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THE DEVELOPMENT OF A FOSSIL FUEL FIRED
HEAT PIPE FOR USE WITH THERMIONIC ENERGY CONVERTERS

Report No. 1
Contract DA28-043-AMC-01507(E)
First Quarterly Technical Report

by

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Prepared by

Radio Corporation of America
Electronic Components and Devices
Direct Energy Conversion Department
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ABSTRACT

The subject contract was initiated 1 July 1965 to develop the most efficient method of coupling a simulated thermionic converter to a heat pipe. The heat pipe incorporates a gas barrier and is used to conduct the heat from a fossil fuel burner to the simulated converter. A theoretical analysis of the operation of the heat pipe will be made and confirmed experimentally.

During this first report period, progress was made on the following pertinent tasks: Potential working fluids were evaluated; structural materials and fabrication techniques were investigated; barrier materials were evaluated; permeation tests were started using the most promising barrier materials and a theoretical analysis of getter materials to eliminate unwanted contaminants has been started.

Technical Report ECOM-01507-1

THE DEVELOPMENT OF A FOSSIL FUEL FIRED
HEAT PIPE FOR USE WITH THERMIONIC ENERGY CONVERTERS

FIRST QUARTERLY REPORT

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THE DEVELOPMENT OF A FOSSIL FUEL FIRED HEAT PIPE
FOR USE WITH THERMIONIC ENERGY CONVERTERS

SECTION I
INTRODUCTION AND SUMMARY

For several years there has been a widespread effort to develop a thermionic converter capable of producing electric power directly from the combustion heat of a burning fossil fuel. The recent achievement at RCA of 1020 hours of flame-heated converter operation has indicated the potential of this approach. In addition, the technical experience leading to this achievement has defined several areas where marked improvements in performance are both possible and desirable. In each case the advantage to be obtained is related to the method of heating the converter emitter through the permeation barrier structure. The insertion of a heat pipe in the thermal flow path between the burner and converter shows great promise of achieving more efficient and reliable performance.

In July 1965, this one year engineering program was initiated to evaluate the best method of coupling a heat pipe to a simulated thermionic energy converter.

The current program provides a theoretical analysis of heat pipe operation from a fossil fuel heat source with an extensive investigative program providing experimental and design data in the following areas: (a) heat transfer fluids, (b) heat pipe envelope and capillary materials, (c) high temperature gas permeation and corrosion barrier materials, (d) techniques for coupling the fossil fuel fired heat pipe and thermionic converters, (e) measurement of gas permeation rates and the development of means of minimizing any deleterious effects of permeating gases, (f) determination of the thermal transfer capacity of heat pipes at surface temperatures up to 1450°C, (g) the distribution of temperatures and heat flux over the useable surface of a heat pipe, (h) the efficiency of heat transfer by means of a heat pipe, and finally, (i) the cycled operating life of a heat pipe.

The information derived from the analytical and experimental portions of the program form the basis for the design of the heat pipes to be tested. A fossil fuel burner will be employed for the tests. Quarterly and Final Technical Reports will be prepared at appropriate intervals. Delivery will be made of two heat pipes representative of the work carried out during the program.

SECTION II

FACTUAL DATA

A. <u>Heat Pipe Advantages</u>

The bases for the current program stem from the demonstrated advantages of heat pipes when used to drive thermionic converters.

The heat pipe is a static device which couples the outstanding heat transfer properties of a liquid-vapor, two-phase system with capillary return of the condensate to the boiler. RCA has designed, fabricated and tested heat pipes for operation at thermionic conditions. The tests, and the analysis of the results, have revealed the following heat pipe characteristics which are useful in this application:

1. Efficient heat transfer
2. Thermal flux transformation
3. Temperature flattening
4. Isolation of heat source
5. Low sensitivity to contaminants
6. Geometric flexibility

These characteristics yield the following advantages in a fossil fuel heated thermionic generator.

1. <u>Uniform Emitter Temperature</u>

It is difficult to achieve uniform temperature on the emitter of a thermionic converter heated directly from any practical heat source. Even if the heat source supplies a quite uniform heat flux, substantial temperature non-uniformity will exist on the emitter because of conductive end losses. These problems are magnified with the moving hot gas heat transfer of a fossil fuel burner. Since thermionic emission is a steep

function of emitter temperature, the performance of a converter with the ideal isothermal temperature distribution attainable with a heat pipe is substantially greater than can be achieved from a converter with a non-uniform emitter temperature.

2. Optimum Burner Efficiency

The heat flux required to operate a thermionic converter in the 1400°C temperature region is approximately 30 watts per square centimeter. This high heat flux is attainable with existing burners, but is available only at an appreciable cost in efficiency. Reduction of the heat flux requirement to one-third or one-half of this maximum level will permit optimum burner operation and result in a burner efficiency increase of ten percent or more. This reduction in the heat flux requirement can be obtained easily through the use of the transformation capability of the heat pipe. Simultaneous optimization of burner and converter efficiencies can then be achieved.

3. Reduced Temperature Drop

Since the heat flux through the heat pipe surface and its permeation barrier can be reduced, as discussed above, the temperature drop will be reduced since it is proportional to heat flux. Thermally induced stresses will be reduced. Improved thermal shock resistance can be expected to result.

4. Reduced Sensitivity to Contaminants

The heat pipe contains no electronically active surfaces and is thus less sensitive to contaminants than a thermionic converter. The intense vapor stream in the heat pipe will sweep any gaseous contaminant to the low pressure end where it can be processed by "windows"

(such as palladium for hydrogen) or by more conventional gettering techniques.

5. <u>Optimum Converter Design</u>

From the heat transfer, burner design, and barrier fabrication viewpoints it is preferable to supply heat to the outer surface of a heat transfer device which is inserted into the burner. For optimum converter efficiency, minimum electrical lead losses, minimum converter cooling power requirement and minimum converter weight, an internal emitter (and heat source) are preferable. The use of the heat pipe makes possible the simultaneous realization of these otherwise conflicting design considerations. The heat pipe can project into the burner on one end and into the converter on the other.

Through the use of the heat pipe it is therefore possible to solve many of the existing problems in fossil fuel heated thermionic converters and reduce the effect of others. The enhancement of converter performance will more than offset the slight additional weight of the heat pipe. The difficult barrier problem is rendered less acute. It becomes possible to match the performance of the converter and burner in a way not otherwise possible so as to gain optimum efficiency from both, leading to very worthwhile gains in system weight, efficiency and fuel consumption.

B. <u>Heat Pipe Design</u>

In order to evaluate the various items covered in the program, the basic heat pipe-thermionic converter design shown in Figure 1 was modified to investigate two different heat pipe system concepts. These modifications are shown in Figures 2 and 3. These systems are designed to furnish

Sapphire Window

Cesium Reservoir

Ceramic Fossil Fuel Barrier

Heat Pipe

Wick

Emitter Heat Dam

Emitter

Emitter Contact Terminal
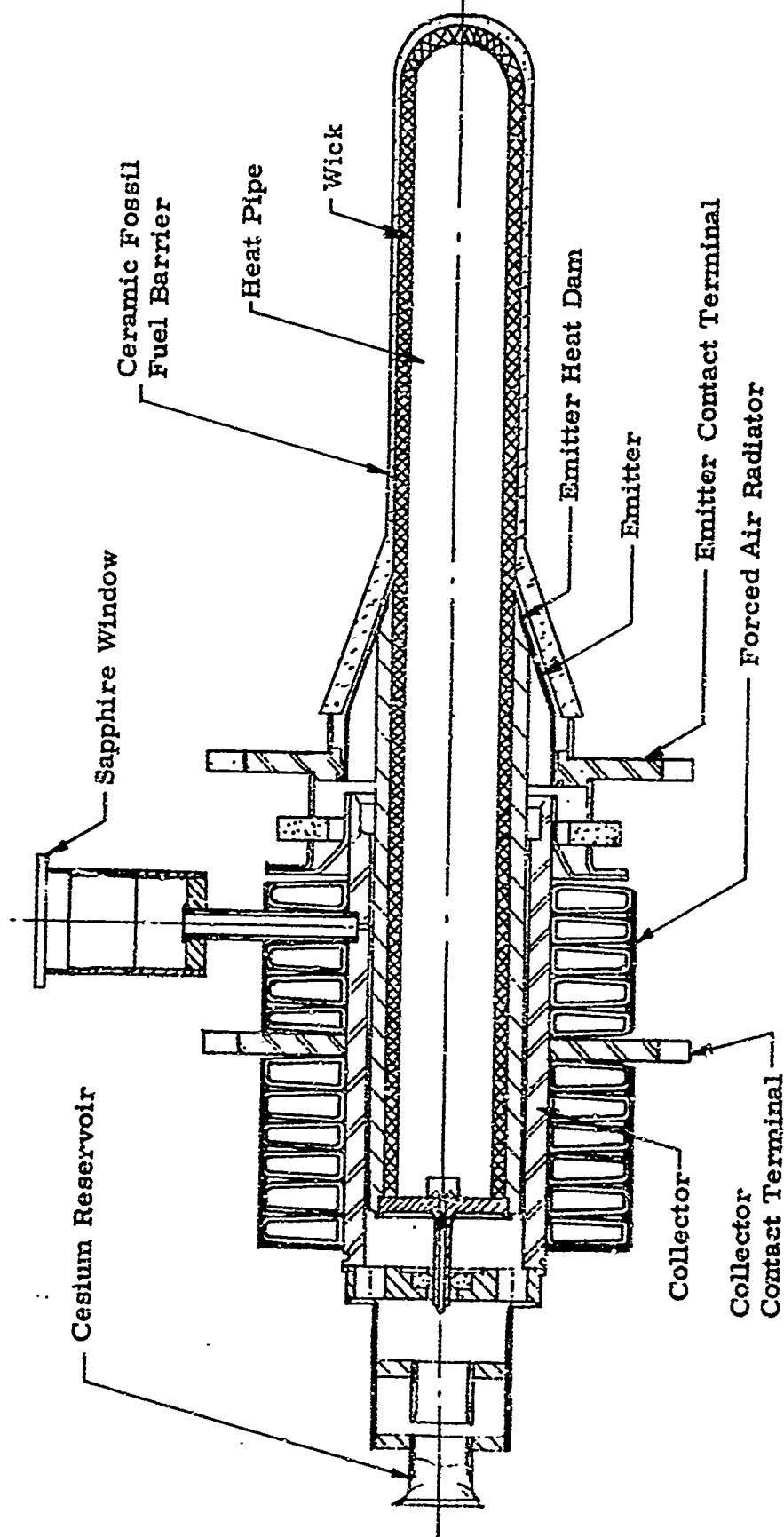
Forced Air Radiator

