

**DURABILITY TESTING OF CERAMIC CANDLE FILTERS IN
PRESSURIZED-FLUIDIZED BED COMBUSTION ENVIRONMENTS**

by

Karen Rose Valentino

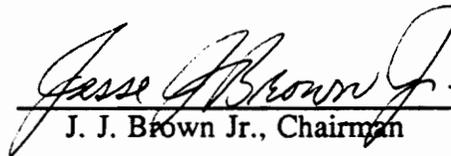
Thesis submitted to the Faculty of the
Virginia Polytechnic Institute and State University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

in

Material Science and Engineering

APPROVED:


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February, 1993

Blacksburg, Virginia

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(ABSTRACT)

Ceramic candle filters were subjected to 500 hour high temperature/ high pressure (HTHP) exposure tests to examine their extended durability in simulated coal pressurized-fluidized bed combustion (PFBC) environments. The candle filter materials analyzed included two SiC filters, one with clay binder and one with a minimal amount of clay binder, a cordierite filter, a mullite candle filter and an aluminosilicate refractory concrete filter. Exposure testing conditions included a range of temperature from 700-850°C and a pressure ranging from 1.7-1.8 MPa. The HTHP tests included exposing the ceramic filter materials to steam and steam-alkali environments. The presence of alkali significantly accelerated the deterioration of the filters. The results of the analysis show that significant crushing strength losses were exhibited by the SiC filters after exposure to HTHP alkali-steam conditions at temperatures as low as 700°C. The expansive and destructive cristobalite phase developed in the SiC filters after most of the treatments. The cordierite candle filter showed a decrease in crushing strength associated with grain growth after each high temperature exposure but few other signs of deterioration were detected. The mullite candle filter and the refractory concrete candle filter showed the least amount of change in crushing strength and overall the most candle stability.

ACKNOWLEDGEMENTS

I would like to express much appreciation to Dr. Jesse Brown for giving me the opportunity to work with him and having confidence in my ability to be a graduate student while already being a wife and mother.

I am deeply indebted to Mrs. Nancy Brown for her guidance, assistance, immense patience and understanding through out this project. I also thank my thesis committee members, Dr. R. S. Gordon and Dr. R. D. Law, for critical comments and review of this manuscript.

I am very grateful for the assistance of Min Kang as she painstakingly collected data, cut samples and helped so much in many other ways. I am also very grateful for the help of Ron Dodd who devoted many hours late into the night to keep the experimental apparatus running.

I am thankful for the friendship of my office mates Shannon Namboodri, Lauren Shea and Diane Raque who all set an appreciated example of diligent and thoughtful work.

I would like to express thanks to my father and mother who all my life have stressed and sacrificed much for education.

I am immensely grateful to my wonderful husband, Dave, for his enthusiasm for my project, confidence in me and especially for his continuous support and love. I thank my dear sons, Joshua and Benjamin, for the joyful reprieves from graduate work that they have brought me.

Finally, I give many thanks to my God in whom I have been able to accomplish this task.

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INTRODUCTION

Coal is the most abundant natural energy resource in the United States. Research efforts have concentrated on developing highly efficient and clean coal conversion technology in order to take advantage of our large coal reserves. New coal conversion technology such as pressurized-fluidized bed combustion (PFBC) utilize energy produced during the combustion of coal by generating energy in a high temperature gas turbine, as well as by the traditional method of energy production by a steam generated turbine. The successful operation of the gas turbine requires that particulates such as dust and other contaminants produced during coal combustion be removed before the hot gas enters the turbine in order to protect the turbine from premature failure due to erosion and corrosion. The conventional method of hot gas particulate removal, a cyclone, is not able to remove submicrometer size particles with a high efficiency and further cleaning would be required down gas stream in order to meet environmental standards.

Ceramic candle filters offer a highly efficient particulate removal technology that is capable of operating at the high temperature (590-1000°C) and pressure (150-450 psig) conditions present in combined cycle power generation plants such as a PFBC. The candle filters are also required to be resistant to the harsh and chemically corrosive atmosphere present in a PFBC. Steam and alkali phases have been identified as the chemical factors most threatening to the long-term durability of the candle filters (Sadler et al.,1984; Gentile et al.,1987; Brown et al.,1988). The materials selected for the candle filters need to exhibit temperature and pressure resistance, strength, and chemical stability to survive in the environments they will be subjected to in a PFBC.

An analysis of various candle filter materials after exposure to high-temperature and high-pressure (HTHP) steam and steam-alkali environments was undertaken in this

research in order to evaluate which ceramic material may be best suited for application in PFBC plants.

LITERATURE SURVEY

Coal conversion processes such as pressurized fluidized-bed combustion (PFBC) and integrated gasification combined cycle (IGCC) are ideal for the utilization of ceramic filters to clean hot gases. Particulates consisting mostly of ash fines and spent sorbent need to be removed before the hot gas stream reaches the turbine in order to protect the turbine components from abrasion and corrosion (Brown et al.,1991). Plant efficiency is improved because the gas does not need to be cooled before it enters the gas turbine.

Particulate removal is also necessary in order to meet the strict environmental regulation standards which require the dramatic reduction of all particulates including respirable matter (15 micrometers in size and less) from coal exhaust streams (New Source Performance Standards). Zievers et al. (1991) compared the efficiency of eight current particulate removal systems such as cyclones, scrubbers, electrostatic precipitators (ESPs) and porous ceramic candle filters (Figure 1). The ceramic candle filters are distinctly different from other technologies in that they have a collection efficiency range of 99.5-99.9% and possess the capacity of regularly filtering submicrometer size particles. In addition, ceramic candle filters are able to operate at very high temperatures whereas scrubbers and ESPs are not. Cyclones, the hot gas cleanup method currently used, are not able to meet necessary efficiency standards (Oakey and Reed,1987). Of the new hot gas cleanup technologies being developed, candle filters are considered to have the most promising characteristics (Reed,1985; Oakey and Reed, 1987).

Materials need to have a low thermal expansion and be resistant to high temperatures and chemical corrosion to be considered for filtering applications in coal conversion plants. Current materials under consideration are silicon carbide, silicon nitride, chemically infiltrated silicon carbide, and aluminosilicates such as fireclay, mullite,

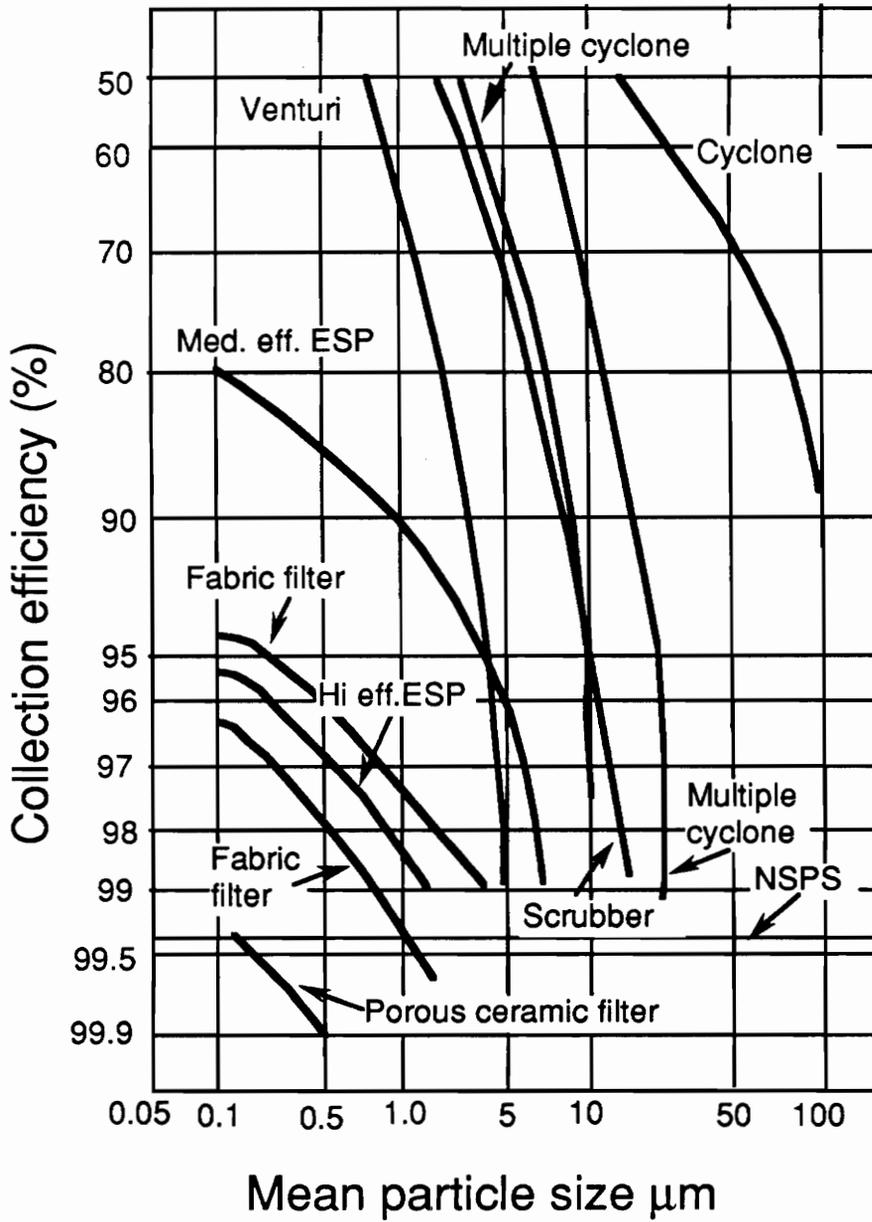


Figure 1. Graph of collection efficiency for various filter materials used in coal conversion processes.

cordierite, aluminosilicate fibers, aluminum titanate and a refractory concrete composed of calcium aluminate cement and mullite aggregate (Brown et al., 1991; Holcombe et al., 1991). Commercially manufactured candle filters are made of SiC and mullite and the very similar tube filter is made of cordierite. Research is under way to produce commercially viable candle filters out of aluminosilicates including mixtures of cordierite, mullite and alumina (Alvin et al., 1991).

