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Metals and Ceramics Division

**CRADA Final Report
For CRADA Number ORNL 97-0476**

**Design and Development of a
Ceramic Hot-Gas Filter For
Fossil Energy**

**V. Vaubert, B. L. Armstrong, and
D. P. Stinton
Oak Ridge National Laboratory**

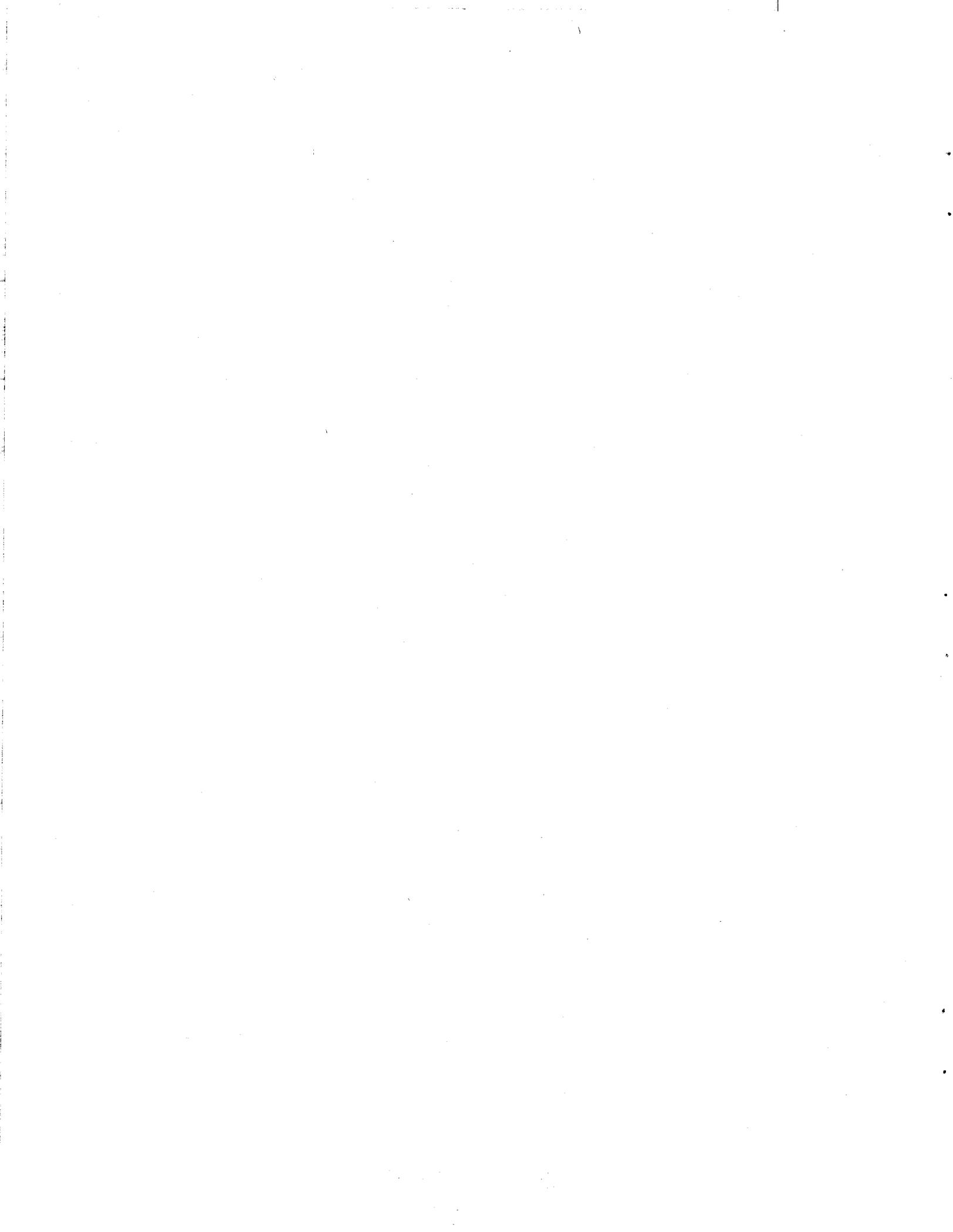
**R. Nagesvaran
LoTEC, Inc.**

Date Published – January 2001

**Prepared by the
OAK RIDGE NATIONAL LABORATORY
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DESIGN AND DEVELOPMENT OF A CERAMIC HOT-GAS FILTER FOR FOSSIL ENERGY

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ABSTRACT

Advanced coal-fueled, power generation systems utilizing pressurized fluidized bed combustion (PFBC) and integrated gasification combined cycle (IGCC) technologies are currently being developed for high-efficiency, low emissions, and low-cost power generation. In spite of the advantages of these promising technologies, the severe operating environment often leads to material degradation and loss of performance in the barrier filters used for particle entrapment. To address this problem a monolithic cross-flow ceramic hot-gas filter is being designed and developed. Because of testing necessities, a hot-gas candle-filter which integrates the requirements of the cross-flow filter will be fabricated first. As a result, a high-purity, stoichiometric mullite, nine inch long, closed-end, candle-filter prototype was fabricated at Oak Ridge National Laboratory (ORNL) using gelcasting technology.

PROGRAM OBJECTIVES

The objective of this CRADA was to develop a high surface area, monolithic cross-flow ceramic hot-gas filter for IGCC and PFBC systems. Full-scale power plants would require thousands of the currently used candle filters costing several million dollars to accommodate the large volumes of gases. The filters, whether candle or cross-flow, must be capable of withstanding severe thermal shocks created by cleaning with ambient air and be corrosion resistant. The development of high surface area cross-flow filters would significantly reduce the capital cost of the hot-gas filter system.

BENEFITS TO THE FUNDING DOE OFFICE'S MISSION

The Fossil Energy Materials Program has, for many years, been supporting the development of thermal shock- and corrosion-resistant materials for use in high-temperature fossil environments. The development of corrosion and thermal shock-resistant cross-flow filters compliments the work being funded by the Fossil Energy Materials Program. This was a 100% funds-in CRADA and therefore, no funding from the Fossil Energy Materials Program was required.

TECHINICAL DISCUSSION

Introduction

Cleaning of the combustion gas stream is a key issue for the successful development of several advanced, coal-fueled, gas turbine technologies. Effective removal of the fly-ash is necessary in order to protect the turbines, minimize deterioration of chemical clean-up process units, and meet environmental standards.

The thermal efficiency of power generation is maximized when the removal of all impurities (gas, liquid, and solid) is conducted at or above the operating temperature of the combustor or gasifier. In PFBC systems, hot-gas filters must operate in a temperature range of 840 to 870°C and at a pressure of 1 MPa. For IGCC systems, the operating temperature will be 650° to 870°C at a pressure of about 3 MPa. The gas stream may contain chloride, sulfide, phosphate and alkali species. The ash particles

may contain mixed and pure oxides of silicon, aluminum, calcium, iron, and alkali elements; sulfates of sodium, potassium, and calcium; and compounds of trace elements. Thus, prospective filter elements must be resistant to a wide variety of chemistries.

As the ash layer builds up on the filter surface, the pressure drop across the filter increases and the ash layer must therefore, be periodically dislodged and collected. This operation is performed by pulsing with a clean, typically cooler, gas stream from the downstream side of the filter element. This pulse cleaning and other process transients expose the filter element to cyclic mechanical and thermal stresses. The filter elements must have, therefore, excellent thermal shock resistance and significant toughness.

Many commercially available, porous ceramic materials are currently being evaluated for use in PFBC and IGCC power generation systems¹. While several of these materials demonstrate sufficient filtration capability, virtually all of the ceramics tested show signs of thermal fatigue and/or excessive corrosion in accelerated testing environments that potentially limit their survivability. Research conducted during the past decade has shown that different failure mechanisms exist for oxide and non-oxide materials. In oxide-based candle filters, failure occurs by thermal fatigue. Failure occurs in non-oxide-based candle filters primarily due to the reaction of the silica in the grain boundary or binder phases with the effluent gases that contain volatile alkali vapors that form lower melting amorphous phases^{2,3,4,5}.

