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EFFECT OF THERMAL TREATMENT OF RICE HUSK ASH ON THE SURFACE PROPERTIES OF HYDRATED LIME-RICE HUSK ASH BINDERS

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Abstract

Rice husk ash fired at different temperatures, 450, 700 and 1000°C, was mixed with different concentrations of lime (molar lime/silica ash ratio of 0.2, 0.5 and 1.0). Each dry mixture was first ground and hydrated in the suspension form (water/solid ratio = 10) for various time intervals within the range of 1 to 365 days. The surface properties of the unhydrated and hydrated samples were studied by means of nitrogen adsorption measurements. The results indicated that the surface areas and total pore volumes of unhydrated solid mixtures and hydrated lime-rice husk ash samples, prepared with lime/silica ash ratio of 1.0, decrease with increasing firing temperature of rice husk ash. The effect of varying the lime/silica ash ratio of the solid mixture on the surface area and pore structure was fully discussed. The results of surface area and pore volume measurements could also be related to the crystal structure of silica produced from rice husk ash.

Keywords: hydrated lime-rice husk, surface properties, thermal treatment

Introduction

The constituents of rice husks are both organic and inorganic compounds. Analysis reported in the literature showed that the organic matter present in the husks generally consists of lignin and cutin, but carbohydrates and nitrogen compounds are also reported such as lipids, organic acids and traces of vitamins. The inorganic constituents determined in the ash comprise about 13.29% of the husk [1]. The predominant compound of rice husk ash (RHA) is silica. The IR-absorption patterns for white RHA were also studied at different temperatures between 100 and 1400°C [2]. The effect of firing temperature on the crystallite size of the formed silica was explained by means of X-ray diffraction technique [3].

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The reactions between amorphous SiO_2 and lime solutions of variable concentrations were studied and related to the initial lime content [4]. The effect of lime/silica ratio on the kinetics of the reaction of silica with saturated lime has also been investigated [5]. Look and Suwanvioys [6] studied pastes made from $Ca(OH)_2$ and RHA hydrated at 22°C. The rate of hydration of ash-lime mixtures is dependent on the reactivity of the ash and the initial ash/lime ratio [7]. The physical characteristics and the chemical reactivity of SiO_2 in RHA was found to be affected by the temperature of heating and of the time of soaking [8]. Reaction of the amorphous SiO_2 in the rice husk ash with lime yields Ca-silicate hydrates in the presence of water [9].

The internal surface and the total porosity were first measured by Powers and Brownyard [10] using water vapour adsorption. Both water and nitrogen adsorptions were employed later by others [11, 12]. Skalny and Odler [13] compared the results of pore structure determination using nitrogen and water vapours on a variety of calcium silicate hydrates prepared under various conditions.

Experimental

Rice husk ash (RHA) fired at different temperatures and finely ground $Ca(OH)_2$ were used as starting materials for this study; green rice husk was burned in air. The washed rice husk with a grain size of 0.5 mm was burned in a muffle furnace in an atmosphere of air at a constant heating rate of 10 $deg \cdot min^{-1}$, up to the required temperature ranging from 450 to 1000°C for 2 h, with sudden cooling in air. The weight of the resulting ash was 18% of that of the rice husk. Chemical analysis of RHA is as follows:

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%.

RHA samples fired at different temperatures (450, 700 and 1000°C) were mixed with different quantities of lime (0.2, 0.5 and 1 molar ratio). Each dry mixture was ground, then introduced into air-tight bottles containing 100 ml of distilled water (about 10 g of mixture). The bottles were stoppered tightly and sealed with paraffin wax to avoid loss of material or carbonation from the atmosphere. The bottles were shaken from time to time to attain complete mixing with water. Hydration was carried out up to one year. The contents of the bottles were filtered after 1, 3, 7, 28, 90, 180 or 365 days, then the hydration was stopped by chemical method [14–16].

Specific surface areas and total pore volumes of dried specimens were measured volumetrically from the adsorption of nitrogen gas at liquid nitrogen temperature (–195.8°C).

