Applied Mechanics and Materials Vol. 679 (2014) pp 228-236
Online available since 2014/Okt/08 at www.scientific.net
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doi:10.4028/www.scientific.net/AMM.679.228

Submitted: 12.08.2014
Accepted: 13.08.2014

The effect of three different types of rice husk ash as Ad mixture for ordinary Portland Cement

[1]Karya Sinulingga ,[2]Harry Agusnar ,
[3]Zakaria Mohd Amin and [4]Basuki Wirjosentono

[1]Deparment of Physics, Universiti Negeri Medan,

[2,4]Department Of Chemistry, University of North Sumatera, Medan, Indonesia,

[3]Allianze University College of Medical Sciences, Waziria Medical Square, Penang,Malaysia.

Keywords: rice husk ash, ordinary Portland cement, cement paste, hydration temperature

Abstract: The effect of three different types of rice husk ash which distinguish by color, pink, grey and white ashes were used as admixture to ordinary Portland cement paste was studied. Six batches of cement paste was prepared by adding 0-50 wt % RHA. The chemical and mineralogical characteristics of RHA were first analyzed. The characteristic of cement paste was investigated using IR, TGA and XRD. Hydration temperature also recorded. Chemical analysis shows higher amount of silica in RHA which is in range of 95-98wt. %. XRD and IR confirmed the white RHA is amorphous silica. The optimum amount of RHA addition was 10 wt. % which produced comparable properties with cement paste control. Based on Calorimetery Studied, IR, TG and hydration temperature results, white silica was found the most reactive silica but plays limited role as admixture in OPC paste.

1. Introduction

Pozzolans from industrial and agricultural by-products such as rice husk and fly ash are receiving more attention now since their uses generally improve the properties of the blended cement mortar, the cost and the reduction of negative environmental effects. Pozzolanic material when used in conjunction with a Portland cement, the calcium hydroxide produced by cement hydration reacts with pozzolan and produces additional calcium silicate hydrate (C-S-H) gel, blocking existing pores and altering the pore structure. The hydration reactions particularly during the setting and early hardening period are exothermic, and measurement of the rate of heat output at constant temperature is a direct indication of the rate of reaction. The products of reactions are primarily calcium silicate hydrate, calcium hydroxide and ettringite according to the following equations:

C_3S + Water -→ C-S-H + CH + Heat (1)
C_3A + Water + Gypsum → Ettringite + Heat (2)
C_3A + Water + Ettringite→ Monosulfoaluminate (3)

Where C_3S is tricalcium silicate, C_2S is dicalcium silicate, C_4A is tetracalcium aluminate, C_4AF is tetracalcium aluminium ferrite, and CH is calcium hydroxide.

The advantage of using rice husk ash in concrete such as increased compressive and flexural strengths [1,2,3], reduced permeability [1,4], increased resistance to chemical attack [5] and increased durability [6]. Based on unique and important contribution of RHA to cement and concrete research, this paper evaluates the effect of different type of rice husk ash (RHA) and the limitation role its plays to properties of cement paste during hydration.
Even though a lot of researches have been reported on using RHA and ordinary Portland cement(OPC), but the limitation of RHA is able to be used as admixture is still far from clear. In this paper we are studied the effect and the limitation role of RHA as a cement admixture.

2. Materials and methodology

2.1 Materials

Three different color of RHA, gray ,white and pink supplied by local supplier was used in this experiment. The ashes were primary sieves 200 mesh (75µm) to ensure the particles homogeneity of the ashes. Ordinary Portland cement was used to produce cement paste in this study. Ordinary Portland cement was obtained from local cement supplier.

2.2 Method

Preparation of cement paste for Calorimeter

Cement paste samples was prepared in 200g of samples by mixing OPC with different amount of RHA (0, 10, 20, 30, 40 and 50%). The ratio water to cement was chose constant at 0.5. The mixture was mold in cup and placed in thermos, the hydration temperatures were recorded for every hour for 24 hrs. After de-mold, samples were covered by parafilm and stored for 3, 7 and 14 hydration time. Samples then analyzed using Calorimeter, IR, TGA and XRD techniques.

3. Results and Discussion

3.1 Characterization of raw materials

3.1.1 Chemical analysis of OPC and RHA

The chemical analysis of OPC and RHA by wet chemical method shows in Table 1. It was found that CaO (64.30 wt.%) is the major component in OPC and other oxide content in cement is suitable with range of chemical composition Portland cement Type I and complies with British standard -12-1958 [7]. Chemical analysis confirmed silica is the main constituent in RHA which is in range of 95 to 97%. Pink RHA shows higher silica contents among other. Beside silica, RHA also contained minor oxides of other elements such as potassium, sodium, calcium, magnesium, iron, aluminum. Loss on ignition seem to be high in grey RHA which means that organic constituents is well remove compared to Pink and White RHA. Overall, the loss of ignition of these RHA was in range of 0.90 to 2.30%.

