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B. Document Number HNF-11207

C. Title
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HNF-11207
Revision 0

Thermal Property Evaluation Of Cerium Dioxide And Cerium Dioxide-Magnesium Oxide

Powders For Testing Plutonium Stabilization Furnaces

Prepared for the U.S. Department of Energy
Assistant Secretary for Environmental Management

Project Hanford Management Contractor for the
U.S. Department of Energy under Contract DE-AC06-96RL13200

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Richland, Washington

Approved for public release; further dissemination unlimited.

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1.0 Summary

Ceric oxide (CeO_2) and mixtures of CeO_2 -magnesium oxide (MgO) have been utilized at the Plutonium Finishing Plant (PFP) as surrogate materials to represent plutonium dioxide (PuO_2) and impure PuO_2 containing impurities such as MgO during verification tests on PFP's stabilization furnaces. Magnesium oxide was selected during furnace testing as the impurity of interest since much of the impure PuO_2 to be stabilized and packaged at the PFP contains significant amounts of MgO from solution stabilization work. The issue being addressed in this study is whether or not heating the surrogate materials to 950 °C adequately simulates heating PuO_2 powders to 950 °C. This paper evaluates some of the thermal properties of these oxides, as related to the heating of powders of these materials where heat transfer within the powders is governed primarily by conduction. Detailed heat transfer modeling was outside the scope of this paper.

This study has made a reasonable assessment of available data to compare the thermal properties of CeO_2, MgO, and PuO_2. Results of this study indicate that the use of CeO_2 and CeO_2 with MgO is a good representation of how various plutonium oxides would heat up. Results of furnace tests with these surrogate oxides that demonstrate they achieve the desired temperature for the appropriate time should provide assurances that the PuO_2 will behave in similar manner.

The thermal conductivity of PuO_2 is approximately the same as that of CeO_2, and is approximately 3 times less than that of MgO. The thermal conductivities when in powder form are significantly less than when in solid form because of the low thermal conductivity of air. This study considered two of the equations reported in the literature for calculating effective thermal conductivities of powders. Results from the different equations, while somewhat different, were consistent in estimating the effects of a powder form. The effective thermal conductivity of PuO_2 powder is equal to or greater than both that of the CeO_2 and CeO_2-MgO mixed powders used as surrogate material in testing PFP's stabilization furnaces to represent PuO_2 and impure PuO_2 containing MgO.

Additional calculations were performed to estimate the effective thermal diffusivities of all three powders. The effective thermal diffusivity essentially describes the rate of penetration of a high temperature into the material, and takes into account the thermal conductivity, heat capacity, and bulk density of a material. Materials with a higher thermal diffusivity will reach a higher temperature more quickly upon heating than material with a lower thermal diffusivity. Results of effective thermal diffusivity calculations indicated that the CeO_2 surrogate powder and the CeO_2-MgO mixed surrogate powders heat up at rates similar to or less than those for PuO_2 and PuO_2-MgO powders.

It is concluded from this thermal analysis that the CeO_2 surrogate powder containing up to 50wt% MgO used during the testing of PFP's stabilization furnaces provided excellent representations of how PuO_2 containing up to 50wt% MgO would behave under similar conditions. It is believed that lesser quantities of other impurities would not significantly alter the findings of this study.

2.0 Introduction

2.1 Purpose

The purpose of this paper is to assess the viability of utilizing CeO_2 powder and mixtures of CeO_2 and MgO powders as surrogate materials simulating powders of PuO_2 and PuO_2 containing MgO for furnace testing. The issue being addressed in this study is whether or not heating the surrogate materials to 950 °C adequately simulates heating PuO_2 powders to 950 °C. This assessment involved comparison of the thermal properties of these materials, first addressing the thermal conductivities of the solid materials, then the effective thermal conductivities of these materials in powder form, and finally addressing the effective thermal diffusivities of the powders.

2.2 Background Information

The stabilizations furnaces at the Plutonium Finishing Plant (PFP) are required to be able to heat both pure and impure PuO_2 powders to 950 °C and hold it there for a minimum of two hours to assure that the material has been stabilized. Furnace testing is required to assure that they will function as designed. It is preferable that this testing be accomplished without contaminating the equipment with plutonium and hence a stand-in material was identified and selected. It is desirable that the surrogate materials have thermal properties that are reasonably close to those for PuO_2.

The thermal properties of interest are: thermal conductivity, heat capacity, and thermal diffusivity. These properties are important not only for the materials of interest but primarily for powders of these materials, as the thermal conductivity of the powders will approach that of the gas which is inter-dispersed within the powder, in this case air.

Frequently, cerium compounds are selected as a stand-in material for plutonium process testing because they have similar chemical properties [Dworzak, 1981 & 1982]. Much of the plutonium to be stabilized and packaged at the PFP is impure oxide and one of the significant impurities for some of the material is MgO from solution stabilization work. Consequently, CeO_2 powder and mixtures of CeO_2-MgO powders were selected as surrogate materials for stabilization furnace testing in the Plutonium Process Support Laboratories (PPSL) and in the W-460 thermal stabilization furnaces in the new stabilization and packaging process. These tests were performed in PPSL during the year 2000 and in the W-460 furnaces in 2002.

An initial thermal analysis of these powders was included in the laboratory work evaluating the thermal stabilization furnaces [Compton]. This paper provides a more thorough analysis of the thermal properties of these powders and their adequacy as PuO_2 surrogates for furnace testing.

2.2.1 3013 Stabilization Requirement

The United States Department of Energy (DOE) has developed a standard for long-term storage of plutonium materials [DOE-STD-3013-2000], "DOE Standard- Stabilization, Packaging, and Storage Of Plutonium-Bearing Materials". This standard identifies the stabilization and packing requirements for plutonium materials to be placed into long-term storage.

The standard specifies that plutonium materials to be placed into long-term storage be heated to at least 950 °C in an oxidizing atmosphere and held at that temperature for a minimum of two hours. This material is then to be cooled, sampled for moisture content, and packaged in acceptable 3013 inner and outer containers, if the moisture content is <0.5 wt% at the time of container loading.

2.2.2 Furnace Testing In Plutonium Process Support Laboratories

The PPSL was requested to demonstrate that the stabilization process in use at PFP meets the stabilization requirements [Compton]. This was accomplished through a series of tests utilizing a spare furnace that was identical to the production furnaces, and CeO_2 and mixtures of CeO_2-MgO were selected as surrogate materials representing PuO_2 and impure PuO_2 containing MgO. The furnace boat used to hold the oxide materials was made of Hastelloy X®. The tests involved various furnace conditions using powders involving 100% CeO_2, CeO_2 with 10-20% MgO, and CeO_2 containing various amounts of salts that decompose exothermically. Temperatures in the powder beds were measured using 2 or 3 thermocouples.

Results of the PPSL stabilization furnace tests demonstrated that the furnace could heat ~2500 grams of the CeO_2 and ~1900 grams CeO_2 – MgO surrogate powders to the required 950 °C and maintain this temperature for at least two hours. The large volume of the CeO_2-MgO mixed powders caused unusually high powder depths in the boat, making it necessary to reduce the quantity below 2500 grams to achieve >950 °C throughout the powder bed. Even at this amount the powder bed exceeded the 1-1/2 inch depth limit allowed for the production furnaces.

2.2.3 Furnace Testing In 2736-ZB Process Line

The adequacy of the new W-460 thermal stabilization and packaging process for stabilization was also demonstrated using surrogate powder in one of the actual production furnaces [HNF-10527, Rev. 0]. These test involved using pure CeO_2 powder, and two mixtures of CeO_2/MgO powder, 75/25 wt% and 50/50 wt%. Thermocouples were utilized to measure the temperature of the furnace, Hastelloy X® boats, and powder bed. In addition, minimum powder bed temperatures were determined using indication vials containing pure silver wire. The 20 gauge silver wire was demonstrated to melt at 962 °C and form a ball or bead when held at 976.5 °C. Nine of these indicator vials were placed in each test boat of powder, all at a depth of ~3/4 inch.

Results of the tests indicated that the furnaces were effective in heating the surrogate material to the required 950 °C.

3.0 Thermal Data From Literature

3.1 Thermal Conductivity Data

The thermal conductivity discussion presented in this section relates to the conductivity within a particle or single crystal of the material. If the material is present as a powder, then an effective thermal conductivity must be determined, since the dispersion fluid can have a very significant effect. This is discussed in Section 4.0.

Thermal conductivity depends on both temperature and density of the solid material. Limited thermal conductivity data has been reported in the literature for CeO_2, MgO, and PuO_2. This conductivity data is for the pure materials having specific solid densities: 6.2-6.87 g/cc for CeO_2, 10-10.66 g/cc for PuO_2, and for solid MgO having an unknown density. The thermal conductivity for these pure materials is plotted as a function of temperature in Figure 1. Scatter

