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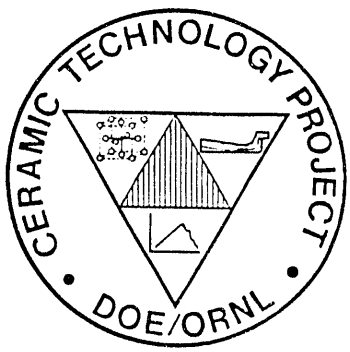
Development Of A Zirconia-Mullite Based Ceramic For Recuperator Applications

J. M. Gonazlez

CERAMIC TECHNOLOGY PROJECT



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DEVELOPMENT OF A ZIRCONIA-MULLITE BASED CERAMIC FOR RECUPERATOR APPLICATIONS

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EXECUTIVE SUMMARY

GTE Products Corporation, under a jointly funded program with the U.S. Department of Energy (DOE), developed a compact ceramic high temperature recuperator that could recover heat from relatively clean exhaust gases at temperatures up to of 2500°F. The DOE program was very successful in that it allowed GTE to improve the technical and economic characteristics of the recuperator and stimulate industrial acceptance of the recuperator as an energy-saving technology.

The success of the DOE Program was measured by the fact that from January 1981 to December 1984, 561 recuperators were installed by GTE on new or retrofitted furnaces. One objective of this contract was to conduct a telephone survey of the industrial plants that use the recuperator to determine their operating experience, present status, and common problems, and thus to complete the historical picture.

The ceramic matrix material is made of cordierite, a magnesium aluminum silicate, in 10-in. cubes, 12-in. cubes, and 12- x 12- x 18-in. units that are rated at 0.6, 1.0, and 1.5 million Btu/h respectively. The exhaust gases from the furnace flow straight through the recuperator, while the air to be heated makes three passes. This arrangement allows air to be heated to 1300°F with exhaust gas temperatures of 2400°F. The three pass arrangement is counterflow with respect to the exhaust flow path. The design helps minimize temperature-induced stresses in the cordierite material, thus improving the reliability of the unit.

The thrust of the marketing effort was in the metal processing industries. This focus appears to be correct in view of the energy consumption and number of furnaces in these industries. The durability of the recuperators is indicated by their survival rate. Among 561 units installed on 165 new or retrofitted furnaces in 89 plants, 405 units (72%) were operating after 4 years. There are 117 units (21%) that are not in use either because of failure, poor business climate, or plant shutdown. The combined energy saving of the present operating units is estimated to be about 0.5×10^{12} Btu/year.

The reliability of the recuperated furnace is high in the lower temperature applications. Most of the recuperators (87%) installed on furnaces operating at 2000°F and below were operational through June 1988, while only 57% were being used on furnaces operating above 2000°F. Regarding recuperator size, the smallest unit seems to be more reliable. Of the three sizes of recuperators installed, 89% of the small 10-in.cubes, 72% of the intermediate 12-in. cubes and only 56% of the large units were operational. Possibly the large units are more severely stressed during operation or flaws may develop during the fabrication process.

The initial problems with hot air burners and combustion controls were solved by GTE

and the burner manufacturers. The current problems are recuperator plugging and corrosive attack by alkali compounds, both of which depend on the specific application. In most cases, plugged recuperators could be cleaned with an air lance during normal shutdown and reused. The alkali compounds appear to form lower temperature eutectics with the cordierite material, and if the furnace operating temperatures exceeded the softening point of the eutectic, failure occurred.

Sources of alkali compounds are fluxes used in aluminum remelt furnaces or pottery kilns, topping compounds used on steel ingots, and effluents from organic materials (trace concentrations) generated over extended periods of operation (16,000 hours). Task 1 of this study (reported in ref. #3) confirmed the effect of temperature on the life cycle of the recuperator. At temperatures above 2150°F life cycles can be reduced to weeks if the concentration of a reactive contaminant is high. Designs must reduce the alkali concentration (process modification), and/or reduce the exhaust inlet temperature below 2100°F. Injection of a sufficient quantity of ambient air into the exhaust gas stream before it enters the recuperator is one method utilized to maximize the life cycle of the ceramic. The reduced exhaust inlet temperature reduces the reaction rate of the contaminant. The recuperator efficiency is reduced only nominally. The decrease in exhaust inlet temperature and the increase in mass flow rate balance each other, resulting in negligible loss in preheat air temperature. The exhaust gas-flow inducement device (eductor) can generally accommodate the increased volume of exhaust gases, usually less than 10%. A combustion system designer must include ceramic matrix replacement costs based upon reduced life cycles into a projects economic feasibility analysis. Since there is no easy solution to alkali attack, applications generating large amounts of alkali should be avoided.

About 48,000 furnaces were identified that were similar to those in the 89 plants where the recuperators were installed. Based on the industrial users experience with this recuperator, the following industries are potential markets: metal heat treating, aluminum foundries, steel mills, steel forging, and structural clay products. Because of contaminated exhaust gas streams, the following applications should be avoided: tunnel kilns in the pottery and related industries, ladle preheaters in the ferrous and nonferrous industries, remelt and kettle furnaces in the secondary nonferrous industries and reheat/forge furnaces processing steel ingots with topping compounds.

This study investigated a series of zirconia-mullite based mixed -oxide ceramic materials. This family of ceramic materials have been used in borosilicate glass tanks successfully, and was shown to offer potential during a previous contract effort, ("Ceramic Heat Recuperators for Industrial Heat Recovery")[1]. A corrosion test furnace was used to determine the potential for a series of compositions. A series of milling trials, compounding and extrusion experiments

were then undertaken. Manufacturing techniques were based upon the desire to fabricate cross flow matrix elements similar to GTE's commercially available cordierite ceramic. Thin wall (plate-fin) extruded sheets were manufactured and sintered to 2642, 2777 and 2912°F. MOR bars were extracted from the material sintered to 2777°F. Phase content, thermal expansion, microstructure, and pore size distribution were evaluated. The process developed is considered suitable for manufacture of crossflow matrix elements, and thin wall tubes. Corrosion resistance was not determined for monolithic shapes of the Z-1000 ceramic, however coating tests did show that the ceramic, when applied as a coating, protected cordierite (MAS-8400) ceramic matrix elements when exposed to alkali and lead @ 2450°F. A recuperator design concept capable of exploiting monolithic Z-1000's potential corrosion resistance is summarized.

DEVELOPMENT OF A ZIRCONIA-MULLITE BASED CERAMIC FOR RECUPERATOR APPLICATIONS*

Jeffrey M. Gonzalez

ABSTRACT

GTE Products Corporation, under a jointly funded program with the U.S. Department of Energy (DOE), developed a compact ceramic high temperature recuperator that could recover heat from relatively clean exhaust gases at temperatures up to 2500°F. The DOE program was very successful in that it allowed GTE to improve the technical and economic characteristics of the recuperator and stimulate industrial acceptance of the recuperator as an energy-saving technology. The success of the DOE Program was measured by the fact that from January 1981 to December 1984, 561 recuperators were installed by GTE on new or retrofitted furnaces. With over 1200 units sold commercially between 1981 and 1990, GTE has documented the effect (long and short term) of corrosive attack (from alkalies and lead). One objective of this contract was to develop Z-1000, a zirconia-mixed oxide ceramic for use in ceramic recuperator applications that are susceptible to corrosion due to this attack. The incorporation of this material into the GTE crossflow recuperator housing would entail development of extrusion technology similar to that currently used by GTE for their cordierite-mixed-oxide ceramic recuperator system. The first and second pass of the ceramic recuperator would utilize the current cordierite-mixed-oxide ceramic. A Z-1000 matrix element would be used in the preheated air side's third pass (the exhaust inlet section). Thermal stresses on the Z-1000 cross flow module could be minimized by selecting appropriate heat transfer surface areas for each pass. A large surface area for the first and second pass (cordierite section) could provide for sufficient heat transfer to achieve 50% effectiveness. A surface area that generates minimal heat transfer in the third pass (Z-1000) section is envisioned. The heat transferred in this section reduces the differential temperature across the matrix, and therefore thermally induced stresses are minimized. Reduced heat transfer in this section means that thermal shock resistance (TSR) of the material in the third pass becomes less critical; however, its corrosion resistance must be sufficient to withstand corrosive attack. This modular design could utilize a field repairable, disposable matrix. This report concerns itself with the development of process technology for fabricating such a matrix, and a series of corrosion tests that established the potential corrosion resistance of the Z-1000 ceramic.

* Research sponsored by the Industrial Energy Efficiency Division, Office of Industrial Technologies, U.S. Department of Energy.

1. INTRODUCTION

GTE Products Corporation began development of ceramic heat exchangers in 1973. This activity resulted in a high-temperature compact cross-flow recuperator made of cordierite which functions well in relatively clean exhaust gases at temperatures up to 2500°F. Part of the development work, which was jointly funded by DOE and GTE under Contract EX-76-C-01-2612 began in October 1976. A final report[1] published by DOE in August 1980 described development and field testing.

In August 1980, the DOE and GTE started a cooperative program titled a Technology Acceleration Program for High Temperature Recuperators (TAPHTR)[2]. The primary goals of the cooperative agreement were to test, install, and collect baseline and operating data for 175 industrial applications of the high-temperature recuperator. The specific tasks of that program were to accurately assess the industrial high-temperature process requirements; to improve the technical and economic characteristics of the recuperator; to stimulate the industrial acceptance of the recuperator for waste heat recovery; and, by saving energy and increasing productivity, to further DOE's Office of Industrial Programs industrial conservation efforts.

During the TAPHTR program, 175 recuperators were installed on 38 furnaces in 30 industrial plants. With the exception of six newly designed furnaces, the furnaces were retrofitted with recuperators. These furnaces were operated at temperatures ranging from 1600°F to 2500°F and air preheat temperatures of 700°F to 1300°F were obtained. Four furnaces were fired by # 2 fuel oil, one by # 4 fuel oil, and the others with natural gas. Preheated air burners were manufactured by Eclipse Inc., Hauck Manufacturing Company, North American Manufacturing Co., and Selas Corporation. The combustion control systems which regulate temperature and fuel:air ratio were modified to accommodate the preheated air from the recuperator. Pneumatic pressure control, pressure balanced mass-flow control and electronic mass-flow control systems were used.

The TAPHTR program was successful in that it provided the following benefits to the host sites:

- Fuel savings of 12% to 61% made the retrofits economically attractive.
- Productivity increases resulted because of higher product throughputs, lower furnace reheat times, and, in the case of batch furnaces, more cycles per shift.
- In some cases, materials savings resulted from decreased scale formation.

The TAPHTR program also revealed system problems, some of which were solved during the course of the program or soon after. These were as follows:

- Inherent leakage around the seals could be tolerated provided fuel-rich conditions did not exist in the furnace.

- The initial hot air burners deposited carbon and had flame instability, but these were later corrected by the burner companies.

- Combustion controls on the cold-air side were not adequate to prevent excess gas conditions in the furnace. This was corrected after the TAPHTR program by development of a simple but novel hot-air side control system.

- In some cases, plugging of the compact recuperator passages necessitated the use of an on-line or periodic air-lance cleaning system.

- Some furnaces produce alkali or lead-based materials that can degrade the magnesium aluminum silicate (cordierite) recuperator at tempertures above 2100°F. Many furnaces, originally categorized as producing clean exhaust, volatilize these materials as a result of the specific process or the furnace design. Degradation of the ceramic can often be eliminated or reduced by careful system design; however, experience has shown that subtle process or system design changes can produce greatly different exhaust gas constituents.

- A recuperator capable of withstanding the attack of common contaminants (alkali compounds) could accelerate the market acceptability of the ceramic heat exchanger, because a more confident estimate of life cycle could be offered for various applications.

The success of the DOE/GTE TAPHTR program is indicated by the fact that between January 1981, when the first DOE installation was started, and December 1984, about 560 recuperators sold by GTE were installed on new furnaces or were retrofitted to furnaces. Since the start of the DOE TAPHTR program, about 1200 recuperators were sold as either new or replacement units. A telephone survey was made of the industrial plants that installed the ceramic recuperator to determine their operating experience, present status, and common problems, and thus to complete the historical perspective of the recuperator. The report[3] details the results of the telephone survey

of the industrial users, provides some comparative analysis of ceramic recuperator applications, and details corrosive attack from alkalies and lead. A series of case studies detail the mechanism of corrosive attack. This report describes a method to screen potential corrosion resistant ceramic materials, and process development activities associated with the compounding, extrusion, and densification of a zirconia-mullite based ceramic.

1.1 The GTE Recuperator System Design

Ceramic recuperators are manufactured in three sizes: a 10 x 10 x 10 in. ceramic core with a recommended capacity of 0.6 million Btu/h, a 12 x 12 x 12 in. core with a capacity of 1.0 million Btu/h and a 12 x 12 x 18 in. core with a recommended capacity of 1.5 million Btu/h The ceramic cores are constructed of cordierite, a magnesium aluminum silicate (MAS), which was selected because of ease of fabrication, relatively low thermal expansion, good thermal shock resistance, and certain corrosion-resistant characteristics. The recuperator is manufactured by bonding extruded MAS ribbed-sheets with a cordierite ceramic bonding material. The sheets and ribs are arranged to form a cross-flow heat exchanger (Figure 1). The ceramic

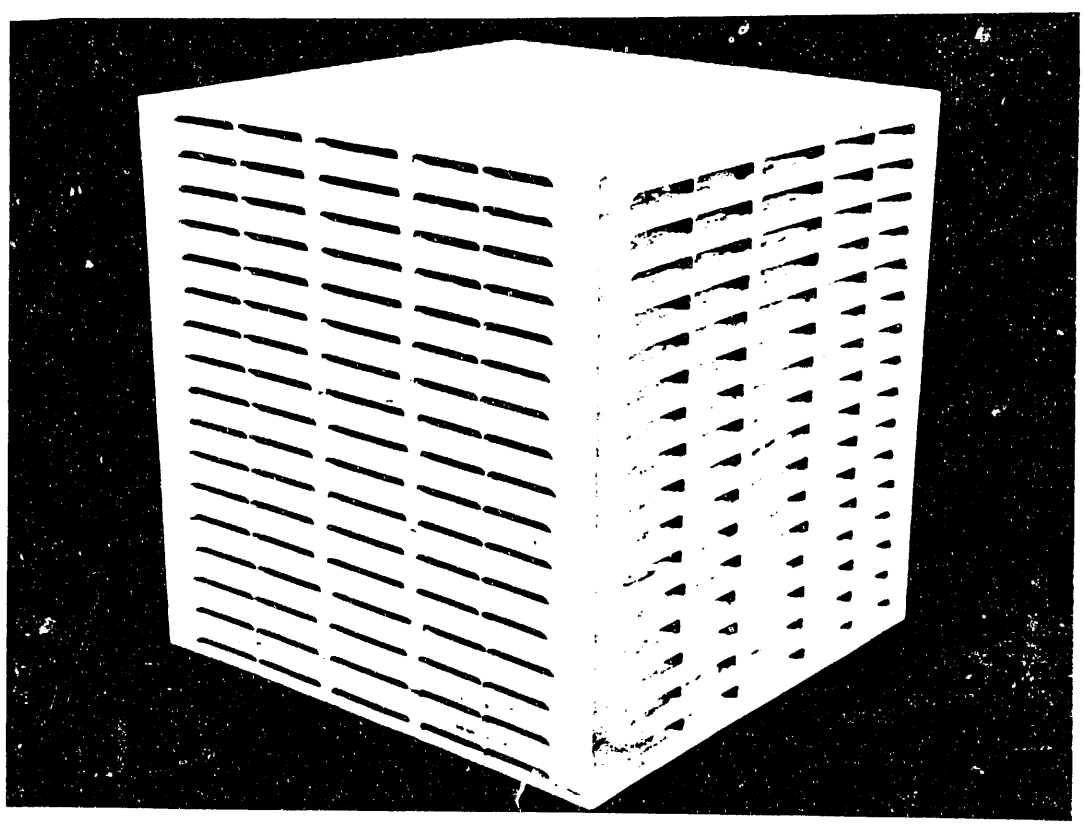


Figure 1
GTE Ceramic Recuperator Matrix

core unit and resilient refractory seal are contained in a metallic housing. The unit is under a slight compression from a spring assembly. A key feature of current recuperators is that the preheat air makes three passes in the recuperator while the exhaust gas passes through once. The air side passes are made possible by baffles in the metal housing (Figure 2). The areas of each pass are selected to optimize the heat transfer for a given pressure drop*. Figure 3 shows the anticipated performance of a model R1000 (12 x 12 x 12 in.) recuperator. The triple-pass recuperator provides higher preheated air temperatures than the earlier single-pass model. An added advantage of the triple-pass recuperator is that the maximum temperature difference between the exhaust gases and the preheated air is reduced. Temperature-induced stresses are therefore lower, thus increasing the reliability of the recuperator.

