U. S. DEPARTMENT OF ENERGY
SMALL BUSINESS INNOVATION RESEARCH PROGRAM
PHASE II-FY 1997-1
PROJECT SUMMARY

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FIRM NAME, ADDRESS, TELEPHONE NUMBER:

Selee Corporation, 700 Shepherd Street, Hendersonville, NC 28792 (704)697-2411

TITLE OF PROJECT: Novel High Strength Ceria-Zirconia Toughened Alumina Ceramic with Superior High Temperature Corrosion and Erosion Resistance

NAME AND TITLE OF PRINCIPAL INVESTIGATOR: Dr. Giulio A. Rossi, Senior R & D Scientist

TECHNICAL ABSTRACT (limited to space provided):

Composite Ce-TZP/ Al_2O_3 (CeZTA) foams were developed and tested in a variety of conditions to determine their suitability as particulate filters in hot gaseous conditions generated by coal combustion in electric power plants. The optimized ceramic foam compositions exhibit superior high-strength and corrosion resistance. In an effort to optimize the CeZTA composition and production process, several potentially important variables were investigated, including the addition of spinel to the matrix. It was determined that the density, cell size and the mixing method had the strongest influence on foam strength. The spinel compositions (CeZTS) failed to outperform the 30%vol CeZTA or the 10%vol CeZTA foams. The CeZTA foams have demonstrated excellent room temperature (RT) strength, thermal shock resistance, and strength retention at 1000°C. Exposure to extreme corrosive conditions that simulated environments found in coal gasification/combustion processes, such as IGCC (Integrated Gasified Combined Cycle) and PFBC (Pressurized Fluid Bed Combustion) did not cause significant degradation of CeZTA strength. The CeZTA foams that were thermally cycled in temperatures that simulated IGCC and PFBC conditions retained their high strengths while the same conditions had a deleterious affect on Alumina foam strengths. The superior properties of these foams suggest that they could be used for a variety of applications in the environmental, energy and chemical fields.

KEY WORDS:

Ceramics, Foam, Zirconia, Alumina, Transformation Toughening, Thermal Shock, Corrosion, Ceria

ANTICIPATED RESULTS/POTENTIAL COMMERCIAL APPLICATION as described by the applicant (limited to space provided)

The Ce-TZP/ Al_2O_3 ceramic foam developed in Phase I of this award is a promising candidate for particulate filtration in coal-derived hot gas, for light weight kiln furniture, as catalyst support, for radiant burners of natural gas and for other uses in the environmental, energy and chemical fields.

DOE SBIR PHASE II AWARD

DE-FG05--94ER81859

**Novel High Strength Ceria-Zirconia Toughened Alumina
Ceramic with Superior High Temperature Corrosion
and Erosion Resistance**

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FINAL REPORT

DOE Patent Clearance Granted

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1. Executive Summary

The production process and composition of the two-phase, composite Ceria-Zirconia Toughened Alumina (CeZTA) foam that was developed in Phase I of this contract has been successfully optimized. By testing several potentially important variables and characterizing the foam samples, we were able to produce a superior high-temperature, corrosion resistant ceramic foam, which is the strongest foam ever made by Selee Corp. In addition, a composition (CeZTS) was developed in which spinel replaced most of the Alumina present in the matrix. It was theorized that a lower thermal expansion and thus a better thermal shock resistance would result.

The Ce-ZTA foams have shown superior room temperature (RT) strength, excellent thermal shock resistance (94% strength retention after shock), very good strength retention at 1000°C (80% of RT strength), extreme corrosive conditions resistance and high retention of strength during thermal cycling from 750°C to 950°C. The 15%CeZTS foams performed much better in all testing than the 40%CeZTS composition, but failed to outperform either CeZTA composition. In addition, it was found that working with the spinel compositions was difficult to due their troublesome rheology.

Of the eight variables evaluated in the Experimental Design 1, the density and the cell size (PPI #) had the strongest influence on the foam strength. The Modulus of Rupture (MOR) increases with density (in the range 10% to 25% of theoretical density) and with cell size (from 65 PPI to 30 PPI). Reducing the volume fraction of $\text{CeO}_2\text{-ZrO}_2$ in the Ce-ZTA from 30% to 10% did not result in significantly lower strength. The RT MOR, the thermal shock resistance and the retained strength at 1000°C were virtually unaffected. This is an important discovery, since the 10 vol% CeZ material is 2-3 times less expensive versus the 30 vol% material. The mixing method was found to be an important variable.

A thermal cycling apparatus was set up at Selee in order to compare the results obtained to the results from thermal cycling tests performed at Pennsylvania State University. The samples were cycled in conditions that would be likely to be found in actual operating conditions. Although the strengths of the Ceria composites were not initially as high as they could have been, their retention of strength was superior to Alumina, which had a significant decrease in strength. 40%CeZTA, 15%CeZTA and 15%CeZTS demonstrated no significant change in strength.

The encouraging results obtained from the In-House cycling were somewhat confusing when contrasted with those obtained from Penn State. The retained strengths of Experimental Design 1 samples that were thermally cycled at Penn State showed surprisingly low retention of strengths. For example, 15%CeZTA made with Daichi powder only retained 60% of its initial strength (MOR), while Alumina retained 69%. Experimental Design 2 samples, exhibited similar results; however, initial strengths of these samples were considerably lower than expected. The cycling parameters chosen (25-1000C) may have had a much more deleterious effect on the foams' strengths than those chosen based on simulated operating conditions (750-950C).

The foam samples that were exposed to simulated IGCC (Integrated Gasified Combined Cycle) and PFBC (Pressurized Fluid Bed Combustion) conditions exhibited excellent strength retention. In fact, both the 15% CeZ composites from Experimental Design 1, showed a significant increase in strength upon exposure to the PFBC conditions. Only the 40% CeZTA foam with an alumina coating showed any degradation in strength when exposed to the PFBC conditions, dropping from a superior strength of 1873 psi to 1193 psi. The samples tested from Experimental Design 2 also displayed high strength retention even though their initial strengths were low due to an insufficient mixing method. 40%CeZTS was the only composition that demonstrated a significant decrease in strength when exposed to the corrosive conditions.

2. Project Title and Objectives

The title of the research program is:

“Novel High Strength Ceria-Zirconia Toughened Alumina Ceramic with Superior High Temperature Corrosion and Erosion Resistance”

The main objective of this research program was to develop and test a unique composition for reticulated, open-cell ceramic foams that can be used as a particulate (fly ash) filter in hot gases generated by coal combustion in electric power plants. This material may also be of interest for other high temperature applications. This material should exhibit sufficient strength at high temperature, good thermal shock resistance, microstructural and phase stability in use, and corrosion resistance in the presence of aggressive chemical species.

The Phase I specific objectives were:

- 1) Develop a Ce-ZTA foam with 30 vol% $\text{CeO}_2\text{-ZrO}_2$, 30 ppi, and approximately 20% of theoretical density.
- 2) Achieve minimum strength of 1000 psi at RT and 500 psi at 1000°C.
- 3) Characterize the Ce-ZTA foam for physical, chemical and mechanical properties.
- 4) Evaluate alkali and sulfate corrosion resistance of the Ce-ZTA foam at 1000°C, versus Alumina and Mullite foams of similar density.
- 5) Evaluate the thermal shock resistance of the Ce-ZTA foam, versus Alumina and Mullite foams of similar density.

Summary of Phase I Results

1. More than 90% of the $\text{CeO}_2\text{-ZrO}_2$ in the Ce-ZTA foam was present in the tetragonal form (Ce-TZP). This provides high toughness and strength at RT.
2. The average RT MOR was about 1200 psi, much higher than Alumina (570 psi) and Mullite (340 psi) foams of similar density.
3. After thermal shock (RT-1000°C-RT) the residual strength for Ce-ZTA was almost 600 psi, but only 200 psi for Alumina and 140 psi for Mullite.
4. The strength at 1000°C was 690 psi for Ce-ZTA, higher than Alumina (520 psi) and Mullite (170 psi).
5. The corrosion resistance at 1000°C in the presence of NaCl and KCl vapors was very good. Also, the resistance to sodium sulfate vapors at 1000°C was excellent. There was no loss in strength found after exposure.

The Phase II specific objectives were:

- 1) Optimize the Ce-ZTA composition and production process.
- 2) Evaluate the effect of several variables on strength and thermal shock resistance.
- 3) Characterize foam for physical, chemical and mechanical properties.
- 4) Evaluate foam performance in severe conditions simulating environments found in coal gasification/combustion processes, such as IGCC (Integrated Gasified Combined Cycle) and PFBC (Pressurized Fluid Bed Combustion).
- 5) Evaluate effect of thermal cycling on strength and elastic modulus.

3. Background

Ce-TZP/ Al_2O_3 composites have been the subject of extensive investigation, due to their excellent mechanical properties. Ce-TZP (CeO_2 -stabilized Tetragonal Zirconia Polycrystals) ceramics have been produced that exhibit high strength and toughness (1). The main advantage of Ce-TZP's vs. Y-TZP's (Y_2O_3 -stabilized) is the better resistance to t- ZrO_2 destabilization induced by moisture at 150°C - 250°C (Low Temperature Degradation), which results in microcracking and strength loss. The Y-TZP ceramics are, however, stronger and less prone to plastic deformation. Mixed Ce, Y-TZP's have been made (2) to combine the best properties of the two materials.

CeTZP/ Al_2O_3 composites combine the advantages of strength and toughness of Ce-TZP with the hardness and cost advantages of Al_2O_3 . For instance, abrasive grits of CeO_2 - ZrO_2 - Al_2O_3 have shown better performance in grinding wheels vs. conventional abrasives (3). Two phase Ce-TZP/ Al_2O_3 composites can be produced with a variety of compositions, depending upon the desired mechanical properties. A composite with Al_2O_3 matrix, (major phase) is less expensive and the minimum volume fraction of Ce-TZP should be used to achieve the desired strength and toughness. Typically, Ce-TZP volume fractions of 0.2 to 0.4 have been used, with a CeO_2 content of 10-12 mol % in solid solution with ZrO_2 . The best properties are obtained for dense materials with grain size of 1-3 μm . A small grain size is necessary to retain the t- ZrO_2 after fabrication, which enhances toughness by transforming to m- ZrO_2 under stress. However, microcrack toughening is another important toughening mechanism in these materials. Whereas transformation toughening becomes inoperative at high temperatures, when t- ZrO_2 is thermodynamically stable, microcrack toughening is still viable.

A recent study by the principal investigator of this program (4) had shown that a dense Ce-TZP/ Al_2O_3 composite with 30 vol% Ce-TZP (12 mol% CeO_2) pressureless sintered at 1600 C exhibited a 25 C MOR of 634 Mpa and a K_{Ic} of $7.4 \text{ Mpa}\cdot\text{m}^{1/2}$. More importantly, MOR of 315 Mpa and K_{Ic} of $3.5 \text{ Mpa}\cdot\text{m}^{1/2}$ were measured at 1000°C . Furthermore, aging at 1000°C in air for 1000 hrs showed no microstructural changes and no strength degradation.

