EFFECT OF THERMAL TREATMENT OF RICE HUSK ASH ON SURFACE PROPERTIES OF HYDRATED PORTLAND CEMENT-RICE HUSK ASH PASTES

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Abstract

Portland cement was mixed with rice husk ash (RHA) fired at 450, 700 and 1000°C, in ratios of 5, 15 and 25% of RHA by mass. Cement-RHA pastes were made by using a water/solid mixture ratio of 0.30 by mass and then cured for various hydration periods within the range 3 to 90 days. The surface properties of the hydrated samples were studied by means of the nitrogen adsorption technique. The results indicated that the hydrated cement-RHA samples made from rice husks fired at 450 and 700°C gave higher values of surface area than that for the hydrated cement-RHA sample made from rice husks fired at 1000°C. The surface area and pore volume results could be related to the pore structure of the silica produced in the RHA, as controlled by its predicted degree of crystallinity.

Introduction

Detailed studies on the surface area and pore structure of thermally treated silica gel and rice husk ash (RHA) silicas have been reported in the literature [1–3].

Al-Khalaf *et al.* [4] investigated the effect of RHA used as an admixture in Portland cement (PC) concrete. The physicochemical properties of blended cements made from PC and RHA have also been studied [5]. The internal surface area and the total porosity were first measured by Powers and Brownyard [6], using the technique of water vapour adsorption. Both water and nitrogen adsorption were later employed by others [7, 8]. Mikhail *et al.* [9] analysed various hardened cement pastes, using surface area and pore structure analysis techniques to achieve a consistent interpretation of the results. Skalny and Odler [10] compared the results of pore structure determinations involving the use of nitrogen and water vapour on a variety of calcium silicate hydrates prepared under various conditions. Nitrogen and butane sorption data were obtained for a wide range of hardened cement pastes [11]. The pore structure of hydrated cement pastes was studied by water vapour sorption at 25°C up to a relative pressure of 0.98 [12].

Experimental

RHA fired at different temperatures and ordinary PC were used as starting materials for this study; green rice husks were burned in air. The washed rice husks with a grain size of 0.5 mm were burned in a muffle furnace in an atmosphere of air at a constant rate of $10°C$ min^{-1} up to the required temperature, ranging from 450 to $1000°C$, for 2 h, with sudden cooling in air. The mass of the resulting ash was 18% of the rice husk mass. Chemical analysis of the RHA gave the following results: $SiO_2=94.47$; $Al_2O_3=2.03$; $Fe_2O_3=0.4$; $CaO=1.14$; $MgO=0.89$; $Na_2O=0.67$; and $K_2O=0.85\%$. The chemical composition of the PC was as follows: $CaO=62.49$; $SiO_2=20.82$; $Al_2O_3=6.53$; $Fe_2O_3=3.02$; $MgO=2.86$; $SO_3=2.25$; and ignition loss=0.76%, respectively. The Blaine area was 3300 cm^2 g^{-1}.

PC was mixed with RHA fired at 450, 700 or $1000°C$ in ratios of 5, 15 and 25% by mass. PC-RHA pastes were made by using a water/solid ratio of 0.30 by mass. The samples were moulded into one-inch cubes and cured in a moist atmosphere at 100% relative humidity for hydration periods of 3, 7, 28 or 90 days. After each time interval, the hydration of the hardened cement pastes was stopped [13–15], and the samples were then dried and kept in a desiccator.

Results and discussion

Effect of rice husk ash firing temperature

Three mixes made from RHA fired at 450, 700 or $1000°C$ and admixed with PC in a PC:RHA ratio of 85:15 by mass were studied after hydration for 3, 7, 28 or 90 days. RHA fired at 450, 700 or $1000°C$ was used as representing the active silica reactant.

The nitrogen adsorption isotherms of 85:15 PC-RHA samples made from RHA fired at $450°C$ are shown in Fig. 1. This Figure can be regarded as representative of all samples made from other mixes.

