

Hydration of bamboo leaf ash blended Portland cement

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Bamboo leaf ash (BLA) obtained at 600°C was found to be pozzolanic material. The pozzolanic activity was studied by using chemical methods, differential scanning calorimetry, X-ray diffraction and scanning electron microscopic techniques. Hydration behaviour of 20 wt% BLA blended ordinary Portland cement (OPC) was studied by using different experimental techniques and it was found that at 28 days of hydration the compressive strength value for 20 wt% BLA blended cement mortar was quite comparable to that of mortar made from OPC. The mechanism of pozzolanic activity has been discussed.

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Ordinary Portland cement is one of the most important binding materials in terms of quantity produced. Since it is manufactured at a very high temperature (~1500°C), it consumes lot of energy. Besides huge amount of energy consumption, it emits harmful gases, which pollute the atmosphere. The production of every ton of Portland cement contributes about one ton of CO₂ in the atmosphere. Small amounts of NO_x and CH₄ gases are also emitted. Apart from energy consumption and emission of harmful gases, calcium hydroxide, one of the hydration products, obtained during the hydration of cement, is a nuisance for construction industry. This affects the durability characteristics of Portland cement pastes, mortars and concretes.

There are large number of industrial by-products which are practically considered to be waste (although nothing is waste), when mixed in an appropriate amounts with Portland cement, improves the properties of the cement. Some such materials are – blast furnace slag, fly ash and silica fume. These materials also known as mineral admixtures are latent hydraulic or pozzolanic in nature. Apart from industrial by-products, there are certain ashes obtained from agriculture based industries which have pozzolanic properties. Rice husk ash and sugarcane bagasse ash are already in use in construction industry¹⁻⁴ in the form of blended cements.

Blended cements also known as composite cements are obtained when these materials are mixed with

Portland cement. Many times these blended cements show properties better than Portland cement provided proper optimization is done. These cements reduce energy consumption, protect atmosphere and reduce the amount of calcium hydroxide by converting it into a useful hydration product¹⁻¹². There is a continuous search for alternative supplementary materials, which may have hydraulic/pozzolanic properties. This is much more important in developing countries like India, where there is shortage of good quality coal and limestone. In an attempt to this, we found that ash obtained from bamboo leaf is amorphous in nature and has pozzolanic properties.

In the present paper, a detailed investigation regarding the pozzolanic activity of BLA and hydration behaviour of BLA blended OPC has been reported. Attempts have been made to understand the mechanism of action of BLA during the hydration of OPC.

Experimental Procedure

Materials

Dry bamboo leaves were burnt in an open air and then heated in a muffle furnace at 600°C for 2 h. Vikram premium OPC 53 was used for hydration studies. Ca(OH)₂ (Qualigence) was used for studying pozzolanic reactions.

The chemical composition of BLA and OPC are given in Table 1 and the mineralogical compositions of OPC are given in Table 2. The particle size distributions determined by laser granulometer are given in Fig. 1.

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Methods

Pozzolanic reactivity in suspension

100 mL of saturated $\text{Ca}(\text{OH})_2$ solution was mixed with 20 g BLA and stirred magnetically. 10 mL of the solution was filtered at different intervals of time (1, 2, 3 and 4 h) and was titrated against N/4 HCl using phenolphthalein as an indicator. From the titre values the amount of $\text{Ca}(\text{OH})_2$ reacted with BLA was calculated. The experiment was performed at room temperature ($\approx 30^\circ\text{C}$) and 75°C .

Reaction between calcium hydroxide and BLA

Equal mass of $\text{Ca}(\text{OH})_2$ and BLA were mixed thoroughly in polythene bags and then mixed with water in such a way that w/s ratio was 1.0. The reactions were stopped at different intervals of time (1, 3, 7, 14, 28, 45 and 90 days) with isopropyl alcohol and ether. The samples were dried at 100°C and subjected to different analysis.

Water consistency measurement

The water consistency was determined by Vicat apparatus (I S: 4031 part 4, 1988) and was found to be 27.5% for OPC and 40% for OPC+20 wt% BLA blended cement. So water/solid (w/s) ratio was kept 0.4 in both the cases.

Setting time measurement

Initial and final setting times in the presence of different amounts of BLA was determined with Vicat apparatus (I S: 4031 part 5, 1988) and are given in Table 3. In the presence of 10 wt% BLA the setting times increased whereas in the presence of 20 wt%

BLA, the setting times were almost equal to that of control (OPC without BLA). Therefore, 20 wt% BLA blended cement was used for detailed investigation in the present study.