In addition to having excellent mechanical properties, a Ce-TZP/ Al_2O_3 composite was expected to exhibit superior corrosion resistance to alkalis (Na, K) and sulfur species (SO_2 , SO_3) present in the aggressive atmosphere of coal-derived gases. Plasma sprayed CeO_2 - ZrO_2 , for instance, has been patented for protection of superalloys against attack by vanadium and SO_x impurities in gas turbines (5). CeO_2 appears to enhance corrosion resistance in ZrO_2 -based ceramics. For example, in materials tests for MHD channels, CeO_2 - ZrO_2 has shown good resistance to 1200 C K_2SO_4 - K_2CO_3 melts (6). Additions of CeO_2 as dispersed particles in the

metal reduces sulfidation-oxidation attack on nickel based turbine blades, presumably by reducing the sulfur activity through formation of $\text{Ce}_2\text{O}_3\text{S}$ (7). More recently (8) the sulfation behavior of CeO_2 (50 mol%) in the presence of Na_2SO_4 has been studied. It was concluded that a liquid eutectic was formed only at temperatures of 800 C or higher and that a high SO_3 partial pressure (1200 Pa) for CeO_2 sulfation was needed. In the same study it was determined that the sulfation resistance of ZrO_2 was more resistant than CeO_2 to SO_3 - Na_2SO_4 attack.

Another study (9) has confirmed the excellent corrosion resistance of CeO_2 to alkalis. Dense CeO_2 pellets were submerged in eutectic Li, K carbonates at 650°C for 500 hours and showed no microstructural changes.

It has been reported in the literature (10) that in a reducing atmosphere at high temperature (1000°C-1400°C) t- CeO_2 - ZrO_2 can transform to monoclinic due to the Ce^{4+} reduction to Ce^{3+} . This has been confirmed by experiments performed by G.A. Rossi (4), where a dense billet of CeTZP/ Al_2O_3 , after HIP'ing in N_2 at 200 Mpa, showed an orange discoloration and formation of m- ZrO_2 , as shown by XRD. However, the transformed layer was found to be only 5 μm thick. The original ivory color was restored after reoxidation at 1000°C. The strength of the reduced material was found to be slightly higher, which was explained by the surface compressive stress created by the t-m transformation. It is therefore concluded that destabilization of the first grain layers, induced by reducing gases or reactions of CeO_2 with SO_2 , SiO_2 or other species, will not cause strength reduction. It must be remembered that the Ce-TZP grains are surrounded and constrained by Al_2O_3 grains and that catastrophic crack propagation will not occur.

Hot gas streams contain a host of contaminants (particulates, nitrogen, sulfur, alkalis, halogens, and tars) which must be removed to prevent damage to equipment (corrosion, erosion, deposits) and to the environment. Fine particles removal has been proposed using porous ceramic filters, which should exhibit a set of properties, often mutually exclusive, such as strength at low and high temperature, thermal shock resistance, low pressure drop, ease of cleaning by back pulsing, corrosion and erosion resistance. Ceramic filters tested thus far present problems related to three main areas, i.e. fabrication costs, system design and materials durability. For instance, candle filters are expensive and susceptible to fatigue rupture during use, due to mechanical stresses resulting from a high aspect ratio. Furthermore, creep at high temperature is a serious problem (11). Cross-flow cordierite honeycombs coated with aluminosilicate ceramic membranes (12) are expensive to make, due to the laborious process of coating and plugging alternate channels, and are vulnerable to alkali attack in extended use. Cross-flow stack type filters made with Alumina/Mullite (13) have shown serious alkali corrosion in prolonged tests.

Because of this research being performed on Ceria composites, it was deemed viable that a ceramic foam containing Ceria-Zirconia Toughened Alumina would have the characteristics necessary to make an excellent choice for a filter material. Reticulated ceramic foams are potentially excellent filter materials, because they exhibit low pressure drop, due to high porosity and large pore size, and good thermal shock resistance thanks to a low elastic modulus. Additionally, because of the catalytic activity of ceria, this Ceria-Zirconia Toughened Alumina has the potential to have some self-cleaning tendencies with respect to tar particles. However, commercial applications are not limited to coal gas purification, other potential uses include catalyst supports, especially for HCN and nitric acid production, light weight kiln furniture, and radiant burners.

SELEE's technical approach was to produce an open cell Ce-TZP/ Al_2O_3 composite ceramic foam. The SELEE ceramic foam is an open cell, reticulated foam made by a replication process, which uses a thermoset polyurethane (PU) foam. The PU foam is impregnated with an aqueous slurry of ceramic particles, which are deposited on the PU foam webs. The final ceramic foam density is controlled by the amount of slurry deposited on the webs and by the density of the ceramic struts after firing. The foam cell size is regulated by the original cell size of the PU foam and by the firing shrinkage.

The typical foam density is in the range 10-25% of Theoretical Density (TD). In general, densities lower than 10% result in very low, unacceptable strength, while densities higher than

25% result in "blind" cells and loss of permeability. A typical SELEE foam is shown in Figs. 1 and 2.

Foam strengths are controlled by the flaws present in the struts. Therefore minimizing flaw size and population density is imperative to achieve high strengths. Most flaws are present as impurities (i.e. foreign particles), agglomerates, air bubbles, or cracks. It is therefore important to control and minimize the sources of potential flaws, by controlling the properties of the slurry, which, in turn, will be largely responsible for the fired foam properties.

The ideal slurry for foam impregnation should exhibit the following properties:

1. Pseudoplastic (or shear thinning) behavior
2. Thixotropy (viscosity increase when shear strain is removed)
3. Highest solids content (to limit firing shrinkage and prevent cracking)
4. Broad particle size distribution, in order to maximize packing density and minimize the firing shrinkage and possible cracking.
5. Absence of air bubbles
6. Purity (absence of foreign contaminants)
7. Absence of agglomerates.
8. Uniform powder particle dispersion. This is crucial when a multiphase ceramic foam is fabricated, as in this program, where a uniform dispersion of Ce-TZP grains in the Alumina matrix is desired.

Figure 1. Typical Selee Foam Disk, 30 ppi.

Figure 2. Typical Selee Ceramic Foam, same as above.

4. Experimental Procedures

Overview

In order to optimize the Ce-ZTA composition, which was developed in Phase I of this program, an experimental design matrix, Experimental Design 1, (Table 1) was created in which several potentially important variables were tested for their affect on the foam properties. Eight variables were chosen to study their affect on the foam strength and thermal shock resistance. To test the foams' mechanical properties, strength tests were performed both at room temperature and at 1000°C. The original plan for Phase II of this program had specified the use of two experimental design matrices to optimize the composition and production processes of the Ce-ZTA foams. The second design was to be derived based primarily upon the results of Experimental Design 1. However, because of an interest in spinel (MgAl_2O_4) as a toughening agent, the second experimental design matrix, Experimental Design 2 (Table 2), had spinel introduced as an added variable. After extensive investigation, samples were prepared from this design. These samples were subsequently thermally shocked and tested to determine the modulus of rupture at room temperature and after shock. Furthermore, samples were characterized by SEM and XRD analysis. To determine those variables that significantly affected foam strength, statistical evaluations of the data were performed.

To evaluate the effect of thermal cycling on strength and elastic modulus and to evaluate foam performance in corrosive conditions, compositions from Experimental Designs 1 and 2 were prepared. Several samples were sent to Pennsylvania State University where they were tested in a thermal cycling apparatus. The cycling effects on both the strength and the Dynamic Young's Modulus were determined. Corrosive conditions testing was performed at the Research Triangle Institute (RTI) where they are equipped with an apparatus that can be used to simulate environments found in coal combustion processes. Several samples of varying compositions from Experimental Designs 1 and 2 were chosen to be tested in both IGCC (Integrated Gasified Combined Cycle) and PFBC (Pressurized Fluid Bed Combustion) simulated environments. Compositions with CeZ powder from two sources were tested in an effort to qualify a second source of CeZ powder. The exposed samples were then sent back to SELEE to determine the strengths of the exposed samples. As well, a gas burner apparatus was set up at SELEE to thermally cycle several samples from Experimental Design 2 to compare with the data obtained from Pennsylvania State University.

While the various samples from Experimental Design 2 were being tested at RTI and Penn State, it was discovered that the method used to prepare the samples from this design was not optimal. It was determined that the mixing method used, while sufficient for most other slurries prepared here at Selee, failed to properly disperse the CeZ and Spinel powders. Consequently, additional samples were prepared using the attrition mill. Finally, with much experimentation, various methods were tested in which it was attempted to further optimize the spinel compositions. These samples were also tested and characterized so that a better evaluation of the effect of spinel as a toughening agent could be realized.

Fractional Factorial Design of Experiments to Determine Relative Importance of Main Variables on Ce-TZP/Al₂O₃ foam bending strength.

Exp.#	Vol% CeZ	Mix. Method	Boric Acid	De-Airing Cpd.	Coating	Coat. Type	PPI #	% Density
1	10	Attritor	No	No	No	N.A.	30	10
2	30	Attritor	No	No	Yes	CeZA	30	20
3	10	Mixer	No	No	Yes	CeZA	65	10
4	30	Mixer	No	No	No	N.A.	65	20
5	10	Attritor	Yes	No	Yes	A	65	20
6	30	Attritor	Yes	No	No	N.A.	65	10
7	10	Mixer	Yes	No	No	N.A.	30	20
8	30	Mixer	Yes	No	Yes	A	30	10
9	10	Attritor	No	Yes	No	N.A.	65	20
10	30	Attritor	No	Yes	Yes	A	65	10
11	10	Mixer	No	Yes	Yes	A	30	20
12	30	Mixer	No	Yes	No	N.A.	30	10
13	10	Attritor	Yes	Yes	Yes	CeZA	30	10
14	30	Attritor	Yes	Yes	No	N.A.	30	20
15	10	Mixer	Yes	Yes	No	N.A.	65	10
16	30	Mixer	Yes	Yes	Yes	CeZA	65	20

Explanation of Table:

1. Vol% CeZ : Volume percent of 10 mol% CeO₂-ZrO₂ in the CeO₂-ZrO₂-Al₂O₃ composite
2. Attritor : Union Process Attrition Mill containing 3 mm Mg-PSZ balls.
3. Mixer : Silverson Abramix High Shear Mixer.
4. Boric Acid : 0.05% by weight of H₃BO₃ added , based on fired ceramic weight.
5. De-Airing Cpd. = Foamaster A (Henckel Corp.) in the amount of 0.2 % by weight , based on fired ceramic weight.
6. Coating = Application of coating to foam by dipping impregnated and dried foam into ceramic slurry.
7. Coating Type = Either Al₂O₃ or CeO₂-ZrO₂-Al₂O₃ (CeZA) , same composition of the bulk material.
8. PPI # = Polyurethane foam cell size in pores per inch (PPI).
9. % Density = Percent of Theoretical Density of the Ceramic Foam.
10. N.A. = Not Applicable.