Collector

Collector Contact Terminal

FIGURE 1   CROSS-SECTION OF FOSSIL FUEL FIRED CONVERTER DESIGN

FIGURE 2 INITIAL HEAT PIPE SYSTEM

FIGURE 3 SECOND HEAT PIPE SYSTEM

Condenser

Columbium
Tubing
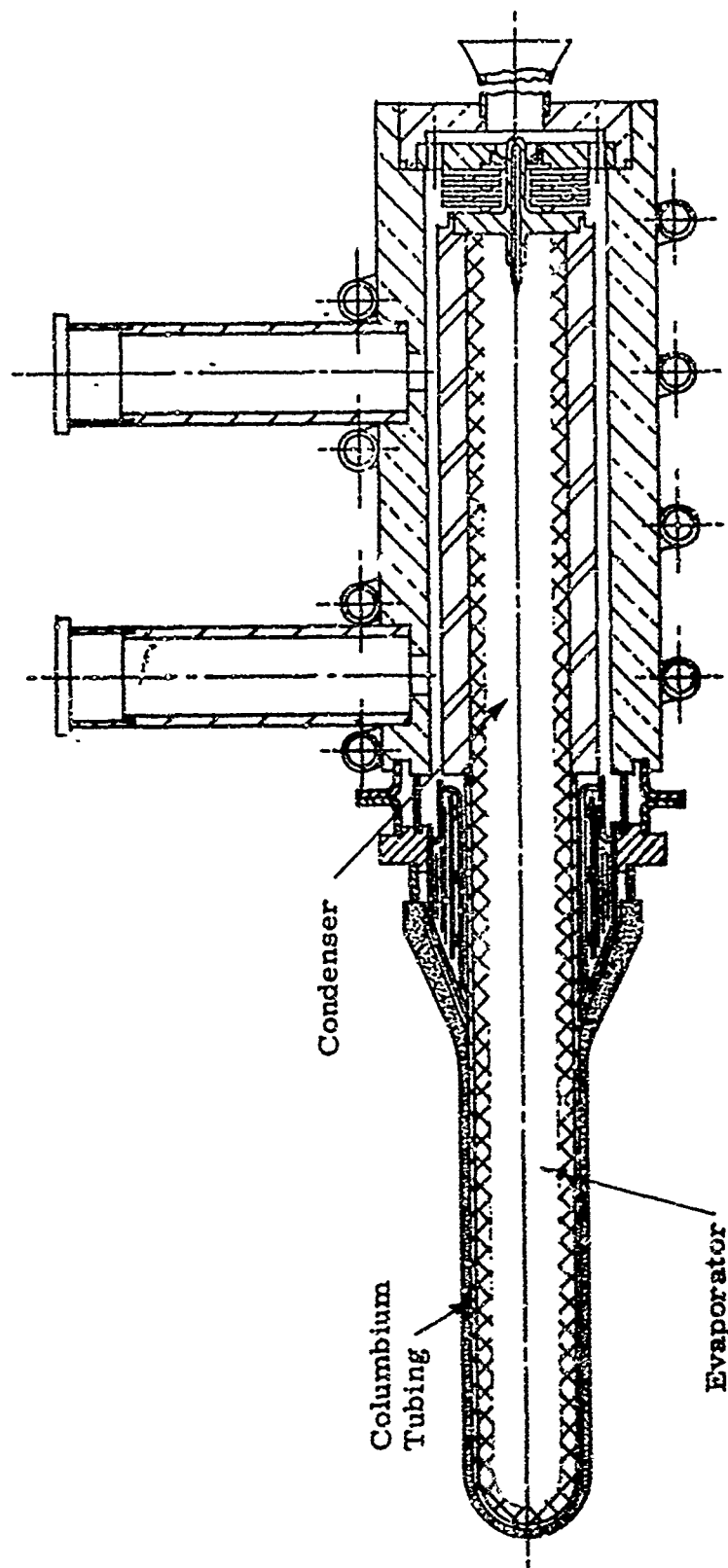
Evaporator

sufficient thermal power to deliver 100 electrical watts from a converter. In both systems the working fluid in the heat pipe is in solid thermal contact with the barrier. With solid thermal contact the major temperature gradient between the outside of the barrier and the working fluid occurs through the wall of the barrier and is less than 46°C.

The cone section of the barrier and its associated heat shields makes it possible to operate the seal between the converter and the barrier at 400°C while the heat pipe is operating at 1450°C.

In the first system, Figure 2, the barrier and the emitter form the heat pipe. This system requires that the barrier, the emitter and the joint between them be compatible with the working fluid. The space between the heat shield and barrier is narrow enough that stagnant working fluid will be held in the gap by capillary forces. In the second system, Figure 3, the working fluid does not come in contact with the barrier. Assembly is made by shrinking the barrier onto a columbium tube to which the emitter is later welded. The requirements of this system are that the working fluid be compatible with columbium and the emitter material, and that the differential thermal expansion between columbium and the barrier be small enough not to crack the barrier.

In the design of the heat pipe it is assumed the converter will operate at 10% efficiency or 1000 watts of power must be transferred from the boiler to emitter. Some heat will also be lost at the jointure of the boiler to converter. An estimate of this loss was made by vectorially adding the longitudinal heat losses to the radial losses. To determine the longitudinal heat loss, the cone was treated as a cylinder with one end operating at 1450°C while the other end was at 400°C. Using the average thermal conductivity and the average cross-sectional area of the cone, the longitudinal heat

loss was 53 watts. The radial heat loss was determined by treating the cone as a disk with the inside radius being the inside radius of the barrier and the outside radius the radius at the base of the cone. The length of the disk was the average wall thickness of the cone. With the same assumed temperature, the radial heat loss was 34 watts. The total heat loss is 63 watts when the longitudinal and radial heat loss are vectorially added. Adding 63 watts loss at the jointure to the heat which must be supplied to the emitter, 1063 watts of energy must be transferred from the boiler.

To simulate the operation of a converter, the emitter will radiate to the water-cooled calorimeter. The power transferred by the heat pipe can be calculated from the change in temperature of the cooling water. A molybdenum emitter 2.8 cm in diameter and 10 cm long operating at 1450°C will radiate 1063 watts at a power density of 11.4 watts/cm^2. The temperature gradient through the wall of the emitter is 6.5°C. These simulated converter and heat pipe structures shown will be temperature cycled 50 times from room temperature to 1450°C.

C.   Working Fluids

Potential working fluids for the heat pipe are required to have the following characteristics.

1.   The vapor pressure and the latent heat of vaporization of the working fluid must be high enough that heat can be transferred from the boiler with laminar flow in the vapor.

2.   The vapor pressure of the working fluid must be low enough that there are no undue stresses in the barrier from excessive internal pressure.

3.   The melting point of the working fluid must be low so that stresses from differential thermal expansion between solid working fluid and barrier do not crack the barrier.

4. The working fluid must wet the wick material and preferably the inside wall of the heat pipe.

5. The working fluid must be compatible with the materials with which it comes in contact.

In light of these requirements, bismuth and lead are the best working fluids for the first design with the liquid metal in contact with the alumina barrier. Lithium is the best working fluid for the second design where the working fluid does not come in direct contact with the barrier. Lithium is not compatible with alumina.

Table I lists the working characteristics of bismuth, lead and lithium. All of the values are calculated using equations derived by T. P. Cotter[1] in his paper on "Theory of Heat Pipes". For completeness of this report, the equations are repeated in the Appendix and sample calculations are made using bismuth as the working fluid. Lithium is the best of the three materials for a heat pipe operating at 1450°C even though the pressure is slightly greater than two atmospheres. At 1660 torr the hoop stresses in a barrier with a 0.060 inch wall are only 200 psi. Lithium has the smallest temperature gradient (0.08°C) and pressure gradient (0.0088 torr) over the entire length of the pipe. Lithium's Reynold's number is small enough to assure laminar flow. Lithium is also a desirable working fluid because of its large latent heat of vaporization and low density.

For a heat pipe operating in contact with the alumina barrier, bismuth is the best choice. Although bismuth's temperature gradient (0.81°C) and pressure gradient (0.42 torr) are more than an order of magnitude greater than lithium's, they are small enough to assure that the vapor in the heat pipe is the same temperature from one end of the pipe to the other. The

TABLE II
THE CHARACTERISTICS OF POTENTIAL WORKING FLUIDS

		Bi	Pb	Li	Units
L	Heat of Vaporization at 1450°C	1.14	.745	19.0	kwatt-sec/g
ρ_v	Density of the vapor at 1450°C	7.05×10^{-4}	2.52×10^{-4}	1.22×10^{-4}	g/cm^3
v_v	Velocity of the vapor	1040	4480	360	cm/sec
η_v	Viscosity of the vapor	1.78×10^{-3}	1.40×10^{-3}	2.04×10^{-4}	poises
R	Reynolds number for the vapor	260	510	118	
p	Vapor pressure at 1450°C	320	124	1660	mm Hg
Δp_v	Pressure gradient in the vapor	-0.42	-2.75	-0.00875	mm Hg
ΔT_v	Temperature gradient in the vapor	0.81	7.73	0.0795	°K
ρ_ℓ	Density of the liquid at 1450°C	8.55	9.3	0.433	g/cm^3
v_ℓ	Velocity of the liquid	0.062	0.130	0.0110	cm/sec
η_ℓ	Viscosity of the liquid at 1450°C	5.7×10^{-3}	8.5×10	1.85×10^{-3}	poises
γ	Surface tension of liquid 1450°C	275	335	155	dyne/cm
r_c	Optimum pore radius for the wick	0.0078	0.0086	0.0089	cm

Fixed Quantities and Dimensions

			Units
Q_e	Heat transferred from the boiler	1.063	kwatts
ℓ	heat pipe length	24.68	cm
ℓ_e	Boiler length	8.1	cm
r_v	Inside radius of wick	0.63	cm
T_o	Temperature of heat pipe	1723	°K
A_v	Cross-sectional area of vapor region	1.27	cm^2
r_w	Inside radius of heat pipe	0.95	cm

most severe temperature gradient (¼°C) occurs in the barrier's radial direction along the path heat flows into the heat pipe.

Lead will also operate the heat pipe, but is a poor choice because the temperature gradient along the pipe is 7.7°C.

D. **Materials and Assembly Techniques**

Two important structural items were considered during the report period; the design of the capillary structure and the achievement of a reliable seal to join the heat pipe sections.

1. **Capillary Structure**

A wick is necessary in the heat pipe to return the condensed vapor to the boiler for reevaporation. For the designs which have been discussed, the optimum pore size is 0.006 to 0.007 inches in diameter for all the liquids considered as shown in the Appendix. The wick can be made of either 80 mesh molybdenum screening or molybdenum sponge. Eighty mesh screening is made using 0.0055 inch diameter wire and an opening with a width of 0.007 inch. A photograph of sponged tungsten is shown in Figure 4.

2. **Ceramic-to-Metal Seal**

The two-piece heat pipe in which the working fluid is in contact with the ceramic barrier requires a ceramic-to-metal seal compatible with lead or bismuth. Liquid lead and bismuth are very corrosive and can readily dissolve brazing alloys containing copper, nickel, or any of the precious metals. Attempts to braze seal assemblies with refractory metal alloys such as the molybdenum-iron eutectic have failed because they lack the ductility of conventional brazing alloys. For these reasons an effort has been made to develop a ram seal using a refractory metal compatible with bismuth and lead.

