EMISSIVITY DATA FOR URANIUM DIOXIDE

by

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A THESIS

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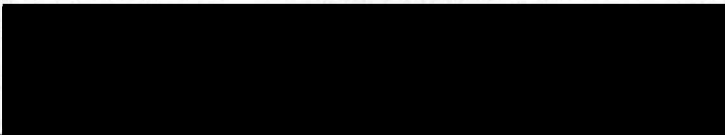
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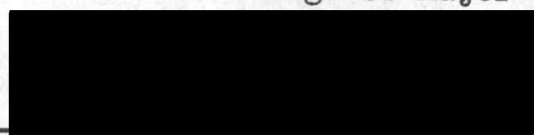degree of

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PURPOSE

The purpose of the work for this thesis was to determine the value for the emissivity of uranium dioxide in the temperature range of $900^\circ C - 1800^\circ C$.

INTRODUCTION

In order to produce electrical power from nuclear reactors economically, the fuel costs for the reactor must be extremely low and the overall efficiency of the nuclear power station must be high. One method to reduce fuel cost is to run the fuel to longer exposure thereby increasing the recycle time required for the fuel. To achieve a high overall efficiency the nuclear reactor must operate at high temperatures. Even by alloying, metallic nuclear fuels are limited by both exposure time and operating temperature.

The use of ceramic nuclear fuel is one solution to this problem, uranium dioxide being the most common in use today. Where metallic fuels are limited to exposures of hundreds of megawatts days and low operating temperatures, uranium dioxide fuel elements may be exposed to thousands of megawatt days and operate at temperatures of $1000^\circ C$ to $1500^\circ C$ without disastrous effects.

The design and development of a nuclear ceramic fuel

requires a thorough knowledge of its heat transmission properties. There are three methods of transferring heat; conduction, convection, and radiation. For the application of ceramic fuels operating at high temperatures, contact of the ceramic to its metallic container may not be possible due to the decrease in strength properties of the metal. Heat transfer in such cases will then be primarily by radiation. Radiant energy from a hot body is emitted in all directions. When this energy strikes another body, a part may be reflected, a part transmitted, or a part absorbed. The Stefan Boltzmann Law has been derived to determine the amount of energy transferred by radiation. This law states that the amount of heat transferred from a radiating body to another body in an enclosure is proportional to the area of the radiating body, to the fourth power of its absolute temperature and to its emissivity. The proportionality constant is known as the Stefan Boltzmann constant and is equal to 0.1713×10^{-8} Btu/hr ft^2 $^oR^4$. It is then necessary to determine the emissivity factor for uranium dioxide in order to determine the amount of heat transferred under certain operating conditions. The Stefan Boltzmann equation may be written as:

$$q_{12} = \sigma \mathcal{F}_{12} F_{12} A_1 \left[T_1^4 - T_2^4 \right] \tag{1}$$

where:

$q_{1,2}$ = net energy interchange Btu/hr

$\mathcal{F}_{1,2}$ = gray body factor

A_1 = area of the radiating body, F_T^2

T_1 = absolute temperature of the radiating body, ^{o}R

T_2 = absolute temperature of the second body, ^{o}R

σ = Stefan Boltzmann constant, Btu/hr F_T^2 $^{o}R^4$

The view factor, F_{12}, is defined as the fraction of radiation emitted by a black body of area A_1 which is intercepted directly by a second body of area A_2. Since from the geometry of the experimental apparatus for this project a body of area A_2 has an unobstructed view of the radiating body of area A_1, the form factor F_{12} is equal to unity. In the actual experimental apparatus the net energy interchange, q, was determined by placing a thick walled cylinder (hereafter called the heat shield) of a proposed nuclear fuel cladding around the test specimen. Embedded at different radii from the center of the heat shield were two stainless steel sheathed chromel-alumel thermocouples. Thus by measuring a temperature difference between known radii through the cylinder and knowing the thermoconductivity of the heat shield material, the net energy interchange of the system could be calculated by the standard conduction formula.

$$q = \frac{k \, 2\pi L(t_1 - t_2)}{\ln r_2/r_1}$$

By using the same equation and extending the limits the

temperature at the inner surface of the cylinder was also calculated, thus determining T_2.

Before any progress could be made in determining the emissivity, a method of measuring the temperature of the uranium dioxide had to be found. A device was needed to read true temperatures independent of emissivity and environmental effects. Such a device is the two color optical pyrometer. The basis of operation of a two color optical pyrometer is on the principle that as the temperature of a body increases the energy radiated at each wave length increases. From this basic principle the following equation may be derived.

$$\frac{1}{T} = \frac{1}{T_{RB}} + \frac{\lambda R}{C_2} \ln e \qquad (3)$$

$$\frac{1}{T} = \frac{1}{T_{GB}} + \frac{\lambda G}{C_2} \ln e \qquad (4)$$

where:

T = true absolute temperature, ^{o}R

T_{RB} = Brightness temperature at .654 micron

T_{GB} = Brightness temperature at .54 micron

λR = wavelength of .654 micron

λG = wavelength of .54 micron

e = spectral emissivity

C_2 = 1.4388 cm degree

The actual temperature measuring procedure consisted of taking one reading from two optical pyrometers having optical filters of .654 and .54 micron, respectfully.

