ORNL/CP-102173

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

Virginie Vaubert and David P. Stinton
Oak Ridge National Laboratory

Chris Barra and Santosh Limaye
LoTEC, Inc

RECEIVED
MAR 25 1999
OSTI

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 $Ca_{0.5}Sr_{0.5}Zr_4P_6O_{24}$ (CS-50) and $2Al_2O_3$-$3SiO_2$ (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 systems[1]. 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 expensive[6]. 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 [$NaZr_2P_3O_{12}$ and its isostructural analogs (e.g., $CaZr_4P_6O_{24}$)] 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, $Ca_{1-x}Sr_xZr_4P_6O_{24}$ (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.

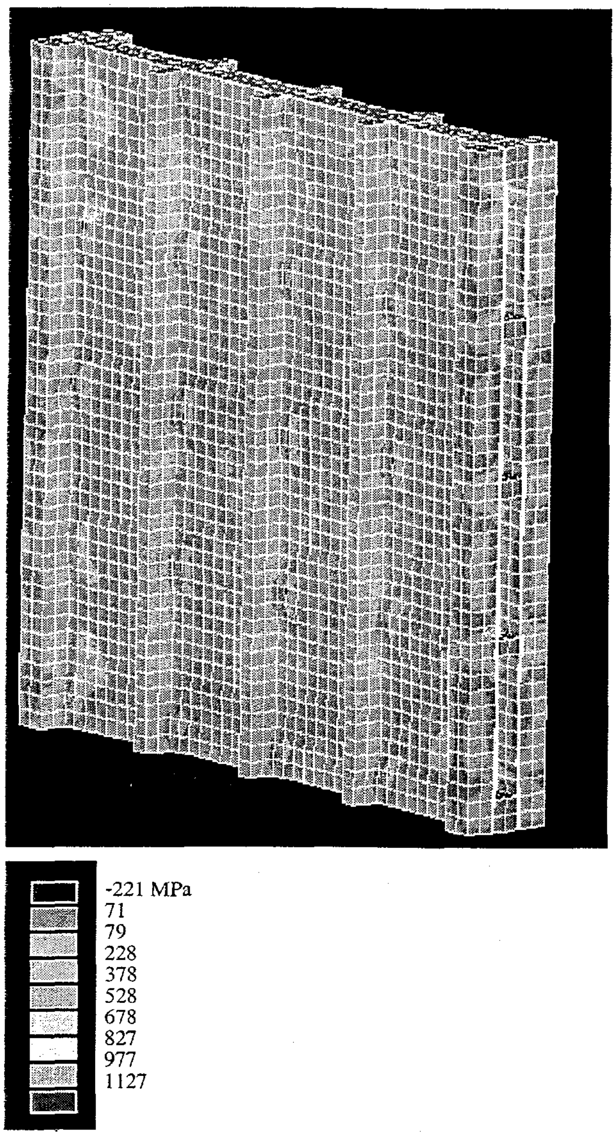

Figure 1: Thermal stresses distribution in alumina

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.