Results and discussion

Effect of firing temperature of rice husk ash

In this section three mixes made from rice husk ash (RHA) fired at 450, 700 and 1000°C mixed with lime having lime-silica ash [CaO/SiO_2] molar ratio of 1 were studied before and after hydration for various time intervals: 1, 3, 7, 28, 90, 180 or 365 days.

The nitrogen adsorption isotherms of the lime-RHA specimens made from RHA fired at 450°C with a CaO/SiO_2 molar ratio of 1 for unhydrated solid mixture and after hydration for various time intervals are shown in Fig. 1. The Figure is considered to represent all specimens made from other mixes. All isotherms show common characteristics and are similar in shape to type II of Brunauer's classification [17]. The adsorption–desorption isotherms indicate the existence of closed hysteresis loops in 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 ares (S_{BET}) could be evaluated by applying the BET-equation and using the molecular area of nitrogen, 16.2 $Å^2$ [18].

The total pore volumes, V_p, were taken as the saturation values of the isotherms and were expressed in ml of liquid adsorbate (nitrogen) per one gram of the adsorbent (V_p, mL/g).

The BET-C constant, the specific surface areas (S_{BET}, m^2/g), the total pore volumes (V_p, mL/g), as well as the mean hydraulic radii of the total pore system (r_h, Å) are all given in Tables 1–4 for various specimens made from lime-RHA mixtures fired at 450, 700 and 1000°C before and after hydration. All results were referred to the ignited weight basis.

The total surface areas and total pore volumes obtained for unhydrated solid mixtures indicate a decrease in the values of S_{BET} (m^2/g) and V_p (mL/g) with increasing firing temperature from 450 to 1000°C (Table 1). Also the values of mean hydraulic radii (r_h, Å) of the total pore system accessible to nitrogen molecules show a small continuous decrease with increasing firing temperature up to 1000°C. These variations are mainly attributed to the increase in the degree of

Table 1 Some surface characteristics of unhydrated solid mixtures of lime-RHA specimens made from rice husk fired at different temperatures (C/S = 1)

T_{firing} / °C	BET-C constant	S_{BET} /	S_t /	V_p / mL(g ign. wt.)$^{-1}$
		m^2(g ign. wt.)$^{-1}$		
450	6	90.34	88.92	0.202
700	9	77.22	77.92	0.188
1000	3	70.54	69.74	0.127

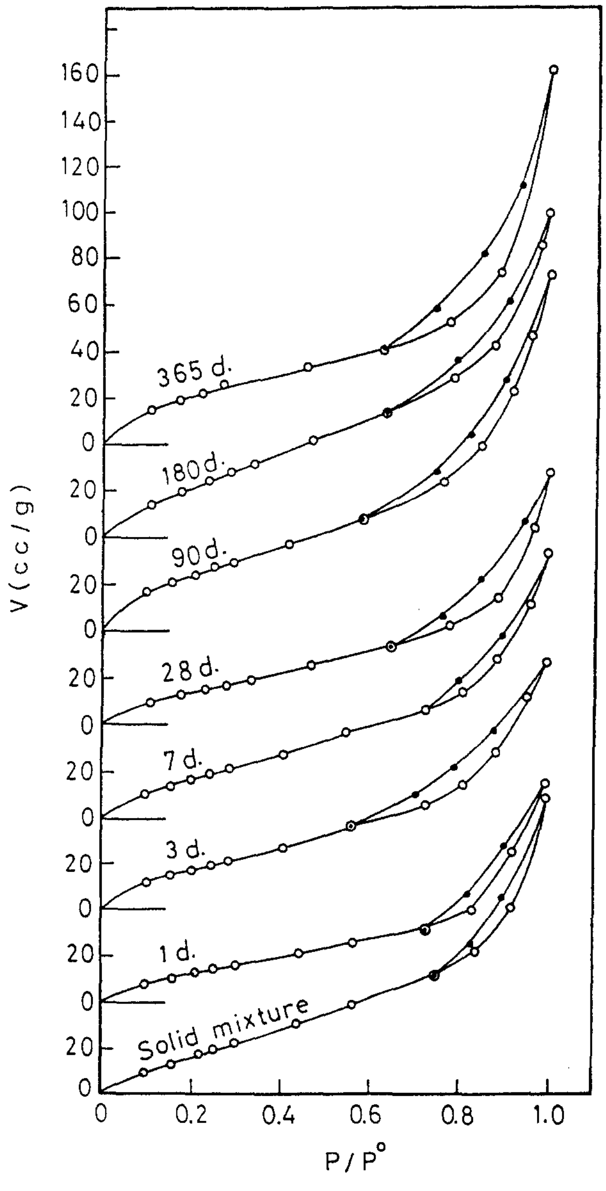

Fig. 1 Adsorption–desorption isotherms of nitrogen gas on unhydrated solid mixture and hydrated lime-RHA specimens made from rice husk fired at 450°C (C/S = 1)

