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Disclaimer

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FILTER MANUFACTURING ASSESSMENTS

EXECUTIVE SUMMARY

The develoment of advanced filtration media for advanced fossil-fueled power generating systems is a critical step in meeting the performance and emissions requirements for these systems. While porous metal and ceramic candle-filters have been available for some time, the next generation of filters will include ceramic-matrix composites (CMCs) (Techniweave/Westinghouse, Babcock & Wilcox (B&W), DuPont Lanxide Composites), intermetallic alloys (Pall Corporation), and alternate filter geometries (CeraMem Separations). The goal of this effort was to perform a cursory review of the manufacturing processes used by 5 companies developing advanced filters from the perspective of process repeatability and the ability for their processes to be scale-up to production volumes. Given the brief nature of the on-site reviews, only an overview of the processes and systems could be obtained. Each of the 5 companies had developed some level of manufacturing and quality assurance documentation, with most of the companies leveraging the procedures from other products they manufacture. It was found that all of the filter manufacturers had a solid understanding of the product development path. Given that these filters are largely developmental, significant additional work is necessary to understand the process-performance relationships and projecting manufacturing costs. An exception to this is the Pall filter, since it is strongly aligned with their current manufacturing processes and experience. CeraMem has developed a filter product that strongly leverages the manufacturing base for a commercial product, which greatly simplifies their internal filter development effort. B&W, DuPont Lanxide Composites, and Techniweave/Westinghouse all have experience manufacturing a variety of products, but do not currently sell a CMC product. Their experience with the manufacture of other products provides significant leverage for the filter development, since existing quality assurance/quality control and manufacturing procedures can be adapted to this new product line. While each organization had specific needs, some common among all of the filter manufacturers were access to performance testing of the filters to aide process/product development, a better understanding of the stresses the filters will see in service for use in structural design of the components, and a strong process sensitivity study to allow optimization of processing.

1.0 INTRODUCTION

A number of advanced coal-fired power systems, such as fluidized-bed combustion, coal gasification, direct coal-fired turbine concepts, and fuel cells, require high-efficiency particulate removal from the hot-gas stream to both protect down stream equipment and to meet emissions requirements[1]. Monolithic ceramic filters, such as clay-bonded SiC, reaction-bonded Si_3N_4, mullite/alumina, cordierite, alumina, have been used as either candle or cross-flow filters. These filter systems provide excellent particulate removal characteristics with up to 99.9 percent removal of 0.5 μm particulates reported[2]. The performance of these filters has been studied extensively, and it has been a subject of a number of demonstration programs sponsored by the Department of Energy. Westinghouse has reviewed the environmental stability of candidate filter materials[1], and identified the key factors in determining filter life as thermochemical stability of the ceramic phases with the gas stream, oxidation of non-oxide ceramics, phase transformations in oxide systems, and thermal shock during pulse cleaning or system upsets.

With hot-gas filters critical to the successful commercialization of advanced coal-fired power systems, the Department of Energy (DOE) Federal Energy Technology Center at Morgantown (FETC-M) has driven the development of advanced hot-gas filters. FETC-M has championed the development and demonstration of both monolithic, discontinuous-fiber reinforced, and continuous-fiber reinforced ceramic filters.

Improved filter elements for both oxidizing and reducing environments are needed to meet the needs of the advanced coal-fired power systems, as well as other industrial applications. A number of promising filter systems have been developed over the years, but several of them have encountered significant problems with process variability and others have not been able to reproduce their bench-scale results on full-size filter elements. With this perspective, FETC-M has contracted with BIRL, Northwestern University's industrial research laboratory, to perform manufacturing assessments of five advanced filter development programs. The manufacturing assessments focused on process monitoring and control, process documentation, quality control methods, identifying key process steps for filter performance, and identifying potential scale-up issues.

The five filter programs that were selected for this effort included Westinghouse/ Techniweave - a mullite-based CFCC candle filter produced by sol-gel; Babcock & Wilcox - an alumina-based CFCC candle filter produced by filament winding; Pall Corporation - an iron aluminide candle filter produced by powder metallurgy; DuPont Lanxide Composites - a cordierite-based composite candle filter produced by filament winding, and CeraMem - a cordierite dead-end flow filter produced by a combination of extrusion and solution processing. Each of these advanced filter development programs underwent a one day review of their manufacturing processes solely from the perspective of process monitoring/repeatability, process documentation, identification of critical processing steps in relation to filter performance, and a discussion of scale-up issues associated with their processes. It was not the intent or purpose of these visits to assess the technical approach, actual processing conditions, or filter costs. A discussion of each of the visits is provided in the following sections.

2.0 TECHNIWEAVE/WESTINGHOUSE

A team between Westinghouse and Techniweave has been formed to focus on the development of low-cost advanced hot-gas filters based upon three-dimensional (3-D) woven preforms and sol-gel matrix processing. Westinghouse has substantial expertise in ceramics processing and production, particularly in sol-gel methods. Techniweave is a recognized leader in weaving of ceramic fabrics and preforms, and has been expanding their product line to include matrix processing. Over the past two years, Techniweave has developed the sol-gel process for the mullite matrix used in this project. All of the filter processing is done at Techniweave, with Westinghouse providing expertise on testing of the filters and the application environment. This project is another example of Techniweave's effort to vertically integrate their product line to include finished composites (polymer- and ceramic-matrix composites), as well as woven fabrics and preforms.

2.1 Filter Description and Process Overview

The Techniweave-Westinghouse filter consists of 3-D woven Nextel 550 fiber preform infiltrated with a mullite matrix. The key performance features of the filters were identified by Techniweave-Westinghouse as: 1) flange area strength and tolerance, 2) straightness, 3) permeability, and 4) absence of holes. The geometric features (flange area and straightness) are very easily determined using simple measurements. Permeability can be measured through pressure drop tests, while bubble testing offers additional information on permeability and the pore size distribution (absence of hole). Tube strength can not be measured without destructive testing, and no correlation between processing and strength had been developed. A measure for the allowable variation within any of the process steps which still resulted in an acceptable tube had not been developed. The lack of information on process tolerances was apparently due to the early state of development for the process. Process conditions were still being defined, and it would be premature to begin to develop a complete understanding of process tolerances.

However, they are trying to develop a process for the filters with limited bench-scale testing (400 hours at the Westinghouse test facility) and no field testing to date. With the level of development for the filters, the limited level of testing is to be expected. As the filter process is developed, significantly more testing will be necessary to aide process optimization for performance and product cost. Techniweave/Westinghouse recognize the need for feedback from end-users on critical features and the need to eventually develop specifications.

An outline of the filter production process, process variables, and types of inspection carried out at each step are presented in Table 2.1. Performance features of the filter that were defined by Techniweave/Westinghouse are geometrical control (flange dimensions and straightness), filter permeability, the uniformity of matrix loading and fiber architecture, and the processing of the membrane layer.

2.2 Process Monitoring and Control

2.2.1 - Preform

Before an order is released to the floor for production, it is reviewed for completeness by QA manager, a job summary sheet is prepared, work instructions are prepared, the schedule is documented, material identification tags are prepared, and the QA manager approves the package. It is then sent to the production manager for review with QA manager to establish QA inspection points (start-up, in-process, and final inspection). Start-up inspection consists of setting the weave pattern and warp and pic counts. The counters set to "0" and one foot of material is produced. This sample is taken to QC for inspection (weight/area, thickness, and pattern). If the sample is within specifications, production is continued. Daily loom inspections are made after start-up to verify actuals versus required for width, pic count, yarn type, and edge quality. No more than three feet of fabric is woven that is out of specification, and the non compliant area is either spliced out or tagged before delivery to the customer. If the fabric cannot be produced correctly within three feet, the machine is stopped until the correction is made. A sample of relevant weaving work orders and quality control documentation is provided in Appendix A.

Table 2.1 - Techniweave Filter Process

Description	Variables	Inspection
Preform Fabrication	Serving Yarns	lot # of yarn and verify type
	Beaming	approve weaving instructions
	Loom Set-Up	weave pattern check
	Weaving	surface pic count
		final inspection: weight/area, fill & warp count, weight, fiber volume, and geometric inspection
Matrix Infiltration	sol preparation	record lot # of raw materials
		precursor weights
		time, temperature
		solids content
		XRD of dried and fired matrix
	infiltration	weight gain
	calcining	time and temperature
		weight gain
Machining		
Final Inspection		geometrical inspection
		permeability

2.2.2 - Sol-Gel Processing of the Matrix

The sol is prepared through the hydrolysis of alkoxides or salts, and the solids loading is adjusted via evaporation of water. The control of the incoming raw materials is seen as key to sol quality and repeatability. Analysis of raw materials is performed using x-ray diffraction (XRD) to qualify materials suppliers. Solids content in the sol is measured using standard off-line methods (measure out a known volume and weigh, then dry and weigh the residuals). All mixing of the sol is done on a mass basis with calibrated scales. Currently, the sol is mixed in a 55 gallon drum with temperature control and stirring equipment. The pH (determines sol stability) is checked occasionally, but it is assumed that if the correct precursor weights are added to the tank, the pH will be correct. The stoichiometery of the sol, and hence the matrix, is controlled at the time of sol mixing. Thus, the quality and consistency of the starting materials and repeatably weighing the sol precursors is critical to the consistency of the sol. They have encountered variability from lot-to-lot with raw materials suppliers, and they are working with them to improve quality. The sol chemistry itself has a narrow window for compositional control. They were still working to better define the desired matrix composition. Once they define the matrix composition, they believe it will be easy achieve it repeatably with only modest control of precursor weighing for the sol batching and mixing conditions, and raw materials control.

