate fiber architectures were selected for fabrication into CMC panels for characterization. For each architecture, preforms are being fabricated from Nextel 550 fiber. The preforms are then infiltrated with the matrix solution to form filter material composite plates. The matrix solution is either sol-gel mullite with mullite filler powders, or sol-gel mullite without mullite filler powders.

To date, 12 plates have been fabricated from the first six architecture designs and have been shipped to Westinghouse for evaluation. These six candidate architectures are shown in Figure 2. Two sizes were fabricated for each architecture:

1) 4 in. x 6 in. panels were made using Techniweave's baseline matrix fabrication process combining mullite sol and mullite powder infiltration. These panels were fabricated with an *in-situ* formed membrane layer. The 6 in. length of these panels is parallel to the fill direction. The warp direction, which is the 4 in. length, generally has a higher strength than the fill direction. This is of importance for those candidate architectures which have unequal fiber volume fractions in the fill and warp directions. Permeability test specimens, 41 mm diameter disks, and 4-pt bend specimens, machined according to ASTM C1161-90, were prepared for testing. Bend strength will be measured in each direction.

2) 2 in. x 2 in. plates for composite fabrication using just the mullite sol. The mullite powder is not used for the composite matrix in these samples. Thus, these samples will determine the permeability of the fiber architecture without the additional influence of the powder. Permeability test specimens have been machined from these samples.

Permeability Test Results. The gas flow resistance for each disc sample was measured with the Westinghouse permeability test rig. Acceptable permeability results from this test rig are gas flow resistance values < 1 in-wg/fpm at room temperature.

The samples were evaluated in this rig in two positions: a) "up" position, this is the normal expected filter material orientation where the expected external surface of the filter material is the face exposed directly to the flowing gas stream, as it would be in use, and b) "down" position, this refers to directly exposing the face of the filter material that would normally be the internal surface of the candle filter to the flowing gas stream. The intent of this evaluation is note if there are significant differences in the flow resistance through the material based on its orientation in the test rig; there should not be any differences.

