184
3-6-78
UC-96

Lh. 1883

CONS/9698-1
NASA CR-135292

IMPROVED CERAMIC HEAT EXCHANGER MATERIAL

H.W.Rauch, Sr.
GENERAL ELECTRIC COMPANY
Philadelphia, Pennsylvania

MASTER

NOVEMBER 1977

Prepared for the
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
Lewis Research Center
Cleveland, Ohio 44135

Contract NAS 3-19698

As a part of the
DEPARTMENT OF ENERGY
Division of Transportation Energy Conservation
Heat Engine Highway Vehicle Systems Program

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

NOTICE

This report was prepared to document work sponsored by the United States Government. Neither the United States nor its agent, the United States Energy Research and Development Administration, nor any Federal employees, nor any of their contractors, subcontractors or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

1. Report No. NASA CR-135292	2. Government Accession No.	3. Recipient's Catalog No.
4. Title and Subtitle IMPROVED CERAMIC HEAT EXCHANGER MATERIALS		5. Report Date November 1977 6. Performing Organization Code
7. Author(s) H. W. Rauch, Sr.		8. Performing Organization Report No.
9. Performing Organization Name and Address General Electric Company P. O. Box 8555 Philadelphia, Pa. 19101		10. Work Unit No. 11. Contract or Grant No. NAS3-19698
12. Sponsoring Agency Name and Address Department of Energy Division of Transportation Energy Conservation Washington, D. C. 20545		13. Type of Report and Period Covered Contractor Report 14. Sponsoring Agency Code CONS/9698-1

15. Supplementary Notes

Interim Report. Prepared under Interagency Agreement EC-77-A-31-1011
Project Manager, Dr. Thomas P. Herbell, Materials and Structures Division,
NASA Lewis Research Center, Cleveland, Ohio 44135

16. Abstract

Various ceramic materials in the form of small, monolithic bars were screened as candidate materials in heat exchanger structures for automotive gas turbine engines. The material finally selected consists of 60 w/o* petalite (LAS) and 40 w/o of a recrystallizable glass which converts during thermal processing to cordierite (MAS). This new material, GE-3200, was fabricated by Coors Porcelain Company into a circular honeycomb structure 53.3 cm diameter and 10.2 cm thick (21" x 4") and having 69.8 holes/cm^2 (450 holes/in^2) of rectangular geometry. Dimensions of each cell are about 2.5 mm x 0.5 mm (0.1" x 0.02") with wall thicknesses about 0.20 mm (0.008").

Small bar-shaped specimens of the honeycomb were used to measure thermal, chemical, and mechanical properties and for macro- and microstructure examination. Cylindrical honeycomb specimens about 15.2 cm diameter and 10.2 in. thick (6" x 4") were sent to Ford Motor Company and are currently being tested in a gas turbine engine.

Data obtained from testing the bar-shaped honeycomb specimens of GE-3200 and from testing bar-shaped honeycomb specimens of Corning 9455 were compared. Results indicate that GE-3200 has significantly better resistance to sulfuric acid and to sodium chloride than Corning 9455; thermal expansion of GE-3200 is higher than that of Corning 9455 ($1.7 \times 10^{-6}/^{\circ}C$ vs. $0.65 \times 10^{-6}/^{\circ}C$ over the temperature range 25°C - 1000°C); mechanical properties of GE-3200 are higher in the tangential direction, but lower in the radial direction than Corning 9455; and during thermal cycling between R.T. 1000°C and R.T. - 1100°C, GE-3200 tends to elongate while Corning 9455 tends to slightly contract.

Overall assessment of GE-3200 properties, ease of material preparation, ready adaptability to honeycomb fabrication, and refractoriness qualify this new material as a candidate for heat exchanger application in automotive gas turbine engines.

* Weight percent

17. Key Words (Suggested by Author(s)) Ceramics, Thermal, Mechanical, Chemical Properties Lithium Aluminosilicates (LAS) Magnesium Aluminosilicates (MAS) Honeycomb Structures Heat Exchangers, Gas Turbine Engines	18. Distribution Statement

19. Security Classif. (of this report) UNCLASSIFIED	20. Security Classif. (of this page) UNCLASSIFIED	21. No. of Pages 35	22. Price* A03

* For sale by the National Technical Information Service, Springfield, Virginia 22161

NASA-C-168 (Rev. 10-75)

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

TABLE OF CONTENTS

Section — Page

Summary 1

Introduction 2

Materials Development 4

Materials Testing and Results 6

Corrosion Resistance 9

Mechanical Properties 10

Porosity and Microstructure 11

Discussion of Results 12

Conclusions 14

References 15

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

LIST OF ILLUSTRATIONS

Figure		Page
1	Particle Size Distribution of Petalite and 266M as Received and of Two Different Batches of Milled GE-3200	16
2	Cross-Section of GE-3200 Honeycomb from Wheel Fired at 1100°C (2012°F) by Fabricator, Coors Porcelain Company	17
3	Cross-Section of GE-3200 Honeycomb from Wheel Fired at 1100°C (2012°F) by Fabricator, Then Fired at 1260°C (2300°F) by GE	17
4	Thermal Expansion Behavior of Fusion Sintered Monolithic GE-3200 and Corning 9454	18
5	Thermal Expansion of Monolithic GE-3200 Fired Under Different Conditions of Time at Temperatures Below Fusion	19
6	Typical Thermal Expansion Behavior of Monolithic and Honeycomb GE-3200	20
7	The Effect of Thermal Cycling on the Coefficient of Linear Thermal Expansion of GE-3200 Honeycomb	20
8	Effect of Corrosion Testing on Thermal Expansion of GE-3200 Honeycomb	21
9	X-ray Diffraction Patterns of Monolithic GE-3200 Before (Upper) and After (Lower) Ten Hour Exposure to 1100°C	22
10	X-ray Diffraction Patterns of Corning 9454 Before (Upper) and After (Lower) Ten Hour Exposure to 1100°C	23
11	The Effect of Thermal Cycling on Length Stability of Monolithic GE-3200 and Corning 9454	24
12	The Effect of Thermal Cycling on Length Stability of GE-3200 Honeycomb	24
13	The Effect of Molten Sea Salt (Sodium) and Sulfuric Acid on Monolithic Specimens of Candidate Heat Exchanger Materials	25
14	The Resistance to 1% Sulfuric Acid of GE-3200 and Corning 9455 Honeycomb	26
15	The Resistance to Boiling 3.43% Sodium Chloride Solution of GE-3200 and Corning 9455 Honeycomb	26
16	Schematic of a Circular Honeycomb Structure Showing Required Orientation of Mechanical Test Specimens	27
17	Microstructure of GE-3200 and Corning 9455 Honeycomb Before and After Corrosion Testing in Boiling 3.43% Sodium Chloride Solution (Mag. 1,000 X, Specimens Etched with 10% H.F.	28

LIST OF TABLES

Table		Page
I	Composition of Sea Salt Used to Evaluate Monolithic Specimens for Sodium Resistance	29
II	Mechanical Properties of GE-3200 and Corning 9454/9455 Monolithic and Honeycomb Material	29
III	Porosimetry Data for GE-3200 Honeycomb Specimens Fired at Various Temperatures	30
IV	Oxide Composition in Weight Percent of Individual and Mixed Raw Materials and of Various Fired GE-3200 Specimens	30

SUMMARY

The objective of this program was to develop a material suitable for heat exchanger applications in automotive gas turbine engines. The material had to be fabricable in honeycomb form and had to have low thermal expansion, be resistant to sulfuric acid and sodium, be thermally stable both structurally and dimensionally for long times at 1000°C (1832°F) and for short excursions to 1100°C (2012°F), and have sufficient mechanical integrity to withstand the tangential and radial loads encountered in gas turbine engine useage.

Several materials, including aluminum titanate, iron aluminum titanate, mixtures of these materials with cordierite, and several recrystallizable glasses, were evaluated and rejected because their thermal expansion behavior was undesirable. The material selected for further development is a combination of petalite (LAS) and a powdered glass which recrystallizes to cordierite (MAS). This new material, GE-3200, is made by ball milling 60 w/o of the LAS phase with 40 w/o of MAS phase, forming the material by an extrusion/embossing method into a honeycomb structure and firing to 1260°C (2300°F). The fired material, essentially beta spodumene and alpha cordierite, was comparatively tested against Corning 9455, which is an LAS honeycomb material. Testing included thermal expansion measurements from ambient to 1000°C (1832°F), cyclic immersion in sulfuric acid followed by heating at 300°C (572°F), immersion in boiling sodium chloride solution followed by heating at 800°C (1472°F) for 21 days, cycling at 1100°C (2012°F) for one hour intervals up to ten hours, cycling at 1000°C (1832°F) in seven minute intervals for 5000 cycles, measurement of modulus of rupture and flexure modulus, and determination of porosity and microstructure.

The results obtained indicate that:

1. GE-3200 is significantly more resistant to sulfuric acid and sodium chloride than Corning 9455
2. GE-3200 is stronger tangentially, but weaker radially than Corning 9455.
3. The coefficient of thermal expansion over the temperature range 25°C-1000°C (77°F-1832°F), of GE-3200 is $1.7 \times 10^{-6}/^{\circ}C$ compared to $0.65 \times 10^{-6}/^{\circ}C$ for Corning 9455.
4. During thermal cycling from ambient to 1000°C (1832°F) and ambient to 1100°C (2012°F), GE-3200 tends to elongate and Corning 9455 tends to contract slightly.

In addition to these comparative test data, our overall assessment of GE-3200 includes comments from the honeycomb fabricator, Coors Porcelain Company. Coors personnel indicated that this new material is more slump resistant and contains less residual stress after firing than the MAS materials they had previously fabricated into honeycomb structures. Together with the good corrosion resistance and mechanical properties, and the relatively low thermal expansion, the acknowledged ease of fabrication and availability of materials should qualify GE-3200 as a candidate material for heat exchanger applications in automotive gas turbine engines.

INTRODUCTION

Automobile manufacturers have been interested in ceramics for vehicular gas turbine engines since the early 1950's, and the availability of low expansion glass-ceramics about a decade later intensified that interest. Today, the demand for greater efficiency through higher operating temperatures, along with low cost more available materials has given even more impetus to the use of ceramics in automotive gas turbine engines.

During the past five years, about half a dozen ceramic manufacturers and several automobile manufacturers have been developing materials and processes suitable for the fabrication of ceramic honeycomb structure for use as heat exchangers. The materials, of current interest, (none of which is without certain limitations) are lithium aluminosilicates (LAS), magnesium aluminosilicates (MAS), an acid-leached and heat-treated lithium aluminosilicate (AS), and combinations of LAS/MAS. Some of these materials are processed by conventional glass-ceramic techniques; some are prepared by heat-treating initimately mixed mineral combinations; and, some utilize portions of each technology.

The three primary fabricating processes for making honeycomb structures are corrugating, extrusion-embossing (calendering), and extrusion. The first method, uses paper which has been impregnated with ceramic powder to form a structure similar to corrugated cardboard. Embossing consists of drawing a thin ceramic film onto a plastic substrate or extruding a thin ceramic tape into which a subsequent treatment impresses spaced ridges which act as separators between concentric tape layers thus forming the cellular structure common to honeycomb materials. When the ceramic film is extruded by itself and later embossed, the process is also known as calendering. The third method is one in which a ceramic powder is forced through a die to immediately form a honeycomb structure. The first two methods can produce circular shapes typically in diameters of 71.1 cm (28 in) and 10.2 cm (4 in) thick, while extrusion is limited to smaller sizes which can be bonded together to form larger shapes.