2.2.3 Matrix Densification:

Processing of the filter is done with tooling which defines the shape. At the time of this visit, Techniweave had made less than 10 filters, so a significant amount of development was still to be done within the current program. Techniweave is producing high-temperature structural components with a simple geometry for another application using the same sol-gel process. With the filter concept being developed by Westinghouse/Techniweave, the preform is both structural and shape defining, the quality of the matrix is less critical. Typically, less than 20 percent of the final filter is matrix. During matrix densification, the sol is infiltrated into the preform and calcined several times with the weigh gain with each cycle recorded. A slurry is then infiltrated into the preform as the basis for the membrane layer. The powder size distribution, amount of powder, membrane thickness, and change in weight are all recorded. After calcining, the weight of the filter is recorded again. Additional infiltration and calcine cycles are performed as needed to tailor the matrix volume fraction. A final sintering step is performed to complete the process. For sintering, the change in weight, time-temperature profile, geometric features, and density of the filter are all recorded. Lot numbers of the precursors are recorded on the filter processing records throughout the process. The key matrix densification step is the formation of the membrane layer during one of the infiltration cycles. Recycling of the sol is a future goal when the filters are brought to a production level. Bubble testing of the filters is used to check for holes and matrix inconsistencies, and it is considered a key test of fiber uniformity and mean pore diameter. The fiber uniformity is critical since the matrix volume fraction is very low.

2.3 Existing QA/QC Systems

All of the filter processing is performed at Techniweave, which has a quality program in place. They currently manufacture woven products to MIL-I-42508, MIL-Q-9858, and are preparing for ISO certification. All orders are inspected to at least MIL-I-45208 and any additional customer specifications. Inspection equipment (counters, gauge blocks, micrometers, scales, vernier calipers, test stands, furnaces, and recorders) is calibrated to ANSI NCSL Z540-1 at qualified outside vendors. Statistical ratings of weavers is performed by collecting data on every roll they produce. The weavers are then rated to qualify them for different production jobs (difficulty of weave, types and number of defects, and qualified weaves). If a weaver falls below a minimum rating on a fabric or weave, they must go through additional training before they can work on that fabric again. Weavers receive initial training, and then annual training and review with the QA manager. These procedures clearly demonstrate their commitment to quality, and their expertise in producing woven products for the military, biomedical, and commercial markets.

Process instruction records for matrix processing have been developed that include many of the features from the woven products quality system. Part of this is driven by the need to have all jobs in the facility meet a minimum quality system required by MIL-I-45208. However, the matrix process is much less developed than the weaving processes, and no information relating filter performance to processing variations has been developed yet. Matrix processing is done by one or two people, and is not yet ready to shift to a more production oriented training and documentation process as has been done with weaving. Process records include listing actual process parameters (time, temperature, weights, etc.) versus desired, tracking of raw materials lot numbers, and appropriate test results. Since the process was still in early development at the time of this visit, no fixed set of process parameters had been developed, nor had the experimental plan to determine the effect of process changes on directly measurable properties, such as strength or permeability, been completed.

2.4 Scale-Up Experience

Preforms

Techniweave is a leading supplier of specialty woven cloth and 3-D preforms. To date, their production of 3-dimensional preforms (all types) is relatively small with a total accumulated production of a few thousand. However, they believe that the thin nature of the filter preforms makes them more akin to fabric which they routinely produce for a variety of commercial products. For example, Techniweave produces filter bags which have a similar degree of difficulty. Production lots for the filterbags are done in 6,000 feet per run units. Adaptation of QA for production may include using MIL-I-105 (sampling plan), which includes daily inspections of weave. Other woven products that Techniweave has taken to production include those for knee braces, radomes, tethers, and an insulating fabric for the space shuttle.

Matrix

Westinghouse has taken a number of ceramic products to production, primarily for electronics applications. However, the production is being done at Techniweave, and the processing of ceramic matrices by sol-gel and slurry methods is a very recent technology addition. Sol-gel and slurry processing are also a relatively new technical area for the Principal Investigator (PI). The PI at Techniweave has taken CMC to production at SEP, and has worked with other CMC systems while at Textron Specialty Materials. At SEP, the process used was chemical vapor deposition, and at Textron it was polymeric precursors for ceramics. This experience base is complementary to the current effort, in that issues of process development, manufacturing floor practices, and process repeatability were addressed. The processing of ceramics by sol-gel and slurries has been studied extensively, and it can be, and is, done on a large scale for a variety of monolithic ceramic products. However, significant effort has gone into developing each of those processes, and the scale-up of the process will require substantial effort to produce a commercial product, despite the apparent simplicity of the process. The continued collaboration of Westinghouse, with their substantial experience in manufacturing ceramics, will be an important factor in scaling-up the matrix processing.

2.5 Observations and Recommendations

The assessment visit to Techniweave led to the following observations:

- Filter development is clearly at the bench-scale level
- While the development of process tolerances is not appropriate at this time, a better understanding of which step(s) is key to filter performance would benefit the development effort.
- The team recognizes that performance criteria for filters need to drive identification of and process control for key steps, and the definition of process tolerances.
- Intermediate-scale testing (between bench and slip-stream) to determine effect of operating environment on filter properties is required for process optimization.

Preform Weaving

- The proposed filter design assumes that the fiber dominates mechanical properties of the filter, so the preform is key to filter mechanical performance.
- Weaving is the more mature technology in this program.
- Quality systems are well established for the weaving processes.
- A variety of woven goods are in production, and the path to scale-up appears well established.
- Further development of the preform will depend upon feedback from performance tests.

Matrix Processing

- The difficulties in scaling-up the sol-gel process were oversimplified during discussions. The basis for this is that the filter is fiber dominated. And while that is certainly the case for the mechanical properties, the matrix uniformity will have a strong influence on permeability and pore size distribution. While bag filters certainly provide high efficiency cleaning, no data on just the preform meeting the particle emissions requirements was presented.

- The planned re-use of sol is driven by economics, but it necessitates tracking of multiple lots, better assay of sol composition and solids content on line, and the ability to remove the membrane forming materials (unless separate sol sources are used for general matrix and membrane layer processing)
- Techniweave has made significant progress over the past two years in developing a sol-gel process for processing of the filters and other components. Westinghouse has expertise in the scale-up of sol-gel processes, and their continued close collaboration with Techniweave would benefit the project.
- No discussion of interface coatings for the fiber was presented. For this application, an interface coating may be expected to protect the fibers from degradation during matrix processing.

The following recommendations were drawn from the assessment visit to Techniweave:

1. Continued teaming with Westinghouse is very important, particularly to provide the experience in scale-up and manufacturing of sol-gel ceramics.
2. At some point in the development effort (Phase II or III), the tools and systems necessary to reuse of sol will require development/demonstration.
3. A design of experiments approach to identify critical processing step(s) and the sensitivity of each as it relates to filter performance would benefit the development effort.
4. While mixing larger batches of sol is not a major problem, a lack of feedback on key performance factors and their influence by processing oversimplifies the process and the issues associated with scale-up. A plan to obtain performance feedback for process development should be implemented in follow-on efforts.
5. While the composite is fiber dominated, the uniformity of the membrane layer is critical to functionality. A better understanding of how processing effects this feature of the filter is required.
6. A comparison retained strength data for the composite processed with and without and fiber interface coating would be useful to optimize the filter and preform design. If a greater strength can be achieved with a fiber coating (fugitive), then less fiber may be utilized in the preform.

3.0 BABCOCK & WILCOX

Babcock & Wilcox (B&W) is a leading supplier of coal-fired power systems. During the past three years, they have been a contractor in the DOE Continuous-Fiber Ceramic Composite Program with a focus on developing oxide-fiber reinforced oxide-matrix composites by sol-gel and slurry impregnation processes. The current program on hot-gas filters is a joint effort between the Lynchburg Research Center, Lynchburg facility, and the Utility and Environmental Power Division. ERI is becoming the focus of composites manufacturing for B&W and is currently producing several polymer-matrix composite components for the Navy, and has committed to becoming the manufacturing group for all CMC components, including hot-gas filters. The Utility and Environmental Power Division is providing the market driver and product path for the hot-gas filters.

