Recent Developments on Improved Materials and Low-cost Fabrication Options for Candle Filters

K. Uznanski (Kuznanski@aol.com)
G. Hanus (76424.1606@compuserve.com)

PHOENIX Solutions Company
5900 Olson Memorial Highway
Minneapolis, MN 55422

Contract Information

Contract Number	DE-FG02-95ER81971
Contractor	Fluidyne Engineering Corporation d.b.a. Phoenix Solutions Company 5900 Olson Memorial Highway Minneapolis, MN 55422 (612) 544-2721 (612) 546-5617 (fax) 76424.1606@compuserve.com
Subcontractor	Exotherm Corporation 1035 Line Street Camden, NJ 08103
FETC Program Manager	Richard A. Dennis
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Abstract

Development work continues on the use of self-propagating high temperature synthesis (SHS) or combustion synthesis of inorganic materials (CSIM) to produce oxide based candle filter elements for hot gas clean-up (HGCU). Material combinations possessing suitable mechanical properties and corrosion resistance were identified and studied within the context of combustion synthesis. These combinations were selected to match the temperature, strength and corrosion resistance requirements of operation in pressurized, fluidized bed combustion (PFBC) environments. Filter permeability and capture efficiency was also examined. In addition, molding techniques to maximize oxygen diffusion/reaction completion and heating/re-heating cycles have been examined to reduce the cost of fabrication while maximizing simplicity.

Introduction

Both the Department of Energy and the private sector have extensive ongoing programs for the development of hot gas cleanup (HGCU) methods for coal utilization with emphasis on pressurized fluidized bed combustion (PFBC) and integrated gasification combined cycle (IGCC) equipment. A successful filter will eliminate typical downstream filtration elements such as cyclones, baghouses and/or electrostatic precipitators, giving an overall reduction in pressure loss and equipment cost.

Objective

Current production candle filters suffer from long-term reliability problems due to reactions between the tube material/binder and the corrosive IGCC/PFBC environments [1,2]. Current manufacturing/processing technology is somewhat limited in producing corrosion resistant and mechanically tough materials. Using self-propagating high-temperature synthesis (SHS) or combustion synthesis of inorganic materials (CSIM), unique combinations of materials are possible, with suitable properties for the demanding filtration environment. In addition to desirable mechanical properties and corrosion resistance, SHS/CSIM process methods offer manufacturing simplicity, versatility, and cost-effectiveness when compared to other manufacturing techniques.

The purpose of this work is to demonstrate the ability of SHS/CSIM to produce unique materials that exhibit candle filter performance characteristics within the context of simplified, innovative fabrication techniques. The SHS/CSIM process can easily be tailored to the needs of the PFBC/IGCC community.

Specific objectives are:

- Demonstration of filtration efficiency of better than 99.9%
- Operational capability to 2000 deg F
- Resistance to thermal and mechanical shock of back-flushing and system upsets
- Chemical resistance to hot gas environment of typical PFBC/IGCC power systems
- Operational life of two years or more in a HGCU environment
- Competitive price potential relative to current competing technologies

Approach

The SHS/CSIM method is a combustion driven, material synthesis technique, which offers many advantages over traditional fabrication methods of metallic, ceramic, and composite phase materials. The reaction is energy efficient, simple, adaptive to complex shape development, and controllable for selective material properties (i.e. porosity, thermal conductivity, density, pore size, etc.). These characteristics make SHS/CSIM ideal for candle filter element development.

SHS/CSIM is a material processing method that utilizes energy from a highly exothermic reaction to sustain a chemical reaction in a combustion wave [3,4]. The process is initiated by either locally igniting the powder mixture or heating the mixture to some elevated temperature at which a "thermal explosion" occurs. Either method produces a chemical reaction that is sufficiently exothermic to sustain a combustion wave that converts the reactant powder into the desired product. The speed of the combustion wave typically varies from 0.1 cm/sec to 10 cm/sec. The powder composition and initial conditions (i.e.: geometry, reactive volume, heating rate, etc.) determine the maximum reaction temperature which usually ranges from 1000 deg C to 3000 deg C. The following figure is an illustration of the SHS/CSIM process.