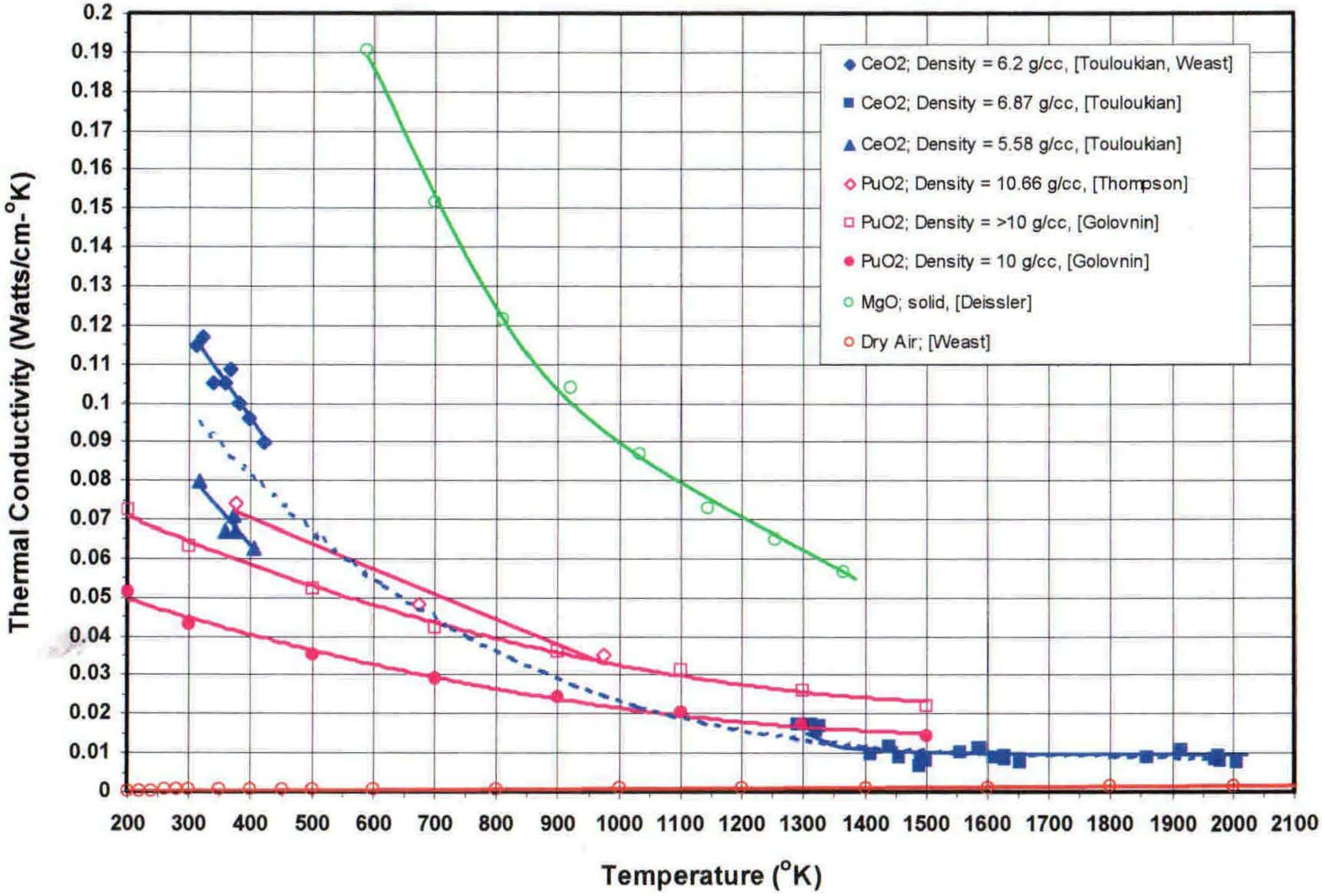

Figure 1. Thermal Conductivities For Air And Solid CeO_2, PuO_2, And MgO

in some of the data is the result of variations in the material porosity, as noted from the solid densities listed in the legend for the figure. The dashed line represents an overall interpolation for the thermal conductivity data for CeO_2 having slightly different solid densities. This data indicates that CeO_2 and PuO_2 have very similar thermal conductivities, while the thermal conductivity of MgO is higher by a factor of approximately 3.

As it was noted above, the thermal conductivity is known to be dependent upon the solid density. J. W. Jerrell, and P. Lam [Jerrell] have estimated the effect of solid density on the thermal conductivity of PuO_2. Their work involved thermal analysis of storage containers of special nuclear material. They used estimates and interpolations of thermal conductivity data available in the literature, and they assumed that the thermal conductivity was independent of temperature over their temperature range of interest (~30-225 °C). Figure 2 shows their estimated effects of density on the thermal conductivity of PuO_2. It can be seen by examining this figure that the thermal conductivity can increase substantially as the solid density increases over the temperature range shown. Estimates of density effects were not made for the high temperature range of interest in this study.

The thermal conductivity of air is also presented in Figure 1, which is significantly less than those for the oxides shown. This fact has a significant effect on the thermal analysis discussed later on in this paper on effective thermal conductivities and effective thermal diffusivities. It should also be noted that the thermal conductivity of a solid typically decreases with increased temperature while that of a gas typically increases.

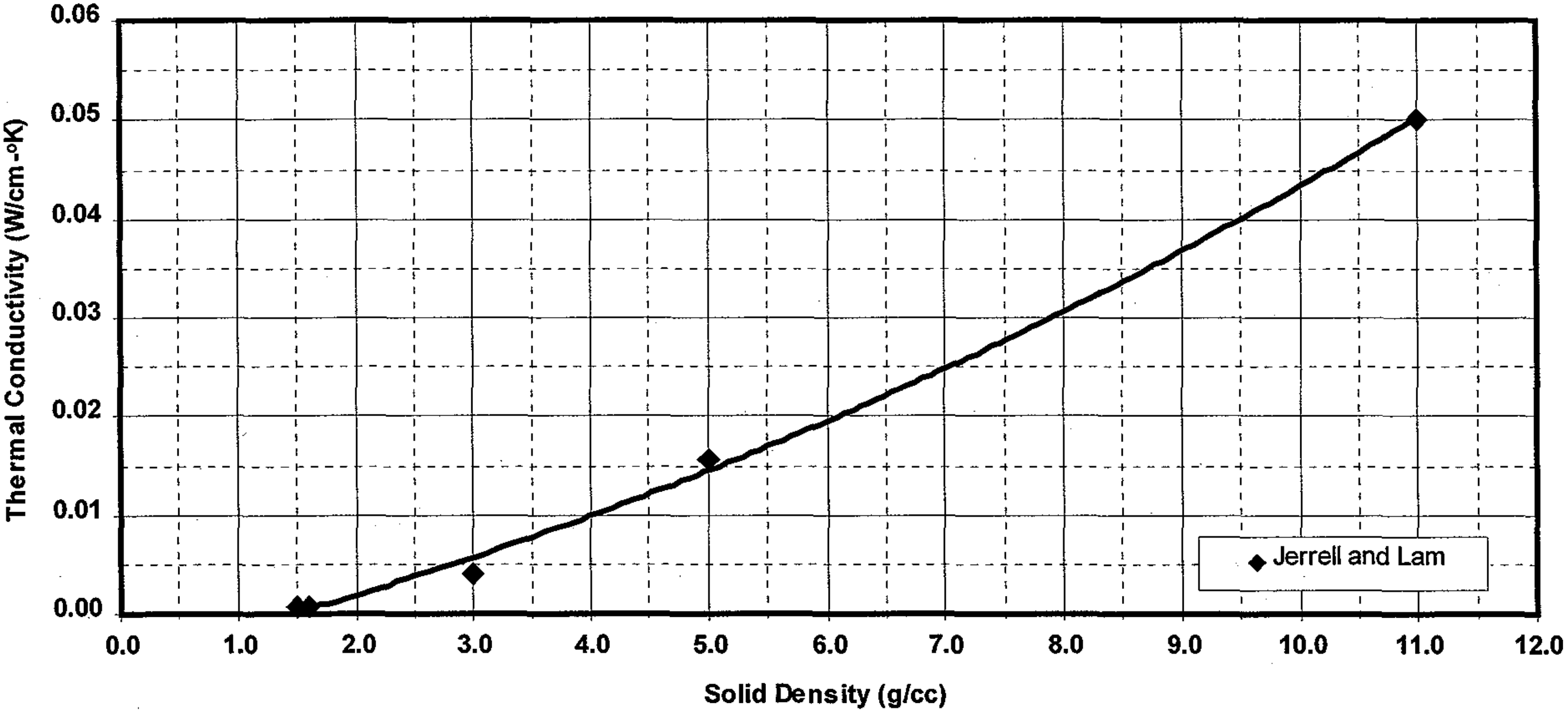

Figure 2. Effects Of Solid Density On The Thermal Conductivity Of PuO_2

3.2 Heat Capacity Data

In addition to thermal conductivity, the heat capacity of the powders also has an effect on the time and energy required to heat a material to a desired temperature. This thermal parameter has a significant effect on the thermal diffusivity of the material, as discussed in Section 6.0. Data on heat capacities as a function of temperature were taken from L. B. Pankratz's book, Thermodynamic Properties Of The Elements And Oxides [Pankratz]. Heat capacities that were calculated for the analysis discussed in this paper were from the following equations presented by Pankratz:

$$C_p(\text{cal/mole-°K}) \text{ for } CeO_2 = 16.761 + 2.216\text{x}10^{-3}T - 2.392\text{x}10^{5}T^{-2} \qquad (298.15 - 2000\ °K)$$

$$C_p(\text{cal/mole-°K}) \text{ for } PuO_2 = 20.677 + 1.906\text{x}10^{-3}T - 4.810\text{x}10^{5}T^{-2} \qquad (298.15 - 2000\ °K)$$

$$C_p(\text{cal/mole-°K}) \text{ for } MgO = 11.357 + 1.030\text{x}10^{-3}T - 2.473\text{x}10^{5}T^{-2} \qquad (298.15 - 2000\ °K)$$

Heat capacity temperature dependencies using these equations are shown in Figure 3.

4.0 Effective Thermal Conductivity Of Powders

It is well known that the thermal conductivity of powders is best represented by an effective thermal conductivity that is highly dependent upon the thermal conductivity of the material, void fraction, the type of the gas in the void spaces, and the gas pressure [ANL-6800, McLain, Deissler, and Kingery]. Numerous equations representing this effective thermal conductivity have been derived and reported in the literature. Two of these equations have been considered in this analysis in order to help visualize potential analytical differences. Maxwell developed one of the equations selected for two-phase mixtures [Etherington, Kingerly], and Krupiczka developed another for an analysis of the thermal conductivity of granular materials [Krupiczka].

Maxwell's equation:

$$k_{eff} = k_c\left[\frac{2k_c + k_d - 2x_d(k_c - k_d)}{2k_c + k_d + x_d(k_c - k_d)}\right]$$

where k_c represents the thermal conductivity of the continuous phase (air in this study), k_d the discontinuous phase (the oxides in this study), and x_d is the volume fraction of the discontinuous phase.

Krupiczka's equation:

$$k_{eff} = k_c\left(\frac{k_d}{k_c}\right)^{A + B\log\left(\frac{k_d}{k_c}\right)} \qquad \text{where } A = 0.280 - 0.757\log(1 - x_d), B = -0.057$$

and other terms are defined as for Maxwell's equation.