Since the TAPHTR program ended in 1982, the techniques for production, firing, and encasement of the ceramic cube in the metallic housing have been improved, which have resulted in a more reliable product. Another improvement in the recuperator system is related to the method of controlling the air:fuel ratio to the burner. The common methods of mass flow control, if applied to the cold-air side, do not compensate for changes in recuperator leakage and, if applied to the hot preheated air side, do not account for variations in the preheated air temperature. In case the recuperator leaks, the cold-side control would not correct the air:fuel ratio and the furnace could run fuel rich, if the leakage was large. In the case of controls applied to the preheated air, as the preheated air temperature increases, the air:fuel ratio decreases and fuel rich conditions could result depending on the air:fuel ratio established at system calibration. In the patented GTE temperature compensator[5], a bimetallic strip in the preheated air stream compensates the pressure signal which controls the fuel flow, thus preventing a fuel-rich condition. This simple, relatively inexpensive device is now offered as part of the standard recuperator package.

1.2 Industrial Operating Experience Summary

This report is the summary of the second Task of an ORNL subcontract (N0. 86-22044). The first Task summarized the "Industrial Operating Experience of the GTE Ceramic Recuperator"[7] by conducting a survey of users and a chemical analysis on recuperators that were exposed to corrosives . A listing of the furnace types and number of recuperators are presented in Table 1. Of the total 561 new recuperators, 405 or 72% are still operating and 117 are not in use at present either because of failure, poor performance, or plant shutdown. The box-type furnace used either for forging, reheating, or heat-treating metals was the most common type that GTE selected for heat recovery, accounting for 26% of the furnaces. One hundred seventy-eight recuperators were installed on these box furnaces, of which 104 or 58%

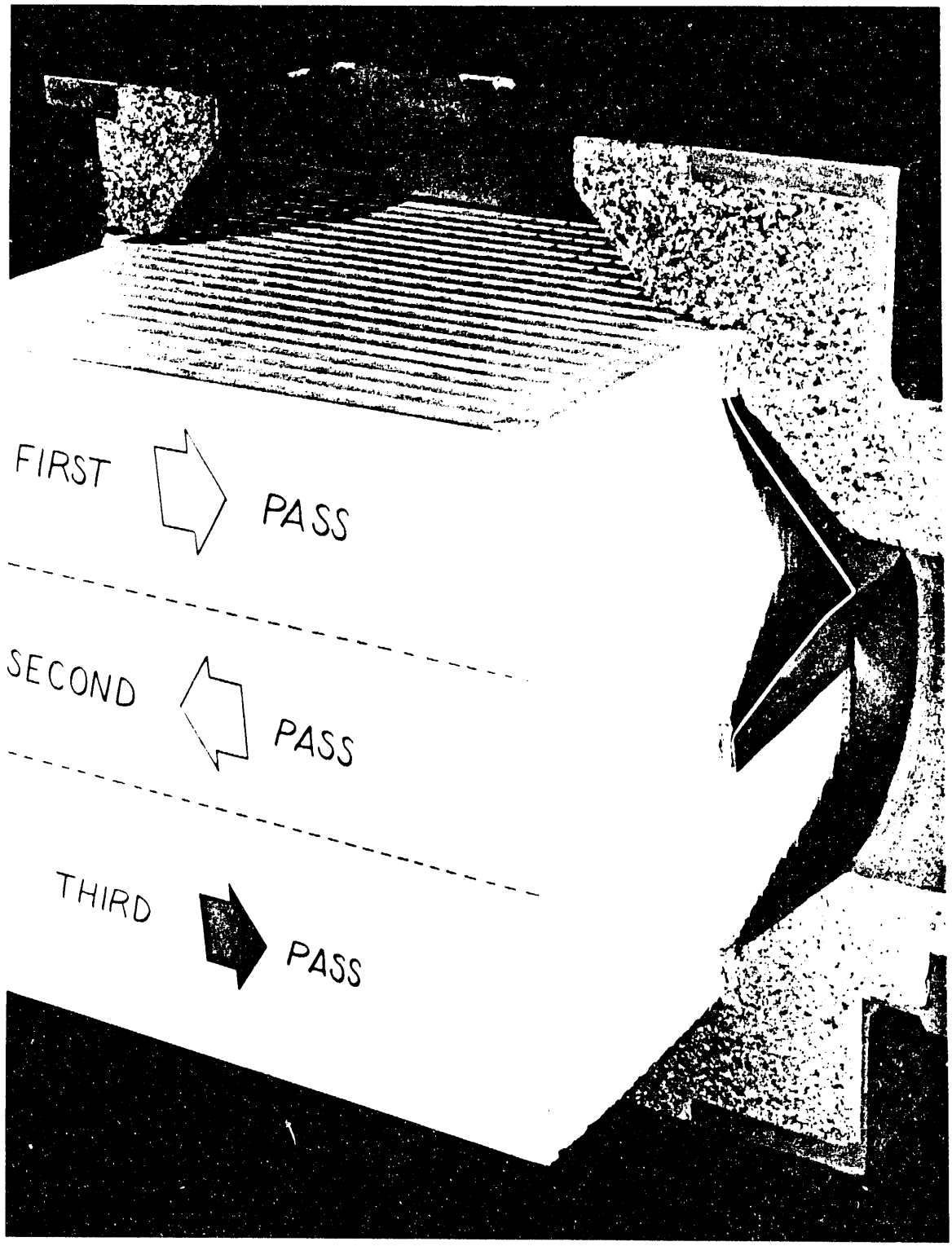


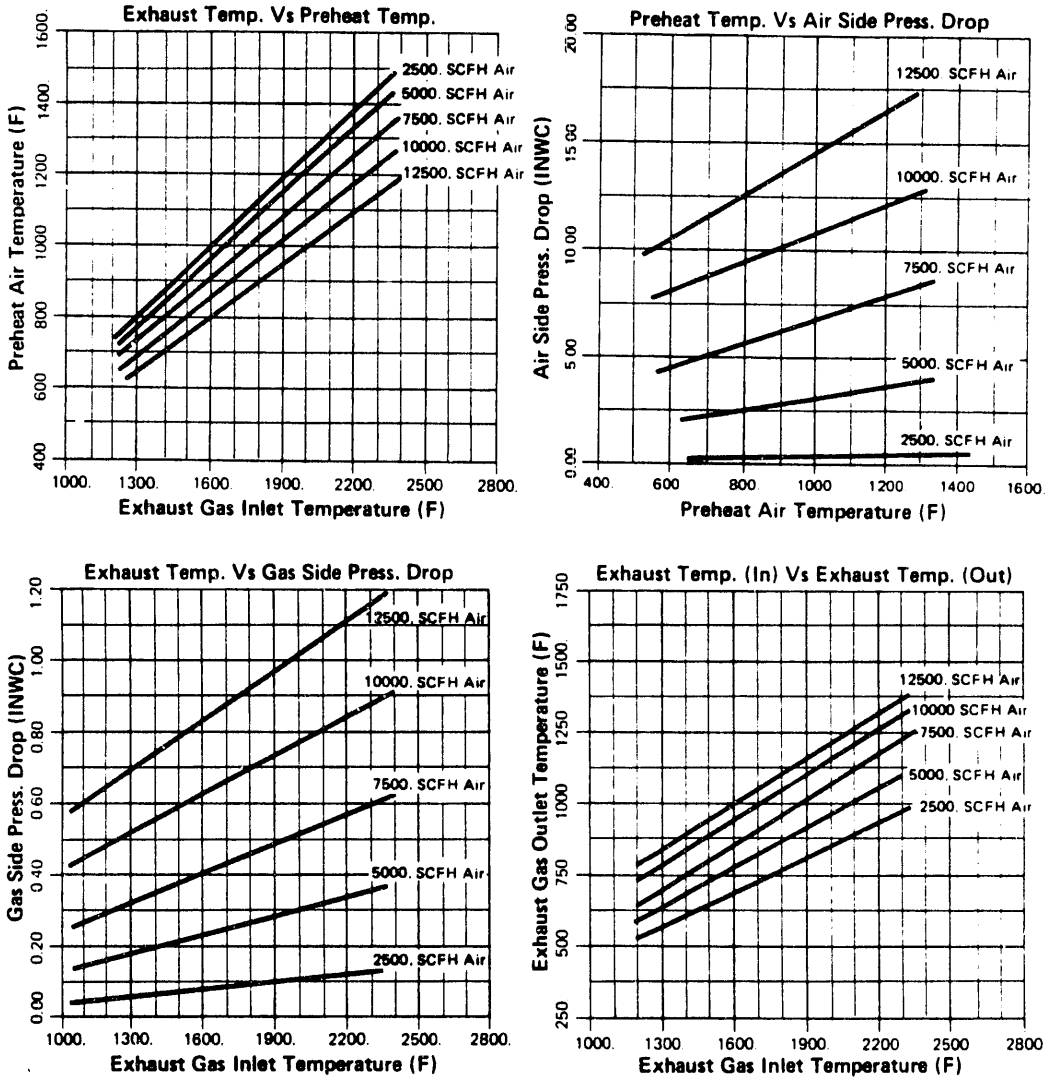
Figure 2
Housed GTE Recuperator with Cutaway Section

GTE
R1000TPXB

- Product Code: 8163222
- Air Hole Size: .200"x .680"
- Exhaust Hole Size: .200"x .680"
- Flow Ratio = 0.917 ±5% = $\frac{\text{Air Flow}}{\text{Exhaust Flow}}$

Example:

1 mm BTU Burner using 10% excess air.
Air Flow = 11000 SCFH
Gas Flow = 1000 SCFH
Exhaust Flow = 12000 SCFH
Preheated Air Temp. at 2000°F Exhaust = 1070°F
Pressure Drop Exhaust .87" H_2O Column
Pressure Drop Air 12½" H_2O Column



SYLVANIA Chemicals/Metals GTE

Figure 3
Typical Thermal Performance of GTE Ceramic Recuperator

Table 1
GTE Industrial Furnaces/Recuperators

	Furnace Type	Number of Furnaces	Number of Recuperators		
			Operational	Not in Use	Status Unknown
1	Box Forge/Reheat/Heat Treat.	43	104	61	13
2	Slot Forges	18	17	22	0
3	Aluminum Pot Melters	16	14	2	0
4	Mold/Die Reheat Furnaces	15	34	0	0
5	Indirect Tube-type Reduction Furnaces	13	71	0	0
6	Rotary Calciners	9	29	0	0
7	Retorts	9	44	0	0
8	Carbottom Forge/Heat Treat.	7	43	8	12
9	Aluminum Reverberatory	5	0	7	1
10	Solder Pots	5	5	0	0
11	Annealing	4	5	1	1
12	Muffle	4	14	2	0
13	Lead Melters/Heat Treat.	4	10	2	0
14	Pusher	2	14	4	0
15	Rotary Hearth	2	8	0	8
16	Ladle Preheaters	2	0	2	0
17	Clay/Pottery Kilns	2	2	2	0
18	Misc.	5	1	4	4
	TOTALS	**165**	**405**	**117**	**39**

are still operational. The slot forge furnaces were the next popular category with 18 furnaces outfitted with 39 recuperators of which only 43% are in operation. None of the aluminum reverberatory furnaces or ladle preheaters are currently recuperated. However, the success rate on pot melters, tube furnaces, rotary , retorts, and heat-treating furnaces was high.

If one considered the performance of the recuperators based on their operating temperature, shown in Table 2, one finds that 87% of those installed on furnaces at 2000°F and below are still operating, while only 57% of those installed at temperatures above 2000°F are still operating. The recuperator performance based on size is shown in Table 3. GTE manufactured the recuperators in three sizes, 0.6, 1.0, and 1.5 million Btu/h and these are 10 x 10 x 10 in., 12 x 12 x 12 in., and 12 x 12 x 18 in., respectively. Eighty-nine percent of the small units are still operating, while 77% of the medium size units are operational and only 56% of the larger units are still operating.

1.3. Corrosive Attack

One application that GTE has concentrated on is alloy steel forging furnaces. These are mostly box-type furnaces that operate at between 2250°F and 2350°F depending on the type of alloy being worked. Most of the furnaces were natural gas fired and the exhaust gases were expected to be clean. However, at ten facilities problems arose with the leaking recuperators causing the preheat air temperatures to drop. As the leaks got gradually worse, the furnaces would run fuel-rich and then the recuperators rapidly deteriorated. In the beginning, it was thought that the recuperators may have been faulty or that the furnace operators had run the furnace at fuel-rich conditions, causing the recuperators to crack. What was puzzling was that there were several plants where similar box forge furnaces were operating satisfactorily with the same fuel and at the same temperatures. Initially, the problem recuperators were replaced, but replaced matrices soon suffered the same fate.

GTE analyzed several of the failed recuperators in the laboratory and found traces of sodium and potassium. The source of the sodium and potassium was traced to the ingots that were processed through the furnace. All of the furnaces at the ten plants processed raw ingots either continuously or on occasion. When raw steel is poured into an ingot, salts of sodium, potassium, calcium, etc., are placed on the top of the ingot. These are referred to as topping compounds. When these raw ingots are reheated in the recuperated furnace, the alkali deposits in the cordierite matrix and corrosive attack begins. The alkali metals form lower temperature eutectics with cordierite resulting in softening and cracking of the matrix. Scott Forge, a large progressive forge shop outside Chicago, installed five sets of the GTE recuperators on one of their forge furnaces, all of which failed. They sent a failed matrix to an independent laboratory and found that 2100°F eutectics were formed. With exhaust gases at 2350°F, it is easy to

Table 2
Recuperator Performance By Operating Range

	≥2000°F	≤ 2000°F	Totals
Operating	155	250	405
Not in Use	93	24	117
Unknown	25	14	39
Totals	**273**	**288**	**56**

Table 3
Recuperator Performance by Size

Size MM Btu/h	**0.6**	**1.0**	**1.5**	**Totals**
Operating	180	90	135	405
Not in Use	6	19	92	117
Unknown	17	7	15	39
Totals	**203**	**116**	**242**	**561**

understand why the recuperators failed. Scott Forge installed 6 sets of Hague International's Sic tubular recuperators on a furnace, all of which failed due to alkali attack. Because of their interest in conservation, they then installed Hotworks metalic units and all four failed relatively quickly. They concluded that it was not economical to recuperate furnaces that processed raw ingots containing topping compounds.

Several of the forge shops tried cutting off the tops of these ingots but could not completely get rid of the alkali metals, and the cordierite matrix failed. One plant that is satisfied with their fuel savings but would like longer recuperator life is Hawker Siddeley in Nova Scotia, Canada. This plant is supplied with hot ingots shipped in insulated containers, therefore they are unable to cut off the tops. Their furnaces are oil-fired and their paybacks (with 50% savings) are less than a year. Their engineer would continue to replace the failed cubes as long as it was economical to do so. In the case of Cape Ann Forge, the plant is located by the seashore and salt in the air may have further contributed to the cube failure.