All the isotherms exhibit common characteristics and are similar in shape to type II of Brunauer's classification [16]. The adsorption-desorption isotherms indicate the existence of closed hysteresis loops at the high-pressure end of the isotherms. The existence of such hysteresis is mainly explained in terms of capillary condensation in mesopores. The specific surface areas, S_{BET}, could be evaluated by applying the BET equation and using the molecular area of nitrogen of 16.2 Å [17].

The total pore volumes, V_p, were taken as the saturation values of the isotherms and are expressed in ml liquid adsorbate (nitrogen) per gram of adsorbent (V_p/ml g^{-1}).

The BET-C constants, S_{BET} (m^2 g^{-1}), V_p (ml g^{-1}), and mean hydraulic radii of the total pore system (r_h, Å) are given in Tables 1–3 for hydrated samples made from PC-RHA fired at 450, 700 or $1000°C$. All results are referred to the ignited mass basis.

S_{BET} and V_p data are shown in Fig. 2. There is an initial marked increase in both S_{BET} and V_p on increase of the period of hydration from 3 to 7 days for all PC-RHA
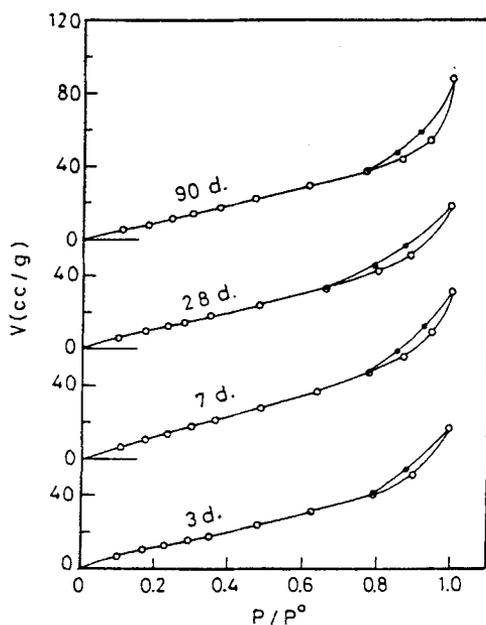
Fig. 1 Adsorption–desorption isotherms of nitrogen gas on hardened cement pastes made from an 85:15 mixture by mass of PC and RHA fired at 450°C

Table 1 Some surface characteristics cf hardened cement pastes made from 85:15 mass percent of PC and RHA fired at 450°C

Curing time/ days	BET-C constant	S_{BET} $m^2(g\ ign\ wt)^{-1}$	S_t	$V_p/$ ml (g ign wt)$^{-1}$	Mean $r_h/$ Å
3	6	75.94	74.80	0.1412	18.57
7	4	103.26	102.21	0.1652	15.95
28	5	82.82	81.75	0.1473	17.75
90	5	78.59	76.52	0.1867	23.76

Table 2 Some surface characteristics of hardened cement pastes made from 85:15 mass percent of PC and RHA fired at 700°C

Curing time/ days	BET-C constant	S_{BET} ml (g ign wt)$^{-1}$	S_t	$V_p/$ $m^2(g\ ign\ wt)^{-1}$	Mean $r_h/$ Å
3	6	74.26	66.21	0.1404	18.91
7	4	100.78	98.17	0.2143	21.23
28	5	96.96	93.14	0.1968	20.29
90	5	90.46	87.12	0.1885	20.78

Table 3 Some surface characteristics of hardened cement pastes made from 85:15 mass percent of PC and RHA fired at 1000°C

Curing time/ days	BET-C constant	S_{BET}	S_t	V_p/	Mean r_h/
		$m^2(g\ ign\ wt)^{-1}$		$ml\ (g\ ign\ wt)^{-1}$	Å
3	6	75.51	73.12	0.1364	18.01
7	4	79.42	75.44	0.1769	18.15
28	5	73.78	70.99	0.1545	20.94
90	5	72.88	72.23	0.1375·	18.87