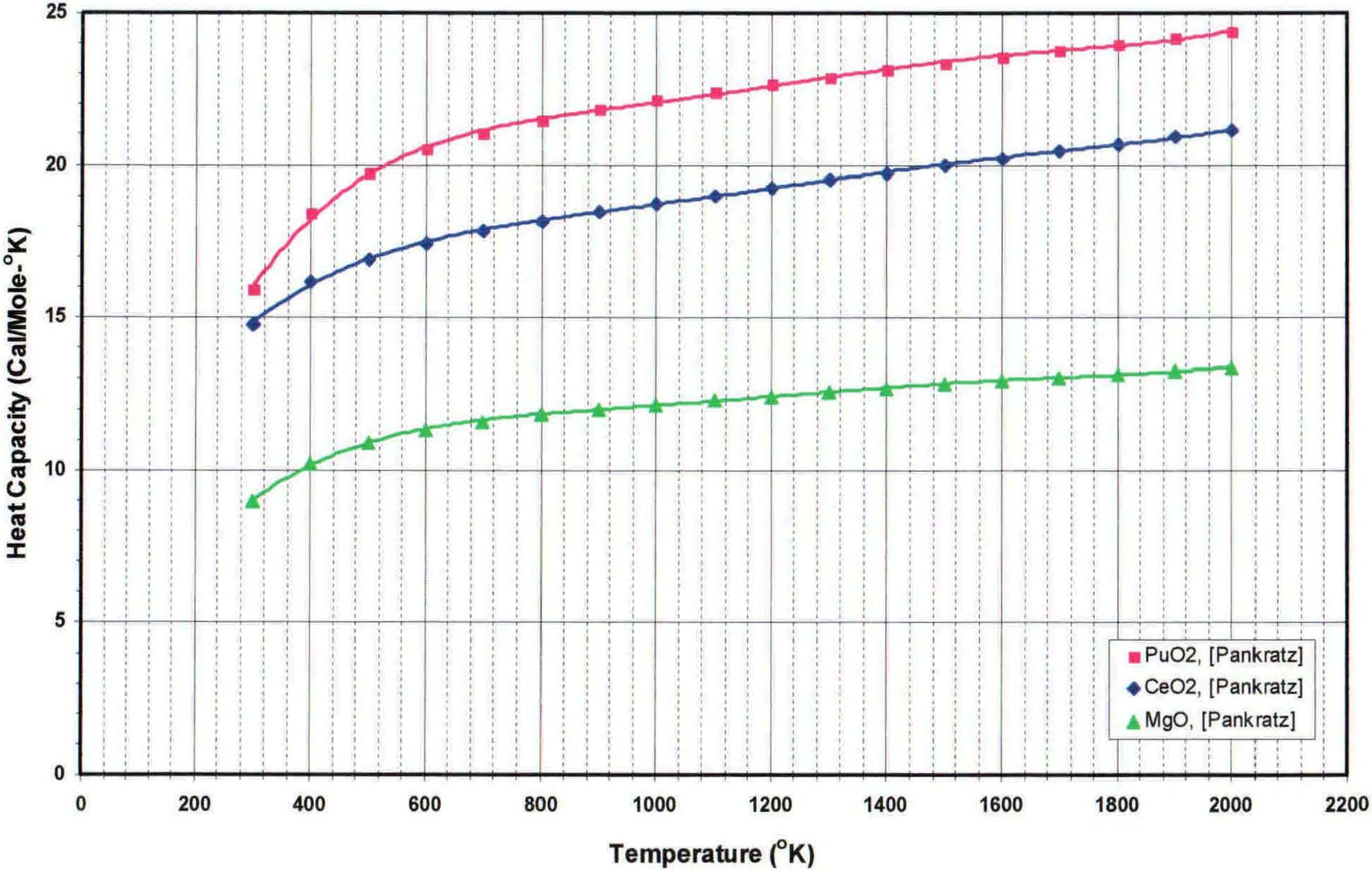

Figure 3. Heat Capacity Temperature Dependencies

These equations require a determination of the mass fraction or void fraction of the powder, which basically established how much air is mixed with the powder particles. Thus knowledge of the particle density (g/cc) and bulk density (g/cc) of the powder is necessary.

4.1 Material Characteristics

It was previously discussed in Section 3 that thermal conductivity depends upon the density of the solid material, as well as temperature. Estimating the effective thermal conductivity of powders brings in the additional particle and powder characteristics of particle density and powder bulk density. This section discusses particle and bulk densities. These parameters establish the porosity or void fractions for the CeO_2, MgO, and PuO_2 powders of interest.

The particle density depends upon the crystal theoretical density and porosity. For this study, the particle density is taken to be the same as the solid density. The bulk density depends upon the particle density, particle size distribution, particle shape, and particle structure. Typically only some of this information is available on material that has had the results of thermal conductivity measurements reported in the literature. Usually solid density is reported.

It was discussed in Section 3.1 that the thermal conductivity data reported in the literature was found for solid densities of 6.2-6.87 g/cc for CeO_2 and 10-10.66 g/cc for PuO_2. Solid density information was not reported for solid MgO for which thermal conductivity data was available. Since the solid density is usually less than the theoretical density (TD), it was assumed for this study the solid density was 75% TD, or 2.69 g/cc for MgO.

Bulk densities for CeO_2 and MgO used in this study were the results of measurements during the PPSL laboratory furnace testing work [Compton]: 1.84 g/cc for CeO_2 and 0.34 for MgO. Particle densities for the surrogate materials were not measured. It is assumed that the particle densities for the surrogate materials are the same as the solid densities for the CeO_2 and MgO oxides for which thermal conductivity data has been reported. Void fractions were calculated by dividing the bulk densities by the solid densities.

For thermal property comparison to PuO_2, the bulk densities were established from some of the Pu oxide characterization work done by the Los Alamos National Laboratory for the Materials Identification and Surveillance (MIS) Program [Mason]. This work involved characterization of Pu oxides generated from a wide range of different processes, including measurements of both bulk and particle densities. Data from this work was utilized to provide a general estimate of the bulk density for PuO_2 that has high particle densities similar to that for which thermal conductivity data is available. Results from the MIS particle density measurements were plotted against results for bulk density measurements on the same material, see Figure 4. As one would expect, this data is clearly scattered since these oxides were generated from a variety of different processing methods. There is, however, a definite trend for increased bulk density with increased particle density.

Recognizing that the PuO_2 at PFP has also been generated from numerous different processes and that this oxide is also represented in the MIS characterization work, the statistical relationship shown in Figure 4 was used to estimate bulk densities. For PuO_2 oxide having

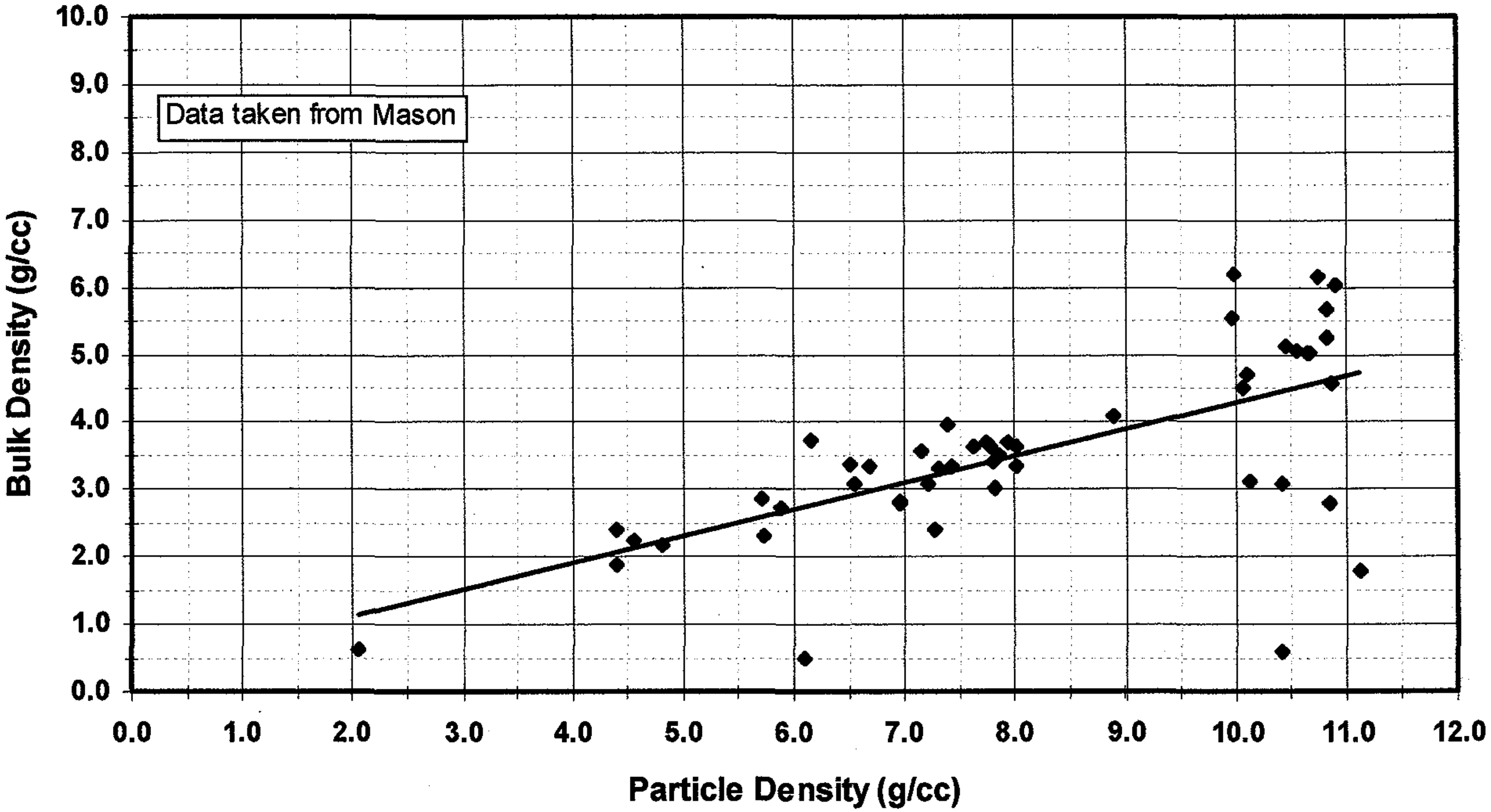

Figure 4. Statistical Correlation Between Measured Particle Density And Bulk Density For PuO_2

particle (or solid) densities of 10, 10.6, and 10.66 g/cc, bulk densities were estimated at 4.25, 4.5, and 4.55 g/cc, respectively.

A summary of the densities for these oxide materials is given in Table 1. Additional bulk densities for PuO_2 powder were also considered for sensitivity analysis in the calculation of the effective thermal conductivity and the effective thermal diffusivity of PuO_2. These bulk densities ranged from 1 g/cc to 8 g/cc, as discussed in Sections 4.2 and 5.0.

Table 1. Densities Of CeO_2, MgO, And PuO_2

Oxide	**Theoretical Solid Density[1] (g/cc)**	**Solid Density[3] (g/cc)**	**Bulk Density (g/cc)**
CeO_2	7.13	6.2-6.87	1.84[2]
MgO	3.58	2.69[4]	0.34[2]
PuO_2	11.46	10	4.25[5]
		10.6	4.5[5]
		10.66	4.55[5]

(1) CRC Handbook of Chenistry and Physics
(2) Measured during PFP furnace testing (Compton)
(3) Densities reported with thermal conductivity data
(4) Not reported; used estimate based upon 75% of the theoretical solid density
(5) Based upon statistical correlation shown in Figure 4

4.2 Estimates Of Effective Thermal Conductivities

The effective thermal conductivities for CeO_2, MgO, and PuO_2 powders have been estimated using the information discussed above. Calculations of the effective thermal conductivities included the temperature dependence of the thermal conductivities of the oxides and air, as shown in Figure 1. Figure 5 illustrates the effective thermal conductivities using Maxwell's equation, and Figure 6 provides the effective thermal conductivities utilizing Krupiczka's equation. Scatter in the data is a result of scatter in the reported thermal conductivities that is probably related to slight variances in solid porosities (see Figure 1) and curves were fit through the calculated data. Somewhat different effective thermal conductivities were calculated by the two equations. Both indicate that, for the powder properties considered, the effective thermal conductivity for the PuO_2 powder is greater than for either the MgO or CeO_2 powders. At first glance this seems unexpected. However, the void fraction of the PuO_2 powder is significantly less than the CeO_2 or MgO powders. This results in a higher powder effective thermal conductivity since less air is present.

