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THERMAL CONDUCTIVITY OF ALUMINA PRODUCED BY
THE FLUIDIZED BED PROCESS

Paul N. Kelly

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US ATOMIC ENERGY COMMISSION

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A B S T R A C T

The thermal conductivity of granular, free-flowing alumina produced by fluidized bed calcination of simulated aqueous waste from uranium-aluminum alloy fuels at the Idaho Chemical Processing Plant was determined experimentally in the temperature range of 100° F to 2800° F. The thermal conductivity varied from 0.08 BTU/(hr)(ft²)(°F/ft) at 100° F to 0.30 BTU/(hr)(ft²)(°F/ft) at 2800° F.

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SUMMARY

A promising approach to increasing the safe disposal of liquid radioactive wastes from chemical reprocessing of atomic reactor fuels is fluidized bed calcination to a solid. One facet of the engineering studies involved for waste disposal by such means is the design of equipment and methods for dissipation of fission product decay heat from the calcined material. Adequate designs require knowledge of the thermal conductivity of granular, free-flowing alumina produced by fluidized bed calcining of simulated waste from uranium-aluminum fuels at the Idaho Chemical Processing Plant (ICPP).

Thermal conductivity was measured over the temperature range from 100° F to 2800° F. The method of determination involved steady-state conditions, i.e., the measurements of heat flux and temperature were made after the system had reached temperature equilibrium. Heat flux measurements for experiments above 1000° F were complex because the flux was not uniform along the length of the heating element. The method of measurement was affected by a change in physical state of the material being investigated, and absolute values for conductivity could not be obtained in some experiments. However, because the value of heat flux does not affect the slope of the conductivity versus temperature curves, no data were completely invalidated for this reason. The particle size of the alumina ranged from 14 to 150 Tyler mesh.

The experimentally determined values of the thermal conductivity varied from 0.08 to 0.30 BTU/(hr)(ft²)(° F/ft) at 100° and 2800° F respectively. Above a temperature of 1800° F, the alumina converted from amorphous to alpha crystalline structure, and the curve of thermal conductivity versus temperature is discontinuous in the region of 1800° F.

I. INTRODUCTION

A continually growing problem in the application of atomic energy is the safe disposal of radioactive waste from the recovery of uranium from spent fuel elements. A great amount of research and development effort is being expended on the problem (1, 2). The principal objective of these efforts is the biologically safe storage on a permanent basis. Present radioactive liquid waste storage in the United States is in underground tanks; however, because of corrosion and rupture possibilities, these tanks are not considered an ultimate solution to the disposal problem. For the past several years, the Atomic Energy Division of Phillips Petroleum Company has investigated the fluid bed technique for the conversion of radioactive liquid wastes to solids (3, 4, 5). Simulated wastes from uranium-aluminum fuel elements have been calcined in a pilot plant fluid bed calciner to produce a granular, free-flowing alumina.

As part of the fluid bed calcining program, the problem of removal of nuclide decay heat from the stored solids was investigated. Although the heat generation is not great (an estimated 1.8 BTU/(hr)(lb) of alumina for two-year-cooled MTR wastes)(6), the low thermal conductivity of granular alumina limits the rate of heat flow creating the possibility of extremely high temperatures in bulk storage. Storage above calcining temperature may be operationally undesirable because of possible fission product migration (7); thus, thermal conductivity data are necessary for design of safe, economical storage containers.

This work is a continuation of studies initiated at ICPP by Chase (8) who reported thermal conductivities over the temperature range from 100 to 1500° F. In the work reported here, Chase's data were recalculated by an independent method and the experimental error was determined. In an attempt to improve the accuracy of results in this new method of calculation, only the data in the range from 100 to 1000° F were considered. Further experimental work was performed to determine the conductivity up to a temperature of 2800° F. The method used for conductivity determination involved steady-state heat transfer, and all measurements were taken after thermal equilibrium was reached.

The calcined alumina used in this work was produced in a pilot plant fluidized bed calciner operated at 750° F with a liquid feed of the composition shown in Table 1.