Candle filters are flanged porous tubes that are closed at one end and commonly 1-1.5 meters in length. Figure 2 schematically shows a typical candle filter and how it is situated in a cleaning module. The candle filters are suspended from a metal tube sheet by the flange. The tube sheet acts as both a support for the candle filters and as a physical barrier between the incoming dirty gas and the exiting clean gas. The candle filters are covered on the surface with a thin membrane with a mean pore size of 25-30 micrometers that primarily performs the filtering. The bulk of the material is aggregate with a mean pore size of 125 μm that acts as a structural support for the filtering membrane (Sheppard, 1991; Zievers et al., 1991). As the unprocessed gas passes through the cleaning module the gas is able to pass through the micrometer size pores while particles are trapped on the surface. Experiments performed with 4 micrometer dust showed that particle impregnation takes place in only the first 10-15% of wall thickness (Zievers et al., 1991). During the filtering process a 'cake' subsequently builds up on the filters' outer surface which is periodically removed by a pulse of air that is forced down the center of the tube in the opposite direction as gas flow. Although particle impregnation does not severely block the filtering ability of the candle, the permeability of the unused filter is never fully recovered even after cleaning (Stringer and Leitch, 1991). Removal of the particulates during cleaning will usually cause a fracture in the cake itself and not at the candle surface which helps prevent reexposure of the filter surface to dirty gas and further impregnation of particles. The remaining cake that

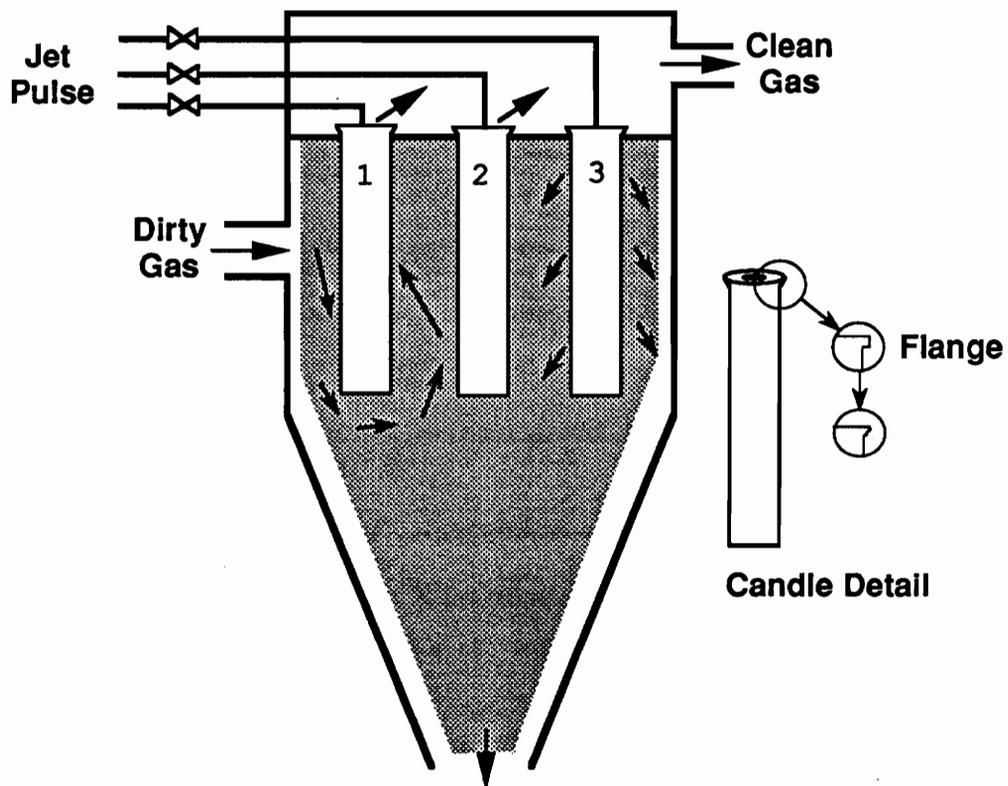


Figure 2. Schematic of a candle filter situated in a cleaning module.

is adhered to the filter after cleaning has been observed to be up to 2 mm thick in places and will serve along with the candle as the filtering mechanism (Stringer and Leitch, 1991; Oakey and Reed, 1990).

The high temperature thermal, mechanical and chemical stability of candle filters are essential characteristics that still need to be determined. Figure 3 schematically represents the sources of stress on a candle filter. Candle filters experience internal stresses due to internal thermal gradients during startup and shutdown of the system, but the most damaging thermal gradients that the filter experiences is during reverse pulse cleaning where room temperature air is forced down the center of the filter which may be operating at temperatures between 800-1000°C. Microcracks that develop in the inner tube region of the filter are attributed to thermal shock produced during reverse pulse cleaning. These microcracks are considered to contribute to the overall weakening of the candle filters by thermal fatigue (Stringer and Leitch, 1991).

Candle filters experience mechanical stresses from installation and handling, the weight of the candle and the accumulated dust, differential pressure across the filter, and through system vibrations and upsets (Sawyer, 1989). Candle filter experience to date shows that the primary cause of filter failure in short term exposures (<1000 hours) is from mechanical stresses such as inadequacies in the present filter mounting and sealing design (Stringer and Leitch, 1991) and from thermal stresses such as an accidental injection of water before the filter module (Holcombe et al., 1991). The candle filter is particularly vulnerable at the flanged region, where filter breaks have frequently occurred (Stringer and Leitch, 1991; Sawyer et al, 1990).

The unknown, long-term chemical stability of candle filters is presently the most limiting factor to their immediate application. The projected chemical corrosion response of ceramic filter materials is given by Sheppard (1991) in Table 1. The evaluation of the

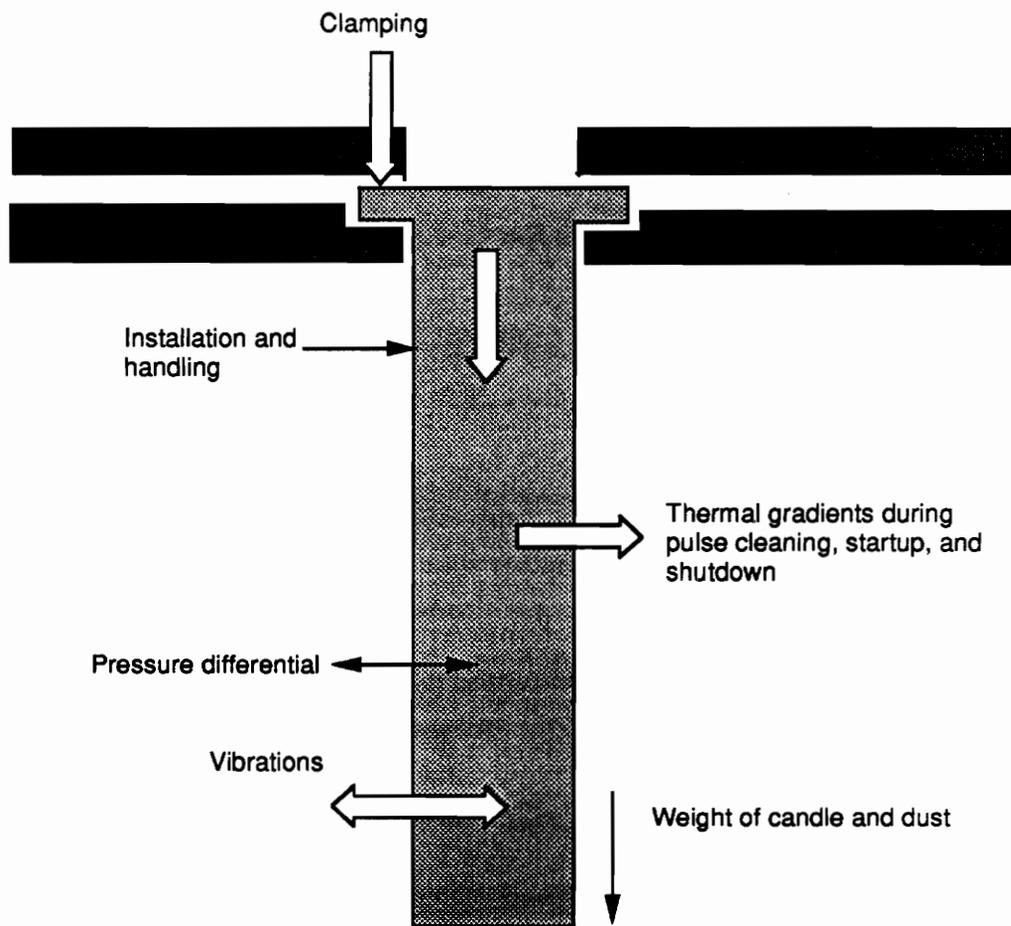


Figure 3. Schematic diagram of the various causes of stress on a candle filter during operation (Sawyer, 1989).