Another technique, which is still in the development stage, utilizes recrystallizable glass tubing of very small diameter. Short lengths of tubing are packed into a circular arrangement which self-bonds during the heat treatment cycle to convert the tubing into a glass-ceramic and forms an in situ honeycomb structure.

The lack of corrosion resistance exhibited by LAS materials and the relatively high thermal expansion of MAS materials are serious disadvantages. The relatively new AS material represents a major improvement in corrosion resistance while retaining the low expansion of the parent LAS, but its limitation to operating temperatures between 800°C (1472°F) and 1000°C (1832°F) is undesirable. The LAS/MAS combinations investigated during this program exhibited good corrosion, mechanical, and refractory properties depending on the LAS:MAS ratio but they all have higher thermal expansion than either the LAS or AS materials.

The present work was aimed at developing a material which would be chemically and thermally stable during long-term exposure to 1000°C (1832°F) with the ability to survive short excursions to 1100°C (2012°F). In addition, the material must have a low coefficient of thermal expansion between ambient and 1000°C (1832°F). Progress toward these goals was determined by comparing the developed materials with Corning LAS 9454 (monolithic) and Corning LAS 9455 (honeycomb).

The initial approach was to prepare melts consisting of MgO, Al_2O_3, SiO_2 and TiO_2 and processing the resulting glasses by appropriate heat treatment to obtain glass-ceramics consisting essentially of cordierite and aluminum titanate (AT). The absence of microstructures conducive to low thermal expansion in these materials prompted the study of combinations of MAS and other materials which could provide anisotropic second phases. Aluminum titanate and iron aluminum titanate were utilized for this prupose, but large and unpredictable thermal hysteresis effects shifted the program focus to LAS/MAS mixtures. It is from this combination that a material has been developed which appears to have potential for service in automotive gas turbine engine heat exchangers.

MATERIALS DEVELOPMENT

An LMAS material consisting of 60 w/o petalite and 40 w/o of a thermally crystallizable glass has been developed for heat exchanger applications in automotive gas turbine engines. This new material, designated as GE-3200, was selected over other LAS/MAS combinations because of its corrosion resistance, good mechanical properties, and low thermal expansion. During the program, other materials combinations such as MAS/aluminum titanate, MAS/iron aluminum titanate, and several recrystallizable glasses were evaluated. However, none of these appeared to have the potential for low expansion that the LAS/MAS combinations displayed.

Petalite was selected because it is a readily available, naturally occurring mineral ($Li_2O \cdot Al_2O_3 \cdot 8SiO_2$) which converts when heated to 1093°C (2000°F) to beta spodumene and amorphous silica in solid solution. This thermally converted phase has an irreversible expansion coefficient near zero and is the basis for most of the current LAS glass-ceramics. The MAS phase of GE-3200 is supplied from a crystallizable glass (Ferro 266M) which converts to essentially 100% cordierite when heated at 1050°C-1100°C (1922°F-2012°F). Cordierite ($2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$) ceramics are well known for their excellent thermal shock resistance. Since there are no known large deposits of natural cordierite and the Ferro 266M is readily available, it was selected as the MAS source for our work.

Petalite and 266M frit in a weight ratio of 3:2 were thoroughly mixed by ball milling for 16 hours in a porcelain mill jar containing high density alumina grinding media. This process thoroughly blends the two ingredients and further reduces their particle size as seen in Figure 1 which shows the particle size distribution of both starting materials, of a sample from a 400 gram (0.88 lb) batch milled in-house, and of a sample from a 90.8 kilogram (200 lb) batch milled by a local ceramic firm in production-sized equipment.

The use of stearic acid in amounts up to 1.0% of the total batch weight serves as a milling aid and prevents contamination of the mill batch by the mill lining and grinding media. Batch weights were recorded before and after milling on numerous 400 gram (0.9 lb), 800 gram (1.8 lb), and 1500 gram (3.3 lb) batches with some batches milled as long as 72 hours. Weight changes less than 1.0% were repeatedly observed which was interpreted as contamination-free milling. Batch homogeneity was demonstrated by the reproducibility of properties in fired specimens made from different mill batches and by x-ray diffraction patterns which consistently showed the same amounts of two primary phases, α-cordierite and β-spodumene.

Coors Porcelain Company was selected to fabricate a honeycomb structure representative in size and cell geometry of the rotary ceramic heat exchangers being currently evaluated by various automobile manufacturers. A 45.4 kilogram (100 lb) mix of GE-3200 was sent to Coors who used an extrusion-embossing technique to fabricate a circular honeycomb structure about 53.3 cm in diameter (including about 5 cm of sacrificial material) and 10.2 cm thick (21 in x 4 in). Coors fired the honeycomb wheel to 1100°C (2012°F), at our request, so that the structure would be strong enough for shipment to our laboratory. In this pre-fired condition, the structure contained 69.8 holes/cm^2 (450 holes/in^2) which were rectangular with dimensions of about 2.5 mm by 0.5 mm (0.1 in x 0.02 in). Cell wall thickness was about 0.28 mm (0.011 in) which reduced to about 0.20 cm (0.008 in) when the honeycomb was subsequently fired at 1260°C (2300°F). Figures 2 and 3 show typical cell geometry of specimens fired at 1100°C (2012°F) and at 1260°C (2300°F). Some distortion of the cell walls is evident in the higher fired material.

Coors Porcelain Company personnel commented that the GE-3200 material was more slump resistant and contained less residual stress after the 1100°C (2012°F) firing than any of the MAS materials they has fired previously.

MATERIALS TESTING AND RESULTS

Although a honeycomb structure was the ultimate materials form to be tested, the properties of each material were initially determined on monolithic shapes for economic considerations and to expedite materials screening. Only those materials which surpassed the performance of Corning 9454 (monolithic LAS reference material) were considered for fabrication into honeycomb form. Several materials exhibited better corrosion resistance, but failed to match, or exceed, the thermal expansion behavior of the LAS reference material. However, GE-3200, exhibited sufficiently good performance in the screening tests to warrant fabricating it into the circular honeycomb structure previously described. This geometry is representative of the rotary ceramic heat exchangers currently being evaluated by several automobile manufacturers and served as the source of the many small specimens required for measuring various properties and for two 15.2 cm diameter (6 in) core specimens sent to Ford Motor Company for engine testing.

Thermal Expansion

This property was measured over the temperature range, ambient to 1000°C (1832°F), at a heating rate of 2°C/minute on the monolithic and honeycomb specimens. Sample contraction was also recorded during a cooling rate maintained at 2°C/minute. Early in the program a Theta Dilatronic II dilatometer was used to measure expansion, but near the mid-point of the investigation all subsequent specimens were sent to a commercial testing laboratory which utilized a Harrop TDA-H1-MP6 dilatometer. Both units employed fused silica standards obtained from the National Bureau of Standards.

Early in the program, a goal of 800 ppm expansion at 800°C (1472°F) was established. The first material which met this goal was a monolithic specimen of GE-3200, which had been isostatically pressed, then heated to 1320°C (2408°F). This heat treatment caused the edges and corners of the specimen to become rounded due to incipient melting. Following this initial heat treatment, the specimen was subjected to nucleation and crystallization cycles of 900°C (1652°F) for 2 hours and 1000°C (1832°F) for 17 hours, respectively. Thermal expansion measurements on this specimen revealed that it had a fairly large thermal hysteresis and a negative coefficient of expansion over a large part of the measurement range. The average coefficient of linear thermal expansion between ambient and 1000°C (1832°F) was determined to be $0.88 \times 10^{-6}/^{\circ}C$ and the expansion at 800°C (1472°F) was 420 ppm. These data were reproduced on several specimens and a typical expansion curve is shown in Figure 4A. For comparison, the expansion behavior of Corning 9454 is shown in Figure 4B.

Since the process used to prepare the specimens described above requires incipient fusion, it would not be practical for honeycomb production because slumping of the cell structure would be detrimental. Therefore long-term firing at temperatures just below fusion, followed by appropriate nucleation and crystallization treatments, were investigated in an effort to obtain the same expansion characteristics. The thermal expansion behavior of specimens subjected to various firing schedules is shown in Figure 5. Although none of these treatments produced an expansion as low as that of the "fusion sintered" GE-3200, there is a significant decrease in thermal hysteresis in each of the long-term fired specimens.

The coefficient of thermal expansion of GE-3200 honeycomb is consistently higher than monolithic GE-3200. It is believed that this unexpected behavior is related to lithia (Li_2O) losses during firing and a more detailed explanation is presented in the Discussion of Results section.

Thermal expansion data from GE-3200 honeycomb specimens revealed a typical expansion of 1080 ppm at 800°C (1472°F) and a linear coefficient of thermal expansion of $1.7 \times 10^{-6}/^{\circ}C$ from 25°C - 1000°C (77°F - 1832°F). By comparison, typical expansion data for GE-3200 monolithic specimens are: 880 ppm at 800°C and $1.48 \times 10^{-6}/^{\circ}C$. These data are shown in Figure 6.

The effect of thermal cycling on the expansion behavior of honeycomb GE-3200 was investigated by two cycling techniques. One series of specimens was placed into a 1000°C (1832°F) furnace, held at that temperature according to a pre-selected schedule, removed and cooled to ambient temperature, then re-heated at 1000°C (1832°F) according to a pre-selected schedule. The actual cycles used were:

1. 10 cycles, hold one hour at 1000°C.
2. 3 cycles, hold six hours at 1000°C.
3. 1 cycle, hold 22 hours at 1000°C.
4. 2 cycles, hold 25 hours at 1000°C.

Thermal expansion was measured on each specimen after total exposure times of 1, 10, 28, 50, 75, and 100 hours. A second series of specimens was thermally cycled from ambient to 1000°C (1832°F) by inserting each specimen into a tube furnace pre-heated to 1000°C (1832°F), and holding the specimen at temperature for 3.6 minutes. The times to insert and retract the specimens were 1.7 minutes each, thus one cycle required seven minutes for completion. Each specimen was subjected to a total of 5000 such cycles. The results of both types of cycling on the thermal expansion of GE-3200 are shown in Figure 7.

Thermal expansion measurements were also made on honeycomb specimens of GE-3200 which had been subjected to corrosion resistance testing. The exact details of testing are given in a subsequent section of this report, but consist essentially of cyclic immersion in a hot sulfuric acid solution followed by exposure to increasing temperature to 1000°C (1832°F) and of impregnation in an aqueous solution of sodium chloride followed by long-term heating at 800°C (1472°F). The results of this phase of testing on thermal expansion are shown in Figure 8.

Thermal Phase Stability

The stability of monolithic GE-3200 was determined by x-ray diffraction analysis on specimens which had been cycled for 1, 5, and 10 hours at 1100°C, with each cycle consisting of a one hour hold at temperature. No significant differences in amounts or kinds of phases were observed at the end of 1, 5, and 10 hours. The diffraction patterns for monolithic specimens of GE-3200 and Corning 9454 at the start of cycling and after 10 hours at 1100°C are shown in Figures 9 and 10.