FIGURE 4 TUNGSTEN SPONGE

This material represents a pore size of
0.020 inch and ten percent density

A ram seal is made by pushing a metal band over the outside diameter of a ceramic cylinder as shown in Figure 5. Sealing is accomplished by the residual stresses resulting from the interference between the two parts.

The selection of the materials, the required surface finishes, and the seal forces are all important parameters determining the quality of the seal and are discussed as follows:

The sealing force, V_o per linear inch of seal circumference, can be calculated using the equation:

$$V_o = 0.38 \sigma_t \frac{t^{3/2}}{\sqrt{R}} \frac{1}{4\sqrt{1-\nu}}$$

where

σ_t = the hoop stress

t = the wall thickness of the metal

R = the mean radius of the metal

ν = Poisson's ratio

The interference ΔR can be calculated from the equation

$$\Delta R = \frac{\sigma_t R}{E}$$

where E = the modulus of elasticity of the metal band.

The six seals listed in Table II were made and leaked. An analysis of them is discussed later.

The metal selected for the seal is D-43, a columbium alloy with a nominal composition of 10 percent tungsten, 1 percent zirconium,
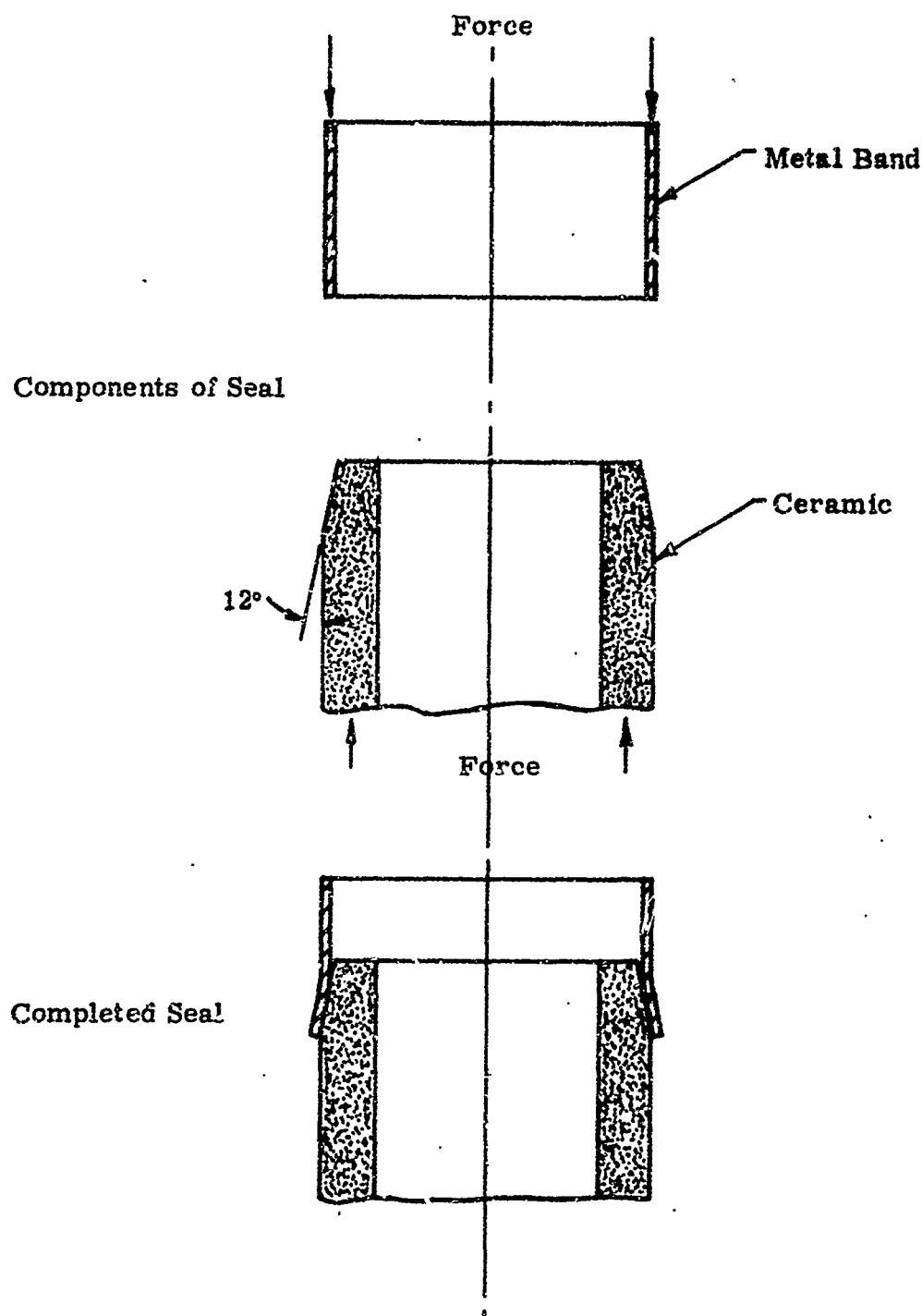
Force

Metal Band

Components of Seal

12°

Ceramic

Force

Completed Seal

FIGURE 5 RAM SEAL BETWEEN METAL BAND AND CERAMIC

TABLE II

CHARACTERISTICS OF FABRICATED SEALS

Wall Thickness t	Surface Preparation	Stress	Sealing Force	ΔR
0.020	as drawn	40,000 psi	50# /in	0.0037 in
0.020	polished	60,000	75	0.0055
0.020	iron plated .00'" thick	40,000	50	0.0037
0.033	polished	40,000	100	0.0037
0.033	polished	60,000	150	0.0055
0.033	polished	>80,000*	> 150*	0.010

*This seal was designed to exceed the yield point of B-43.

0.1 percent carbon and the balance columbium. It has a thermal expansion nearly the same as pure alumina, Figure 6, a yield strength above 58,000 psi from room temperature to 800°C, Figure 7, a modulus of elasticity of 17.8×10^6 psi, Figure 8, and an elongation prior to rupture of 20 percent at room temperature.

With a thermal expansion nearly the same as alumina, and the high yield strength at 800°C, the sealing force would change little with temperature. Also, the small modulus of elasticity makes it possible to design parts with a relatively large interference.

Rings were formed from D-43 sheet 0.020 and 0.033 inch thick by drawing and by spinning. Spinning was tried first, without success. It was necessary to anneal parts before reaching the final dimension, and the rings cracked during the second operation. The rings were finally made by drawing, which could be done in a single operation without an anneal.

The surface finishes on the joining parts are very important because complete contact must be made for the seal to be vacuum tight. The first ceramics were ground with a 320 grit diamond wheel followed by 600 grit rubber bonded silicon carbide wheel and 2 micron diamond paste. This procedure tended to pull grains from the ceramic body creating an undesirable surface. By following 320 grit diamond wheel with decreasing grit sizes (45, 15, 9, 3 and 1 microns) of diamond paste applied to a copper wheel, pulling out of the grains was avoided. The surface of the metal was then polished using standard metallurgical practices.

One of the first seals made is shown in Figure 9 after it was pushed apart to observe the deformation to the metals surface. The wall