Table 1. Chemical properties of OPC and different type of RHA

Content	**Wt. %**			
	OPC	**Grey RHA**	**White RHA**	**Pink RHA**
SiO_2	21.34	95.60	97.00	97.50
Al_2O_3	4.45	0.50	0.41	0.32
CaO	64.30	0.42	0.08	0.05
Fe_2O_3	3.57	0.09	0.09	0.03
MgO	2.08	0.32	0.30	0.29
Na_2O	0.63	0.10	0.04	0.04
K_2O	0.30	0.50	0.46	0.42
SO_3	1.90	-	-	-
Loss of ignition	1.10	2.30	1.40	0.90
Insoluble residue	0.20	0. 16	0.22	0.45
TOTAL	**99.87**	**100.00**	**100.00**	**100.00**

3.1.2 Phase analysis of RHA

XRD pattern for different RHA shows the similar pattern which is represents the tridymite phase (SiO_2) ICDD 98-006-6154.

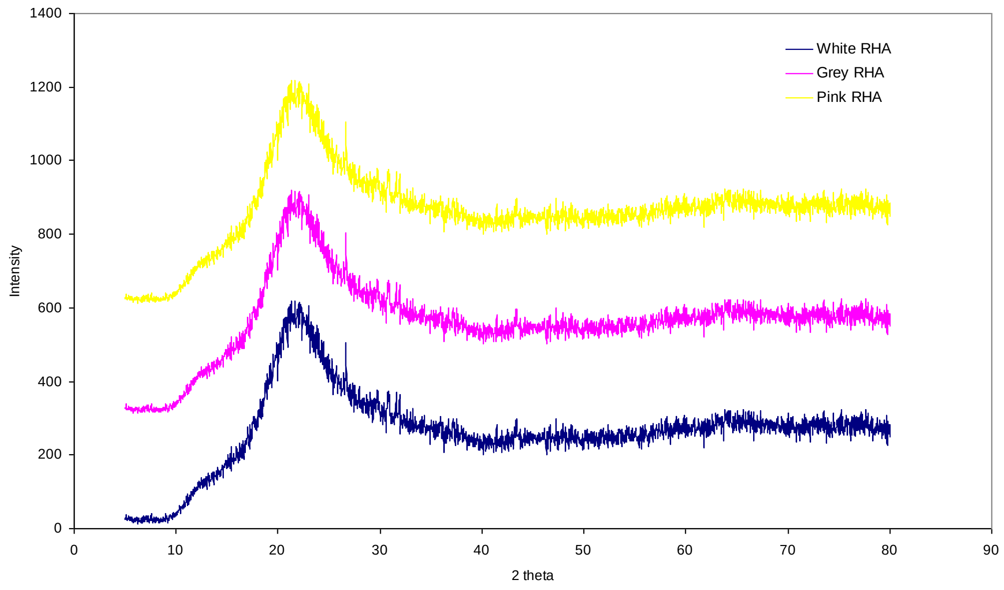

Fig. 1 XRD patterns of different RHA represent tridymite phase (SiO2) ICDD 98-006-6154.

3.1.3 IR Spectra

IR spectra for each RHA were shown in Fig. 2. It is clearly seen a broad main peak was at between (1000 -1300cm^{-1}) which represents the amorphous characteristic of silica for both samples grey and white RHA. But a sharp peaks at 1100 cm^{-1} is indicated the pink RHA is more crystalline than the two other RHA. This could be due the presence of cristabolite as reported [8]. What is interesting here, one can used IR in certain region to tell the crystalinity for solid compounds. Where Si – O-Si bond and it is indicating amorphous if broad peak.