3.1 Filter Description and Process Overview

The B&W filter is fabricated by filament winding, and consists of both continuous- and chopped-oxide fibers. The chopped fiber, Saffil, acts as a rigid porous matrix which is reinforced by the continuous fiber, Nextel 610. The filament winding process results in a simultaneous deposition of both the continuous and chopped fibers throughout the cross section of the filter element. The basic process consists of fiber coating, chopped slurry preparation, filament winding, heat treating, and final machining. The general process steps, variables, and controls for each process step are shown in Table 3.1. An example of a typical data sheet for a filter is shown in Table 3.2

Table 3.1 B&W Hot Gas Filter Fabrication Process

Operation	Variables	Measured Values	Controls
fiber coating	rate pyrolysis temperature number of passes solution concentration	total fiber length temperature fixed batch weights	spool drive speed furnace controller fixed fixed
chopped fiber slurry preparation	pre-mixing speed time concentration	no time water and fiber weights	mixer control timer switch fixed aspect ratio
filament winding	fiber tension continuous fiber content chopped fiber content	tension fiber spool weight slurry tank weight	tension controller winding speed slurry pump rate none
Rigidization	binder concentration number of saturations binder retained in preform curing reaction time curing temperature	water and binder weights time temperature	fixed at set up specified manual dryer temp controller
heat treating	temperature time atmosphere	temperature time purge gas	furnace temp controller furnace temp controller gas supply

Table 3.2 - Process Run Sheet

WINDING RECORD Date: ____________
Preform ID: ____________
Dimensions: ID: ____________ OD: ____________ Length: ____________
Continuous Fiber: ____________ Fiber Lot No.: ____________
As Rec'd Coating: Winding Coating: ____________
Fiber Architecture (attach computer output): ____________
Chopped Fiber: Saffil Dry Hobart Milling Time: ____________
Fiber Wt.: ____________ Premixing Water Wt.: ____________ Premix Binder: ____________
Premix Binder Wt.: ____________ Premix speed: ____________ Premixing Time: ____________
Slurry Dilution Water Wt.: ____________ Percent: ____________
Mixer: ____________ Speed: ____________ Time: ____________
Mandrel Set-up: Fiber base: ____________ Tension: ____________ Mix speed: ____________ %
Bobbin Wt. (start): ____________ Wt. (finish): ____________
Binder type: ____________ Concentration: ____________ Final Wt.: ____________

Time	**Count**	**Cont. Fiber Wt.**	**Pump**	**Closure**	**Slurry Weight**	**Flange Od**	**Body Od**
rate 1 C/min	level 1	hold 1 min	rate 2 C/min	level 2 C	hold 2 min	atmos.	notes
←			Heat				→
←			Treating				→
←			Parameters				→

3.2 Discussion Process Monitoring and Control

Continuous Fiber Coating:

The immiscible-liquid fiber coating process is used to apply the interface coating to the continuous fiber. The fiber tow is desized, passed through the immiscible layer bath to apply the coating, and then the coating is pyrolyzed. Multiple coatings may be applied. A sizing is applied before rewinding the fiber. The process has been scale-up to prototype level and is largely automated. The potential need to monitor the fiber coating thickness was discussed with B&W. The coating does need to be a minimum thickness to protect the fiber during processing, but a study to determine the overall sensitivity of the filter mechanical properties to variation in coating uniformity is not part of the Phase I effort. Some concern exists over the long-term stability of the coating solution, and the effect on coating quality and uniformity. Several concepts may be amenable to on-line monitoring of coating thickness. Thermocouples and controllers are all calibrated in accordance with the QA system requirements.

Chopped-Fiber Slurry Preparation:

The Saffil fiber slurry is prepared by mixing the desired fiber:solution ratio in a standard mixer with the mix time being controlled. The slurry is then added to the feed tank and diluted to the working concentration. The feed tank is mounted on a digital scale and the dilution process is controlled by the weight fraction. The scale is calibrated as part of QA system requirements. The mixing time has been varied somewhat, and there appears to be a minimum time to achieve the desired slurry properties. Longer mixing times do not seem to change the slurry significantly. Characterization of the Saffil particles may be useful as a baseline measurement and as a standard for the process over time.

Filament Winding:

An En-tec 4-axis filament winder is used to fabricate the closed-end tubes with integral flange preforms. The filament winding process features the simultaneous deposition of continuous and chopped fiber. A peristaltic pump is used to transfer the chopped-fiber slurry. The amount of continuous fiber is monitored by weighing the supply fiber spool. The amount of chopped fiber is calculated from the slurry concentration and the weight change of the slurry tank. The relative amount of continuous and chopped fiber are controlled by the winding speed and the slurry pumping rate. The dimensions of the body and flange are measured after each closure, and the process is stopped when the dimensions are within Westinghouse specifications. As with the other measuring equipment, the scales are all calibrated as part of the existing QA system.

Rigidization:

The rigidization is performed while the preform is still on the winding mandrel by saturating the preform with the binder solution several times. The hole created in the closed-end of the preform during winding by the mandrel support fitting is sealed at this time. The preform/mandrel assembly is dried, and then an initial heat treatment is used to rigidize the preform enough to allow mandrel removal. After removal of the mandrel, additional heat treatments are performed to complete the processing. All furnaces use calibrated thermocouples. The obvious area for improvement is in determining how much of the rigidizing material is in the preform and its distribution. Currently, it is determined to be "saturated" by visual inspection. Better measurement of the amount and distribution of the rigidizer would be an important improvement in process understanding.

Final Machining and Inspection:

The flange end of the filter element is machined to the Westinghouse configuration and dimensions. Standard geometric inspection methods are used for the flange and filter sections. The permeability is determined from the pressure drop associated with a given face velocity.

During subsequent discussion, the B&W staff identified the following attributes as important to the functionality of filter: permeability, thermal fatigue, thermal shock resistance, chemical and thermal stability, and the flange sealing area mechanical properties and geometric tolerance. These factors all influence the reliability of the filter elements. As with other filter programs, it is to early in development to understand the effect of process conditions on these properties. The need for feedback from field and intermediate testing will be important to developing a reliable filter. Access to a suitable filter test facility has limited the understanding of process-performance interaction. Relating process variables to the performance of the filter, through a design of experiments in order to minimize the number of tests, will be critical to understanding the relative sensitivity of each process step. It is also believed that a better definition of mechanical and thermal loads for tubes is needed. A justifiable concern with the filters being over designed or under designed exists, and this cannot be determined until modeling of the loads is performed and long term environmental exposure data is obtained for the filter materials.

3.3 Existing QA/QC systems and documentation

The ERI division currently in production with a number of components for the military. These components require working to several military specifications on quality (Mil-I-45208 and Mil-Q-9858). These specifications require certain levels of inspection, recording process information, tracking materials, control of production documentation, and the use of calibrated inspection and measurement equipment. This covers temperature, pressure, mass flow, and weighing equipment used to produce the filters. Also, B&W uses an approved vendor list for materials and services. To be approved, the vendor must conform to required certain quality system requirements. A facility ISO certification is also in progress. As part of the current filter development effort, procedures are being developed to formalize the filter manufacturing process. The actuals processing information for heat-treatments, firing, and fiber coating operations are recorded (either strip charts or computer files) and associated with the filter run sheets.

3.4 Previous Experience with Scale-up and Manufacturing

B&W does not currently sell ceramics. At one time, B&W produced vacuum formed ceramic insulation and cutting tools. They have also supplied UO_2 fuel pellets to both DOD and commercial nuclear reactors. The fuel pellet process made the full transition from R&D to a commercial product. B&W currently manufactures a variety of advance polymer-matrix composites, including torpedo casing at the ERI facility. They are planning the development and introduction of other CFCC components in addition to the hot-gas filter. These CFCC products, which are being developed in parallel, include low NOx burner components, hot structures, turbine combustor cans, thermal photovoltaic devices, recuperators, combustors, and emitters. B&W is an end-user of the materials/components which may benefit the commercialization of these products.

3.5 Observations and Recommendations

The following observations on the B&W filter program resulted from our assessment visit:

- The quality systems in place at ERI appear to be sufficient for process repeatability.
- The process documentation for filament winding and heat treating operations records the necessary process variables and the monitoring equipment is calibrated.
- The filament winding manufacturing method is readily scaleable, and similar processes have been used to produce commercial products.
- Additional work on understanding the effect of process variables on filter performance is needed, especially for identifying the critical process steps and there tolerances.
- They do not manufacture ceramic products currently, but they have brought other products (metals and polymer-matrix composites) from R&D to production.
- Strong understanding of performance requirements because of company expertise with coal-fired power systems.

The following recommendations are made based upon our assessment visit:

1. Additional environmental stability and field performance data is necessary to drive process optimization and process tolerance definition.
2. A process sensitivity study should be included in future efforts.
3. Improved process monitoring and control of the rigidization step is required.
4. Improved monitoring of the fiber-interface coating process is necessary, and a determination of the sensitivity of filter mechanical properties to this step.

