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Authors:

Theodore J. McMahon (METC)
Mary Ann Alvin (Westinghouse Electric Corporation)
H. Stuart Starrett (Southern Research Institute)

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CERAMIC BARRIER FILTERS FOR ADVANCED
COAL-BASED POWER GENERATION SYSTEMS

THEODORE J. MCMAHON
U.S. DEPARTMENT OF ENERGY
MORGANTOWN ENERGY TECHNOLOGY CENTER
P.O. BOX 880
MORGANTOWN, WV 26507

MARY ANNE ALVIN
WESTINGHOUSE ELECTRIC CORPORATION
SCIENCE AND TECHNOLOGY CENTER
PITTSBURGH, PA 15235

H. STUART STARRETT
SOUTHERN RESEARCH INSTITUTE
2000 NINTH AVENUE
BIRMINGHAM, AL 35255

OBJECTIVES

The objectives of this program are to identify the potential long-term thermal, chemical, and mechanical effects that advanced coal-based power generating systems have on the stability of porous ceramic filter materials. These objectives are achieved through a test program that consists of laboratory testing and analysis of field exposed filter elements. Laboratory analyses involve measurement of basic filter material properties in order to predict behavior seen in service performance. In addition, full filter elements are exposed to simulated operating conditions in order to separate the effects of the thermal, chemical, and mechanical loads experienced by the filter elements in service.

The focus of this paper will be to highlight results of the analyses of filter elements that have seen service in the circulating fluidized-bed combustion (CFBC) test facility in Karhula, Finland, and in the pressurized fluidized-bed combustion (PFBC) test facility at the American Electric Power (AEP) demonstration plant in Brilliant, Ohio. Results of laboratory testing performed in support of pilot scale filter testing will also be presented. These results indicate current generation filter materials are subject to damage from thermal stresses caused by pulse cleaning. Results of laboratory testing are also presented that explain creep behavior of clay bonded silicon carbide filter materials.

BACKGROUND INFORMATION

Westinghouse Advanced Particulate Filtration (W-APF) systems have been operated at temperatures of 690 °C to 900 °C in the CFBC pilot

scale test facility in Karhula, Finland, and 540 °C to 810 °C in the PFBC demonstration facility in Brilliant, Ohio, both under oxidizing conditions. First generation Coors alumina/mullite and clay bonded silicon carbide Pall Vitropore 442T and Schumacher Dia Schumalith F40 candle filters have been utilized in these installations.

The porous alumina/mullite filter material consists principally of mullite in addition to an amorphous phase, anorthite, and corundum. Both the Vitropore 442T and Dia Schumalith F40 candle filters consist of silicon carbide grains that are bonded together by a silica-rich binder phase. Both clay bonded silicon carbide candle filters have outer membrane coatings, a finer grain silicon carbide layer along the Vitropore 442T candles; an aluminosilicate fibrous mat along the Dia Schumalith F40 candles, while the alumina/mullite candle filter is currently manufactured without an external membrane or coating.

RESULTS

Field Testing

Characterization of the Alumina/Mullite Candle Filters after Exposure in the W-APF System at the Ahlstrom CFBC Test Facility in Karhula, Finland (Test Segment 1). One hundred twenty-eight (128), 1.5 m full length alumina/mullite candle filters were installed in the W-APF system in the Ahlstrom circulating fluidized-bed combustion (CFBC) pilot plant in Karhula, Finland prior to October 1992. The W-APF operated for a period of 716 hours at nominal temperatures of 900 °C.

Figure 1 illustrates the residual bulk strength of the CFBC-exposed alumina/mullite filter material as a function of process operating time. An initial loss of the bulk strength of the alumina/mullite filter material is experienced within the first 50 to 100 hours of operation in the CFBC process gas environment. The bulk strength of the material then appears to stabilize, remaining relatively constant throughout the remainder of the 616 to 666 hours of test operation.

Typically a greater loss of bulk material strength is experienced along the inner surface of the CFBC-exposed alumina/mullite filter material (i.e., tensile c-ring testing: 46-49% residual inner wall strength as opposed to compressive c-ring testing: 71-83% residual outer wall strength). Increased strength reduction along the inner filter wall is principally attributed to thermal fatigue of the alumina/mullite filter material due to the inner wall being contacted with the cold pulse cleaning gas.