Preparation of hydrated samples of OPC and BLA blended cement

10 g of OPC or BLA blended cements were weighed separately in different polythene bags and mixed with 4 mL water so that w/s ratio became 0.4 and the air inside the bags was removed in order to avoid carbonations. The hydration reactions were allowed to continue at room temperature ($\approx 30^\circ\text{C}$). The hydrations at different interval of time (1, 3, 7, 14 and 28 days) were stopped with isopropyl alcohol and ether and the hydrated samples were heated at 105°C for 1 h. The dried samples were stored in polythene bags and kept in a desiccator.

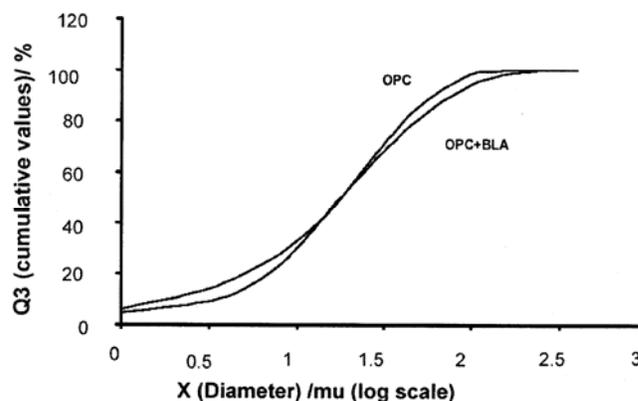


Fig. 1 — Particle size distribution

Table 1 — Oxide compositions

| System | Composition (wt%) | | | | | | | | | | |
|--------|-------------------|-------------------------|-------------------------|--------------|--------------|----------------------|-----------------------|----------------|---------------|------|-------|
| | SiO_2 | Al_2O_3 | Fe_2O_3 | CaO | MgO | K_2O | Na_2O | TiO_2 | SO_3 | IR* | LOI** |
| OPC | 21.40 | 5.03 | 4.40 | 61.14 | 1.35 | 0.48 | 0.24 | - | 2.53 | 1.65 | 1.29 |
| BLA | 75.90 | 4.13 | 1.22 | 7.47 | 1.85 | 5.62 | 0.21 | 0.20 | 1.06 | - | - |

* IR – insoluble residue, ** LOI – loss of ignition

Table 2 — Mineralogical composition of OPC-53

| Mineral phase | Composition (wt%) |
|-----------------------|-------------------|
| C_3S | 38.89 |
| C_2S | 31.83 |
| C_3A | 6.06 |
| C_4AF | 13.37 |

Table 3 — Setting times

| Amount of BLA (mass %) | Initial Setting time (min) | Final setting time (min) |
|------------------------|----------------------------|--------------------------|
| 0.0 | 155 | 190 |
| 10.0 | 200 | 260 |
| 20.0 | 155 | 200 |

Non-evaporable water content (W_n)

Approximately one gram of the hydrated OPC or blended cement were weighed in ceramic crucibles and heated at 105°C for 1 h and then at 1000°C for 1 h. From mass losses the non-evaporable contents were calculated.

Free lime determination

One gram of hydrated cements were refluxed with 40 mL of isopropyl alcohol and acetoacetic ester mixture (20:3) for one hour. The solutions were filtered and titrated against 0.1N HCl using bromophenol blue as an indicator.

Analysis of liquid phase for Ca^{++} ions

10 g cements were taken in polythene bags and mixed with 20 mL water ($w/s=2.0$) and liquid was filtered at different intervals of time and titrated against standard EDTA solution. Care was taken to avoid carbonation.

X-ray diffraction studies

X-ray diffraction studies of the reaction products obtained from reaction of CH and BLA and the hydrated samples (prepared as mentioned above) were recorded with the help of a Philips PW1710 diffractograph using CuK_{α} radiation.

