PROJECT TITLE: CFCC

CONTRACT NUMBER: DE0FC02-92CE40945

PRINCIPLE INVESTIGATOR: R. A. WAGNER, MTI

PROGRAM MANAGER: R. G. TRIMBERGER

REPORTING PERIOD: 1992 - 2002

Prepared by Richard A. Wagner____________________ date: December 18, 2002

1 Executive summary

This report summarizes work to develop CFCC's for various applications in the Industries of the Future (IOF) and power generation areas. Performance requirements range from relatively modest for hot gas filters to severe for turbine combustor liners and infrared burners. The McDermott Technology Inc. (MTI) CFCC program focused on oxide/oxide composite systems because they are known to be stable in the application environments of interest. The work is broadly focused on dense and porous composite systems depending on the specific application. Dense composites were targeted at corrosion resistant components, molten aluminum handling components and gas turbine combustor liners. The development work on dense composites led to significant advances in fiber coatings for oxide fibers and matrix densification. Additionally, a one-step fabrication process was developed to produce low cost composite components. The program also supported key developments in advanced oxide fibers that resulted in an improved version of Nextel 610 fiber (commercially available as Nextel 650) and significant progress in the development of a YAG/alumina fiber. Porous composite development focused on the vacuum winding process used to produce hot gas filters and infrared burner components.

IR burner development resulted in a number of burner configurations that exhibited significantly higher efficiency than the commercial metal burner. A commercial black body coating produced the most efficient heating of any burner configuration. Fabrication developments included a net shape vacuum forming method to produce perforated burner blocks that eliminated flashback and exhibited good thermal stability and strength. Reverberation screens were filament wound and coated to control the emittance. Final burner assessment was performed under prototypical paper machine conditions at the Institute of Paper Science and Technology. Testing revealed that while the burner blocks performed well, the reverberation screens did not possess sufficient thermal-mechanical stability for this application.

Significant progress was achieved in the development of a CFCC aluminum casting riser tube. A slurry-winding fabrication method was used to produce low porosity CFCC tubes. The process is based on the use of high solids content slurries that were developed by optimizing the particle size distribution. A hydraulic binder used to stabilize the structure during drying has the potential to produce unfired composites. The resulting CFCC tubes exhibited good strength and non-brittle failure behavior. With a fiber content of 10 – 15%, the resulting production costs could be very competitive with monolithic components. The hermetic sealing requirement was met by applying a borosilicate based surface coating. Additional work is needed to develop a mounting flange configuration for this application.

In the final phase of the YAG development task, two-phase Al_2O_3-YAG fibers with up to 50% YAG were developed. These fibers exhibited good strength and a fine-grained, two-phase microstructure with high density. The fibers had improved strength and flexibility compared to YAG fibers synthesized previously. No grain growth or other microstructural degradation occurred in these fibers at temperatures up to 1300 °C for 100 hours. However, the creep rate of these fibers was not as good as 100% YAG fibers; instead, the creep rate was similar to Nextel 650 fibers. This concluded the YAG fiber development program.

Hot gas filter development activities under the CFCC program complimented the initial work performed under contract DE-AC21-94MC31212. Specifically, the CFCC program supported crucial field test activities that provided an early demonstration of the unique thermal shock resistance of the vacuum wound filter structure. If the DOE Clean Coal project at Lakeland, Florida had proceeded as planned, MTI would have set up a pilot manufacturing line under Phase III of the CFCC program to supply filter elements for this facility. The vacuum wound hot gas filter continues to generate a low level of interest in the power generation market. The unique combination of moderate strength and low elastic modulus results a very thermal shock resistant component. Furthermore, the structure is mechanically tough and highly resistant to surface flaws or damage.

Although the classified application was terminated because the process requiring these parts was not selected by the customer, significant progress was achieved in the fabrication of thin gage CFCC's. A pilot production line was also planned for this component under Phase III. Significant developments related to this work include:

- an improved commercial fiber was developed by 3M (Nextel 650)
- implementation of immiscible liquid fiber coating (> 40 pounds of carbon coated fiber produced)
- successful production of thin gage CFCC panels
- a more durable and corrosion resistant and cost effective replacement for existing component

2 Application Assessment

Potential CFCC applications were assessed throughout the program. This included market analysis, and contacts with potential customers and potential partners in order to build a portfolio of products for future CFCC manufacturing capability. Emphasis was placed on completing the development and testing of selected components. Table 1 lists the applications identified in Phase 1[1] of the MTI program along with their current status. After reviewing the potential for commercial and technical success, the following applications were selected for further development in Phase 2:

- Porous composites
  - Hot gas filters
  - IR radiant emitters for industrial heating applications
- Dense Composites
  - Corrosion resistant component (classified application)
  - Low NOx burner components
  - Turbine combustor liners
  - Casting riser tubes for low pressure aluminum casting

These applications will be described in more detail in the sections that follow.

2.1 Hot Gas Filters

Despite the increasing utilization of combined cycle gas turbine plants, advanced coal based power generation systems such as PFBC and IGCC are expected to play an important role in future power generating capacity in both the domestic and international markets. A critical feature of advanced coal fired power generation systems such as pressurized fluid bed combustors (PFBC) and integrated gasification combined cycle (IGCC) is the high temperature high-pressure gas stream utilized by the gas turbine. In order to protect the gas turbine components from erosion, it is necessary to remove the ash/sorbent particulates from the turbine inlet gas stream. The high temperature barrier filters are therefore considered to be one of the enabling technologies for the high efficiency cycles. Testing at various DOE and private facilities has demonstrated that the level of mechanical durability exhibited by the currently available filters may not be adequate to meet the reliability demands of large power generation systems.

Hot gas filter elements must be sufficiently rugged to withstand the mechanical abuse associated with a power plant environment. Element failures have occurred during shipping, installation, and inspection/removal. Although failures during shipping or installation would not result in plant downtime, filter elements may be damaged to the extent that even normal operating conditions could lead to failure. During normal operations, the filter elements are exposed to temperatures up to 850 °C in a combustion atmosphere containing alkali, sulfur, and water vapor. As in many material applications, the nominal operating conditions of 750 to 860°C in a coal combustion atmosphere present only part of the challenge. Plant upset conditions, on the other hand, typically present the most serious threat and account for the bulk of the filter element failures. For example in PFBC plants, the transition from startup burners to coal firing may result in the carryover of unburned coal to the filter system and subsequent ignition on the surface of the filter element. The resulting severe thermal gradients produced at the surface of the filter element often generate a highly localized stress that causes failure of the element. In monolithic materials, the combination of a high elastic modulus and high coefficient of thermal expansion often results in excessive thermal stresses that produce catastrophic failure of the filter element.

Monolithic silicon carbide (SiC) is currently the most common material used in the fabrication of candle filters. Because of their monolithic structure, SiC candle filter elements exhibit brittle or catastrophic failure. The combination of relatively high thermal conductivity and moderate thermal expansion (5 ppm/°C) of SiC contributes to good thermal shock resistance. Excessive creep elongation and distortion of SiC candle filter elements was attributed to the clay based bond phase used in some compositions. New bond systems have eliminated the creep problem; however, element elongation due to oxidation remains an issue at higher temperatures.

Mullite and cordierite oxide materials have also been utilized for monolithic ceramic barrier filters. Mullite systems suffer from low thermal shock resistance as a result of a moderate thermal conductivity and moderate thermal expansion (5 ppm/°C). The low thermal expansion (1 to 1.5 ppm/°C) of cordierite systems results in increased thermal shock resistance; however, brittle failures remain a problem.

Continued development of the MTI hot gas filter element through the DOE/NETL and CFCC programs has resulted in a product that has performed very well in pilot-scale field-testing. The unique combination of moderate strength and low elastic modulus has resulted in a filter with superior strain tolerance and non-catastrophic failure behavior. In addition, this combination of properties also results in extremely good thermal shock resistance that was demonstrated in the severe thermal upsets that occurred in a current pilot-scale test program. The MTI filter elements are fabricated as flanged-closed end tubes or candles approximately 60 mm diameter by 1.5 M long using a vacuum winding process. In order to transfer the fabrication technology to production scale, a number of process operations were streamlined to improve product consistency, reduce the labor content, and minimize capital equipment requirements.

Although the filter element market for power generation is clouded by fuel costs and deregulation issues, a reasonable market for filter elements exists in the larger scale advanced coal power system test facilities now coming on line. At the beginning of Phase II, the 240 MWe Foster Wheeler pressurized fluidized bed combustion (PFBC) Clean Coal plant was planned to be built in Lakeland, FL. The first filter element order was expected in late 2001 with delivery scheduled for the last quarter of 2002. The Lakeland CCT project was eventually cancelled and no new PFBC plants are expected in the near term. Furthermore, as part of a DOE Clean Coal Technology (CCT) proposal effort in the Spring of 2002, no domestic OEM's would bid on a PFBC plant design. This is a clear indication that PFBC based plants are not a near term hot gas filter market.

Gasification systems (i.e. IGCC) appear to be the most near term market for hot gas filters. The Wabash River Coal Gasification Repowering Project is a 262 MWe commercial scale IGCC plant that began operating in 1995. Additionally, the 540 MWe Kentucky Pioneer Energy IGCC Demonstration Project is now in the planning stage. The Wabash system utilized SiC elements during startup and currently uses metal filters. Because of concerns regarding the corrosion resistance of the metal filters, there is continued interest in a more durable ceramic filter element.

MTI was also contacted to supply hot gas filters for testing in a low-level nuclear waste processing facility. The facility was commissioned in 1999 and requires over 160 filter elements in the filter array. This application is very cost sensitive and currently uses SiC filter elements.

A hot gas filter application in the chemical industry was identified by ORNL. Subsequent testing performed by ORNL demonstrated that the alumina CFCC composition was unacceptable for this application.

2.2 Infrared Burners

The use of high porosity reticulated or fibrous ceramic structures for gas-fired IR burner elements has been the subject of substantial development in recent years. The benefits of improved heat transfer and reduced pollutant emissions has been widely recognized. For example, when preheating before the press section, a 10°C web temperature increase yields a one point solids increase out of press. This one point increase in solids content going into the dryer yields a 4% energy savings or production increase. Current practice is to use a steambox that has the advantage of high energy content. Disadvantages of the steambox include the vacuum requirement and the fact that the efficiency is affected by sheet "openness". The trend to increased recyled fiber decreases sheet "openness" thus further limiting the applicability of the steambox.

Furthermore, incremental increases in web temperature decreases with increasing steam flow. Preheating the web just prior to the first dryer allows all dryers to operate at maximum temperature without web sticking. However, a number of studies have shown that significant gains in energy efficiency (by 10-25%) and productivity, via enhanced heat transfer, can be obtained through the use of high-temperature, spectrally-controlled ceramic emitters. Thus, the use of one or more selective emitters in the burner element may allow for tailoring of the IR emission spectra to match specific materials and processes, and thereby optimize energy and equipment utilization.

Target industries which consume substantial quantities of natural gas, and other fuels, for process heat and which appear to be potential candidates for enhanced IR radiant burners include paper products, textiles, paint/coating curing, thermoplastic forming, food processing and waste treatment. Based on preliminary evaluations of potential markets, MTI selected IR drying of paper products as the initial application for spectrally controlled emitters. Fibrous metal and ceramic emitters are already being used in existing IR heating equipment produced by OEMs. Thus, there is an existing market for drying equipment with a high-temperature, spectrally-controlled CFCC emitter to enhance performance.

The objective of the infrared drying application is to develop a spectrally matched burner system with improved heat transfer to the wet paper web. The essential requirements of a composite IR emitter designed to optimize the transfer of thermal energy to the wet paper web include the following elements:

- low mass
- controlled emittance component
- acceptable strength, thermal stability, and durability
- cost effectiveness

The benefits of such a burner are increased efficiency and safety. In addition, the production rate of many paper machines is limited by the dryer capacity so increasing the efficiency of the dryer results in increased machine capacity. Current IR burners consist of all metal fabrications and operate at a metal temperature of 870 to 940C at typical firing conditions. The primary disadvantage of metal burners is the slow heating and cooling rates that result from the large thermal mass. In order to prevent equipment damage and fires, the burners must have low thermal mass in order to cool rapidly in the event of a web break.

2.3 Corrosion Resistant Component (MTI Classified Application)

A classified application for corrosion resistant CFCC's showed promise as the nearest term market for dense CFCC materials in sizable quantities. The use of an oxide-oxide CFCC material solved a critical corrosion problem that limited system operation. A CFCC material using Nextel 610 fiber, a fugitive interface, and an alumina-yttria matrix performed well in several system tests. However, improved creep resistance and chemical stability will be needed for long-term operation in the system. As such, MTI worked with 3M to develop a modified 610 fiber having 1-2 orders of magnitude reduction in creep. The development of the modified fiber; CFCC component fabrication and testing using this fiber; and development of the YAG matrix was supported by MTI's customer. MTI has received more than $1 million in funding to support the development effort. In order to meet the anticipated volume and cost requirements, MTI investigated scale-up issues and manufacturing process development for dense structural CFCCs under Task 4.

The MTI classified application was utilized in an advanced processing system that was recently suspended by the ultimate customer. Based on the results of a recent series of test runs, the customer identified continuing issues that would take at least another year to address satisfactorily and, once addressed, would increase new plant construction costs beyond the previous estimate. Even if these issues were resolved, the resulting economics, weighed against the market price trends, would provide too low a rate of return on investment for the risk involved. The decision to suspend the project was driven by clear cost/benefit and long-term considerations. This was a business decision that was not related to the MTI CFCC material.

2.4 Structural CFCC's: Low NOx Burner Components and Turbine Combustor Liners

Discussions with the B&W Power Generation Group identified low NOx burners as a potential CFCC application. Existing metallic burner components may exhibit severe wastage in some oil-fired low-NOx burner applications as a result of the sulfur, vanadium, and sodium in the atmosphere. Typical operating temperature of the burner components is approximately 1000 to 1100C. Other key design issues include complex shapes and attachment methods. Laboratory corrosion tests were performed on CFCC coupons to identify suitable compositions. Because of the complex shape of the burner component, fabrication development activities were initiated in parallel with the corrosion testing.

Ceramic fiber properties such as strength and creep resistance in conjunction with the debonding behavior of the fiber coatings control the properties of structural CFCC's. Although much of the coating development has been focused on non-oxide fiber systems, MTI and others have made substantial progress in the development of non-reactive coatings with acceptable de-bonding properties. Coating methods utilized at MTI include solution based and slurry systems. In order to minimize bridging between fibers, considerable effort was devoted to implementing the immiscible liquid coating method proposed by Hay.

2.5 Aluminum Casting Riser Tube

Casting riser tubes are used to transfer molten aluminum from a ladle to the mold in a low pressure casting process. Pressurization of the gas space above the aluminum melt causes the metal to flow up through the riser tube and into the mold. The riser tube must therefore be gas-tight in order to function as the pressure boundary needed to force the molten metal up into the mold. Other performance requirements and conditions include:

- Molten aluminum (750C) resistance
- Thermal shock resistant
- Low cost per unit of production (wheel)
- Non-wetting by molten aluminum
- Low dross adherence
- Mechanically durable
- Low thermal mass

Current industry practice is to use porcelain coated cast iron and monolithic fused silica tubes. The cast iron typically exhibits longer service life at a higher cost than fused silica. Furthermore, cast iron tubes would require more extensive preheating to prevent solidification in the tube. Fused silica tubes are fabricated with thick walls to meet the durability and gas-tightness requirements. With cast iron setting a high material durability standard at a low cost per wheel cast, it is necessary to rethink the design of a CFCC tube. The mechanical properties of conventional ceramic composites are generally fiber dominated. Therefore, the typical approach is to maximize composite strength by increasing the fiber volume. For example, the thin gage corrosion resistant panels utilized an unbalanced weave fabric to increase the axial fiber concentration in order to improve creep resistance. Because cost is such a critical consideration for the casting riser tube, the technical approach and design must be modified to develop a successful product. The cost of the primary reinforcement fibers is 682 per kg ($0.11 per meter). In comparison, matrix raw material costs are $2.30 to 50.00 per kg. Furthermore, the fabrication method has a significant impact on the potential fiber volume in the component. Therefore composite designs that minimized fiber volume while maintaining acceptable strength and toughness were investigated. It was also critical that the number and complexity of processing steps be minimized to control labor costs.

3 Supporting Technologies

Nondestructive evaluation (NDE) techniques developed at Argonne National Laboratory (ANL) were used to evaluate the flange and body sections of MTI hot gas filters. In addition, Oak Ridge National Laboratory (ORNL) tested MTI hot gas filters in a simulated Dow Corning process environment. The results of the ORNL study indicated that the alumina composite used for the filter was not suitable for this application. In addition, Northwestern University supported fiber coating development that led to an Air Force program on Robust Fiber Coatings. Finally, MTI worked closely with Virginia Tech on mechanical testing and modeling of various CFCC components. A ligature model of the hot gas filter provided valuable insight on the unique mechanical properties of the vacuum wound structure.

4 Materials and Process Development

4.1 Process Feasibility

Process details are described in the Process Engineering section below.

4.2 Process Engineering

4.2.1 Hot Gas Filters

Although the bulk of the hot gas filter process engineering activity was performed under the FETC Advanced Hot Gas Filter Development program, it is useful to describe the fabrication process. As described previously, the hot gas filters were fabricated by a vacuum winding process developed by MTI. The essential requirements of a composite material designed to meet the program objective for a toughened hot gas filter include the following:

- stable continuous fiber
- engineered fiber coating (if required)
- rigid porous matrix
- cost effectiveness
- appropriate filtration properties

In the MTI hot gas filter, structural reinforcement is provided by the continuous ceramic fibers while the discontinuous fibers perform the filtration function and form the rigid porous matrix of the filter element. The pure alumina Nextel™ 610 fiber was supplied as 400 filament tows with a unit weight of 1500 denier. The Saffil™ discontinuous fiber (95-97% alumina, 3-5% silica) was supplied as bulk fiber and exhibited a mean diameter of 3.5 microns. A modified filament winding process, shown in Figure 1, was developed to simultaneously deposit both continuous and discontinuous fibers on a mandrel. An En-Tec computer controlled filament winder was used for all samples. The continuous fiber was wound onto a mandrel while a dilute slurry of discontinuous fiber was pumped onto the mandrel. The excess water from the slurry was removed by the system to deposit the discontinuous fiber. The resulting preform exhibits a controlled distribution of the Nextel continuous fiber and Saffil discontinuous fiber through the wall thickness. The relative distribution of the continuous and discontinuous fibers was controlled to optimize the cost and/or performance of the filter element. Figure 2 shows the amounts of Nextel 610 continuous fiber and Saffil chopped fiber as a function of the number of layers or closures from the inside diameter to the outside diameter of the filter element. This demonstrates how the Nextel 610 was concentrated in regions of high stress near the filter element ID and OD and decreased near the center of the filter element wall. The ease of producing graded structures is unique to the vacuum winding process. An example of a vacuum wound microstructure is shown in Figure 3. The flange section was initially formed oversize and machined to the appropriate size and shape. The resulting flange exhibited low strength because the continuous fibers were cut in the machining operation and were therefore not anchored to the body of the element. The independent control of the relative amounts of continuous and discontinuous fibers can also be varied along the element axis to form an integral flange that required only trimming to length. During initial tests, the sealing gaskets on filters with the machined flange leaked because the mounting loads were reduced to accommodate the lower flange strength. In the net shape flange shown in Figure 4, the continuous fibers remain intact to effectively transfer the collaring loads to the body of the element and greatly enhance the integrity of the flange section.