Table 1. Experimental Design 1 Matrix

Table 2. Experimental Design 2 Matrix

Sample I.D.	vol% CeZ	w/spinel
15%CeZTA	10	no
40%CeZTA	30	no
15%CeZTS	10	yes
40%CeZTS	30	yes

*This design encompassed the most promising compositions derived from Experimental Design 1 (15CeZTA and 40CeZTA), as well as, compositions created from extensive investigation of spinel toughening (15 CeZTS and 40CeZTS). The samples were subsequently used for the first rounds of testing at RTI and Penn State, as well as for in-house thermal cycling and characterization. 100% Spinel and Alumina compositions were made to compare the effects on strength of the in-house cycling.

Outline of experimental procedures contained in this section:

1. Sample Preparation
 - a) Powders Used
 - b) Slurry Preparation
 - c) Foam Impregnation
 - d) Foam Drying/Firing
 - e) Slip-Cast Tile Preparation
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1. Sample Preparation

a) Powders Used.

The $\text{CeO}_2\text{-ZrO}_2$ powder used for Experimental Design 1 (Table 1) was the 10 mol% CeO_2 - ZrO_2 made by Unitec, U.K. During the course of the program, a shortage of the Unitec powder was experienced and it was decided to qualify a second source of CeZ powder. The powder chosen was made by Daichi KKK (Japan). This DKKK powder was used as a variable in the first set of samples that were sent to Penn State and to the Research Triangle Institute.

After the first set of samples were sent to be tested, compositions were created in which spinel was added as a variable. Spinel was utilized because current literature cites that spinel has been shown to increase the strength of ZrO_2 - toughened ceramics by precipitate hardening. Furthermore, the thermal expansion coefficient is lower than that of alumina, suggesting that a greater resistance to thermal shock could be obtained. The spinels used were made by Baikowski International, USA and Atlantic Equipment Engineers, USA. After some experimentation, it was noted that to obtain a high solids loading with a broad spectrum of particle sizes, a portion of the spinel that was added to the compositions needed to be attrited for an 8 hour period to acquire a finer particle size.

A more detailed description of the powders used can be found in Appendix 1.

b) Slurry Preparation:

Using either Unitec or DKKK powder, the aqueous slurry for making the CeZTA foams was prepared by adding the dry CeZ powder to a slurry of Alumina powders routinely made by Selee for the manufacture of Alumina foam filters. This slurry is electrostatically stabilized and contains about 80% solids by weight. Several types of alumina powders are used to make up this slurry, in order to obtain high solids loading, good rheological behavior and a broad particle size distribution which are all essential in order to limit the firing shrinkage and avoid cracking.

When preparing the samples from Experimental Design 1, the CeZ powder was dispersed in the Alumina slurry using either the attrition mill or the Silverson high shear mixer. In all cases

(10 or 30 vol% CeZ, Unitec or DKKK powder) the CeZTA slurry contained 78-80 % solids and exhibited excellent rheology, as shown by a typical Shear stress/Shear strain curve obtained with Haake (Model RV3) viscometer (See Fig. 3, p.16).

Once spinel was introduced as a variable into Experimental Design 2, compositions were created in which the fired product was approximately 80% spinel and 15% CeZ or 57% spinel and 40% CeZ, by weight (15CeZTS and 40CeZTS). Here again, several alumina powders were chosen in order to create a composition with a high solids loading. There was evidence that magnesium was precipitating out of the solid solution. To remedy this, tetramethyl ammonium hydroxalate was added and used additionally when the viscosity was found to be too high, whereas, nitric acid was used in an analogous capacity for the CeZTA compositions. All of the original samples made from Experimental Design 2 were originally made using a standard variable high shear mixer that is regularly used by our pilot plant to make larger batches than is possible using the attrition mill or the Silverson. Once it was discovered that this mixer was insufficiently mixing the slurries, the attrition mill was used. The attrition mill was chosen because it produces slurries free of agglomerates and because the Silverson, although easier to operate, was inoperative.

c) Foam Impregnation :

The CeZTA slurry was used to impregnate the PU foam using the standard Selee procedure. The foam is impregnated by dipping for a sufficient length of time for the foam to be saturated. A roller setup was used to remove excess material and to obtain the desired weight. This step is critical in that it, together with the slurry properties, determines the uniformity and the relative density of the final product. The spinel slurries had a greater tendency to dry quickly compared to the CeZTA slurries.

d) Foam Drying /Firing:

The impregnated foam pieces, which were either blanks which would be cut after firing to the desired size or foam which was precut to the desired size were air dried overnight and dried further in an industrial convection oven when necessary. In an electric furnace with MoSi_2 elements, they were then fired with the following schedule:

RT to 1600°C : 15 hrs
1600°C soak : 4 hrs
1600°C to RT : 15 hrs.

During this step, the polyurethane foam was decomposed and volatilized. The typical linear firing shrinkage was 10-11 %. The foam color after firing was yellow when the Unitec powder was used, but ivory, almost white, when the DKKK powder was used. The samples containing spinel powder exhibited evidence of photosensitivity, changing from slightly orange to tan upon exposure to light.

Figure 3. Shear Stress/ Shear strain curve for a typical $\text{CeO}_2\text{-ZrO}_2\text{-Al}_2\text{O}_3$ slurry 80 % solids by weight).

e) Slip-Cast Tiles :

For XRD and SEM (microstructure) analysis, slip-cast tiles (5x5x1 cm) were made in a plaster mold, using the same slurry used for the foam. Sintered tiles allow the determination of m-ZrO₂ in the as-fired, ground and ground/annealed states. These tiles were ground using a Blanchard grinder, polished and then annealed at 1150°C for 1 hour to create as closely as possible the as-fired state of the foams. It is felt that this method avoids the effect of zirconia destabilization caused by the mechanical stress of grinding. Furthermore, they are convenient for mounting and polishing for the SEM. The slip-cast tiles were dried and fired together with the foam squares.

2. Characterization of Samples:

The fired Ce-ZTA and Ce-ZTS foams were characterized using the following procedures:

- Calculating Density as a Percentage of the Theoretical Density
- Microstructure Analysis by SEM
- X-Ray Diffractometry
- Strength Testing (MOR) at RT and 1000°C
- Thermal Shock Testing
- Statistical Evaluation of Data

Appendix B contains a detailed description of these methods.

3. Exposure to Corrosive Conditions Testing at the Research Triangle Institute :

RTI had an available reactor from previous work related to coal burning problems. Fig. 4 describes the high-temperature, high-pressure bench-scale test facility. A stainless steel pressure vessel houses a quartz reactor. The hot zone of this reactor measures approximately 3.4 inches in diameter by 18 inches in length. The reactor was loaded with small disks slightly smaller than 3.0 inches in diameter. The fired sizes of the foams were 3.0 inches in diameter, but because the actual reactor vessel was slightly out of round the samples were ground individually to get a tight fit.

The reactor temperature was continuously monitored using a type-k thermocouple. The system pressure was regulated by a control valve which was located at the reactor exit. Different gas compositions were created by blending metered quantities of pure component gases. An HPLC pump was utilized in order to feed water to generate steam. The coal gas and the steam formed in a preheater are further heated before entering the sorbent bed. The H₂S/H₂ mixture was fed through a bubble cap distributor.

Samples from each of the four compositions chosen were exposed for 100 hours in the simulated conditions. After the two runs, the samples were returned to Selee for in-house evaluation. Unexposed control samples were also evaluated to assess the extent of degradation suffered by the foam discs exposed to the simulated IGCC and PFBC conditions. Table 3 lists the conditions that were used for each test.

Figure 4. Schematic of Reactor used for Exposure to Simulated IGCC and PFBC Conditions

Table 3. Simulated IGCC and PFBC Conditions for Corrosive Exposure Tests

Process	IGCC	PFBC
Temperature, °C	650	850
Pressure, Atms	25	15
Gas Composition		
CO ₂ , %	8	14
CO, %	39	0
H ₂ O, %	25	10
H ₂ S, %	1	0
SO ₂ , %	230ppm	0
H ₂ , %	27	0
O ₂ , %	0	6
N ₂ , %	0	70
HCl, %	100/ Not Available	100/ Not Available
Alkalies, ppm	30	30

From the sample set derived from Experimental Design 1 (Table 1), approximately 15 samples were tested of each composition in the IGCC environment and 15 of each in the PFBC gas composition. A total of 44 samples from Experimental Design 2 were tested. During Experimental design 1 testing, HCl flow was only continued for the first 30 hours of the PFBC exposure and unavailable during the IGCC exposure due to corrosion of the HCl supply line. Due to the fact that there was discoloration around the edges of the disks, it is thought that there may have been some channeling of the gas mixture during this experiment. The gas flow rate for both environments was set corresponding to a linear velocity of 3.5 ft/min. This flow rate is typically used for commercial candle filter designs.

Experimental Design 1: Four of the most promising samples were chosen from the results of Experimental Design 1. As well, because it was necessary to quantify another source of CeZ powder, DKKK powder was used to prepare one of the four compositions. The first set of samples that were sent for exposure testing were prepared as follows; Foam discs, 50cm x 0.25cm, with composition 10 vol% and 30 vol% CeZ were made and shipped to the Research Triangle Institute (RTI) for testing in their simulated IGCC and PFBC reactor conditions. Both Unitec and DKKK CeZ powders were used to make the Ce-ZTA with 10 vol% CeZ. In addition, Ce-ZTA samples with 30 vol% CeZ (Unitec powder) were coated with an Alumina coating, which was expected to enhance strength and resistance to the IGCC and PFBC severe environments. The target % theoretical density for the prepared foams was 18-20% . Table 4 summarizes the compositions chosen.

Table 4. Experimental Design 1 for Exposure Testing and Thermal Cycling at Penn State

Sample I.D.	vol% CeZ	w/DKKK CeZ	w/alumina coating
40UCeZTA w/c	30	no	yes
40UCeZTA	30	no	no
15UCeZTA	10	no	no
15DCeZTA	10	yes	no

Note: These compositions were deemed the most promising samples derived from Design 1.

Experimental Design 2: The second set of samples, (Table 2), to be exposed to simulated IGCC and PFBC conditions had the addition of spinel as a variable in the compositions. All of

the samples were prepared using the Unitec powder. The samples were of the same dimensions as those sent previously; however, the target % theoretical density was 15% instead of 20%.

4. Thermal Cycling

a) Thermal Cycling Effects on Strength and Elastic Modulus Performed at Penn State

The Thermal Cycling Apparatus at Penn State is shown in Fig. 5. In this apparatus, which was developed at Penn State, specimens were irradiated from both sides using Infrared heaters (Research Inc.). Cooling was obtained by air jets. The high density heaters have six tungsten filament quartz lamps arranged in a compact array. This allows specimen temperatures close to 1500 C, combined with very fast heating and cooling rates. The temperature profile is controlled by a process controller driving a Phase Angle Silicon Controlled Rectifier. The air flow rate for cooling is controlled by a combination of solenoid and metering valves. Fine gauge thermocouples (0.005") were used to measure the temperature and give feedback to the controller.