Differential scanning calorimetric (DSC) studies

DSC studies of the reaction products obtained from reaction of $Ca(OH)_2$ (CH) and BLA and the hydrated

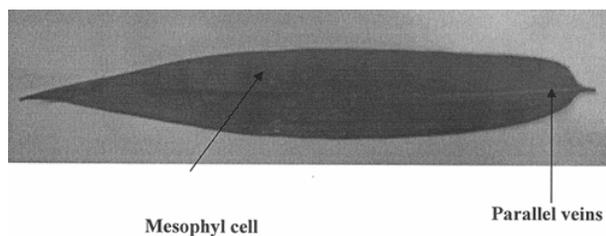


Fig. 2 — Photograph of bamboo leaf

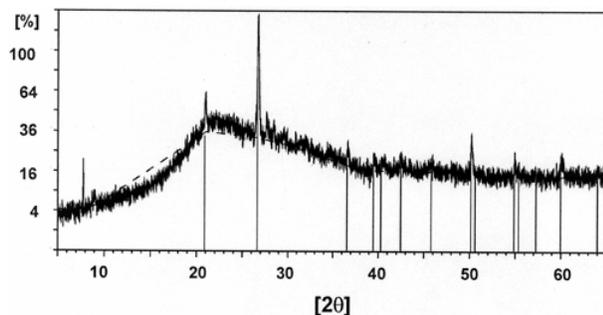


Fig. 3 — X-ray diffraction pattern of bamboo leaf ash

samples were recorded with a TG-DTG-DSC NETZSCH STA 409 PC instrument in the temperature range of 30-1000°C in nitrogen atmosphere with a heating rate of 10°C/min. using Al_2O_3 as reference.

In order to determine the amount of calcium hydroxide reacted, calibration curve was plotted. $Ca(OH)_2$ was mixed thoroughly with different amounts of Al_2O_3 and DSC studies were made. A curve between heat of fusion of $Ca(OH)_2$ versus amount of $Ca(OH)_2$ was plotted, from which the amount of $Ca(OH)_2$ reacted was calculated.

SEM studies

Hydrated samples (CH+BLA) were coated first with carbon and then with gold in an argon atmosphere and SEM images were recorded with the help of Philips XL 30i scanning electron microscope.

In the case of hydrated cement (OPC and OPC+BLA blended cement) only carbon coating was made and SEM images and EDAX spectra were recorded.

Compressive strength measurement

OPC/BLA blended cement were mixed with sand in 1:3 ratio and then mixed with water (I S: 4031 part 4, 1988). The mortars were placed in steel moulds of 70.6 mm³ dimension. These cubes were demoulded after one day and stored in water at 27°C at a relative humidity of 100%. These cubes were then taken out from water prior to testing. The compressive strengths were determined at 3, 7 and 28 days as per I S: 4031 part 6, 1988 method.

Results and Discussion

Bamboo leaf (Fig. 2) consists of two parts (i) mesophyl cell and (ii) parallel veins. The X-ray diffraction pattern (Fig. 3) of bamboo leaf ash heated at 600°C for 2 h shows that it is amorphous in nature. The SEM pictures of the ash (both parts) are shown in Fig. 4. Since the ash contains amorphous SiO_2 , it is expected to be a pozzolanic material and was allowed to react with calcium hydroxide in solution as well as in paste. In case of reaction in solution, BLA was mixed with saturated solution of calcium hydroxide and a definite volume of the solution (filtered) was titrated against standard HCl at different intervals of time. The amount of calcium hydroxide reacted with BLA was determined. The amount of reacted calcium hydroxide is plotted against time (Fig. 5). The curve shows that as the time progressed, the amount of calcium hydroxide reacted increased. Further the