Since the pyrometer containing the .54 micron filter was not calibrated for a known emissivity and the second pyrometer was, it was necessary to calibrate the first to a know emissivity. A tungsten filament was used and the calibration curve is shown in figure 1. Solving equations 3 and 4 simultaneously and substituting in known values the following equation to determine the true temperature is formed.

$$\frac{1}{T} = \frac{5.88}{T_{GB}} - \frac{4.88}{T_{RB}} \quad {}^{\circ}R$$

Referring to equation (1) all terms are either measured or calculated except the gray body factor $\mathscr{F}_{12}$. This term may be calculated. By the following derivation it may be shown that:

$$\mathscr{F}_{12} = \frac{1}{\frac{1}{e_1} + \frac{A_1}{A_2}\left[\frac{1}{e_2} - 1\right]}$$

where subscripts 1 and 2 refer to the radiating inner body and outer body respectfully. For the case of diffusely reflecting concentric cylinders of radius R_1 and R_2 assume the following.

    a) Body 1 is radiating

    b) Body 2 is a diffuse reflector

    c) F_{12} = Fraction of energy leaving body 1 and falls on body 2 = $\frac{A_1}{A_2} = \frac{R_1}{R_2}$

    d) Subscript 12 is mean from body 1 to body 2

e) K = Energy leaving body 1 and being reflected
   back is absorbed by body 1

f) a = Absorbtivity

g) r = Reflectivity

h) H = Energy per unit time

i) P = Energy that leaving a body comes back to
   that body after being reflected

j) h = Heat per unit area

Consider first the expression for K_{11}. The fraction of the emission E_1 from body 1 that falls on body 1 again after the first reflection from body 2 is $r_{21} F_{21}$. The remainder of the reflected radiation, $E_1 r_{21}(1 - F_{21})$, falls on body 2 and is again diffusely reflected so that an amount $E_1 r_{21}(1 - F_{21})r_{21} F_{21}$ falls on body 1. This process continues and the fraction of the radiation leaving body 1 that falls again on body 1 after a series of reflections is:

$$P_{11} = r_{21} F_{21} + r_{21}(1 - F_{21})r_{21} F_{21} +$$
$$r_{21}(1 - F_{21})(r_{21})(1 - F_{21})(r_{21})(F_{21}) + \ldots$$

or $P_{11} = \dfrac{(r_{21})(F_{21})}{1 - (1 - F_{21})(r_{21})}$

Similarly to the previous case, at each step in the process a part a_{11} of the radiation is being absorbed, and a part $(r_{11} + \tau_{11})$ is reflected and transmitted. Taking the ultimate sum of this series as before,
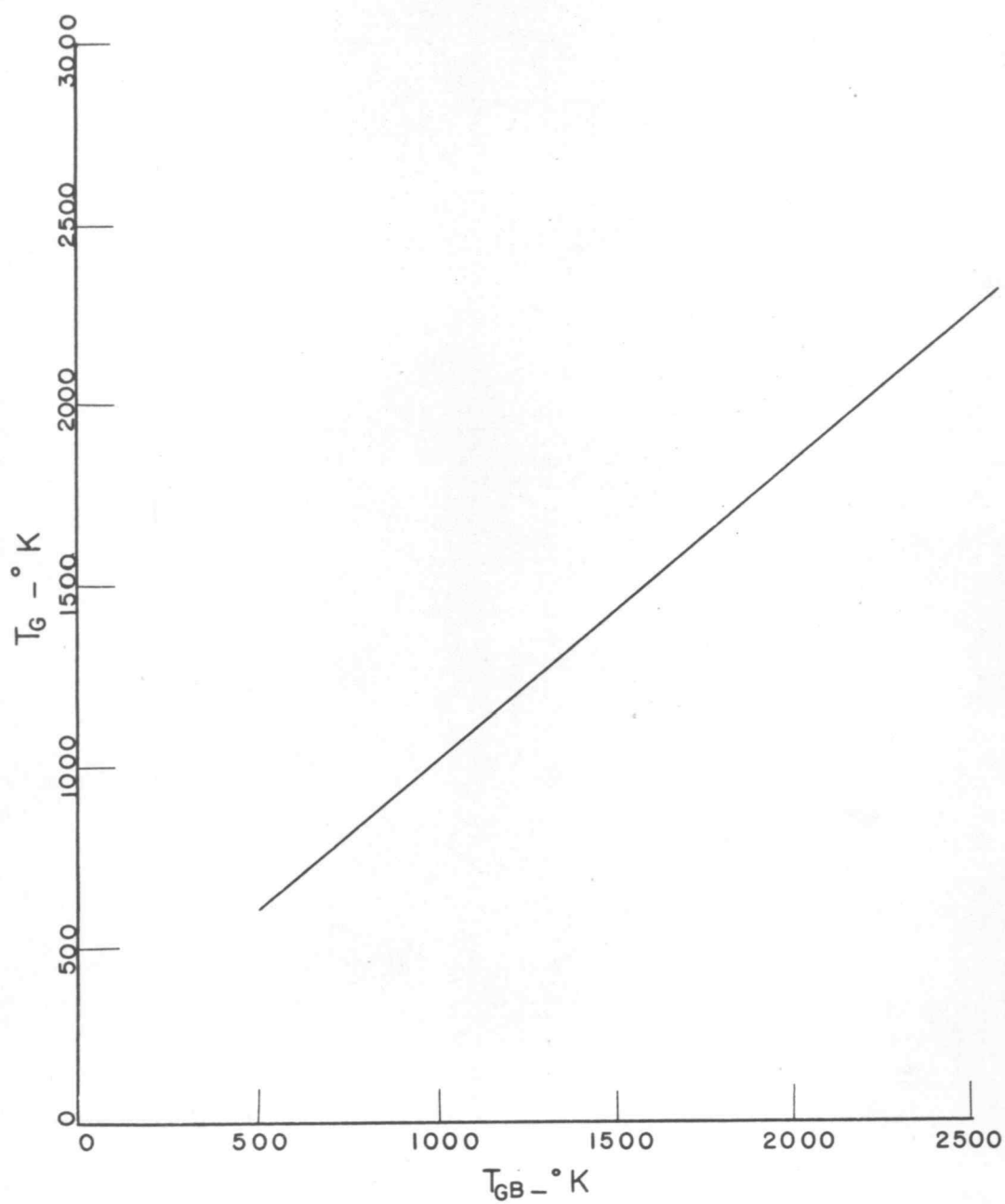
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FIGURE I