The fabrication process is completed by the addition of a bond component in the form of a sol or liquid chemical binder to the filter element preform followed by heat treatments to convert the sol to a stable bond phase. An ideal bond system must develop bonds at fiber to fiber contact points without plugging or filling the open or continuous porosity of the filter element. The development of a uniform distribution of the bond phase is critical to developing high strength without compromising the permeability of the filter. Phosphoric acid was used as the bond system in the early part of the program. The phosphoric acid reacts with the alumina to form a gel around the fibers that bonds the fibers at contact points. Subsequent heat treatment converted the gel to monoaluminum phosphate, a very refractory bond phase. Although the phosphoric acid resulted in high strength and the desired bond morphology, a fiber coating was required to minimize degradation of the continuous fiber. Various fiber coatings and application methods were investigated under the NETL program. A fugitive fiber coating based on furfuryl alcohol was applied by the immiscible liquid process described in section 3.2.3. A disadvantage of the carbon coating is the requirement to perform all heat treatments in an inert atmosphere. Furthermore, the available inert gas furnaces could not accommodate the 1.5 meter long filters required for the PFBC application. Additionally, some compositions utilizing the phosphoric acid bond system exhibited brittle failure behavior at elevated temperature.

Alternate bond systems were therefore investigated to simplify the fabrication process. An oxyhydroxide of aluminum, AlOOH or boehmite was selected for further development. A principal advantage of the boehmite bond is that no fiber coating is required because the boehmite sol does not react with the Nextel fiber. The boehmite-bonded filters were dried and fired to 1150°C to stabilize the structure prior to the final inspection.

4.2.2 IR Burner Emitters

The IR emitter activity was focused on developing a durable CFCC emitter for the Krieger burner system. Spectral control coating materials were selected to match the infrared absorption of water[2] as shown in Figure 5. In order to achieve some penetration through the thickness of the paper web, the initial work focused on the two absorption peaks at 1.5 and 2.0 microns. Erbium and holmium were selected for further study because they exhibit emittance peaks at 1.5 and 2.0 microns, respectively as shown in Figure 5. In addition, unlike other elements, the emittance peak of rare earth elements is related to an inner electron shell transition that is relatively unaffected by crystal structure. Aluminum oxide composite systems provide a good substrate for spectral control coatings because they typically exhibit very low emittance in this spectral range.

Preliminary burner testing demonstrated that the original flow through burner design resulted in severe composite degradation because the material temperatures were far above the fiber use temperature. Testing at IPST and MTI confirmed that a perforated burner block combined with a reverberation screen produced significantly more radiant power. Subsequent material development was then focused on this burner design.

The configuration of the burner block was re-examined to improve the effectiveness of the reverberation screen. In particular, the work was focused on the development of a burner block configuration that produced a uniform temperature on the reverberation screen while eliminating flash back inside the burner. After several attempts to stabilize the flame position by controlling the porosity of the burner block, a ported block configuration was developed because it exhibited more flexibility in terms of flow and distribution. Burner block perforations of 1 to 2 mm were positioned at 3 and 6 mm center to center spacing, respectively. Several burner blocks were drilled manually and with numerically controlled machines but the machining cost was prohibitive either way.

Furthermore, it was difficult to achieve clean holes because of fiber pull out during the drilling operation.

Efforts were then directed at developing a net shape vacuum forming method that was capable of producing the desired perforation pattern and increased block thickness. Although vacuum forming is normally used for relatively simple shapes such as blocks and tubes, more complex shapes can be produced if the fiber length is short enough. Saffil fiber was prepared by mixing in a Hobart style mixer to shorten the fiber. Final grinding was performed in a high-shear mixer. This practice typically produced fiber lengths of 100 to 200μ. Grinding times were varied to determine the maximum fiber length consistent with good forming behavior and strength properties. The pin array can be changed to vary the number and distribution of ports to control the flame pattern. The goal was to achieve sufficient gas velocity to prevent flash back while keeping the flame attached to the burner block. The current burner block mold configuration uses an array of 414 pins 2.1 mm diameter that should give a port velocity of 0.9 M/sec at a firing rate of 15,000 Btu/hr. Considering the porous burner block material, the actual port velocity would be somewhat less than 0.9M/sec.

After the vacuum forming operation, the wet preform was saturated with an alumina sol and gelled with ammonia gas to minimize sol migration during drying. The ammonia gas gelling time was extended to increase the stability of the preform and to facilitate removal from the mold box. The amount of bond phase was controlled by the concentration of the sol and by the amount of sol left in the preform. Increasing the amount of bond phase in the burner block not only decreases the bulk porosity but also can also adversely affect the brittleness and thermal shock resistance of the block. The challenge is to develop sufficient bond phase to ensure good handling strength while maintaining the excellent thermal shock resistance that is inherent in an open-fibrous structure.

Emittance control was achieved by coating the burner blocks and reverberation screens with an inorganic polymer prepared by digesting selected rare earth oxides in glycolic acid and formic acid. Excess water was boiled off to control the rare earth concentration and viscosity. The resulting precursors were applied to the fibers using an on-line coating system during the screen winding operation. The high viscosity and good film forming characteristics of the rare earth precursor resulted in significantly more compact fiber tows than with as-received fibers. After winding the pattern on the hexagon mandrel, the individual screens were bonded along the edges to stabilize the fiber and to facilitate mounting the screen on the burner. Individual screens were recoated several times before firing to 538C. The good film forming also resulted in significantly improved coating coverage after firing compared to slurry based coatings. Spectral control on the burner block was achieved by spraying the outer surface of the dried perform with the rare-earth polymer. Thin coatings are necessary to minimize penetration into the block and to prevent foaming of the polymer during the drying step. More importantly, a burner block failed during rapid cooling on the burner test stand. Typical gas stream temperature went from about 871C to under 204C in 1.5 minutes. Visual examination of the cross section of the block revealed that the rare earth polymer penetrated and densified approximately 1/3 to 1/2 of the block thickness. Cracks formed at the surface during cooling and propagated through the thickness. The polymer is now applied in multiple thin coats, dried between coats and fired at 44C/hour to 538C to minimize foaming.

A more direct form of spectral control involved the production of chopped $(Er,Ho)_3Al_5O_{12}$ garnet fibers by the centrifugal spinning process at MTI. Although fabrication of green fibers does not seem to be a problem, firing to form dense, fine-grained fibers has proven difficult. Initial results have shown larger grains (0.5-1.0 microns) and weak fibers after firing to 1500°C. Such fibers are very friable, and thus are inadequate for emitter fabrication. This approach was abandoned because the precursor coating or powder additions to the burner block and screen appeared to be more durable.

In a parallel effort, two approaches were considered to increase the radiant output of the burner. Although the rare earth oxides provide a means to control the peak wavelength of the radiated power, the peaks are very narrow and high material temperatures are needed to generate output comparable to metal burners. In order to get a more direct comparison with the metal burner, a "gray-body" emitting burner block was fabricated by adding SiC powder to a portion of the fiber slurry used in the vacuum forming process. The overall emittance of the SiC containing burner block is expected to be lower than a pure SiC or metal emitter because of the dilution of the SiC by the Saffil fiber. The SiC based emitter should have a broad gray body radiant output and exhibit the rapid cool down characteristics of a low-mass burner. In addition, a commercial high emittance coating, Aremco 840C, was used on six sets of burner blocks and screens and tested at IPST. Three coats of the Aremco 840C were sufficient to achieve complete coverage on the screens and burner blocks. A final heat treatment to 538C was used to stabilize the coating prior to testing.

A number of ceramic fibers were used in the screen fabrication work. The 3M Nextel family of fibers included Nextel 610, a pure alumina fiber; Nextel 650, a zirconia modified alumina fiber; and Nextel 720, an alumina/mullite fiber. Nextel 610 was supplied as 1500 denier and 10,000 denier tow sizes. The bulk of the screens were fabricated using rayon served Nextel 610 because the served fiber was much more compact than any of the sized fibers. The compact fiber tow allowed more flexibility in terms of screen patterns. Finally, Textron SCS-6, a 142 micron diameter CVD silicon carbide fiber, was used as gray body emitting fiber. The Textron fiber was wound as a single filament without a bond phase and the resulting screens were somewhat fragile compared to the coated fiber screens.

Initial burner screens were fabricated by hand weaving fiber tows that were rigidized with the rare earth polymer. The hand weaving process was very time consuming and the resulting screens were limited to relatively large openings (~6 mm). In order to increase the flexibility and speed of screen fabrication, developmental reverberation screen preforms were fabricated by filament winding a helical pattern on a hexagonal mandrel. As currently configured, twelve screens (150 by 200 mm) can be fabricated at one time. An En-Tec computer controlled filament winder facilitated screen development because it permitted exploration of a variety of fiber spacings and patterns. Compared to woven screens that are interlocked with adjacent or nearby fibers, filament wound screens typically exhibit loose fiber strands that extend out of the plane of the screen because they lack the anchoring provided by woven patterns. Various filament-winding patterns were investigated to improve screen stability through increased fiber interlocking. Screens were fabricated with open areas of 25 to 75 percent.

4.2.3 Dense Composites

Continuous fibers were coated as described in section 4.3.2 with the appropriate interfacial coating prior to fabricating the preform. Dense composite preforms were produced by the following methods:

- filament winding
- 3D weaving
- 2D fabric lay-up

The preforms were densified by a two-step process. In the first step, the voids between the fibers were filled by pressure casting a slurry of fine powder through the cross-section of the part. In order to fill the voids in the preform, the particle size of the slurry must be much smaller than the fiber diameter. Figure 6 illustrates the elements of the pressure casting process and shows a partially filled preform. In this process a filter cake forms at the filter paper surface and builds up through the preform. The water passes through the filter paper and drains from the system. By applying pressure above the slurry, reasonable casting rates are possible even with thick parts. Because sol-gel or chemical precursors have such low volume yields it is essential to perform the initial densification using pressure casting if reasonable process times are to be achieved. Final densification of the component is achieved by sol-gel vacuum impregnation to form additional matrix material within the voids of the pressure cast powder matrix. Approximately 15 to 20 sol-gel impregnation/drying/firing cycles are required to achieve an 80 to 85% dense composite.

The pressure casting process described above was initially developed for flat plate components for the corrosion resistant components and later adapted by MTI to produce cylinders and complex 3D parts for burners. Flat plates up to 15 mm thick using approximately 40 plies of carbon coated fabric were fabricated. In order to achieve the desired fiber loading, it was necessary to compress the preform while maintaining the appropriate pressure seals. Cylindrical performs produced by filament winding or 3D weaving required special tooling that provided the necessary sealing to control slurry flow and water extraction. Tubes with wall thickness up to 2.5 cm thick were successfully pressure cast.

4.2.4 Aluminum casting riser tubes

Fabrication development of aluminum casting riser tubes utilized filament winding and either pressure casting or slurry winding to form the initial matrix. The emphasis must be to keep production cost low in order to compete with the existing materials. Therefore, either low cost fibers or low fiber content and probably both will be required to meet the market requirements for the finished product. A simplified fabrication process is also necessary to minimize the labor content.

Candidate reinforcement fibers include the Nextel family of oxide fibers discussed above. 3M's Nextel 610 alumina fiber in rayon served 1500 denier and 10,000 denier were selected for the alumina system. Note that the rayon fiber used as a serving is approximately 100 u diameter. For the silica composition, Quartzel fused quartz fiber produced by St. Gobain was used as a twisted two end yarn or a 20 end roving. The fibers were filament wound in a helical pattern using a 45° winding angle and a fiber spacing that depended on the width of the fiber tow. A filter paper covered mandrel was used for both approaches.

Pressure casting utilized Sumitomo AKP 53 high purity fine alumina with a median particle size of 0.2 microns. AKP 20 alumina with a median particle size 0.5 microns was also blended with the AKP 53 in an attempt to increase the packing density. Although increased packing was achieved with the blended powder, significantly higher packing efficiency results when a much broader size distribution is used in a slurry winding process.

In order to minimize the porosity of the finished composite, it is essential to maximize the solids content of the slurries used in the forming process. Andreassen[3] developed an empirical particle packing theory that can be used to design high solids slurries. The Andreassen equation:

$$CPFT = (d/d_{max})^q * 100 \qquad (1)$$

CPFT = cumulative percent finer than
d = particle diameter
d_{max} = maximum particle size
q = exponent

A plot of log(CPFT) versus log (d/d_{max}) will have a slope of q. Using computer packing models, Funk and Dinger[4] determined that optimum packing occurred at q = 0.37. In practice[5], lower values of q between 0.20 and 0.25 produce free flowing slurries at high solids loading. MTI developed an optimization routine that blends powders of various size distributions to achieve the best fit to the Andreassen equation for a given q value and maximum particle size d_{max}.

Particle size distributions for the candidate alumina raw materials are shown in Figure 7. Microsilica supplied by Elkem was added to some of the alumina batches to improve rheology. An example of an alumina slurry design with a q of 0.2 and a d_{max} of 250 microns is shown in Figure 8. The following raw materials were blended to get this particle size distribution: Alcoa A3000FL alumina, Alcoa CTC50 alumina, Elkem 971 microsilica, Sumitomo AKP53 alumina, T64 tabular alumina (minus 100 mesh), and T64 tabular alumina (+48-200 mesh). Citric acid was added at a concentration of 0.28 mg/m^2 as a dispersant. Samples were prepared with d_{max} ranging from 10 microns to 700 microns. Slurry preparation involved dry mixing in a Hobart planetary mixer followed by a two-stage water addition. The initial water addition was sufficient to get a fully wetted paste of about 80 to 82 percent solids that developed high shear to break up the agglomerates. The final water addition produced a solids content of 74 to79 percent at a pumpable viscosity. Pileggi and Pandolfelli[6] recently reported that a q of 0.26 resulted in improved rheology for large scale pumping applications but this value resulted in excessive water content and higher porosity. A vacuum de-airing step was performed to remove trapped bubbles that would produce flaws in the part.

The slurry pumping system was designed to ensure complete coverage of the fiber as it was wound on the mandrel. A vacuum was applied to the mandrel to remove excess water but the high solids slurries were not sufficiently permeable to de-water fast enough to keep up with the winding speed. Matrix porosity was highly dependent on the size and shape of the fiber tows used. Although well separated de-sized fibers are normally used to achieve a uniform fiber distribution, tubes produced with these fibers were usually brittle. Furthermore, the 10,000 denier fiber tows often trapped porosity at fiber cross-over locations. The best mechanical behavior was achieved using served or twisted fibers that formed discrete reinforcement. Even with high solids slurries, problems were encountered with excessive porosity caused by the migration of fines during drying. Calcium aluminate cement bonded compositions were developed to stabilize the matrix prior to drying. A blend of set controlling additives was used to delay the setting of the cement enough to complete the preform winding. If a collapsible mandrel was used, unfired composites could be produced with the calcium aluminate cement bonded compositions. An initial heat treatment to 538C was used to burn off the filter paper in order to remove the part from the mandrel. After the initial 538 C heat treatment, the alumina and silica composites were sintered at 1000C and 750C, respectively.

Preliminary tests were performed to characterize the baseline properties of the composites. These tests included C-ring strength, porosity, bulk density, and permeability. Composite samples were also sectioned to evaluate fiber and matrix distribution. The fiber distribution was greatly improved by using fine gage fibers such as the rayon served Nextel 610 alumina fiber or the twisted Quartzel yarn. A typical cross-section of a slurry wound alumina tube is shown in Figures 9 – 11. The matrix cracks visible in Figures 9 and 10 were attributed to the thermal expansion of the rayon serving on the fiber tow. In addition, the gap around each fiber tow produced by burning out the rayon appears to improve the mechanical behavior by increasing the fiber pull-out. C-ring strength of the alumina composition after the 1000C firing was in the range 73 to 103 MPa with non-brittle failure. An example of the fracture behavior of the alumina composite is shown in Figure 12. As shown in Figure 13, the alumina sample exhibited substantial fiber pullout. In contrast, the fused silica sample exhibited brittle failure and no significant fiber pullout. Quartzel fiber with HT-1 sizing exhibited non-brittle failure and about an order of magnitude lower than the alumina composites. The fused silica composition was not investigated further as a result of the low strength and low corrosion resistance.

Initial permeability tests performed on the baseline material demonstrated that neither the pressure cast nor the slurry wound parts meet the specification of a leak down time of five minutes to drop from 20 psi to 15 psi. Partially hydrolyzed ethyl silicate was tested as a sealant but resulted in little improvement. The ethyl silicate did however improve the strength from 69 MPa to 97 MPa for the alumina compsosition.

Surface coatings were also evaluated as a sealing method. The focus was on developing a borosilicate glaze that matched the thermal expansion of the alumina composite structure. Slurries were prepared at about 50 weight percent solids and applied to the tube by dipping. After drying, the parts were recoated, dried and fired at temperatures up to 1050C. The resulting glaze was fully vitrified and met the sealing requirement of a leak down time of at least 5 minutes from a pressure of 138 to 103 Pa (20 to 15 psi). Figure 14 shows a cross section of coated sample.

Corrosion resistance was assessed by a static aluminum exposure test. Sections of riser tubes were cemented to alumina plates to form the test crucibles. A quantity of aluminum alloy 6061 bar stock was located on top of a perforated plate over the crucible. This configuration allowed the aluminum to melt and flow into the test crucible without forming an oxide shell that would prevent direct contact between the molten metal and sample. The test was performed in a cold wall vacuum furnace at approximately 740C for 72 hours. Following the test, the crucible containing the sample was sectioned and photographed. Figures 15 and 16 show the test crucible configuration and a macrophoto of the metal/wall interface. The separation of the coating in Figure 16 was probably caused by expansion of the bubbles in the glass phase under the prolonged high temperature vacuum conditions in the test.

4.3 Subtask 3.2.2 CFCC Process Optimization

4.3.1 Hot Gas Filter

Process optimization activities for hot gas filters are described in section 4.1, Process Scale-up and Manufacturability.

4.3.2 Fiber Coating Development

A weak fiber/matrix interface is required to prevent matrix cracks from propagating through the fiber in order to impart damage tolerance to the composite. Obviously, if a weak bond is not developed at the fiber/matrix interface, one is left with a very high cost monolithic material. Because the fiber/matrix interface is such a critical element of a CFCC, a significant effort was devoted to the development of interface control methods for the oxide/oxide system. Essential characteristics of the fiber/matrix interface include:

- Weak bond
- Chemically stable
- Mechanically stable

Several approaches were investigated to develop a weak fiber/matrix interface. The simplest approach uses no fiber coating and relies on a porous matrix to prevent crack propagation[7]. In order to keep costs low, the aluminum casting riser tube development relied on a porous matrix to avoid excessive fiber/matrix bonding. A fugitive interface was utilized for the corrosion resistant components in the classified application. The fugitive carbon coating protected the fiber during processing and provided a controlled gap between the fiber and matrix after a final oxidizing heat treatment. Neither fugitive coatings nor porous matrix approaches provide any fiber protection from the service environment and long term exposure effects need to be assessed for specific applications.