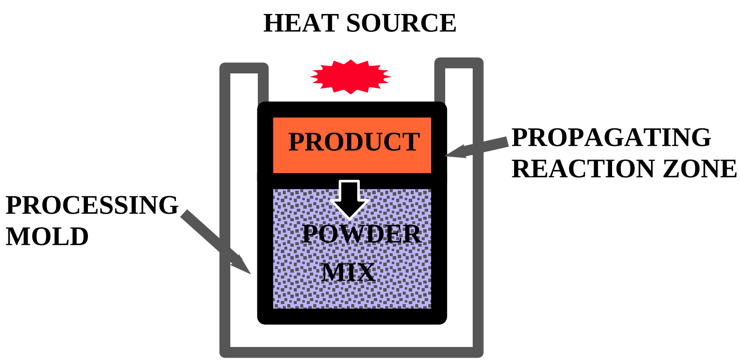

Figure 1 SHS/CSIM Reaction Schematic

The mechanical and filtration properties of the product are dependent upon the nature of the initial mixture, dispersion of constituents, pre-heat temperature, combustion rate, and other secondary process parameters. Up to 14 process parameters have been identified. By varying the quantity and size of reactants, one can alter the final composition and vary the porosity. Another factor controlling the structure of the final product is the combustion mode. As stated above, the process is initiated by either igniting the powder and allowing the combustion wave to propagate through the mixture or by heating the mixture and allowing rapid combustion or "thermal explosion" to occur. The advantage of the "propagation" mode is a slow process requiring very little energy input to initiate the reaction. The advantage of the "explosion" mode is quick transformation of the powder mixture into the final product with uniform properties. The explosion mode is characterized by a near instantaneous, isotropic reaction.

Four major classes of SHS materials are under investigation for use in hot gas clean up. Phase I work concentrated on glass binder or traditional SHS/CSIM to produce ceramic oxide materials. It is convenient to think of glass binder materials consisting of large mullite "bricks" held in place by glass mortar. Phase II work has focused on other classes of SHS/CSIM materials. The second class of SHS is the glass ceramic material. Consisting of ceramic oxides, this material is similar to the glass binder except the glass reacts with the "bricks" causing some sintering between the neighboring bricks. In general, these materials are more dense and stronger. In addition, the glass ceramics are less prone to creep than the glass binder materials. The third and fourth classes of materials are advanced oxide materials with alumina and mullite dispersed within the material matrix. These advanced oxide materials offer excellent creep resistance above 1093C (2000F) with good corrosion resistance.

Results

Preliminary results for SHS/CSIM materials are well documented [5,6]. These results include filtration efficiency in excess of 99.5%, resistance to hot corrosive media, and desirable pressure drop characteristics. Computational chemical analyses and sample material processing were conducted to demonstrate the ability of the SHS/CSIM process to produce materials with the desired end products. To date, over 80 different material combinations have been synthesized, tested and optimized. The “explosion” mode was determined to be the best candidate for application to high volume manufacturing processes with the capability to achieve uniform synthesized product with the desired properties. Figure 2 depicts a typical temperature profile for SHS/CSIM explosion mode synthesis of a sample in a processing furnace.