Information on past plutonium processing work and the characterization work done at LANL in the MIS program [Mason] clearly shows that the bulk densities of PuO_2 powders can vary considerably, depending upon how the oxide is generated. To address the impact of PuO_2 bulk densities different than those established in Section 4.1 (4.25, 4.5, and 4.55 g/cc), effective thermal conductivities for PuO_2 powder was also estimated for a range of bulk densities. Particle

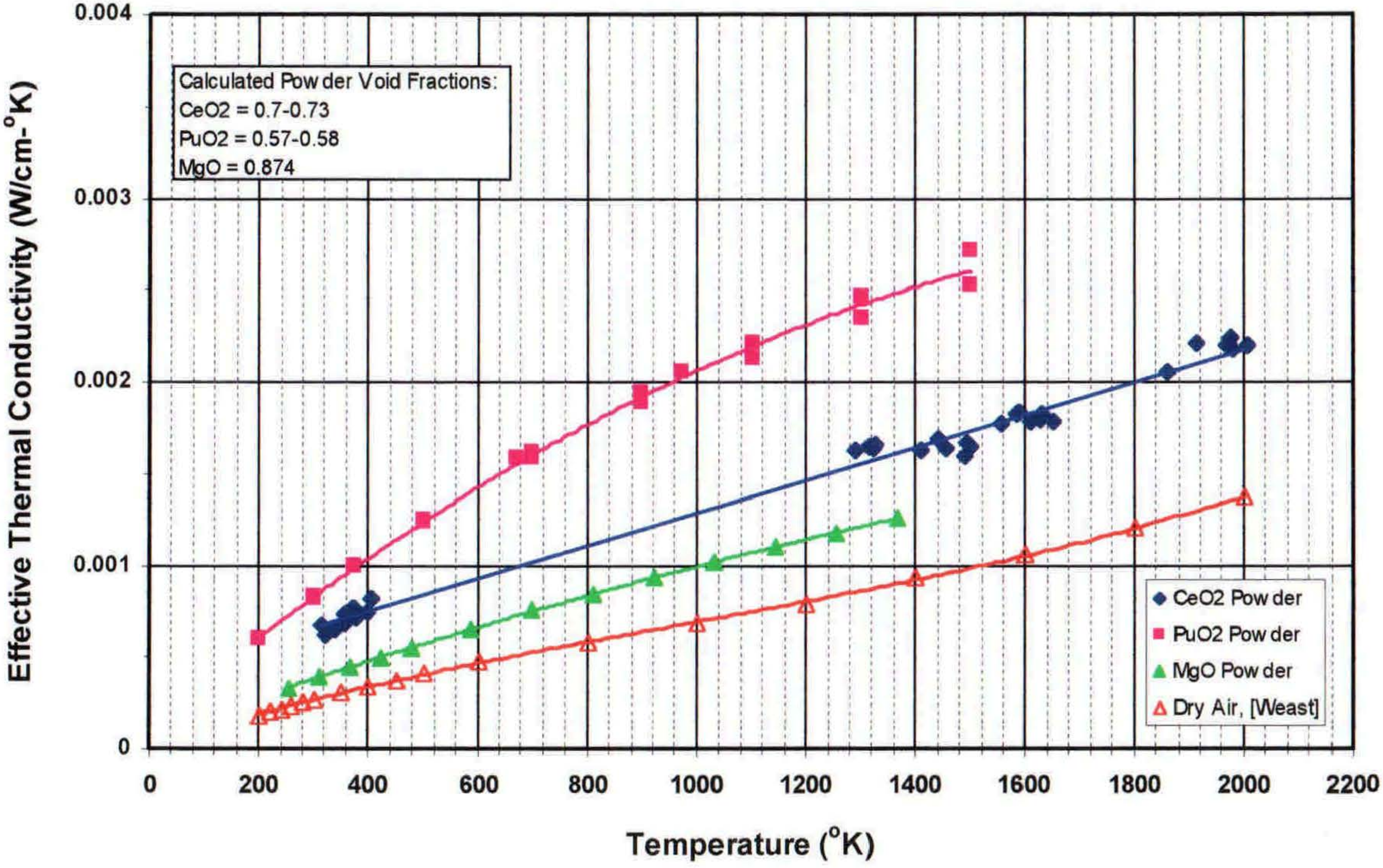

Figure 5. Estimates Of Effective Thermal Conductivities Using Maxwell's Equation

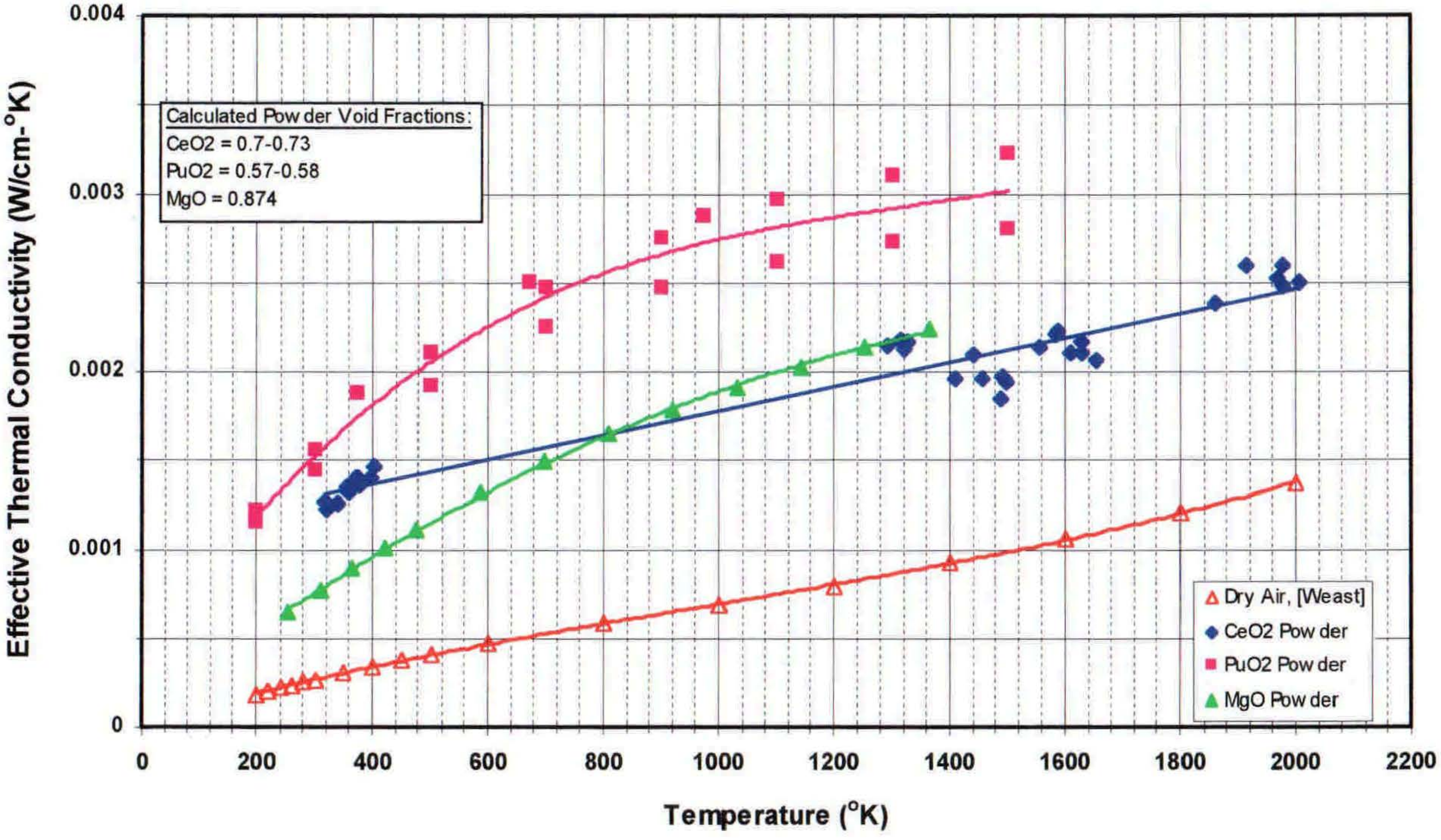

Figure 6. Estimates Of Effective Thermal Conductivities Using Krupiczka's Equation

densities were held constant and at values consistent with the reported thermal conductivities for the solid materials. These effective thermal conductivities were then plotted for PuO_2 bulk densities that resulted in 'high' and 'low' values of the effective thermal conductivity to show potential ranges. This 'high and low' determination was done by examining the effective thermal conductivity at a temperature of ~1300 °K, which is close to the operating temperature of the stabilization furnaces. The bulk densities that resulted in the 'high and low' values at that temperature were used to calculate the effective thermal conductivities for PuO_2 over the entire temperature range. This data is presented in Figure 7 and Figure 8 using both the Maxwell and Krupiczka equations. The PuO_2 bulk densities that resulted in the 'high' and 'low' effective thermal conductivities were 8 g/cc and 1 g/cc, respectively.

The data in Figures 7 and 8 clearly indicate that the PuO_2 effective thermal conductivities that are possible completely bracket those of the CeO_2 and MgO powders. Scatter in the data is a result of scatter in the reported solid thermal conductivities relating to slight variances in solid porosities. The CeO_2 surrogate powder and the MgO powder have effective thermal conductivities that are almost identical to that of a low bulk density PuO_2 powder. Plutonium dioxide powders having higher bulk densities have higher effective thermal conductivities than the CeO_2 and MgO powders used for furnace testing.

As was previously mentioned, thermal conductivity information is only part of the picture in addressing thermal properties. The effects of heat capacity must also be considered. Typically this is done through the analysis of thermal diffusivities. This is discussed in the next section.