CALIBRATION CURVE

$$K_{11} = \frac{a_{11} \, P_{11}}{1 - (1 - a_{11}) P_{11}}$$

Substituting for P_{11},

$$K_{11} = \frac{a_{11} \, r_{21} \, F_{21}}{1 - [1 - (a_{11})(F_{21})] \, r_{21}}$$

In the same manner determine P_{21} and K_{21}.

$$P_{21} = \frac{F_{21}}{1 - (1 - F_{21}) r_{22}}$$

$$K_{21} = \frac{a_{12} \, P_{21}}{1 - (1 - a_{12})(r_{22})(P_{21})}$$

Substituting for P_{21}

$$K_{21} = \frac{a_{12} \, F_{21}}{1 - [1 - (a_{12})(F_{21})] \, (r_{22})}$$

Using the equation that

$$H_1 = K_{21} E_2 - (1 - K_{11}) E_1$$

The total net gain of energy/unit time by body 1 is

$$H_1 = \frac{a_{12} \, F_{21} \, A_2 \, E_{22} \, T_2^4}{1 - (1 - a_{12} \, F_{21}) r_{22}} - \frac{(1 - r_{21})(A_1) E_{11} \, T_1^4}{1 - (1 - a_{11} \, F_{21}) r_{21}}$$

$$h_1 = \frac{H_1}{A_1} = \sigma \left[\frac{a_{12} \, E_{22} \, T_2^4}{1 - [1 - a_{12}(R_1/R_2) \, r_{22}]} - \frac{(1 - r_{21})(E_{11})(T_1)^4}{1 - [1 - a_{11}(R_1/R_2)] \, r_{21}} \right]$$

Similar to this example is the case of gray opaque surfaces.

$$K_{11} = \frac{e_1(1 - e_2)F_{21}}{e_2 - e_1(1 - e_2)F_{21}}$$

and

$$K_{21} = \frac{e_1 F_{21}}{e_2 + e_1(1 - e_2)F_{21}}$$

or

$$h_1 = \frac{e_1 e_2(T_2^4 - T_1^4)}{e_2 + e_1(1 - e_2)R_1/R_2}$$

or

$$q_{1\,2} = A_1 \frac{1}{\frac{1}{e_1} + \frac{R_1}{R_2}\left(\frac{1}{e_2} - 1\right)}(T_1^4 - T_2^4)$$

$$\therefore \quad \mathscr{F}_{12} = \frac{1}{\frac{1}{e_1} + \frac{R_1}{R_2}\left(\frac{1}{e_2} - 1\right)}$$

From this gray body factor and knowing the emissivity of the heat shield material the emissivity of body 1, the uranium dioxide, may be calculated. The material used in these experiments was reactor grade uranium dioxide. In powder form it is dark brown in appearance and will adhere to the skin like talc. Its crystal structure is the face centered cubic with the uranium ions occupying corners and faces. Figure 2 shows a unit cell. The cell dimension has been determined as 5.469Å. From this dimension a theoretical density of 10.95 is calculated. It may be noted that the lattice is relatively open. The index of refraction is 2.355. Figure 3 presents the latest equilibrium diagram for uranium dioxide.
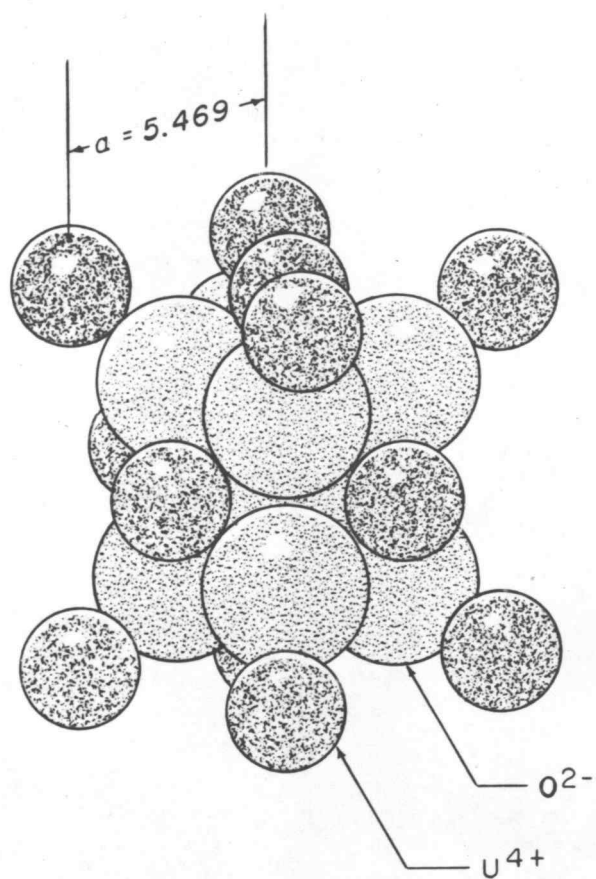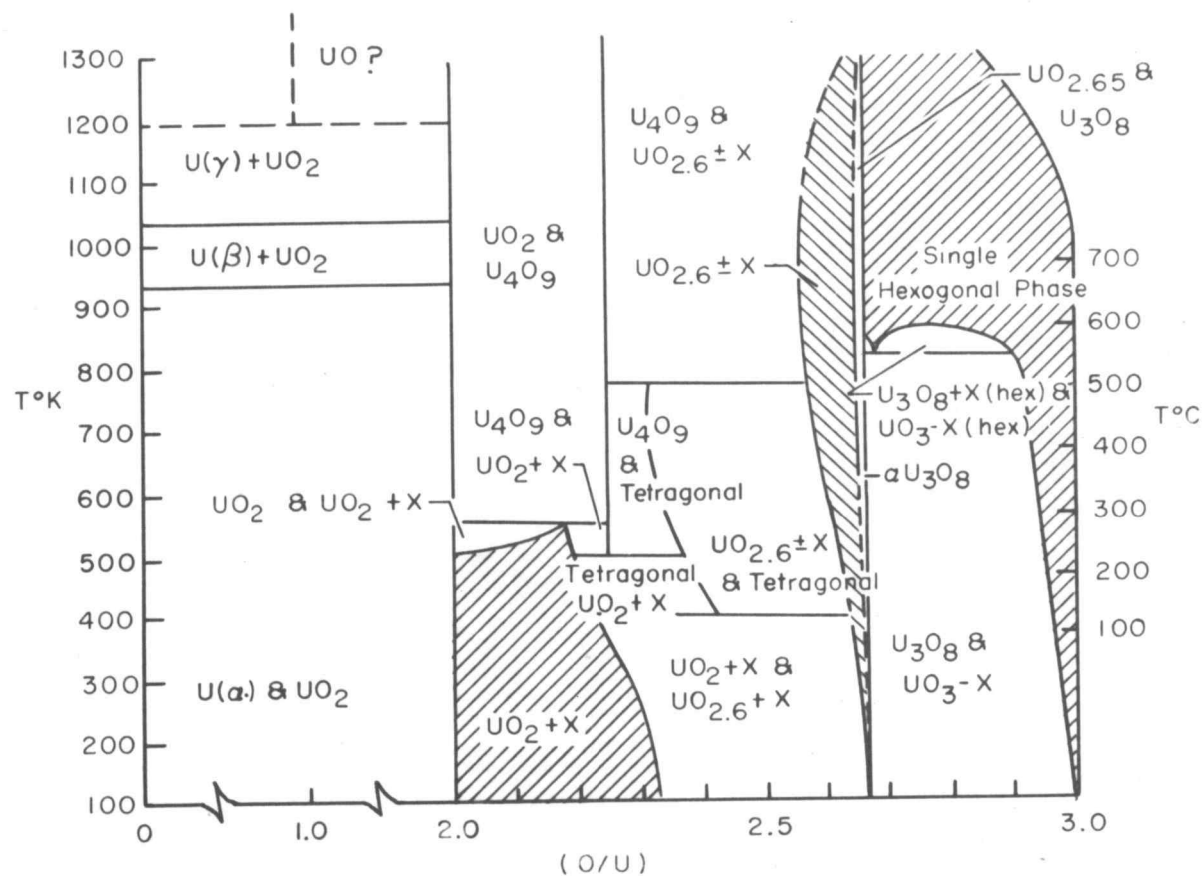
Although the melting point of uranium dioxide has not