FIGURE 6 THERMAL EXPANSION OF MATERIALS

Temperature – Degrees Centigrade

Expansion – Mils per Inch

——— D43 Columbium Alloy

——— Al_2O_3 Aluminum Oxide
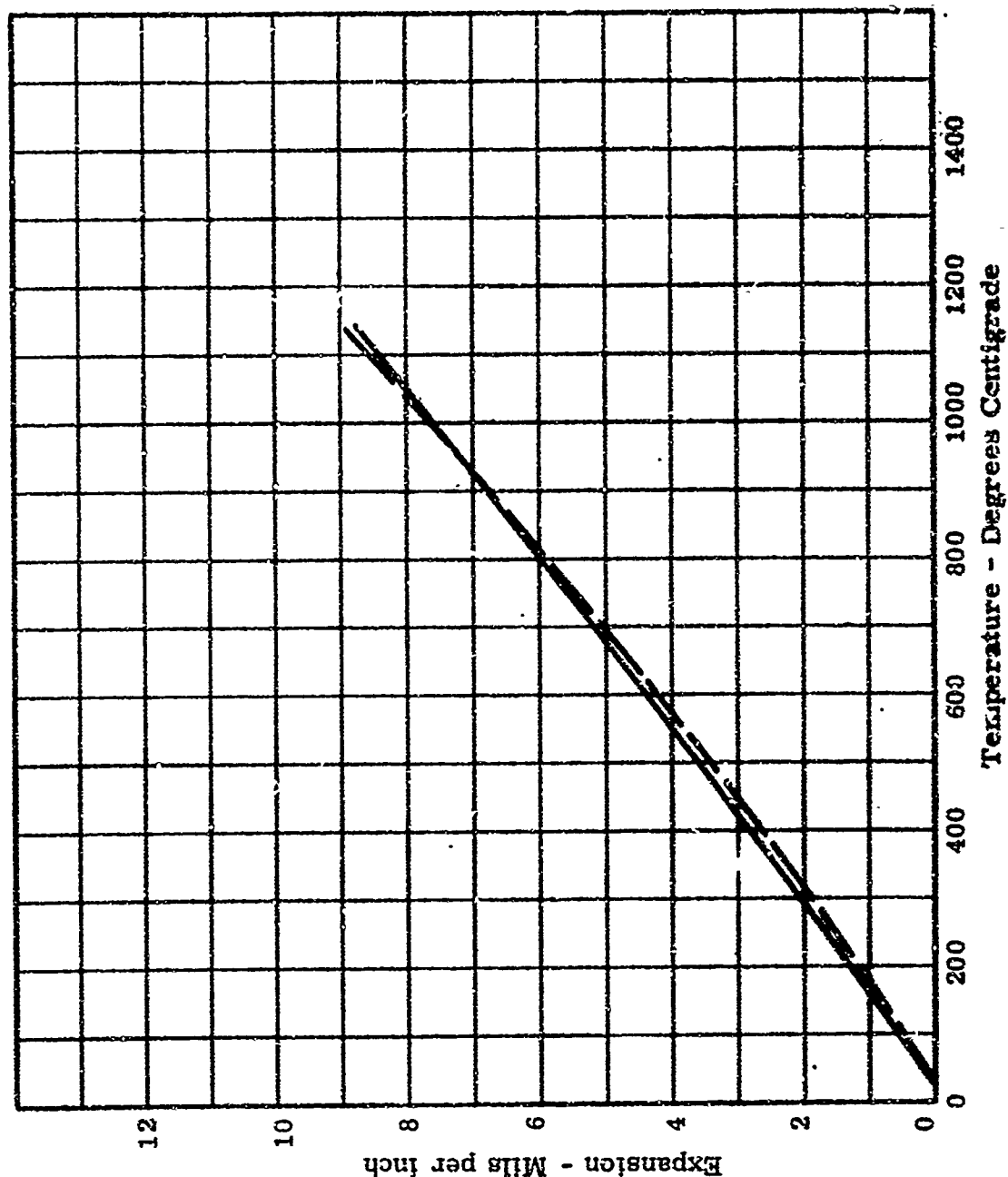
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Contract DA28-043-AMC-01507(E)
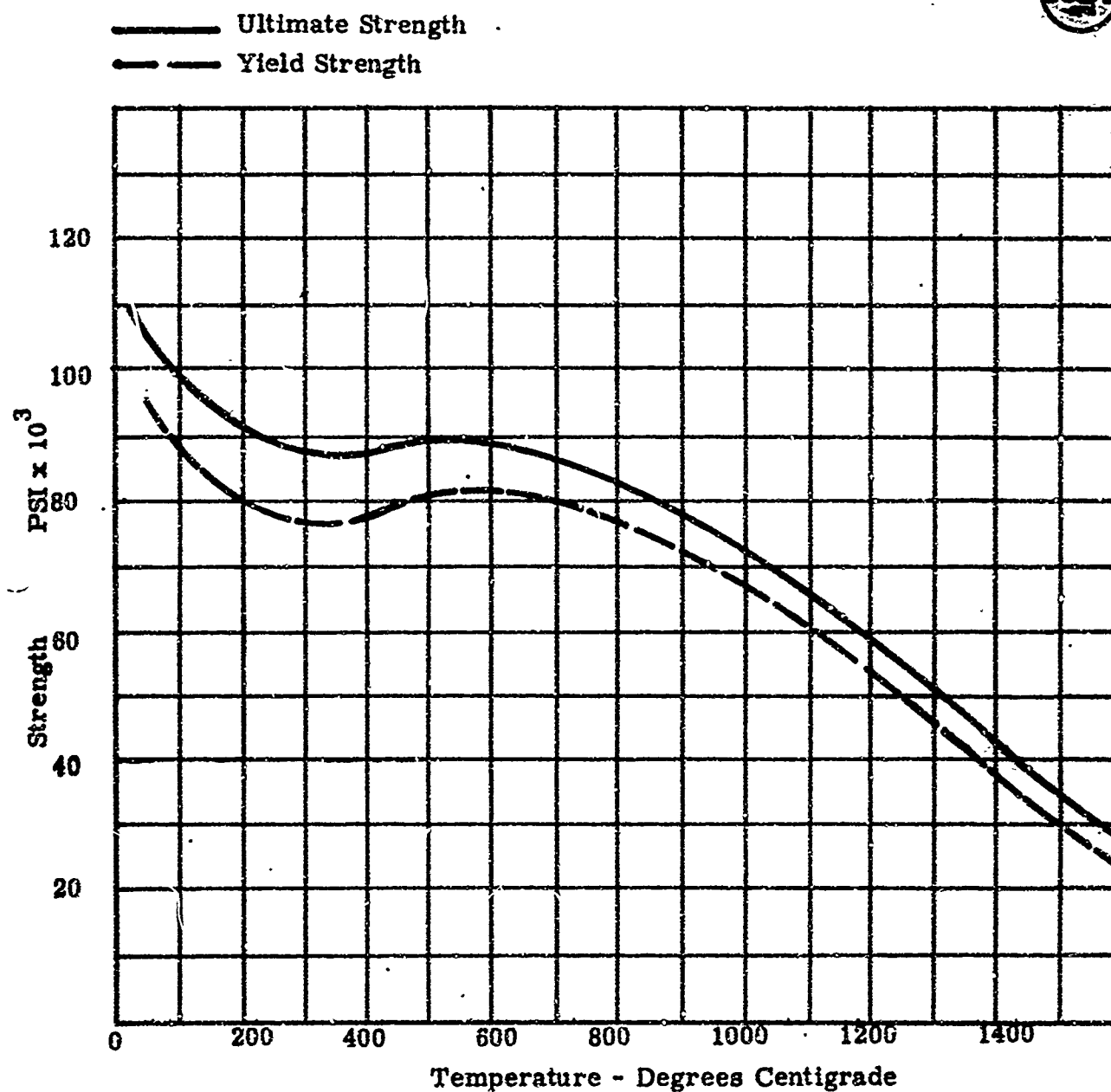31 October 1965

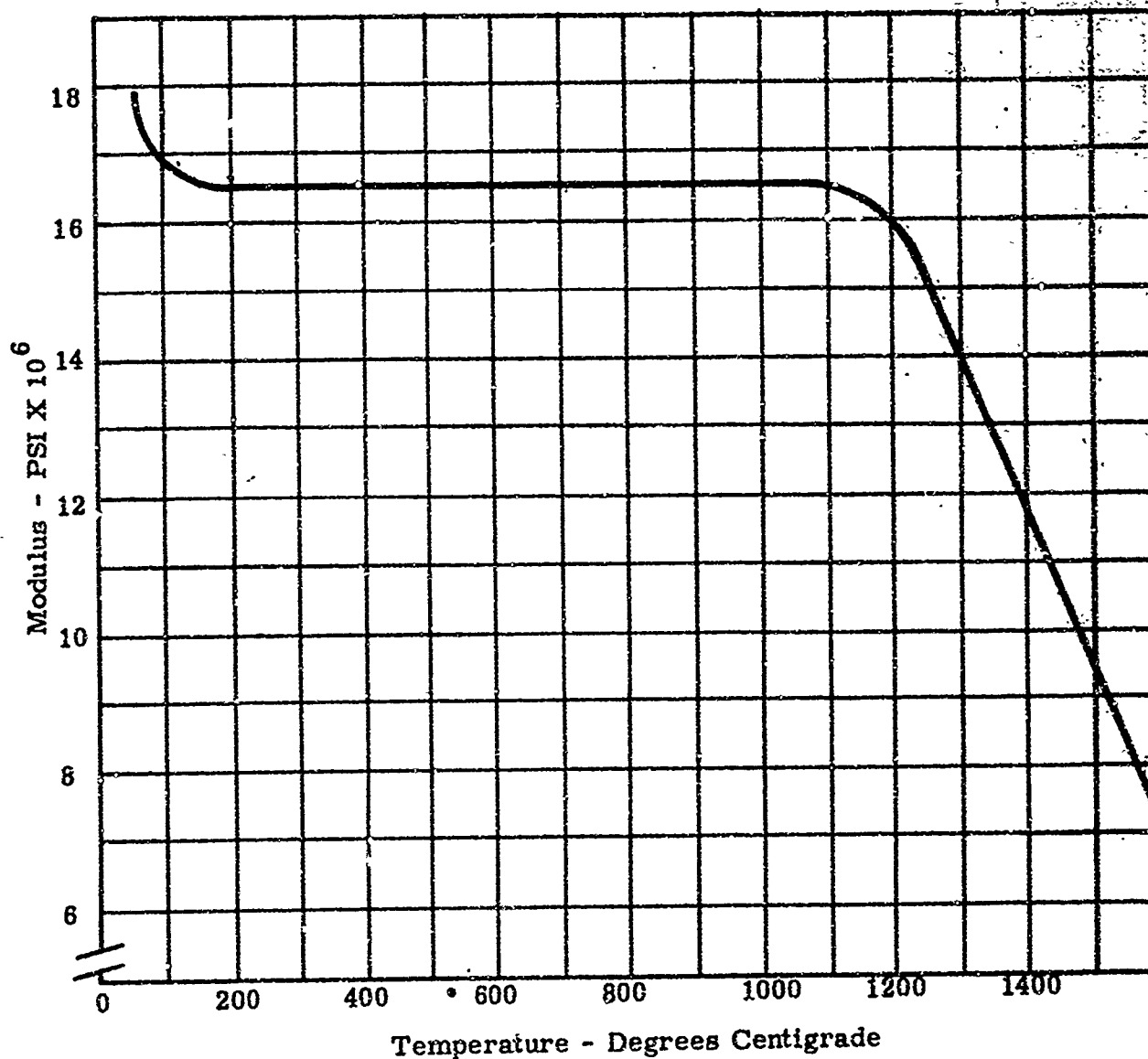-19-

FIGURE 7 YIELD STRENGTH OF D43 MATERIAL

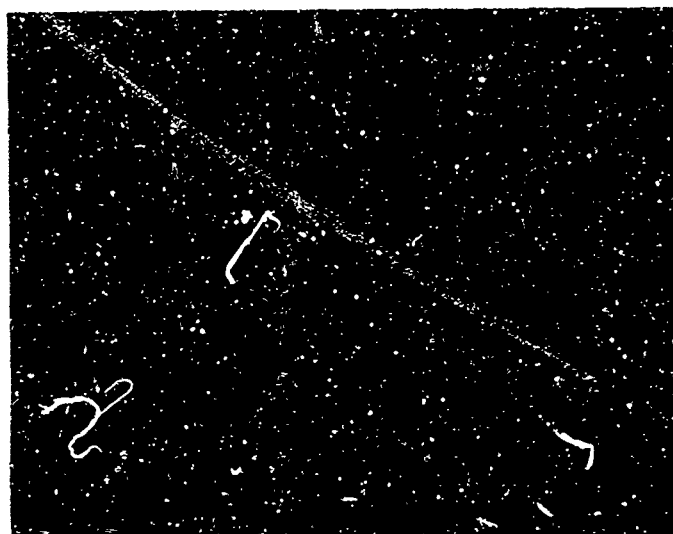FIGURE 6 MODULUS OF ELASTICITY OF D43
COLUMBIUM ALLOY

FIGURE 9 D43 BOND AFTER REMOVAL FROM
CORAM RING

NOTE: The score lines are obvious on the
inside diameter of the ring

thickness of the ring is 0.030 inch. This seal leaked because of the scoring. From latter test with the 0.033 inch wall it was concluded that the scoring is the result of gauling and that the metal pilling-up in front of the ceramics sealing edge is pushing the metal band away from the ceramic, preventing a seal in neighboring regions. Test with the heavier wall only broaden the scored regions. Shown in Figure 10 is an iron plated 0.020 inch thick metal band after it was pushed apart. It should be noticed the metal is not scored because the softer iron acts as lubricant when the band is pushed onto the ceramic. This seal had a small leak and is believed to be the result of insufficient sealing force. Iron plating the D-43 is very difficult because the adherence is poor, and thermal expansion mismatch is great.

From these preliminary tests, iron plating appears to be necessary and the wall thickness of D-43 must be increased to obtain vacuum tight joints.

3. Barrier Materials

    The requirements of the barrier, that it be impervious to all gases at 1450°C for more than 1000 hours, and be capable of withstanding thermal shock, limits the choice of materials to a few, which are discussed as follows: (Most of the correspondence and tests were performed with RCA funds and are being reported here to add continuity to this report).