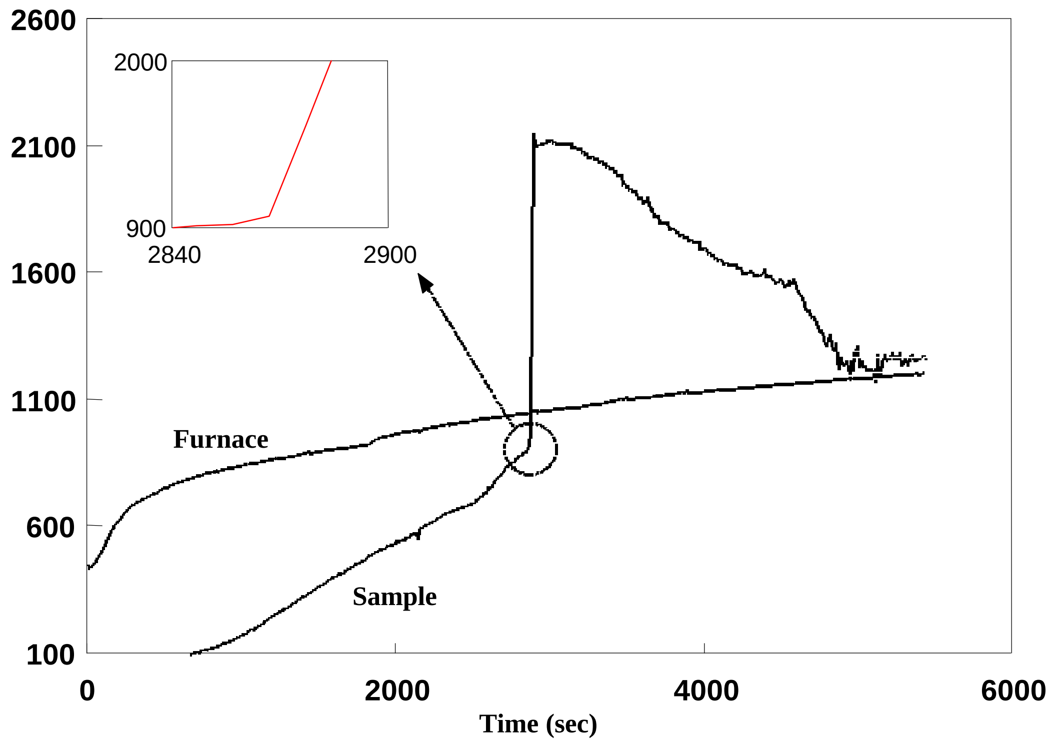

Figure 2 Typical SHS/CSIM Temperature Profile

Both the SHS/CSIM powder temperature and furnace temperature are shown as a function of processing time. The SHS/CSIM temperature lags the furnace temperature up to approximately 900 deg C. At this temperature the combustion synthesis process occurs, causing the sample temperature to rise to approximately 2100 deg C, at a rate of greater than 50 deg C per second. At this point, the SHS/CSIM process is complete and the sample is allowed to cool. By optimizing the SHS reaction, one can produce materials that react in the explosive mode at approximately 400 deg C. This leads to great savings in both processing time and equipment expense as heat input is minimized. Figure 3 is a picture of a typical tube-shape produced using the SHS/CSIM explosion mode.

Figure 3 SHS/CSIM explosion mode sample

Current work has focused on the fabrication process. Of particular interest is the diffusion of oxygen into the sample during the reaction. One advantage of the SHS/CSIM technique is the production of the ceramic oxides in-situ. It is possible to produce zirconia, titanium dioxide, magnesium oxide, alumina, mullite and several complex oxides from elemental powders. The advantages of this are twofold. First, the cost of the reactant powder is greatly reduced by using elemental materials. Second, the oxidation of the elemental material provides exothermic energy to complete the SHS/CSIM reaction. It is difficult to provide enough oxygen from other reactants to complete the oxidation process and "black coring" occurs. Thus, the required oxygen must diffuse through the powder from the furnace environment, making rigid, solid molds undesirable. The free flowing nature of the SHS powder simplifies the molding process, as it requires little or no packing pressure.

