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Cement and Concrete Research 34 (2004) 521–526

CEMENT AND CONCRETE RESEARCH

Study on the pozzolanic properties of rice husk ash by hydrochloric acid pretreatment

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Received 9 October 2002; accepted 8 September 2003

Abstract

The pozzolanic properties of rice husk ash by hydrochloric acid pretreatment are reported in the paper. Three methods have been used to estimate the pozzolanic activity of rice husk ash. The heat evolution and the hydration heat of cement, the $Ca(OH)_2$ content in the mortar and the pore size distribution of mortar are determined. It is shown that compare with the rice husk ash heated untreated rice husk, the sensitivity of pozzolanic activity of the rice husk ash heated hydrochloric acid pretreatment rice husk to burning conditions is reduced. The pozzolanic activity of rice husk ash by pretreatment is not only stabilized but also enhanced obviously. The kinetics of reaction of rice husk ash with lime is consistent with diffusion control and can be represented by the Jander diffusion equation. A significant increase in the strength of the rice husk ash (pretreated) specimen is observed. The results of heat evolution indicate that the rice husk ash by pretreatment shows the behavior in the increase of hydration of cement. The cement mortar added with the rice husk ash by pretreatment has lower $Ca(OH)_2$ content after 7 days and the pore size distribution of the mortar with the rice husk ash with pretreatment shows a tendency to shift towards the smaller pore size.

Keywords: Rice husk ash; Hydrochloric acid pretreatment; Pozzolanic activity; Heat evolution; Strength

1. Introduction

As an agricultural product, rice husk contains considerable amount of SiO_2. Recent investigations on the production of the rice husk ash with high activity and the possible application of it in cement and concrete have been made by many researches [1–4]. All the results of which reveal that a well-burnt and a well-ground rice husk ash is very active and considerably improves the strength and durability of cement and concrete. The results also reveal that this pozzolanic material with good and constant properties can be obtained only by burning rice husk under well-defined conditions. The sensitivity of burning conditions is the primary reason that prevents the widespread use of this material as pozzolan [5,6].

It has been reported that acid leaching of the husk helps to obtain relative pure silica with high specific surface area [7]. It is possible to enhance the pozzolanic properties and decrease the sensitivity of burning conditions of this material. However, the effect of hydrochloric acid pretreatment on the pozzolanic properties of rice husk ash has not been systematically investigated.

In this study, the effect of hydrochloric acid pretreatment and heating course on the pozzolanic activity of rice husk ash is determined. Furthermore, the heat evolution, the hydration heat of cement added with rice husk ash and the pore size distributions of the mortar containing rice husk ash are also tested.

2. Experimental section

2.1. Pozzolanic activity experiment

The estimation of pozzolanic activity of rice husk ash is obtained as follows:

1. Rapid evaluation method—conductivity measurement, the conductivity method proposed by Luxan et al. [8]. The greater the change in the conductivity of the saturated $Ca(OH)_2$ solution added with rice husk ash, the more active rice husk ash is. This method is valid to evaluate the pozzolanic activity of rice husk ash [9].

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0008-8846/$ – see front matter
doi:10.1016/j.cemconres.2003.09.005

Table 1
Chemical composition[a] and physical properties of RHA, ADR and cement used

	ADR	RHA	Cement
Loss on ignition (%)	2.65	2.31	3.10
SiO_2 (%)	96	92.40	21.29
Al_2O_3 (%)	0.1	0.30	5.60
Fe_2O_3 (%)	0.2	0.40	3.00
CaO (%)	0.2	0.70	62.69
MgO (%)	< 0.1	0.30	2.24
Na_2O (%)	0.03	0.07	0.30
K_2O (%)	0.16	2.54	0.31
SO_3 (%)			1.47
P_2O_5 (%)	0.18	0.51	
MnO (%)	0.02	0.11	
Cl (%)	0.01	0.11	
Specific gravity (g/cm^3)	2.12	2.10	3.16
Specific surface, Blaine (m^2/kg)			330
Nitrogen adsorption (m^2/g)	311	110	
Median grain size (μm)	7.2	7.40	26
Change in electrical conductivity (mS/cm)	8.43	4.75	

[a] Conducted by X-ray fluorescence analysis.