An improved fiber coating process based on the work of Hay[8] was implemented for dense composites. This process utilized the differences in the interfacial energies of immiscible liquids to minimize the coating bridges that normally occur within the fiber tow. Furfuryl alcohol catalyzed with citric acid was used as the carbon precursor. Hexadecane is immiscible with the furfuryl alcohol and provided the difference in interfacial energy required to minimize bridging within the fiber tow bundle. The as-received Nextel 610 fiber was de-sized by heating to approximately 815 °C in air. The fiber tow then entered the catalyzed furfuryl alcohol solution and then continued up through the hexadecane to separate the filaments. An argon purged furnace operated at about 815 °C was used to first cross-link and then pyrolyze the fiber coating. Up to six coating passes were performed on each fiber tow before applying a PVA sizing to improve handling strength. Coating speeds of up to 150 cm/min were achieved with this equipment. The coating speed would have to increased by about a factor of ten to allow reasonable filament winding speeds. MTI coated more than 40 pounds of Nextel 610 fiber using the immiscible liquid system.

MTI investigated several approaches that utilized dense non-reactive oxide coatings. MTI identified a new class of dense non-reactive oxide coatings in the ABO_4 family. The emphasis was on the tungstates ($Me^{+2}WO_4$) family, specifically, calcium tungstate or scheelite. The immiscible liquid coating process was used to apply the scheelite coating to Nextel 610 and 720 fibers. Transmission and scanning electron microscopy demonstrated that this coating provided an effective de-bond between the fiber and matrix. In addition, single filament strength testing was used to determine if the coating caused any degradation of the fibers. Generally, at least 30 single filament tests were used to perform Weibul analysis of the fiber strength distribution.

The heterocoagulation method of fiber coating was also utilized to apply $LaPO_4$ coatings to Nextel 720 fiber. In this method, surfactants are used to shift the isoelectric point of either the fiber or the coating particles to cause electrostatic attraction. By directly depositing the desired coating material, this method avoids possible fiber degradation that has been related to precursor stoichiometry.

4.3.3 Advanced Fiber Development

Although oxide fibers are thermodynamically stable in many industrial environments, they often lack sufficient creep resistance. In order to improve the creep strength of the corrosion resistant components for the classified application, 3m was funded by MTI's customer to improve the creep performance of Nextel 610 fiber. Yttria was added because it segregates at grain boundaries and decreases the creep rate by controlling grain boundary diffusivity. In addition, Zirconia was added to improve thermal stability by inhibiting grain growth at high temperature. The resulting fiber exhibited a creep rate that is approximately one to two orders of magnitude lower than standard Nextel 610 fiber. This fiber is commercially available as Nextel 650.[9]

MTI, 3M and stationary gas turbine OEMs encouraged the funding of a program to show the feasibility of a yttrium aluminum garnet (YAG) fiber program for use in a multiple of applications. The fibers are of most interest to the turbine industry; however, they would also positively impact the development of CFCCs for IR burners, TPV power systems and various industrial applications requiring high-temperature structural materials. YAG fibers are of interest because of their potential greater creep resistance than the current commercially available oxide fibers from 3M (Nextel 610 and Nextel 720). Alternate garnet fiber compositions could also be formulated with special spectral emission properties that are important for the IR burner and TPV applications.

The major accomplishments under the Investigative Program can be summarized in the following:

1. MTI's precursor chemistry for YAG fiber was successfully transferred to 3M. 3M performed some additional investigation of the precursor to better understand its chemical make-up. 3M also made some slight modifications to the chemistry to improve the shelf life of the precursor. 3M also continued development of their own precursor. By the end of the program, they had reached a formulation that is as good, if not better in some respects, to the MTI precursor.
2. Many batches of fiber were spun in 3M's development laboratory from the MTI precursor. These green fibers were then fired, in air, using different heating schedules to convert it to YAG polycrystalline fiber. Regardless of the heating schedule, the fiber invariably had larger grains (up to 1 micron in size) and poor strengths.
3. Because of the difficulty in achieving a fine-grained, strong fiber, 3M and MTI determined that dopants were likely required to assist in the conversion of the amorphous fiber to a crystalline fiber, which typically occurs near 900°C. The highly exothermic crystallization to YAG seems to create large "mosaic" crystals that

   weaken the fiber. In addition, the low densification rate for YAG caused by its low diffusivity suggests the need for effective sintering aids. It was determined that by doping the fiber with chromia and silica, formation of the “mosaic” crystals could be minimized, and much higher quality fibers could be produced. These doped fibers also exhibited a very smooth surface in contrast to undoped fibers that had a very textured or bumpy surface caused by large sub-surface crystals.

4. While the success with chromia and silica doping was encouraging, problems remained. Using standard fiber processing methods (sol concentration, fiber spinning and firing), results were erratic. In some cases, relatively high strength, fine-grained fibers were produced above 900°C; however, results could rarely be reproduced. To eliminate this variability, fiber process conditions were investigated to identify critical experiments. The experiments suggested the need for an improved pyrolysis cycle. It was determined that performing the pyrolysis in nitrogen greatly improved the quality of the fibers, with improved reproducibility.

Using the new heat treatment, 3M has produced an inventory of fiber batches that had decent strength and that are fine-grained. Actually, even undoped fibers heated in nitrogen showed good strengths indicating that the dopant issue may need revisiting; at least relative to crystallization control. Fibers that have been heat-treated to 1200°C show strengths of up to 100 ksi. These values are quite encouraging at this stage of development. In early stages of fiber development, laboratory fibers such as these have many defects such as kinks and bends that can be readily eliminated by focussed process development.

When the nitrogen-pyrolyzed fibers were fired in air to 1500°C and above, the grain coarsening and porosity experienced throughout this development effort were again apparent. Doped and undoped fiber heated to 1600°C had larger amounts of porosity and a much larger grain size than fibers heated at <1500°C. The doped YAG had a lower porosity, indicating improved sintering, but grain size was larger (>2 microns) than for undoped YAG fiber, which had grains <1 micron in size.

5. Scaling up the MTI precursor system even to a pilot scale will present a formidable challenge (e.g., nitrogen pyrolysis capability does not exist in the 3M fiber pilot plant or in factory processing equipment). The 3M YAG precursor could avoid thus problem. Fibers made from such a precursor using air firings are very comparable to those made with the MTI precursor using nitrogen firings. This remains a promising route for rapid scale-up to continuous YAG fiber tows.

The creep resistance of YAG fiber has been evaluated by Greg Morscher of NASA-Glenn using the bend-stress-relaxation (BSR) test method. The BSR test does not give an actual creep rate, but instead compares relative creep performance of fibers. The

test measures the amount that fibers relax about a constrained radius during a set heat-treatment. A extremely creep resistant fiber would should no relaxation (an M value of 1 according to the test) and straighten out completely when removed from the fixture. A fiber with very poor creep properties would fully relax (an M value of 0) and conform to the radius of the fixture during the heat-treatment time. The BSR test for the YAG fiber was run at 1200°C for one hour. An M value of 0.27 was measured. This should be compared to Nextel 720 that fully relaxes under these conditions. The YAG fiber is fully relaxed at 1250°C for one hour. These early results would indicate that a YAG fiber might exhibit about a 50°C higher use temperature than Nextel 720 fiber. This is probably a very conservative estimate. The YAG fiber that was tested still contained a large fraction of residual microporosity, and the fiber was only heat treated to 1300°C prior to the BSR test. We would expect denser fiber that has been heat-treated to a higher temperature to exhibit even better creep properties.

In the final phase of the YAG fiber program, two-phase Al_2O_3-YAG fibers with up to 50% YAG were developed. These fibers exhibited good strength and a fine-grained, two-phase microstructure with high density. The fibers had improved strength and flexibility compared to YAG fibers synthesized previously. No grain growth or other microstructural degradation occurred in these fibers at temperatures up to 1300 °C for 100 hours. However, the creep rate of these fibers was not as good as 100% YAG fibers; instead, the creep rate was similar to Nextel 650 fibers. This concluded the YAG fiber development program.

4.4 Component Fabrication and Testing

4.4.1 Hot Gas Filters

An early critical test was performed at the 55 MWe CFB located in Ebensburg, PA. The CFCC program supported the thermal fatigue segment of this test. Sub-scale filter elements were given 1000 back pulses with 90 psi air during the 250 hour test. Because this was an operating power boiler, the samples were installed in observation ports in the sidewall while the boiler was on line. The thermal shock caused by inserting the sample probes directly into the hot gas stream was probably the most severe aspect of the entire test exposure. The superior thermal shock resistance of the vacuum wound structure first demonstrated in the Ebensburg test would turnout to be a key advantage of the MTI hot gas filter. At the time of the test, the thermal shock caused by rapid heating of the filter element was not considered to be representative of typical service conditions. Subsequent testing at the Power Systems Development Facility (PSDF) in Wilsonville, AL demonstrated that thermal shock was indeed a

determining factor in hot gas filter survival.

A summary of filter testing is given in Table 2. Based on the initial test results, twelve full-size MTI filter elements were fabricated and tested for 581 hours in the Foster Wheeler pressurized circulating fluid bed combustor located in Karhula, Finland. The pressure drop and composition of each of these filters is shown in Figure 17. All of MTI elements survived the test with only minor surface defects consisting of small regions of missing chopped fiber. The MTI CFCC elements retained about 87 percent of the as-fabricated C-ring strength following the test as shown in Figure 18.

The primary filter element qualification testing was conducted in pilot scale testing at the DOE/Southern Company Services Inc. (SCS) Power Systems Development Facility (PSDF) in Wilsonville, AL. This $271 million facility was designed to develop and improve advanced coal-based electric generating technologies and environmental cleanup systems. The PSDF is sized to allow integrated testing of advanced power systems and components at a scale that can be confidently scaled up to commercial units. Initial testing at the PSDF utilized the M. W. Kellogg transport reactor module as the pressurized combustion unit and a Westinghouse hot gas filter system containing 91 filter elements as shown in Figure 19. No gas turbine is used on this system. Candidate filter elements for this system were purchased and installed by the Southern Company operators. As filter testing progressed, the PSDF staff provided detailed run data at regularly scheduled workshops and were particularly candid regarding system upsets. The availability of this information was critical to the filter element development process. MTI filter elements were included in test campaigns TC02, TC03, TC04, and TC05. During tests TC02 and TC04, coal carry-over and combustion on the surface of the elements resulted in the failures of monolithic oxide and non-oxide filter elements due to thermal shock. The MTI elements survived both upsets with no apparent damage. During test TC05, an end-plug on one of the MTI elements failed under conditions of higher than normal pressure drop and associated back-pulse pressures. The end-plug was re-designed to improve the integrity of the plug anchoring. A laboratory high-pressure back-pulse test was conducted to evaluate the durability of the revised end plug.

Filters were also tested at the Wabash River IGCC slip stream. Seven CFCC filter elements were tested for approximately 150 hours. The test was terminated because two of the filters developed leaks. Post test examination of the filters revealed that the inside surface near the flange was severely eroded. It appeared to have been caused by direct impingement by the cleaning pulse. This type of failure was never observed on the Westinghouse filter system which used a fail-safe/regenerator insert in the top of the filter that pre-heated and diffused the back pulse gas. Wabash has since included a filter fail safe device but it is not known if this would protect the filter from pulse

impingement. Additional testing in IGCC systems is unlikely because the process temperature has been decreased to permit the use of metal filters.

4.4.2 IR Burners

Preliminary laboratory testing of full-sized IR burner elements was performed on a Krieger burner test stand at MTI shown in Figure 20. The burner test stand consists of a Krieger burner and associated manifolds and pressure taps. The goal of the initial testing was to identify material and hardware issues that affected the lifetime of the burner element. A two-color pyrometer was used to measure the surface temperature of the emitter as a function of equivalent air flow at various gas flow rates. Equivalent air flow is defined as the ratio of the actual air flow to the air flow required for complete combustion or stoichiometric air flow. The MTI test stand was subsequently modified to include a water calorimeter in order to measure heat flux and burner efficiency because pyrometer temperature measurements alone were an unreliable indication of burner performance. An estimate of the burner efficiency was determined from the heat absorbed by the water and the energy input to the burner. In the MTI test, the temperature of a weighed amount of water is measured as a function of the heating time. The emitter surface was positioned 2.5 inches from the surface of the water. A summary of the calorimeter results is shown in Figure 21. It is apparent from this graph that the holmium and silicon carbide CFCC burner systems transferred significantly more energy to the water than the metal burner at the 15,000 Btu/hr firing rate. The results tended to converge at 20,000 Btu/hr. Photographs of the holmium coated CFCC and Krieger metal burners in operation are shown in Figures 22 and 23. It is clear that the more gray body emitting metal burners operate at a lower temperature than the holmium coated CFCC burners.

Candidate emitters (both selective emittance and grey-body emitters) were supplied to the Institute of Paper Science and Technology (IPST) and Georgia Tech for characterization. Krieger supplied a six-burner test stand to IPST to support this activity. Georgia Tech measured the spectral response of the standard Krieger metal burner and various rare earth coated CFCC emitter systems. IPST performed drying tests of the candidate burner systems on their flywheel driven test sled shown in Figure 24. Drying tests were performed at typical paper machine speeds of up to 3000 feet per minute using an instrumented section of wet paper web. A standard Krieger metal burner was used as a baseline for these tests. R. Speyer, Georgia Tech, initially characterized the spectral transmission/absorption properties of target furnishes (i.e. web materials). At wavelengths of 2μ or less, the web materials exhibited reasonable transmittance levels of 15 to 20%. The spectral response of the standard Krieger metal burners was measured to establish the baseline properties. MTI supplied the candidate emitters for spectral characterization and drying testing. T. Patterson, IPST, performed initial drying tests using the Krieger metal burners to determine a set of test conditions that resulted in a measurable temperature rise while maintaining acceptable discrimination between radiation and conduction heat transfer modes.

The final IPST test results shown in Figure 25 confirmed that the CFCC burner blocks and screens exhibited superior drying performance compared to the standard metal burner. The best drying performance over a range of paper solids contents was achieved by the black body radiant CFCC systems. Given that the radiant output of the black/gray body CFCC and metal burners would have similar spectral distributions, the advantage of the CFCC system must result from the higher operating temperature. The results for the holmium coated burners were very close to that of the metal burners. Although the holmium coated emitter operated at higher temperature, the radiant energy was focused at 2 microns where the water absorption coefficient is much lower than the absorption at about 3 microns as shown in Figure 26. For nearly all of the conditions tested, the black body CFCC burners (both silicon carbide and emitters coated with the commercial black body coating) delivered significantly more energy to the paper web than the holmium coated CFCC or metal burners.

The mechanical durability and thermal stability of the CFCC reverberation screens proved to be inadequate for this burner design. Although the light gauge fiber provided a large radiant surface with low pressure drop, it exhibited significant degradation during the IPST testing. In tests performed at MTI, pyrometer measurements indicated temperatures over 1300C for the screen and/or burner block. SEM examination of post-test reverberation screens confirmed that the fibers had undergone significant grain growth which accounted for the low strength. In addition, the holmium coating failed to adhere to the fiber. The Aremco “black body” coated screen shown in Figure 27 exhibited somewhat better durability than the rare earth coated screens but it is still considered to fragile for industrial applications. The post-test condition of the Aremco 840C black body coating on the burner block is shown in Figure 28. Although extensively cracked, the coating appears to be well bonded to the surface of the vacuum formed burner block. It may be possible to design an improved burner block with a corrugated surface that would not require a reverberation screen to develop increased heating efficiency while maintaining the advantages of a low thermal mass configuration. Alternatively, the Krieger ceramic burner block could be coated with the commercial “black body” coating to increase the radiant output. Since this burner uses a metal reverberation screen, the durability should be unaffected. Furthermore, the “black body” coating should increase service life of the Krieger burner block by decreasing the surface temperature. The primary disadvantage is that retaining the metal reverberation screen would undoubtedly result in extended heat up and cool down times that may be unacceptable in some applications.

4.4.3 Corrosion Resistant Components

CFCC samples were subjected to stressed-corrosion testing at 1100C and 2000 psi for a total of 1400 hours. No failures were reported for this test in which the baseline material seldom survives for more than 400 hours.

4.5 Composite Property Evaluation

4.5.1 Hot Gas Filters and IR Burners

The Materials Response Group of the Department of Engineering Science and Mechanics at Virginia Tech was subcontracted to perform specialized testing and durability modeling of various CFCC components. Initial work focused on the unique structure and properties of vacuum wound hot gas filters and IR burner emitters. Filter testing included tube tensile testing, 4 point bending, flange compression, flange bending, and hoop testing. The flange bend test configuration and a plot of load versus displacement are shown in Figures 29 and 30, respectively. The extended strain and non-brittle behavior of the CFCC filter element is very apparent in these results. IR burner emitter samples were also characterized through tensile, 3 point bending, and pseudo-hydrostatic loading. A ligature model of the vacuum wound structure was developed based on the mechanical test results and used to predict the material response to typical in-service loads.

5 PROCESS SCALE-UP AND MANUFACTURABILITY

5.1 Hot Gas Filters

Hot gas filter scale-up activities focused on both process and raw material costs. The hot gas filter development status given in Table 3 was used as the first stage of the process scale-up and manufacturability analysis. In anticipation of a large filter order for the Lakeland 240 MWe project, each unit operation of the hot gas filter process was analyzed in terms of labor content, operation yield, and equipment production rate. Figure 31 illustrates one scenario for the labor per unit sold for each operation. The filament winding operation clearly dominates the labor requirements of the hot gas filter production process. The analysis was based on using the EnTec filament winder as it was initially configured at MTI. The first process scale-up activity was therefore focused on the implementation of two-strand winding. Issues related to the chopped fiber deposition required a maximum separation of the two strands as they were applied to the preform and a more complicated fiber routing path. Several filters were successfully produced using two-strand winding. An attempt to increase the speed of the EnTec winder from 100 rpm to 200 rpm was unsuccessful because of unacceptable tracking errors on one or more axes on the winder. The tracking error is defined as the difference between the programmed position of an axis and the actual position. MTI also has access to a Cobra chain driven filament winder that would be suitable for filter element production. A significant advantage of the Cobra winder is that it is capable of winding 2 meter filter performs. If the market justified, a multi-spindle filament winder could be purchased with obvious impact on the labor per filter. The biggest benefit would result from automation of the winding operation thus limiting the labor to loading and unloading. The addition of a programmable controller on the slurry pump will require less operator surveillance and allow the winder operator to perform other activities such as mandrel preparation and fiber slurry mixing. Other automation options include online diameter measurement of the body and flange sections to control the completion point of the winding. Finally, the addition of fiber break monitors interlocked to the winder and slurry pump would be required for unattended operation. Clearly, as one operation is streamlined others become more dominant and need to be addressed. From a process control standpoint, the most critical variables are the average length and length distribution of the chopped fiber. The bulk density of the preform is very sensitive to variations in the chopped fiber slurry preparation process. The type of online fiber length monitoring used in the paper industry might be utilized to monitor and control the chopped fiber milling operation. Alternatively, Saffil chopped fiber is commercially available as a milled product form that would eliminate this processing step. Additional work is needed to develop a reliable QA test to ensure consistent properties of the chopped fiber.

5.2 Corrosion Resistant Components

A similar manufacturing analysis was performed for the production of the classified corrosion resistant components. Prior to the cancellation of this application, production plans were initiated to set up a manufacturing line for both the hot gas filters and various types of corrosion resistant components. A key element of the corrosion resistant component is the fiber coating process. MTI successfully implemented a continuous immiscible-liquid coating process to apply a fugitive carbon coating on Nextel 610 fiber. Approximately 40 pounds of fiber were coated using this process and then woven into fabric by a commercial weaver. Numerous pressure casting tool sets were produced for the various components. These were used to fabricate single and multiply flat performs. Tool designs that were better suited for production were being evaluated at the time the task was terminated. Finally, considerable progress was achieved in the production of very complex shapes using water jet machining at a commercial vendor.