FIGURE 2
UNIT CELL UO$_2$

THE TENTATIVE CONDENSED PHASE DIAGRAM OF THE URANIUM-OXYGEN SYSTEM FOR
COMPOSITION VS. TEMPERATURE

(The lined areas represent single phase regions)

FIGURE 3

been definitely determined, most investigators have noted
it to be about 2800°C. It develops an appreciable vapor
pressure much below this temperature with weight losses
being noted at 1400°C. It was also noted during this
investigation that a partial loss in vacuum occurred at
temperatures of 1400 - 1600°C. The presence of foreign
material such as BeO seems to increase the volatility.
The vapor pressure of uranium dioxide as reported by Kelin
and Cefola is shown in Table 1.

Table 1.

Vapor Pressure of UO_2

Temperature-°C	Pressure (mmHg x 10^{-3})
1600	0.071
1750	1.7
1800	4.0
1900	18.0
2000	72.0

The thermal conductivity of uranium dioxide is
relatively low among the oxides. Debyes' theoretical
treatment of the thermoconductivity is given as:

$$K = \tfrac{1}{4} C V \rho \lambda \qquad (7)$$

where: K = thermoconductivity

ρ = density

C = specific heat

V = velocity of the heat wave

λ = mean free path of the wave

Recent work done in the field has found, however, that the thermoconductivity is a function of the sintering temperature and the ratio of the actual density to the theoretical density. The empirical formula derived is given as:

$$K = \frac{1.327}{(T + 350)}\frac{\rho}{\rho_o} \tag{8}$$

where:

K = thermoconductivity $\frac{KW}{FT - {}^oC}$

ρ = actual density

ρ_o = theoretical density

T = sintering temperature, ${}^oK$

In general the strength and modulus of elasticity of uranium dioxide are of the same order as most oxides while its thermal expansion is relatively high increasing with increasing temperature. It is interesting to note that the strength of uranium dioxide also increases with increasing temperature up to $1000{}^oC$. The moduli of rupture values are given from 12,000 psi at room temperature to 18,000 psi at $1000{}^oC$. At temperatures above $1400{}^oC$, uranium dioxide seems to become subject to plastic deformation and rapidly looses strength with further increase in temperature. A summary of physical property data is given in Table 2.

Table 2.

Physical Properties of Uranium Dioxide

Property	Uranium Dioxide
Crystal Structure	F.C.C.
X-Ray Density	10.95
Thermal Conductivity	.008 1000°C
	.02 20°C
Melting Point	2800°C
Expansivity	10×10^{-6} °C^{-1}(0 - 1000°C)
Specific Heat	0.056 Cal/g - °C(0 - 200°C)
Tensile Strength	5000 psi
Modulus of Elasticity	25×10^{6} psi
Metal Atoms/cc in oxide	51.5%
Index of Refraction	2.355

To prepare test samples, uranium dioxide of the type just described was coated around a 1/8 inch tungsten rod. The final diameter of the sample was designed for 1/4 inch. Several methods were tried in an attempt to place a 1/16 inch coating of uranium dioxide on the tungsten rod. These included electroplating from a uranium nitrate solution; the casting and sintering of rings, dipping the rod into a uranium dioxide slurry, and hydrostatically pressing the oxide on the rod. The latter method was the only one found to be successful and was accomplished in the following

manner.