In addition, specimen length was measured initially and after total exposure times of one, five, and ten hours at 1100°C (2012°F). These results are shown in Figure 11.

The effect of long-term cycling at 1000°C (1832°F) on the dimensional stability of GE-3200 honeycomb specimens was also recorded as shown in Figure 12.

CORROSION RESISTANCE

Monolithic specimens were evaluated for resistance to sodium and sulfuric acid attack primarily by determining whether specimen weight changes occurred. Specimens were also examined for evidence of cracks and etching. The corrosion resistance of honeycomb specimens, however, was evaluated on the basis of changes in specimen length and thermal expansion as well as visual evidence of etching and cracks.

Monolithic specimens were immersed for two hours in 300°C (572°F) concentrated sulfuric acid, then removed and heated for two hours at 320°C (608°F). The specimens were then re-immersed in the hot acid for an additional two hours, removed and heated for two hours at 650°C (1202°F). A final two hour immersion in the hot acid was followed by heating for two hours at 1000°C (1832°F). Therefore, each specimen received a total immersion time of six hours in the 300°C (572°F) acid.

Evaluation of monolithic specimens to sodium was made by placing a specimen in a 100 cc platinum crucible, covering the specimen with dry, -20 mesh sea salt and placing the crucible in a furnace heated to 750°C (1382°F). As the sea salt melted, additional salt was added to maintain the liquid level above the specimen during the two hour test duration. Results of acid and salt testing on the monolithic specimens are shown in Figure 13 which includes data for an MAS (Corning 9606) material. The composition of the sea salt is shown in Table I.

Honeycomb material was evaluated for acid resistance by immersing specimens in a 1% sulfuric acid solution for two hours at room temperature. Only one specimen was tested in a given solution which was always freshly prepared and the solution was evacuated for two minutes at the beginning of the cycle to remove entrapped air from the honeycomb cells. At the end of the immersion cycle, the specimen was removed, excess solution was gravity drained and the specimen was heated for two hours at 300°C (572°F). Each specimen was subjected to a minimum of three such cycles and $\Delta L/L$ was recorded after each cycle. Comparison of GE-3200 and Corning 9455 specimens after acid evaluation is shown in Figure 14.

The sodium resistance of honeycomb specimens was evaluated as follows:

1. Immerse specimen for five minutes in a boiling 3.43% NaCl solution in a reflux condenser.
2. Blow excess solution out of specimen for five minutes using filtered, oil-free nitrogen or air at 5 psig.
3. Dry specimen at 200°C (392°F).
4. Heat specimen at 800°C (1472°F) for three weeks, measuring $\Delta L/L$ after 1, 3, 7, 14 and 21 days.

The data obtained are shown in Figure 15.

MECHANICAL PROPERTIES

Monolithic specimens, 51 mm x 6 mm x 6 mm, (2 in. x 0.25 in. x 0.25 in) were prepared as previously described and their surfaces were ground flat to a tolerance of ± 0.025 mm (± 0.001 in).

Modulus of rupture (MOR) was measured by loading the specimens in four-point flexure using a 51 mm x 6 mm surface as the tensile surface. The outer knife edge span was 38.1 mm (1.5 in) and the inside span was 12.7 mm (0.5 in). A cross-head speed of 0.051 mm/min (0.002 in/min) was used for all tests.

An average value (based on a minimum of six tests) for the MOR of monolithic GE-3200 is 77.6 MPa (11,260 psi), while the average MOR for Corning 9454 was determined to be 83.8 MPa (12,160 psi).

Specimens of the same geometry as those just described were used to determine elastic modulus by the sonic resonance technique according to ASTM Standard C623-69T. An average value (based on a minimum of six tests) for the elastic modulus of monolithic GE-3200 is 72,400 MPa (10.5×10^6 psi), while the Corning 9454 material displayed an average elastic modulus of 71,700 MPa (10.4×10^6 psi).

Mechanical properties of the honeycomb material were measured on two different specimen sizes. Modulus of rupture specimens were 63.5 mm x 9.5 mm x 9.5 mm (2.5 in x 0.375 in x 0.375 in). Flexure modulus was measured instead of elastic modulus because of the difficulty in using the sonic technique on honeycomb material. Flexure modulus specimens, 114 mm x 12.7 mm x 19 mm (4.5 in x 0.5 in x 0.75 in), were loaded in four point flexure and a deflectometer was used to determine specimen deflection.

Test conditions for MOR were identical for both the monolithic and honeycomb specimens, but a cross-head speed of 0.51 mm/min (0.02 in/min) was used during flexure modulus measurements on honeycomb specimens.

The directional nature of honeycomb structures makes it necessary to measure mechanical properties on specimens which reflect this directionality. Accordingly, specimens were cut in both a tangential and a radial orientation as shown schematically in Figure 16. Table II summarizes the mechanical properties of both GE-3200 and Corning 9454/9455 in both monolithic and honeycomb form.

POROSITY AND MICROSTRUCTURE

The pore volume and associated structural characteristics were determined by the Micromeritics Instrument Corporation using the mercury penetration method. Three different speciments of GE-3200 honeycomb which had been fired at 1100°C (2012°F), 1240°C (2264°F), and 1260°C (2300°F), respectively, were analyzed by this technique. The data, summarized in Table III, show that pore volume, porosity, and density at 345 MPa (50,000 psia) decrease as firing temperature increases, but increased thermal treatment also increases the average pore diameter and the bulk density.

The microstructures of GE-3200 and Corning 9455 honeycomb before and after exposure to sodium chloride solution are shown in Figure 17. Standard metallographic procedures were used to prepare the specimens for examination and for the photomicrographs. Figure 17 reveals that Corning 9455 exhibits the typical fine grained structure of a glass-ceramic while

GE-3200, a two phase, sintered material, consists of considerably larger particles. There does not appear to be any grain growth in the specimens exposed to the salt tests, but the more clearly defined grain boundaries suggest sodium decoration.

DISCUSSION OF RESULTS

The difference in thermal expansion of GE-3200 when heated for a few minutes at a temperature which produces incipient fusion and of the same material when heated for one to three hours at a temperature just below incipient fusion is somewhat puzzling. It was initially believed that the higher fired material contained different phases than the lower fired material and that these phases were causing microcracking. However, x-ray diffraction data revealed no significant differences in amounts or kinds of phases present in both materials.

In the development of low-iron spodumene, Fishwick (1) observed that a decrease in lithia (Li_2O) content from about 6% to about 1% produced an increase in expansion coefficient from about $1 \times 10^{-6}/^{o}C$ to about $8 \times 10^{-6}/^{o}C$. We believe this behavior partially explains our results. Spodumene, when heated converts to beta spodumene, while petalite converts to beta spodumene and amorphous silica in solid solution. Therefore, the loss of lithia from a petalite-containing material probably has less effect on expansion because of the influence of the silica solid solution. In addition, Fishwick's data indicate that the expansion coefficient changes very slightly as the lithia content reduces from 6% to about 2.5%, but as further lithia is lost, the expansion increases rapidly.

GE-3200 does lose lithia during firing. This was first observed when the results of acid tests on "as fired" monolithic specimens revealed less attack than on specimens whose surfaces had been ground and polished prior to acid testing. Subsequent chemical analyses on similar specimens and on a fired honeycomb specimen confirmed that substantial loss of Li_2O can occur. Two techniques for suppressing the loss of Li_2O were immediately investigated. One involved a shorter firing cycle; the other utilized a lithia-enriched atmosphere during firing. This work was initiated near the end of this phase of the study and will be continued during the next phase.

Complete chemical analyses of the variously fired GE-3200 specimens appear in Table IV which also contains complete analyses of the raw materials used to make GE-3200, and of milled, unfired GE-3200. The theoretical compositions of both raw materials, of milled, unfired GE-3200, and the supplier's typical analysis of petalite are also included. The data in Table IV show that lithia losses during firing can be reduced, but they also show that a significant amount of alkali is present in the petalite. The indicated amounts of Na_2O and K_2O could be detrimental to corrosion resistance and to low thermal expansion.

We believe that the tendency for GE-3200 to elongate during thermal cycling is related to specimen thermal history. Both the monolithic and honeycomb specimens were cut from larger pieces of GE-3200 which had been pre-fired to 1100°C (2012°F), cooled to room temperature, and subsequently fully fired to 1260°C (2300°F). Pre-firing provides sufficient mechanical integrity to the material so that sample preparation is facilitated. However, an interruption in the sintering process such as described in the above cycle might be detrimental to dimensional stability. We plan to investigate this possibility in the next phase of study by firing specimens from the "green" state directly to the fully fired condition.

The improved corrosion resistance of GE-3200 (LAS/MAS) compared to Corning 9455 (LAS) is a function of the cordierite phase (MAS) of GE-3200. Early in the program, the excellent corrosion resistance of MAS alone was demonstrated in both acid and salt environments. Subsequent combinations of MAS and other materials also exhibited very good corrosion resistance, but we observed that increased amounts of MAS produced increased thermal expansion. For this reason, the LAS/MAS ratio of 3:2 was selected as the combination to be fabricated into honeycomb.

The mechanical properties of GE-3200 are dependent to some extent on the geometry of the honeycomb structure (e.g., cell size and shape, wall thickness, number of cells per unit of surface area, etc.). In addition, the mechanical properties are greatly affected by the degree of bonding between the ribs and tape segments of a rectangular or sinusoidal honeycomb configuration. We believe the lower radial strength and higher tangential strength of GE-3200 compared to Corning 9455 reflects differences in honeycomb configuration and possibly incomplete rib/tape bonding in GE-3200. This latter factor can most likely be improved by firing directly from the "green" state to 1260°C (2300°F) and possibly also by more tightly wrapping the honeycomb during fabrication.

Examination of the porosity data (Table III) and microstructure (Figure 17) of GE-3200 reveals that it consists of relatively small grains (~6 μm) and is slightly less dense than most silicate glasses. The increase in pore diameter with increased firing temperature is not an unexpected behavior when the decrease in porosity is considered. In the higher fired material, there are indeed larger pores, but the number is very significantly reduced.

The relatively small grain size and low density of GE-3200 are desirable materials features from the standpoint of lightweight, strong ceramic structures for gas turbine engine heat exchanger applications.

CONCLUSIONS

A mixed phase material, GE-3200, has been demonstrated for heat exchanger applications in automotive gas turbine engines. The material consists of 60 w/o lithium aluminosilicate (LAS) and 40 w/o magnesium aluminosilicate (MAS) and can be fabricated, by conventional techniques, into honeycomb structures similar to the rotary ceramic heat exchangers being currently evaluated by various automobile manufacturers.

Thermal, chemical, and mechanical properties were measured on small, honeycomb specimens of this new material and were compared to the same properties measured on similar specimens of Corning 9455 (LAS).

The following results were obtained:

1. GE-3200 is significantly more resistant to sulfuric acid and sodium chloride than Corning 9455.
2. The mechanical properties of both materials are about equal, although GE-3200 honeycomb is less strong in the radial direction, but stronger in the tangential direction than Corning 9455.
3. GE-3200 has a higher linear coefficient of thermal expansion than Corning 9455.
4. GE-3200 tends to elongate during thermal cycling while Corning 9455 tends to contract slightly.

In addition to these measured results, the ease of fabrication, resistance to slumping and residual stresses in the pre-fired honeycomb, and the greater refractoriness of GE-3200, suggest its potential as a candidate heat exchanger material for gas turbine engine applications.