6 Conclusions and Recommendations

6.1 Porous Composites

6.1.1 IR Burners

Although significant improvements in thermal efficiency were produced by controlling the emittance of the burner components, the CFCC structures lacked the ruggedness required to survive in an industrial environment. A commercial black body type coating was identified that could be applied to existing burners to improve the radiant output.

6.1.2 Hot Gas Filters

Significant improvements in the fabrication and properties of vacuum wound hot gas filters were demonstrated. Approximately 2000 hours of successful testing in a pilot scale pressurized fluid bed combustion facility was achieved. The unique combination of low modulus and good toughness of the vacuum wound structure results in a very thermal shock resistant filter. Testing in a gasification facility was unsuccessful due to excessive gas impingement on the ID of the filters. Significant modifications to the filter system back pulse cleaning system would be needed to eliminate the gas impingement. Alternatively, a significant development program to increase the erosion resistance of the filter element would be required. The power generation market for hot gas filters is currently restricted to low temperature gasification applications where low cost silicon carbide or metal alloy filters are more cost effective.

6.2 Dense Composites

6.2.1 Aluminum Casting Riser Tubes

A simplified slurry winding process was developed to produce low cost CFCC's. High solids slurries (72-79 % solids) were developed to fabricate dense filament wound performs. Good strength (80 to 90 MPa) and toughness were achieved at very low fiber contents. Furthermore, a hydraulic binder was utilized to produce unfired composite structures. Borosilicate based coatings were developed to meet the gas sealing requirements of this application. Additional work is needed to develop an effective flange and to scale the process up to full size riser tubes.

6.2.2 Corrosion Resistant Components

Although the classified application was terminated because the process requiring these parts was not selected by the customer, significant progress was achieved in the fabrication of thin gage CFCC's. A pilot production line was also planned for this

component under Phase III. Significant developments related to this work include:

- an improved commercial fiber was developed by 3M (Nextel 650)
- implementation of immiscible liquid fiber coating (> 40 pounds of carbon coated fiber produced)
- successful production of thin gage CFCC panels
- a more durable and corrosion resistant and cost effective replacement for existing component

6.2.3 YAG Fiber

In the final phase of the YAG development task, two-phase Al_2O_3-YAG fibers with up to 50% YAG were developed. These fibers exhibited good strength and a fine-grained, two-phase microstructure with high density. The fibers had improved strength and flexibility compared to YAG fibers synthesized previously. No grain growth or other microstructural degradation occurred in these fibers at temperatures up to 1300 °C for 100 hours. However, the creep rate of these fibers was not as good as 100% YAG fibers; instead, the creep rate was similar to Nextel 650 fibers.

Table 1. MTI CFCC applications.

APPLICATION	COMPONENT DESCRIPTION	PERFORMANCE TARGETS/COND.	STATUS
1. Boiler Components	Tube shield	Temp: 1500-1800°F Erosion Lifetime: > 1 year	
	Burner tips	Temp: 1400 to 1600°F Combustion Environment Lifetime: > 1 year	
	Condensing Heat Exchanger	Temp: < 300°F Sulfuric/Carbonic Acids Lifetime: > 4 years	B&W acquired teflon coated condensing heat exchanger technology
	U-Beam channels in CFB	Erosion & Corrosion: Vanadium	
	Burner Components	Temp: 2200°F Corrosion/reducing environment	Laboratory testing demonstrated fiber and coating attack.
	Hot Gas Filter (PFBC)	Temp: 1600°F Combustion environment	test time: >1900 hours; production status: final development and planning in progress
2. Turbine Components	Combustor Liner	Temp: ~2300°F	Tested at Solar; limited by fiber properties
	Shroud		Considered for GE turbine
3. Radiant Heater Tubes	13" diameter x 4 to 8' long	Temp: 2500°F Combustion environment	Limited by fiber properties.
4. Pulp and Paper	Gas fired infrared dryers	Temp: 2300°F Spectral match to paper	Fabrication process developed; IPST testing in progress
5. Classified application	Process components	Temp: 2000°F corrosive environment	Alternate process selected by customer
6. Heat Exchangers	5 to 6" diameter x 6 to 8 ' long tubes	Temp: 2200°F corrosive environment; lifetime: 3 to 5 years	Market limited for atmospheric HX
7. Chemical Industry (dimethyldichlorosiliane)	Hot Gas Filter	Temp: 500 to 1800°F oxidizing/reducing	Process economics unfavorable
8. Petrochemical Industry	Burners for Refinery Heaters	Temp: 2300°F Lifetime: > 4 years	

Table 2. MTI hot gas filter test summary.

Test Facility	Filter Type	# of elements	Duration (hours)	Comments
Ebensburg CFB	C1, C2, C3, C4	3 of each	250	
Westinghouse HTHP	C3	4	100	
FETC Combustor	C3	3	24	
Westinghouse HTHP	C4M	1	100	
Karhula	C4M	6	581	Surface defects
Karhula/PSDF TC02/TC03	C4M	3	1800	Coal carry-over event: no failures
PSDF TC02/TC03	C4M	6	1219	Coal carry-over event: no failures
PSDF TC03	C4M	2	660	
PSDF TC04	C4M	8	175	Coal carry-over event: no failures
PSDF TC05	C4M	8	179	End plug failure
PSDF TC06	C4M	8		Gasification conditions

Table 3. MTI hot gas filter development status.

Property	Req't.	Status	Challenge
size	2.4 x 60"	2.4 x 60"	complete
shape	flanged, closed end tube	closed end tube with integral flange	complete
pressure drop @10ft/min	10	5	complete
strength	1 - 4 ksi	0.8 - 1.2 ksi	moderate
Toughness	non-brittle failure	non-brittle failure with high strain tolerance	Complete
Thermal shock	survive severe plant upsets	MTI filter exhibits very high thermal shock resistance	complete
corrosion resistance	3 year life	No corrosion issues identified; all oxide system expected to stable	complete
scale-up	thousands/yr	Planning	No major issues identified
cost	$500-1000	Nextel fiber cost is expected to decrease with increased fiber production	moderate

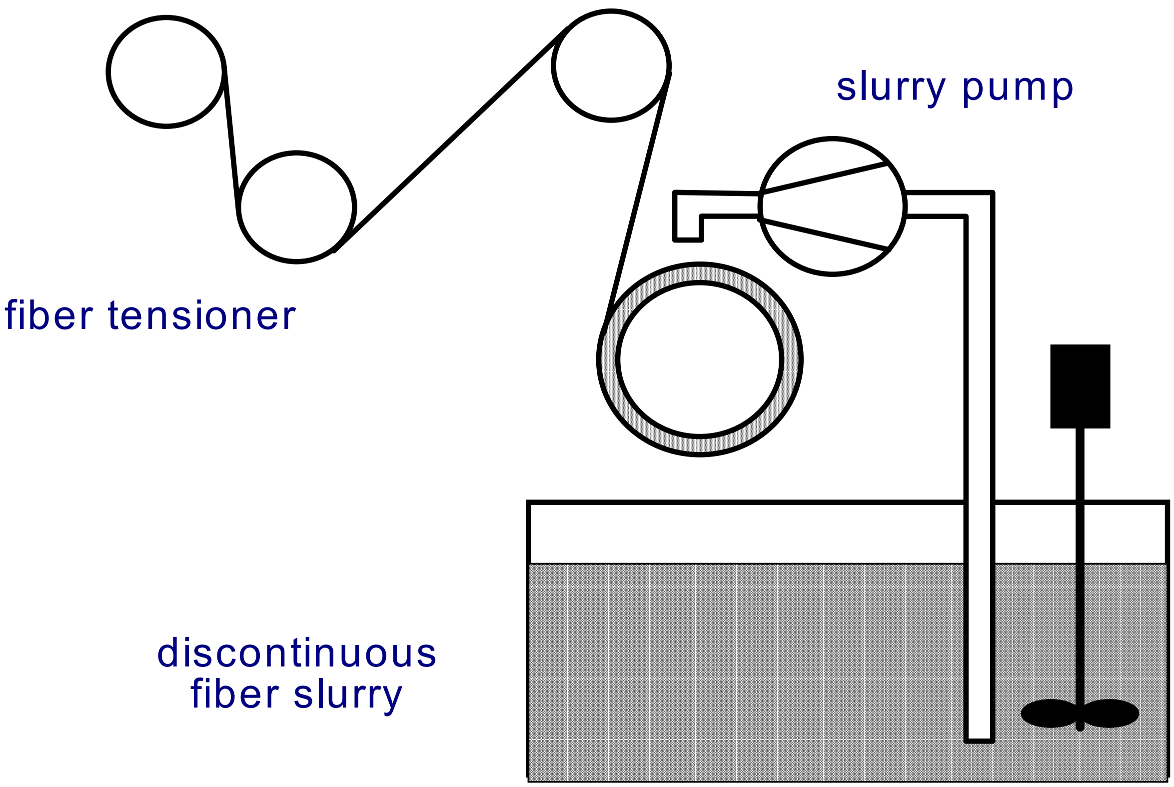


Figure 1. Schematic diagram of vacuum winding fabrication process.

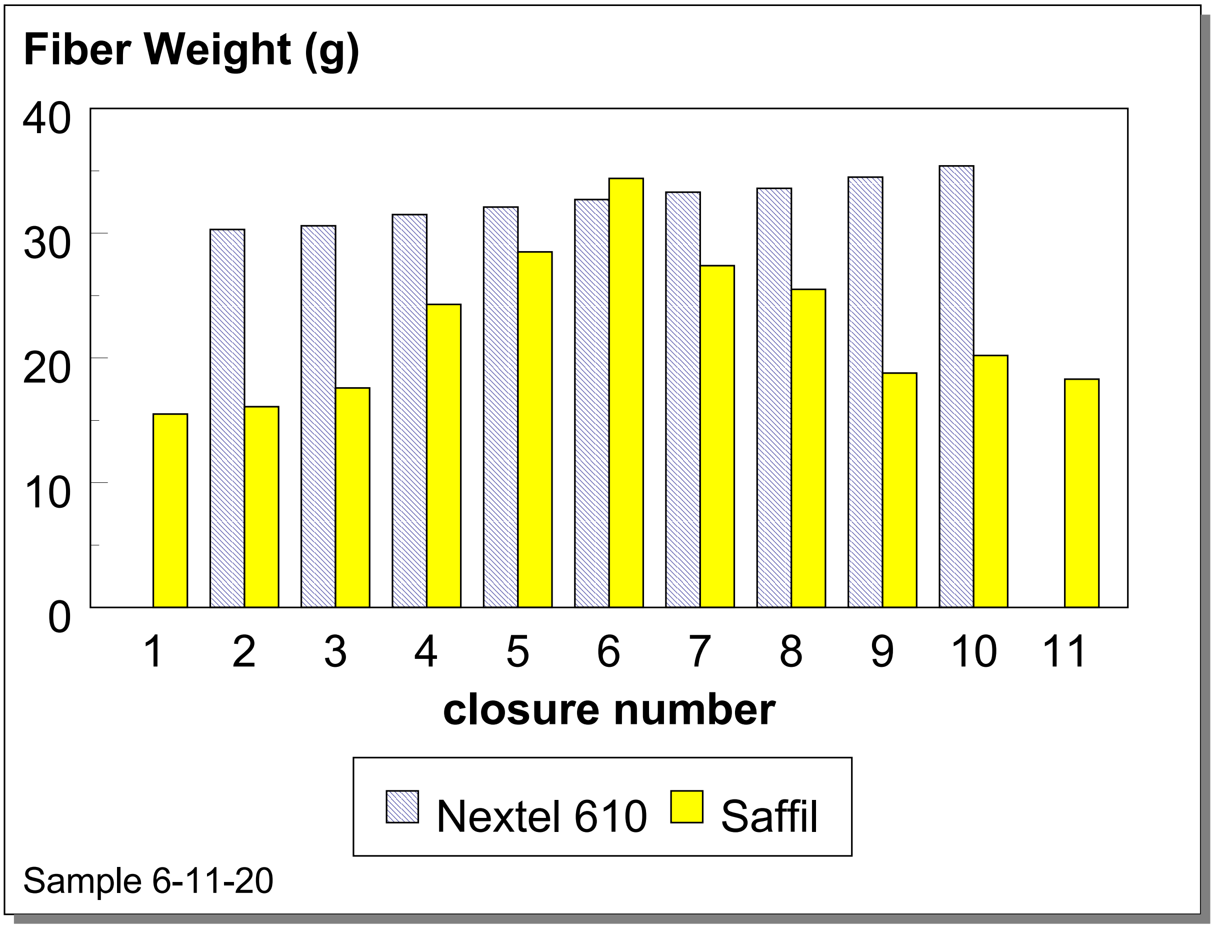


Figure 2. Example of control of the distribution of the continuous and chopped fibers available in the vacuum winding process.

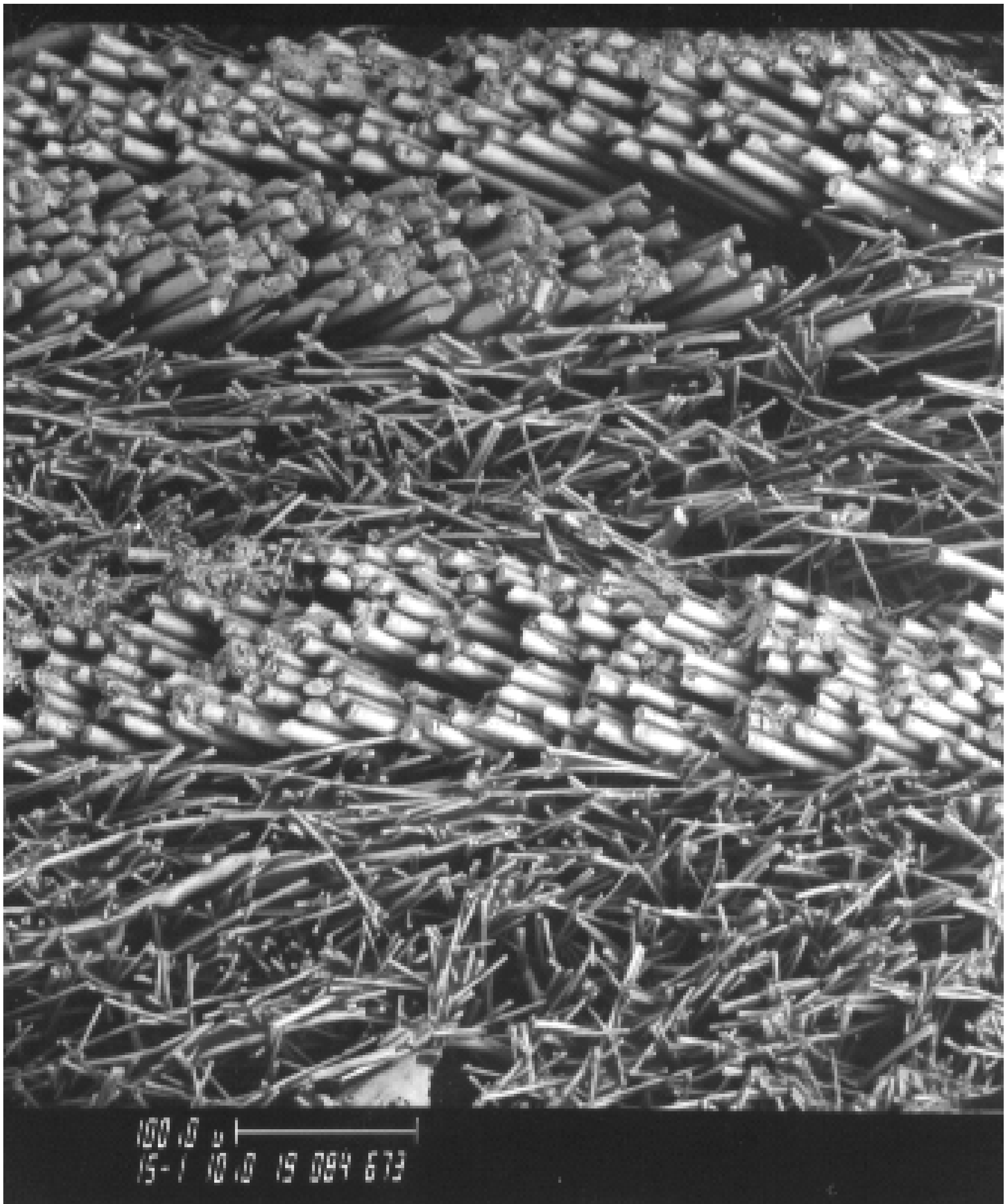


Figure 3. Cross section of vacuum wound hot gas filter.

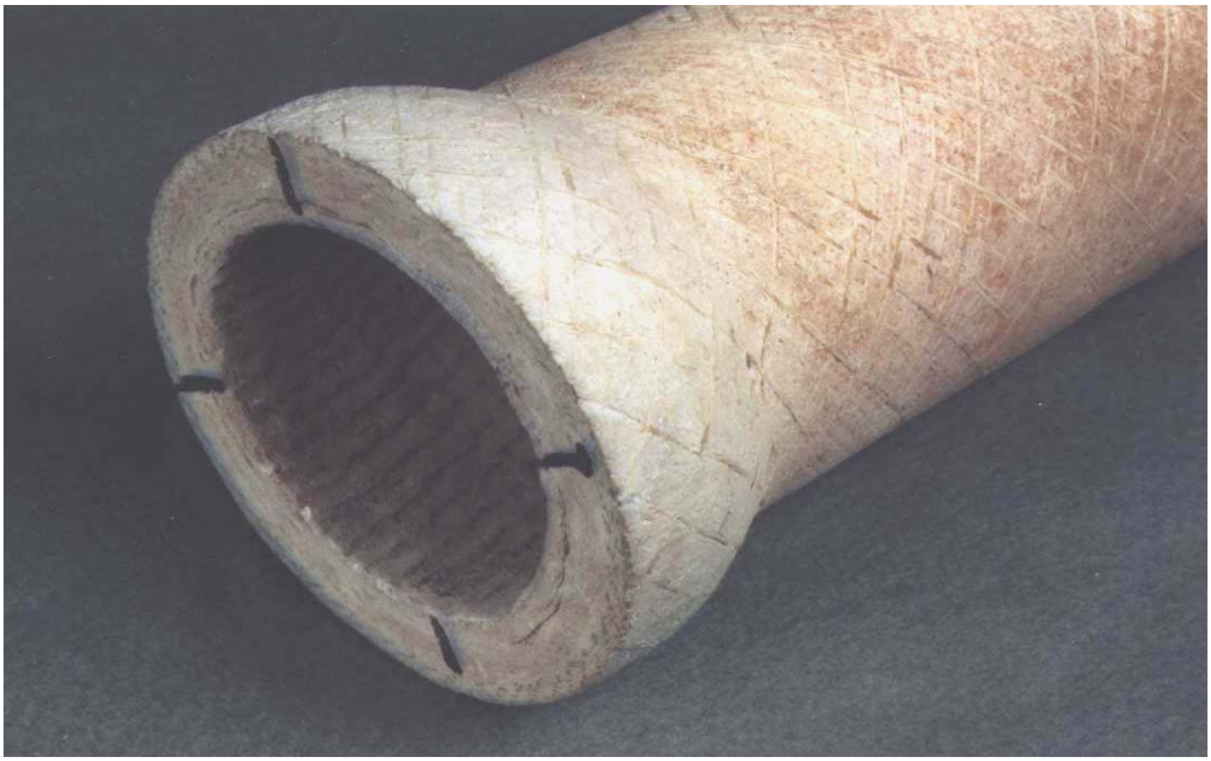


Figure 4. Net shape flange produced by vacuum winding.

