STUDIES IN THE PROPERTIES OF HEAT INSULATING BUILDING MATERIALS

Part III.—Analysis of the Anomalous Thermal Conductivity of Blocks of Cement and Rice Husk Ash

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The new $K^{\frac{1}{3}}$ formula derived in an earlier paper for the thermal conductivity of simple binary mixtures of two components has now been applied to the case of concretes of cement and rice husk ash. A proper allowance for the anomalous contraction is necessary, and a theoretical evaluation of this rather large correction is carried out. When this correction is made, the calculated values are in approximate agreement with the observed data. The outstanding error of 17±17% is correlated with the formulation of new products by chemical reaction of the activated silica (of the ash) with the cement, but could be partly due to a suspected anomaly in the properties of the local cement itself.

1. Theoretical Conductivity without Allowance for Contraction

In Part II of this series,[1,2] an analysis was presented for the thermal conductivity of a simple mixture of x_a and x_b parts by volume of two components with thermal conductivities K_a and K_b respectively, and the following experession was obtained:[2]

$$K_{mix}^{\frac{1}{3}} = \frac{x_a}{x_a+x_b} K_a^{\frac{1}{3}} + \frac{x_b}{x_a+x_b} K_b^{\frac{1}{3}} \qquad (1)$$

Experimental evidence for the correctness of this formula was obtained both from the standard data on cellular concretes and from our measured values for rice husk ash, assuming that both these materials are binary mixtures of air with the solid component.

Formula (1) when applied to binary mixtures of cement with rice husk ash gives the values of conductivity shown in the third row of Table 1 for various compositions by volume. A comparison of these calculated values with those determined experimentally for concretes of rice husk ash[1] is shown in Fig. 1(a). It is at once apparent that the experimental values are all higher than those calculated in Table 1, and that the ratio of the two rises to a maximum of nearly 2½ at about 80% of ash by volume. Now, if we ignore the anomalous maximum and minimum in the experimental curve and draw a monotonically decreasing graph, we obtain the broken line curve Fig. 1(a). The relation between this curve and the calculated one is very similar to that between the measured densities and those expected on the basis of simple mixing without contraction (Fig. 1 (b)), thus suggesting that the major part of the discrepancy observed in Fig. 1(a) can be explained by the large contraction in volume.

TABLE 1.—VALUES OF K ideal OBTAINED ON THE BASIS OF AN IDEAL BINARY MIXTURE.

Vol % ash:	0	20	40	60	80	100
$10 \times K_{ideal}^{\frac{1}{3}}$:	0.87_1	0.80_2	0.73_3	0.66_3	0.59_4	0.52_5
$10^3 \times K_{ideal}$:	0.66_0	0.51_5	0.39_3	0.29_1	0.21_0	0.14_5

2. Analysis of the Volume Contraction of the Rice Husk Ash Cement Blocks

If the apparent densities of the ash and the cement are ρ_{ash} and ρ_c, respectively, then the density of a simple mixture of x_{ash} parts by volume

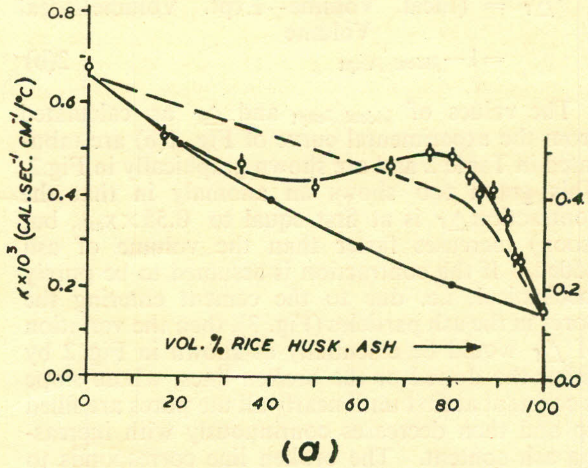

Fig. 1(a).—Comparison of experimentally measured thermal conductivities for concretes of rice husk ash (hollow circles) with K_{ideal} (solid circles) i.e. the values calculated on the basis of an ideal binary mixture. The broken line indicates the averaged monotonically decreasing component of the experimentally observed variation.