REFERENCES

1. Fishwick, J.H., Applications of Lithium in Ceramics, Cahners Books, Boston, 1974, 156 pp.

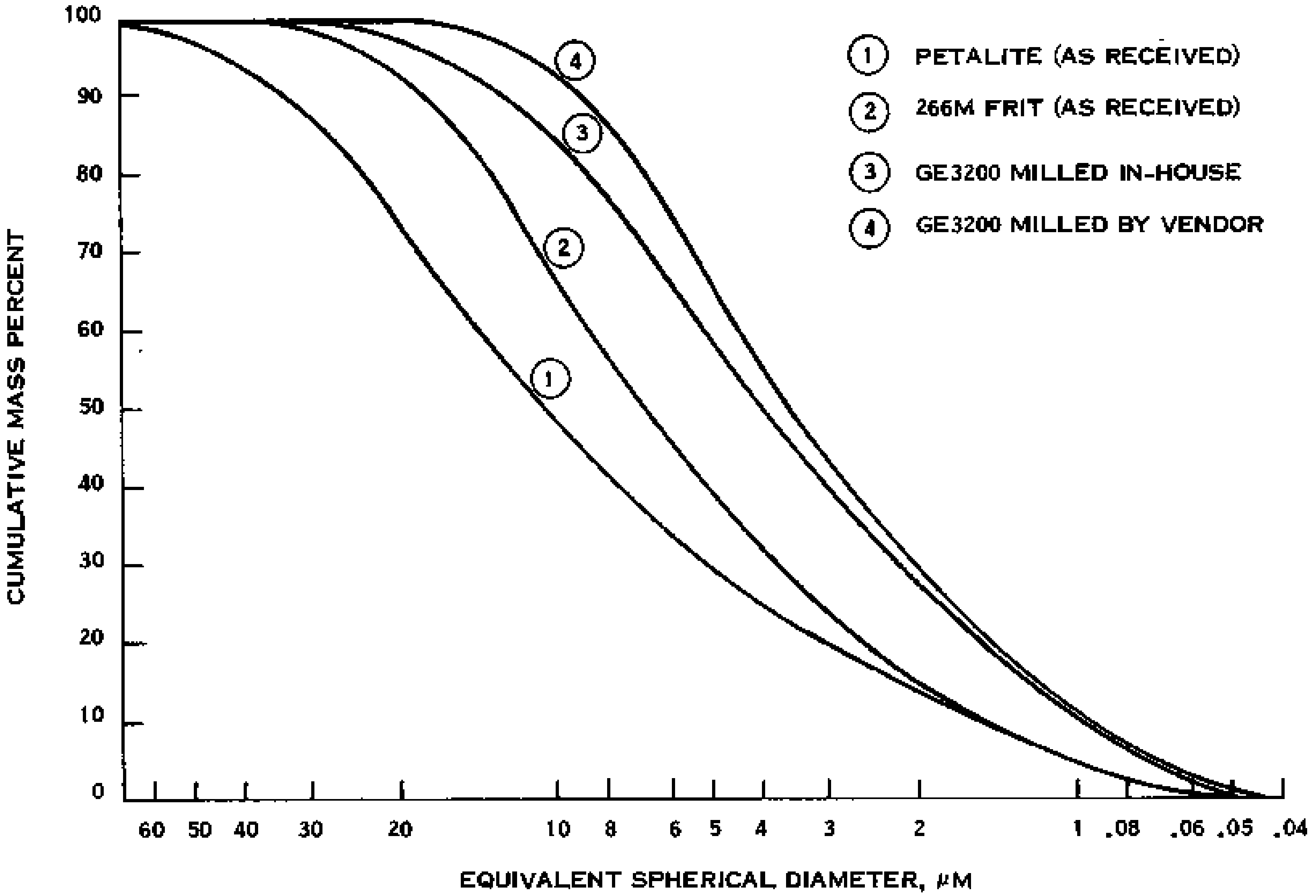


Figure 1. Particle Size Distribution of Petalite and 266M as Received and of Two Different Batches of Milled GE-3200

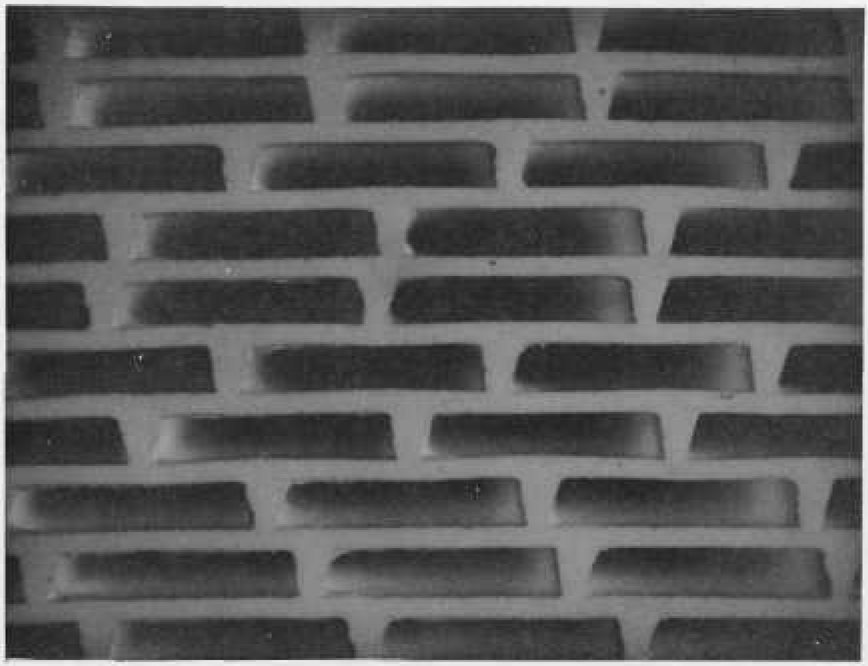


Figure 2. Cross-Section of GE-3200 Honeycomb from Wheel Fired at 1100°C (2012°F) by the Fabricator, Coors Porcelain Company

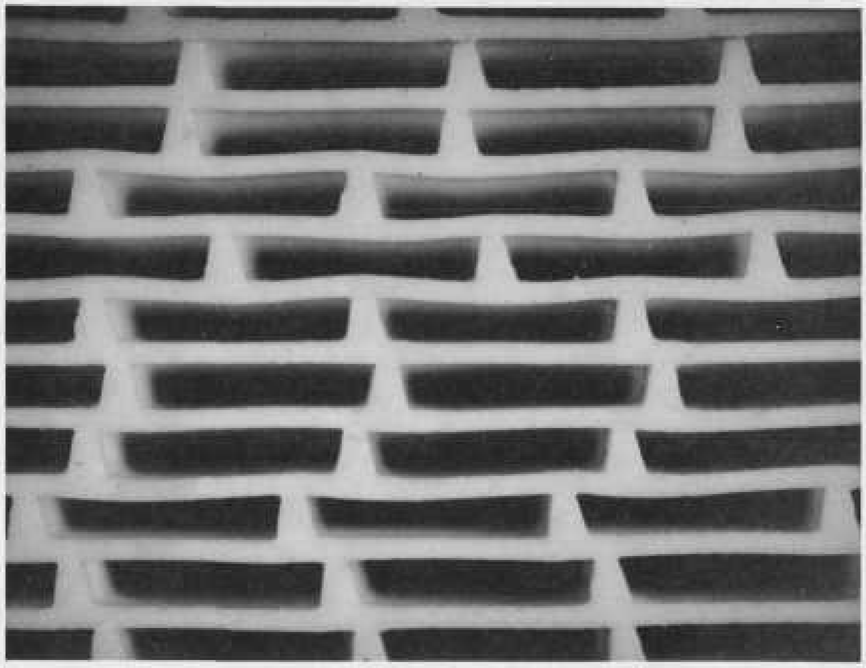


Figure 3. Cross-Section of GE-3200 Honeycomb from Wheel Fired at 1100°C (2012°F) by Fabricator, Then Fired at 1260°C (2300°F) by GE

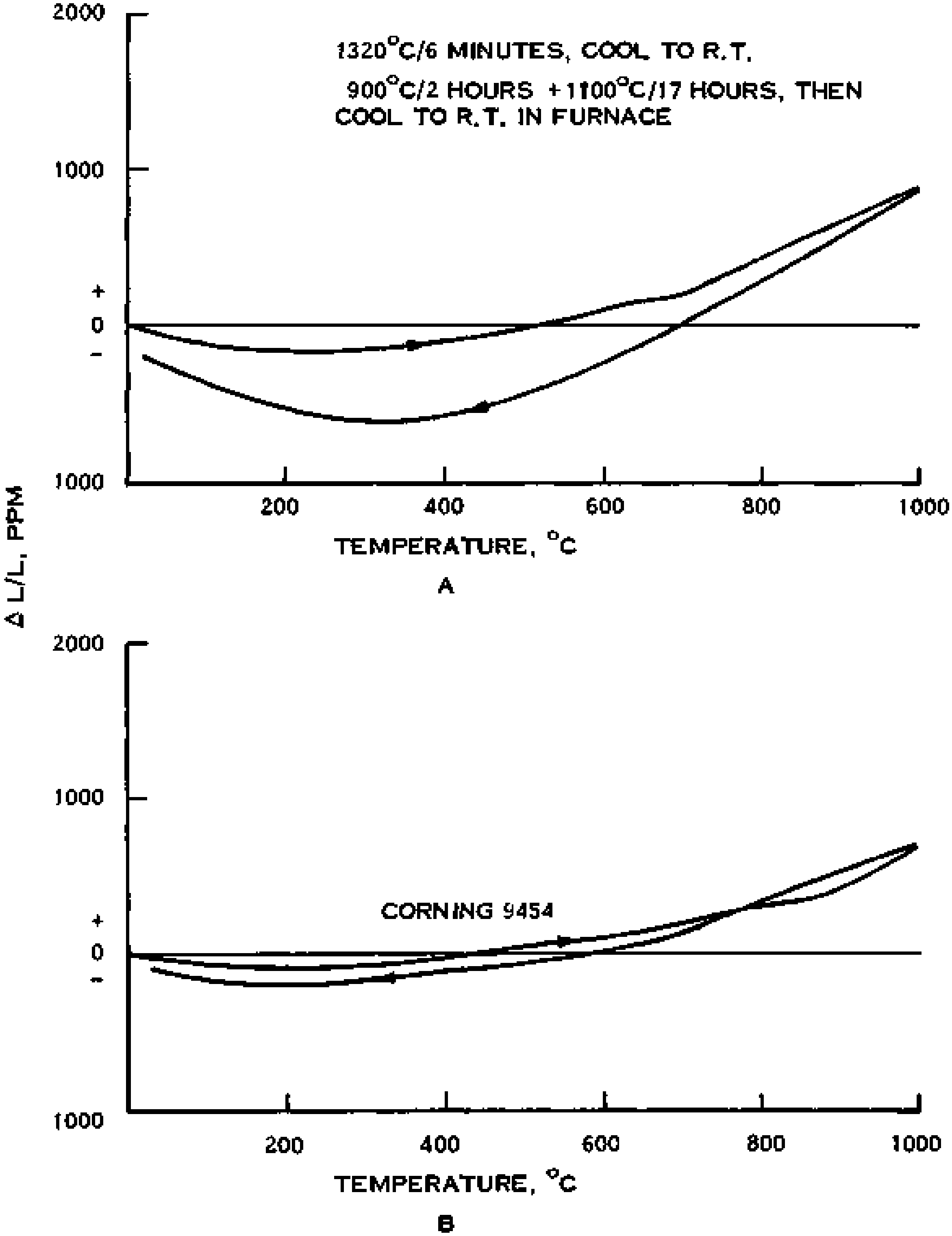


Figure 4. Thermal Expansion Behavior of Fusion Sintered Monolithic GE-3200 and Corning 9454