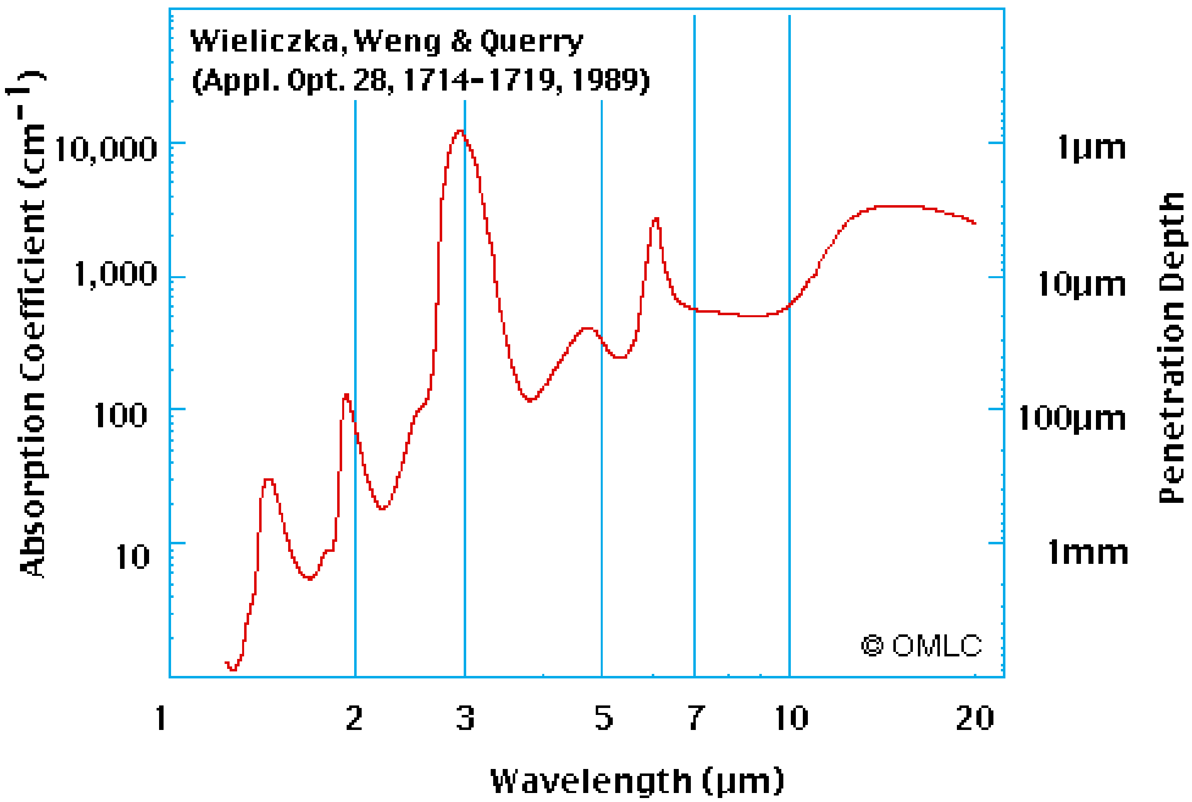


Figure 5. Infrared absorption of water.

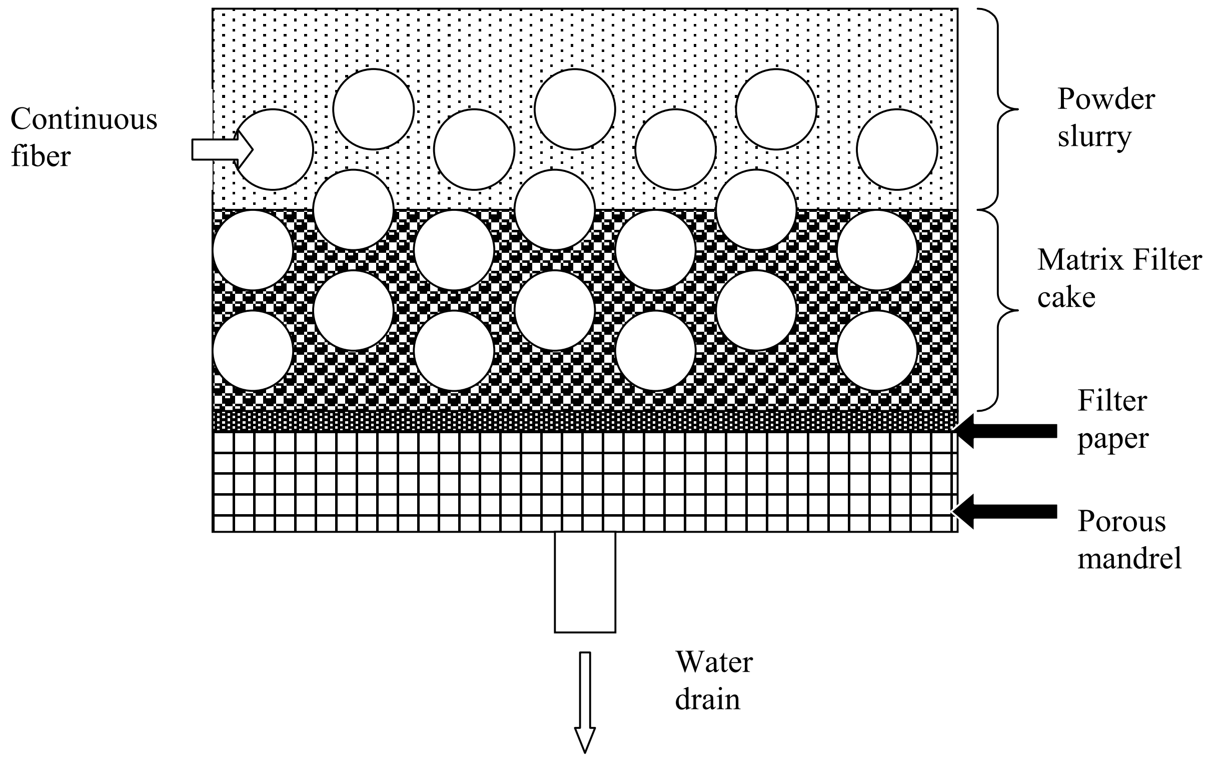


Figure 6. Schematic diagram of initial matrix formation by pressure casting process.

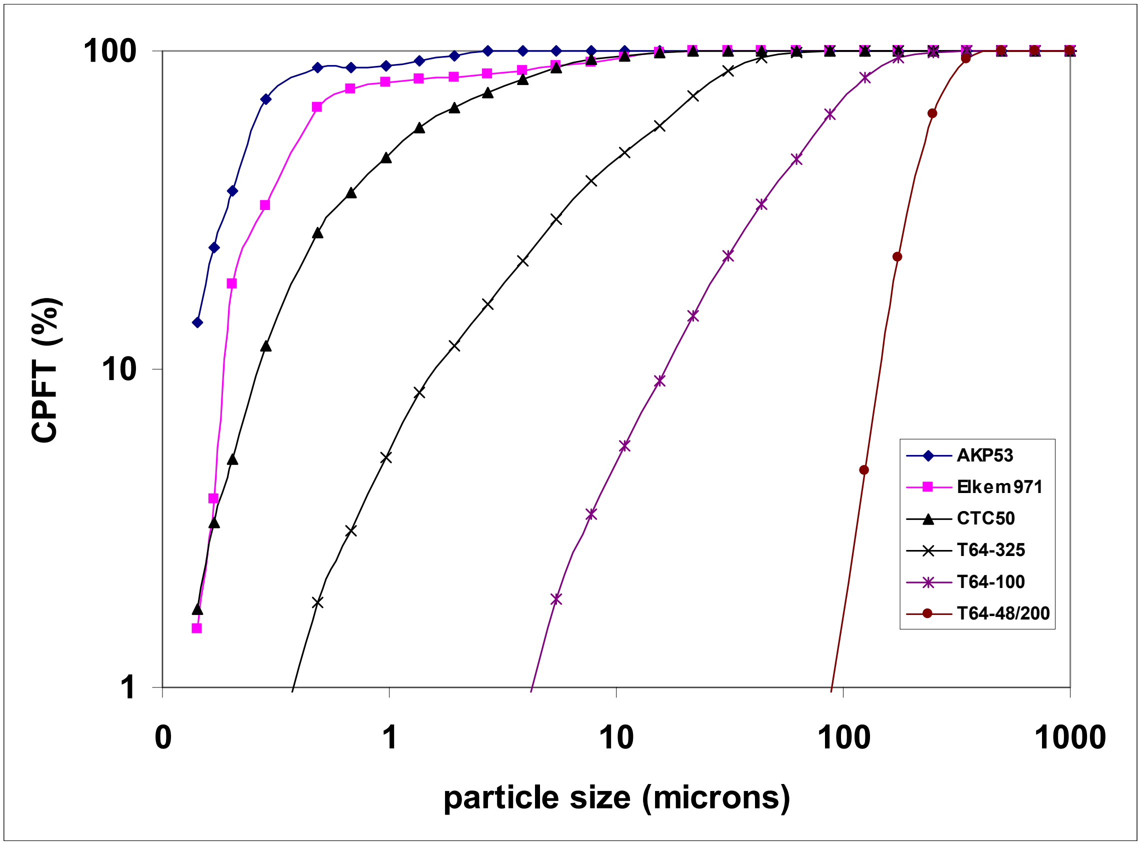


Figure 7. Particle size distribution of alumina raw materials.

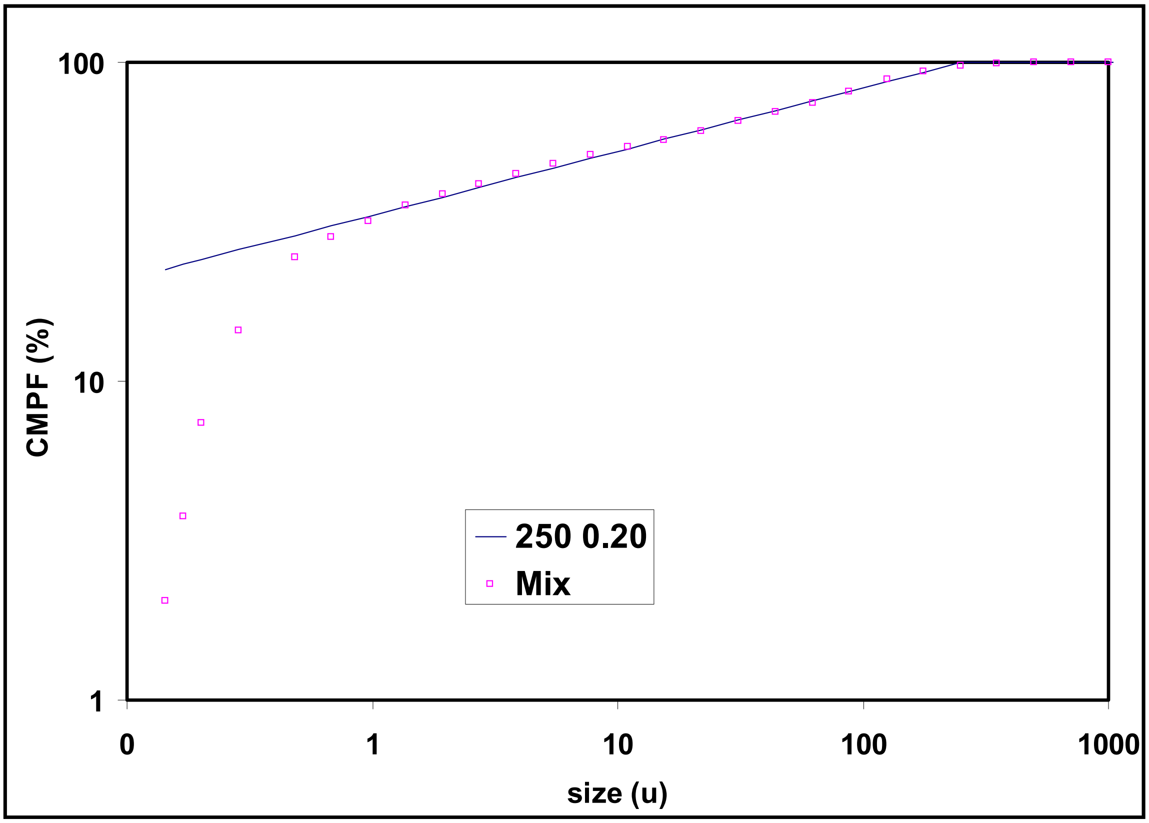


Figure 8. Particle size distribution of optimized alumina batch.

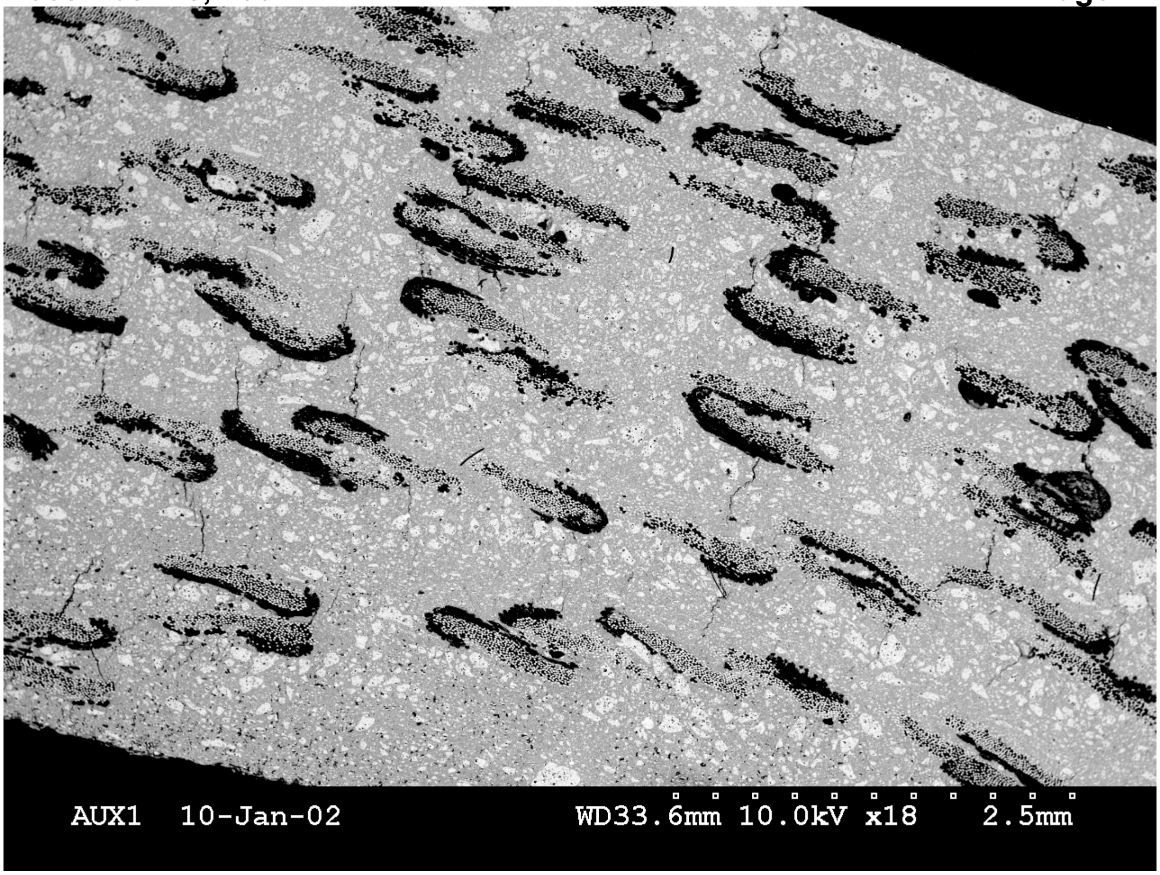


Figure 9. Scanning electron micrograph of alumina casting riser tube.

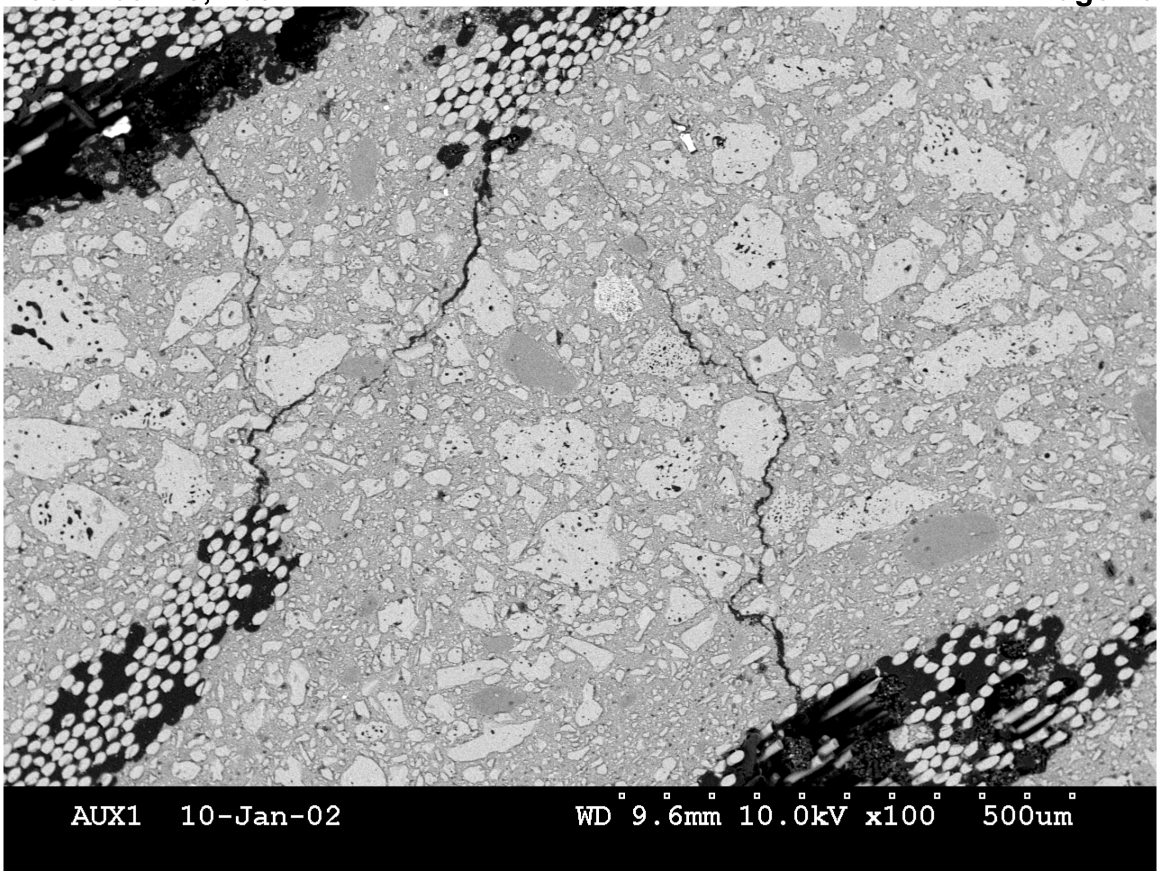


Figure 10. SEM micrograph of cracking between fiber tows.

