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# HYDRATION OF PORTLAND BLENDED CEMENTS

By

N.B. Singh, K.N. Bhattacharjee and A.K. Shukla
Department of Chemistry
University of Gorakhpur
Gorakhpur 273009, India

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## ABSTRACT

Hydration of portland cement blended with granulated blast furnace slag and rice husk ash in presence of bag house dust has been studied by measuring non-evaporable water contents, heat of hydration and compressive strengths. Analysis of liquid phase for $Ca^{++}$ ion estimations has been made. Hydration characteristics have been discussed.

## INTRODUCTION

In order to save resource and energy, it is now a common practice to use portland blended cements made from portland cement and agricultural/industrial wastes(1-4). Further with increasing demand on specific performance characteristics in concrete such as improved strength, low heat, sulphate resistance, improved impermeability and certain other applications, these waste materials have imparted superior qualities to portland cements(5,6). In a previous communication(7) we have reported the hydration of portland blended cements made from alkali bypass dust and granulated blast furnace slag. This paper describes the hydration characteristics of portland blended cements made from bag house dust, granulated blast furnace slag and rice husk ash.

## EXPERIMENTAL

Materials:

Portland cement clinker was obtained from VSK plant, Bhutan, bag house dust was a waste material of a calcium carbide plant, Bhutan, granulated blast furnace slag was taken from M/S Indian Iron and Steel Co. Ltd., Burnpur, Asansole. Rice husk was obtained from a local rice mill at Gorakhpur and burnt in an open heap to have the ash. This ash was further heated at 700°C for 2 hours. The chemical composition of all the materials are given in table 1.

**Table 1**
Chemical Composition of Materials (Mass%)

| Materials | LOI | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | CaO | MgO | Others |
|---|---|---|---|---|---|---|---|
| PCC | 1.0 | 20.5 | 6.5 | 4.5 | 63.5 | 3.5 | Alk. traces |
| BHD | 18.2 | 12.3 | 2.8 | 2.2 | 56.2 | 0.8 | - |
| GBFS | 0.3 | 35.0 | 21.3 | 1.1 | 33.1 | 8.0 | 0.8% $S^{-}$ |
| RHA | 10.0 | 81.0 | 2.6 | 1.9 | 1.8 | 1.2 | Alk. traces |
| RHA-700 | 0.5 | 89.0 | 2.8 | 2.1 | 2.2 | 1.3 | Alk. traces |

For different materials we used the following symbols
Portland cement clinker - PCC
Bag house dust - BHD
Granulated blast furnace slag - GBFS
Rice husk ash fired in open heap - RHA
Rice husk ash heated at 700°C for 2 hours - RHA-700
The composition of different blended cements are given in table 2.

**Table 2**
Composition and number of blended cements

| Composition | 98%PCC +2% Gyps. | R-1 +5% BHD | R-2 +5% BHD | R-2 +5% GBFS | R-2 +5% RHA | R-2+5% RHA-700 |
|---|---|---|---|---|---|---|
| Number | R-1 | R-2 | R-3 | R-4 | R-5 | R-6 |

Methods:

Specific surface area of each blend was determined by Blaine area meter. Water requirements, setting times, compressive strengths of mortars, soundness by LeChatelier expansion method and autoclave test were performed as per Indian Standard IS 4031-1988 (Methods of Physical Tests for Hydraulic Cements).

Hydration in polythene bags(W/S=0.4) at room temperature (30±2°C) were stopped at different intervals of time with the help of isopropyl alcohol and ether. The samples were dried at 105°C for 1 h, sealed in polythene bags and stored in desiccator.

Non-evaporable water contents of the hydrated samples were determined by drying them at 105°C to constant weight and then from the weight loss at 1000°C for one hour.

Heat of hydration of the cements were determined with the help of a conduction calorimeter at 25°C at W/S=0.5.

The liquid phase of the hydrating cement paste (W/S=1.0) was extracted by applying a nitrogen pressure at different intervals of time and the solutions were immediately titrated against standard EDTA to determine the $Ca^{++}$ ion concentrations.