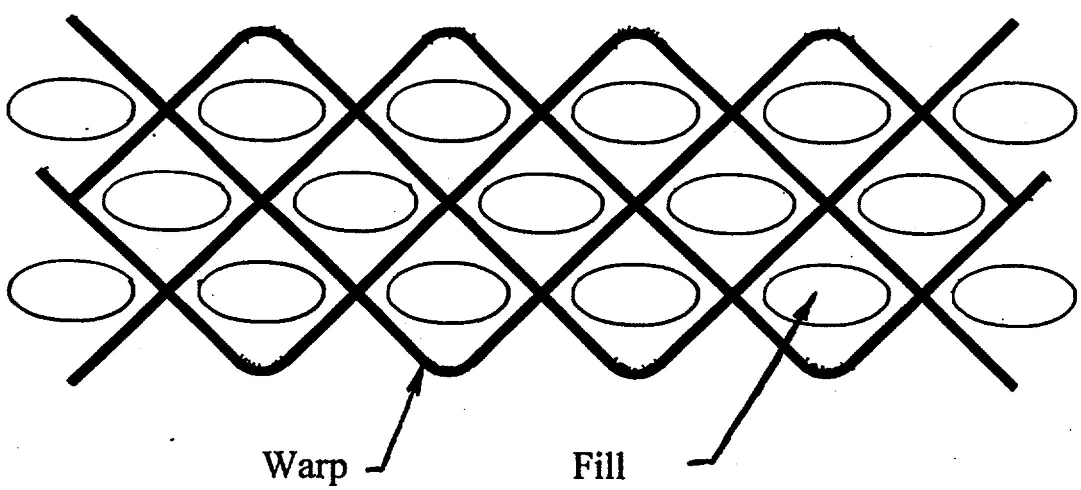
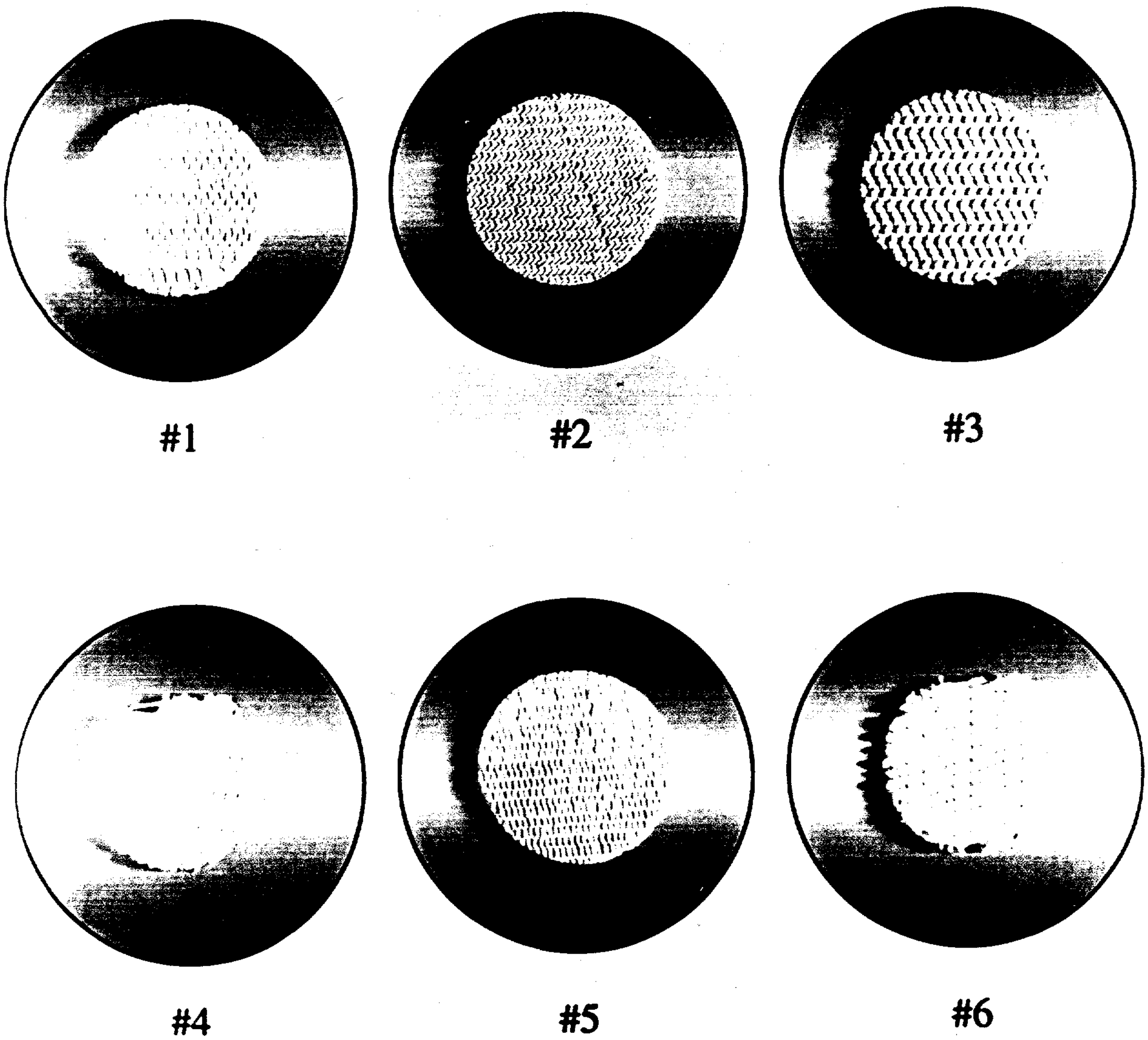


Figure 1. Schematic of multi-layer fabric where the warp yarns provide axial and radial reinforcement while fill yarns provide hoop reinforcement.



Candidate Fiber Architectures

Figure 2. Photographs of Candidate Fiber Architectures 1-6

During testing, six of the twelve samples had leaks at the edges or were poor fits in the test rig. These samples will be re-machined, as-needed, and edge sealed with a ceramic adhesive, then re-tested.

The data for the remaining samples is shown in Table 1. All measured architectures, in both test orientations, met the gas flow resistance requirement of < 1 in-wg/fpm at room temperature. A higher gas flow resistance was measured in the "up" position. It is hypothesized that when in this position some leak may have occurred around the periphery of the sample. Even though an attempt was made to seal the edge with Teflon tape, it is conceivable that some leak may have still occurred.

TABLE 1. Gas Flow Resistance as a Function of Fiber Architecture

Architecture*	Gas Flow Resistance (in-wg/fpm at 70 °F)	
	Up	Down
1	0.434	0.657
2	0.129	0.750
3	0.193	0.442
5	0.425	0.759
6	0.264	0.248
4 (sol only)	0.332	0.622

*samples 1,2,3,5,& 6 were made with powder + sol

To confirm the results in Table 1, and to eliminate any potential leaks when placed in the sample holder, all samples will have their perimeters and edges sealed with a ceramic adhesive prior to being re-tested.