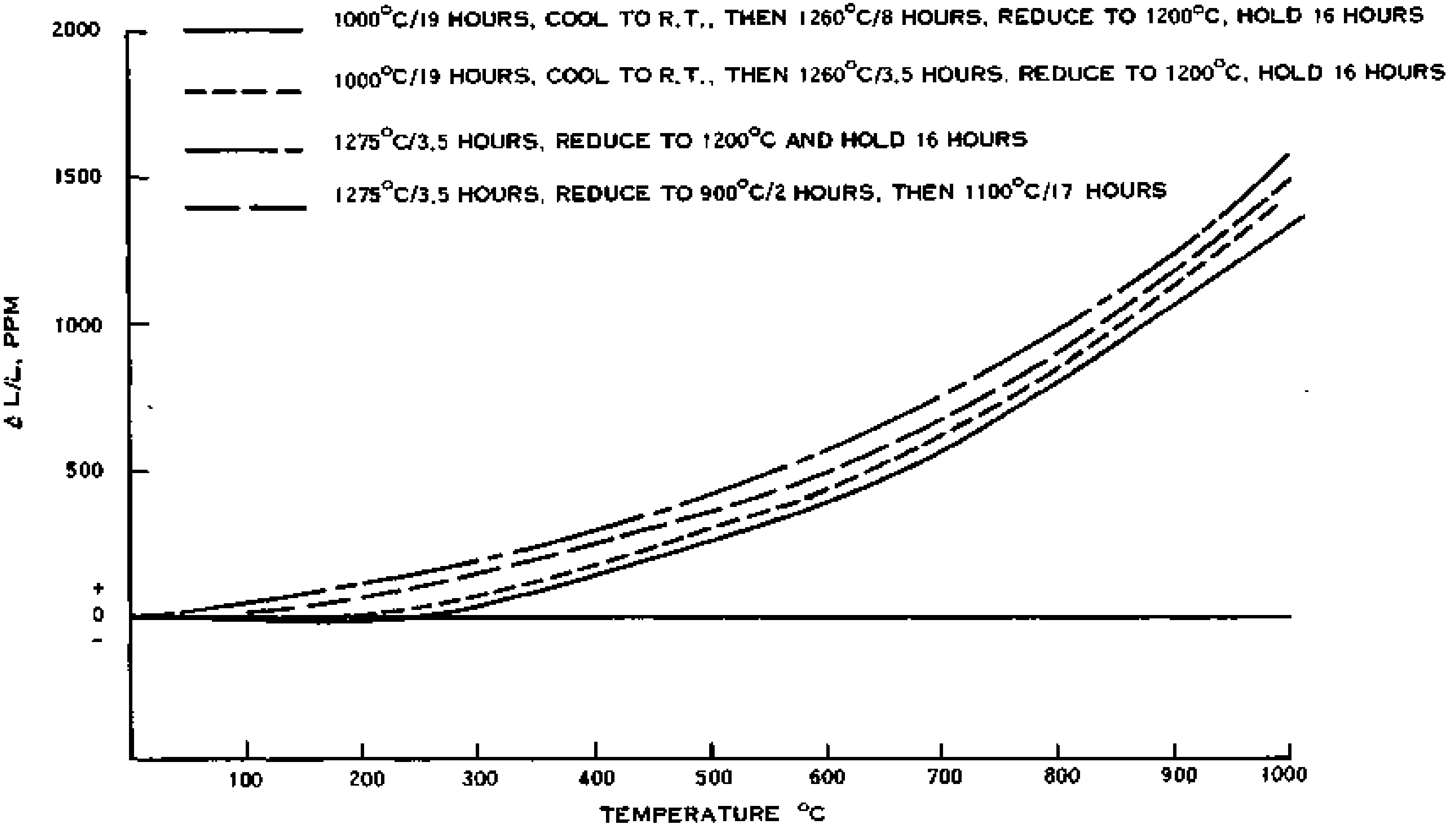


Figure 5. Thermal Expansion of Monolithic GE-3200 Fired Under Different Conditions of Time at Temperatures Below Fusion

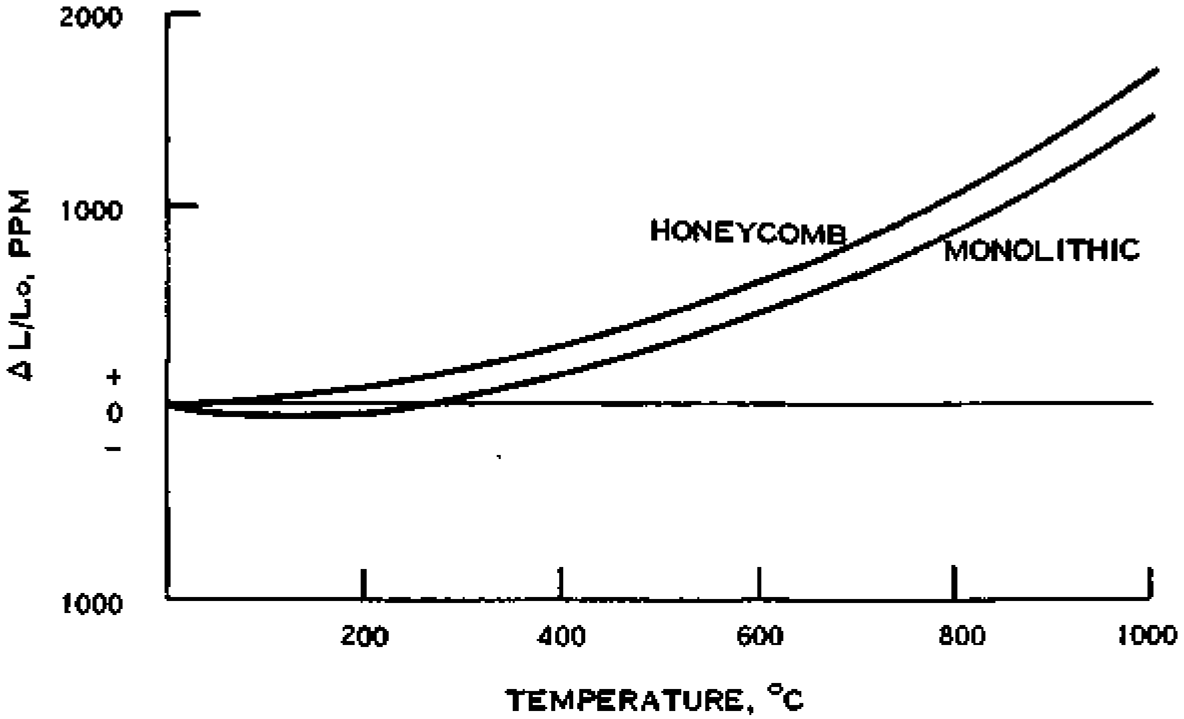
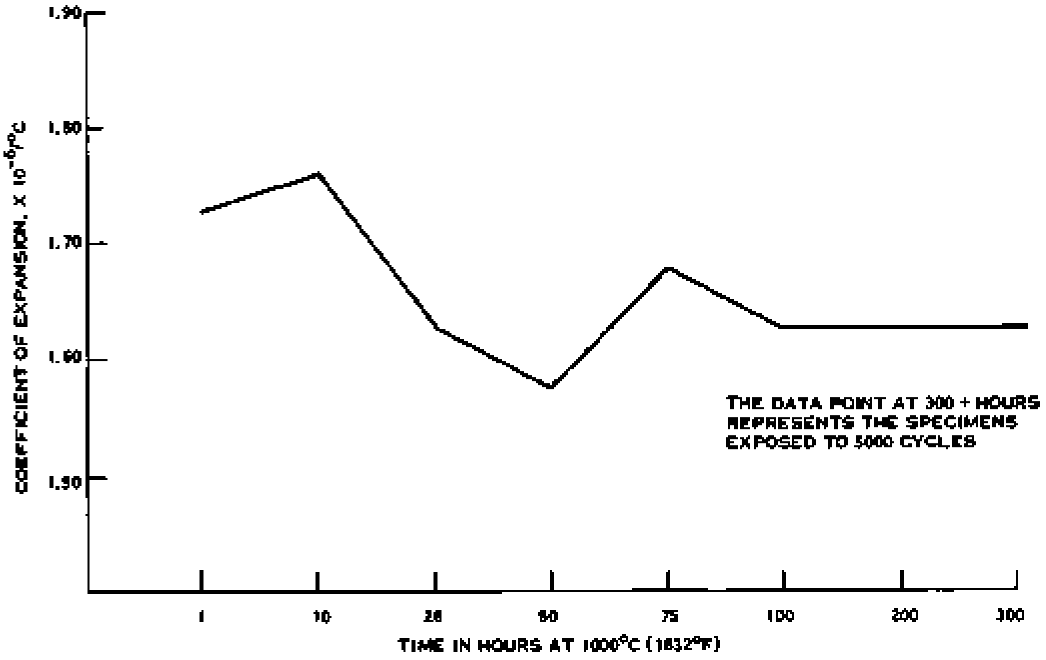


Figure 6. Typical Thermal Expansion Behavior of Monolithic and Honeycomb GE-3200



THE DATA POINT AT 300 + HOURS REPRESENTS THE SPECIMENS EXPOSED TO 5000 CYCLES

Figure 7. The Effect of Thermal Cycling on the Coefficient of Linear Thermal Expansion of GE-3200 Honeycomb