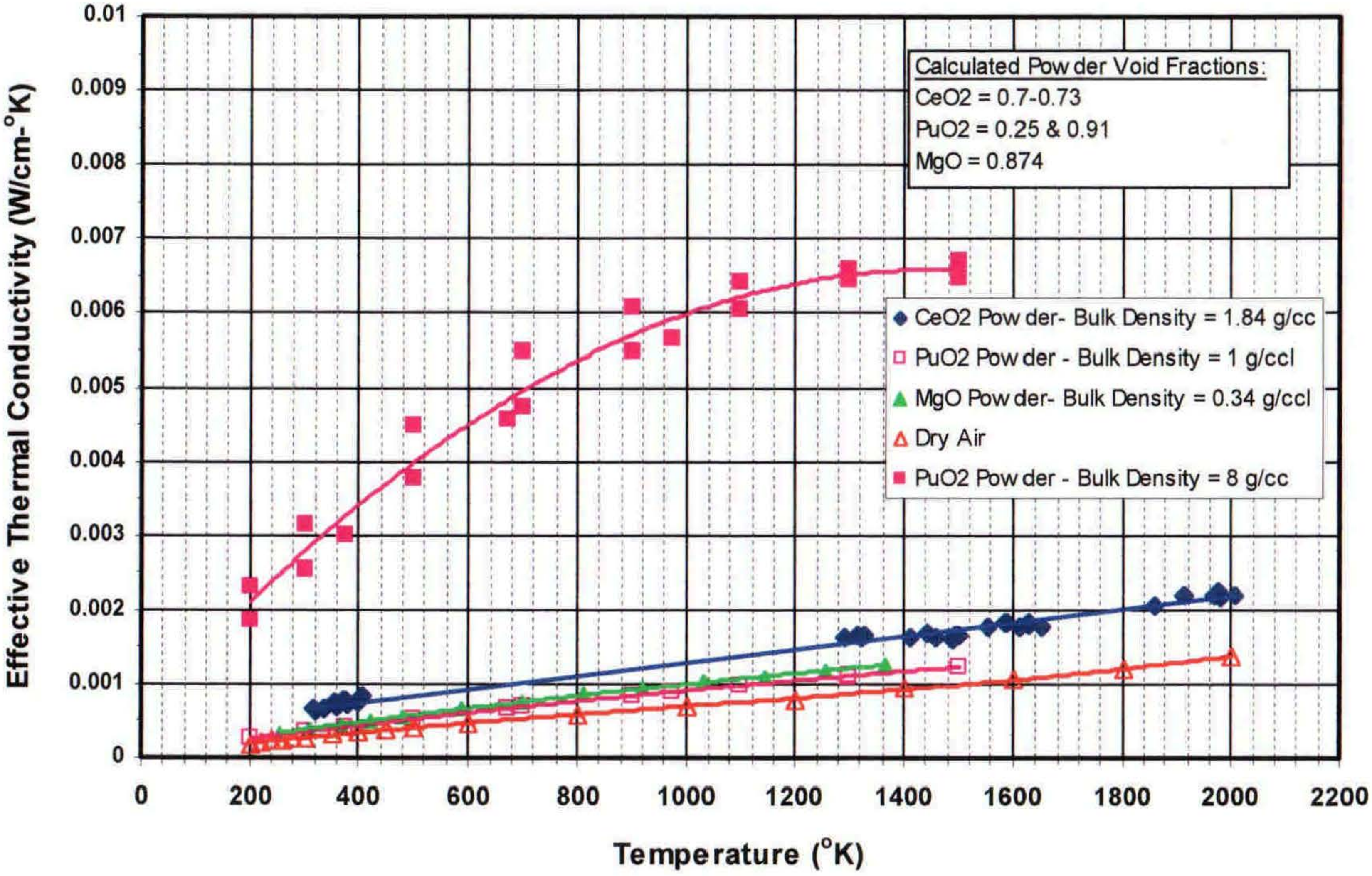

Figure 7. Effective Thermal Conductivities With Ranges For PuO_2 Having Different Bulk Densities
(Using Maxwell's Equation)

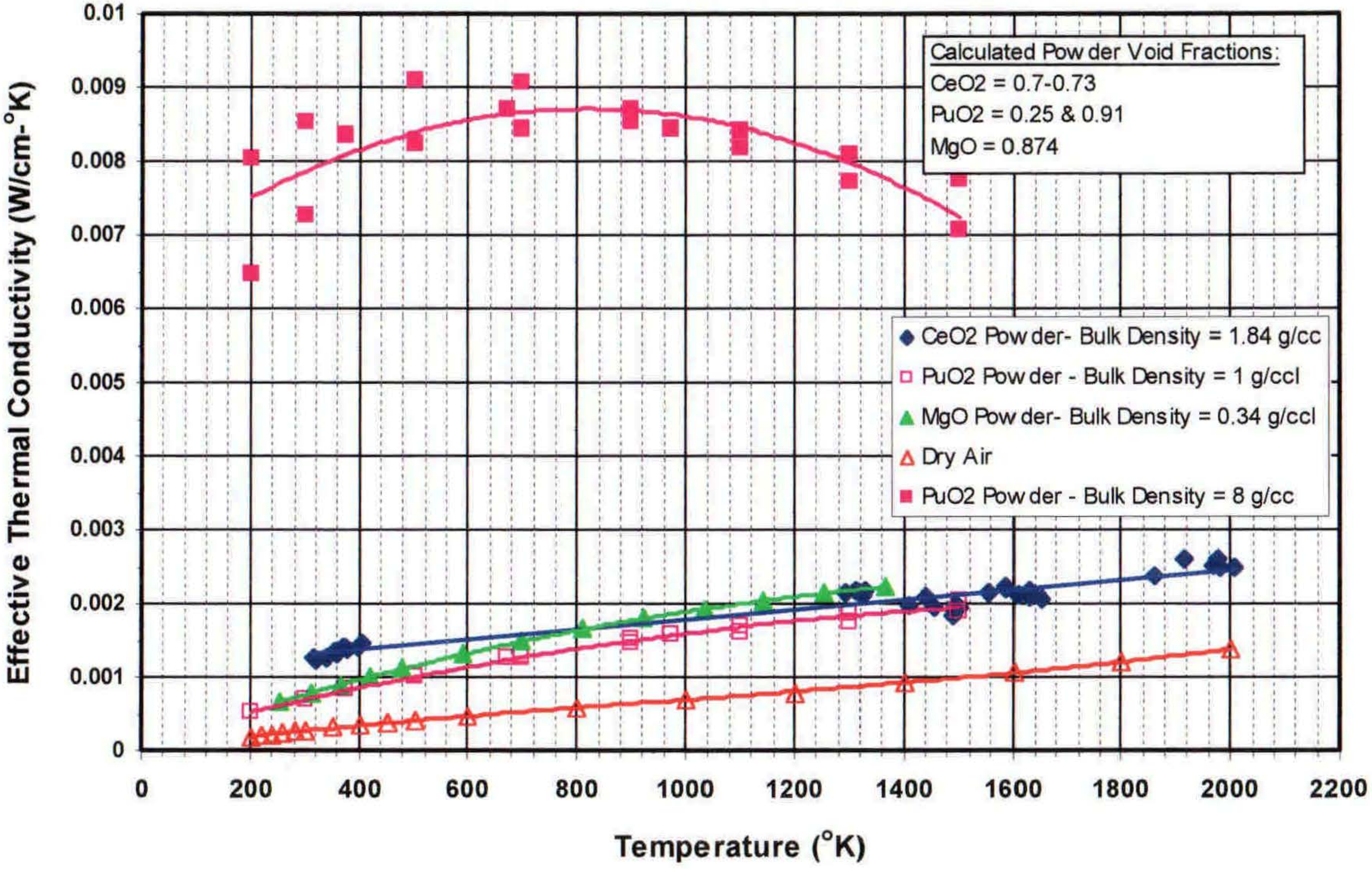

Figure 8. Effective Thermal Conductivities With Ranges For PuO_2 Having Different Bulk Densities
(Using Krupiczka's Equation)

5.0 Effective Thermal Diffusivities

In considering energy transport in a situation where there is no fluid motion, such as in the case where air is entrained within a powder, heat transfer through the material is predominantly by conduction. The general heat transfer equation is

$$\frac{\partial T}{\partial t} = \nabla^2(\alpha T)$$

where α (which is a function of temperature) is defined as the 'thermal diffusivity' and is equal to the thermal conductivity divided by the heat capacity and the density [Welty].

$$\alpha = \frac{k}{C_p \rho} \quad \text{where the units are } \left(\frac{area}{time}\right)$$

In the case of a powder where the thermal conductivity is represented by an effective conductivity, the effective thermal diffusivity can be written as

$$\alpha_{eff} = \frac{k_{eff}}{C_p \rho_{bulk}}$$

The thermal diffusivity describes the rate of penetration of a higher temperature into matter by absorption of heat. The rate of increase in temperature depends both on the rate energy is absorbed, which is controlled by the thermal conductivity, and the temperature rise per energy absorbed, which is controlled by the product of density and heat capacity. The ratio of these attributes is the thermal diffusivity. The time required to reach a given temperature rise at a given distance into a solid is inversely proportional to the thermal diffusivity. The distance a given temperature rise penetrates in a given time is proportional to the square root of the thermal diffusivity. Materials with a higher thermal diffusivity will reach a higher temperature more quickly upon heating than material with a lower thermal diffusivity. Therefore, a comparison of the effective thermal diffusivities for CeO_2, MgO, and PuO_2 provides insight into their relative heating rates as the material approaches the desired temperature.

Estimates of the effective thermal diffusivities for the oxides of interest are shown in Figure 9 for effective thermal conductivities calculated using Maxwell's equation, and in Figure 10 for effective thermal conductivities calculated using Krupiczka's equation. The scatter in the data is a result of scatter in the reported solid thermal conductivities that is probably related to slight variances in solid porosities, as previously noted. The calculated effective thermal diffusivities are somewhat different when using the different equations for the effective thermal conductivity. These series of calculations indicate for the powder properties considered (see Table 1 in Section 4.1), that the effective thermal diffusivity for the PuO_2 powder is very close to that for the CeO_2 powder and a factor of 2 to 3 less than that of MgO.

It was previously discussed that the bulk densities of PuO_2 powders can vary considerably, depending upon how the oxide is generated. To address the impact of PuO_2 bulk densities different than those established in Section 4.1 (4.25, 4.5, and 4.55 g/cc), effective thermal

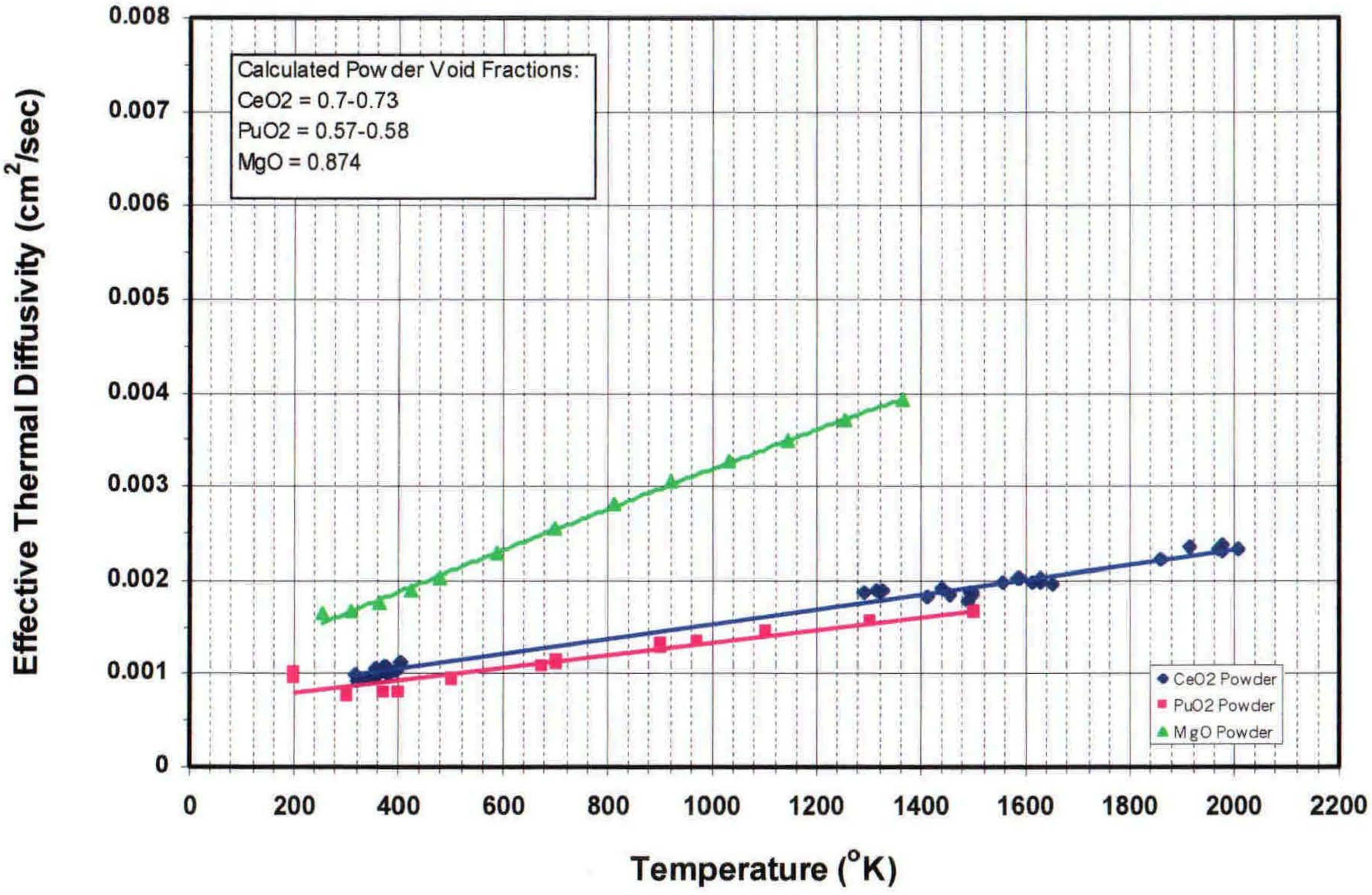

Figure 9. Effective Thermal Diffusivities Using Maxwell's Equation For Effective Thermal Conductivities