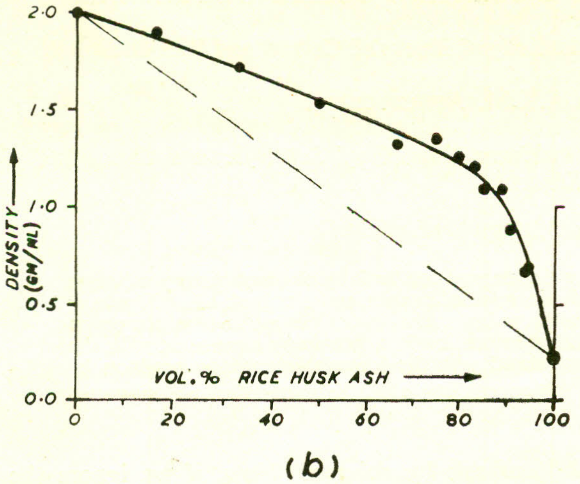

Fig. 1 (b).—The solid circles and full line show the experimental variation of the density of concretes of rice husk ash, while the broken line shows the variation for simple mixing without contraction.

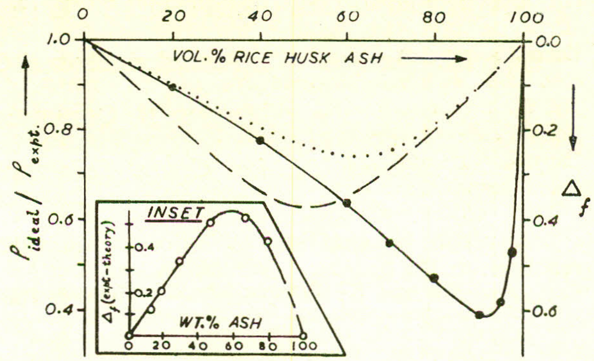

Fig. 2.—Solid circles and full line show the observed values of ρ_{ideal}/ρ_{expt} and the fractional contraction on mixing, Δf. The other lines show the expected contraction for filling up of (i) all the available space in the pores of the ash (broken line) and (ii) about 50% of the available space (dotted line).

Inset shows the excess of the experimental over the expected contraction, plotted against weight percent ash in the concrete.

of ash and $(1-x_{ash})$ parts of cement should be

$$\rho_{ideal} = \left[x_{ash}\,\rho_{ash} + (1-x_{ash})\,\rho_c \right] / \left[x_{ash} + (1-x_{ash}) \right] = \rho_c + (\rho_{ash} - \rho_c)\,x_{ash}, \qquad 2(a)$$

which corresponds to the broken line of Fig. 1(b). In order to study the contraction taking place on mixing various volumes of cement and rice husk ash, it is advantageous to calculate the quantity ρ_{ideal}/ρ_{expt} because the fractional volume contraction, Δ_f, is given by

$$\Delta_f = \text{(Ideal Volume—Expt. Volume)/Ideal Volume}$$
$$= 1 - \rho_{ideal}/\rho_{expt} \qquad 2(b)$$

The values of ρ_{ideal}/ρ_{expt} and Δ_f as calculated from the experimental curve of Fig. 1(b) are tabulated in Table 2 and are shown graphically in Fig.2. This graph too shows an anomaly in that the contraction Δ_f is at first equal to $0.55 \times x_{ash}$, but (soon) increases faster than the volume of ash added. If the contraction is assumed to be purely mechanical, i.e. due to the cement entering the pores in the ash particles (Fig. 3), then the variation of Δ_f would be essentially as shown in Fig. 2 by either the dotted or the broken lines, whose slope is constant at first until nearly all the pores are filled up and then decreases continuously with increasing ash content. The broken line corresponds to filling up of all the vacant space available, which is 90% of the volume of the ash (whose apparent bulk density is one-tenth of that of silica), while the dotted curve corresponds to filling up of about 50% of the available space, which is comparable