The uranium dioxide as it came from the manufacturer in powder form was ball milled and sifted through 600 mesh screens. For a binder 5-7% by weight of carbaloy wax was thoroughly mixed into the powder. The powder was then packed around a 1/8 inch diameter tunsten rod enclosed by a rubber tube. Neoprene washers were placed over the tungsten rod to act as pistons and the ends of the rubber tube sealed. The entire assembly was then hydrostatically pressed in oil to 50,000 psi. After pressing, the uranium dioxide now packed against the tungsten rod, was centerless ground to a final dimension of 0.250 inches. Figure 4 is a schematic sketch of the final test specimen positioned in the heat shield.

A schematic drawing of the emissivity furnace is shown in figure 5. The furnace and auxilliary equipment used in the tests are shown in figure 7. It consists basically of two concentric tubes between which flows cooling water. Water cooled electrodes entering from each end of the inner tube connect to the tungsten rod of the test specimen thus holding it in place and providing for electrical contact. The inner tube was evacuated by means of a vacuum pump through outlets on each end of the furnace. Since temperature measurements were to be made optically, a viewing port was located centrally on the furnace.
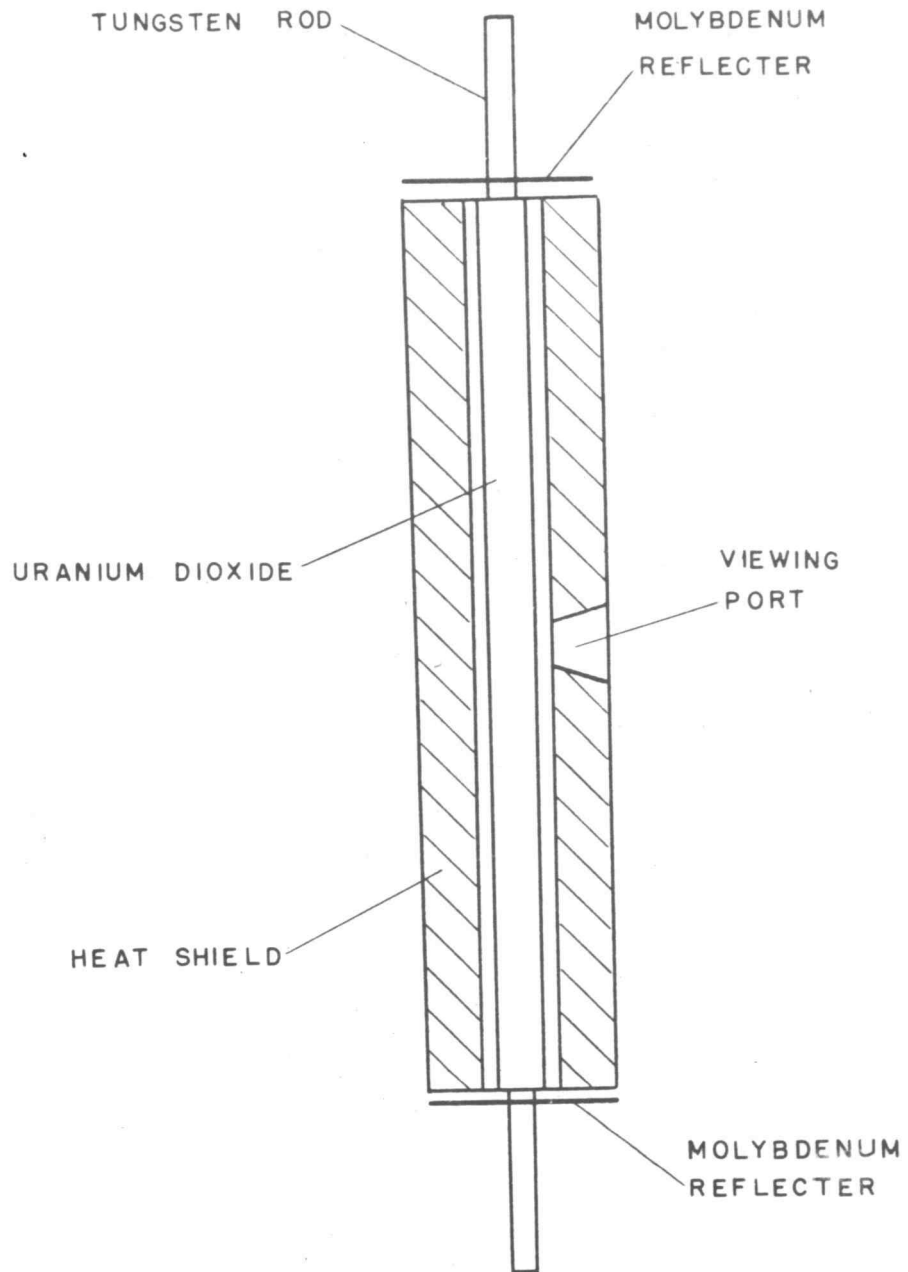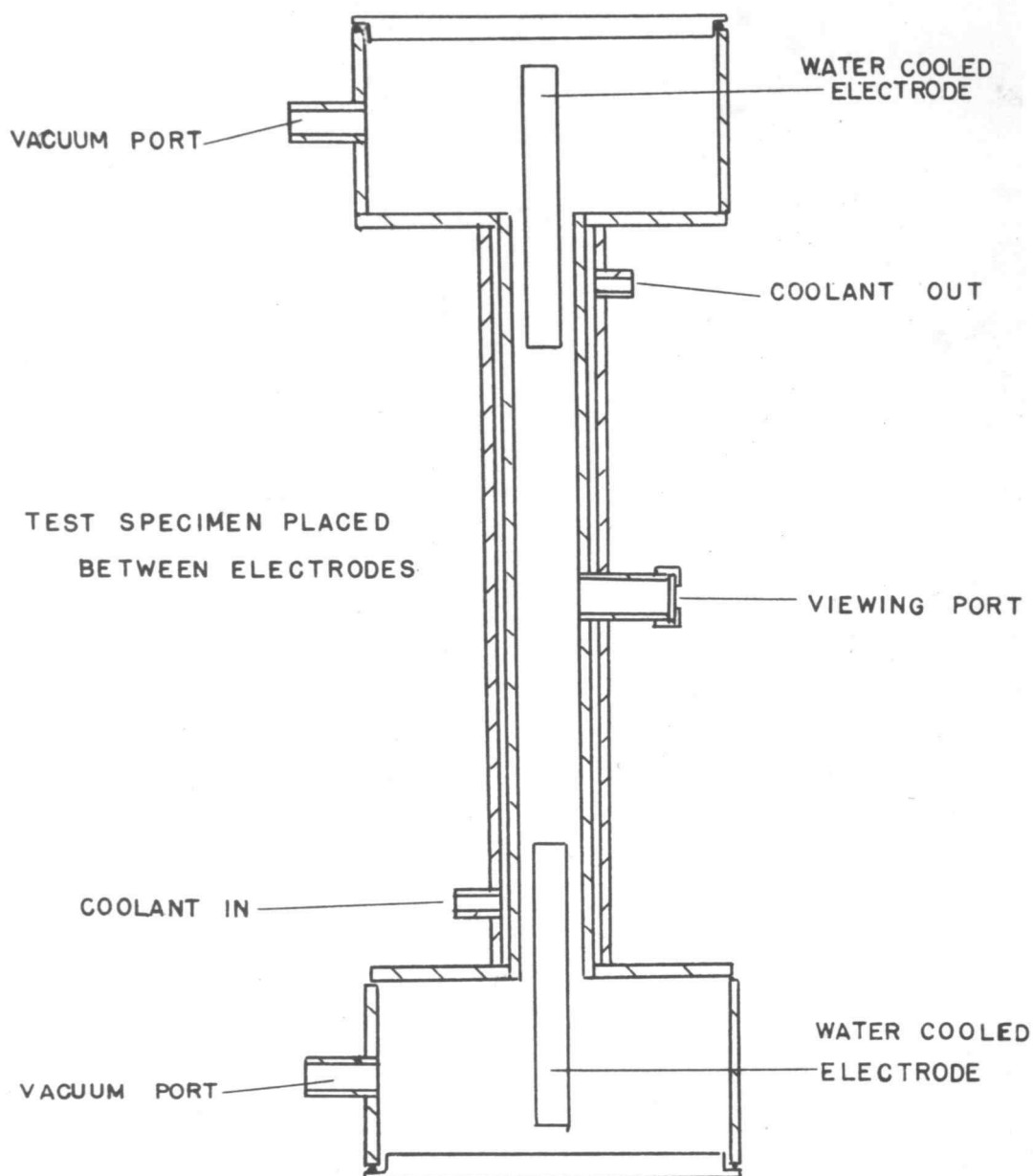
FIGURE 4

