Advanced Ceramic Hot Gas Filters

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Introduction

Advanced power generation systems based on pressurized bed combustion (PFBC) and integrated gas combined cycle (IGCC) are being developed as alternatives to the current coal-fired boiler systems. Ash minerals in coal end up in the gas stream as flyash. Removal of these fine particles is necessary to comply with environmental regulations, to prevent erosion of gas turbine components, and to minimize build-up of ash particles and other chemically corrosive species. Ceramic filters are being used as particle filtration devices in such advanced power generation systems. Conventional ceramic filters, either candle or the cross-flow type have been plagued by design and/or material limitations.

LoTEC, Inc. and Oak Ridge National Laboratory are jointly developing a new cross flow hot-gas filter that addresses most of the limitations associated with the existing technology. 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 materials make-up. The materials currently being examined viz. Mullite and CS-50 ($Ca_{0.5}Sr_{0.5}Zr_4P_6O_{24}$) have low thermal expansion, good thermal shock resistance, and corrosion resistance. Research is underway to optimize the material and physical make up of the cross flow got-gas filter in an iterative manner using engineering analysis and actual testing. In actual service, the hot gas filter is also subjected to severe thermal shock during back-pulse cleaning of the filtrate ash. Finite element analysis is being employed to assess thermal gradients and thermo-mechanical stresses in the filter during actual operation. The ultimate goal of this research is to develop a robust hot gas filter

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design and a filter material optimized for good chemical stability, high thermal shock resistance, and superior thermo-mechanical properties.

Objectives

The overall primary objective of this effort is to develop a high surface area, cross-flow, hot-gas filter that is resistant to delamination and thermal shock. Some of the specific objectives are:

- Identify specific materials that are thermal shock and corrosion resistant.
- Develop a preliminary finite element analysis model that will serve as a guideline for future efforts.
- Develop fabrication technology for a truly monolithic hot-gas filter.

Approach

In order to address many of the challenges discussed above, LoTEC, Inc. and Oak Ridge National Laboratory have started working together to develop a new materials and design strategy. To date, the efforts were focused on identifying materials, establishing an understanding of the design, and fabricating a monolithic cross-flow component.

Monolithic Cross-Flow Design

The primary advantage of the cross flow design stems from the high-volume specific surface area of the filter. In the past, the cross-flow filters were fabricated by laminating "ribbed" layers and sintering them at high temperatures. Filters fabricated in such a manner tend to delaminate during the high temperature operation. Over the last few years, LoTEC, Inc. has developed a unique fabrication technique that allows fabrication of these cross-flow filters in a single step without using any lamination. Such a process yields a true monolithic cross-flow geometry and is shown in Figure 1. The flexibility of such a process allows the control of various geometric parameters including channel size, shape, wall thickness, and taper. Unlike tubular or laminated cross flow filters, this design flexibility in LoTEC's monolithic filter could accommodate various changes dictated by the analytical work to further reduce the thermo-mechanical stresses, improve the gas flow and reduce the plugging or fouling of the filter. Additionally, the

high-volume specific surface area of the filter would reduce the overall footprint of the filtration system, leading to enormous savings in capital costs. It will be apparent from the following discussions that overall thermal gradients and the associated stresses are also very small for such a filter. The focus of this research will be oriented towards improving this cross flow design such that it will be easy to insert these filters in the existing systems used for IGCC/PFBC hot gas clean-up.