Filter designs include candle, fabric, and cross-flow. Filter systems large enough to clean the typical volume of gas produced by an IGCC and PFBC systems will require large surface areas⁶. Therefore cross-flow filters, which have a very high filter area/volume ratio, are of particular interest. However, they are complex in design and extensive development will be required to bring the technology to commercialization. Typically, such a filter is fabricated by laminating several layers of material containing channels in orthogonal directions. As a result, such filters tend to delaminate and are susceptible to breakage during operation⁷. Engineered Ceramics Inc. (ECI) and ORNL are jointly developing a new cross-flow, hot-gas filter that addresses most of the challenges associated with hot-gas filtration. This filter design is based on fabricating a monolithic, cross-flow ceramic body using gelcasting technology to avoid delamination problems⁸. Current testing facilities are not configured yet for the evaluation of cross-flow filters, therefore the focus of this project was to first develop a candle filter to validate our filter technology. The design was based on mechanical and thermal modeling of the cross-flow filter⁹, which helped determine the optimum filter properties as well as materials selection. (Attached as Appendix A)

Gelcasting was selected as the fabrication technology for the project. Gelcasting is a ceramic forming process developed at Oak Ridge National Laboratory which enables the formation of near-net-shape parts of complex geometry. Gelcasting involves the addition of two monomers to a water-based ceramic slurry followed by polymerization of these monomers using appropriate activator and catalyst. The polymerization process rigidizes the slurry, transforming it from a liquid to a semi-rigid gel. Once the gelation process is complete, the component is dried and sintered. The steps involved during the gelcasting process do not essentially differ from traditional slip-casting and are schematically presented on figure 1. Wax, plastic or metal can be used as mold material, so relatively inexpensive, and very diverse (e.g. dissolvable) molds can be utilized. Because of the complex shape of a monolithic cross-flow filter, gelcasting was chosen as the forming process. Gelcasting also enabled the use of more versatile pore-forming methods.

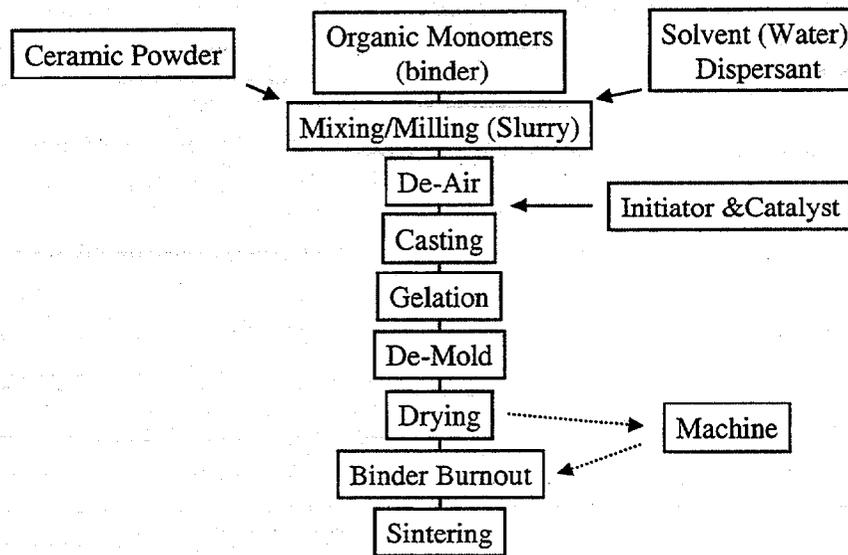


Figure 1: Schematic of the gelcasting process

The primary criteria for selecting materials for hot-gas filters include corrosion resistance, thermal shock resistance, high strength, and high toughness. Candidate materials that provide a good compromise among all these criteria are mullite, and NZP. The NZP family of ceramics [NaZr₂P₃O₁₂ and its isostructural analogs (e.g., Ca_{0.5}Sr_{0.5}Zr₄P₆O₂₄), CS-50] provides compositions with ultra-low thermal expansion (1 ppm/°C) and high melting temperatures (1850°C)¹⁰. Mullite (3Al₂O₃-2SiO₂) presents a high resistance to thermal shock and is stable in corrosive environment^{11, 12}. The major properties of mullite and CS-50 are summarized in Table 1.

	Mullite	CS-50
Strength, σ_f (MPa)	200	75
Young's modulus, (MPa)	180	75
Coeff. Th. Exp. (ppm/°C)	5	3
Th. shock, ΔT (°C)	400	750

Table 1: Properties of mullite and CS-50

DISCUSSION OF CURRENT ACTIVITIES

EXPERIMENTAL PROCEDURE

Screening Tests

Material Selection. Since high corrosion/oxidation resistance of the filter components is needed, the selection of the optimum candidate material was continued by corrosion testing of CS-50 and three different commercially available mullite powders. The mullite powders tested were: a) Mullite A, stoichiometric, high-purity mullite (MULSM Baikowski, Charlotte, NC); b) Mullite B, stoichiometric, 99.7 wt% pure mullite (Duramul, Washington Mills Electro Minerals Corporation, Niagara Falls, NY); Mullite C, mullite and alumina mixture (Aremco Products Inc., Ossining, NY).

Slip-cast and isopressed pellets were prepared, sintered and machined into 4x3x50 mm flexure bars. For each material, 10 samples were kept as reference and 10 samples were subjected to alkali environment. The flexure bars dedicated to the corrosion test were thoroughly cleaned in acetone and dried. Once dry, the specimens were weighed and dimensionally measured. The sodium sulfate loading was performed by heating the specimens on a hot plate at 90°C and dispensing drops of saturated Na₂SO₄ solution onto the surface. The samples were left to dry for an hour, weighed, and more sodium sulfate was added until the loading reaches 8 mg/cm². The samples were then heated in a furnace at 1000°C for 100 hr with O₂ at 200 cm³/min flowing over them. The samples were weighed, washed in hot distilled water for two hours to dissolve any residual salt, and then weighed again.

Pore Former Process Selection. Much work has been devoted to obtaining acceptable porosity to achieve optimum permeability for hot-gas filtration. Several pore-forming techniques, including liquid phase separation, air entrapment, and pore formation by fugitive organic addition, have been evaluated⁹ but none of these methods yield sufficient open porosity. However, by using a bimodal powder distribution, high porosity levels are now obtained. The first group of powder is comprised of particles with a diameter between 177 and 150 μm (sieve 80-100) and the second group of powder, that acts as a binder-phase between the coarse particles, has a sub-micron average particle size centered around 0.8 μm.

PROCESS

Powder Preparation

Duramul mullite was selected as the candidate material (cf. results section). Duramul is a fused high purity mullite produced by the electric furnace fusion of Bayer process alumina and high purity silica. According to the manufacturer, there is an excess of aluminum oxide above the normal mullite ratio (3Al₂O₃: 2SiO₂) to ensure that all of the SiO₂ is contained within the mullite phase and is not present as a glass phase. The as-received powders were characterized by X-ray diffraction and no free alumina phase was detected. The chemical analysis of the manufacturer indicates the presence of 0.3 wt % Na₂O and the reported coefficient of thermal expansion at room temperature is 4.63 X 10⁻⁶ per °C. Duramul is ordered as - 80 grit powder from the manufacturer to obtain sufficiently coarse particles and to keep as low as possible the amount of impurities introduced during particle size reduction. The coarse fraction is obtained by sieving the as-received powder to -80 +100 mesh, and the fine fraction is obtained by milling the - 100 mesh powder. The sub-micron particle size is reached after 24 hr of wet milling in isopropanol with 3 mm diameter partially stabilized zirconia media (ZrO₂ - 5 mol% Y₂O₃, Tosoh Soda, Tokyo Japan). The media to powder ratio is 10 to 1 in weight. Mullite particles are measured using a Horiba LA-700 (Kyoto, Japan) particle size analyzer. The mullite and isopropanol mixture is then placed in a large pan, covered with pierced aluminum foil and dried overnight at 60°C.

Slurry Preparation

The first step of the slurry preparation is the fabrication of the monomer premix. The monofunctional monomers are a blend of methylacrylamide (MAM) (Aldrich Chemical Company, Inc.; Milwaukee, WI) and N-Vinyl-2-pyrrolidone (NVP) (Polyscience, Inc.; Warrington, PA). The crosslinker is N, N'-methylenebisacrylamide (MBAM) (Aldrich Chemical Company, Inc.; Milwaukee, WI). The weight ratio of the monomers is MAM:NVP:MBAM = 3:1:1. The monomer system constitutes 25 wt% of the liquid phase, the rest being water. First, MAM is added to the high purity water, then the liquid is rolled for 30 min., next NVP is incorporated followed by 30 min of rolling, finally MBAM is added and the liquid is rolled for 2 hr. After filtering the monomer-water solution 2 wt% (based on powder weight) DuramaxTM D-3021 (Rohm and Haas, Philadelphia, PA) is added as a dispersant.

Then 2 wt% Polyethylene Glycol (PEG-400, EM Science, Gibbstown, NJ) is added as a plasticizer. The fine mullite powder is incorporated into the solution and the slurry is rolled for 2 hours in a polyethylene jar with a few pieces of 10 mm diameter alumina media to ensure proper mixing and dispersion of the particles. The weight of the fines is based on a 9:1 coarse to fine ratio and a slip with a 48 vol% solids loading (coarse and fine powder).