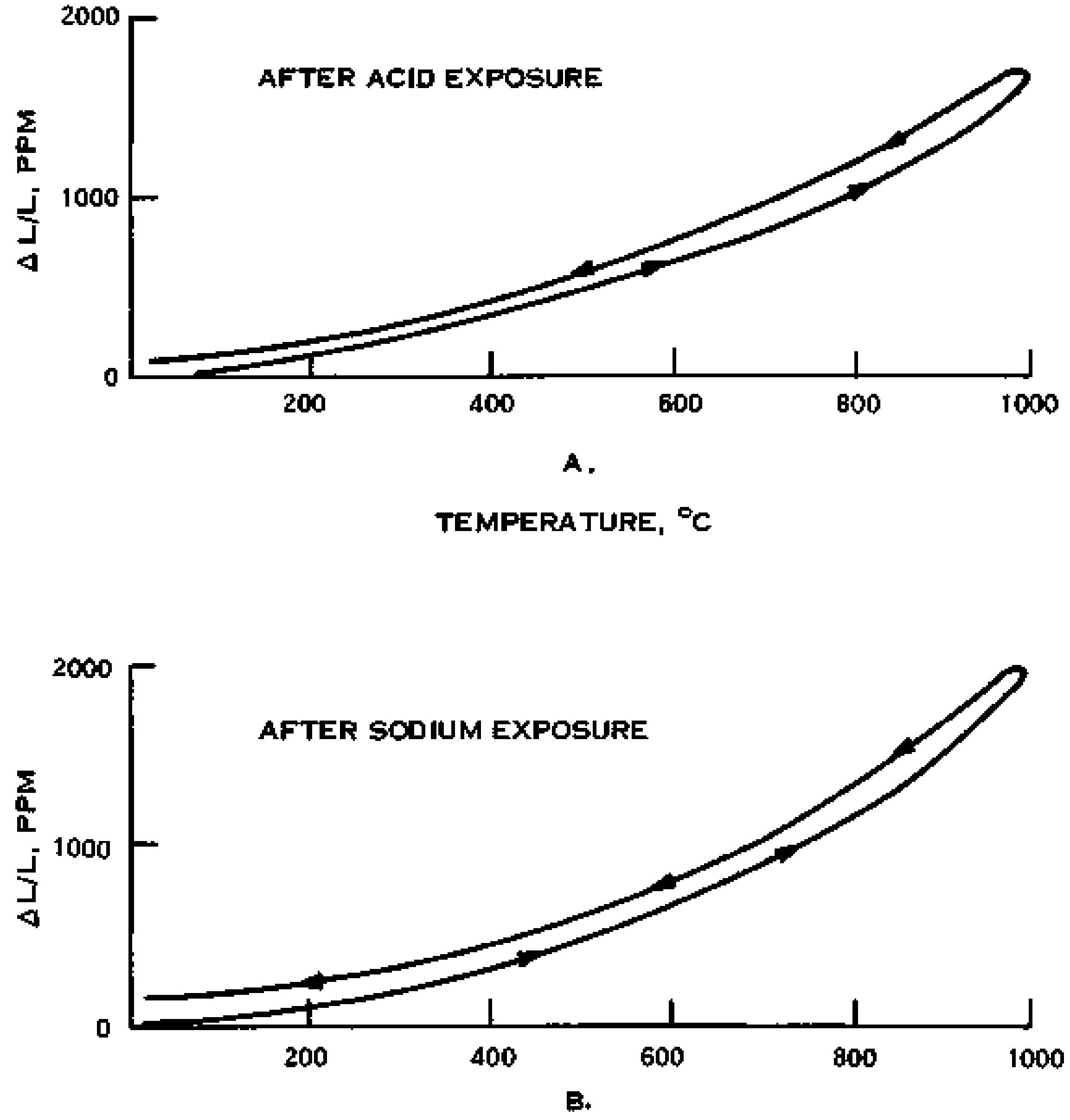


Figure 8. Effect of Corrosion Testing on Thermal Expansion of GE-3200 Honeycomb

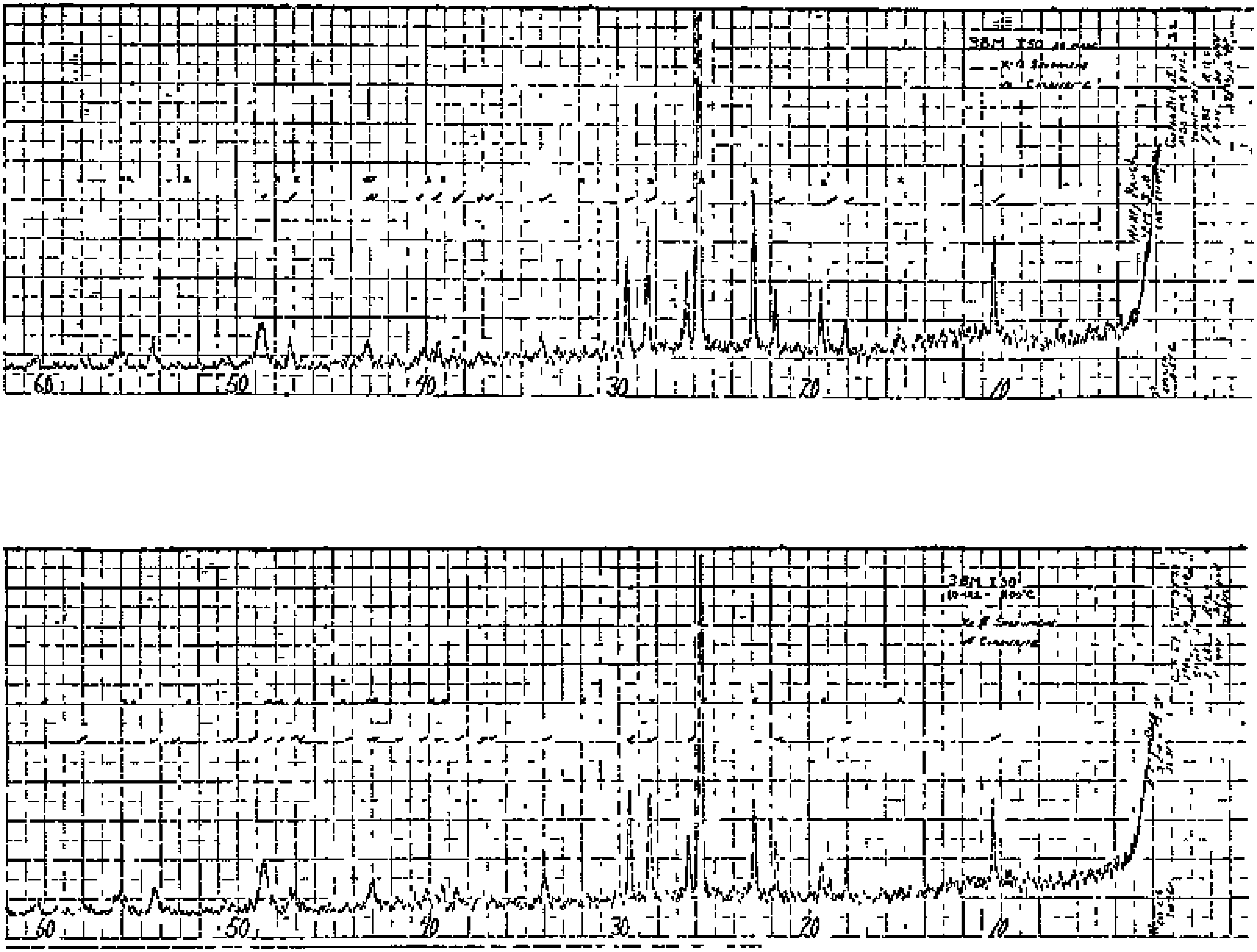


Figure 9. X-ray Diffraction Patterns of Monolithic GE-3200 Before (Upper) and After (Lower) Ten Hour Exposure to 1100°C

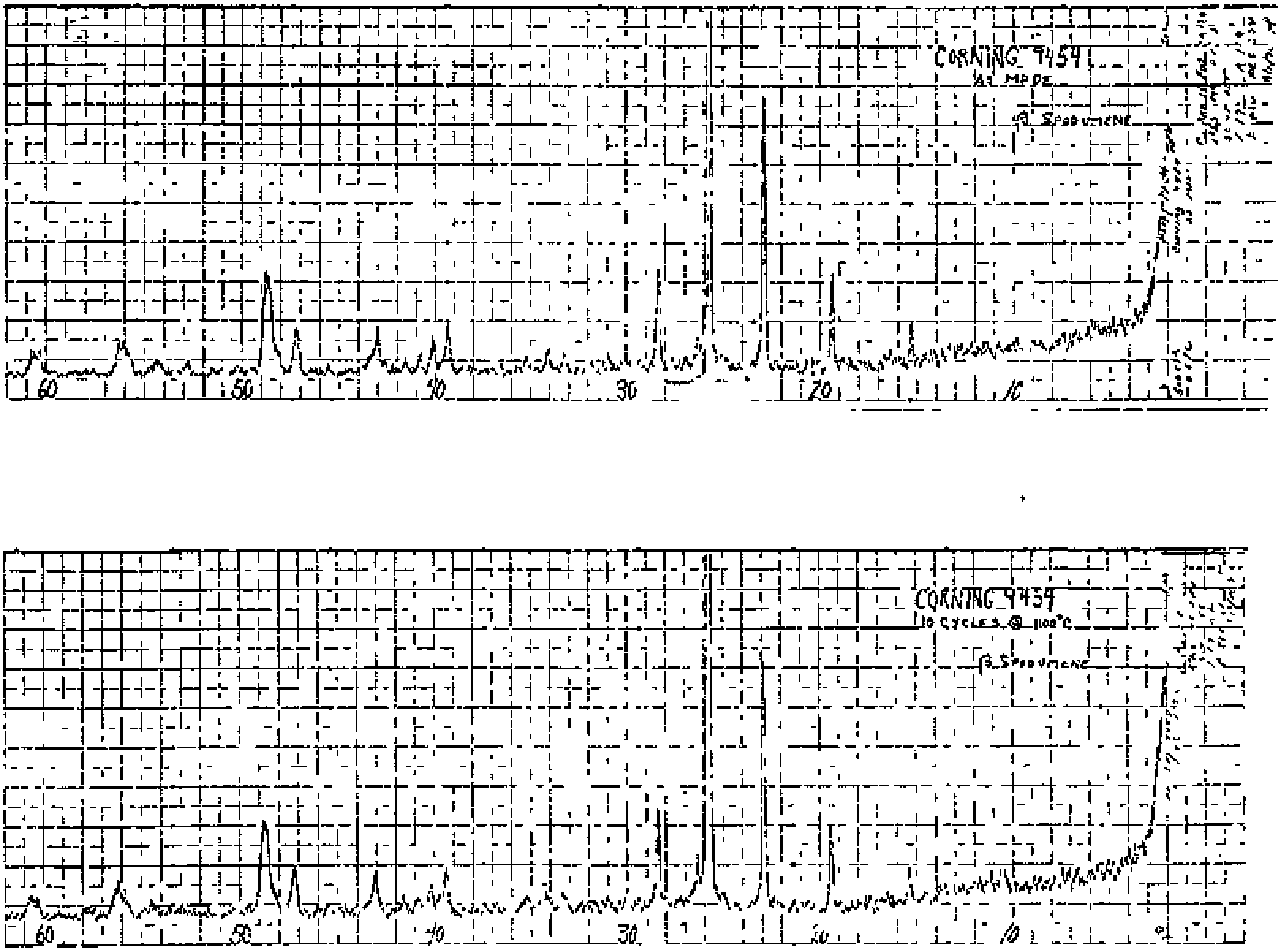


Figure 10. X-ray Diffraction Patterns of Corning 9454 Before (Upper) and After (Lower) Ten Hour Exposure to 1100°C

