Recuperator Materials Technology Assessment

V. J. Tennery
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V. J. Tennery and G. C. Wei

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CONTENTS

LIST OF SYMBOLS	v
LIST OF FIGURES	vii
LIST OF TABLES	vii
ABSTRACT	1
INTRODUCTION	2
RECUPERATOR DESIGNS AND APPLICATIONS	4
Radiation Recuperator	5
Convection Recuperators	7
Recuperator Performance	13
Recuperator Applications	20
RECUPERATOR MATERIALS SELECTION AND OPERATING EXPERIENCE	23
Metals	24
Ceramics	28
CRITICAL AREAS FOR CERAMIC MATERIALS	34
Mechanical Properties	35
Gas Permeability	36
Chemical Stability	36
Joining	37
Specifications, Materials Codes, and Standard Tests	39
FABRICATION AND COST OF CERAMIC COMPONENTS	40
Ceramic Tubes	41
Extended-Surface Ceramic Structures (Honeycomb)	47
ADVANCED METALLIC CONCEPTS	55
CONCLUSIONS	57
Metallic Recuperators	57
Ceramic Recuperators	58
ACKNOWLEDGMENTS	59
REFERENCES	60

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LIST OF SYMBOLS

a	= Partition thickness.
A	= Heat exchange surface area.
C_p	= Specific heat of gas at constant pressure.
C_{pg}	= Average specific heat of flue gas.
C_{pa}	= Average specific heat of air.
ϵ	= Effectiveness.
h	= Heat transfer coefficient.
h_h	= Convective film coefficient on the hot side.
h_c	= Convective film coefficient on the cold side.
k_p	= Partition thermal conductivity.
N_{tu}	= Number of heat transfer units.
ΔP	= Pressure difference between flue gas and air.
ΔP_a	= Pressure difference between preheated air and ambient.
P	= Pressure.
$\dot{Q}$	= Heat transferred per unit time.
$\dot{Q}_{\max}$	= Maximum transferable heat per unit time.
$\dot{Q}_{\text{actual}}$	= Actual amount of heat transferred per unit time.
T_{1g}	= Temperature of flue gas entering the recuperator.
T_{2g}	= Temperature of flue gas leaving the recuperator.
T_{1a}	= Ambient air temperature.
T_{2a}	= Maximum air temperature.
T'_a	= Average temperature of air.
T'_g	= Average temperature of flue gas.
ΔT_g	= $T_{1g} - T_{2g}$.
ΔT_a	= $T_{2a} - T_{1a}$.
T_g	= Flue gas temperature.
T_a	= Air temperature.
U	= Average heat transmission coefficient in the heat exchanger.
U_a	= Heat transmission coefficient from the recuperator wall to the air.
U_g	= Heat transmission coefficient from the hot flue gas to the recuperator wall.

LIST OF SYMBOLS (Continued)

U_w	= Heat transmission coefficient through the recuperator wall.
W	= Mass flow rate.
W_a	= Mass flow rate of air.
W_g	= Mass flow rate of flue gas.
$(WC)_p a$	= Product of mass flow rate and specific heat of air.
$(WC)_p g$	= Product of mass flow rate and specific heat of flue gas.
$(WC)_p \max$	= Maximum product of mass flow rate and specific heat in the recuperators; that is, $(WC)_p g$ or $(WC)_p a$, whichever is larger.
$(WC)_p \min$	= Minimum product of mass flow rate and specific heat in the recuperator; that is, $(WC)_p g$ or $(WC)_p a$, whichever is smaller.
$(WC)_p \min / (WC)_p \max$	= Ratio of $(WC)_p \min$ to $(WC)_p \max$.

LIST OF FIGURES

Figure		Page
1	Three Types of Gas Flow Paths Used in Recuperators	4
2	Example of Present Commercial Suspended Tube-Type Recuperator Design	8
3	Core Structure of Plate-and-Fin Cross-Flow Heat Exchanger . .	9
4	Design Features of Amsler-Morton Type of Ceramic Recuperator	11
5	Design Features of the Cross-Flow Ceramic Recuperator Marketed in the United Kingdom	12
6	Dependence of the Effectiveness of a Counter-Flow Heat Exchanger upon the Number of Heat Transfer Units and Ratio $(WC)_{p \text{ min}} / (WC)_{p \text{ max}}$	19
7	Dependence of the Effectiveness of the Three Types of Heat Exchangers upon the Number of Heat Transfer Units at a Constant $(WC)_{p \text{ min}} / (WC)_{p \text{ max}}$ Ratio	19
8	Schematic of Hague International Type Ceramic Recuperator	31
9	Schematic of Coated-Paper Process for Fabrication of Extended-Surface Ceramic Structures	50
10	Schematic of Extrusion Process for Fabrication of Extended-Surface Ceramic Structures	51
11	Schematic of Embossing Process for Fabrication of Extended-Surface Ceramic Structures	51
12	Schematic of Calendaring Process for Fabrication of Extended-Surface Ceramic Structures	52

LIST OF TABLES

Table		Page
1	Costs of Silicon Carbide Tubes from Vendor A	42
2	Available Sizes for Tubes of Selected Silicon Carbide Materials from Vendors A and B	42
3	Costs and Maximum Sizes of Mullite and Alumina Ceramic Tubes from Vendor C	45

RECUPERATOR MATERIALS TECHNOLOGY ASSESSMENT

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ABSTRACT

Recuperators are a particular type of heat exchanger designed to recover waste heat from hot flue gases for preheating combustion air or low-joule gases. Recuperation can provide very significant fuel savings (up to 40%) in various industrial fossil fired processes. This report is the result of an assessment of recuperator materials technology conducted between January and August 1977, and includes both metals and ceramics. Most present recuperators used in the United States are constructed of 300 and 400 series stainless steels. Creep, corrosion, and oxidation properties of available alloys limit the maximum metal partition temperature in present recuperators to about 980°C (1800°F). Use of metallic recuperators with higher flue gas temperatures normally dictates selection of units designed primarily for radiation heat transfer and parallel flow of the gas streams. These designs operate with the maximum recuperator wall temperature considerably below the maximum gas temperature. Their major disadvantage is that they recover heat less efficiently than do other designs, such as the cross-flow convection type. Specific standards for use by vendors in quantifying recuperator performance do not exist at present. Specific test standards for identification of recuperator leakage and other characteristics have not been adopted by the United States. The recuperator industry and various manufacturers now use internally developed tests.

Use of ceramic materials in recuperator construction could, in principle, permit the design of recuperators capable of operating with partition temperatures well above the 980°C limit for available alloys and in a gas flow mode able to remove more of the available heat from the waste gas stream. This is possible because of the lower creep and better oxidation and corrosion resistance of selected ceramic materials compared with stainless steels. Siliconized and recrystallized types of silicon carbide have shown promising initial results for tubular heat exchanger application. Few data of this nature exist for other candidate ceramic materials. Extended-surface ceramic structures offer promise for use in constructing compact high-temperature recuperators if leakage, fouling, and fabrication costs can be adequately controlled. Fabrication costs of candidate ceramic recuperator materials, their brittleness, their sensitivity to thermal shock fracture,

the lack of adequate shop and field joining and repair techniques, generally inadequate nondestructive examination techniques, and the lack of appropriate specifications for structural ceramics for use in recuperators and other heat exchangers were all identified during this assessment as major impediments to more serious consideration of ceramics for this structural application.

INTRODUCTION

Increasing fuel costs and natural gas shortfalls are making an increase in fuel-use efficiencies of paramount importance to the industrial sector. One method of conserving energy or increasing the fuel usage efficiency of a process that derives its heat directly from fuel combustion is to transfer some of the heat from the combustion gases to the air used for subsequent combustion of fuel. This air-heating process can be accomplished by the use of one of two devices, one commonly called a recuperator and another referred to as a regenerator. A standard nomenclature for these devices, which relates to a specific design, is not currently applicable to all industries. Therefore, in this report, the term "recuperator" will be used to refer to a heat exchanger in which heat is transferred from hot gases in one section of the device through a material partition to air in a different section of the device. This convention distinguishes "recuperators" from "regenerators." In the latter, combustion gases and cooler air are made to pass alternately through the same sections.

The current fuel availability situation in the U.S. and the prospects for future fuel supplies and costs clearly indicate that use of some type of heat recovery device will become more favorable from an industrial economic viewpoint. The technical status of this heat recovery device technology, specifically that for recuperators, is of interest to (1) identify the current status of the industry that markets such devices and its potential for meeting significantly larger demand, and (2) assess the current materials technology applicable to recuperators. The latter is necessary to identify the current

maximum flue gas and air preheat temperatures as well as to determine prospects for handling higher flue gas temperatures and attaining higher air preheat temperatures in the future.

This report is the result of an assessment of both ceramic and metallic materials technologies appropriate to industrial recuperator applications. The assessment was conducted during the period January through August 1977. The assessment was conducted by means of meetings and discussions with various recuperator vendors in the U.S., with firms who are conversant with sophisticated heat exchanger technology, and with ceramic vendors as well as through an extensive review of the literature. The cooperation of persons from numerous industrial firms in providing information pertinent to this assessment was vital to the effort.

Several different types of heat recovery devices are available for application to industrial furnaces. Some of the factors that dictate an industrial firm's selection of a particular type include (1) the economic situation of the firm at the time a design is selected, (2) cost of fuel and anticipated future costs of fuel, (3) current fuel availability and anticipated future fuel availability, (4) maximum combustion gas temperature, (5) composition and mass flow of hot exhaust gas from the process, (6) ability of the available furnace and burner to use preheated air at various temperatures, (7) design of installed ducts and burners, and (8) available plant space near present furnaces to accommodate the heat recovery equipment.

In general, the thermal efficiency of a heating process involving hydrocarbon fuel combustion can be markedly improved by the use of heat recuperation, and the higher the temperature of the process exhaust gas, the greater the effectiveness of the recuperator from a fuel economy standpoint. Currently, some U.S. industries employing extensive process heat widely use recuperation or regeneration, while others do not. Reasons identified during this assessment for lack of use of waste heat recovery vary considerably, but in many cases implementation of heat recuperation or regeneration has been restrained by economic considerations, such as a perception of unacceptably low return on the investment by industrial managers and ready availability of fuel supplies at relatively low cost.

RECUPERATOR DESIGNS AND APPLICATIONS

Three basic recuperator gas flow designs consist of counter flow, parallel flow, and cross flow for the paths of the two gas streams.¹ Each of these designs has particular technical and economic advantages under certain conditions, and some of the technical factors dictating a recuperator design choice are the high-temperature properties of the material used in the separating wall of the recuperator. The three basic recuperator designs are shown in Fig. 1. The counter flow recuperator allows the highest temperature of air preheat, while the parallel-flow design gives the lowest maximum temperature of the recuperator walls. For relatively high-temperature flue gases, the parallel-flow design is often employed for metallic recuperators, at least in the high-temperature section, because of the temperature limitations of the alloys used. Some designs employ a combination of these types.

Fig. 1. Three Types of Gas Flow Paths Used in Recuperators.

The heat transfers from the hot flue gas to the recuperator wall principally by two processes in all current recuperators, (1) convection and (2) radiation. In essentially all current recuperators, the unit is designed to optimize heat transfer by one process or the other. Some recuperators are designed such that the hot exhaust gas passes sequentially through two sections, the first designed for radiative transfer and the second for convective transfer.

Radiation Recuperators

All metallic recuperators currently available commercially for use with gases of temperatures above about 1000°C (1800°F) depend on the radiation transfer process, because radiation is most effective at the higher gas temperatures. By using a parallel flow scheme, such units can operate with gas temperatures considerably higher than the maximum allowable service temperature of the alloys typically used for construction. The reason for this is that during operation of a recuperator designed for radiative transfer, the material partition in the device operates at temperatures considerably below the maximum gas temperature. Such units almost always incorporate a protective air bleed or water bleed system near the flue gas and/or air inlet to protect the recuperator from meltdown in case the air supply fan on the secondary side fails.