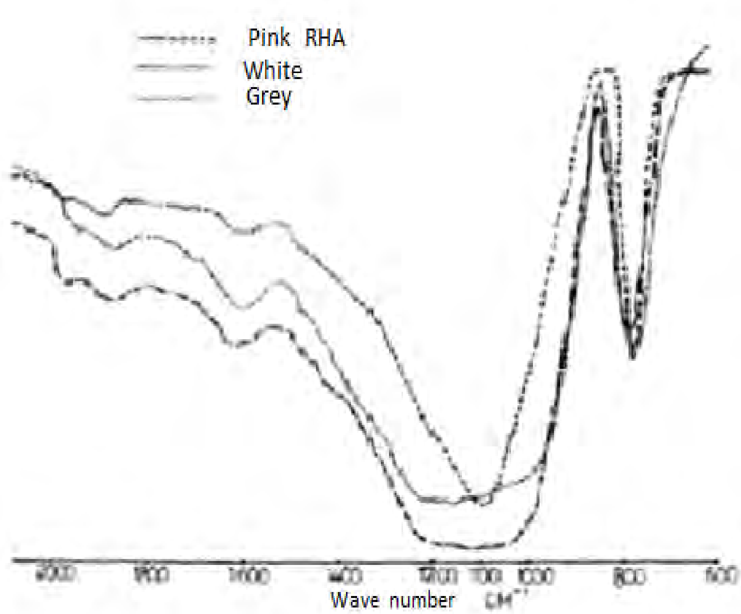

Fig. 2. IR spectra of different type of RHA

3.2 Effect of RHA to properties of cement paste

3.2.1 Calorimeter measurement during hydration

Due to heat is liberated when cement is mixed with water as a result of process cement hydration, one can monitor the heat changes with time using calorimeter. Fig. 3 shows the temperatures recorded during hydration of cement paste for different amounts and types of RHA. It is clearly indicated that all type of RHA shows the same trend of temperature versus hydration time (Fig. 3a-c). The temperature was steeply increased with increasing hydration time until reach optimum level and decreases again. The optimum temperatures recorded were found varies with different type and amount of RHA contents. The optimum temperature at 10wt.% RHA was similar to the control cement paste. However, as the contents of RHA increases to 20-50wt.%, the optimum temperature was reduced and longer time is taken to achieve this point. As a comparisons, cement paste with 10 wt% of RHA have shorter time (7-9 hrs) to reach optimum temperature compare 50wt% of RHA (10-16hrs).

It is clearly observed that, 10wt% of white RHA is the best composition which produced a similar trend with control cement pasted to other. This finding shows that addition of 10wt.% of white RHA not alter the composition of cement paste and suitable for used in as admixture materials.