Next, the slurry is poured in a high-shear Kitchen-Aid™ mixer which provides the necessary high shear mixing power. The coarse powders settle out of the suspension making the slip impossible to utilize. Our approach was to increase the viscosity of the slurry by adding a binder to obtain a strongly pseudoplastic solution. Due to its high viscosity grade and low thixotropicity, hydroxyethyl cellulose¹³ (Cellosize^R, Union Carbide Chemicals and Plastics Company Inc., Danbury, CT) was chosen as a binder. A 1:1 weight ratio mixture between two types of hydroxyethyl cellulose QP-4400H and QP-100MH is used and 0.125 wt % based on powder weight is added to the slurry. The coarse powder is then incorporated under shear mixing. Next, the slurry is poured under vibration into a deairing mixer. After adding Surfynol^R 104-E Surfactant (Air Products - Allentown, PA) to the slurry as a defoamer, the slip is defoamed by pulling vacuum under vibration. Then, N,N,N',N'-tetramethyl-ethylenediamine (TEMED; Aldrich Chemical Company, Inc.; Milwaukee, WI) is added as an initiator and ammonium persulfate (APS; Aldrich Chemical Company, Inc.; Milwaukee, WI) as a catalyst. A thin layer of petroleum jelly is first applied on the anodized aluminum mold, most of it is wiped off, and a layer of Mold WIZ AZN release agent (Axel, Woodside, NY) is sprayed over the mold surface. Afterward, the slurry is poured into the mold under high vibration, and the part is gelled at 55°C for 30 min. Lastly, the part is de-molded and left to dry for 48 hr at room temperature and ambient humidity.

The parts are bisqued fired in air according to the schedule presented in Figure 4. The sintering is performed at 1750°C in a tungsten element furnace Model 901 (RDBrew and Co, Concord, NH) under an Ar-4% H₂ atmosphere.

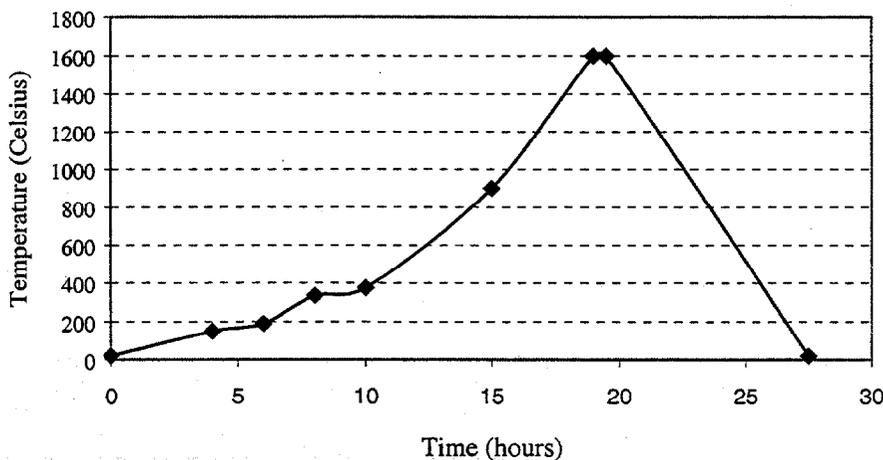


Figure 4: Binder burn-out schedule

CHARACTERIZATION

Permeability Measurements

The permeability of the filter rings was measured by recording the pressure drop across the porous specimen for different volumetric flows. The viscous flow through a porous media is expressed by Darcy's law:

$$N = cu = \frac{-\beta}{\mu} \times \frac{P}{RT} \nabla P$$

Where N = total molar flux

c = molar concentration

u = average velocity

β = permeability

μ = gas viscosity

∇P = pressure gradient

The average velocity through a porous medium is:

$$u = \frac{Q}{A} = \frac{-\beta}{\mu} \times \frac{\Delta P}{T}$$

Where Q = volumetric flow rate

A = cross-sectional area

ΔP = pressure drop

T = Filter ring thickness

$$\beta = \frac{Q}{\Delta P} \times \frac{\mu T}{A}$$

$$A = \Pi(r_o + r_i)L \quad T = r_o - r_i$$

Where L = length of the filter ring

r_o = outside diameter

r_i = inside diameter

$\frac{Q}{\Delta P}$ is obtained by flowing air through the filter rings and recording the pressure drop with a baratron (224HA-10000BB, MKS instruments Inc., Burlington, MA). The experimental setup is shown on Figure 6. The permeability of filters rings presenting different coarse to fine powder weight ratios was measured. The following coarse to fine powder weight ratios were evaluated: 80:20, 85:15, and 90:10. For comparison purposes, the pressure drop as a function of gas flow of three commercial or experimental filter rings was measured.

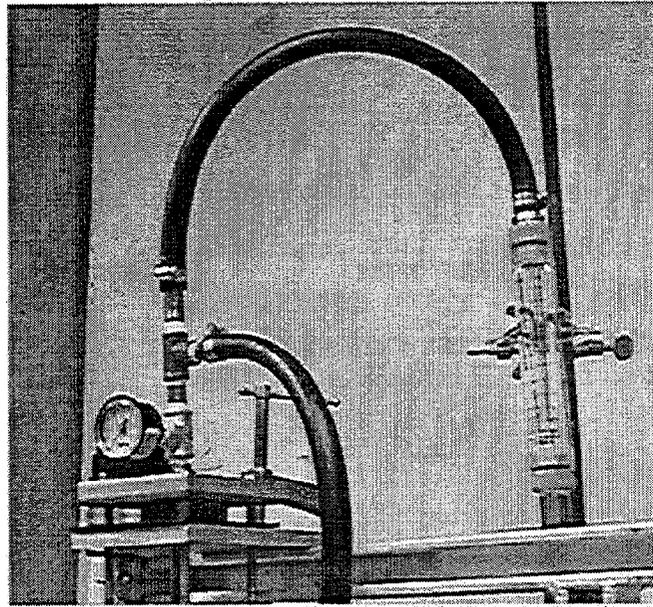


Figure 6: Experimental setup used for permeability measurement

Thermal Diffusivity Measurements

The thermal diffusivity of several porous ceramic samples was measured at room temperature by xenon flash and at 850°C by laser flash technique¹⁴. Three-millimeter thick by twelve-millimeter diameter disks were machined out of commercially available or experimental filters. Nine different samples were tested at room temperature and six of them were tested at 850°C. The test was performed according to the ASTM standard E-1461¹⁵.

Scanning Electronic Microscopy Evaluation

Samples processed with a 80:20, 85:15, and 90:10 coarse: fine powder weight ratio were observed by scanning electron microscopy (S-800, Hitachi, Tokyo, Japan).

Mechanical Evaluation

Ten filter rings presenting a 90/10 coarse to fine powder weight ratio were fabricated and tested for strength. The rings are filled with rubber (Silastic[®], Dow Corning Co., Midland, MI) and a compressive strength is applied on both surfaces of the incompressible elastomeric insert to obtain a uniform pressure all around the inside of the filter ring. The test was performed according to the standard test method ASTM C28.7. The maximum internal pressure is calculated according the following equation:

$$P_{\max} = \frac{T_{\max}}{A}$$

Where T_{\max} is the maximum applied compressive load and A is the initial cross-sectional area of the rubber insert.

Corrosion Evaluation

Ten filter rings are currently being exposed to a combustion environment and ten more are planned to be tested in a gasification environment both at the University of North Dakota Energy and Environmental Research Center. The goal of this test is to determine the material's behavior in a realistic fossil atmosphere. The samples will be tested for mechanical strength and characterized by X-ray diffraction and scanning electronic microscopy.

RESULTS

Screening Tests

Material Selection. The elastic modulus of the alkali-exposed and reference samples was measured by a sonic method (grindo-sonic MK4i model, J.W. Lemmens Inc., St Louis, MO). The modulus of rupture was measured by breaking the samples in four point bending with an inner span of 20 mm and an outer span of 40 mm (Applied Test Systems, Inc., Butler, PA). The phases present on the sample surface were identified before and after corrosion by standard x-ray diffraction (PAD V, Scintag, Sunnyvale, CA) and scanning electron microscopy (S-800, Hitachi, Tokyo, Japan). Significant elastic modulus and strength losses were measured for CS-50 and mullite C. No statistically significant variation was recorded for mullite A and B. The mechanical property measurements are presented in Figure 2 for the elastic modulus and in Figure 3 for the strength. Mullite B, (Duramul) was chosen as the candidate material over mullite A due to economical considerations since the price of mullite B was close to a hundred times cheaper.

