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Thermal Conductivity of Coal Ashes and Slags

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DISCLAIMER

Thermal Conductivity of Coal Ashes and Slags

CONTRACT INFORMATION

FY'92 Program Schedule

	J	A	S	O	N	D	J	F	M	A	M	J
Physical Properties												

OBJECTIVES

The purpose of this work is twofold: 1) to gain an understanding of the effects of mineralogical inhomogeneity and porosity of coal ash deposits on the heat-transfer phenomena, and 2) to determine the relationship between thermal and electrical conductivities in the temperature range of 25°-500°C. This new program was initiated at the Energy and Environmental Research Center (EERC) in 1991 to elucidate the cause of significant heat-transfer problems in the convective pass of utility boilers.

BACKGROUND INFORMATION

In combustion and gasification systems, a buildup of deposits on heat-transfer surfaces in the convective pass reduces the heat transfer. It is important to know the thermal conductivity of the deposited coal ashes to predict the energy loss on the nondeposited heat-transfer surfaces. Very little data on the thermal conductivity of coal ashes exist in open literature. The problems result from the extremely inhomogeneous chemical and mineralogical compositions of the ash.

Thermal conductivity is defined as the proportionality coefficient between the heat flux passing through a material and the temperature gradient resulting from the causative heat flux. This arises from the lattice thermal conduction, k_l; the electronic thermal conduction, k_e; and the ionic thermal conduction, k_i.[1] The latter factor in silicate/aluminosilicate glasses usually occurs at high temperatures and is a result of the transport of mobile alkali metal ions.

The appropriate method is determined by the physical nature of the material, the geometry of the samples available, the required accuracy of results, the speed of operation, and the time and funds entailed. The supplied heat must flow through the defined area of the sample without gain or loss. To achieve such precise cancellation in practice is simply impossible. However, from the practical point of view, it is important to carry out experiments under the same conditions to allow a reliable comparison of obtained results. The nonsteady-state method is applied to measure thermal diffusivity.[2,3]

The heat flux, Q/t, can be lost by means of radiative heat. This effect is mostly observed in large sample sizes.[4] Also, one measurement on a large sample takes a long time. Generally, a small length-to-width ratio of sample for poor conductors is recommended, in literature, to measure thermal conductivity at high temperatures.[2,3] To minimize error in temperature gradient measurements and to save time, the thin-plate method was selected for thermal conductivity measurements. The applied method is based on the assumption that there is the same heat flow, Q, through both a sample of unknown conductivity and a standard of known conductivity.[5]

PROJECT DESCRIPTION

A striking feature of thermal conductivity of nonmetallic solids is its relation to structure, composition, and microstructure.

Influence of Structure

The structure effect is visualized by the nature of atomic vibrations in real crystals that depend on the bond energy and the mass of atoms/ions. Generally, a decrease in the bond energy is accompanied by a noticeable decrease in the lattice heat conductivity.[6] Also, the lighter elements (such as B, C, N, Si) cause an increase in thermal conductivity.[7] Amorphous ceramic materials, in turn, usually have lower thermal conductivities than those in crystalline form.[8]

Composition

Materials with complex compositions have a lower conductivity than their components.[9] However, thermal conductivity of silicate/aluminosilicate glasses is not influenced much by composition and usually is about 1 $Wm^{-1}K^{-1}$ at room temperature.[10]

Microstructure

The picture of the thermal conductivities of ceramics may totally be changed when pores are introduced into the materials. In most cases, the radiation process across the pores causes a decrease of k.[11] Moreover, grain boundaries, mineralogical inhomogeneities, the distribution of individual phases, crystallographic orientations of grains in the matrix, and adhesional contact at the grain-grain and/or grain-glass-grain interfaces affect the thermal conductivity values. The thermal conductivity of a multiphase material may be significantly reduced if the second phase

completely isolates the high thermal conductivity phase.