crystallinity of RHA with firing temperature. El-Didamony *et al.* [19] showed the effect of firing temperature on the crystallinity of RHA. The silica in the ash is almost amorphous at lower firing temperatures up to 700°C. The crystallization of silica starts at 700°C and increases at 1000°C. In these unhydrated lime-RHA mixtures, the entire pore system is completely accessible to nitrogen molecules. Therefore, the increase in the degree of crystallization of RHA silica is accompanied by a decrease in the total surface area and total pore volume as well as in the mean hydraulic radius of the total pore system [20, 21].

Table 2 Some surface characteristics of hydrated lime-RHA specimens made from rice husk fired at 450°C (C/S = 1)

Curing time/day	BET-C constant	S_{BET} /	S_t /	V_p / mL(g ign. wt.)$^{-1}$	mean r_h / Å
		m^2(g ign. wt.)$^{-1}$			
1	9	60.61	62.01	0.140	23.09
3	7	69.90	65.22	0.151	21.60
7	14	86.04	83.41	0.157	18.24
28	11	73.96	70.44	0.134	18.11
90	22	115.27	108.11	0.227	19.69
180	6	141.66	130.48	0.137	9.60
365	8	129.74	128.55	0.175	13.49

Table 3 Some surface characteristics of hydrated lime-RHA specimens made from rice husk fired at 700°C (C/S = 1)

Curing time/day	BET-C constant	S_{BET} /	S_t /	V_p / mL(g ign. wt.)$^{-1}$	mean r_h / Å
		m^2(g ign. wt.)$^{-1}$			
1	6	71.81	73.04	0.138	19.22
3	8	65.66	63.42	0.164	24.98
7	8	79.06	73.33	0.165	20.87
28	7	91.64	85.72	0.177	19.44
90	18	103.09	102.01	0.180	17.46
180	14	105.58	114.02	0.202	19.13
365	9	115.41	109.24	0.257	22.27

Table 4 Some surface characteristics of hydrated lime-RHA specimens made from rice husk fired at 1000°C (C/S = 1)

Curing time/day	BET-C constant	S_{BET} /	S_t /	V_p / mL(g ign. wt.)$^{-1}$	mean r_h / Å
		m^2(g ign. wt.)$^{-1}$			
1	3	75.44	70.12	0.099	13.12
3	4	69.15	66.97	0.092	13.30
7	6	69.54	73.44	0.150	21.57
28	6	81.22	80.52	0.156	19.20
90	8	75.04	73.32	0.140	18.65
180	4	75.62	70.46	0.101	13.36
365	5	79.29	80.02	0.151	19.04

The values of specific surface areas (S_{BET}, m^2/g) and the total pore volumes (V_p, mL/g) of hydrated lime-RHA silica specimens made from RHA fired at 450, 700 and 1000°C and hydrated for various times are shown in Fig. 2.

The results in Fig. 2 reveal an initial increase in both the surface areas and pore volumes with increasing time of hydration for lime-RHA silica specimens made from RHA fired at 450°C during the initial stage of hydration (up to 7 days of hydration). This result can be explained by the formation and later stabilization of the initial hydration products; these hydrates seem to have a nearly amorphous character, mainly as calcium silicate hydrates (C–S–H–I and C–S–H–II). After 28 days of hydration, the accumulation of larger amounts of the nearly amorphous calcium silicate hydrates within the pore system and around the silica grains might hinder the access of nitrogen molecules into the pore system of these hydrates leading to a decrease in the measured surface area and pore volume. Later, the stabilization of the hydration products, via crystallization causes an increase in the access of nitrogen molecules to a major fraction of total pore system leading to an increase in the surface area and total pore volume of these hydrated specimens up to 180 days of hydration. Finally the deposition of large amounts of hydration products within the pore system might decrease the access of nitrogen molecules to the pore system of the hardened pastes leading to a decrease in the surface area after 365 days of hydration.