Table 1. Response of ceramic material to processing conditions.

Process	Alumina/ mullite	Cordierite	Aluminosilicate foam or fiber	Cordierite- Si ₃ N ₄	Reaction- bonded Si ₃ N ₄	Silicon carbide/ fireclay	CVD- SiC
Fixed-bed gasification (590°C)	None						
Fluid-bed gasification (700°C)	Limited glassy grain boundary phase reactions					-Reaction with clay binderphase	
Entrained-bed gasification (870°C)	-React with grain boundary glass phases -Dissolution of adjacent grains -Loss of material strength		-Reaction with uncoated glass fibers	-Reaction with grain boundary glass phases -MgSiAlON stabilizes grain/glass interface		-Reaction with clay binderphase -Dissolution of binder and adjacent grains -Loss of material strength	
Direct coal-fired turbine (980°C)					-Reaction with SiO ₂ Si ₂ ON ₂ layer	-Reaction with SiO ₂ layer -Reaction with clay binder phase	-Reaction with SiO ₂ layer
Pressurized fluidized bed combustion (870°)					-Small pore closure	-Dissolution of binder and adjacent grains -Loss of material strength	-Small pore closure

corrosion on the materials has been broken up into an evaluation of aluminosilicate materials and an evaluation of SiC materials.

Aluminosilicate Corrosion

Alkali, present in all coals in amounts commonly in the range of 20-100ppm, is released during coal gasification and combustion and has been recognized as a key element in the failure of aluminosilicate refractory linings (Sadler et al.,1984; Brown et al.,1988). Table 2 provides typical gas compositions for an IGCC and a PFBC. The alkali corrosion process takes place in a series of reactions, often expansive, which degrade the refractory. Farris et al. (1973) concluded that damage of aluminous refractories was primarily caused by the formation of alkali compounds that produced volume expansion and consequent refractory spalling and disruption. In an extreme case a mullite refractory lining failed after 125 hours of exposure to NaOH at $1000\pm 200^{\circ}\text{C}$ (Kennedy, 1981).

The presence of the alkali lowers the liquidus temperature allowing for localized melting to occur where the alkali has penetrated the filter (Gentile et al., 1987). Unlike alkali solids which remain on the filters surface, alkali vapors and liquid alkali have the ability to penetrate deep into the porous filter causing undesirable compounds to form inside the filter which increases internal stresses (Gentile et al., 1987). Entrained-bed gasification, direct coal fired turbine and pressurized fluidized bed combustion temperatures often operate in the high temperature ranges where vapor phase Na compounds exist. An increase in porosity produces an increase in the rate of corrosion as alkali vapors are able to penetrate deeply into the candle filter. The depth of alkali penetration is dependent on the permeability which is characterized by the size, number and interconnectivity of the pores (Brown, et al.,1988).

Table 2. Typical gas compositions for PFBC and IGCC (after Oakey and Reed, 1987).

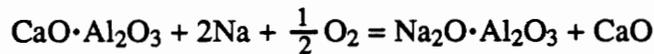
Component	Composition	
	PFBC	IGCC
Nitrogen	74.9 vol %	57.8 vol %
Carbon dioxide	13.0 vol %	8.9 vol %
Carbon monoxide	100 VPM	17.9 vol %
Hydrogen	—	10.3 vol %
Oxygen	7 vol %	—
Sulphur dioxide	200VPM	—
Sulphur trioxide	5 VPM	—
Hydrogen sulphide	—	250 VPM
Hydrogen chloride	50-100 VPM	500 VPM
Nitrogen oxides (NOx)	200 VPM	—
Water	5 vol %	3.3 vol %
Alkali metals (total Na + K)	2 PPM (wt)	10 PPM (wt)
Dust loading after cyclonic cleaning	200 PPM (wt)	2000 PPM (wt)
Dust composition Ash	99%	30%
Carbon	1%	70%
Dust size, d50	3 micrometers	6 micrometers

VPM- parts per million by volume

A likely reaction to occur between the alkali and a mullite refractory is given by,



which Kennedy (1981) estimates to have around a 30% volume expansion associated with it. Gentile et al. (1987) gives the equation,



to describe the reaction between calcium aluminate cement and sodium, and estimates the formation of the sodium aluminate to have a 47% volume expansion. Lee (1988) observed volume expansion in an alumina brick that when exposed to moderate amounts of Na_2O produced beta- Al_2O_3 with mild amounts of volume expansion, however; with increasing amounts of Na_2O irreversible phases of $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3$ were formed causing severe, irreversible volume expansion. Due to pure alumina's poor alkali resistance as well as its high thermal shock behavior it is not adequate as a filter material alone, however; attention to the response of alumina in alkali is valid since it is frequently considered as a component material for these applications (Brown et al., 1991).

Cordierite ($\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_8$) upon firing will form mullite, spinels, corundum and glass. The glass is stable if temperatures are below 1120°C (Alvin et al., 1991). Glass in general is a damaging element of a filter composition because it absorbs alkali readily and increases thermal expansion and fluidity (Brown et al., 1991). Glass commonly used in candle filter binder needs to be recrystallized to minimize thermally expanding phases (Brown et al., 1991). Crystalline mullite (70% Al_2O_3 , 30% SiO_2), with less free silica, is

expected to have slightly better alkali resistance than compositional mullite because the severity of alkali attack increases with an increase in the amount of silica present in an aluminosilicate material (Brown et al., 1988).

The concentration of sodium in the coal plays an important part in determining the severity of the degradation of these filters. The reactivity of aluminosilicate phases with alkali and the associated large volume expansion, is the largest threat to the life of this type of candle filter as prolonged exposure increases the propensity for these reactions to occur.

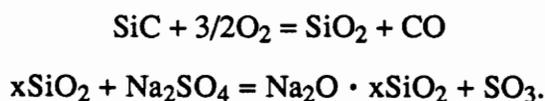
Reactions of aluminosilicate filters in steam environments can be anticipated by the response of refractory materials in similar conditions. Sadler et al. (1984) exposed aluminosilicate refractories (ranging in Al_2O_3 content from 50-90%) to steam partial pressures up to 7 MPa and at temperatures up to 1400°C. The effects of steam below 1000°C were insignificant and caused only minor amounts of silica loss. At temperatures above 1000°C and high steam partial pressures, steam-induced silica loss was slightly enhanced and a maximum weight loss of 3% was observed. The aluminosilicate filters being already composed of stable oxide phases, are less likely to undergo extensive chemical changes with exposure to steam (Alvin, 1991). Evidence of vapor-phase silica migration was seen in the loss of silica in the high-silica refractories and a gain in silica in the low-silica refractories. Lower alumina refractories (40-60 % Al_2O_3) even showed increases in strength after exposure to steam due to the transition from a bulk composition of quartz and kyanite to one of mullite (Sadler et al., 1984). Although the aluminosilicate refractories are relatively resistant to steam degradation, the steam can work as a transport for destructive alkali compounds.

Exposure of mullite/alumina materials to alkali gas species at temperatures of 870°C and 1100°C at Westinghouse, indicates this material has the ability to retain its physical and structural integrity and remains relatively chemically inert (Alvin, 1991). An important

consideration, however, is whether the candle filters will remain resistant to chemical deterioration after prolonged exposure.

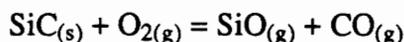
SiC Corrosion

The aluminosilicate binder, often kaolinite clay, in the SiC filters will tend to form the same expansive reaction products as seen in the aluminosilicate filters described previously. The SiC candle filters are coated on the outside with a layer of silica (usually cristobalite) or aluminosilicate which acts as a protective boundary between the SiC grains and oxidizing gases. Alkali corrosion of the protective SiO₂ phase covering the SiC was found to take place at temperatures as low as 877°C, where Fox et al. (1986) noted the formation of a glassy reaction product that contained bubbles. Under the sodium silicate-glass phase, the SiC refractory was found to have large pores that were attributed to the oxidation of the SiC after the protective coating was corroded. Sawyer et al. (1990) proposed the following reactions to describe the corrosion of the SiO₂ coating and the oxidation of SiC:

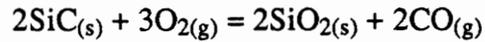


Estimates of up to a 50% loss in strength are proposed for this corrosion process (Smialek et al., 1987), making the long-term viability of SiC candle filters questionable.