TEST SPECIMEN—HEAT SHIELD

FIGURE 5

EMISSIVITY FURNACE

The furnace electrodes were connected to a high ampere transformer with a capacity of 2500 amperes at 4 volts or 10 KW. Power was controlled through a 0 - 440 volts variac and was measured by means of a current meter and a volt meter. About 2 KW was required to bring the test specimens up to temperature.

Because of the high temperature involved, thermostats set at 180°F were placed at each point where cooling water left the furnace. These thermostats were connected in series with the power supply to shut down power when their limit was exceeded. In addition, a panellit pressure gage would shut the power off if coolant pressure dropped below 25 psig.

TEST PROCEDURE

The heat shield was first placed into the furnace and positioned in line with the viewing port by means of expansion rings located fore and aft of the shield. Thermocouple lead wires brought out through a vacuum seal provided and connected to an appropriate potentiometer. Molybdenum heat reflectors were placed on each end of the test specimen to insure that the heat path would be radical from the specimen and lessen the amount of heat traveling longitudinally.

The test specimen was positioned in the furnace by adjusting the electrodes so that the specimen was exactly in the center of the heat shield and free of any bending stress. The position of the test specimen was found to be critical in obtaining good experimental data because the method used depended upon the geometry being symmetrical. Any stress imparted to the tungsten rod by the electrodes would bend the rod when at high temperatures. This not only distorted the symmetry but also cracked the uranium oxide.

After loading the sample, the furnace sealed and a vacuum of 5 - 35 micron drawn. The sample was then heated at a rate of about 250°C per hour. This slow rate was used to prevent thermal stresses from cracking the uranium oxide and also to control the severe outgassing

associated with a rapid heating of the sample.

After the test specimen reached the incandescent temperature, about 800°C, readings were taken at about every 100°C. One half hour was allowed after every temperature increase for the system to come to equilibrium. Two separate readings of power to the furnace, millivolt readings from the thermocouples, and vacuum were taken. Several readings were taken of the temperatures of the test specimen until one value could be read consistantly. It was felt that some human error could be eliminated in this manner.

DATA

From the data obtained, $\mathcal{F}_{12}$ was calculated from
equation 3. Within experimental error, this factor proved
to be the value of one and indicated that the system was
acting as if it were a black body. From the geometry of
the test apparatus, this seemed to be a reasonable
assumption. Further calculations were based upon black
body radiation and the following equation was used.

$$q_{12} = \sigma A_1 e T_1^{4}$$

Since q, A_1, σ, and T_1 are known, the emissivity factor
e can be calculated directly. Figure 6 is a plot of the
emissivity of uranium dioxide, e, versus its temperature,
$^{\circ}C$, based upon the data taken during this test. From this
plot it is shown that the emissivity of uranium dioxide
varies from 0.95 at 600°C to 0.4 at 1800°C. These values,
although slightly higher than expected, do show correlation
to other ceramics used in industry. Table 3 is presented
showing the data obtained from the tests and from which
the plot on figure 6 is taken.