2. Measuring the rate of consumption of $Ca(OH)_2$ that reacted with rice husk ash. Rice husk ash/$Ca(OH)_2$ = 1:1, W/C = 1.0, 20 °C, the $Ca(OH)_2$ used was analytical grade $Ca(OH)_2$.
3. Comparing the strength of mortar made with and without rice husk ash, guided by JIS R5201.

Furthermore, the heat evolution and hydration heat of cement added with 30% rice husk ash or ground silica sand are determined by thermal conductivity calorimeter (Calvet calorimeter), W/C = 1.0, 25 °C.

The pore size distributions of the samples are determined by mercury intrusion porosimetry. The $Ca(OH)_2$ content is calculated by using thermogravimetry (TG) curves. The TG analyses are carried out at temperature from 30 to 1050 °C and the heating rate of 10 °C/min.

2.2. Raw material preparation

Hydrochloric acid-treated rice husk was prepared by immersing rice husk in 1 N HCl aqueous solution. The husks were washed repeatedly with water until hydrochloric acid was undetected in the filtrate and then air-dried at room temperature. Two kinds of rice husk ash were obtained by heating rice husk in a batch furnace under oxidizing atmosphere by which rice husk ash can be produced about 300 g at a time. One kind of rice husk ash (ADR for short in the following) was obtained by heating hydrochloric acid-treated rice husk, and another kind of rice husk ash (RHA for short in the following) was obtained by heating untreated rice husk. The heating temperature ranged from 350 to 1100 °C and the maintaining time was 4 h, and then the rice husk ash was ground in a ball mill for 60 min with grinding agent addition.

The chemical and particle properties of the normal Portland cement and the rice husk ashes used for the test of the rate of $Ca(OH)_2$ consumption and the test of the strength of mortar are shown in Table 1.

3. Results and discussion

3.1. Reaction between rice husk ash and saturated $Ca(OH)_2$ solution

Fig. 1 shows the change in the conductivity of the saturated $Ca(OH)_2$ solution added with the rice husk ashes heated at different temperatures. The change in the conductivity of the saturated $Ca(OH)_2$ solution added with ADR is larger than that added with RHA over a wider temperature range. Up to 950 °C, the saturated $Ca(OH)_2$ solution added with ADR still has a large change in the conductivity (5.41 mS/cm). But the change in the conductivity of the saturated $Ca(OH)_2$ solution added with RHA drops significantly when heated over 700 °C; for example, the conductivity change was only 0.96 ms/cm at 750 °C. It shows that when heated over 750 °C, RHA will not have good pozzolanic activity. At 1000 °C, the change in the conductivity of the saturated $Ca(OH)_2$ solution added with ADR drops significantly. Moreover, at the critical crystallization temperature, the change in the conductivity of the saturated $Ca(OH)_2$ solution added with ADR heated at 950 °C with different maintaining time (from 4 to 12 h) varied from 5.42 to 5.02 mS/cm. But the change in the conductivity of the saturated $Ca(OH)_2$ solution added with RHA heated at 700 °C with different maintaining time (from 4 to 12 h) varied from 5.62 to 0.85 ms/cm. The result shows

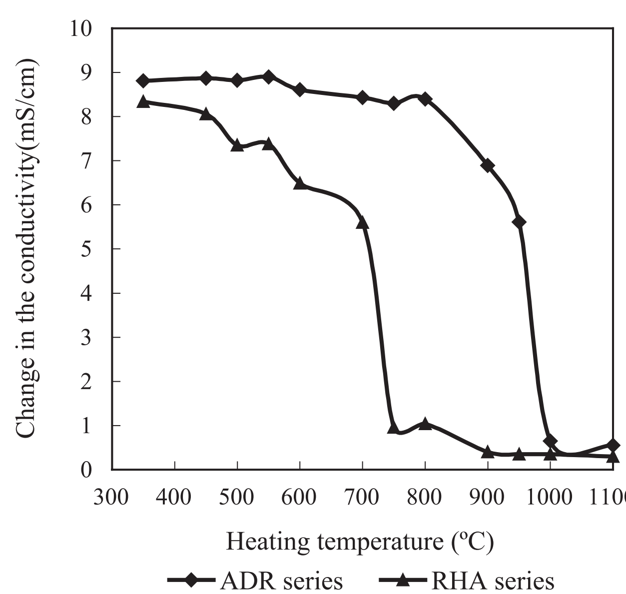

Fig. 1. Relation between the change in conductivity and the heating temperature.