4.0 PALL CORPORATION

Pall Corporation is a supplier of porous metal filtration elements used in the chemical, pharmaceutical, medical, aerospace, paper, food, and beverage industries. They have been manufacturing porous sintered metal filters since the company was founded in 1946. Current products involve porous metal media consisting of mainly stainless steels and nickel-based superalloys. Using this expertise, Pall has been working on the development of porous media hot-gas filters based on Fe-Al intermetallics for approximately 4 years. The Fe-Al intermetallics offer excellent oxidation and sulfidation resistance with greater ductility than available from ceramic-based filters. The development environment uses production equipment, and is performed in a "job shop" setting. Pall Trinity Micro (of which the Micro Metallic Division is a part) is ISO 9001 certified.

4.1 Filter Description and Process Overview

The Fe-Al intermetallic porous metal filter under development by Pall Aerospace is a seamless tube construction. The general processing steps and their associated inspection points are summarized in Table 1. There are four major process steps in the manufacture of the porous metal filters consisting of: 1) Preform Production, 2) Isostatic Compression, 3) Sintering, and 4) Welding and Fabrication. In summary, 24 inch sections of seamless tube performs are produced by centrifugally spinning a prepared slurry and then dried. The green bodies are then isostatically pressed and then sintered. These sections are then cut to size circumferentially welded and end fittings attached to form the filter.

Processing Step	Inspected Features
Perform Production	
— Receive Powders	— Size distribution, composition, sintering behavior
— Mix Slurry	— pH, ratio of weights
— Spin Tubes	— RPM profile
— Dry	— time, temperature
Isostatic Press	pressure, green density
Sinter	temperature, pressure, time, density
Welding and Fabrication	welding parameters
Final Inspection	porosity distribution, strength, pressure drop

4.2 Discussion of Process Monitoring and Control

During our discussions, the Pall staff identified the key performance factors for the hot-gas filters as strength in the operating environment, blow-back stability, pressure drop in forward flow, and thermocyclic fatigue resistance. They believe the strength of the material is strongly influenced by the isostatic compression step. While it is key to this property, they believe that their experiments to date show that as long as a minimum force is applied it is not very sensitive to process fluctuations. The blow back and pressure drop performance of the filter is related to a stable porosity and filter cake interaction with the surface of the filter. These factors are strongly influenced by sintering. Testing of the ash-surface interaction is scheduled for later stages of product development. Of particular significance will be the ash release tests scheduled for the pilot production phase of the current program. With the high thermal conductivity of Fe-Al alloys, thermocyclic fatigue is not seen as a major problem. Of the two key steps (isostatic compression and sintering), sintering is seen as the process which is most sensitive to fluctuations. Pall recognizes that development of the sintering parameters is necessary to understand the process-performance relationship for the filters.

4.2.1 Preform Production

Several Fe-Al powder compositions are being evaluated by Pall Corporation in the filter development program. The powders are synthesized by an outside vendor using water atomization. The Fe-Al powders come with certifications on composition, oxygen content, and particle size distribution. Pall performs several additional tests on the powder before releasing it for use in the project. The additional tests include determining the sintered strength of the material and void volume after sintering. Powders from different lots are cross blended to minimize lot to lot variation. The powder characteristics that have been found to be critical in processing are oxygen content and the particle size distribution. They have found that a broad cut of powder is acceptable with respect to filter performance.

The preform is produced by spinning a slurry inside a ceramic tube. The centrifugal force produced by spinning forms a uniform deposit of the Fe-Al powder on the interior of the tube. The operator prepares the appropriate binder and records the viscosity and pH (see Appendix C). For each preform, the powder is weighed and added to a fixed amount of binder. The scale used for weighing the slurry materials is calibrated. Traceability is maintained for all materials on a per lot basis. The operator mixes the slurry by hand and then pours it into a ceramic tube that has been taped closed on one end. The operator them similarly closes the other end and distributes the slurry within the tube which is then placed in the spinning apparatus. The spinning apparatus is computer controlled and a two stage spinning operation is used. The tubes are then air dried for a specified minimum time and then kiln dried. Production parameter are maintained on a Seamless Cylinder Production Traceability Chart and include the operator name, binder bucket number, viscosity, pH, and type, the job number, part number and powder lot number. For each cylinder the tube ID, cylinder weight after breakdown and any spinning notes are also recorded. Operator procedures are standardized and each job is given a work order detailing the process and conditions for each job. These procedures are under development for the Fe-Al product. The spinning parameters used to make the stainless steel filter product have been adapted to produce an acceptable filter with the Fe-Al system. However, the parameters have not been optimized, and Pall feels that type of effort is outside the scope of the current project.

4.2.2 Isostatic Compression

Isostatic compression is performed by at an outside vendor, who provides certification of the process cycle for each batch of filters. Pall prepares each tube using standard wet bag methods. Both inner and outer rubber bladders are used which minimizes leaks. Pall suggests that this step is essential to the final sintering process and, ultimately, the performance of the filter. They propose that the effect this process has on the microstructure of the powder strongly influences the strength and performance of the filters. Three isostatic pressures were evaluated for filter processing, with the results of sintering and handleability tests driving the selection of the pressure used for further development. No other process optimization has been accomplished. Tubes are received from the vendor and the rubber bladders removed. The ends of each filter are modified using a simple procedure which improves dimensional stability of the tube ends during sintering.

4.2.3 Sintering

Sintering is done in a batch type vacuum furnace, and all of the Fe-Al filters are processed in the same furnace. Charts are kept for all runs which record pressure, temperature, and time. Periodic calibration of the furnace controls is performed. The tubes are arranged vertically on a pallet with an outside row of bare ceramic tubes and then insulated. For the most recent sintering run a thermocouple was placed in the center of the assembly. It was used to follow temperature changes overtime in the furnace chamber as well as inside the charge. Initially the binder remaining in the powder is pyrolyzed and then the tubes are slowly brought up to sintering temperature. The sintering conditions are currently being optimized. Time and temperature are recorded for this process. The sintering temperature is deemed by Pall as critical to the performance of the filter. However, no measurements of the actual temperature variation within a furnace load has been made. A study to measure the uniformity of the process conditions within the assembled furnace load would be advantageous. For their stainless steel product, Pall has found little variation in filter performance with position in the furnace. Pall is planning a systematic study of the sintering cycle, with performance measured by filter strength, strain-to-failure of the Fe-Al, shrinkage, and filtration performance. The strength and strain-to-failure of the filters is evaluated using an "in house" tensile test method, which Pall uses to determine the effect of sintering time on the mechanical properties of the filters. Due to the shrinkage of the Fe-Al powder preform during sintering the porous seamless tubes are easily removed from the ceramic support tubes. Again, standardized procedures are used for this process and provided for each job number. The porous tubes are then tested using a proprietary bubble test apparatus. Results of this test are recorded and failures are set aside for either scrap or rework. All documentation and procedures are ISO 9000 certified.

4.2.4 Welding and Fabrication

The porous tubes are then cut to length, assembled and welded to fittings to produce the desired filter geometry. They are currently in the process of developing procedures for the welding of the intermetallics to the solid stainless steel fitting hardware and have a number of alternatives under consideration. The process sheets will include surface preparation, welding parameters, preheating requirements/methods, post-weld heating, and all other relevant information. They have considerable experience with welding their stainless products. The welds are visually inspected, and some destructive testing is being done during process development. Cracks in the Fe-Al to stainless steel joints can occur hours after processing.

Since weld cracks are larger than the filter pore diameter, the bubble testing of the final filter assembly tests both the filter element and the welds.

4.3 Existing QA/QC Systems and Documentation

Pall has a quality control system that is ISO 9001 certified. Documentation for the key production parameters of each process is available for the processes for which they are known. During process development, parameters are tracked on production-type documents, and modified versions of standard process instructions are used by the production floor. Welding and final assembly instructions are still under development and documentation is not yet available. Work procedures have not yet been finalized, but, given examples of currently manufactured products, when the documents are ready they should be satisfactory. Pall is currently modifying a hot- gas test apparatus that allows small filter elements to be exposed to the combustion gas environment under controlled conditions. The capability to introduce fly ash in to this simulator, however, is not available. On-site capabilities for testing and analysis are extensive including analytical services, microscopy, and performance testing. The facilities for characterizing all aspects of the filter (materials, porosity, pressure drop, environmental stability, and mechanical properties) are extensive and are a strong asset to Pall's development efforts.