Heat transfer by radiation from hot gases to the recuperator partition is therefore of particular significance to state-of-the-art devices for use with high-temperature flue gases. A quantitative description of heat transfer from nonluminous gases (the general case for gases entering a recuperator) is quite complex and depends on several factors, which will be briefly enumerated because some are strongly related to the material chosen for use in the partition.

Many gases — including oxygen, nitrogen, and hydrogen — have a very low radiative capability at high temperatures. However, water vapor, carbon dioxide, carbon monoxide, hydrocarbons, hydrogen chloride, and ammonia can each contribute to gas radiation. The

most common case is radiation from carbon dioxide and water vapor, since these are common combustion products present in relatively large amounts in flue gases.

Radiation recuperators are generally cylindrical and usually are made a part of the flue system of the furnace to which they are connected. One usually consists of two concentric cylindrical shells. The flue gases pass up the central portion of the recuperator, which usually has a diameter up to 1 or 2 m, and the hot gases radiate their energy to the walls, where the passages containing the combustion air to be preheated are located. Heat transfer calculations generally assume that the recuperator material has an emissivity value of unity. No material presently used in recuperators does, and a more typical value is in the range 0.7 to 0.8 for most of the alloys used in these devices, following some oxidation of their surfaces. Relatively clean metal would have a considerably lower value, but following a few hours of operation with high-temperature flue gases, the oxide layer that forms on the metal will effectively increase the emissivity, and thereby the heat transfer rate of the recuperator for a given flue gas composition and temperature. Specific data documenting changes of the emissivity of radiation recuperator surfaces during service were not located during this assessment.

As the temperature difference between the flue gas and recuperator wall decreases, the heat transfer rate by radiation decreases significantly. Also, the temperature of the metal partition in this type of recuperator is usually limited to $T_{\max}$ of about 800°C (1500°F). A typical maximum flue gas temperature at the recuperator is in the range 1370 to 1430°C (2500–2600°F), even for a process temperature near 1650°C (3000°F), because of duct conduction losses.² This situation limits the maximum temperature difference between the flue gas and the partition to about 800°C (1500°F) in a radiation recuperator.

As the hot gas passes through a radiation recuperator, it transfers energy to the recuperator partition and thus cools. This

results in a considerable temperature gradient along the unit, and a critical aspect of designing such a unit is involved in accommodating the stresses induced by the temperature gradient.

Once the thermal energy is transferred to the recuperator partition by radiation, the heat is conducted through the metal wall to the secondary side, where it is transferred to the combustion air. On the air side of this recuperator type, the heat is transferred by a convection process like that operative in a convection recuperator.

From the foregoing discussion, it is clear that the effectiveness with which a radiation recuperator extracts heat from a flue gas stream decreases rapidly with decreasing flue gas temperature and depends strongly upon the flue gas composition and the emissivity of the recuperator surfaces on the flue gas side.

Convection Recuperators

Recuperators designed to utilize convective heat transfer usually have considerably different designs from those dependent upon radiative transfer. These typically have a design resembling Fig. 1(c) although, as we shall see later, that in Fig. 1(a) will have the highest theoretical effectiveness. An important aspect of this type of recuperator is the fact that the temperature of the partition is very close to the temperature of the flue gas. For metallic convection recuperators, this limits the maximum permissible flue gas temperature to 980°C (1800°F) because of rapid degradation of the oxidation resistance and mechanical properties of available alloys at higher temperatures. For applications in which the flue gas is above this temperature, the gas is often diluted with ambient air or water spray to protect the recuperator.

Convective heat transfer between a gas and the wall of a tube depends on several parameters involving properties of the gas as well as its velocity and the geometric relation between the direction of gas flow and the tube axis. For a recuperator design including air flowing through tubes on the secondary side, the air velocity

on the secondary side must be much greater than the flue gas velocity on the primary side, if maximum heat extraction to the secondary side is to occur in the recuperator.

The convection recuperator functions by the use of tubes placed across or along the flue gas stream through which air is forced at a relatively high velocity compared with that of the flue gas stream. The tubes are joined together by use of manifolds or tube sheets. In some designs, such as the Hazen* recuperator, the tubes are suspended from one end in order to better accommodate the thermal expansion strains in the unit. This design, illustrated in Fig. 2, uses a counter flow configuration of double tubes, which are in turn used in cross flow in the flue gas stream. This system is reportedly usable with flue gas temperatures up to 1260°C (2300°F) by use of a protection thermocouple connected to the inner wall and an air bleed system, which keeps the metal temperature within acceptable limits.

*Hazen, Combustion Engineering, Inc., Wellsville, New York.

Fig. 2. Example of Present Commercial Suspended Tube-Type Recuperator Design.

Another type of heat exchanger design, which is widely used presently, but mostly for engine applications, is the so-called plate-fin type. At present, this type of unit is available commercially for a wide variety of applications for transferring heat between liquids or between one liquid and a gas. This type of heat exchanger is constructed from flat plates and corrugated sheets, which are called the fins. The passages formed when the corrugated sheets are bonded to the plates are used as the primary (hot) and the secondary (cold) side of the unit as illustrated in Fig. 3. This type of heat exchanger could be a particularly effective recuperator because of the very efficient heat transfer between the primary and secondary sides due to the high heat transfer area per unit volume for this design. The fabrication technology is well established for construction of plate-fin heat exchangers from various aluminum alloys and some stainless steels. The metal fins are brazed to the plates in this type, and this can presently be done sufficiently well to allow essentially no leakage between the primary and secondary sides. The analytical description of the plate-fin design is well developed, and this background plus the extensive manufacturing experience in constructing these units of metal make this design appear as a reasonable candidate for future application to high-temperature recuperation if suitable materials

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Fig. 3. Core Structure of Plate-and-Fin Cross-Flow Heat Exchanger.

are available. Materials limitations and the higher tendency of this design for fouling in dirty flue gas environments are presently the potential impediments to future use. The plate-fin design very effectively utilizes space in which to accomplish heat transfer and also has the potential for economical fabrication.

Another distinctive type of recuperator that has been employed in the U.S. is the ceramic unit, which relies largely upon convection for heat transfer. This type of recuperator employs ceramic pipe and tile and typically operates in a crossflow mode. The two types of ceramic recuperators that have been used commercially to date in the U.S. are the Carborundum and Amco types.³ In the Carborundum type, ceramic tubes are supported horizontally between vertical ceramic walls such that the tubes span the flue gas duct. Air to be preheated passes through the tubes. The tubes are sealed to the ceramic walls by use of fibrous aluminosilicate packings, which allow slight movement of the tube ends in the region of the seal to accommodate thermal expansion strains. Multiple air passes are accomplished in this design by the use of header boxes, which carry the air to subsequent tube banks located vertically above the first bank, which is at the bottom of the recuperator. The ceramic tubes are typically 1.2 m (4 ft) long and 0.1 m (4 in.) in diameter. This design was found difficult to apply to large installations because of difficulties in distributing the air reasonably equally to a large number of tubes and subsequently collecting the heated air and directing it to the burner ports.

The Amco recuperator was introduced in the U.S. in the late 1930s, and several installations are still operating.⁴ This unit consists of octagonal ceramic tubes oriented vertically with their ends located in fiber sealed recesses in ceramic tile. The recuperator is built up vertically from tiles and tubes, with a typical unit consisting of six or more vertical tube sets. The waste gases pass down the tubes and the air flows around the tubes. A section of this type of recuperator is shown in Fig. 4. The tiles establish and maintain the alignment of the ceramic tubes in the unit. A large number of tubes and tiles is required in the construction

Fig. 4. Design Features of Amsler-Morton Type of Ceramic Recuperator.

of such recuperators because the size of tile or tube that can be manufactured within reasonably accurate limits is limited. Various types of refractory fiber seals have been used at the tile-tube interfaces to isolate the primary and secondary sides of the recuperator. These seals have worked with varying degrees of success, and a typical maximum pressure differential, ΔP , achievable between the two sides with these units is 500 to 750 Pa (2 to 3 in. of water column). This leakage problem places design limitations on both the Carborundum and Amco ceramic recuperators. As noted earlier, a relatively high air velocity within the tube relative to the flue gas velocity is desirable so heat transfer within the tubes does not limit heat transfer in the recuperator. Practically, the recuperator designer would prefer to be able to use high air velocities within the tubes with the resultant positive ΔP (cold side to hot side) required to accomplish this flow. Leakage of 10 to 15% or more from the cold to hot side, which will occur at higher ΔP for the type of seals

used in these recuperators, reduces the effectiveness of the unit in extracting waste heat from the flue gas. Another difficulty accompanying the leakage is a restriction on the burner design. Burner designs introduced within the past few years tend to require a ΔP_a (air stream to ambient) of 1.25 kPa (5 in. of water column) or more, and this is not compatible with this type of recuperator if many of the seals leak appreciably.

A third ceramic recuperator design was reported to have originated in the United Kingdom⁵ and can sustain a significant ΔP across the seals. This unit is illustrated in Fig. 5. It is of the cross-flow type and employs a header box to serve as the manifold that directs the heated air from one set of tubes into the adjacent set located further down the flue gas duct. This type of recuperator reportedly has less than 3% leakage and has demonstrated the capability of functioning at high air preheat temperatures. Tubes made of SiC bonded with Al_2O_3 as well as some glazed fireclay-based ceramic tubes have been used.

Fig. 5. Design Features of the Cross-Flow Ceramic Recuperator Marketed in the United Kingdom.

The tubes used at present have 0.1 m (4 in.) OD and a 20 mm (3/4-in.) wall thickness.⁵ Eleven of these units are reportedly now in operation in the U.K. in steel soaking pits, steel reheat furnaces, and at least one oil refinery. Air temperatures of 600 to 900°C (1100–1650°F) have been demonstrated in reheating furnaces, while 1200 to 1300°C (2200–2400°F) air has been produced from soaking pits. Inserts are typically used inside the ceramic tubes to perturb air flow and, thus, to enhance heat transfer to the air.

Recuperator Performance

One aspect of recuperators that became apparent during this assessment was a general lack of universally accepted parameters or data that allow a simple direct comparison of recuperator designs and performance for various industrial waste heat recovery applications.

One reason for this situation is related to the different bases that various present and potential recuperator customers use to decide whether recuperation is economical. A relatively universal parameter is the importance of present and projected costs of fuel and its availability. Another significant factor is whether a potential recuperation system is to be an add-on to an already existing furnace system or whether it is to be incorporated into a new plant design. The increasing costs of plant space has favored recuperator facilities that require minimal floor space or excavation and construction below plant floor level. Both floor area and below ground structural requirements were identified during this assessment as impediments to new installations of ceramic recuperators of the Amco and Carborundum designs. The potential customer's required return-on-investment policy, capital availability, and current and potential Federal and local government fuel policies were also cited as variables of importance in the recuperation decision. Detailed analysis of these factors were not within the scope of this assessment.

An attempt was made however, to assess more directly amenable technical factors in determining whether recuperation should be employed and, if so, what type of recuperator would be selected. A convenient technical measure currently available in the industry whereby one recuperator could be compared with another was not identified. Various parameters based on heat exchanger theory allow recuperators to be compared on the basis of their ability to transfer heat from a stream of flue gas to air. In general, specific data of this type are not readily available for recuperator units now on the market. Several recuperator vendors expressed the view during this assessment that such a standardization would be helpful to this industry.