Table 2
The amount of solute ion in ash (conducted by ion chromatograph)

Composition		Cl	F	K	Na	Ca	Mg	pH
Content	RHA	0.946	0.035	32.209	1.345	2.034	0.630	6.60
(mg/g ash)	ADR	0.471	0.102	1.187	0.846	0.684	0.219	5.89

RHA is obtained from heating untreated rice husk, ADR is obtained from heating acid treated rice husk.

that with simple hydrochloric acid pretreatment of the rice husk, the pozzolanic activity of the rice husk ash is enhanced and maintained at larger burning temperature scale. The pozzolanic activity of the RHA is greatly affected by the change of the maintaining time, but the pozzolanic activity of the ADR is slightly affected by the change of the maintaining time. The sensitivity of the pozzolanic activity to burning condition is reduced by the pretreatment. The faster change in the conductivity of the saturated $Ca(OH)_2$ solution added with ADR did not result from the reaction between the saturated $Ca(OH)_2$ solution and the hydrochloric acid residue or other impurity ions in ADR. From Table 2, it can be seen that with hydrochloric acid pretreatment and washing, the amount of the impurity ion stripping from rice husk ash is decreased. Table 3 shows the specific surface area and the amount of amorphous silica in the rice husk ash heated at different temperatures. The larger change in the conductivity of the saturated $Ca(OH)_2$ solution added with ADR is due to the fact that ADR has larger specific surface area and great amount of amorphous SiO_2 in it which can produce greater pozzolanic activity. However, heating hydrochloric acid-treated rice husks at 1000 °C or above resulted in the formation of crystalline SiO_2 from amorphous SiO_2 in the rice husk ash, which leads to appreciable decrease of the change in the conductivity of the saturated $Ca(OH)_2$ solution. It indicates that rice husk ash with low specific surface area containing crystalline silica shows low initial pozzolanic reactivity. This is in agreement with the results reported by James and Rao [10].

Table 3
Specific surface area[a] and amount of amorphous silica[b] in rice husk ash

Sample	Heating temperature (°C)	Specific surface area (m^2/g)	Amount of amorphous silica (%)
ADR	550	210	94.8
	600	270	95.1
	700	311	95
	800	257	95.7
	900	154	90.9
	1000	7.31	50.8
RHA	550	164	88.6
	600	86	89.6
	700	73	75.4
	800	9.24	40.2

[a] Determined by nitrogen adsorption method.
[b] Determined by glycerol method [11].

3.2. Mechanism of reaction between rice husk ash and $Ca(OH)_2$

To study the reaction of rice husk ash with lime, measurement of lime consumed at different reaction times are obtained by TG. The results are shown in Fig. 2. It can be seen that the lime is consumed at a very rapid rate in the initial period of reaction, almost 50% of the lime reacted within the first 24 h. The two kinds of the rice husk ashes have the same rate of lime consumption within the first 24 h. After 24 h, the reacted lime in the sample incorporating ADR is more than that in the sample incorporating RHA. The previous research has shown that the mechanism of the pozzolanic reaction can be satisfactorily described by diffusion equation [12]—the Jander equation that is based on Fick's parabolic law of diffusion. The following is the Jander equation [13]:

$$F(G) = [1 - (1 - G)^{1/3}]^2 = 2kt/r^2 = Kt$$

Where: $F(G)$ represents the equation $[1-(1-G)^{1/3}]^2$; G = fraction of the sphere that has reacted; r = initial radius of the starting sphere; k = parabolic rate constant; K = constant proportional to k, it indicates the reaction rate constant.