4.4 Previous Experience with Scale-up and Manufacturing

Pall Aerospace currently makes approximately 18,000 seamless tubes per year of stainless steel and nickel-based alloy porous metals. The differing metallurgy of Fe-Al alloys will require Pall to modify processes and procedures to accommodate this product. However, the QC/QA systems used for other products should be suitable. The manufacturing process used by Pall is batch-oriented and current prototypes are produced on production line equipment. This represents a minimal risk for scale-up development hurdles. Large volume production can be initiated by increasing the number of batches scheduled for the existing equipment. Pall's internal estimates have determined the a production level need to outfit up to 52 Tampa Electric plants can be maintained on the current equipment without any significant capital outlays. It is unknown if this figure resembles a plausible estimate of market demand. If additional equipment is needed to expand production capacity, risk increases and it is dependent on Pall Aerospace's ability to plan, finance, and execute and appropriate capital expansion plan. Outside vendor capabilities to supply the power metal and the isostatic pressing operation for large scale production is unknown but not unrealistic.

4.5 Observations and Recommendations

The following observations can be made based upon our site visit:

- Pall Aerospace is currently producing Fe-Al porous metal seamless tubes with acceptable quality using production scale equipment.
- Fabrication of full scale filter assemblies using these tubes has not yet been demonstrated.

- They possess a good understanding of the process variables which most strongly affect the performance of the filter, however, the underlying analysis of these relationships are less clear or were not communicated during the assessment.
- Sintering is recognized as the most critical and sensitive processing step.
- Quality control, documentation, and procedures are in place and representative of their ISO 9000 certification.
- Development hurdles remain, most notably in the fabrication and welding of full scale filter prototypes, but once these are accomplished, scale-up to full production represents minimal risk.
- Testing at Pall has demonstrated the ability of these filter to withstand the temperature and corrosion of the service environment.
- Performance in actual combustion gas streams is still unknown

The following recommendations are made based upon our site visit:

1. The composition of the slurry for spinning the green bodies should be evaluated for sensitivity to composition.
2. An effort to understand the effect of sintering cycle changes on filter structure and properties is needed.
3. Additional performance testing of the sub-scale filters is needed, particularly on the ash release behavior and ash-filter stability in the hot-gas environment.
4. Access to an accelerated aging test facility and/or exposure of filters to the application environment is needed to understand the sensitivity of key fabrication steps on filter performance.

5.0 DUPONT LANXIDE COMPOSITES

DuPont Lanxide Composites, Inc. (DLC) is a joint venture between the DuPont Company and Lanxide Corporation dedicated to the development and manufacture of advanced materials, including ceramics and ceramic composites. For their hot-gas filter development project, they have selected a unique material system, PRD-66, which offers a combination of thermochemical stability, thermal shock resistance, and potentially low manufacturing costs. PRD-66 was developed nearly 30 years ago, and has been demonstrated and used in a variety of applications, including catalyst supports and filter media. This substantial base of processing experience is being applied to the development of hot-gas filters. The process development work being done by DLC largely incorporates the equipment that would be expected to be used in production, and in many cases the same equipment. DLC is currently going through ISO 9002 certification for other ceramic-matrix composite products, and, as necessary, the PRD-66 filter process will be added to this system.

5.1 Filter Description and Process Overview

PRD-66 is a composite material in which each filament in the final product has a layered microstructure consisting of an exterior alumina layer, an intermediate mullite ($3Al_2O_3{\bullet}2SiO_2$) region, and an interior of cordierite ($2MgO{\bullet}2Al_2O_3{\bullet}5SiO_2$). This layered structure provides for the exceptional thermal shock resistance, thermochemical stability, and thermophysical stability of the material. The basic processing steps for the PRD-66 hot-gas filters, along with the inspection points for each step, are shown in Table 5.1. In summary, larger batches of slurry are prepared, and the yarn is impregnated with the slurry as it is filament wound. The flange and filter tip sections are fabricated and bonded into place, and the membrane layer is filament wound onto the filter body. The filter is then dried, fired, and the ends are over-coated with a slurry to insure they do not interfere with the performance of the active filter area. If necessary, final machining of the filter is done at this time. A final firing step is then performed.

Table 5.1 - DLC Hot-Gas Filter Process Summary

Processing Step	Inspected Features
Slurry Preparation	weights, pH, viscosity
Filament Winding	winding speed, weight change, humidity, uniformity, geometric features
Flange and Tip Reinforcement	winding speed, weight change, humidity, area "blinded" with slurry
Surface Membrane	winding speed, weight change, humidity
Drying	drying agents, time
Firing	temperature, time
End Sealing	slurry preparation
Final Machining	geometric features
Final Firing	time, temperature, pyrometric cones
Final Inspection	geometric features

5.2 Discussion of Process Monitoring and Control

The key properties for filter performance were identified by DLC as permeability, particle collection, flange reinforcement, and strength. A summary of the test method used to evaluate these properties and the critical processing step(s) is presented in Table 5.2. The identification of these important processing steps has come not only from the current filter program, but also with almost 30 years of company experience with processing PRD-66. The optimization of the process for candle filters is planned to take place begin in the next few months. To date, only limited process variation has been done, except to address specific issues that may have occurred. The optimization effort is to be done as part of Task 4 of the current program.

Table 5.2 - Property - Processing Relationship

Property	Measured Feature	Governing Step(s)
permeability	pressure drop	membrane layer drying firing
particle collection	25 cycle filtration test	membrane layer drying firing
flange reinforcement	visual saturation with slurry	flange reinforcement
strength	o-ring compression	filament winding firing winding pattern

5.2.1 Slurry Preparation

For each batch of slurry, the components are measured out by weight, mixed, and then the pH is adjusted to stabilize the slurry. The weights for each batch, mix date, and its use history are recorded on a run sheet. The slurry components are commercial products. The viscosity of the slurry is measured after initial mixing using the rotating disk method, and then it is checked and adjusted before each winding trial. The scales are calibrated by an accredited vendor. The pH sensors are tested using buffer solutions to insure accuracy for stabilizing the slurry.

5.2.2 Filament Winding

The main body of the filter is filament wound with the slurry being impregnated into the tow with an in-line bath. The amount of slurry picked up by the tow is controlled using a stripper die. The amount of fiber wound onto the filter is measured by the change in weight of the fiber spool. The amount of slurry picked up by the filter is also calculated by knowing the total weight (after intermediate firing) of the filter body and the amount of fiber used. All of the scales used to measure the precursor and filter weights are calibrated by an outside vendor. Humidity control in the winding area is important to maintaining geometric tolerances. At the time of the assessment visit, the humidity control for the winding area was crude, but appeared to be sufficient for prototype development. DLC recognizes the limitations of the current facility, and when the filters move into/toward production a facility would be built for this process.

5.2.3 Flange and Tip Reinforcement

The flange is wound separately from the main filter body using similar techniques to those described earlier. After winding, it is stored in a designated area until it is incorporated into a filter body. During the winding and subsequent drying of the filter body, a strong bond develops at the interface with the flange. The flange and tip area are strengthened and "blinded" (i.e. sealed so they are not an active filtering area) by applying more slurry to these areas. Because the change in diameter that occurs in these regions degrades filter performance, and due to the higher mechanical loads on the flange, blinding is necessary to make a durable filter that meets the emission requirements. For both areas, a known amount of slurry is added that has been shown to seal the areas and increase the strength of the composite. However, if the blinding layer is not present, DLC stated that the surface membrane may keep the filter within the emissions requirements. This is because the body of the filter is a bulk filter whose performance is not dependent upon the membrane layer. The membrane layer does enhance the release of the ash from the filter during blow-back.

5.2.4 Surface Membrane

Limited discussion of the membrane layer was possible during the visit, except to note that the current method will likely be changed in the foreseeable future. Three alternate technologies have been evaluated and passed DLC's internal performance testing. The selection of one technology will be driven by achieving the pressure differential goals for the filter. There is some technical concern with being able to achieve the necessary pressure drop.

5.2.5 Drying

After winding, the filters are dried at ambient conditions, typically overnight. No monitoring of drying process is done, but insufficient drying may lead to cracking of the membrane layer during firing.

5.2.6 Firing

During the intermediate firing step, filters are heated to a temperature that stabilizes the structure without significantly altering its nature (which occurs later in "final firing"). In this intermediate state, Steps 5.2.7 and 5.2.8 can be performed without damaging the unit. A thermocouple control loop is used to keep the candles at the recommended temperature for a specified time. After intermediate firing, candles are weighed to determine how much solid material was added to the yarn during the filament winding (5.2.2). This "percent pickup" is tracked to evaluate process stability. Candles can be rejected at this point for "low pickup" which could reduce the strength of the product.

5.2.7 End Sealing

The mandrels used in filament winding the filters have a support rod at the tip of the closed end. This support pin leaves a hole in the end of the filter which must be plugged for the filter to operate properly. A thick slurry of the PRD-66 precursor materials is prepared, mixing it by weight using calibrated scales, and the hole is filled by hand. It is allowed to dry before the next processing step.

5.2.8 Final Machining

The high porosity level in the PRD-66 makes machining the filters very simple, since it can be performed with standard methods, and even with hacksaws if appropriate. Since the process is near-net shape, the filters are cut to length and any requisite machining of the flange area is performed to comply with the specifications. After machining the filter is geometrically inspected using standard methods.