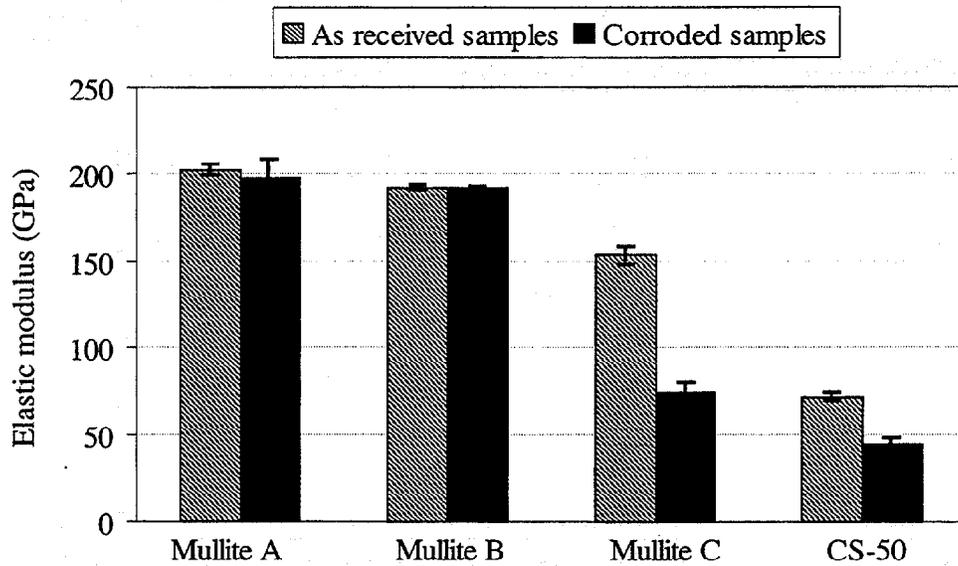


Figure 2 Elastic modulus for corroded and non-corroded ceramic candidates

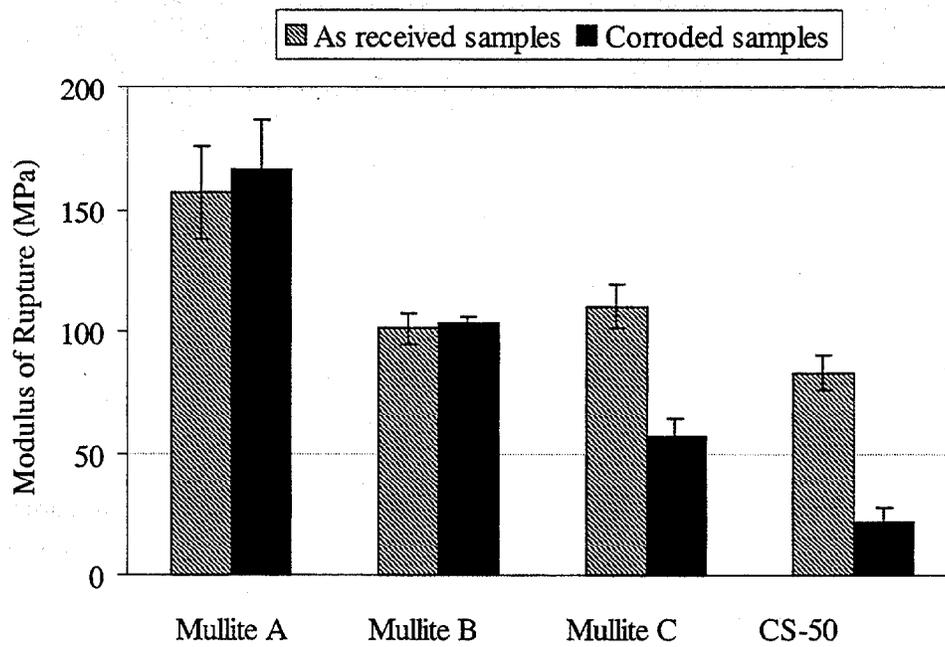


Figure 3: Modulus of rupture for corroded and non-corroded ceramic candidates

Closed-end, twenty-five-centimeter long filters were fabricated. Examples of sintered parts are shown in Figure 7.

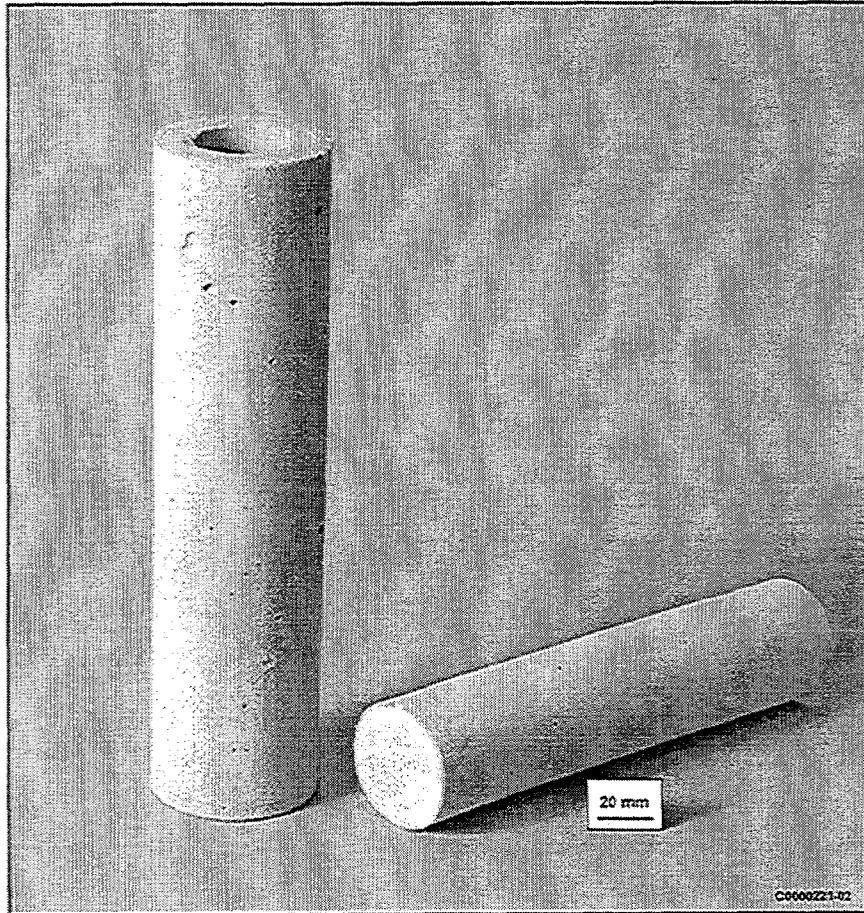


Figure 7: Filter obtained by gelcasting

Permeability Measurements

The permeabilities were calculated relative to the permeability of a commercial candle filter (Schumacher, Germany). The results are shown on Figure 8.

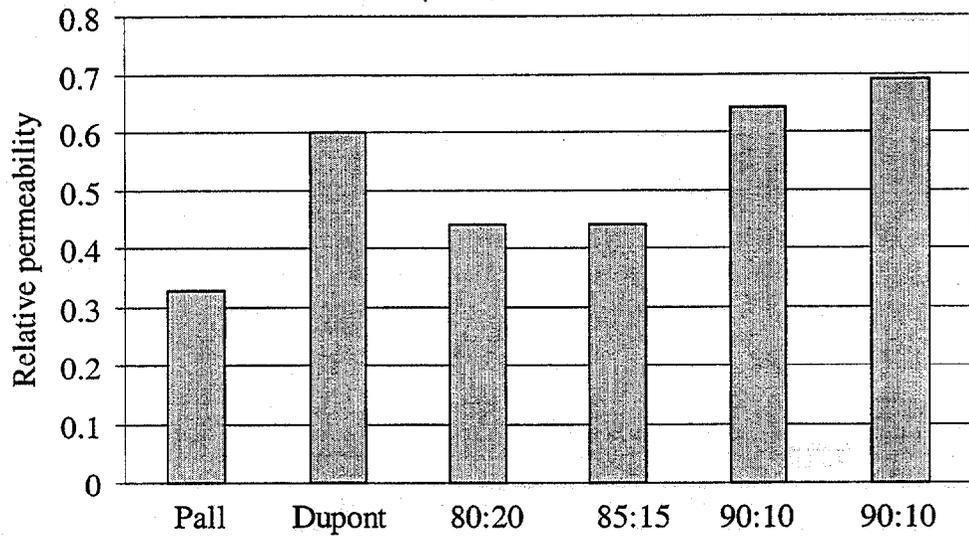


Figure 8: Relative permeability of different filter rings

The permeability of the fabricated filters is in the same range as the commercially available candle filters. The coarse to fine ratio 90:10 yield higher permeability than the 80:20 and 85: 15 powder ratios. We wanted to evaluate higher coarse to fine ratios, but processing has not been possible at this point. The fine particles are providing the structural strength after binder burn-out and the parts were too weak to be handled. The room temperature permeability was also measured by Siemens-Westinghouse and was 0.25 in-wg/fpm which is within the tolerance for hot gas filter applications.