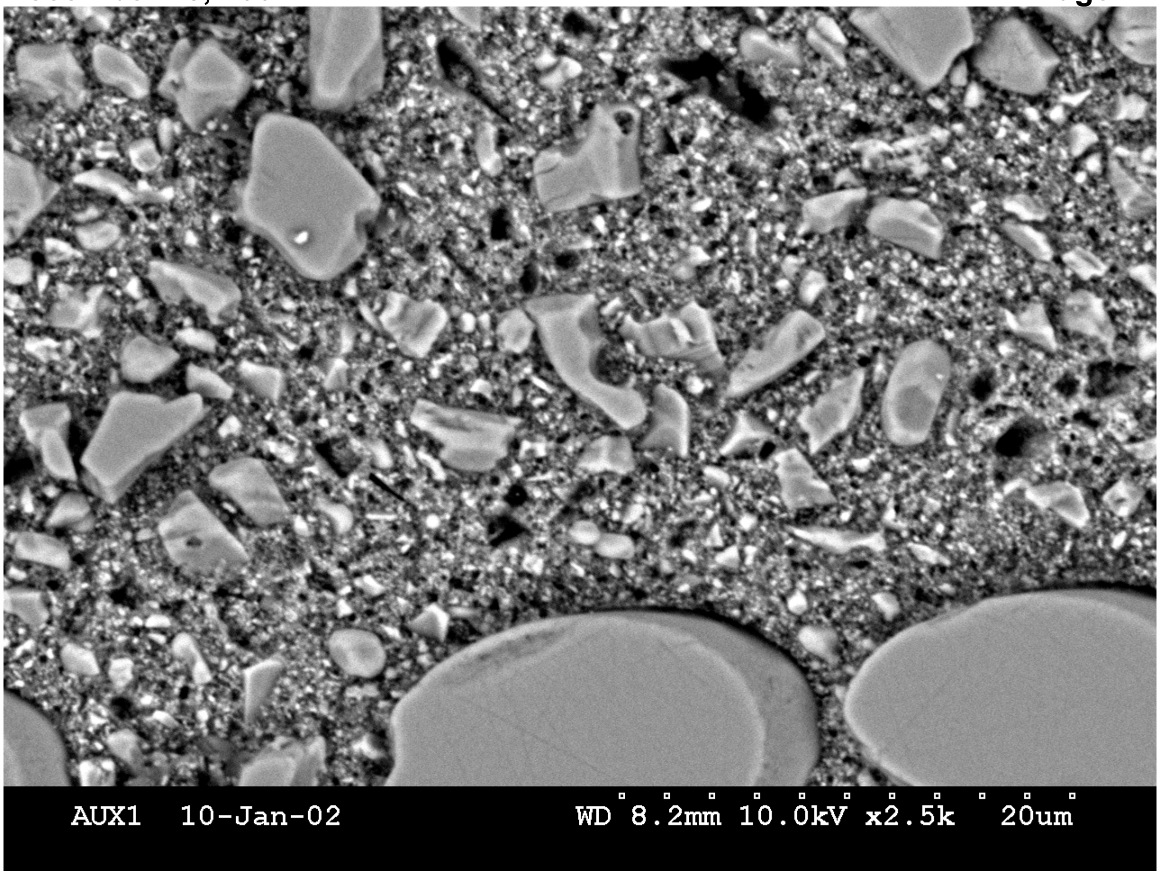


Figure 11. High magnification of fiber/matrix region of alumina CFCC riser tube.

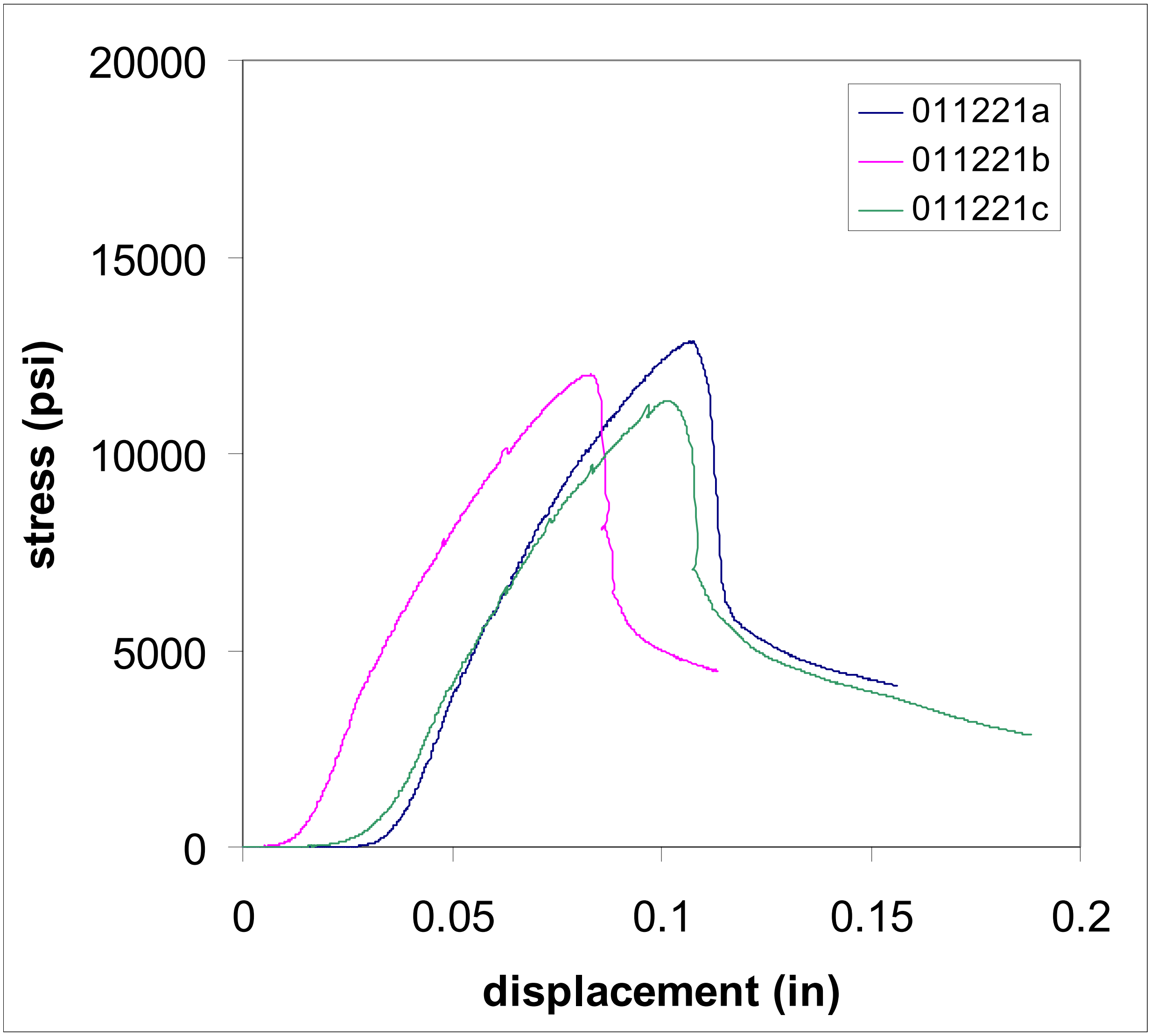


Figure 12. Compressive C-ring results for alumina casting riser tube.

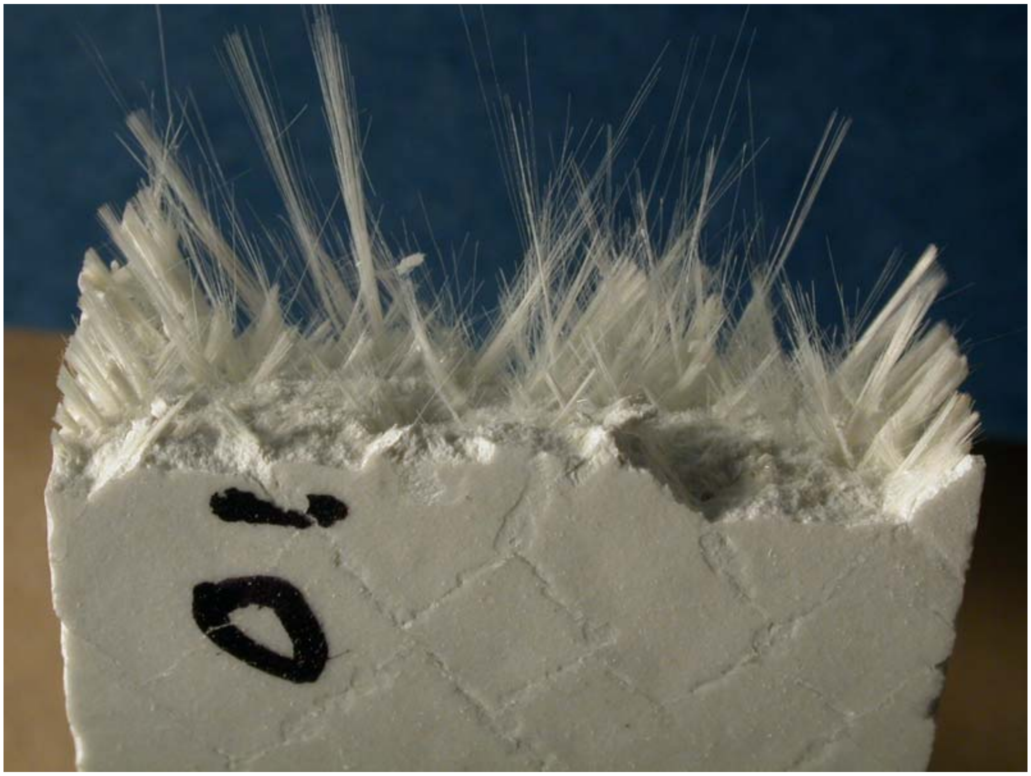


Figure 13. Fracture surface of C-ring sample showing extensive fiber pull-out (7X).

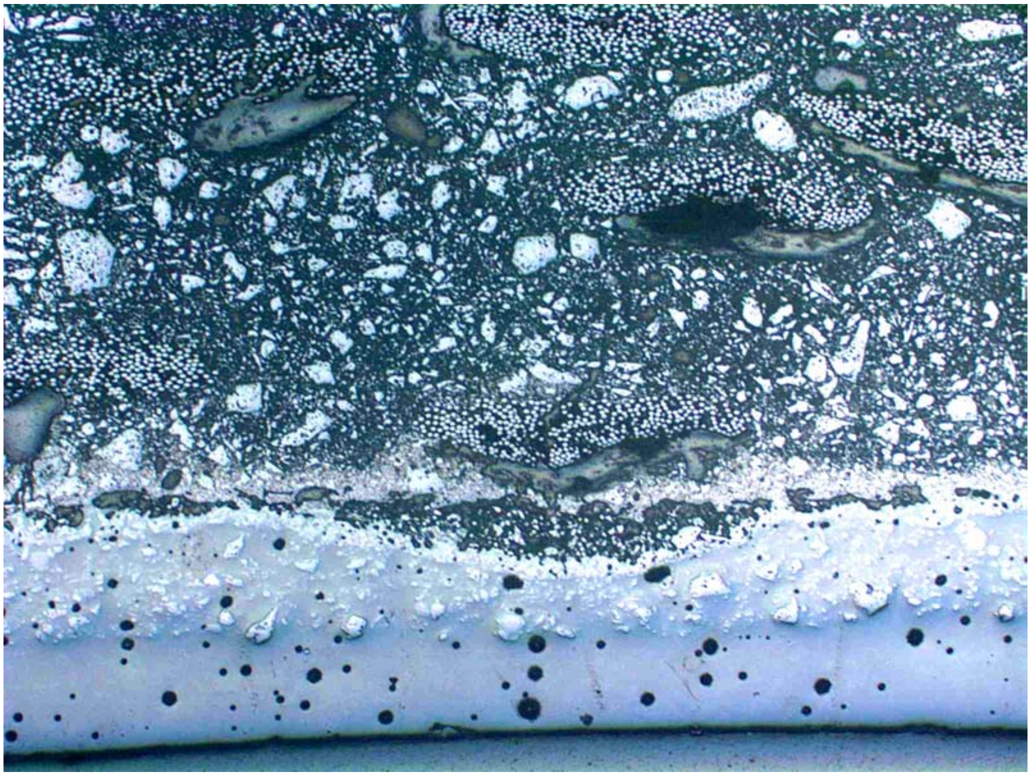


Figure 14. Cross-section of borosilicate sealed ID of casting riser tube.

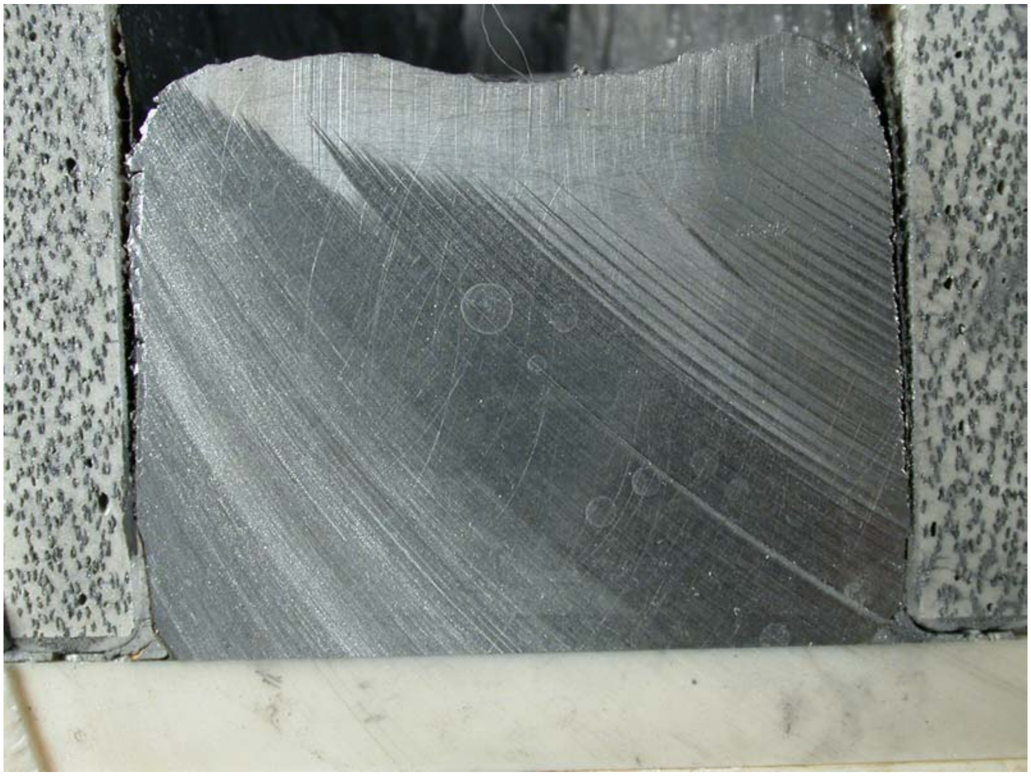


Figure 15. Cross-section (2X) of molten aluminum exposure sample.

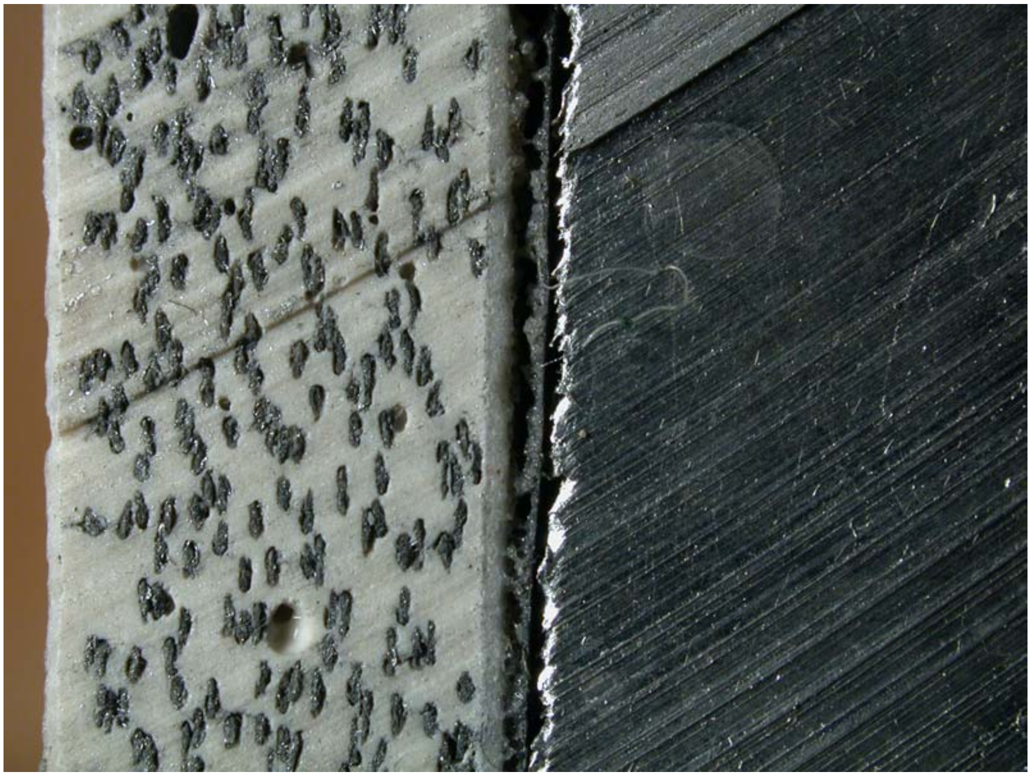


Figure 16. 6X macrophoto of sample/metal interface after 72 hour aluminum exposure test.