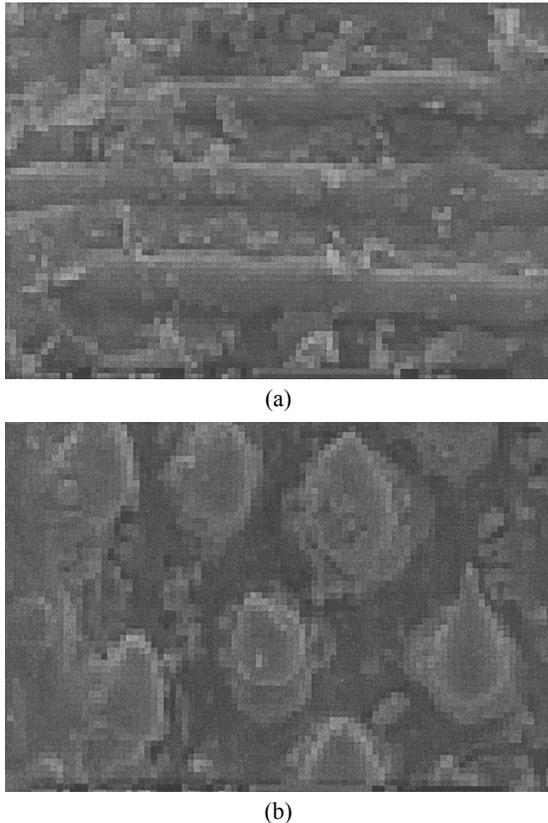


Fig. 4 — SEM pictures of bamboo leaf ash (a) parallel veins (b) mesophyl cell

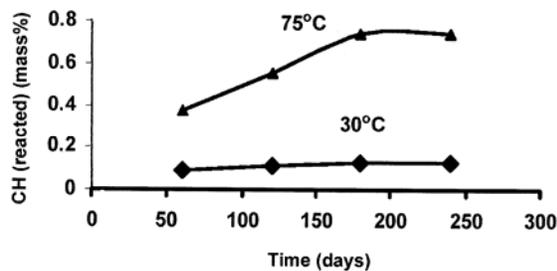


Fig. 5 — Amount of calcium hydroxide reacted at different time with BLA in suspension at different temperatures

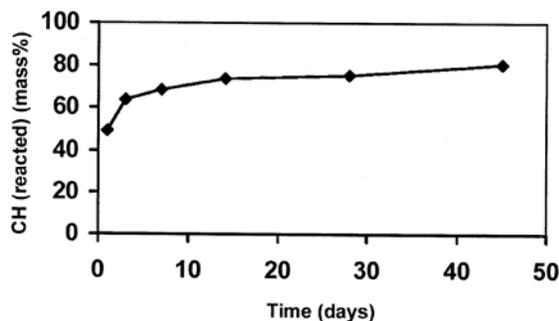
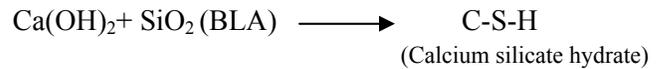


Fig. 6 — Amount of calcium hydroxide reacted with BLA in a paste at different time as determined by DSC technique

experiment was performed at 75°C and the amount of calcium hydroxide reacted with time is also shown in Fig. 5. The results suggest that BLA is a pozzolanic material and its pozzolanic activity increases with the increase of temperature. The pozzolanic reaction can be expressed as



The increase of rate of above reaction with temperature may be due to increase of dissociation of Ca(OH)_2 in solution giving more Ca^{++} and OH^- ions. The larger number of ions react with a faster rate with amorphous silica.

BLA was also allowed to react with calcium hydroxide in paste and the amount of calcium hydroxide reacted at different intervals of time was determined by DSC technique and is shown in Fig. 6. The curve shows that the amount of reacted calcium hydroxide increased with time indicating that the pozzolanic activity of BLA increased with time. However, the rate of increase of pozzolanic reactivity is much higher in the suspension. In suspension larger number of Ca^{++} and OH^- ions are available and as a result higher pozzolanic reaction occurs.

The X-ray diffraction pattern of sample (CH+BLA) hydrated at 28 days is shown in Fig. 7. The figure shows unreacted calcium hydroxide and the formation of calcium silicate hydrate (C-S-H) phase. The diffraction pattern confirms that BLA is a pozzolanic material and during the course of reaction calcium silicate hydrate is formed.

SEM images of samples (CH+BLA) hydrated at different intervals of time are shown in Fig. 8. The results show that as the time progressed, the amount of C-S-H phase increased.

In order to understand the role of BLA as a pozzolanic material during the hydration of Portland