The heat transmission in a recuperator is basically given by the expression:

$$W_g(T_{1g} - T_{2g})(C_{pg}) = AU(T'_g - T'_a) = W_a(T_{2a} - T_{1a})C_{pa}, \quad (1)$$

where

- W_g = mass of flue gas flowing in unit time,
- C_{pg} = average specific heat of flue gas,
- C_{pa} = average specific heat of air,
- A = heat exchange surface area,
- U = average heat transmission coefficient in the heat exchanger,
- T'_g = average temperature of flue gas,
- T'_a = average temperature of air,
- W_a = mass of air flowing in unit time,
- T_{2a} = maximum air temperature,
- T_{1a} = ambient air temperature,
- T_{1g} = temperature of flue gas entering the recuperator,
- T_{2g} = temperature of flue gas leaving the recuperator.

For the recuperator to have maximum effectiveness, no leaks are allowed between the section containing the hot flue gas and the air to be heated.

The heat transfer coefficient, U , in Eq. (1) consists of at least three components, which can be represented by the expression

$$U^{-1} = U_g^{-1} + U_w^{-1} + U_a^{-1}, \quad (2)$$

where

- U_g = heat transmission coefficient from the hot flue gas to the recuperator wall,
- U_w = heat transmission coefficient through the recuperator wall,
- U_a = heat transmission coefficient from the recuperator wall to the air within the device.

The economics and operation of a recuperator are quite sensitive to the particular value of U that controls or limits heat transfer within the unit. When heat is transferred within a system where several coefficients (U_g , U_w , and U_a) operate sequentially, the coefficient having the smallest value has a strong influence on the value of total heat transmission through a particular recuperator section. Later, this aspect of heat transfer will be seen to have an important bearing on recuperator design.

The properties of the recuperator wall enter these analyses via an expression for U of the form:

$$\frac{1}{U} = \frac{1}{h_h} + \frac{a}{k_p} + \frac{1}{h_c}, \quad (3)$$

where

- a = partition thickness,
- k_p = partition thermal conductivity,
- h_h = convective film coefficient on hot side,
- h_c = convective film coefficient on cold side.

Equation (3) is explicitly correct for the case where the available area on the hot and cold sides are equal and no extended surfaces are used.

The thermal conductivities of alloys and the wall thicknesses used in metallic heat exchangers or recuperators are typically such that the α/k_p term is neglected in the design. In the case of ceramic materials being considered for use in high-temperature recuperators, such an assumption may not be valid because of the relatively low thermal conductivity of ceramic materials compared with metals. No specific analysis of this situation was found in the literature or acknowledged as being available from the recuperator vendors or other respondents.

The maximum heat that can be transferred from the hot side to the cold side of a heat exchanger is limited to a maximum value dictated by thermodynamics. The maximum amount of heat that can be transferred per unit time is given by

$$\dot{Q}_{\max} = (WC_p)_{\min} (T_{1g} - T_{1a}) , \quad (4)$$

where

- $\dot{Q}_{\max}$ = maximum transferable heat per unit time,
- $(WC_p)_{\min}$ = minimum product of mass flow rate and specific heat in the system,
- T_{1g} = flue gas inlet temperature,
- T_{1a} = combustion air inlet temperature.

The quantity $(WC_p)_{\min}$ in Eq. 4 is the smaller of the two quantities $(WC_p)_g$ and $(WC_p)_a$, where these two values are the product of the mass flow rate W on the flue gas side or air side and the corresponding specific heat of the gas.

Equation (4) defines the maximum possible thermodynamically limited heat transfer rate for a counter-flow heat exchanger of infinite heat transfer area. The actual amount of heat that is transferred per unit time within the recuperator is given by

$$\dot{Q}_{\text{actual}} = W_g C_{pg} (\Delta T_g) = W_a C_{pa} (\Delta T_a) , \quad (5)$$

where

$$\begin{aligned} \Delta T_g &= T_{1g} - T_{2g}, \\ \Delta T_a &= T_{2a} - T_{1a}. \end{aligned}$$

Using $\dot{Q}_{\text{max}}$ and $\dot{Q}_{\text{actual}}$, a heat transfer effectiveness ϵ can be defined⁶ as

$$\epsilon = \frac{\dot{Q}_{\text{actual}}}{\dot{Q}_{\text{max}}} = \frac{W_g C_{pg} (\Delta T_g)}{(WC_p)_{\min} (T_{1g} - T_{1a})} = \frac{W_a C_{pa} (\Delta T_a)}{(WC_p)_{\min} (T_{1g} - T_{1a})} \quad (6)$$

where all the quantities are defined as previously. The heat transfer effectiveness, ϵ , is a property of any heat exchanger that allows comparison with any other unit, and it is apparent from this assessment that presentation of data of this type for recuperators would make comparisons of the performance of different designs much simpler.

Kays and London⁷ describe a general function that relates the effectiveness, ϵ , for any heat exchanger to three parameters, N_{tu} , the number of heat transfer units of an exchanger, the ratio $(WC_p)_{\min} / (WC_p)_{\max}$, and the flow arrangement. The quantity N_{tu} is defined as

$$N_{tu} = \frac{AU}{(WC_p)_{\min}} , \quad (7)$$

where

- A = the heat transfer area,
- U = average thermal transmission coefficient between the hot and cold sides,
- $(WC_p)_{\min}$ = minimum product of mass flow and specific heat in the system, as defined previously.

For a recuperator, N_{tu} can be stated as⁸

$$N_{tu} = \frac{UA}{(WC_p)_g}, \quad (8)$$

since $(WC_p)_g < (WC_p)_a$ is typical for a recuperator.

Kays and London⁷ reported graphs for numerous heat exchanger geometries that relate the effectiveness, ϵ , to the number of heat transfer units, N_{tu} , for various ratios of $(WC_p)_{\min}/(WC_p)_{\max}$. Analysis of graphs of this type permits rapid and reasonably unambiguous comparisons of various designs.

Figure 6 shows the dependence of the effectiveness, ϵ , on N_{tu} for the important case of counter flow at selected $(WC_p)_{\min}/(WC_p)_{\max}$ ratios. This case typically provides the maximum ϵ achievable. From Fig. 6 the heat transfer effectiveness, ϵ , is obviously largest at lower ratios of $(WC_p)_{\min}/(WC_p)_{\max}$, and for values of this ratio in the range 1 to 0.25, ϵ increases rapidly with values of N_{tu} up to at least 3. The design procedure for making ϵ as large as possible for a recuperator of this type then is to make the ratio $(WC_p)_{\min}/(WC_p)_{\max}$ as small as practical while incorporating a value of N_{tu} in the range 2 to 3. In the case of a recuperator, where $(WC_p)_a = (WC_p)_{\min}$ is typical, ϵ is obviously greatest when the (WC_p) product for the flue gas is very small relative to (WC_p) on the air side.

Figure 7 compares the dependence of ϵ on these parameters for the case of simple counter flow, parallel flow, and cross flow with both streams unmixed for a $(WC_p)_{\min}/(WC_p)_{\max} = 0.5$. Similar trends occur for other ratios. The term "mixing" is used to denote agitation or stirring of the flow medium so that the temperature at any section perpendicular to the flow is uniform. The effectiveness is typically greater for a given set of conditions when both streams are unmixed. At $N_{tu} = 2.0$, the ratios of ϵ for the parallel flow and cross flow to that for counter flow are approximately 0.81 and 0.94, respectively. If both streams are mixed in the cross-flow design, the ratio for cross flow is decreased to 0.88. One recuperator vendor estimated that his radiation recuperators operated with a typical effectiveness in the range 0.3 to 0.4.

Fig. 6. Dependence of the Effectiveness of a Counter-Flow Heat Exchanger upon the Number of Heat Transfer Units and Ratio $(WC_p)_{min}/(WC_p)_{max}$.

Fig. 7. Dependence of the Effectiveness of the Three Types of Heat Exchangers upon the Number of Heat Transfer Units at a Constant $(WC_p)_{min}/(WC_p)_{max}$ Ratio.

The methodology discussed in this section for evaluating recuperator performance is based on an assumption that the heat transfer occurs primarily by convection and conduction. In the case where significant radiation transfer occurs on the hot side, the analytical treatment becomes more complicated, and a specific treatment of this case was not available. However, for any case where the heat transfer is described reasonably accurately by the differential equation,

$$\frac{d\dot{Q}}{dA} = U(T_g - T_a) , \quad (9)$$

where the overall thermal conductance, U , can be treated approximately as a constant, the foregoing treatment should be adequate as a first approximation.

The general design methodology for any recuperator then is to maximize ϵ while keeping the pressure drop and the size of the unit acceptable. Numerous other factors must be used in an actual design, but the reader is referred to ref. 7 for a summary of these.

Recuperator Applications

Effort was made during the assessment to identify which industries with high-temperature processes have historically utilized recuperation or other waste heat recovery extensively and which industries have not. This information was obtained primarily from information sources involved with the marketing of recuperators. In general, the steel industry appears to have adopted waste heat recovery systems extensively. One respondent estimated that 90% of the current soaking pits have some kind of heat recovery system in place and that essentially all of these are recuperators, both metallic and ceramic. Steel reheating furnaces, on the other hand, were estimated to have waste heat recovery on only about 80% of the current furnaces.

The glass industry has historically made extensive use of regenerators for recovering waste heat from the combustion exhaust of

large continuous glass melting furnaces. These regenerators have apparently not been replaced to any significant extent by recuperators. Historically, glass tank regenerators have evolved to the point where their performance is relatively well understood, and to replace them with recuperators would involve very significant capital investments, in most cases due to the present furnace designs. In this particular case, regenerators are desired over recuperators. Although a recuperator has the advantages of being relatively simple, requiring less space and no gas flow reversal, plus providing a constant air temperature, its main disadvantage is a lower air preheat than that provided by a regenerator, and this is considered undesirable for a glass furnace. On the other hand, most fiber glass melting furnaces reportedly have been equipped with metallic recuperators. Other types of glass furnaces, such as some unit melters, were reported to have a very limited number of waste heat recovery systems installed. Many day tanks (relatively small glass melting furnaces usually operated on a periodic basis) were reported to be equipped with regenerators. A case study of a metallic radiation recuperator installed on a glass day tank recently reported⁹ that the installation resulted in a 25% fuel savings.

Aluminum melting and remelting furnaces are generally lacking in waste heat recovery systems; one respondent estimates that about 5% of the current furnaces are presently so equipped. It should be emphasized that these comments regarding the extent of installation of waste heat recovery systems in various industrial sectors have been obtained from a limited number of sources.

Because of the current U.S. industrial economic situation, the purchase and installation of waste heat recovery systems is not generally an automatic decision being made by corporate management. The principal factor is economic, and until the industrial fuel selection, energy conservation, and taxing policies are resolved at the Federal level, no clear-cut decision process is available that would clearly favor widespread installation of recuperators on high-temperature furnaces previously operated without them. Also,

although it was not an objective of this assessment, no major industrial sector was identified that should but presently does not use any high-temperature waste heat recovery, except perhaps for some parts of the aluminum industry.

There are obvious material limitations that presently prevent the maximum heat extraction from industrial high-temperature combustion gas streams. We found no detailed analysis that identified the *new* net energy savings possible annually in the U.S. if advanced recuperators were available at competitive prices and installed on the appropriate furnaces. One respondent pointed out that if such so-called advanced recuperators were to become available in the marketplace in the next two to five years, and were to be extensively installed, most of the currently used fuel burners would also have to be replaced. This would represent a significant incremental capital cost in most cases. Another interesting aspect of the burner situation was the observation that most of the currently used high-temperature burners (capable of using highly preheated air) are limited to air at about 540°C (1000°F) or lower. Therefore, if recuperators capable of preheating air to temperatures in the range 800 to 1000°C (1500–1800°F) were to be demonstrated and employed, then burners capable of operating under these conditions would be required. Only one burner design was identified during this assessment as being capable of operating with air above 800°C (1500°F) and this unit reportedly can operate with air at temperatures up to 980°C (1800°F).