McWilliams Forge operates a box forge to reheat copper for forging into aircraft parts. The furnace has three recuperators. While the copper is being reheated, charcoal is thrown into the back of the furnace probably to prevent the formation of copper oxide. However, the two recuperators closest to the back of the furnace failed, and their replacements failed as well. It was found that the charcoal contained potassium which was the cause of the failure.

None of the recuperators on the aluminum remelt furnance or aluminum reverberatory furnaces are in operation because of attack by sodium. Callen Mfg. Corp. in North Lake, Illinois uses a white powder called "Smokeless Flux" for fluxing in their remelt furnace. Some of the powder deposited in the recuperator and could not be removed by an air lance. The flux may also have contained some sodium which could have attacked the cordierite, since the exhaust gases entered the recuperator at 2200°F. The aluminum reverberatory furnace recuperators were failures as well because of the fluxing agents used. It soon became evident that aluminum remelt/reverberatory exhaust gases are dirty gases and these applications are not suitable for the GTE recuperator.

The metal lead may also be considered a poor application with respect to attack on cordierite. Two lead melters operating at 1800°F were recuperated. In both cases, the recuperators plugged and were destroyed. The other two lead operations were annealing furnaces where steel spring wire and steel bailing straps are tempered. In both these plants the operations are similar although furnace temperatures are 2300°F and about 2000°F to 2100°F, respectively. Both furnaces are still operating, but the recuperators have done better on the furnace operating at the lower temperature. Large stainless steel pots, 4 ft wide and 12 ft long, contain the molten lead at 1600°F for tempering steel and are supported at the bottom by piers

made of firebrick. The natural gas burners fire low and the exhaust gases blow by the steel pot. Multiple straps, at least 14, and wires continuously pass through the lead. Molten lead falling on the firebrick forms a eutectic that destroys the brick rapidly. The brickwork on these furnaces is rebuilt every 6 to 12 months at American Spring Wire (ASW) but (as a rule) lasts longer at Stanley Works. Both recuperator systems are exposed to lead, but only the system with a high operational temperature (ASW) experiences shortened life cycles.

There are three distinct problems with the recuperators. First, if the lead on occasion falls into the combustion chamber, it vaporizes and deposits in the recuperator, causing some plugging. The second problem relates to the firebrick which contains some potassium and sodium that is released in firing the brick and deposits in the ceramic matrix. Regular replacement of the fire- brick would hasten the demise of the ceramic matrix. Finally, it is possible that the lead and cordierite form lower melting eutectics that may soften or crack the matrix. If lead can cause the firebrick to deteriorate that fast, it surely must have an affect on the cordierite. It is possible that the eutectics formed with lead could soften at temperatures as low as 2200 or 2300°F. The fact that American Spring Wire operates at 2300°F while Stanley Works operates between 2000 and 2100°F may explain why the former's recuperators have to be replaced more often. It would appear that American Spring Wire should operate the furnace at a lower temperature unless this would adversely affect their production. It would appear that applications involving molten lead are not the best for the GTE recuperator.

2. Z-1000 MATERIAL DEVELOPMENT STUDY

GTE engineer's designed and built a corrosion test facility that simulates the corrosion that occurs during exposure of the ceramic recuperator to contaminated exhaust gases. Development of a test method required that we first understand the type of corrosion that typically destroys ceramic matrix elements. Alkalies were found to be the most prevalent contaminant identified in recuperators returned to GTE for rebuilding. The "Industrial Operating Experience of the GTE Recuperator" task of this contract effort (Reference #3) confirmed this.

2.1 Corrosion Resistant Coatings of Z-1000

GTE operates a test furnace capable of testing recuperators at temperatures from 1000-2450°F, and flow rates from 2,000 - 40,000 scfh A new refractory liner was required for the exhaust plenum area of the furnace. Prior to rebuilding the exhaust section, a series of tests was undertaken. Various amounts of sodium hydroxide (NaOH) were vaporized under a

R1500 (1.5 million Btu/h rating) at temperatures between 2200 and 2500°F. A pressure of 1 psi was maintained in the preheat outlet side of the recuperator. The leakage of the recuperator was monitored. Tests were generally abandoned after combustion air flow rates could no longer maintain an outlet pressure of 1 psi. This indicated that corrosion (or melting) or a significant crack on the exhaust inlet of the recuperator had penetrated through the "dead zone" of the ceramic matrix as shown in Figure 4.

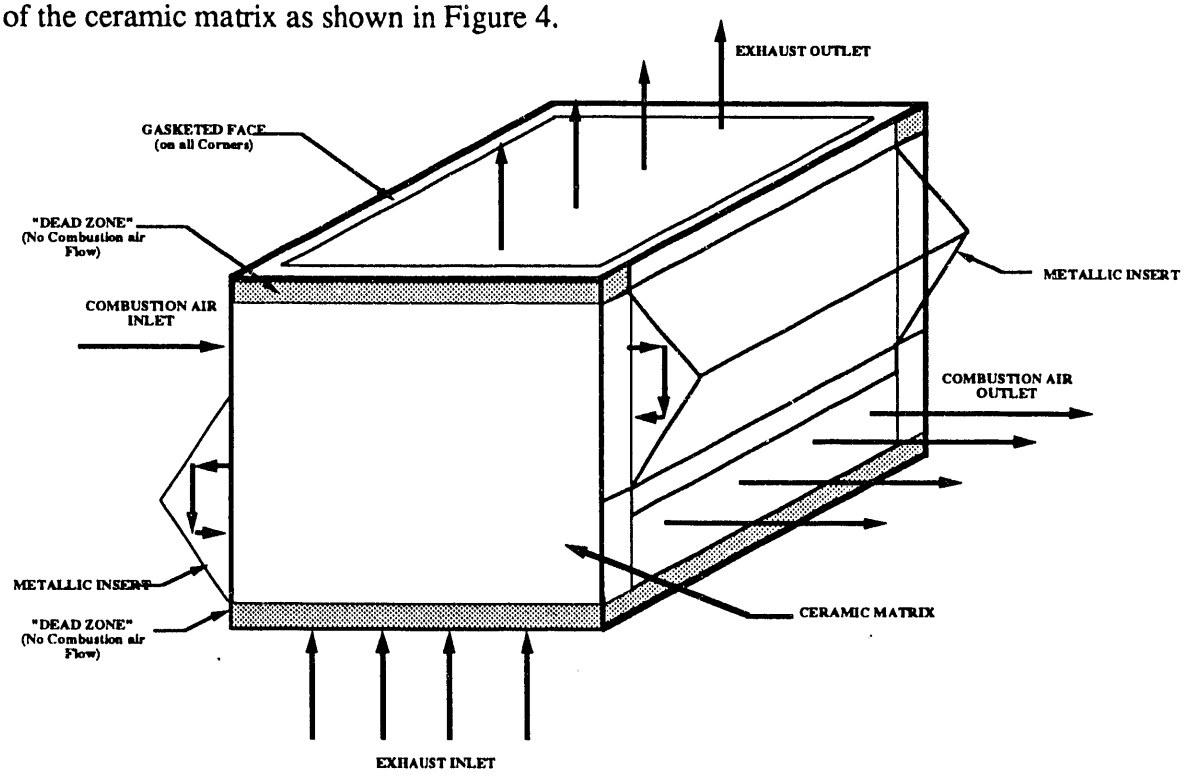


Figure 4

GTE Ceramic Recuperator Flow Arrangement

Seventeen tests were performed. A new cordierite ceramic matrix (MAS-8400) was utilized for each test. Table 4 details the type of matrix element tested, its flow configuration and type of coating evaluated (if any). Table 5 describes the operating conditions varied during each test and summarizes the leakages rates of the housed recuperator at various stages during the cycle. Our goal was the establishment of a short duration test (<24 h) capable of simulating the long term effects of alkali's on the ceramic matrix. Commercially available materials were screened by coating sections of the matrix, to determine their effectiveness and potential for a field test. Heat up times took less than 20 minutes, due to the low mass of the refractory fiber lining of the furnace.

The test furnace is not a closed loop, as the combustion air flow rate is independent of the flow of the exhaust air flow rate. A typical furnace operates in a closed loop. The exhaust gas

TABLE 4

Corrosion tests on GTE R1500 TPX Cramic Matrix

Test #	Recuperator Model #	Matrix Size	Configuration	Coating Type(s) Notes
1	R-1500-TPX-B	.200 x .200	parallel flow TPX	none
2	R-1500-TPX-B	.200 x .200	counter flow TPX	Pyromack 2500 and Cerama Preg (in 3" sections)
3	R-1500-TPX-B	.200 x .200	counter flow TPX	none
4	R-1500-TPX-B	.200 x .200	counter flow TPX	none, matrix had 56 cracks before test
5	R-1500-TPX-A	.125x .200	counter flow TPX	none
6	R-1500-TPX-B	.200 x .200	counter flow TPX	pass 3 is segretated from 1 and 2
7	R-1500-TPX-B	.200 x .200	counter flow TPX	none, "solid edge" matrix
8	R-1500-TPX-B	200 x .200	counter flow TPX	Zirmul-361 dip coated
9-10	R-1500-TPX-B	200 x .200	counter flow TPX	Zirmul-361 dip coated, baked on
11-13	R-1500-TPX-B	200 x .200	counter flow TPX	none
14	R-1500-TPX-B	200 x .200	counter flow TPX	Zirmul on a solid edge matrix
15	R-1500-TPX-B	200 x .200	counter flow TPX	MAS-8400 with Zirmul "glue"
16	R-1500-TPX-B	200 x .200	counter flow TPX	none (solid edge matrix)
17	R-1500-TPX-B	200 x .200	counter flow TPX	Zirmul on a solid edge matrix

inlet temperature, the mass flow rate and the (mass) flow ratio all determine the thermal gradients throughout the ceramic matrix, and the mean temperature of the ceramic matrix. A flow ratio of 0.917 is achieved when a furnace is operating at 10% excess air (stoichiometry) in a closed loop manner. Combustion air can be looked at as "cooling air" for the purpose of determining its effect on chemical attack during operational conditions. As the flow ratio increases ("cooling air" flow rate), the mean temperature of the ceramic matrix decreases. A furnace that has an open slot, or an opening that allows products of combustion to escape, operates at flow ratios greater the .917. In summary, flow ratio is defined as:

Flow Ratio = Q(a) / Q(e)

where:

Q(a) = Flow (SCFH) of the combustion air into the recuperator

Q(e) = Flow (SCFH) of exhaust gases into the recuperator

Q(e) = Flow of combustion air into furnace + Flow of Natural gas into furnace

The tests described also attempted to:

- determine if reducing the mean matrix temperature could extend life cycles.
- determine the effectiveness of commercially available coatings.
- evaluate "solid edge" ceramic matrix elements.

The "solid edge" matrix is based upon a modified plate/fin sheet system. This system produces a ceramic matrix with a flat face (solid edge), as illustrated in Figure 5. The reduced

surface area, and the fact that the refractory glue (bonding agent) is not exposed to the exhaust gases offered the potential for extended life cycles, and afforded reduced edge leakage of the ceramic matrix elements. The solid edge also provided a more consistent surface topography that facilitated improved uniformity of surface coatings. The tests did not confirm or refute life cycle enhancements based upon incorporation of the "solid edge" process. Results of the tests are listed in Table 5.

Figure 6 shows the exhaust inlet section of a recuperator exposed for 8 hours to 400 grams of NaOH @ 2450°F. This effect is similar to those documented in reference 3.

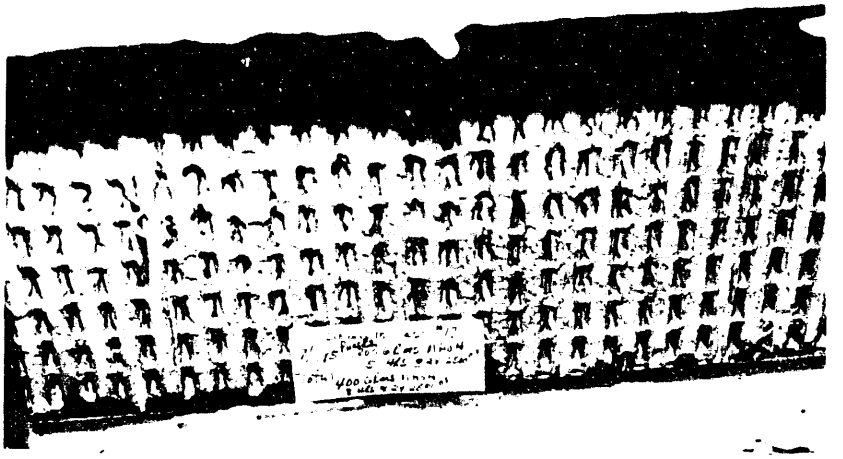


Figure 5
GTE R1500 "Solid Edge" Ceramic Recuperator after Exposure to 400 grams of NaOH for 8 h @ 2450°F

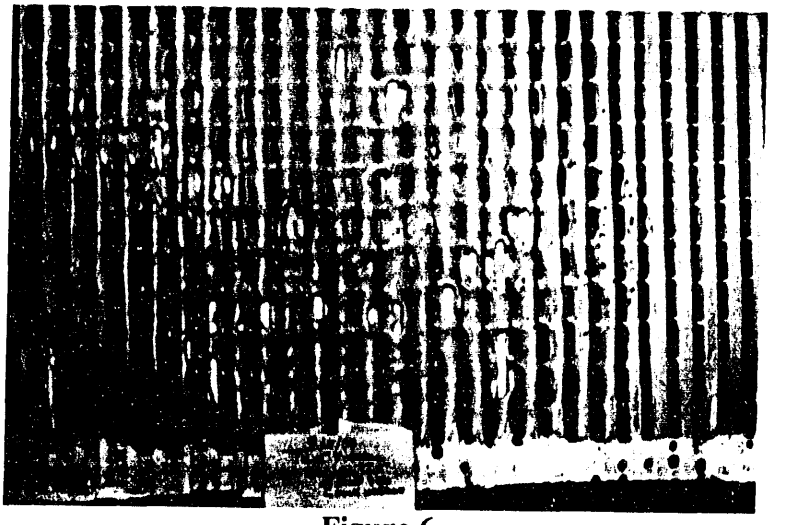


Figure 6
GTE R1500 (standard) Ceramic Recuperator after Exposure to 400 grams of NaOH for 8 h @ 2450°F

TABLE 5

Corrosion tests on GTE R1500 TPX Cramic Matrix

Test #	Q (e) SCFH	Flow Ratio Q(a) / Q(e)	Corrosive Type	Corrosive g	Temp. °F	Time H	Leakage %Q(a)	Pressure osi
Test 1 used a standard unit (B) with a parallel flow triple pass								
1a	TIB*	.917,1.1	-	0	2500	150		
1b	12,000	.46	NaOH	200	2400	3		
1c	12,000	.42	-	0	2500	5		
1d	10,000	.1	-	0	2500	.1	55	16
Test 2 used a standard matrix (B) and has two 3 in. sections coated								
2a	12,000	.46	NaOH	200	2500	2		
2b	12000	.46	-	0	2500	.1	L=86	9
3a	12,000	1.0	NaOH	200	2500	11	23	16
3b	12,000	1.0	NaOH	200	2500	3	29	16
3c	12,000	1.0	NaOH	200	2500	3	40	16
3d	12000	1.	NaOH	200	2500	11	47	16
Test 4 used a standard matrix (B) with 56 cracks. . .								
4	-	-	-	0	100	.1	14	16
4a	12,000	.917	-	0	2450	.1	22	16
4b	13,000	.5	NaOH	200	2500	3	44	16
4c	13,000	.55	-	0	2500	5	37	16
4d	13,000	.5	NaOH	200	2500	6	54	16
Test 5 used a standard matrix (A)								
5	-	-	-	0	100	.1	6	16
5a	11,500	.917	-	0	2450	.1	24	16
5b	13,700	1.1	NaOH	200	2450	2	32	16
5c	8,400	1.1	-	0	2450	6	34	15.5
5d	11,000	1.1	NaOH	200	2450	3	36	16
5e	11,000	1.1	NaOH	200	2450	3	36	16
5f	7,700	.917	NaOH	200	2350	3	44	16.2
5g	7,700	.917	NaOH	200	2350	5	52	16.4
Test 6 used a segretated matrix in the third pass (B)								
6a	11,000	.917	-	0	2450	.1	21	12
6b	12,000	1.1	NaOH	200	2450	3	2	16
6c	12,000	.5	NaOH	200	2450	5	35	16
Test 7 used a "solid edge" matrix (B)								
7a	11,000	.917	-	0	2450	.1	10	16
7b	13,000	.5	NaOH	200	2450	2	21	16
7c	13,000	.5	NaOH	200	2450	6	26	16
7d	13,000	.5	NaOH	200	2450	5	73	16