Fig. 3 shows the plots of $F(G)$ versus time of hydration for ADR and RHA. The rate constants are obtained:

For ADR: $K = 18.41 \times 10^{-4}$.
For RHA: $K = 10.99 \times 10^{-4}$.

The present results show that the kinetics of reaction of rice husk ash with lime is clearly consistent with diffusion control and ADR has a faster reaction rate with lime than RHA has. The lime consumption of the samples added with ADR was completed within 72 h, while the lime consumption of the sample added with RHA was completed within 168 h. The amount of amorphous SiO_2 in RHA is similar to

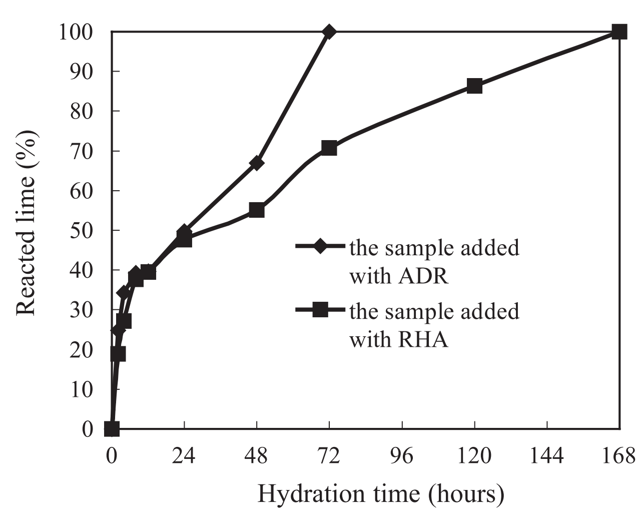

Fig. 2. The amount of lime reacted at different hydration times as determined from TG.

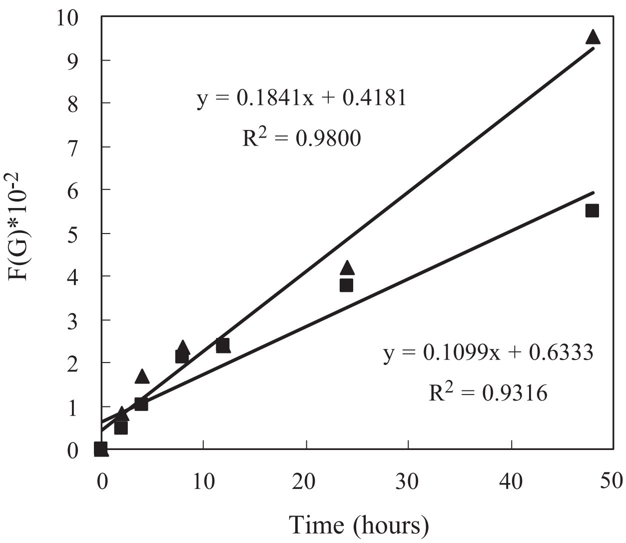

Fig. 3. Regression lines for the results obtained by samples added with RHA and ADR.

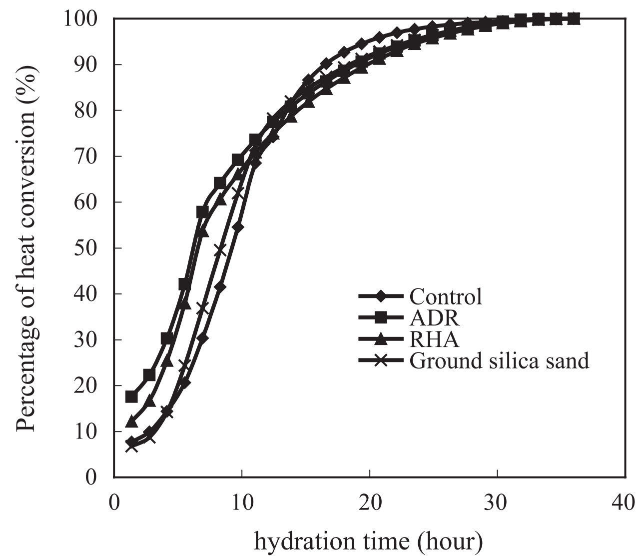

Fig. 5. Percentage of heat conversion of the samples.

that in ADR, but the specific surface area of ADR is about twice that of RHA. Therefore, ADR has faster reaction rate than RHA has.