Recuperators can be used for preheating low-joule gases as well as combustion air. Preheating low-joule gases generally imposes more severe corrosion conditions on the secondary side of the recuperator than the case of preheating combustion air because of the corrosive and detrimental species, such as H₂ and CO, which are typically present in the low-joule gases. At present, there is no operating or experimental data on recuperators that are designed and used for preheating low-joule gases such as producer gas, blast furnace gas, coke oven gas, Lurgi low-joule gas, and fluidized-bed coal gas. It is anticipated that in the long term preheating low-joule

gases will become very important and offer substantial economic advantage as fuel costs continue to increase and natural gas and petroleum become gradually depleted. A critical temperature above which a low-joule gas becomes unstable needs to be established before a recuperator to preheat this fuel is designed and constructed. The critical temperature is the upper limit for the temperature of the low-joule gas leaving the recuperator. A stringent condition of absolutely no leakage between the flue gas side and the low-joule gas side in a recuperator is required because of the danger of combustion within the recuperator as a result of mixing of the two gases there. The stable oxide film on the surfaces of stainless steel and other high-temperature alloys, which provides their oxidation resistance, could be decomposed because of the reduction of these oxide films by H_2 and CO in the low-joule gases. The service life of metals and alloys in an environment containing H_2 and CO could, therefore, be drastically shortened compared with service in more oxidizing atmospheres. Hydrogen permeability and metal embrittlement due to hydrogen-metal reactions are also potential problem areas. The use of ceramics, including oxides and carbides, in recuperators for preheating low-joule gases does not seem to offer any significant advantage over metals, because oxides and the oxide films on carbides (e.g., SiO_2 on silicon carbide) are also potentially subject to reduction by H_2 and CO. Recuperators for preheating low-joule gases represent an application that can conserve a significant portion of industrial energy in the future if low-joule gases become widely used, but much development work on problems cited above needs to be undertaken to establish the viability of recuperators for this application.

RECUPERATOR MATERIALS SELECTION AND OPERATING EXPERIENCE

During this assessment, groups in the U.S. who have had direct experience in heat exchanger design and construction, recuperator design and fabrication, ceramic recuperator design and installation, and ceramic tube fabrication were contacted by phone and several were visited. In general the purpose of this assessment was

acknowledged by these respondents as being potentially useful by these organizations, who are either presently marketing high-temperature recuperators or who are considering the possibility of marketing such devices. Firms involved in ceramic manufacturing and who were considered as typical candidates for fabrication of tubes required for use in advanced tubular recuperators were also very helpful in providing information on current availability of long tubes etc.

The materials technology as identified during this assessment and as it applies to recuperator applications will now be discussed. These conclusions are the summation of the expressions of technical people currently active in the field. Details of the economic constraints on materials choices for recuperator use will not be reviewed in depth, as these data were not readily available for most cases.

Metals

The temperatures encountered in recuperators for waste heat recovery restrict the choice of available alloys. Stainless steels or compositional variations on these are used almost exclusively for present state-of-the-art metallic recuperator construction. The major materials used for constructing radiation-type recuperators are austenitic types 304 and 309 stainless steel as reported to us during this assessment. The slightly higher chromium and nickel contents of 22-24 and 12-15 wt % respectively in type 309 makes it favored for use where higher temperatures are encountered. One recuperator vendor uses type 304 or 330 stainless steel in radiation recuperators, depending on whether the flue gas temperature is less or greater than 980°C (1800°F). Another respondent who markets radiation recuperators, on the other hand, strongly favors use of the strongly oxidation resistant ferritic type 446 and generally uses type 304 or 309 only on recuperators designed for use on steel soaking pits.

Another respondent, who currently does not market recuperators but has extensive high-temperature heat exchanger design and

manufacturing experience, expressed the view that ferritic stainless steels such as type 430 or 446 would be selected for applications in the temperature range 650–700°C (1200–1300°F) (metal temperature) while austenitic steels (300 series) would be used in applications up to 980°C (1800°F). For temperatures above 760°C (1400°F) high-nickel-content alloys such as Incolloys* and alloys containing 14% Cr and 4% Mo had been found to have the best creep resistance. High vanadium contents in the flue gas would, in this respondent's view, dictate use of a stainless steel containing at least 18% Cr, also with the lowest possible nickel content because of the relatively high incremental cost associated with high-nickel-content stainless steels. Two respondents indicated that they generally use an aluminum-coated steel called "Alonized"[†] in recuperators on furnaces fired with dirty fuels such as No. 6 fuel oil. Applications in flue gas atmospheres having high sulfur contents generally favor use of the ferritic steels of the 400 series, which have zero or very low contents of nickel, because of the tendency for corrosion of austenitic type steels via nickel-sulfur reactions at high temperatures.

The high cost of Inconel,[‡] Incoloy, and Hastelloy[§] materials was cited by all the recuperator manufacturers interviewed as a severe impediment to their consideration for use in recuperators. High-temperature instability of various properties of these alloys was also cited as a major concern of one respondent. Another concern that discouraged consideration of the more refractory metals was currently prevailing long delivery times. Of the three metallic recuperator vendors visited during this assessment, two had constructed devices of Inconel 601 once and the other had used Hastelloy X once as part of a government contract.

One of the metallic recuperator vendors visited had rather extensive experience with cross-flow convection recuperators of the

*Incolloys, product of Huntington Alloys, Co., Division of Int. Nickel Co., Huntington, W.V.

[†]Alonized, products of Alon Processing, Inc., Tarentum, Penn.

[‡]Inconel, products of Huntington Alloys Co., Division of Int. Nickel Co., Huntington, W.V.

[§]Hastelloy, products of Cabot Corp., Haynes Stellite Co., Kokomo, Ind.

variety sometimes referred to as the canal type. Several of these had been installed in steel soaking pits fired with No. 6 oil, and this application has been found to be very severe on convection recuperators because of fouling and corrosion of the tube banks by products from fuel combustion as well as oxide scale carry-over from the pit. The recuperator design used for this application consists of tube banks welded to a header or plenum, which is generally outside the flue gas stream. The alloy found to function best for this corrosive application is a stainless steel casting alloy designated as HD, containing 26 to 30 wt % Cr and 4 to 7 wt % Ni according to the respondent. The major failure mode observed in the recuperator tubes during service is by cracking, which was thought to be caused by the severe embrittlement of the alloy due to the formation of sigma phase during high-temperature service. The tubes of HD stainless steel are presently fabricated by a proprietary centrifugal casting process. There are reportedly presently three or four vendors in the country who can fabricate these tubes. The present casting process limits the maximum tube length to about 2.5 m (100 in.) and a maximum diameter of about 90 mm (3.5 in.)

Another respondent who had considerable experience with fabrication and performance of radiation recuperators expressed the view that any recuperator application involving No. 6 oil as a fuel should be limited to metal temperatures below 620°C (1150°F). Higher metal temperatures in the presence of the vanadium, sulfur, and other impurities in the combustion gas from No. 6 fuel oil has resulted in rapid corrosion of ferritic stainless steels. Type 446 stainless steel has also been observed by this recuperator manufacturer to become very brittle after being used for some time in a radiation unit operating with 1320–1370°C (2400–2500°F) flue gas and producing 700°C (1300°F) air. This firm has installed several radiation recuperators made of austenitic stainless steels on fiber glass furnaces. These typically last about seven years.

Examples of extensive corrosion of the HD stainless steel casting alloy tubes from cross-flow recuperators used in steel

soaking pits fired with No. 6 oil were observed during a visit at the plant of one of the recuperator vendors. The corrosive attack occurred on the exterior of the tubes and, in the advanced stage, consisted of gross pits, which grew laterally and radially in the tube wall from the exterior tube surface that was exposed to the flue gas. Gross deposits collected on the tubes, with the lead tube rows showing the most extensive corrosion. These recuperators typically consisted of ten or more rows of tubes in a staggered configuration. Several units had been returned to the vendor for "reworking." Most of the examined tube banks contained massive fouling deposits or plugging of the passages between the tubes after being in service in a soaking pit for times ranging from two to five years. The vendor who built these units speculated that the corrosion was due to reactions between the steel and vanadium, sulfur, and other impurities from the fuel as well as some possible carry-over from the pit.

A radiation recuperator vendor described his experience with serious corrosion of units made of type 446 stainless steel in aluminum furnace applications, where chlorine-bearing vapor species were present in the flue gas. The vendor was not aware of a readily available alternate alloy to substitute for type 446 stainless steel for this application. Lead-bearing vapor species in flue gases were identified by another vendor as being very corrosive to convective recuperators made of type 304, 309, or 446 stainless steel, while vendors of radiation recuperators stated that they had not observed this corrosion problem. They felt this lack of corrosion in radiation units was probably due to the relatively short residence time of the flue gas and/or its relatively poor physical contact with the metal in the radiation-type unit. No quantitative data base for this conclusion was identified during this assessment. Corrosion of stainless steel recuperators by boron in applications to borosilicate glass melting furnaces was also cited as a potential problem area.

No specific information was identified pertaining to the corrosion resistance of such alloys as Incoloy 800 (32% Ni, 21% Cr, 46% Fe) or Inconel 601 (60% Ni, 23% Cr, 16% Fe) in recuperator applications involving flue gases containing significant impurity levels. Much of the metallic recuperator operating experience in the U.S. has involved use of relatively clean fuels, such as natural gas or distillate oils, except for the residual-oil-fired soaking pit usage cited previously. If incentives are provided in the future to make industrial use of higher air preheat temperatures and/or use of relatively impure fuels more economically attractive, an increase in recuperator corrosion can be anticipated.

Ceramics

As indicated earlier, the data base for use of ceramic materials in recuperator construction is much more limited than that for metals. The severe leakage problem, the lack of flexibility of installation and operation, and the large weight and volume required of the older types of ceramic recuperator have not made it as attractive for new plant installation as the metal units. Conceptually, a ceramic recuperator potentially offers some clear advantages over a metal unit, if the objective is to maximize the energy conservation of the process. Because of the ability of certain ceramic materials to maintain their physical integrity at temperatures in the range 1100 to 1650°C (2000–3000°F) in oxidizing atmospheres, they obviously are candidates for use in very high-temperature flue gas streams. In principle, a ceramic recuperator could function in a mixed radiation-convective mode at flue gas temperatures above 980°C (1800°F) such that appreciably more heat is extracted from the flue gas than is presently achievable with metallic radiation recuperators. Such a recuperator would also not need an over-temperature protection system because of the use of high-temperature ceramics. The absence of danger of the ceramic recuperators becoming damaged by overheating due to failure of the air supply indicates that the ceramic recuperators are particularly valuable in providing fuel savings and lowering

recuperator maintenance and materials costs as well as providing improved furnace productivity. Also, a listing of candidate ceramic materials that might be considered for use in recuperators contains no material, such as chromium, whose supply must rely heavily on imports.

Information regarding ceramic materials presently or previously used in actual recuperator installations was obtained from firms that either now market such units or have in the past. Other information was obtained from a firm that only recently has developed a ceramic recuperator and is in the process of marketing the unit.