Samples with the same compositions as those shipped to RTI were sent to Pennsylvania State University for thermal cycling and measurement of the residual Young's modulus and strength. Dynamic resonance testing generated the data for the normalized elastic modulus. A digitally generated wide band frequency sine wave was used to excite vibrations at one end of the specimen. The vibration spectra was collected at the other end. Excitation and response was measured by piezoelectric transducers in contact with the specimen. The elastic modulus was tested because it is a non-destructive process which enables one to monitor a cycling process, and because a decrease in the elastic modulus indicates overall damage to the sample while a strength test is, in some instances, merely related to the largest crack produced during shock.

The samples were heated rapidly to 1000°C, held for 2 mins , then cooled by the forced air jets to room temp. The elastic modulus of the samples was measured in as-received condition, after 1,2,5 and 10 cycles. The elastic modulus was normalized with the elastic modulus of the as-received specimens. Strength of the samples was measured at Penn State using a three-point bend test. 6 samples were used to measure as-received strength. 3 samples were thermally cycled. This procedure was utilized for both Experimental Design 1 and 2 samples.

Schematic of the thermal cycling apparatus

Schematic of elastic modulus measurement setup

Figure 5. Schematic of Thermal Cycling Apparatus and Elastic Modulus Measurement Set-Up used at Pennsylvania State University

b) Thermal Cycling Effects on Strength Performed In-House at SELEE

In order to cycle the samples at conditions which are more attuned with actual IGCC and PFBC operating conditions, Selee set up a gas burner test rig to thermally cycle samples. Fig. 6 describes the apparatus used. In this apparatus, specimens were inserted in a cylindrical sample chamber. The exhaust from a gas burner operating at excess air conditions was blown through the porous sample. The disks are held in place by wrapping the circumference with alumina fiber, thus allowing the heat to disperse evenly across the face of the sample. Two thermocouples were set up so as to track the temperature on either side of the sample during the test. Burner shields made of Silicon Carbide foam were placed at both the intake and exhaust to further control even heat dispersment. The air flow rate for cooling and heating is controlled by a combination of solenoid and metering valves. The samples were cycled from 750°C to 950°C for a total of 15 cycles, the temperature ranges being based on actual operating conditions. Fig. 7 gives an example of a cycling curve generated for this project. The number of cycles was based upon the behavior of similar compositions when exposed to thermal cycling. For instance, the majority of the damage to alumina foams occurs within the first few cycles and then tapers off. It was felt that 15 cycles would give a good indication of the maximum amount of strength decrease, if any, that would occur in the sample. 5 samples each of the following compositions were cycled 15 times from 750°C to 950°C, and then broken at RT to determine the impact on the strength: 15%CeZTA; 40%CeZTA; 15%CeZTS; 40%CeZTS; Alumina; and 100%Spinel.

Figure 6. Schematic of Gas Burner Rig located at Selee

Figure 7. Typical Heating and Cooling Curve for In-House Thermal Cycling

5. Experimental Design 1 Matrix

5.1. Strategy for Experimental Design 1

The Phase II proposal had identified several potentially important variables that could affect the Ce-ZTA foam properties and a tentative partial factorial design had been proposed. After receiving the Phase II grant, it was decided to study the effect of eight variables on the foam strength (MOR) at room temperature (RT), at 1000°C and at RT after thermal shock.

The choice of the eight variables shown in Table 1 was dictated by the following considerations:

1. CeZ volume fraction :

This was thought to be the most important variable. The CeZ powder, dispersed in the Alumina matrix, after firing at 1600°C will produce small Ce-TZP (Tetragonal Zirconia Polycrystals) grains. It is expected that the majority of these grains would remain tetragonal after cooling to RT, provided that they did not exceed a critical size (about 2 μm). The t-CeZ grains impart toughness (transformation toughening) and strength to the foam.

In Phase I a 30 vol % volume fraction of CeZ was used (40 weight percent) with good results. In Phase II it was decided to choose two levels of CeZ concentration, i.e. 10 vol% and 30 vol% with the hope that a significant reduction in the CeZ fraction, from 30 to 10 vol%, would not significantly affect the mechanical properties. A foam with 10 vol% CeZ is less expensive to manufacture, since the CeZ powder price (Unitec, U.K.) is about 17\$/lb, compared to less than 1 \$/lb for Alumina powder.

2. Mixing Method :

In Phase I the slurry with the 30 vol % CeZ composition was prepared by adding the Unitec CeZ powder to a Selee Alumina slurry (with 80 weight percent solids) in an attrition mill (Union Process). Although this method had shown good results, the use of the attritor can change the particle size distribution of the two powders and, in addition, cleaning the mill is difficult and part of the powder is lost. As an alternative method, it was decided to use for Phase II a high shear mixer made by Silverson (U.K.), Model Abramix RBXL, specifically designed for abrasive slurries. This machine, constructed in stainless steel, is made up of an inner rotor and an outer stator, separated by a small gap. During the mixing operation, the ceramic particles are sucked from the bottom up and ejected radially through a series of holes in the stator. Since the gap size is much larger than the particle size, particle size reduction should not occur, but efficient mixing of the powders and agglomerate break-up was expected. An additional advantage is the ease of cleaning.

3. Addition of Boric Acid :

Past experiments at Selee have shown that addition of Boric Acid to Alumina slurries lower the final impurity content in the fired foam, especially the sodium level. The boric acid volatilizes at the high firing temperature and apparently promotes the volatilization of other impurities. This is desirable both for increasing strength, particularly at high temperature, and for the enhancement of chemical resistance. The use of Boric Acid had not been tried with this specific composition. In Phase II 0.05% of Boric Acid was added to selected compositions, based

on the fired ceramic weight.

4. De-Airing Compound:

As previously mentioned , air bubbles in the slurry can result in flaws and strength reduction. Past experience at Selee has shown that , among various de-airing agents, Foamaster A (Henkel Corp.) is one of the best. This compound was used in selected experiments at the concentration of 0.2 % by weight, based on fired foam weight.

5. Coating of the Foam Struts :

It was hypothesized that coating the foam struts with a thin layer of a ceramic material might have the effect of enhancing the strength, by eliminating or reducing the surface flaws, and also increasing the chemical resistance to various environments. For example, if the foam were to be used in a reducing atmosphere, an Alumina coating , preferably dense and impervious to gases, could be desirable, to prevent the reduction of Ce^{4+} to Ce^{3+} . An additional advantage would be the presence of surface compressive stresses caused by the presence of the alumina coating, with an expansion coefficient smaller than Ce-ZTA. In oxidizing atmospheres, on the other hand, a Ce-ZTA, CeZ or CeO_2 coating could be advantageous, to reduce surface flaws and also to promote burning of carbon deposits (CeO_2 is known to be an oxidation catalyst).

6. Type of Coating for the Foam Struts :

In Phase II the following types of coating were tested; Alumina and Ce-ZTA. Each with the same composition of the bulk material.

7. PPI # :

The foam mechanical properties depend, among other parameters, upon the cell size, or PPI number. It is known that the strength decreases when the PPI number increases. However, no data was available on thermal shock resistance and strength retention at high temperature as a function of cell size. In the Phase II program, 30 ppi and 65 ppi foams were prepared and tested .

8. Density :

It is known that strength increases with density, everything else being the same. During Phase II , we prepared Ce-ZTA foams of two densities, i.e. 10% and 20% of theoretical, to determine how density affects not only strength, but also thermal shock resistance and percentage of strength retained at 1000°C .

5.2. Results and Discussion of Data obtained from Experimental Design 1

5.2.1. Physical and Chemical Characterization:

Strength data at 25°C, at 1000°C and at 25°C after thermal shock: Table 5 (p. 29) shows the strength data for the Ce-ZTA foam samples at RT, at 1000°C and at RT after the up and down thermal shock (RT-1000°C-RT). It is clear from the data shown in the last row that the Ce-ZTA foam has very good thermal shock resistance and excellent strength retention at high temperature (1000°C).

Tables 6, 7 and 8 (pp. 30, 31 and 32) report the effect of the variables on the modulus of rupture at room temperature, measured on the as-fabricated samples (Table 6), after the thermal shock test (Table 7) and at 1000°C (Table 8). In these tables the relative importance of the variable decreases from top to bottom, on the basis of the MOR difference at the two levels of each variable. It can be observed that the most important variables are the density, the PPI number and the addition of boric acid.

Table 9 (p. 33) shows a summary of the results shown in Tables 6, 7 and 8. In addition, the results of the t-test at 95% confidence level are shown. This test indicates that the MOR difference is always significant for the three variables density, boric acid and PPI #. There is also an indication that the coating might be beneficial and that the de-airing agent is not.

Table 10 (p.34) shows the percentage of room temperature strength retained after thermal shock. Very high retention was found (average = 94%) . This result is much better than that obtained in Phase 1, where only 40% retention was found. At present the reason for the discrepancy is not known. The T-Ratio Test results have shown no significant difference for all variables, when the variable level was changed.

Table 11 (p. 35) shows the percentage of room temperature strength retained at 1000°C. The average of 82% is higher than the 56% measured in Phase 1. The T-Ratio Test, as in the previous case, has shown no significant difference between the two variable levels, for all variables.

Figure 8 shows a strong linear dependence of the bending strength on the foam density. The slope of the line is 83% PSI/%TD for the As-fabricated samples tested at RTI.

The multiple regression analysis revealed that, for the as-fabricated samples, density, boric acid and PPI # are significant. An equation was obtained that allows the calculation of RT MOR from density, PPI# and Boric Acid (BA) data. The equation is :

$$\text{Log}_e (\text{RT MOR}) = 5.065 - 0.13 (-1 \text{ w/o BA; } +1 \text{ with BA}) - 0.00565 (\text{PPI \#}) + 0.113 D \%$$

For EXP. #1, for instance, the RT MOR predicted by this equation is 469.1 PSI, whereas the experimental value is 477 PSI.

The same regression analysis applied to the shocked samples and to the samples tested at 1000°C has shown that: 1) for the shocked samples, density and PPI# are judged to be significant; whereas, Boric Acid may be significant. Also, coating may be significant. 2) for the samples tested at 1000°C, significant variables are density and PPI #.

Ce-ZTA foam made with Daichi CeZ powder: Table 12 shows the RT strength of Ce-ZTA foam samples made with the Daichi CeZ powder. For comparison purpose, the strength of foam made with the Unitec CeZ powder is also reported. It can be seen that the Daichi powder is as good or better than the Unitec powder. However, because it is much less expensive, the Unitec powder was used for the remainder of the program.

XRD Results: The results of the XRD analysis on sintered tiles derived from Experimental Design I are reported in Table 13.

The data in Table 13, p.37, indicates that 1) the Ce-ZTA with 30 vol% CeZ volume fraction contains more m-ZrO₂ vs. the 10 vol% and the t-ZrO₂ is more transformable under the grinding stresses and 2) the Ce-ZTA made with the high shear mixer (M) appears to contain more m-ZrO₂ vs. that made with the attritor (A), both in the as-fired and in the as-ground state. Annealing at 1000° C brings the % m-ZrO₂ close to the original as-fired values .