5.2.9 Final Firing

The filters are run through a multi-step firing cycle in a commercial-scale furnace. The system does not currently use calibrated thermocouples. The system is controlled from the output of the controllers. To monitor the temperature history of the filters in every run, pyrometric cones are used. The microstructure, and hence the mechanical properties, of the filters is highly dependent upon the firing process. Also, the performance of the membrane layer is strongly effected by the firing cycle. While pyrometric cones are very useful for post-process verification of the maximum temperature of the process, reliance on them for production seems less than optimum since no active control is possible. If the thermocouples are deemed unreliable, or at least insufficient, other temperature monitoring methods should start being used during the process development program.

5.2.10 Inspection

After the filter has completed processing, it is dimensionally inspected for compliance with the filter specifications. This includes geometric and pressure drop inspections. Standard techniques are used for the dimensional inspection and calibrated tools are used. For pressure drop determination, a in-house system is used to test either the sub-scale or full-scale filters. It consists of a air flow regulator and a differential pressure gauge. The appropriate air flow is supplied to the inside of the filter to produce the required face velocity, and the pressure drop produced under these conditions is measured. Standards are measured prior to making measurements on production units. All processing and inspection records for the filter are collected and filed.

5.3 Existing QA/QC Systems and Documentation

DLC is working towards ISO 9001 certification for their facility. The model they are using includes modules for Administration & Control, Product Realization, and Support Activities. This model has a total of 20 discrete areas that cover all aspects of manufacturing, including management responsibility, document control, purchasing, inspection, training, and statistical methods. DLC has selected this model for use in limited production and production of several CMC products, including rocket thrust nozzles, tip shrouds, and engine seals. DLC has built a quality system that readily allows products to be brought into the system with only moderate effort. The Quality Assurance manager has extensive experience in developing QA systems. Much of the basic quality system being implemented at DLC will be directly applicable to filter production. After reviewing the status of the PRD-66 filter effort, they have estimated that 9 of the 20 areas would need additional work to make them fully compliant, and that this effort would likely take three to four man-months of effort. The table of contents from the DLC Quality Manual and several relevant operating procedures is provided in the Appendix.

5.4 Previous Experience with Scale-up and Manufacturing

DLC has brought several CMC products to the limited production stage, including rocket thrust nozzles, tip shrouds, and engine seals. However, these composites are produced using chemical vapor infiltration. PRD-66 is produced commercially (honeycomb structures), but it is not made within a quality system. The experience of the key technical and management staff at DLC with bringing other products into production provides a strong background to support the transition of the PRD-66 filters.

5.5 Observations and Recommendations

The following observations can be made based upon our site visit:

- DuPont Lanxide Composites is currently producing prototype filters with the anticipated strength and filtering performance.
- Full-scale prototypes (approximately 6 feet long) are made for testing and characterization.
- They have a nearly 30 year history of processing PRD-66 into a variety of components, including filters, which provides a solid base for this project.
- They recognize that control of the winding environment is critical to achieving a repeatable product. However, the current facility is lacking in control of at least one key variable, although it is monitored.
- A study of the parameters effecting drying of the filters may be useful, since this step is strongly linked to ambient conditions which vary with the seasons.
- A shift to a reliance on in-process temperature/process control for the final firing step, instead of inspecting pyrometric cones after firing is complete, is suggested as the process moves towards higher volume production.
- Quality control, documentation, and procedures are in place for other DuPont Lanxide Composites products. Approximately 70 % of the documentation/procedures already in place are applicable to the filters, with the balance being process/application specific procedures.
- Several proprietary developmental hurdles need to be addressed, though they do not appear to be major activities.
- An innovative and proprietary solution has been developed to address the cause of failure found in one of their full-scale filter sets that has been tested.
- At least one successful demonstration of full-scale filters has been achieved.

- While full-scale components are produced, improvements in the processing equipment can certainly be made. Also, despite their long history of processing PRD-66, only one product is sold from it, and it does not require and quality program. The methods and equipment used to produce the filters are common in the manufacturing environment. However, it will still requirement significant development to scale-up the equipment and processes to the production level anticipated for these filters. The strong experience of DuPont in scaling up other processes should be a significant benefit to this effort.

The following recommendations are made based upon our site visit:

1. A processing area with improved environmental control should be considered for these filters, with a study to determine the sensitivity of the processing and drying steps to environmental changes being done within the current program.
2. A correlation between the internal test used by DuPont Lanxide Composites and the filter application environment should be developed to better guide process and component development.
3. Access to an accelerated aging test facility and/or exposure of filters to the application environment is needed to understand the sensitivity of key fabrication steps on filter performance.

CERAMEM SEPARATIONS

CeraMem Separations Inc. (CeraMem) manufactures ceramic membrane filters for both liquid and gas process streams. CeraMem is a joint venture between CeraMem Corporation, Exxon Corporation/Enjay Inc., and Corning Inc. CeraMem Corp. was founded in 1986 to commercialize ceramic membrane technology and to continue as a source of new membrane technology for CeraMem. Corning provides CeraMem with a secure supply of the honeycomb ceramic monoliths that are the basis of the filters. Exxon provides access to the petrochemical market for these ceramic filters. The filters being developed by CeraMem modifies the commercially available honeycomb structure available from Corning. The modification of the honeycomb includes sealing selected channels on both ends (to produce a dead-end flow configuration) and application of a membrane layer onto the surfaces of the substrate to tailor the filter efficiency and enhance cleaning. Purchasing the honeycombs from Corning, greatly simplifies the production of the filters for CeraMem. CeraMem is developing enhanced manufacturing methods, including additional process automation and implementation of quality systems, and working with their materials suppliers to improve product quality and performance. A quality system is being developed that, if implemented as planned, will likely provide a repeatable manufacturing process.

6.1 Filter Description and Process Overview

CeraMem filters are a modified form a the commercially available cordierite honeycomb structures available from Corning. Purchasing the honeycomb core structure instead of producing it internally greatly simplifies the manufacturing process. The modifications of the honeycomb that are performed by CeraMem include, application of the engineered membrane layer for efficient gas clean-up and back-pulse cleaning, and sealing alternating passages in the structure to produce a dead-end filter. The basic processing steps for the CeraMem hot-gas filters are shown in Table 6.1. In summary, the honeycomb substrates are inspected for defects using both visual and graphite powder flow through tests. They are then coated with the membrane layer by a slip casting method, dried, and fired. The ends of the honeycomb core are then sealed to produce the dead-end flow configuration. The filter is then tested for pressure drop versus air flow and for defects in the passageways. A final firing step is used to burn off any trapped graphite powder and to sinter the seals on the channels. The filters are then wrapped in an insulating blanket and placed inside metallic can. Final inspection consists of a powder leakage test for gross defects and collecting the process documentation.

Table 6.1 - Summary of CeraMem Filter Process

Process Step	Inspected Features
Receiving Inspection	dimensions, bow, gross defects, interchannel defects, part/chemical certifications
Membrane application	composition weight fraction), specific gravity, solids content, weight gain, pH, number of uses
Firing	time, temperature, ramp rates
Cement Passages	visual inspection (light transmission), drying time
Testing	pressure drop vs. face velocity, powder leakage
Final burnout	time, temperature, ramp rate
Final inspection	dimensions, gross interpassage defects, certification package
Canning	force, thickness of padding

6.2 Discussion of Process Monitoring and Control

The key processing steps for filter performance were identified by CeraMem as the application and firing of the membrane layer(s). These result of these steps are not immediately obvious, as a machining operation would be, because they effect the microstructure of the membrane layer. Variations in these steps effect the ability of the ash to release on back-pulse, particulate removal, and durability of the filter. These steps are controlled by monitoring the weight pickup (wet and dried) from the membrane application, a number of slip characteristics, and the temperature profile during firing. The normal variations that occur during process development are being tracked and initial efforts to correlate these results to the filter performance are being made. However, no systematic sensitivity study has been made.