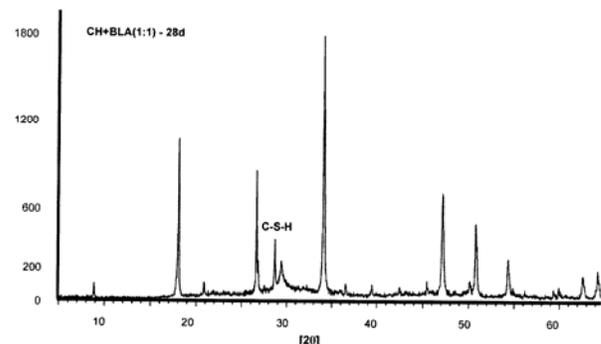


Fig. 7 — X-ray diffraction pattern of CH+BLA hydrated for 28 days

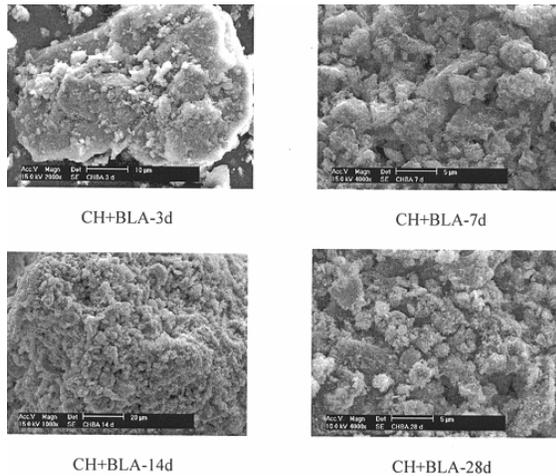
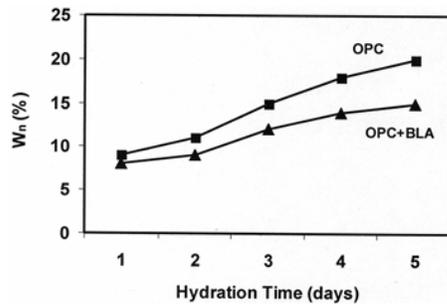


Fig. 8 — SEM pictures of hydrated CH+BLA pastes

Fig. 9 — Variation of non-evaporable water content (W_n) with hydration time

cement, the hydration studies of 20 wt% BLA blended Portland cement were made. The non-evaporable water contents (W_n) (Fig. 9) of the hydrated OPC increased with time indicating an increase in hydration. W_n values of BLA blended OPC also increased with time but the values were found to be lower. The lower values of W_n may be due to dilution effect. Free lime values (Fig. 10) were also found to increase with time indicating an increase in hydration. In blended cement the values also increased with time but the values are much lower than that of OPC. This is due to reaction of $\text{Ca}(\text{OH})_2$ obtained during hydration with amorphous silica of BLA.

In order to understand the mechanism of hydration, Ca^{++} ion concentrations of the liquid phase were determined at different intervals of hydration time (Fig. 11). From the figure it is seen that as soon as cement comes in contact to water, Ca^{++} ion concentrations in the liquid phase increased and reached to a maximum value within 5 min of hydration. The solution becomes saturated or supersaturated with respect to Ca^{++} ion

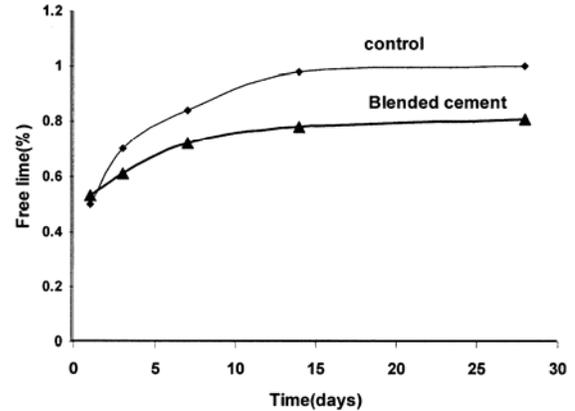


Fig. 10 — Variation of free lime with hydration time

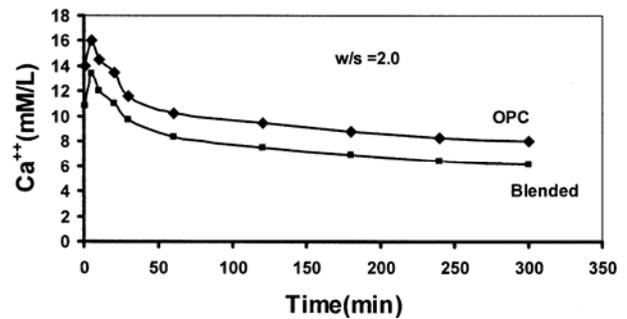
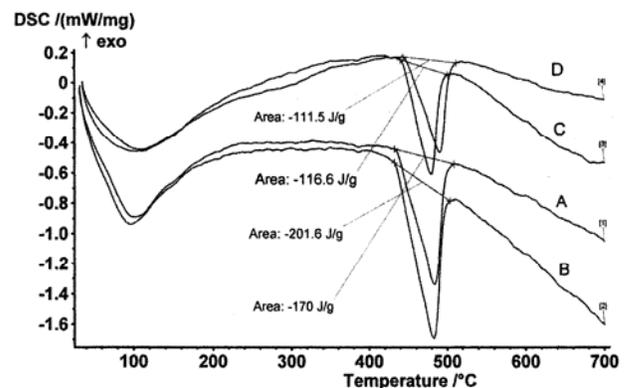
Fig. 11 — Variation of Ca^{++} ions in the liquid phase with hydration time

Fig. 12 — DSC curves of hydrated samples: A- OPC-7d. B-OPC-14d, C-OPC+BLA-7d and D-OPC+BLA-14d

concentrations. After the maximum value, the concentration decreases due to precipitation of different hydration products of calcium. The curve is similar with lower values in the case of blended cement. This indicates that the blended cement behaves in a similar way as the OPC.