The conclusion to be drawn from this data is that the attritor gives a more uniform distribution of CeZ powder in the Alumina matrix vs. the high shear mixer . It should be remembered that a critical grain size exists (about 2 um) above which spontaneous transformation of t-CeZ to m-CeZ takes place on cooling from the firing temperature. Since the attritor not only mixes the powders but also reduces the particle size, the probability of exceeding the critical grain size after firing (due to grain growth and/or to clustering) is decreased and a higher fraction of t-ZrO₂ at RT is expected. However, the difference between the two mixing methods appears only marginal . The microstructures (SEM) , shown in the next section, support this conclusion.

Microstructure by SEM: All microstructures were taken with back scattered electrons. No etching was done to reveal the grain boundaries. Figs. 9 and 10 (p. 38) shows two microstructures (300 X) of tiles from Exp. # 1 and Exp. # 3. The two Ce-ZTA ceramics were made with the attritor mill (Fig. 9) and high shear mixer (Fig. 10), respectively. (See Table 1). Both materials contain 10 vol% CeZ. The CeZ grains are light , whereas the Alumina grains are dark. It appears that the grain size of CeZ in material 3M is slightly larger , due to more clustering. (The Alumina grains are much larger than the CeZ grains in both materials). This seems to indicate that the attritor did a better job in dispersing the CeZ powder. At higher magnification (1000X) , Figs. 11 and 12 (p.39) show that most of the CeZ grains are intergranular. No dramatic difference between the two microstructures is evident.

Figs. 13 and 14 (p.40) show the microstructures (300 X) of the Ce-ZTA tiles from Exp. #2 and Exp. #4. These two materials contain 30 vol% CeZ phase. No appreciable difference can be noticed. At higher magnification (1000 X) , Figs. 15 and 16 (p. 41) show that the two microstructures are similar, with very little intragranular CeZ grains. At higher concentration (30 vol %), the CeZ phase could better inhibit the growth of the Alumina grains at 1600°C , which are smaller compared to those observable in the 10 vol% Ce-ZTA. It was concluded that the Silverson high shear mixer could be used instead of the attritor for the preparation of Ce-ZTA slurries.

Table 5. Modulus of Rupture of Samples Made According to Experimental Design 1 Matrix

MODULUS OF RUPTURE OF SAMPLES MADE ACCORDING TO EXPERIMENTS OF TABLE 1

RT MOR (as fabricated)					RT MOR (after shock)				1000°C MOR (as fabricated)					
Exp. #	Max	Min	Avg	SD %	Max	Min	Avg	% SD	Max	Min	Avg	% SD		
1	686	304	477	26	684	251	465	29	533	251	442	18		
2	2435	1203	1693	23	2646	1217	1625	22	1325	734	1300	15		
3	380	219	309	17	469	226	314	23	405	168	244	30		
4	1294	760	1031	17	1294	682	971	16	996	531	641	24		
5	1498	920	1159	18	1737	846	1170	25	1161	668	991	20		
6	554	171	327	44	500	205	332	31	275	151	215	20		
7	1247	848	1034	12	1120	608	846	22	1209	724	909	20		
8	576	210	391	31	509	165	339	29	646	251	413	28		
9	1224	794	1020	13	1215	465	813	29	1078	608	856	18		
10	946	224	525	40	617	195	372	34	365	179	301	26		
11	2033	971	1501	22	2162	1004	1587	25	1950	965	1288	27		
12	693	229	463	31	634	216	368	34	379	241	305	18		
13	443	225	316	22	465	128	322	30	302	146	236	21		
14	1772	397	1043	37	1791	575	1082	34	1132	493	823	25		
15	346	166	260	20	340	102	196	31	300	133	212	24		
16														
Average of averages			770	25				720	28				632	22

Explanation and notes: Exp. # 16 was not performed due to unavailability of CeO₂-ZrO₂ powder
SD% = standard deviation as percent of the average.
15 samples tested for R.T. MOR as fabricated, 15 samples for R.T. MOR after shock and 9 samples for 1000°C MOR.
MOR values are in p.s.i.

Percentage of RT strength retained after 1000°C thermal shock : 94%

Percentage of RT strength retained at 1000°C : 82%

Table 6. Room Temperature Modulus Of Rupture (MOR) Before Thermal Shock
Effect of the Variables on the Bending Strength of Ce-TZP/Al₂O₃ Foam Samples

VARIABLE	LEVEL	MOR (PSI)
PERCENT OF T. D.	12.3	384
	22.5	1212
BORIC ACID	Y	647
	N	877
PPI #	30	865
	65	662
COATING	Y	842
	N	707
COATING TYPE	A	894
	CeZA	773
MIXING METHOD	A	820
	M	713
DE-AIRING AGENT	Y	733
	N	803
VOL% CeZ	10	760
	30	782

Table 7. Room Temperature Modulus Of Rupture (MOR) After Thermal Shock

Effect of the Variables on the Bending Strength of Ce-TZP/ Al_2O_3 Foam Samples

VARIABLE	LEVEL	MOR (PSI)
PERCENT OF T.D.	12.1	339
	22.1	1156
PPI #	30	830
	65	595
BORIC ACID	Y	612
	N	814
COATING	Y	818
	N	634
COATING TYPE	A	867
	CeZA	754
MIXING METHOD	A	773
	M	660
DE-AIRING AGENT	Y	677
	N	758
VOL % CeZ	10	714
	30	727

Table 8. Effect of the Variables on the Bending Strength of Ce-TZP/ Al_2O_3 Foam Samples ,
(MOR) AT 1000°C

VARIABLE	LEVEL	MOR (PSI)
PERCENT OF T.D.	12.1	296
	22.1	973
PPI #	30	715
	65	494
DE-AIRING AGENT	Y	441
	N	644
COATING TYPE	A	748
	CeZA	593
COATING	Y	682
	N	550
BORIC ACID	Y	543
	N	672
MIXING METHOD	A	646
	M	573
VOL % CeZ	10	647
	30	571

Table 9. Effect of the Variables on the Bending Strength of Ce-TZP/Al₂O₃ Foam Samples

ROOM TEMPERATURE MODULUS OF RUPTURE (MOR) BEFORE THERMAL SHOCK

	Vol% CeZ	Mixing Method	Boric Acid	De-airing Compound	Coating	Coating Type	PPI #	% of T.D.
Difference of avg. MOR's	22	107	230	70	135	121	203	828
t-Test result	N	N	S	N	N	N	S	S
Higher MOR	30	A	N	N	N	A	30	20
Normalized MOR diff.	3	13	28	9	16	15	25	100
Rank	8	6	2	7	4	5	3	1

ROOM TEMPERATURE MODULUS OF RUPTURE (MOR) AFTER THERMAL SHOCK

	Vol % CeZ	Mixing Method	Boric Acid	De-airing Compound	Coatin g	Coatin g Type	PPI #	% of T.D.
Difference of avg. MOR's	13	113	202	81	184	113	234	817
t-Test result	N	N	S	N	N	N	S	S
Higher MOR	30	A	N	N	Y	A	30	20
Normalized MOR diff.	2	14	25	10	23	14	29	100
Rank	8	6	3	7	4	5	2	1

1000 ° C MODULUS OF RUPTURE (MOR)

	Vol% CeZ	Mixing Method	Boric Acid	De-airing Compound	Coatin g	Coatin g Type	PPI #	% of T.D.
Difference of avg. MOR's	76	73	19	204	132	155	220	677
t-Test result	N	N	S	S	S	N	S	S
Higher MOR	10	A	N	N	Y	A	30	20
Normalized MOR diff.	12	11	19	30	20	23	32	100
Rank	8	7	6	3	5	4	2	1

Note: The row entitled "Higher MOR" shows which variable level gave a higher average MOR. The t-Test was performed at a 95 % confidence level. N = Not significant; S = Significant . Note the predominant effect of the foam density over the other variables.

**Table 10. Effect of the Variables on the Thermal Shock Resistance of Ce-TZP/Al₂O₃ Foam Samples:
PERCENT STRENGTH RETAINED AFTER THERMAL SHOCK**

Variable	Level	RT MOR Before shock	RT MOR After shock	% RS	t-Test Result
Vol% CeZ	10	760	714	94	N
	30	782	727	93	
Mix. Method	A	820	773	94	N
	M	713	660	93	
Boric Acid	N	877	814	93	N
	Y	647	612	95	
De-airing	N	803	758	94	N
	Y	733	677	92	
Coating	N	707	634	90	N
	Y	842	818	97	
Coat. Type	A	894	867	97	N
	CeZA	773	754	98	
PPI #	30	865	830	96	N
	65	662	595	90	
% of T.D.	10	384	339	88	N
	20	1212	1156	95	

Note: The t-Test showed insignificant difference at the 95% confidence level in all cases.

N = Not significant ; S = Significant. % RS = Percent retained strength after thermal shock.

Table 11. Effect of the Variables on the Percentage of Room Temp. Strength Retained at 1000°C by Ce-TZP/Al₂O₃ Foam Samples

PERCENT OF STRENGTH RETAINED AT 1000°C

Variable	Level	RT MOR	1000° C MOR	% RS	t-Test Result
Vol% CeZ	10	760	647	85	N
	30	782	571	73	
Mixing Method	A	820	646	79	N
	M	713	573	80	
Boric Acid	N	877	672	77	N
	Y	647	543	84	
De-Airing	N	803	644	80	N
	Y	733	441	60	
Coating	N	707	550	78	N
	Y	842	682	81	
Coat. Type	A	894	748	84	N
	CeZA	773	593	77	
PPI #	30	865	715	83	N
	65	662	494	75	
% of T.D.	10	384	296	77	N
	20	1212	973	80	

Note: The t-Test showed insignificant difference at the 95% confidence level in all cases.
 N = Not significant ; S = Significant. % RS = Percentage of strength retained at 1000°C.

RT MOR VS. DENSITY (AS FABRICATED)

Figure 8 Strength/density relationship for as fabricated Ce-ZTA foam samples

Table 12. Effect of Powder Source on Strength of Foams

Powder	Percent of T.D.	10 vol% CeZ	30 vol% CeZ
UNITEC	23.1	1267	
UNITEC	23.8		1368
DAICHI	21.1	1140	
DAICHI	22.3		1656

Note: MOR in PSI. TD = Theoretical Density. Strength numbers are averages of 15 samples.

Table 13. Effect of Mixing Method on the Transformation Toughening Contribution

Exp. #	Vol% CeZ	A or M	% m-ZrO ₂ as fired	% m-ZrO ₂ ground	% m-ZrO ₂ annealed
1	10	A	10	36	14
2	30	A	17	56	18
3	10	M	14	42	19
4	30	M	24	63	23

Note: Exp. # is the same described in Table 1. A or M refers to the mixing method, Attritor or Mixer.