* Technical Information Bulletin (various flows, flow ratios, and temperatures)

TABLE 5 (cont'd)

Corrosion tests on GTE R1500 TPX Cramic Matrix

Test #	Q (e) SCFH	Flow Ratio Q(a) / Q(e)	Corrosive Type	Corrosive g	Temp. °F	Time H	Leakage %Q(a)	Pressure osi
Test 8 used a standard matrix (B) coated with Zirmul (dipped)								
8a	11,000	.917	-	0	2450	.1	27	16
8b	11,000	.5	NaOH	200	2450	2	33	16
8c	11,000	.5	NaOH	200	2450	5	49	16
8d	11,000	.5	NaOH	200	2450	5	71	16
Test 9 used a standard matrix (B) coated with Zirmul (dipped,baked on)								
9	-	-	-	0	100	.1	4	16
9a	12,000	.917	-	0	2450	.1	14	16
9b	13,000	.5	NaOH	200	2450	2	13	16
9c	12,000	.5	NaOH	200	2450	5	13	16
9d	12,000	.5	NaOH	200	2450	5	11	16
9e	12,000	.5	NaOH	200	2450	5	18	16
9e	12,000	.5	NaOH	200	2450	5	12	16
9f	12,000	.5	-	0	100	.1	21	16
Test 10 used a standard matrix (B) coated with Zirmul (dipped,baked on)								
10	-	-	-	0	100	.1	4	16
10a	12,000	.917	-	0	2450	.1	18	16
10b	12,000	.5	NaOH	300	2450	3	14	16
10c	12,000	.5	NaOH	200	2450	5	28	16
10d	12,000	.5	NaOH	200	2450	5	39	16
10e	12,000	.5	NaOH	200	2450	5	45	16
10e	12,000	.5	-	0	100	.1	54	16
Test 11 used a standard matrix (B)								
11	-	-	-	0	100	.1	5	16
11a	12,000	.917	-	0	2450	.1	29	16
11b	15,000	.4	NaOH	200	2450	3	38	16
11c	15,000	.4	NaOH	200	2450	5	37	16
11d	15,000	.4	NaOH	200	2450	5	35	16
11e	15,000	.4	NaOH	200	2450	5	36	16
11f	15,000	.4	NaOH	200	2450	5	40	16
11g	15,000	.4	-	0	100	.1	62	16
Test 12 used a standard matrix (B)								
12	-	-	-	0	100	.1	7	16
12a	12,000	.917	-	0	2450	.1	13	16
12b	12,000	.5	NaOH	200	2450	2	25	16
12c	12,000	.5	NaOH	200	2450	5	63	16
12d	12,000	.5	-	0	100	5	71	16

TABLE 5 (cont'd)

Corrosion tests on GTE R1500 TPX Ceramic Matrix

Test #	Q (e) SCFH	Flow Ratio Q(a) / Q(e)	Corrosive Type	Corrosive g	Temp. °F	Time H	Leakage %Q(a)	Pressure osi
Test 13 used a standard matrix (B)								
13	-	.-	-	0	100	.1	3	16
13a	12,000	.917	-	0	2450	.1	9	16
13b	12,000	.5	NaOH	200	2450	2	24	16
13c	12,000	.5	NaOH	200	2450	5	33	16
13d	12,000	.5	NaOH	200	2450	5	91	16
13e	12,000	.5	-	0	1005	.1	100	16
Test 14 used a "solid edge" matrix (B), with Zirmul (baked on), cube delaminated								
14	-	-	-	0	100	.1	6	16
14a	11,000	.917	-	0	2450	.1	100	16
Test 15 used a MAS-8400 matrix with Zirmul Glue (B), extreme ambient leakage								
15	-	-	-	0	100	.1	120	11
15a	12,000	.917	-	0	2450	.1	24	16
15b	12,000	.5	NaOH	200	2450	3	40	16
15c	12,000	.5	NaOH	200	2450	2.5	56	16
15d	12,000	.5	-	0	100	.1	64	16
Test 16 used a "solid edge" matrix (B), coated with Zirmul (dipped, baked on)								
16	-	-	-	0	100	.1	4	16
16a	11,000	.917	-	0	2450	.1	6	16
16b	11,000	.5	NaOH	200	2450	2	7	16
16c	11,000	.5	NaOH	200	2450	5	11	16
16d	11,000	.5	NaOH	200	2450	5	14	16
16e	11,000	.5	NaOH	200	2450	5	17	16
16f	11,000	.5	NaOH	200	2450	5	22	16
16g	11,000	.5	-	0	100	.1	25	16
Test 17 used a standard matrix (B)								
17	-	.-	-	0	100	3	15	16
17a	12,000	.917	-	0	2450	.1	40.7	16
17b	12,000	.5	NaOH	200	2450	3	42	16
17c	12,000	.5	NaOH	200	2450	5	82	14
17d	12,000	.5	-	0	100	.1	100	16

To allow for expeditious review and evaluation of potential materials and corrosion resistant coatings a corrosion test facility was fabricated. The test bed would evaluate cross flow matrix shapes in sizes of 3 x 3 x 3 in. Coatings could be applied to the existing cordierite-mixed -oxide ceramic (MAS-8400) or a matrix of alternate materials could be evaluated. The furnace would expose both a sample and one or two controls (standard MAS-8400 ceramic matrix elements). Comparisons would be based upon qualitative results (degree of melting or softening). If possible quantitative comparisons would be made by measuring the amount of change in thermal expansion coefficient of the matrix substrate. If corrosive attack creates a glassy phase a dramatic increase in the thermal expansion of the material would be observed.

A GTE funded test program to evaluate coatings (commercially available and ones developed by GTE such as Al_2O_3) was established. The contract effort did not call for the fabrication of full matrix elements of Z-1000 or testing Z-1000 coatings via this test method, however GTE was able to run these inexpensive experiments concurrently with the process development tasks described in section 3 of this report. The technique offered the potential for early determination of the merit of the zirconia-mullite based ceramic (Z-1000).

The corrosion test stand has the following specifications:

- Chamber size (internal) 8 x 8 x 24 (in.)
- K-3000 refractory brick with tie rod support
- Two 35,000 Btu/h nozzle mix burners fire from opposite ends (24 in.)
- Automatic purge, ignition, temperature control and flame safety
- Three exhaust flues (2 x 2 in.) spaced evenly along the units length
- Thermocouples (type S) at each flue
- On ratio or excess air temperature control

The furnace utilizes a 3 x 3 x 3 in. (test matrix), located on each flue. A small alumina crucible is located directly under each flue, and sits on a refractory platform. A refractory baffle hangs down from the refractory roof 4 in. Its function is to help direct the contaminant (generally NaOH) directly into the exhaust flue above the crucible. The burners are located on opposite side of the walls but are offset from one another as illustrated in the flow diagram depicted in Figure 7 and the cross-section schematic shown in Figure 8. The flames do not directly impinge in the crucibles, which are centrally located below each flue during a test. The burners are located approximately 4.5 in. above the refractory hearth.

A series of tests was run with MAS-8400 matrix elements (control) on each flue. Unlike the matrix shown in Figure 5, these elements do not have combustion air flow passing through them during the test. The "dead zone" of a recuperator has no air flow, however it is cooler than

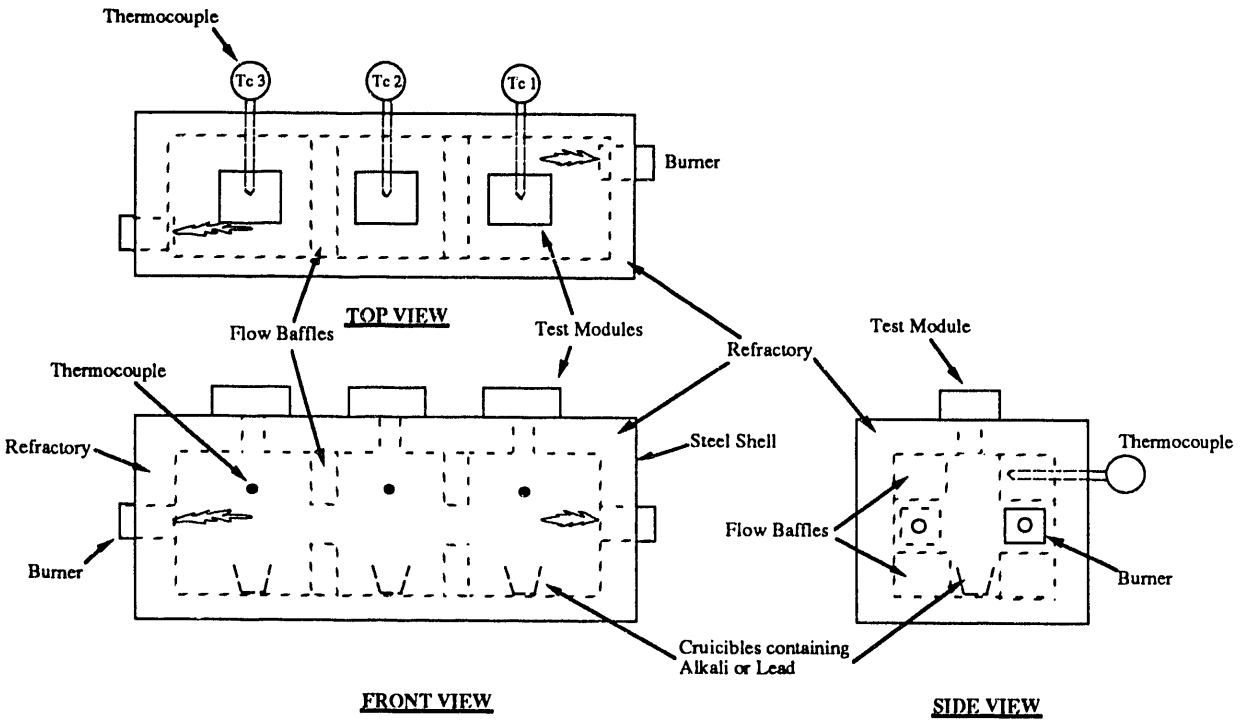
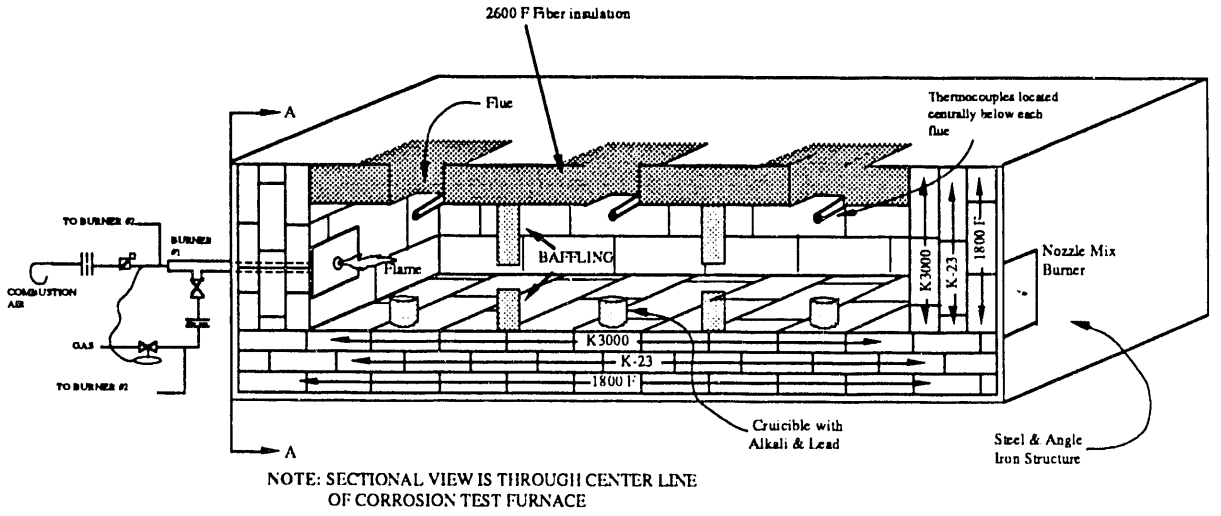


Figure 7
Corrosion Test Stand

the exhaust inlet due to the heat transferred to the section that participates in heat exchange. The net result is that the test performed on the test stand will actually be more severe. The corrosion rate may increase resulting in the need for a lower temperature, shorter exposure duration or both. The use of controls eliminates the need to fully duplicate what occurs on a full scale test. It was determined that a 10g sample of NaOH run at 2450°F for 6 h produced a surface similar to that shown in Figure 5. Additionally, the thermal expansion of the "glassy" material showed a 350% increase in expansion in the room-temperature to 600°F range which compares to historical data obtained from "post mortem analysis" (technique is detailed in reference 3) of recuperators returned for rebuild and refurbishing. Figure 9 shows the exhaust inlet of the exposed test elements. The rounding of the corners, and melting of the ribs is evident.

A test with the central flue plugged off was run to determine the consistency of the corrosion comparison test. Furnace adjustments were made to insure balanced input, exhaust flow, and temperature. Figure 10 illustrates the consistency between the corrosion experienced by the matrix elements placed on each of the two flues. The test was repeated several times to insure consistency.