Conditions with low oxygen partial pressures exhibit active oxidation where the reaction,



is favorable . The SiC material shows a weight loss due to the formation of the gaseous reaction products. At higher partial pressures, passive oxidation takes place and is described by the reaction,



where a protective scale of SiO₂(s) is formed at the reaction surface of the SiC and acts as an inhibitor to further oxidation (Easler, 1985). Higher partial pressures of oxygen would seem to be better since passive oxidation would occur and a SiO₂ scale would form. However, the corrosion of the scale by alkali would reexpose the SiC to further high concentrations of oxygen and subsequent oxidation.

Tressler et al. (1985) stated that the presence of steam greatly accelerates the oxidation rates of SiC when compared to the oxidation rates of SiC by O₂. The authors compared the relationship between temperature and the parabolic rate constants of SiC in O₂ , in 3% H₂O in O₂ and in steam atmospheres and demonstrated the accelerating oxidation effect of water vapor which exhibits a parabolic rate constant 20 times greater than is seen for dry O₂ . The steam has two important effects in that it permeates the material, dissociates and acts as an oxidizer. The incorporation of OH- into the SiO₂ phase cause a reduction in viscosity and the acceleration of the incorporation of molecular oxygen (Tressler et al., 1985).

Plant Exposure Tests

Candle filters have only recently been considered for hot gas cleaning in coal gasifiers and combustion plants. Therefore, a comparison of candle filter performance can not be made by a correlation between previous less severe applications and the very severe conditions of a ICGG and a PFBC. Filter testing in pilot cleaning systems has taken

place on a limited basis. Table 3 lists a summation of candle filter field experience to date. Three significant tests of the clay-bonded SiC candle filter are the Grimethorpe, the KRW and the Solar Turbine exposures. The longest exposure of the SiC filter was at the Grimethorpe pressurized fluidized bed combustor where the pressure conditions ranged from 8-10.5 atm and temperature ranged from 850-900°C. The test lasted for a total of 860 hours with 790 hours at the designated process conditions of 850°C and 145 psi (Alvin et al., 1991). Of the 130 candle filters used, 5 candles failed from excessive mechanical stresses produced by the lifting and falling of the candle against the tube sheet due to the existence of a large pressure differential. No evidence of deterioration was detected on the surface of the filters. However, a pervasive weakening of the entire filter was observed with the center of the filter showing a slightly lower strength than the outside. Microcracks found at the interface between the binder and the aggregate may have been caused by thermal shock produced during reverse pulse cleaning. The microcracks are thought to then contribute to the overall weakening of the candles by thermal fatigue (Stringer and Leitch, 1991). Few signs of chemical attack were detected. Having achieved high cleaning efficiency, the general conclusions about the candle filter performance at Grimethorpe were positive (Stringer and Leitch, 1991).

The Kellogg Rust-Westinghouse (KRW) gasifier facility tested 33 clay-bonded SiC candle filters for 653 hours at designated process conditions. 13 filter failures occurred from thermal shock when the water quenching system failed causing the hot filters to be exposed to water. Seven filters failed from the mechanical shock of a slug of material impacting the filter elements and 1 filter failed from excessive compressive forces on the flanged region after approximately 650 hours of operation (Holcombe et al., 1991).

Table 3. Candle filter field experience (modified after Alvin et al., 1991).

CRE (U.K.)	1984-85	Filter Coupons	
Grimethorpe	1987	Clay-bound SiC filters	130 Schumacher Dia Schumalith (1.5 m) filter element capacity 4 candles broke after 800 h of operation; solenoid valve jammed; pulse reservoir opened 1 candle broke after 300 h of operation Ca/S crystallites found on internal surface of candle-surface interactions only
KRW	1985-87	Clay-bound SiC filters	33 Schumacher Dia Schumalith (1 m) filter element capacity 13 elements failed after 6 h operation due to water quench system failure; thermal shock induced by water droplet impact 7 elements failed after 50 h of operation due to plug formation in cyclone upstream of filter vessel; momentum impact
DOE-METC	On-going	Clay-bound SiC filters	Pressurized entrained combustor at METC using NYU reinjected particles Laycer Industrial Filter and Pump Candles
Solar Turbine	Early 1990	Clay-bound SiC filters	14 filters- Laycer and Schumacher Dia Schumalith candles
IGT	1983-85	Clay-bound SiC filters	~150 h on Industrial Filter and Pump Candles
Calvert			700 operational hours 2 tiers; 6 candles/ tier
Aachen		Clay-bound SiC	6 candles 5800 h (3600 air/2200 gas)
Deutsch Babcock		Clay-bound SiC	2 candles operated in parallel 3500 cycles at 700°C
Rheinbraun-Berrenrath		Clay-bound SiC	9 filter elements
Rheinbraun-Wesselery		Clay-bound SiC	90 filter elements
Electric Power Development Corp.		Clay-bound SiC and cordierite	
Ahstorm-Finland		Cordierite	
Internal Energy Agency /ABB Carbon		Cordierite and others	

Solar Turbines' direct coal fired turbine facility tested 14 filters at 1000°C and 130 psi. After 6 hours of operation at 600°C, 2 candle failed from flaws in the filters created during manufacturing (Holcombe et al.,1991).

Exposures of the cordierite filter has taken place in 23 pilot plants, such as oxygen converter, coal gasification and PFBC, with few problems reported (Mimori and Maeno, 1989). An extensive test facility has been installed at Ahlstorm, Finland but no published information on the tube filters performance is available.

A large scale pilot test system has been set up at the 70 MWe Tidd PFBC in Brilliant, Ohio to test 384 clay-bonded SiC candle filters over a two year period from 1993 to 1995. Operating conditions will be at 150 psi (1.1 MPa) and 843°C and one-seventh of the plants' generated gas will be processed through the candle filter cleaning system (Mudd and Durner, 1991). The goal of the test program is to evaluate the performance and reliability of commercial scale candle filter cleaning technology (Mudd and Durner, 1991).

EXPERIMENTAL PROCEDURE

Materials

Ceramic candles are rigid tubular filters consisting of ceramic grains or fibers bonded together with a ceramic binder material to form a porous structure. Typically, candles are 1 to 2 m long, and have a 60-mm O.D. and a 10 to 15-mm wall thickness. Descriptions of the commercial ceramic filter materials evaluated in the exposure tests in the present study are summarized in Table 4. A photograph of four of the candle filters is shown in Figure 4.

Apparatus

A schematic diagram of the high-temperature and high-pressure (HTHP) test apparatus is shown in Figure 5. The 347 stainless steel reaction vessel has an internal volume of $383 \times 10^{-5} \text{ m}^3$ and is capable of holding approximately 120, 15 x 15 x 30-mm test specimens, separated from each other by thin alumina sheets.

The HTHP vessel is mounted within a high temperature box furnace, secured into place with cut firebrick. The exposed area of the vessel where inlet and outlet piping are attached is surrounded by tightly packed ceramic fiber insulation. The test chamber temperature is constantly monitored by an internal thermocouple. A high pressure liquid metering pump delivers the appropriate amount of aqueous NaNO_3 solution of the proper concentration to produce the desired NaNO_3 : steam ratio. The steam- and alkali-laden air is introduced to the sample container from one side and travels across the container past the test specimens to the opposite side where it is vented from the vessel. In all exposure tests,

Table 4. Descriptions of the material used during the current investigation.

Filter Material	Source	Description
SiC1	Schumacher Umwelt und Trenntechnik	Clay bonded SiC aggregate; OD-60 mm, ID-30 mm
SiC2	Refractron Technologies, Inc.	Clay bonded SiC aggregate with a minimal binder content; OD-60 mm, ID-40 mm
Cordierite	Asahi Glass Co.	Fused cordierite aggregate with crystalline beta-spodumene as a minor phase in the binder; OD-170 mm, ID-140 mm
Refractory Concrete	Virginia Tech	Calcined fireclay aggregate with intermediate purity calcium aluminate cement binder; OD-60 mm, ID-40 mm
Mullite	Coors, Inc.	Interlocking grains of crystalline mullite with a needle-like crystal habit; OD-60 mm, ID-40 mm

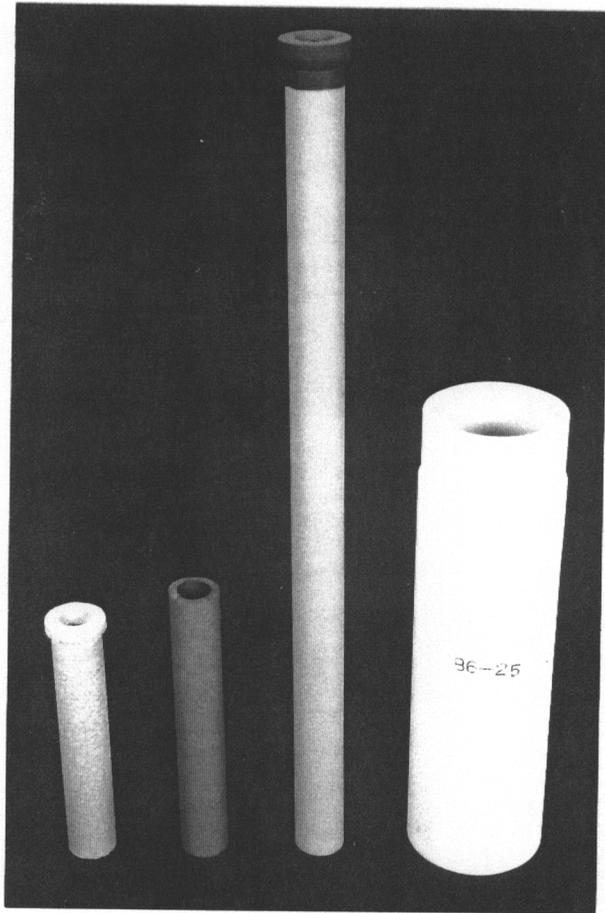


Figure 4. Photograph of the candle filters from left to right: Refractory Concrete, SiC2, SiC1 (about 1 meter long for scale), and Cordierite.