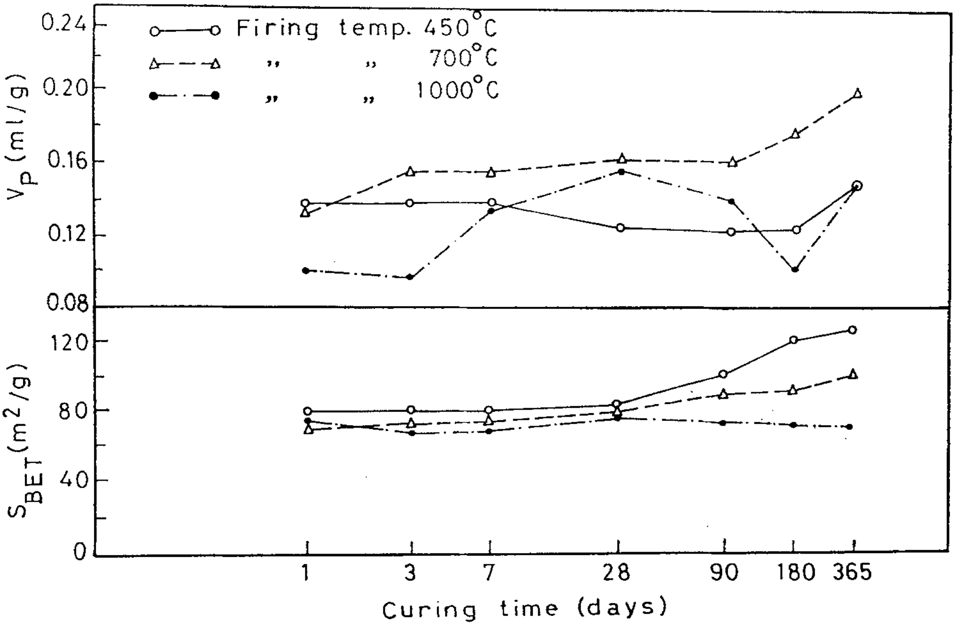

Fig. 2 Variation of surface area and total pore volume with curing time for nitrogen gas adsorption on hydrated lime-RHA specimens made from rice husk fired at different temperatures

Nitrogen molecules are almost excluded from a major part of the total pore system of the hydrated cement pastes by two mechanisms: either the pores are too narrow or have too narrow entrances to admit nitrogen molecules [22].

The lime-ash specimens made from rice husk ash fired at 700°C and cured for various periods exhibit the same trend as the ash prepared at 450°C (cf. Fig. 2). This can be explained by considering that the silica of rice husk fired in the range of 450–700°C is similar in structure to silica gel (amorphous silica).

Figure 2 shows also the variations in both of S_{BET} and V_p with time of hydration for lime-rice husk silica specimens made from husk ash fired at 1000°C. This can be explained by considering that the rice husk silica fired at 1000°C is mainly crystalline cristobalite; therefore it is expected that the amorphous form of silica will be more active hydraulically than that in the crystalline form. Again, S_{BET} decreases with increasing hydration time; meanwhile V_p gives an irregular variation with hydration time for lime-rice husk ash fired at 1000°C. This can be attributed to an increase in the degree of crystallinity of the initially formed calcium silicate hydrates and/or the later accumulation of stable hydrates with increasing time of hydration.

For the lime-silica specimens made from RHA fired at 450°C, the mean hydraulic radius of the total pore system accessible to nitrogen molecules lies in the range 18.11–23.09 Å up to 90 days of hydration. This represents the average width of the total pore system of the initial hydration products; these hydrates are initially formed as nearly amorphous hydrates and later stabilized as ill-crystallized and crystalline hydrates. After 180 and 365 days of hydration, the mean hydraulic radii are 9.6 and 13.49 Å, respectively. These smaller values of the mean hydraulic radii (mean r_h) reflect the formation of inner (newly-formed) hydrates located deeper on the partly hydrated silica grains; such inner hydrates are almost amorphous in character and contain almost micropores within their pore system.