NOTE: SECTIONAL VIEW IS THROUGH CENTER LINE OF CORROSION TEST FURNACE

Figure 8
Schematic of the Corrosion Test Stand

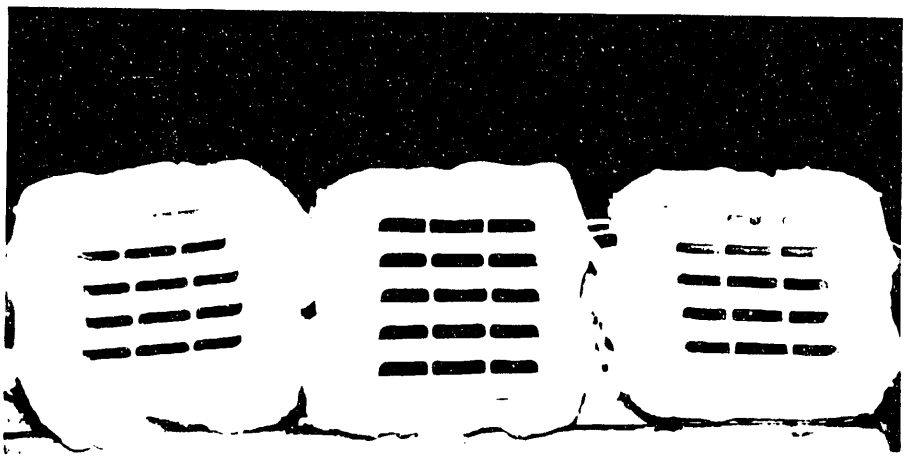


Figure 9
MAS - 8400 (Cordierite-Mixed-Oxide) Test Modules
after Exposure to 10 g (each) NaOH at 2450°F for 6 h

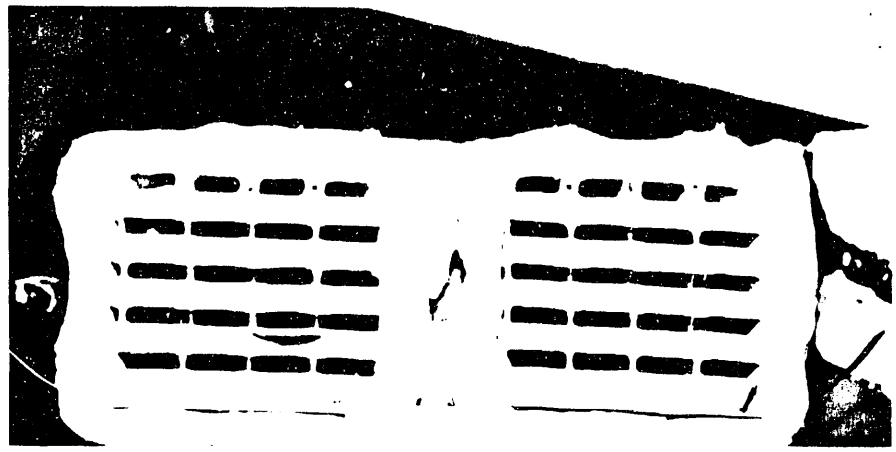


Figure 10
MAS - 8400 (Cordierite-Mixed-Oxide) Test Modules
after Exposure to 10 g (each) NaOH at 2450°F for 6 h

A series of compositions were prepared with various mixtures of zirconia-mullite based material (Zirmul*) and a Staywhite Talc+ (required to "flux" the Zirmul). The following procedure was used:

- The compositions were all milled for 40 h in a Sweco DM-10 (urethane) vibratory mill. The media utilized was 1/2 in. capped cylinders of alumina (Coors 99.5% Al_2O_3). The mill was set to 30° angle and utilized 2 top plates and 3 bottom plates. A media:load charge ratio (by weight) of approximately 18:1 was utilized. Contamination (Al_2O_3 addition) to the Z-1000 was measured at approximately 1.3% (by weight).
- Additions of 5,10,15, and 20% talc+ were made subsequent to the milling. Each sample was then milled for 8 h on a Sweco (model # DM 18/5) mill in 1 gallon (urethane lined) stainless steel containers. A charge ratio of 10:1 was utilized, and the media was identical to that utilized in the DM-10 mill.
- After milling the compositions were pelletized in a jar mill with the addition of approximately 5 weight percent water.
- The pellets were then fired to 2650, 2700 and 2750°F on alumina trays.
- The sintered agglomerates were then wet milled for 8 hours in 1 gallon vibratory mills with 2500 cc deionized water
- The slurry was then screened through a 100 mesh screen.

* Taylor Refractories Grade 361 and 362

\+ Cyprus Industrial Minerals Co, Talc Division

- The sample was heated to 140°F until dry.
- A 20% (volume) suspension in deionized-H_2O was prepared.
- Polyvinyl-alcohol (PVOH) was added (1% by weight of solids).
- The suspensions were dip coated onto 3 x 3 x 3 in. MAS-8400 ceramic test elements that were dried at 140°F prior to dipping. The slurry was thinned and dip time was adjusted to foster a coating less than .010 in. thick. The matrix were air dried while suspended on the wire used for dipping.
- The Zirmul based coated matrix elements were all fired to 2500°F in air to foster a bond and assure that the material would not spall off the matrix during the test (at 2450°F). The ramp was 100°F/h with a 2 h hold at temperature. Several attempts were often made to bond the coating to the matrix, as the mismatch in thermal expansion between the MAS-8400 and the Zirmul based coatings often caused the coating to spall off. As a rule, the thinner the coating, the better the adherence.

This application technique was similar to one developed for testing other corrosion resistant coatings. CVD SiC, alumina precipitated on the matrix via an alkoxide process and the other coatings (detailed in Table 5) were evaluated by GTE during the aforementioned internally funded project. None of the materials performed as well as the Zirmul based materials.

Figure 11 shows the result of a side-by-side comparison test on the corrosion test stand. The standard test (10g NaOH @ 2450°F for 6 h) was run and repeated two times with this material. Vaporization rates for the NaOH were not determined, however the degree of melting (on an uncoated matrix) did continue to increase throughout the duration of the test. Additional tests were done with lead oxide. These tests were done prior to a refractory rebuild. The results were similar to those with the NaOH (Figure 12). X-ray diffraction patterns of the material found on the exposed face of matrix samples of full-scale and sub-scale tests showed the presence of a typical MAS-8400 cordierite pattern and PDF19-1227. This pattern is either (Na or K) -Al - $Si_{13}O_8$ or Pb-$Al_2Si_{12}O_8$. Review of appropriate phase equilibria data suggest that low temperature eutectics would be formed, and melting and/or softening of the ceramic is predictable.

Full-scale test # 16, (detailed in Table 5), illustrated the potential of Zirmul to extend life cycles. During sub-scale tests the positions of the control matrix (uncoated) and the test matrix (coated) reversed. A significant reduction in the degree of softening of the MAS matrix substrate (similar to that observed in full scale tests) was observed. The material used in this test was **Zirmul-361** with 15% talc addition, which was milled and presintered at 2700°F. This

material seemed to adhere to the MAS-8400 substrate better than other coatings. The softening of the leading edges, and the formation of a glassy phase evident in the control sample was not observed in the coated test matrix. A sample of MAS-8400 sample was extracted from the leading face of the coated matrix.

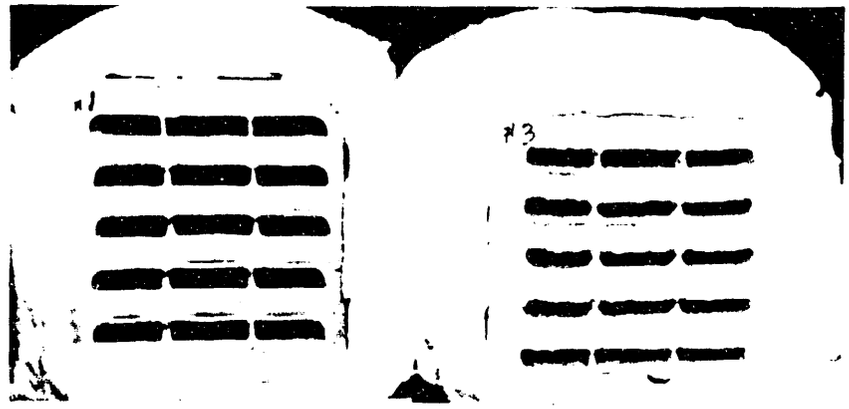


Figure 11
Uncoated MAS - 8400 (Cordierite-Mixed-Oxide) Test Module (Left) and MAS-8400 module coated with Zirmul-361 with 15% Talc (2777° F) after exposure to 10 g (each) NaOH at 2450°F for 6 h

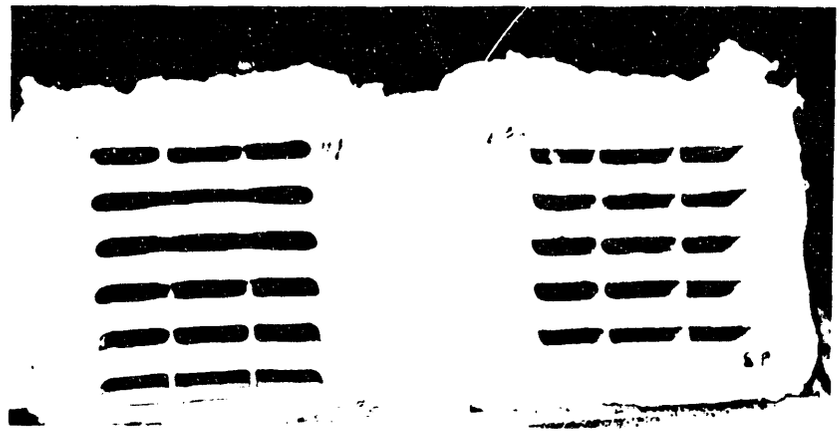


Figure 12
Uncoated MAS - 8400 (Cordierite-Mixed-Oxide) Test Module (Left) and MAS-8400 module coated with Zirmul-361 with 15% Talc (2777° F) after exposure to 10 g (each) PbO at 2450°F for 6 h

Optical micrographs (Figure 13) contrast the coated and uncoated substrate after the exposure test. The coating was ground off and the coefficient of linear thermal expansion of the cordierite (RT - 800°F) was measured at approximately 2.1 x 10^{-6}/°F. This is similar to that measured for MAS-8400 prior to exposure to corrosive materials. This is dramatically lower than those measured in the glassy area (tests up to 500°F were done and expansion rates up to 6.0 x 10^{-6}/°F have been measured, when samples were corrosion-tested). The positive results obtained here focused the development effort for the Zirmul based materials on the Z-361 with 15% additions, sintered at 2777°F.

Figure 13 Not Available

2.2 Z-1000 Extrusion Process Development

2.2.1 Summary of the MAS-8400 Manufacturing Process

The process used to manufacture the MAS-8400 cordierite ceramic crossflow recuperator matrix was used as a model for extrusion process development, fabrication, green machining, binder removal / sintering / annealing and inspection procedures envisioned for the zirconia - mullite mixed-oxide composition. The MAS-8400 matrix is manufactured via the following procedure:

1. The following materials are added to an Eirich Mixer Model (dust collector on):
   - Inorganic Additives:
     - Alumina (after hammer-milling)
     - Staywhite Talc
     - Pyrax B
     - M-23 Ball Clay (<2% for extrudability enhancement)
   - Organic Additives (Dry):
     - Polyethylene-glycol (PEG)
     - Hydro-ethyl-cellulose (HEC)
2. Mix for 10 minutes, counter-rotating drum, impeller at low speed.
3. Add the following solution to the blended powders (wet mix):
   - Tri-ethylene-glycol (TEG)
   - de-ionized H_20
   - Polyethylene-glycol (PEG)
4. Mix for 10 minutes, counter rotating drum, impeller at high speed.
5. Mix until material balls up into 1-2 in. spheres at low speed, co-rotation (approximately 15 minutes). Temperature should not exceed 135°F.
6. Discharge mixture into doubled plastic bags, seal and store at room temperature.
7. Charge 200T, 8 in. extruder with 30 kg (approximately) compounded mixture.
8. Close ram and compress mixture into die holder assembly, until material begins to extrude through the .200 die (Fig 14).
9. Open ram and fill extrusion barrel completely (approximately 30 kg).
10. Close ram to minimal compression of the mix, but enough to assure that the vacuum ring seal is inside the barrel.
11. Turn on vacuum pump, verify that a vacuum seal exists at the die end of the barrel (indicated by negative gauge pressure) and run 10 minutes.
12. Extend ram until compounded material begins to flow, withdraw ram, fill barrel with compounded material and repeat vacuum cycle (approximately 20 kg).

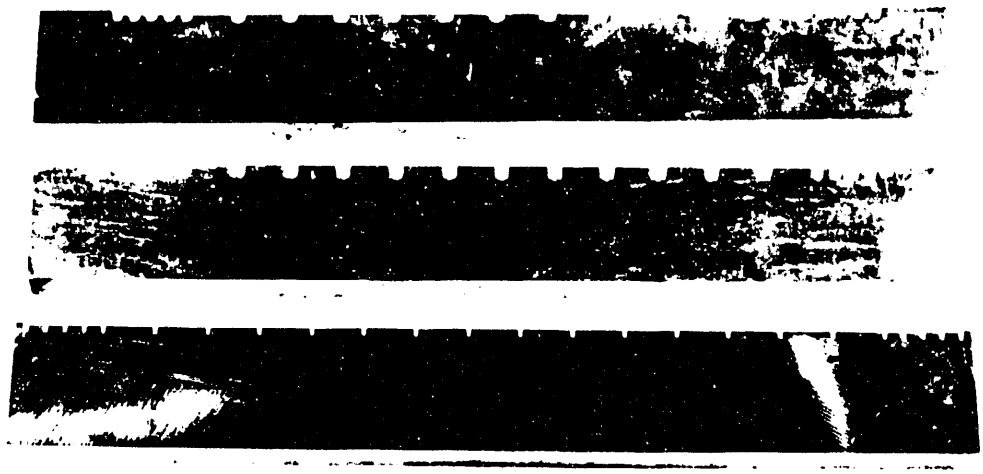


Figure 14
Extrusion dies for Extrusion of plate/fin sheets of Ceramic

13. Adjust extrusion pressure to 60T (bypass valve), and set extrusion die flow-restriction adjustment screws to foster uniform flow of the sheet. Objective is flatness, uniform thickness and tear-free sheets running continuously.
14. Monitor extrusion wall thickness to insure that the differential thickness between the center of the sheet and the outside edges is less than .002 in. If it exceeds this replace the worn die insert.
15. Extrude sheets to 38 or 44 in. lengths (for 10 x 10 or 12 x 12 in. widths, respectively) onto 24 x 48 x 0.5 in. trays. (trays are plastic light diffusers with .020 in.wall thickness and .375 x .375 in.holes)*
16. Cut sheets to length (10 or 12 in.).
17. Place into air dryer for 45 minutes (trays are stacked 2 in. apart in a box with ambient air circulating above and below each tray)
18. Dry in high volume replacement air oven (Dispatch) at 140°F for 2h
19. Remove from oven and stack sheets in 12 in. heights. The base sheet is comprised of a sheet with the rips facing up with a second sheet placed over it with its ribs parallel to the base sheet's ribs (interlocked), facing down (Figure 15). Sheets are then stacked with ribs facing down, in an alternating manner that fosters a crossflow shape.

* The actual die sizes are made oversized to accommodate shrinkage. Sheet widths and lengths are 11.0 in. for the 10 x 10 x 10 in. unit and 13. 0 in. for the 12 x 12 x 12 in recuperator.

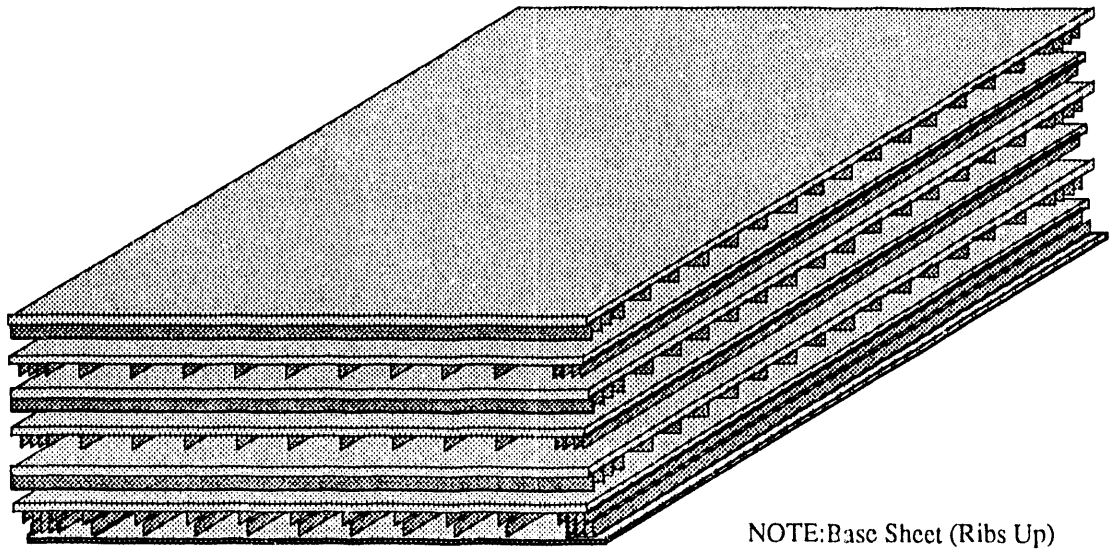


Figure 15
Assembly Illustration for GTE Ceramic Crossflow Recuperator

20. Place 11 x 11 x .5 or 13 x 13 x .5 in. steel plates on the stack (for 10 x 10 or 12 x 12 in. sheet extrusions, respectively).
21. Units are constructed in a jig that ensures that alternate layers are normal (90°) to one another. Sheets are inspected for flatness, and only sheets that are cut square are used.
22. Each sheet is positioned then coated with a deflocculated MAS-8400 slurry (Darvan C in a 40 volume percent aqueous (deionized H_2O) suspension containing PEG and HEC). The slurry is rolled on with a thin nap roller. Another sheet is then placed on it (at 90°) immediately. Process is repeated for 10 sheets, and then weight is applied using steel plates for 10 minutes. Process is continued until the appropriate height is obtained (10.2, 12.3 or 18.5 in. for models R0600, R1000 or R1500, respectively).
23. The units are then cut to the proper widths. A 0.5 in. cut is made in each of the walls that contacted the building jig. The other walls are trimmed to create 9.9 x 9.9 in. or 11.9 x 11.9 in. thickness (for 10 x 10 or 12 x 12 in. units, respectively).
24. Units are placed on a set of interlocked MAS-8400 ceramic sheets with an **alumina** sand layer and positioned in the Bickley High Temperature Furnace. An **alumina** sand layer is placed on the top of the recuperator matrix, and MAS-8400 ceramic sheets are placed on top. Units are stacked up to 48 in. high, 3 abreast. The unit on top has an 1 in. thick alumina setter that covers the entire matrix. Care is taken to ensure that the units are positioned on level flat surfaces.