Yu et al. [14] studied the reaction between the rice husk ash and $Ca(OH)_2$ solution and the nature of its product at 40 °C. They suggested that in the presence of water, RHA could react with $Ca(OH)_2$ to form a kind of fine C-S-H gel. The results of the present investigation by differential thermal analysis (DTA) are summarized in Fig. 4, which is used to study the nature of the reaction products at 20 °C. The main phase is CSH gel. It is in agreement with the findings of Yu et al. [14].

3.3. Heat evolution and hydration heat of cement added with ADR

The determination of the heat evolution rate is a sensitive and useful tool to characterize the way in which a pozzolanic material influences the early hydration of cement. In this study, the heat evolution and the hydration heat of cement pastes containing 0% and 30% of RHA, ADR or ground silica sand are studied with thermal conductivity calorimeter. The percentage of heat conversion and the curves of the rate of the heat evolution of samples are shown in Figs. 5 and 6, respectively. The percentage of heat conversion is the percentage of hydration heat evolved in time t to that in total hydration times (in this study, the total time to measure hydration time was 36 h); the higher the percentage of heat conversion of the sample, the faster the rate of hydration heat of the cement is. It can be seen that during the first 12 h, RHA and ADR show similar behavior in the increase of hydration heat (positive values). The rate of hydration heat of the cement added with pozzolanic material mainly depends on three factors, i.e., alite hydration, aluminate hydration and pozzolanic reaction [5,15]. Therefore, the reason for the increase in the hydration heat

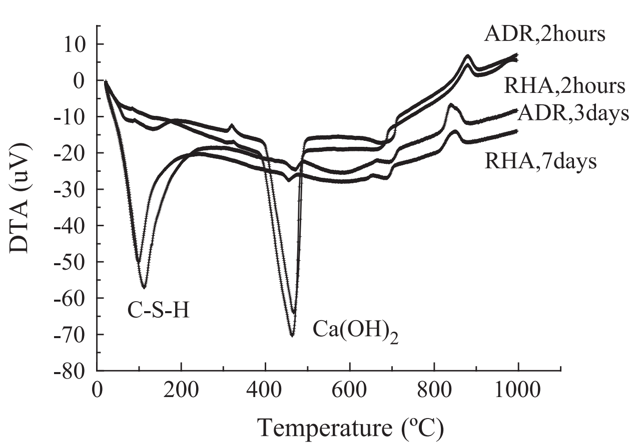

Fig. 4. DTA curves show the formation of reaction products with time of hydration.

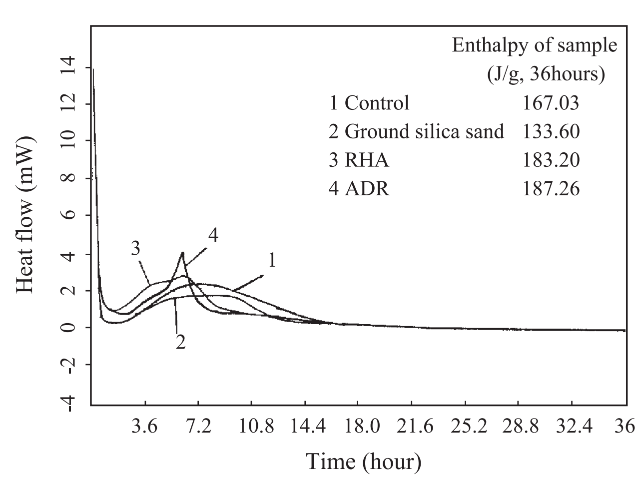

Fig. 6. Calorimetric curves from the hydration of cement with 30% by weight of additive.

