MARCH 1965

RESEARCH STUDIES ON THERMIONIC CONVERTERS, EMITTER SHELL PHASE

REPORT NUMBER 5

FINAL REPORT

1 JULY 1963 THROUGH 28 FEBRUARY 1965

CONTRACT NO. DA-36-039-AMC-03197 (E)
DA TASK NO. 1G6-22001-A-055-02

PREPARED FOR:

U.S. ARMY ELECTRONICS COMMAND
FORT MONMOUTH, NEW JERSEY

PREPARED BY:

RADIO CORPORATION OF AMERICA
ELECTRONIC COMPONENTS AND DEVICES
DIRECT ENERGY CONVERSION DEPARTMENT
LANCASTER, PENNSYLVANIA

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March 1965

RESEARCH STUDIES ON THERMIONIC CONVERTERS, EMITTER SHELL PHASE

Report Number 5

Final Report
1 July 1963 through 28 February 1965

Program Objective: The development of an emitter shell that will permit the operation of a fossil-fuel-heated thermionic converter at temperatures as high as 1400° Centigrade with an attendant improvement in performance.

Contract DA-36-039-AMC-03197(E)

In Accordance With

Technical Guidelines 11 December 1963
DA Task No. 1G6-22001-A-055-02

Author: G. Y. Eastman

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RESEARCH STUDIES ON THERMIONIC CONVERTERS, EMITTER SHELL PHASE

SECTION I

PURPOSE

The principal objective of the program under the subject contract was to evaluate materials for use as a protective shell around the emitter of a thermionic energy converter to be heated by a fossil fuel. For this application an unusual number of material properties are important, but the two most significant are impermeability to the gas products of fuel combustion, and resistance to corrosion by gaseous vapors from the burner.

The program consisted of:(1) a materials investigation, including a comprehensive literature search; (2) materials selection; (3) preliminary evaluation of test samples heated to temperatures in excess of 1400° Centigrade; (4) design, development, and fabrication of a fossil-fuel-heated converter incorporating a shell of the material selected; (5) performance evaluation of the converter; and (6) life testing of the converter at an emitter temperature of 1400° Centigrade for a period of 1,000 hours.

In November 1964, the contract was extended to include further permeation testing of three promising barier materials and the fabrication and testing of a converter having a palladium thimble for the venting of hydrogen gas.

30 March 1965

SECTION II

ABSTRACT

The objective of the program was the development of a barrier shell to protect thermionic energy converters from the combustion products of a fossil fuel flame. Two material properties are of prime importance; impermeability, and corrosion resistance.

A literature survey was performed to select promising materials from the standpoint of properties, availability, and fabrication potential. Three types of materials were selected for extensive testing; alumina, beryllia and silicon carbide

Equipment of very high sensitivity (10^{-12} liter torr/cm^2 second) was developed which permitted the determination of gas permeation rates. The identification of individual gases was made possible by the latest mass spectrometer equipment.

It was determined that high purity alumina has the lowest permeation rate, the highest material strength, good thermal shock resistance and is resistant to corrosion. Beryllium oxide had a poor corrosion resistance and a high permeation rate for carbon monoxide. The pyrolytic silicon carbide samples obtained for this program evidenced high permeation rates for carbon monoxide and showed a tendency toward unpredictable fracture after extended periods at elevated temperatures.

Converters were fabricated which operated at power levels up to 33 watts. One converter delivered useful output power for more than 1000 hours through seven complete thermal cycles and 56 short, abrupt interruptions of the burner operation.

This program has demonstrated the feasibility of long reliable thermionic energy converter operation from a fossil fuel flame.

SECTION III

PUBLICATIONS, LECTURES, REPORTS, AND CONFERENCES

A. Lectures and Publications

A technical paper entitled "Emitter-Shell Materials for Fossil-Fuel-Heated Thermionic Converters" was presented at the 18th Annual Power Sources Conference 21 May 1964 and subsequently published in the proceedings of the conference. The paper described the progress of work on this contract at the time of presentation.

A second such paper is scheduled for presentation at the 19th Annual Power Sources Conference in May, 1965. The subject matter will contain a description of work carried out during the latter portions of the contractual effort.

B. Reports

The First Quarterly Report dated 15 October 1963 for the subject contract was distributed in accordance with instructions of Mr. J. E. Creedon, USAEL.

The Second Quarterly Report dated 15 January 1964 for the subject contract was distributed in accordance with instructions of Mr. J. E. Creedon, USAEL.

The Third Quarterly Report, dated 15 April 1964, for the subject contract was distributed in accordance with the instructions of Mr. S. Levy, USAEL.

The Fourth Quarterly Report, dated 15 December 1964 for the subject contract, was distributed in accordance with the instructions of Mr. J. E. Creedon, USAEL.

C. Conferences

Eleven conferences were held during the contractual period.

1. On 10 July 1963, G. Y. Eastman, J. J. Polkosky, and H. A. Stern, of RCA, reviewed the proposed work program with J. E. Creedon, USAEL, Fort Monmouth, New Jersey. The principal areas of discussion included the experimental method for permeation measurement as well as possible converter geometries. It was agreed that the collection chamber approach would be adopted for the permeation measurements in order to achieve the highest possible sensitivity. A mass spectrometer would not be employed because of its outgassing contribution to the system and consequent limiting of the system sensitivity. Secondly, it was agreed that the converter geometry should be chosen so as to accommodate most satisfactorily the materials selected as the permeation barrier. Both single-ended cup and double-ended cylindrical designs were discussed.

2. On 11 September 1963, the following USAEL representatives conferred with RCA personnel at the Lancaster Plant: J. Angello, S. Levy, J. E. Creedon, and H. Guetzlaff. The status of thermionic energy converter work at RCA was reviewed, information was exchanged on the general level of development in the field of fossil-fueled converters, and the ultra-high vacuum permeation measuring equipment developed by RCA was demonstrated.

3. On 4 November 1963, G. Y. Eastman, J. J. Polkosky, J. A. Fox, and P. D. Strubhar of RCA met with S. Schneider, S. Levy, J. E.

Creedon, and J. Angello of USAEL at Fort Monmouth, New Jersey. The latest RCA progress in thermionic converter development was reviewed along with the status of the work program of the subject contract. The initial operation of the permeation measuring equipment was described, including an estimate of ultimate detection sensitivity. The calibration measurement of hydrogen permeation through molybdenum was described along with the initial permeation runs for the high alumina samples.

4. On 20 December 1963, a status review meeting was held at the Lancaster RCA Plant. In attendance were: J. Angello and S. Levy for USAEL and P. D. Strubhar, J. A. Fox, J. L. Rhoads, H. A. Stern, G. Y. Eastman, and J. J. Polkosky for RCA. The progress of the technical work program was reviewed. Delays due to supplier's inabilities to meet delivery schedules for the high density alumina and pyrolytic silicon carbide materials were noted. The feeling was expressed that through acceleration of the remaining portions of the program, it may be possible to absorb these delays. The hydrogen permeation measurements on the sintered and high density alumina samples and the beryllia sample were presented. The difficulties experienced in obtaining a reliable vacuum seal to the pyrolytic silicon carbide samples were discussed, including the apparent relationship of these difficulties to the structure of the material. The design of the proposed thermionic converter test vehicle was presented and discussed, including the use of sintered alumina as the emitter shell material in the initial version. The fabrication of the converter now will aid the desired acceleration of the program by permitting early evaluation of the basic converter geometry and construction procedures. The design allows

substitution of the optimum barrier material when the selection is made following the completion of the permeation measurement phase of the program.

5. On 24 February 1964, G. Y. Eastman, J. J. Polkosky, J. A. Fox, and J. L. Rhoads of RCA met with S. Schneider, S. Levy, J. E. Creedon, and J. Angello of USAEL at Fort Monmouth, New Jersey. The status of the technical work program was reviewed. The permeation measurements of helium, argon, nitrogen, and fossil fuel combustion gases on SC98D alumina were presented. The hydrogen permeation measurements on beryllia were reviewed. The toxicity problems of beryllia were discussed. Delays in the program due to suppliers' inabilities to meet delivery schedules were noted, and a possible extension in the time of the contract was discussed.

6. On 21 April 1964 a status review meeting was held at the RCA-Lancaster Plant. In attendance were J. Angello, J. E. Creedon, and S. Levy for USAEL and F. G. Block, J. A. Fox, J. J. Polkosky, J. L. Rhoads, M. N. Slater, and G. Y. Eastman for RCA. The progress of the technical work program was reviewed. Delays in the fabrication and delivery of materials and components were noted, and the request for a two-month extension of the contract was discussed. Results of the completed permeation studies on alumina, beryllia, and silicon carbide were presented with the conclusion that alumina is the best barrier material. The apparent selectivity of the permeation process was discussed. Thermionic converter test vehicle designs were reviewed, including the recent double-wall cup modification. Electrical and physical test results were presented, and proposed design and construction modifica-

tions were discussed.

7. On 27 May 1964 a contractor's meeting to discuss the status of emitter shell development was held at USAEL, Fort Monmouth, New Jersey. Those present were J. E. Creedon, S. Levy, S. Schneider, and M. H. Zinn of the Electron Tube Division, Electronic Components Department, USAEL; J. P. Angello, G. Hunrath, Dr. Kittl, and D. Linden of the Power Sources Division, Electronic Components Department, USAEL; J. E. Teti and G. C. Uchrin of the Electronic Components Department, USAEL; B. B. Rosenbaum of the Bureau of Ships; A. B. Neild and C. F. Krolick of the USN Engineering Experimental Laboratory; H. N. Hatsopoulos, S. Kitrilakis, F. Lyczko, and P. G. Pantazelos of Thermo Electron Engineering Corporation (TEECO); W. R. Clendenning of Texas Instruments (TI); and G. Y. Eastman, J. A. Fox, J. J. Polkosky, M. N. Slater, and H. A. Stern of RCA.

The results of the complete RCA gas permeation study of alumina, beryllia, and silicon carbide were presented with the conclusion that alumina was the best barrier material studied. Some disagreement in theoretical approach by TI, which had studied only silicon carbide, was apparently resolved when it was shown that the numerical results obtained were essentially similar.

Results of efforts to incorporate the emitter shell material into an operating converter were also discussed. Over 400 hours of power-producing life plus an additional 200 hours in-flame without apparent shell deterioration were reported by RCA on a double-wall converter with an alumina barrier. TEECO reported 255 hours of constant output life on a converter with a silicon carbide barrier.

Results of calculations were presented by USAEL which showed that permeation data from various sources were in substantial agreement and confirmed the data reported by RCA.

8. On 26 June 1964 J. E. Creedon and S. Levy of USAEL met with F. G. Block, G. Y. Eastman, J. J. Polkosky, and M. N. Slater of RCA at the RCA-Lancaster Plant. Processing and life test results on nine fossil-fuel thermionic converters were discussed with an analysis of failure modes. Planned design modifications were presented. Data from the successfully completed thermal shock tests were offered, and a demonstration of a thermal shock test was made on a randomly selected converter.

9. A meeting was held 18 September 1964 at Fort Monmouth, New Jersey. Those present were S. Schneider, J. E. Creedon, S. Levy, Lt. D. McMaster, Dr. E. Kittl, and J. P. Angello of USAEL and F. G. Block, H. A. Stern, J. J. Polkosky, and G. Y. Eastman of RCA. The progress of the work grogram, including the fabrication problems and first life test results was reviewed. Design improvements on the collector cooling course and emitter "heat dam" area were discussed in detail. Also reviewed were the industry's views concerning the use of both alumina and pyrolytic silicon carbide permeation barriers, and the relative progress in this area.

10. On 21 December 1964, a meeting was held at the RCA-Lancaster Plant. Present were Mr. S. Levy and Mr. J. E. Creedon of USAEL. RCA was represented by J. A. Fox, H. A. Stern, J. J. Polkosky, F. G. Block and G. Y. Eastman. The results of the 1000 hour and 200 hour converter life tests were discussed along

with a review of the thermal shock and corrosion data obtained to date. The first portions of the analysis of the 200 hour life test converter were presented. Permeation data on Frenchtown alumina and Texas Instruments' silicon carbide were reviewed. The failure mechanism of the silicon carbide sample was discussed. Difficulties in obtaining a second silicon carbide sample of the Battelle Memorial Institute-Thermo Electron Engineering Corp style were also discussed.

11. The eleventh meeting of the contract was held at Fort Monmouth on 5 March 1965. Present were S. Schneider, J. E. Creedon, S. Levy and J. P. Angello of USAEL and H. A. Stern, J. A. Fox, J. J. Polkosky and G. Y. Eastman of RCA. Delivery was made at this time of two converters representative of work under the contract and three copies of drawings for the parts and assemblies of the converters, in accordance with contractual requirements. The status of the contract work was reviewed, including the results of physical analysis of the 200 hour life test converter, the operation of the converter having a palladium thimble, and the assembly and test the converters. Also discussed were the data on outgassing, premeation and corrosion collected during the permeation testing of the Frenchtown alumina, Coors Beryllia and Texas Instrument pyrolytic silicon carbide samples. The extensive, but unsuccessful efforts to obtain a tungsten-pyrolytic silicon carbide emitter shell of the type manufactured by Battelle Memorial Institute for Thermo Electron Engineering Corp were also described in detail. It was pointed out by the RCA personnel that the delivery of this part was approximately two months overdue, with little chance of delivery before April 1, 1965. The delay made it impossible for reasons of equipment and personnel availability to include this sample in the work program of the subject contract.

SECTION IV
FACTUAL DATA

A. Literature Survey

The eventual development of an operable fossil-fuel-heated thermionic energy converter is largely dependent on a successful search for a functional barrier material to protect the emitter of the converter. The material must be vacuum tight, impermeable, and oxidation resistant in the 1400° to 1600° Centigrade range. In actual operation, the emitter portion of the converter will be placed in the flame of a fossil-fuel (gasoline, methane, propane, etc.) burning in air and will be heated to 1400° Centigrade. The refractory barrier-layer must be impervious to the initial fuel mixture and the gas products of the fossil-fuel flame (hydrogen, carbon monoxide, carbon dioxide, water vapor, oxygen, and nitrogen), and must be chemically and physically resistant to attack by any of the gas vapors or condensible liquids from the burner. The converter was required to have an operational life of 1000 hours.

Little published work was found on the permeation characteristics of refractory materials. Concern for the problem with regard to electron tube envelopes led Turnbull, Collins, and Kirkpatrick[1] to study the permeation characteristics of both metals and ceramics. The gases used in the investigation are common in a fossil fuel flame. Hydrogen permeation of the metals studied was found to be rapid even at temperatures approaching room ambient. No permeation of the metals by the other gases studied was found at 750° Centigrade. The ceramic materials, alumina and forsterite, were found to be impermeable to all of the gases at a temperature of 750° Centigrade.

Continuing this work, Conklin and Turnbull[2] studied the permeation of materials suitable for thermionic energy converter construction. A mass spectrometer was used to make measurements of the rates of fossil-fuel gas permeation through several metals, with and without protective coatings, and one ceramic. These tests showed no detectable permeation of high alumina ceramic by any gas at temperatures up to 1600° Centigrade. All other materials tested showed catastrophic hydrogen permeation rates throughout the desired temperature range. The rates were in general agreement with those measured by Smithells and Ransley.[3] Hayes, Budworth, and Roberts[4] investigated the permeability of dense sintered alumina materials with respect to oxygen, nitrogen, and argon at temperatures in the region of 1700° Centigrade. They reported that the alumina materials showed no permeation of oxygen or nitrogen below 1500° Centigrade. Above 1500° Centigrade an appreciable and reproducible permeation of oxygen was found, smaller and unreproducible permeation of nitrogen was noted, and no permeation of argon was detected. In continuing their work Hayes, et al.[5] reported that two of the three aluminas tested exhibited only oxygen permeation at 1500° to 1750° Centigrade, while under identical conditions the third alumina was permeable to both oxygen and nitrogen.

The General Electric Company supplied permeation information on its high density Lucalox ceramic. In its laboratories, General Electric determined that this high density alumina is impermeable to oxygen and nitrogen to 1600° Centigrade. J. P. Roberts has verbally reported that Lucalox is impermeable to helium, argon, nitrogen, and iodine up to 1600° Centigrade. He has measured oxygen permeation at 1630° to 1650° Centigrade.

Cunningham, Pfeifer, Carmichael, and Hodge[6] have measured diffusion of oxygen through the aluminum oxide coating used on uranium dioxide microspheres at temperatures lower than 1500° Centigrade. Lower diffusion rates have been reported verbally for beryllium oxide under similar conditions. While this work is not directly related to the present application, it does show that oxygen transfer is possible through certain refractory oxides under selected conditions.

Reports were privately received from two sources concerning the permeation of pyrolytic silicon carbide by gases of interest. In one case no permeation of hydrogen was detected to the limit of the spectrometer sensitivity (5 x 10^{-9} liter torr per cm^2 second) in the 1200 to 1500° Centigrade range. In the second case, a vacuum of 10^{-8} torr was maintained inside a silicon carbide vessel heated for several hundred hours to 1400° Centigrade in a fossil-fuel flame. In a third similar case, low permeation rates have been reported verbally for a composite barrier consisting of silicon carbide pyrolytically deposited over a molybdenum disilicide coated molybdenum member. Undocumented verbal reports of low permeation rates for pyrolytic graphite have also been received.

No other applicable permeation measurements were found after extensive literature searches and contact with a large number of suppliers, users, and independent authorities in the refractory materials field. It is evident from the limited information available that the most promising results are to be obtained in the area of the nonmetals. However, no definitive analytical treatment of permeation of nonmetals by gases at high temperatures is known to exist. This no doubt is due to the newness of the problem and the lack of reliable data.

It was felt than an attempt to develop such an analysis was beyond the scope of the present program. Lacking an analytical treatment that is based on other known or measurable properties, it is impossible to establish valid criteria by which materials can be judged for the probability or extent of permeation. The search was continued, however, in an effort to find other materials which are available in useful shapes and whose known properties make them appear attractive from the viewpoints of heat transfer, corrosion resistance, thermal shock resistance, vacuum integrity at room temperature, etc.

The results of the survey are presented in Table I. Most of these data were obtained from published literature of refractory ceramics.[7, 8, 9] The remainder were extracted from information provided by numerous suppliers. In some cases conflicting data were found for the properties being considered. As a result, several values for some properties are listed in Table I.

The following materials were considered to have potential use for this application: alumina, beryllia, thoria, zirconia, pyrolytic silicon carbide, silicon nitride, boron nitride, zirconium diboride, titanium boride, molybdenum disilcide, tungsten disilicide, tantalum beryllide, and pyrolytic graphite. Suppliers specializing in each of the above materials were contacted, and known properties, commercial availability, and present uses of each material were discussed. From the information compiled, it was evident that alumina, beryllia, and pyrolytic silicon carbide were the only three materials having the full range of properties required by the barrier, that are commercially available, can be made into vacuum-tight components, and show some promise of being impermeable. Commercial sintered silicon carbide is not vacuum-tight. Thoria and zirconia are weak and have poor

MATERIAL	Sources of Info.*	PERMEATION	CORROSION	SHOCK RESISTANCE	VAPOR PRESSURE	THERMAL CONDUCTIVITY (Watts/CM/°C/CM)	MODULUS OF RUPTURE (1000 PSI)	CK TANC
ALUMINA	1, 2, 3, 4, 5, 6, 7, 8	Good to at least 1350°C	Good to 1800°C	Good	1.2×10^{-2} mm at 2327°C (2600°K)	.30 @ 100°C .06 @ 1000°C	34 @ 20°C 24 @ 1000°C	od
BERYLLIA	1, 2, 3, 4, 5, 9, 10	Diffusion of oxygen reported equal to alumina. Permeation anticipated to be equal to or better than alumina.	Good in O_2, N, H, He, CO to 1700°C No good in H_2O vapor	Excellent @ low temp.	2.95×10^{-3} mm at 1950°C (2223°K)	2.1 @ 100°C .19 @ 1000°C	30 @ 20°C 25 @ 1000°C	ellent ow te
THORIA	1, 2, 3, 5	No data available	Unstable in carbonaceous atmosphere at high temperature	Poor	3.7×10^{-6} mm at 1777°C (2050°K)	.09 @ 100°C .03 @ 1000°C	15 @ 20°C 15 @ 1000°C	or
ZIRCONIA	1, 2, 3, 5, 11	No data available	Same as Thoria	Fair		.22 @ 20°C .02 @ 20°C .02 @ 1000°C	20 @ 20°C 15 @ 1000°C	ir
SILICON CARBIDE PYROLYTIC	1, 2, 12 13, 14, 15, 16, 17	Reported impermeable to 1400°C	Good in air to 1400-1500°C. In neutral, reducing, or vacuum to 2000°C	Excellent		.54 @ 100°C .21 @ 1000°C .92 @ 1000°C .14 @ 1500°C .16 to .4 no temp.	50 @ 20°C 64 @ 1400°C 24 @ 25°C 25 @ 1200°C 18 @ 1500°C	ellent
SILICON NITRIDE	1, 2, 18	No data available	Good in neutral and reducing ATM. to 1650°C Good in air to 1200°C (1 source to 1500°C)	Good		.15 - no temp.	16 - 20 over Range 25 to 1200°C	od
BORON NITRIDE	1, 4, 19, 20, 21	No data available	Hydrolizes Good neutral ATM. to 1650°C Good in O_2 to 1000°C	Good (Anisotripic)		.28 ⊥ to grain .15 ∥ to grain .16 to .28 @ 100°C .12 to .24 @ 1000°C	16 NITH Grain 7.3 ⊥ to Grain	od tripic
ZIRCONIUM DIBORIDE	1, 2	No data available	Good in O_2 to 1300°C	Fair to good		.23 @ 200°C	29 @ 20°C	to good
TITANIUM BORIDE	1, 2	No data available	Good in O_2 to 1400°C	Fair to good		.26 @ 200°C	19 @ 20°C	to good
MOLY DISILICIDE	1, 2, 4, 22	Permeable when evaluated as a coating over molybdenum.	Good neutral and reducing ATM. at high temp. Good in air to 1500°C - poor in air below 900°C.	Good		.31 @ 100°C .126 @ 1000°C .31 @ 100°C .14 @ 1200°C	50 @ 20°C 13 @ 1500°C	od
TUNGSTEN DISILICIDE	2, 4, 22	No data available	Max. temp. of resistance to oxidation for short time use. 5 hrs. 1760°C 10 hrs. 1650°C	Good		.32 @ 600°C .31 @ 1425°C	57.5 @ 1260°C 70 @ 1370°C 51 @ 1510°C	d
TANTALUM BERYLLIDE	2, 22, 23	No data available	Resistant to oxidation at temperatures ranging from 1480°-1600°C	Good		.30 @ 760°C .34 @ 1480°C	30 @ 20°C 40 @ 870°C 78 @ 1260°C 56 @ 1370°C 35 @ 1510°C	d
PYROLYTIC GRAPHITE	1, 24, 25, 26, 27, 28	Reported impermeable to 1400°C	Oxidation resistance Poor above 650°C. Poor resistance to cesium vapor.	Good	10^{-8} mm at 1677°C (1950°K)	3.72 ∥ to grain .019 ⊥ to grain 1.75 ∥ to grain @ 1000°C .012 ⊥ to grain @ 1000°C	Loaded ∥ to Basal Plane 7 @ 21°C 13 @ 600°C Loaded ⊥ to Basal plane 13 @ 21°C 12.5 @ 600°C	d

*Sources identified in Table I Notes

A

OCK TANCE	VAPOR PRESSURE	THERMAL CONDUCTIVITY (Watts/CM/°C/CM)	MODULUS OF RUPTURE (1000 PSI)	THERMAL EXPANSION (IN/IN/°C x 10^{-6})	ELECTRICAL RESISTIVITY (ohms/CM)	HARDNESS KNOOP (100 gm)	COMMENTS
d	1.2×10^{-2} mm at 2327°C (2600°K)	.30 @ 100°C .06 @ 1000°C	34 @ 20°C 24 @ 1000°C	8.5 @ 800°C	$> 10^{14}$ @ 20°C 10^{8} @ 1000°C	2260	Good
ellent ow temp.	2.95×10^{-3} mm at 1950°C (2223°K)	2.1 @ 100°C .19 @ 1000°C	30 @ 20°C 25 @ 1000°C	9.4 @ 1400°C	$> 10^{14}$ @ 20°C 5×10^{7} @ 1000°C	9 (MOHS)	Good Except Toxic in Water Vapor
r	3.7×10^{-6} mm at 1777°C (2050°K)	.09 @ 100°C .03 @ 1000°C	15 @ 20°C 15 @ 1000°C	9.0 @ 1000°C 9.55 @ 1400°C	$> 10^{14}$ @ 20°C 10^{5} @ 1000°C	640 (500 g)	Strength & Shock Resistance too low
r		.22 @ 20°C .02 @ 20°C .02 @ 1000°C	20 @ 20°C 15 @ 1000°C	5.6 @ 1200°C	10^{8} @ 20°C 500 @ 1000°C	7 (MOHS)	Strength & Shock Resistance too low
ellent		.54 @ 100°C .21 @ 1000°C .92 @ 1000°C .14 @ 1500°C .16 to .4 no temp.	50 @ 20°C 64 @ 1400°C 24 @ 25°C 25 @ 1200°C 18 @ 1500°C	4.0 @ 1000°C 4.8 @ 1000°C	10^{-3} to 10^{-1} 10 @ 20°C 4 @ 1000°C 2×10^{-4} @ 20°C 7.9×10^{-3} @ 1100°C	2740	Good
d		.15 - no temp.	16 - 20 over Range 25 to 1200°C	2.5 @ 1000°C 3.0 @ 1000°C	No Data Available	9 (MOHS)	Requires Oxidation Protection Can not be purchased in vacuum tight components.
d tripic)		.28 ⊥ to grain .15 ∥ to grain .16 to .28 @ 100°C .12 to .24 @ 1000°C	16 NITH Grain 7.3 ⊥ to Grain	.77 ⊥ to Grain @ 1000°C 7.51 ∥ to Grain @ 1000°C	10^{10} @ 20°C 10^{4} @ 1000°C	230	Anisotropic - not useful unless Pyrolytic Form has better corrosion resistance No known sealing methods
o good		.23 @ 200°C	29 @ 20°C	7.5 @ 1350°C	$9\text{-}16 \times 10^{-6}$	2300	Requires Oxidation Protection Not commercially available in shapes
o good		.26 @ 200°C	19 @ 20°C	6.4 @ 1350°C	15.3×10^{-6}	3370	Requires Oxidation Protection Not commercially available in shapes
d		.31 @ 100°C .126 @ 1000°C .31 @ 100°C .14 @ 1200°C	50 @ 20°C 13 @ 1500°C	8.9 @ 1425°C 9.2 @ 1000°C	$75\text{-}80 \times 10^{-6}$ @ 1500°C 22×10^{-6} @ 20°C	1260	Useful as coating for oxidation protection. Not commercially available in shapes
d		.32 @ 600°C .31 @ 1425°C	57.5 @ 1260°C 70 @ 1370°C 51 @ 1510°C	8.5 @ 1510°C		1100	Not commercially available in shapes
d		.30 @ 760°C .34 @ 1480°C	30 @ 20°C 40 @ 870°C 78 @ 1260°C 56 @ 1370°C 35 @ 1510°C	15.2 @ 1510°C	43.5×10^{-6} @ 20°C 111.1×10^{-6} @ 650°C 138.5×10^{-6} @ 1260°C	1120 Vickers (2.5KG)	Requires oxidation Protection
d	10^{-8} mm at 1677°C (1950°K)	3.72 ∥ to grain .019 ⊥ to grain 1.75 ∥ to grain @ 1000°C .012 ⊥ to grain @ 1000°C	Loaded ∥ to Basal Plane 7 @ 21°C 13 @ 600°C Loaded ⊥ to Basal plane 13 @ 21°C 12.5 @ 600°C	2.9 @ 21°C 1.8 ∥ to grain @ 1000°C 39.6 ⊥ to grain @ 1000°C	5×10^{-4} ∥ to grain 4×10^{-1} ⊥ to grain	28 ∥ to grain 91 ⊥ to grain	Anisotropic requires Oxidation and Corrosion Protection

B

TABLE I NOTES

1. W. D. Kingery, "Property Measurements at High Temperatures", Chapter 2 - Laboratory Refractories, John Wiley & Sons, New York, 1959.
2. J. E. Hauck, "Guide to Refractory Ceramics", Materials in Design Engineering, Vol. 58, No. 1, 1963.
3. W. H. Kohl, "Materials and Techniques for Electron Tubes", Chapter 2 - Ceramics, Reinhold Publishing Corporation, New York, 1960.
4. J. D. Latva, "Selection and Fabrication of Nonmetallics - Oxides, Beryllides, and Silicides", Metal Progress, November 1962.
5. "Technical Data Sheets - Oxide Ceramics", National Beryllia Corporation, Haskell, New Jersey.
6. "Mechanical and Electrical Properties of Alsimag Ceramics", American Lava Corporation, Chattanooga, Tennessee.
7. "Technical Data Sheets - Oxide Ceramics", Frenchtown Porcelain Company, Frenchtown, New Jersey.
8. "Technical Data Sheet - Lucalox Ceramic", General Electric Company, Nela Park, Cleveland, Ohio.
9. "Technical Data Sheet - Beryllia Ceramics", Coors Porcelain Company, Golden, Colorado.
10. "Technical Data Sheets - Beryllia Ceramics", Brush Beryllium Company, Cleveland, Ohio.
11. "Technical Data Sheets - Zirconium Oxide", Zirconium Corporation of America, Cleveland, Ohio.

12. R. W. Brown, "High-Temperature Nonmetallics", Chemical Engineering, 21 April 1958.

13. "Technical Data Sheets - Silicon Carbide Coatings", Texas Instruments Incorporated, Dallas, Texas.

14. "Technical Data Sheets - Pyrolytic Carbides", High Temperature Materials, Incorporated, Boston, Massachusetts.

15. "Technical Data Sheets - Silicon Carbide", Carborundum Company, Niagara Falls, New York.

16. E. G. Kendall, "High-Temperature Demands Turn Attention to Refractory Carbides", Ceramic News, July 1963.

17. "Technical Data Sheets - Silicon Carbide", Norton Company, Worcester, Massachusetts.

18. "Technical Data Sheets - Silicon Nitride", Union Carbide Stellite Company, Kokomo, Indiana.

19. "Technical Data Sheets - Boron Nitride", Carborundum Company, Latrobe, Pennsylvania.

20. "Technical Data Sheets - Boron Nitride", National Carbon Company, New York, New York.

21. "Technical Data Sheets - Pyrolytic Boron Nitride", High Temperature Materials, Incorporated, Boston, Massachusetts.

22. WADD Technical Report TR 60-889, Parts 1 and 2.

23. "Technical Data Sheets - Beryllides", Brush Beryllium Company, Cleveland, Ohio.

24. M. W. Riley, "Carbon and Graphite", Materials in Design Engineering, Vol. 56, No. 3, 1962.

25. "Technical Data Sheets - Pyrolytic Graphite", High Temperature Materials, Incorporated, Boston, Massachusetts.

26. "Technical Data Sheets - Graphite", Great Lakes Carbon Corporation, New York, New York.

27. "Technical Data Sheets - Carbon-Graphite Mechanical Materials", National Carbon Company, New York, New York.