The presently used ceramic tube-and-tile recuperators of the vertical tube type are constructed from either sintered fireclay or silicon carbide (SiC) tubes and sintered fireclay tiles. In steel soaking pit applications, these recuperators reportedly used to have a typical service life of about eight years, but recent experience shows that these units presently have a three-year lifetime. The recuperator vendor did not have specific information to explain this reduction in performance. This recuperator builder presently obtains all the ceramic tubes and tiles from one ceramic fabricator. The fireclay-based tubes are favored over silicon carbide because the carbide tubes cost about twice as much as the fireclay equivalents, although silicon carbide parts potentially can offer a higher heat transfer rate because of its higher thermal conductivity (about ten times that of fireclay). Fibrous gaskets, washers, and ropes are used as an expansion joint and seal between the tubes and the tiles. Mortar based on sodium silicate is also used as seals between tubes and tile to isolate the hot side from the cold side of the recuperator. The fibrous seals and the mortar often leak or fail in an unpredictable matter, as mentioned earlier. The design of this recuperator makes it nearly impossible to repair such a seal without dismantling the entire unit. A removable upper tube course allows rapid replacement of the top course rather than the entire setting, and in most cases plugging the failed tubes is often the only practical means of repair.

Two types of SiC tubes have been fabricated for this use and these are (1) fireclay-bonded SiC fabricated by extrusion, and (2) SiC bonded with a minimal amount of fireclay and fabricated by ramming the powder into molds. Both the SiC tube types are subsequently fired at high temperature, as are the fireclay-based tubes.

Longitudinal and circumferential cracking of the fireclay and fireclay-bonded tubes often occurs during service, with the result that the ability of the tube to support compressive loads at the recuperator temperatures is decreased and leakage across the recuperator is increased. The tubes often crack before they start to plug from furnace carry-over condensation and slags formed in the fireclay running down the inside wall of the tube. The principal reason for premature preheating efficiency decline is thus tube cracking. In the later stage of the recuperator life, plugging becomes a more significant problem in many steel industry applications.

Materials used in ceramic recuperators of the horizontal-tube cross-flow type have consisted primarily of SiC using either a fireclay bond as for the vertical tube design, just discussed, or a silicon nitride bond. No specific information on the operating experience of these two types of tubes in this horizontal-tube recuperator could be identified during this assessment.

A third recently developed type of ceramic heat exchanger or recuperator using finned ceramic tubes is of direct interest in this assessment. The tubes in this heat exchanger consist of about 85 wt % SiC, but their specific composition and other characteristics are proprietary at this time.¹⁰ This SiC is reportedly not bonded with either clay or silicon. The tubes have extended surfaces on both the inside and outside walls to enhance heat transfer. Full-size tubes have been laboratory temperature-cycle tested as well as evaluated in a forge furnace recuperator for two years of cyclic service with no reported tube failures.¹¹ A schematic of this type of ceramic recuperator is shown in Fig. 8. A typical finned tube for this type of recuperator is about 1.2 m long. An early design of these SiC tubes included an OD measured to the tip of the fins

Fig. 8. Schematic of Hague International Type Ceramic Recuperator.

of 90 mm (3.5 in.), but this has recently been changed to 95 mm (3.75 in.). Both smooth-bore and extended-inner-surface tubes have been employed in these units. The smooth bore tubes have an ID of 39 mm (1.55 in.), while the extended inner surface tubes have a minimum ID of 30 mm (1.35 in.) and a maximum OD of 39 mm (1.55 in.). The inner extended surface consists of 36 longitudinal serrations running the length of the inner tube surface. There has been no experience to date using relatively dirty fuel, such as No. 6 residual oil, with these ceramic recuperator tubes, but no problems have been observed with use of No. 2 distillate oil in early testing.

Other ceramic materials that were cited by respondents as potential candidates for use in recuperators included alumina, zirconia, mullite, spodumene, cordierite, silicon nitride, and sialon (Si-Al-O-N compounds) compositions. Apparently none of these materials have been employed in practical recuperators, but some, such as spodumene (lithium aluminosilicate, LAS) and cordierite

(magnesium aluminosilicate, MAS) have been evaluated rather extensively in heat wheel regenerator applications.

In the past several years, about six ceramic manufacturers and several automobile manufacturers have been developing materials and processes suitable for the fabrication of honeycomb structures for use as regenerators. The materials of present interest are LAS, MAS, and acid-leached and heat-treated lithium aluminosilicate (AS), and combinations of LAS and MAS. However, all these materials have certain limitations concerning their usefulness as recuperator parts. Lithium aluminosilicate ceramics are prone to reaction with sulfur, which is commonly present in fuel oils. The relatively higher linear thermal expansion coefficient of MAS as compared with LAS and the relatively low mechanical strength of MAS [modulus of rupture is 48 MPa (7000 psi) are undesirable. The AS material resists corrosion better than LAS and retains the low expansion of the parent LAS, but it is limited to operating temperatures between 800 and 1000°C (1470 and 1830°F). Combinations or mixtures of LAS and MAS exhibit good corrosion, mechanical, and refractory properties, depending on the ratio of LAS and MAS, but they all have higher expansion than either LAS or AS materials. The technology for the fabrication of LAS and MAS in the form of multiple-cell units appropriate to the plate-fin heat exchanger geometry is reasonably well established.

In general, the thermal shock resistance of a brittle ceramic will be quite important in determining its ultimate usefulness in a recuperator application. The thermal shock resistance of a brittle solid is not an intrinsic property. It is a function of the heat transfer conditions at the surface of the material during a thermal excursion as well as of the geometry and the microstructure of the solid that is being subjected to the thermal transient. The ceramics' resistance to thermal shock and thermal stress is a function of thermal expansion coefficient, thermal conductivity, elastic modulus, modulus of rupture, fracture toughness, tensile strength, compressive strength, heat capacity, density, Poisson's ratio, sample thickness,

and the surface-heat-transfer coefficient. A general feature of the thermal shock resistance phenomenology of brittle solids can, however, be used to qualitatively rank candidate materials.

All solids that do not exhibit appreciable stress relaxation at crack tips due to plastic deformation can respond to high stresses by brittle fracture. For all practical purposes, all the ceramic materials considered as candidates for recuperator use fail in brittle fracture and are quite sensitive to surface and internal flaws. The surface flaws serve as crack initiation sites when the surface is under tension.

Thermal stresses developed from the temperature gradient and the thermal expansion of the ceramic parts in a recuperator may be sufficient to cause slow crack growth. Resistance to such slow crack growth is quite important, and the understanding of slow crack growth in candidate ceramics and availability of means to minimize it are of major importance to large-scale use of ceramics in recuperators. Resistance to thermal shock fracture, resistance to slow crack growth due to thermal stresses, acceptable low gas permeation, suitable maximum service temperature, and the ability to join the ceramic components to other parts of the recuperator are five important technical attributes for any candidate ceramic material for recuperator use. A satisfactory data base to use for ranking candidate ceramics for recuperator design on this basis was not identified during this assessment. There is definitely a need to establish such a data base for the selection and development of ceramic parts for recuperators.

The status of the data base for ceramics in each of these property categories will be briefly reviewed. Specific and useful comparisons of the thermal shock resistance of even more widely used and relatively pure ceramic materials are not generally available. This is partly due to the complexity of defining the thermal shock resistance of a brittle solid and partly due to the sensitivity of the properties of ceramics to their impurity content, their microstructure, and the relation between the final properties and the fabrication process used to make the part. The need for a practical thermal shock

parameter data base usable for comparison and consideration of candidate ceramics in various recuperator designs and applications will be discussed in more detail in the following section.

CRITICAL AREAS FOR CERAMIC MATERIALS

Information presented earlier in this report clearly indicates that high-temperature recuperators [flue gas temperature $>980^{\circ}\text{C}$ (1800°F)] having greater effectiveness than current metallic radiation units would be possible and desirable if higher temperature materials were available for use. The only class of materials that appear to have potential for this application according to this assessment are refractory ceramics, and the number of candidates is relatively limited.

As noted in the previous section, five important general attributes are necessary for any ceramic material to be considered seriously for use in recuperators. These attributes are (1) suitable mechanical properties at the desired operating temperature and the ability to withstand thermal cycling during the service life, (2) resistance to slow crack growth, (3) sufficiently low gas permeability at the use conditions for all sections as well as joints, (4) satisfactory chemical stability toward chemical species in the combustion gas and to air at service conditions, and (5) the ability to be joined to form strong gastight joints with itself or possibly with some metals in the shop and the field. A sixth important attribute for any serious material candidate is also that it must be fabricable into the required shapes at acceptable cost.

Refining some of the qualitative phrases in the statement of these attributes into specific engineering and/or economic terms can be attempted for some ceramic materials at the present time, while for others, the data base is insufficient.

Obviously, ceramic recuperators *per se* have metallic recuperators as direct competitors, and only when ceramic units have been demonstrated to have an economic advantage over the metallic units will they be of interest to U.S. industry. Clearly, the ceramic units have a

potential advantage over metallic units at recuperator temperatures much above 1000°C (1800°F), because they conceptually could have a higher effectiveness than the present radiation units. At lower gas temperatures, ceramic recuperators could have an advantage over metallic convection units when relatively impure fuels are used due to a projected longer service life derived from their greater resistance to chemical reaction with such flue gas impurity species as S, V, Zn, Pb, B, and Fe. This advantage can have value only when the other attributes are satisfied. This assessment indicates that in the area of high-temperature applications ceramic recuperators offer the greatest promise. The amount of heat that could be recovered and utilized by such recuperators if applied extensively by U.S. industry was not established during this assessment, but in the view of the authors, this estimate should be made to assess the energy conservation potential of this technology.

Mechanical Properties

Ceramic materials have notoriously unpredictable mechanical properties; for example, the tensile strength values measured on seemingly identical samples may show a wide variability at a given test condition. This is due primarily to the considerable sensitivity of the mechanical properties to the microstructure, impurities, porosity, and various internal flaws. This unpredictability makes it very difficult to utilize ceramics in design methodologies well established for metals and metallic alloys. In addition, ceramics are notoriously low in ductility, and brittle materials design methodologies are required. Manufacturers of ceramic materials that can be considered as candidates for use in recuperators usually do not have the property data for their products that are required for brittle design methods. Recent mechanical properties studies of silicon nitride at high temperatures have shown that even this extensively studied material can exhibit unpredictable mechanical behavior after being maintained at 1200°C (2200°F) for several hours

in air.¹² A data base including, as a minimum, tensile strength, fracture toughness, compressive strength, creep properties, elastic modulus, thermal expansion, and Poisson's ratio over a temperature range from 25°C (77°F) to at least 1400°C (2500°F) in air and representative combustion gas environments for a few select materials deemed capable of reproducible manufacture is required. Data exist for some candidates, but most of the strength and fracture toughness data are not available. Well-defined thermal shock resistance parameters for ceramic candidates would also be very useful.

Gas Permeability

As noted earlier, if a recuperator is to sustain any appreciable pressure differential from the cold to the hot side, leakage must be minimal or the effectiveness will be seriously reduced. Leakage can occur by physical permeation through bulk material, and of course through cracks, leaking joints, etc. Dense oxide and carbide ceramics typically have been demonstrated to have low permeabilities over limited temperature ranges as long as they remain crack free. The permeability test method and the data base for crack-free specimens including joints should be developed for air and combustion gases up to 1400°C (2550°F).

Chemical Stability

Oxide ceramics such as Al_2O_3 , mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$), ZrO_2 , MAS, and LAS are already in stable oxidation states. Carbide ceramics such as SiC are prone to oxidation, and this is well known to occur by the formation of a silica layer, which tends to reduce the oxidation rate of the carbide. In air, silicon carbide can be used to temperatures up to 1530°C (2800°F), above which the protective oxide (SiO_2) can react with silicon carbide to form volatile silicon monoxide (SiO). Sufficient data are probably available to identify any potential oxidation problems for ceramic recuperator candidates on the air side. Much less information is available concerning the

stability of various ceramic materials in the presence of species derived from fuel impurities or process carry-over. Most of these refractory phases are thermodynamically unstable in the presence of vanadium, sulfur, and other metallic species at high temperatures. Data specific to recuperator environments would be most useful. The oxygen potential in a typical flue gas stream is sufficiently high that concern over reduction of the oxides is not warranted, but some oxide systems such as $\text{Na}_2\text{O}-\text{V}_2\text{O}_5$ have liquidus temperatures that vary significantly with the oxygen pressure.¹³ Typically, impurities can strongly flux many of the refractory oxides, and any candidate materials should be analyzed from this viewpoint. Data relative to many fuel impurities and refractory ceramics were recently reviewed.¹⁴ This data base is not considered sufficient for some of the candidates such as mullite, MAS, and LAS.