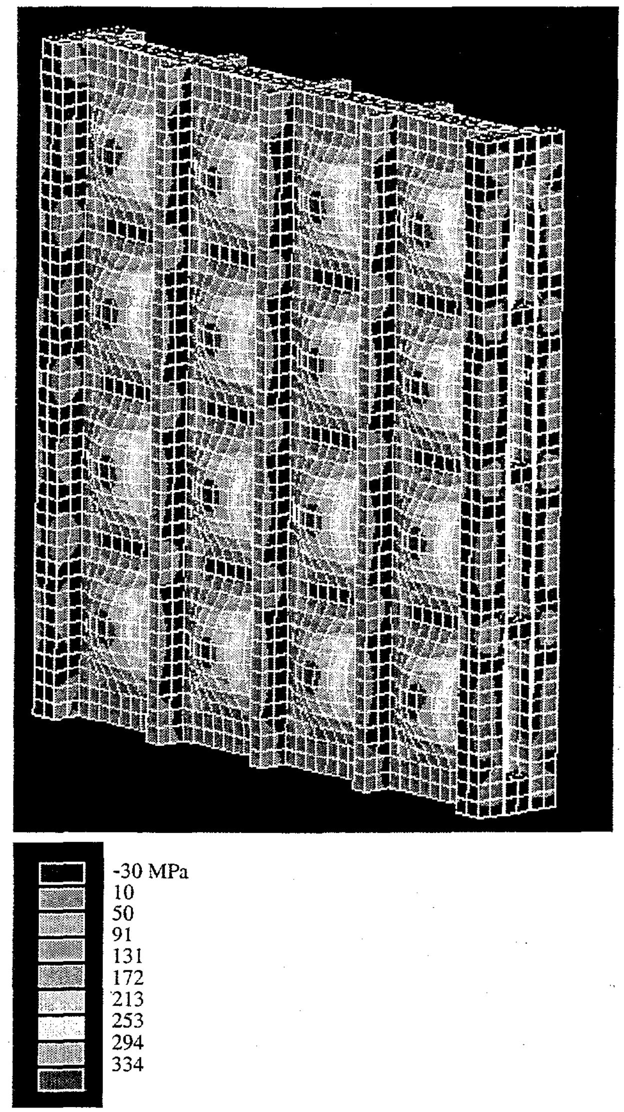

Figure 2: Mechanical stresses in alumina

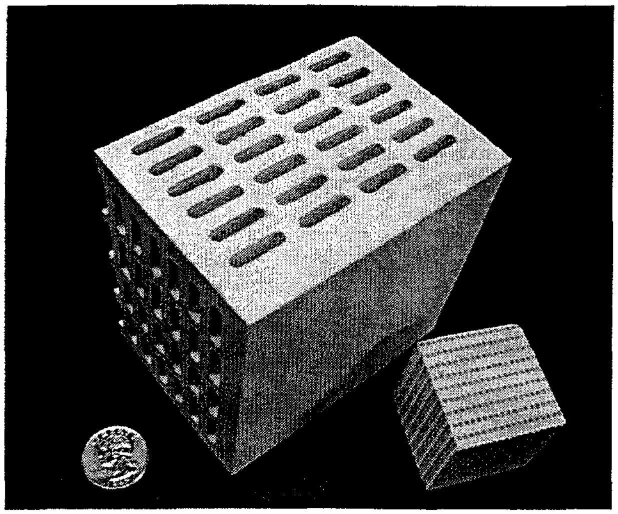

Figure 3: Comparison of first generation (smaller) to current hot gas filter design.

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, 3) fabrication of both simple and complex shapes, 4) 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 Brezny[11] that pore volumes as high as 70% with pore sizes in the 10 to100-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 starch[13] obtained from Lyckeby Stärkelsen, Sweden. LoTEC, Inc., was supplied with two separate starches, Mikrolys and

Trecomex, with average particle sizes of 20 and 55μm, respectively. Both Mikrolys 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.

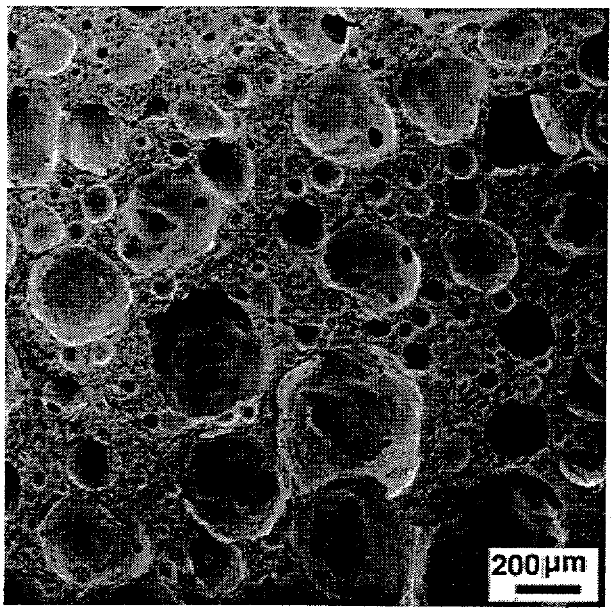

Figure 4: SEM picture of CS-50 gelcast foam

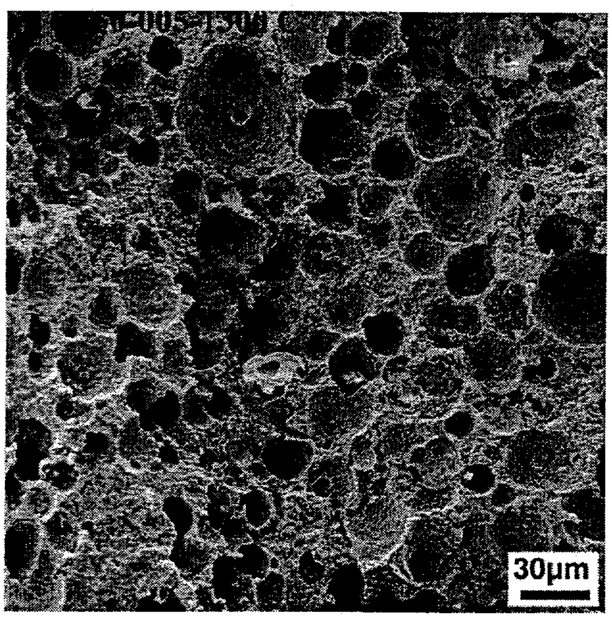

Figure 5: CS-50, + 50 vol% starch, sintered at 1300°C.