Figure 9. Microstructure (SEM) of polished, unetched sample from Exp. #1 in Table 1. Attritor used, 10 vol% CeZ₂, backscattered electrons.

Figure 10. Microstructure (SEM) of polished, unetched sample from Exp. #3 in Table 1. High Shear Mixer used, 10 vol% CeZ₂, backscattered electrons.

Figure 11. Same sample shown in Fig.9, higher magnification (1010 X).

Figure 12. Same sample shown in Fig. 10, higher magnification (1000 X)

Figure 13. Microstructure (SEM) of polished, unetched sample from Exp. #2 in Table 1. Attritor used, 30 vol% CeZ₂, backscattered electrons.

Figure 14. Microstructure (SEM) of polished, unetched sample from Exp. #4 in Table 1. High Shear mixer used, 30 vol% CeZ₂, backscattered electrons.

Figure 15. Same sample shown in Fig. 13, higher magnification.

Figure 16. Same sample shown in Fig. 14, higher magnification.

5.2.1.1. Thermal Cycling Tests at Penn State using Experimental Design 1 Samples:

Alumina was utilized in this design as a standard for comparison. Although 41 to 61% of the strength (MOR) was retained after the cycling procedure for the ceria stabilized compositions, more testing was desired after these initial results were obtained. This was due to the fact that other testing, such as thermal cycling tests performed in-house and corrosion tests, showed much higher percentages for retained strength when compared to Alumina. For instance, a test performed in Phase I of this project involved thermally shocking samples of similar composition for 1500 hours cycling up to 1400°C for a total of 500 cycles using a gas burner rig. The Ce-TZP/ Al_2O_3 foams used showed little degradation after this severe shock test, while Alumina generally only lasted 100 cycles before extensive cracking and warping were detected. Because of these early results, the percentages of strength retained after the thermal cycling done at Penn State were expected to be much higher. And because the IR heaters used by Penn State were thought to have heated the sample irregularly, it was decided that samples from Experimental Design 2 would also be tested at Penn State to see if similar results were obtained. As well, an in-house thermal cycling apparatus was set up to obtain comparative data. The cycling procedure for the In-house cycling was changed to reflect more closely the actual conditions that would be encountered during operation. Table 14 and Fig. 17 demonstrate these results.

The normalized elastic modulus was obtained using dynamic resonance testing during the cycling process. It was expected that the CeZTA composites would have a lower initial elastic modulus than alumina due to microcracks that are thought to be inherent to the material. (Table 15) These would help to explain the high strengths previously obtained from the CeZTA material. The experimental results were found to corroborate this prediction very well. In fact the initial values for the elastic modulus of the 40CeZTA and 15CeZTA composites was 9.78 GPa and 11.78 GPa, respectively, while alumina was reported to have an initial elastic modulus of 13.21 GPa. This was despite the fact that the Ceria compounds have an initial strength which is much greater than alumina. Figure 18 shows the normalized elastic modulus for both the ceria compounds and the alumina as it relates to the number of thermal cycles.

Table 14. Retained Strength After Thermal Cycling to 1000°C: Experimental Design 1

Sample	As Received (psi)	After 10 Cycles to 650°C (psi)	% Strength Retained
40UC-CeZTA	702	311	44.3
40U-CeZTA	1109	457	41.2
15U-CeZTA	874	532	60.8
15D-CeZTA	843	513	60.9
Alumina	696	481	69.1

Note: Only three samples of each composition were cycled. 6 samples were used for the as-received strength tests. All samples had relative densities between 18 and 20 %.

Thermal Cycling Effects on Strength: Experimental Design 1

Figure 17. Effect of Thermal Cycling on Strength: Experimental Design 1

Table 15. Dynamic Young's Modulus and Strength Comparisons for Alumina and Ce-ZTA Compositions

Sample Type	Dynamic Young's Modulus (GPa)		Strength (MPa)	
	As-received	After 10 cycles	As-received	After 10 cycles
40CeZTA	9.78	4.32	7.65	0.98
15CeZTA	11.78	7.15	6.03	1.65
Alumina	13.21	10.76	4.80	2.73

Note: These results were reported by Penn State. They were derived from their investigation of the compounds sent for thermal cycling .

Figure 18. Change in Elastic Modulus After Thermal Cycling: Experimental Design 1

5.2.1.2. IGCC and PFBC Simulated Conditions Test Results:

Table 16 describes the results obtained from the samples exposed at RTI. Unfortunately, due to corrosion of the stainless steel apparatus, Hydrogen Chloride gas was unavailable, although it is specified as one of the components of the exposure testing. The samples were sent back and tested using a ring-on-ring, bi-axial strength test apparatus. A description of this procedure can be found in Appendix B. Approximately 15 samples of each were tested. The samples were analyzed to discern the relationship between the %-m Zirconia and the strength of the sample. Indeed, the stronger the sample, the less monoclinic was present in the sample type. Because of the coating applied, the 40%Unitec samples with the Alumina coating were not X-rayed.

The results of the T-Ratio test utilized to analyze the data indicate that there was not a significant decrease in any of the foams except for the 40% CeZ with an alumina coating (40UC) when exposed to the PFBC conditions. Dropping from a superior strength of 1873psi to 1193psi. However, this same composition did not show any significant decrease in strength under IGCC conditions. In fact, there was evidence that both the 15% CeZ composites (15U and 15D) had a significant increase in strength upon exposure to PFBC conditions. It was demonstrated that the CeZTA compositions have excellent resistance to IGCC and PFBC simulated conditions, with the 40%CeZTA composition with an applied Alumina coating having the highest strength after exposure, followed by the 15%CeZTA made with the Daichi powder. It is unfortunate that the Daichi powder is the more expensive of the two CeZ powders; however, the Daichi sample did not significantly outperform the Unitec sample during the thermal cycling tests.

Table 16. Strength and Transformation Toughening Contribution on Samples Exposed to Simulated IGCC and PFBC Conditions.

(Experimental Design 1)

Exposure Conditions	STRENGTH MOR (psi)	Significant Difference	%Theoretical Density Average	%m-Zirconia /Annealed
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40%CeZTA-Unitec w/Alumina Coating

Unexposed	1873		23	--
PFBC	1193	Yes-Decrease	23	--
IGCC	1890	No	23	--

40%CeZTA-Unitec

Unexposed	974		17	26.4
PFBC	907	No	17	34.1
IGCC	857	No	17	22.2

15%CeZTA-Unitec

Unexposed	512		16	61.3
PFBC	731	Yes-Increase	16	54.3
IGCC	512	No	16	53.9

15%CeZTA-Daichi

Unexposed	823		18	42.6
PFBC	1084	Yes-Increase	19	36.4
IGCC	722	No	19	34.3

Explanatory Notes:

1. Significant Difference: As determined from T-Ratio test at 95% confidence level Compares unexposed sample to exposed sample. Relates whether difference was an increase or a decrease.
2. % m/Ann. means percent m-ZrO₂ in the powder (325/400 mesh cut) obtained from ground discs, after annealing at 1000° C /1 hr.

6. Experimental Design 2 Matrix

6.1. Strategy for Experimental Design 2

The original plan for phase II included two experimental designs. The second was to be based directly upon the results of the first. However, other research at Selee suggested that the same toughening mechanism could be created using spinel as a variable in the composition. Current literature reported that the addition of hard high modulus particles would be conducive towards creating a ceramic with high strength properties at high temperatures. Presently ZrO_2 -toughened ceramics are considered to be low temperature ceramics due to the stress-induced phase transformation which decreases near the equilibrium transformation temperature. Some strengthening at room temperature by precipitate hardening has been reported. The addition of spinel has been shown to be effective if the zirconia particles remain in the tetragonal phase and if the spinel particles are large enough so that fracture would occur at the application temperature. The most promising samples reported involved the preparation of samples by attriting reactive stoichiometric spinel with an appropriate amount of Al_2O_3 . This led to an investigation of similar compositions of CeZTA being prepared with the added variable of spinel. Because the thermal expansion coefficient of magnesia alumina spinel is lower than that of alumina, it seemed likely that a better resistance to thermal shock and thermal cycling would result. After extensive investigation, two compositions of Ce-ZTS, (with spinel), were prepared to be included in the second experimental design matrix (Table 2).

As with the samples that were derived from the first experimental design matrix, 30 samples of each composition were shipped to be tested at the Research Triangle Institute under IGCC and PFBC conditions. Samples were also sent to Penn State for thermal cycling tests. In-house thermal cycling was performed on these new compositions and their characteristics were investigated.

6.2. Results and Discussion of Experimental Design 2

6.2.1. Physical and Chemical Characterization:

Effects of the Variable High Speed Mixer:

The Ce-ZTA compositions that were prepared according to the Experimental Design 2 failed to exhibit the same initial and retention of strengths as those prepared in Experimental Design 1. The standard deviation within the CeZTA batches was also much higher than the deviations found in Experimental Design 1. Because of the deviation in strengths found between batches made during Experimental Design 2, it was thought that an unspecified variable was creating too small of an operating window for consistent production. For example, one batch of 40CeZTA prepared from experimental Design 2 had an average strength of 552 psi, while another batch only had an average of 317 psi. These strengths, while inconsistent, were also considerably lower in strength than similar compositions formed in Experimental Design 1.

It was determined that the amount of time a slurry is mixed and the difference encountered from person to person when operating the variable high speed mixer has a serious effect. Early on in this program, variability of this type was not encountered as often, most likely due to the fact that small batches were being prepared utilizing the one-speed high shear mixer or the attritor, both of which, independent of the operator, will produce consistent batches of slurry. When larger batches were produced, the procedure was changed and the variable high-speed

mixer was used. In most cases, for other slurry preparation procedures, the high-speed mixer is a suitable choice. It is largely up to the operators discretion and experience to determine when a slurry is well-mixed when operating this particular mixer due to the fact that there are no precise speed controls available. Due to microstructure analysis of the samples, which revealed large agglomerates within the composites, it was determined that the variable speed mixer was unable to produce the high shear necessary to properly mix the powders.

A major detriment in having these agglomerates within the matrix is that they have different densification kinetics than the surrounding substance, creating voids. As well, these agglomerates tend to produce larger grain sizes. Figs. 20 and 21 show an example of the large agglomerate of CeZ powder found in a sample of 40CeZTA in which densification differences are apparent. Fig 22 presents us with an example of a extremely large spinel agglomerate. Samples with the same compositions were remade without changing the dispersant but using instead the attritor to thoroughly mix the slurry. The strengths of these materials were considerably greater than those made using the variable high-speed mixer. For instance, the MOR of 40CeZTA was increased from 552 psi (std. deviation 200) to 953 psi (std. deviation 200). The microstructure analysis of these attrited samples revealed none of the large agglomerates, see Figures 23, 24 and 25.

Figure 19. Microstructure (SEM of polished, unetched sample from Experimental Design 2. Variable speed mixer used, 40%CeZTA 60X.

Figure 20. Microstructure (SEM of polished, unetched sample from Experimental Design 2. Variable speed mixer used, agglomerates present. 40%CeZTS.