Joining

For any solid substance to develop to the status of an engineering material, it must be capable of being joined to itself. Preferably it should also be joinable to other materials common to the structural design of the device in question. The common joining methods for alloys include welding and brazing. Present metallic recuperators are constructed with welding as the primary joining technique. Brazing can be used when the service temperature is sufficiently low. Both these techniques as applied to metals are well established technologies. Neither of these joining methods as applied to metals is directly applicable to most ceramic materials.

The electrical properties, high melting points, and thermal shock sensitivity of ceramics makes direct fusion joining (welding) impossible in most cases. Ceramics can be brazed to each other or to some metals if satisfactory metallizing and brazing alloys are available and if the ceramic material is not placed in tension upon cooling from the brazing temperature. Ceramic-to-ceramic or ceramic-to-metal brazed joints are usually designed to operate at ambient or modestly elevated temperatures. Some ceramic-to-metal

joints have been demonstrated¹⁵ to be usable to temperatures as high as about 1400C° (2550°F), but such applications are very specialized. Brazing systems stable to oxidation, typical fuel impurities, and thermal cycles over wide temperature ranges are not generally available for ceramic materials.

Joining of ceramics for shop construction of devices or for field repair is clearly an area where major information deficiencies currently exist. These will, in the view of the authors, seriously impede wide implementation of ceramics in recuperators and other heat exchangers. This conclusion is based on results of this assessment and was also a general conclusion of a recent meeting on ceramic heat exchangers.¹⁵

In the authors' view, some of the most advanced ceramic joining work relevant to recuperator and heat exchanger applications has been conducted recently as part of a program sponsored by Electric Power Research Institute (EPRI).¹⁶ The candidate ceramic material involved is recrystallized or siliconized silicon carbide, and ceramic-to-ceramic joints have been produced with a modulus of rupture equivalent to that of the bulk ceramic: about 276 MPa (40×10^3 psi). Joints of this type offer the advantage that complex ceramic parts can be fabricated in sections and then joined to make a much larger component. This work is part of a current EPRI program to demonstrate the feasibility of a ceramic heat exchanger capable of heating helium for a 300 MW(e) system via direct coal combustion on the hot side of the heat exchanger. Both butt and lap joints have been fabricated for SiC tubes in this program. The tubes are 25 mm (1 in.) OD with a 3.20 mm (0.126 in.) wall thickness.

This type of technology should be extended to other selected ceramic candidate materials if they are to have real potential for industrial recuperator use. Field repair of tubes or ability to replace single tubes without interrupting the operation of furnace and recuperator will probably be required for tube-type ceramic recuperators unless they can be economically designed to have a

very low probability of tube failure during the service life. Accomplishment of the latter objective appears to be unlikely at the present time.

The need for direct bond joints in a ceramic recuperator design may be obviated by judicious use of mechanical compression joints. This approach has been used in the finned-tube SiC ceramic recuperator described previously¹⁰ and in a ceramic heat exchanger design conducted recently for a solar power tower air driven turbine unit.¹⁷ Because the introduction of such a joint on a ceramic recuperator is so recent and the operating data are limited, long-term performance figures are not available. The vendor of the finned-tube SiC recuperator unit with mechanical compression joints reported that present leakage of the recuperator is in the 2 to 3% range and is optimistic that it can be reduced to 1% with a ΔP across the compression seals of at least 0.35 MPa (50 psia). Details concerning this joint are presently proprietary.⁶

Specifications, Materials Codes, and Standard Tests

We assessed the status of ceramic materials specifications, available codes, and tests for ceramic recuperators. Information on this area was solicited from major ceramic and recuperator vendors. In regard to ceramic materials, all three of these areas are far less developed than is the case for commercially available alloys presently used in recuperators.

Specification sets for application of ceramic materials in recuperators do not exist at the present time. The only specification identified relevant to application of ceramics in heat recovery devices is one for procurement of ceramic honeycomb regenerator wheels for application in advanced gas turbine and vehicular Stirling engines.¹⁸

The lack of specifications for structural ceramics for use in recuperators is related to the historical lack of technical activity in ceramic recuperators. With the growing interest in improvements

in industrial fuel use efficiency and the potential contribution of ceramic recuperators in this area, we anticipate that technical advancement in ceramic material specification development for recuperators could be quite rapid if sufficient incentive is provided.

A representative of one recuperator vendor stated that there are no current recuperator leakage standards, even for metallic recuperators, and that vendors usually use internally developed test procedures. This particular firm uses a German standard developed for recuperator testing. The measurement includes both dynamic and static tests. The static test involves pressurizing one side of the recuperator to 0.13 MPa (10^3 torr) followed by measurement of the pressure decay with time. The dynamic test involves the measurement of the air mass flow through one side of the recuperator necessary to maintain a pressure differential of 0.13 MPa (10^3 torr) between the primary and secondary sides. Specific accept or reject levels of the recuperator used for these test results were not provided by this vendor.

FABRICATION AND COST OF CERAMIC COMPONENTS

Significant application of ceramics in recuperators or other high-temperature heat exchanger use will require not only a clear demonstration of the ability of these materials to perform adequately under the intended application conditions and environments, but they must also have a demonstrated fabricability at a cost judged acceptable under the conditions of the economic analysis used for analyzing the recuperator investment.

During this assessment, several ceramic vendors were contacted to solicit their views regarding present fabrication capabilities for ceramic shapes that appear to be of most interest for present conceptual ceramic recuperator and heat exchanger designs. Presently, the shapes of most interest are tubes with or without extended surfaces on the inside and outside and plate-and-fin or cellular geometries.

Ceramic Tubes

Two current major vendors of silicon carbide ceramics and a third major vendor of mullite- and alumina-based ceramic tubes provided information as a result of our requests. The information provided by these vendors will be presented in some detail and the vendors will be identified by the code A, B, or C. Vendor A presently markets a comprehensive range of tubes of various types of silicon carbide. As noted earlier, silicon carbide based ceramics have to date been identified in other DOE (Department of Energy) and EPRI supported programs as having desirable properties for use in recuperators and heat exchangers. These silicon carbide products include (1) oxide bonded, (2) oxynitride bonded, (3) silicon nitride bonded, and (4) siliconized or recrystallized materials. The last type of silicon carbide has received major attention in heat exchanger applications because it offers higher strength, higher thermal conductivity, and lower permeability to gases at high temperature than silicon carbide products made with the other bonding systems. However, it should be noted that, since silicon melts at 1410°C (2570°F), siliconized silicon carbide should be used at temperatures below this level.

Examples of the cost of currently available tubular shapes of these silicon carbide materials and prices of vendor A as of April 1977 are listed in Table 1. The largest currently available dimensions for tubes from vendor A of some of these silicon carbide materials are given in Table 2. The cost of the impervious silicon carbide listed in Table 1 is about \$130/kg (\$60/lb) in large quantities. This price compares with a current nominal price of \$7-11/kg (\$3-5/lb) for 300 series stainless steels. From this comparison, it is obvious that impervious silicon carbide, which is a candidate material for use in ceramic heat exchangers, presently costs at least ten times the price of alloys now used extensively in recuperators. According to opinions of recuperator vendors obtained during the current assessment, the cost of silicon carbide or other ceramic candidates for high-temperature recuperators must eventually be reduced and become

Table 1. Costs of Silicon Carbide Tubes from Vendor A

Material	Wall Thickness (mm)	Price per Tube, \$, for Each Quantity ^a		
		100	1000	10,000
Oxide bond	15.9	65	64	60
Oxynitride bond	15.9	72	71	66
Nitride bond	12.7	105	103	96
Recrystallized bond	6.4	483	451	360
Recrystallized bond, impervious	6.4	966	810	522

^aCost as of April 1977 for 1.22-m lengths of 0.1-m-ID tubes.

Table 2. Available Sizes for Tubes of Selected Silicon Carbide Materials from Vendors A and B

Material	Dimensions, m		
	Wall Thickness	ID	Length
<u>Vendor A</u>			
Oxide bond	0.0095-0.0254	0.152	1.524
Oxynitride bond	0.0095-0.0254	0.152	1.524
Nitride bond	0.0095-0.0254	0.0254-0.102	1.524
Recrystallized bond	0.0048-0.008	0.0254-0.114	2.44
Recrystallized bond imper- vious	0.0048-0.008	0.0254-0.114	2.44
<u>Vendor B</u>			
Siliconized	0.0062	0.114	1.626

appreciably closer to the cost range of currently available stainless steels if the current recuperator industry is to seriously consider eventual use of ceramics.

Costs estimates made by vendor A for the silicon carbide tubes required for the ceramic heat exchanger tubes in the current EPRI Coal-Fired Prototype High-Temperature Continuous Flow Heat Exchanger program are in the \$9-11/kg (\$4-6/lb) range for production of tubes 6.7 m long at a level of 0.57 Gg (1.25×10^6 lb) per year.¹⁹ This represents approximately a tenfold cost reduction from current costs while tripling the maximum tube length. To be accomplished, such a cost reduction will probably require significant improvements in production technology in the ceramic industry. Present processes used for manufacturing silicon carbide tubes of the type considered here have a labor-to-material cost ratio of about 4 according to vendor A. Improved production processes could be expected to reduce this ratio, and, in the authors' opinion, such a reduction would be essential if tubular silicon carbide parts are to eventually be seriously considered for extensive application in recuperators and other heat exchangers.

A second major vendor (vendor B) of silicon carbide ceramics was requested to provide information on available maximum sizes of tubes that can currently be fabricated. The maximum tube size of dense siliconized silicon carbide that is currently available from vendor B is 114 mm OD by 102 mm ID with a maximum length of 1.63 m (4.5 by 4 by 64 in.). Tubes of slightly smaller outside diameter [i.e., 92 mm (3.625 in.)] can be fabricated with slightly greater lengths of 1.68 m (66 in.). Tolerances stated for these dimensions are: diameter and wall thickness ± 1.6 mm (0.0625 in.); length ± 3 mm (0.125 in.); warpage 9.5×10^{-3} (0.3 in./ft); maximum out-of-roundness 1.6 mm (0.0625 in.).

Vendor B stated that the current production costs for siliconized silicon carbide tubes are about five times as great as the raw material costs if no machining or other special handling is required. If machining operations are required for the tubes, this ratio increases

to about ten. It is clear from the data obtained from these two vendors that labor and other manufacturing costs represent a very significant fraction of the quoted costs of the types of silicon carbide tubes that can be considered as near-term candidates for use in ceramic recuperators.

Comparison of the costs of silicon carbide tubes from Vendor A with current costs for relatively short fireclay-bonded silicon carbide tubes used by one of the vendors of ceramic recuperators of the Amsler-Morton type described earlier shows that the silicon carbide costs are very comparable from these two sources. The tubes used in the Amsler-Morton recuperators are about 0.6 m (2 ft) long and about 100 mm (4 in.) in diameter. These tubes currently cost about \$140/kg (\$65/lb), a value very close to the earlier value stated for large production quantities of siliconized silicon carbide from vendor A. The fireclay-bonded silicon carbide does not have the high-temperature strength or low gas permeability typical of siliconized silicon carbide.