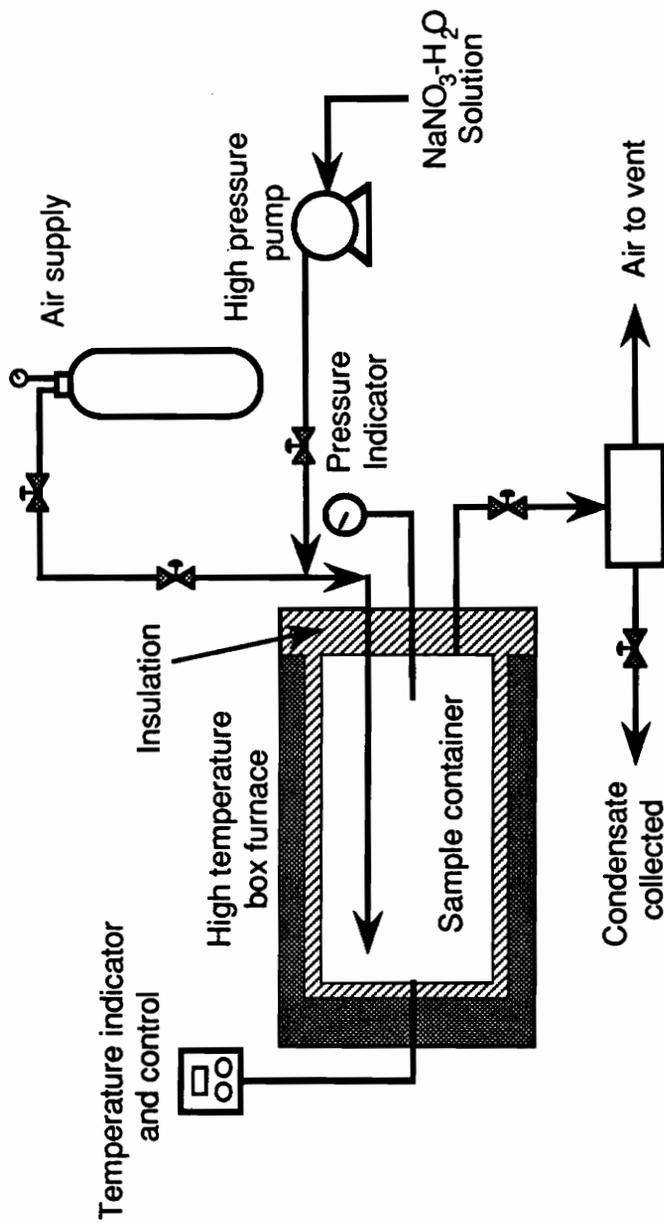


Figure 5. Schematic of the high-temperature and high-pressure experimental apparatus

gas flow rate across the test specimens is maintained at 420 milliliters/hour. The gas leaving the sample container is cooled, passed through a liquid-gas separator, metered, and then vented. Condensate collected is analyzed to monitor exiting gas composition.

Procedure

Pressures, temperatures, and levels of steam and alkali investigated represent conditions anticipated in hot gas clean-up systems of PFBC facilities. Table 5 provides the specific conditions for the five 500-h exposure tests.

In each exposure test run, more than twenty specimens of each filter were positioned in the test chamber. The vessel was then heated at a rate of 150°C/min to exposure test temperature (700-850°C). An adjustable pressure regulator dispensed air directly to the sample container from a compressed gas cylinder at the desired pressure. Once the vessel equilibrated at the designated partial pressure of air, total pressure was increased to the desired exposure pressure by pumping water into the air line entering the test vessel. This setup generated the air-steam exposure conditions. When an alkali-steam-air atmosphere was desired, an aqueous solution of NaNO₃ was pumped into the chamber at a rate such that when the solution vaporized (NaNO₃ decomposes at 380°C), the desired steam and Na concentrations were achieved.

At the termination of an exposure, air and solution delivery was stopped and the vessel was vented of any remaining gases before lowering the temperature at a rate of about 10°C/min.

Table 5. Experimental conditions for five 500 hour exposure tests.

Gas (Volume %)	Alkali Content (ppm)	Temperature (°C)	Pressure (MPa)
1. Steam (15)/air (85)	0	810	1.8
2. NaNO ₃ in steam (25)/ air (75)	3.4	800	1.7
3. NaNO ₃ in steam (8)/ air (92)	9	830	1.8
4. NaNO ₃ in steam (8)/ air (92)	10	700	1.8
5. NaNO ₃ in steam (9)/ air (91)	10	850	1.8

Evaluation

Properties of filter specimens after exposure tests are compared to properties of identical specimens that have been fired in air at the same temperature for the same length of time at atmospheric pressure. The properties evaluated for each filter were the bulk density, apparent porosity, hot and cold compressive strengths, pressure drop, microscopic features and X-ray diffraction patterns.

Bulk Density, Apparent Porosity, and Pressure Drop

ASTM C20-87 was used to evaluate bulk density and apparent porosity. Samples used for measuring bulk density and apparent porosity did not need special preparation or attention to size due to the testing procedure.

Samples were prepared for pressure drop analysis by cutting samples with a minimum face surface area of about 6.45 cm^2 (1 inch²). Openings on both sides of a sample were maintained to allow for the passage of air during the test and the rest of the sample was sealed with GE red enamel glyptal paint. The prepared samples were attached to the pressure drop test apparatus so that one manometer measured the air pressure before entering the sample and a second manometer measured the air pressure after passing through the sample. The differential height of the water in the manometers indicated the sample pressure drop. Air flow rate across the specimens was monitored with a flowmeter and was determined at a face velocity of 220 meters/hour.

Crushing Strength

Samples were prepared for crushing analysis by cutting the filters into concave wedge pieces in a 1:1:2 ratio of width, length and height respectively on a trim saw. Careful attention was taken to produce parallel specimen ends.

ASTM C133-84 was used for evaluating hot (850°C) and cold (room temperature) crushing strengths. For the crushing strength tests, a head speed of 1.3 mm/min was used in applying specimen loads with a mechanical testing machine (Figure 6). Loads were applied to the two end surfaces having the smallest dimensions (10x10 or 15x15 millimeters). For room temperature tests, corrugated cardboard pieces were used as bedding material, whereas for elevated temperature tests, ceramic wool fiber was the bedding material used. Eight to ten samples of each filter were tested in order to attain a mean compressive strength value. The observed differences in average strength values were examined statistically using the Student's t-test at the 99% level of confidence.

Optical microscopy and X-ray diffraction

Microstructural characterization was primarily accomplished by transmitted light optical microscopy examination of thin sections. For optical microscopy analysis to be performed, thin sections were prepared from samples of each filter in an "as received" condition and after each exposure. Due to the porous and friable nature of the ceramic materials, heated samples of the filters were initially impregnated with optically clear epoxy in order to hold the fragile samples together during thin sectioning. A flat polished surface of the impregnated filter sample is attached to a glass slide with epoxy. The ceramic sample chip is trimmed from the glass slide leaving only a sub-millimeter thick section. The thick