samples made from RHA fired at 450°C. This result can be explained by the formation and later stabilization of the initial hydration products, due to the interaction between the amorphous SiO_2 in RHA fired at 450°C and the lime released from the hydration of PC; this forms calcium silicate hydrate phases. These hydrates possess a nearly amorphous character, mainly as calcium silicate hydrates C–S–H(I) and (II). After 28 days of hydration, S_{BET} and V_p decrease; this is due to the accumulation of larger amounts of nearly amorphous calcium silicate hydrates within the system and around the unhydrated grains. This effect might hinder the accessibility of nitrogen molecules to the pore system of these hydrates. During the final stage of
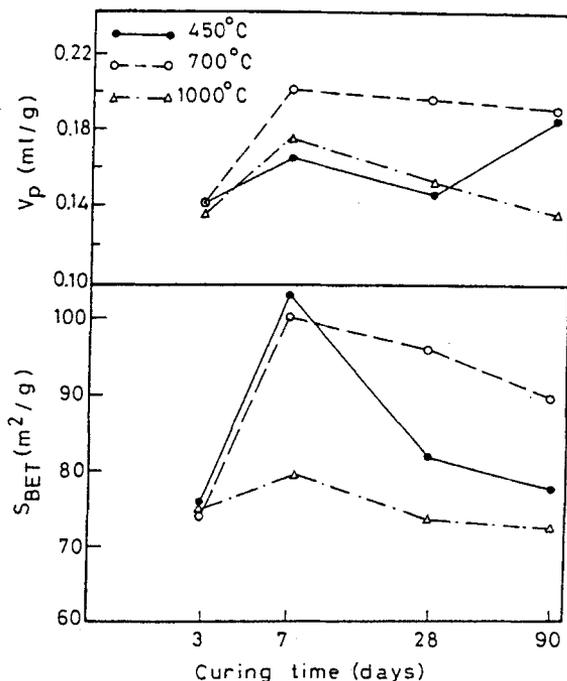
Fig. 2 Variation of surface area and total pure volume with curing time for hardened cement pastes made from an 85:15 mixture by mass of PC and RHA fired at different temperature

hydration (90 days), S_{BET} slightly decreases for the stabilization of the final hydration products, V_p increases.

Almost the same trend of variation was observed for S_{BET} of PC–RHA samples made from RHA fired at 700°C and hydrated for various periods (cf. Fig. 2). These results can be explained by considering that the silica of rice husks fired in the range 450–700°C is closely similar to silica gel (amorphous silica).

Figure 2 also shows the variations in S_{BET} and V_p with the duration of hydration for PC–RHA samples made from rice husks fired at 1000°C. S_{BET} slightly increases with increasing hydration time from 3 to 7 days. This can be explained by considering that the RHA silica fired at 1000°C is mainly crystalline cristobalite; it is therefore expected that the amorphous form of silica (RHA fired in the range 450–700°C) will be more hydraulically active than the crystalline form (RHA fired at 1000°C). V_p increases between 3 and 7 days of hydration. Both S_{BET} and V_p continuously decreased with increasing duration of hydration from 7 days up to the final stage of hydration (90 days). This can be explained by the increase in the degree of crystallinity of the initially formed hydration products with increasing length of hydration, the crystallization process resulting in a decrease in the total surface area of the hydrates formed. Additionally, V_p decreased with increasing time of hydration. The mean hydraulic radii of the total pore system of the hydrated PC–RHA silica fired at 1000°C accessible to nitrogen molecules were found to be within the range 18.01–20.94 Å.

In general, hydrated PC–RHA samples made from RHA fired at 450 or 700°C gave higher S_{BET} values in the early stages (7 days) of the hydration reaction than the hydrated PC–RHA samples made from RHA fired at 1000°C. This is due to the formation of larger amounts of hydration products produced from the hydration interaction between: RHA fired at 450 or 700°C, which is considered to be an amorphous silica (active silica), and the lime released from the hydration of PC, whereas the RHA silica fired at 1000°C is mainly crystalline, as cristobalite. It is therefore expected that the amorphous form of silica will be more hydraulically active than the crystalline form.