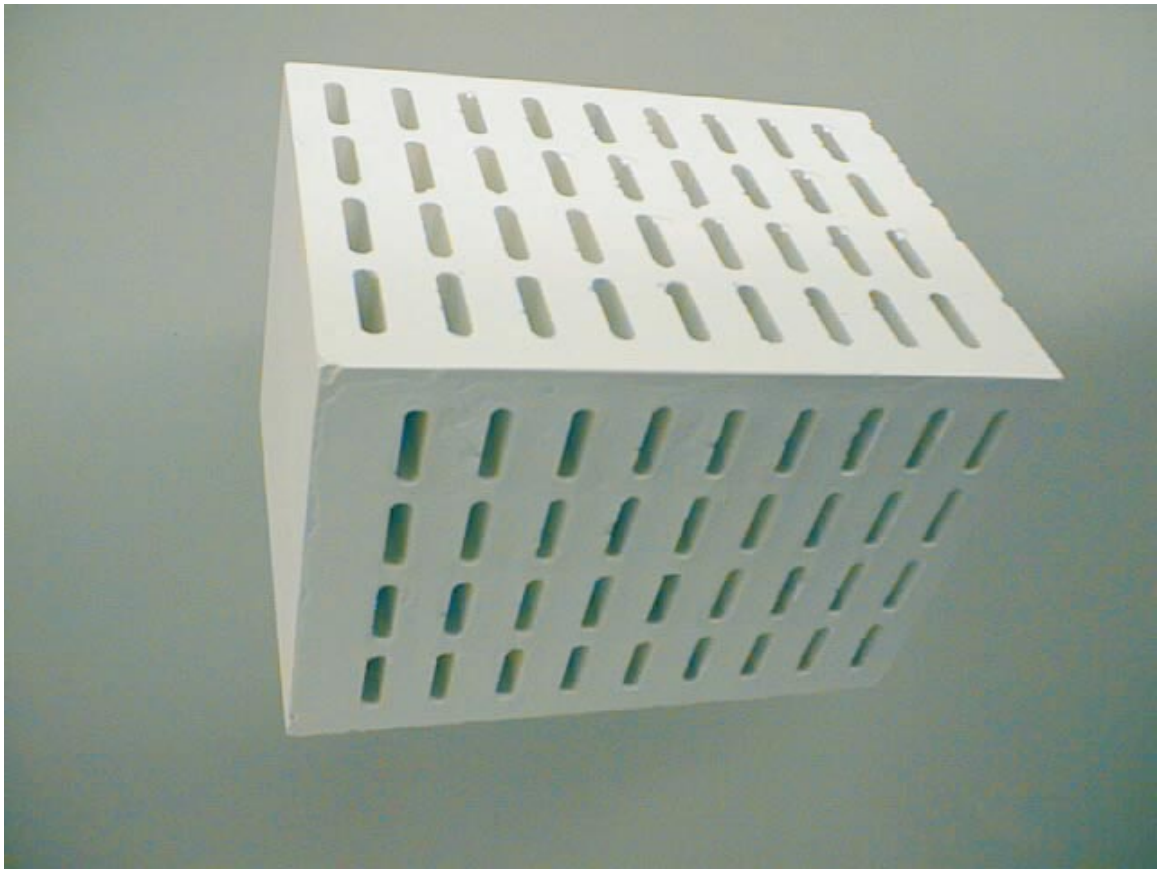


Figure 1: Prototype monolithic cross-flow hot-gas filter.

Alternate Materials

The primary criteria for selecting materials for hot gas filters include: corrosion resistance, thermal shock resistance, high strength and high toughness. There are very few materials that simultaneously meet all these criteria. During the early stages of this work it was decided that the materials which would be examined were mullite and [NZP]. It is well known that alumina-rich mullite exhibits moderate thermal expansion, good

thermal shock resistance, high strength, and high corrosion resistance under hot-gas filter conditions. Mullite is also a prime candidate due to its relatively low economic cost.

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). These materials exhibit very low CTE, and thus very high thermal shock resistance, higher melting temperature and superior thermal insulation capabilities compared to most of the 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. The thermal shock resistance of these materials is also very high. These materials can be quenched from 1400°C without any significant loss of strength.

Fabrication Technology

Fabrication of LoTEC's unique monolithic cross flow filter was possible due to a unique process called gelcasting. LoTEC has licensed this technology from Oak Ridge National Laboratory. 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 provides the rigidity to the slurry, thus transforming it from a liquid slurry form to a semi-rigid gel state. Once the gelation process is complete, the component is dried and sintered. The advantages of the gelcasting process are: 1) it produces strong, machinable green body ceramic, 2) slurries can have high solids loading while maintaining low viscosity, 3) both simple and complex shapes can be fabricated, and 4) it produces near-net shape parts, decreasing machining time and cost. As a result, gelcasting has become an attractive and cost effective solution for fabricating complex shaped components. LoTEC has acquired a license to manufacture various ceramic components using this gelcasting technology.