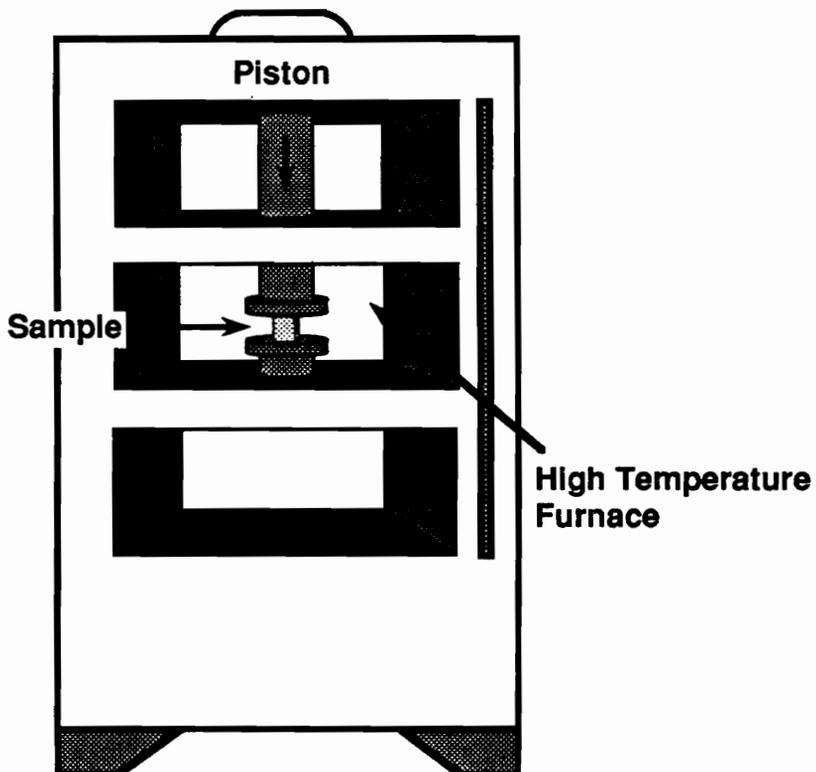


Figure 6. Diagram of the crushing apparatus used to test crushing strength of the candle filter materials.

section is polished by hand on a glass plate with SiC grit for the aluminosilicate castable, the cordierite and the mullite filters, and alumina powder for SiC filters. The sections are polished approximately to the standard thin section thickness of 0.03 millimeters.

In addition, X-ray diffraction (XRD) phase identifications were made for many of the specimens and used to interpret results from strength measurements. A Philips X-ray diffractometer with $\text{CuK}\alpha$ radiation was used.

RESULTS

Effect of Heat Treatment

Results of property determinations of the four ceramic filter specimens following the 500-h heat treatment in air at 850°C and atmospheric pressure are presented in Table 6. Figures 7a, 7b, 7c, 8a, and 8b are optical photomicrographs of the five filters used in this study after heat treatment. The cordierite filter was the only filter to show significant variation from the as received to the heat treated condition. The cordierite filter exhibited a loss in cold and hot crushing strengths after the heat treatment in air. Optical microscopy examination of the as-received cordierite filter revealed an interlocking matrix of crystalline cordierite grains. After 500 h at 850°C, the cordierite filter showed extensive grain growth (Figure 7c and d). Strength losses were most likely associated with the grain growth since there was no change in XRD mineralogy.

Although the mullite candle filter showed a significant decrease in hot crushing strength after the heat treatment, a similar decrease in strength was not detected in the cold crushing strength and no variation in other characteristics was detected.

Effect of 500 h Steam Exposure

85% air- 15% steam, 810°C, 1.8 MPa

After exposure of filter specimens to 85% air-15% steam for 500 h at 810°C and 1.8 MPa, no visual evidence of physical changes was observed. Table 6 contains bulk

Table 6a. Property characterization of SiC1, SiC2 and Mullite candle filters after 500-hour exposure tests.

Sample and Treatment	Bulk Density (g/cm ³)	Apparent Porosity (%)	Crushing Strength (cold)* (MPa)	Crushing Strength (850°C)* (MPa)	Pressure Drop+ (Pa)
SiC 1					
As-received	1.79**	41.4**	42.7±5.7	29.2±3.9	623
Heat treatment	1.83	40.0	39.7±2.6	30.0±4.5	722
Steam treatment	1.88	37.7**	23.9±3.4**	28.7±3.7	648
Alkali/steam treatment #1	1.69**	44.0**	5.6±1.3**	9.1±3.0**	598
Alkali/steam treatment #2	1.90**	37.3	18.4±1.9**	15.0±3.7**	—
Alkali/steam treatment #3	1.79**	41.3	19.8±2.0**	23.5±2.3**	548
Alkali/steam treatment #4	—	—	19.0±0.8**	22.5±7.1	—
SiC 2					
As-received	1.69**	44.1	44.3±3.0	41.4±4.3	1046
Heat treatment	1.62	46.3	46.0±3.3	34.1±5.4	1220
Steam treatment	1.73**	42.0**	31.3±4.4**	28.1±4.8	1170
Alkali/steam treatment #1	1.60	46.0	25.6±2.4**	17.8±2.2**	1170
Alkali/steam treatment #2	1.65	43.5**	25.2±1.2**	20.2±2.5**	1245
Alkali/steam treatment #3	1.62	46.1	27.5±2.7**	22.6±4.0**	946
Alkali/steam treatment #4	—	—	19.9±3.5**	18.9±3.0**	1445
Mullite					
As-received	1.76	39.5	68.0±7.1	47.8±7.8**	772
Heat treatment	1.70	40.9	58.7±7.3	35.9±5.0	772
Alkali/steam treatment #2	1.70	41.2	53.3±5.5	37.8±7.7	897
Alkali/steam treatment #3	1.63**	43.5**	64.8±7.1	31.6±3.3	697
Alkali/steam treatment #4	1.59**	45.7**	56.4±9.3	27.6±6.5	822

*95% confidence intervals shown

**denotes significantly different from companion heat treatment samples (in bold print) at 99% confidence level using Student's t-test

+ pressure drop value determined from measurement made on one sample

Heat treatment: 850°C; 0.1 MPa

Steam treatment: 810°C; 85% air-15% steam; 1.8 MPa

Alkali/steam treatment #1: 800°C; 75% air-25% steam-3.4 ppm Na; 1.7 MPa

Alkali/steam treatment #2: 830°C; 92% air-8% steam-9 ppm Na; 1.8 MPa

Alkali/steam treatment #3: 700°C; 92% air-8% steam-10 ppm Na; 1.8 MPa

Alkali/steam treatment #4: 850°C; 91% air-9% steam-10 ppm Na; 1.8 MPa

Table 6b. Property characterization of Cordierite and Refractory Concrete candle filters after 500-hour exposure tests.

Sample and Treatment	Bulk Density (g/cm ³)	Apparent Porosity (%)	Crushing Strength (cold)* (MPa)	Crushing Strength (850°C)* (MPa)	Pressure Drop+ (Pa)
<u>Cordierite</u>					
As-received	1.40	44.4	35.8±2.3**	21.6±3.3**	2640
Heat treatment	1.42	43.6	29.7±3.6	15.2±1.8	2715
Steam treatment	1.40	41.8**	26.7±4.1	17.7±2.0	2715
Alkali/steam treatment #1	1.43	42.9	25.6±2.0	14.4±1.5	1570
Alkali/steam treatment #2	1.42	43.0	27.0±1.9	14.2±1.8	1719
Alkali/steam treatment #3	1.38**	45.1**	27.3±2.5	17.2±2.7	2042
Alkali/steam treatment #4	1.41	43.9	26.7±2.0	15.7±2.3	648
<u>Refractory Concrete</u>					
As-received	1.27	54.9	16.5±0.9	13.6±1.0	349
Heat treatment	1.31 ((1.37))	53.3 ((51.5))	17.8±1.3 (13.5±0.9) ((13.0±1.6))	11.9±2.0 (9.0±1.1) ((10.0±1.4))	374
Steam treatment	1.45**	45.6**	15.1±2.1	13.4±1.8	448
Alkali/steam treatment #1	1.35	53.8	13.9±2.0**	9.5±2.0	398
Alkali/steam treatment #2	1.33	53.5	(14.5±1.1)	(8.7±1.3)	473
Alkali/steam treatment #3	((1.39))	((50.8))	((13.2±1.3))	((11.5±2.2))	—
Alkali/steam treatment #4	—	—	((14.2±2.8))	((9.9±1.5))	498

* 95% confidence intervals shown

** denotes significantly different from companion heat treatment samples (in bold print) at 99% confidence level using Student's t-test

+ pressure drop value determined from measurement made on one sample

() indicates a second refractory concrete filter was used with a different mean strength

(()) indicates a third refractory concrete filter was used with a different mean strength