One molding method is depicted in figure 4a. A loose granular matrix defines the tubeshape. This matrix consists of a material, which does not react with the SHS/CSIM powder, is highly porous and reusable. A thin expendable membrane separates the mold matrix and the SHS/CSIM mixture. The matrix is contained within a ceramic outer shell. Although the membrane pyrolizes during the SHS/CSIM process, its surface finish determines the surface finish of the final product. After firing, the final product is easily removed from the matrix. Although reusable and relatively inexpensive, this molding technique is somewhat cumbersome and limited in the amount of oxygen available to the SHS/CSIM powder. In addition, the entire system has greater mass, which must be heated, resulting in increased fabrication cost.

A second method is depicted in figure 4b. The granular matrix and ceramic outer tube have been replaced with a metallic mesh. As the interface membrane pyrolizes, it releases enough heat to sinter the SHS/CSIM powder locally leaving behind a surface that is rigid enough to define the shape of the final product and hold the reactant powder in place until the reaction occurs. This method increase the availability of oxygen for the reaction with a reduction in overall energy required to complete the reaction.

The third method replaces the metallic mesh with a porous ceramic tube (figure 4c). The ceramic allows oxygen to diffuse into powder while maintaining a well-defined shape. In addition, greater dimensional tolerance is attainable due to the rigid structure of the porous ceramic tube. Due to shrinkage of the powder during the SHS/CSIM process, care must be taken when selecting the mold material to define the inner diameter.

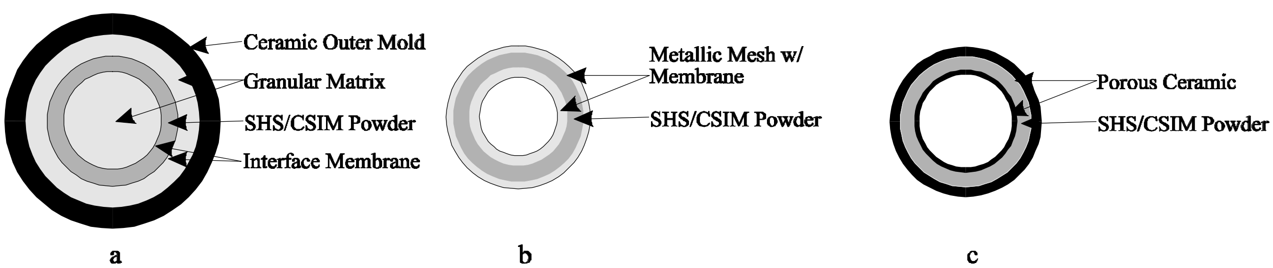

Figure 4 Molding Methods

An alternative to exotic molding techniques is to re-heat the SHS/CSIM material in the absence of the mold. By heating and soaking the material at approximately 1100 deg. C, the remaining reactants will fully oxidize to produce the desired complex ceramic oxides. Materials show a 10% increase in MOR when fully oxidized. The re-heat process is undesirable as it adds an additional step to the process.

Another area of interest is particle size distribution. By varying the size of a constituent, say mullite, the porosity and strength of the processed material can be varied. Small particles of metal reactants are desirable as they react completely. Large particles of ingredients like mullite are desirable and somewhat inert, as only the particle's surface reacts and sinters, while the center of the particle retains its initial properties. The use of large particles leads to large pores and high porosity. By introducing smaller particles, the porosity can be controlled.

The porosity and properties of the material can be varied through the reaction temperature. By increasing the reaction temperature or by providing re-heat, one can increase the amount of sintering of the glass materials and decrease the porosity. Figure T shows the porosity of a given material as a function of re-heat temperature. In addition to allowing for accurate control of the porosity, this data give some insight into the maximum continuous operating temperature of the material. Typically, the material can operate continuously at 85% of the softening temperature, as defined by a sudden drop in porosity due to glass filling the pore structure. In the case of the material shown above, the operating temperature is approximately 980 deg C.