Figure 21. Microstructure (SEM, polished, no etching), 40% CeZTS. Mixed using variable high-speed mixer. Exhibits large spinel agglomerate, almost 100 microns wide. 70X

Figure 22. Microstructure (SEM polished, no etching) Mixed using Attrition Mill. No evidence of Large Agglomerates. 15%CeZTS, Significant increase in strength . 60X

Figure 23. Microstructure (SEM) 40%CeZTA, mixed with Attrition Mill, 660X. Exhibits two-phases, light areas are 80% ZrO₂ and 20% Ce₂O₃. Darker areas are Alumina phase.

Figure 24. Same sample as above. 60X. MOR strength was 952 psi.

Figure 25. 40CeZTS 660X. Exhibits the following three phases: Alumina (grey areas), Ceria-Zirconia (light areas) and Magnesia Oxide Alumina (dark areas). Mixed using Attrition mill.

XRD Results for Experimental Design 2:

These samples were annealed so that any mechanical stresses caused by grinding were corrected. Previously in this study it was found that when powder samples were needed for XRD, neglecting to anneal samples before x-ray diffraction had a significant effect on the amounts of monoclinic and tetragonal zirconia present. This finding was critical in the attempt to properly characterize and compare the samples.

Table 17 summarizes the results obtained for Experimental Design 2 samples. Those compositions with spinel were found to have a much lower percentage of tetragonal zirconia. Subsequently, strengths were generally lower because transformation toughening did not occur to as great of an extent as in the CeZTA compositions.

Table 17. Transformation Toughening Contribution and Strength at RT: Experimental Design 2

Composition	percent t-ZrO ₂	Strength at RT (psi)
15CeZTA	42%	651
40CeZTA	63%	553
15CeZTS	5%	403
40CeZTS	9%	160
15CeZTS batch*	16%	732

*This batch was made using the attritor. In contrast to the other spinel batches, all of the spinel powder that was added was attrited in order to break down the particle sizes. The spinel was attrited for 6 hours before being added to an alumina matrix with 15% CeZ powder. This slurry has a very short shelf life and must be used immediately. However, it did provide for the strongest spinel composition.

Thermal Expansion Coefficient:

The average thermal coefficient of expansion of 15CeZTA and 40 CeZTA between 25-1000 C was found to be 6.42×10^{-6} and $7.51 \times 10^{-6} \text{ K}^{-1}$ respectively. 15CeZTS displayed a thermal expansion of $5.73 \times 10^{-6} \text{ K}^{-1}$ with only a small phase change present at 900°C. Between 0°C and 675°C, 40CeZTS had a thermal expansion of $2.98 \times 10^{-6} \text{ K}^{-1}$, with a phase change occurring between 675 and 834°C with an expansion of $12.3 \times 10^{-6} \text{ K}^{-1}$. It would seem that the addition of spinel, did in fact, result in a lower thermal expansion in the 15CeZTS composition, although there is evidence of a slight phase change.

Thermal Shock/Hot MOR Tests:

The spinel compositions had considerably high Thermal Shock/Hot MOR strengths. 15%CeZTS compositions retained an average of 93% of their initial strength after being placed in a 1000C furnace and broken after one minute. This test is described in Appendix B and has become the Selee standard for determining Thermal Shock and Hot MOR data. The 40%CeZTS samples retained 88% of their initial strength. Experimental Design 1 demonstrated that the CeZTA compositions had 94% strength retention after shock and 80 % of RT strength 1000°C.

6.2.1.1. Thermal Cycling Using Gas Burner Apparatus at Selee

The results of thermal cycling at Selee are reported in Figure 26. The data was analyzed using both a student T-test and by calculating the retained strengths. These samples were cycled from 750°C to 950°C for fifteen cycles. Alumina was tested for comparison purposes. In contrast to the first set of samples that were cycled at Penn State, in which Alumina had a greater strength retention after cycling than the CeZTA compounds, in these cycling conditions, the CeZTA compounds, as well as, the 15%CeZTS exhibited a higher retention than Alumina. In fact, the samples that were tested were found later to be of considerably lower strength than compositions made previous to Design 2. It was discovered that using the variable high-speed mixer, as opposed to the Attrition Mill or the Silverson High Shear mixer, failed to properly disperse the powders. For instance, because of the mixing method used, and thus the agglomerates present in the matrix, the 15%CeZTA samples that were cycled only had 76% of the average strength found for similar compositions in Experimental Design 1. The 40%CeZTA samples had only 94% of Experimental Design 1 strengths. It is suggested that the retained strengths might have been even higher had the initial structures been free of agglomerates.

When the data was analyzed using a student T-Test to determine the statistical significance of the data, keeping in mind the small samples sets, it was determined at the 95% confidence level that the differences found for 40%CeZTA, 15%CeZTA and 15%CeZTS were not significant differences, while the differences found for the Alumina, 100%spinel, and 40%CeZTS samples were significant. It was surprising to note that the anticipated effect of spinel imparting a better resistance to thermal shock failed considerably in that the 100% spinel composition retained only 33% of its initial strength.

Some of the strengths were corrected for density variation among the samples. Since it is difficult to compare samples of differing density, some of the CeZTA strengths in this set were normalized using the relationship between density and strength found for the compositions in Experimental Design 1 (Figure 8, p.36).

From this test, it was concluded that the CeZTA compositions and the 15%CeZTS samples clearly have a much better thermal shock resistance than the 40%CeZTS and pure Alumina.

**Effect of In-House Thermal Cycling on Strength (MOR):
Experimental Design 2**

Figure 26. Effect on Strengths (MOR) After Thermally Cycling Samples from 750°C to 950°C for 15 Cycles: In-House (Experimental Design 2)

6.2.1.2. Thermal Cycling at Pennsylvania State University

While the change in the Dynamic Young's Modulus exhibited similar results to those found from Experimental Design 1 samples, the retention of strength tested using a three-point bending tests yielded rather poor results. Table 18 and Figures 27 and 28 disclose the information found from these tests. The results were in stark contrast to those found here at Selee after thermally cycling in conditions similar to actual operating conditions. For example, 40%CeZTA, which had an MOR strength retention of 94% (not a statistically significant difference) when exposed to In-House thermal cycling conditions only had a 49% retained strength when tested at Penn State. Disregarding the low retention of strengths, 40%CeZTA did outperform the other compositions during Design 2 testing.

The correlation between the elastic modulus and the modulus of rupture is not precise. For example, the percent of elastic modulus retained for 15%CeZTS was nearly the same as the MOR (48% and 47 %, respectively). Yet, the Alumina and CeZTA compositions had much lower percentages for the MOR tests than for the elastic modulus tests.

It is important to note that the strengths of these samples, like those cycled In-house, had large agglomerates present in their matrix because of the mixing method chosen. This led to decreased initial strengths for all of the samples and possibly made them more susceptible to thermal shock. Yet, those samples cycled In-house, still showed no significant decrease in strength. It is thought that perhaps the difference in cycling conditions could have a serious effect. The method of heating the sample at Penn State could also have a deleterious effect due to rapid heating of the surface of the sample because of its close proximity to the IR heaters. The Penn State samples were cycled from 25-1000C, while the condition for the In-house testing more closely simulated actual IGCC and PFBC operating conditions, cycling from 750-950C. Even this does not sufficiently explain why Alumina would outperform the experimental compositions in these tests.

Table 18. Percent Retained Strength, MOR and Dynamic Young's Modulus, After Thermal Cycling to 1000°C at Penn State: Experimental Designs 1 and 2

Composition	% Retained of Initial Dynamic Young's Modulus		% Retained of Initial Modulus of Rupture	
	Design 1	Design 2	Design 1	Design 2
Alumina	96	-	69	-
40%CeZTA w/C	77	-	44	-
40%CeZTA	76	75	41	49
15%CeZTA-D	95	-	61	-
15%CeZTA	86	67	61	41
40%CeZTS	-	12	-	32
15%CeZTS	-	48	-	47

Notes: 40%CeZTA w/C designates the samples with Alumina Coating. 15%CeZTA-D is the samples made with Daichi powder as opposed to Unitec powder.

Change in Dynamic Young's Modulus with Thermal Cycling

Figure 27. Effect of Thermal Cycling (RT to 1000°C) on Dynamic Young's Modulus:
Experimental Design 2

Figure 28. Percentage of Initial Strength Retained After Thermal Cycling (RT to 1000°C):
Experimental Design 2

6.2.1.3. Results of Corrosive Conditions Exposure Testing: Experimental Design 2

Eleven samples of each composition were tested in the IGCC conditions, and then eleven more were tested in PFBC conditions. No HCl was present, due to corrosion of the apparatus, but the other conditions were the same as specified in Table 3, p.19. In the initial attempt to expose samples to the PFBC conditions, when the samples were being removed from the reactor, it was discovered that the extremely high temperature and the strongly oxidizing atmosphere had destroyed the grafoil seal. This allowed the gas to bypass the disks, and only the first few disks in the chamber had any discoloration, suggesting only the first few had any gas exposure. Hence, the disks were exposed again, this time for only a 76 hour period due to a power outage. Rather than expose the disks to further thermal cycling, the test was terminated. All of the disks exposed to the PFBC exposure test were discolored, ranging from a light gray to a greenish black color.

Although the initial strengths of these samples were considerably lower than strengths found in Experimental Design 1, due to the mixing method, they still performed exceptionally well. Table 19 and Figure 29 display the results found. The 15CeZTA, 40CeZTA and 15CeZTS compositions showed no statistically significant difference between their initial MOR strength and their strength after exposure. Statistical analysis of the exposure testing only suggested a significant difference was only found for the 40CeZTS samples.

The low strength of the 15CeZTA sample in comparison to the 40CeZTA sample can be disregarded since it was demonstrated in Experimental Design 1 that there was no statistically significant difference in strength when the volume fraction of CeZ was lowered from 30% to 10%. The difference in strength and retention between the 40%CeZTS and the 15%CeZTS is significant. And while we were able to prepare a 15%CeZTA composition with a strength of 734 psi, the benefit of utilizing the 15%CeZTS composition over the 15%CeZTA has yet to be proven. While it was thought that it would have a better thermal shock resistance because of its lower thermal expansion coefficient, it failed to outperform the CeZTA compositions during the cycling tests.

Table 19. Strength of Samples Exposed to Simulated IGCC and PFBC Conditions.

(Experimental Design 2)

Exposure Condition	STRENGTH (psi)	T-Ratio Result	Significant Difference- 95% Confidence Level	%TD Average
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15CeZTA

Unexposed	664			20
PFBC	541	1.57	No	21
IGCC	603	0.78	No	20

40CeZTA

Unexposed	320			13
PFBC	302	0.61	No	13
IGCC	353	0.73	No	14

15CeZTS

Unexposed	290			18
PFBC	285	0.22	No	17
IGCC	294	0.18	No	16

40CeZTS

Unexposed	124			13
PFBC	97	2.26	Yes	13
IGCC	97	2.26	Yes	11

Notes:

1. Significant Difference: As determined from T-Ratio test at 95% confidence level. Compares unexposed sample to exposed sample. Relates whether difference was significant.
2. Each set had eleven test points. Low initial strengths were caused by poor mixing method.