Differential scanning calorimetric studies of hydrated samples (Fig. 12) have shown that there are two endothermic peaks at $\approx 101^{\circ}\text{C}$ and $\approx 480^{\circ}\text{C}$ in all

the hydrated samples. The first peak is broad and correspond to the elimination of adsorbed water molecules, decomposition of ettringite and calcium silicate hydrate. The broadening is more in the case of blended cement, which increased with hydration time. This indicates the decomposition of more hydration products. In the presence of BLA more C-S-H phase will be formed which will increase with hydration time. The second endothermic peak corresponds to the decomposition of calcium hydroxide formed during the hydration. In the case of control, the peak area (represented as heat of decomposition) corresponding to the decomposition of $\text{Ca}(\text{OH})_2$ increased with hydration time. However in the case of BLA blended cement, the peak area for the decomposition of calcium hydroxide decreased with time indicating lesser amount of calcium hydroxide. This is due to pozzolanic reaction between BLA and OPC, which increases with time and as a result lesser amount of free calcium hydroxide was left.

The X-ray diffraction patterns of hydrated cement are shown in Figs 13 and 14. In the case of control (Fig. 10) the intensity of mineral phases decreases whereas that of $\text{Ca}(\text{OH})_2$ increases with hydration time. This simply indicates that hydration of OPC (control) increases with time, In the case of BLA blended Portland cement the intensity of mineral phases also decrease with time indicating increase of hydration with time. However the increase in the intensity of $\text{Ca}(\text{OH})_2$ peak is lower as compared to the corresponding peaks in the case of control. This is due to pozzolanic reaction between BLA and $\text{Ca}(\text{OH})_2$ liberated during the hydration of OPC. The X-ray diffraction patterns of OPC/20 wt% BLA blended Portland cement do not show peaks due to gypsum. This may be due to the fact that either gypsum is converted into anhydrite during grinding or it is present below the detectable limit.

SEM images of the hydrated samples are shown in Fig. 15 and indicate that the amount of hydration products increase with time in the case of control as well as in blended cement. EDAX studies (Fig. 16) show that in both the cases ettringite is formed which is stable even up to 28 days of hydration. This suggests that probably gypsum is converted to anhydrite and the sulphate of anhydrite reacts with aluminate phase forming ettringite.

The variation of compressive strength with time is shown in Fig. 17. The compressive strength values increase with time but the values are lower in the case