    Titanium diboride and zirconium diboride are two relatively new materials. They are primarily employed for coating thermocouple protection tubes made of either tantalum or columbium. They are capable of withstanding the thermal shocks of being submerged in molten steel from room temperatures. Samples of these materials
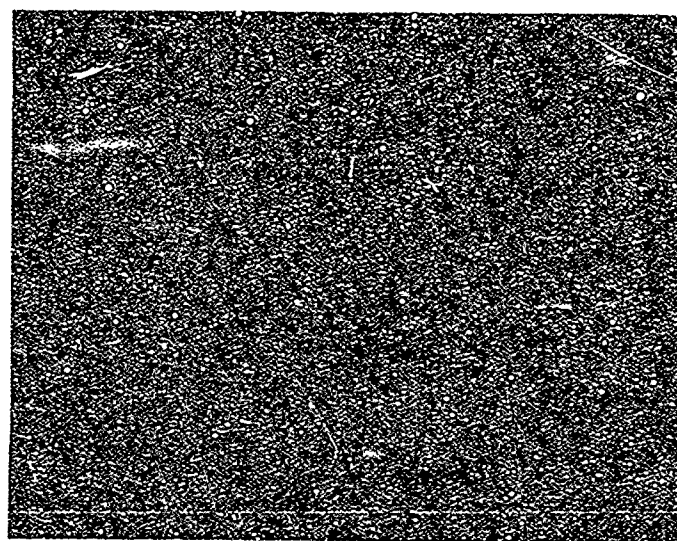
FIGURE 10 IRON PLATED D-43 METAL BAND

AFTER REMOVAL FROM CORAM RING

NOTE: The highly polished inside diameter is obvious. It resulted from the interference between the parts. A second seal was obtained with the opposite end of the metal band with less interference and thus is less highly polished.

were obtained for thermal cycling. The titanium diboride was received as a free standing tube which was not vacuum tight. It was temperature cycled six times from room temperature to 1500°C without cracking. At 1500°C a loose white oxide formed on the exposed surface which indicated titanium diboride would be marginal for continuous exposure at 1500°C. The sample of zirconium diboride was plasma sprayed onto a tantalum tube. An attempt was made to join the tantalum tube to a vacuum system. In brazing this material the zirconium diboride coating delaminated and peeled off the tantalum tube. The vendor replaced this sample, but the second sample failed the same way.

A sample of Kanthal Super was also obtained and tested for thermal shock. Kanthal Super is a molybdenum disilicide bonded together with dispersion of ceramic and metal. A photomicrograph of its structure is shown in Figure 11. Normally Kanthal Super is used as a heater element for 2000°C operation in air. The sample was temperature cycled six times successfully to 1500°C and the only change in its appearance is a glazing of the exposed surface. Attempts to metalize the Kanthal Super so that it could be brazed to a vacuum system failed. The vendor also disclosed it would be impossible to make parts with a diameter greater than one inch or in the shape of the cone at the end of the barrier.

Samples of high purity mullite were also obtained, but failed during the thermal shock test. A crude measurement of the permeation of gases through mullite was obtained by sealing a vac-ion pump and ion gauge to a mullite tube closed at one end. After degassing the tube for 24 hours, the vac-ion pump was turned off and the pressure of the system raised more than two orders of magnitude in less than one-half hour.
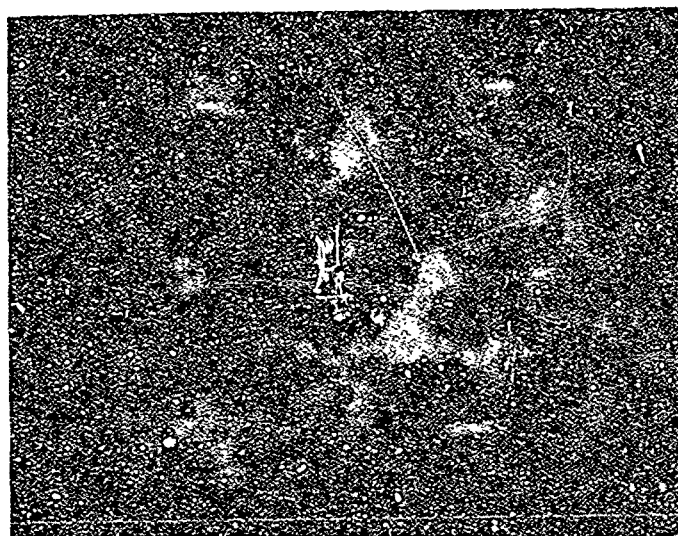
FIGURE 11 PHOTOMICROGRAPH OF KANTHAL SUPER
(Magnification 1380x)

Silicon carbide has also been considered as a permeation barrier, but like the titanium diboride, vacuum integrity cannot be assured as a pressed and sinter part. However, it can be obtained vacuum tight by vapor plating. Unfortunately, vapor plating produces the columnar grain structure shown in the photomicrograph Figure 12. Such a grain structure caused the material to be very weak because there are no grains to interfere with the propagation of cracks along grain boundaries. The average modulus of rupture of samples of pyrolytic silicon carbide was 19,650 psi. Also, since grain boundaries are regions of a relatively loose molecular structure having diffusion coefficients sometimes several orders of magnitude higher than the bulk diffusion coefficient, the columnar structure provides a shorter diffusion path for impurities than a fine pressed and sintered structure. Vapor plated silicon carbide is also difficult to join to a metal member because induced thermal stresses which cause the SiC to crack along the columnar grain boundaries.

In light of the short comings of the materials discussed above, alumina still appears to be the best material for the barrier. Currently there is more published data on the properties of alumina than any other refractory material. The tube industry has accumulated years of experience in working with alumina, and the permeation rate has been proven to be low enough as demonstrated by life testing a converter, Type A-1192B, for more than 1000 hours. Several suppliers are capable of furnishing high alumina bodies in the required geometry. The properties of the alumina, as received from different suppliers, vary sufficiently that they must be discussed separately.

Lucalox, Coram, and Frenchtown 7325 are the three bodies considered for this program. Lucalox is a high purity alumina body made by the
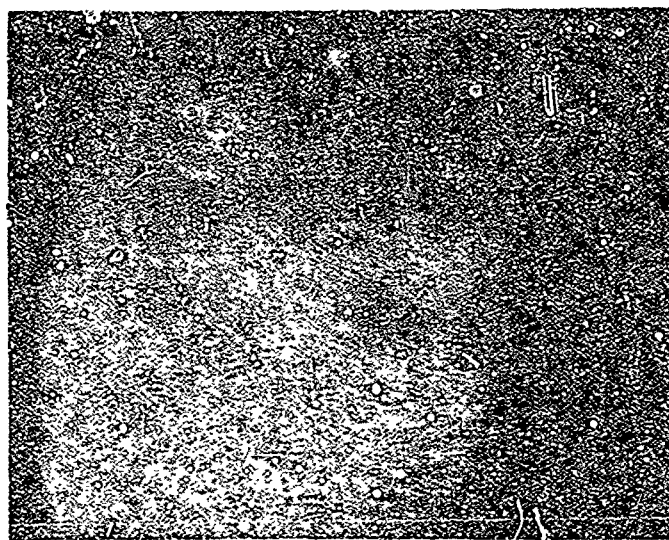
FIGURE 12 PHOTOMICROGRAPH OF VAPOR-
DEPOSITED SILICON CARBIDE

(Magnification 69x)

NOTE: The columnar grain growth is accentuated

General Electric Co. It is translucent and will transmit infrared energy with a wavelength as long as 6.5 microns. Lucalox's modulus of rupture strength is in the range of 35,000 to 40,000 psi. Barriers made of Lucalox are shown in Figure 13.

Coram is similar to Lucalox and made by the Corning Glass Co. under a General Electric license. They claim to have improved the thermal shock resistance of the body. A barrier made of Coram is shown in Figure 14. Their body is sintered in vacuum.

Frenchtown 7325 is manufactured by the Frenchtown Porcelain Co. and was used in the A-1192B converter. Frenchtown has not been able to furnish barriers of the size necessary in this program because of equipment limitations, so RCA has undertaken the task of aiding them. By a joint effort the isostatic pressing mold shown in Figure 15 was designed. Frenchtown is furnishing 7325 powder which will be used to fabricate barriers at RCA.

All of these alumina bodies have similar modulus of rupture strengths of 30 to 40,000 psi. If the strength of the body can be increased there will be a corresponding increase in the shock resistance of the barrier. Passmore[2] and his associates have shown that by hot pressing alumina, a high purity body may be obtained with a very fine grain size and modulus of rupture strength greater than 100,000 psi.

Unfortunately, these samples were made by pressing in an unidirectional carbon die which is not amendable to manufacturing barriers. A search is being made for a vendor with hot-isostatic pressing equipment operable in the temperature and pressure ranges where alumina bodies are fabricated.
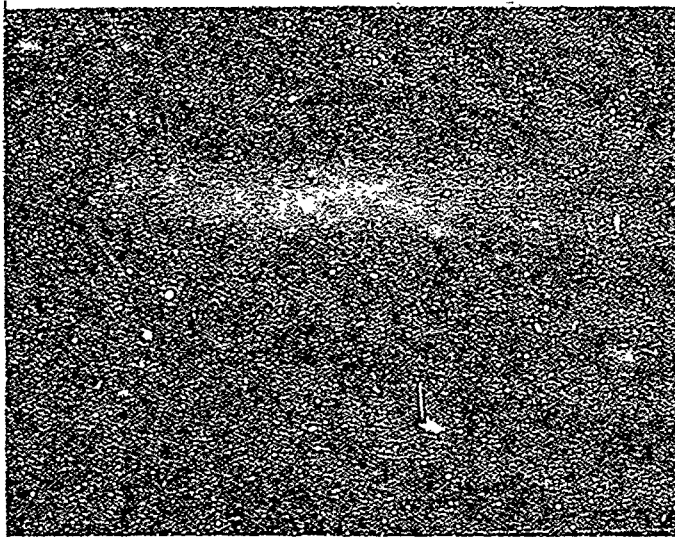
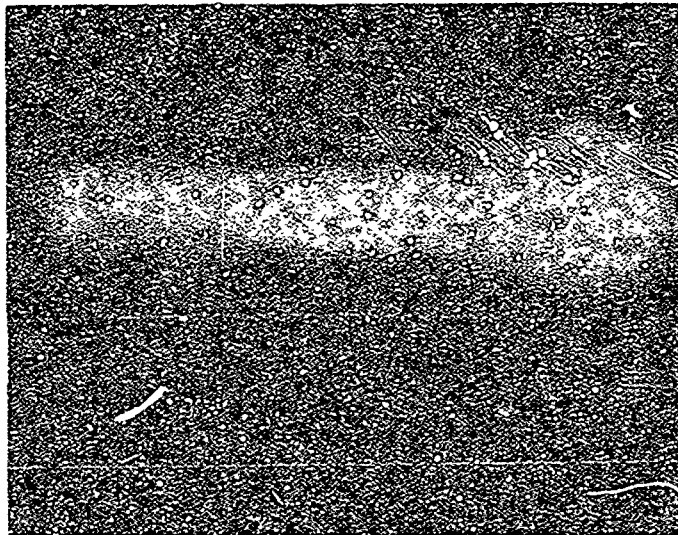FIGURE 13   FOSSIL FUEL BARRIER MADE OF LUCALOX

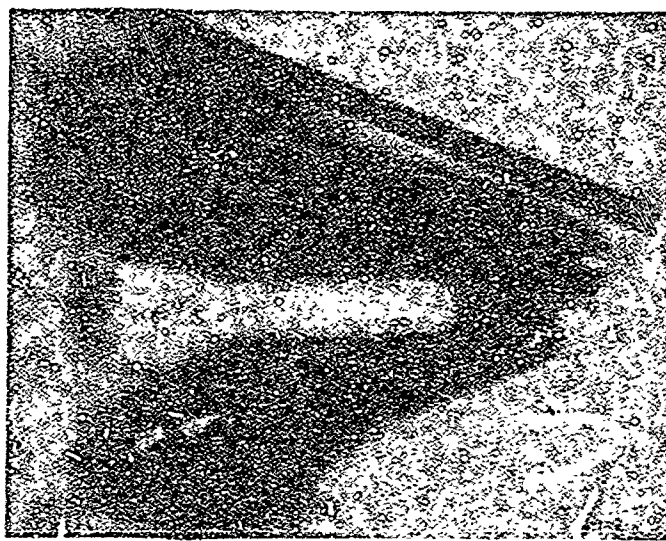FIGURE 14 FOSSIL FUEL BARRIER MADE OF CORAM

FIGURE 15   ISOTATIC MOLD FOR FORMING
CERAMIC BARRIER

NOTE: Designed for use with Frenchtown 7325 body material.   A barrier in
the "green" state is shown between the rubber bag and the steel mandrel.