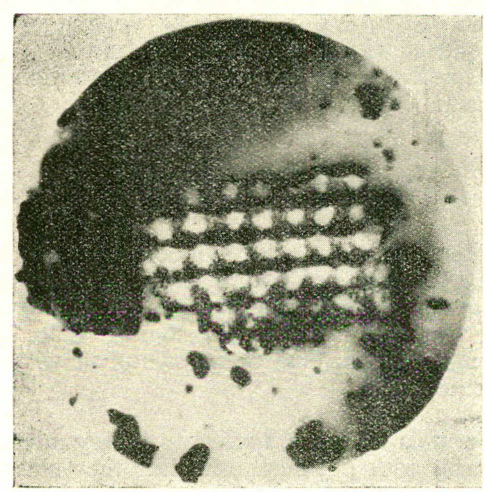

Fig. 3.—A photomicrograph of a flake of the ash, showing the cellular structure ($\times$100 approximately).

with the volume of the open region of the silical lattice-work of the ash seen magnified in Fig. 3.

In either case, the curve for a purely mechanical contraction should be essentially of a parabolic character with a maximum value of about 0.3 for Δ_f at 50% to 60% ash by volume. The experimental curve is comparable with the theory only for less than 60% ash, and the very prominent bump in the region of 80 to 100% ash must therefore be attributed largely to a contraction caused by a chemical reaction between the silica and the cement. This excess contraction can be estimated from the figure, and is seen to reach a maximum of over 0.5 at 93% ash by volume, i.e. 60% by weight (*cf.* inset to Fig. 2). Such a reaction in the cold is to be expected because the silica of the ash becomes activated in the course of burning the rice husk (where temperatures of the order of 700°C. are usual), and indeed use has previously been made of this type of reaction in the manufacture of 'Pozzolana' cements[3] from burnt clays, bricks, etc.

In order to examine the influence of this reaction on the thermal conductivity, we must at first separate out the effect produced through the purely mechanical contraction on the thermal conductivity of the composite concrete mixture.

3. Effect of Mechanical Contraction on Thermal Conductivity

If K_{ideal} is the thermal conductivity of a particular mixture as calculated in Table 1, ρ_{ideal} is the density calculated on the basis of no contraction, and ρ_{expt} is the actual density, then one might expect the experimental value of the conductivity to be increased to

$$K_{calc} = K_{ideal} \times \frac{\rho_{expt}}{\rho_{ideal}}$$

the line of argument being that there is now $(\rho_{expt}/\rho_{ideal})$ times as much conducting material in a unit cube as before. This naive reasoning, ignores the varying influence of the large volume of air entrained inside the ash by virtue of its cellular structure. Since the measurements were made on samples oven-dried at about 110°C., of which water content was found to be between 4 and 10%, we may in the first instance, ignore its presence and consider the blocks as a three-component system comprising cement, silica, and air in varying proportions, x_c, x_s and x_a by volume. If the (effective) conductivities of these three materials are K_c, K_s and K_a, respectively, then from equation(1), the conductivity of the ash will be

$$K_{ash}^{\frac{1}{3}} = \frac{x_s}{x_s+x_a} K_s^{\frac{1}{3}} + \frac{x_a}{x_s+x_a} K_a^{\frac{1}{3}},$$

and thence the conductivity of the composite mixture will be

$$K_{ideal}^{\frac{1}{3}} = \frac{x_c}{x_c+(x_s+x_a)} K_c^{\frac{1}{3}} + \frac{x_s+x_a}{x_c+(x_s+x_a)} K_{ash}^{\frac{1}{3}}$$