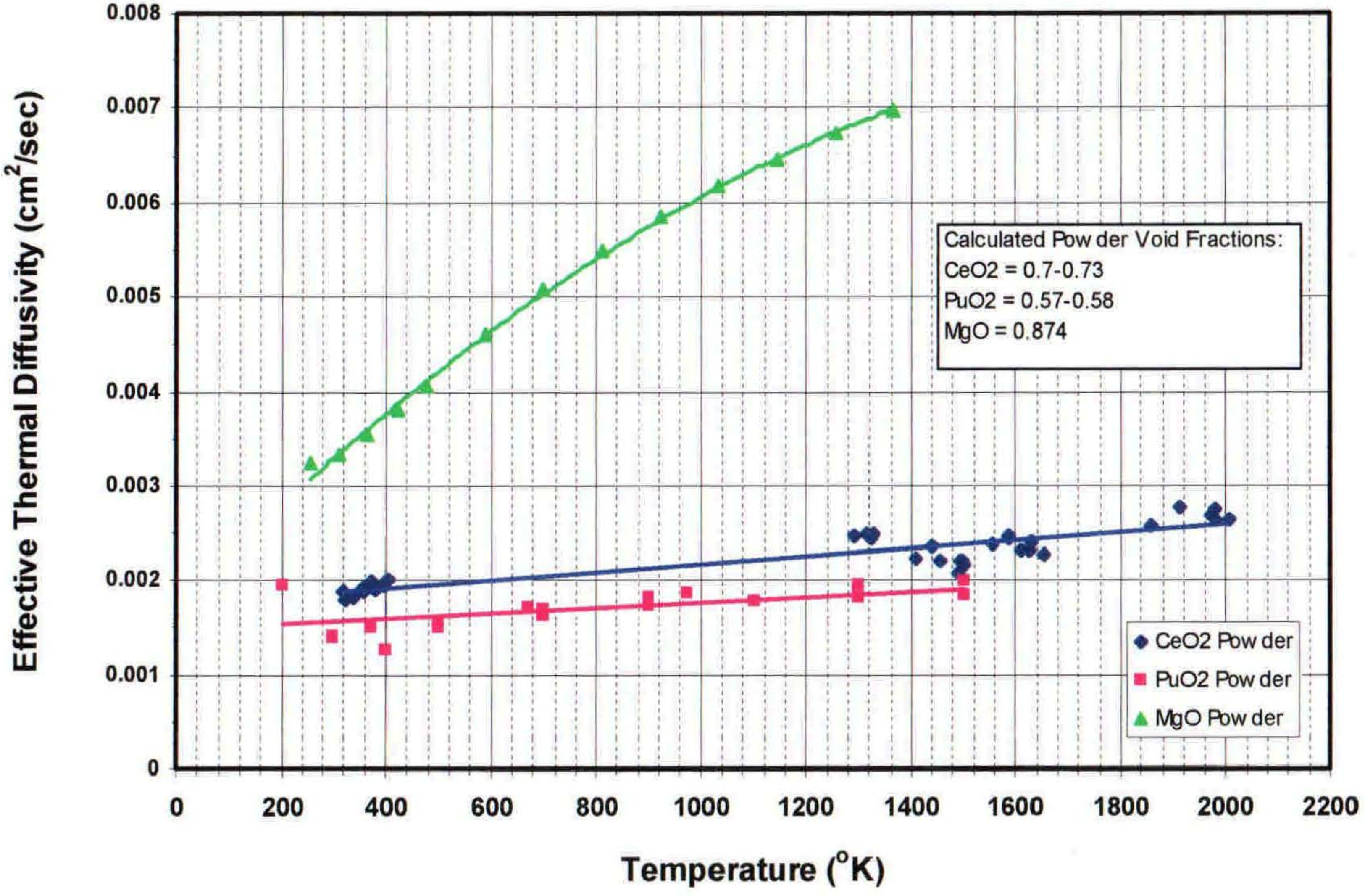

Figure 10. Effective Thermal Diffusivities Using Krupiczka's Equation For Effective Thermal Conductivities

diffusivities for PuO_2 powder was also estimated for a range of bulk densities, as was done for the effective thermal conductivities discussed in Section 4.2. The PuO_2 effective thermal diffusivities were calculated with bulk densities that resulted in 'high' and 'low' values to show potential ranges. This 'high and low' determination was done by examining the effective thermal diffusivity at a temperature of ~1300 °K, which is close to the operating temperature of the stabilization furnaces. The bulk densities that resulted in the 'high and low' values at that temperature were used to calculate the effective thermal diffusivities for PuO_2 over the entire temperature range. The PuO_2 bulk densities that resulted in 'high' and 'low' effective thermal diffusivities were 1 g/cc and 5 g/cc, respectively. This data is presented in Figure 11 and Figure 12 using the Maxwell and Krupiczka equations, respectively.

The data in Figure 11 clearly indicates that the PuO_2 effective thermal diffusivities that are possible for variances in bulk density completely brackets those of the CeO_2 powder and is quite close to those of MgO powder, when using Maxwell's equation for calculating the effective thermal conductivities. Use of Krupcizka's equation for calculating the effective thermal conductivities results in a similar trend for the effective thermal diffusivities, see Figure 12. The range of effective thermal diffusivities for PuO_2 is wider but still brackets those of CeO_2. The effective thermal diffusivity of MgO is calculated to be a factor of 1.5 to 2 times greater when using Krupiczka's equation for the effective thermal conductivities.

Recognizing that the surrogate powders used in PFP furnace testing, were either pure CeO_2 to represent PuO_2, or a mix of CeO_2 with up to 50% MgO to represent impure PuO_2 containing MgO, the average effective thermal diffusivities for mixed CeO_2-MgO powder was compared to the range possible for those of mixed PuO_2-MgO powders. This comparison was done assuming that the average effective thermal diffusivity of a mix of powders is equal to the effective thermal diffusivities of the individual powders weighted by their respective mass fraction in the powder mix. The powder mix used for this comparison was a 50-50wt%, the highest weight percent MgO used during PFP furnace testing. The average effective thermal diffusivities for the mix powders is shown in Figure 13, when using Maxwell's equation for calculating the effective thermal conductivities, and in Figure 14 when using Krupiczka's equation for the effective thermal conductivities. These results indicate that the possible PuO_2-MgO average effective thermal diffusivities completed brackets those of the CeO_2-MgO mixed powder. The average effective thermal diffusivities for the CeO_2-MgO mixed powder are close to those for mixed powders of PuO_2-MgO having a high PuO_2 bulk density and are less than those having a low PuO_2 bulk density.

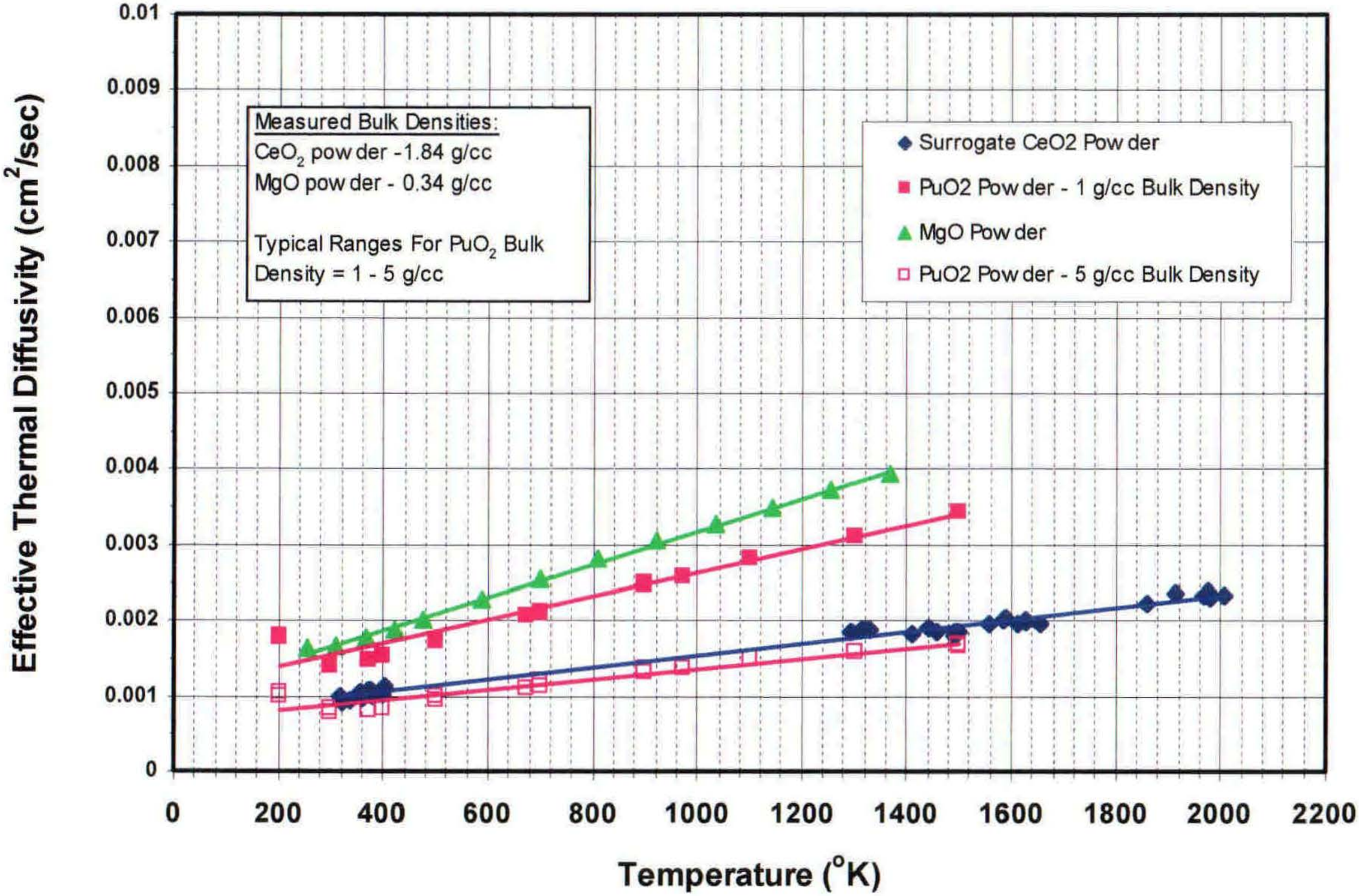

Figure 11. Effective Thermal Diffusivities With Ranges For PuO_2 Having Different Bulk Densities, Using Maxwell's Equation For Effective Thermal Conductivities

