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RESEARCH ARTICLE

HYDRATION ANALYSIS OF AGRICULTURAL RESIDUE ASH ADMIXTURED CEMENT PASTE

*¹Barathan, S. and ²Gobinath, B.

¹Department of Physics, Annamalai University, Annamalai Nagar, Tamilnadu, India

²Central Instrumentation and Service Laboratory, Annamalai University, Annamalai Nagar, Tamilnadu, India

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ABSTRACT

Rice straw ash and wood ash were admixed at various weight percentages with cement and its effect on hydration was explored in this report. The ash particles under 75 micron size were mixed together at four different percentages and added to cement as a partial replacement and the samples were hydrated for various time periods from 1 hour to 4 weeks. The samples were analyzed with FTIR, XRD and SEM techniques to characterize the hydration kinetics and to understand the changes occurring in mineral compounds during their modification into hydrated mineral compounds. The results were compared with the compressive strength measurements in the light of available literature. The result obtained reveal a definite possibility of RSA and WA reuse.

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INTRODUCTION

The phenomenal development in science and technology and the unprecedented growth in the construction industry drives the requirement for cement to many folds in the last century. The industry had grown throughout the world with an annual output of 3736 Mt. in 2012. Cement industry plays a vital role in the development of any country, but its growth has also its own hazardous effects. The emission of CO₂ from various stages of cement production is alarming. For 1000kg of cement produced 930 kg of CO₂ is emitted into the atmosphere. Overall the cement industry is accountable for 5% manmade CO₂ emission globally. Many possible ways were being explored to reduce the CO₂ emission around the globe and one such option open to us is to reduce the usage of cement by replacing it with some suitable Supplementary Cementing Materials (SCM). They are finely divided materials that supplement Portland cement partially which reduce the cost and increase the cementing behavior. The common examples are fly ash, silica fume, granulated blast furnace slag, lime stone dust, and ashes from bio, agro and other wastages. In order to reduce the emission of greenhouse gases cement companies have turned to the use of supplementary cementitious materials. Since cement is the most expensive fraction in concrete and difficult to obtain for third world countries, other ash materials have been used to help extend cement supplies and allow more development.

Replacing the cement with these materials with higher percentage to obtain higher strength or making them suitable to versatile conditions is one of the prominent areas in current research. Wood Ash (WA) is tested for its suitability as an admixture by Abdullahi (2006) and he suggested that 20% replacement of wood ash has considerably increased the strength of the concrete. Sivakumar, et al., 2009 analyzed RHA for cement replacement and suggested that the amorphous silica present in the RHA is effectively reacting with Ca(OH)₂ in hydrated cement matrix to product CSH. Cheah, Ramli (2012) had investigated the high calcium wood ash and silica fume mixture to replace cement partially by measuring various elastic moduli. Kevern, (2010) had analyzed the corn ash as supplementary cementitious material and suggested that the corn ash may have potential to be used as an admixture in third world countries.

Rice straw ash (RSA) was used as a pozzolanic material in cement mortars by Munshi, Dey & Sharma, 2013. They found that compressive strength has increased upto 12.5% by replacing 10% RSA in cement. Being the second largest producer of rice in the world and using wood as a primary fuel source, India is producing an enormous quantity of ash part of which was land filled. Land filling such a fine particle is highly hazardous to life stock. So the possibility of admixturing those ashes with cement which address environment issues on either way was explored in this work. Since 20% wood ash replacement is recommended already and 10% RSA is also suggested, it was decided to replace 20% or

*Corresponding author: Barathan, S.

Department of Physics, Annamalai University, Annamalai Nagar,
Tamilnadu, India

more replacement for cement by mixing wood ash and rice straw ash.