In order to produce an efficient filter, the permeability must be optimized. By carefully tailoring pore-related variables such as morphology, orientation and volume, this optimization can be achieved. In doing so, however, careful attention must be given to interdependent variables such as strength and modulus to ensure that they are not sacrificed. This balance of variables is crucial for the development of an efficient, stable, and durable hot gas filter system. In order to achieve greater control over these variables,

it is very important to select the appropriate pore forming technique. There are several techniques, including fugitive pore forming, liquid phase separation, air-entrapment, etc., all of which are capable of forming a porous structure. However, appropriate technique selection must be made so that the permeability can be enhanced without sacrificing the strength. For example, a particular technique could produce monodispersed, spherical, equiaxed pores, resulting in a perfectly linear strength/modulus relationship. On the other hand, disk-shaped, or elliptical pores could result in anisotropic properties, which could be desirable providing that the orientation of the pores provides maximum permeability and strength along the required directions.

Project Description

There are three main components of the proposed effort. These are 1) Fabrication Technology, 2) Materials Characterization, and 3) Engineering Analysis. Each of these is explained in detail in the following paragraphs.

Fabrication Technology

Much of the work in this area was devoted to obtaining acceptable porosity characteristics of the ceramic in order to achieve optimum permeability for hot gas filtration. Controlled levels of porosity were incorporated into the ceramic materials via additions of an organic phase that would later be burned off during firing. The resulting fraction of porosity and pore size were determined by factors such as the volume fraction of organic filler added, the size of the organic particles, and the final sintering temperature. Initially, monolithic samples were gelcast to establish a porosity baseline. The baseline samples were then used to determine what changes needed to be made in order to optimize the filtration properties. The three fugitive pore formers examined during phase I research were carbon black, Elvacite™, and potato starch.

Materials Characterization

Corrosion resistance in an alkali environment

Corrosion resistance was measured by the application of a thin film of sodium sulfite or sodium carbonate and heating the coated specimen to a temperature resembling

an actual hot gas filter environment. The specimens were then 1) checked for weight loss, 2) examined for the presence of second phases through x-ray diffraction, and 3) checked for the penetration of sodium compounds into the samples using a scanning electron microscope.

Mechanical Properties

Flexural strength measurements were taken on baseline monolithic samples and compared to porous samples fabricated through the use of fugitive organic additions.

Thermal Properties

The thermal shock resistance of the ceramic materials was measured by water quenching. Flexural bars were tested for flexure strength before and after water quenching from different soaking temperatures. Specimens were also subjected to several thermal cycles, without quenching, and tested for flexure strength.

Engineering Analysis

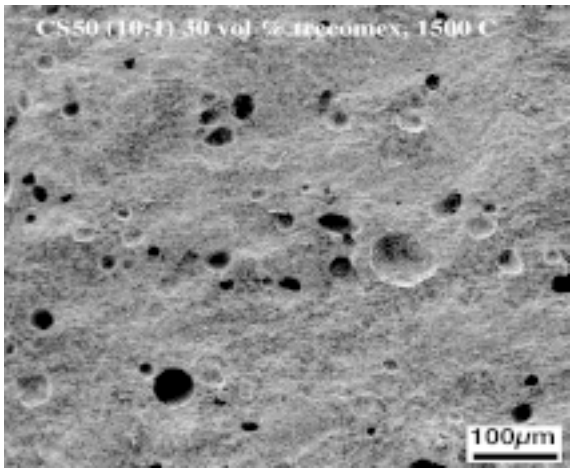
A thermo-mechanical analysis was conducted on a preliminary design of the hot-gas filter using finite element techniques. Results from materials characterization and dimensions of the preliminary filter design were used as inputs into the analysis. The objective of the analysis was to determine how the hot gas filter responded both thermally and mechanically to a series of thermal and mechanical loads. The results of the analysis were used to predict problem areas in the current design and to further dictate the overall design of the cross flow hot gas filter.