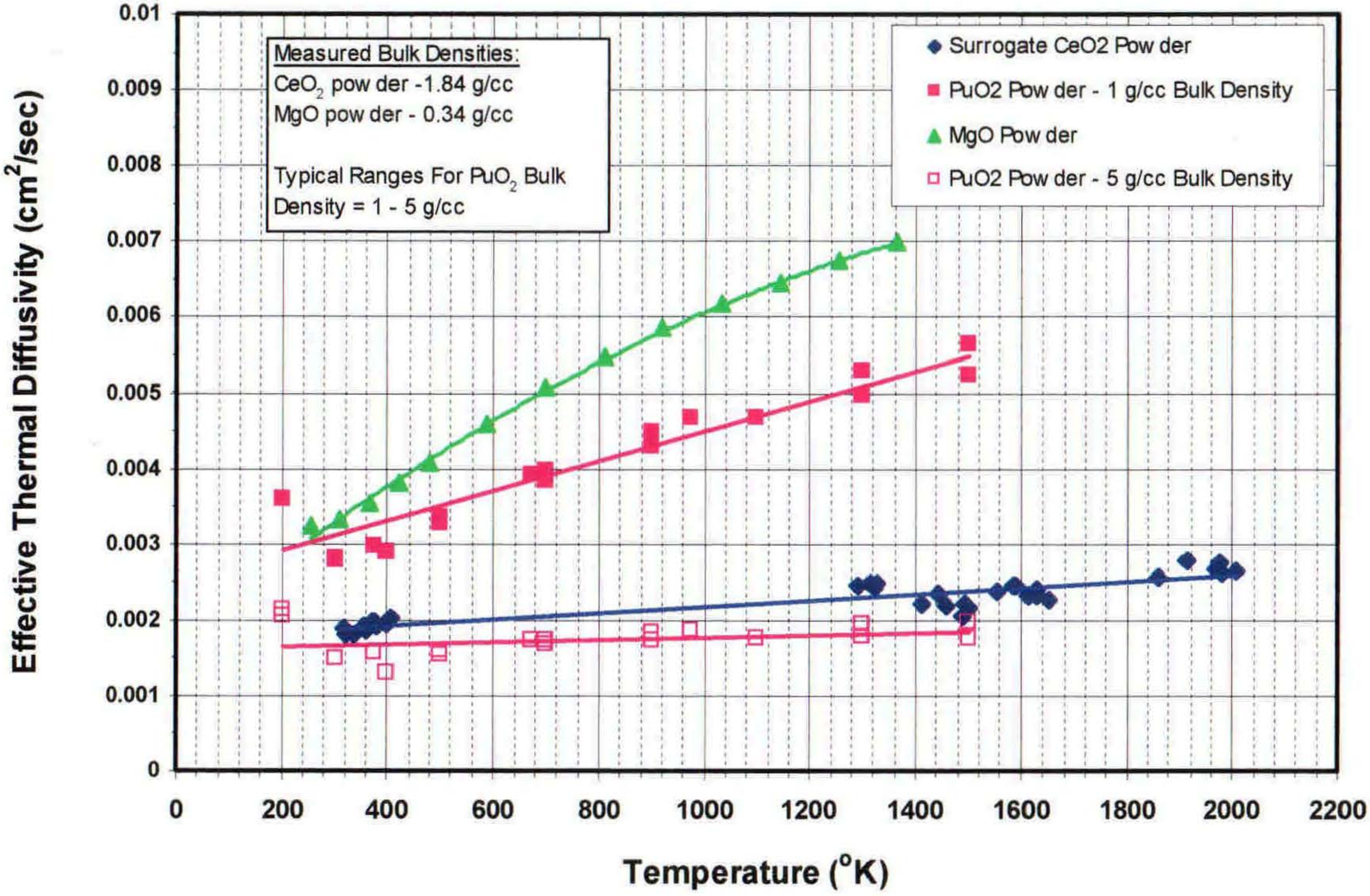

Figure 12. Effective Thermal Diffusivities With Ranges For PuO_2 Having Different Bulk Densities, Using Krupiczka's Equation For Effective Thermal Conductivities

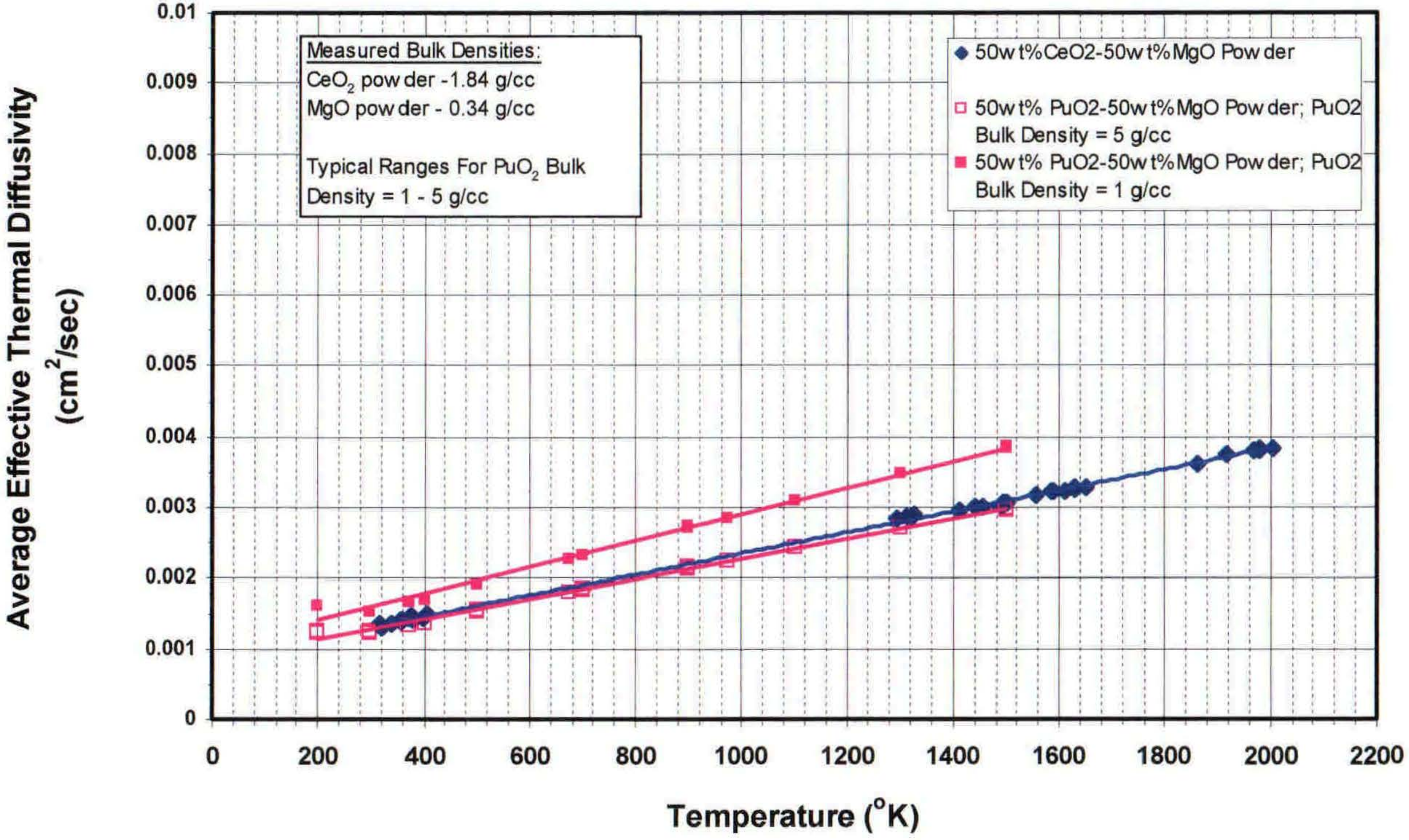

Figure 13. Comparison Of Effective Thermal Diffusivities, Average For Mixed Powders; Using Maxwell's Equation For Effective Thermal Conductivities

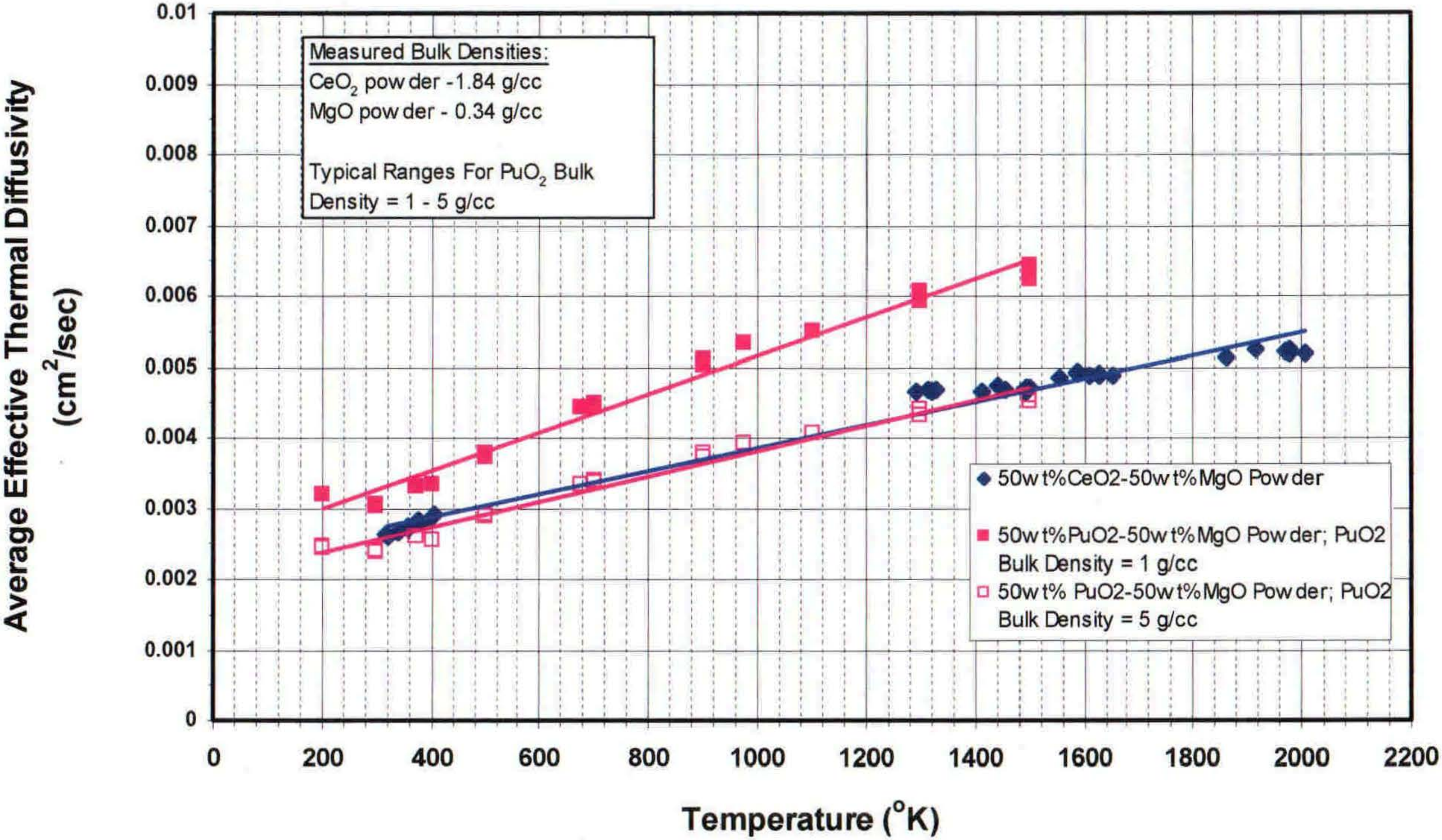

Figure 14. Comparison Of Effective Thermal Diffusivities, Average For Mixed Powders; Using Krupiczka's Equation For Effective Thermal Conductivities