Table 4
Strength[a] of cement-rice husk ash Mortar

Sample	Rice husk ash (%)	Compressive Strength (Mpa)				Flexural Strength (Mpa)			
		3 days	7 days	28 days	91 days	3 days	7 days	28 days	91 days
Control	0	21.9 (100)[b]	32.4 (100)	39.3 (100)	44.0 (100)	5.16 (100)	6.40 (100)	8.10 (100)	8.45 (100)
RHA	10	26.6 (122)	44.3 (137)	52.3 (133)	55.7 (126)	5.71 (111)	7.61 (119)	9.45 (117)	10.00 (117)
ADR	10	28.7 (131)	48.4 (149)	56.3 (143)	62.4 (142)	6.21 (120)	8.03 (126)	9.82 (121)	10.80 (126)

[a] JIS R 5201mix proportions are used, cement/sand = 1:3, water/cement = 0.5.
[b] Figures in parenthesis show the relative strength of cement rice husk ash mortar to the strength of respective control mortar with no rice husk ash, expressed in percent.

of cement with rice husk ash added is due to (1) the acceleration of the early hydration of C_3S and (2) pozzolanic reaction. The acceleration of early hydration of C_3S is ascribed to the high specific surface area of the rice husk ash, which provides a large number of nucleation sites for precipitation of hydration products of C_3S. The pozzolanic reaction corresponds to the second peak on the exothermic curve. The height of the second peak initially shows marked increases in incorporating ADR than in incorporating RHA or the control cement but then decreases. At the same time, the sample with ADR shows shortened dormant period. This is due to the large amount of amorphous SiO_2. The silica from the rice husk ash can react with Ca^{2+}, OH^- ions and calcium hydroxide from the cement hydration to form more C-S-H gel. In concrete, these reactions are known to contribute to the improvement in the properties of concrete. The result also indicates that the pozzolanic activity of ADR is higher than that of RHA. In addition, the exothermic rate of hydration of the cement sample added with ADR is more rapid than that of the cement added with RHA. It is mainly because ADR has larger specific surface area and higher chemical activity, which is proved by the results from measuring the change of the conductivity of the saturated $Ca(OH)_2$ solution added with the rice husk ashes. Moreover, from Fig. 6, the cement added with ADR or RHA has larger enthalpy compare to the base cement (within 36 h).

3.4. Strength

Another evaluation of the pozzolanic activity of ADR (RHA as the comparative object) is based on the comparison of the strength of mortar specimens made with and without the rice husk ashes. In the test, ADR and RHA replaced 10% of the cement by mass. The result is shown in Table 4. It can be seen that compared with the control, a significant increase in the strength of ADR specimen is observed even after 3 days. This is because of the high amount of amorphous SiO_2 with high specific surface area and high activity of ADR, which can react with calcium hydroxide produced from cement hydration. This increase in ratio does not decrease during the whole hydration time to 91 days.

When cement is replaced by RHA, there is a similar trend. However, the increase in the strengths is lower than that with ADR, although still higher than that of the control. This is because the content of active silica in RHA and the specific surface area of RHA are lower than that of ADR.

Table 4 also shows the flexural strength results, which show the similar trend.

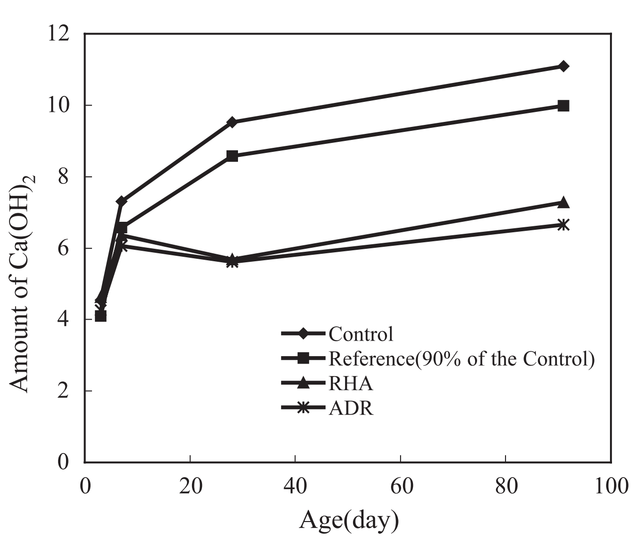

Fig. 7. Amount of $Ca(OH)_2$ in hardened cement pastes.