$$= \left\{ x_c K_c^{\frac{1}{3}} + (x_s+x_a)\left(\frac{x_s}{x_s+x_a} K_s^{\frac{1}{3}} + \frac{x_a}{x_s+x_a} K_a^{\frac{1}{3}}\right)\right\} \div (x_c+x_s+x_a)$$

$$= \frac{x_c}{x_c+x_s+x_a} K_c^{\frac{1}{3}} + \frac{x_s}{x_c+x_s+x_a} K_s^{\frac{1}{3}} + \frac{x_a}{x_c+x_s+x_a} K_a^{\frac{1}{3}} \quad 3\text{ (a)}$$

$$= x_c K_c^{\frac{1}{3}} + x_s K_s^{\frac{1}{3}} + x_a K_a^{\frac{1}{3}} \quad 3\text{ (b)}$$

if $x_c + x_s + x_a = 1$

Now suppose that a contraction occurs on forming the mixture; this means that a fraction, say α, of the air is removed. We must therefore replace x_a by $(1-\alpha)\, x_a$, and $(x_c + x_s + x_a(1-\alpha))$ will be equal to $(1-\alpha x_a)$. So that the conductivity K_{calc} will be given by

$$K_{calc}^{\frac{1}{3}} = \frac{x_c}{1-\alpha x_a} K_c^{\frac{1}{3}} + \frac{x_s}{1-\alpha x_a} K_s^{\frac{1}{3}} + \frac{(1-\alpha)\, x_a}{1-\alpha x_a} K_a^{\frac{1}{3}}$$

$$= \left\{ (x_c K_c^{\frac{1}{3}} + x_s K_s^{\frac{1}{3}} + x_a K_a^{\frac{1}{3}}) - \alpha x_a K_a^{\frac{1}{3}} \right\} \div (1-\alpha x_a)$$

$$= (K_{ideal}^{\frac{1}{3}} - \alpha x_a K_a^{\frac{1}{3}}) / (1-\alpha x_a) \quad 4\text{ (a)}$$

Thus

$$(K_{calc}^{\frac{1}{3}} / K_{ideal}^{\frac{1}{3}}) = \left[1 - \alpha x_a \left(K_a^{\frac{1}{3}} / K_{ideal}^{\frac{1}{3}}\right)\right] / (1-\alpha x_a)$$

$$= 1 + \left\{ 1 - (K_a / K_{ideal})^{\frac{1}{3}} \right\} \times \frac{\alpha x_a}{1-\alpha x_a} \quad 4\text{ (b)}$$

TABLE 2.—THE FRACTIONAL CONTRACTION, Δ_f, OBSERVED IN CONCRETES OF RICE HUSK ASH.

$100\, x_a$ = Vol % of ash :	0	20	40	60	70	80	90	95	97.5	100
$(\rho_{idea}/\rho_{expt})$	1.000	0.897	0.777	0.633	0.547	0.470	0.390	0.420	0.52	1.000
Δ_f	0.000	0.103	0.223	0.367	0.453	0.530	0.610	0.580	0.48	0.000
Δ_f/x_a	—	0.52	0.56	0.61	0.65	0.66	0.68	0.61	0.50	0.00

Now αx_a is merely the fractional contraction, measured as a fraction of the ideal volume for simple mixing. We therefore get.

$$\alpha\, x_a = \frac{\text{Ideal volume} - \text{Experimental volume}}{\text{Ideal volume}}$$

$$= \Delta_f$$
$$= 1 - (\rho_{ideal}/\rho_{expt}),$$

whence

$$\frac{\alpha\, x_a}{1-\alpha\, x_a} = (\rho_{expt}/\rho_{ideal}) - 1,$$

so that equation (4) becomes,

$$\left\{\frac{K_{calc}}{K_{ideal}}\right\}^{\frac{1}{3}} = 1 + \left\{\frac{\rho_{expt}}{\rho_{ideal}} - 1\right\}\left\{1 - \left\{\frac{K_a}{K_{ideal}}\right\}^{\frac{1}{3}}\right\} \quad (5)$$