6.0 Discussion

The thermal properties of CeO_2, MgO, and PuO_2 have been analyzed to address whether or not CeO_2 and CeO_2 - MgO mixtures are adequate surrogates for PuO_2 and impure PuO_2 containing MgO in simulating the heating of PuO_2 powders to 950 °C. This assessment involved comparing four thermal properties for each of the oxides: (1) thermal conductivity when in a solid/crystal state, (2) effective thermal conductivity when in a powder form, (3) heat capacity, and (5) the effective thermal diffusivity. The thermal properties of mixtures of CeO_2 and MgO powders are anticipated to reside somewhere between those of the individual powders and proportional to their amount, recognizing that one of the driving parameter will be the thermal conductivity of air, which is in all of the powders. Detailed heat transfer modeling was outside the scope of this paper.

Thermal conductivity depends on both temperature and particle density. Limited thermal conductivity data has been reported in the literature for CeO_2, MgO, and PuO_2. This conductivity data is for the pure materials having specific particle densities: 6.2-6.87 g/cc for CeO_2, 10-10.66 g/cc for PuO_2, and for solid MgO having an unknown particle density. This data indicates that CeO_2 and PuO_2 have very similar thermal conductivities, while the thermal conductivity of MgO is higher by a factor of approximately 3. Data is not available on the thermal conductivity of these oxides at significantly different solid densities.

The thermal conductivity of powders is best represented by an 'effective thermal conductivity' that is highly dependent upon the thermal conductivity of the material, the powder void fraction, the type of the gas in the void spaces, and the gas pressure. The effective thermal conductivities of the powders are significantly less than those for the solid materials because air, which is the continuous phase, has such a low thermal conductivity. The fraction of void space depends upon the particle size distribution, solid/particle density, and bulk densities of the materials. Typically very little data on material physical characteristics is provided in conjunction with thermal conductivity data reported in the literature. In addition, neither particle densities (g/cc) nor thermal conductivities were measured for the CeO_2 and MgO powders that were used in testing PFP stabilization furnaces. Therefore, it has been assumed for this study that particle densities of the CeO_2 and MgO powders used to make surrogate powders are the same as the solid densities for which thermal conductivity data is available. It has also been assumed that the bulk densities of CeO_2 and MgO powders which could be made from the solid oxides for which thermal conductivity data is available is the same as that measured on the oxides used to make surrogate powders.

Numerous equations representing an effective thermal conductivity for a powder have been derived and reported in the literature. Two of these equations have been considered in this analysis in order to help visualize potential analytical differences in estimating the effective thermal conductivities for CeO_2, MgO, and PuO_2 powders. Somewhat different effective thermal conductivities were calculated from the two equations. Results from both equations indicate that, for the powder properties considered, the effective thermal conductivity for the PuO_2 powder is greater than that for either the MgO or CeO_2 powders. At first glance this seems unexpected. However, the void fraction of the PuO_2 powder is significantly less than that of the surrogate CeO_2 or MgO powders that were used for testing. This results in a higher powder effective thermal conductivity since less air is present.

Plutonium processing experience within the DOE Complex and the characterization work done at LANL in the MIS program (Mason) clearly shows that the bulk densities of PuO_2 powders can vary considerably, depending upon how the oxide is generated. To address the impact of PuO_2 bulk densities different than those established in Section 4.1 (4.25, 4.5, and 4.55 g/cc), effective thermal conductivities for PuO_2 powder were calculated for a range of bulk densities to determine a "high and low' range for the PuO_2 effective thermal conductivity. This 'high and low' determination was done by examining the effective thermal conductivity at a temperature of ~1300 °K, which is close to the operating temperature of the stabilization furnaces. The bulk densities that resulted in the 'high and low' values at that temperature were used to calculate the effective thermal conductivities for PuO_2 over the entire temperature range.

Results indicated that the possible PuO_2 effective thermal conductivities arising from different bulk densities completely bracket those of the CeO_2 and MgO powders used as surrogate oxide representing PuO_2 powder and impure PuO_2 powder containing MgO. These powders have effective thermal conductivities that are almost identical to that of a low bulk density PuO_2 powder. Plutonium dioxide powders having higher bulk densities have higher effective thermal conductivities than the surrogate powders used. Thus the rate at which energy is absorbed into the surrogate powders is approximately the same for low bulk density PuO_2 and is significantly less than for high bulk density PuO_2 powder. This means that energy transfer into the surrogate powders is the same as or more difficult than for PuO_2 powders, depending on the PuO_2 bulk density.

A relative assessment of the rate of temperature rise for the CeO_2, MgO, and PuO_2 powders of interest was accomplished by evaluating their effective thermal diffusivities. The effective thermal diffusivity is defined as the effective thermal conductivity divided by the product of the heat capacity and bulk density. The thermal diffusivity describes the rate of penetration of a higher temperature into matter by absorption of heat. The rate of increase in temperature depends both on the rate energy is absorbed, which is controlled by the thermal conductivity, and on the temperature rise per energy absorbed, which is controlled by the product of density and heat capacity. The ratio of these attributes is the thermal diffusivity. The time required to reach a given temperature rise at a given distance into a solid is inversely proportional to the thermal diffusivity. Materials with a higher thermal diffusivity will reach a higher temperature more quickly upon heating than material with a lower thermal diffusivity.

The heat capacities for most oxides are readily available in the literature. Data used for calculation of the effective thermal diffusivities indicates that, on a gram-mole basis, the heat capacity of PuO_2 is ~15 % greater than that of CeO_2 and ~73 % greater than that of MgO at a temperature near 1000 °C.

Estimates of the effective thermal diffusivities for the oxides of interest were calculated using Maxwell's equation for the effective thermal conductivity, and for the effective thermal conductivity as calculated using Krupiczka's equation. The calculated effective thermal diffusivities are somewhat different when using the different equations for the effective thermal conductivity. However, the overall trend and relationships of the effective thermal diffusivities are very similar. Results of these calculations indicate that the effective thermal diffusivity for the PuO_2 powder is very close to that for the CeO_2 powder and may be a factor of 2 to 3 less than that of MgO powder.

The impact of PuO_2 bulk densities different than those established in Section 4.1 (4.25, 4.5, and 4.55 g/cc), on the effective thermal diffusivities for PuO_2 powder was also estimated for a range of bulk densities, as was done for the calculations of effective thermal conductivities. Results of these calculations clearly indicate that the PuO_2 effective thermal diffusivities that are possible completely brackets those of the CeO_2 powder used and are fairly close to those of the MgO powder, when using Maxwell's equation for calculating effective thermal conductivities. The use of Krupcizka's equation for calculating effective thermal conductivities results in similar trends, although somewhat different effective thermal diffusivities are calculated. In both cases the effective thermal diffusivities for MgO are higher than those possible for PuO_2 at temperatures above 300 °C. The MgO powder, however, is anticipated to heat up at the same rate, whether mixed with CeO_2 or PuO_2 powder.

The surrogate powders used in PFP furnace testing, were either pure CeO_2 to represent PuO_2, or a mix of CeO_2 with up to 50% MgO to represent impure PuO_2 containing MgO. A comparison of the average effective thermal diffusivities for mixed CeO_2-MgO powder was compared to the range possible for those of mixed PuO_2-MgO powders. This comparison was done assuming that the average effective thermal diffusivity of a mix of powders is equal to the effective thermal diffusivities of the individual powders weighted by their respective mass fraction in the powder mix. The potential range of the average effective thermal diffusivities for PuO_2-MgO powders was based upon variances in the PuO_2 bulk density, keeping material or particle densities unchanged. Results of this comparison indicate that the possible PuO_2-MgO mixed powder average effective thermal diffusivities completed brackets those of the CeO_2-MgO mixed powder.

Although the thermal and physical property data that was available for this study was lacking in a few areas, the results of this study indicate that the CeO_2 surrogate powder will heat up at the same rate or less than that of PuO_2, and surrogate mixtures with up to 50 wt% MgO will heat up at the same rate or less than that of PuO_2 containing up to 50wt% MgO, for the surrogate powders used in testing PFP's stabilization furnaces. If further conformation is felt necessary, actual measurements on PuO_2 powder could be performed in the W-460 stabilization furnaces. Another option, although more expensive, would involve detailed thermal analysis utilizing finite-difference modeling. This, however, would probably still require validation with actual measurements on PuO_2 powder.

This paper compared the thermal properties of CeO_2 powder containing up to 50wt% MgO impurity to that of PuO_2 containing up to 50wt% MgO impurity. The results of this analysis indicate that CeO_2 powder and CeO_2-MgO powder mixtures are excellent surrogates for PuO_2 powder and PuO_2-MgO powder mixtures for testing PuO_2 stabilization furnaces. Magnesium oxide was selected as the impurity of interest during PFP furnace testing since much of the impure PuO_2 to be stabilized and packaged at the PFP contains significant amounts of MgO from solution stabilization work. It is believed that lesser quantities of other impurities would not significantly alter the findings of this study.

7.0 Conclusions

- The thermal conductivity of solid PuO_2 is approximately the same as that of solid CeO_2, and is approximately 3 times less than that of solid MgO.
- The effective thermal conductivity of a powder is significantly less than that of solid material because of the low thermal conductivity of air.
- The effective thermal conductivity of PuO_2 powder is equal to or greater than that for both CeO_2 powder and CeO_2-MgO mix powders used as surrogate material to represent PuO_2 and impure PuO_2 containing MgO in testing PFP's stabilization furnaces.
- The CeO_2 surrogate powder and the CeO_2-MgO surrogate mix powders heat up at rates similar to or less than that for PuO_2 and PuO_2-MgO powders, based upon evaluation of their effective thermal diffusivities.
- The CeO_2 surrogate powder and the CeO_2-MgO mixed surrogate powders used during the testing of PFP's stabilization furnaces were excellent representations of how PuO_2 and impure PuO_2 containing MgO would behave under similar conditions.

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