28. "Technical Data Sheets - Carbon-Graphite", Stackpole Carbon Company, St. Marys, Pennsylvania.

thermal shock resistance. Silicon nitride was available commercially but it could not be fabricated into vacuum-tight components. Boron nitride has poor corrosion resistance, it hydrolizes, and there are as yet no known joining techniques by which it could be made a part of a vacuum envelope.

Zirconium diboride, titanium boride, and tungsten disilicide were not commercially available in the shapes required at the time of the survey. Molybdenum disilicide was available in coating form only, and previous work has shown that molybdenum disilicide coating over molybdenum is permeable,perhaps due to micro-cracks. Its use would therefore be restricted to that of a corrosion resistant coating. Tungsten disilicide was considered to be similar. Tantalum beryllide is available but will not meet the temperature requirements of this application. Pyrolytic graphite, while possibly impermeable, is subject to corrosion by both the external gases and the cesium contained in the converter. It would have to be protected from both. The anisotropic properties of pyrolytic graphite make the development of a reliable protective coating unlikely. In addition, the thermal conductivity in the desired direction is relatively low while the conductivity down the length of a deposited cylinder or cup is undesirably high.

Nickel aluminide was also considered on the basis of its ability to protect molybdenum against oxidation; however, because of its metallic structure it is felt that it would not be impermeable to hydrogen.

As noted briefly above, the effort was limited by two important factors. The first was the lack of a thorough, qualitative expression for the several processes which comprise permeation: adsorption, dissociation, solution, diffusion, recombination, and desorption. This situation was complicated by, if not the result of, a general shortage of high-temperature data on which to base such a theory or analysis. Second, a number of potentially promising materials were not available in useful shapes at the time, although rapid progress was being made in this area. This shortage of fabrication skills limits not only the scope of the present search for a permeation barrier but the development of an expression on which prediction of performance could be made in the future.

B. Permeation Investigation

1. Experimental Method

Experimental permeation systems generally belong to two categories:

(1) Systems employing a mass spectrometer to measure increases in partial pressures of permeating gases.

(2) Collection chambers where increases in total pressure are related to permeation rates.

Conklin and Turnbull[2] in earlier work at RCA, using the first method, studied the permeation rates of various gases through several materials. In their investigation of the permeation of gases through Al_2O_3, however, the sensitivity of the mass spectrometer was not sufficient to give quantitative data, but did supply an upper limit for permeation rates. Dr. Turnbull suggested that to improve the sensitivity for the current study the mass spectrometer technique should be abandoned in favor of the collection chamber technique. With this approach and by working in the ultra-high vacuum range, the sensitivity of the study would be improved by several orders of magnitude. Recent advances in equipment and technology have made this approach feasible. Such a system was designed, constructed, and successfully tested. The mathematics of the collection chamber approach follow the equation:

$$\text{Permeation rate} = \frac{V}{A} \frac{dP_c(t)}{dt} \tag{1}$$

where V is the volume of the chamber (liters); A is the heated surface area of the sample (cm^2); and $\frac{dP_c(t)}{dt}$ is the time rate of pressure rise in the chamber because of permeation (torr/sec). This yields a permeation rate with the units $\frac{\text{liter torr}}{\text{cm}^2 \text{ sec}}$, which are familiar and useful to vacuum engineers.

The consideration of wall thickness involves an assumption of a mechanism which is not fully established; therefore, this parameter was eliminated from the equation by using a wall thickness which closely simulates conditions in converter operation.

This definition of the measured permeation rate assumes negligible pumping effects of the pressure-measuring Bayard-Alpert type ion gauges in the system. In practice this effect cannot be overlooked and a more general definition was derived which, in the special case of no gauge pumping, reduces to the previous definition.

$$K = \frac{1}{A} \frac{dQ(t)}{dt} \tag{2}$$

$$Q(t) = P(t)V(t) \tag{3}$$

$$\frac{dQ}{dt} = \frac{PdV}{dt} + \frac{VdP}{dt} \tag{4}$$

The term $\frac{dV}{dt}$ is the pumping speed S of the ion gauge. This leads to

$$K = \frac{PS}{A} + \frac{V}{A}\frac{dP}{dt} \qquad (5)$$

When S is zero, this expression reduces to the previous definition. However, from the general relationship, a second equation is possible:

$$K = \frac{PS}{A} \qquad (6)$$

when $\frac{dP}{dt}$ equals zero. This proved to be the most applicable equation for this experiment.

In order to evaluate the pumping speed of the gauge(s), a relationship was established to determine this quantity from experimental data. The mathematical formulation is as follows:

$$S = \frac{V}{(P_u - P)}\frac{dP}{dt} \qquad (7)\ \text{(Ref. 10)}$$

S = pumping speed of gauge (liter/sec)

V = volume of system (liters)

P = P(t) is pressure in system (torr)

P_u = the ultimate, or equilibrium, pressure of the system (torr)

$$\frac{dP}{dt} + \frac{S_P}{V} = \frac{S_{P_u}}{V} \qquad (8)$$

The solution of this differential equation is of the form,

$$P = Me^{-(S/V)t} + P_u \qquad (9)$$

and allowing $P = P_o$; when $t = 0$; the solution becomes

$$P = (P_o - P_u)e^{-(S/V)t} + P_u \tag{10}$$

Solving for S explicitly yields

$$S = -\frac{V \ln \frac{P - P_o}{P_o - P_u}}{t} \tag{11}$$

Bayard-Alpert ion gauge pumping speeds obtained from the literature[11] were independently checked and confirmed for:

Gas	Pumping speed
H_2	1×10^{-2} liters/sec
He	3×10^{-3} liters/sec
A	3×10^{-2} liters/sec
N_2	2×10^{-1} liters/sec

2. Permeation Measurement System

a. Vacuum Equipment

The concept of the system is straightforward. A sample tubing, closed at one end, is connected to a vacuum pumping system by means of a gold-seal fitting. Incorporated into this pumping system are three bakeable, ultra-high vacuum valves which divide the manifold into two separate chambers, each with an ionization gauge attached. The upper chamber is the collection chamber; the second cavity will serve as a control, and is included to monitor outgassing rate and ensure that the valve isolating the collection system is not leaking. Surrounding the sample is a second vacuum system capable of achieving a pressure in the high-vacuum range. After this system is evacuated it is back-filled with the test gas. By means of an electrical heating element, the sample is then heated to the desired temperature. Monitoring of pressure increases in the collection system will determine the associated permeation rates. Typical operation provided a collection system base pressure of 10^{-9} torr and a bell pressure of 10^{-7} torr. The measurement sensitivity of the equipment was established as 10^{-12} liter-torr/cm^2 sec during the testing of the Frenchtown 7325 alumina sample. This corresponds to the design objective. The sensitivity was calculated by the use of Equation (6) as follows.

$$K = \frac{PS}{A} \tag{6}$$

where

P = outgassing background pressure

S = pumping speed of ion gauge for hydrogen

A = area of sample hot zone

$$K = \frac{(3 \times 10^{-9} \text{ torr})\ (10^{-2} \text{ liter/sec})}{30 \text{ cm}^2}$$

$$K = 1 \times 10^{-12} \text{ liter-torr/cm}^2 \text{ sec}$$

A schematic of the basic system is shown in Figure 1. Photographs of the completed system are included in Figures 2 through 7 with the more interesting features noted.

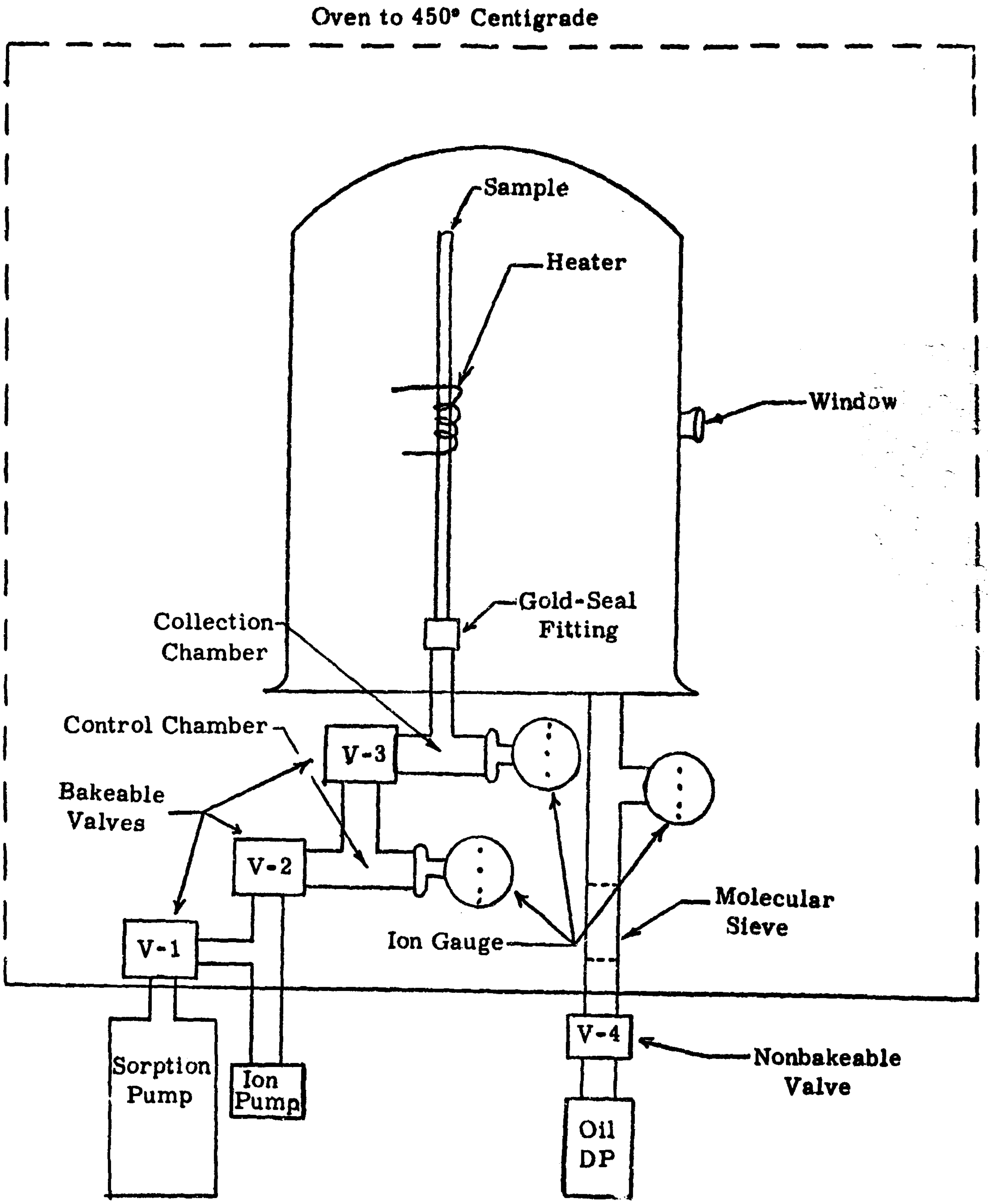


FIGURE 1. SCHEMATIC OF COLLECTION CHAMBER SYSTEM

Notes for Figure 2:

1. The bell is made of 8-inch I. P. S. seamless Type 304 stainless steel.

2. An aluminum seal is used between the bell and the baseplate. This type of seal was pioneered and developed by Holden, Holland, Laurenson, and Elsworth[12, 13] of Edwards High Vacuum Ltd. In this application, 0.064-inch diameter, dead-soft aluminum wire is used and is "pulled down" to 0.030-inch thickness.

3. The window is an adaptation of a faceplate from RCA Tube Type 6032.

4. The heart of the test system is the group of three ultra-high vacuum valves which isolate the collection chamber, control chamber, and sorption pump respectively. The valves used are RCA Type J1870-1 Ultra High Vacuum Valves.

5. Three Alpert-type ionization gauges are employed. Two of these gauges are in the ultra-high vacuum system, while the third is in the "outside" system.

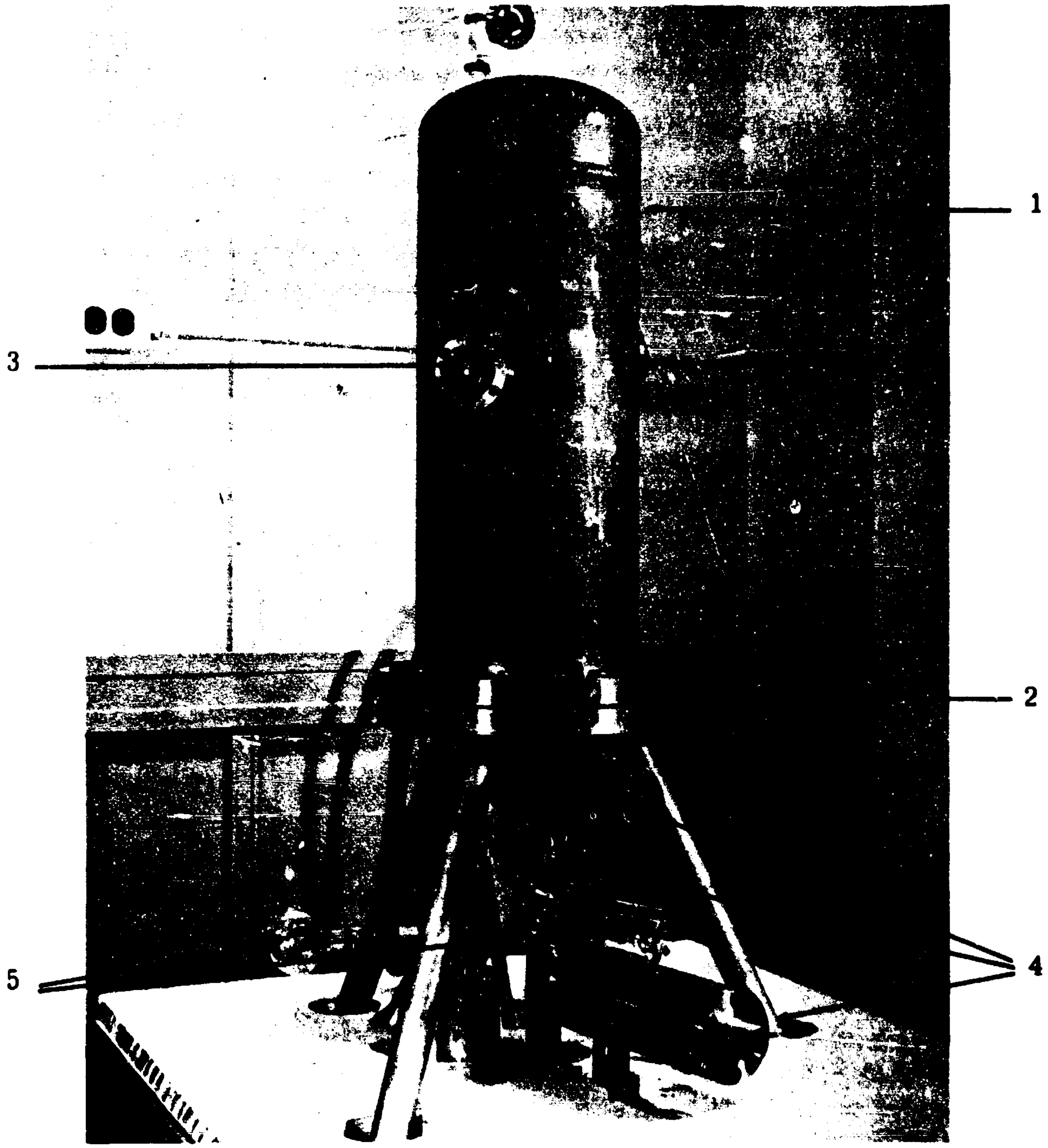


FIGURE 2. VIEW SHOWING BELL, VACUUM VALVES, AND IONIZATION GAUGES

Notes for Figure 3:

6. The test gas in-out tubes are made of Type 304 stainless steel tubulation.

7. The ceramic feedthroughs in the baseplate are modified parts used on RCA Tube Type 6448. Two are used for water-cooled heater leads, the third (not shown) for water cooling a baffle.

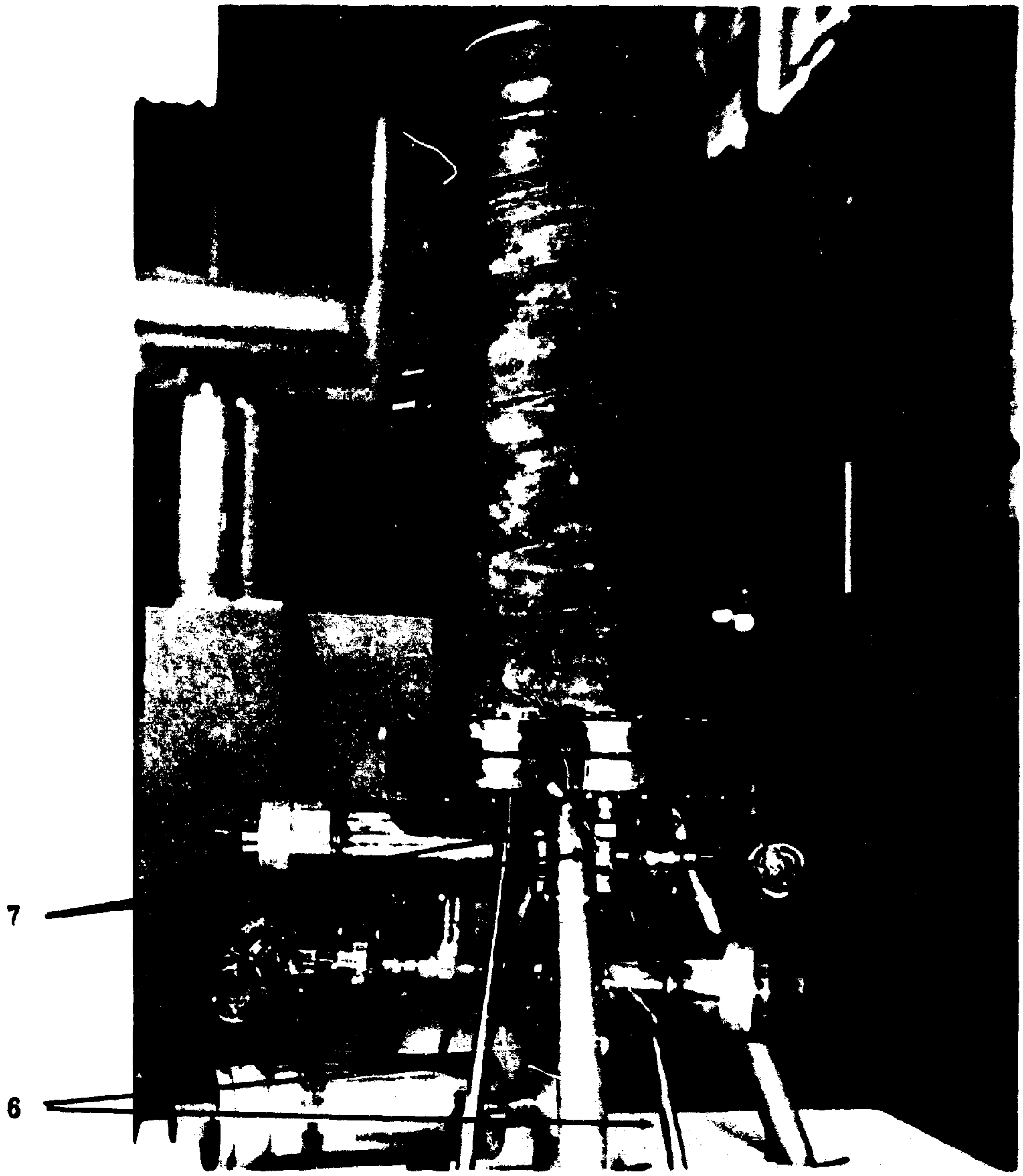


FIGURE 3. VIEW SHOWING GAS IN-OUT TUBES AND CERAMIC FEEDTHROUGHS

Notes for Figure 4:

8. A 15 liter/sec, high-throughput, Vac Ion pump, model 911-5010, was selected for this application.
9. The sorption pump is a model 941-5610 Vac-Sorb pump.
10. A slide valve was included in the oil diffusion system to isolate the pump while the bell is filled with test gas.
11. The gas inlet and outlet valves are Veeco #R25SS bellows sealed, all stainless steel valves with Teflon washers.

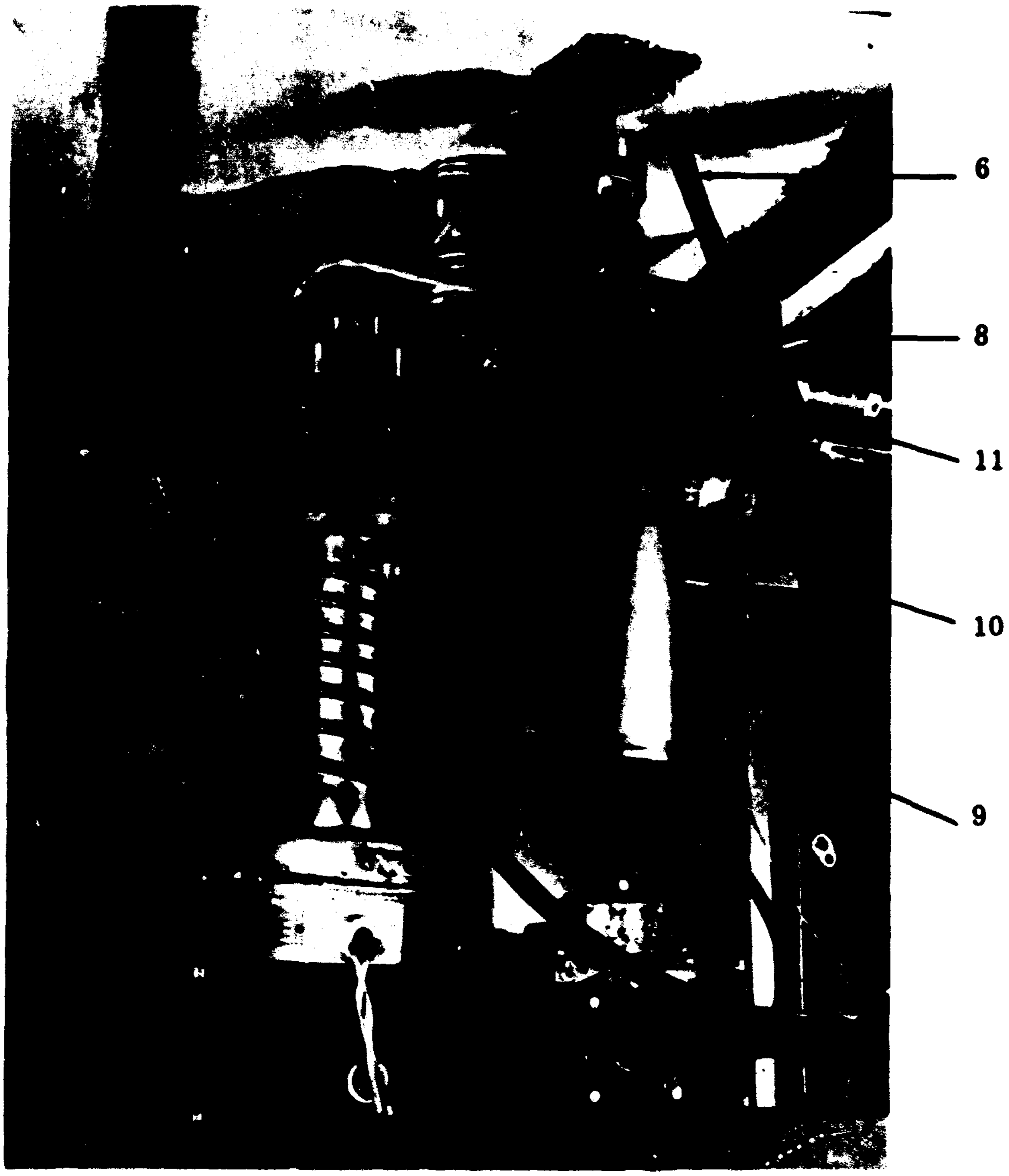


FIGURE 4. VIEW SHOWING VACUUM SYSTEM

Notes for Figure 5:

12. Sample tubes are discussed in the paragraph describing the permeation test assembly.

13. A series of molybdenum cylinders and plates form four demountable "cans" which serve as heat shields.

14. Copper tubing, brazed to the bottom of a stainless steel plate, constitutes a water-cooled baffle which protects the sample-to-system seal.

15. The heater connectors are comprised of three sections of OFHC copper. By bolting these pieces together, solid connection is made between feedthrough and heating element.

16. This connector is a Parker fitting especially machined to accept a gold gasket.

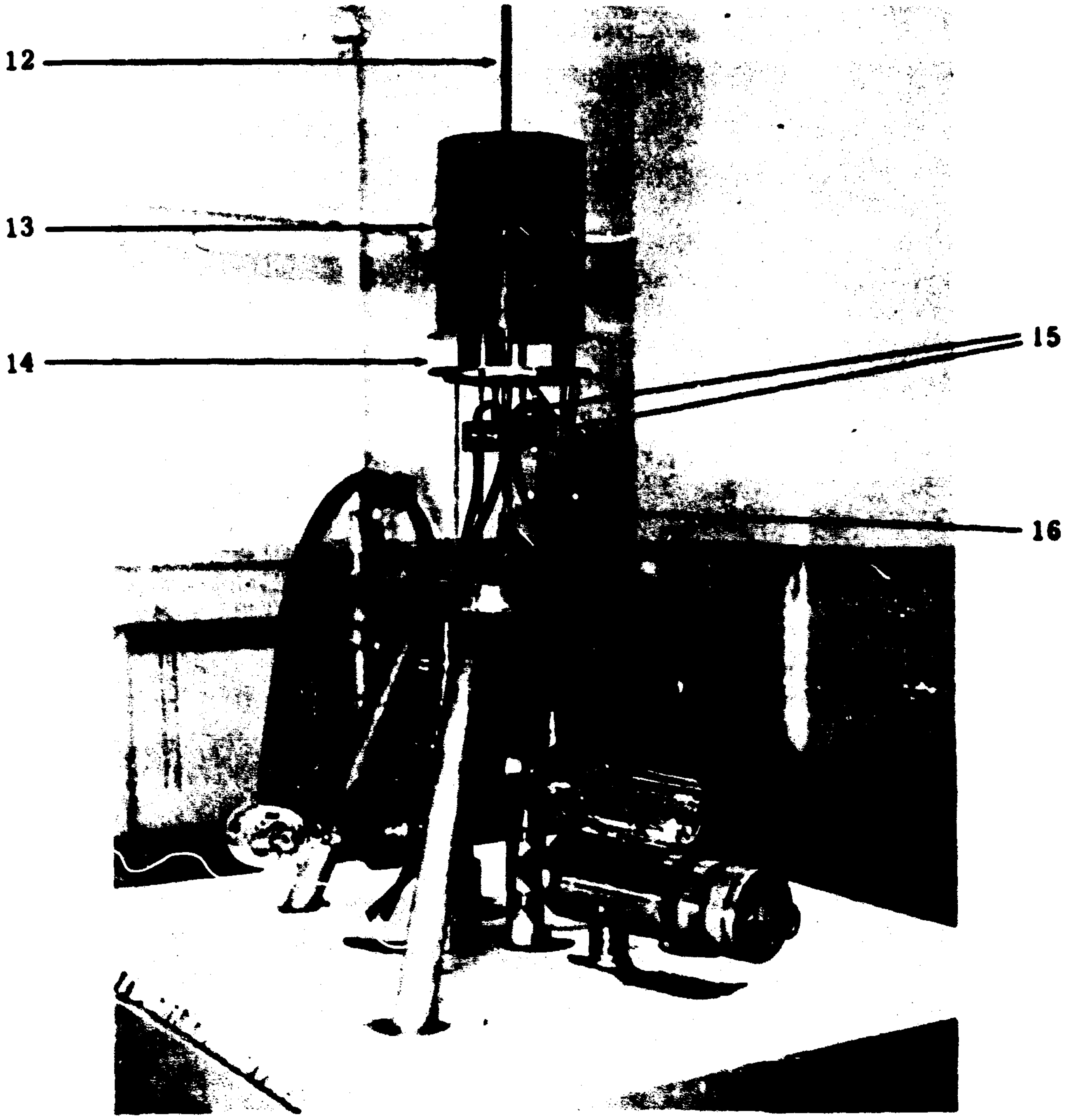


FIGURE 5. VIEW SHOWING SAMPLE MOUNTING AND HEAT SHIELDS

Notes for Figure 6:

17. For a heating element a hairpin-type heater was fabricated from 0.103-inch diameter pure tungsten wire.

18. Ceramic cylinders were ground to form supports for the heat shields. The spacing between the molybdenum discs is 0.25 inch.

19. In the first shield area, molybdenum rods were used instead of ceramic as a support for the first shield because of excessive temperature and thermal shock.

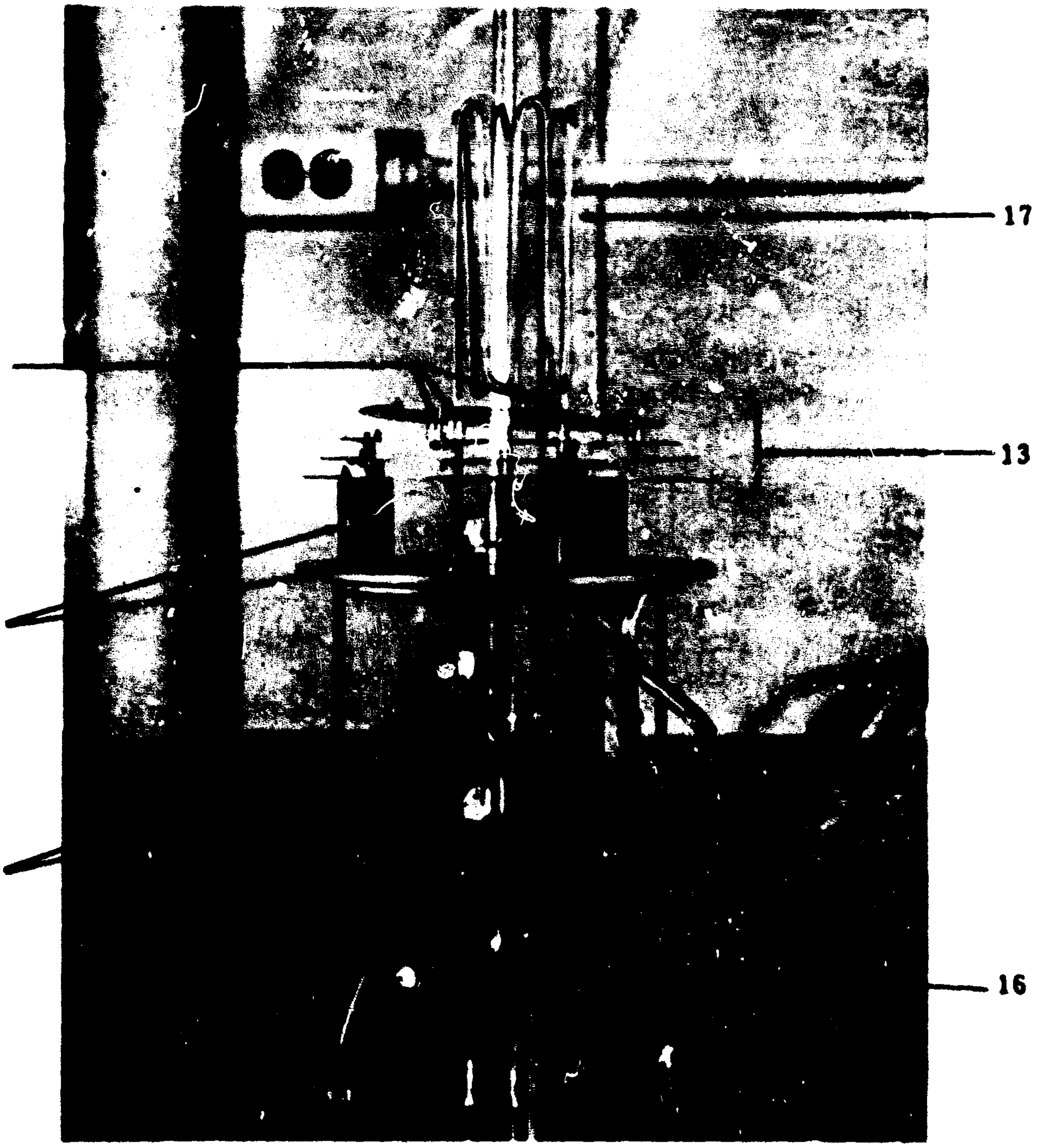


FIGURE 6. VIEW SHOWING HEATING ELEMENT AND STAND FOR HEAT SHIELDS

Figure 7 shows the system being baked with a portable oven. The control circuit of the oven contains a proportional timer so that the rate of temperature rise can be closely controlled.