Weaving Trials for Manufacturing Issues. Separately, weaving trials of tubular sections have been initiated to determine the manufacturing issues for the tubular, closed-end, and flange sections of the candle filter. This information is one of the factors which will be used to select the best and lowest cost architecture for candle filters. Initial trials have demonstrated the feasiblity of continuously weaving tube sections with an integrated closed end.

Develop Composite Filter Material Fabrication Process

The objective of this effort is to optimize the matrix infiltration step and matrix sintering conditions in order to minimize the fabrication costs of ceramic hot gas filters and maintain acceptable filter performance. Our goal is to fabricate the filter material using only two matrix processing steps:

1) Infiltration of the ceramic preform with a water-based mullite sol (no mullite filler powder) to rigidize the ceramic preform and provide a protective coating on the fibers.
2) Infiltration of the ceramic preform with a water-based mullite sol with mullite filler powder added. The purpose of the filler is to create a tortuous porosity network.

Several processing variables, listed below, can influence the density/porosity, mechanical properties and performance of the ceramic hot gas filter.

- Processing method
- Mullite sol concentration
- Sol viscosity
- Particle size distribution
- Concentration of mullite filler powder added to sol
- Calcining temperature
- Sintering temperature

The evaluation of the effects of these processing variables on the matrix infiltration efficiency, filter performance and mechanical properties have been undertaken in this subtask. A Taguchi design of experiments approach has been selected to provide a systematic analysis of the effects of the processing variables.

The intent of the Taguchi process is to identify the major effects (variables) and the most optimum values for these effects to give the desired response. In this case, the desired response is meeting the permeability specification.

Permeability is the primary response to be measured and these results will be used in the Taguchi analysis for determining the best values for the matrix processing variables. Permeability was selected because it is the most important parameter. Regardless of strength, surface condition, etc., if the candidate material does not meet the permeability requirement, it cannot be considered for filter applications.

Secondary factors being using for evaluating the results of the Taguchi test matrix are the ability to form a membrane *in-situ* and the composite density. Strength is an additional factor which will be considered in additional experiments.

Prior to conducting the first experimental design, two sets of screening studies were necessary in order to establish experimental values for the sol viscosity and mullite powder particle size distribution.

Modification of Sol Viscosity. Westinghouse experience indicates that a higher viscosity will help to keep ceramic filler powders in suspension and provide for a more homogeneous infiltration of the ceramic preform. Additionally, eliminating the currently required mechanical agitation to keep the powder dispersed will simplify fabrication and reduce production and capital equipment costs.

Several water-soluble polymers were evaluated in terms of their effectiveness for increasing the viscosity of the water-based mullite sol. These additives include: Carbopol by Goodyear (cross-linked polyacrylic acid polymer), Surfynol CT-324 by Air Products (pigment grind additive of proprietary composition), and Elvanol by Dupont (Polyvinyl Alcohol). Unfortunately, these products were found to be either incompatible with the water-based mullite sol or were ineffective for increasing the sol viscosity. Carbopol and Elvanol were not able to be dissolved in the Westinghouse water-based mullite sol.

Surfynol CT-324, did not completely dissolve in the water-based mullite sol, but was found to significantly improve the dispersability of the mullite powder in the sol. Concentrations in the range of 5 - 10% by mullite powder weight were found to be beneficial. The viscosity of the sol increased from 20 cp to 400-800 cp, depending on the mullite powder concentration in the sol. Unfortunately, the undissolved portions of Surfynol were in the form of large, fat-like globules. During preform infiltration, these Surfynol globules clogged the pores of the composite preform and formed a coating on the preform surface which inhibited infiltration of the mullite sol and mullite filler powder.

Vendors of dispersing and thickening agents were contacted to discuss the compatibility difficulties that were encountered. The vendors indicated that such water-soluble additives are geared towards use in systems having a pH in excess of 3. Water-based mullite sols typically have a pH less than 2. This pH difference causes a chemical incompatibility between the additives and the sol.

Polyethylene imine and polyvinylpyrrolidone have been suggested as possible compatible additives. Polyethylene immine retains its charge in acidic conditions and hence may work in conjunction with this low pH sol. Polyvinylpyrrolidone has good solubility and chemical stability in both water and many organic solvents. These additives are under evaluation.

Other methods evaluated for either improving powder dispersion or increasing sol viscosity included: 1) The application of an "ionic" polyvinyl alcohol (PVA) coating to the surface of the mullite filler powder, prior to dispersion in the sol, as a means to improve the dispersability of the mullite powder, and 2) the use of a thermal treatment of the water-based sol to increase sol viscosity. Neither approach was successful.