During the 716 hours of CFBC test operation in Karhula, Finland, the W-APF vessel experienced a fuel ignition event, isolated ash bridging, and a shift in the vessel shroud position -- all of which

Figure 1. Residual Bulk Material Strength of the Alumina Mullite Filter Material After Exposure to the CFBC Process Conditions in the W-APF System

Figure 2. Residual Bulk Material Strength of the Vitropore 442T Clay Bonded Silicon Carbide Filter Material After Exposure to the CFBC Process Conditions in the W-APF System

were considered to contribute to failure of thirty-six (36) candle filter elements throughout the entire test period. As shown in Figure 1 the fractured candle sections exhibited a lower residual bulk strength in comparison to candles that remained intact throughout the course CFBC testing.

Characterization of the alumina/mullite filter material utilizing SEM/EDAX analytical techniques indicated that during the initial several hundred hours of test operation, crystallization of the amorphous phase occurs in the CFBC-exposed filter material. Mullite formation, growth of rod-like grains, is evident along the inner wall pore cavities. Nucleation or grain growth within the amorphous phase of the material leading to the formation of mullite, appears to be enhanced as a result of repetitive exposure to cold pulse gas cycling conditions.

X-Ray diffraction results show that after 716 hours of CFBC-exposure, the alumina/mullite filter material appears to be nearly fully crystallized. Grain growth is evident throughout the entire ligament structure of the filter body. Extensive mullite formation is also evident, particularly along the pulse cycled surface (i.e., 2-4 microns from the inner wall). Crystallization of the amorphous phase in the alumina/mullite filter element is thought to contribute to the stabilization of the material strength.

Characterization of the Vitropore 442T Clay Bonded Silicon Carbide Candle Filters after Exposure in the W-APF System at the Ahlstrom CFBC Test Facility in Karhula, Finland (Test Segments 2 and 3). The W-APF vessel was entirely re-candled in the fall of 1993 with new Vitropore 442T candle filters for use in testing in Test Segment 2. Testing was initiated on November 6, 1993, and continued for 512 hours at nominal temperatures of 830 °C. Post-test inspection of ten (10) Vitropore 442T candle filters from the bottom plenum indicated that one candle showed evidence of creep crack growth directly below the hemispherical flange. All ten candles removed were replaced with new Vitropore 442T candle filters prior to reinitiation of testing in Test Segment 2.

Testing was reinitiated in February 1994, and continued until March 1994, accumulating an additional 514 hours of operation at nominal temperatures of 830 °C. Post-test inspection of the Vitropore 442T candles included the removal of fourteen (14) candles from the bottom plenum, six (6) of which showed evidence of creep crack growth, crack formation and elongation of the candle filter body. Since these candles were identified to have been manufactured by a certain production method, and similarly processed candles remained within the bottom array, all bottom plenum candles were removed, and the unit was re-candled once again with new Vitropore 442T candle filters. Post-test inspection of the removed candles indicated that eighteen (18) of the fifty-two (52) bottom plenum candles had developed cracks below their flanges. Based on the manner in which the Vitropore 442T candles had been manufactured, elongation of the

candle body ranged between 0-2 mm for manufacturing process No. 1 and No. 2, and 1-12 mm for manufacturing process No. 3, for candles which had been operated in the later 514 hours of CFBC operation. Similar elongation measurements were made for candles that had experienced the entire 1026 hours of 830 °C CFBC operation. These measurements indicated that candles which were produced by manufacturing process No. 1 elongated by 1-12 mm, while candles produced by manufacturing process No. 2 elongated by 9-14 mm, and candles produced by manufacturing process No. 3 elongated by 13-26 mm.

Figure 2 illustrates the residual bulk strength of the Vitropore 442T candle filters as a function of filter manufacturing process, and-operating time in the CFBC process gas environment. Irrespective of how the Vitropore 442T candle filters were manufactured, all candles appear to lose bulk material strength as a function of time at 830 °C. Initial scatter in strength values due to differences in manufacturing are apparently overcome by a conditioning effect at 1,000 hours of operation in the 830 °C CFBC gas environment. A nearly equivalent loss of bulk material strength is indicated along both the inner and outer surfaces of the Vitropore 442T material. This is in contrast with the residual bulk material strength of the Vitropore 442T matrix after 227 hours of exposure in the 900 °C CFBC process environment in Test Segment 1.

SEM/EDAX analyses illustrate the progression of the changes that occurs within the microstructure of the Vitropore 442T candle filter material as a function of process operating time. After 512 hours of exposure in the 830 °C CFBC process environment, holes and voids are evident in the binder ligaments that bond adjacent silicon carbide grains together. Crystallization of the binder phase occurs along both the fine membrane layer and coarse support layer silicon carbide grains. Typically along the coarse support layer grains where silica enriched crystalline phases form, are associated depressions which often mark the initiation site for microcrack formation(s) along the binder coating surface.