MATERIALS AND METHODS

For the present study commercially available 43 grade OPC (Type I) is selected. Wood ash is collected from Sri Manakula Vinayagar Rice Bran Oil Mill, Thirubuvanai, India. Rice straw is collected for the nearby field and burnt in clay pit for 1 hour. Both ashes were collected and sieved using a 75micrometer test sieve. Then they were mixed in four different combinations and is tabulated in Table 1 along with their names.

Table 1. Ash Combination and Sample Names

Sl. No	% of RSA	% of WA	Total Replacement (%)	Name of Sample
1	15	5	20	A1
2	15	10	25	A2
3	10	20	30	A3
4	5	20	25	A4

Table 2. Chemical composition of OPC, RSA and WA

Oxides	OPC	RSA	WA
SiO ₂	25.9	66.72	46.05
CaO	59.31	4.78	18.23
Fe ₂ O ₃	4.11	0.76	8.12
Al ₂ O ₃	5.33	3.26	7.55
MgO	0.81	1.48	2.1
K ₂ O	1.08	9.16	4.2
Na ₂ O	0.23	1.12	1.5
TiO ₂	0.6	0.68	0.1
MnO	0.11	0.7	2.85
P ₂ O ₅	0.2	0.59	1.7
SO ₃	1.67	1.35	1.4
Loi	0.65	9.4	6.2

The oxide composition is tested for the sample using Bruker S4 Pioneer XRF Spectrometer and given in Table 2. For hydration analysis, the mentioned mixture samples were replaced with cement by the method of replacement of weight. The prepared samples were added with water at a water to cement ratio of 0.45 and mixed thoroughly for two minutes in a plastic container and allowed to hydrate for different periods from 1 hour (1h), 1 day (1d), 1 week (1w) and 4 weeks (4w). Hydration was stopped by soaking them in acetone for two minutes to remove any evaporable water content. Then the samples were oven dried for two hours at 120° C and grounded to a fine powder using an agate mortar by grinding for half an hour. Care had been taken to apply uniform pressure and the time period of grinding to maintain uniform grain size.

The grounded samples were stored in a desiccator for further study. The admixed samples were mixed with fine grained river sand at sand to cement ratio of 1.3 and W/C of 0.45 to prepare a 7cm³ test cube for compressive strength measurements. The cubes were cured for 1d, 1w and 4w before measuring compressive strength using Unico compressive strength testing machine. The FTIR spectra were recorded in transmission mode using KBr pellet as a standard in the region of 4000cm⁻¹ to 400cm⁻¹ with a resolution of ±4cm⁻¹ at room temperature using Perkin Elmer FTIR Spectrometer model RX1. The identification of the crystal phases were carried out using Xpert-Pro SRDML Gonio X-ray Diffractometer with Cu-Kα radiation (λ=1.54060Å)

RESULTS AND DISCUSSION

The chemical composition from the table 2. Suggests that both the samples have significant quantity of SiO₂. From XRD data the silica present in RSA is in amorphous phase. The compressive strength measurements were plotted for all the samples from A1 to A4 admixed with ashes and the control paste were given in Fig. 1. From the compressive strength diagram (Fig. 1) it is clear that all the admixed samples show higher strength irrespective of ash percentage except A3 than the control paste. It is a clear indication of the effectiveness of the admixture. The XRD spectra of anhydrous OPC, RSA and WA were presented in Fig.2 a, b, and c respectively. The XRD spectra of control paste and admixed paste hydrated for different time periods were given in Fig. 3-7 In Fig. 2 (a) anhydrous OPC has peaks at 2θ = 29.4°, 32.3°, 34.4°, 51.7° representing the C₃S phase in cement (Harchand, et al., 1980), (Kjellsen, K.O., and Fjallberg, L, 1999). The peak at 32.5° represent the C₂S phase the peak at 2θ=11.7° is assigned to gypsum and the peak at 2θ=44.3° is assigned to C₄AF(Prince, Espagne, & Aitcin, 2003). The carbonate has a prominent peaks at 2θ=39.4° and 47.3° (Mollaha, MYM. et.al., 1995).