Apparatus

Thermal conductivity measurement was based on the axial one-dimensional heat flow method.[12,13] The apparatus used for the thermal and electrical conductivity measurements is shown in Figure 1. A cylindrical pellet with an unknown thermal conductivity was placed between a heater at one end and a reference material (Pyrex 7740) with known thermal conductivity[14] at the second end. The hot source was built with a Pt disc and was warmed by a heating element in a stainless steel block with a peripheral guard shield to assure uniform heat flow. The metal block was kept at a constant temperature by a direct current supplied to the main heater. The platinum disc and the metal block were called the heat sink. The second platinum disc on top of the sample was called the cold sink. A small force was applied to the top of the column to improve the connectivity between the pellets and simultaneously reduce the radiation processes.

The thickness and the area of the coal ash specimens were 0.4-0.5 cm and 1.8-1.9 cm^2, respectively. The platinum discs and Pyrex 7740 had the same area. Their thicknesses were 0.254 cm and 0.325 cm, respectively.

In order to get correct temperature measurements and to minimize error, the Pt-PtRh thermocouples were made with fine wires that had fabrication diameters of 0.1 mm. The temperatures were recorded from the central zones.

To prevent radial heat losses, two guard cylinders were used. The inside cylinder surrounding the specimen was made with ircar and located around the heater and samples. The outside cylinder was a mullite tube. Additionally, the space between the inside guard shield and the specimen was filled with bubbled alumina, which had a low thermal conductivity coefficient.[5] This reduced heat losses resulting from the convection process.

T_1, T_2, T_3, T_4 thermocouples
S sintered coal ash pellet
P Pyrex 7740
R for measurements of resistivity
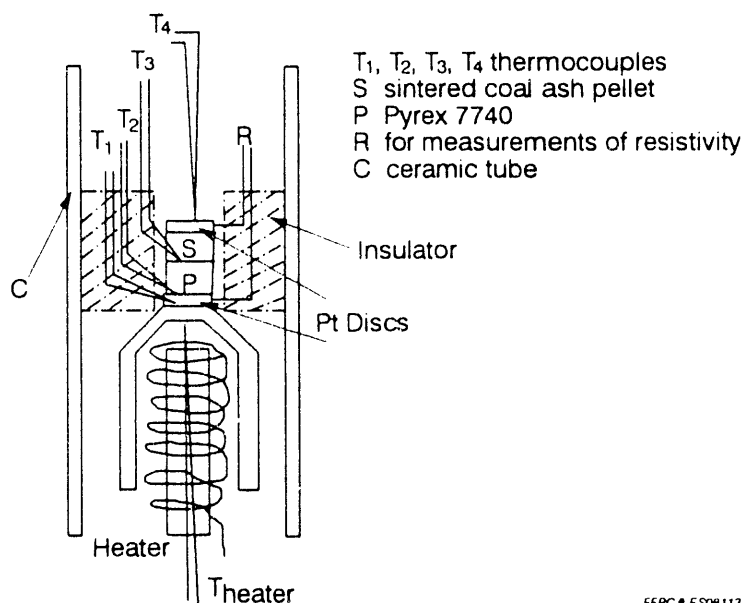C ceramic tube

Figure 1. Scheme of Thermal and Electrical Conductivity Apparatus

Experimental Procedure

Five Pt-PtRh thermocouples were arranged to measure and to regulate the temperatures; T_1 read the temperature of the heater (first platinum disc) at the bottom of a sample; T_2 read the temperature between the reference sample and the Pt disc; T_3 read the temperature between the reference sample and the coal ash sample; and T_4 read the temperature of the cold sink.

The direct current in the heating element, the switching mechanism for reading temperatures, and "beaded" thermocouples have shown that the reproducibility of measuring temperatures on Pt discs was superior. The temperature reading accuracy was evaluated on Pt/Pyrex/Pt sandwich specimens with two fine-wire thermocouples at each interface. The precision of measured temperature was $\pm 0.05\,°C$.