Thermal Diffusivity Measurements

The thermal diffusivity results at room temperature and 850°C are reported in Table 1.

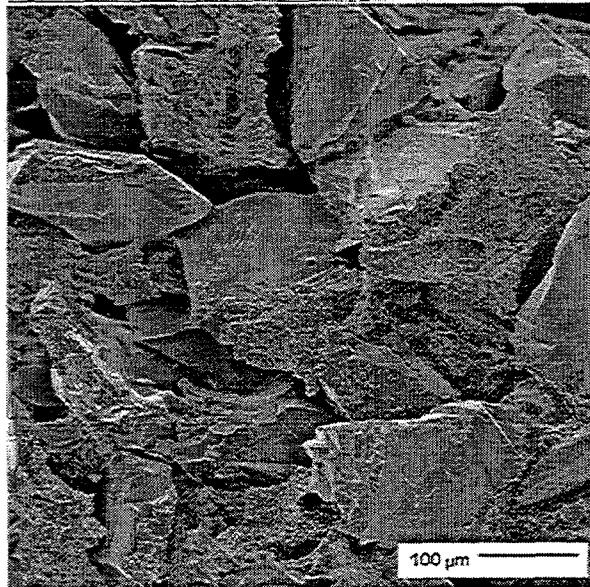
Room temperature measurements (xenon flash) T = 20°C, Unit: cm ² /s									
	Mullite 1 Duramul 90:10	Mullite 2 Duramul 90:10	Mullite 3 Duramul 3% Al ₂ O ₃	Mullite Cercona foam	Mullite Coors (filter)	Babcock and Wilcox (filter)	DuPont Lanxide (filter)	Pall Corp SiC (filter)	Shumacher SiC (filter)
Average	0.0098	0.0087	0.0067	0.0105	0.0083	0.0031	0.0076	0.0587	0.0456
Error (%)	1.9973	1.3166	0.6695	0.6734	0.6006	1.7899	0.7647	1.1258	1.8690
High Temperature Laser Flash tests T= 850°C Unit: cm ² /S									
Test 1	0.0043		0.0046	0.0045	0.0037			0.0237	0.0264
Test 2	0.0046		0.0025	0.0045	0.0045			0.0227	0.0249
Test 3	0.0041		0.0033	0.0045	0.0054			0.0227	0.0253
Average	0.0043		0.0035	0.0045	0.0045			0.0230	0.0255

Table 1: Thermal diffusivity measurements of porous ceramics

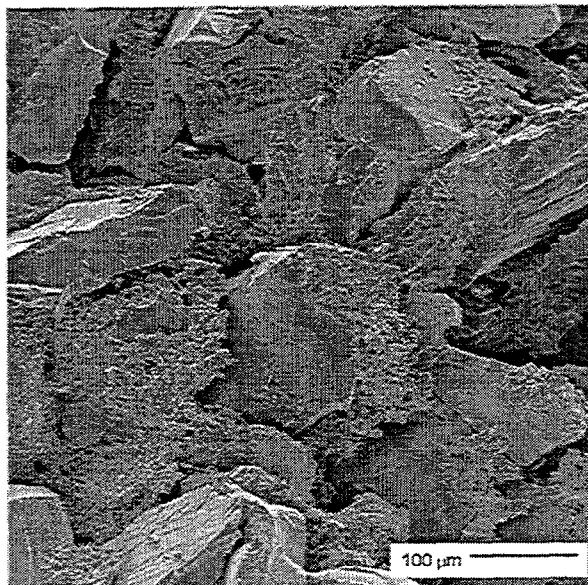
As expected, the thermal diffusivity of the mullite samples is very low compared to the thermal diffusivity of the porous SiC samples.

Scanning Electronic Microscopy Evaluation

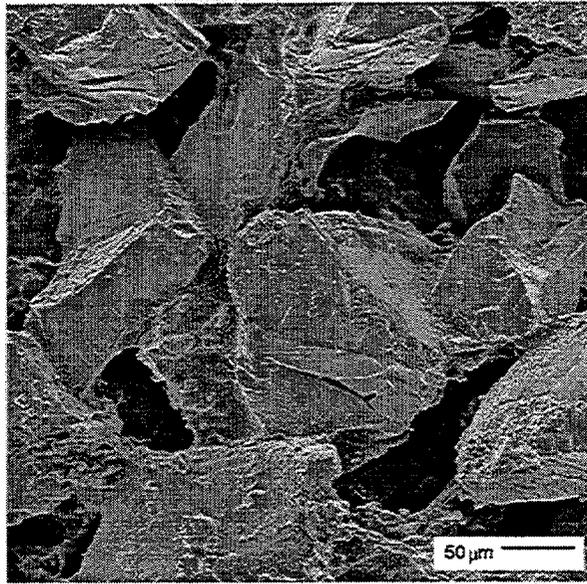
Micrographs of the filter samples are shown on Figure 9, 10 and 11. The fine particles are obstructing the pores, which explains the increase in permeability as the amount of fine decreases. Even for the 90:10 coarse to fine weight ratio some of the fine particles are limiting the permeability without playing a structural role, an effort is ongoing to better disperse the fine particles around the coarse particles.



Figures 9: Scanning electron micrograph of an 80:20 coarse: fine mullite sample shows that the fine particles fill up the pores



Figures 10: Scanning electron micrograph of an 85:15 coarse: fine mullite sample shows that the fine particles fill up the pores



Figures 11: Scanning electron micrograph of a 90:10 coarse: fine mullite sample shows that there is no obstruction of the pores

Mechanical Evaluation

The results of the mechanical strength measurements are reported in table 2.

	Mullite Duramul 90:10	Dupont SiC/SiC	Dupont PRD66-C	Dupont PRD-66M	Babcock and Wilcox	Smart Ceramics	3 M
Av Max P (MPa)	1.60	2.87	1.85	1.27	2.01	0.39	1.70
Stdev (MPa)	0.29	0.20	0.09	0.42	0.20	0.04	0.04

Table 2: Maximum pressure strength for the fabricated filter rings and various other experimental filter samples developed elsewhere

The average mechanical strength of the experimental 90:10 samples is within the range of other commercial/experimental hot-gas filters. A better dispersion of the fine particles around the coarse particles should yield stronger inter-particle bonds and should result in an overall increase of the filter strength.

INVENTIONS

The development of monolithic cross-flow filters resulted from the combination of existing technologies at LoTEC and at ORNL. Both technologies had already been patented and therefore, no additional inventions were required.

COMMERCIALIZATION POSSIBILITIES

Researchers at ORNL were very disappointed with the work done LoTEC at over the last several years. Filter materials with carefully controlled grain size and surface area that were developed at ORNL, were never able to be duplicated at LoTEC. We do not feel that this

was the result of scale-up issues. We are convinced that this project did not receive a very high priority after LoTEC was purchased (see below). The Principal Investigator at LoTEC was changed several times. Unfortunately, the new researchers were always less experienced and less qualified than the previous investigator. We do not feel that there is any possibility of commercialization of this technology by LoTEC.

PLANS FOR FUTURE COLLABORATION

LoTEC and ORNL have collaborated on a number of programs in the last 5 to 10 years. A number of these programs have been quite successful and contributed to the growth of LoTEC from 4 to about 15 employees. Because of this success, LoTEC was purchased by Composite Optics Incorporated and most of the employees were relocated to San Diego. Unfortunately, the reorganization changed the focus of the work from commercial or industrial programs to ones funded by DOD. Furthermore, our primary collaborator, Santosh Limaye, is no longer with the company. Therefore, we plan no further collaboration with LoTEC or Composite Optics Inc.

CONCLUSIONS

A material selection has been performed to determine the best candidate material for hot-gas applications. Stoichiometric mullite has been selected as the best compromise between strength, thermal-shock resistance and resistance to alkali containing environment.

A pore forming method has been developed which uses a mixture of very coarse mullite particles and very fine mullite particle. This technique yields acceptable permeability for hot-gas filter applications and also enables the use of a single material, therefore limiting the number of compounds which could experience degradation from hot corrosion.

A processing technique was also developed and nine-inch long filter tubes were fabricated accordingly. The ratio of the coarse and fine ratio was optimized by permeability measurements, microstructural characterization and processing limitations.