Table 3.

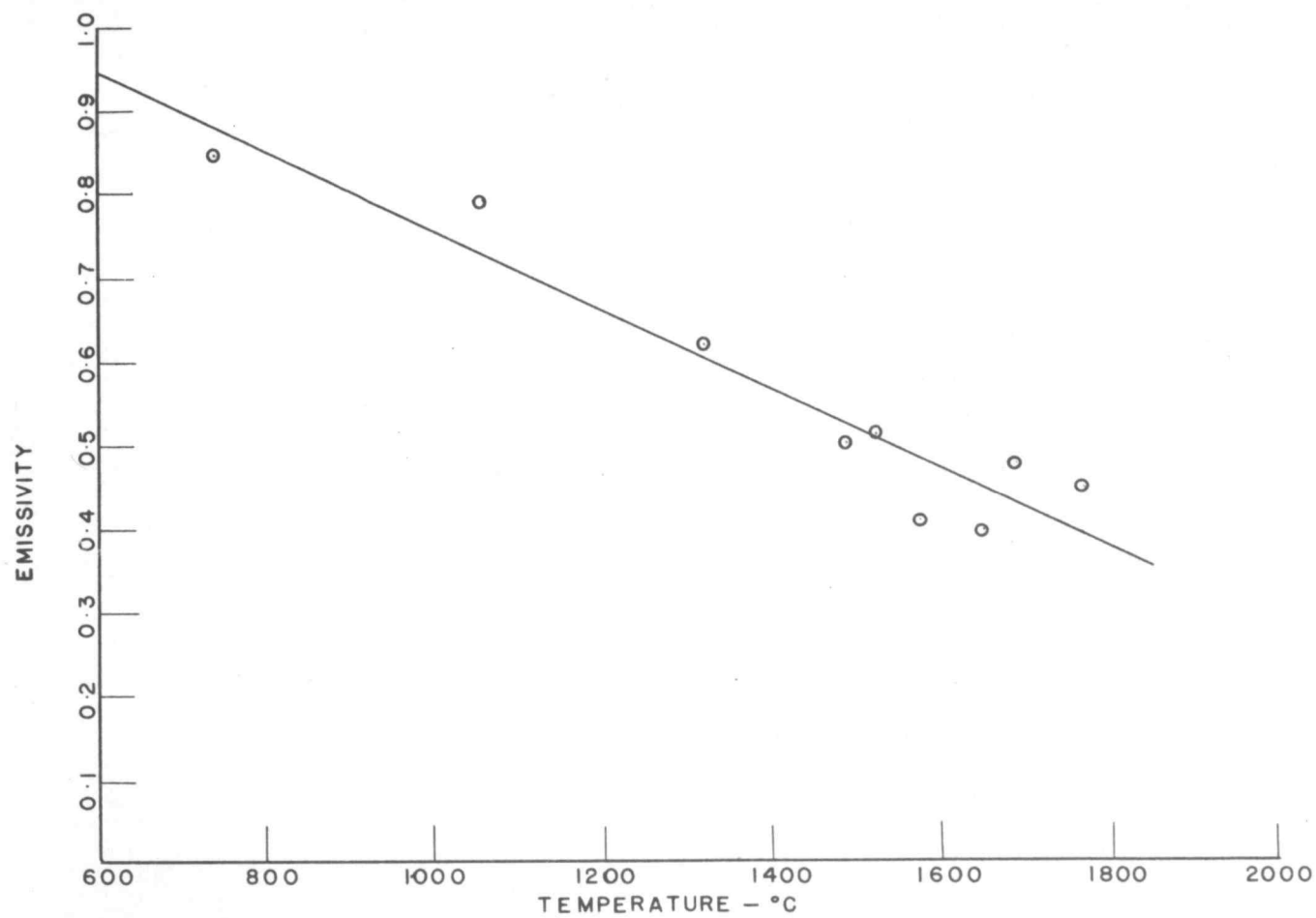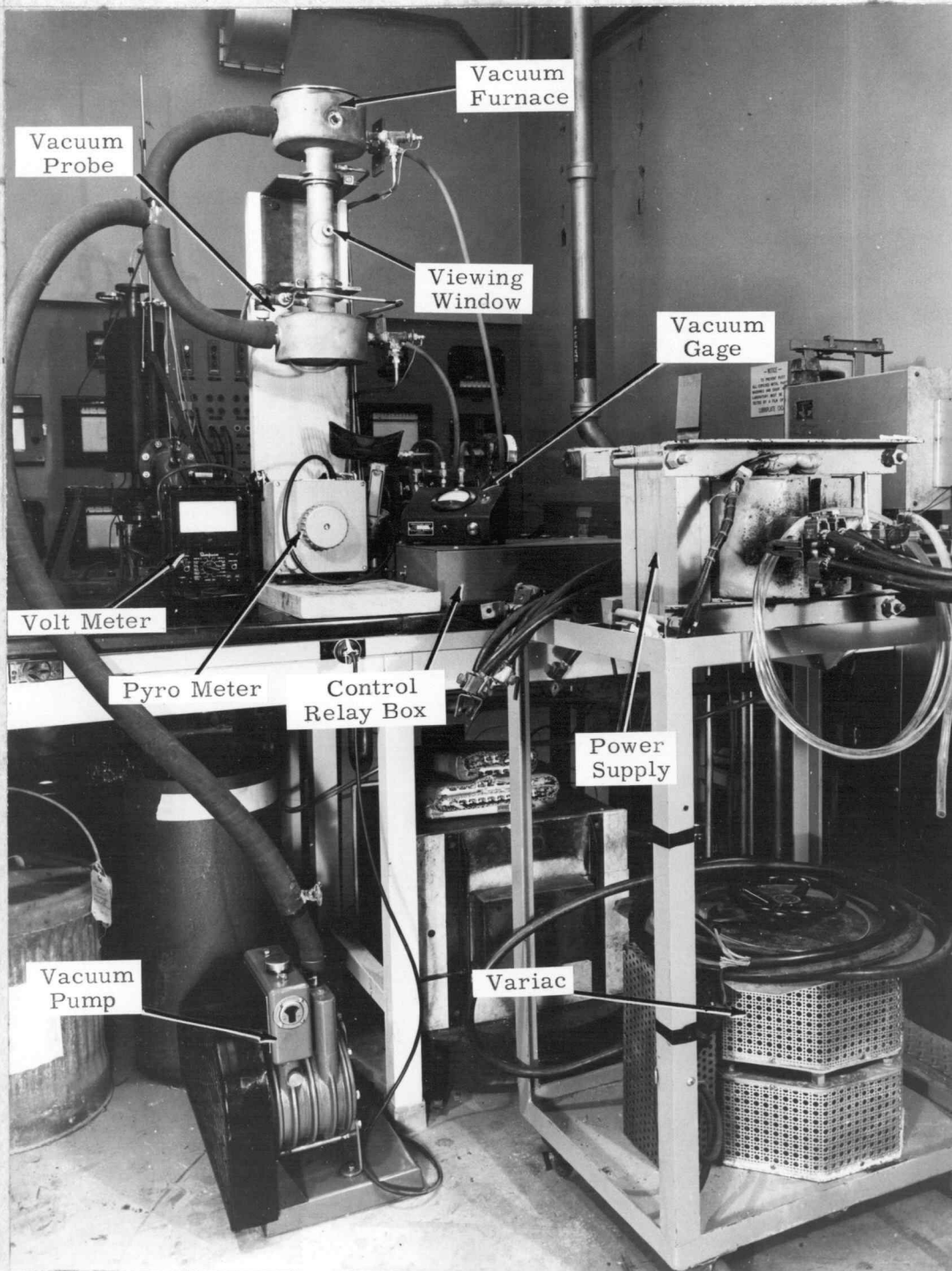| Temperature-$^{\circ}$C	Emissivity
727	.850
1047	.798
1320	.628
1482	.510
1522	.515
1580	.417
1647	.402
1682	.484
1780	.446
1947	.370