Tests on all specimens were run for a fixed time (usually 5 min), and the outputs at that time were recorded until equilibrium was achieved. The EERC has developed a computer program to allow recording and saving all data to a disc.

All tests were run on well-polished pellets, previously sintered in an air atmosphere at appropriate temperatures and times to assure good surface contact. As mentioned above, Pyrex 7740 was selected as a reference material because its conduction area well matched those in coal ash deposits. Pyrex conductivities were controlled using a specimen of fused silica. The thermal conductivity values of Pyrex 7740 differed from literature values by about 5%.

Electrical resistivity was measured in separate experiments in the same apparatus on the same coal ash samples without a reference sample using a Hewlett Packard model 3478A multimeter. This allowed the electrical conductivity to be calculated and compared with the thermal conductivity of coal ashes.

Chemical and mineralogical compositions of tested coal ashes were determined by x-ray fluorescence and x-ray diffraction techniques, respectively.

Porosity of sintered samples was estimated (after measuring thermal and electrical conductivities) using the automated image analysis of backscattered electron images. Closed porosity was evaluated for sintered coal ashes from the weight gain of the samples after keeping them in anhydrous methanol for 24 h.

Densities were determined from the displacement of anhydrous methanol at room temperature using a pycnometric method with an accuracy of ± 0.02 g/cm^3. Duplicate samples were used in the experiments, and average values are presented.

Since the thermal conductivity of materials is very sensitive to the inhomogeneity of chemical and mineralogical compositions, a special processing technique was developed. Homogeneous amorphous coal ashes were prepared by melting at 1500°C, homogenizing at that temperature for 3 h, and quenching at room temperature (Table 1). The obtained glass was ground to -30 mesh and sintered at an appropriate temperature for a specific time. After sintering, the crystalline phases were determined. The mineralogical compositions of the tested samples are listed in Table 2.

Model sodium silicate glass and gehlenite with the chemical compositions listed in Table 1 were also used. They were prepared from oxides/carbonates by melting at 1500°C,

Table 1. Composition of Coal Ashes and Model Glasses

Sample	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	Na_2O	K_2O	P_2O_5
Beulah	30.1	16.2	12.3	1.7	23.8	7.2	7.4	0.1	1.2
Gascoyne	35.2	11.5	8.8	1.5	27.6	7.5	6.7	0.1	1.0
Illinois #6	50.7	18.7	21.3	0.7	5.3	0.8	0.6	1.8	0.1
Glass	61.7	14.9	--	--	11.9	1.9	9.5	--	--
Gehlenite	19.9	10.7	5.9	--	57.8	3.8	0.5	--	--

Table 2. Mineralogical Compositions of Sintered Coal Ashes

Coal Ash	Treatment	Major Phases
Beulah	900°C/3 h	Nepheline ($NaAlSiO_4$)
		Gehlenite ($Ca_2Al_2SiO_7$)
	1000°C/3 h	Gehlenite
	1100°C/3 h	Gehlenite
	1100°C/20 h	Gehlenite
		Haüyne ($[Na,Ca]_8[Al_2Si_2O_{24}][SO_4]_2$)
Gascoyne	1100°C/15 h	Gehlenite
		Merwinite ($Ca_3Mg[SiO_4]_2$)
Illinois #6	1100°C/15 h	Anorthite ($CaAl_2Si_2O_8$)
		Hematite (Fe_2O_3)
Gehlenite	1300°C/3 and 5 h	Gehlenite

homogenizing at that temperature, and quenching at room temperature. The glass was ground to -38 mesh before sintering.