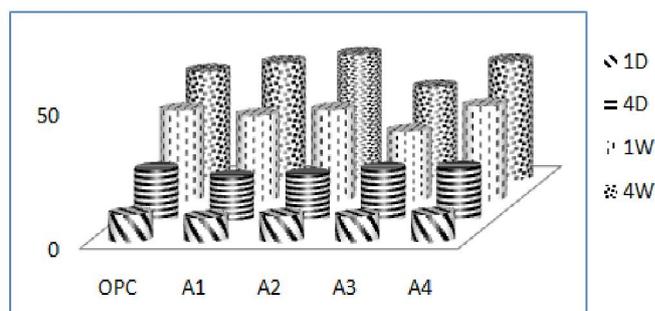


Fig. 1 Compressive strength of OPC and Admixed samples

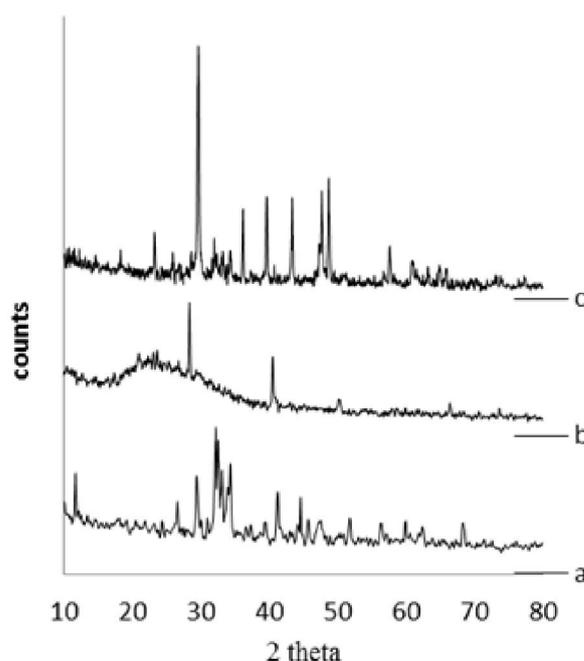


Fig. 2 XRD Spectra of anhydrous (a), OPC, (b) RSA and (c) WA

The anhydrous wood ash has a characteristic peak at $2\theta=26.62^\circ$ representing SiO_2 and $2\theta=29.6^\circ$, 47.50° and 48.55° representing calcite, peak at 36.4° and 43.38° representing CaCO_3 . The anhydrous RSA has a broad hump in between 21° and 34° angle showing the presence of amorphous silica and peaks at 28.07° , 40.20° and 49.87° for sylvite (Thy *et al.*, 2006). In the one hour spectra of OPC (Fig. 3a), the peaks representing gypsum and C_3A were reducing in intensity slowly and new peaks at 15.8° and 22.7° were emerging. It represents the reaction between gypsum and the Aluminate phase with water to produce ettringite. It is the first and a rapid reaction occurring in cement when water is introduced. In the 1d (Fig. 3b) diffractogram, the gypsum peak had reduced further in intensity and ettringite peaks begin to reduce in intensity. It shows that the gypsum is fully consumed in first day of hydration and the ettringite which is a semi stable state is converting to a more stable monosulfate. During that time the paste has completed initial and final set and begin to harden and is visualized in the emergence of a peak at 23.0° (Dyer & Dhir, 2004). The peaks representing C_3S were reducing in intensity from 1h onwards due to hydration reaction. Simultaneously new peaks are emerging due to hydration namely CH at $2\theta=18^\circ$, 34° , 47° and 50.7° (Antiohos, 2007). A partially crystalline