For lime-silica samples made by firing RHA at 700°C, the average values of the mean hydraulic radii are within the range 19.2–25 Å for the pastes hydrated up to 28 days; this represents the average width of the total pore system of these hydrated pastes during the early stages of hydration. After 90 days of hydration, a sort of pore-narrowing is observed and the mean r_h-value is reduced to 17.64 Å; this stage represents the new formation of inner hydrate with an ill-crystallized character and smaller pore size. Later, the stabilization of these inner hydrates, via crystallization, causes opening of the pore system, with an increase of the mean hydraulic radius to 19.13 and 22.27 Å with increasing time of hydration of the pastes to 180 days and 365 days, respectively (cf. Table 3); this effect results in an increase in the accessibility of pores to nitrogen, i.e. larger fractions of the total pore system become accessible which leads to an increase in the measured surface area of these hydrated specimens.

The lime-rice husk ash silica pastes prepared from RHA fired at 1000°C, possess a mean hydraulic radius of about 13.10–13.30 Å during the early stage

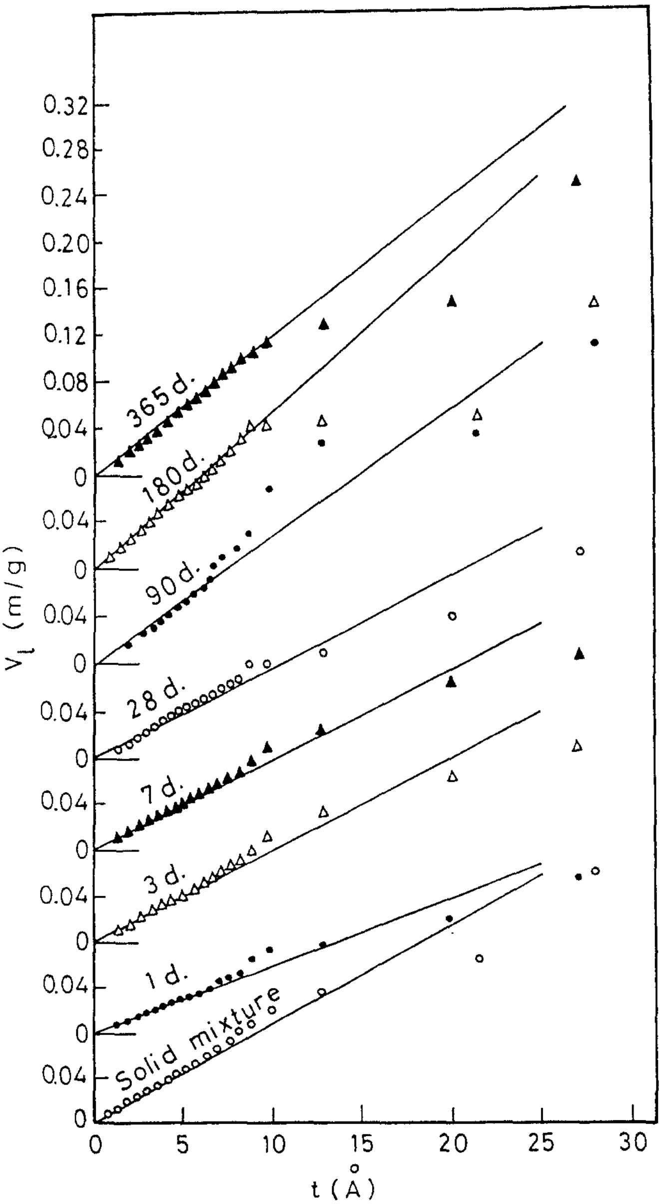

Fig. 3 $V_l - t$ plots for adsorption of nitrogen gas on unhydrated solid mixture and hydrated lime-RHA specimens made from rice husk fired at 450°C (C/S = 1)