Figure 29. Effect of Exposure Condition on Percentage of Retained Strengths

7. Conclusions

From the work done in Phase II of this program, the following conclusions were drawn:

1. The Ce-ZTA foams exhibited superior room temperature strength (1200 psi for 20%TD foams), excellent thermal shock resistance (94% strength retention after shock) and very good strength retention at 1000°C (80 % of RT strength).
2. The 15%CeZTS foams performed much better in all testing than the 40%CeZTS composition, but failed to outperform either CeZTA composition.
3. Of the eight variables evaluated in Experiment Design 1, the density and the cell size (PPI #) had the strongest influence on the foam strength. The MOR increases with density (in the range 10% to 25% of theoretical) and with cell size (from 65 PPI to 30 PPI).
4. It was found that reducing the volume fraction of CeO₂-ZrO₂ in the Ce-ZTA from 30% to 10% did not result in significantly lower strengths. The RT MOR, the thermal shock resistance and the retained strength at 1000°C were virtually unaffected. This is an important result, since the 10 vol% CeZ material is 2-3 times less expensive versus the 30 vol% material.
5. The variable high speed mixer, which is routinely used in the pilot plant, was unable to properly mix the slurry compositions. The Silverson high shear mixer was able to blend uniformly the CeZ powder with the Alumina slurry, although, it appears that the attritor can provide a slightly more uniform distribution of the t-ZrO₂ grains in the Al₂O₃ matrix.
6. There were some slight strength differences encountered in the foams made with the different CeZ powders (Unitec versus Daichi); however, after the qualifying testing was performed the Unitec powder was used because it is much less expensive than the Daichi powder.
7. Literature had suggested that spinel might be included in the CeZTA compositions to act as a toughening agent and it was hoped that it would help to impart a lower thermal expansion coefficient. A 15%CeZTS composition was fabricated that had considerably high strength (RT MOR, 734 psi) and a thermal expansion coefficient of $5.73 \times 10^{-6} \text{ K}^{-1}$ between 25 and 1000°C. It did, indeed, perform almost as well as the 15%CeZTA composition in many of the tests, yet it still failed to have a significantly better resistance to thermal shock.
8. The foams that were sent to RTI to be exposed to simulated coal gasification and combustion conditions exhibited excellent strength retention.
9. The thermal cycling tests that were performed In-House yielded encouraging results. Although the strengths of the CeZTA composites and the 15%CeZTS compositions were not initially as high as they could have been, they were clearly superior to Alumina. The thermal cycling tests which were performed at Penn State showed poor thermal shock resistance. The reason for this is not known.
10. The foam compositions which were investigated in this program have a reasonable cost when compared to other materials which are being considered for flue gas filtration devices.
11. Because of the high strengths and corrosion resistance investigated in this program and their relatively low cost, CeZTA foams are a promising candidate for particulate filtration in coal gasification and combustion processes. In addition, these unique properties would allow the foams to be suitable for many other applications in the environmental, energy and chemical fields.

Appendix A: Powders

Powders Used

The Unitec CeZ powder is made by electrofusion, solidification and milling. The impurities are: $\text{SiO}_2 = 0.13 \%$; $\text{Al}_2\text{O}_3 = 0.05\%$; $\text{Fe}_2\text{O}_3 = 0.10 \%$; $\text{TiO}_2 = 0.20 \%$; $\text{MgO} = 0.05\%$; $\text{BaO} = 0.04 \%$. The particle size distribution (Sedigraph) has shown $d_{90} = 1.34 \text{ }\mu\text{m}$; $d_{50} = 0.56 \text{ }\mu\text{m}$; $d_{10} = 0.30 \text{ }\mu\text{m}$. The powder is light yellow in color and free flowing. Due to the method of preparation, the individual particles are solid, without internal nanoporosity. This is an advantage for the slurry preparation, since it fosters the ability to obtain high solids loading for a certain viscosity. Another advantage is the relatively low price, i.e. 17 \$/lb.

The CeZ powder made by Daichi KKK, is chemically derived and therefore purer, but more expensive (about 34 \$/lb). It contains 12 mol% CeO_2 and the impurities, as reported by the manufacturer, are only CaO (0.005 %) and Na_2O (0.005%). The surface area is $13.4 \text{ m}^2/\text{g}$ and the average particle size is $0.24 \text{ }\mu\text{m}$. The powder color is very light yellow.

The particle size distribution (Sedigraph) of the Baikowski spinel shows $d_{90} = 3.22 \text{ }\mu\text{m}$; $d_{50} = 0.30 \text{ }\mu\text{m}$; $d_{20} = 0.11 \text{ }\mu\text{m}$. The chemical analysis displayed 9ppm Na; 24ppm K; 6ppm Fe; 17ppm Si; and 2ppm Ca. The surface area was found to be $28.6 \text{ m}^2/\text{g}$. The particle size distribution found using an in-house sedigraph showed the AEE spinel to have the following characteristics; $d_{90} = 32.67 \text{ }\mu\text{m}$; $d_{50} = 9.97 \text{ }\mu\text{m}$; and $d_{10} = 1.46 \text{ }\mu\text{m}$. After some experimentation, it was noted that to obtain a high solids loading, with a broad spectrum of particle sizes, a portion of the spinel that was added to the compositions needed to be attrited down to a particle size distribution of approximately 90% finer than 4.53; 50% finer than 1.46; 10% finer than 0.49, using an attrition mill.

Appendix B: Standard methods of Characterization

a. Density as % of Theoretical Density: This was done by measuring weight and volume and dividing by the theoretical density. The theoretical density is calculated by knowing the volume fraction of CeZ and the m/t ZrO₂ ratio.

b. Microstructure by SEM: This was done by one of two methods, the first method involved mounted and polished pieces of the slip-cast sintered tiles. The second involved vacuum impregnating the sample with epoxy resin, followed by polishing. A film of gold is sputtered onto the surface to prevent the sample from accumulating an electric charge in the scanning electron microscope. Selee's S.E.M. is an Amray model 1810 equipped with an EDAX with a light element window capable of detecting to carbon in atomic weight. Samples were examined for homogeneity of phase distribution, cracks and other flaws, particle packing, evidence of grain growth, impurities at the grain boundaries, and porosity.

c. Percent of m-ZrO₂ (XRD): The percentage of m-ZrO₂ was calculated from the peaks at $2\theta = 28.2^\circ$ (m), 30.2° (t) and 31.6° (m), on the same tiles used for SEM. (In the Ce-ZTA foam (and tiles) the ZrO₂ is present as t-ZrO₂ and/or m-ZrO₂). The XRD patterns were obtained from the as-fired surface, the wet-ground surface and the ground/annealed (1000°C) surface of the tiles utilizing a Siemens diffractometer. The main information sought was to what extent the transformability of the Ce-TZP grains under mechanical stress would depend on the composition (i.e. volume fraction of CeZ) and on the mixing method used (Attritor vs. Shear Mixer).

d. Strength (MOR) at RT and 1000°C: If the fired sizes of the foams were too large for strength testing, the foam squares were cut with a diamond saw into coupons of suitable size. The MOR was measured using a three point loading apparatus as shown in Fig. ****. The load is applied using an Instron universal tester. The Modulus of Rupture is calculated from the load and the geometry of the fixture and the sample bar according to the formula:

$$\text{M.O.R.} = \frac{3(\text{load})(\text{span})}{2(\text{width})(\text{height})^2}$$

Figure 30. Three Point Loading Apparatus Used to Determine Modulus of Rupture

The cross-head speed was 0.1 cm/min during the room temperature (RT) tests. For each one of the 15 experiments of Experimental Design 1 (Table 1, Exp.# 16 could not be performed due to unavailability of CeZ powder) 15 samples as-fabricated were tested at RT, 15 samples at RT after thermal shock, and 10 samples as-fabricated at 1000°C. The average MOR and standard deviation were calculated. For all samples, except for those that were returned to us from RTI,

and those samples used for in-house thermal cycling tests, a three point bend test was used instead of a crushing strength measurement because it was felt that the bend test was more germane to field failures.

The samples that were sent to the Research Triangle Institute for exposure and the disks that were used for in-house thermal cycling tests were tested using a ring-on-ring strength testing apparatus (See Fig. 31) because the samples were small and circular. The equation used to determine the modulus of rupture when utilizing the ring-on-ring apparatus is as follows:

$$\sigma_{\max} = 3P / 4\pi h^2 (2 (1 + \nu) \ln(a/b) + ((1 - \nu)(a^2 - b^2)/R^2))$$

where P is the axial load applied by the load ring

h is the thickness of the sample disk

ν is Poisson's ratio

b is the radius of the load ring

a is the radius of the support ring

R is the radius of the sample disk

A bi-axial (ring-on-ring) strength test was used instead of the traditional 3-point bend test because it was possible that performing the 3-point test on such small parts would be more likely to yield compression data instead of true strength data. The ring-on ring flexural test was performed utilizing an Instron machine. A disk sample was placed on a supporting ring. Pressure was applied normally to the sample by pushing a smaller loading ring slowly onto the sample.

During the course of this project, our methods of determining the hot strength and the thermal shock strength were combined into a single test in which the sample was placed inside a furnace that was kept at 1000°C. The sample is kept in the furnace for one minute and then a three point bend test is performed on the sample while it is still in the 1000°C furnace. The crosshead speed was kept at 0.5cm/min. The MOR was measured on samples having a length of 3 in, with varying widths and heights depending upon the original sample size. Having become a SELEE standard for obtaining thermal shock and hot MOR data, for comparison purposes, it was thought best to utilize this method for the remainder of Phase II. This was the method used on all samples fabricated from Experimental Design 2. Samples from Experimental Design 1 were thermally shocked using the procedure stated in Section E of this Appendix.

Figure 31. Ring-on Ring Apparatus Used For Bi-Axial Strength Testing

e. Thermal Shock Test : The following method was used for the samples of Experimental Design 1. All the subsequent data, from Experimental Design 2, was obtained utilizing the procedure stated in Section D. The coupons were up-shocked by plunging them, while attached to a Nichrome wire, into an electric furnace (crucible type) whose temperature was held constant at 1000°C. After covering the furnace with a lid, the samples were kept inside until the temperature rose again to 1000°C and remained constant for 5 min. Then the lid was removed and the samples were down-shocked by taking them out and holding them in static air until they reached room temperature. After this, the samples were broken at Room Temperature (RT) utilizing the Instron machine.

f. Statistical Evaluation of Data :

A student t-test was performed on the MOR data to determine whether differences in MOR were significant. In addition, a multiple regression analysis was performed to identify the significant or main variables and possible variable interactions in Experimental Design 1, (Table 1). Unless otherwise specified, a confidence level of 95% was used to determine significance in the t-test analysis.

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