Mullite Filler Powder Particle Size Distribution. Based on prior Westinghouse and Techniweave research, three particle size distributions were identified for the initial experimental design: 1 - 10 μm, 5 - 20 μm and 10 - 45 μm. These three desired particle sizes were not available "off-the-shelf." The three particles size distributions were obtained by classifying -200 mesh (< 70 microns) mullite powder feedstock.

Because of the additional cost of size classification of the filler powder, the test matrix was expanded to include the evaluation of the -200 mesh mullite powder. If this powder is suitable, a significant cost savings would result.

Processing Development for Sol-Only Infiltration Step. As previously discussed, the current objective is to fabricate filter materials using only two matrix processing steps. The first step is a sol-only infiltration to rigidize the preform and provide a protective coating on the fibers.

Westinghouse experience indicates that if the initial infiltration yields a coating which is too thick, the resulting preform will be stiff and difficult to process in subsequent steps. Furthermore, to optimize the mechanical properties of the composite filter material, it is desirable to have a thin, uniform crack-free coating with minimal bridging between fibers.

The suitability of the water-based mullite sol for forming a uniform, thin coating was evaluated by dip coating woven Nextel 550 fabric in three sol concentrations: 10, 5, and 2.5 wt%. The fabrics were then air dried, calcined at 800 °C for 1 hour and then examined using a scanning electron microscope.

The 10 wt% mullite sol resulted in a very thick and cracked coating; significant fiber bridging was observed. The 5 wt% sol also yielded a thick cracked coating. The 2.5 wt% mullite sol was found to give the most uniform crack-free mullite coating with minimal bridging. The 2.5 wt% sol was selected for use in all subsequent CMC fabrication.

Selection of Infiltration Method. Prior to proceeding with the initial design of experiments, the infiltration efficiency (weight gain/infiltration cycle) and permeability ratio were compared for a more conventional vacuum infiltration approach to a one-sided vacuum infiltration method. In the conventional method, the infiltrant enters the composite preform from all exposed surfaces. In the one-sided approach, vacuum was used to pull the infiltrant from one exposed surface through the composite, see Figure 3.

Each composite was infiltrated with a 10 wt% water-based mullite sol to which 10 wt% additional mullite powder was added. The particle size of the mullite powder was 10-44 microns. The infiltration efficiency was slightly greater for the conventional vacuum infiltration process.

After 5 infiltration cycles, the immersion densities of the samples were 1.80 g/cm^3 and 1.68 g/cm^3 for the conventional and one-sided infiltrated samples, respectively. These values correspond to 58 % and 54 % of theoretical density (3.11 g/cm^3), respectively.

The gas flow resistance was measured for each sample. As shown in Table 2, the sample infiltrated from one-side only is within the Westinghouse filter specification for gas flow resistance (i.e., < 1 in-wg/fpm), while the conventionally infiltrated sample had a gas flow resistance exceeding the target specification.

TABLE 2. Gas Flow Resistance as a Function of Infiltration Method

Infiltration Method	Gas Flow Resistance (in-wg/fpm at 70 °F)	
	Up	Down
Conventional Vacuum	2.160	2.637
One-Sided	0.283	0.332

The one-sided infiltration approach was selected for all CMC fabrication. This approach is also expected to give the lowest manufacturing cost.

Taguchi Experimental Design The results of the screening studies for sol viscosity and mullite filler particle size distributions, as well as processing information from Techniweave, led to the formulation of the first experimental design. The variables are listed below.

- Sol Viscosity: At this time, a suitable additive or method has not been identified for increasing the sol viscosity (for the purpose of providing a uniform dispersion of mullite filler powder in the sol). Because the mullite powder can be maintained in a dispersed state through continuous agitation, this technique will be used to maintain the powder dispersion until an alternate means is identified.
- Mullite Powder Particle Size Distributions: The initially targeted distributions of 1 - 10 µm, 5 - 20 µm, and 10 - 45 mm will be utilized. Additionally, the -200 mesh mullite feedstock will also be evaluated due to the potential cost savings.
- Concentration of Mullite Filler Powder: A low, 10 wt%, and a high, 30 wt%, concentrations were selected for evaluation.
- Concentration of Mullite in Aqueous Base Sol: A low, 5 wt%, and a high, 10 wt%, concentrations were selected for evaluation.