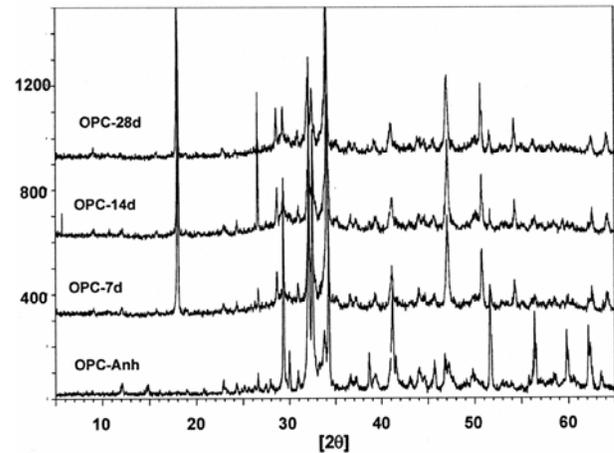


Fig. 13 — X-ray diffraction patterns of OPC hydrated for different periods

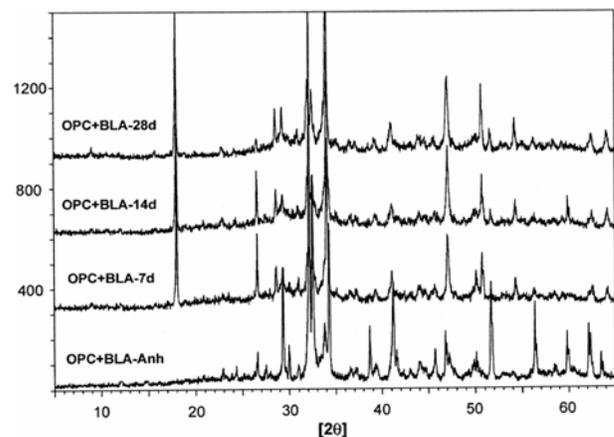


Fig. 14 — X-ray diffraction patterns of OPC+BLA hydrated for different periods

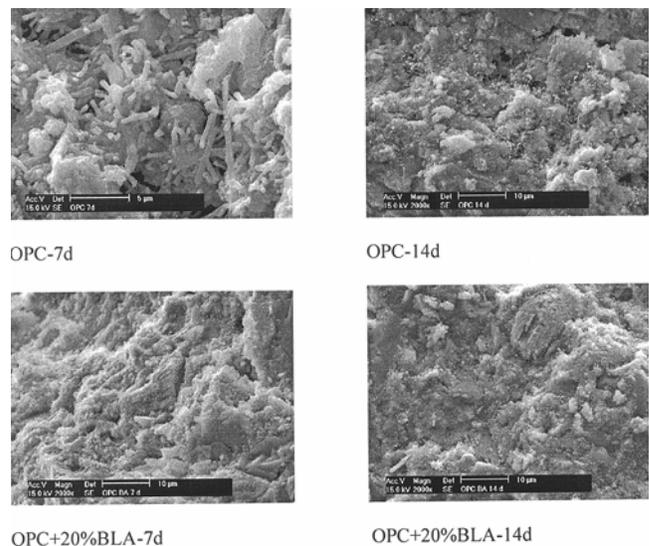


Fig. 15 — SEM pictures of hydrated OPC and OPC+BLA

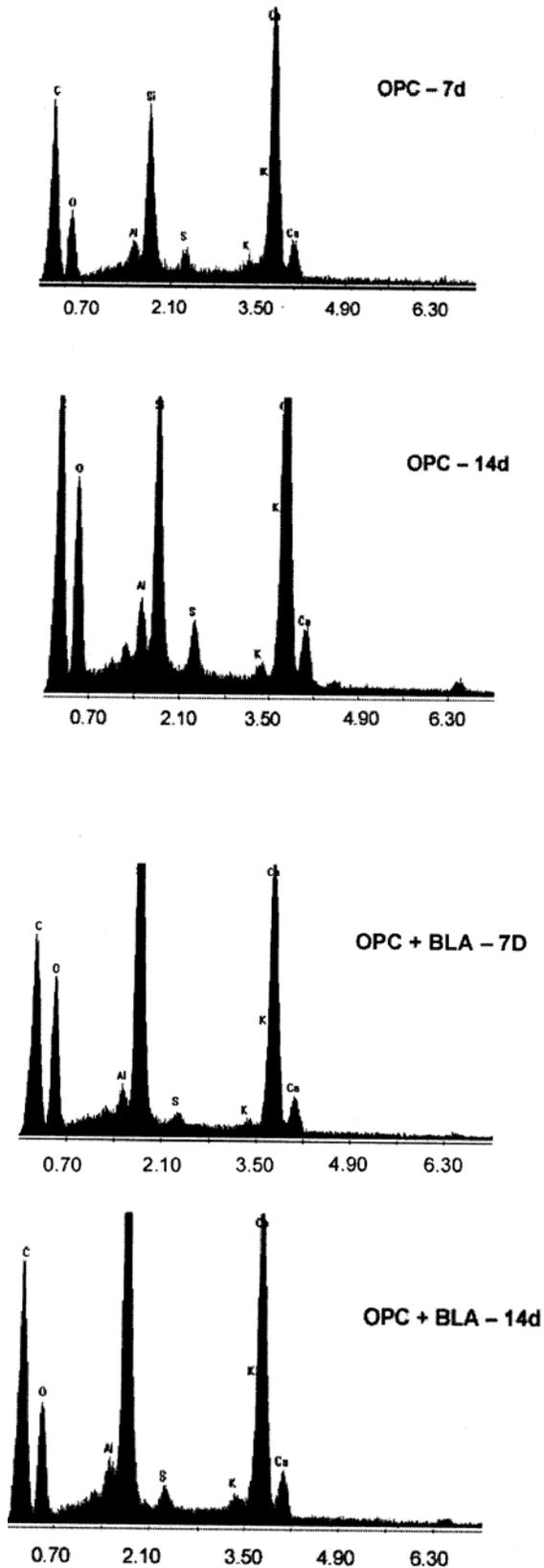


Fig. 16 — EDAX spectra of hydrated OPC and OPC+BLA

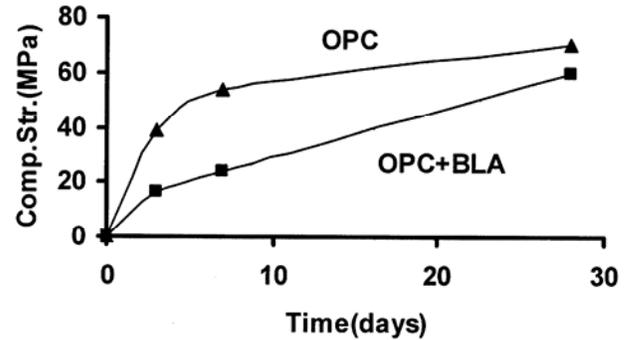


Fig. 17 — Variation of compressive strength with time.

of blended cement. However, at 28 days of hydration the compressive strength value of the blended cement is very close to that of the control. The lower values of compressive strength in the case of BLA blended cement may be due to lower pozzolanic reactivity at early time of hydration. However, the compressive strength value at 28 days of hydration is quite comparable to that of control, which may be due to additional amount of calcium silicate hydrate formed as a result of pozzolanic reaction.

Structure developments leading to strength in hydrating cement pastes are due to formation of different hydration products, which are both crystalline and amorphous in nature. Thus different surfaces are in contact. The increase in cohesion is then due to increase in facing surfaces. According to Powers¹³, physical forces (between surfaces) are responsible for the development of strength. However, chemical forces contribute little. In the presence of BLA, quantities of hydration products change and as a result, surface contacts also change. Thus it appears that in the presence of BLA, surface forces change leading to microstructural and strength changes. Nachbaur *et al.*¹⁴ have also shown that physical forces between particles are responsible for mechanical properties of the cement pastes from mixing to setting and even later.

Conclusions