Bubble formations in the binder phase are evident at the silicon carbide grain-binder ligament post areas. Frequently cracks occur along the surface of the bubbles, indicating that out-gassing has occurred from what was expected to be the release of carbon dioxide from reaction of diffused oxygen and/or steam through the binder coating with the surface of the silicon carbide grain. Infrequently "patchy" rod-like crystalline phases (i.e., mullite) are evident within the binder phase that coats the coarse support layer silicon carbide grains of the Vitropore 442T filter material.

Moving toward the inner surface of the 512 hour, 830 °C CFBC-exposed candle are areas of the binder phase that have undergone extensive crystallization. In these areas the crystallized binder appears to be lifted and is somewhat detached from the underlying binder phase and/or surface of the silicon carbide grain.

After 1,026 hours of exposure to the 830 °C CFBC gas environment, extensive crystallization of the Vitropore 442T binder phase is evident. Crystallization continues to result in the formation of a silica-enriched phase (i.e., cristobalite). Void formations are readily evident along the surface, as well as throughout the binder ligament posts. Degradation of the binder phase due to formation of microcracks, bubbles, and separation of the binder from the silicon carbide grains, is most likely the cause of strength reduction in the CFBC exposed clay bonded filter materials.

Characterization of the Dia Schumalith F40 Clay Bonded Silicon Carbide Candle Filters after Exposure in tile W-APF System at the AEP PFBC Test Facility at Brilliant, Ohio (Test Segments 1, 2, and 3). Hot gas filter operation of the W-APF system at the AEP PFBC Demonstration plant was conducted in three test campaigns in which Schumacher Dia Schumalith F40 clay bonded silicon carbide candle filters were exposed to PFBC process gases at temperatures of 732 °C for periods of 464, 1,296, and 1,278 hours (i.e., 3,038 hours of total test operation). Irrespective of the manner in which the Dia Schumalith F40 material was manufactured (i.e., higher initial bulk material strength as a result of high firing procedures) the clay bonded silicon carbide material tends to initially lose bulk material strength, and stabilize to a conditioned strength after extended operating time (Figure 3). Bulk material strength characterization as determined by room temperature and process temperature C-ring compressive and tensile testing indicates comparable strengths of the material after 3,038 hours of hot gas filtration as after 1,760 hours. Typically a greater loss of bulk material strength appears to occur along the inner surface of the 15 mm Dia Schumalith F40 filter wall, implying that the material has undergone thermal fatigue as a result of contact with the cold pulse cleaning gas.

During the course of 3,038 hour PFBC exposure, the fibrous aluminosilicate outer wall membrane remained intact, preventing fines penetration into the candle filter wall. SEM/EDAX characterization of the material indicates that with prolonged filtration at temperatures of 732 °C, the clay bonded silicon carbide material undergoes extensive crystallization of the binder phase that coats the silicon carbide grains. A silica-enriched phase (i.e., cristobalite) forms as a continuous layer or "crust" (i.e., 5 microns) along the binder coating that originally encapsulated the silicon carbide grains. Below the silica-enriched phase are what appears to be mullite-like rod formations. Further effort will be required to determine if oxidation of the silicon carbide grain has occurred, as well as any variations in the microstructure that may have resulted throughout the 15 mm Dia Schumalith F40 candle filter wall.

The complete or nearly complete crystallization of the binder phase, leading to what appears to be a stable binder phase, is

Figure 3. Residual Bulk Material Strength of the Dia Schumalith F40 Clay Bonded Silicon Carbide Filter Material After Exposure to the PFBC Process Conditions in the W-APF System

considered to be responsible for the bulk material strength conditioning that results after extended exposure of the Dia Schumalith F40 material in the 732 °C PFBC gas environment.

Laboratory Testing and Analysis

High Temperature Static Air Exposure. When the alumina/mullite, Vitropore 442T or Dia Schumalith F40 filter materials are subjected to 870 °C process temperatures in a static air environment, the bulk material strength of these porous ceramic filter materials is retained during the first 3,000 hours of exposure. The as fabricated morphology of the oxide and nonoxide-based materials is also retained, with negligible observable changes occurring in the ceramic microstructure (i.e., crystallization, bubble formation, etc.). These results are expected in view of the substantially higher manufacturing temperatures that are used to produce the various candle filter elements.