Results

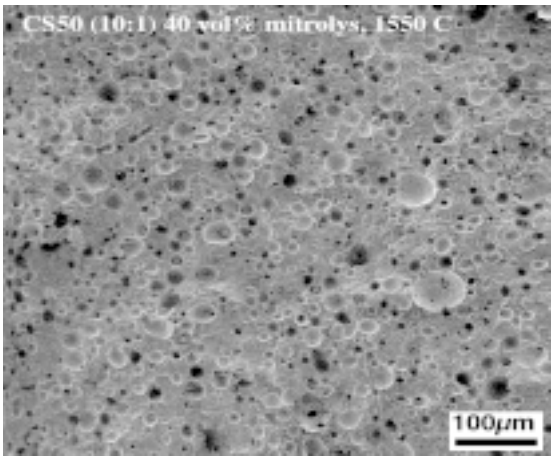
Fabrication Technology Development

The most effective fugitive pore former was potato starch obtained from Lyckeby Stärkelsen, Sweden. LoTEC, Inc. was supplied with two separate starches termed Mikrolys and Trecomex, with average particle sizes of 20μm and 55μm respectively. Both Mikrolys and Trecomex starch were added to CS-50 slurry in amounts of 30, 40, and 50 volume percent. With the smaller sized Mikrolys starch, all but the 50 volume percent samples were crack free through the sintering process. Samples with the larger Trecomex starch presented some cracking in the 40 and 50 volume percentage loading after sintering. Firing temperatures ranged from 1000°C while bisquing to 1500°C

during sintering. Scanning electron microscope images of various samples showing the progress from little or no porosity, to high levels of uniform porosity are shown in Figure 2. From the Figure it can be seen that in the highly porous samples, the porosity is both spherically shaped and uniform throughout the sample, both, which are desirable for hot gas filtration.



(a)



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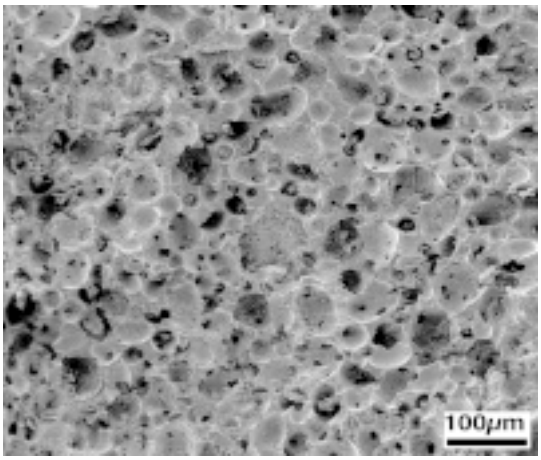


(c)

Figure 2: SEM Micrographs of CS-50 with starch additions showing increased porosity; (a) 30 vol% starch, (b) 40 vol% starch, (c) 50 vol% starch.

Materials Characterization

Corrosion Resistance

All of the samples remained intact in terms of visual evaluation. The weight after testing was in between the initial weight and the weight with sodium sulfate loading. The weight increase might be explained by a slight penetration of sodium into the material. No statistical difference was found between the weight variations of samples with or without porosity.

Determination of the phases present on the coating surface was determined before and after corrosion by standard x-ray diffraction. The tests indicated that no new crystalline phases were created during the corrosion tests.

Characterization of the microstructure was performed using a scanning electron microscope. An energy dispersive x-ray analysis (EDX) was also used to evaluate the penetration depth of sodium compounds into the samples. The microstructure of CS-50 appeared to not be affected by the corrosion test. However, as can be seen in Figure 3, sodium was detected in the samples after exposure and inclusions were visible on the microstructure especially near the sodium exposed surface, and more particularly in the porous samples.