ACKNOWLEDGMENTS

This work was supported by the U.S. Department of Energy SBIR/STTR program. We would like to thank Paul Menchhofer for his extremely valuable help on processing coarse particulate material. The authors would also like to thank Mary Anne Alvin from Siemens Westinghouse for her help and advice, John Hurley from the University of North Dakota for the corrosion test, Edgar Lara Curzio from Oak Ridge National Laboratory for the mechanical evaluation, and Hsin Wang from Oak Ridge National Laboratory for the thermal diffusivity measurements. We would also like to thank Beth Armstrong for her help and advice during the project.

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APPENDIX A: DESIGN AND INITIAL DEVELOPMENT OF MONOLITHIC CROSS-FLOW CERAMIC HOT-GAS FILTERS

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ABSTRACT

Advanced, coal-fueled, power generation systems utilizing pressurized fluidized bed combustion (PFBC) and integrated gasification combined cycle (IGCC) technologies are currently being developed for high-efficiency, low emissions, and low-cost power generation. In spite of the advantages of these promising technologies, the severe operating environment often leads to material degradation and loss of performance in the barrier filters used for particle entrapment. To address this problem, LoTEC Inc., and Oak Ridge National Laboratory are jointly designing and developing a monolithic cross-flow ceramic hot-gas filter. The filter concept involves a truly monolithic cross-flow design that is resistant to delamination, can be easily fabricated, and offers flexibility of geometry and material make-up.

During Phase I of the program, a thermo-mechanical analysis was performed to determine how a cross-flow filter would respond both thermally and mechanically to a series of thermal and mechanical loads. The cross-flow filter mold was designed accordingly, and the materials selection was narrowed down to $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{Zr}_4\text{P}_6\text{O}_{24}$ (CS-50) and $2\text{Al}_2\text{O}_3\text{-}3\text{SiO}_2$ (mullite). A fabrication process was developed using gelcasting technology and monolithic cross-flow filters were fabricated. The program focuses on obtaining optimum filter permeability and testing the corrosion resistance of the candidate materials.

INTRODUCTION

Cleaning of the combustion gas stream is a key issue for the successful development of several advanced, coal-fueled, gas turbine technologies. Effective removal of the flyash is necessary in order to protect the turbines, minimize deterioration of chemical clean-up process units, and meet environmental standards.

The thermal efficiency of power generation is maximized when the removal of all (gas, liquid, and solid) impurities is conducted at or above the operating temperature of the combustor or gasifier. In PFBC systems, hot-gas filters must operate in a temperature range of 840 to 870°C and at a pressure of 1 MPa. For IGCC systems, the operating temperature will be 650° to 870°C at a pressure of about 3 MPa. The gas stream may contain chloride, sulfide, phosphate and alkali species. The ash particles may contain mixed and pure oxides of Si, Al, Ca, Fe, and alkali elements; sulfates of sodium, potassium, and calcium; and compounds of trace elements. Thus, prospective filter elements must be resistant to a wide variety of chemistries.

As the ash layer builds up on the filter surface, the pressure drop across the filter increases and the ash layer must be periodically dislodged and collected. This operation is performed by pulsing a clean, typically cooler, gas stream from the downstream side of the filter element. This pulse cleaning and other process transients expose the filter element to cyclic mechanical and thermal stresses. The filter elements must have, therefore, excellent thermal shock resistance and significant toughness.

Many commercially available, porous ceramic materials are currently being evaluated for use in PFBC and IGCC power generation systems¹. While several of these materials demonstrate sufficient filtration capability, virtually all of the ceramics tested show signs of thermal fatigue and/or excessive corrosion in accelerated testing environments that potentially limit their survivability. Research conducted during the past decade has shown that different failure mechanisms exist for oxide and non-oxide materials. In oxide-based candle filters, failure occurs by thermal fatigue. Corrosion occurs in nonoxide-based candle filters primarily due to the reaction of the silica in the grain boundary or binder phases with the effluent gases that contain volatile alkali vapors that form lower melting amorphous phases^{2,3,4,5}.

In summary, suitable filter materials must have sufficient strength and toughness to tolerate thermal stresses caused by pulse cleaning and process transients. They must be relatively inert toward the ash components so that ash filter cake can be easily dislodged and the pressure drop across the filter can be kept within acceptable limits. The materials must also have sufficient chemical resistance to survive in high-pressure gas streams containing steam and alkali vapor.

Filter designs include candle, fabric, and cross-flow. Filter systems large enough to clean the typical volume of gas produced by an IGCC and PFBC systems will be very expensive⁶. Therefore cross-flow filters, which have a very high filter area/volume ratio, are of particular interest. However, they are complex in design and extensive development will be required to bring the technology to commercialization. Typically, such a filter is fabricated by laminating several layers of material containing channels in orthogonal directions. As a result, such filters tend to delaminate and are susceptible to breakage during operation.⁷ LoTEC, Inc. and ORNL are jointly developing a new cross-flow, hot-gas filter that addresses most of the challenges associated with hot-gas filtration. This filter design is based on fabricating a monolithic, cross-flow ceramic body using gelcasting technology to avoid delamination problem.⁸ The materials considered for this design have low thermal

expansion resulting in excellent thermal shock resistance. The two primary candidate materials being considered for this application are mullite (as a benchmark) and alkaline or alkaline earth zirconium phosphates (NZP) ceramics that have a very low thermal expansion. If successful, this research is expected to result in a robust hot-gas filter that has excellent chemical stability and a very high resistance to thermal shock and delamination.

PROJECT DESCRIPTION

Over the last few years, LoTEC, Inc. has developed a unique method for fabricating cross-flow filters in a single step without using laminates. The flexibility of the process allows control of various geometric parameters including channel size, shape, wall thickness, and taper. The fabrication of LoTEC's monolithic, cross-flow filter utilizes gelcasting, a process licensed from ORNL. The constraints of the PFBC test facility at Westinghouse require ceramic filters of specific dimensions (30.5x30.5x10.2 cm). However, the rest of the variables -channel size, shape, material properties (strength, toughness, and thermal expansion)- can be optimized. The optimization of the filter was realized by improving its design and fabrication process.

The design development was based on mechanical and thermal modeling of the filter, which helped determine the optimum filter properties as well as materials selection. The process development effort focused on identifying parameters that improve the overall mechanical strength, increase the strain to failure, and increase the number of connected pores since the low pressure drop required during gas cleaning necessitates significant porosity levels. Several porosity-forming techniques have been pursued: porosity formation by liquid-phase separation, air entrapment, and pore formation by fugitive additives. The current effort also includes mechanical testing of corroded mullite and NZP samples.

DESIGN DEVELOPMENT

Materials Selection. The primary criteria for selecting materials for hot-gas filters include corrosion resistance, thermal shock resistance, high strength, and high toughness. Candidate materials that provide a good compromise among all these criteria are mullite, NZP, and high-purity alumina.

The NZP family of ceramics [$\text{NaZr}_2\text{P}_3\text{O}_{12}$ and its isostructural analogs (e.g., $\text{CaZr}_4\text{P}_6\text{O}_{24}$)] provides compositions with ultra-low thermal expansion (1 ppm/°C) and high melting temperatures (1850°C). The very low coefficient of thermal expansion (CTE) results in very high thermal shock resistance. The materials also have high melting temperatures and superior thermal insulation capabilities compared to most low thermal expansion ceramics.⁹ In addition to low and tailorable thermal expansion, NZP materials can be chemically altered to reduce the thermal expansion anisotropy. It has been shown that the thermal expansion, as well as the thermal expansion anisotropy of these materials, can be reduced significantly by tailoring the chemical composition within the NZP family of ceramics. The composition, $\text{Ca}_{1-x}\text{Sr}_x\text{Zr}_4\text{P}_6\text{O}_{24}$ ($x = 0.5$, CS-50) exhibits minimal microcracking, whereas compositions of values $x = 0$ and $x = 1.0$, exhibit a high degree of anisotropy

and microcracking. Thus, one can control the microcracking associated with the thermal expansion anisotropy to improve the mechanical properties by controlling the chemistry of NZP materials. Typically, compositions with a high degree of anisotropy show low flexural strength (30 MPa), while compositions that have lower anisotropy have higher flexural strength (75 MPa).¹⁰ In addition, the thermal shock resistance of these materials is very high. These materials can be quenched from 1400°C without any significant loss of strength. The major properties of alumina, mullite and CS-50 are summarized in Table 1.

Thermo-mechanical analysis

The finite-element model contained three layers of the cross-flow filter and is shown in Figure 2. The middle layer was exposed to the cold backpulse used for dislodging ash particulate buildup, while the two surrounding layers were exposed to the particulate containing hot gas. The initial temperature of the hot gas was assumed to be 870°C for the entire filter. The model examined three thermal-loading conditions with cold backpulses of 25°C for one second, 25°C for five seconds, and 100°C for one second.