Method of Calculation

The heat flow between two isothermal surfaces and heat losses due to radiation were assumed to be the same in all experiments. This assumption allows the determination of the thermal conductivity coefficients for unknown materials with the same range of error. Under such ideal conditions, the thermal conductivity coefficient of the sample was calculated from the following equation:

$$k_s = k_{ref} \frac{S_{ref}}{S_s} \frac{\left(\frac{\Delta T}{X}\right)_{ref}}{\left(\frac{\Delta T}{X}\right)_s} \quad [Wm^{-1}K^{-1}] \qquad 3$$

where k_s and k_{ref} are the thermal conductivities of the specimen and the reference material, S_s and S_{ref} are the surfaces of the specimen and the reference material, respectively, and x_s and x_{ref} are the appropriate lengths.

Electrical conductivity ($\Omega^{-1}m^{-1}$), was calculated separately from the resistivity results.

RESULTS

Thermal and Electrical Conductivities of Selected Coal Ashes and Model Silicates

Generally, the thermal and electrical conductivities increase with temperature and are dependent on both the chemical and mineralogical compositions (Figures 2-6). Thermal and electrical conductivity results presented in the figures correspond to those measured at equilibrium. Calculations of the thermal conductivities of amorphous forms of coal ashes are included in the figures. Usually, they are lower than that measured on crystalline forms. Calculations were performed by steady-state methods using factors representing the contribution of individual oxides (on a wt% basis) at 30°C, as provided by literature.[14,15] The micro-porosity as determined by the automated image analysis of backscattered electron images was lower than 4%. However, the microporosity of gehlenite, sintered at 1300°C for 3 h, was higher than 10%, and this corresponds with a sample density of 3.039 g/cm³.

Results of the thermal conductivity of model silicate glass shown in Figure 5 are compared with two selected from literature with compositions that match as closely as possible to our specimen.[16] However, some discrepancy between our results and that from the literature exists. Also, a discrepancy exists between the literature values of thermal conductivities, if measured as a function of temperature, and it is in the order of 10% or higher.

Generally, heat in solids is conducted by the free electrons in metals and alloys at low temperatures, by thermal vibrations of atoms that are observed in the stoichiometric dielectrics, by the free electrons and holes as well as lattice vibrations at the sufficiently

high temperatures recorded in semiconductors, and also by ions in amorphous materials at high temperatures. In our case, the linear variations of both thermal and electrical conductivities suggest also that ionization of point defects related to nonstoichiometry, impurities, and dopants plays some role in the thermal conductivity at intermediate and high temperatures. They create free carriers, such as electrons and holes, with concentrations that increase with temperature. The magnitude of this electronic component of thermal conductivity is very low, since σ/k is about 10^{-6}. Also, there is reason to expect the existence of electrically charged ceramic particles in a liquid-phase sintering medium that may introduce free charges.[17] The ionic component in heat transfer, related to the diffusion of alkali ions, does not play any major role in this range of temperature and can be neglected. This component may take place above some critical temperature, across the surface, or through the volume of the material and is strongly dependent on the glass structure.