Creep Testing and Characterization of the Microstructure of the Vitropore 442T Material. In order to better understand the behavior in general, and the creep behavior in particular, of the Vitropore 442T material, an analysis of the filter material microstructure was performed. A similar analysis was performed for the Dia Schumalith F40 material. Quantitative optical microscopy techniques were employed to characterize the features of the two microstructures (Figure 4). The Schumacher material was found to consist of silicon carbide particles 450 microns (18 mils) in diameter which are connected by bridges of binder material that are 125 microns (5 mils) in diameter by 6 microns (0.25 mils) in length. In contrast, the Vitropore 442T material is found to consist of groupings of particles 760 microns (30 mils) in diameter, which consist of silicon carbide grains embedded in a matrix of binder material. These groupings are connected by bridges of binder material that are 225 microns (9 mils) in diameter by 15 microns (0.6 mil) in length. Characterization of these features allows for the calculation of local stresses and strains in the binder material for a given applied load.

Creep testing was performed at 200 psi at temperatures of 815 °C, 843 °C, and 870 °C (1500 °F, 1550 °F and 1600 °F). The load is significantly higher than loads expected in service, and is chosen to minimize time of experiments and provide insight into the properties of the binder phase (Figure 5). Testing at 815 °C (1500 °F) was terminated at 100 hours due to minimal creep that had occurred. Several samples were tested at 843 °C (1550 °F) and were found to fall along the same line, which showed substantially higher creep than at the lower temperature. Finally the material was found to creep significantly at 870°C (1600 °F). Thus the creep behavior of the Vitropore 442T is found to increase rapidly over the operating temperature range of the CFBC test facility.

Figure 4. Schematic of Schumacher Dia Schumalith F40 and Vitropore 442T (Refractron) Microstructures

Figure 5. Tensile Creep Testing of the Vitropore 442T (Refractron) Material

Results of this testing and other testing at various temperatures allows for calculation of the viscosity using the relation (viscosity = stress / 3 creep rate), keeping in mind that the actual stresses and strains in the binder phase are used (Figure 6). This viscosity temperature relation is compared with similar curves for various commercial glasses in Figure 7. The curve falls in between curves R and L, which are high silica glasses, and curves D, H, B, A, and P, which are aluminosilicate, borosilicate, soda-lime, and two lead alkali silica glasses respectively. Analysis of these types of curves may lead to an understanding of the requirements for the binder phase composition.

The Vitropore 442T viscosity temperature curve crosses the strain point at roughly 800 °C, which is in the temperature range where the CFBC facility operates, indicating that the binder phase is relatively soft at operating temperature, which could lead to the elongation of the filter elements observed in the CFBC test facility. The source of the mechanical load leading to the creep is not known at this time. The relatively minor differences in manufacturing procedure may have a slight impact on binder viscosity, which may account for differences in creep behavior seen in the candles exposed to the CFBC conditions. Creep testing and analysis of the temperature viscosity curve may provide insight into the temperature limitations of the clay-bonded silicon carbide materials. Similar temperature viscosity curves are expected for the Dia Schumalith F40 material.

Accelerated Thermal Fatigue Testing. Accelerated pulse testing of Coors alumina/mullite, Schumacher Dia Schumalith F40 clay bonded silicon carbide, and Pall Vitropore 442T clay bonded silicon carbide 1.5 m candle filters was completed under high temperature, high pressure (HTHP), simulated pressurized fluidized-bed combustion (PFBC) gas conditions at Westinghouse. Each filter was subjected to temperatures of 843 °C (1,550 °F), system pressures of 100 psig, and either 771 or 10,000 simulated pulse cleaning cycles. Pulse conditions were typical of those utilized in the W-APF system at AEP. All of the first generation monolithic candle filters remained intact during the entire 10,000 pulse cycle test. Cracks were not visibly evident along any of the filters after testing had been completed.

As shown in Figure 8, a greater loss of bulk material strength in the alumina/mullite, Vitropore 442T and Dia Schumalith F40 materials generally resulted along the inner wall surface of the candle filters, implying thermal fatigue of the material had occurred primarily as a result of contact with the cold pulse gas. Conditioning of the materials appears to rapidly occur during the accelerated thermal cycling life of the filters (i.e., <771 pulse cycles). Similar conditioning of the filter materials was evident in the field-tested filter materials.