The same-finite element model used for determining temperature differentials throughout the filter was also used to determine the thermal and mechanical stresses induced during hot-gas filtration. The analysis was performed using NZP, mullite, and alumina, to provide a comparison among candidate hot-gas filter materials.

Results

The finite-element analysis results indicate that the minimum temperature of the filter due to the pulse is 854°C, which corresponds to a temperature gradient over the membrane of only 16°C. In actual environment, cold-gas backpulsing is on the order of a tenth of a second, which would lead to even smaller temperature gradients.

Thermal stresses generated by the cold-gas pulses were found to be as high as 355 MPa for alumina. This eliminated alumina as a candidate material to be used for the design of cross-flow filters. The values of the thermal stresses found for mullite and CS-50 were respectively 75 and 15 MPa.

Table 1: Properties of alumina, mullite and CS-50

	Alumina	Mullite	CS-50
Strength, σ_f (MPa)	350	200	75
Young's modulus, (MPa)	375	180	75
Coeff. Th. Exp. (ppm/°C)	8	5	3
Th. shock, ΔT (°C)	300	400	750
Thermal σ (MPa)	355	75	15

Channel and filter design

Initially, a mold was designed which allowed fabrication by gelcasting of a 5x5x5cm, cross-flow body with rectangular cross-flow channels of 0.4 mm. The thermo-mechanical analysis was based on this initial mold design. As shown in Figure 1, the thermal stresses found with the model were extremely large at the corners of the channels; these should be diminished by rounding off the corners in the next design iteration.

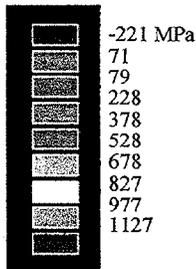
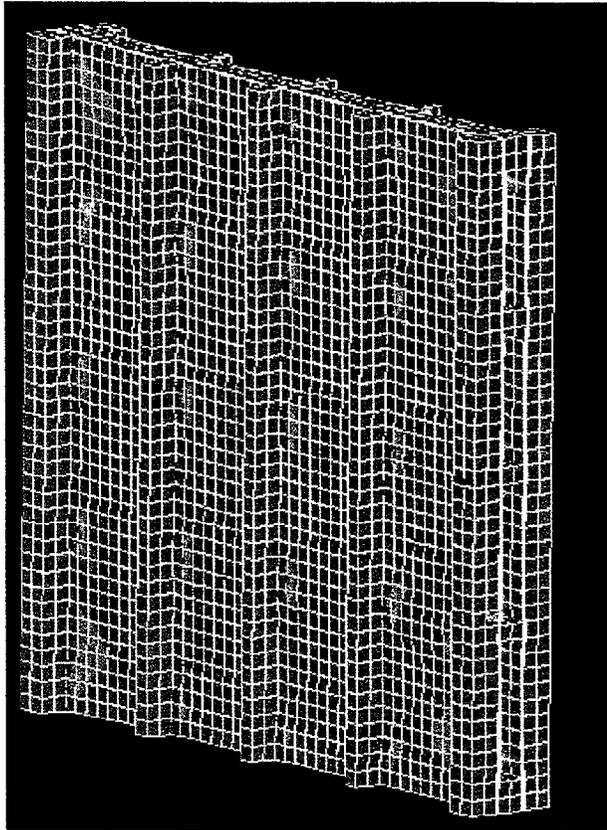


Figure 1: Thermal stresses distribution in alumina

As shown in Figure 2 the maximum mechanical stresses occur in the center of the wall. The mechanical stresses applied on the membrane are proportional to the inverse of the square of the thickness, so by increasing the thickness of the membrane, the mechanical stresses will diminish. The initial finite element analysis has demonstrated that the thermal gradients for a thin-walled (0.4 mm), hot-gas filter are

relatively small (less than 50°C). However, as the wall thickness is increased to accommodate higher mechanical stresses, the thermal gradients are expected to be more severe.

A new mold has been designed with larger dimensions 10x10x15cm, and thicker walls of 3 mm. The channel shape has been changed from circular to more rectangular in order to increase the overall surface area. A photograph of prototypes made with both the old (small) and new (large) mold designs is shown in Figure 3. Along with dimensional changes in the mold, there have been minor changes in the mold materials. The mold walls have changed from plain aluminum to an anodized aluminum in order to increase surface scratch resistance and improve mold release.

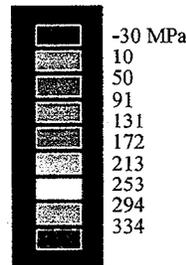
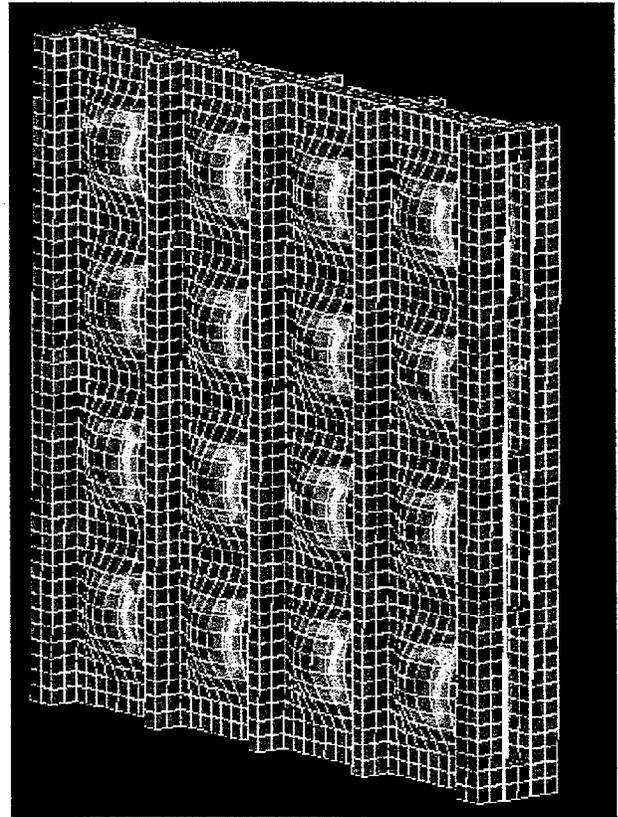


Figure 2: Mechanical stresses in alumina

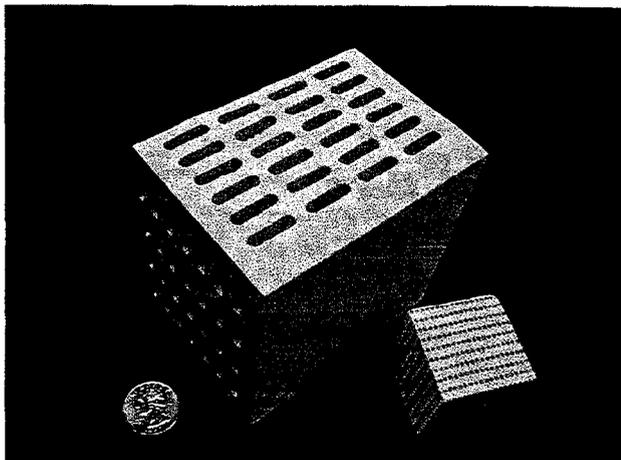


Figure 3: Comparison of first generation (smaller) to current hot gas filter design.

PROCESS DEVELOPMENT

Fabrication Technology

Gelcasting. As mentioned earlier, fabrication of LoTEC's, monolithic, cross-flow filter was possible due to a unique process called gelcasting. Gelcasting involves the addition of two monomers to a water-based ceramic slurry followed by polymerization of these monomers using appropriate activators and a catalyst. The polymerization process rigidizes the slurry, transforming it from a liquid to a semi-rigid gel. Once the gelation process is complete, the component is dried and sintered. The advantages of the gelcasting process are 1) production of a strong, machinable, green-body ceramic, 2) fabrication of both simple and complex shapes, 3) production of near-net shape parts resulting in a decrease of the machining time and cost. As a result, gelcasting has become an attractive and cost-effective solution for fabricating complex-shaped components.

Powder processing. To achieve a strong, interconnected matrix for porous material, it was necessary to reduce the particle size of CS-50 in order to increase particle packing and sinterability. An average particle size of 1.5 μm was obtained and solids loading of 78 wt% solids were obtained without significantly increasing the viscosity of the slurry. Submicron mullite powder was obtained commercially (MULSM, Baikowski, Charlotte, NC) and used as received. Other commercial mullite powders (Aremco) used essentially for the corrosion study were wet milled down to 1 μm in size.