Effect of Porosity on Thermal Conductivity

Figure 7 shows the effect of porosity on the thermal conductivity of Beulah coal ash. Thermal conductivity decreases with the increase of porosity. Two kinds of pores are distinguished: two large pores and fine pores inside the large ones. The latter pores are likely formed from necks. Listed in Table 3 are porosity numbers estimated after measuring thermal conductivity.
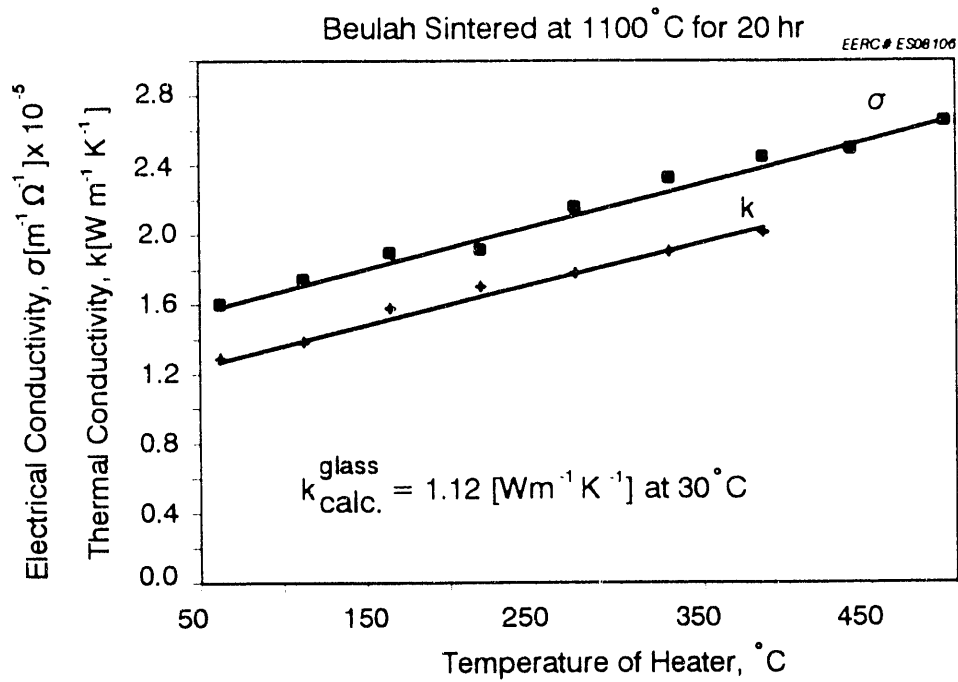
Beulah Sintered at 1100°C for 20 hr

Thermal Conductivity, k[W m⁻¹ K⁻¹]
Electrical Conductivity, σ[m⁻¹ Ω⁻¹]x 10⁻⁵

$k^{glass}_{calc.}$ = 1.12 [Wm⁻¹K⁻¹] at 30°C

Temperature of Heater, °C

EERC# ES08106

Figure 2. Thermal and Electrical Conductivities of Beulah Coal Ash Sintered at 1100°C for 20 h, in Air

Gascoyne sintered at 1100°C for 15 hr

Thermal Conductivity, k [Wm⁻¹K⁻¹]
Electrical Conductivity, σ[Ω⁻¹ m⁻¹]x 10⁻⁸

$k^{glass}_{calc.}$ = 1.134 [Wm⁻¹K⁻¹] at 30°C
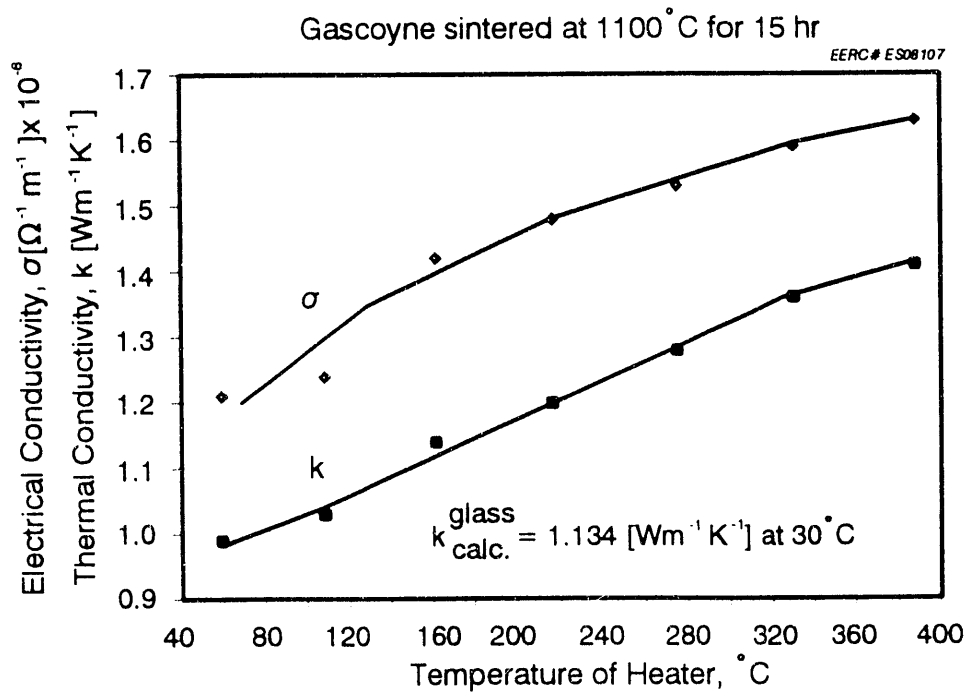
Temperature of Heater, °C