The baseplate of the bell system was machined from Type 304 stainless steel. All parts were heliarc welded with full penetration welds.

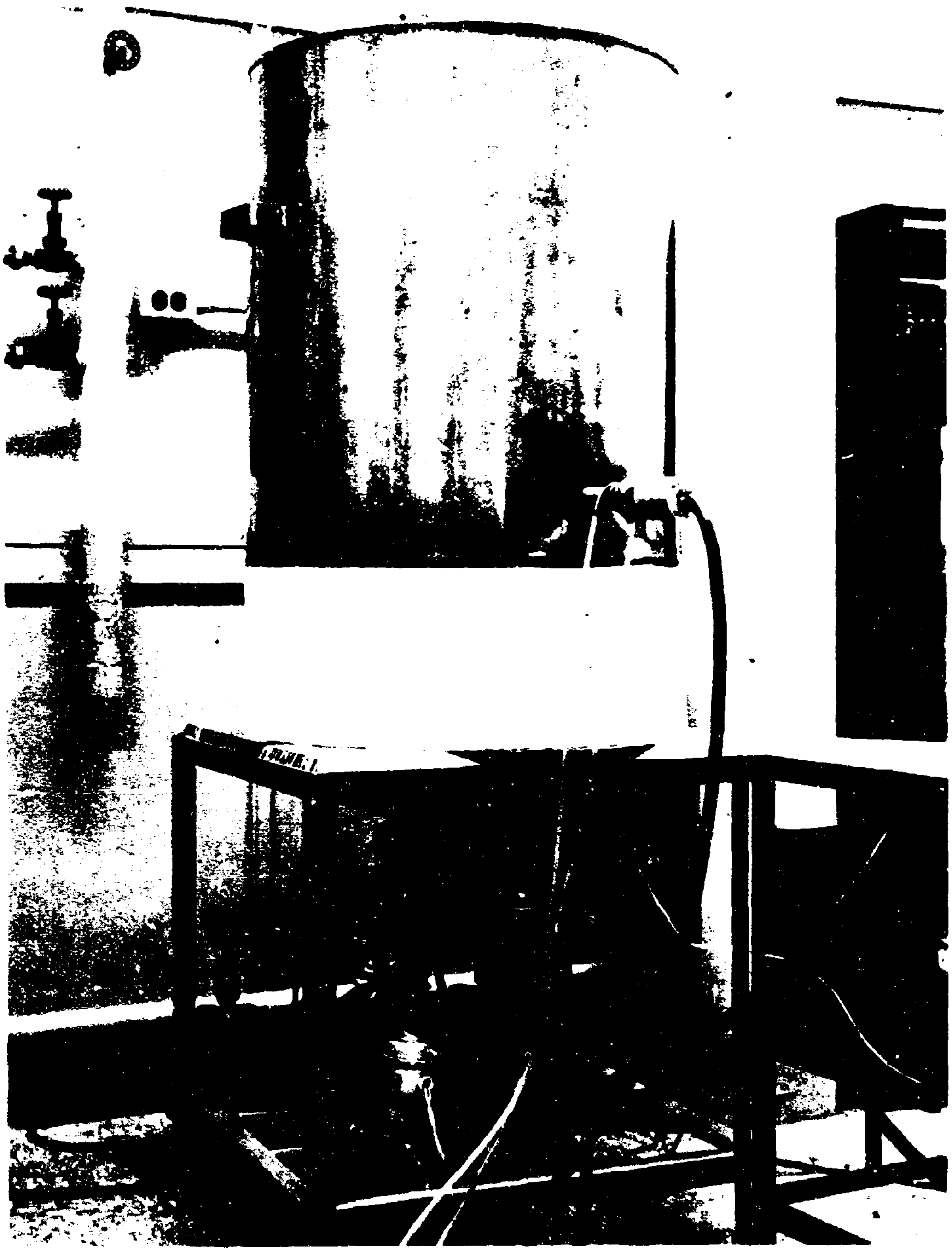


FIGURE 7. VIEW SHOWING BAKEOUT OVEN IN TEST POSITION

b. Permeation Test Assemblies

The resistance of sample materials to permeation of gases was measured by mounting test assemblies, fabricated from each of the materials to be evaluated, on the collection chamber system. These test assemblies were closed-end tubes having the following nominal dimensions: 5/16-inch OD x 3/16-inch ID x 10-inch minimum length. The construction of this assembly is illustrated in Figure 8.

Vacuum-tight closed-end tubes to the nominal dimension specified were commercially available in each of the three basic materials chosen for study (alumina, beryllia, and pyrolytic silicon carbide).

Numberous high alumina ceramics were available and four were chosen for evaluation. One alumina was of the high density type

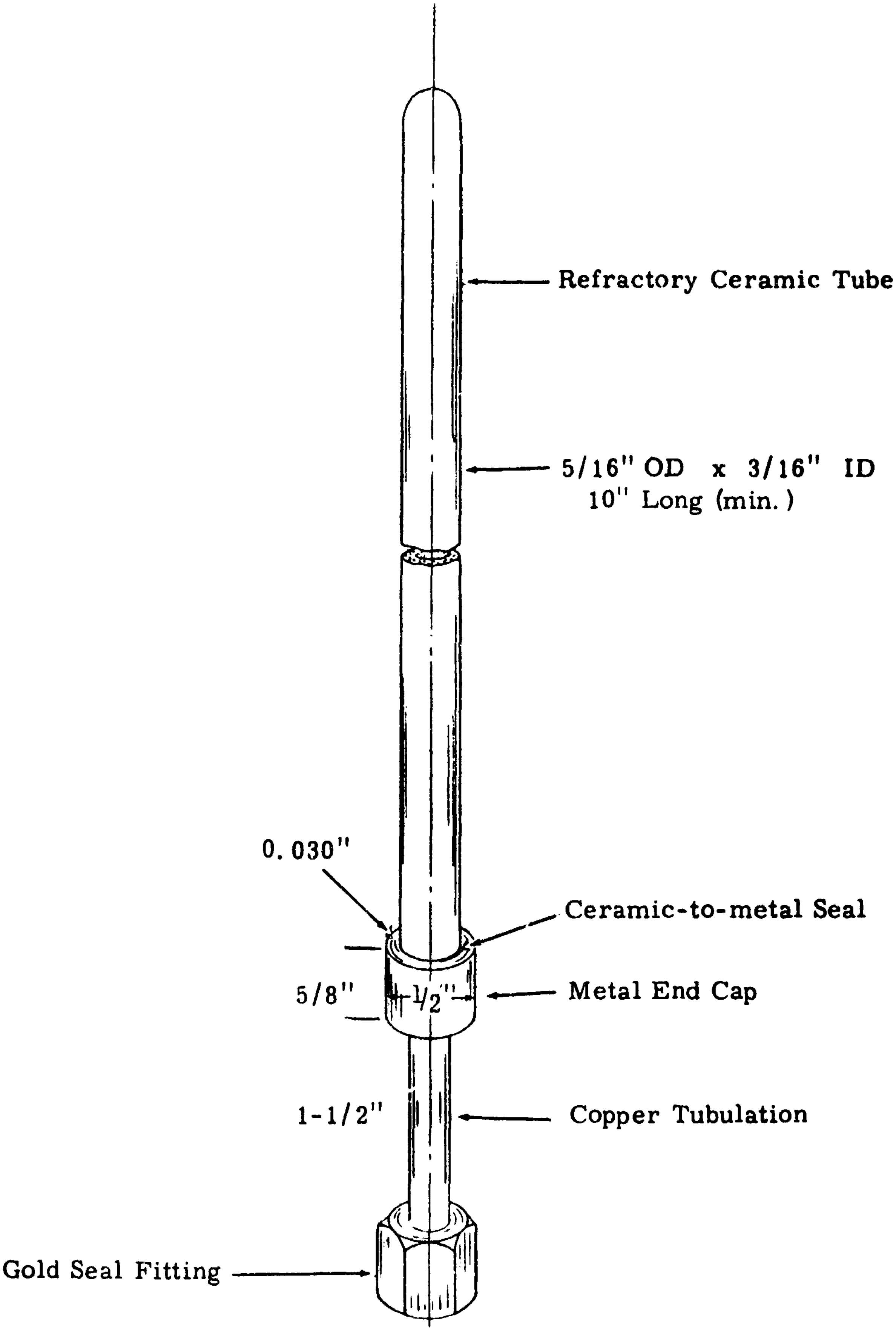


FIGURE 8 - PERMEATION TEST ASSEMBLY

(Lucalox, General Electric Co.) having a purity of 99.9% and no appreciable pore volume. The other three aluminas were of the conventional type and 99.8% Al_2O_3 (Frenchtown 7325), 99% Al_2O_3 (Frenchtown 7258) and 98% Al_2O_3 (Silk City SC98D) respectively. This series was chosen because of the different amounts of fluxing agents present in the ceramics, to determine the effect of fluxing agents on both the permeation and thermal decomposition characteristics of the materials. All assemblies were satisfactorily metalized and brazed to their respective metal members. One Lucalox sample leaked in the area of several small but visible markings in the central portion of the tubing wall.

A beryllia body having a purity of 99.5% BeO (Coors BD-995) was chosen because it contained the least amount of glassy phase material of any available sample. Because of the toxicity hazard involved in metalizing beryllia, the vendor fabricated the complete permeation assembly.

Pyrolytic silicon carbide samples in the desired shape proved extremely difficult to acquire, delays of several months beyond the scheduled delivery dates being encountered with the suppliers, Texas Instruments and San Fernando Laboratories. The fabrication problems were reported to be associated with non-stoichiometric composition of the deposited material, poor reproducibility of the process, non-uniformity of deposition over the surface of the samples, internal stresses in the parts, difficulty in obtaining reproducible carbon mandrel material and, with deposition on a metallic substrate, poor bonding of the two layers.

Additional difficulties were experienced in sealing the first pyrolytic silicon carbide sample, Texas Instrument's ScS. Seal strengths equal to that of the silicon carbide were obtained using both single refractory metal and a combined refractory metal-reactive metal metalizing techniques; however, only one vacuum tight test seal was produced. Vacuum failure of the seals was traced to micro-cracks in the silicon carbide. It is RCA's engineering opinion that the micro-cracks are closely related to the radially oriented crystal structure of the material and may be induced by the reaction between the metalizing and the silicon carbide, and the stresses set-up by the dissimilar material (tungsten) components used in the seal.

Of the three samples obtained from Texas Instrument, two were metalized and brazed. Both units leaked. The third assembly was sent to San Fernando Laboratories for tungsten vapor coating on the seal area, then sealed at RCA. It was vacuum tight on the helium leak detector, but leaked on the permeation system. The failure occurred at the tungsten-silicon carbide interface.

Four silicon carbide samples were then obtained from San Fernando Laboratories.

Two were metalized and brazed. The third was coated with tungsten and then sealed. The fourth sample was coated with rhenium and sealed. All units leaked.

Repeated attempts were made to recover these assemblies by cutting off the defective seal areas and resealing. All efforts were without success. Compression seals were attempted by shrink-fitting copper and stainless steel members to the silicon carbide, but none was vacuum tight. Useable assemblies were finally obtained by coating two of the better seals with General Electric SR-82 silicone varnish.

The first useable assembly, made with SFL silicon carbide, failed in bakeout when a power failur in one heater element caused partial cooling. The relatively small thermal shock caused extensive cracking in the hot zone in the apparently highly stressed silicon carbide. The second assembly, made with T. I. ScS material, was testable. A water-cooling course was used on this assembly during testing to assure the integrity of the silicone resin seal.

c. Fossil Fuel Burner

For the series of experiments on permeation in a fossil fuel combustion environment, a three-stage ring burner was designed, constructed, and fitted around the test sample coaxially, as shown in Figure 9. During the test the burner was operated with a mixture of city gas (mainly methane), oxygen, and low-pressure air and produced a heat zone of 40 cm^2 with a temperature range of 1440-1500° Centigrade.

3. Permeation Measurements

The measurements of gas permeation rates were divided chronologically into two parts. Initial measurements of gas permeation rates for alumina, beryllia, and pyrolytic silicon carbide were

FIGURE 9. FOSSIL FUEL BURNER FOR PERMEATION TESTS

carried out between November, 1963 and March, 1964. In November, 1964, a contract extension was received to include identification of the individual gas species which permeated the samples. For this work, a highly sensitive mass spectrometer (General Electric Model 514 Partial Pressure Analyzer) tube was substituted for the ionization gauge opposite valve V-2, Figure 1. This approach retained the high sensitivity inherent in the gas collection approach by integrating small amounts of gas flow over long time periods and provided for the ultimate identification of the collection products. Actual tests, made by collecting the outgassing products of a test sample, showed this technique to be satisfactory. A schematic diagram of the revised system is shown in Figure 10. For simplicity, the work is discussed here by material rather than chronologically.

a. Testing Technique

The detailed test procedure was as follows:

(1) Sample tubing attached to test system with gold-seal fitting.

(2) Sample pumped to high-vacuum range with no heating or baking.

(3) Entire sample system checked for leaks using conventional leak detection methods.

(4) Bell placed over sample (heater and heat shields in place) and evacuated to 10^{-7} torr range.

(5) Sample and system outgassed extensively.

(6) With sample at 1500° Centigrade and bell evacuated, valves V-2 and V-3 are closed.

(7) Sample, pumped only by ion gauge, achieves outgassing

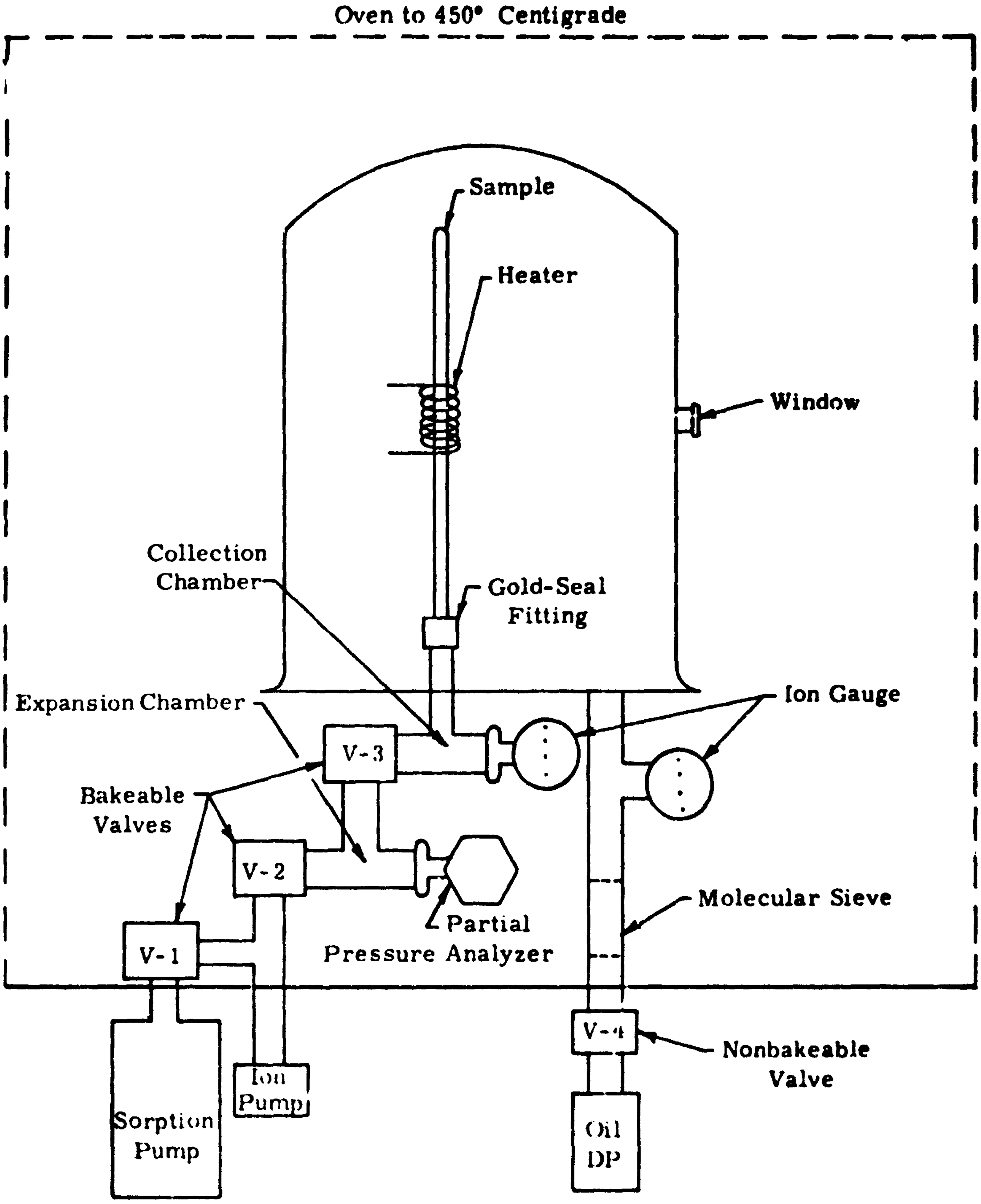


FIGURE 10. SCHEMATIC OF MODIFIED COLLECTION CHAMBER SYSTEM

equilibrium in 10^{-9} torr range.

(8) Temperature of sample is systematically changed from 1500° Centigrade to 1300° Centigrade in steps of 50° Centigrade to establish outgassing rates.

(9) Valve V-4 is closed and the bell is backfilled with the test gas.

(10) The pressures in both the collection chamber, P_1, and the expansion chamber, P_2, are closely monitored and plotted.

(11) Permeation is evidenced by an appropriate rise in the pressure of the collection chamber. When the permeation reaches equilibrium with the pumping speed of the ion gauge "pump", a plateau appears in the pressure plot; i. e., dP/dt approaches zero.

(12) At this time a "pumping check" is taken to determine the pumping speed of the ion gauge. This measurement is discussed in more detail below.

(13) Following the pumping check, the temperature of the sample is increased until a limiting permeation or temperature is reached. At each temperature, steps (10) through (12) are repeated.

A pressure versus time plot of a typical test is given in Figure 11.

For the fossil fuel tests, this same basic procedure was used for the sample insertion, attachment, and outgassing with the following differences in the permeation phase:

(1) The sample was outgassed extensively inside the evacuated bell, using the electrical heater at 1700° Centigrade.

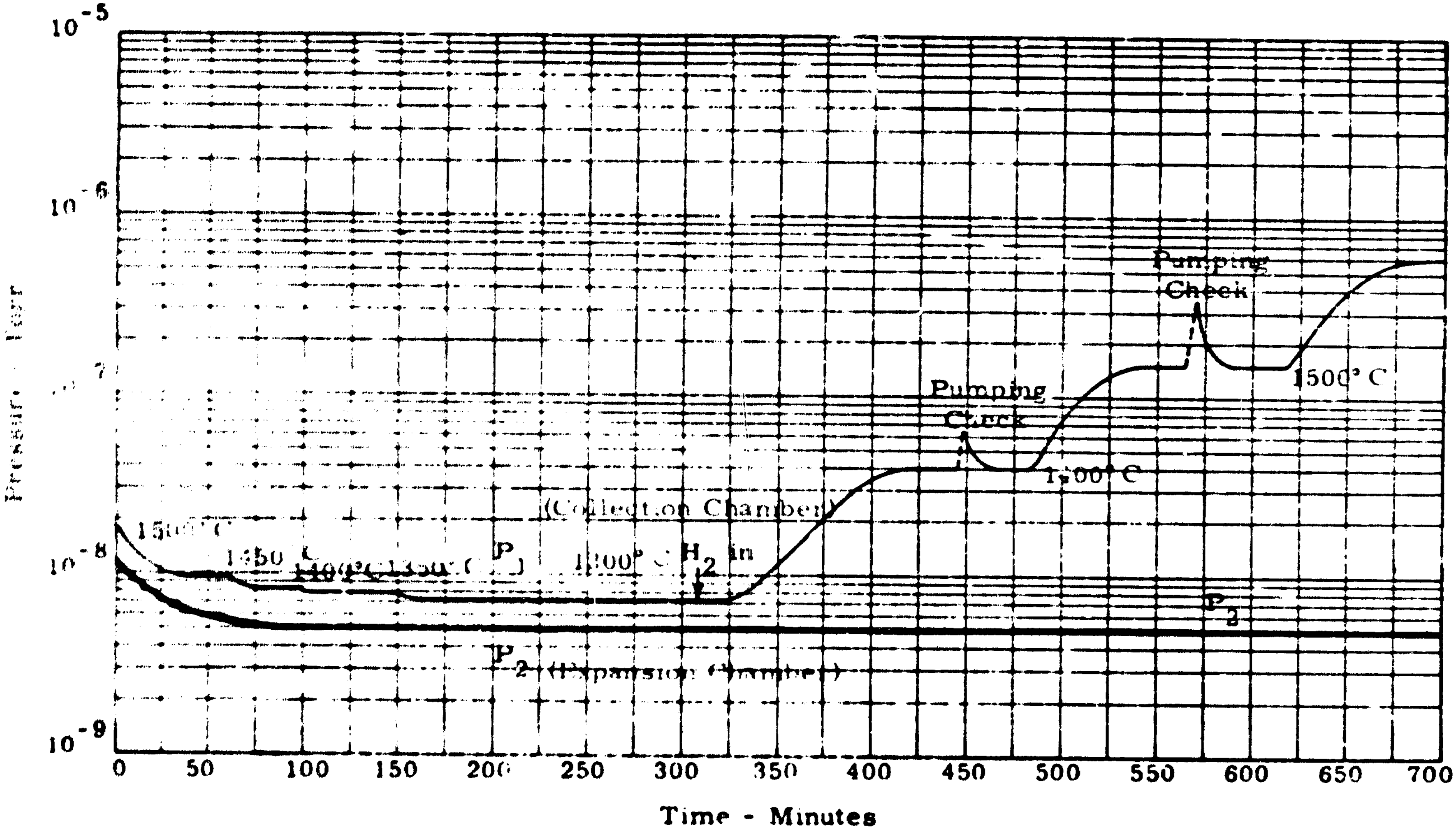


FIGURE 11. TYPICAL TIME-PRESSURE CURVE

(2) After outgassing, the sample was cooled to room temperature and the bell opened to air. The bell, the electric heater, and the heat shields were removed. At this point the pressure inside the samples was about 1×10^{-8} torr.

(3) The burner was placed around the sample, ignited, and slowly raised in temperature until the sample hot zone reached 1440-1500° Centigrade.

(4) Valve V-2 (see Figure 10) was then closed and the pressure in the collection chamber was monitored.

(5) Valve V-3 was then opened and the constituents of the gas determined in the Partial Pressure Analyzer.

In order to determine the pumping speed of the ion gauge, Equation (11) was applied to experimental pumping checks. These checks were made by simply turning off the gauge while the system was in equilibrium and after several minutes returning the gauge to operation. The strip-chart record of the pumpdown (Figure 12) yields directly, the information needed to compute the pumping speed, S (Equation 11, page 23). The choice of P_o is, of course, arbitrary and in these checks was always chosen so as to eliminate obvious transient effects.

The value of S calculated in these experiments approached 1.0×10^{-2} liters/sec for H_2, which is in agreement with the value of 9.4×10^{-3} liter/sec calculated from Alpert's equation for determining the ion-pumping speed of an ion gauge.[14]

b. Sample Testing and Results

(1) Molybdenum Control Sample

The first sample investigated was molybdenum. The object

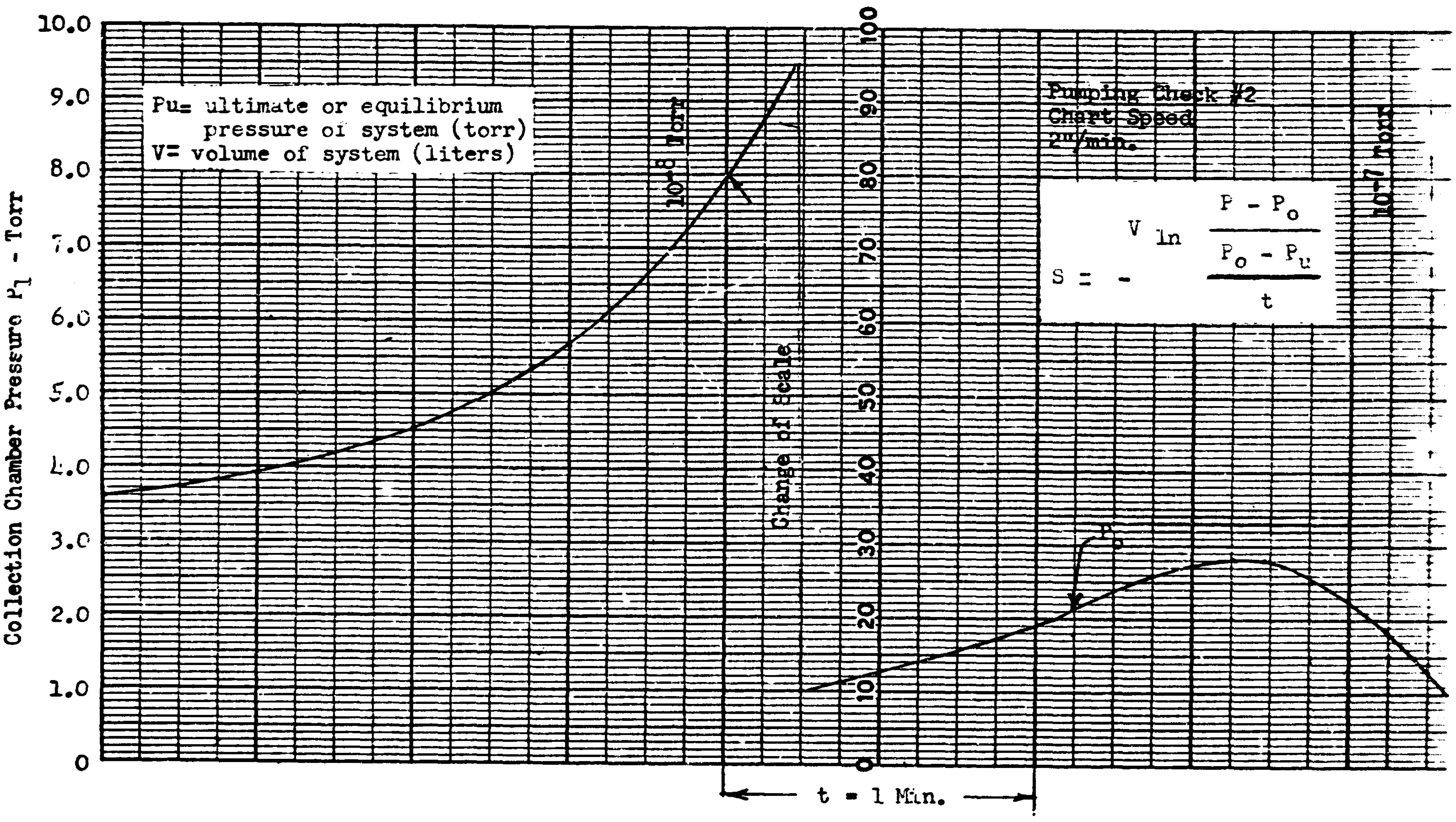


FIGURE 12. STRIP CHART RECORDING OF A TYPICAL PUMPING CHECK

of this test was to show the system to be capable of reproducing values determined by other investigators. The high permeation characteristic of molybdenum approaches the limit of usefulness of the test equipment. By evaluating the sample at 500° Centigrade the permeation was held within the range of the system. Temperature was measured with a Thermo-Dot Infra-Red Detector. A value of permeation was obtained which correlated with extrapolations made from data previously reported by Conklin and Turnbull.[2] This result is shown graphically in Figure 13. Note that all curves, in the region of interest, are extrapolated.