The results show that BLA is a pozzolanic material, which reacts with calcium hydroxide forming calcium silicate hydrate. The pozzolanic activity of BLA increased with increase of time and temperature. When 20 wt% BLA was mixed with OPC the hydration properties were quite similar to that of OPC. The compressive strength values of mortar at 28 days of hydration were found to be quite comparable. Before BLA is recommended as a

blending component, further experiments under different conditions are needed.

Acknowledgements

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References

- 1 Rice Husk Ash Cement, Proc Workshop on Production of cement- like materials from Agro-wastes, Peshawar, Pakistan, 22-26 Jan. 1979.
- 2 Mehta P K, *J Am Concr Inst*, 74(9), (1977) 440-442.
- 3 Singh N B, Singh V D & Rai Sarita, *Cem Concr Res*, 30 (2000) 1485-1488
- 4 Martirena Hernandez J F, Middendorf B, Gehrke M & Budelmaun H, *Cem Concr Res*, 28(11) (1998) 1528-1536
- 5 Mehta P K, Natural pozzolanas in supplementary cementing materials for concrete, edited by Malhotra V M, (SCANMET, Canada), 1987, 3-33
- 6 Schmidt M, Middendorf B, Velmer C & Geisenhanslueke C, *Blended Cements in Innovations in Portland cement manufacturing*, edited by Bhatti J I, MacGregor F & Kosmatka S H, (Portland Cement Association, Skokie, Illinois), 2004, 1107-1148
- 7 Helmuth R A, *Fly ash in cement and concrete*, SP 040, (Portland Cement Association, Skokie, Illinois), 1987, 203
- 8 Roy D M, Fly ash and silica fume-chemistry and hydration, fly ash, silica fume, slag and natural pozzolanas in concrete, Third Int.Conf.Trondheim, Norway, 1, (1989) 117-138
- 9 Taylor H F W, *Cement Chemistry*, (Academic Press Ltd.), 1990, 277-344
- 10 Uchikawa H, *Proc 8th Int Cong Chem Cem*, Rio, Brazil, vol. 1, (1986) 249-280
- 11 Narang D C, *Proc 9th Int Cong Chem Cem*, New Delhi, vol. 1, (1992) 213-257
- 12 Sersale R, *Proc 9th Int Cong Chem Cem*, New Delhi, vol. 1 (1992) 261-302
- 13 Powers T C, *J Am Ceram Soc*, 41(1) (1958) 1-6
- 14 Nachbaur L, Mutin J C, Nonat A & Choplin L, *Cem Conc Res*, 31 (2001) 183-192.