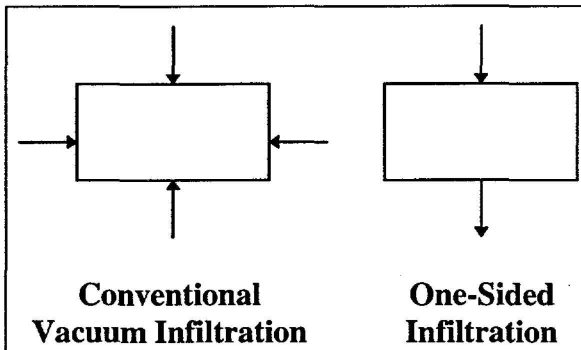


Figure 3. Comparison of Conventional Vacuum Infiltration and One-Sided Infiltration Techniques

- Calcining Temperature: Temperatures of 600 and 800 °C were selected.
- Sintering Temperature: Temperatures of 1050 and 1150 °C were selected.

After establishing the values of the experimental variables, a Taguchi design of experiments was set up, Table 3, to permit a systematic analysis of the variables with a minimum number of experiments. For this initial experimental design, both the calcining and sintering temperatures are being held constant at 2 and 4 hours, respectively. Only the calcining and sintering temperatures are being varied because temperature has a more significant impact on microstructure development, than does time at temperature. The times were chosen conservatively to provide sufficient time for all significant reactions to occur.

Nextel 550 preforms, using an angle interlock architecture, are being used for this test matrix. Sections of preform were first dip coated using a 2.5 wt% concentration of mullite sol. The preforms were then air dried and calcined at 800 °C for 1 hour. Permeability disks were then cut from the coated preform. The weights of each starting disk were measured.

Matrix infiltration processing of these disks is in progress. Each permeability disk is being infiltrated using the appropriate slurry composition with the one-sided infiltration method. The goal is to infiltrate until a thin, uniform membrane layer is formed on the disk surface. The infiltration efficiency of the various slurries is monitored. Upon completion of the infiltration processing, the gas flow resistance values of each disk will be measured. These data will be analyzed using standard Taguchi methods.

Thus far, the following observations about infiltration efficiency and membrane layer formation have been noted:

- The finest particle size distribution, 1-10 microns, is easily pulled through the coarse porosity network of the standard angle interlock fiber architecture. A membrane layer on the surface of the composite is unable to be formed after several infiltration cycles.
- The medium particle size distribution, 5 - 20 microns, at a loading of 10 wt%, will form a membrane layer after numerous

TABLE 3. Design of Experiments Matrix for Filter Processing

Factor / Trial No.	Mullite Powder Particle Size Distribution				Mullite Sol Conc. (wt%)		Conc. of Mullite Powder in Sol (wt%)		Calcining Temp. (°C)		Sintering Temp. (°C)	
Code	1-10 µm	5-20 µm	10-35 µm	-200 mesh	5	10	10	30	600	800	1050	1150
FD-1	X				X		X		X		X	
FD-2	X					X		X		X		X
FD-3		X			X		X			X		X
FD-4		X				X		X	X		X	
FD-5			X		X			X	X			X
FD-6			X			X	X			X	X	
FD-7				X	X			X		X	X	
FD-8				X		X	X		X			X

infiltration cycles (7-15). The number of cycles required to form this layer is not practical. At a loading of 30 wt%, this particle size distribution can be used to form a membrane layer within one to two cycles.

- The use of the coarse -200 mesh powder (< 70 microns) allows a membrane to be readily formed (# of cycles is dependent on powder loading and sol concentration).
- When a film is formed, pinholes are often observed. This pinhole formation is a processing issue that is also related to the coarse surface porosity of the angle interlock architecture. It is not a characteristic of any of the particle size distributions. These pinholes do not imply a potential leak as the architecture in its own right has quite tortuous porosity and would stop any penetration of the ash. The disadvantage of pinholes is that they would be more likely to plug up with ash. Thus a large number of pinholes, if plugged with ash, would reduce the available filtering surface area.

FUTURE WORK

The remaining candidate architectures will be woven into preform panels and used to fabricate CMCs for test and evaluation. Weaving trials will be conducted to evaluate the feasibility of continuously forming tubes with integrated flanges and closed ends. Matrix processing optimization studies will be completed with the results from the first experimental matrix being used to guide additional experiments to evaluate flexure strength as a function of the processing variables.

The results from the above will be used to select the best architecture and matrix processing approach. CMC test panels will then be fabricated using the best architecture and matrix processing technique. These panels will undergo permeability testing, 4-pt bend testing, Weibull modulus determination, and high temperature flow-through corrosion tests.