Flexural Strength

The modulus of rupture of porous CS-50 (with 30 vol % mikrolys starch) was measured to verify that the material was strong enough for the hot-gas filter application. The average modulus of rupture was 40.6 MPa with a stdev of 1.6 MPa. The samples failed in two pieces, at a 90° angle in the middle, indicating a low energy type of failure. Also the fracture seemed preferentially initiated from the region of highest stress (middle) rather than by a defect site. Additionally the variation in the flexure strength between the specimens is very small indicating a good uniformity in the mechanical properties of the material. The flexure strength of CS-50 was reduced by half by introducing 30 vol % of porosity. However the modulus of rupture of porous CS-50 is still acceptable according to the finite element model.

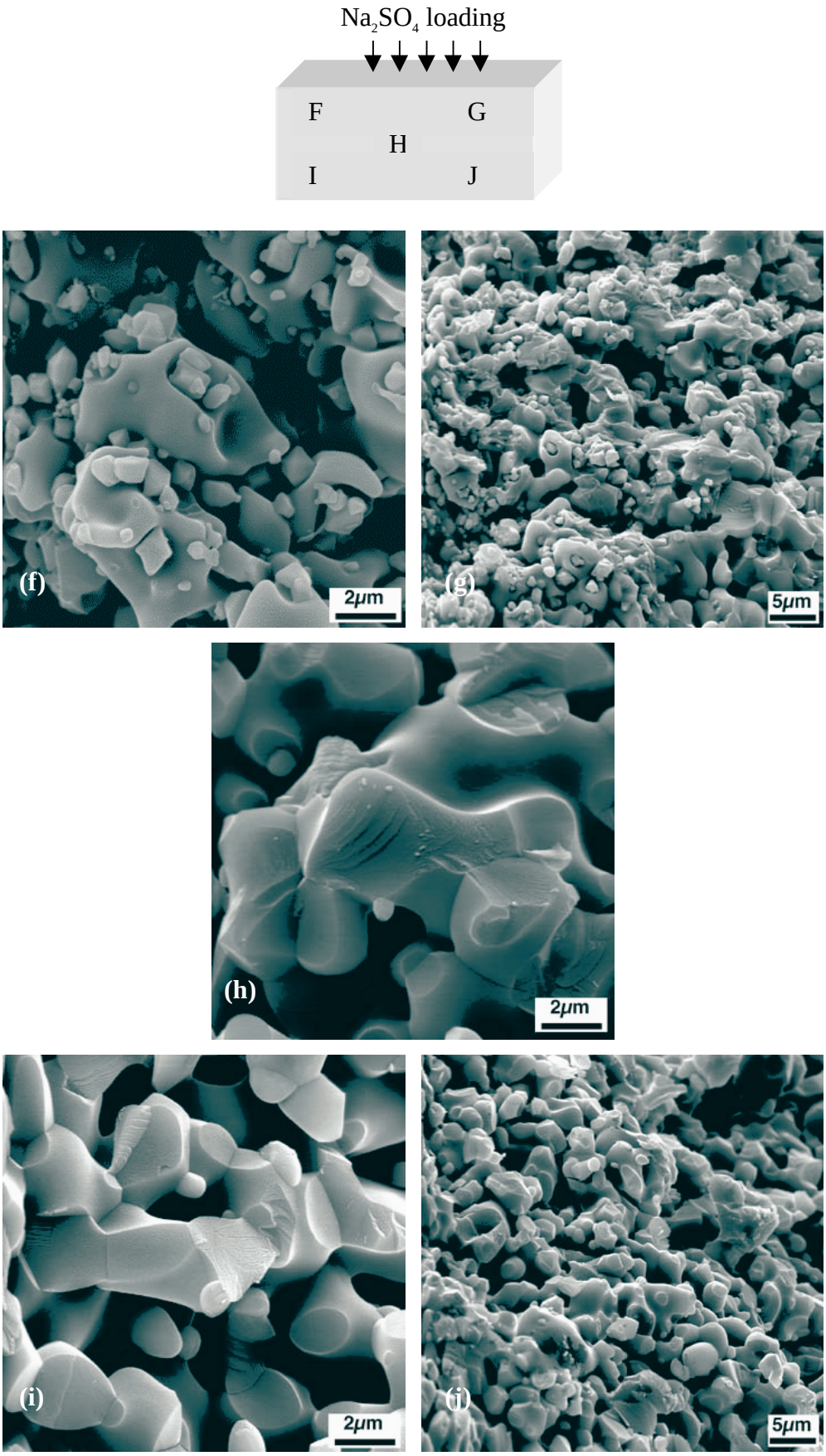


Figure 3: SEM pictures of 10 vol% porous corroded CS-50.