(2) Aluminum Oxide

Three aluminum oxide ceramic materials were initially subjected to permeation testing; Silk City SC98D, Frenchtown 7325 and General Electric Lucalox. The fourth alumina sample, Frenchtown 7258, was not tested since a concurrent cesium compatibility study showed it to have unsatisfactory resistance to cesium attack.[15]

It was initially believed that hydrogen was likely to show the highest permeation rate. The materials were, therefore, first subjected to testing in hydrogen. The Silk City SC98D and Frenchtown 7325 showed comparable low rates, in the order of 2 to 7 x 10^{-11} liter-torr/cm^2 sec at 1400° Centigrade. The permeation followed a characteristic time profile in which introduction of the hydrogen was followed by a delay of several minutes to over one-half hour before permeation became evident on the inside of the

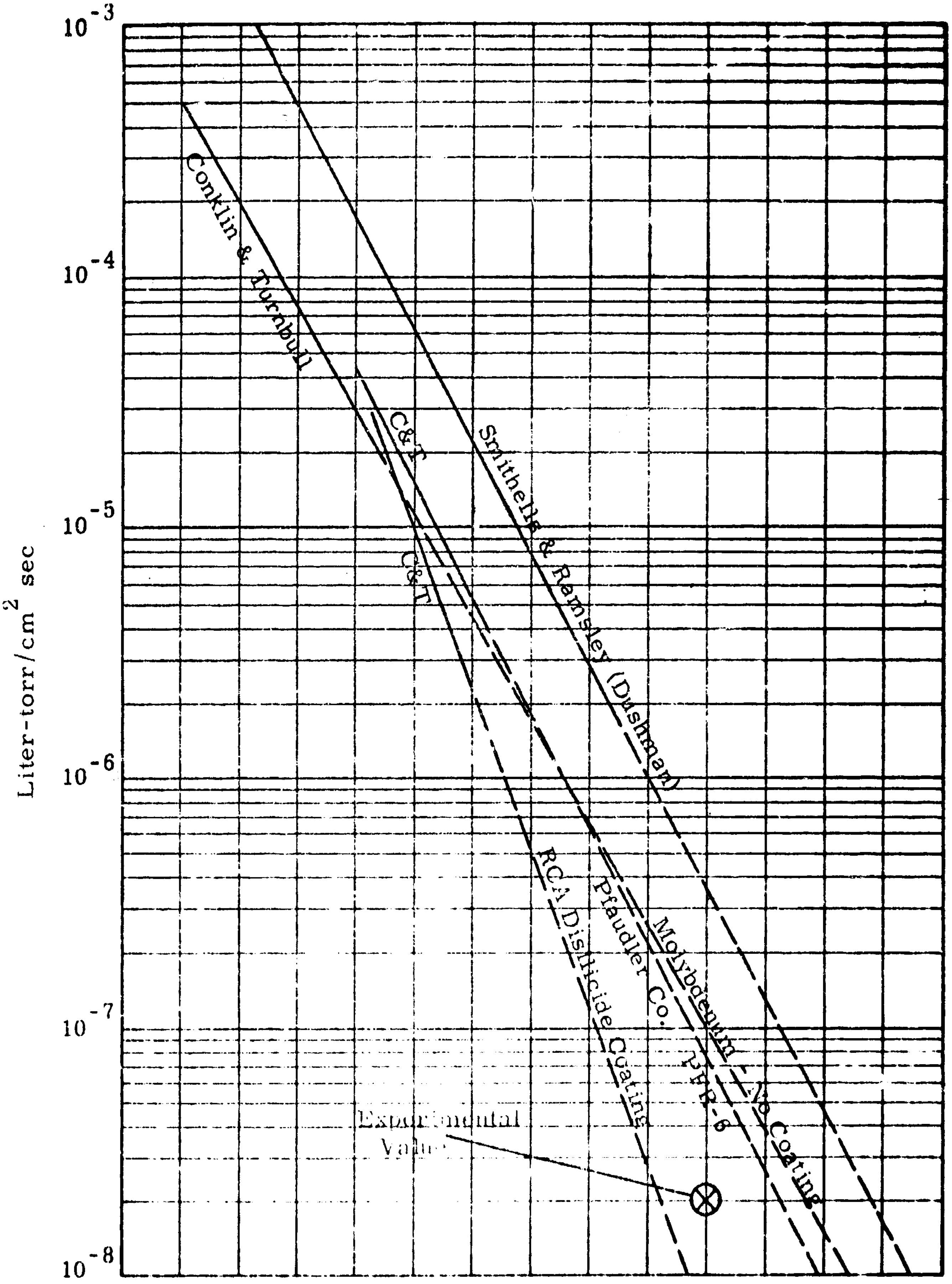


FIGURE 13. GRAPHIC RESULTS OF MOLYBDENUM-HYDROGEN TESTS

sample

With Lucalox the permeation began with the introduction of the hydrogen Following the permeation test, the sample was again leak checked at room temperature with a helium mass spectrometer leak detector to insure that no ordinary leak had developed. No leak was found. It is felt that this unexpected behavior is related to the observed structural non-uniformities in the samples received Since these samples are apparently representative, further work with this otherwise promising material was discontinued.

The Silk City SC98D sample was then subjected to testing with a spectrum of gases helium, argon, nitrogen and, finally, a burning fossil fuel. The results are indicated graphically in Figure 14 and are tabulated in Table II. While the helium rate is relatively high, there is relatively little helium present in a normal converter environment, so that this is not considered to be a serious detriment. The fossil fuel result, showing a rate greater than the sum of the total of the previously measured rates, presented the possibility that an unmeasured gas, possibly oxygen has a significant permeation rate in alumina.

The Frenchtown 7325 body was eventually selected for use in actual converters For this reason it was also selected as the alumina sample for subsequent mass spectrometric testing using a fossil fuel heat source. The gases released during the outgassing of the sample, elec-

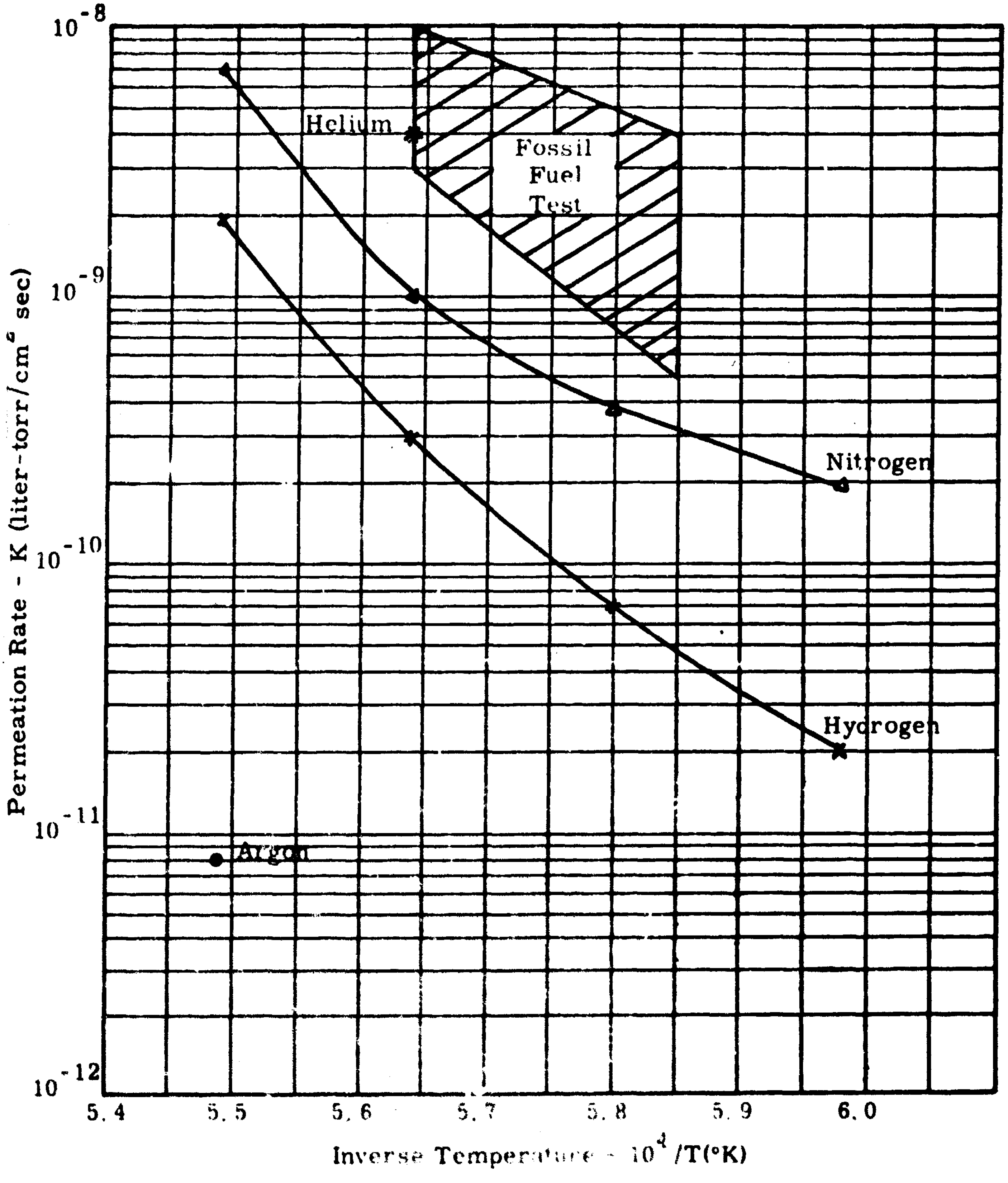


FIGURE 14. PERMEATION TEST RESULTS FOR SC98D ALUMINA

TABLE II. PERMEATION TEST RESULTS

		Permeation Rate K (liter-torr/cm^2 sec)			
Sample/Gas	1300° C	1400° C	1450° C	1500° C	1550° C
Frenchtown 7325					
H_2		7×10^{-11}*			
GE Lucalox					
H_2		7×10^{-10}**			
Silk City SC98D					
H_2		2×10^{-11}	8×10^{-11}	3×10^{-10}	2×10^{-9}
He				$\geq 4 \times 10^{-9}$	
A		No detectable permeation			8×10^{-12}
N_2		2×10^{-10}	4×10^{-10}	1×10^{-9}	7×10^{-9}
Fossil Fuel			$\geq 5 \times 10^{-9}$	$\leq 1 \times 10^{-8}$	

* Only one point was measured on Frenchtown 7325 to obtain correlation with the similar Silk City SC98D.

**While this sample did not exhibit usual characteristics, a value of permeation rate is included for comparison.

trically heated and surrounded by a vacuum, were those typically observed when degassing ceramics. Carbon monoxide, water vapor, and carbon dioxide represent the bulk of the desorbed gases. A normalized mass scan taken during the degassing period is shown in Figure 15. The gases collected during the lighting of the fossil-fuel burner[5] and the raising of the temperature, were those which had been observed during the vacuum bake. After the sample was at a temperature of 1500° Centigrade for approximately 30 minutes, the recorded spectra showed marked and significant changes inasmuch as masses 16, 32, and 44 (O^+ and O_2^{++}, O_2^+, CO_2^+) became dominant (see Figure 16) At this time the normal testing procedure was changed in order to show direct correlation between the sample temperature and the amount of mass 32 (O_2) present in the system. This was accomplished by focusing the mass spectrometer on the mass 32 peak maximum and recording this maximum peak height as a function of temperature. Figure 17 shows the discontinuities which resulted when the temperature of the sample was changed. Although the temperatures given in Figure 17 are close approximations, they contain errors such as time lag and temperature gradients within the heat zone, which are inherent in the rapid manipulation of a fossil-fuel burner. Similar tests on other gas peaks showed that only CO_2 followed the same pattern. The level of oxygen permeation observed falls within the range reported earlier for the fossil-fuel operation of SC951 alumina, 1×10^{-8} liter torr/cm^2 sec.

During the initial mass spectrometric testing of the Frenchtown 7325 sample, a maladjustment of the spectrometer

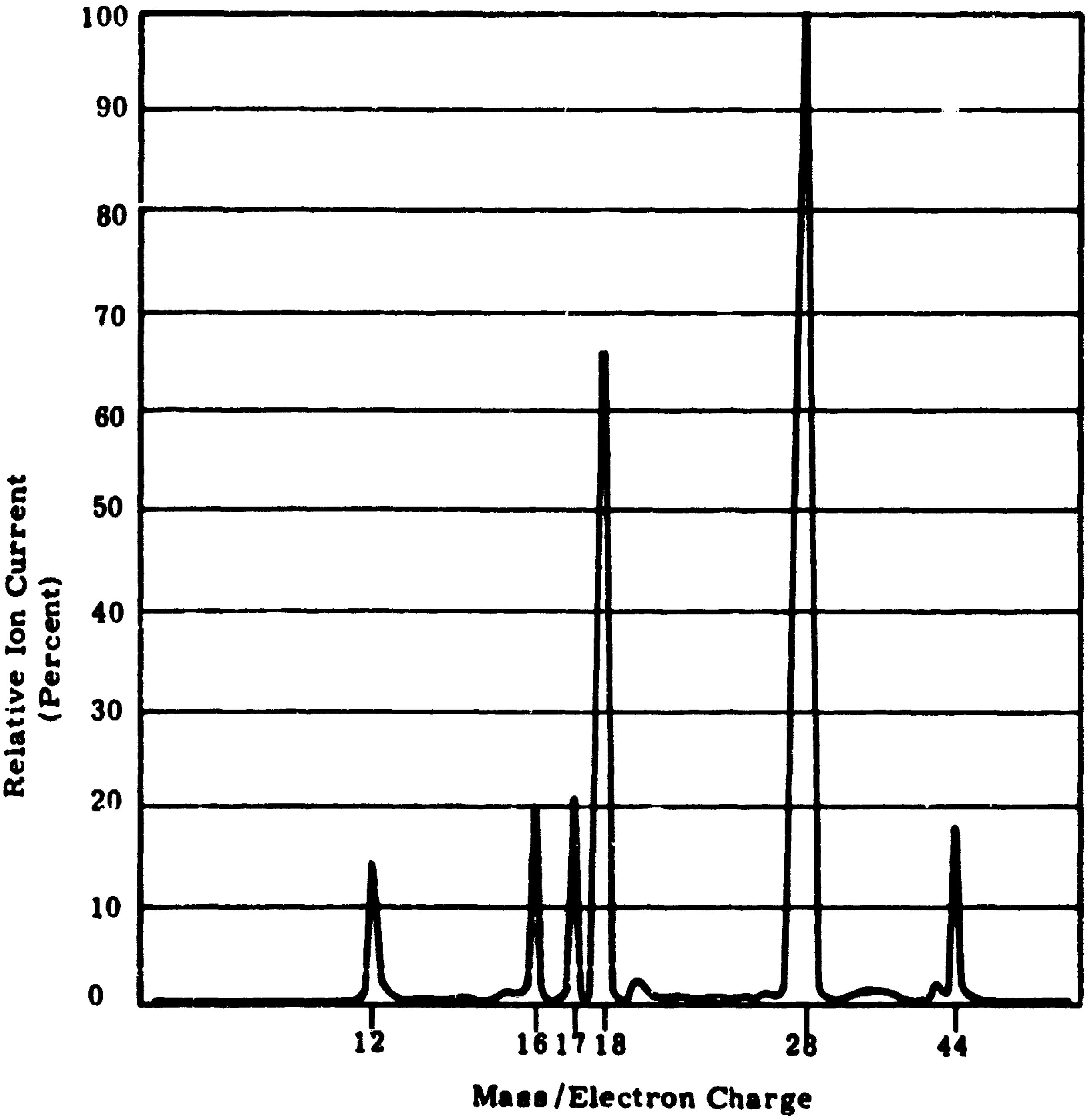

Body, Frenchtown 7325 as measured during degassing in vacuum

FIGURE 15. MASS SPECTRUM FOR Al_2O_3 CERAMIC
(Initial Run)

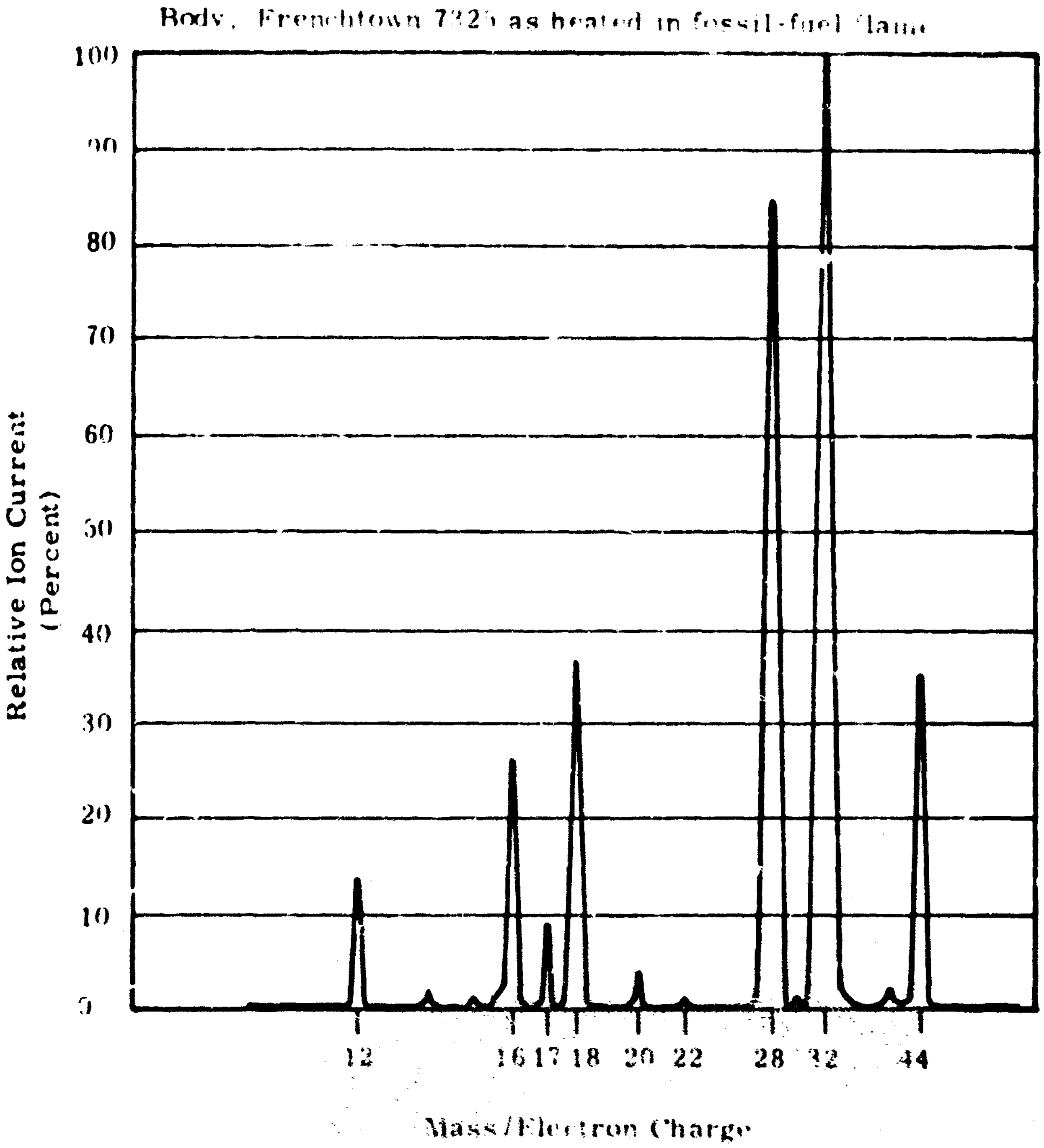


FIGURE 16. MASS SPECTRUM FOR Al_2O_3 CERAMIC

(Initial Run)

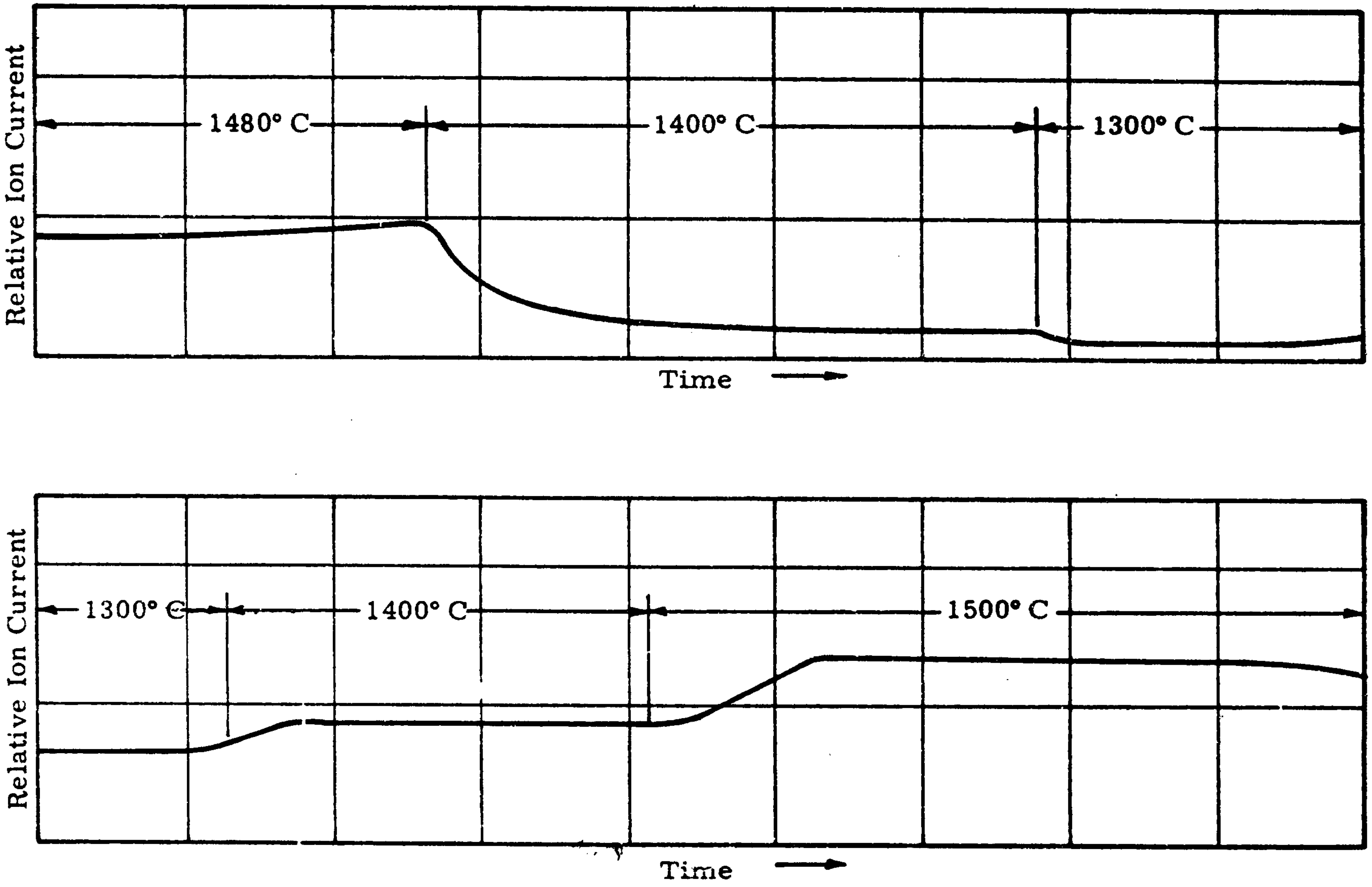


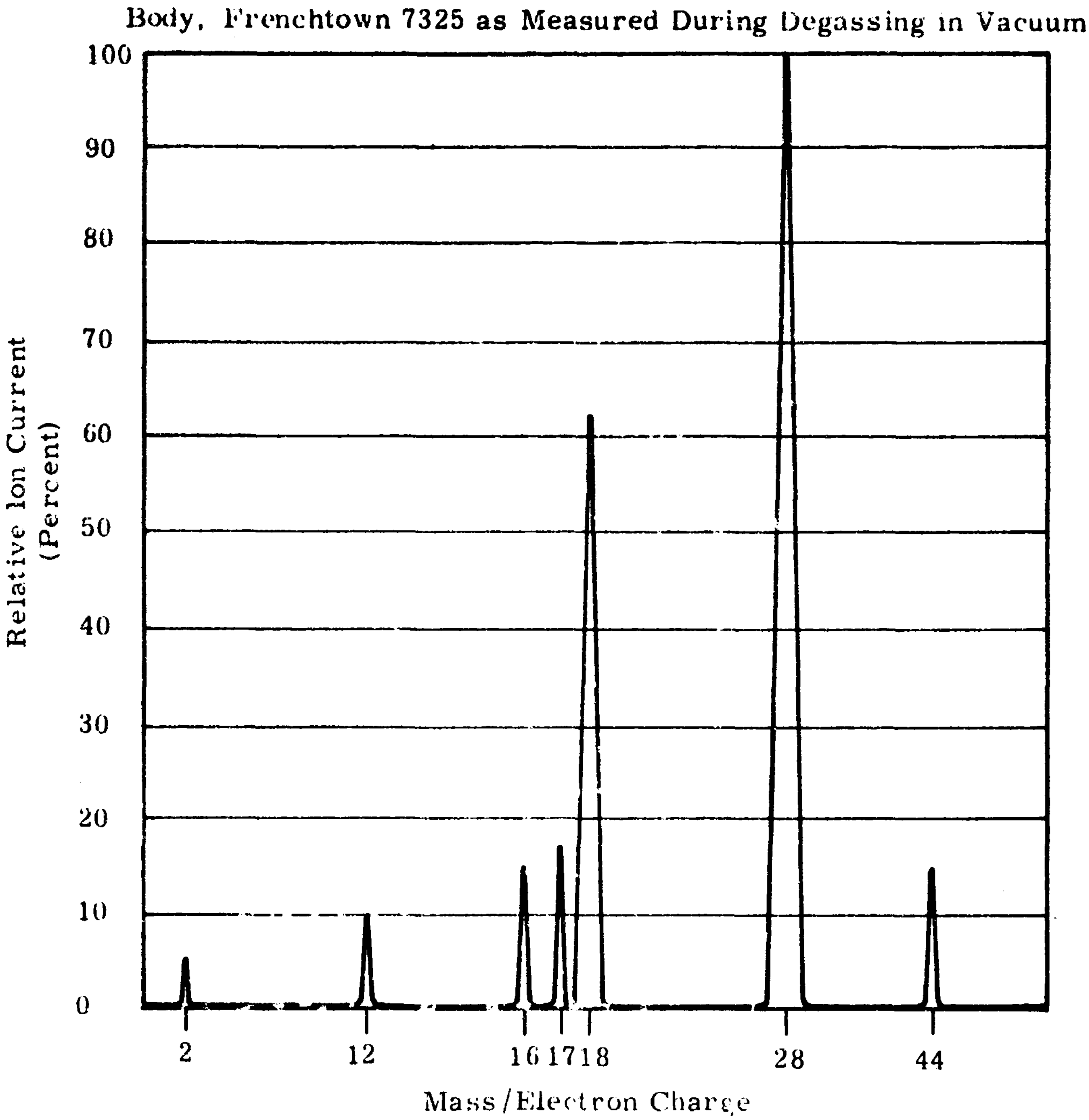
FIGURE 17. SCAN OF M/e = 32 VERSUS TIME AT VARIOUS TEMPERATURES

prevented the observation of the mass 2 peak, that is, hydrogen permeation could not be observed. The test was subsequently repeated with the equipment in proper adjustment All previous values were repeated with the hydrogen permeation rate in the fossil fuel shown to be approximately 10^{-10} liter torr/cm^2 sec at a temperature of 1500° Centigrade. Normalized scans showing the full mass range during the degassing and permeation tests are given in Figures 18 and 19.

(3) Beryllium Oxide

The testing of the sample of Coors BD-955 Beryllia involved special problems of isolation of any toxic vapors which were produced. After consultation with representatives of Coors Porcelain Company, the following procedures were worked out. When testing individual gases in the bell, the effluent gas was bubbled through a sulphuric acid solution before venting. During fossil fuel heated tests a special exhaust hood and scrubber were installed over the sample and burner. Subsequent checks revealed no dangerous quantities of beryllium compounds except as noted in the section on sample corrosion below.

The beryllia showed a very low level of permeation in a hydrogen environment, it was, in fact, undetectable at 1500° Centigrade. The rate was 1×10^{-10} liter torr/cm^2 sec at 1550° Centigrade. In spite of this promising result, an extremely high permeation rate was observed in the fossil fuel heated test, as shown in Figure 20. In fact, an equilibrium was not reached. The chamber pressure rose beyond the upper pressure tolerance of the system. A sample was later subjected to mass



Body, Frenchtown 7325 as Measured During Degassing in Vacuum

FIGURE 18. MASS SPECTRUM FOR Al_2O_3 CERAMIC

(Repeat Run)

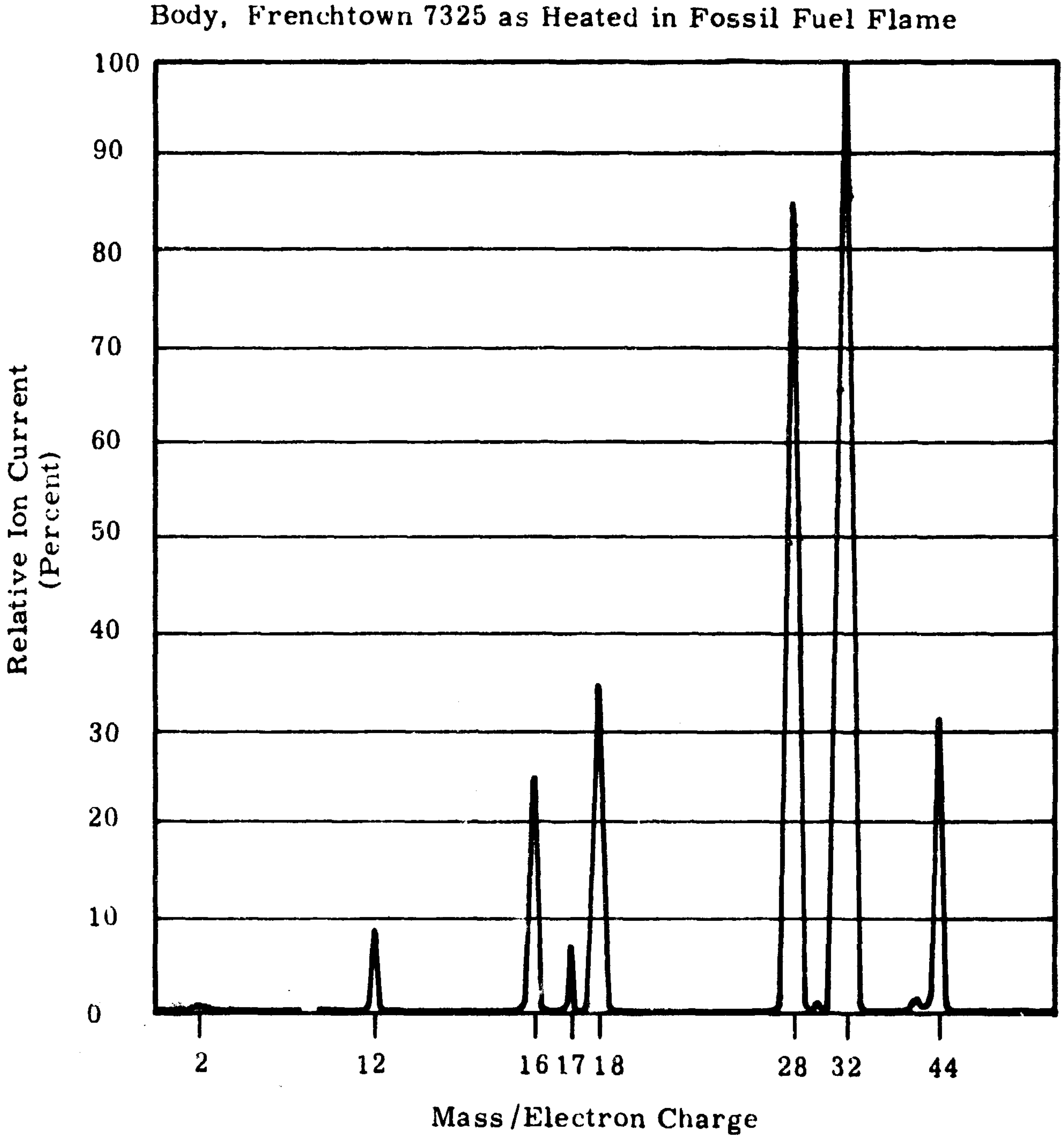


FIGURE 19. MASS SPECTRUM FOR Al_2O_3 CERAMIC

(Repeat Run)

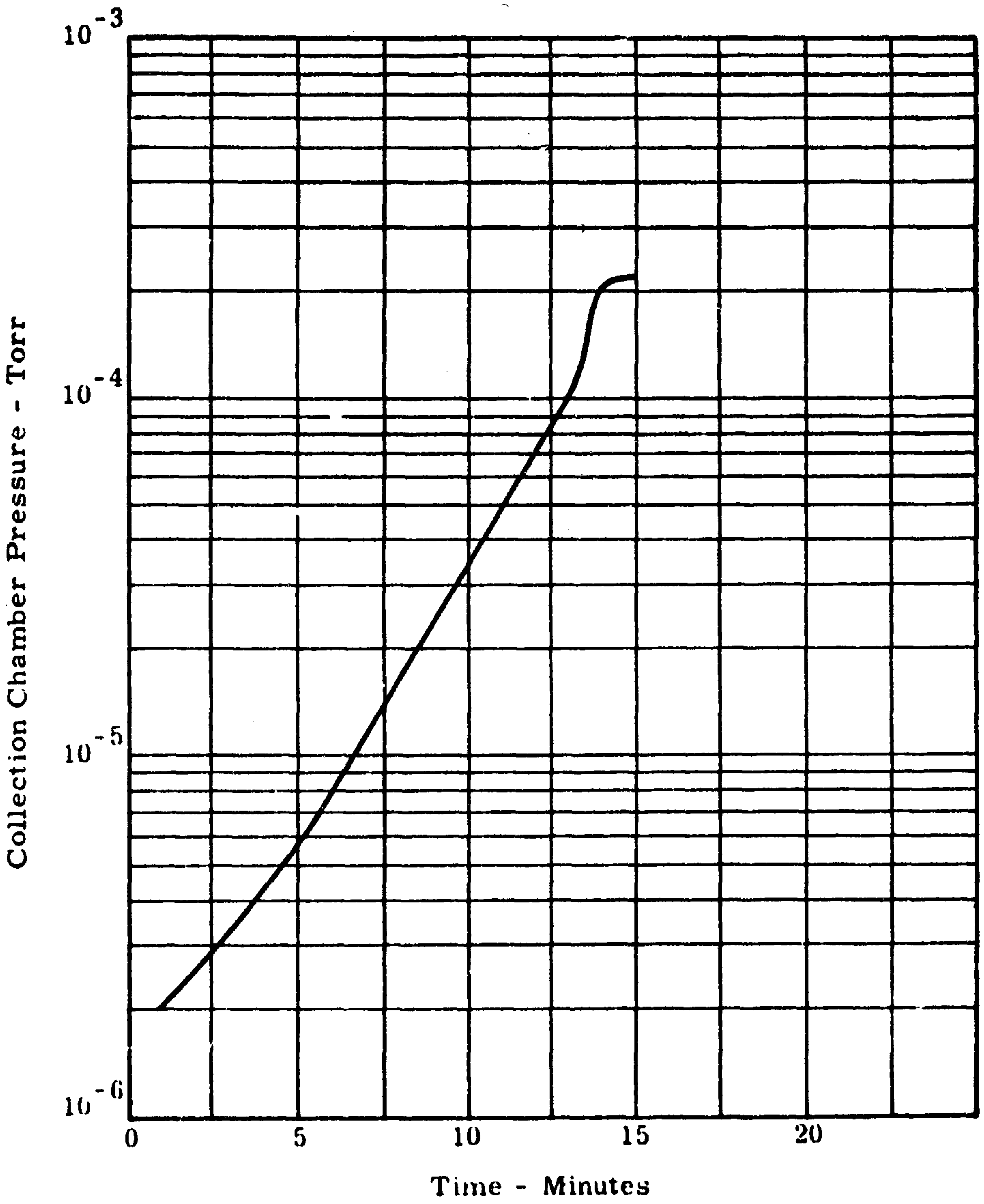


FIGURE 20. PERMEATION TEST RESULTS
FOSSIL FUEL PRODUCTS THROUGH BERYLLIA

spectrometric tests according to the following procedure.