25. The Bickley Bell Kiln is lowered, and then the hearth rotation apparatus, environmental protection devices and power supply are turned on. The four zone control system is pre-programed to carry out a proprietary one step binder-burnout/ sintering/anneal thermal cycle. The entire cycle takes place under an air atmosphere, however, the binder removal cycle requires that the furnace be starved of oxygen during the exothermic portions of the binder burnout cycle (oxygen is consumed by the oxidized organics). Ramp rates were selected to minimize the differential temperature across a matrix element to <18F° (the center actually gets hotter than the outside of the matrix). Sintering temperatures require an extended hold at 2525°F. A controlled cool to an annealing temperature fosters crystallization of any glass formed at the high soak temperature. Final cooling rates are limited to the ability of the furnaces dense alumina refractory to dissipate its stored heat (approximately 24h). Up to 36 cubic feet (800 pounds) of ceramic heat exchanger matrix elements can be sintered simultaneously. Automatic controls determine the time temperature profile, ensure zone-to-zone thermal uniformity (+/- 8°F) control damper positions, exhaust gas flow, and environmental systems. Status is remotely monitored and recorded on local and remote strip chart recorders.
26. Units are unloaded, inspected for cracks (no visible cracks are accepted), pressure tested to determine structural integrity (to 5-8 psi) and leak tested (must be less than 10% of it nominal rating during operation). Leakage rates are generally in the <1% range.

2.2.2 Milling Studies

The particle size distribution (PSD via Micrometrics sedigraph), surface area (SA via Quantachrome Monosorb BET), and density (via Quantachrome Null-pycnometer) determined for Zirmul 361, Staywhite talc and MAS-8400 mixture and are shown in Table 6. GTE has had prior experience relating to extrusion with the aforementioned binder system, and decided to attempt to match (approximate) the volume loading, mean particle size and surface area of the production MAS-8400 material.

Milling experiments were undertaken because of the course nature of the Zirmul-361 powder. A Sweco mill (M18-5) was used for a 40h milling experiment. A sample was extracted every 8 hours, and surface areas (BET) and particle size distributions were determined (via sedigraph). Table 7 shows the results of the draw trials. The same test was repeated using a rolling mill and one gallon polypropylene bottles (Table 8). The charge ratio (media:charge) was 8:1 (by weight) and 0.25 in. diameter capped cylinders (Coors 99.5%

Table 6

Properties of MAS-8400, Zirmul-361 and Staywhite Talc

MATERIAL	DENSITY (abs.) g/cm^3	SURFACE AREA m^2/g	mean-PSD μm
MAS-8400	2.99	10.028	5.005
Zirmul-361	3.77	0.588	12.400
Staywhite Talc	2.94	11.120	

Table 7

Sweco Milling Effectiveness (model - M-18/5) of Zirmul-361, A Time Study, 1 Gallon Lined Containers with 4.0 Kg of 0.25 in. capped Al_2O_3 Cylinders. The media:charge ratio was 8:1 (by weight).

TIME (hours)	SURFACE AREA m^2/g	CALCULATED DIAMETER (μm)	BULK DENSITY g/cm^3	SEDIGRAPH (PSD) Mean-Diameter (μm)
0	0.44	3.56	1.034	N/a
8	1.29	1.23	1.040	6.799
16	1.82	0.88	1.017	3.813
24	2.04	0.78	1.052	3.317
32	2.03	0.78	1.024	3.119
40	2.52	0.63	1.044	2.651

Table 8

Ball Milling Effectiveness of Zirmul-361, A Time Study, 1 Gallon Polypropylene Bottles with 4.0 Kg of 0.25 in. capped Al_2O_3 Cylinders The media:charge ratio was 8:1 (by weight).

TIME (hours)	SURFACE AREA m^2/g	CALCULATED DIAMETER (μm)	BULK DENSITY g/cm^3	SEDIGRAPH (PSD) Mean-Diameter (μm)
0	0.44	3.56	1.034	N/a
8	1.14	1.40	1.040	5.661
16	1.40	1.14	1.017	4.779
24	1.86	0.86	1.052	4.098
32	1.98	0.81	1.024	3.698
40	2.37	0.67	1.044	3.425

Al_2O_3) were used. The goai was to obtain a surface area in the range of 5-10 m^2/g. MAS-8400 is compounded using raw material with a surface area of approximately 10.0 m^2/g. GTE has successfully compounded and extruded materials with surface areas as low as 5 m^2/g using the binder system described earlier. MAS-8400 contains 63.8% (weight) talc, which has a platy crystal structure which yields a large surface area:mass ratio. Extrusion of more spherical materials can be accomplished at a higher solids loading levels (less organic additives). Courser materials have a lower surface area:mass ratio than fine materials.

Sweco milling was the more effective attrition process and was selected for process upscale. The 40h milling time (upper limit) selected for the experiments was based upon equipment availability and required department usage.

2.2.3 Compounding and Extrusion Studies

A Sweco DM-3 mill was loaded with 20.45 Kg Zirmul-361 and clean 0.5 in. capped cylinders (363.6 kg of Coors 99.5% Al_2O_3), and run for 21h for the purpose of cleaning out the mill and checking the operation of the mill at full load. After cleaning, three batches of Zirmul-361 were then milled according to the following procedure:

- Sweco DM-3 (urethane)
  - angle = 30°
  - 3 plates on bottom
  - 2 plates on top
- 363.6 kg (Coors 99.5% Al_2O_3) 0.5 in. capped cylinders
- 20.45 kg raw material (media charge:load = 18:1)
- Mill for 40 h, discharge for 1h

The material was removed from the mill and the three batches were blended together (cone blender with an intensifier bar) for 30 minutes). This material was used for the six compounding experiments shown in Table 7. The properties of the milled Zirmul-361 blend were as follows:

- Surface Area (Zirmul-361).....5.72 m^2/g (via BET)
- Average Particle Size Distribution....2.667 µm (via sedigraph)
- Bulk Density.....0.955 g/cm^3

The compositions detailed in Table 9 were prepared for a compounding/extrusion trial. Additions of 0, 5, 10, 15, 20, and 25 % Staywhite talc were made to Zirmul-361. The solids loading of each batch was modified as indicated. The modifications were required to insure

Table 9

COMPOSITION OF COMPOUNDING TRIALS (Batch 1-6)

SIMPSON MULLER MIXER - RIBBON EXTRUSION PRESS

BATCH 1

MATERIAL	AMOUNT Inorganics kg	AMOUNT Inorganics %	AMOUNT (Dry) Components kg	AMOUNT(Dry) Components %	AMOUNT Total kg	AMOUNT Total %
Zirmul -361	10.0	100.0	10.000	91.74	10.000	80.30
Staywhite Talc	0.0	0.0	0.000	0.00	0.000	0.00
	10.0	100.0				
HEC (dry)			0.600	5.51	.600	4.82
PEG (dry)			0.300	2.75	.300	2.41
			10.900	100.00		
di.-H_2O (wet mix)					1.311	10.53
PEG (wet mix)					.066	0.53
TEG (wet mix)					.175	1.41
					12.452	100.00

BATCH 2

MATERIAL	AMOUNT Inorganics kg	AMOUNT Inorganics %	AMOUNT (Dry) Components kg	AMOUNT(Dry) Components %	AMOUNT Total kg	AMOUNT Total %
Zirmul -361	9.5	95.0	9.500	87.16	9.500	76.29
Staywhite Talc	0.5	5.0	0.500	4.58	0.500	4.01
	10.0	100.0				
HEC (dry)			0.600	5.51	.600	4.82
PEG (dry)			0.300	2.75	.300	2.41
			10.900	100.00		
di.-H_2O (wet mix)					1.311	10.53
PEG (wet mix)					.066	0.53
TEG (wet mix)					.175	1.41
					12.452	100.00

BATCH 3

(modified wet mix, added 10% additional wet mix)

MATERIAL	AMOUNT Inorganics kg	AMOUNT Inorganics %	AMOUNT (Dry) Components kg	AMOUNT(Dry) Components %	AMOUNT Total kg	AMOUNT Total %
Zirmul -361	8.5	85.0	10.000	91.74	10.000	71.39
Staywhite Talc	1.5	15.0	0.000	0.00	0.000	7.93
	10.0	100.0				
HEC (dry)			0.600	5.51	.600	4.76
PEG (dry)			0.300	2.75	.300	2.38
			10.900	100.00		
di.-H_2O (wet mix)					1.421	11.28
PEG (wet mix)					.071	0.56
TEG (wet mix)					.215	1.7
					12.607	100.00

Table 9 (continued)
COMPOSITION OF COMPOUNDING TRIALS
SIMPSON MULLER MIXER - RIBBON EXTRUSION PRESS

BATCH 4

(increased the amount of dry organic binder, PEG and HEC)

MATERIAL	AMOUNT Inorganics kg	AMOUNT Inorganics %	AMOUNT (Dry) Components kg	AMOUNT(Dry) Components %	AMOUNT Total kg	AMOUNT Total %
Zirmul -361	8.5	85.0	8.500	77.34	8.500	66.95
Staywhite Talc	1.5	15.0	1.500	13.65	1.500	11.81
	10.0	100.0				
HEC (dry)			0.660	6.01	.660	5.20
PEG (dry)			0.330	3.00	.330	2.60
			10.990	100.00		
di.-H_2O (wet mix)					1.421	11.20
PEG (wet mix)					.071	0.56
TEG (wet mix)					.215	1.68
					12.697	100.00

BATCH 5

MATERIAL	AMOUNT Inorganics kg	AMOUNT Inorganics %	AMOUNT (Dry) Components kg	AMOUNT(Dry) Components %	AMOUNT Total kg	AMOUNT Total %
Zirmul -361	8.0	80.0	8.000	72.79	8.000	63.01
Staywhite Talc	2.0	20.0	2.000	18.20	2.000	15.75
	10.0	100.0				
HEC (dry)			0.660	6.01	.660	5.20
PEG (dry)			0.330	3.00	.330	2.60
			10.990	100.00		
di.-H_2O (wet mix)					1.421	11.20
PEG (wet mix)					.071	0.56
TEG (wet mix)					.215	1.68
					12.697	100.00

BATCH 6

MATERIAL	AMOUNT Inorganics kg	AMOUNT Inorganics %	AMOUNT (Dry) Components kg	AMOUNT(Dry) Components %	AMOUNT Total kg	AMOUNT Total %
Zirmul -361	7.5	75.0	7.500	68.24	7.500	59.08
Staywhite Talc	2.5	25.0	2.500	22.75	2.500	19.70
	10.0	100.0				
HEC (dry)			0.660	6.01	.660	5.20
PEG (dry)			0.330	3.00	.330	2.60
			10.990	100.00		
di.-H_2O (wet mix)					1.421	11.20
PEG (wet mix)					.071	0.56
TEG (wet mix)					.215	1.68
					12.697	100.00

that the mixture was homogeneous, and had a consistency similar to GTE's MAS-8400 compounded mixture (or commercially available "plastic" modeling clay).

Extrusion trials were performed on a 2.5 in. diameter manual extrusion press. The results were used to determine the base composition for a pilot scale designed experiment planned for the production sized equipment (Eirich mixer and 200T extruder). Table 8 shows the results of the extrusion test matrix. Mixing was completed when the material formed a solid ball, or the muller (Simpson) rollers began to rock. Mixing time increases as a function of the talc added. If, after 2 minutes the components appeared to be dry, additional "wet mix" was added. Table 7 illustrates the compositional changes made during the mixing. Figure 10 summarizes the compositions made, and the results of the extrusion tests. In every case the extruded material and the dried material was of acceptable quality. One reason for the increase in the required binder levels is the increased surface area associated with increased talc concentrations.

A designed experiment was formulated with a goal to optimize the composition of the organics materials added to the Z-361/Staywhite Talc mixture . An early focus on a single composition was made based upon corrosion resistance of a series of zirconia-mullite coating placed on MAS-8400. These tests are detailed in section 2 of this report. The composition is as follows:

- 85% Zirmul - 361 (Taylor refractories)
- 15% Staywhite Talc (Cyprus Minerals)

Table 10
Extrusion Capability of Zirmul-361, Batch 1-6

Batch #	Z-361 %	Staywhite Talc %	Dry PEG %	Dry HEC %	DiH_20 %	Wet PEG %	TEG %	% Z-361 in Tot. Inorganics
1	80.31	0.00	2.41	4.82	10.52	0.53	1.41	100.
2	76.30	4.01	2.41	4.82	10.52	0.53	1.41	95.
3	71.39	7.93	2.38	4.76	11.28	0.56	1.70	90.
4	66.95	11.81	2.56	5.20	11.20	0.56	1.69	85.
5	63.01	15.75	2.56	5.20	11.20	0.56	1.69	80.
6	59.07	19.69	2.56	5.20	11.20	0.56	1.69	75.

Batch #	Z-361 %	Talc %	% Z-361 in Inorganics	Calculated SA* m^2/g	Mixing Time (m)	0.25 x 0.25 x 2 in. Bars Produced	0.050 x .625 x 4.0 in. Ribbons
1	80.31	0.00	100.	5.72	7	47	3
2	76.30	4.01	95.	5.99	9	39	3
3	71.39	7.93	90.	6.26	12	33	3
4	66.95	11.81	85.	6.53	27	25	3
5	63.01	15.75	80.	6.80	30	36	3
6	59.07	19.69	75.	7.07	32	40	2

* Rule of Mixtures

The selected experiment is a 16 run fractional factorial for 5, 6, 7, or 8 variables. Five factors (variables) were identified, they are shown (A-E) in Table 11. The selected experimental design has all variables free of two factor interactions (they are aliased with 3 factor interactions only). Randomization of the experiment was required at all levels. The following procedures were followed to established randomization:

- Run order for experiment 1-16 was randomized
- 23 batches of Z-361 were milled. Raw material were extracted from each of the 23 batches (Table 12). This eliminated the effect of milling.
- The mixer was completely cleaned between runs, and 20 kg of a milled 30 kg batch of Z-361 (identical to that shown in Table 10) was blended at high speed for three minutes (to pre-coat the internal drum).
- The extruder was run at 60T. One hundred inches of material was extruded prior to making any adjustments in the die restrictions. Measurements were made on the best (flattest, tear free) 48 in. of subsequent extrusion produced.