EERC# ES08107

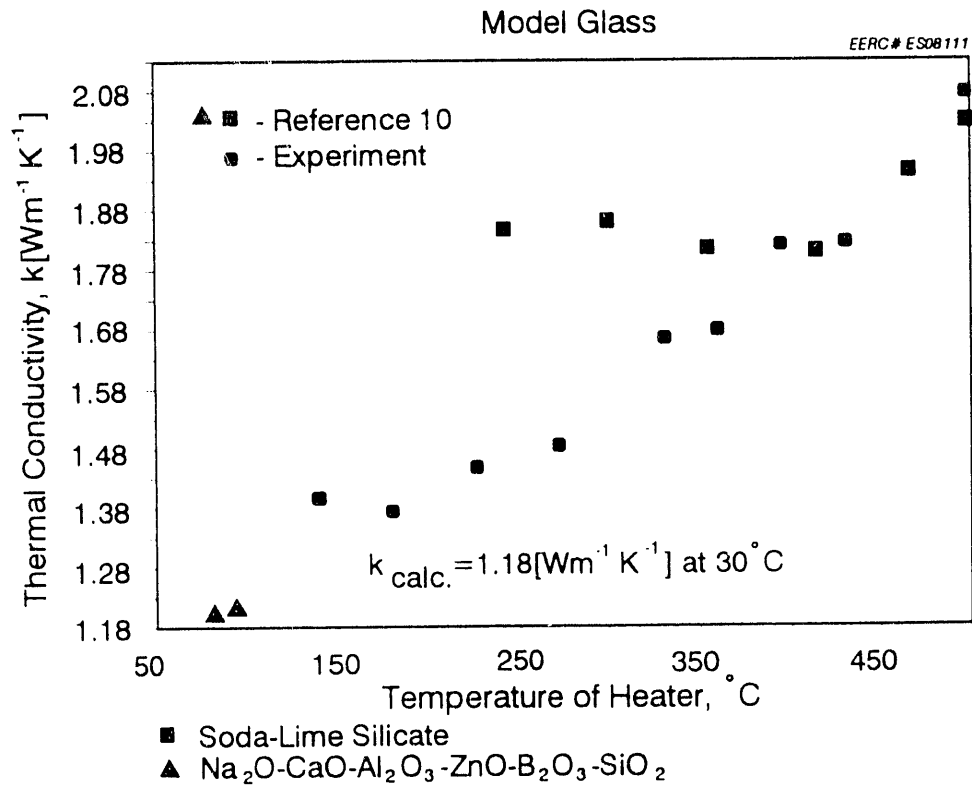**Figure 3. Thermal and Electrical Conductivities of Gascoyne Coal Ash Sintered at 1100°C for 15 h, in Air**
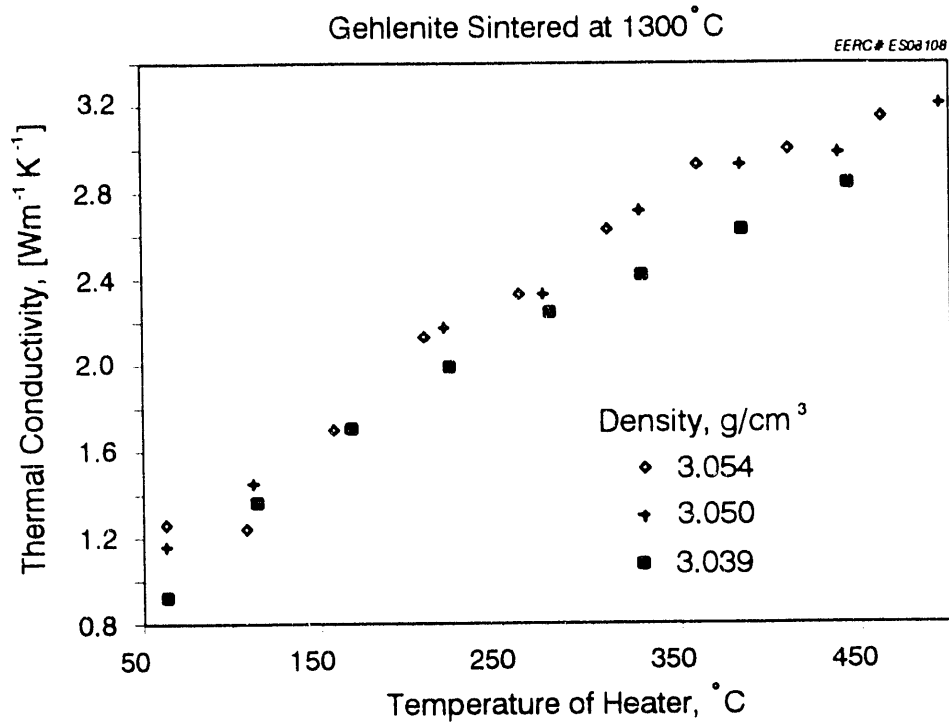
Illinois #6 sintered at 1100°C for 15 hr