V_1 vs. t plots were constructed on the basis of the adsorption branches of the nitrogen isotherms for each of the samples investigated at liquid nitrogen temperature. Such plots are shown in Fig. 3 for hydrated PC–RHA sample made from RHA fired at 450°C; this Figure can be regarded as representative of all samples made from all other mixes.

The initial straight line which passess through the origin in the V_1 vs. t plots could be used as a measure of the surface area, known as S_t, and these values are also given in Tables 1–3 for all hydrated samples of PC with RHA fired at 450, 700 or 1000°C. The close agreement between S_{BET} and S_t is good evidence of the correctness of the t values used in this investigation.

There was a slight upward deviation in the V_1 vs. t plots, which were almost linear, indicating that the pore system was composed mainly of micropores and some mesopores of limited size and number.
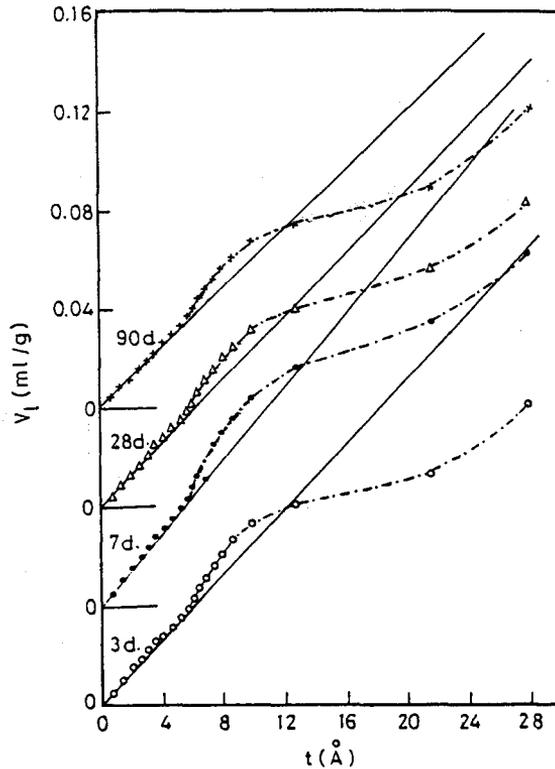
Fig. 3 V_l vs. t plots for adsorption of nitrogen gas on hardened cement pastes made from an 85:15 mixture by mass of PC and RHA fired at 450°C

Effect of amount of rice husk ash

The hydrated PC–RHA mixtures made from RHA fired at 450°C were investigated for hydration periods of 3, 7, 28 and 90 days. These mixes had PC–RHA mass percentage ratios of 100:0; 95:5, 85:15 and 75:25.

The BET-C constant, the specific surface areas, S_{BET} (m^2 g^{-1}, ignited mass basis), the total pore volume, V_p (ml g^{-1}, ignited mass basis) and the mean hydraulic radii of the total pore systems, r_h (Å), are all given in Tables 1, 4 and 5 for hydrated neat PC pastes and also PC–RHA samples with various contents of RHA fired at 450°C (5, 15 and 25 mass per cent).

The values of S_{BET} and V_p, for hydrated PC–RHA samples with various amounts of RHA (5, 15 and 25 mass per cent) are shown in Fig. 4.

The values of S_{BET} and V_p for hydrated PC–RHA silica samples with a PC–RHA mass ratio of 95:5 decreased continuously with increasing duration of hydration. This can be explained by the increase in the degree of crystallinity of the hydration products initially formed and/or the later accumulation of more stable hydrates with

Table 4 Some surface characteristics of hardened neat cement pastes

Curing time/ days	BET-C constant	S_{BET}	S_t	$V_p/$	Mean $r_h/$
		$m^2(g\ ign\ wt)^{-1}$		$ml\ (g\ ign\ wt)^{-1}$	Å
3	6	71.61	70.68	0.1772	24.73
7	4	83.61	81.62	0.1483	17.66
28	5	74.09	73.19	0.1441	19.50
90	5	74.60	73.64	0.1472	19.75

Table 5 Some surface characteristics of hardened cement pastes made from 95:5 mass percent of PC and RHA fired at 450°C