E. **Permeation**

The permeation test system constructed under contract DA-36-039-AMC-03197(E) and described in the Summary Technical Report[3], was reactivated with the following modifications as shown in Figure 16.

1. The gold-seal fitting used for attaching test samples was replaced by a stainless steel flange using a copper gasket.

2. The concept of an independent electrical heater inside a series of "stacked" heat shields has been replaced with a new integrated heater-heat shield construction, completely enclosed within a water-cooled jacket as shown in Figure 17. This modified system has been successfully pumped to the ultra-high vacuum region. Currently, a Coram sample is attached and is being outgassed at 1600°C prior to testing in a fossil fuel flame environment.

A recently acquired GE Partial Pressure Analyzer[4], Model #22 PC120, has been installed on the system and is undergoing checkout. According to manufacturer's specifications, the instrument is capable of resolving adjacent peaks in the range 2 - 50 AMU (3K gauss magnet) .

The forthcoming permeation tests will be conducted in the following manner:

1. Sample mounted and checked for leaks.

2. Sample outgassed extensively inside the evacuated bell, using the electrical heater at 1800° Centigrade.

3. After outgassing, the sample will be cooled to room temperature and the bell opened to air. The bell and the electric heater will be removed.

4. Burner will be placed around the sample, ignited and slowly raised in temperature until the sample hot zone reaches 1450° Centigrade.
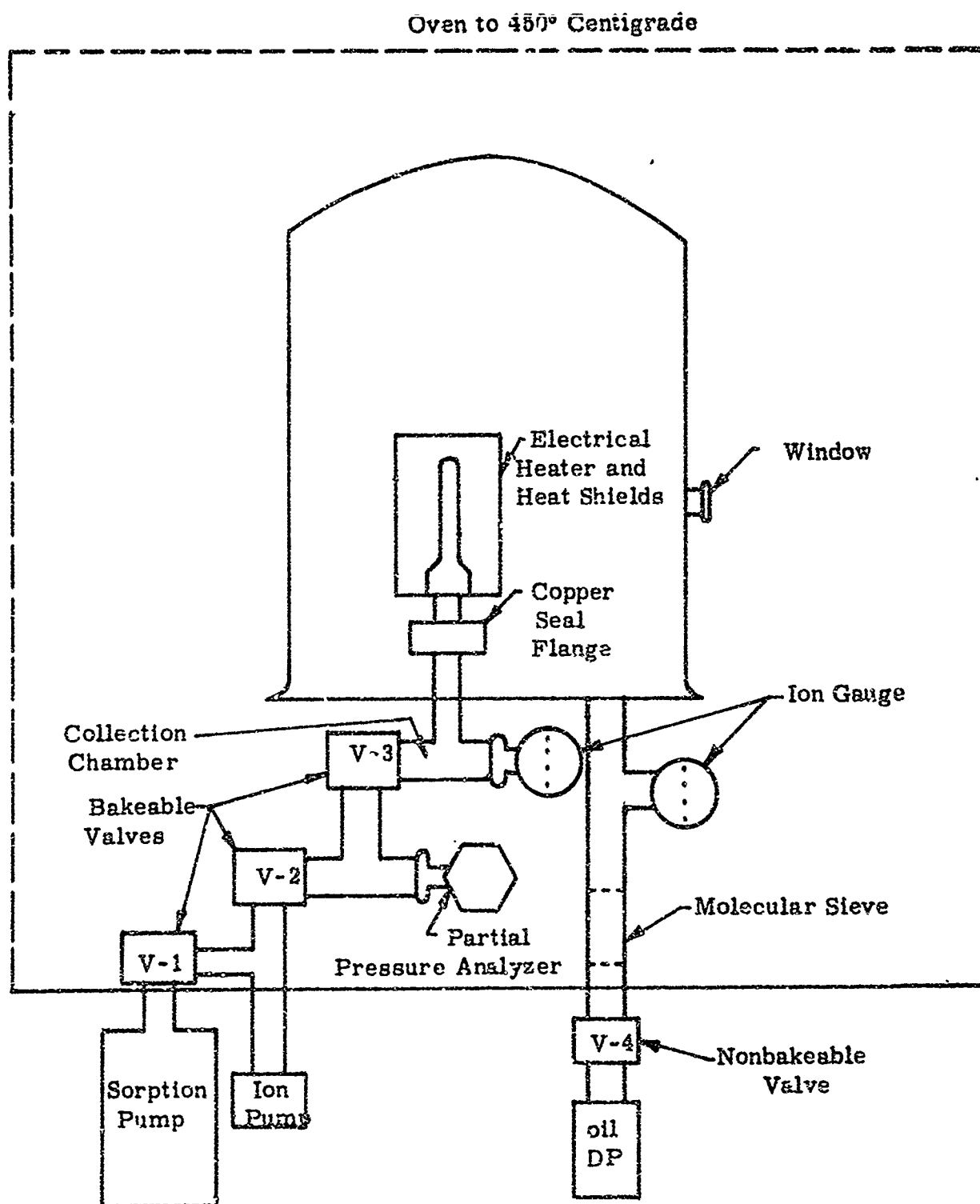
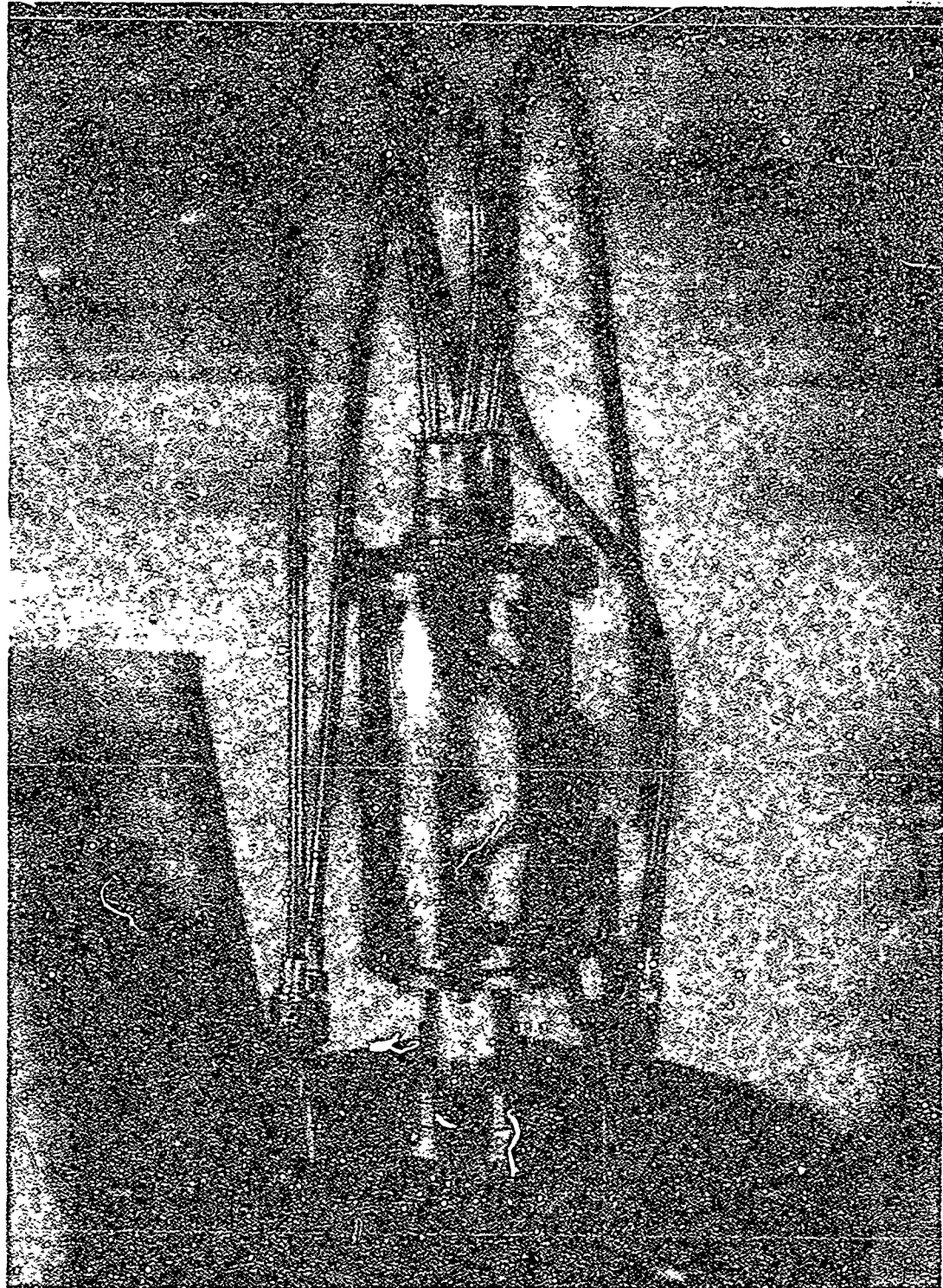FIGURE 16 SCHEMATIC OF MODIFIED COLLECTION CHAMBER SYSTEM

FIGURE 17 HEATER-HEAT SHIELD ASSEMBLY

-35-

5.   Valve V-2 (See Figure 16) will then be closed and the pressure in the collection chamber monitored.

6.   Valve V-3 then will be opened and the constituents of the gas determined by the Partial Pressure Analyzer.

F.   Gettering

In an attempt to minimize the effects of permeating gases on the operation of a heat pipe, an investigation has been launched into various getters or gettering techniques applicable to a heat pipe environment. Specifically, this environment consists of a metal vapor at a pressure of 10-1000 microns of Hg and a temperature of 1400° Centigrade.