Thermal properties

A thermal shock resistance ($\Delta T_{2/3}$) of 800°C was found for CS-50 medium density and the ultimate thermal shock resistance ((ΔT_f of fracture) was found to be higher than 1200°C. Presented in Figure 4 are the results of thermal cycling for two different soaking temperatures: 600°C and 1200°C. The residual strength after 50 cycles of quenching from 600°C is just below two thirds of the original strength. CS-50 offers a very good resistance to thermal cycling. Additionally, with the thermal shock resistance of porous CS-50 being higher than dense CS-50, the thermal fatigue resistance should also be higher.

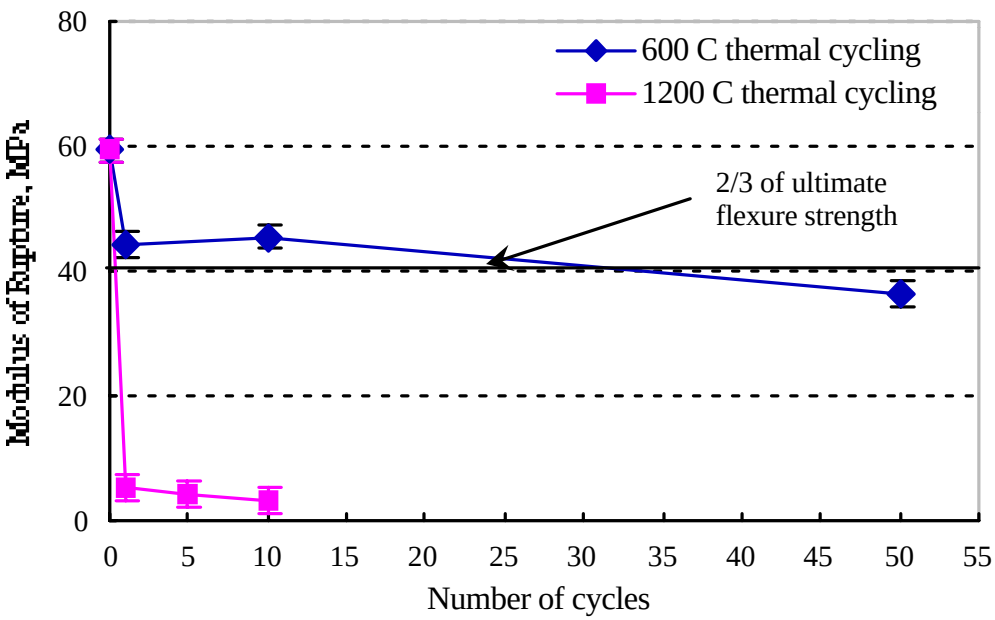


Figure 4: Thermal Cycling of CS-50

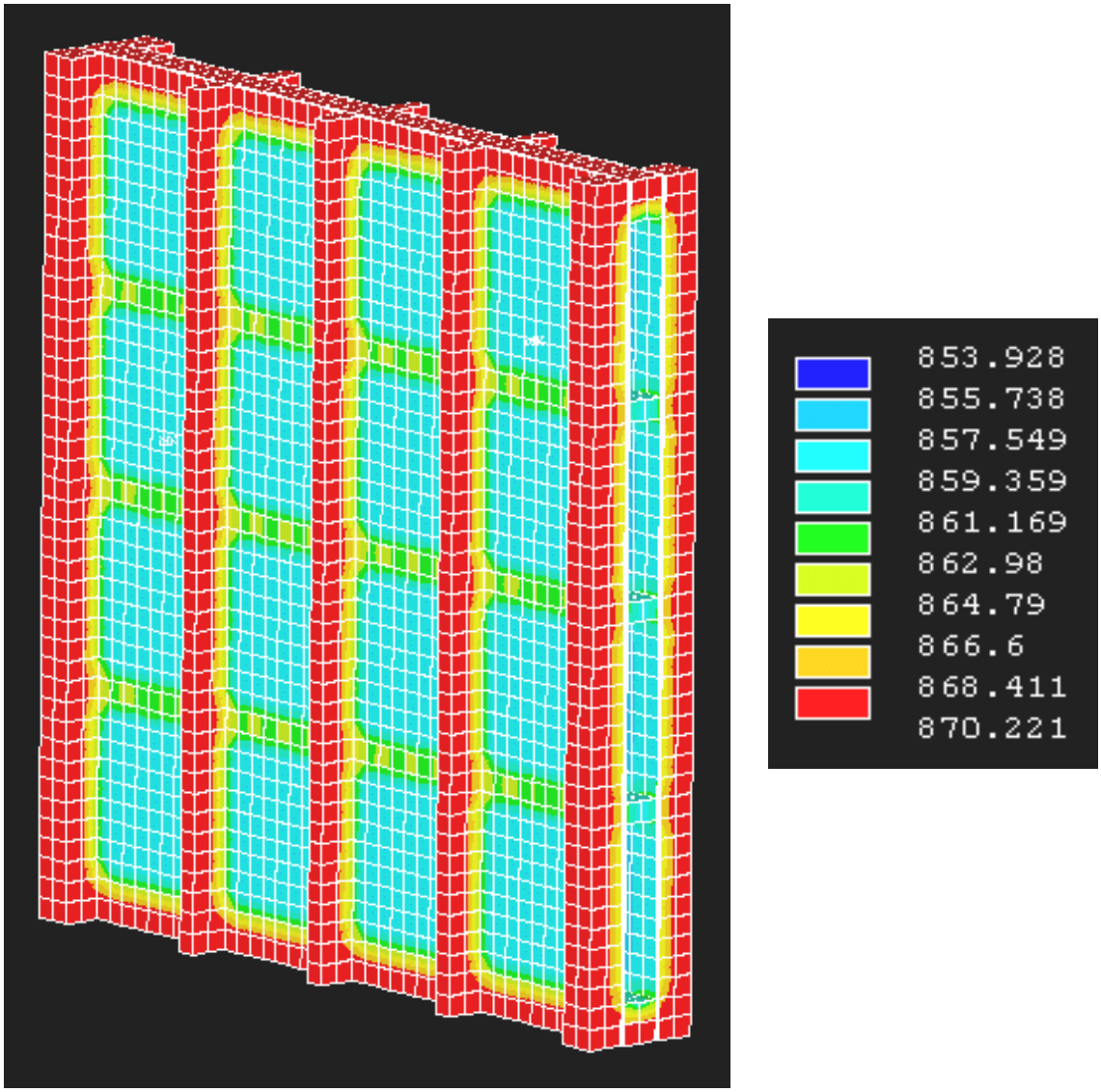
Engineering Analysis

Thermal Modeling

The purpose of the thermal model was to determine the temperature drop of the filter during cold gas backpulsing, and therefore obtain the degree of thermal cycling that the filter would encounter during normal operation. The finite element model consisted of three layers of the cross flow filter. 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 model.. The model examined three thermal loading conditions with cold gas backpulses of: a) 25°C for one second; b) 25°C for five seconds; and c) 100°C for one second.

The finite element analysis graphical result of the change in temperature of the filter due to a cold gas backpulse of 25°C for one second is shown in Figure 5. It can be seen that the minimum temperature of the filter due to the pulse is 854°C, which is corresponds to only a 16°C temperature differential across the filter membrane. The one second 100°C pulse reveals a minimum temperature of 852.6°C, which is slightly lower than the 25°C pulse. This is explained by the slight difference in film coefficients used in the calculations for each temperature. The longer, five second pulse of 25°C shows a minimum temperature of 805°C, corresponding to a temperature differential of a 65°C across the filtration membrane. Cold gas backpulsing conditions in an actual testing environment are on the order of one tenth of one second, rather then one full second, which would lead to an even smaller temperature drop. The temperature differentials calculated here are well within the capabilities of CS-50, which are discussed earlier in the characterization section.