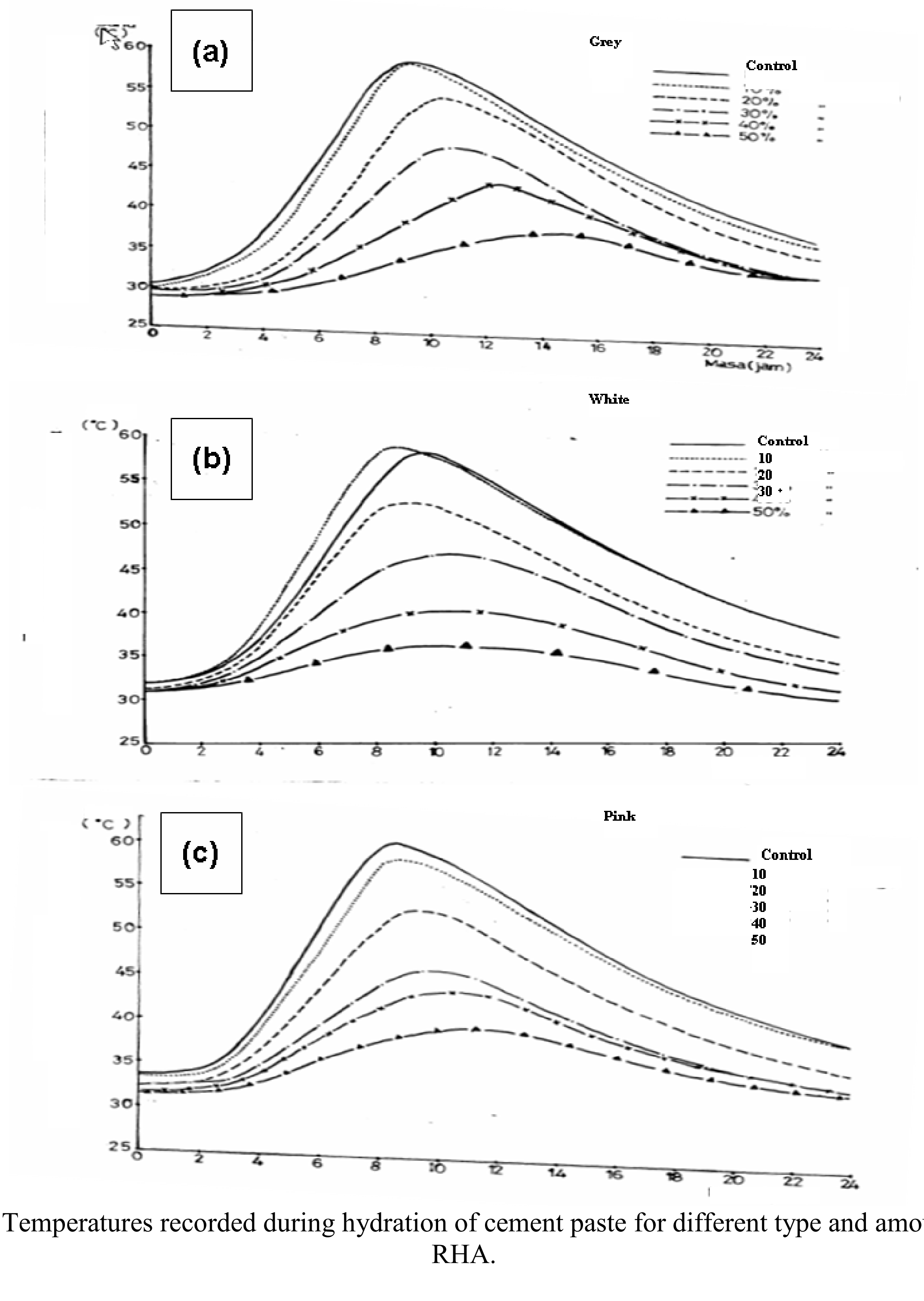

Fig 3. Temperatures recorded during hydration of cement paste for different type and amounts of RHA.

3.2.2 IR Spectra

Since 10wt.% RHA shows a comparable results with control cement paste, only these samples was characterized using IR technique. IR spectra for 10wt.% RHA and control cement paste at 3, 7 and 14 days hydration was shown in Fig. 2. It is clearly seen that the IR spectra peak of RHA cement pastes at 3, 7 and 14 days hydration are similar to control. However, for 10wt% of white RHA at 14 days hydration shows a clearer and broad peak at 960 cm^{-1} compared to control. This broad peak was mainly contributed by formation of additional of C-S-H in cement paste since C-S-H is amorphous in nature .

It is clearly seen that IR peak at 3640 cm^{-1} is sharp in pink RHA indicated the presence of $Ca(OH)_2$ in cement hydration this peak is disappeared in all white RHA. However, peak at 1480-1410 cm^{-1} which represents C-S-H are weak compared to white and grey RHA especially when hydration time increases. These suggested that grey RHA are less reactive compared to white and pink RHA. The less reactivity of grey RHA will contribute to less silica reactions with $Ca(OH)_2$ which yield from cement hydration which contribute to lesser addition of sodium silicate hydrate which unable to reduce the presence of $Ca(OH)_2$ in the paste.

For white RHA additions, adsorption peak which represent $Ca(OH)_2$ seams disappears in all cases with increase of hydration time while peak which represent of C-S-H become more broader and clearer. The high reactivity of white RHA react with $Ca(OH)_2$ from cement hydration to form additional C-S-H which reduced the amount of $Ca(OH)_2$. Detail IR spectra peak and its absorbance characteristic is simplified in Table 2.

Table 2. IR spectra peaks and its absorbance characteristic

IR Spectra peak (cm^{-1})	**Absorbance characteristic**
860 (weak)	Calcite
1100	Amorphous silica
1640	O-H bending
3420	O-H stretching
960 (Ca-O-Si)	C-S-H adsorption
1480 - 1410	C-S-H adsorption
3640 (sharp)	O-H stretching of $Ca(OH)_2$
1430 (double peaks)	$Ca(OH)_2$
870 (weak)	$Ca(OH)_2$