Heat treatment: 850°C; 0.1 MPa

Steam treatment: 810°C; 85% air-15% steam; 1.8 MPa

Alkali/steam treatment #1: 800°C; 75% air-25% steam-3.4 ppm Na; 1.7 MPa

Alkali/steam treatment #2: 830°C; 92% air-8% steam-9 ppm Na; 1.8 MPa

Alkali/steam treatment #3: 700°C; 92% air-8% steam-10 ppm Na; 1.8 MPa

Alkali/steam treatment #4: 850°C; 91% air-9% steam-10 ppm Na; 1.8 MPa

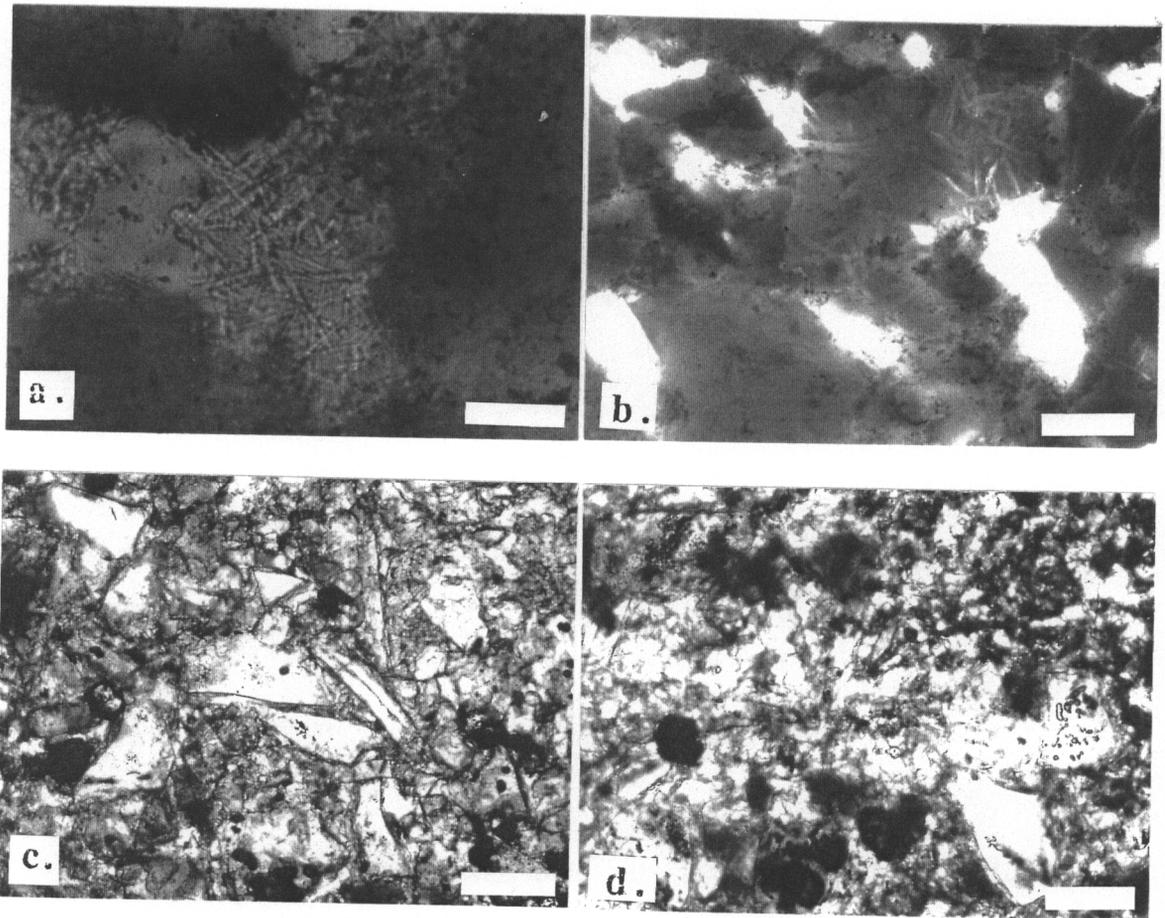


Figure 7. Optical photomicrographs of the ceramic filters **a-** the mullite filter after 500 h heat treatment (bar=25 μ m), **b-** the refractory concrete filter after 500 h heat treatment (bar=100 μ m), **c-** the cordierite filter after 500 h heat treatment (bar=100 μ m), **d-** the cordierite filter as received (bar=100 μ m).

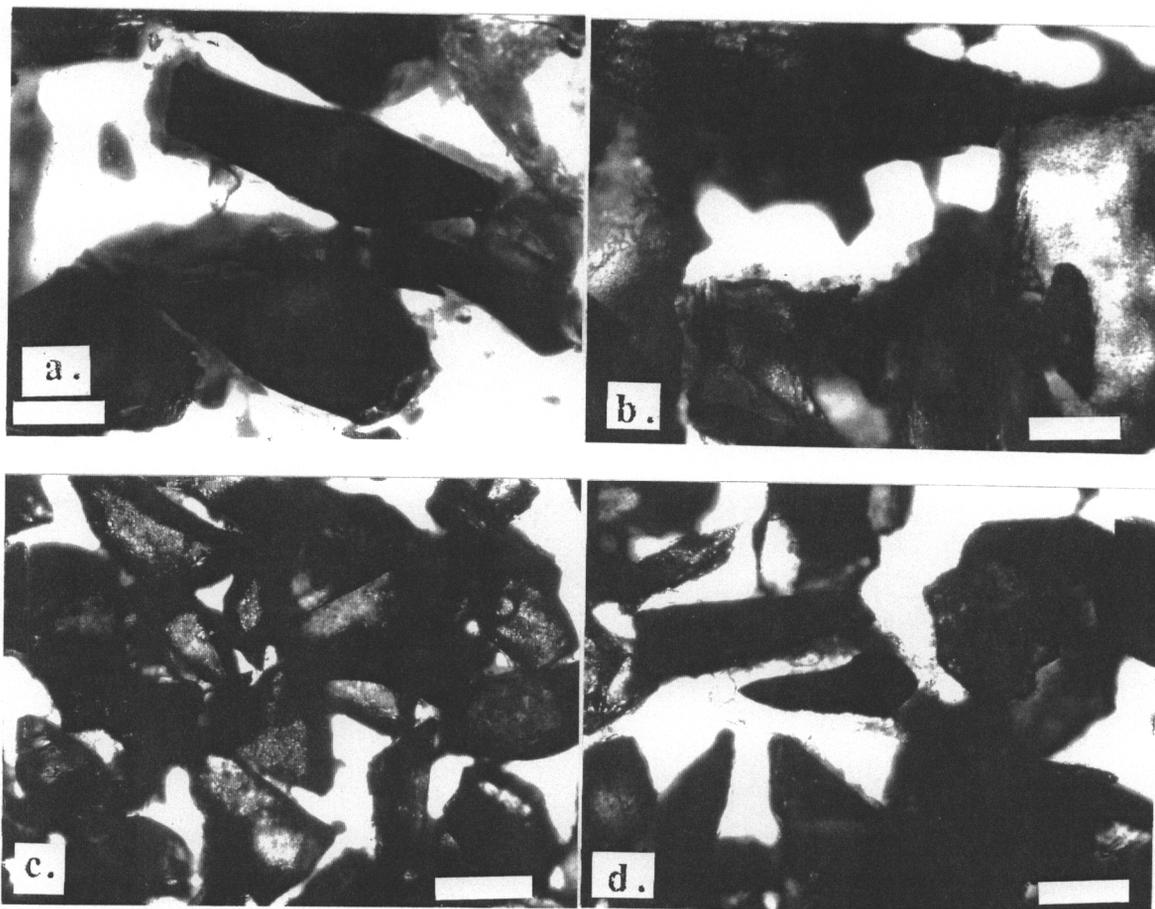


Figure 8. The SiC candle filters **a-** the SiC1 filter after heat treatment, **b-** the SiC1 filter after alkali/steam treatment #1 showing binder depletion and thinning, **c-** the SiC2 filter after 500 h heat treatment, **d-** the SiC2 candle filter after alkali/steam treatment #1 showing an extensive reaction rim surrounding an SiC grain. (Bar= 100 μ m in all photos)

density, apparent porosity, cold and hot crushing strength, and permeability data for the filter specimens following this exposure.

The data show that the air-steam exposure significantly lowered the cold crushing strengths of both types of SiC filter specimens when compared to companion air-fired samples. However, hot strengths of the SiC filters did not appear to be affected by the steam environments. Both SiC filters showed a decrease in apparent porosity with the SiC2 filter showing an increase in bulk density as well. XRD phase identification of the SiC1 filter indicated the presence of a small amount of cristobalite which is in agreement with microscopic observations. No cristobalite was detected in the SiC2 filter through XRD examination, however, microscopic evaluation did reveal crystallites of cristobalite around the SiC grains.

The cordierite and refractory concrete filter materials exhibited no strength changes after the air-steam exposure when compared to the air-fired specimen. However, reductions in apparent porosities were noted in both materials with the refractory concrete filter showing an accompanying increase in bulk density. XRD phase identification analyses indicated no change in mineralogy in the filter materials.

Optical microscopy examination of thin sections of the cordierite filter after exposure to the air-15% steam environment for 500 h revealed that grain growth had occurred. The refractory concrete filter showed no visual change after the air-steam exposure.

Effects of 500 h Alkali-Steam Exposures

75% air- 25% steam, 800°C, 1.7 MPa, 3.4 ppm Na

After exposure to 75% air- 25% steam- 3.4 ppm Na for 500 h at 800°C and 1.7 MPa (alkali/steam treatment #1), other than some discoloration, no visual evidence of physical changes in the filter specimens was observed. Table 6 presents results of bulk density, apparent porosity, cold and hot compressive strengths, and permeability determinations.

The data show that the alkali/steam treatment #1 significantly lowered the cold and hot compressive strengths of both types of SiC filter specimens when compared to companion air-fired samples. In addition, the SiC1 filter registered a significant increase in porosity and associated decrease in bulk density following the air-steam-alkali exposure. Optical microscopy examination of the SiC1 filter revealed that the binder phase had deteriorated and flowed away from the grains, likely causing the noted increase in porosity through binder loss and thinning (Figure 8b). Similar deterioration of binder was observed in the SiC2 filter. Reaction rims surrounding some of the SiC grains of both SiC filters were observed and are associated with the formation of cristobalite. XRD indicated significant growth of cristobalite in both SiC filters after exposure to alkali/ steam treatment #1 (Figure 8d).