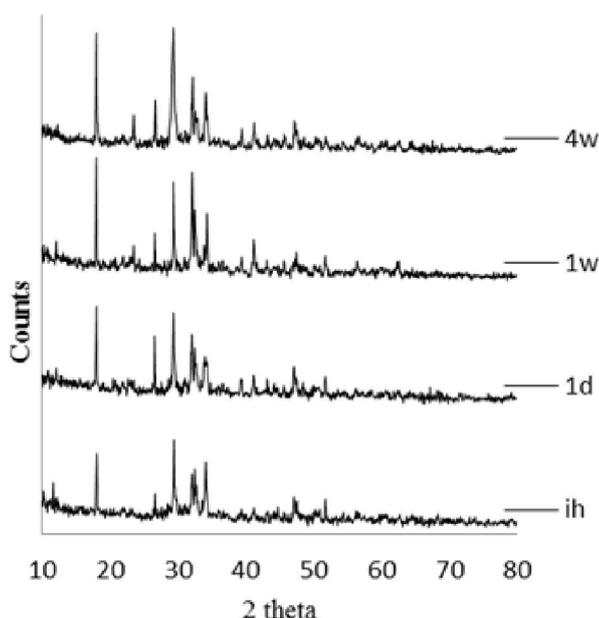


Fig. 3. XRD Spectra of OPC hydrated for 1h, 1d, 1w and 4w

peak at 29° was observed which is assigned to main hydration product Calcium Silicate Hydrate (CSH) (Heikal, 2004). The CSH is responsible for the strength of the cement and the growth of the peak is directly related to strength gain. The C_2S peak shows a slight decrease only in 1 w sample representing the delayed reaction of C_2S phase and in 4w C_3S is almost consumed and C_2S is partially consumed. The existence of the C_2S in 4w hydrated sample represent the incompleteness of the hydration reaction. In the 4 week sample the CH and monosulphate and CSH peaks had significant increase in intensity and the ettringite peak is almost consumed representing the conversion from ettringite to monosulfate. From Fig. 4-7 admixed samples show the same trend as

OPC hydrated sample and the reaction rate indicating the progress of the hydration. From Fig. 4-7 the CH peak which has a maximum intensity in 1w sample shows a reduction in 4w hydrated samples which indicates the consumption of CH between 1 and 4 week. This may be due to the pozzolanic reaction between the silica present in the ash sample and the CH produced during hydration. During the hydration reaction in the early stages C_3S reacts with water producing CSH. After 1d C_2S begin to react with water to produce CSH which is explained by the following equations 1 and 2. After one week, the CH produced by hydration reaction reacts with the silica present in the ash particle to produce CSH called secondary CSH. It was explained in equation 3 (Fajun, Grutzeck, & Roy, 1985). In samples A1, A2, A4 the CH peak diminishes significantly. The rate of decrease was more in the case of A1 and A2 but it was less pronounced in A4. But these transitions were not well pronounced in A3 sample whose strength was less than control paste. The same results were substantiated in FTIR measurements. The FTIR spectra of all the samples hydrated for 1 day and 4 w are presented for comparison in Fig 8. For convenience part of the spectra alone presented. The significant peak at 920cm^{-1} represent the ν_3 silicate indicate the progress of hydration reaction. In control paste ν_3 silicate peak shifted from 920cm^{-1} to 972cm^{-1} in 4 weeks of hydration and also the intensity had increased substantially (Mollah *et al.*, 2000). ν_2 silicate peak at 462cm^{-1} which also reflects the hydration reaction has also grown significantly. In A1, A2 and A4 samples both the peaks were developed well in 4 week duration but the growth is not well pronounced in A3 sample. CH peak at 3629cm^{-1} is also a good indicator for monitoring the pozzolanic reaction in hydrated paste (Mollah, *et al.*, 2004). The peak intensity reduced from 1w and subsequently the intensity of the silicate peaks increased more than the control paste in A1 and A2. This indicates the rate of pozzolanic reaction in those samples are progressing well which was conformed in XRD and Compressive strength measurements.