FIGURE 6

EMISSIVITY OF URANIUM DIOXIDE

TEST EQUIPMENT

FIGURE 7

CONCLUSIONS

The emissivity of uranium dioxide as prepared and
tested by the procedures outlined in this thesis has been
determined to vary from 0.95 at 600°C to 0.4 at 1800°C
in the temperature range of 600 - 1800 °C.

The method used in determining the emissivity factor
of uranium dioxide was chosen since it was felt to be a
straight forward approach in obtaining the necessary data
without a large amount of intricate and expensive equip-
ment. The method as well as the equipment used functioned
well but because of the nature of the radiation phenomena,
obtaining accurate data is extremely difficult. For this
reason the possible percentage error involved is large.

Since the emissivity factor is a function of the
fourth power of its absolute temperature, an error in
reading the pyrometers of plus or minus $2\frac{1}{2}\%$ at the upper
temperature range would lead to an error of plus or minus
10% in the final calculation of the emissivity factor.
This latter percentage can make the difference between
acceptable data and data that is unreasonable. It is for
this reason that only approximately 10% of the data
collected was felt acceptable. One other source of error,
beside the human factor, is that of the thermocouple
readings. It is generally felt that thermocouples when
used correctly under good conditions are accurate within

plus or minus 2%. Judging from the calculated heat being transferred out of the system versus the known power input, it is felt that the thermocouples were giving satisfactory readings within this range of error.

The instrumentation used throughout the experiments was very sensitive. The potentiometer used to record the thermocouples were sensitive to changes of 0.01 milli-volts. The optical pyrometers used were commercial Leeds and Northrop Optical Pyrometers. These instruments will note changes in temperatures of five degrees centigrade.

It is believed by this author that the results of these experiments gives a good representation for the value of the emissivity of uranium dioxide within the temperature range studies. Further refined data is needed to either substantiate these values or disprove them. Several suggestions for improving the accuracy of the data are given later in this report. Duplication of results proved very difficult, especially at low temperatures. This was due mainly to the number of variables which enter into the obtaining of heat transfer data and to the human error involved. Pyrometer readings are very difficult to read accurately at low temperatures.

Problems in outgassing at temperatures up to $300^{\circ}C$ were attributed to the binder used in preparing the uranium dioxide. Further outgassing problems became serious in the temperature range of 1400 - $1600^{\circ}C$. The cause of this was

unknown until data on the vapor pressure of uranium dioxide presented previously was located. By increasing the pumping capacity, sufficient vacuum was attained to reach the higher temperatures.

Although the general procedure and method used is felt acceptable, there was found that considerable improvements could be made. Basically, these include the acquiring of better and more expensive equipment. The use of an electronically operated two color optical pyrometer would greatly improve the accuracy of the results. This along with a continuous multipoint recording device to which the thermocouples could be attached would eliminate any human error associated to these devices. The use of noble metal for thermocouples would also improve the experimental data and would increase the life of the heat shield.

It was found very difficult to read the pyrometers accurately in the lower temperature range. Possibly an improvement here would be the location of a thermocouple in the uranium dioxide itself. This would entail a great deal of effort in locating such a device but the results would be beneficial.

The results of these experiments indicate emissivity values that are in the order of magnitude of other similar material. It is worth while to mention that most nonmetals in general have emissivity values which vary from 0.3 to

0.8 at furnace refractory temperatures. If anything,
they are probably a little high. Further refined experi-
mentation will no doubt be carried out in the near future.
The accuracy of these results will also be shown as the
results of experimental work on ceramic nuclear fuels
are received.

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