CORROSION RESISTANCE

Corrosion/oxidation resistance of the filter components is needed for durability and reliability. SiC and Si_3N_4 are expected to form a surface layer of SiO_2 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 Na_2SO_4 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 SiO_2-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 Na_2SO_4 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/cm^2. The samples are then heated in a furnace at 1000°C for 100 hr with O_2 at 200 cm^3/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.

ACKNOWLEDGMENTS

This work was sponsored by the U.S. Department of Energy SBIR/STTR program.

REFERENCES

[1] Alvin, M. A., "Performance and Stability of Porous Ceramic Candle Filters During PFBC Operation", Materials at High Temperature, Proceedings of the 2nd International Workshop on Corrosion in Advanced Power Plants Mar 3-5, **14**, (3), 355-364, 1997.

[2] Alvin, M. A., Lippert, T. E., and Lane, J. E., "Assessment of Porous Ceramic Materials for Hot Gas Filtration Applications," Ceram. Bull., **70**, (9), 1491-1498, 1991.

[3] Jacobson, N.S., "Corrosion of Silicon-Based Ceramics in Combustion Environments," J. Am. Ceram. Soc., **76**, (1), 3-28, 1993.

[4] Pickrell, G.R., Sun, T., Brown, J. J., "High Temperature Corrosion of SiC and Si_3N_4," Fuel Processing Technology, **44**, 213-236, 1995.

[5] Fox, D.S., Smialek, J. L., "Burner Rig Hot Corrosion of Silicon Carbide and Silicon Nitride," J. Am. Ceram. Soc., **73** (2), 303-311, 1990.

[6] Epstein, M., " Overview of Dust Filtration of Dust from Coal-Derived Reducing Gases at High Temperature, " in: Proc. Second EPRI Worshop on Filtration of Dust From Coal-Derived Reducing and Combustion Gases at High Temperature, R. C. Bedick, M. Epstein, and R. A. Brown, eds., Electric Power Research Institute, Palo Alto, CA, Mar. 11-13, 1992.

[7] Alvin, M. A., Tressler, R. A., Lippert, T. E., and Diaz, E. S., "Evaluation of Ceramic Filter Material, Selection for Application." Proceedings of the Coal-Fired Power Systems -- Advances in IGCC and PFBC Review Meeting, DOE/METC-93/6131, 1993. NTIS DE93000289, National Technical Information Service, Springfield, VA.

[8] Janney, M. A., Omatete, O. O., Walls, C. A., Nunn, S. D., Ogle, R. J., Westmoreland, G, "Development of Low-toxicity Gelcasting Systems", J. Am. Ceram. Soc., **81**, (3), 1998.

[9] Limaye, S. Y., "New Ultra-Low Thermal Expansion, Highly Thermal Shock-Resistant Ceramic," U.S. Pat. No. 5488018, 1989.

[10] Jackson, T. B., Limaye S. Y., and Porter W. D. "The effects of thermal cycling on the physical and mechanical properties of [NZP] ceramics", Ceram. Trans., **52**, 63-79, 1995.

[11] Brezney, R., Spotnitz, R. M., "Method of Making Microcellular Ceramic Bodies," U.S. Patent No. 5,427,721, 1995.

[12] Sepulveda. P., "Gelcasting Foams for Porous Ceramics," Am. Ceram. Soc. Bull., **76**, (10), 61-65, 1997.

[13] Lyckfeldt, O., Ferreira, J. M. F., "Processing of Porous Ceramics by Starch Consolidation," J. Eur. Ceram. Soc., **18**, 131-140, 1998.

[14] Lee, W. Y., Stinton, D. P., and Joslin, D. L., "Interaction of Low-Expansion NZP Ceramics with Na_2SO_4 at 1000 C," J. Am. Ceram. Soc., **79**, (2), 484-86, 1996.

[15] Lee, W.Y., Cooley, K. M., Brendt, C.C., Joslin, D.L., and Stinton, D.P., "High Temperature Chemical Stability of Plasma Sprayed $Ca_{0.5}Sr_{0.5}Zr_4P_6O_{24}$ Coatings on Nicalon/SiC Ceramic Matrix Composites and Ni-Based Superalloy Substrates, J. Am. Ceram. Soc., **79**, (10), 2759-62, 1996.