The surface area of the designed experiment mixture is calculated (via rule of mixtures) as follows:

- Measured surface area of milled Z-361 blend .....5.60 m^2/g
- Measured surface area Staywhite Talc .....11.12 m^2/g
- % Z-361 blend in extrusion mix .....85 %
- % Staywhite Talc in extrusion mix .....15 %
- Calculated surface area of extrusion mix .....6.428 m^2/g

Results of the designed experiment are listed in Table 11. The shrinkage data reported reflects large variations in measurement capability, and is therefore, not considered reliable. The compliant nature of the extruded sheet made accurate measurement impossible with the instruments selected (calipers and micrometer). If these experiments were repeated, a profile metering device would be useful. The negative shrinkages reported result when material swells after it passes through the die cavity. Negative shrinkages may also the result of poor measurement techniques. The only response evaluated statistically was Extrusion Quality Factor (goodness). No single factor or 2 factor interactions were found to be significant at the 95% confidence level. Variable C was found to be a significant negative effect at the 90% confidence level. Decreasing the amount of di-H_2O increases extrudability (most rejects were found to be too wet). Variable C was aliased with three level interactions only, (their occurrence are considered unlikely, statistically). Experiments 9 and 10 and 3 (in descending quality order) exhibited the best extrusion characteristics.

Table 11
Compounding / Extrusion Designed Experiment
16 Experiment Fractional Factorial with 5 Variables

Variable #	Variable Description	Lo Level %	Lo Level kg	High Level %	High Level kg	Nominal %	Nominal kg
A	di-H_2O	90%	3.892	110%	4.757	100	4.325
B	Dry PEG	90%	0.826	110%	1.000	100	0.913
C	Wet PEG	90%	0.193	110%	0.236	100	0.2145
D	TEG	90%	0.549	110%	0.671	100	0.610
E	Dry HEC	90%	1.652	110%	2.019	100	1.836

Design Matrix

Experiment	A	B	C	D	E
1	-	-	-	+	+
2	+	-	-	-	-
3	-	+	-	-	+
4	+	+	-	+	-
5	-	-	+	+	-
6	+	-	+	-	+
7	-	+	+	-	-
8	+	+	+	+	+
9	+	+	+	-	-
10	-	+	+	+	+
11	+	-	+	+	-
12	-	-	+	-	+
13	+	+	-	-	+
14	-	+	-	+	-
15	+	-	-	+	+
16	-	-	-	-	-

Example of Batch Compositions (Extracted from design matrix)

Variable Name	Material Description	Batch 1 kg	Batch 1 %	Batch 8 kg	Batch 8 %	Batch 16 kg	Batch 16 %
	Z-361	23.654	66.73	23.654	64.74	23.654	67.66
	Staywhite Talc	4.192	11.83	4.192	11.47	4.192	11.99
E	Dry HEC	2.019	5.70	2.019	5.53	1.652	4.73
B	Dry PEG	0.826	2.33	1.000	2.76	0.826	2.36
A	di-H_2O	3.892	10.98	4.757	13.02	3.892	11.13
C	Wet PEG	0.193	0.54	0.236	0.65	0.193	0.55
D	TEG	0.671	1.89	0.671	1.84	0.549	1.57
		35.477	100.00	36.538	100.00	34.958	100.00

Table 11 (continued)
Compounding / Extrusion Designed Experiment
16 Experiment Fractional Factorial with 5 Variables

Aliases

Variable #	Nominal Description	Factor kg	Aliases
A	di-H_2O	4.325	3-Factor only
B	Dry PEG	0.913	3-Factor only
C	Wet PEG	0.2145	3-Factor only
D	TEG	0.610	3-Factor only
E	Dry HEC	1.836	3-Factor only

Responses Measured

RESPONSE	MEASURE
%SHRINKAGE: RIB WIDTH	EXTRUDED RIB WIDTH & DRY RIB WIDTH
%SHRINKAGE: THICKNESS	DIE GAP FOR SHEET & DRY THICKNESS
%SHRINKAGE:LENGTH	CUT LENGTH AND SHRINKAGE LENGTH
EXTRUDABILITY	QUALITATIVE MEASURE (1=GOOD, 5=POOR)

2.2.4 Binder Removal and Sintering of Z-1000

Extruded samples (sheets) were cut, air dried, oven dried and stacked as described in 2.2.1 (steps 15-20). Dried sheets were measured (shrinkages were recorded in Table 13). Extruded sheets from test 3, 9, and 10 were placed into a standard MAS-8400 binder fire / sintering / annealing (process step #24 in section 2.2.1) and processed along side of a 600 pound load of production ceramic recuperator matrix elements. The sintering cycle called for a final temperature of 2525°F, a temperature well below that required to fully react the Inorganic materials. No cracking was observed on the sintered sheets. Those sheets stacked in contact with and normal to one another showed evidence of bonding to each other, despite the fact that no additional inorganic material was placed at the interface. Shrinkage of the presintered material was measured in the 12-13% range. Individual sheets and bonded matrix sections (4-6 plate-fin sections high) were then divided into three groups. Three sintering runs were then run to temperatures of 2642, 2777, and 2912°F (1450, 1525, and 1600°C). Ramp rates were 90 F°/h to the soak temperature, and the soak temperature was held for 4 hours. Programmed cooling rates were 100 F°/h to room temperature (however actual cooling rates were much slower below 800°F). Visual inspection showed that regardless of sintering temperature, no cracking was evident.

Table 12

SWECO MILLING OF 23 BATCHES OF Z-361

20.45 kg MILLED FOR 40 HR WITH ALUMINA MEDIA
Model DM-10: Angle = 30 degrees, 3 bottom plates, 2 top plates
360 kg of 1/2 in. 99.5 % Alumina Capped Cylinders (18:1 media:charge)

MILLING BATCH # 207-42-	SURFACE AREA BET (m^2/g)	BULK DENSITY (g/cm^3)	SEDIGRAPH MEAN (µm)	SEDIGRAPH MEDIAN (µm)	WEIGHT DISCHARGED (kg)	% of TOTAL WEIGHT	WEIGHT ADDED (kg)	WEIGHT ADDED %
A	5.35	0.988	2.600	1.883	15.880	3.334%	-4.570	-22.35%
B	5.41	0.930	2.681	1.976	23.700	4.976%	3.250	15.89%
C	5.23	0.897	2.632	1.915	23.700	4.976%	3.250	15.89%
D	5.70	0.914	2.580	1.894	20.460	4.295%	0.010	0.05%
E	5.69	0.937	2.691	2.061	21.000	4.409%	0.550	2.69%
F	5.54	0.914	2.555	1.957	20.645	4.334%	0.195	0.95%
G	5.54	0.914	2.510	1.909	20.100	4.220%	-0.350	-1.71%
H	5.75	0.981	2.585	1.929	21.100	4.430%	0.650	3.18%
I	5.39	0.960	2.561	2.000	20.500	4.304%	0.050	0.24%
J	5.54	0.957	2.492	1.949	20.600	4.325%	0.150	0.73%
K	5.93	1.097	2.469	1.897	18.700	3.926%	-1.750	-8.56%
L	5.83	1.052	2.460	1.900	22.600	4.745%	2.150	10.51%
M	5.64	1.053	2.492	1.949	20.500	4.304%	0.050	0.24%
N	5.97	1.063	2.646	2.000	21.500	4.514%	1.050	5.13%
O	5.82	1.012	2.606	1.953	20.600	4.325%	0.150	0.73%
P	5.95	1.045	2.604	2.000	20.400	4.283%	-0.050	-0.24%
Q	5.90	1.008	2.746	2.133	20.400	4.283%	-0.050	-0.24%
R	5.81	1.079	2.683	2.000	20.900	4.388%	0.450	2.20%
S	5.73	1.108	2.601	2.000	20.750	4.356%	0.300	1.47%
T	5.77	0.940	2.643	2.063	19.850	4.167%	-0.600	-2.93%
U	5.67	0.936	2.798	2.187	21.300	4.472%	0.850	4.16%
V	4.56	0.895	2.777	2.235	20.670	4.339%	0.220	1.08%
W	5.00	1.020	3.499	2.563	20.470	4.297%	0.020	0.10%
MEAN (a-w)	**5.60**	**0.987**	**2.648**	**2.015**	**476.325**	**100.00%**	**5.975**	**29.22%**
Weighted Mean	**5.60**	**0.986**	**2.649**	**2.016**				

Table 13

RESULTS OF 16 EXPERIMENT FRACTIONAL FACTORIAL DESIGNED EXPERIMENT FOR 5 VARIABLES

COMPOUNDING AND EXTRUSION STUDY
Extrusion Quality Factor: 1=Good, 5 = Poor
(All results are the average of 2 measurements)

LOT # 207-42 BATCH #	RIB WIDTH EXTRUDED in.	RIB WIDTH DRY in.	RIB WIDTH SHRINKAGE %	THICKNESS EXTRUDED in.	THICKNESS DRY in.	THICKNESS SHRINKAGE %	LENGTH DRY in.	SHRINKAGE LENGTH %	Extrusion Quality Factor
1	0.179	0.176	1.67%	0.081	0.079	2.44%	12.210	5.86%	4.5
2	0.172	0.169	1.73%	0.076	0.087	-14.52%	12.294	5.21%	4.75
3	0.178	0.183	-3.10%	0.082	0.078	4.07%	12.245	5.59%	2
4	0.177	0.175	0.85%	0.082	0.083	-0.62%	12.380	4.55%	4.75
5	0.184	0.202	-9.80%	0.089	0.092	-3.95%	12.320	5.01%	4
6	0.184	0.187	-1.36%	0.081	0.086	-6.15%	12.203	5.92%	3
7	0.182	0.186	-2.48%	0.088	0.089	-1.11%	12.388	4.49%	2.5
8	0.178	0.180	-1.45%	0.082	0.082	-0.05%	12.225	5.75%	2.5
9	0.180	0.170	5.54%	0.081	0.095	-18.05%	12.355	4.74%	1
10	0.181	0.187	-3.33%	0.085	0.088	-4.15%	12.368	4.65%	1.5
11	0.162	0.159	2.09%	0.071	0.065	9.65%	12.193	6.00%	4.5
12	0.176	0.178	-1.14%	0.075	0.084	-11.17%	12.167	6.20%	2.5
13	0.187	0.188	-0.27%	0.079	0.080	-1.28%	12.195	5.98%	5
14	0.171	0.171	0.28%	0.069	0.070	-0.74%	12.260	5.48%	3.5
15	0.188	0.180	3.99%	0.077	0.078	-0.66%	12.136	6.43%	3.5
16	0.184	0.183	0.82%	0.083	0.083	0.61%	12.398	4.41%	2.5

2.2.4 Physical Properties of Z-1000

Thermal expansion, flexural strength (transverse rupture), and porosity (via mercury porosimeter) was measured for the material sintered at 2777°F as shown in Table 14. A micrograph of the material is shown in Figure 16.

Table 14

Properties of Z-1000 (85% milled Zirmul-361, 15% Talc)
Sintered at 2777°F.

Thermal Expansion	**4.8×10^{-6}/ °F (RT - 800°F)**		
Modules of Rupture (4 pt.)	**24.4 Ksi (σ = 4.2)**		
Porosity	**16 %**	**(range .003-180μm)**	
		90 % <	**180. μm**
		80 % <	**40. μm**
		75% <	**.02 μm**
		50% <	**.015 μm**
		10 % <	**.01 μm**
Phase Content	**Major**	**Al_2O_3**	**Corundum**
	Major	**$Al_6Si_2O_{13}$**	**Mullite**
	Minor	**$ZrSiO_4$**	**Zircon**
	Minor	**ZrO_2**	**Baddeleyite**

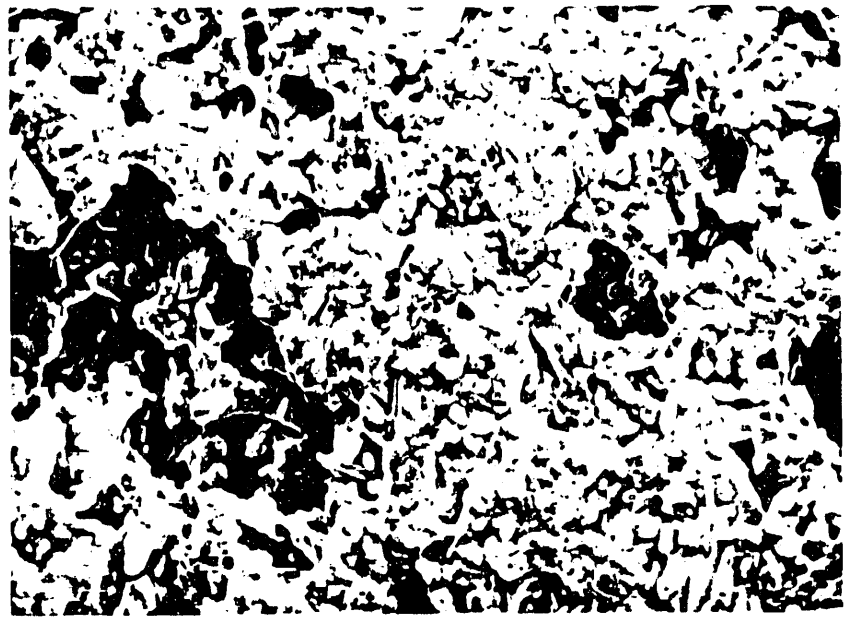


Figure 16

Micrograph of Z-1000 (85% milled Zirmul-361, 15% Talc)
Sintered at 2777°F, 1000x

Strength measurements (modulus of rupure) were performed using 4 point loading with inner and outer loading spans of 0.4 in. (10.16 mm) and 0.9 in. (22.86 mm) respectively. Load was applied using " knife edges" in the form of cylindrical rods 0.25 in. (6.35 mm) in diameter made from hot pressed SiC. The self aligning fixture used for testing is illustrated in Figure 17. A schematic of the loading arrangement is shown in Figure 18. The test specimens used were rectangular bars of length 1.2 +/- 0.05 in. (30.5mm), width 0.1 +/- 0.0005 in. (2.54mm), and thickness 0.05 +/- 0.0005 in. (1.27mm). Opposing faces of the bars were ground flat and parallel within 0.005 in. and were chamfered 0.006 +/- 0.002 in. at 45° as illustrated in Figure 19. Testing was performed using a Tinius Olsen universal testing machine with DS-30 computer control. Test samples were aligned in the fixture and then were loaded to failure at a crosshead speed of 0.05 in./minute. Modulus of rupture was calculated from the following expression;

$$S_{mor} = 1.5\, L\, (J-I) / (w\, t^2)$$

where

S_{mor} = Maximum outer fiber tensile stress of test specimen at fracture (psi)
L = Load at fracture (pounds)
J = Outer loading span (in.)
I = Inner loading span (in.)
w = Width of bar (in.)
t = Thickness of bar (in.)

The modulus of rupture was measured for 10 samples. A mean fracture strength of 24.4 ksi (σ = 4.2) was calculated. The data was not considered reliable due to the distributed porosity identified in the microstructural analysis. By comparison MAS-8400 has a strength of 8.5 Ksi. The sample number was considered too small to include Weibull statistics, as n>25 are generally required for this measure. The large standard deviation is typical of a material with a large pore fraction, and has been observed in data obtained from other compositions fabricated with this binder system. The distributed porosity is not considered detrimental for this application, in that it has been shown to increase the thermal shock resistance (TSR), despite its obvious negative impact on fracture strength. One explanation for this observation may be that the distributed porosity also decreases the elastic modulus (which would increase TSR). A dry press and sinter fabrication technique that yielded a part with negligible porosity would be required to determine the "intrinsic" strength of this material. No attempt was made to determine the strength of a "fully dense" Zirmul-361:Talc (85:15) blend.