It is interesting to note here that $(K_a/K_{ideal})^{\frac{1}{3}}$ is equal to 0.6 ± 0.1 for blocks with K_{ideal} between 0.5×10^{-3} and 0.17×10^{-3} cal. cm^{-1} sec^{-1}/°C., and therefore we also get the approximation

$$\frac{K_{calc}}{K_{ideal}} \simeq \left\{1 + \left\{\frac{\rho_{expt}}{\rho_{ideal}} - 1\right\}(1 - 0{\cdot}6)\right\}^3$$

$$= \left\{0{\cdot}4 \quad \rho_{expt}/\rho_{ideal} + 0{\cdot}6\right\}^3$$

$$\simeq \left\{\rho_{expt}/\rho_{ideal}\right\}^{1{\cdot}5} \quad \text{for } 1 < \rho_{expt}/\rho_{ideal} < 2.5,$$

which result is to be compared with the elementary notion mentioned previously that K_{calc}/K_{ideal} should be proportional to ρ_{expt}/ρ_{ideal}.

Formula (5) can be used to make an accurate allowance for the mechanical effect of the contraction in the case of concretes of rice husk ash, taking $K_a = 0.06_0 \times 10^{-3}$ cal cm^{-1} sec^{-1}/°C. Table 3 gives the values of ρ_{expt}/ρ_{ideal} obtained from Fig. 1, of K_{ideal} (i.e. without contraction) and of K_{calc} i.e. with allowance for contraction, together with the ratio K_{expt}/K_{calc}, while Fig. 4 shows a comparison of K_{ideal} and K_{calc} with the experimentally determined values, K_{expt}.

4. Discussion of the Residual Effect

It is seen that, whereas the values of K_{ideal} are considerably lower than the experimental values (K_{expt}), the introduction of the effect of contraction brings K_{calc} into approximate agreement with experiment. However, the error is now in the opposite direction, K_{expt} being consistently lower than K_{calc}, with a mean value of about 0.83 for the ratio K_{expt}/K_{calc} which is a minimum in the region of 96% by volume of rice husk ash (about 70% by weight). This discrepancy may well be a result of some departures from the foregoing theory, or more probably of anomalous behaviour of the local cement, for which there is some evidence from other sources. Moreover, it generally follows the variation of Δ_f (expt—theory), and can therefore also be connected with the change in thermal conductivity brought about by the 'Pozzolana' type of reaction. If we take the abnormal fractional contraction observed in Fig. 2, i.e. Δ_f (expt.—theory) as being equal to β times the quantity of this new compound with thermal conductivity K_p, then to a first approximation, the ratio K_{expt}/K_{calc} in Table 3 should be given by

TABLE 3.—COMPARISON WITH EXPERIMENT OF THE VARIOUS THEORETICALLY CALCULATED VALUES OF K WITH AND WITHOUT ALLOWANCE FOR THE AIR IN THE PORES; $K_{air} = 0.060 \times 10^{-3}$ cal. cm^{-1} sec^{-1}°C.

Vol. % ash	0	20	40	60	70	80	90	95	97.5	100
ρ_{expt}/ρ_{ideal}	1.000	1.114	1.287	1.580	1.828	2.126	2.563	2.38	1.83	1.000
$K_{ideal} \times 10^3$ from eq. (1) ..	0.660	0.515	0.393	0.291	0.249	0.210	0.175	0.159	0.152	0.145
$(K_a/K_{ideal})^{\frac{1}{3}}$	0.450	0.488	0.535	0.592	0.622	0.658	0.700	0.723	0.734	0.746
$K_{calc} \times 10^3$ from eq. (5)	0.660	0.610	0.570	0.550	0.564	0.555	0.555	0.420	0.276	0.145
$K_{expt} \times 10^3$ (from graph) ..	0.66	0.525	0.44	0.46	0.485	0.485	0.37	0.26	0.20	0.145
K_{expt}/K_{calc}	1.00	0.86	0.77	0.84	0.86	0.87	0.67	0.62	0.72	1.00
Wt. % ash	0	2.5	6.2	13	19	29	47	66	80	100