Table 1

PILOT PLANT CALCINER FEED COMPOSITION					
Component	Al ⁺⁺⁺	NO ₃ ⁻	H ⁺	Na ⁺	Hg ⁺⁺
Concentration (gm-moles/liter)	2.2	8.0	1.25	0.15	0.008

No attempt was made to include fission product chemicals in the feed, since they constitute only a small portion of the chemical composition. The calcined alumina had an amorphous crystalline structure and a slightly yellow appearance due to a residual nitrate concentration of 1.4 milli-equivalent per gram. The poured bulk density was estimated at about 50 pounds per cubic foot. More thorough investigations of the bulk density of alumina produced by the ICPP pilot plant calciner have been made since these conductivity tests (9). These investigations reveal that the intra-particle porosity varies within a range from 4 to 60 per cent voids and affects the bulk density which varies from 1.5 to 0.6 gm/cc. The particle size distribution for two series of experiments is given in Table 2. These distributions were typical of all but two series of experiments which were conducted with size extremes, +28 and -100 mesh.

Table 2

CALCINED ALUMINA SIZE DISTRIBUTION (weight per cent)							
Tyler Mesh	+14	+20	+28	+35	+60	+100	-100
Sphere Series A	9.6	16.2	18.7	20.4	23.5	7.3	4.2
Sphere Series C		5.9	19.1	34.5	28.0	8.8	3.7

II. MATHEMATICAL CONSIDERATIONS

The two generally acceptable physical configurations for the apparatus used for determining thermal conductivity are the spherical and the cylindrical. Both configurations were used in these experiments.

In a thermal conductivity determination such as this, the conductivity obtained is an apparent conductivity which may be described as a summation of all possible methods of heat transfer; it includes radiation and convection effects in combination with pure conduction (10). In this experiment the heat transfer by convection was no doubt negligible because of the small particle size (10, 11). The contribution of radiant heat transfer, which increases with temperature, was minimized because the void spaces were small and the particles served to block this type of heat transfer (11).

To avoid temperature error due to conduction in wire leads, thermocouples were placed in the bed with the first three or four inches of lead equidistant from the heater. Temperature deviation due to conduction in wire leads can be significant even at moderate temperature (12, 13).

a. Spherical

The mathematical relationships for determining conductivity from radial heat flow in spheres at steady-state conditions are straightforward. A workable relation is obtained from a differential form of Fourier's Law applied to a sphere:

$$q_x = -k_m A \frac{dt}{dx} \quad (1)$$

substituting for surface in terms of radius and rearranging:

$$\int dt = - \frac{q_x}{4\pi k_m} \int \frac{dr}{r^2} \quad (2)$$

then integrating:

$$t = \frac{q_x}{4\pi k_m} \frac{1}{r} + C \quad (3)$$

A list of nomenclature is given on page 24. Using equation (3), the thermal conductivity can be calculated from energy input and temperature measurements at steady-state, i.e., a plot of (t) versus ($\frac{1}{r}$) giving a slope of $q_x/4\pi k_m$. To perform the integration, a mean thermal conductivity (k_m) must be used since conductivity varies with temperature.

b. Cylindrical

A workable relationship for determining cylindrical heat flow at steady-state is obtained from a differential form of Fourier's Law as follows:

$$\int q_x = -k_m A \int \frac{dt}{dx} \quad (4)$$

substituting for surface and rearranging:

$$\int dt = - \frac{q_x}{2\pi l k_m} \int \frac{dr}{r} \quad (5)$$

then, integrating:

$$t = - \frac{q_x}{2\pi l k_m} (\ln r) + C \quad (6)$$

Using equation (6), the conductivity may be calculated from heat flux and temperature data. This equation assumes no heat loss from the ends of the cylinder, i.e., a cylinder of infinite length.

III. EXPERIMENTAL

A. Spherical Apparatus

In experiments with spherical configuration, twelve- and eighteen-inch-diameter spheres with 100 watt heating elements, three-eighths-inch in diameter by one inch long, were used. Figure 1 shows a view of the lower hemisphere of the eighteen-inch sphere with the heating element and thermocouples in place. Both assembled spheres are shown in Figure 2. Temperature measurements were made on alumina with typical size distribution in two series of experiments in the eighteen-inch sphere while measurements for two series of experiments with -100 mesh and one series with +28 mesh were made in the twelve-inch sphere. Each series of experiments constituted measurements at thermal equilibrium for four or five conditions of heat flux.