Vendor C is a major vendor of mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) and alumina (Al_2O_3) ceramics. Long tubes of these materials offer some promise for ceramic heat exchanger applications due to their strength at high temperature and relative inertness in oxidizing and corrosive atmospheres. The cost and size availability of tubes of these ceramics are of interest for comparison with those for silicon carbide to determine if these materials currently have any cost advantage. The potentially lower thermal shock resistance of these oxide ceramics is of major concern for heat exchanger application with many recuperator vendor respondents contacted during this assessment. However, if adequate material performance is available for these ceramics, they could be considered as reasonable candidates for further recuperator demonstration activity.

Examples of the largest tubular shapes available from vendor C for both mullite and 99.8% alumina compositions are given in Table 3. The cost of both mullite and the high-purity alumina tubes based on vendor C data for the longest tubes available at this time are essentially identical at about \$113/kg (\$47/lb).

Table 3. Costs and Maximum Sizes of Mullite and Alumina Ceramic Tubes from Vendor C

Material	Dimensions, m			Price ^a Per Tube (\$)
	OD	ID	Length	
Mullite	0.1	0.095	2.13	588
99.8% Al ₂ O ₃	0.133	0.124	1.83	1431
96% Al ₂ O ₃	0.133	0.124	1.83	1062

^aAs of April 1977.

The current cost for large tubes of impervious silicon carbide, high purity alumina, and mullite tubes on a mass basis are essentially the same; [i.e., in the \$110–120/kg (\$50–60/lb) range]. If significant demand were to develop for one of these materials for recuperator or other heat exchanger applications, price reductions could be anticipated, but an estimate of the magnitude of such a decrease based on assumed demand scenarios was not done within the present assessment. Two widely used fabrication methods are currently employed for manufacturing the silicon carbide, mullite, and high-alumina ceramic tubes discussed previously. The two fabrication methods are extrusion and slip casting. The extrusion process involves the formulation of the base composition into an extrudable mass by use of organic additives and plasticizers followed by formation of the annular cylindrical tube by extruding the plastic mass through appropriate dies by means of hydraulically or mechanically applied pressure. The extruded tubes are dried and fired under appropriate conditions to develop a ceramic material having satisfactory strength and other properties. This method has the advantage that in principle very large diameter and/or long tubes can be fabricated.

With sufficient control of the powders used in the batch formulation, along with proper composition and extrusion aid control, diametral control within about $\pm 4\%$ is possible for ceramic tubes. Tube straightness and ovality control ranges for long extruded tubes are typically 5×10^{-3} and $\pm 4\%$ respectively.

The slip casting process involves preparation of the base composition in the form of a suitable stable solid suspension (slip) and subsequent casting of a solid shape by applying the liquid slip in a suitable plaster mold. Tubular shapes would normally be cast with the outer tube surface depositing against the mold surface. The inner tube surface would be generated in this case within the slip by the consolidation of solids in the slip during the casting process. Under these conditions, the inner surface of such a slip cast tube will be somewhat irregular compared with the inner surface of an extruded tube. Standard slip casting procedures require that the cylindrical axis of the tube be vertical, otherwise the tube wall thickness on the bottom side of the tube would be significantly greater than that on the top side. This gravitationally accelerated casting rate also will slightly enhance the casting rate at the bottom of a long vertically cast tube. Wall thickness control is more difficult with the casting process than with extrusion. The values of the chemical parameters necessary to produce a satisfactorily stable slip depend strongly on the material, and special compositions must be used for ceramic systems such as silicon carbide, mullite, and alumina that contain no clay minerals.

As noted previously, the use of ceramic tubes in a recuperator design requires a high-integrity joint between the ends of the tube and an appropriate header, manifold, or tubesheet. Designs employing U-tube geometry have the potential advantage of allowing the tubes to hang inside the waste gas stream while allowing the thermal expansion stress to be accommodated via dilation of the hanging tubes within the gas duct. Such a design does require the joining of two straight tube sections to a U section or fabrication of the tube as an integral unit such as by casting or shaping the U following extrusion. Both slip cast and extruded U-tubes of siliconized silicon carbide having good integrity have been fabricated as part of the previously referenced EPRI ceramic heat exchanger program.^{20,21} A recuperator design based on U-tubes hanging into a hot gas duct also requires that the tubes be joined to appropriate air distribution ducts. If the application warrants use of ceramic tubes, then the distribution ducts must also be lined with a refractory ceramic, and

probably made of the same material as the U tubes. This material choice will help to minimize the joining problems associated with connecting the U tubes to the distribution ducts. As noted earlier in the section on ceramic joining, the ability to make at least some of these joints in the field, either for initial installation or for required repair of fractured tubes will, in the authors' opinion, have a significant effect on future considerations for use of this type of ceramic recuperator design.

Extended-Surface Ceramic Structures (Honeycomb)

The only other geometry for a ceramic based recuperator or heat exchanger for which there is a technological data base at present is the cellular type. This is much like the plate-and-fin geometry used in construction of current metallic compact heat exchangers. Work on ceramic systems with this geometry has been conducted rather extensively in regenerator development for vehicular gas turbine and vehicular Stirling engines.²² This design uses the ceramic material in the form of a heat wheel regenerator, which rotates alternately in a hot exhaust gas stream and then into the incoming air stream. Heat absorbed in the ceramic honeycomb from the waste gas is transferred to the combustion air during wheel rotation. Ceramic honeycombs intended for turbine or Stirling engine applications must be able to withstand thousands of thermal cycles while being inert to various impurities from the fuel at the maximum honeycomb wall temperature and under the stresses required by the regenerator design. The honeycomb design appropriate to regenerator wheel application requires unidirectional cavity structures with the axis of the cells oriented parallel to the cylindrical axis of the wheel. This is obvious, since this is the direction of gas flow in the regenerator.

Use of ceramic honeycomb structures for recuperator applications will require more complex geometrical structures because of the required gas flow paths discussed earlier. In principle, ceramic honeycomb structures appropriate to either parallel or perpendicular gas flow paths for the primary and secondary sides could be considered.

Earlier, it was pointed out that counter-flow designs provide the highest value of ϵ when convective heat transfer is operative. A counter-flow or parallel-flow ceramic honeycomb recuperator would generally use the same core geometry; the basic difference would appear in the header attachment scheme. Due to the honeycomb cell size probably appropriate to consideration for recuperator application, 6 to 7 mm (~ 0.25 in.), the header attachment and sealing scheme for parallel or counter-flow streams will probably be more complicated than for the case of cross flow. In this latter design, the headers for the two flow streams can be physically separated by distances of at least 0.2 m and this should be easier to accommodate physically. An example of this type of design is shown in Fig. 3 for a triangular honeycomb crossflow design.

Fabrication of ceramic honeycombs has been extensively evaluated for three systems, the aluminosilicate (AS), the magnesium aluminosilicate (MAS), and the lithium aluminosilicate (LAS). Work on these materials started with LAS in 1965 by the Ford Motor Co.²³ By 1971, data for LAS indicated that regenerator wheels should have a life of 4000 to 5000 hr in an industrial gas turbine engine. Follow-on testing of LAS cores, however, resulted in a high incidence of failures. In 1974, work on AS and MAS materials was started with the objective of demonstrating regenerator wheel materials superior to LAS. Ceramics of LAS were found to be susceptible to two sources of chemical attack. Hydrogen in the form of sulfuric acid or other sulfur-bearing gaseous species reacts with LAS in such a way to markedly change the thermal expansion and dimensional stability of this ceramic material. Sodium from the fuel or the local environment reacts with LAS and produces detrimental changes similar to hydrogen. The degradation is observed in the form of gross warpage of the regenerator wheel plus radial cracking. Leaching of LAS in hot sulfuric acid improved its resistance to hydrogen and sodium degradation at high temperatures, and this material is referred to as AS in the literature. Ceramics of LAS are based on development of the spodumene phase, $\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$, in the ceramic material with its inherently low bulk thermal expansion

properties. These bodies usually contain an appreciable concentration of microcracks after being cooled from the firing temperature. Ceramics of MAS are based on the properties of the cordierite phase, $2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$. This phase has a total thermal expansion dilation of about 0.003 ($\Delta L/L$) from 25 to 1200°C (70–2200°F). This ceramic is much more resistant to sodium and sulfur reactions at high temperatures and, therefore, is now considered a major candidate material for advanced automotive engine regenerator applications.

The technology developed in the past few years for fabrication of ceramic honeycomb cores for regenerator wheels is of direct interest for potential application to the manufacture of ceramic honeycomb heat exchangers. One of the major incentives of the ceramic honeycomb development has been to produce the cores economically on a mass production basis. The fabrication methods appear to be applicable to a wide variety of ceramic compositions. The general nature of these fabrication methods will be reviewed and the results of some fabrication cost analyses for LAS, AS, and MAS wheels performed for Ford by industrial fabricators will be presented to provide some comparison with ceramic tube costs presented earlier.

The two forms of raw material used to make LAS, AS, and MAS ceramic honeycomb matrices are glass frit and raw mineral. Use of a glass frit offers advantages of better compositional control and hence final property control of the ceramic. Frit has the disadvantage of being more expensive than using oxides as the starting material. The basic approach in using a glass frit is to fabricate the honeycomb with the frit and to subsequently recrystallize the glass to produce the phases desired in the final ceramic component. This approach is viable for either LAS, AS, or MAS compositions, but is not a potential route for more refractory ceramic compositions such as silicon carbide. The mineral preparation approach for MAS, for example, involves weighing and mixing proper mixtures of talcs, clays, and aluminum oxide, followed by calcining, grinding, adding binders, plasticizing, fabrication, and sintering. Cordierite is difficult to obtain in a fully densified condition. Fabrication of a silicon carbide honeycomb would obviously start with a suitable silicon carbide powder.

Basically four fabrication processes have been used for preparation of ceramic honeycomb structures.²⁴ These are (1) coated paper, (2) extrusion, (3) embossing, and (4) calendering. Schematic diagrams of these processes are shown in Figs. 9 through 12.

Each process has certain advantages and disadvantages relative to its use for regenerator wheel fabrication. A critical analysis of these processes and their potential technical and economic application to ceramic recuperator core fabrication was not identified during this assessment and apparently has not been done. Features of these fabrication processes relevant to regenerator production are discussed in the following.

In the coated paper process, a low-ash paper is coated on both sides with a slurry of the ceramic composition, dried, and passed through crimping rolls to form the crimped sheet. Another sheet of low-ash paper is passed through an identical slurry, dried, and used as the separator layer between the crimped sheets. For heat wheel fabrication the crimped sheet and flat sheets are rolled alternately

Fig. 9. Schematic of Coated-Paper Process for Fabrication of Extended-Surface Ceramic Structures.

ORNL-DWG 77-21217

Fig. 10. Schematic of Extrusion Process for Fabrication of Extended-Surface Ceramic Structures.

ORNL-DWG 77-21216

Fig. 11. Schematic of Embossing Process for Fabrication of Extended-Surface Ceramic Structures.

Fig. 12. Schematic of Calendaring Process for Fabrication of Extended-Surface Ceramic Structures.

into a disk to form a green wheel. The green wheel is then dried and fired so as to burn out the paper and then to sinter the ceramic. The coated paper process yields matrices with sheet thicknesses as low as 0.1 mm (0.003 in.) with uniform cell geometry and good joint bonds. The use of nonrecoverable paper is a cost factor for this method, and the triangular cell produced by this process is not the optimum configuration for regenerator wheel performance.

The simplest of the four fabrication methods is the extrusion process. This process yields the most uniform wall thicknesses and cell structures. It also produces the rectangular opening that is desirable for performance and could be employed to extrude two or more cell configurations along one matrix cell axis. For regenerator wheel requirements, major problem areas include obtaining thin cell walls and large pieces simultaneously, plus the present uncertainty of die wear costs.