6.2.1 - Receiving Inspection

All components (housings, cores, chemicals) are inspected upon receipt. As the materials arrive, they are placed in a segregated storage area until they pass inspection; rejected materials are placed in a separate storage area. The metal housings are produced by commercial vendors and arrive with a certification of compliance to the blueprint. The chemicals are all commercially available and also arrive with certifications. To date, no additional inspection is done on either the metallic components or the chemicals. The ceramic cores undergo both a visual and graphite powder inspection. Visually, the cores are examined for gross defects (chips, cracks in the faces, bowing, diameter). The appropriate geometric inspection tools are used, although they are not calibrated. It is hoped that in FY97 a calibration attainment/maintenance effort will be in place. The graphite powder inspection is used to check for major internal flaws. In this test, clear tape is applied to one end of the core, and a rubber mask that covers every other channel is applied to the other end. Graphite powder is sifted over the masked end, tape is applied over the masked end, and the core is shaken. The pattern produced by the graphite dust on the clear tape is visually examined. If larger cracks or voids exist within the core, the dust pattern is not a "checkerboard". This method is simple and quick screening tool, and, although it does have a finite size detectable flaw, it does detect the defects that can not be sealed with the membrane layer processing. Feedback of the results of the inspection are provided to Corning. Approximately one year ago, less than 50% of the cores met the specification. Since that time CeraMem has worked with Corning to address the problem, including transferring the test method to Corning, and a marked improvement in yield (greater than 75 percent) has been seen. As a result, the specification for the cores has been tightened up, and CeraMem believes that the quality of the cores will continue to improve as Corning continues their development efforts. The sharp increase in yield is attributed to both the improved process experience and quality at Corning and to Corning's parallel inspection which prevents the majority of the deficient cores from being shipped. Cores that have a few cross-channel defects can be acceptable since these channels can be sealed in a later operation. The number of channels that can be sealed is limited by the need for the filter to meet its minimum performance requirements. After passing inspection, a ceramic paint is used to apply a permanent serial number for tracking the core through processing.

6.2.2 - Membrane Application

The membrane layer for the filter is applied using slip technology. The slip is a low viscosity, mixture that is prepared by weighing out the precursors and blending them using standard processing methods. The controlling the composition of the slip by using weights for its constituents is a routine approach that provides good repeatability. The scales used to weigh out the precursors are not calibrated, but no processing problems can be attributed to this step. Utilization sheets are kept for each batch of slip prepared, which track the number of uses, core serial numbers, results of processing (weight gains), and other processing information. Before each use, the slip is checked for specific gravity and solids content, and re-balanced as necessary by adding more liquid (typically) and mixing. The slip is not infinitely reusable, and the weight gain of the cores is tracked against an upper and lower limit. The limits were set by experience, but no systematic effort has been done to determine filter performance versus these limits. To date, these limits have produced reliable filters. The monitoring tools for weight gain, solids content, etc. are not calibrated. Using a simple internal standard (a purchased standard or machined block) with a constant weight may be useful in preventing drift of the weight and solids content measurements. Other internal standards could be readily set aside for some other process parameters. Once the cores are coated, they are allowed to dry at ambient conditions before going to the next processing step. To date, the filters are allowed to dry for at least a minimum time and little is done to monitor temperature, relative humidity, etc. which may influence the uniformity and completeness of the drying. CeraMem recognizes that as production volume is increased, this step will become more critical as they try to reduce cycle time. No systematic effort has been made yet to evaluate the sensitivity of filter performance to the drying parameters.

6.2.3 - Firing

After drying, the filter cores are loaded into a kiln and fired to form the membrane layer. A chart recorder is used to monitor the heating rate and time within certain temperature regimes during the firing cycle. The kiln is controlled via a thermocouple, but pyrometric cones are used to validate the system temperature and to track the temperature variation within the furnace. When the cycle is complete, the critical cycle time information is taken from the chart recorder and entered onto the core processing log sheet. This step is critical to forming a reliable filter and the consequences of process variations (over temperature, variation in time) is better understood. However, as with several other steps, no sensitivity study has been done to determine an acceptable processing envelope. It should also be noted that CeraMem has not noted and recent problems related to this step, and the conditions in use now result in an acceptable core yield.

6.2.4 - Cement Passages

To create the dead-end filter configuration from the cores, alternating passages are sealed on one face using a mask. After sealing the first end, the core is flipped and the mask off-set by one passageway to form blind passages. Before sealing the second, a visual inspection is done by shining a light up the core with the mask in place. If light can be seen through the core, then the mask is not in the correct position or the passages on the other end were not sealed correctly. The ceramic cement used for sealing the ends is injected to a fixed distance using a simple press. The cement is allowed to air dry briefly, smoothed, and then planed in a convection oven to dry. The cement used is a mixture of commercial materials, and the use of a press, with built in stops, repeatable injects the cement into the core. The seals are important, but not critical since the cement is injected a significant distance into the passageways. Thus, even if the cement cracks on firing, gas cross-over does not occur. The cement is fired after final testing of the filter. Except for the light test and visual inspection of the seals, no testing or monitoring of this process step is done.

6.2.5 - Testing

Acceptance testing of the filters consists of two tests; a pressure drop test and a power leakage test. A test stand has been constructed which provides selected volumetric air flows over the operating range of the filters. The pressure drop across the filter as a function of face velocity is measured using differential pressure gauges. The graphite flow through test is performed in the same test fixture. For this test, a fine (0.5 µm median size) is added to the air entering the filter. A white cloth is placed on the outlet side of the filter. The amount of "haze" on the cloth is visually compared to a clean cloth. No correlation between the amount of "haze" and filter performance is available. CeraMem recognizes that this test is best suited to identify larger defects in the filter. If discrete defects are detected, the appropriate channels are sealed with cement, and the filter is tested again. This cycle continues until the filter passes the test. Up to 5 percent of the total surface area can be sealed before the filter falls below its performance specification. As with all of the other measurement devices, the equipment used in these tests is not calibrated. This may not have presented a problem to date, but drift of measurements over time is certainly possible without calibrated tools. This is recognized by CeraMem and they hope to begin introducing calibrated tools sometime in 1997.

6.2.6 - Final Burnout

The filters are fired to both set the cement and remove any material from the acceptance test. The firing is done using the same equipment and monitoring techniques as described in Section 6.2.4.

6.2.7 - Canning

For the filter body to be mounted in filter system, it is placed into a metallic can. The canning process is performed by an outside vendor. To date, this operation has not caused any defects. If it is not done correctly, the potential exists for either cracking the filter body or creating pathways for the gas stream to by-pass the filter. An effort needs to be undertaken to develop a tolerance range for this operation, and develop a specification for the vendor to follow.

6.2.8 - Final Inspection

Final inspection of the filters is the same as the receiving inspection for the cores. It consists of a visual inspection of the filter for obvious defects, the powder leakage test for interpassage defects, and a geometric inspection. The processing documents for that filter are collected and filed in a central storage area. As with the receiving inspection, the gauges used for dimensional inspection are not calibrated.

6.3 Existing QA/QC Systems and Documentation

The areas of process documentation and quality assurance/quality control (QA/QC) have been recognized by CeraMem as high priorities for improvement. The addition of senior management staff with substantial manufacturing and quality experience was a significant step in their plan to address these areas. The Director of Manufacturing, who has been with the company for approximately one-and-a-half years, brings extensive ceramics manufacturing and QA/QC procedure development experience to CeraMem. The Director of Manufacturing is an ASQC Certified Quality Engineer and Manager, and has led efforts at other companies to implement manufacturing and QA/QC documentation and procedures. He has also been involved in the scale-up and high-volume manufacturing of ceramic components. An effort has also been started to train the QC staff, with their quality engineer recently taking the CQE exam. They are moving towards ISO certification, but since they are not being pressured by customers and they have a substantial amount of documentation to perform, it may be more than two years before they apply for certification. Written procedures for all manufacturing and QC operations have been developed and are undergoing internal review. Document control procedures are also being developed. The documents for the liquid filters that CeraMem manufacturers are further along, and serve as a basis for the gas filters. CeraMem hopes to have the process documentation completed for liquid filters in 1997. While these procedures are being developed, the current system does allow traceability of any part manufactured back to its processing log sheets. CeraMem has a substantial amount of work to perform to complete the development and implementation of both the QA/QC and process documentation systems. While progress is being made, it appears that the basic systems may be in place in 1997 for the liquid filters and the gas filters will be added sometime in 1998. The staff is in place that can lead the development and implementation of these systems, but it will take time.

6.4 Previous Experience with Scale-up and Manufacturing

The recent additions that CeraMem has made to their management team brings substantial experience in scaling up and manufacturing ceramic products. They have been directly involved in process and equipment scale-up, development and implementation of quality systems, and transitioning ceramic products from prototype to full production. These additions appear to be strong assets for CeraMem, and will be crucial in transitioning the filters to higher volume production. In our discussions of the issues involved in scaling-up production at CeraMem, they identified the following items:

- Sizes of current filters will be the standard production component, so no scale-up in size is necessary.
- The honeycomb cores are already a high volume manufacturing item, however, the cores used by CeraMem are longer than the standard Corning product. Corning is implementing a quality and technical program to improve the yield of the extrusion process.
- The liquid coating facilities available at CeraMem are the limiting factor for increasing production. Other key process steps, such as core fabrication, filter containers, firing, and canning, are done by outside vendors.
- Expanding the slip handling equipment should be direct, since commercial equipment is currently used and equivalent or larger systems can be purchased off-the-shelf.

As CeraMem moves into production, they will focus on expanding the slip handling equipment, introducing a statistical inspection system instead of the current 100% inspection, further automation of the cement application process, and expand the slip casting capability to allow processing of more than one tube per batch. These are reasonable and realistic assessments of the hurdles that face their transition to full-production. Certainly, significant effort will be required to understand the sensitivity of the process to fluctuations and to optimize the product, but CeraMem appears to have a strong grasp of the realities of process scale-up and the tools to address them.