B. Cylindrical Apparatus

A cylindrical configuration was used to extend the temperature range, making use of commercially available silicon carbide heating rods capable of operating at temperatures up to 2800° F. The cylinder used was 12 inches in diameter by 48 inches long and was jacketed in five sections. Heating rods, 1 and 1-1/2 inches in diameter with active heating sections 34 and 30 inches long, respectively, were utilized and platinum-platinum, 10 per cent rhodium thermocouples were used in high temperature zones. Figure 3 shows the lower half of the cylinder with the heating element and thermocouples in place.

Figure 1

View of the eighteen-inch-diameter spherical apparatus showing the heating element and thermocouples in place

Figure 2

The two spheres assembled with power supply and recorders at right

Figure 3

View of the cylindrical apparatus showing heating element and thermocouples in place

In preliminary experiments, heat fluxes were determined by metering water through the jacket compartments and measuring the temperature rise. Figure 4 shows the assembled apparatus for these measurements (Series AI). For high temperature measurements, the cylinder was wrapped with nichrome heating wire (Figure 5) and covered with six inches of insulation (Figure 6). Heating of the insulated cylinder surface had the effect of extending the high-temperature zone which improved temperature measurements; however, the nichrome heater was used in only one experimental series (Series AII) because the nichrome wire failed in the final experiment of the series. Equipment refinements in a subsequent series of experiments (Series B, C, D, and E) were directed toward attaining a more uniform heat flux along the length of the cylinder. Transite discs, wrapped with nichrome wire, were placed at the ends of the active section of the heating rod and dry insulating material was placed on the outside of these discs. In Figure 7 is shown a comparison of the temperature profiles of the cylinder bed, both before and after addition of the heated discs. Because the heat flux was not completely uniform along the rod, the power input could not be used for the heat flux measurement. In these experiments the heat flux was determined from the outer portion of the cylinder where the thermal conductivity was known, i.e., at the lower temperature. Several power settings were used for each series of experiments and the heater was taken to failure in the final experiment of each series, except C. For Series B and C, the bed was replaced with fresh alumina, but for Series D and E, the only alumina available for testing was that which had been used previously.

Figure 4

Cylinder assembled for low temperature measurements

Figure 5

Cylinder being wrapped with nichrome wire

Figure 6

View of cylinder covered with insulation

Figure 7

Temperature profiles of cylinder before and after insertion of end heating discs

Upon dismantling the bed after each experimental series, the alumina was found to be fused around a section of the heating rod. Figure 8 is a typical view of the rod after disassembly; Figure 9 is a close-up view of the fused section. Radially from the fused section, the alumina was caked to a diameter of about five inches and bleached white as contrasted to the initial off-white color. Chemical analyses established that nitrates originally present had been driven off, and X-ray diffraction studies showed that the alumina structure had changed from the amorphous to alpha crystal structure. Data from the tests indicate this change took place above 1800° F. Because of the nature of the experiments, this temperature must be regarded as approximate only. The caked material contained some beta alumina, formed above 2200° F (also approximate) along with the alpha alumina. The fused material was a mixture of different forms of Al_2SiO_5 and $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, formed when the silicon carbide heater melted or vaporized and fused with the alumina. A summary of these analyses is given in Table 3.

Figure 8

Silicon carbide heating rod after failure

Figure 9

Close-up of fused section of silicon carbide rod shown in Figure 8

Table 3

SUMMARY OF ALUMINA ANALYSES

<u>Temperature (°F)</u>	<u>Crystalline Structure</u>	<u>Nitrate Concentration (meq/gm)</u>	<u>Physical Description</u>
750	amorphous	1.38	Free-flowing, off-white color
1800	alpha	< .05	Free-flowing
2200	alpha and beta	< .05	Caked, bleached white color
2800	Al_2SiO_5 and $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$	< .05	Fused

The change of physical state caused an uncertainty in the absolute value of thermal conductivity for experiments in which the low temperature portion of the bed (from which heat flux values were determined) contained alpha alumina. While this was unfortunate, it did not completely invalidate these data because the value of heat flux does not affect the slope of the conductivity-temperature curve; it determines only the absolute value. In other words, a family of curves, dependent upon the value chosen for heat flux, may be drawn for each set of data.