of hydration, up to 3 days. This smaller value of the mean r_h represents the average width of the total pore system accessible to nitrogen molecules; therefore the new amorphous C–S–H formed during the initial stage of hydration is responsible for this smaller r_h-value. After 7 days of hydration, the mean r_h-value increased to 21.57 Å. This can be explained by a sort of stabilization of the formed hydrates via crystallization, which causes an increase in the average width of the pore system. During the hydration period between 28 and 180 days, the formation of inner C–S–H with an ill-crystallized character on the grains containing silica might lead to a decrease in the average width of the pore system to a mean r_h-value between 19.20 and 13.36 Å. Finally, the crystallization of the newly formed inner C–S–H hydrates is responsible for the increase in the r_h-value to 19.04 Å for the paste hydrated for 365 days.

The $V_l - t$ plots were constructed on the basis of the adsorption branches of the nitrogen isotherms for each of the samples investigated at liquid nitrogen temperature. The t-values used are those suggested by Mikhail *et al.* [23] depending on the values of the BET-C constant. The $V_l - t$ plots are shown in Fig. 3 for lime-RHA specimens made from RHA fired at 450°C with a CaO/SiO_2 molar ratio of 1, for both unhydrated solid mixture and specimens hydrated for various time intervals. The Figure can be considered as representative of all specimens made from all other mixtures.

The initial straight line which passes through the origin in the $V_l - t$ plots could be used as a measure of the total surface area, known as S_t (m^2/g) and the values are also summarized on the ignited weight basis in Table 2 see at page 109 for lime-rice husk ash specimens made from rice husk fired at 450°C before and after hydration for different times. The close agreement between the surface areas derived from $V_l - t$ plots (S_t) and BET surface areas (S_{BET}) is a good evidence for the correctness of the t-values used in this investigation.

For all the samples before and after hydration, the $V_l - t$ plots of nitrogen adsorption indicate that the pore system of the formed calcium silicate hydrates consists mainly of mesopores with limited sizes. This is suggested by the linear $V_l - t$ plots with slight upward deviations.

Effect of the CaO/SiO_2 molar ratio

Three mixtures prepared from lime and RHA fired at 700°C with different CaO/SiO_2 molar ratios (0.2, 0.5 and 1), and hydrated for 28, 90 or 365 days were studied.

The BET-C constants, the specific surface areas, S_{BET} (m^2/g, ignited weight basis), the total pore volumes, V_p (mL/g ignited weight basis) and the mean hydraulic radii of the total pore system, mean r_h (Å), are all given in Table 5 for various mixtures of hydrated lime-RHA specimens.

Table 5 Some surface characteristics of hydrated lime-RHA specimens made from rice husk fired at 700°C with different C/S molar ratios

Curing time/days	BET-C constant	S_{BET} / m^2(g ign. wt.)$^{-1}$	S_t / m^2(g ign. wt.)$^{-1}$	V_p / mL(g ign. wt.)$^{-1}$	Mean r_h / Å
		C/S = 0.2			
28	4	513.78	456.21	0.948	18.45
90	7	192.46	180.44	0.382	19.84
365	9	166.26	155.10	0.351	21.11
		C/S = 0.5			
28	7	175.80	160.27	0.297	16.89
90	11	102.31	91.01	0.202	19.74
365	6	102.10	118.20	0.157	15.38
		C/S = 1			
28	7	91.04	98.45	0.177	19.44
90	15	103.09	102.01	0.180	17.46
365	9	115.41	109.24	0.257	22.27

There appears a continuous decrease in both the surface areas and the pore volumes of the hydrated specimens made from lime-rice husk ash with a molar ratio of 0.2 with increasing time of hydration. This can be explained by the increase in the degree of crystallization and later accumulation of the initially formed hydration products; the crystallization process results in a decrease in the total surface area of the formed hydrates.

The results indicate a decreasing trend in both the surface areas and the pore volumes of the hydrated specimens made from lime-RHA with a molar ratio of 0.5 from 28 to 90 days of hydration. Again, this can be related to the increase in the degree of crystallization and later accumulation of the initially formed hydration products. During the period from 90 to 365 days of hydration, the surface area tends to exhibit a constant value, (characteristic value) for the stabilization of the final hydration product mainly as C–S–H–I. Meanwhile the pore volume decreases.