Curing time/ days	BET-C constant	S_{BET}	S_t	$V_p/$	Mean $r_h/$
		$m^2(g\ ign\ wt)^{-1}$		$ml\ (g\ ign\ wt)^{-1}$	Å
3	6	150.54	149.21	0.245	16.29
7	4	119.14	118.24	0.232	19.43
28	5	101.31	100.28	0.1942	15.96
90	5	87.30	86.22	0.1723	19.66

Table 6 Some surface characteristics of hardened cement pastes made from 75:25 mass percent of PC and RHA fired at 450°C

Curing time/ days	BET-C constant	S_{BET}	S_t	$V_p/$	Mean $r_h/$
		$m^2(g\ ign\ wt)^{-1}$		$ml\ (g\ ign\ wt)^{-1}$	Å
3	6	91.64	90.41	0.1742	18.99
7	4	88.38	86.21	0.1761	19.91
28	5	98.07	96.71	0.1658	16.91
90	5	90.23	88.92	0.1702	18.98

increasing time of hydration; the crystallization process results in a decrease in the total surface area of the hydrates formed. These hydrated samples with a PC–RHA ratio of 95:5 possess higher surface areas and pore volumes as compared with those of hydrated neat PC samples; this might be attributed to the formation of larger amounts of hydration products produced from interaction between the active silica of the RHA fired at 450 °C and the lime released from the hydration of PC, mainly calcium silicate hydrates (C–S–H) products, which possess high surface areas and total pore volumes. The main hydraulic radii (r_h, Å) of hydrated samples made with a PC-silica ratio of 95:5 lie within the range 15.96–19.66 Å. These values are lower than those for hydrated neat PC samples, which were in the range 17.66–24.73 Å, reflecting an increased accessibility of nitrogen molecules to the pore system containing more crystallized, initial hydration product for hydrated samples prepared from a 95:5 PC-silica mixture.
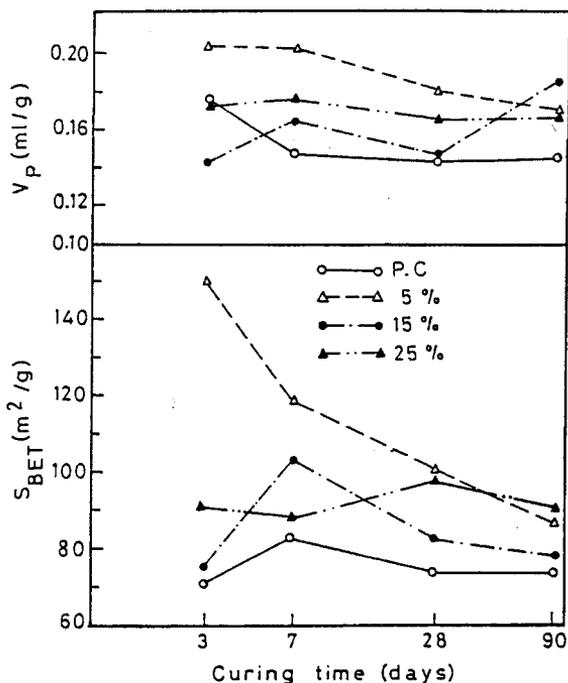
Fig. 4 Variation of surface area and total pore volume with curing time for hardened cement pastes made from different ratios of PC and RHA fired at 450°C

The results in Fig. 4 indicate an initial marked increase in both S_{BET} and V_p with increasing duration of hydration from 3 to 7 days for 85:15 PC–RHA silica samples (cf. Table 1). This result can be explained by the formation of the initial hydration products mainly as C–S–H I and II; these hydrates, with a nearly amorphous character, result from the interaction of the amorphous silica of RHA fired at 450°C and the lime released from the hydration of PC. After 7 days of hydration up to final stage of hydration, the surface areas decreased due to stabilization of the initially formed hydrates via crystallization.

Further, the hydrated 75:25 PC–RHA samples possess higher surface areas and pore volumes than those of hydrated neat PC samples.

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