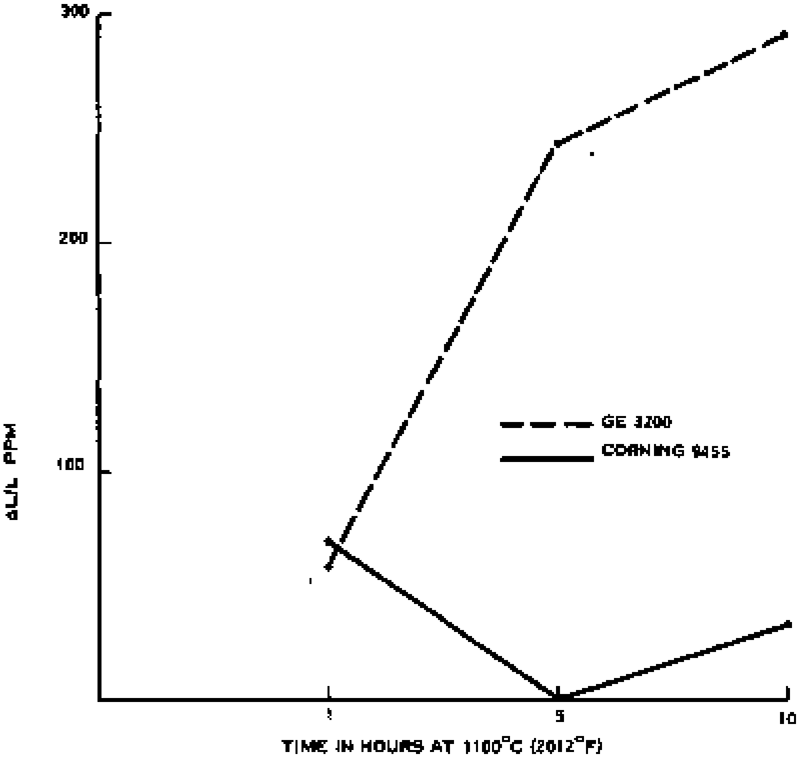
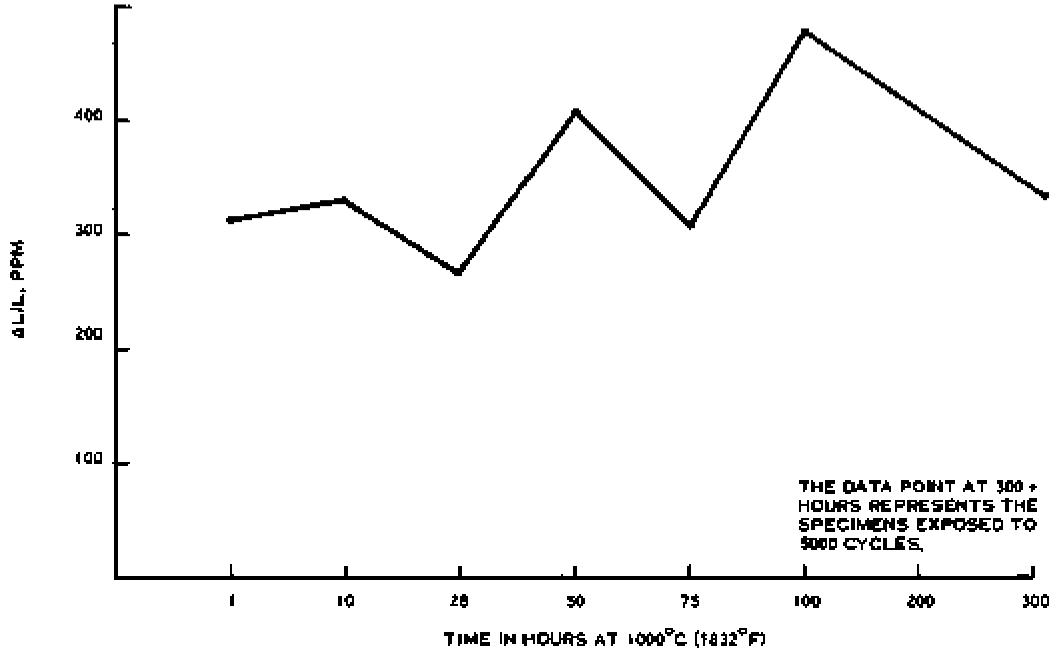


Figure 11. The Effect of Thermal Cycling on Length Stability of Monolithic GE-3200 and Corning 9454



THE DATA POINT AT 300 + HOURS REPRESENTS THE SPECIMENS EXPOSED TO 5000 CYCLES.

Figure 12. The Effect of Thermal Cycling on Length Stability of GE-3200 Honeycomb

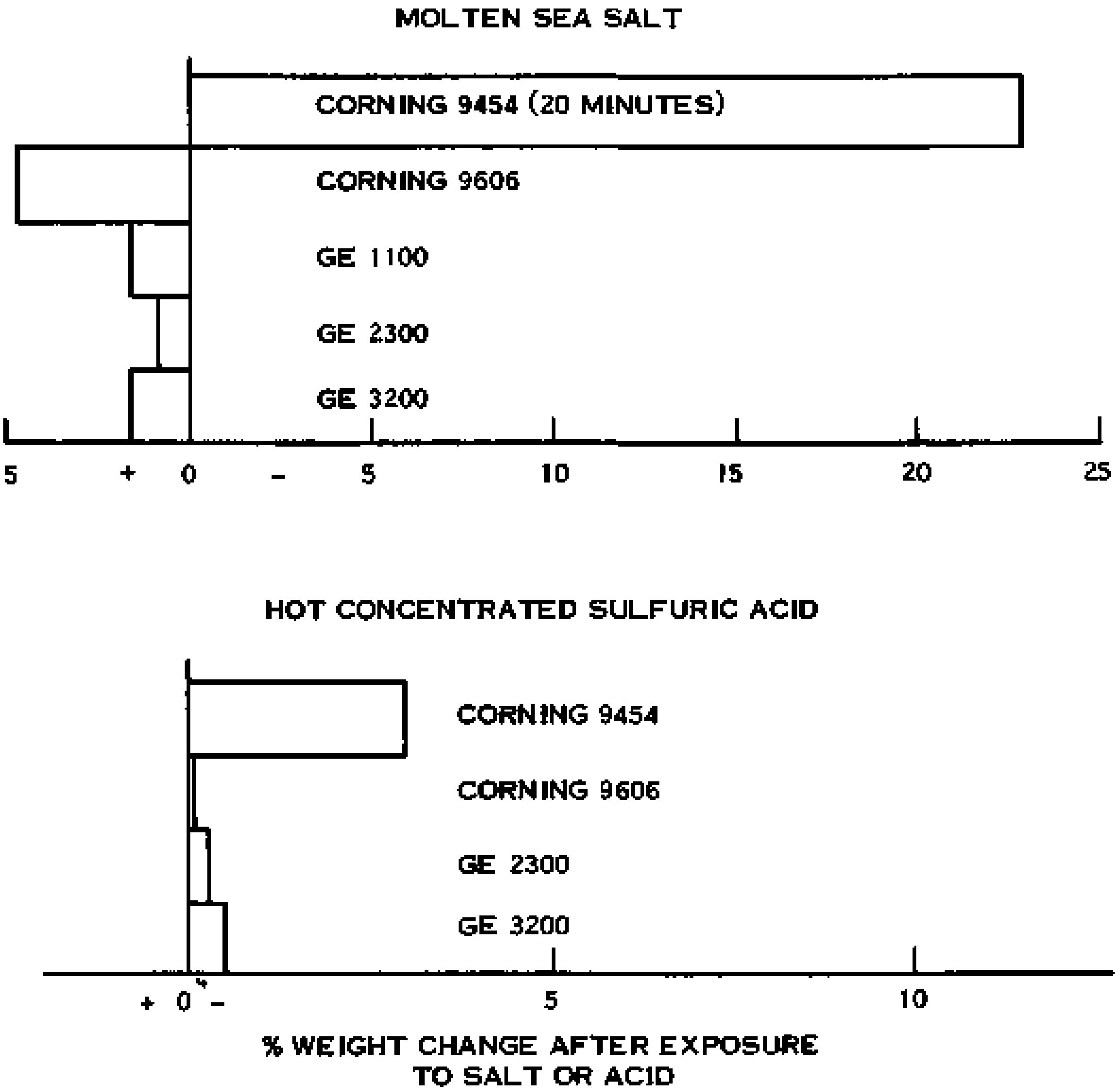


Figure 13. The Effect of Molten Sea Salt (Sodium) and Sulfuric Acid on Monolithic Specimens of Candidate Heat Exchanger Materials

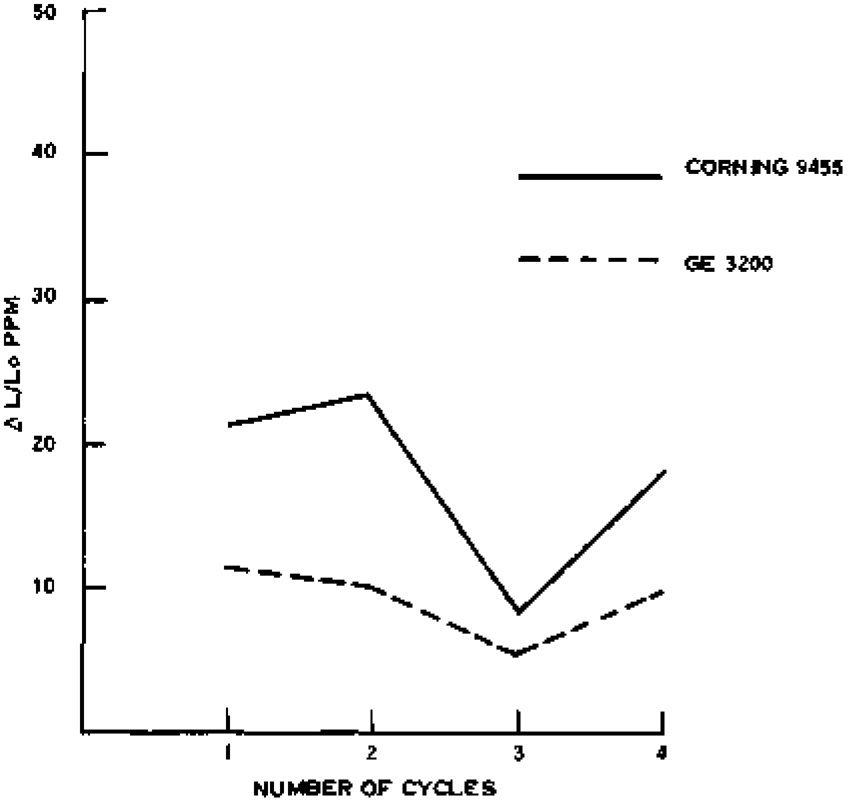


Figure 14. The Resistance to 1% Sulfuric Acid of GE-3200 and Corning 9455 Honeycomb

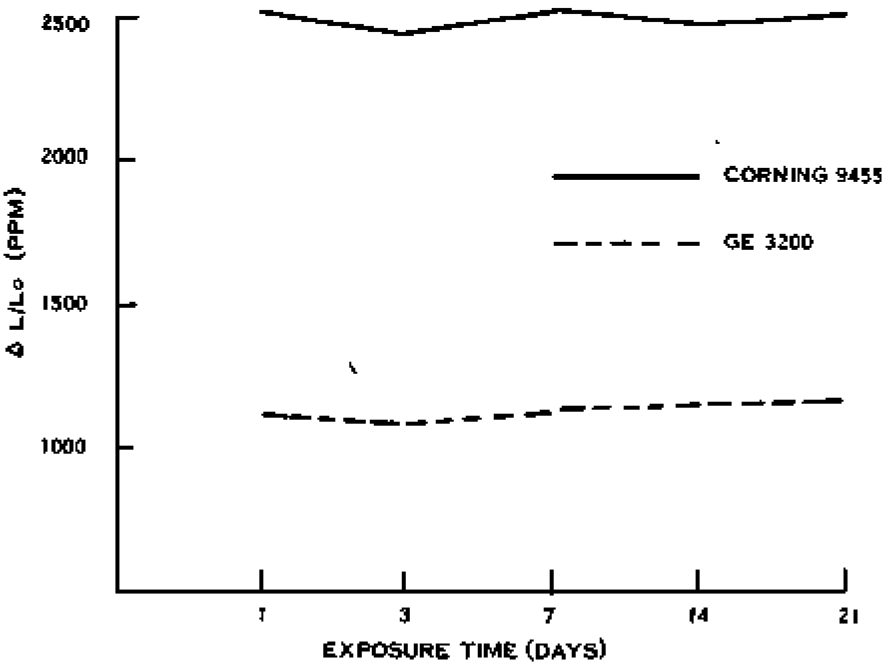


Figure 15. The Resistance to Boiling 3.43% Sodium Chloride Solution of GE-3200 and Corning 9455 Honeycomb