This search is dominated by the following considerations:

1.   Previous work has shown that oxygen selectively permeates alumina barriers[5]. Hence, any material or technique used as a getter must have a high affinity for oxygen and form thermally stable oxides. While hydrogen and hydrides are of interest, they are anticipated to enter only as second-order effects.

2.   No commercial getters are available which operate in the temperature range 1300-1400° Centigrade[6,7].

3.   A literature search has not revealed any getter studies performed under the conditions of interest.

In view of the above facts, the decision was made to approach the problem by considering the thermodynamics and kinetics of possible chemical reactions.

Since thermodynamic parameters dictate the necessary conditions for the reaction, these were studied initially. This study is hampered, however, by inconsistencies in the literature as to nomenclature and notation.

Traditionally, literature in the field of chemistry uses the term "free energy" to describe energy exchange during a reaction in contact with a pressure and heat reservoir; namely, the atmosphere. The thermodynamic function applicable to this condition is the Gibbs Function defined as:

$$G = H - TS$$

where

> H is the enthalpy of the system
>
> T is the temperature of the system
>
> S is the entropy of the system

Many thermodynamics tests, on the other hand, define "free energy" as changes in the Helmholtz Function:

$$A = U - TS$$

where

> U is the internal energy of a system

This function is most applicable to isochoric (at constant volume) processes.

Cognizance of these facts is necessary in analyzing the problem at hand. The processes of interest within the heat pipe are those which occur isothermally and isochorically. This indicates the application of the Helmholtz Function. But most of the information relevant to "free energies" is generated with respect to the Gibbs Function. Such a listing of "free energies" of oxide formation[8] is given as Table III. In addition, an extrapolation of selected portions of this information to 1400°C is presented as Figure 18. The value of this graph is as follows:

1. While not directly applicable to the heat pipe, this information is helpful as an approximation to the correct parameters.

TABLE III

VARIATION OF FREE ENERGY OF FORMATION OF OXIDES WITH TEMPERATURE

Element	Oxide	ΔF at 25°C	ΔF at 500°C	ΔF at 1000°C
Aluminum	Al_2O_3	-366	-330	-298
Antimony	Sb_2O_3	-149	-120*	-92
Arsenic	As_2O_3	-135	-104	-72
Barium	BaO	-126	-115	-104
Beryllium	BeO	-132	-121	-109
Bismuth	Bi_2O_3	-117	-83	-40
Cadmium	CdO	-60	-43	-23
Calcium	CaO	-144	-133	-121
Carbon	CO	-33	-43	-54
Cerium	CeO_2	-220	-198	-176
Cesium	Cs_2O	-79	-74	-69
Chromium	Cr_2O_3	-249	-215	-180
Cobalt	CoO	-51	-43	-34
Columbium	Cb_2O_5	-426	-400	-373
Copper	Cu_2	-35	-28	-21
Gallium	Ga_2O	-75	-64	-53
Germanium	GeO_2	-142	-210	-197
Gold	Au_2O_3	+19	+31	+44
Hafnium	HfO_2	-258	-237	-215
Hydrogen	H_2O	-55	-49	-42
Indium	In_2O_3	-218	-184	-147
Iridium	IrO_2	-28	-9	+51
Iron	FeO	-59	-51	-43
Lanthanum	La_2O_3	-436	-403	-368
Lead	PbO	-45	-34	-22
Lithium	Li_2O	-133	-130	-123
Magnesium	MgO	-138	-127	-114
Manganese	MnC	-89	-82	-75
Mercury	HgO	-14	+2	+25
Molybdenum	MoO_2	-122	-100	-80

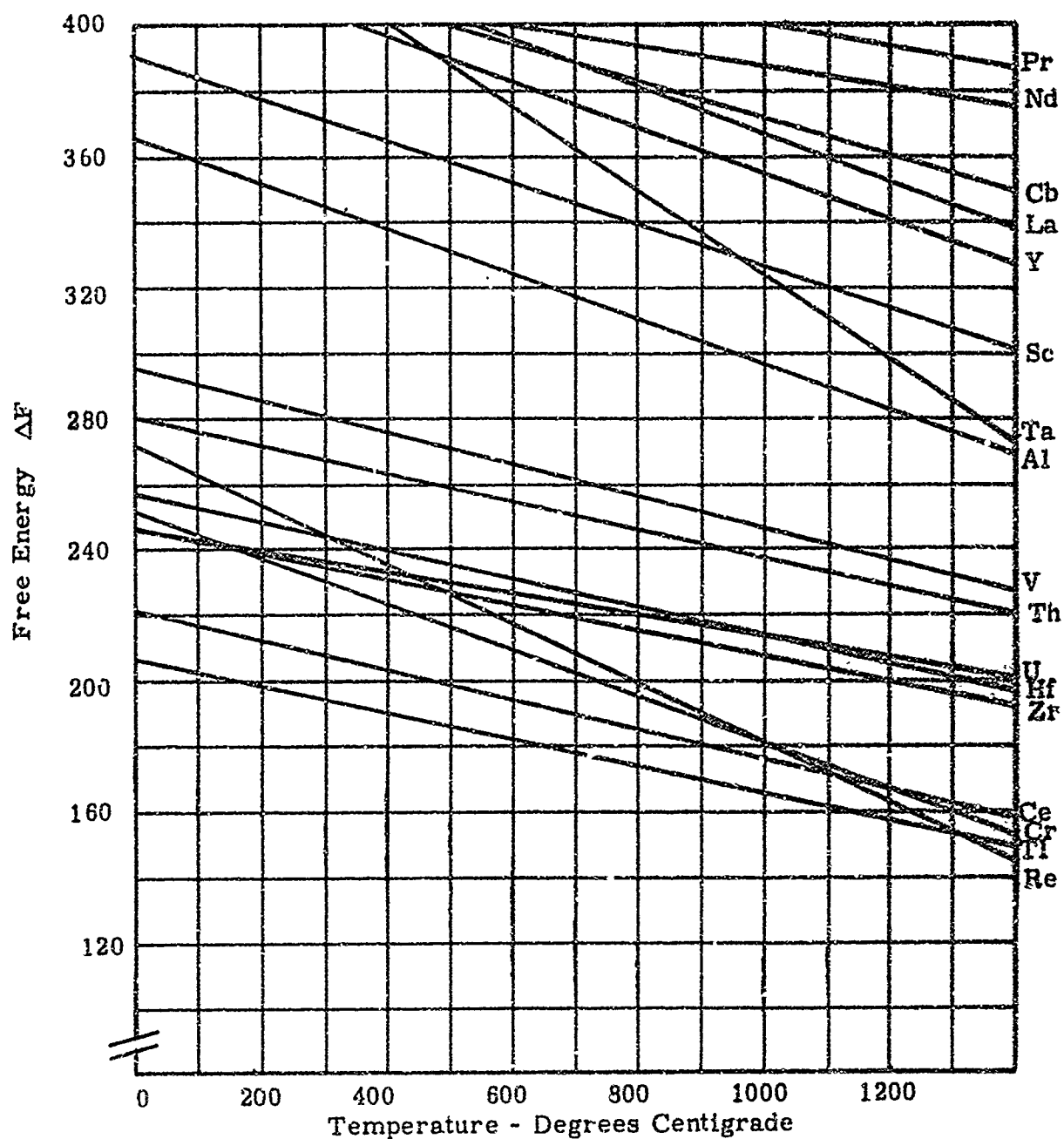| Element	Oxide	ΔF at 25°C	ΔF at 500°C	ΔF at 1000°C
Neodymium	Nd_2O_3	-418	-403	-388
Nickel	NiC	-52	-43	-32
Osmium	OsO	-71	-21	+18
Palladium	PdO	-20	-18	-15
Praseodymium	Pr_2O_3	-430	-416	-400
Potassium	K_2O	-82	-75	-68
Rhenium	Re_2O_7	-270	-227	-181
Rhodium	Rh_2	-17	-12	-6
Rubidium	Rb_2O	-79	-74	-68
Ruthenium	RuO_2	-40	-21	-1
Samarium	Sm_2O_3	-424	-416	-406
Scandium	Sc_2O_3	-391	-360	-327
Silicon	SiO_2	-190	-170	-148
Silver	Ag_2O	-2	+5	+12
Sodium	Na_2O	-90	-75	-54
Strontium	SrO	-133	-122	-109
Tantalum	Ta_2O_5	-447	-388	-325
Tellurium	TeO_2	-64	-44	-25
Thallium	Tl_2O	-43	-44	-39
Thorium	ThO_2	-280	-260	-238
Tin	SnO	-61	-49	-36
Titanium	TiO_2	-205	-185	-164
Tungsten	WO_2	-120	-104	-85
Uranium	UO_2	-244	-225	-213
Vanadium	V_2O_3	-294	-272	-247
Yttrium	Y_2O_3	-76	-66	-49
Zinc	ZnO	-76	-66	-49
Zirconium	ZrO_2	-246	-227	-208

FIGURE 16 VARIATION OF FREE ENERGY WITH TEMPERATURE

2. Thermodynamic properties do not predict the kinetics of a reaction, but they do point out which reaction cannot, or is not likely, to occur.

From this point one is able to intelligently approach a selection process. In addition the the thermodynamic considerations; compatibility with the transfer medium, wick, and envelope is important. Also, the advantages, or disadvantages, of the gettering medium existing as a solid, liquid, or vapor must be evaluated. This selection of several possibilities is now being made.

Following the selection of a group of possible materials, further theoretical investigations are possible. Of particular interest are the speed and extent of appropriate reactions.

Hydride formation and stability will, of course, be considered in a final selection. However, oxygen reactions, being of prime importance, will be exhaustively investigated.

SECTION III

CONCLUSIONS

The following conclusions have resulted from the work accomplished during the First Quarterly Report Period:

1. The operation of a converter, coupled to a heat pipe, can be simulated and studied by substituting a calorimeter for the converter.

2. The two-piece ceramic-to-metal heat pipe system and the integral bonded system are the most efficient methods of thermally coupling a converter to a burner because the working fluid is in direct contact with the parts of the heat pipe.

3. Lead, bismuth and lithium can all be used as working fluids for the heat pipe. Lithium has the smallest temperature gradient along the length of the heat pipe. The optimum pore size for the wick material was the same for all three working fluids; i.e., 0.006 to 0.007 inches.

4. Alumina is the best barrier material because of its low gas permeation rate.

5. The permeation equipment used in Contract DA-36-039-AMC-03197(E) can be modified to measure the permeation rate through the barriers designed for the calorimeter heat pipe systems.

SECTION IV
PERSONNEL

During the report period the following engineering personnel applied the indicated hours to the subject program in accordance with the contractual requirements. Resumes of their experience were included for your review in Technical Proposal RCA DP 6081 dated 30 April 1965.

W. B. Hall Project Engineering Leader	104.0 hours
S. W. Kessler Product Development Engineer	256.5
J. J. O'Grady Engineer	6.0
H. A. Stern Engineering Leader	1.0
J. A. Fox Engineer	69.0

SECTION V

PUBLICATIONS, LECTURES, REPORTS AND CONFERENCES

The subject report is the initial distribution of information accumulated during the program. No publications, lectures or reports were released.