IV. RESULTS

The thermal conductivity varied linearly from 0.08 to 0.27 BTU/(hr)(ft²)(°F/ft) at 100° F and 1500° F, respectively, with an error estimated at ± 0.03 BTU/(hr)(ft²)(°F/ft). In the range 1500 to 1800° F, the results diverged, presumably due to varying degrees of conversion of the alumina from amorphous to alpha crystalline structure. From 1800 to 2800° F, the thermal conductivity was essentially constant between 0.28 and 0.30 BTU/(hr)(ft²)(°F/ft). Figure 10 is a composite curve including the results from all experiments.

The absolute values of thermal conductivity at temperatures above 1500° F were established by only one experimental series, but the nature of the curve was established as well from all experiments in the cylinder. The wide conductivity variation in the range from 1500° F to 1800° F was probably due to temperature variation prior to reaching equilibrium; in some cases this caused a physical-state conversion.

CPP-S-2273

Figure 10

Relationship between thermal conductivity and temperature derived from composite results of all experiments

In some experiments, temperature-datum points in the fused region of alumina caused discrepancies. Single experiments showed a sharp rise in conductivity at 2600° F and 2800° F, while the other experiments failed to show any such rise. Data in this region are of doubtful value when it is considered that silicon from the heater rod combined with the test material to form silica-alumina compounds. Under actual storage conditions, fusion will not produce a similar type of structure, since silicon will not be present.

The results of experiments on +28 and -100 Tyler mesh fractions of the alumina tested are given for the temperature range 100 to 1000° F in Figure 11. In the conductivity-temperature relation of these size extremes, it is significant to note that the thermal conductivity of the +28 mesh fraction increases more rapidly with temperature than unclassified alumina, while the -100 mesh fraction increases less rapidly. This is no doubt due to the effect of particle size on the radiant heat transfer. This mechanism of heat transfer becomes a more significant part of the equivalent conductivity as temperature increases; because, as the experimental results show, with increasing particle size, there are larger void spaces within the mass of solids.

CPP-S-2272

Figure 11

Thermal conductivity of the size extremes (+28 and -100 mesh) of the alumina measured

V. CONCLUSIONS AND RECOMMENDATIONS

The results of this study show that thermal conductivity varies linearly with temperature in the range from 100° F up to 1800° F, and the values reported confirm those previously reported by Chase⁽⁸⁾ for amorphous alumina. The conversion of the physical state of the alumina from amorphous to alpha crystalline structure at about 1800° F causes a change in the thermal conductivity, making its relationship with temperature discontinuous in that temperature area. This conversion of the physical state of the alumina made interpretation of the results difficult. If further studies to obtain more accurate results in the range above 1800° F are warranted, the following recommendations should be considered:

- (1) Use material produced in the Demonstrational Waste Calcining Facility.
- (2) Convert the alumina to the alpha or beta state before performing conductivity experiments.
- (3) Perform experiments to determine more accurately the temperature of the physical state conversion.
- (4) Devise an apparatus for high temperature thermal conductivity measurements in which heat flux can be obtained independent of conductivity.
- (5) Determine the effect of intra-particle porosity on thermal conductivity.
- (6) Determine if there is any significant variation in the thermal conductivity of alpha alumina for extreme size fractions.
- (7) Determine the effect of additives (e.g., boron) on thermal conductivity.
- (8) Devise a heat source which will provide a uniform heat flux.

Future studies on the properties of alumina produced during calcination of fuel reprocessing wastes should include determination of the volatility and migration of fission products.

VI. NOMENCLATURE

A	Area through which heat flows at right angles (ft^2)
C	A constant of integration
k_m	True mean value of thermal conductivity, $\text{BTU}/(\text{hr})(\text{ft}^2)(^\circ\text{F}/\text{ft})$
l	Length (ft)
q_x	Steady rate of heat flow (BTU/hr)
r	Radius (ft)
t	Temperature ($^\circ\text{F}$)
x	Length of conduction path (ft)

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