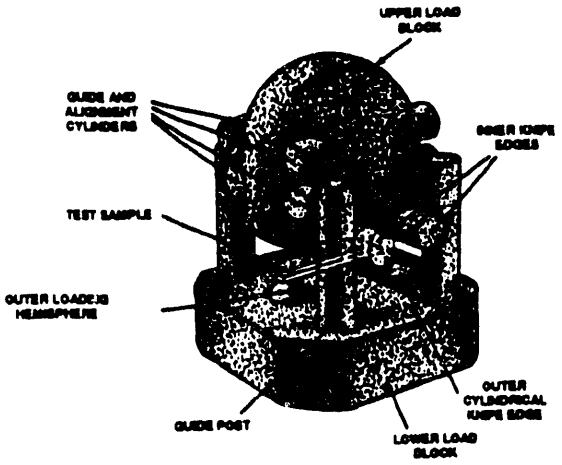


Figure 17
Modulus of Rupture Loading Fixture

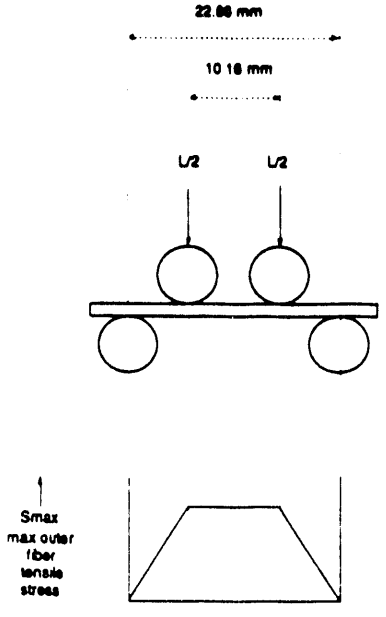


Figure 18
Four Point Bend Test Loading Arrangement

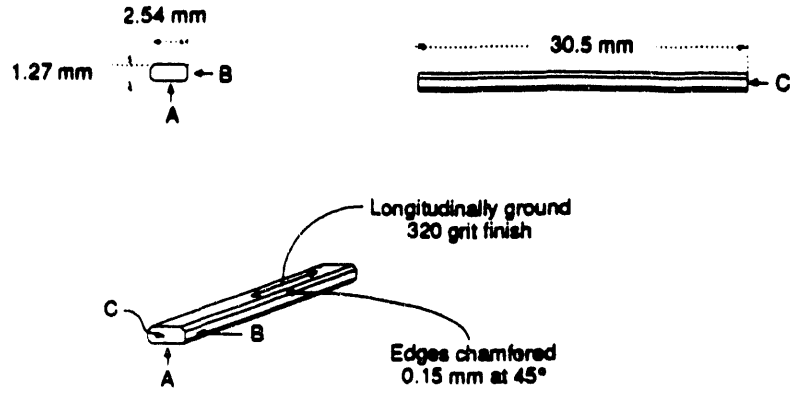


Figure 19
Modulus of Rupture Test Specimen

Phase content of the sintered Zirmul-361:Talc (85:15) material was determined for samples fired at 2642, 2777, and 2912°F. No differences in the phases present were observed, with the exception of the presence of an unidentified phase found only in the material sintered at 2642°F. This is probably a remnant of the talc raw material. The diffraction patterns were done on a Rigaku (USA Inc.) Model D/Max Geigerflex. Phase identification and data reduction was done with the aid of the Rigaku "Peak Finding and Search/Match" software programs run on a DEC PDP-11/23 plus computer. The data base of reference diffraction patterns of the JCPDS - International Center for Diffraction Data was searched. The following phases were identified:

- Al_2O_3 Corundum PDF#10-173* 25.6° = major peak
- $Al_6Si_2O_{13}$ Mullite PDF#15-776 26.3° = major peak
- $ZrSiO_4$ Zircon PDF#6-266 27.0° = major peak
- ZrO_2 Baddeleyite PDF#36-420 28.3° = major peak
- unknown a peak was found @ 19° that is unidentified (2642°F sinter only)
- SiO_2 or ZrO_2 a peak was found @ 30.2° that may be either

The diffraction patterns are shown in Figure 20.

* Powder Diffraction File # (PDF#)

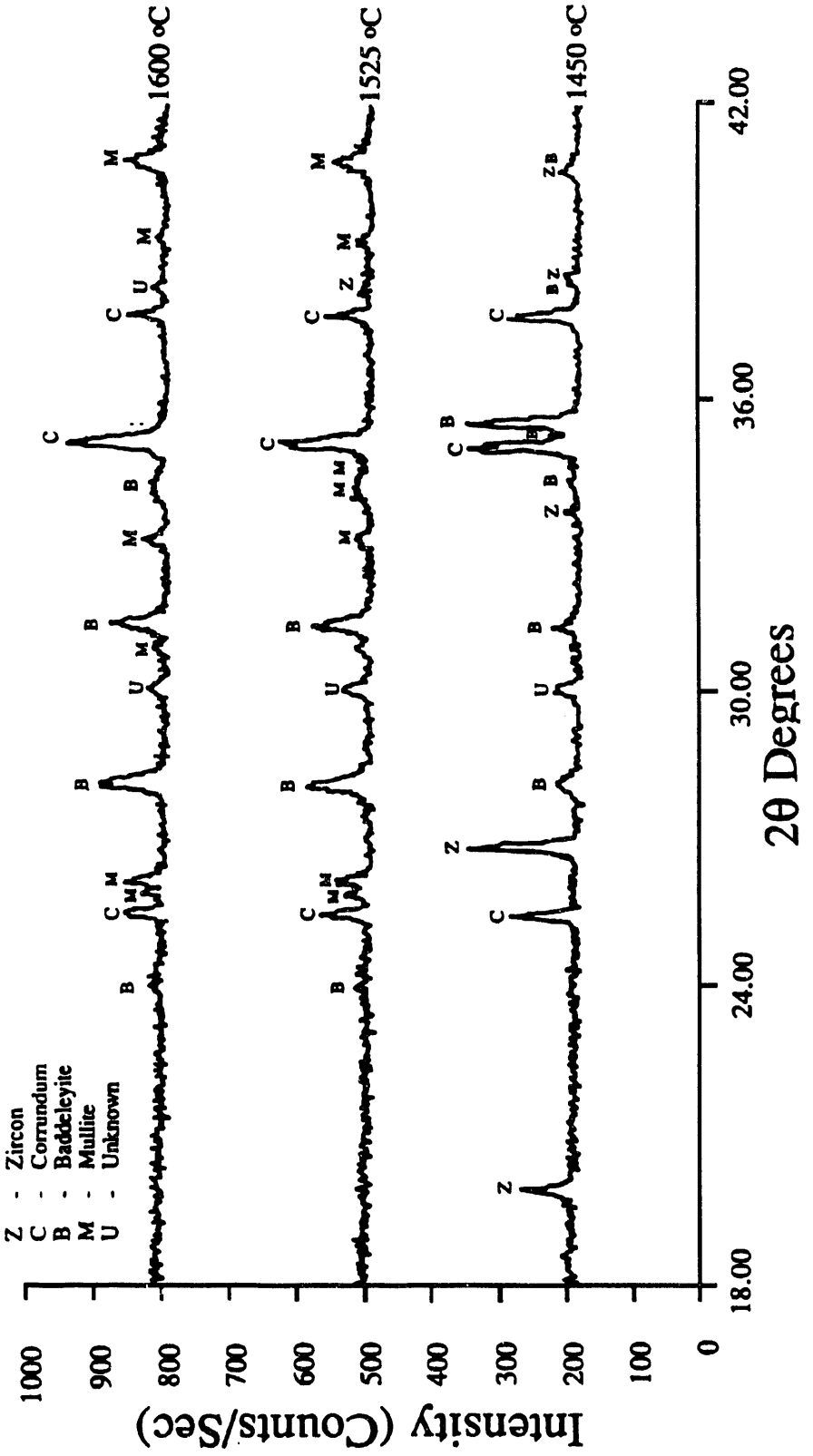


Figure 20
X-Ray Diffraction Patterns of Zirmul-361:Talc (85:15)
Sintered @ 2642, 2777, and 2912°F

2.2.5 Crossflow Recuperator Design for Z-1000 Material

Figure 21 illustrates the anticipated design of a recuperator incorporating a Z-1000 matrix. The low thermal shock resistance of Z-1000 (compared to MAS-8400) necessitates the reduction (minimization) of thermal stresses across the ceramic. The preheated air is counter-flowed with respect to the exhaust gas flow. A design that calls for preheat air temperatures to increase dramatically in the first two passes is anticipated. Surface area (small cell size) and passage free flow area will be selected to maximize differential temperatures between the exhaust gas and the preheated air temperature in pass 1 and 2, and minimize differential temperatures in the third pass. Exhaust gases exiting the third pass (Z-1000) module can mix prior to entry into the MAS-8400 matrix. The design concept shown in the figure has been demonstrated with sectioned MAS-8400 recuperators, and offers merit for use in GTE's standard product, as thermal stresses on a single matrix are extreme during transient conditions found in many industrial applications (when a furnace door opens a matrix cools rapidly, as exhaust gas flow rates drop by 50-90%, when the door closes it is stressed again until equilibrium conditions return). No attempt to develop the technology necessary to bond crossflow sheets (plate-fin) together was made during this contract effort. Therefore the aforementioned design has not been tested with Z-1000. Additionally, the corrosion resistance of a monolithic sample has not been evaluated on the GTE test stand, or in the field.

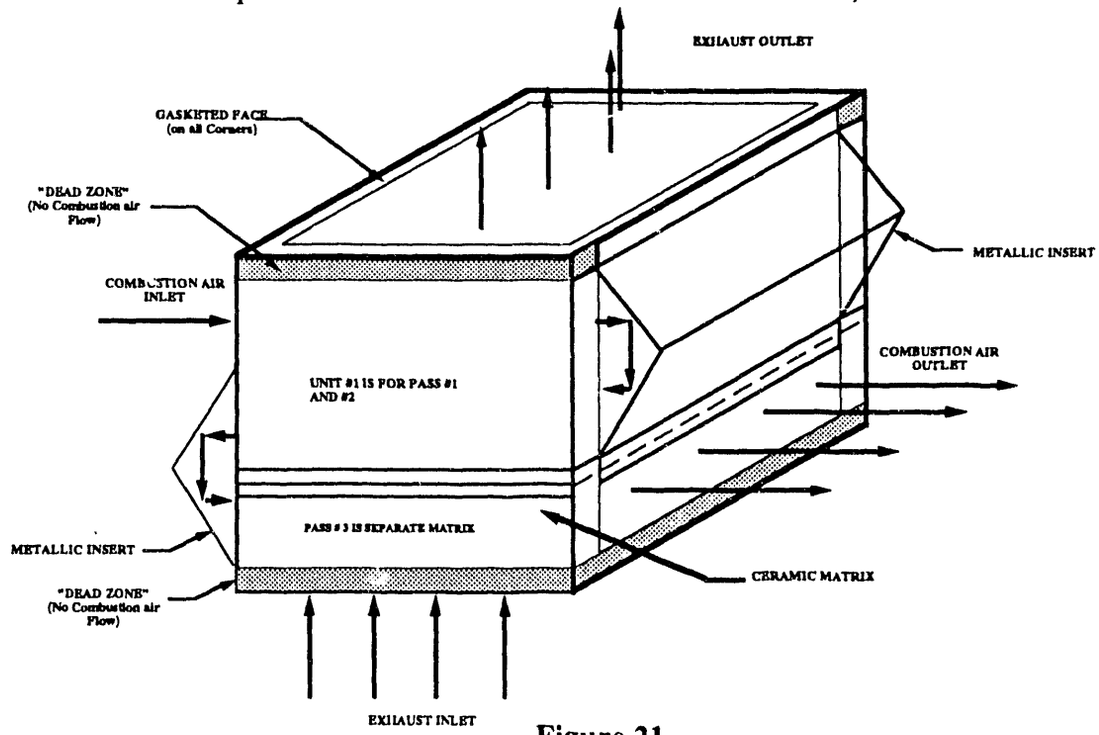


Figure 21

Segmented Recuperator Design for a Z-1000 Ceramic Matrix

3. CONCLUSIONS

The following conclusions can be drawn from the contract effort:

- A GTE Model R1500 recuperator was exposed to sufficient NaOH at elevated temperature to destroy it in 6 h. An analysis of the unit determined its mode of failure was identical to a recuperator that failed from long term alkali attack. This attack was duplicated on a recuperator corrosion test stand fabricated at GTE. The recuperator test stand could expose up to 3 small test samples (3 x 3 x 3 in.) to contaminants.
- A corrosion resistance test method has been established that enables a potential ceramic material to be screened for resistance to high temperature attack (2450°F) of alkali's and lead. The test requires that the test material adhere to MAS-8400 (cordierite).
- A zirconia-mullite mixed oxide ceramic was found to resist alkali attack during a 6 h exposure to PbO and NaOH @2450°F. The same test melted a MAS-8400 substrate. The best protection was afforded by a sintered composition manufactured with 85% Zirmul-361 and 15% Staywhite Talc. The Z-361 was milled in Al_2O_3 to obtain a surface area of approximately 5.5 m^2/g. The mixture was fired to 2777°F, then applied to a MAS-8400 substrate and fired to 2500°F.
- Thin coatings of materials to be evaluated were found to be least likely to spall off during a test.
- A process capable of manufacturing thin wall (plate-fin) shapes of Z-1000 (zirconia-mullite mixed oxide) was developed. The methodology used to develop the process was the bench-marking of the MAS-8400 recuperator matrix production process.
- Plate fin shapes were successfully dewaxed and sintered to three temperatures (2642, 2777, and 2912°F). Phases present were determined. Strength, of the material was 24.4 ksi. Porosity is in the 13.5 % range. Major phases identified include mullite, zircon, baddeleyite, and corundum.
- A ceramic recuperator can be manufactured with a segregated matrix. The corrosion resistant portion can be placed in an area that requires corrosion resistance, but minimizes the need for thermal shock resistance. This design concept was successfully tested by GTE (GTE funded).
- The encouraging performance of the Z-1000 indicates that the technology necessary to manufacture a crossflow matrix should be developed.

- A matrix of Z-1000 should be manufactured and tested on the corrosion test stand, GTE's recuperator test furnace and then field tested.

4. REFERENCES

1. Cleveland J.J., et al, Ceramic Heat Recuperators for Industrial Heat Recovery, Final Report , No. DOE/EC/02162, August 1980.

2. Dorazio, R.E., et al, The GTE Ceramic Recuperator for High Temperature Waste Heat Recovery, 1984 Industrial Energy Conservation Technology Conference, Houston, TX, April 15-18, 1984.

3. Gonzalez, J.M., Ferri, J.L., and Rebello,W.J., Industrial Operating Experienceof the GTE Ceramic Recuperator, Final Report, ORNL/Sub/86-22044, June 1990.

4. Ally, M.R., et al, Optimization of Multi-pass Crossflow Heat Exchangers for Waste Heat Recovery Applications, 1984 National Heat Transfer Conference, Niagara Falls, N.Y., August 5-8, 1984.

5. Ferri, J.L., Temperature Compensated Air/Fuel Ratio Control on a Recuperated Furnace, 1983 Industrial Energy Conservation Technology Conference, Houston, TX, April 17-26, 1983.

6. Gonzalez J.M., and W. J. Rebello, Furnace Controls using High Temperature Preheated Combustion Air, 1981 Industrial Energy Conservation Technology Conference, Houston, TX, April 26-29, 1981.

7. Dorazio, R. E., et al, Technology Acceleration Program for the GTE Ceramic High Temperature Recuperator , Final Report, Contract No. DE-FC01-80CS 40330, January 1983.

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