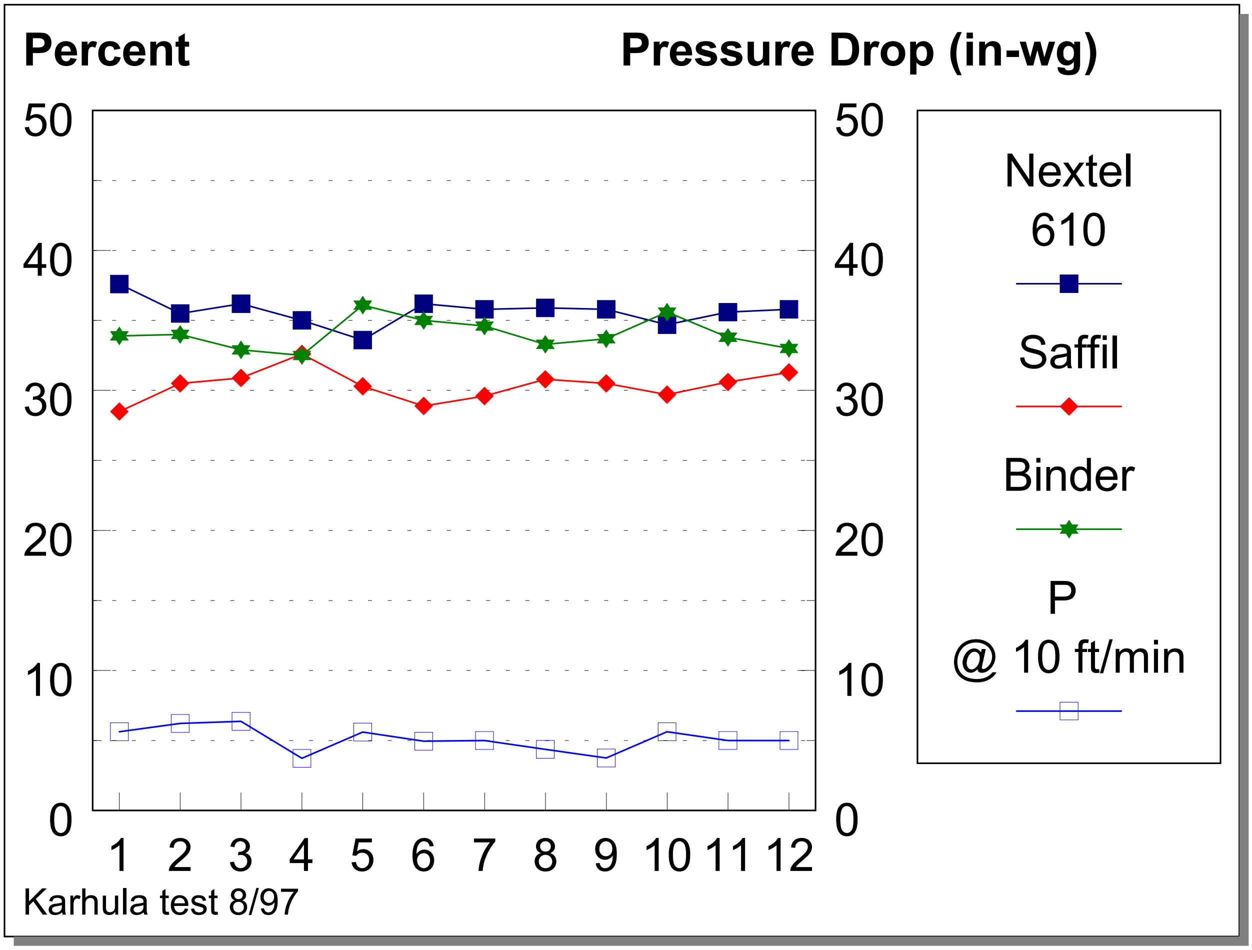
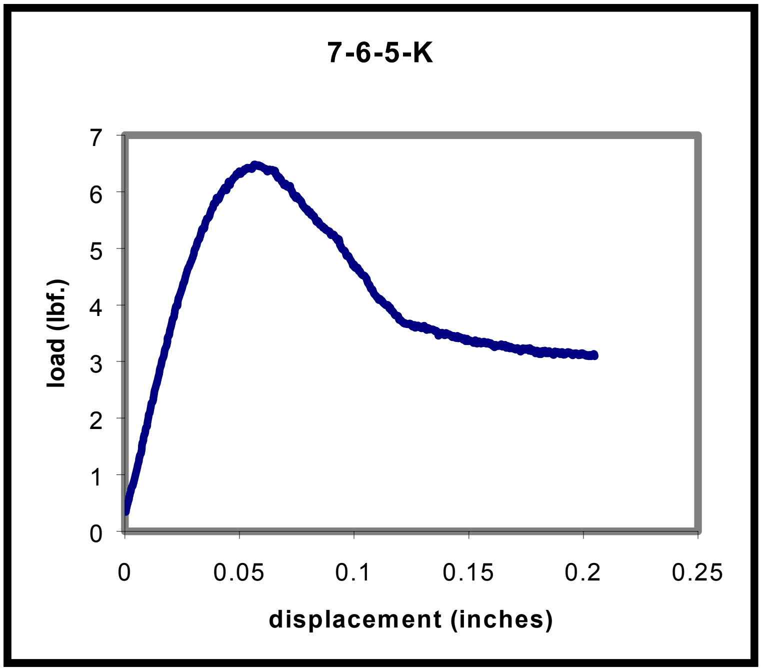


Figure 17. Composition and pressure drop of Karhula filter elements.



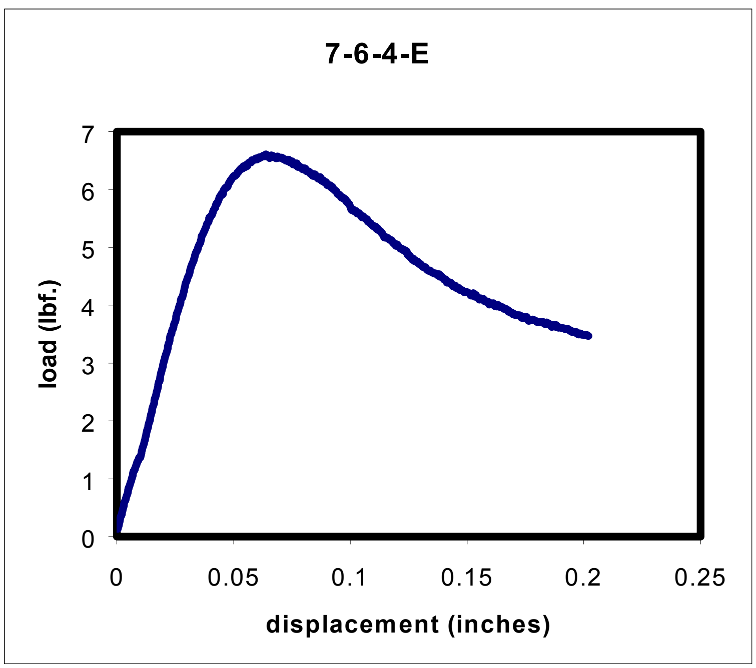


Figure 18. Load versus displacement results for as-fabricated (top) and Karhula tested (bottom) filters.

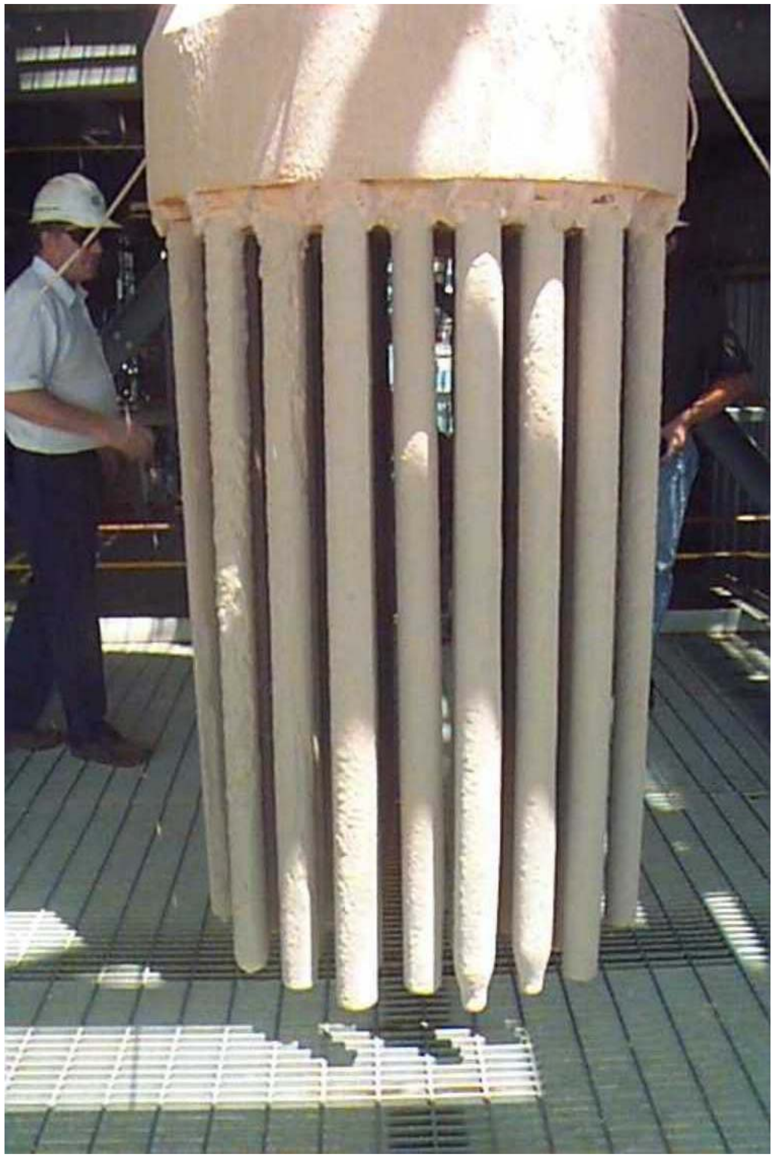
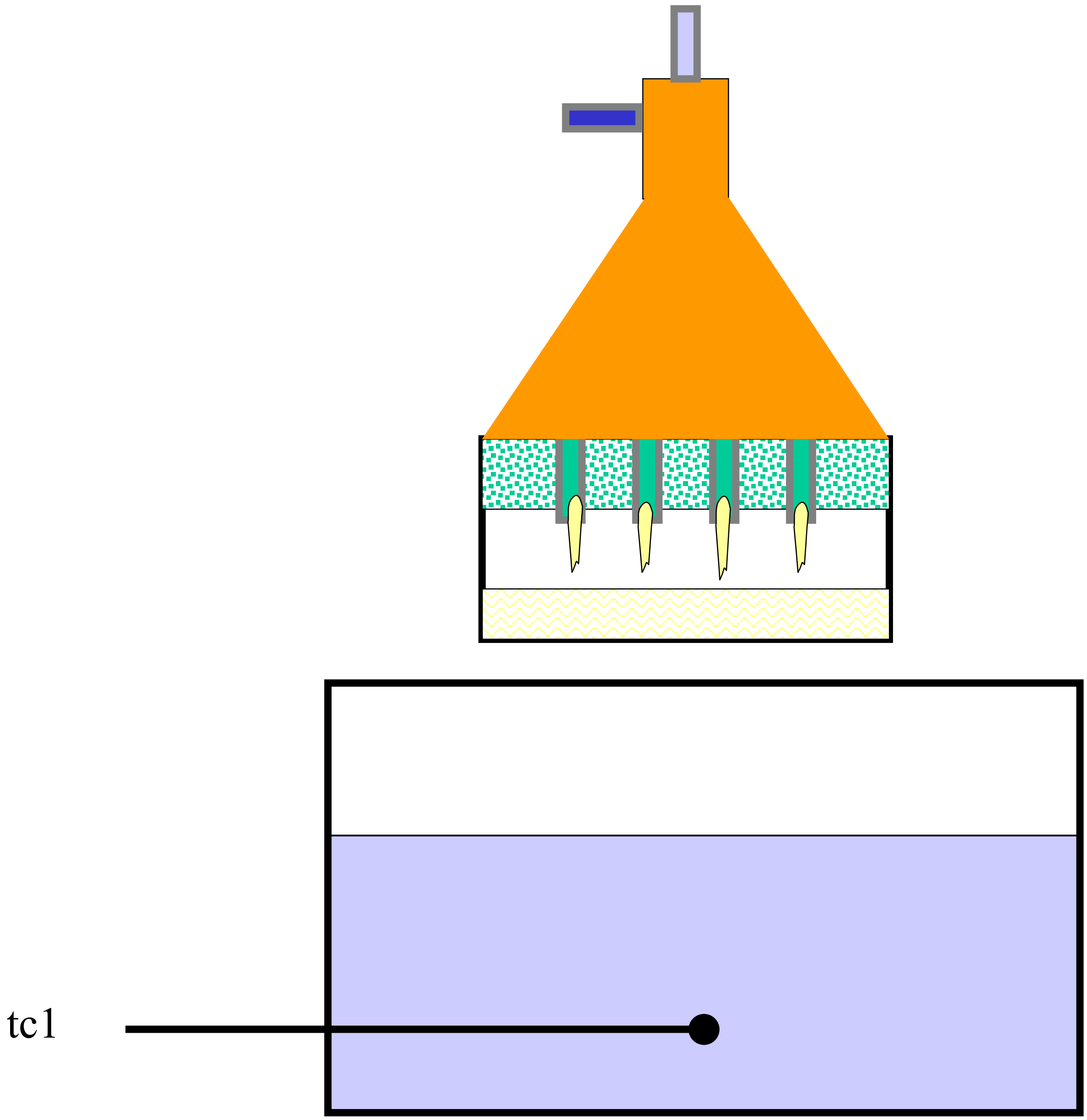


Figure 19. Hot gas filters installed at the PSDF.

Figure 20. Schematic diagram of IR burner calorimeter test.



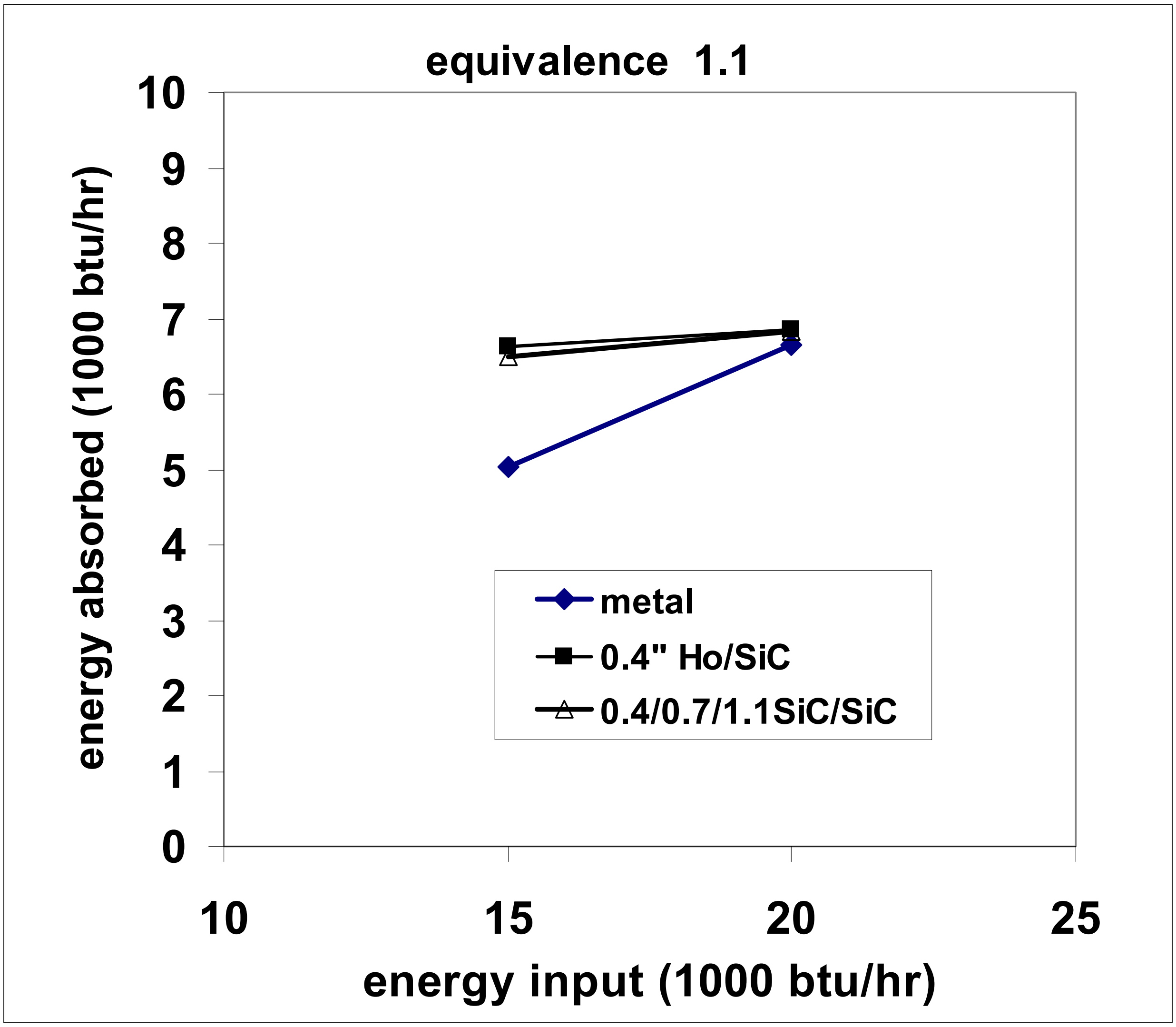


Figure 21. Water calorimeter test results for IR burners.

Figure 22. Photograph of holmium coated CFCC burner at 15,000 Btu/hr firing rate.

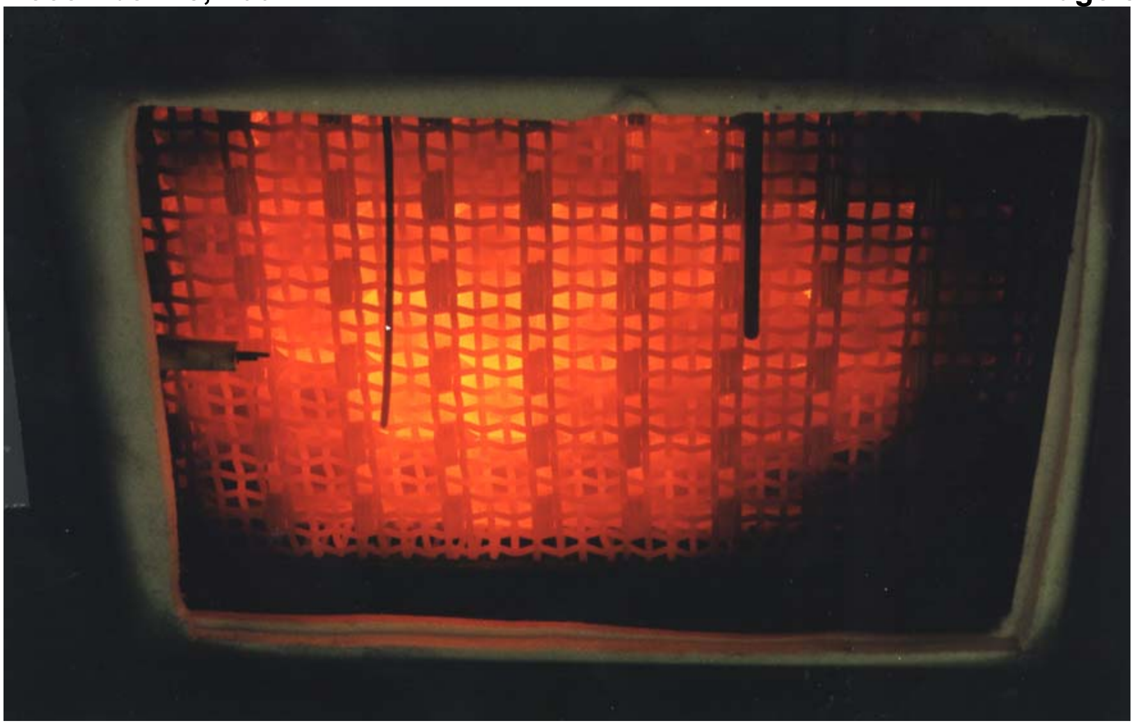


Figure 23. Photograph of Krieger metal burner at 15,000 Btu/hr firing rate.