Drying, bisquing and sintering. Because water is trapped in the gelled polymer network, drying is a slow and critical step in obtaining crack-free gelcast components. Due to the thin-walled nature of the first generation cross-flow filter, drying has not been a major constraint in obtaining crack-free components. However, as indicated by the thermo-mechanical analysis, the thickness of the walls in the second

generation filter was increased, as well as the overall dimensions of the filter. These modifications introduced longer drying schedules using rate-controlled, weight-loss measurements. Binder burn-out schedules were adapted to the new filter dimensions, and sintering times and temperatures were adapted to the particle size utilized.

Porosity Formation

Much work is being devoted to obtaining acceptable porosity in order to achieve optimum permeability for hot-gas filtration. Several pore-forming techniques are still being evaluated.

Porous Ceramics by Liquid Phase Separation. In this process, porous, monolithic, ceramic bodies containing reticulated macropores are produced by first forming a mixture of ceramic powder and two organic polymers, specifically dibutyl sebacate and low-density polyethylene.¹¹ The temperature of this mixture is raised above the miscibility limit to form a liquid solution. While cooling, the polymers phase-separate and the ceramic particles migrate with the polyethylene. Further cooling provides a three-dimensional, interpenetrating structure involving a ceramic-enriched polyethylene phase and dibutyl sebacate. The dibutyl sebacate is then extracted using organic solvents such as hexane, and the remaining porous structure is fired to form a reticulated macroporous body. It has been shown by Brezny¹¹ that pore volumes as high as 70% with pore sizes in the 10 to 100- μm range can be achieved using this technique. The pore volume and size is accurately controlled by adjusting the ratio of polyethylene to dibutyl sebacate. The efficacy of using this technique to form a cross-flow, monolithic filter is still being evaluated, including whether the existing mold can be adapted for this purpose.

Air Entrapment. An air entrapment technique applied to gelcasting to retain air bubbles in the gelled slurry.¹² Several samples of CS-50 and mullite have been successfully foamed, bisqued, and sintered. A scanning electron micrograph of a gelcast CS-50 foam is shown in Figure 4. The entrapped air tends to produce closed porosity unless the bubbles are in close enough proximity so that they eventually join. To increase the connectivity between pores, several processing parameters are being studied to obtain more uniform and smaller bubbles. Variations in the amount of foaming agent, mixing temperatures, speed of the mixer, amounts of catalyst and initiator for polymerizing the slurry are being evaluated. Different sintering temperature and atmospheres are also being evaluated to increase the amount of open porosity during sintering. This process is very promising in terms of volume of pores obtained, shape of the pores, and strength of the cells.

Pore Formation by Fugitive Organic Addition. The most effective fugitive pore former was potato starch¹³ obtained from Lyckeby Stärkelsen, Sweden. LoTEC, Inc., was supplied with two separate starches, Mikrollys and Trecomex, with average particle sizes of 20 and 55 μm , respectively. Both Mikrollys and Trecomex starch were added to CS-50 slurry in amounts of 30, 40, and 50 vol%. With the

smaller-sized Mikrolys starch, all but the 50 vol% samples were crack-free through the sintering process. Samples with the larger Trecomex starch exhibited some cracking in the 40 and 50 vol% loading after sintering. Firing temperatures ranged from 1000°C while bisquing to 1500°C during sintering. Scanning electron microscope images of various samples showing high levels of uniform porosity are shown in Figure 5. It can be seen that in the highly porous samples, the porosity is both spherically shaped and uniform throughout the sample, which is desirable for hot-gas filtration.

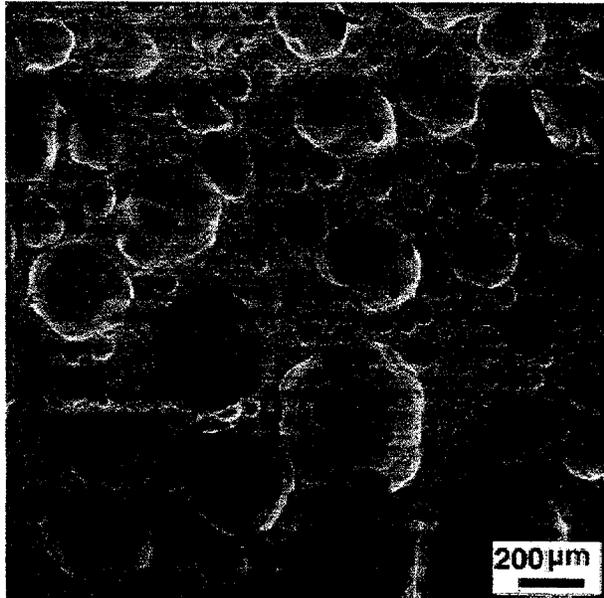


Figure 4: SEM picture of CS-50 gelcast foam

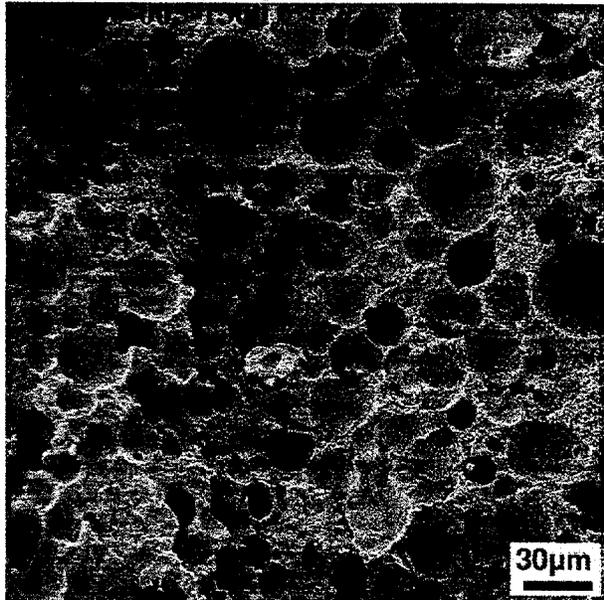


Figure 5: CS-50, + 50 vol% starch, sintered at 1300°C.

CORROSION RESISTANCE

Corrosion/oxidation resistance of the filter components is needed for durability and reliability. SiC and Si₃N₄ are expected to form a surface layer of SiO₂ at high temperatures. This silica layer is responsible for the oxidation resistance of the material. However, any species that reacts with the silica layer will change the transport properties and alter the corrosion resistance of the material^{3,4}. Many Oxide-based materials are inherently stable and are more likely to retain their physical integrity during an alkali attack.²

Recent work at ORNL has shown that CS-50 has a high chemical corrosion resistance to molten salt^{14,15}. Lee et al. have studied the stability of several NZP compositions, including CS-50, in a corrosive environment containing Na₂SO₄ at 1000°C. Their study showed that CS-50 remained structurally intact and did not exhibit significant weight changes after 100 hours of exposure. Current work involves mechanical testing of dense corroded flexure bars of mullite and CS-50 to obtain a more quantitative comparison. Additionally, several mullite compositions have been studied, since it is presumed that SiO₂-rich mullite is more susceptible to corrosion degradation than is alumina-rich. Flexure strength will be measured to evaluate the damage of alkali exposure on the material's strength. The samples are thoroughly cleaned in a solvent such as acetone and dried. Once dry, the specimens are then weighed and dimensionally measured. The sodium sulfate loading is performed by heating the specimens on a hot plate at 90°C and by dispensing drops of saturated Na₂SO₄ solution onto the surface. The samples are left to dry for an hour, weighed, and more sodium sulfate is added until the loading reaches 8 mg/cm². The samples are then heated in a furnace at 1000°C for 100 hr with O₂ at 200 cm³/min flowing over them. The samples are weighed, washed in hot distilled water for two hours to dissolve any residual salt and sodium sulfate, and then weighed again. The identification of the phases present on the sample's surface is performed before and after corrosion by standard x-ray diffraction (XRD) and electron microscopy. The corrosion task will also be extended to include evaluation of filter components tested in the simulated PFBC Facility at Westinghouse for any degradation as well as corrosion.

CONCLUSIONS

Due to excellent thermal shock resistance of the NZP family of ceramics and their promising corrosion resistance, the development of cross-flow hot-gas filters was initiated. During the initial program, the design of a truly monolithic cross-flow filter was improved by the results of a thermo-mechanical analysis. The thickness of the walls was increased, the channels were rounded and the materials selection was reduced to two candidates, CS-50 and mullite. Gelcasting technology was used to fabricate a cross-flow shape without laminations and in a single step.

There have been significant improvements in the porosity levels and uniformity, and more effort will be devoted to further optimize the porosity for hot gas-filters requirements. Future efforts will also involve tailoring the surface porosity to prevent ash penetration and blinding of the material. Evaluation and comparison of the mechanical properties of CS-50 and mullite after corrosion is under way.

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