Figure 6. Calculated Viscosity as a Function of Temperature for the Vitropore 442T Material

Figure 7. Comparison of Viscosity as a Function of Temperature for the Vitropore 442T (Refractron) and Various Commercial Glasses

10,000 Simulated Pulse Cycles

Figure 8. Accelerated Thermal Fatigue Testing

Thermal Stress Analysis. Basic material properties have been measured in order to gain a better understanding of the response of the filter materials to thermal stress. Relevant fundamental properties include tensile stress-strain responses at ambient and elevated temperatures, and thermal expansion (α) as a function of temperature. Data and analysis will be presented for the Coors alumina/mullite material as an example. Tensile stress-strain curves yield the tensile fracture strength (σ), the elastic modulus (E), and the strain at failure (Figure 9). By rearranging the familiar thermal stress expression for a fully restrained body, which includes the Poisson ration (ν) (Figure 10), one can solve for the temperature gradient (ΔT) that will initiate cracking in the material. It is found that for the alumina/mullite material, a temperature difference of roughly 100 °C will initiate cracking.

Thermal stress cracks can be seen in the alumina/mullite material through the use of optical microscopy. A cross section of a filter material seeing exposure at the Karhula CFBC test facility has revealed some 30 regularly spaced radial cracks on the inner wall extending 1 to 3 millimeters into the filter wall. This crack pattern correlates well with stress models that predict tensile stresses extending into the filter wall roughly 3 mm due to cold gas pulse cleaning. The cracking on the inner wall also correlates well with the greater reduction in strength on the filter inner wall that is seen experimentally.

Similar temperature gradients will cause cracking in the clay bonded silicon carbide materials, but microcracking has not been observed using optical microscopy.

CONCLUSIONS

In summary, each of the first generation porous ceramic candle filters have performed as complete barrier filters, preventing fines penetration into the clean gas passages of the W-APF systems. As complex ceramic materials, the alumina/mullite and clay bonded silicon carbide filters undergo numerous microstructural changes that result from contact with the high temperature process gas environment. These progressive phase changes that occur are considered in part to lead to the conditioning or stabilization of the bulk material strength. For both the alumina/mullite and Vitropore 442T materials at 900 °C, thermal fatigue appears to initially reduce the bulk material strength along the candle filter inner surface. The effects of thermal fatigue appears to be mitigated in the Vitropore 442T material at CFBC operating temperatures of 830 °C, while our most recent information indicates that thermal fatigue occurs along the inner surface of the Dia Schumalith F40 material at PFBC temperatures of 732 °C. Evidence of microcrack formations through the structural matrix of the alumina/mullite filter material can be readily seen, while difficulty is encountered in attempting to observe the existence microcracks in the clay bonded silicon carbide filter materials.

Figure 9. Tensile Stress-Strain Curves at 70, 1500, 1600, and 1700 °F for Alumina/Mullite Material

Fully Restrained

$$\sigma = \frac{E}{1 - \nu} \alpha \Delta T$$

at 1500 °F

$$E \cong 2.5 \times 10^6 \text{ psi}$$

$$\nu = 0.25$$

$$\sigma \cong 2250 \text{ psi}$$

$$\alpha \cong 3.5 \times 10^{-6} / ^\circ\text{F}$$

$$\Delta T = \frac{(2250)(1-0.25)}{(2.5 \times 10^6)(3.5 \times 10^{-6})}$$

$$\Delta T = 190 ^\circ\text{F} (\sim 100^\circ\text{C})$$

Figure 10. Thermal Stress Calculations for Alumina Mullite Material

The Vitropore 442T filter material has experienced creep and elongation of the filter body at temperatures of 830 °C which has led to formation of cracks in the candle body directly below the hemispherical flange. Bowing or bending of the Vitropore 442T filter elements was observed in the absence of ash accumulation or bridging. For the Dia Schumalith F40 material, bowing of the filter element can occur at temperatures of 732 °C when extensive ash bridges form between adjacent candle filters. For both materials, this creep behavior is attributed to a relatively low viscosity of the clay-based binder phase at operating temperatures.

As technology moves forward to mitigate ash bridging within the filtration systems, and process operations are maintained to reduce the impact of thermal transients, operation of the filtration systems can be expected to surpass the number of hot gas filtration hours already accumulated for the existing alumina/mullite and clay bonded silicon carbide filters. It will then be possible to demonstrate the actual filter operating life of these materials.

FUTURE WORK

Future work will involve subjecting filter materials to a series of thermal shock exposures, in order to assess the resistance of the individual materials to thermal stresses induced by process related thermal transients. Analysis of filter elements that have been exposed for longer periods of time in both the CFBC and PFBC test facilities will be performed as these filters become available. These analysis are necessary to determine whether filter material microstructures and strength have stabilized. Material properties analysis and exposure to PFBC operating conditions will continue for a second generation of ceramic filter materials that exhibit toughened behavior.

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