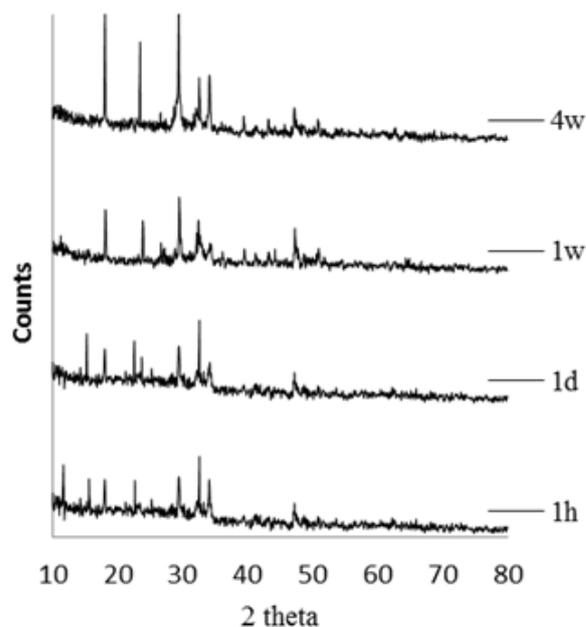


Fig4. XRD Spectra of sample A1 Hydrated for 1h, 1d, 1w and 4w

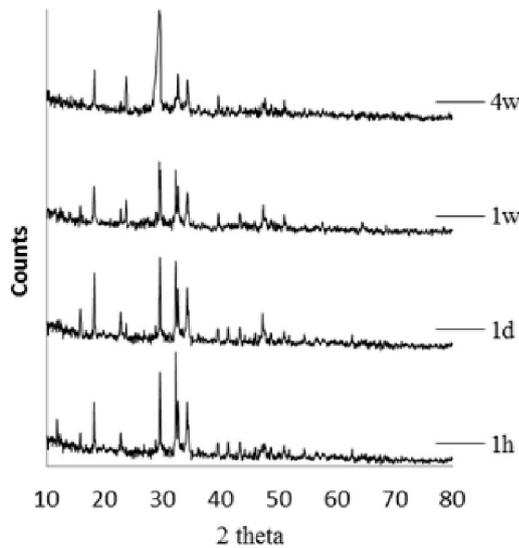


Fig. 5. XRD Spectra of sample A2 Hydrated for 1h, 1d,1w and 4w

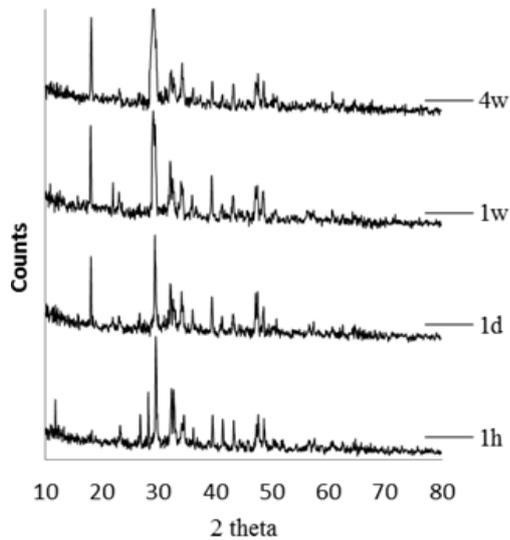


Fig. 6. XRD Spectra of sample A3 Hydrated for 1h, 1d,1w and 4w

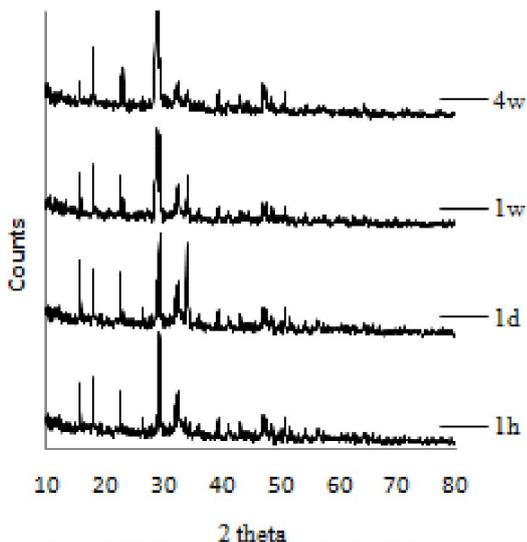


Fig7. XRD Spectra of sample A4 Hydrated for 1h, 1d,1w and 4w

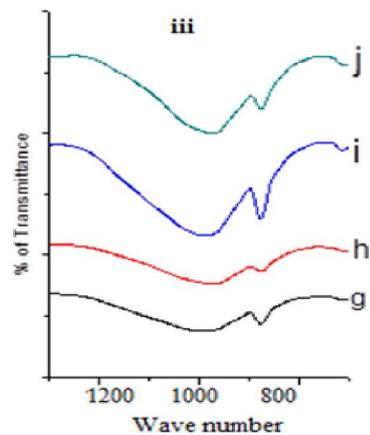
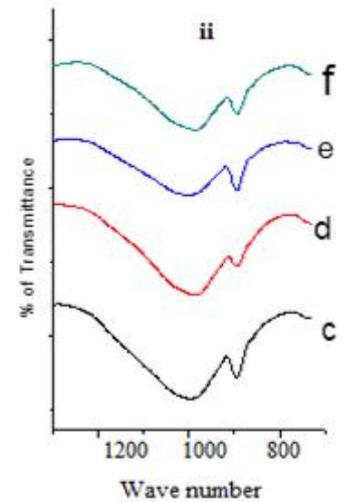
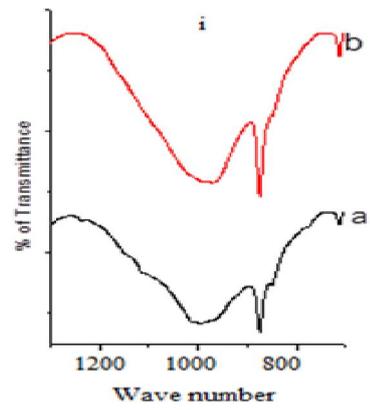


Fig. 8.

- i. FTIR Spectra of OPC Hydrated for (a) 1 day, (b) 4w
- ii. FTIR Spectra of A1 Hydrated for (c) 1d, (d) 4w, A2 hydrated for (e) 1d and (f) 4w
- iii. FTIR Spectra of A3 Hydrated for (g) 1d, (h) 4w, A4 hydrated for (i) 1d and (j) 4w

Apart from the pozzolanic reaction filler effect was also responsible for strength gain. The inert particles in the ash with sufficiently small size drift into the voids and pores, and thereby increase the density solid material consuming the pores. The density increase was reflected in the strength gain. Another type of filler effect is explained where SCM particles act as nucleation site for the CSH to grow further(Taylor, 1990), (Gutteridge & Dalziel, 1990). In either way the density

and the strength is increased. For the A4 sample even though the observed change in CH peak both in XRD and FTIR is less than A1 and A2 it offers nearly same compressive strength. This may be due to the predominance of filler effect than CH – Si interaction. The A4 sample has more WA than RSA. From oxide composition report (Table 2) WA has more CaO content than RSA. The Calcium content may have been a possible reason for strength gain due to filler effect.

Conclusion

By means of three methods FTIR, XRD and Compressive strength, the presence of hydration compounds as well as the changes in mineral phases during hydration was highlighted. The interpretation of the results with the XRD enables a more precise identification of the mineral phases, in all the samples under investigation. A2 sample exhibits higher strength than other samples and A1 and A4 sample show higher strength than control paste. The WA and RSA mixture have better pozzolanic effect upto 25% replacement.

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