On the other hand, the results in Table 5 and Fig. 4 clearly indicate that the specific surface area as well as the total pore volume increase with increasing time of hydration for hydrated lime-rice husk ash specimens with a molar ratio of 1, which is mainly attributed to the conversion of the initially formed C–S–H to another C–S–H with a lower lime content, as well as the formation of a new inner C–S–H product located deeper in the silica grains. Low-lime C–S–H products possess higher surface areas and porosities than high-lime C–S–H products [24, 25].

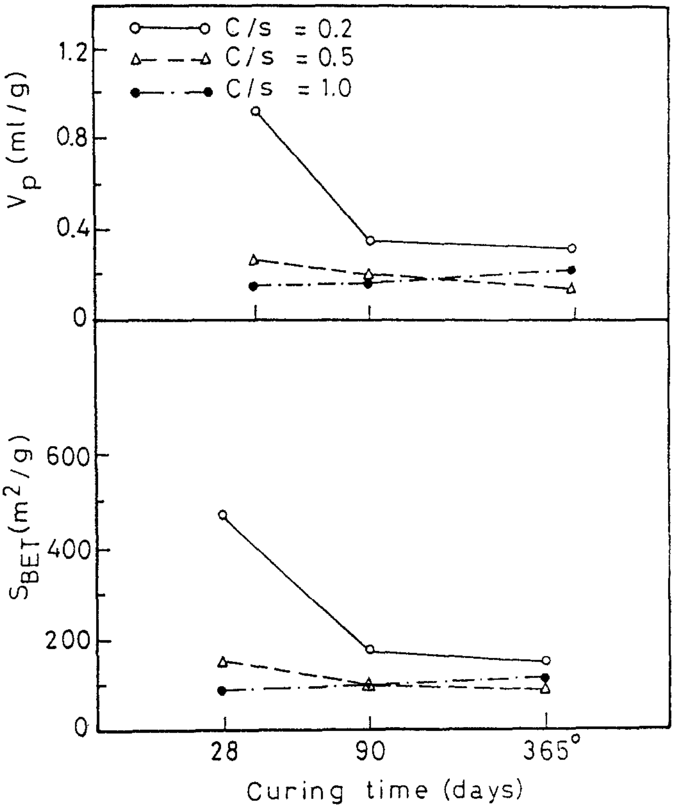

Fig. 4 Variation of surface area and total pore volume with curing time for nitrogen gas adsorption on hydrated lime-RHA specimens made from rice husk ash fired at 700°C with different C/S ratios

The mean hydraulic radius of the total pore system accessible to nitrogen molecules, for the lime-silica pastes made from RHA fired at 700°C with a CaO/SiO_2 molar ratio of 0.2 is increased from 18.4 to 21.11 Å with the time of hydration from 28 to 365 days. This can be explained by the way of stabilization of the formed C–S–H, via crystallization, which causes an opening of the pore system leading to an increase in the mean hydraulic radius with increasing time of hydration up to the final stage of hydration.

For the lime-silica specimens made by firing RHA at 700°C with a CaO/SiO_2 molar ratio of 0.5 the average value of the mean hydraulic radius is 16.89 Å for the paste hydrated up to 28 days; this represents the average width of the total pore system at this time of hydration. After 90 days of hydration the mean r_h-value increased to 19.74 Å; this is attributed to the stabilization of the formed hydrates, via crystallization, causing an opening of the pore system. Later, after 365 days of hydration, some sort of pore narrowing is observed and the mean r_h-value is reduced to 15.38 Å. This process represents the new formation of inner hydrates with an ill-crystallized character and smaller pore size.

The values of the mean r_h of the hydrated lime silica specimens with a CaO/SiO_2 molar ratio of 1 are slightly higher than those of the hydrated specimens made from lime-silica with a CaO/SiO_2 molar ratio of 0.5. This indicates that larger fraction of the total pore system is inaccessible to nitrogen molecules. Therefore, the lower degree of crystallization of the formed hydration products results in an exclusion of nitrogen molecules from a major part of the total pore system; i.e. the access of nitrogen molecules into the pore system of these hydrated lime-silica specimens with a CaO/SiO_2 molar ratio of 1 is decreased.

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