The cordierite filter material exhibited no strength changes after the exposure when compared with the air-fired specimen. Optical microscopy examination of the cordierite filter after exposure to the steam-alkali treatment #1 revealed that grain growth and some discoloration had occurred. Edges of grains seemed slightly deteriorated and XRD analysis indicated no change in mineralogy. A decrease in pressure drop was observed in the cordierite filter after the alkali-steam treatment.

Although a reduction in cold crushing strength was noted in the refractory concrete specimens following the alkali/steam treatment #1, hot crushing strengths and other properties were not affected. Optical microscopy evaluation showed extensive discoloration of the aggregate but XRD analysis indicated the development of no new phases.

92% air- 8% steam, 830°C, 1.8 MPa, 9ppm Na

Following exposure to 92% air-8% steam-9 ppm Na, 830°C, and 1.8 MPa for 500 h (alkali /steam treatment #2), slight discolorations in the filter test specimens were again observed. Results of property determinations (Table 6) show that the exposure to the second alkali/steam environment significantly lowered the cold and hot crushing strengths of both types of SiC filters when compared to companion air-fired specimens, but was perhaps less detrimental than the higher steam-alkali exposure. XRD phase identification indicated the presence of cristobalite in the SiC1 filter following the alkali/steam treatment #2, and optical microscopy examination showed minor amounts of cristobalite along grain rims. No cristobalite was indicated in the post exposure SiC2 filter through XRD analysis, but crystallites were observed in microscopic examination. Both SiC filters showed discoloration of the binder and SiC aggregate.

The cordierite, mullite and refractory concrete filter specimens showed no deterioration in hot or cold strengths following the second steam-alkali exposure. As after exposure to alkali/steam #1, the cordierite filter showed a decrease in pressure drop after the second alkali-steam exposure. Discoloration of grains and a minor amount of grain boundary deterioration were detected. Other than discoloration of the refractory concrete aggregate there was no change in any properties of the refractory concrete filter after

alkali/steam treatment #2. Similarly, the mullite filter showed no changes in the evaluated characteristics after the second alkali-steam exposure.

92% air-8% steam, 700°C, 1.8 MPa, 10ppm Na

After exposure to 500 hours of 92% air- 8% steam- 10 ppm Na, 700°C and 1.8MPa (alkali /steam treatment #3) all the samples showed slight discoloration. The results of property characterization analysis are presented in Table 6. Both types of SiC filters showed a reduction in hot and cold crushing strength after exposure to the lower temperature treatment. XRD analysis revealed cristobalite formation in the SiC1 filter but none was noted in the SiC2 filter. Optical microscopy observations of both SiC filters showed depletion and thinning of the binder as well as minor amounts of cristobalite along grain edges.

The cordierite filter showed no significant change in either hot or cold crushing strength, however a significant decrease in bulk density and an associated increase in apparent porosity were observed. Grain growth and corroded grain edges were observed in post exposure optical microscopy examination of the cordierite filter. The refractory concrete filter showed no change in any of the properties characterized except for discoloration of the aggregate observed in optical microscopy examination. The mullite filter showed an increase in porosity and a decrease in bulk density, but no significant changes in any other properties were detected. XRD analysis indicated no change in the mineralogy of the cordierite, refractory concrete and the mullite filters.

91% air-9% steam, 850°C, 1.8 MPa, 10ppm Na

After exposure to 91% air-9% steam-10ppm Na for 500 hours at 850°C and 1.8 MPa (alkali /steam treatment #4) slight discoloration of all filters was again observed. Property characterization results are presented in Table 6. Exposed samples of the SiC1 filter showed a decrease in cold crushing strength. No statistically significant reduction was noted in hot crushing strength. However, it should be noted that the confidence interval is unusually large for the hot crushed SiC1 samples due to a large amount of variability in the collected data. The SiC2 candle filter showed a significant decrease in both cold and hot crushing strength. XRD indicated the formation of cristobalite in both SiC filters. Optical microscopy examination revealed small amounts of cristobalite along grain rims as well as extensive binder thinning and depletion.

No significant change in crushing strength was noted in the cordierite, refractory concrete and mullite candle filters after exposure to steam and alkali at the slightly higher temperature of 850°C. The cordierite filter showed a large decrease in pressure drop but no change in either bulk density, apparent porosity or XRD mineralogy. Microscopic examination of the cordierite filter revealed grain growth and the development of slightly corroded grain edges after exposure to alkali-steam treatment. Other than discoloration of the aggregate seen in optical microscopic examination, post exposure evaluation of the refractory concrete filter showed no change in any of the properties characterized. The mullite candle filter showed an increase in porosity with an associated decrease in bulk density but no other changes in properties were observed.

Alkali /steam treatment #4 was unique in that it formed about 20 grams of an unknown crystalline, white material against the lid of the reaction vessel. Energy Dispersive X-Ray (EDX) showed that the unknown material consisted of clumps of fine needles and was primarily comprised of Si. A surface analysis, performed using Electron

Spectroscopy for Chemical Analysis (ESCA) detected the following elemental percentages: 22% C, 46% O, 29% Si, 1.3% Na, and 1.6% Al. Cristobalite and SiC peaks were identified through XRD analysis and the material most likely is a compound comprised of a mixture of the two.

The source of the constituent material elements is somewhat unresolved. The migration of C was most likely from the reaction of the SiC with oxygen to produce SiO₂ and CO. An easy source of oxygen would have been the steam /air atmosphere of the reaction chamber. The source of the Si is still unknown. No severe changes in the five filters used in this study were observed. However, the alkali /steam treatment #4 exposure also included a number of other materials that may be the source of the Si migration. The other materials included in the exposure were fibrous aluminosilicate blocks, cordierite honeycomb shaped filters, corundum-mullite-cordierite composites, SiC particulate-reinforced Al₂O₃ composites, and samples of a third SiC filter. No obvious change in these five filters was noted.

DISCUSSION

The most significant property measurements made of the ceramic candle filter samples appear to be crushing strength. Overall, it is evident that steam causes significant filter deterioration primarily because it acts as a mineralizer to promote oxidation and phase changes. Steam with small amounts of alkali present represents the most corrosive environment, with the alkali apparently promoting even faster reaction rates as well as liquid formation in some cases.

SiC Filters

SiC1 is seriously affected by PFBC conditions as reflected in both the hot and cold crushing strength measurements. Some of the binding phase has melted and crystallized to cristobalite, which will probably cause a reduction in thermal shock resistance in the filter with time as more cristobalite forms.

The SiC2 samples appeared to perform somewhat better than SiC1 samples; nonetheless, significant strength deterioration was observed. Microscopic evidence indicates that the same basic corrosion is present as with SiC1 except the kinetics of oxidation of SiC/crystallization of cristobalite are slower.

Cordierite

Corrosion of cordierite samples was not observed to be significant based on the microscopy studies. Grain growth, however, was evident after the air-fired exposures and more so after the PFBC exposure tests. This is significant from the standpoint of pore size change and consequent permeability change of the filter. The decrease in pressure drop in

alkali-steam environments indicates changes in the interconnectivity of the pores which is probably produced from the combined effect of grain growth and deterioration of grains along boundaries.

Refractory Concrete

In spite of the relatively low strength of the as-received porous refractory concrete samples, they exhibited very good resistance to all exposure conditions. No evidence of chemical corrosion or grain growth was noted by the microscopy examinations. A reduction of hot strength after the first alkali/steam exposure of less than 40% was observed. This is less than the hot strength deterioration of the SiC filters and only slightly more than the cordierite filter samples. These results are not surprising in view of the fact that refractory concretes are known to perform well in high-pressure, steam-containing environments (Sadler et al., 1984).

Mullite

The alkali-steam treatment seemed to have little effect on the strength and other characteristics of the mullite filter, although a reduction in hot crushing strength took place after heat treatment. The mullite candle filters showed the greatest initial strengths and showed the capacity to maintain these high strengths after exposure to the steam-alkali treatment. No changes in mineralogy or signs of corrosion were detected after exposure. The mullite filter exhibited the best overall combination of chemical resistance and strength.

CONCLUSIONS

The observations reported here suggest:

- 1) The presence of the combination of steam and alkali in PFBC conditions adversely affects cold and hot strength of SiC filter materials. The magnitude of the strength decrease of the SiC filters after exposure to steam-containing PFBC environments increases with increasing partial pressure of steam.
- 2) The magnitude of the strength decreases of the SiC filters after exposure to the PFBC environments appeared to be independent of temperature in the 700-850°C temperature range tested..
- 3) Cordierite, mullite and refractory concrete filters showed no changes in hot and cold crushing strengths following exposure to high-pressure, steam-containing atmospheres.
- 4) Cordierite, mullite and refractory concrete filters retain their strength at typical alkali-containing PFBC conditions at temperatures ranging from 700-850°C.

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VITA

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Karen Rose Valentino