TABLE 4.—COMPARISON OF HALF THE RESIDUAL ERROR 1/2 $(1-K_{expt}/K_{calc})$ WITH THE ANOMALOUS CONTRACTION Δ_f (EXPT—THEORY)

Weight % ash	10	20	30	40	50	60	70	80	90
Δ_f (expt-theory)	.12	.22	.33	.44	.54	.56	.52	.40	.22
1/2 (1-K_{expt} K_{calc})	.10	.07	.08	.12	.17	.18	.18	.14	.08
0.31 $\times \Delta_f$ (expt—theory)	.04	.07	.10	.13	.17	.17	.16	.12	.07

$$1-(K_{expt}/K_{calc}) \simeq (1-K_p/K_c)\times\beta \times \Delta_f \text{ (expt.—theory)} \qquad (6)$$

If now we proceed on the likely assumption that only one-half of the discrepancy is due to this cause, then it should be possible to make a rough estimate of the quantity $[(1-K_p/K_c)\times\beta)]$ from a comparison of the two quantities 1/2 $(1-K_{expt}/K_{calc})$ and Δ_f (expt—theory). This comparison is made in Table 4, and a value of about 0.31 ± 0.03 can be deduced for$(1-K_pK_c)\times\beta$, cf. the last row of Table 4. From the graphs of Fig. 2, it is clear that β is considerably greater than 0.56, and since it is constrained to be less than 1.0, a fair estimate is 0.85 ± 0.1. It follows that i.e. the thermal conductivity of the new product of reaction with

$$1-K^p/K_c \simeq \frac{0.31\pm0.02}{0.85\pm0.1} = 0.36\pm0.06$$

whence

$$K_p/K_c \simeq 0.64\pm0.06,$$

the activated silica is about 2/3 that of ordinary cement (of zero porosity). The conductivity of the concretes calculated on this is shown in Fig. 4 by the chain-dotted line. Although this estimate may be vitiated very considerably by any major departures of the actual thermal behaviour from the theory outlined in the previous section, we may nevertheless conclude that the above theory taken together with the 'Pozzolana' type of reaction does account (to within about 15% as indicated by Table 4 and Fig. 4) for the anomalous

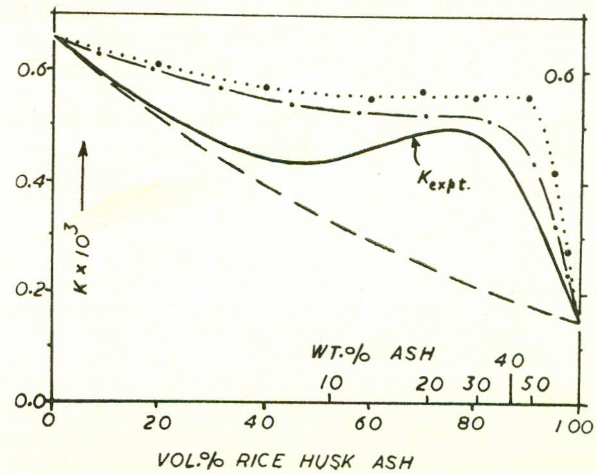

Fig. 4.—Graphs showing the measured thermal conductivity K expt of concretes of rice husk ash (full line) compared with (i) K ideal (broken line) worked out on the basis of an ideal binary mixture, and (ii) K calc (dotted line) calculated with allowance for contraction according to equation (5). The chain dotted curve, further includes an estimated correction for the effects of chemical reaction, and is seen to follow the general trend of the experimental curve.

behaviour of the thermal conductivity of concretes of rice husk ash. The suspected anomaly in the conductivity and other properties of cement at various porosities is being studied further in collaboration with the Building Materials Research Division, and is expected to remove the outstanding 15% discrepancy in the results on concretes of rice husk ash.

References

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