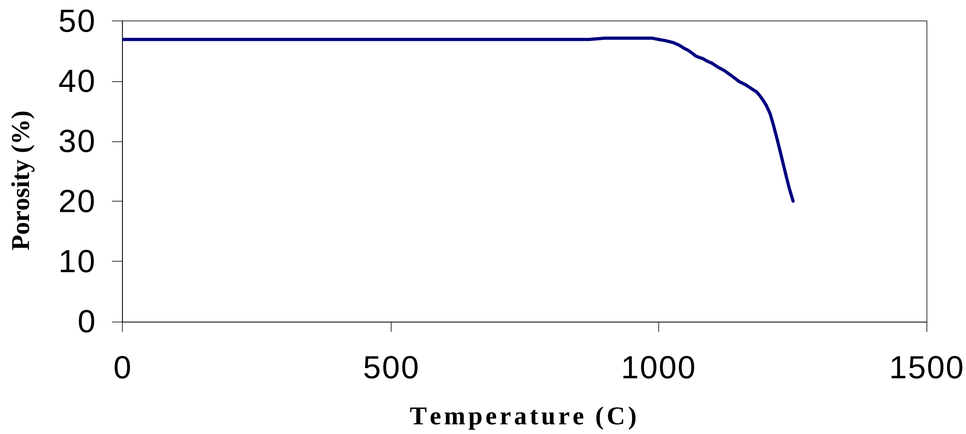

Figure 5 Porosity vs. Re-heat Temperature

Future Activities

Work continues on the production of both 1500 mm and also 500 mm long filter elements made from the glass ceramic materials for internal and outside testing. Testing includes corrosion resistance, filtration efficiency, and thermal shock resistance. In addition, development work continues on the advanced oxide materials. Optimization of molding and heating processes is ongoing to maximize production efficiency while minimizing production cost. Additional material development is planned to reduce the mismatch in thermal expansion between the flange and tube section of the filter, by altering the reactants in the flange region.

A bench-scale processing unit is being installed to evaluate special SHS process aspects which include: heating rate, directionally controlled heating, cooling protocol and geometric issues (e.g. wall thickness, tube aspect ratio, tube length, closed-end constraint, flanging, etc.). Following successful bench-scale testing and full-scale filter element fabrication, a multiple filter element production module/cell will be designed, fabricated, and tested.

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References

1. Epstein, M., "Overview of Dust Filtration From Coal-Derived Reducing Gases at High Temperature", Proceedings: Second EPRI Workshop on Filtration of Dusts Coal Derived Reducing and Combustion Gases at High Temperature, March 11-13, 1992.
2. Judkins, R.R., Stinton, D.P., and DeVan, J.H., "A Review of the Compatibility of Silicon Carbide Hot-Gas Filters in IGCC and PFBC Environments", ASME Paper 94-GT-314, International Gas Turbine and Aeroengine Congress, Netherlands, June 13-16, 1994.
3. Merzhanov, A. and Borovinskaya, I.P., "Self-Propagating High-Temperature Synthesis of Inorganic Compounds", Dokl. Akad. Nauk. SSSR (Chem), Vol. 204, pp. 429-432, 1972.
4. Knight, R., Smith, R.W., Shtessel, E.A., and Koczak, M.J., "Synthesis of Intermetallic Composite Powder Via Self-Propagating Synthesis Reaction", 22nd TMS Annual Meeting, Denver, February 21-25, 1993.
5. Hanus, G.J., Uznanski, K.T., DeCoursin, D.G., Hickel, S.D., Shtessel, E., "Candle Filter Fabrication Using Combustion Synthesis Method", Proceedings: Thirteenth Annual International Pittsburgh Coal Conference, Volume 1, pp. 338-343, September 3-7, 1996.
6. Hanus, G.J., Uznanski, K.T., DeCoursin, D.G., Shtessel, E., "New Materials and Manufacturing Options for Low-cost Candle Filter Production", The Proceedings of the 22nd International Technical Conference on Coal Utilization & Fuel Systems, Clearwater, March 16-19, 1997.