Prior to exposure to the gas flame, the sample was outgassed and low levels of carbon monoxide, water vapor, carbon dioxide and hydrogen were observed. Introduction of the sample into a fossil fuel flame at 1500° Centigrade produced rapid permeation of carbon monoxide, along with lesser amounts of water vapor, hydrogen and carbon dioxide. A normalized mass scan of this test is shown in Figure 21.

The fact that the permeation products were the same as the outgassing products raised a question as to the validity of the results. A second test was therefore performed, after completion of a stringent degassing cycle at 1700° Centigrade maximum temperature, which closely reproduced the initial results. The reproducibility of the consecutive tests, coupled with the extremely low background achieved during the second degas period, confirms the conclusion that the gases collected during the fossil fuel test period are truly permeation products and not sample outgassing. Approximate permeation rates were obtained for the minor constituent gases as follows. The total permeation rate measured independently by the gas storage method was assigned to the major constituent, CO. The relative permeation rates of the other constituents were then deduced from their relative pressures, i. e., ion currents, as indicated by Figure 21, after correcting for the observed outgassing rates as these M/e points. These values are given in Table III.

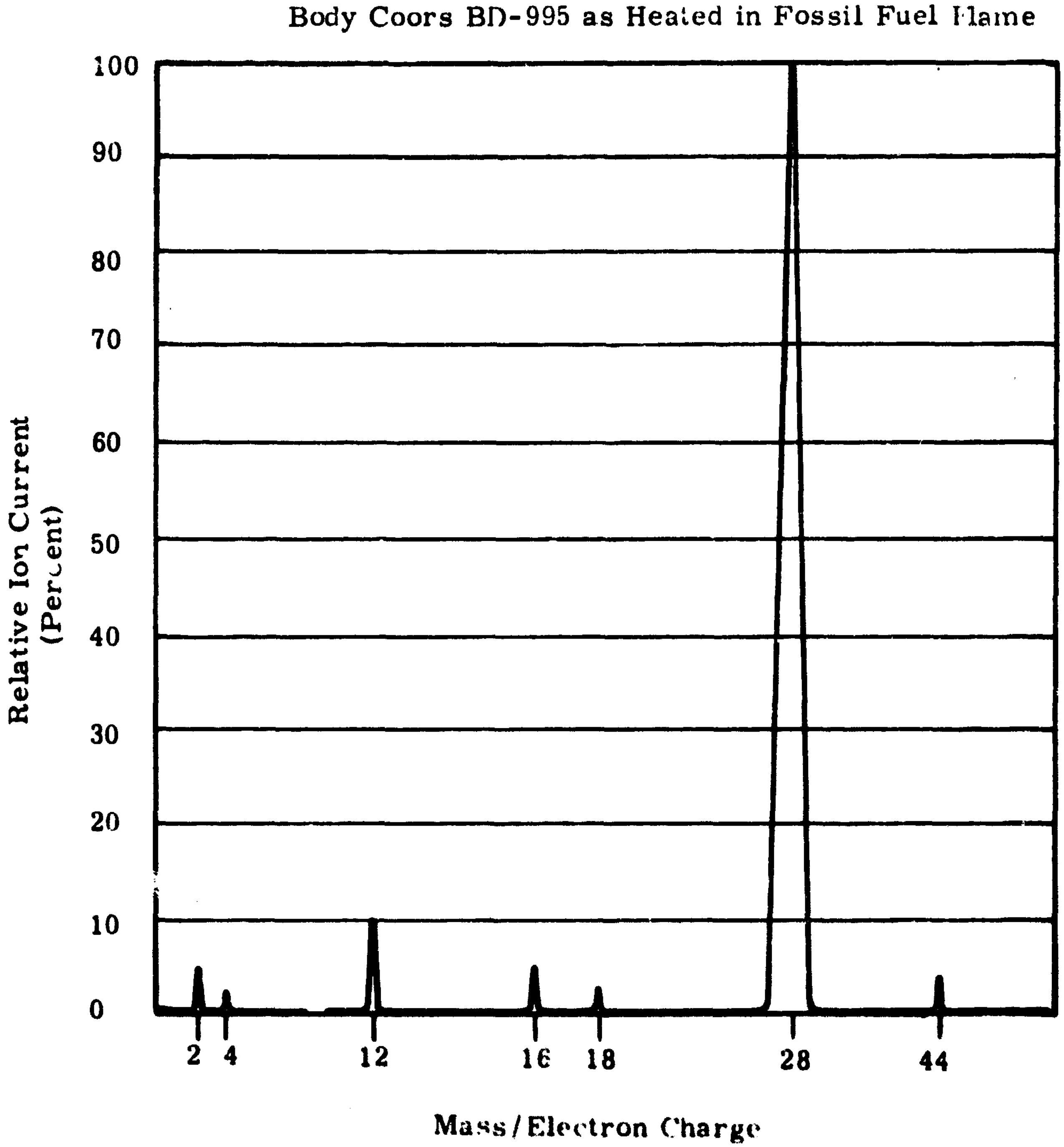


FIGURE 21. MASS SPECTRUM FOR BERYLLIA

TABLE III

BERYLLIA PERMEATION RATES IN FOSSIL FUEL FLAME

Carbon Monoxide	3×10^{-8} liter torr/cm^2 sec
Water Vapor Hydrogen Carbon Dioxide	each approximately 10^{-10}

(4) Pyrolytic Silicon Carbide

A sample of Texas Instrument's ScS silicon carbide was tested initially with hydrogen, following the standard procedure. Hydrogen was introduced into the bell when the sample was at 1300° Centigrade. A 20-minute time lag was observed and within 9 hours the pressure had risen to 1×10^{-4} torr with the sample temperature maintained at 1300° Centigrade. No equilibrium was reached.

In the second experiment the sample was exposed to the fossil fuel flame, with the sample temperature maintained in the range 1275-1375° Centigrade during the experiment. Again no equilibrium was reached - pressure in the sample was still rising when the experiment was ended. The sample checked leak tight after the experiment.

Figure 29 shows the collection chamber pressure versus time plot for both hydrogen and fossil fuel tests. Since no equilibrium was reached between the pumping action of the ionization gauge and the permeation of the gases, no definite value could be assigned to the permeation rate for either experiment. The rate can only be said to exceed the maximum measurable rate of 3×10^{-8} liter torr/cm^2 sec. Two important factors should be noted however:

(a) The permeation rate for hydrogen on the silicon carbide samples was high at relatively low temperatures, when compared to the alumina and beryllia samples.

(b) The time-pressure curves for both hydrogen and fossil fuel flame were substantially identical.

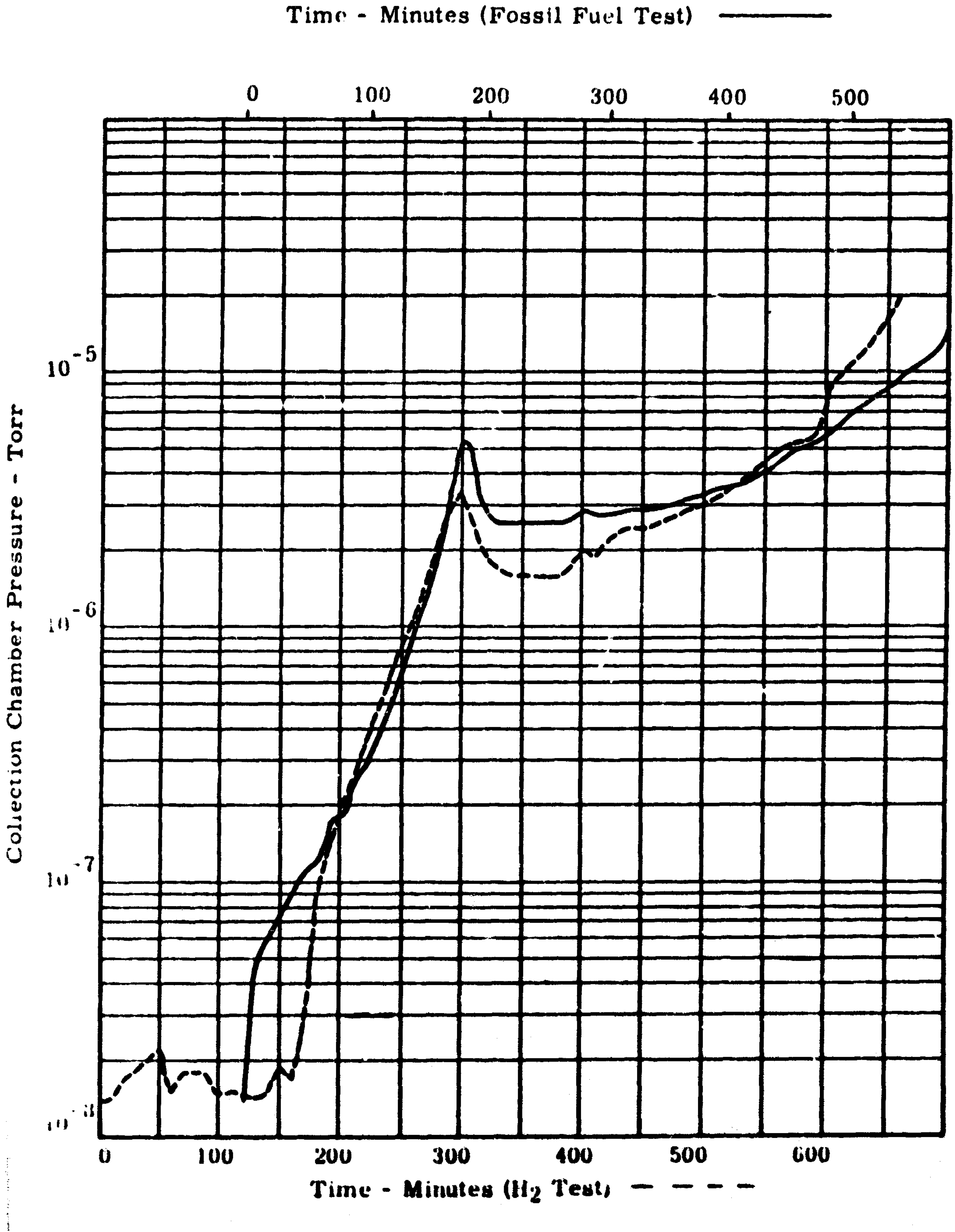


FIGURE 22. PERMEATION TEST RESULTS FOR SILICON CARBIDE

It was primarily this similarity of the fossil fuel and hydrogen results with the silicon carbide and the unexpected fossil fuel behavior of the alumina that led to the program of mass spectrometric examination of the permeating gases during fossil fuel heating of the samples. The following results were obtained in fossil fuel testing of the Texas Instrument sample with the mass spectrometer. The tests began with a thorough vacuum degassing at 1500° Centigrade. The outgassing rate was observed to be high relative to the alumina and beryllia samples previously tested and to experience with common vacuum materials. The products observed during degassing were carbon monoxide, water vapor and hydrogen, with carbon monoxide being predominant.

The testing of the sample in the fossil fuel environment was at a temperature of 1300° Centigrade and yielded an extremely high rate of carbon monoxide permeation, followed by water vapor and hydrogen in somewhat lesser quantities as shown by the mass scan in Figure 23.

Information from previous work indicated that the permeation rate from operating the sample in a fossil fuel environment was the same as for operating in a hydrogen environment and it had been deduced that hydrogen was the permeating gas in both cases. As a result of the current studies, this was shown to be incorrect and, after thorough degassing, the hydrogen environment experiment was repeated. Water vapor was found to be the gas which permeated in the hydrogen environment, with a very low, unex-

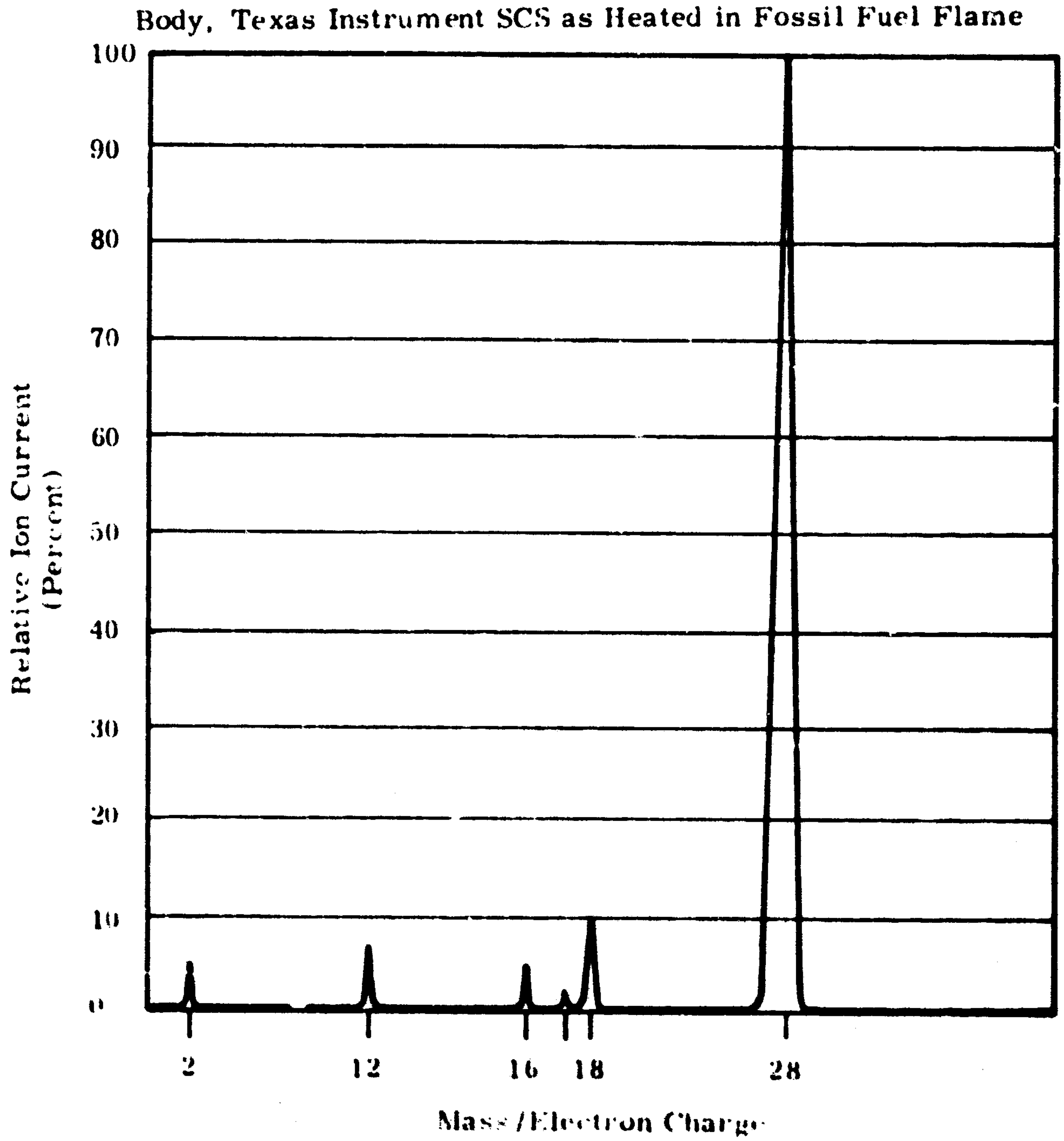


FIGURE 23 MASS SPECTRUM FOR PYROLYTIC SILICON CARBIDE

plained level of helium also present.

The testing continued, following an outgassing cycle, by introducing an atmosphere of nitrogen into the test bell. Results of this test showed that carbon monoxide, helium and water vapor permeated the sample at very low rates. It is possible that these gases were, in fact, outgassing products rather than permeation products. Plans for further experiments were frustrated when the sample developed a large crack during cool-down. Even though no rapid change in temperature had occurred, the failure appeared to be due to thermal shock. The experimental results for all tests are listed in Table IV. The approximate rates assigned to the minor constituent gases were decuced as described previously and are included for general information purposes even though not rigorously derived.

C. Converter Development

1. Initial Design

The detailed design of a fossil-fuel heated thermionic energy converter to evaluate the optimum emitter shell material was completed in December, 1963. A cross-sectional drawing of the converter is shown in Figure 24. The converter employed a cup-shaped emitter, having an area of approximately 16 square centimeters, with the gas permeation barrier shell bonded to its external surface. It was designed to operate at an emitter temperature of 1400° Centigrade. With uniform emitter heating, a power output of 48 watts (equivalent to 3 watts per square centimeter) was expected.

The internal collector contained a central hole through which the emitter surface was viewed and its temperature measured optically. The converter consisted of two major sub-assemblies: emitter and collector, shown in Figures 25 and 26 respectively. The col-

TABLE IV. SUMMARY OF PERMEATION TEST RESULTS

Sample	Environment	Temperature Centigrade	Permeation Product	Rate liter torr/ cm^2 sec
Al_2O_3	Fossil Fuel	1500°	O_2	1×10^{-8}
			H_2	$\sim 10^{-10}$
BeO	Fossil Fuel	1500°	CO	$>3 \times 10^{-8}$
			H_2O	$\sim 10^{-10}$
			H_2	$\sim 10^{-10}$
			CO_2	$\sim 10^{-10}$
SiC	Fossil Fuel	1300°	CO	$>3 \times 10^{-8}$
			H_2O	5×10^{-9}
			H_2	$\sim 10^{-9}$
SiC	H_2	1300°	H_2O	1×10^{-8}
			He	$\sim 10^{-10}$
SiC	N_2	1300°	CO	5×10^{-10}
			He	$\sim 3 \times 10^{-11}$
			H_2O	$\sim 10^{-11}$

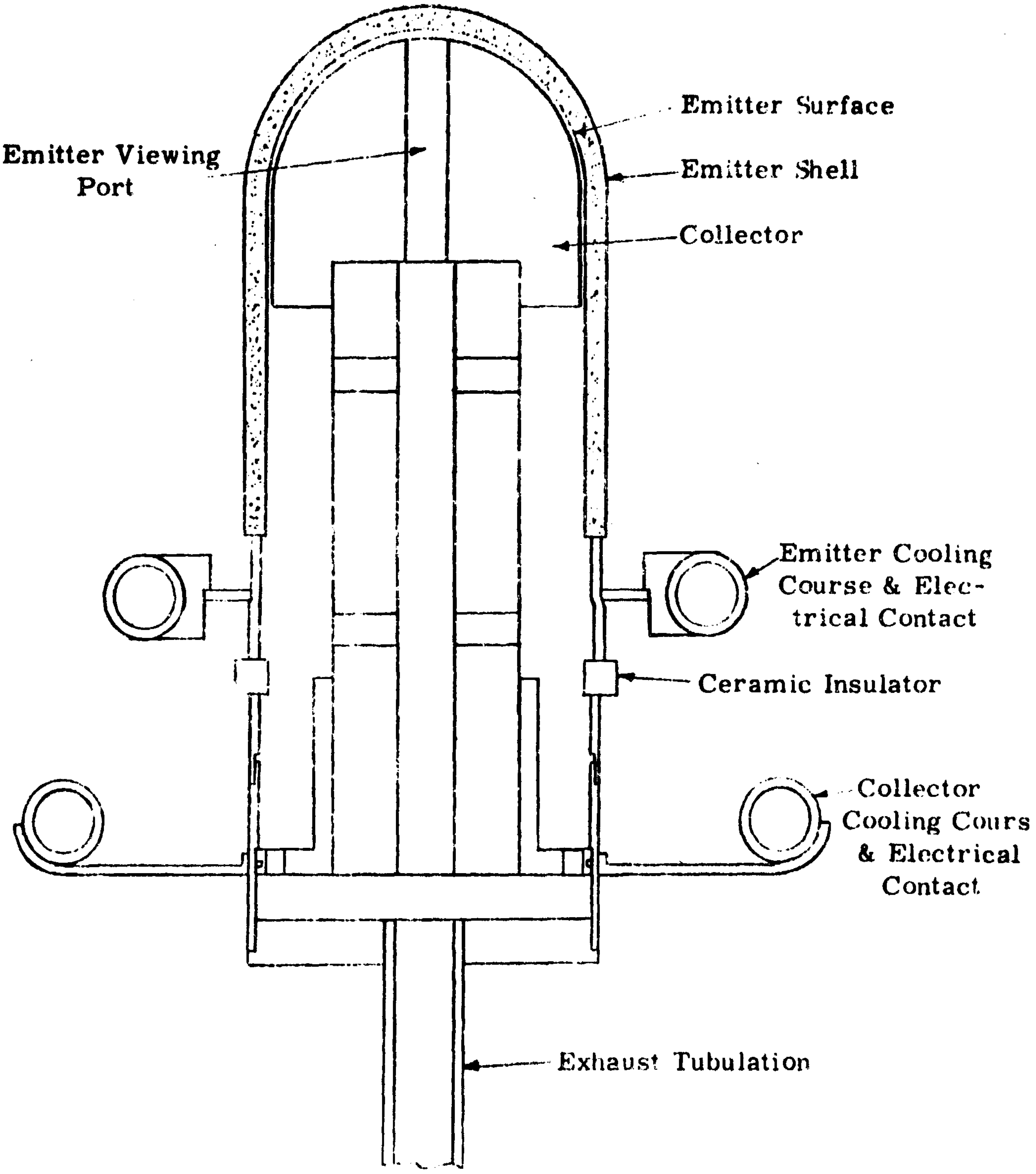


FIGURE 24. THERMIONIC CONVERTER TEST VEHICLE

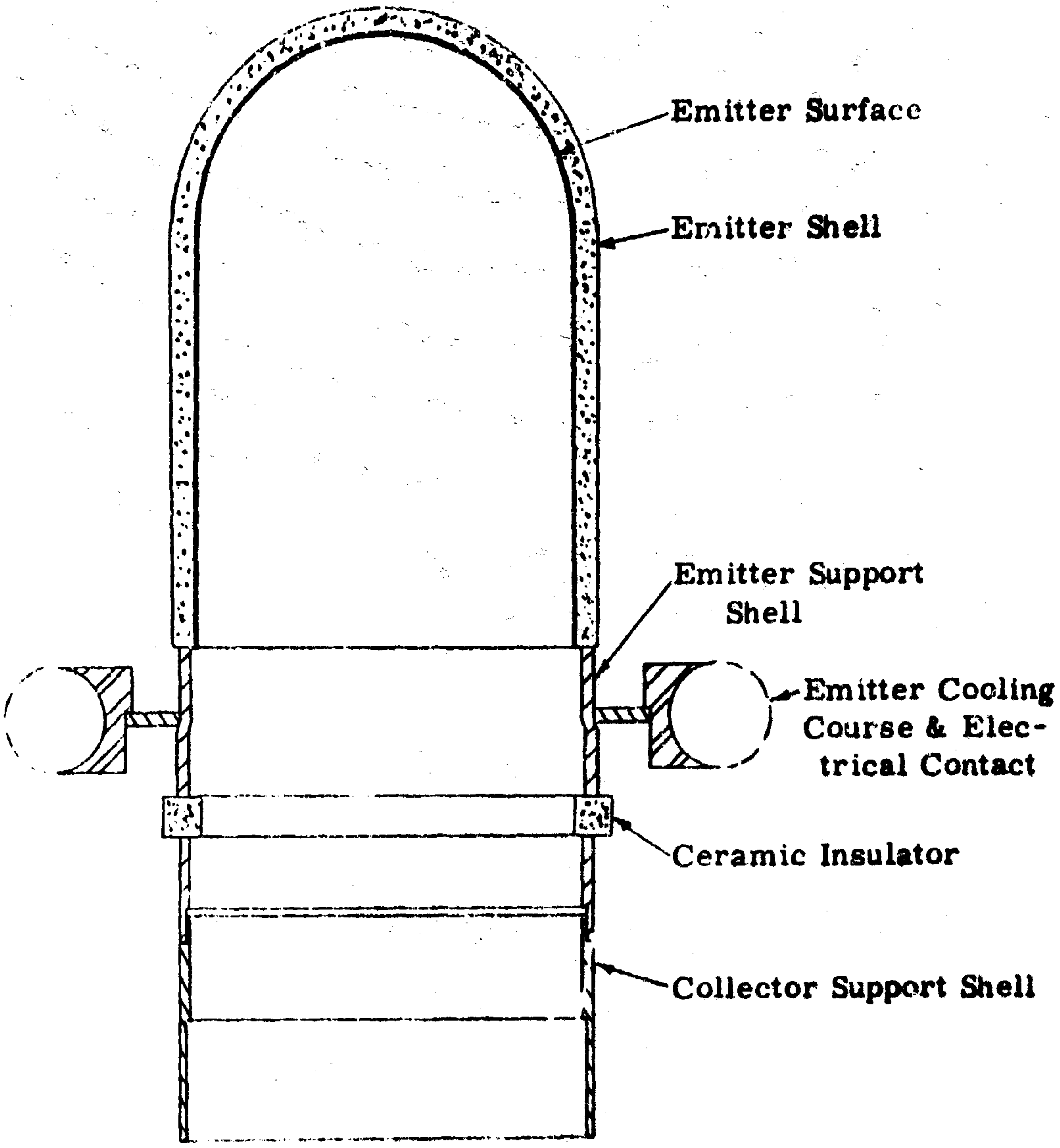


FIGURE 25. EMITTER SUB-ASSEMBLY

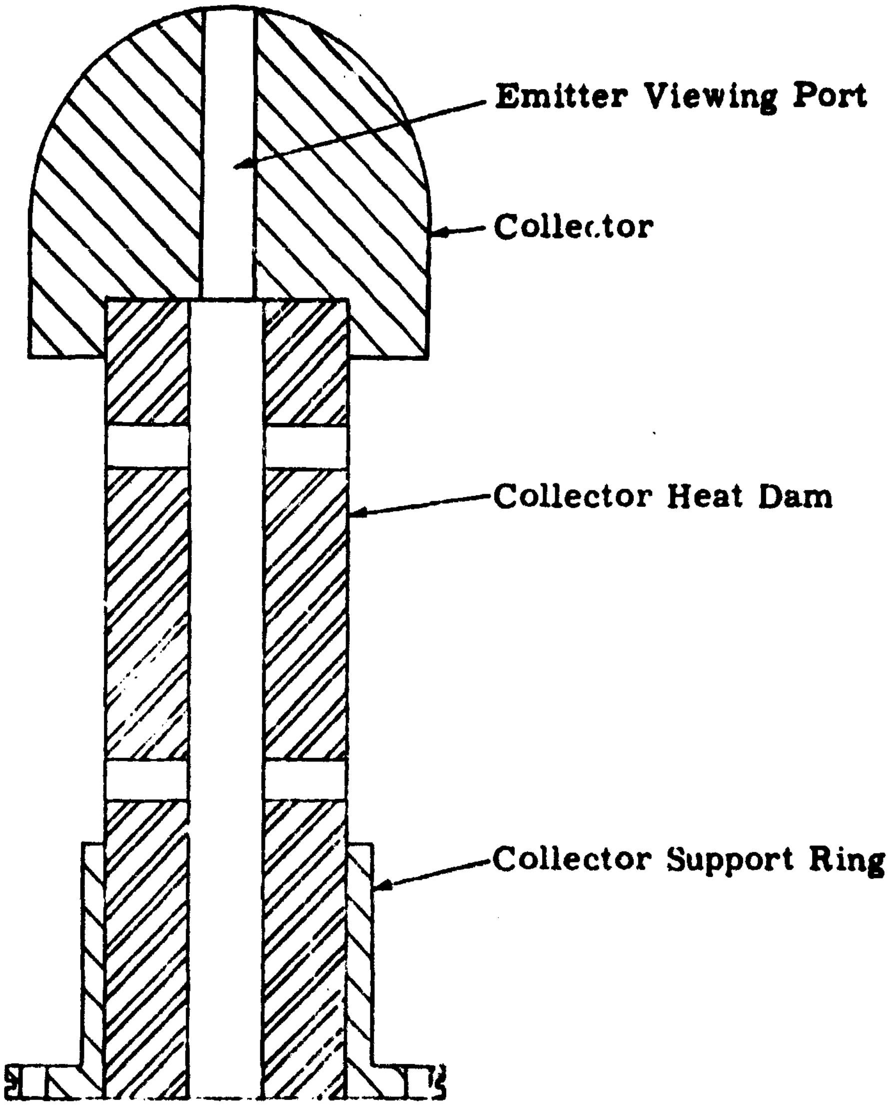


FIGURE 26. COLLECTOR SUB-ASSEMBLY

lector sub-assembly was inserted into the emitter sub-assembly, positioned radially by means of jigging wires and brazed in place. After the wires were withdrawn, the exhaust tubing sub-assembly, shown in Figure 27 was welded in place and the converter evacuated and cesiated. Electrical contact to the converter was made through the emitter and collector coolant courses. Only materials having proven excellent cesium compatibility, (ceramics, metals, and brazing alloys) were employed in converter construction in conjunction with the best known processing techniques.