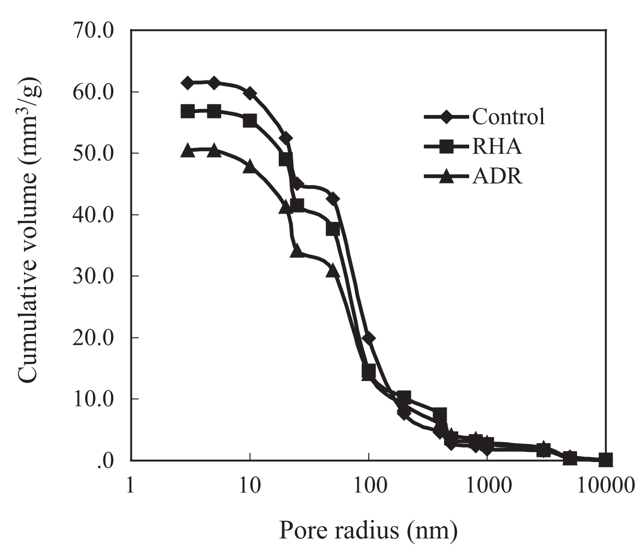

Fig. 8. Pore size distribution of mortar (age: 28 days).

Fig. 7 shows the results of $Ca(OH)_2$ content of the samples. We found that the $Ca(OH)_2$ content in RHA or ADR cement mortar was slightly higher than that in the reference sample at the age of 3 days. The $Ca(OH)_2$ content in the reference sample was 90% of the figure of control (compared to the control, the cement content of the samples with RHA and ADR at 10% replacement level contains 90% cement content). For example, the $Ca(OH)_2$ content in the RHA or ADR cement paste are 4.63% and 4.26%, respectively, and that in the reference sample (90% of the control) is 4.10%. This also shows that the hydration of cement with high activity rice husk ash resulted in the acceleration of the early hydration of C_3S and produced more $Ca(OH)_2$ content. However, from the age of 7 days, the $Ca(OH)_2$ content in the cement pastes with RHA and ADR is lower than that of the control paste, though the cement content in the cement mortar with RHA and ADR at 10% replacement level is lower than that in the control. This is because of the pozzolanic reaction in the cement mortar with RHA and ADR.

The pore size distribution of the mortar is shown in Fig. 8. The pore size distribution of the mortar with ADR shows a tendency of shifting towards the smaller range of pores compared with the control and the sample containing RHA. This may be attributed to the highly dense gel structure due to the high pozzolanic reaction of ADR paste.

4. Conclusions

By means of studying the effect of hydrochloric acid pretreatment on the pozzolanic activity of rice husk ash and the heat evolution of cement added with rice husk ash, the following conclusions can be reached:

1. With hydrochloric acid pretreatment of rice husks, the pozzolanic activity of rice husk ash is not only stabilized, but also enhanced; the sensitivity of the pozzolanic activity of the rice husk ash to burning conditions is reduced. The pozzolanic activity of ADR (pretreated) are slightly affected by the change of maintaining time, but the maintaining time has a great affect on the pozzolanic activity of RHA (no pretreatment).
2. The two kinds of rice husk ashes have the same rate of lime consumption at a very rapid rate in the initial period of reaction. The mechanism of reaction is consistent with diffusion control and ADR has a faster reaction rate with lime than RHA. The main reaction product is C-S-H gel.
3. During the first 12 h, RHA and ADR show similar behavior in the increase of hydration heat of the cement. The height of the second peak shows initially marked increases in incorporating ADR than in of incorporating RHA or the control cement but then decreases. At the same time, the sample added with ADR shows shortened the dormant period. Compare to the base cement, the cement added with ADR or RHA has larger enthalpy and faster exothermic rate of hydration. As a result, the pozzolanic activity of ADR is higher than that of RHA.
4. Because of the high of amorphous SiO_2 content in ADR with high activity, a significant increase in the strength of ADR specimen is observed compared with the strength of control mortar and that made with RHA. The cement mortar added with ADR has lower $Ca(OH)_2$ content after 7 days. The pore size distribution of the mortar with ADR shows a tendency to shift towards the smaller pore size.

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