$k^{glass}_{calc.} = 1.183 [Wm^{-1} K^{-1}]$ at 30°C

Electrical Conductivity, $\sigma[\Omega^{-1} m^{-1}] \times 10^{-6}$ / Thermal Conductivity, $k[Wm^{-1} K^{-1}]$

Temperature of Heater, °C
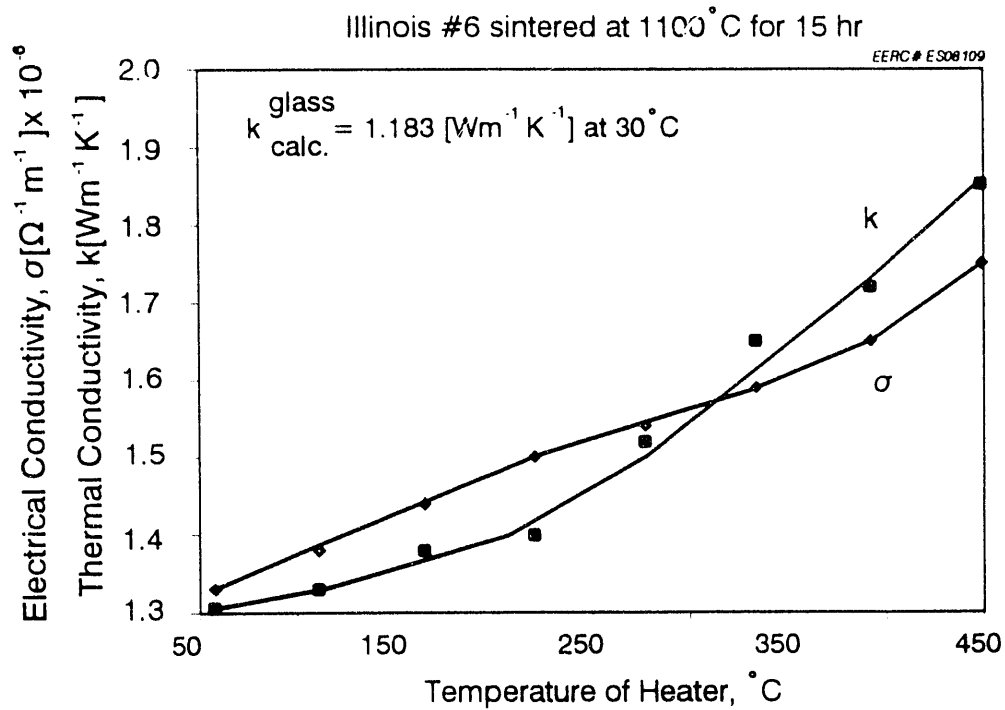
Figure 4. Thermal and Electrical Conductivities of Illinois #6 Coal Ash Sintered at 1100°C, in Air