The embossing and calendaring processes are quite similar and they will be discussed together. Both processes have the advantage

that they can potentially be operated as a high-speed single sheet operation, do not require a paper carrier, and both produce a desirable rectangular cell opening. Sheet thicknesses as thin as 0.1 mm (0.005 in.) have been demonstrated with both these processes, and demonstration of thinner sheets is expected in the near future. These two processes are not presently as well developed as the coated paper and extrusion processes. The processes employ calendaring or embossing rolls as shown in Figs. 11 and 12 to generate the basic cellular geometry. 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. When the ceramic film is extruded by itself and later calendered, the process is known as calendering.

Figures 9 through 12 show schematically how the four processes are employed to lay up the disk geometry required for an engine regenerator wheel. No specific information was located during this assessment relative to the applicability of these methods for fabricating relatively large planar structures. The Stirling engine regenerator wheel design discussed in ref. 24 is approximately 0.46 m (18 in.) in diameter and 40 mm (1.57 in.) thick, so that the fabricated width of the sheet is probably about 43 mm (1.7 in.) wide (allowing for final machining of both disk faces). The wheel design for the Ford 707 turbine regenerator core was 0.71 m (28 in.) in diameter and 76 mm (3 in.) thick. For recuperator applications on large furnaces, sheets with fabricated widths of at least 0.2 m would be required. Significant progress toward fabricating such sheets of MAS for use in a demonstration cross-flow ceramic recuperator has been accomplished recently with fabrication of cubic units as large as 0.28 m (11 in.) on a side.²⁵

Cost data for the ceramic honeycomb recuperator matrix that can be directly compared with potential material costs for ceramic recuperators based on tubular designs was not identified during this assessment. A ceramic wheel heat exchanger cost study²⁴ includes cost estimates for the regenerator for a 127 kW (170 hp)

Stirling engine. Participants in this study included Coors Porcelain, Corning Glass, NGK Insulators, GTE Sylvania, and W. R. Grace. The extrusion process for fabrication of MAS matrices based on use of mineral raw materials was identified as having the greatest potential for producing the regenerator wheels at lowest cost. These cost estimates varied from \$13 to \$69 per matrix, and the authors²⁴ concluded that at production rates of 500,000 units per year, the cost per matrix could be in the \$25 to \$30 range. The mass of this matrix wheel fabricated from MAS is given²⁴ as 4.54 kg (10 lb). For a matrix cost range of \$13 to \$69 stated previously, the minimum estimated ceramic cost is \$2.86/kg (\$1.30/lb). The maximum estimated costs is \$15.20/kg (\$6.90/lb) based on 1975 dollars. These costs will be about 15% higher for comparison with current ceramic tube costs cited previously. This escalation gives matrix costs ranging from \$3.29/kg (\$1.50/lb) on the low side to \$17.48/kg (\$7.94/lb) on the high side. For production levels of about 500,000 matrices per year, a cost in 1977 dollars of \$7.60/kg (\$3.45/lb) appears plausible from ref. 24. Cost differences due to the need for three-dimensional matrices required for recuperator cores compared with the cylindrical geometry requirement for regenerator matrices were not estimated as part of this assessment. The operations required for three-dimensional core layup may be more labor intensive than those appropriate to wheel fabrication. According to available data, presently available large silicon carbide, mullite, or alumina tubes are about ten times as expensive on a mass basis as MAS honeycomb structures. However, cordierite-based ceramic honeycomb may not be satisfactory²⁶ for certain recuperator applications involving temperatures much above 847°C (1550°F). Cordierite is also known to be susceptible to reaction with boron compounds at high temperature, which may make the material unsuitable for certain glass melting furnace applications. Other ceramic compositions capable of fabrication into honeycomb matrices may be required as specific industrial process parameters pertinent to high-temperature recuperators become better defined. According to one of our respondents there presently appear to be no known

technical barriers to fabrication of more refractory ceramics such as silicon carbide into honeycomb matrix structures.²⁷

ADVANCED METALLIC CONCEPTS

This section discusses advanced metallic concepts involving coated refractory alloys, the austenitic iron-base superalloys, and the cobalt- and nickel-base superalloys as to their suitability, practicability, and viability for application in recuperators. These metals and metallic alloys have high melting point, high creep-rupture strength, and/or corrosion resistance at elevated temperatures. However, the economic feasibility, the lack of experimental or operating data, and the maximum usable temperature limit imposed by oxidation have rendered these metallic systems less attractive compared with ceramic materials for the use as parts in advanced high-temperature (>1000°C) recuperators.

Molybdenum, tungsten, niobium, and alloys based on these refractory metals have high melting points. There are three types of commercial molybdenum-base alloys: (1) the precipitation- or dispersion-hardened type containing titanium and zirconium, (2) the solid-solution type with tungsten, and (3) a combination of the first two. For niobium-base alloys, the primary alloying elements are Ti, Zr, V, Ta, Mo, and W. Commercial tungsten alloys include alloys containing thorium or zirconia dispersions; alloys with molybdenum, titanium and zirconium, nickel, or rhenium; and alloys infiltrated with silver and copper. Poor oxidation resistance of these refractory metals and alloys necessitates the use of oxidation-resistant coatings for high-temperature applications in oxidizing environments. Silicide and aluminide coatings, which are thin, impervious layers of silica and alumina, are often applied to the surface of refractory metals and alloys by pack cementation in an atmosphere of silicon or aluminum at 800 to 1200°C for 4 to 12 hr. These coatings provide improved oxidation resistance for the refractory metals and alloys at temperatures from 1100 to 1500°C, depending upon the alloy and coating system.²⁸

New coating systems have been evaluated recently for use on candidate alloys for jet engine applications. The purpose of these coatings is to reduce the metal temperature while permitting higher surface temperatures for engine components. A very promising coating system reported recently is a duplex system consisting of a Ni-16 wt % Cr-6 wt % Al-0.6 wt % Y bond coating plus a ZrO_2 -12 wt % Y_2O_3 thermal barrier coating.²⁹ This system is plasma sprayed onto the alloy and has been evaluated on nickel-base superalloys as well as cobalt-base alloys. This coating has shown promise for jet and utility turbine applications and has reportedly withstood several hundred thermal cycles to coating surface temperatures of about 1490°C (2710°F) in a jet engine burner test rig. The upper critical temperature³⁰ for the ceramic-bond coat interface is near 1090°C (2000°F). At higher temperatures, interaction between the two layers damages the thermal barrier coating.

The present cost for uncoated refractory metals and alloys is in the range of approximately \$90 to 260/kg (\$40-120/lb), which is about ten to forty times more expensive than 300 or 400 series stainless steels. Additional coating costs plus the generally poor fatigue resistance, inadequate ductility, tendency to crack at low stresses, and poor reliability of many coating systems appropriate to refractory alloys makes them impractical for the use as recuperator parts at the present time.

The development of the austenitic, iron-base superalloys as well as the cobalt- and nickel-base super alloys was motivated by the use of turbosuperchargers and turbojet engines in aircraft in the 1940s. More recently, these alloys have been used in the power industry because of the increased steam temperatures and pressures common in newer power system design. The austenitic iron-base superalloys are modifications of 300 series stainless steels. The modifications increase creep-rupture strength and corrosion resistance relative to the parent 300 series stainless steel. The cobalt- and nickel-base superalloys also have high creep-rupture strength and corrosion resistance at temperatures up to 1000°C. The Hastelloy,

Inconel, and Incoloy alloys, which were mentioned earlier, are nickel-base superalloys. All these superalloys may have higher creep-rupture strength, better oxidation resistance, and/or better corrosion resistance than 300 or 400 series stainless steels. However, the lack of experimental or operational data, the lack of experimentally demonstrated improved durability of these alloys, and the higher cost than 300 or 400 series stainless steels are presently the restraints for consideration of these alloys to be used in the severe corrosion and oxidation conditions of a high-temperature ($>1000^{\circ}\text{C}$) recuperator.

CONCLUSIONS

Metallic Recuperators

1. Most recuperators currently used in U.S. industry are constructed of either type 309 or type 446 stainless steel.
2. The performance of a recuperator in transferring heat from waste gas to combustion air can be expressed in terms of a parameter called the effectiveness, which can have a value between unity and zero. Unit effectiveness represents the thermodynamic heat transfer limit for the recuperator.
3. Recuperator vendors do not, in general, describe their products in terms of effectiveness or other parameters that will allow simple performance comparisons of various units.
4. Present recuperators are generally designed for optimum heat transfer by either a convection or radiation process. Radiation types are used for flue gas temperatures above about 980°C (1800°F), as these designs operate with maximum metal temperatures considerably below the maximum gas temperature. The effectiveness for these units is in the range 0.3 to 0.5. Convective types are used for lower temperature waste gas applications and apparently have effectiveness values in the range 0.5 to 0.7.
5. High-temperature creep and oxidation presently limit the maximum metal temperature in current recuperator designs to about 980°C .

6. There are no accepted industrial standards for determining various recuperator characteristics, including leakage across the boundary between the primary and secondary sides.

7. Corrosion, oxidation, and fouling are presently the primary recuperator degradation mechanisms during service. Radiation units are less susceptible to fouling and corrosion because of the simpler waste gas flow path and the short residence time of the hot gas.

8. Advanced metallic concepts including coated refractory metals or alloys, and advanced jet engine alloys such as iron-, cobalt-, or nickel-base superalloys presently do not seem to offer significant advantages over currently available ceramics and alloys for recuperator construction.

Ceramic Recuperators

1. Effectiveness of ceramic recuperators presently used by U.S. industry is less than optimum because of leakage at seals as well as at cracks that develop in the tube walls during service. An estimate of the effectiveness of the ceramic tube and tile recuperators was not available for typical applications. Very limited research and development activity was identified for ceramic recuperation in the recent past in the U.S.

2. Selected refractory ceramics offer promise for use in high-temperature recuperators more effective than present metal radiation type units typically used when waste gas temperatures are above about 980°C (1800°F). Principal candidate ceramic materials for recuperator use at present include silicon carbide, magnesium aluminosilicate (MAS), mullite, and possibly alumina.

3. A very limited data base exists for ceramic recuperator materials from which realistic design or economic analyses can be made. The lack of a material specification base for ceramics for recuperator or heat exchanger application presently precludes an objective comparison of various ceramics for this application except by use of expensive direct comparative tests. Specific tests of small samples whose results will be meaningful to full-scale recuperator performance were not clearly identified during this assessment.

4. Two ceramic recuperators of relatively new design were identified during this assessment. One is being employed in the U.K. in several installations and the other has shown very promising high-temperature performance in demonstrations in the U.S. on a forge furnace. Both these units employ silicon carbide tubes in a cross-flow mode.

5. A major area of concern for ceramic recuperators expressed during this assessment was the obvious brittleness of ceramics, and their presumed tendency to crack or break during service. Designs allowing relatively simple field replacement of portions of the heat transfer surface accompanied by adequate field repair of joints appear to be essential if relatively near-term application of ceramic recuperators is to be realized.

6. The present cost of ceramic tubes and other relatively simple shapes makes serious consideration of ceramics for use in recuperator construction difficult at present. On a mass basis, presently available large tubes of silicon carbide, mullite, or alumina cost about 10 times as much as stainless steel alloys. On a material volume basis, these ceramics now cost about 3.5 to 4 times as much as stainless steels. Whether ceramic costs should be compared with metals on a mass or volume basis depends on specific ceramic recuperator design details, which are not available at present.

7. Viable joining techniques for ceramics including tube-tube, tube-header, tube-tile, cell-matrix-matrix, and cell-matrix-header are needed for the wide use of ceramics in recuperators.

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