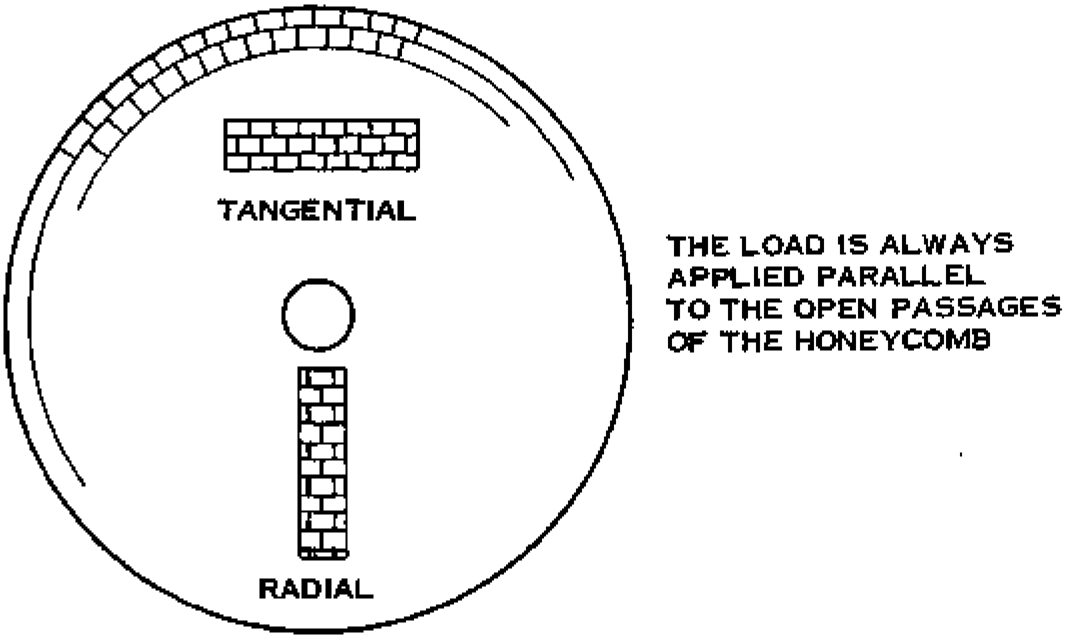


Figure 16. Schematic of a Circular Honeycomb Structure Showing Required Orientation of Mechanical Test Specimens

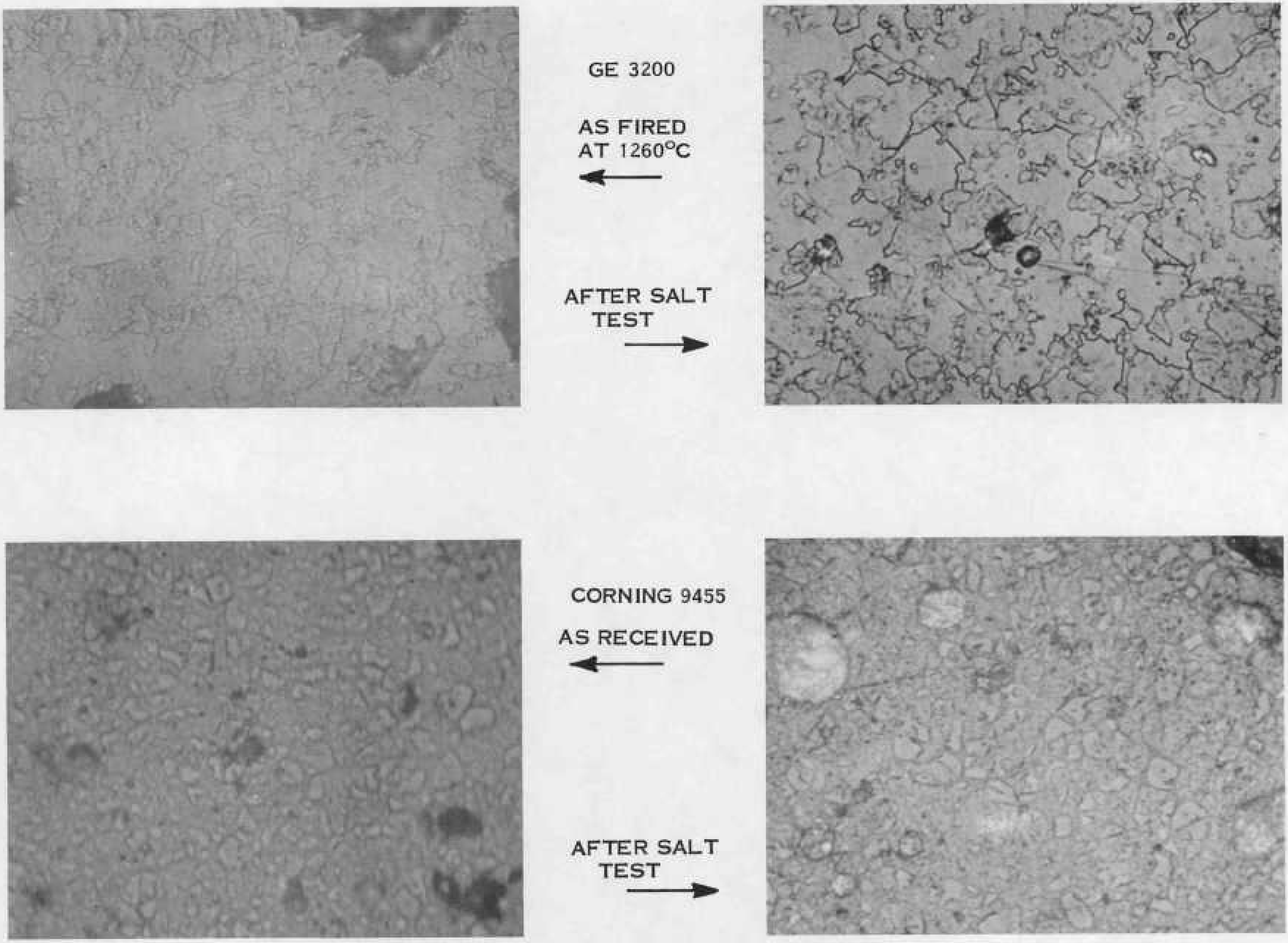


Figure 17. Microstructure of GE-3200 and Corning 9455 Honeycomb Before and After Corrosion Testing in Boiling 3.43% Sodium Chloride Solution (Mag. 1000 X, Specimens Etched with 10% H.F.)

Table I. Composition of Sea Salt Used to Evaluate Monolithic Specimens for Sodium Resistance

	w/o
NaCl	58.5
$MgCl_2 \cdot 6\ H_2O$	26.5
Na_2SO_4	9.8
$CaCl_2$	2.8
KCl	1.6
$NaHCO_3$	0.5
KBr	0.2
H_3BO_3	0.1
$SrCl_2 \cdot 6\ H_2O$	0.1
NaF	0.01

Table II. Mechanical Properties of GE-3200 and Corning 9454/9455 Monolithic and Honeycomb Material

MONOLITHIC	MODULUS OF RUPTURE	ELASTIC MODULUS
GE-3200	77.9 MPa (11.3 X 10^3 PSI)	72400 MPa (10.5 X 10^6 PSI)
CORNING 9454	84.1 MPa (12.2 X 10^3 PSI)	71700 MPa (10.4 X 10^6 PSI)

HONEYCOMB	MODULUS OF RUPTURE		FLEXURE MODULUS	
	TANGENTIAL	RADIAL	TANGENTIAL	RADIAL
GE-3200	8.2 MPa (1189 PSI)	0.65 MPa (94 PSI)	7585 MPa (1.1 X 10^6 PSI)	717 MPa (1.04 X 10^5 PSI)
CORNING 9455	6.1 MPa (881 PSI)	1.3 MPa (191 PSI)	2758 MPa (0.4 X 10^6 PSI)	1103 MPa (1.6 X 10^5 PSI)

Table III. Porosimetry Data for GE-3200 Honeycomb Specimens Fired at Various Temperatures

	1100°C	1240°C	1260°C
Pore Volume (cc/g)	0.197640	0.130662	0.010486
Density at 50,000 psia (g/cc)	2.33	--	2.14
Bulk Density (g/cc)	1.60	--	2.09
Porosity (%)	31.5	--	2.20
Average Pore Diameter (microns)	0.58	4.3	22.0

Table IV. Oxide Composition in Weight Percent of Individual and Mixed Raw Materials and of Various Fired GE-3200 Specimens

		Li_2O	Al_2O_3	SiO_2	Na_2O	K_2O	CaO	MgO	Fe_2O_3	TiO_2
Petalite (LAS) $Li_2O \cdot Al_2O_3 \cdot 8\ SiO_2$	Theoretical	4.9	16.6	78.5	-	-	-	-	-	-
	Supplier	4.3	16.0	77.0	0.4	0.3	0.1		-	-
	Wet Analysis	3.2	18.4	69.9	2.6	0.6	-	-	0.2	-
Cordierite (MAS) $2\ MgO \cdot 2\ Al_2O_3$ $5\ SiO_2$	Theoretical	-	34.9	51.4	-	-	-	13.7	-	-
	Wet Analysis	-	33.4	52.4	-	-	-	13.8	-	0.03
Raw GE-3200 LAS/MAS	Theoretical	2.8	24.0	67.7	-	-	-	5.5	-	-
	Wet Analysis*	2.1	26.0	62.1	2.2	0.4	-	6.0	0.3	-
Monolithic GE-3200 (LAS/MAS) (Wet Analysis)	1320°C/6 minutes	1.59	24.2	67.0	0.8	0.4	-	5.4	0.3	-
	1260°C/1 hour	1.68	26.4	64.1	0.8	0.4	-	5.8	0.4	-
	1260°C/3 hours	1.38	23.7	67.5	0.7	0.4	-	5.6	0.4	-
Honeycomb GE-3200 (LAS/MAS) (Wet Analysis)	1100°C **	1.95	-	-	-	-	-	-	-	-
	1260°C/1 hour ***	1.55	-	-	-	-	-	-	-	-
	1260°C/3 hours	0.97	26.4	59.6	2.1	0.2	-	6.2	0.3	-

* Ball milled 24 hours

** Fired by Coors Porcelain Co.

*** Fired in Lithia-enriched Atmosphere