Design of the converter was undertaken before completion of the permeation studies to allow sufficient time to eliminate the initial fabrication problems inherent in any converter design. The design was so arranged as to permit simple substitution of the optimum shell material when a final selection was made.

The converter was designed with a cup-shaped emitter in order to minimize the surface area of emitter shell exposed to the fossil fuel environment. Completed permeation studies indicated a considerable degree of improbability of finding a totally impermeable material; therefore, it was considered important that the surface area of the hot portion of the emitter shell be held to a minimum.

The emitter shell material chosen for the initial converters was a conventional sintered alumina, Silk City SC98D. This ceramic body showed low permeation and good outgassing characteristics during the materials testing portion of the program. Extended compatibility tests established a satisfactorily high level of

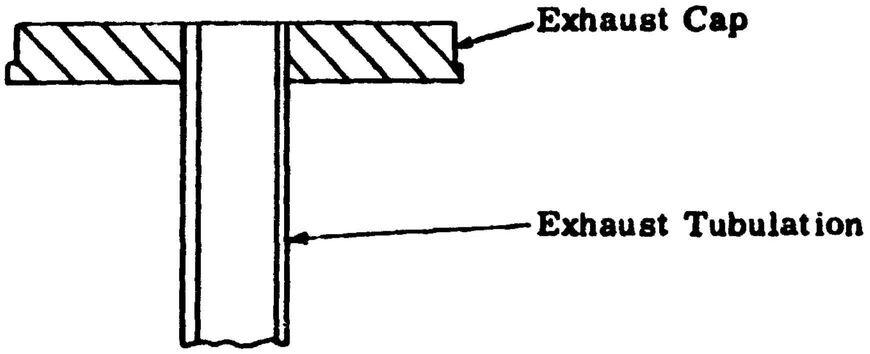


FIGURE 27. EXHAUST TUBING SUB-ASSEMBLY

stability in the presence of cesium vapor

Four converters of the initial design were fabricated. All failed on exhaust or early in the testing period due to cracking of the alumina emitter shell. Tensile tests showed the ceramic parts, the SC98D body of Silk City Ceramics and Tool Company to be of low variable strength. A program was set up with the vendor, using RCA funds, to improve the strength of this ceramic, but did not meet with adequate success. The design approach based on the use of these parts was therefore discontinued.

2. Alternate Emitter-Shell Design

Two converters were constructed utilizing a silica barrier directly coated onto a molybdenum emitter cup. One converter had alumina plasma sprayed on top of the silica. Both failed to survive the exhaust cycle. The failure of the alumina-on-silica converter resulted from a leak in a brazed joint; the failure of the plain silica converter was caused by the rupture of the coating at a deep scratch which was accidentally made in the domed portion. Further work on this approach was discontinued because of greater success shown with the double-walled structure discussed below.

Another general barrier approach involving the use of a molybdenum-molybdenum disilicide-silicon carbide laminated barrier was pursued without success. In spite of encouraging reports in the literature on this construction, the suppliers were unable to produce satisfactory continuous coatings and the approach was abandoned.

3. Double Walled Emitter-Shell Design

As a result of the disappointing emitter-shell failures of the initial converters, a detailed review was undertaken not only of these most recent converters, but of all fabrication and test data related to prior RCA fossil-fuel-heated converters. The following pertinent facts were determined.

a. **Modulus of Rupture**

The highest possible rupture strength is required to prevent failure due to thermal shock or ceramic-to-metal seal stresses.

b. Emitter-Barrier Shell Contact

The incidence of barrier failure due to cracking (as a result of stresses caused by differential thermal expansion) is increased when the emitter and barrier are in intimate physical contact. No incidence of failure was noted during thermal testing of separate barriers without an emitter. While a metalized or vapor-deposited emitter appeared to result in a lower barrier failure rate than solid emitters, in no case were the results fully satisfactory. In order to make satisfactory use of alumina as a barrier material, it was clear that some physical separation of the emitter and barrier was necessary.

The double-walled construction of Figure 28 was employed to overcome these limitations. The barrier was fabricated using the high-alumina body Type 7225 from Frenchtown Porcelain Company.

This ceramic, which has a somewhat lower maximum operating temperature than desired, was known to provide high rupture strength. Its availability permitted rapid evaluation of the basic design approach. Heat transfer to the emitter cup was enhanced by the inclusion of a partial pressure of helium (approxi-

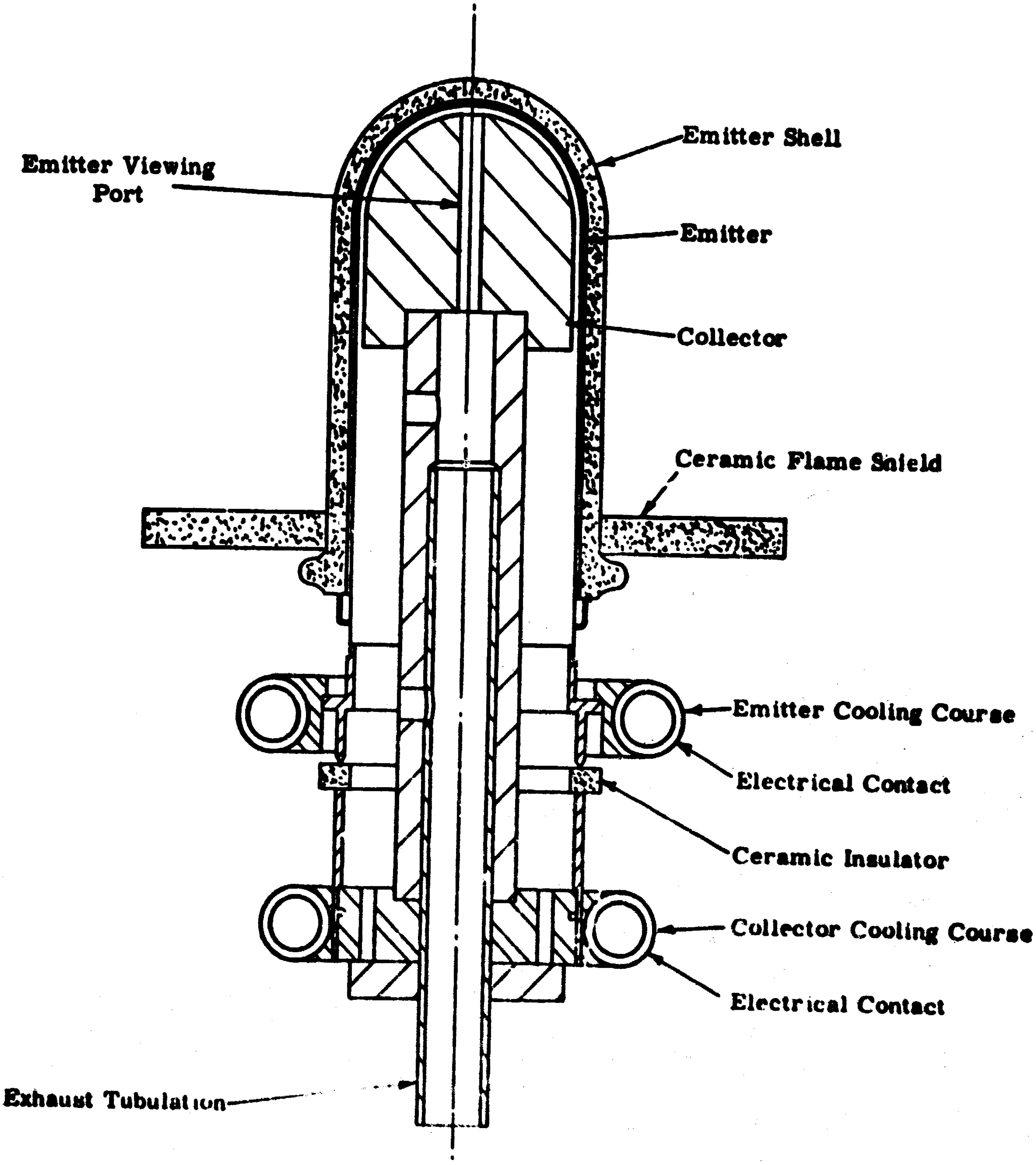


FIGURE 28. DOUBLE WALLED CONVERTER TEST VEHICLE

mately 0.9 atmosphere) in the interspace. The effective emitter area in this design is approximately 12 square centimeters.

The first three converters of this type employed 0.005-inch-thick molybdenum emitter cups. The initial test results were very encouraging. Power output ranging from 4.6 to 11.4 watts were obtained on exhaust at an emitter temperature of approximately 1200° Centigrade. No thermal shock failure of the barriers was observed. However, after a few hours of operation, the thin molybdenum emitter cup of each converter buckled inward toward the collector as a result of creep induced by the external pressure of the helium gas. One of these converters was subjected to severe thermal cycling without emitter shell failure.

The fourth double-walled converter had a reduced helium pressure (approximately 0.1 atmosphere) in the interspace and a 0.015-inch molybdenum emitter wall. This converter was placed on continuous life test at an emitter temperature of approximately 1270° Centigrade. A power output profile for this converter is shown in Figure 29. An increase in circuit resistance due to oxidation of the electrical connections caused the early severe slump at approximately 200 hours. When this condition was corrected, the converter again operated at about 2 watts for a brief period. The power output then dropped rapidly to zero at about the 380-hour point. The reason for this loss of power was not known at the time, and the test was continued to obtain information on the performance of the new design. Analysis at the end of life showed that the converter had lost its vacuum integrity, probably at the 380-hour point, because of porosity in a small area of the ceramic barrier. This, in turn,

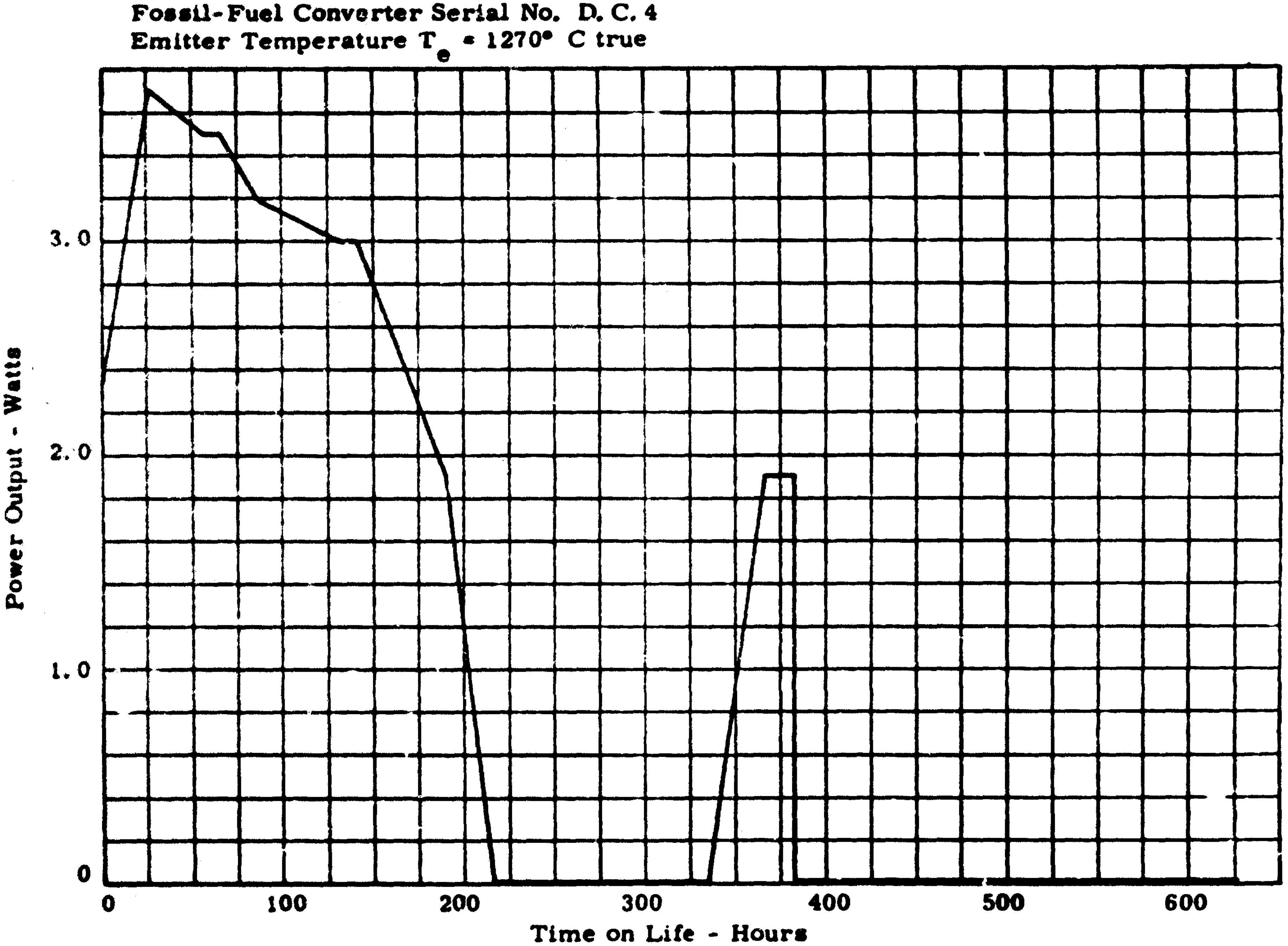


FIGURE 28. LIFE TEST POWER OUTPUT HISTORY

was shown to have resulted from local overheating of the barrier due to burner nonuniformity.

Converters five through nine were of identical construction. All had a 0.015-inch emitter cup with a 0.006-inch-thick "heat dam" section to minimize excessive thermal conduction losses and to improve emitter temperature uniformity. These converters all produced low power output (1.1 to 2.8 watts). Three were subjected to cycled life testing (20 hours on, 4 hours off) and achieved a cumulative total of 586 hours and 15 complete thermal cycles. All failed through either or both of two mechanisms: porosity of the barrier due to local overheating, or destructive oxidation of the short exposed molybdenum "heat dam" section.

The barrier overheating was due to nonuniform operation of the fossil-fuel burner as discussed above. The flow pattern of hot gases over the converter was modified, and more uniform heating was achieved. With the modified burner, a maximum point-to-point temperature variation of 40° Centigrade was observed and was considered acceptable

The converter design was modified to remove the exposed molybdenum "heat dam" from contact witn the surrounding air. The vacuum envelope was completed through the use of a special RCA sealing alloy of excellent corrosion resistance and improved thermal expansion match to the ceramic parts. A section view of this structure is shown in Figure 30.

The tenth converter employed this construction and provided a power output of approximately 7 watts continuously on life test

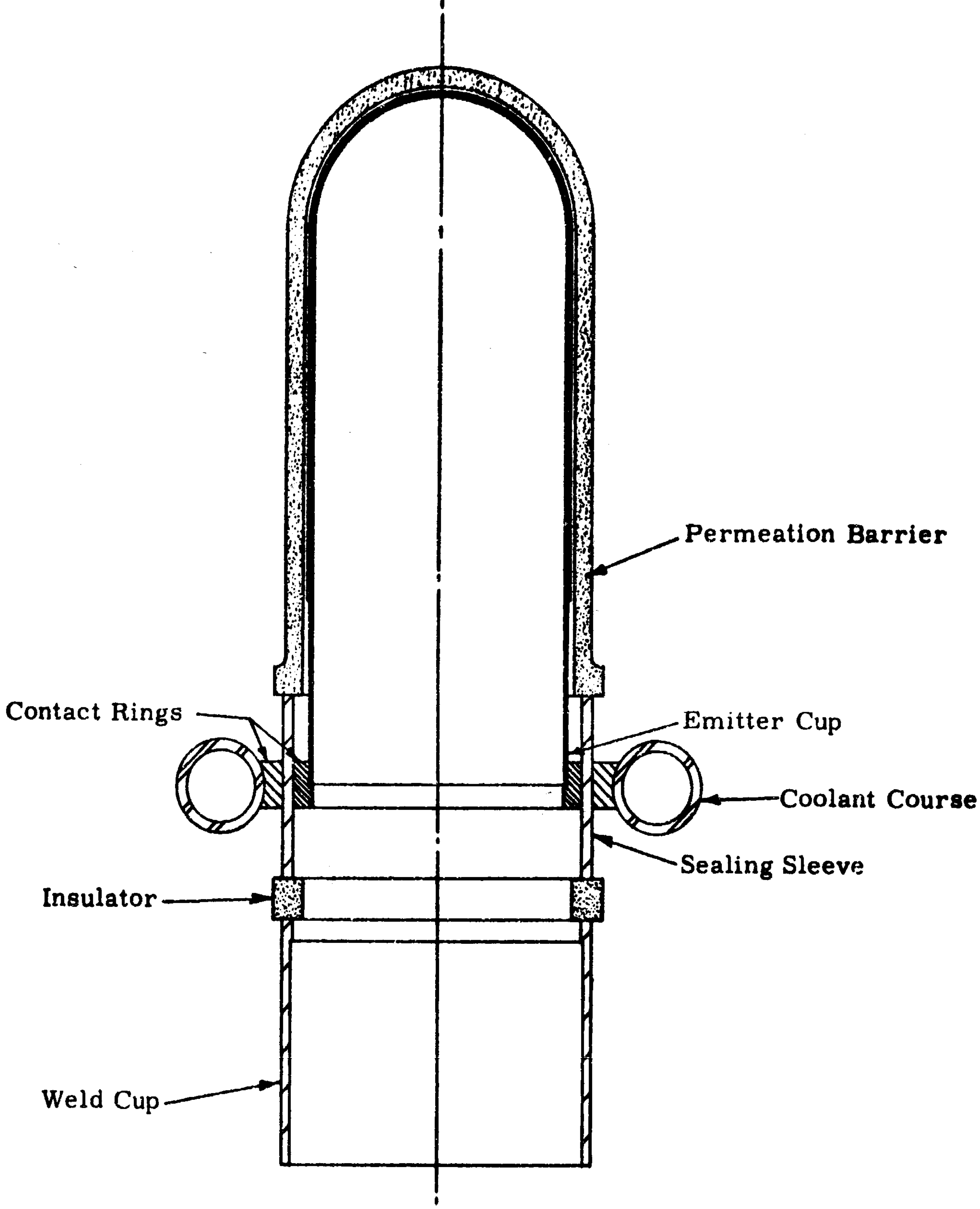


FIGURE 30. IMPROVED EMITTER SUBASSEMBLY

for 44.5 hours. At this time control was lost of the burner temperature which rose several hundred degrees, overheating the barrier shell. The shell collapsed partially around the emitter. While the converter survived this treatment and continued to operate for another 120 hours, the power output dropped to approximately 2 watts due to nonuniform heating of the barrier and emitter. The test was discontinued with the converter still operable at this low level.

An improved barrier material, the Frenchtown 7325 (99.9+ percent alumina body), became available in useable shapes, and all subsequent converters of the double-walled type employed barriers of this material. This improved material combines high strength with an improved margin for high-temperature operation. The eleventh converter, which incorporated the new barrier, failed on the exhaust system due to a leak at the output ceramic seal.

Test experience up to this point had shown that it was difficult to obtain optimized converter operation over the desired range of conditions. The limitation was due to the large temperature differential in the long conductive path in the collector cooling arrangement. Occasionally, the optimum collector temperature could not be obtained because of a cool collector stem, which resulted in a spurious cesium reservoir in that area. The collector structure was revised to eliminate this problem and permit direct cooling of the collector block itself. This re-entrant collector structure, shown in Figure 31, was used on all subsequent converters.

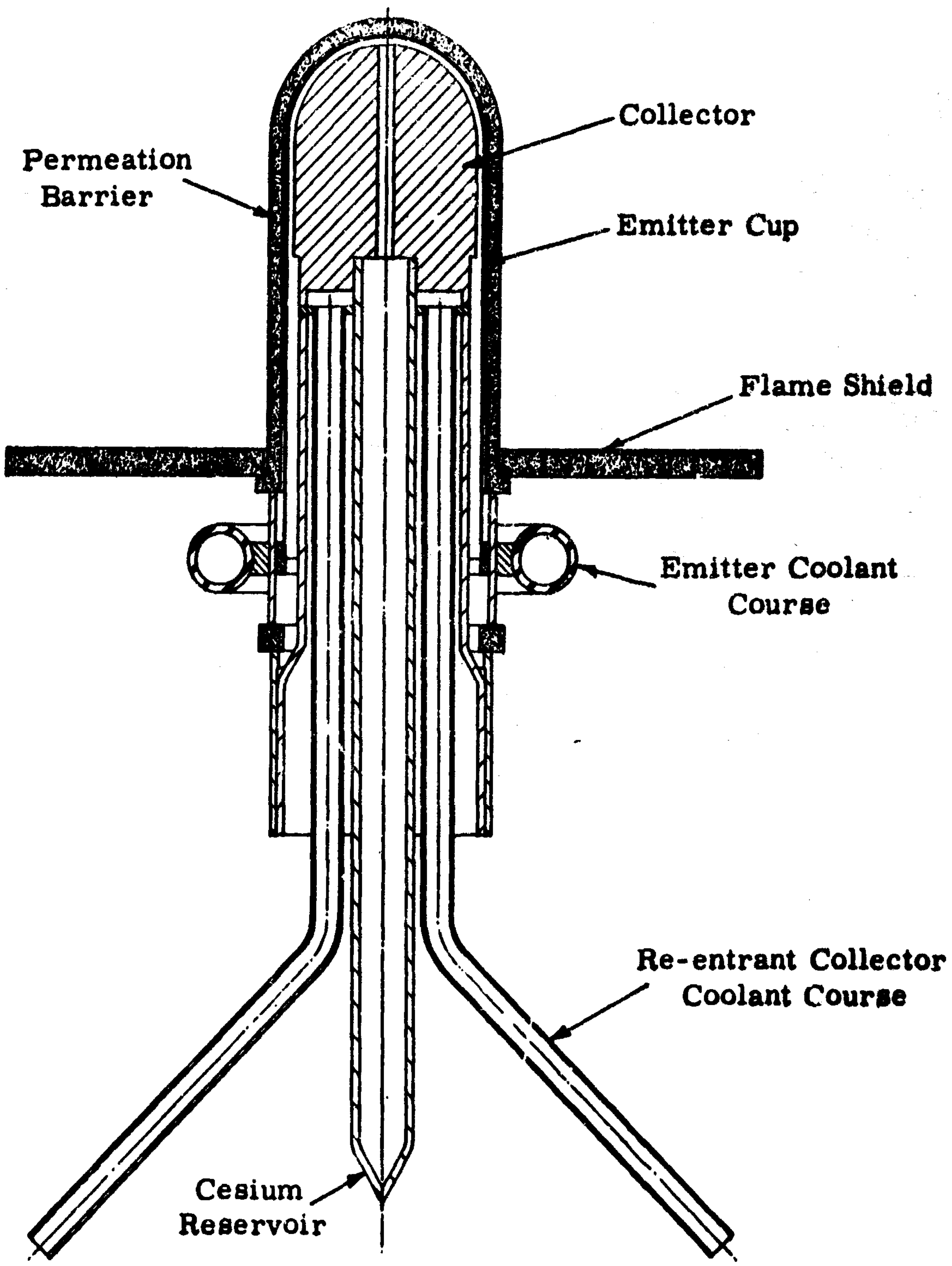


FIGURE 31. FOSSIL-FUELED THERMIONIC CONVERTER

The power output of the twelfth converter, which employed the Frenchtown 7325 barrier, the improved sealing alloy, and the re-entrant collector, was low (less than one watt on test). It was believed that the converter had become contaminated. The converter was cleaned and reprocessed, and when it was rerun it produced a power output of 12 watts during the exhaust cycle. The re-entrant design provided excellent control of the collector temperature. However, the output slumped steadily on test after the converter was sealed off from the exhaust system. Subsequent disassembly and analysis led to the discovery of a minute leak in the collector assembly.

The thirteenth through fifteenth converters failed in assembly. It was shown that the asymetrical geometry and expansion mismatch of the nickel emitter coolant course was responsible for nonuniform ceramic seal stresses and occasional failures, including that in the eleventh converter. A symmetrical molybdenum coolant course was therefore designed.

The sixteenth double-walled converter employed the improvements in the barrier shell material, the special sealing alloy used to attach the shell to the remainder of the converter, the redesigned emitter coolant course, and the re-entrant collector structure. A photograph of the emitter and collector subassemblies is shown in Figure 32. This converter was processed on exhaust with special care. After initial pumpdown, bakeout, and outgassing, the converter was operated from a fossil-fuel burner for 139 hours on a getter-ion pumping system. A cesium distillation apparatus was used to prevent cesium vapor from reaching the getter-ion pump. During this

FIGURE 32. PHOTOGRAPH OF EMITTER AND COLLECTOR SUBASSEMBLIES

period the emitter temperature varied from 1180° to 1295° Centigrade as a result of burner and electrical load variations. Representative power output was 9.3 watts (0.267 volt, 35 amperes) at 1200° Centigrade. During the 139-hour period, the converter was subjected to four complete thermal cycles and two sudden but brief interruptions of burner operation, each lasting a few minutes. After being sealed off from the pump and still, the converter was placed on life test. At this time visual examination of the emitter shell showed no sign of change or deterioration.

The converter was then operated for 1020 hours at an emitter temperature which ranged generally between 1190° and 1290° Centigrade true temperature. A profile of power output versus time at a constant emitter temperature of 1240° Centigrade is shown in Figure 33. Volt-ampere curves were taken periodically throughout life. Several representative curves are shown in Figure 34. It is evident from the curves that operation improved during the initial 200 hours or so and then declined slowly and almost linearly for the remaining 800 hours. A photograph of the converter, taken after 1000 hours of operation, is shown in Figure 35. The rough surface visible on the barrier is due to adherence of flakes of burner insulation which fell onto the converter during life testing. The dark band represents condensed material along the cooler portions of the barrier.

During the life test period, the converter was subjected to seven additional complete thermal cycles and 56 short, abrupt interruptions of burner operation. The converter remained operable, though somewhat low in power output at the end of the test.

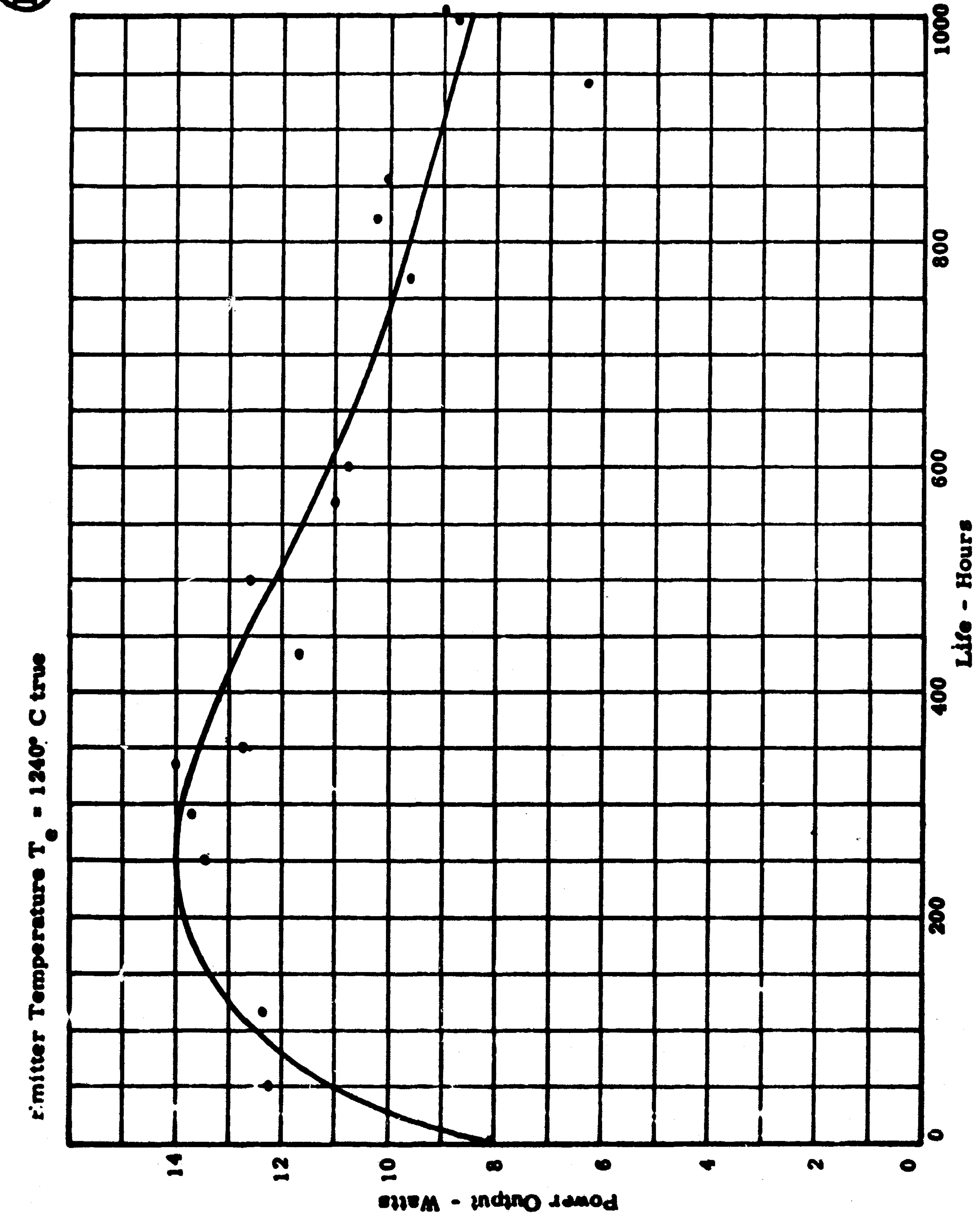


FIGURE 33. LIFE TEST POWER HISTORY

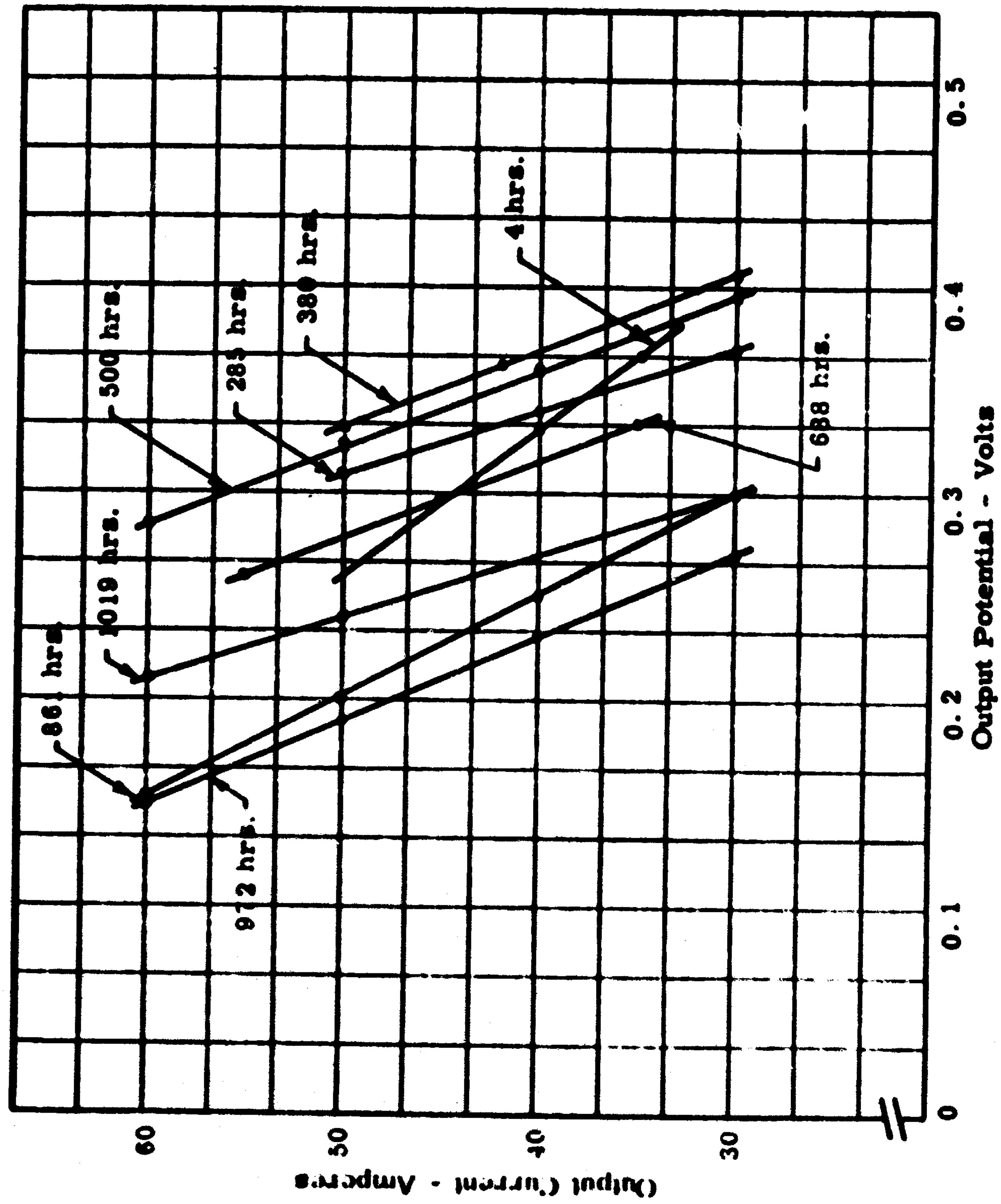


FIGURE 34. VOLT-AMPERE CURVES TAKEN DURING 1000-HOUR LIFE TEST

FIGURE 35. PHOTOGRAPH OF CONVERTER AFTER 1000 HOURS OF LIFE

The next converter was of substantially identical construction. It was exhausted in a similar manner, but a shortage of cesium in the distillation apparatus prevented prolonged operational outgassing on the getter-ion pump. Occasional intermittant short circuiting was observed early in the outgassing period but ceased with time. The converter was accordingly sealed off after 21 hours of outgassing and placed on life test at an emitter temperature which ranged between 1310° and 1360° Centigrade true temperature. After 202 hours of operation and 5 complete thermal cycles, the converter suddenly ceased to operate as the result of an emitter-collector short circuit. A plot of power output versus time at a constant emitter temperature of 1325° Centigrade is given in Figure 36, and representative volt-ampere curves are shown in Figure 37. Figure 38 is a photograph of this converter after 208 hours of operation.