Figure 5: Temperature distribution of hot gas filter after cold gas backpulse of 25°C for one second.



Thermo-Mechanical Stress Modeling

The same finite element model used for determining temperature differentials throughout the filter was also used to determine the thermal and mechanical stresses induced from hot gas filtration. The analysis was performed using CS-50, mullite, and alumina to provide a comparison between candidate hot gas filter materials. Table 2 summarizes the maximum mechanical stress due to the pressure differential between cross flow channels, which is the same for each material, as well as indicates the maximum total combined stress with the addition of thermal stresses which are different for each material.

Stress Description	Maximum Stress (MPa)
Baseline Mechanical Stress	1129
Thermo-Mechanical Stress for CS-50	1144
Thermo-Mechanical Stress for mullite	1201
Thermo-Mechanical Stress for alumina	1484

Table 1: Calculated maximum thermo-mechanical stress during hot gas filtration for different materials using finite element analysis.

It should be noticed that the stresses determined through these analyses are extremely large, and that the thermal stresses make up for a very small percentage of the total for each material. The excessive mechanical stresses are due to two reasons: 1) the distance between cross flow channels was an underestimated 0.4 mm thick; and 2) the channel shape was rectangular, leaving sharp corners for stress concentration. As it turns out, a filtration membrane thickness of 0.4 mm was not possible to fabricate using the gelcasting process. The mechanical stress on the membrane is proportional to the inverse of the square of the thickness, so by increasing the thickness of the membrane the mechanical stress will diminish fairly quickly. By increasing the membrane thickness to 3 mm, the stress is reduced to approximately **20 Mpa**, which is a much more reasonable value.

To diminish stress concentrations in the cross flow channels, all of the corners have been rounded off. By removing the sharp corners there will be another reduction in stress which has yet to be calculated. Overall, by increasing the membrane thickness and rounding off the cross flow channels, the stress level is reduced below the strength values for 70% dense CS-50 (40 Mpa) as described in the characterization section.

Design Optimization and Prototype Fabrication

Overall size of the filters have increased quite significantly. The older filter design had approximate dimensions of 2” x 2” x 2”, while the new filter dimensions are quite larger at 4” x 4” x 6”. The channel shape has been changed from circular to more rectangular in order to increase overall surface area for filtration. The corners of the rectangular shaped channels have been rounded off in order to reduce stress concentration as suggested by finite element analysis.

Along with dimensional changes in the mold, there have also been minor changes in mold materials. The mold walls have been changed from plain aluminum to an anodized aluminum in order to increase surface scratch resistance and to improve mold release characteristics. The pins used to produce the hot gas filter channels were originally made from plain carbon steel. The new pins have been fabricated from D2 tool steel and surface ground on the flat faces in order to assist the release of the pins from the gelcast part. Minor changes have also been made to the mold design to decrease slurry leaking.

Application

With the heightened concerns regarding CO_2 emissions and power generation-related pollution, the need for clean technologies has escalated, and the use of hot gas filters has become critical. If successful, this development will lead to a hot-gas filtration technology which operates at a higher efficiency, producing lower emissions while requiring a lower capital investment and smaller footprint. With the advent of integrated systems, successful entrapment of particulate matter will accommodate the necessary fuel flexibility necessary for technologies such as solid oxide fuel cells and gas turbines. This technology can also be extended to various other industrial emissions including particulate removal from industrial smokestacks and particulate traps for heavy-duty vehicles.

Future Activities

Future activities include more involved engineering analysis, further examination of new materials including mullite and high-purity alumina. Fabrication developments will include the use of low-pressure injection molding to produce filter forms. Alternate pore forming techniques will be of utmost importance in order to increase permeability values. High temperature, high pressure filter testing will be performed on prototype filters at Westinghouse Electric Corporation as the actual components become available for further studies.

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