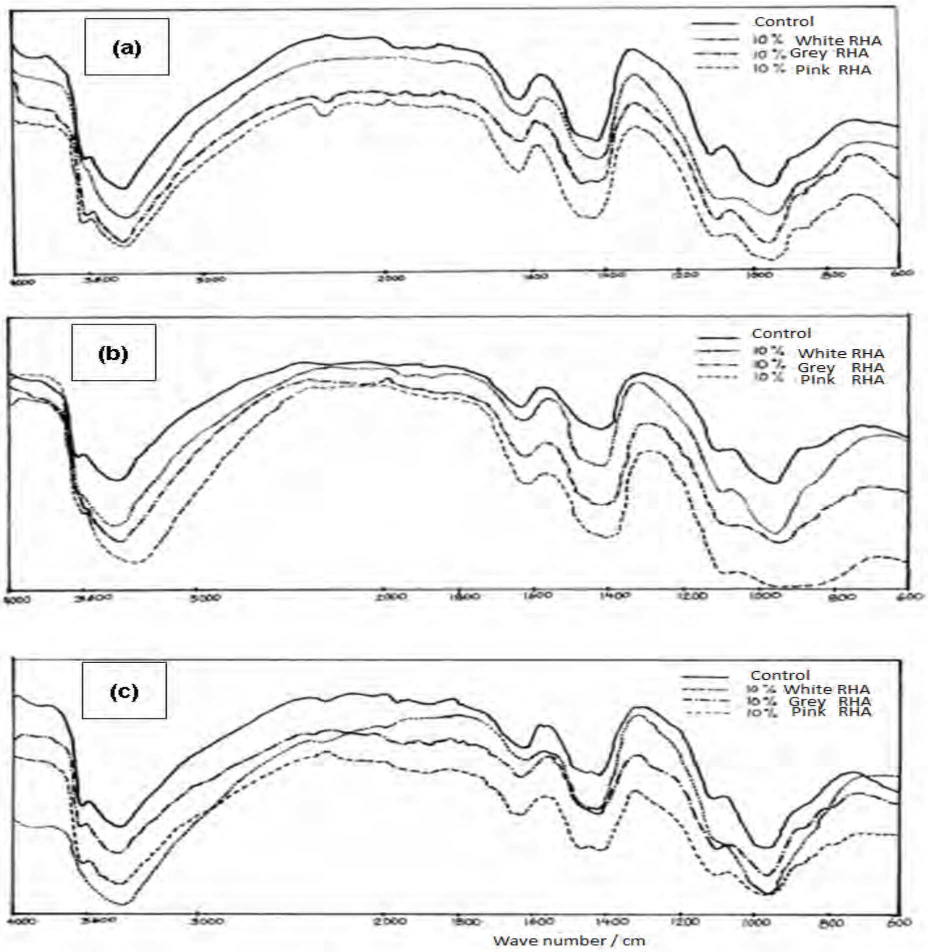

Fig 4. IR spectra of RHA at; (a) 3, (b) 7, and (c) 14 days cement paste hydration.

3.2.3 Thermal gravimetric Analysis

Thermal gravimetric analysis is one of the common tool to be used in analysis phase changes in a solid material. It is also give a great advantage when the instruments of thermal gravimetric (TG) is combined with it derivative (DTG). TG and DTG curves (Fig 5a-c) show two significant curves which represent the weight loss at 50-150°C and at 450 - 500°C. According to Todor [9] (1976), the weight loss at 50-150°C was referred to loss of water hydration while the letter referred to loss of water with presence of $Ca(OH)_2$ in cement paste. Using the TGA peaks in the range of 450 -500^o C, the amount of $Ca(OH)_2$ present during each hydration period was calculated based on relative to the weight loss of water. The amount of total $Ca(OH)_2$ for each reactions is given in the Table 4. It is clearly observed that percentage of $Ca(OH)_2$ produced during cement hydration is almost taken up by silica in white RHA in the first 3 day,(24.00- 10) % and rough estimated left about another 14 % $Ca(OH)_2$ and it retains even until fourteen days. While the pink and grey RHA cement pastes is only about 6% of the total silica are taken up comparable with control cement paste. The higher amount of $Ca(OH)_2$ in pink RHA cement paste may be due to similar reasons that silica present less reactive and as a result the amount of $Ca(OH)_2$ from cement hydration remain or unchanged.

Table 3. Percentage of water and $Ca(OH)_2$ in 10 % RHA cement paste for different hydration time

Cement paste	**% of Water & $Ca(OH)_2$**		
Hydration time (day)	**1**	**3**	**14**
Control	5.71(23.50)	4.52(18.60)	5.84(24.033)
White RHA	3.46(14.24)	3.18(13.09)	3.38(13.91)
Grey RHA	4.14(17.04)	4.59(18.89)	5.19(21.360
Pink RHA	4.20(17.28)	5.39(22.18)	5.38(22.14)

In white RHA cement paste, the percentage of $Ca(OH)_2$ are lesser compared to control and others. Similar to earlier suggestion that the reactive silica in white RHA cement paste is more reactive to react with $Ca(OH)_2$ to form additional C-S-H thus reduced the amount of $Ca(OH)_2$ present in cement paste. The actual percentage of $Ca(OH)_2$ are given in the bracket in (Table 2) and was decreased at 3 day hydration, however increase after 14 days hydration. This could be due slow topographic reaction as a results of solid-solid reaction between dry SiO_2 and dry $Ca(OH)_2$ as the paste is in hardening and gaining the strength.