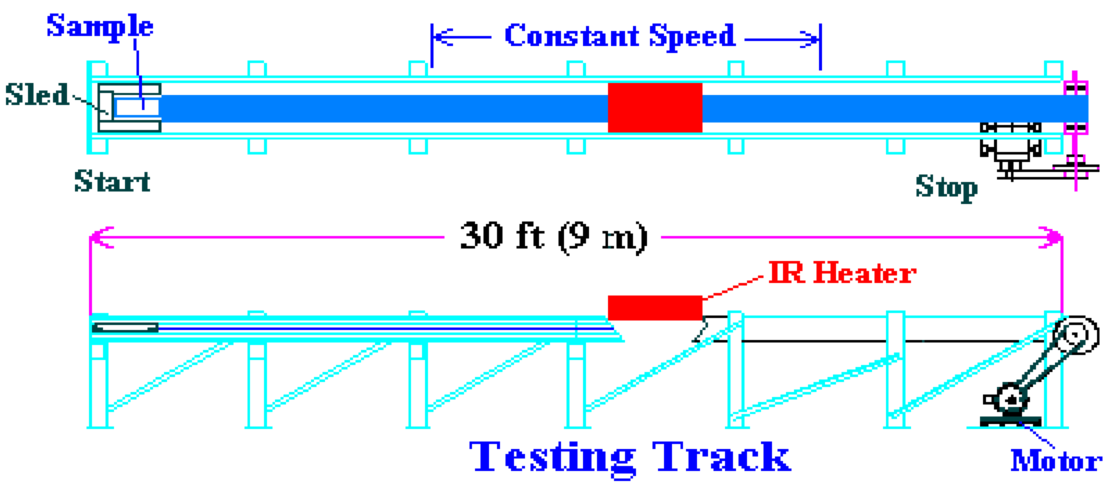


Figure 24. IPST drying track used for IR emitter evaluation.

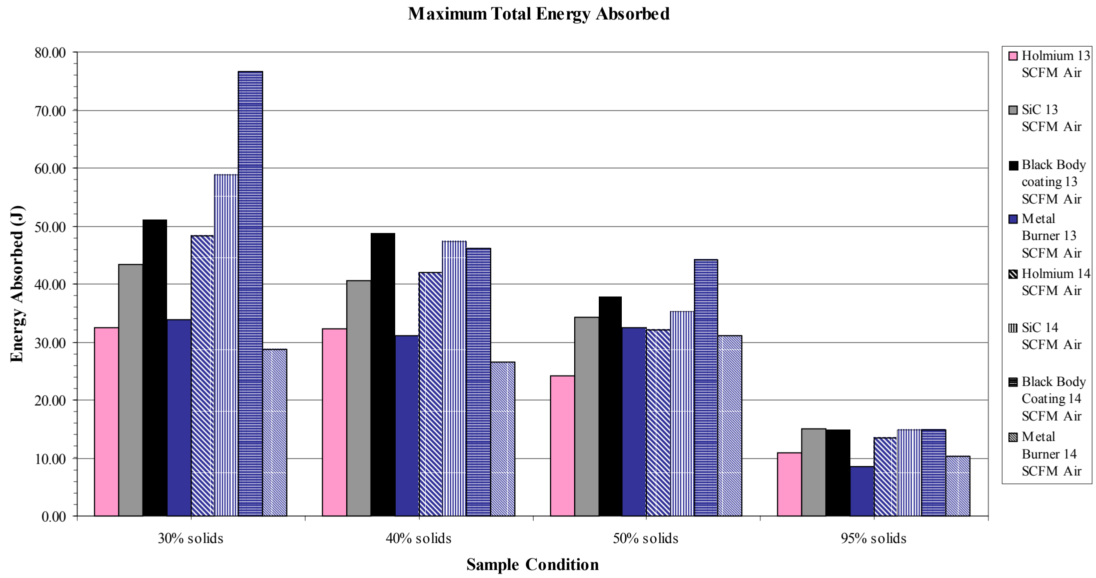


Figure 25. Summary of IPST drying track results.

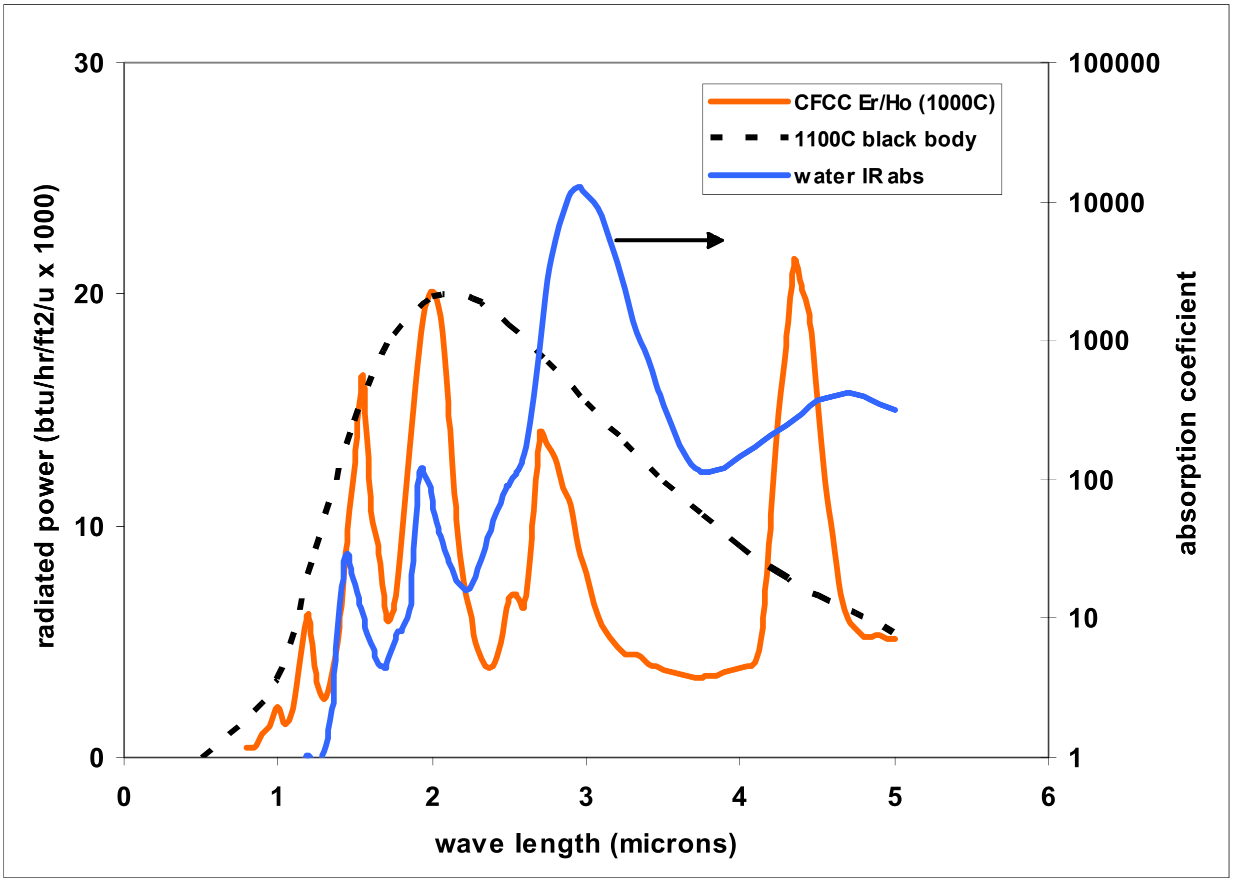


Figure 26. Comparison of burner radiant power to the infrared absorption of water.

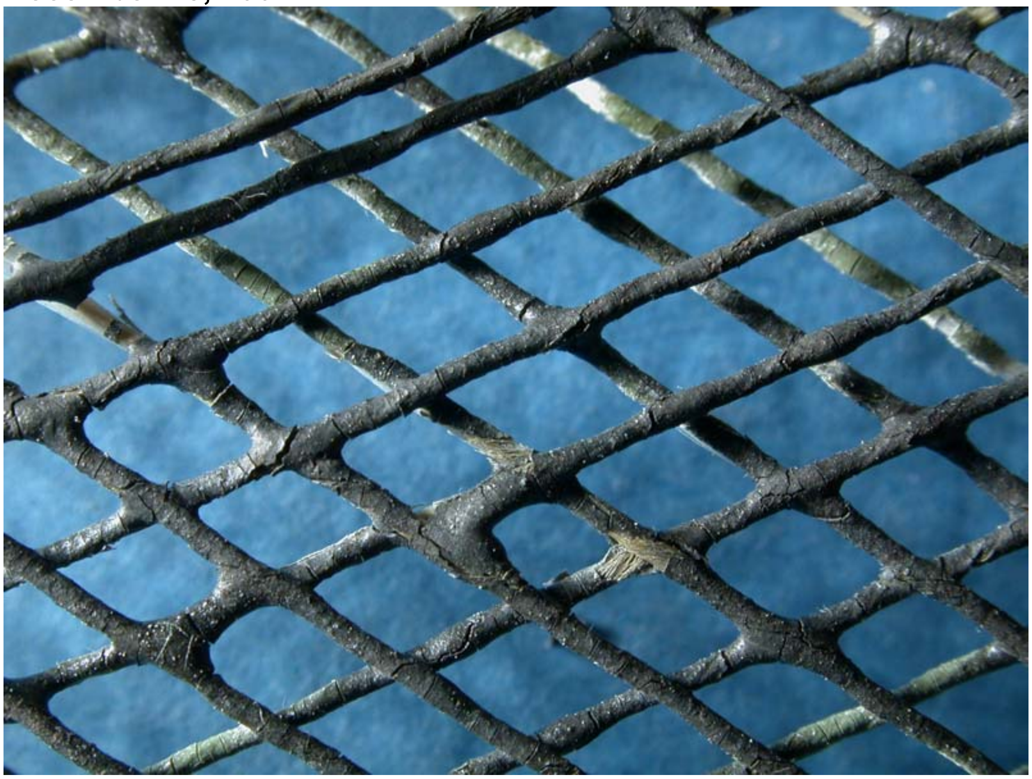


Figure 27. 8X macrophoto of "black body" coated reverberation screen following IPST testing.

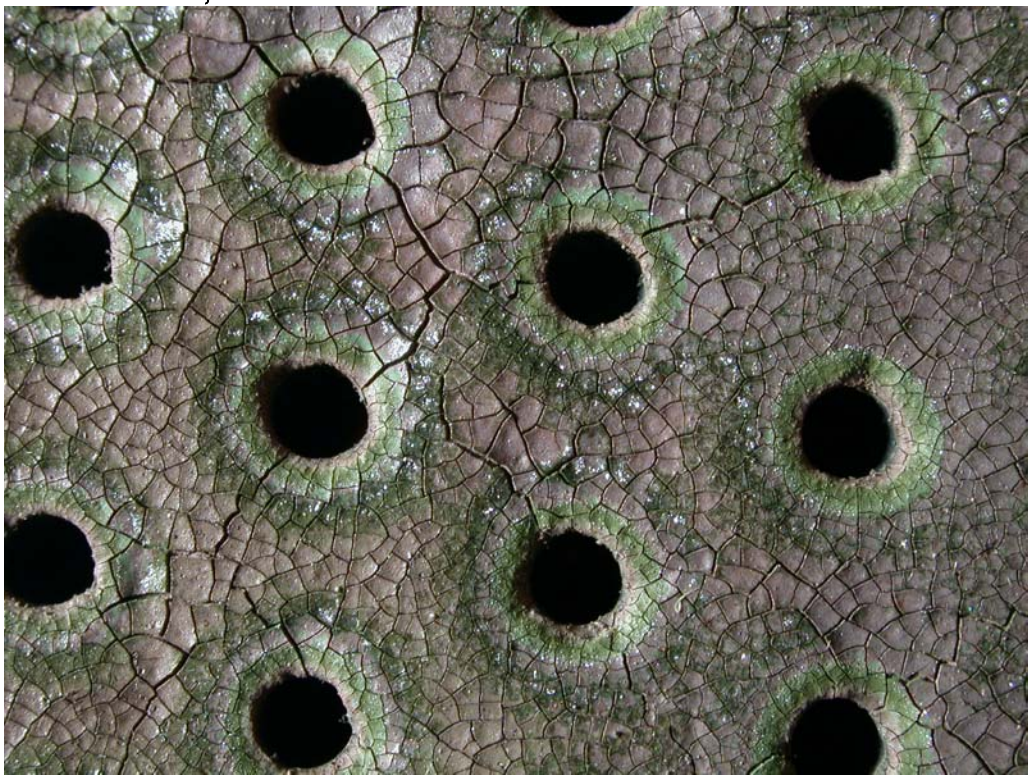


Figure 28. 8X macrophoto of "black body" coated burner block following the IPST testing.

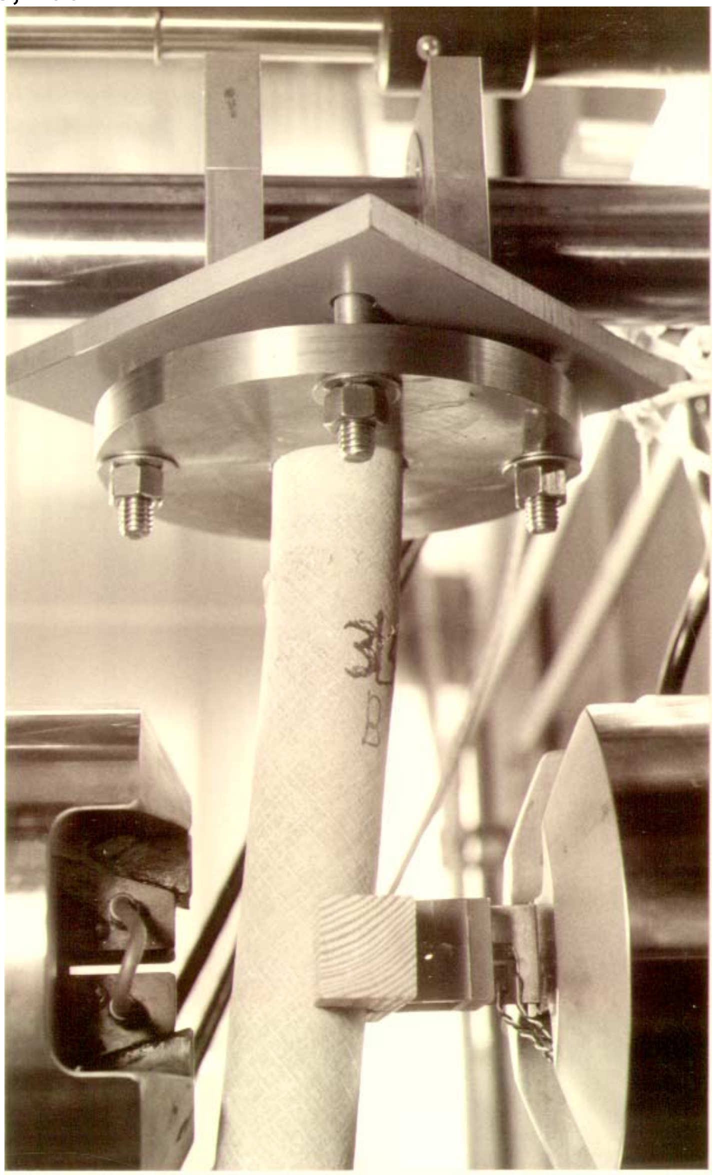


Figure 29. Flange bend test configuration.

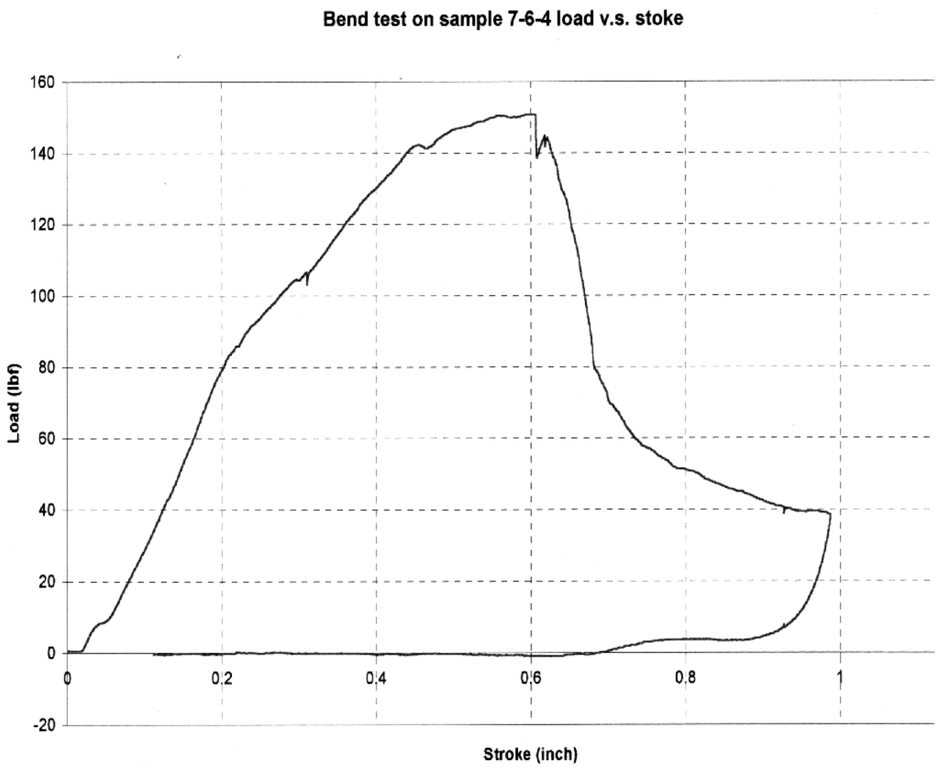


Figure 30. Load versus displacement for flange bend test.

Figure 31. Labor content of each hot gas filter unit operation.

1 Order Materials
2 Receive Materials
3 Release Materials for Production
4 Prepare Chopped Fiber Slurry
5 Prepare Mandrel for Winding
6 Filament Wind Filter
7 Bond Filter
8 Prefire Filter (Prefire #1)
9 Machine Filter Flange
10 Perform Second Filter Bonding
11 Prefire Filter (Prefire #2)
12 Final Fire Filter
13 Identify Filter
14 Inspect Filter
15 Dest. Eval. Filters
16 Package Filter
17 Ship Filters

---

[1] CFCC Phase I Final Report, R. W. Goettler, (1995).
[2] Wieliczka, Weng, and Querry, Appl. Opt. 28, 1714-1719 (1989).
[3] A. H. M. Andreassen and J. Andersen, Kolloid Z. 50 (1930) 217-228.
[4] J. E. Funk and D. R. Dinger, Am. Ceram. Soc. Bull., 73, No. 10 (1994) 66-69.
[5] A. Studart et al., Am. Ceram. Soc. Bull. 78 No. 5 65-72, 1999
[6] R. G. Pileggi and V. C. Pandolfelli, Am. Ceram. Soc. Bull., 80, No. 10, (2001) 52-57.
[7] C. Levi et al. J. Amer. Ceram. Soc, 81 (8) 2077-86 (1998)
[8] R. S. Hay, "Sol-Gel Coating of Fiber Tows", Ceram. Eng. Sci. Proc. 12[7-8] pp. 1064-1074 (1991).
[9] D. M. Wilson and L. R. Visser, "Nextel 650 Ceramic Oxide Fiber: New Alumina-Based Fiber For High Temperature Composite Reinforcement", Ceram. Eng. Sci. Proc. 21 (4) 363-373 (2000).