6.5 Observations and Recommendations

The following observations can be made based upon our site visit:

- The use of commercial substrates produced by Corning greatly reduces the complexity and risk associated with scaling up the filter manufacturing process.
- The strong experience of the management team related to the transition of ceramic manufacturing processes from development to large scale production is a strong asset to this program.
- The initial portions of a quality program are in place, though a substantial amount of work remains to be done on both the quality and manufacturing procedures and documentation.

- The processes used to produce the filters at CeraMem are common in the ceramics industry and larger scale equipment and process control methods are commercially available.
- Several areas of processing may require sensitivity studies, including the slip coating process, drying of the filters after membrane processing, and firing.
- The current size of the filters being produced are the full-scale components.
- The filter test methods used at CeraMem are appropriate for initial quality of the filters, but they provide no indication of the potential performance of the filters in service.
- Exposure test data is required to determine the performance of the filters and to provide feedback for process optimization.

The following recommendations can be made based upon our site visit:

1. A sensitivity study to gauge the effect of variations in membrane application and firing on the performance of the filters is needed.
2. While good experiential data is available for CeraMem's liquid filters, very little data is available on the performance of the hot-gas filters. With the recognized issues of filter regeneration, and pressure profile versus membrane processing, this type of data is very important to developing a viable product.
3. A capability to perform some form of testing representative of the service environment of the filters is needed to guide process development.
4. Access to an accelerated aging test facility and/or exposure of filters to the application environment is needed to understand the sensitivity of key fabrication steps on filter performance

7.0 SUMMARY AND RECOMMENDATIONS

The purpose of this project was to provide a brief overview of the manufacturing processes from the perspective of process repeatability and scale-up of the manufacturing processes used by 5 companies developing advanced filters. Given the brief nature of the on-site reviews, only an overview of the processes and systems could be obtained. Each of the 5 companies had developed some level of manufacturing and quality assurance documentation, with most of the companies leveraging the procedures from other products they manufacture or from the previous experience of their management. It was found that all of the filter manufacturers had a solid understanding of the product development path. However, only limited performance test data is available to aide their filter development and design. This lack of test data highlights a gap in the development path between materials/process development and demonstration of advanced fossil power systems. The materials/process development efforts have very limited application environment testing capability short of inserting filters in a demonstration program test facility. While this has led to success, it has also led to significant failures because the filters could not be realistically tested. In all cases, these filters are largely developmental, and significant additional work is necessary to understand the process-performance relationships and to project manufacturing costs.

The following recommendations would benefit all of the filter manufacturers:

1. Additional environmental stability and field performance data is necessary to drive process optimization and process tolerance definition.
2. A process sensitivity study should be included in future efforts which would relate process variations to filter performance.
3. Access to an accelerated aging test facility and/or exposure of filters to the application environment is needed to understand the sensitivity of key fabrication steps on filter performance.
4. A better understanding of the thermomechanical loads for the filters is necessary for many of the filters to be optimized for performance and cost.

Other specific recommendations for each filter manufacturer are provided in the individual sections of the report.

8.0 REFERENCES

1. M. A. Alvin, T. E. Lippert, and J. E. Lane, "Assessment of Porous Ceramic Materials for Hot Gas Filtration Applications", *Ceramic Bulletin*, vol. 70, No. **9**, 1991, 1491-1498
2. J. F. Zeivers, P. Eggerstedt, and E. C. Zeivers, "Porous Ceramics for Gas Filtration", *Ceramic Bulletin*, Vol. 70, No. **1**, 1991, 108-111

APPENDIX

AS A MINIMUM ALL ORDERS ARE INSPECTED TO:

MIL-I-45208A

WHEN REQUIRED ORDERS ARE PROCESSED TO

MIL-Q-9858
OR
CUSTOMER SPECIFICATIONS

CALIBRATION DONE IN ACCORDANCE WITH:

ANSI/NCSL Z540-1
ISO 10012-1
(REPLACING MIL-STD-45662)

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	SECTION TofC	**PAGE** i

WRITTEN BY	APPROVED BY	DATE ISSUED

Techniweave Quality Control Information

YARN INSPECTION AND IDENTIFICATION TAG

DATE RECEIVED: JOB 1396

YARN DESCRIPTION:

NEXTEL 440 2000 DE 1/2 1.5Z

LOT NUMBER: 3757
CUSTOMER: 3M
OUR P.O. #: CFM
MANUFACTURED BY: 3M
INSPECTED BY: Peter Duquette **DATE:** 12/12/94
APPROVED BY: **DATE:**

APPROVED FOR JOB

INVENTORY

TRANSFERRED TO INVENTORY: 12/12/94

THIS TAG MUST REMAIN WITH YARN AT ALL TIMES!

TECHNIWEAVE, INC.

TEMPORARY WORK STOPPAGE

DATE:

JOB #:

LOOM #:

STOPPED BY:

REASON FOR STOPPAGE:

CORRECTIVE ACTION TAKEN:

CORRECTIVE ACTION PERFORMED BY:

DATE:

QUALITY APPROVAL TO RESTART JOB:
BY:
TITLE AND DATE:

START-UP INSPECTION

DESCRIPTION:

JOB NUMBER:	**DATE:**
LOOM NUMBER:	**PROGRAM MANAGER:**
STYLE NUMBER:	**SPECIFICATION # :**
CUSTOMER NAME:	**CUSTOMER P.O. # :**

DESCRIPTION	REQUIRED DIMENSION	ACTUAL DIMENSION	ACCEPTED BY	REJECTED BY
WARP YARN				
FILL YARN				
SELVEDGE				
LENO				

DOES CREEL/BEAM HAVE MATERIAL I.D. SHEET:[ ]YES [ ]NO

WEAVE PATTERN				
HEDDLES				
HARNESSES				
REED SIZE				
FABRIC WIDTH				
WARP COUNT				
PICK COUNT				
COUNTER @ "O"				
RELEASED TO WEAVE				
THICKNESS				
WEIGHT SAMPLE				
SAMPLE APPROVED				

SPECIAL REQUIREMENTS:

COMMENTS:

YARN I.D./LOT # :

HARNESS SEQUENCE:

SET-UP BY:

INSPECTED BY: ***TITLE:*** ***DATE:***

TECHNIWEAVE

Techniweave Quality Control Information

IN-PROCESS INSPECTION

OPERATOR'S NAME	JOB #	LOOM #	LENGTH	MATERIAL	REQUIRED WIDTH	ACTUAL WIDTH	REQUIRED PICKS	ACTUAL PICKS	EDGE QUALITY	FABRIC QUALITY
									QUALITY RATING	
									A= GOOD	
									B= FAIR	
INSPECTED BY:_______			DATE:____________						C= POOR/ STOP JOB / REPAIR	

HARNESS SEQUENCE

JOB NUMBER: **WEAVE PATTERN:**

STYLE NUMBER:

PICK #	REQUIRED SEQUENCE	PICK #	ACTUAL HARNESS SEQUENCE
1.		1.	
2.		2.	
3.		3.	
4.		4.	
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6.		6.	
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20.		20.	

COMMENTS:

APPROVED BY:______________________________**DATE:**

Techniweave Quality Control Information

WEAVER QUALITY RATING	DATE:	DATE:	DATE:	DATE:	DATE:	DATE:	DATE:	DATE:	DATE:	DATE:
EMPLOYEE NAME										
JOB NUMBER										
STYLE NUMBER										
DEFECT TYPE / QUANTITY PER										
^1		0								
^2										
^3	0	0	0							
^4										
^5										
^6	0	0	0							
^7										
^8										
^9										
^10		0	0							
^11										
^12A	0	0								
^12B										
^12C		0								
^12D	0									
^12E										
^12F	0		0							
DEGREE OF DIFFICULTY	0	0.00	0							
FEET WOVEN THIS ROLL	0	0	0							
FABRIC LENGTH THIS ROLL	0	0	0							
% ROLL WOVEN	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!
PICK PER INCH	0	0	0							
TOTAL MAJOR DEFECTS	0	0	0	0	0	0	0	0	0	0
TOTAL MINOR DEFECTS	0	0	0	0	0	0	0	0	0	0
TOTAL DEDUCT POINTS	0	0	0	0	0	0	0	0	0	0
QUALITY RATING THIS JOB	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
ACCUMULATIVE RATING	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
TOTAL DEFECTS / WOVEN LENGTH	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!
PERCENT POINTS AVAILABLE	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!	#DIV/0!

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MANUFACTURING PROCEDURE

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4	PROCUREMENT SPECIFICATION FOR METAL POWDERS	H	10/11/94
5	MMD PROCESS SHEET CREATING AND REVISION	C	3/17/94
8	PROCUREMENT SPECIFICATION FOR BINDER	B	9/1/93
9	MMD TOOL CONTROL PROCEDURE	NEW	