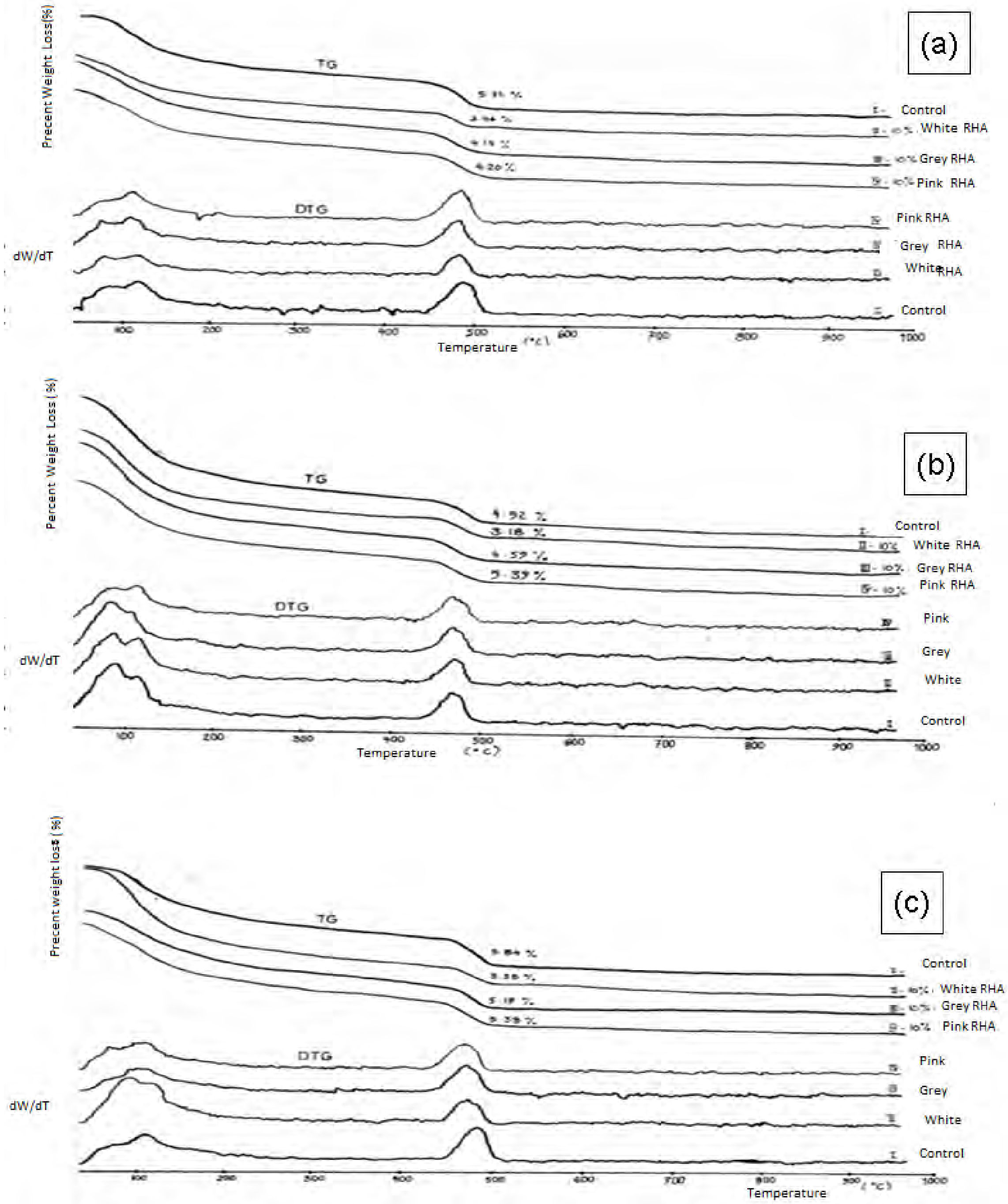

Fig 5 Thermal gravimetric Analysis curves of RHA cement paste hydration; (a) 1, (b) 3 and (c) 14 days

3.3.4 XRD Analysis

XRD pattern in Fig. 6 and Fig. 7 shows the phases obtained from cement paste hydration for 3 and 14 days, respectively. It is clearly seen that the calcium silicate hydrate, C-S-H ($3Ca.SiO_2.3H_2O$) as indicates by poor peaks at d = 3.048 and 9.309, Grangeon and coworkers [10] . While calcium hydroxide, $Ca(OH)_2$ ICDD 98-005-8841 and ettringgite phases, Hesse et.al [11].