One conference was held at RCA Lancaster on 12 July 1965 with the following persons present: Mr. J. Angello and Mr. S. Levy of USAEL and Messrs Block, Hall, Kessler and Polkosky of RCA. The subject matter covered the review of technical plans for the program.

SECTION VI

PROGRAM FOR NEXT REPORT PERIOD

During the next quarter, the program is as follows:

1. Construct a heat pipe demonstrating the effects of bismuth as the working
   fluid in contact with the barrier. This heat pipe will have a limited life
   pending the development of a compatible seal.

2. Start the construction of a heat pipe with a Coram barrier shrunk onto a
   columbium tube.

3. Determine the minimum radial force necessary to make a ram seal vacuum
   tight. D-43 metal bands machined to varying wall thicknesses will be used
   in the test.

4. Optimize the processing schedule necessary to fabricate barriers of
   Frenchtown body 7325.

5. Make permeation test on a Coram barrier.

SECTION VII
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2. E. M. Passmore, R. M. Spriggs and T. Vasilos, "Strength - Grain Size - Porosity Relations in Alumina," Journal of the Amer. Ceramic Soc., Vol. 48, No. 1, Jan. 21, 1965.

3. G. Y. Eastman, Summary Technical Report, Contract DA-36-039-AMC-03197(E), 30 March 1965.

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5. G. Y. Eastman, Summary Technical Report, Contract DA-36-039-AMC-03197(E), 30 March 1965.

6. Private communication with Richard Gollwitzer, Sales Engineer, Union Carbide Corp., Kemet Department.

7. Private communication with Donald H. Nathan, Sales Engineer, Getters Electronics, Inc. (SAES).

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Theoretical Heat Pipe Calculations

The graphical presentation Cotter[1] used in describing the operation of a heat pipe is reproduced in Figure 19. It shows how the driving forces or pressures in the vapor and the liquid varies along the length of the pipe. The pressure drop in the vapor is the driving force for the vapor to travel from the evaporator to the condenser where it gives up its latent heat of vaporization. The pressure drop in the liquid returns the condensed vapor to the evaporator. The equations which quantatively describes the operating parameters of a heat pipe, and their solution using bismuth as the working fluid for the 100 watt fossil fuel converter of the designs shown in Figures 2 and 3 follows.

For an isothermal process $\Delta H = T\Delta S$[1] where ΔH is the change in enthalpy and ΔS is the change in entropy at temperature T. Bismuth vapor at 1450°C is 36.9 percent diatomic with an entropy of 81.12 BTU/lb mole °R[2]. The monatomic phase has an entropy of 53.43 BTU/lb mole °R and the liquid phase and entropy of 31.10 BTU/lb mole °R, so that the heat of vaporization at 1450°C is

$$\Delta H = \frac{0.369(81.12 - 31.10) + .631(53.43 - 31.10)\quad BTU/lb\ mole\ °R \times 3133°R}{209\ lbs/mole}$$

$$\Delta H = 487\ BTU/lb \times \frac{5556}{1000}\ \frac{kcal/g}{BTU/lb} \times 1.163\ \frac{watt\text{-}hr.}{kcal}$$

$$x\ 3600\ sec/hr.\ x\ 10^{-3} = 1.14\ kwatt\text{-}sec/g \qquad (1)$$

Since the best known source[2] of data uses the English units, the conversion into c.g.s. units will be done in the sample calculations.

The quantity of bismuth which must evaporate m_v to transfer 1.063 kwatts, Q_e to the emitter is

$$m_v = \frac{Q_e}{\Delta H} = \frac{1.063\ kwatt}{1.14\ kwatt\text{-}sec/g} = 0.93\ g/sec \qquad (2)$$

FIGURE 19 DISTRIBUTION OF PRESSURES IN A HEAT PIPE

or by dividing quantity flowing by the density of bismuth vapor ρ_v at $1450°C$

$$v_v = \frac{m_v}{v} = \frac{0.93 \text{ g/sec}}{7.05 \times 10^{-4} \text{ g/cm}^3} = 1.32 \times 10^3 \text{ cm}^3/\text{sec} \qquad (3)$$

of bismuth vapor must be transferred from the boiler to the emitter.

According to Cotter the optimum value of r_v/r_w is $2/3$ where r_v is the inside radius of the wick and r_w is the inside radius of the heat pipe. Using this ratio for the heat pipe in Figure 7, $r_w = 0.95$ cm and $r_v = 0.63$ cm and the cross-sectional area, A_v, for conducting the vapor is 1.27 cm^2. Therefore, the velocity of the vapor (v_v) is

$$v_v = \frac{v_v}{A_v} = \frac{1.32 \times 10^3 \text{ cm}^3/\text{sec}}{1.27 \text{ cm}^2} = 1040 \text{ cm/sec} \qquad (4)$$

The velocity of the liquid (v_ℓ) may be calculated the same way

$$v_\ell = \frac{m_v}{0.75 \, \rho_\ell \, A_\ell} = \frac{0.93 \text{ g/sec.}}{0.75 \times 8.55 \text{ g/cm}^3 \times (0.95^2 - 0.65^2) \text{ cm}^2} \qquad (5)$$

$$v_\ell = 0.062 \text{ cm/sec.}$$

The denominator is multiplied by 0.75 assuming that $3/4$ of the wick volume is occupied by liquid metal.

The Reynolds number is important in defining the kind of vapor flow. If the Reynolds number is less than 1000 the flow will be laminar and have the maximum heat transfer efficiency. If the Reynolds number is greater than 2000 the flow will be turbulent. Between 1000 and 2000 the flow may be either laminar or turbulence or a mixture. The Reynolds number is defined as

$$R_E = \frac{\rho_v \quad r_v \quad v_v}{\eta_v} = \frac{7.05 \times 10^{-4} \text{ g/cm}^3 \times 0.63 \text{ cm} \times 1040 \text{ cm/sec}}{1.76 \times 10^{-3} \text{ poises} \times \text{g/sec cm/poises}}$$

$$R_Z = 260 \tag{6}$$

where η_v is the viscosity of the vapor.

The vapor pressure gradient of the liquid along the length of the heat pipe is defined as

$$\Delta p = \Delta p_v - \frac{\ell Q_e \sqrt{RT/2mM}}{\ell_e (\ell - \ell_e) L \, \alpha \, r_v} \tag{7}$$

where

$$\Delta p_v = - \frac{(1 - 4/\pi^2) Q_e^2}{8 \rho_v r_v^4 L^2} \tag{8}$$

or the vapor pressure gradient of the vapor

ℓ = length of the heat pipe

R = gas constant

$\dot{M}$ = molecular weight

ℓ_e = length of the evaporator

L = latent heat of evaporation and is equal to ΔH at 1450°C

α = probability of condensation

The other quantities have been defined in earlier equations.

Substituting values for bismuth in equations 7 and 8

$$\Delta p_v = - \frac{(1 - 4/\pi^2) \, 1.06^2 \text{ kwatt}^2 \times 7.5 \times 10^{-4}) \dfrac{\text{mm of Hg}}{\text{dyne/cm}^2 \times \text{g cm sec}^{-2}/\text{dyne}}}{8 \times 7.05 \times 10^{-4} \text{ g/cm}^3 \times .63^4 \text{ cm}^4 \times 1.14^2 \text{ kwatt}^2 \text{ sec}^2/\text{g}^2}$$

$$\Delta p_v = - .42 \text{ mm of Hg} \tag{8}$$

$$\Delta p = -0.42 - \frac{24.65 \times 1.063 \sqrt{\dfrac{8.3 \times 10^7 \times 1723}{2} \quad \dfrac{}{X\ 209}} \quad \times 7.5 \times 10^{-4}}{8.1(24.65 - 8.1) \times 1.14 \times 1 \times .635} = -2.89 \text{ mm Hg}$$

where the units are

$$\Delta p = \text{mm of Hg} - \frac{\text{cm kwatt} \sqrt{\dfrac{\dfrac{erg}{°K\ mol} \times °K \times \dfrac{dyne\ cm}{erg} \times g \dfrac{cm/sec^2}{dyne}}{\dfrac{g}{mol}}} \quad \dfrac{mm\ of\ Hg}{\dfrac{dyne}{cm^2} \times \dfrac{gcm/sec^2}{dyne}}}{\text{cm} \times \text{cm} \times \text{kwatt sec}/g \times \text{cm}}$$

For small changes in pressure the change in boiling point with pressure is given approximately by the Clausius-Clapeyron equation

$$\Delta T_v = \frac{R\ T^2\ \Delta p}{MLp} \tag{9}$$

where p is the vapor pressure of the bismuth. Substituting values into (9) for bismuth

$$\Delta T_v = -\frac{8.31 \times 10^7 \text{ erg}/°K \text{ mol} \times 1723^2 °K^2 \times 2.50 \quad mm\ of\ Hg \times 10^{-10} \text{ kwatt/erg/sec}}{209 \text{ g/mol} \times 1.14 \text{ kwatt-sec}/g \times mm\ of\ Hg}$$

$$\Delta T_v = .81°K$$

The optimum pore of the wick is dependent upon the operating position of the heat pipe because the capillary forces by the wick must overcome the force of gravity. The most practical terrestrial systems are, a heat pipe operating horizontal where the gravitational force is zero along the length of the pipe and a heat pipe operating vertical with the boiler beneath the condenser. In the case of a vertical heat pipe, gravity will aid the flow of liquid back to the boiler and the only requirement is the wick be saturated with liquid in the boiler. This can be calculated by letting the length of boiler equal the height a liquid with a surface tension γ will rise in a capillary radius of r_c.

$$\ell_e = \frac{2 \gamma \cos \theta}{\rho_\ell \, g \, r_c}$$ (10)

where θ is the wetting angle and assumed to be 0°, g is the acceleration of gravity and ρ_ℓ is the density of the liquid. Substituting values for bismuth in equation (10)

$$r_c = \frac{2 \times 276 \text{ dyne/cm} \times 1 \times \text{gcm/sec}^2/\text{dyne}}{8.6 \text{ cm} \times 8.55 \text{ g/cm}^3 \times 980 \text{ cm/sec}^2}$$

$$r_c = 0.0078 \text{ cm}$$

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13. ABSTRACT

The subject contract was initiated 1 July 1965 to develop the most efficient method of coupling a simulated thermionic converter to a heat pipe. The heat pipe incorporates a gas barrier and is used to conduct the heat from a fossil fuel burner to the simulated converter. A theoretical analysis of the operation of the heat pipe will be made and confirmed experimentally.

During this first report period, progress was made on the following pertinent tasks: Potential working fluids were evaluated; Structural materials and fabrication techniques were investigated; Barrier materials were evaluated; Permeation tests were started using the most promising barrier materials; and A theoretical analysis of getter materials to eliminate unwanted contaminants has been started.

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KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Heat Pipe						
Gas Permeation-Alumina						
Thermionic Converters						
High Temperature Ceramics						
Bismuth						
Metal-to-Ceramic Seals						
Fossil-Fueled Thermionic Converters						

INSTRUCTIONS