The converter was subjected to careful analysis to determine the cause of failure. The short circuiting was shown to be due to the growth of pure molybdenum crystallites on the collector, shown in Figure 39. A deposit of condensed matter on the collector wall opposite the coolant course was shown to contain cesium oxides, molybdenum oxides and molybdenum hydroxide. The presence of the hydroxide is felt to be a strong indication of the operation of a water cycle mass transport mechanism in the converter. This was, no doubt, responsible for the movement of molybdenum from the emitter to the cooler collector. The emitter-shell structure was shown to be vacuum tight, but on mass spectrometric analysis it was found to contain primarily nitrogen. The outer surface of the emitter was oxidized. It is possible that the emitter-shell space was not thoroughly purged

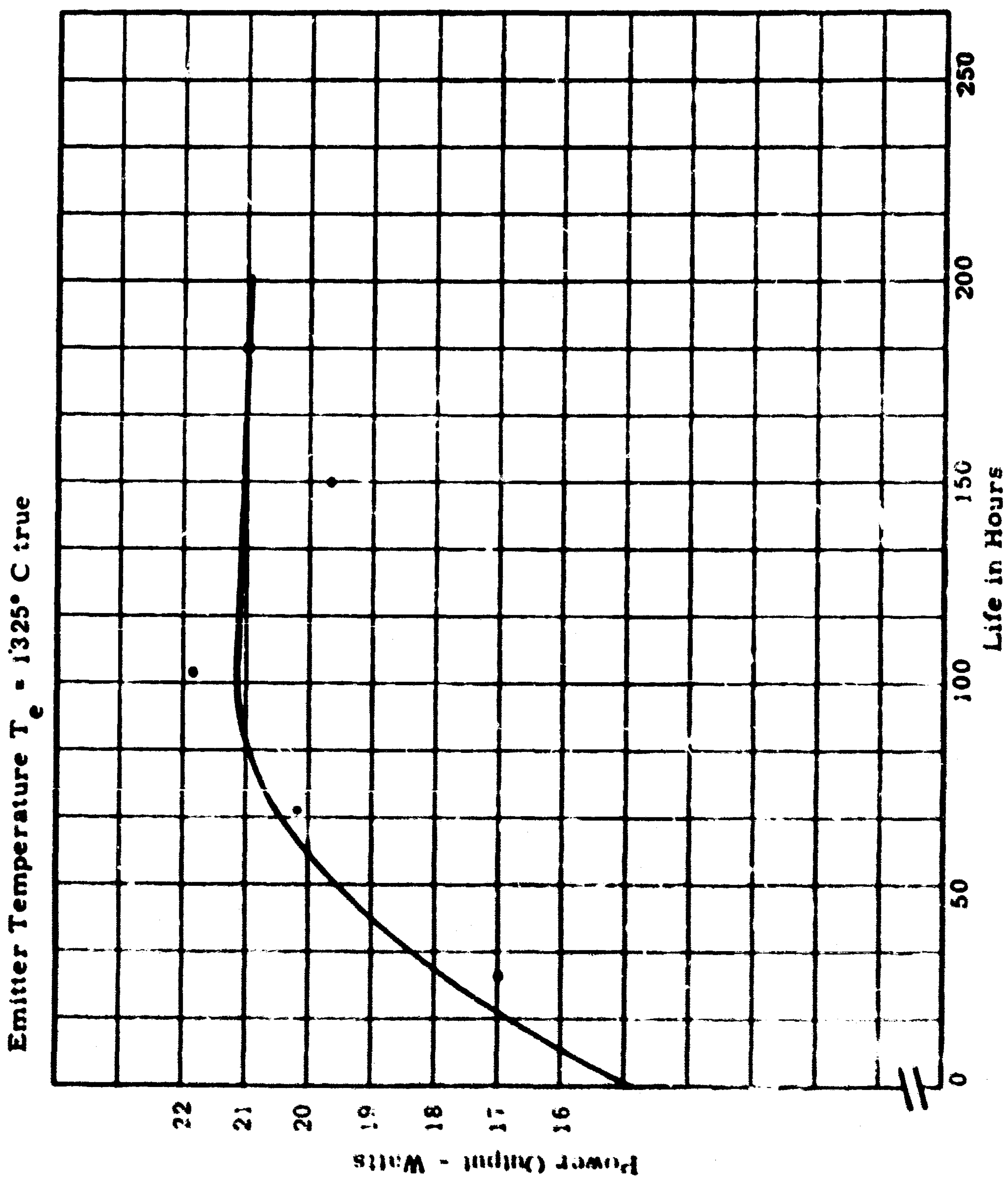


FIGURE 36. POWER OUTPUT VERSUS TIME

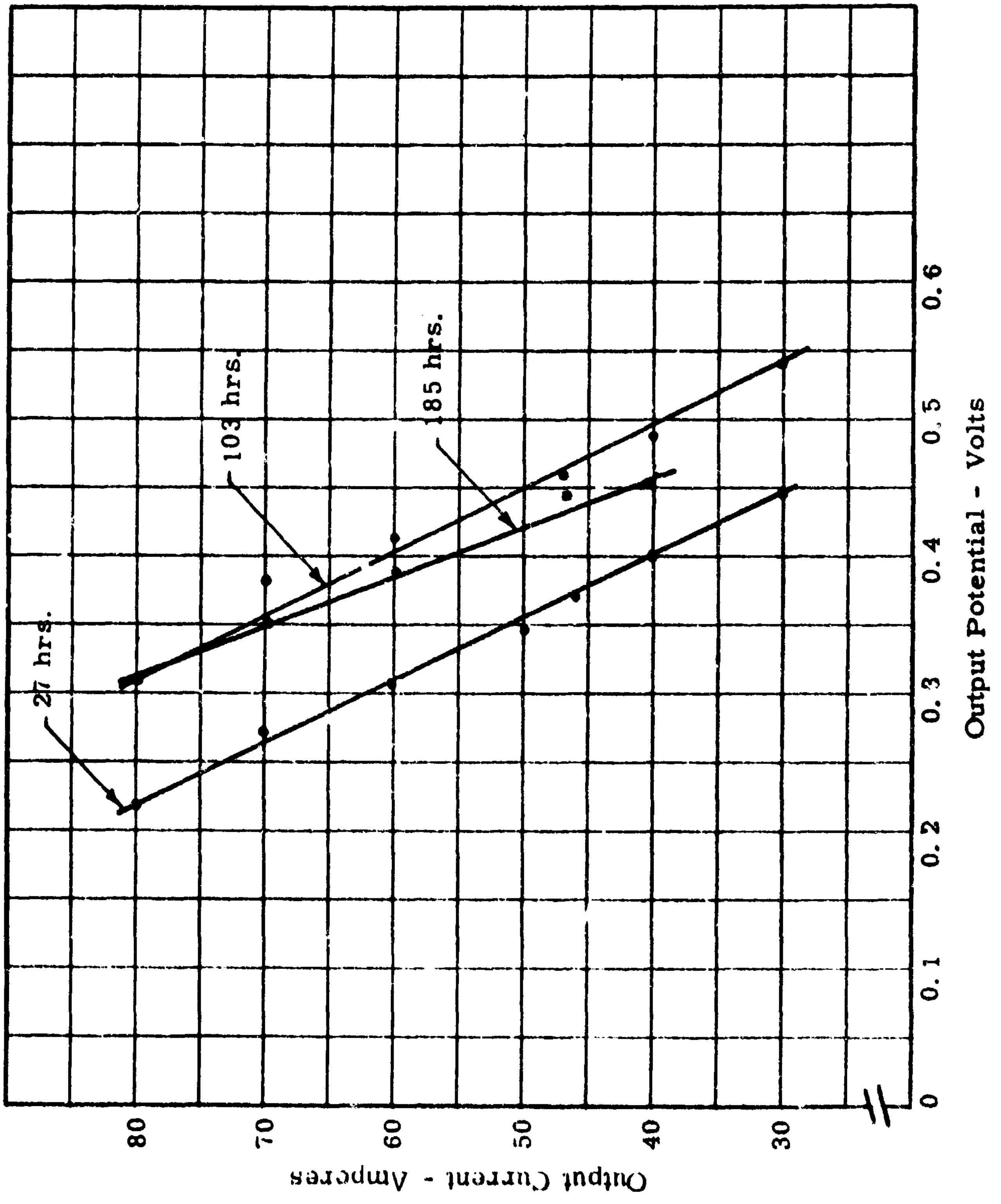


FIGURE 37. REPRESENTATIVE VOLT-AMPERE CURVES FOR VARIOUS POINTS IN LIFE

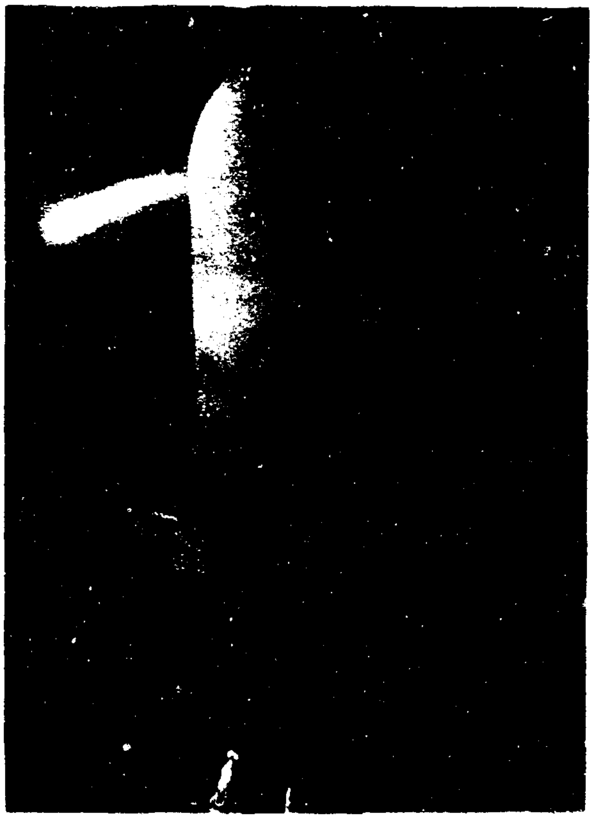


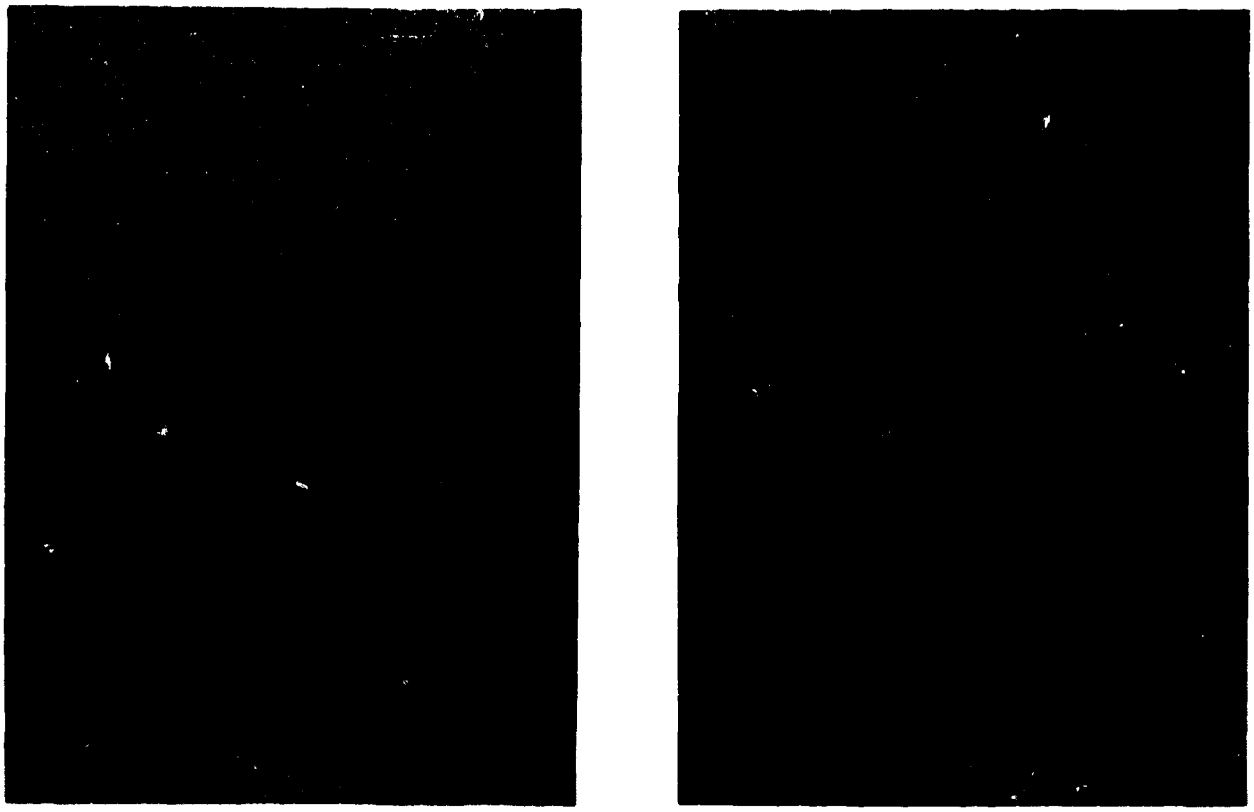
FIGURE 38. PHOTOGRAPH OF CONVERTER AFTER 208 HOURS OF OPERATION

FIGURE 39. MOLYBDENUM DEPOSIT ON COLLECTOR

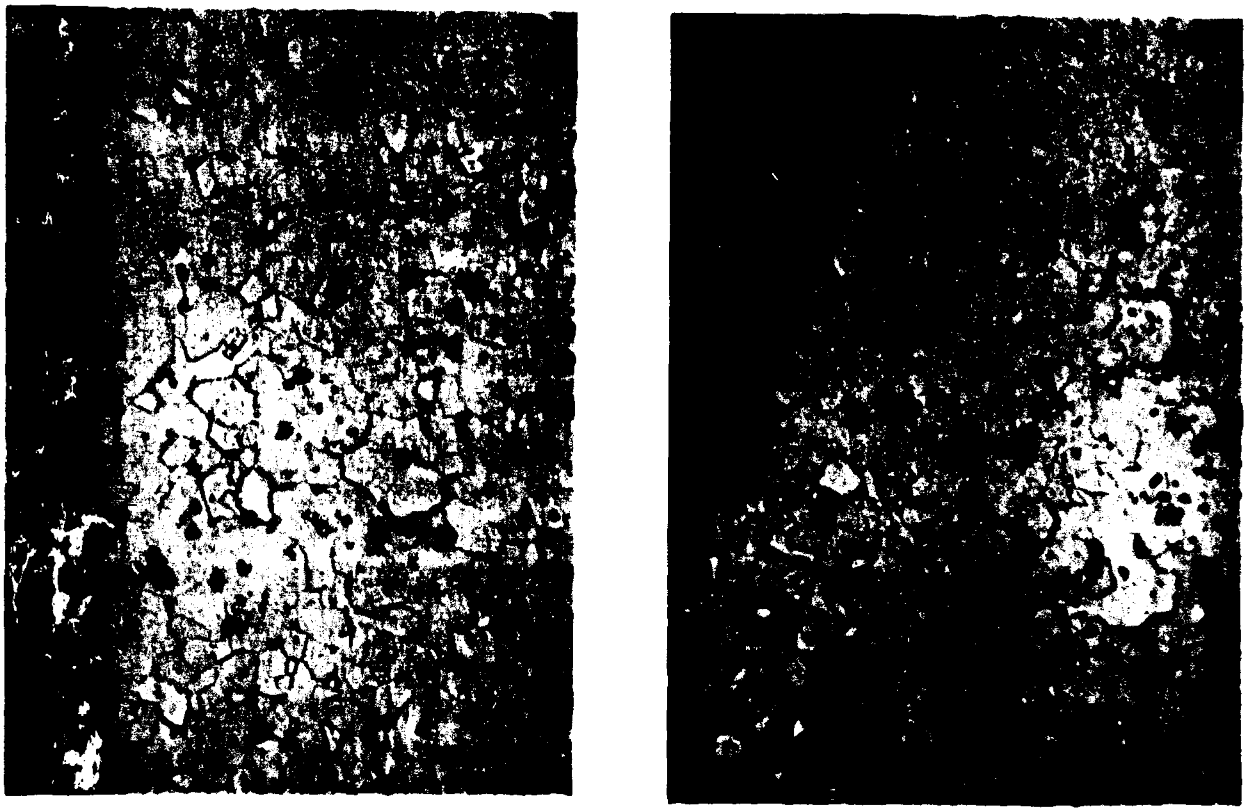
of air prior to brazing and that the subsequent permeation of oxygen and hydrogen into the converter initiated the water cycle. The nitrogen, having an extremely low permeation rate in both molybdenum and alumina, remained in the interface.

The emitter shell of this converter was carefully measured before and after life test and showed no detectable change in dimension. It was subsequently sectioned to determine if its extended operation at high temperature (an estimated 1500° Centigrade) had caused any change in the internal crystal structure. Photomicrographs of the domed area of the shell were taken and are shown in Figure 40 with comparative photographs of an unused shell. Little, if any, change is detectable.

The eighteenth double-walled converter was identical to the preceeding one except for the addition of a 1/8" diameter, 0.010" wall diameter palladium thimble, 2 inches long as shown in Figure 41. The thimble was surrounded by an electrical heater which permitted its temperature to be varied. The purpose of the palladium thimble was to provide a "window" through which any hydrogen in the converter could be vented to the surrounding air by means of the high, selective permeation rate of the palladium, thus preventing the water cycle from proceeding. The converter was operated for 41 hours on the pumping system and then sealed off. The converter was subjected to a simple, 2-variable, 2-level Latin square test in which the emitter (and consequently the emitter shell) and thimble were each operated at two temperature levels. The conditions are outlined in Figure 42. It was hoped through this means, to determine if hydrogen permeation through the emitter shell was a factor in converter opera-



Frenchtown 7325 Emitter Shell as received



Frenchtown 7325 Emitter Shell after 208 hours of operation

FIGURE 40. PHOTOMICROGRAPHS OF DOMED AREAS OF EMITTER SHELLS

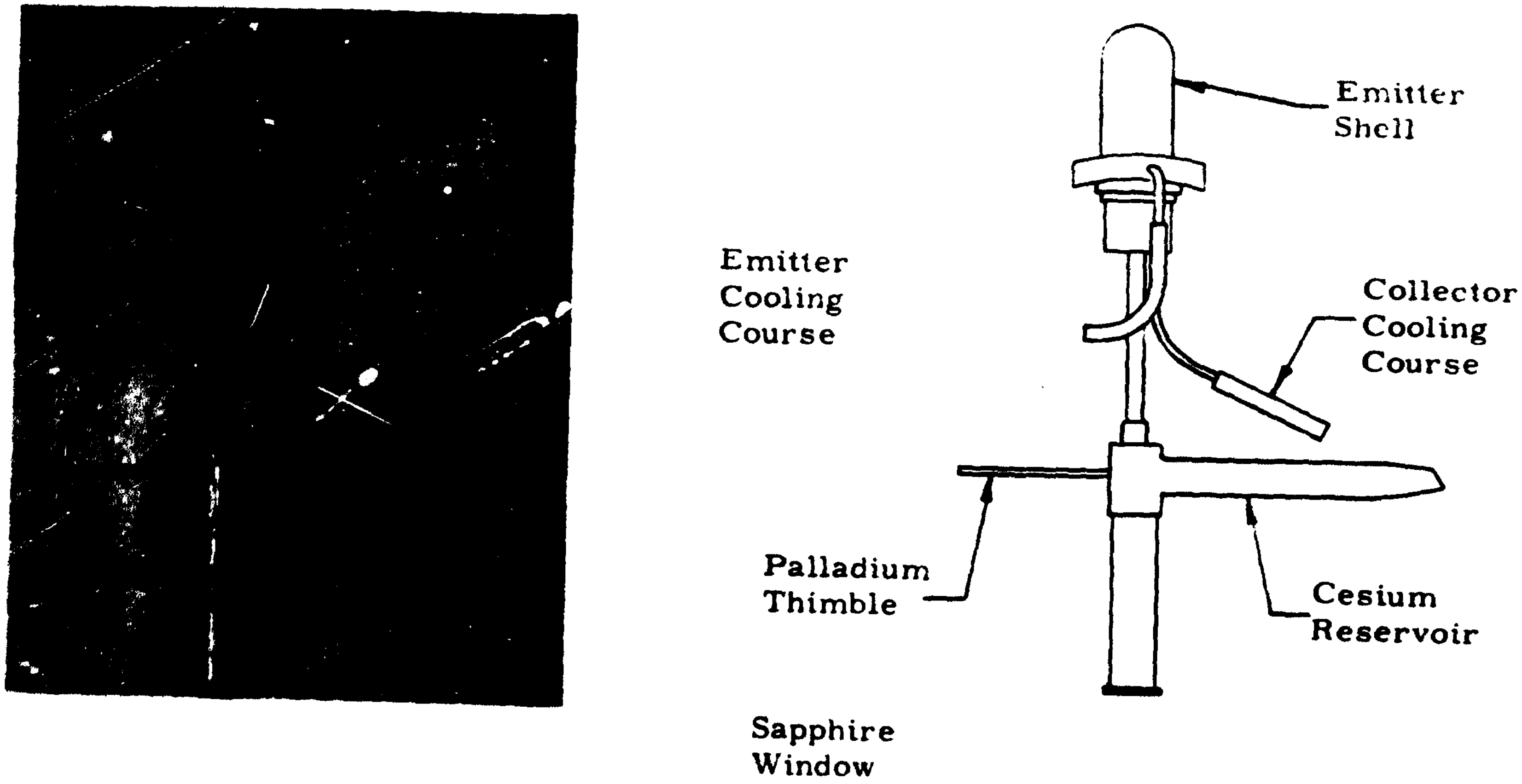
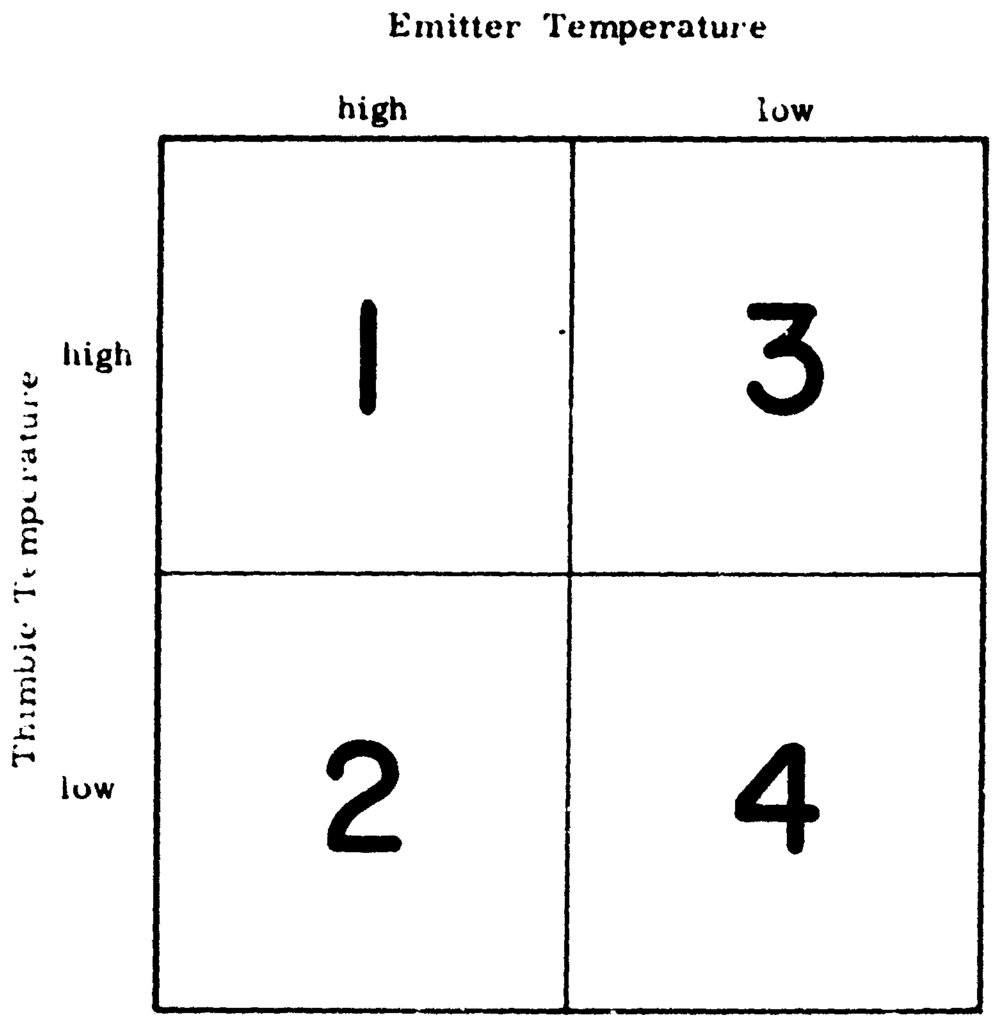


FIGURE 41. FOSSIL FUEL CONVERTER WITH PALLADIUM THIMBLE



		Emitter Temperature	
		high	low
Thimble Temperature	high	1	3
	low	2	4

FIGURE 42. LATIN SQUARE TEST OF PALLADIUM THIMBLE CONVERTER

tion and whether hydrogen permeation out of the converter could be varied by means of the thimble. The converter was operated 24 hours at each condition. Representative volt-ampere curves for the four conditions are given in Figure 43. The results were inconclusive in that the power output was low initially and throughout the test, making the validity of any conclusions somewhat questionable. However, an interesting trend was evident. At each emitter temperature, operation was improved slightly by reduction of the thimble temperature. The only explanations for this unexpected performance seem to be (1) that the hydrogen concentration in the surrounding atmosphere was higher than that in the converter, leading to passage of hydrogen into the converter at the higher thimble temperatures with a resultant loss of power, or (2) that a gas beneficial to converter operation left the converter during the high temperature thimble operation. Further tests with better converters seem to be warranted.

The nineteenth and twentieth double-walled converters (serial numbers 21 and 22) were identical in construction with two exceptions: the first contained a zirconium (0.020"diameter) wire getter located in a moat machined in the collector periphery outside the active area. The second was thoroughly purged in the hydrogen-helium atmosphere to assure the absence of air during the emitter-emitter shell brazing cycle. The converters were operated for 84 and 48 hours respectively on the exhaust system, sealed off and tested approximately 24 hours. Volt ampere curves are shown in Figures 44 and 45. These converters were delivered to USAEL on March 5, 1964.