White RHA has higher intensity at d = 9.309 and d = 3.048 compare to other. This intensity was increase with increasing hydration time from 3 to 14 days. This finding suggest that the formation of additional C-S-H from the reaction between reactive silica (in white RHA) with $Ca(OH)_2$ during cement paste hydration.

$Ca(OH)_2$ pattern is clearly observed at d = 4.928, d = 3.132, d = 2.662. This peak is obvious and high in grey RHA compared to other both at 3 and 14 day hydration time. From this intensity, we can suggest that the content of $Ca(OH)_2$ in cement paste is higher compare to other. This XRD pattern finding support the XRD pattern in raw grey RHA analysis which show that the silica in Grey RHA was less reactive with $Ca(OH)_2$ from cement hydration, hence cannot reduced the amount of $Ca(OH)_2$ as in white RHA additions.

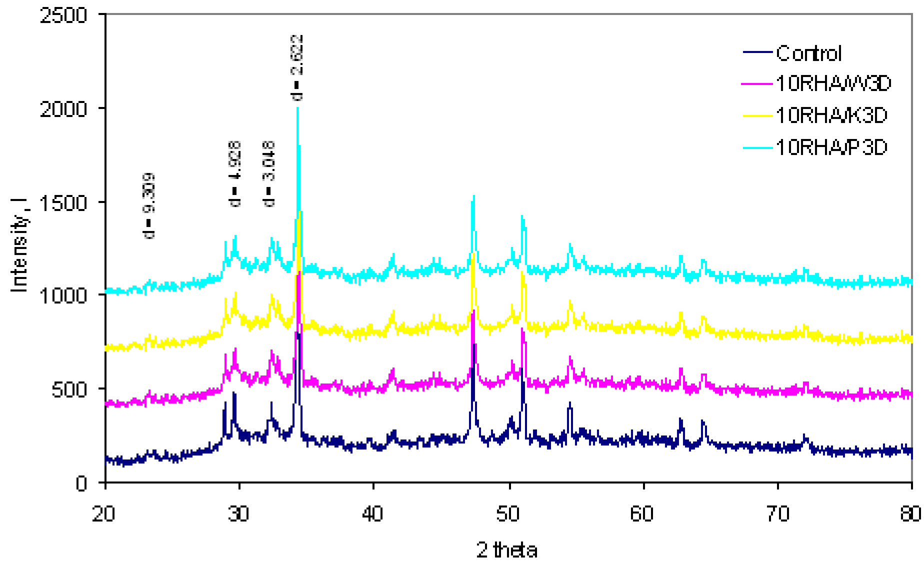

Fig. 6 XRD pattern from cement paste and cement paste with RHA at 3 day hydration time.