Model Glass

▲ ▣ - Reference 10
🔊 - Experiment

$k_{calc.} = 1.18[Wm^{-1} K^{-1}]$ at 30°C

Thermal Conductivity, $k[Wm^{-1} K^{-1}]$

Temperature of Heater, °C

▣ Soda-Lime Silicate
▲ $Na_2O-CaO-Al_2O_3-ZnO-B_2O_3-SiO_2$

Figure 5. Thermal Conductivity of Model Silicate Glass

Figure 6. Thermal Conductivity of Gehlenite Sintered at 1300°C for 3 h (Density 3.039 g/cm^3) and 5 h (Density 3.050 g/cm^3) in Air

Table 3. Porosity of Sintered Beulah Coal Ash

Experimental Conditions	Porosity, in %		Density, g/cm^3
	Large Pores	Fine Pores	
1000°C/3 h	~15	16-17	2.57
1100°C/3 h	~15	17-20	2.54
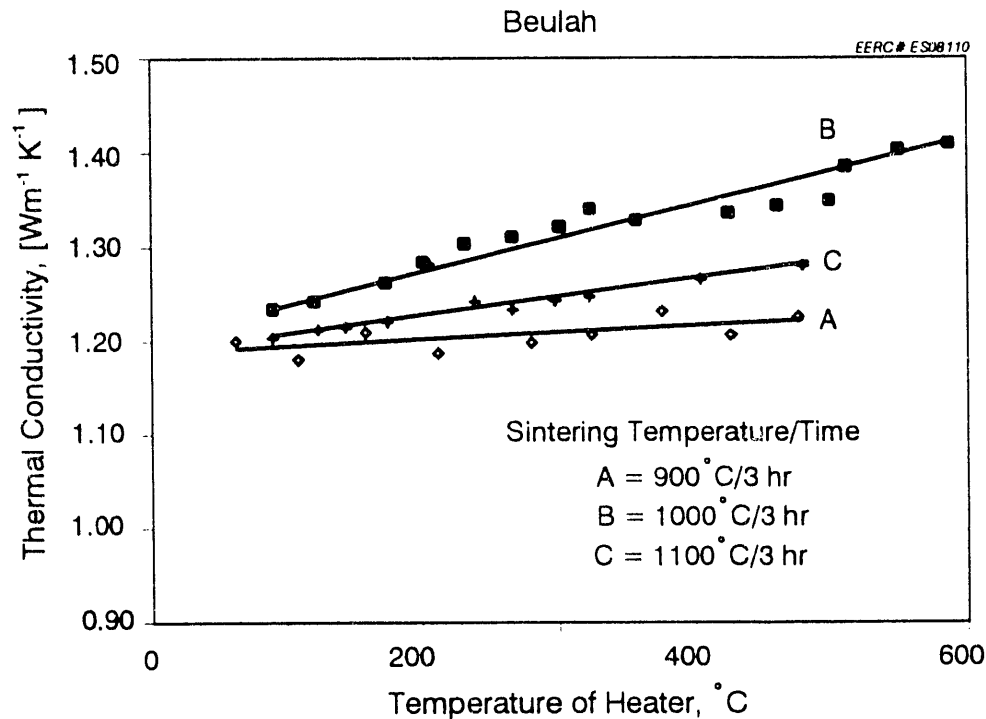
Beulah

Figure 7. Thermal Conductivity of Beulah Coal Ash With Varied Porosity

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