Curve	T_e °C true	Tp_d °C
1	1330	555
2	1330	325
3	1220	560
4	1230	318

Converter
Type A-1192B
Serial No. 20

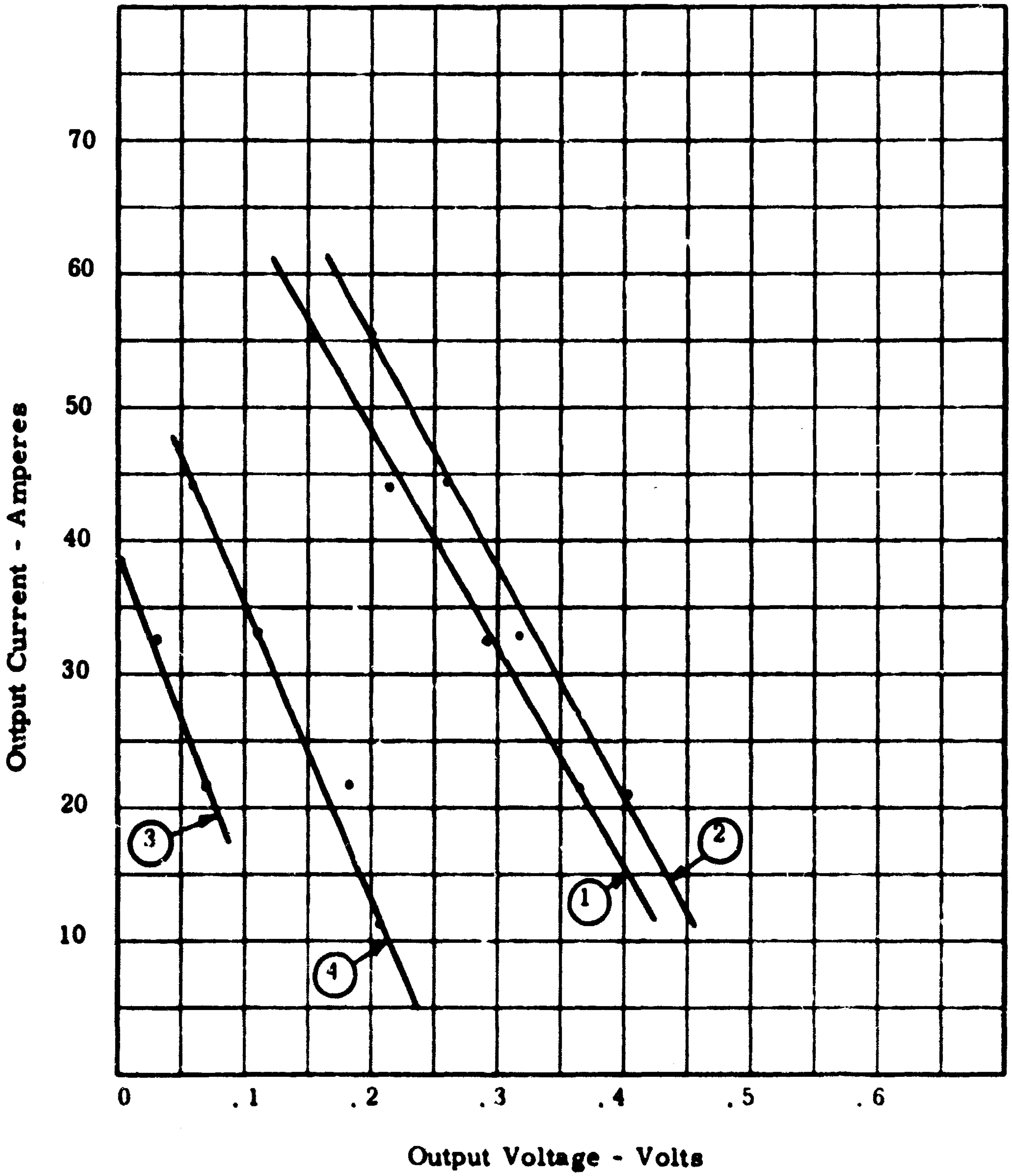


FIGURE 43. VOLT-AMPERE CURVES OF PALLADIUM THIMBLE CONVERTER

Operating Conditions

Collector	Cesium Reservoir
400°C	280°C

Te = True Emitter Temperature °C

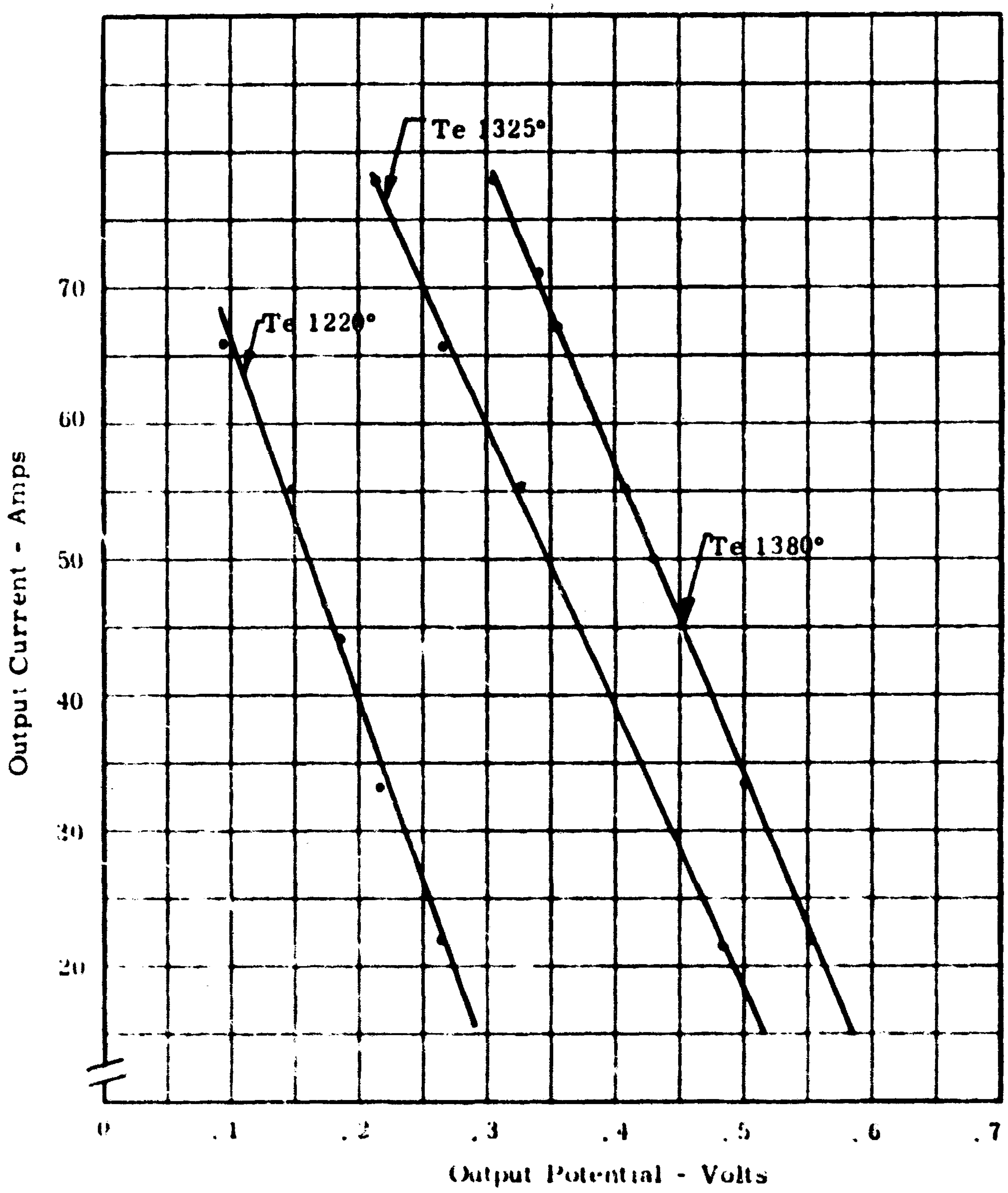


FIGURE 44 VOLT-AMPERE CURVE FOR FOSSIL FUELED THERMIONIC CONVERTER A-1192B, No. DC 21

Operating Conditions

Collector	Cesium Reservoir
380°C	280°C

Te = True Emitter Temperature °C

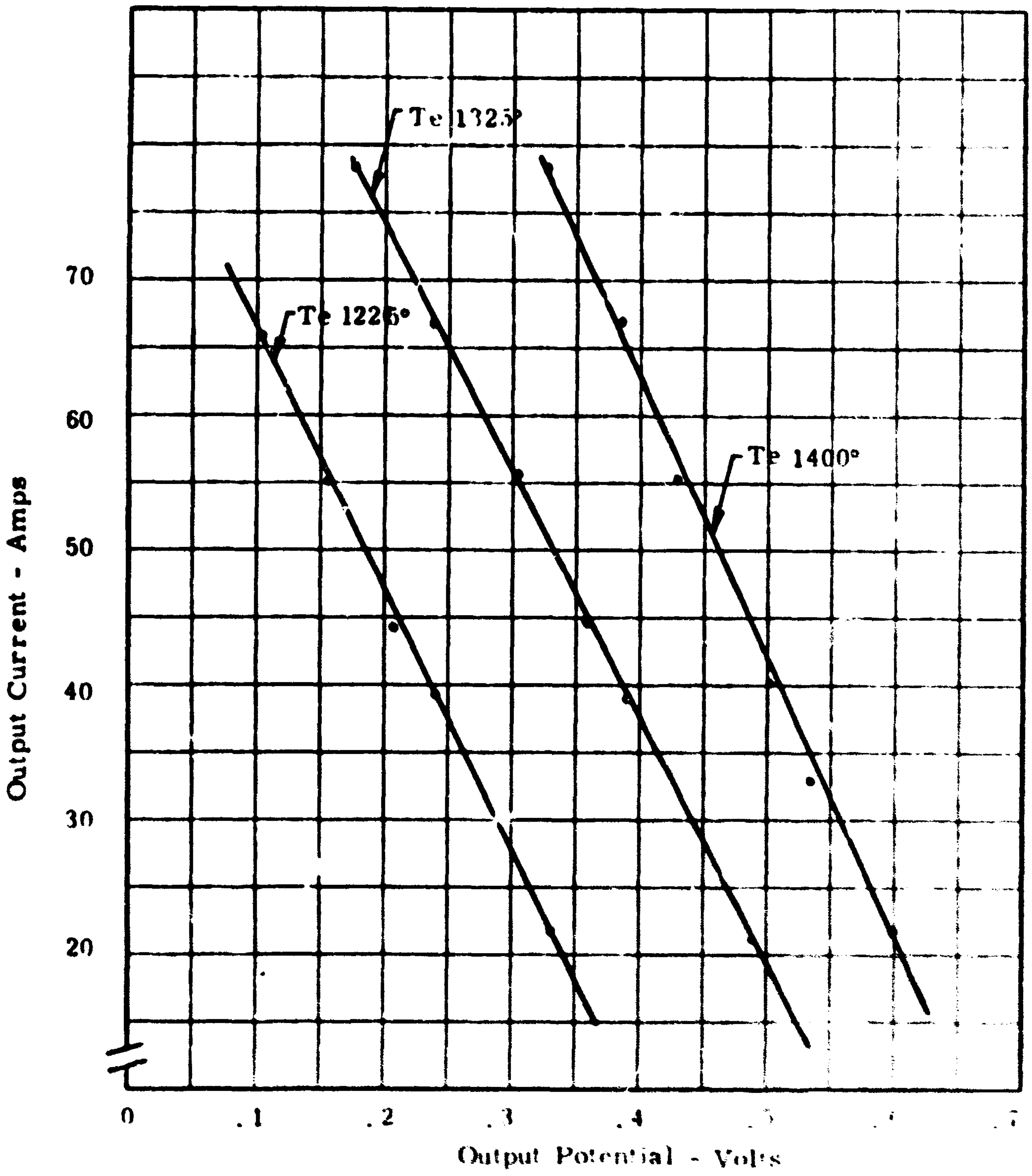


FIGURE 45. VOLT-AMPERE CURVE FOR FOSSIL FUELED THERMIONIC CONVERTER A-1192B, No. DC22

4. Thermal Shock and Corrosion Tests

a. Thermal Shock

Two converters of the double-walled construction were subjected to thermal shock testing. One converter of this type, which had developed an internal emitter-collector short as described above, survived 12 thermal cycles of increasing severity as follows:

TABLE V THERMAL SHOCK TEST DATA

Cycle	Initial Temperature (°C)	Final Temperature (°C)	Time (minutes)
1	25	1400	54
2	25	1000	2
3	25	1400	20
4	25	1375	10
5	25	1325	10
6	25	1430	5
7	25	1410	3.5
8	25	1400	3.5
9	25	1405	4.5
10	25	1400	2
11	-40	1400	7
12	-40	1400	4.5

During the last six cycles, the converter was cooled rapidly by removing it from the burner at approximately 900° Centigrade. The entire converter remained intact throughout these tests. No evidence of impending failure of any kind was noted. The final test in the series exceeds the requirements of the contract.

Another converter, the seventh in this series, was cycled from room temperature to 1400° Centigrade for USAEL representatives. During this test the converter, at room temperature, was inserted directly into a burner operating at full power, allowed to reach the operating temperature, and removed directly into the air, again without failure.

b. Corrosion

(1) Silk City SC98D Alumina

No corrosive effects were noted as a result of the relatively short time periods for which converters with this barrier material were tested in the fossil-fuel burner. The SC98D permeation sample showed some discolorations at the edges of the heated zone after operation in the fossil fuel, but no other change was evident.

(2) Frenchtown 7225 Alumina

As noted above, several samples of Frenchtown 7225 body became porous on overheating. This condition appeared to be related to crystal growth in the body and evaporation of the higher vapor pressure constituents rather than corrosion in the sense of a chemical reaction.

(3) Frenchtown 7325 Alumina

The Frenchtown 7325 high-purity alumina body showed no corrosion or significant change in dimension through the 200-hour life test, although the surface texture of the part was noticeably rough to the touch after life. It was not possible to obtain a complete appraisal of the corrosive effects on the surface of the 1000-hour converter due to the large quantity of firebrick material adhering or completely glazed to it. Both converters showed staining of the ceramic by condensation products in successive bands along the area of thermal gradient where the barrier passed out of the burner. No detrimental effect was found to be associated with these bands, however.

(4) Coors BD995 Beryllia

During the fossil fuel heated permeation tests, there was obvious spalling of material from the BeO sample. A thin film of material, shown by analysis to be BeO, covered the fossil fuel burner and exhaust hood surfaces after the test. It is evident that unprotected BeO cannot be used in a fossil fuel environment without danger to surrounding personnel due to the release of toxic material.

(5) Texas Instrument's ScS Pyrolytic Silicon Carbide

Small grayish-white spots appeared randomly throughout the exposed area. No visible damage to the sample was observed with the exception of cracks previously mentioned.

5. Life Test Positions

Three life test positions were constructed under RCA sponsorship. The positions have chamber-type burners using natural gas and oxygen as the feed gases. Safety controllers were provided against accidental operation of the burner outside the desired temperature range. These positions were utilized for the test and life test portions of the program.

SECTION V

CONCLUSIONS

1. One thousand hours of operation of a fossil fuel heated thermionic converter is possible and was demonstrated using an aluminum oxide emitter shell.

2. Aluminum oxide has the lowest gas permeation rate of the materials tested in a fossil fuel environment and is to be preferred for operation as a permeation barrier.

3. The thermal shock resistance of aluminum oxide is satisfactory for fossil fuel heated thermionic converter service.

4. Beryllium oxide is unsatisfactory for operation in a fossil fuel flame environment because of excessive corrosion leading to the release of highly toxic byproducts. Pyrolytic silicon carbide showed a low and probably insignificant rate of corrosion. Aluminum oxide showed no detectable corrosion.

5. Permeation of the three non-metals tested was shown to be highly selective. It may therefore be possible to fabricate a composite permeation barrier composed of layers of materials which will have a negligible net permeation rate.

6. Reproducible gas permeation rate measurements of very high sensitivity (10^{-12} liter torr/cm^2 sec.) are possible through the use of gas collection techniques coupled with modern ultra-high vacuum techniques. The identification of individual gas species is made possible by the latest high sensitivity mass spectrometric equipment.

SECTION VI

RECOMMENDATIONS

The results obtained to date have defined several areas in which additional effort can be fruitfully devoted. It is felt by RCA that the 1000 hour operation test achieved under this contract is no more than an indication of potential. With this conviction in mind, the following recommendations for further work are made.

A. Fossil Fuel Generator

Initiate development of a prototype lightweight, silent, generator in the 60-300 watt range. The present device life is felt to be sufficient to make this step possible with component replacement every 500-1000 operational hours, i. e., every month or two, which is considered to be a tolerable level. Further converter improvements will follow with resultant extension of this replacement cycle.

B. Device Improvement

1. A plot of power output vs time for the 1000 hour life test of a converter in a fossil fuel shows a non-uniform profile, as discussed in Section IV, above. The cause of the non-uniformity was indeterminate, being possibly related to assembly and exhaust procedures or to gas permeation of the converter envelope. A single test of this kind is an inadequate base for engineering conclusions. It is important that further life testing be performed to determine the reproducibility of the observed results and that carefully controlled tests be carried out to separate the variables. This should

be followed by appropriate processing and/or materials changes.

2. Although aluminum oxide was found to be the best of the emitter shell materials tested, it does display a finite permeation rate. The search for further improved barrier materials should continue. Two directions seem to have merit:

   a. Multi-layer barriers in which a combination of materials is used to exclude all significant permeation. For example, if a material which selectively permeates only oxygen were coupled with a material which permeates hydrogen, but not oxygen, there would be no net permeation.

   b. Improved individual materials are still possible. The range of available refractory materials is expanding steadily, largely as a result of the nuclear and space programs. Zirconium diboride, free-standing molybdenum disilicide and yttrium oxide are a few examples of materials for which it is recommended that permeation measurements be carried out.

   c. The tolerance of a thermionic converter to the various gases has not been quantitatively determined and should be established. This investigation is necessary since all materials measured to date show finite, if low, permeation rates which may cause a reduction in extended life performance. With possible barrier materials showing selective permeation characteristics, it is important to match the gas passed by a particular barrier with a relatively high level of converter tolerance to that gas.

   d. It appears possible to process permeating gases by conventional techniques such as gettering,or to vent them through selective "windows" such as hydrogen through palladium or oxygen through silver. Controlled experiments should be carried out to establish the effectiveness of this approach.

e. The mechanism of permeation in the non-metals is not thoroughly understood. A program of special tests aimed at deducing information on the permeation process and its controlling variables, is strongly recommended. The development of an analytical expression for permeation could lead to the ability to predict barrier performance without the need for resorting to the present "cut and try" approach.

f. The design approach taken in the development of a thermionic converter for this contract involved the physical separation of the emitter and emitter shell to avoid the adverse effects of thermally induced stresses between the two. The result was the achievement of physical stability of the shell and excellent performance under thermal shock. This stability in turn permitted the 1000 hour life test to be successfully carried out. The approach has the disadvantage of placing a relatively high thermal impedance between the emitter shell and the emitter. The result is a temperature drop of approximately 200° Centigrade in this area and consequently, a higher shell temperature than is desirable for a given emitter temperature and level of converter operation. To reduce this differential, a conductively bonded emitter-barrier structure is desirable. Several very promising approaches to this problem are under investigation, or have been proposed. These should be vigorously pursued.

SECTION VII

PERSONNEL

Engineering personnel applied the indicated hours to the project during the contract period.

G. Y. Eastman	325.5
H. A. Stern	176.0
J. L. Rhoads	1383.8
J. A. Fox	1362.0
H. J. Roberts	61.0
M. N. Slater	73.5
S. W. Kessler	9.0

In addition, consultation with engineering personnel was obtained to an amount of 94.5 hours.

Biographies of the above engineers follow.

G. Y. Eastman - Engineering Project Leader

Education:

B. A., Mathematics, Amherst College, 1950

Mr. Eastman's experience in the electron tube field has been unusually broad. He joined RCA at Harrison, New Jersey in 1950 where he worked as an Engineer in Color and Microwave tube design. In 1954, he was transferred to Lancaster as an Engineer to work in Color Kinescope Test Engineering. At Lancaster, his career has encompassed design, development and production engineering. Included in his experience has been: analysis of stress in color kinescope aperture masks; design and development of traveling-wave tubes and continuous-wave magnetrons; process development of multiplier phototubes; process and assembly supervision of developmental power, pick-up, photo and storage tubes construction; design and evaluation of small high-frequency power tubes and supervision of an engineering group charged with advanced development for power tubes.

He has held his current position since 1959, as Engineering Leader, Thermionic Converters, which has given him direct responsibility for the design and development of thermionic energy converters. He was primarily responsible for the successful design of the thermionic converter for rocket engine application. He developed special geometries of converters to evaluate changes in spacing, processing, and materials. He was responsible for the design, construction, and evaluation of the A-1197A nuclear prototype converter tested successfully in-pile under NObs-84823. He was Project Engineer for the development of a solar energy heated converter. He guided an extensive development under RCA sponsorship of a low temperature fossil fuel converter. Mr. Eastman has been responsible for a considerable portion of the investigations of vapor-filled converters carried out by RCA and his varied experience in the fabrication and processing of a wide variety of tubes makes him uniquely qualified for his present position.

Mr. Eastman is a member of the American Physical Society.

Herman A. Stern - Engineer Leader Chemical and Physical Laboratory

Education:

M. S., Chemistry, Franklin & Marshall College, 1960
B. S., Chemical Engineering, University of Cincinnati, 1952

Mr. Stern is an Engineer Leader responsible for the Applied Physics section of the Power Tube Chemical and Physical Laboratory at Lancaster. He was awarded the Bachelor of Science degree in Chemical Engineering by the University of Cincinnati in 1952 and the Master's degree in Chemistry by Franklin and Marshall College in 1960. He joined RCA in 1952, working in the Chemical and Physical Laboratories, first at Lancaster for one year and then at Marion, Indiana, for another year. He spent two years in the U. S. Army from 1954 to 1956 as an instructor in radiological warfare. Since 1956 he has worked in the Chemical and Physical Laboratory at Lancaster, first on general chemical problems, and for the past three years he has been in charge of the Radiotracer Laboratory, and has done extensive work on application of radiotracer techniques to tube problems. This has included investigations of trace quantities of contaminants and their removal from tube parts, of sources of gas components, and of sorption and desorption of gases at very low levels. More recent efforts have been in the area of radiation effects studies. He has been responsible for the investigations employing the mass spectrometer and supervised the permeation analysis of emitter shell materials for thermionic converters.

Mr. Stern holds membership in the American Chemical Society, the Health Physics Society, ASTM & JEDEC on Radiation Effects and is licensed by the states of Ohio and Pennsylvania as a Professional Engineer.

J. L. Rhoads - **Product Development Engineer**

Education:

B. S., Ceramics, Pennsylvania State University, 1953
M. S., Ceramics, Pennsylvania State University, 1954

Immediately upon receiving his B. S. degree Mr. Rhoads was employed by RCA to investigate criteria of metal-to-ceramic seals. He extended this effort to the following areas: Development of a reliable metalizing process for production use, development and construction of reliable furnaces for both metalizing firing and brazing operations, evaluation of high alumina ceramics to obtain best ceramic bodies for seal construction, investigation of brazing materials and metals to produce optimum seals, and handling factory problems relating to the use of ceramic components and ceramic-to-metal seals.

Recently he has applied this knowledge and background toward the development of ceramic metal seals for use with thermionic converters at elevated temperatures. In addition he has made substantial contributions in the development of a ceramic emitter shell for fossil fuel heated converters.

Mr. Rhoads is a member of the American Ceramic Society and Keramos.

J. A. Fox - Chemical and Physical Laboratory Engineer

Education:

B. S., Physics, Lebanon Valley College, 1962
Candidate for M. S., Physics, Franklin and Marshall College

Mr. Fox began his work with RCA as a Production Engineer on Vidicon camera tubes. In this position he gained experience in the area of thin-film evaporation and high-vacuum techniques. Upon transfer to the Chemical and Physical Laboratory, he began a study of residual gases in power tubes which led to improvements of the getter in super-power tubes and a clarification of the gas phenomena observed in Cermolox tubes.

He was responsible for the design of the permeation test equipment and developed the procedure employed on the subject contract to obtain the measurement of outgassing rates; the presence of residual gases and the ion gauge pumping speed.

In addition to his work at RCA, Mr. Fox has experience in the field of inorganic semiconductors. For 18 months he served on the staff of the U. S. Air Attache in Australia as an Electronics Specialist.

H. J. Roberts - Associate Engineer

Education:

B. S., Industrial Arts, Millersville State College, 1952

Mr. Roberts has been with RCA for more than ten years. During this period he has had considerable experience in the production of black and white as well as color kinescopes and the design and installation of vacuum equipment. After a year as a Partsmaker, he became an Assistant Foreman with responsibility for the exhausting and finishing phases of black and white kinescope production. He then spent three years as an Equipment Engineer, designing and constructing equipment for the production of color television tubes. In this capacity he served on a committe responsible for the layout of a new plant for the production of color kinescopes. The committee was also responsible for the estimation of capital equipment costs and the prediction of production capacity.

For the past five years his activities have been concentrated in the vacuum field. He assisted in the design, construction, and testing of the Model C Stellarator, an ultra-high vacuum system for experiments in nuclear fusion. Since 1961 he has been designing mechanical components of vacuum systems and has made a major portion of the vacuum calculations used in the design of the space environmental chambers installed for the National Aeronautics and Space Administration at Langley, Virginia, and Houston, Texas.

Dr. J. C. Turnbull

Education:

B. S., Physics, Massachusetts Institute of Technology, 1934
Ph. D., Physics, Brown University, 1938

Dr. Turnbull was associated with the OSRD Radiation Laboratory, Princeton University from 1938 to 1942, from then until 1945 he was with Preston Laboratories as a Research Physicist.

He has been with RCA since 1945. During this time he has been an Engineer and Leader of the Glass and Ceramic group in the Chemical and Physical Laboratory, a Glass Design Engineer in the Color Kinescope Design section and for the past two years has been Leader of the Applied Physics group in the Chemical and Physical Laboratory. This group is specifically assigned to the investigation of thermionic emission phenomena, gas evolution and permeation and the use of radio tracers in the solution of tube problems. For the past two years he has concentrated on investigations relating to the gas content of tubes. He has done outstanding work in the use of the mass spectrometer for the determination of gas evolution from internal tube parts and the permeation of gas through tube envelope materials. Included in this program was the design and construction of much of the specialized equipment that was required.

Dr. Turnbull is a member of the American Physical Society and the American Ceramic Society. He is also a member of Sigma Xi.

Dr. Turnbull has had one patent granted in the field of metal-to-glass sealing with two additional patents pending.

In addition, he has had numerous papers published on Chemical and Physical Properties of Materials.

M. N. Slater -- Engineering Leader

Education:

B. Sc., Chemistry, University of Manitoba, 1945

After graduation from the University of Manitoba, Mr. Slater did graduate work in physical and organic chemistry at the University of Minnesota until 1951. His thesis work was in surface chemistry, on sorption of halogens.

While at Minnesota he worked as Research Assistant at the Naval Ordnance Research Laboratory doing research on the synthesis of rocket fuels and on the kinetics of fuel combustion. He also worked as the Physicist in the Cancer Research Center of the University of Minnesota Hospitals, preparing radium needles and radon implants for therapy and radioisotope mixtures for both research and therapy.

In 1951 he was employed by the Gates Rubber Company as a Colloid Research Chemist, working on adhesives and coatings and the development of analytical techniques.

In 1952 he joined RCA at Marion, Indiana as a Design and Development Engineer on black and white kinescopes In this function he assisted in the development of the low-carbon steel tube envelope and the investigation of materials and processes for filming and aluminizing of kinescopes. He holds a patent on "Method of Aluminizing Phosphor Screens."

In 1956 he was transferred to RCA-Lancaster as a Product Development Engineer where he worked on tube base adherence, paints, and coatings. He helped to set up the Radiotracer Laboratory and studied parts cleaning and contaminent migration in tubes He presented a paper, "Radiotracers in Parts Cleaning Evaluation," before the American Society for

Testing and Materials which was subsequently published in their book, STP 246, "Cleaning of Electronic Device Components and Materials."

With the opening of the Mountaintop RCA Plant in 1960, he moved there as Engineering Leader to set up and run the Chemical and Physical Laboratory which covered incoming inspection and in-process materials analysis and parts testing, as well as materials and process development, including photoresist and diffusion techniques, gas and liquid purification, etching, ultrasonic cleaning, and plating.

In 1964 he returned to Lancaster as Engineering Leader in the Thermionic Converter Engineering Group.

Mr. Slater is a member of the American Chemical Society, the Electrochemical Society, the American Society for Testing and Materials, and the American Association for Contamination Control.

S. W. Kessler, Jr. - Product Development Engineer

Education:

B. S., Industrial Engineering, University of Pittsburgh, 1949

Mr. Kessler also was engaged in graduate work at Johns Hopkins University from 1949 to 1953, where he worked as a Research Assistant, investigating the kinetics of the solidification of metals.

He joined RCA in 1953 and was assigned to the Chemical and Physical Laboratory at the Lancaster, Pennsylvania plant, where he developed glass-to-metal and ceramic-to-metal seals. He holds one glass-to-metal seal patent. He was later assigned to the RCA Semiconductor and Materials Division, where he specialized in the metallurgical aspects of silicon power rectifier design and the diffusion of doping elements into silicon. Particular areas of investigation included the diffusion, sintering, welding, and brazing characteristics of materials.

He has been associated with the Thermionic Converter Engineering Group in Lancaster since 1962. He has been working on the development of high-temperature, high-strength ceramic-metal seals and the special problems of electrically insulating series-connected converters operating from a high-temperature liquid-metal loop. He is also engaged in the determination of the compatibility of component materials, brazing active metals, and the perfection of electron-beam welding techniques for converter fabrication.

Recently he has been responsible for the development of special metal vapor arc lamps for use in industrial test equipment.

Mr. Kessler is a member of Amercian Society for Metals and American Institute of Metallurgical Engineers.

SECTION VIII

BIBLIOGRAPHY

1. Turnbull, J. C., Collins, R. H., and Kirkpatrick, G. P., "A Study of High Temperature Microwave Tube Design and Processing"; a report prepared for contract AF 33(616)-6563, (1960).

2. Conklin, L. J. and Turnbull, J. C., "Gas Permeation Study of Materials for Use in Thermionic Energy Converters"; a report prepared for contract AF 33(616)-7903, (1961).

3. Smithells and Ransley, "Diffusion of Gases through Metals," Proceedings of Royal Society (1935).

4. Hayes, D., Budworth, D. W., and Roberts, J. P., "Selective Permeation of Gases Through Dense Sintered Alumina," Transactions of the British Ceramic Society, Vol. 60, pp. 494-504, (1961).

5. Hayes, D., Budworth, D. W., and Roberts, J. P., "Permeability of Sintered Alumina Materials to Gases at High Temperatures," Transactions of the British Ceramic Society, Vol. 62, pp. 507-523, (1962).

6. Cunningham, G. W., Pfeifer, W. H., Carmichael, D. C., and Hodge E. S., "Oxidation Resistance of Oxide-Coated UO_2 Microspheres," Battelle Memorial Institute, BMI-1625 (1963).

7. Kingery, W. D., "Property Measurements at High Temperature," Chapter 2, Laboratory Refractories.

8. Haugh, J. E., "Guide to Refractory Ceramics," Materials in Design Engineering, Vol. 58, No. 1, pp. 85-96, (July 1963).

9. Kohl, W. H., "Materials and Techniques for Electron Tubes," Chapter 2, Ceramics, Reinhold Publishing Corp. (1960).

10. D. Alpert, "Production and Measurement of Ultra-High Vacuum," Handbuch der Physik, Sect. 7, p. 621.

11. D. Alpert, "Production and Measurement of Ultra-High Vacuum," Handbuch der Physik, XII, pp. 616-622 (1958).

12. Holden, J., Holland, L. and Laurenson, L., "Bakeable Vacuum Seals

Using Aluminium-wire Gaskets," Journal of Scientific Instruments, Vol. 36, p. 281, (1959).

13. Elsworth, L., Holland, L. and Laurenson, L., "Further Experiences with Aluminium Wire Seals for Bakeable Vacuum Systems, "Journal of Scientific Instruments, Vol. 37, p. 449, (1960).

14. Alpert, D., "Production and Measurement of Ultra-High Vacuum," Handbuch der Physik, Sect. 7, p. 622.

15. Hall, W. B. and Kessler, S. W., "Cesium Compatibility of Thermionic Converter Structural Materials," Report of the Thermionic Conversion Specialist Conference, 7-9 October 1963, the Institute of Electrical and Electronics Engineers, Electron Devices Technical Professional Group, Energy Sources Division.