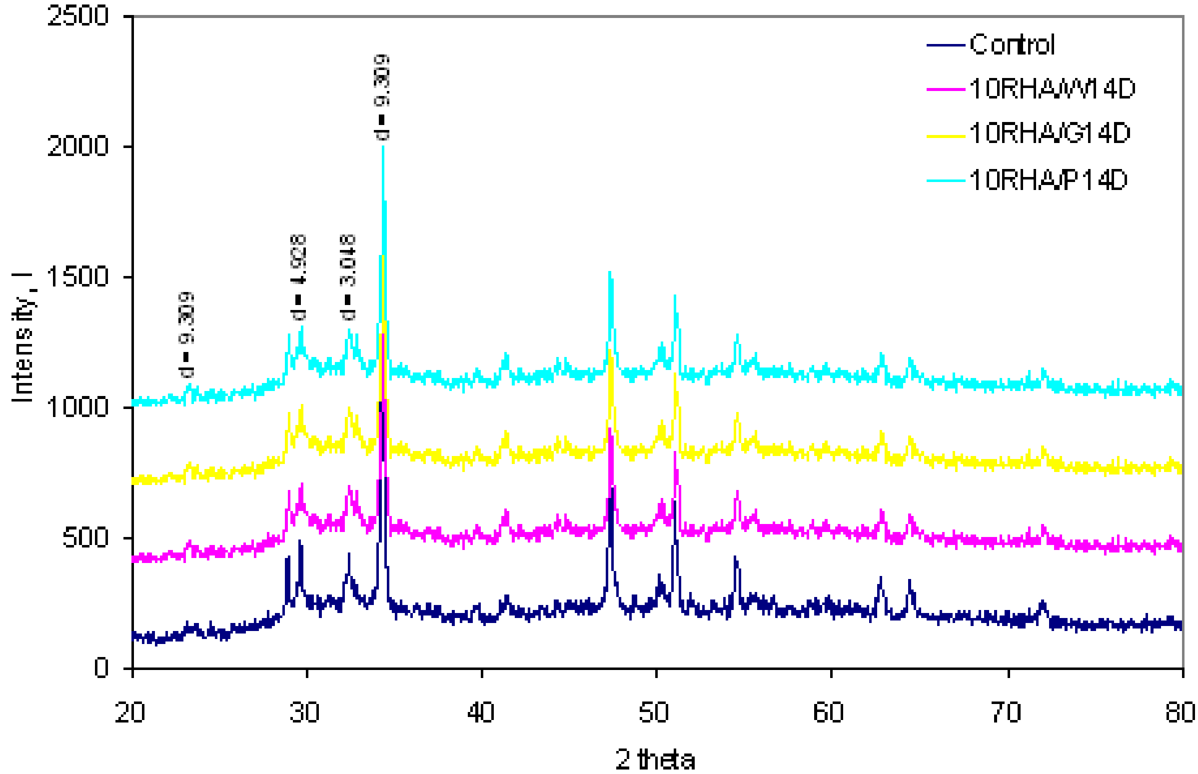

Fig. 7 XRD pattern from cement paste and cement paste with RHA at 14 day hydration time.

4. Conclusion

Effect of three type of RHA on the properties of ordinary Portland cement paste was studied. The following conclusions are derived;

1. White RHA is shows characteristic of reactive silica compare to other
2. The optimum amount of RHA addition was 10 wt. % which produced comparable properties with cement paste control.
3. 10 wt.% of white RHA suitable as admixture in cement paste.

5. Acknowledgement

The authors are grateful to the Universiti Sains Malaysia for financial support.

6. References

[1] Zhang M-H, and Malhotra, M. (1996). High-performance mortar incorporating rice husk ash as a supplementary cementing material. ACI Mater J 93:629–636
[2] Ismaila, M.S., and Waliuddin, A. M.(1996). Effect of rice husk ash on high strength concrete. Construction and Building Materials. 10(7): 521-526.
[3] Rodriguez, G.S. 2006. Strength development of concrete with rice-husk ash. Cement and Concrete Composites. 28(2): 158-160.
[4] Ganesan, K., Rajagopal, K., and Thangavel, K.(2008). Rice husk ash blended cement: Assessment of optimal level of replacement for strength and permeability properties of concrete. Construction and Building Materials. 22(8): 1675–1683.
[5] Chindaprasirta, P., Kanchandaa, P., Sathonsaowaphaka, A., and Caob, H.T.(2007). Sulfate resistance of blended cements containing fly ash and rice husk ash. Construction and Building Materials. 21(6): 1356-1361
[6] Coutinho, J.S. 2002. The combined benefits of CPF and RHA in improving the durability of concrete structures. Cement and Concrete Composites. 25(1): 51-59.
[7] British standard -12-1958, Portland cement (Ordinary) and Rapid Hardening.
[8] Putra Jaya,R., Mohd Al Amin, M.N, Zainal Arifin, A., and Mohd Amin. Z. ,(2013). Properties of Mortar Containing Rice Husk at Different temperature and Exposed To Aggressive Environment, Advanced Material Research, 620, 87-93.
[9] Todor, D. N. (1976). "Thermal analysis of minerals", 1st. ed. Kent
[10] Grangen,S., Claret,F., Lerouge,C., Warnot,F., and Lanso,B. (2013). Cement and Concrete Research, 52 : 31-37.
[11] Hesse,C., Goetz –Neunhoeffer,F.,Neubauer,J., Braeu,M., and Gaeberiein,P. ICDD 2009 ISSN 1097-0002.

Engineering and Technology Research
10.4028/www.scientific.net/AMM.679

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DOI References

[3] Rodriguez, G.S. 2006. Strength development of concrete with rice-husk ash. Cement and Concrete Composites. 28(2): 158-160.
http://dx.doi.org/10.1016/j.cemconcomp.2005.09.005
[6] Coutinho, J.S. 2002. The combined benefits of CPF and RHA in improving the durability of concrete structures. Cement and Concrete Composites. 25(1): 51-59.
http://dx.doi.org/10.1016/S0958-9465(01)00055-5