## RESULTS & DISCUSSION

The variations of non-evaporable water content(Wn) with hydration time are shown in Fig. 1. In the case of R-1 the values of Wn at all ages of hydration are higher as compared to other cements with a value of 14% at 1 day and 17.8% at 28 days of hydration. However the values at one day in the cement R-2 to R-6 lie between 11.0 to 12.4% and at 28 days between 13.3 to 14.1%. From the results it is clear that the

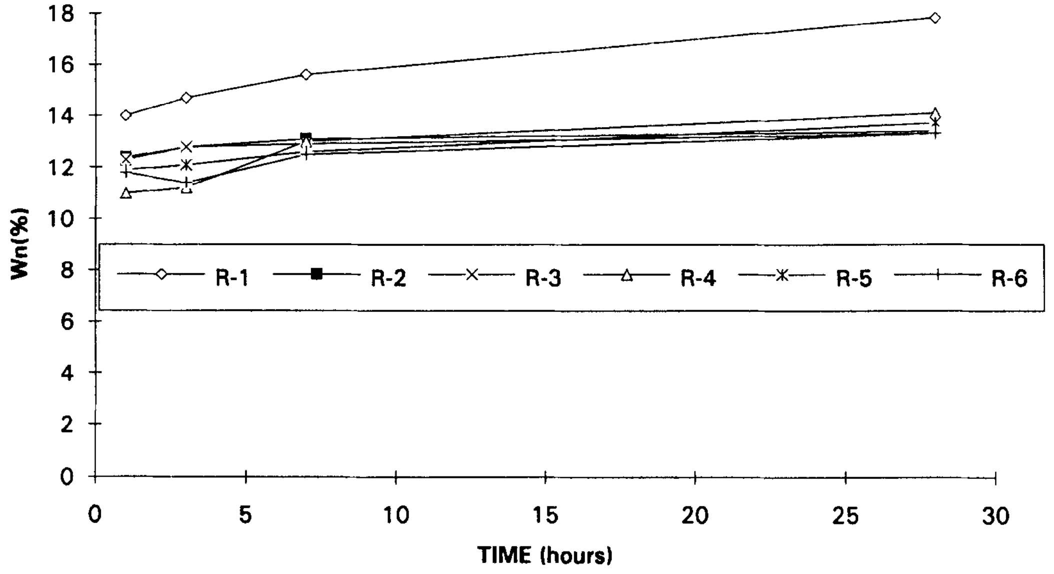

Fig.1. Variation of Wn with hydration time

waste materials decreased the non-evaporable water contents. However it is difficult to have much information with the Wn values about the role of different waste materials in cement. Sometimes these materials change the polymerization characteristics of silicates and water molecules are eliminated and hence Wn values are expected to be lower even if the hydration degree is higher(8).

The variation of heat of hydration with time is given in Fig.2. As soon water is added to the cements rapid heat evolution takes place, which drops within few minutes in all the cements. After this there are dormant periods which are different for different blends and follow the following sequence.

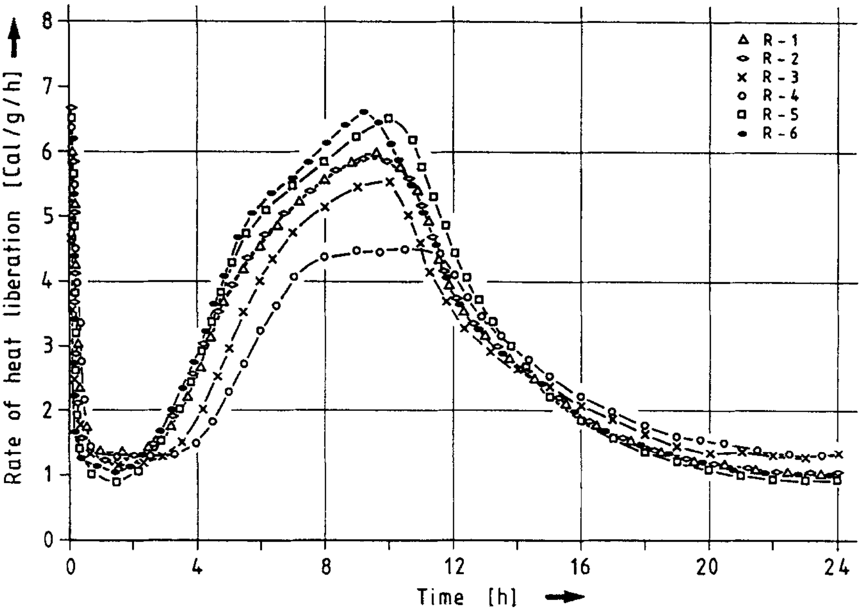

Fig.2. Heat evolution profile during the hydration of cement

R-6<R-5<R-1=R-2<R-3<R-4

After dormant periods are over, the accelerations of hydration start and reach to a maximum value, then decreases and ultimately the hydration reaction become diffusion controlled. In the case of R-1 the acceleratory period consists of one shoulder at around 6 h and a peak at around 10 h of hydration. The shoulder corresponds mainly to the hydration of silicate phases whereas the peak corresponds to the renewed hydration of aluminate phase and conversion of monosulphoaluminate phase. When 5% BHD is added to R-1, the heat evolution profile of the cement R-2 is almost unaffected but when 5% BHD is added to R-2, the peak remains at the same hydration time as those of R-1 and R-2 but the rate of heat evolution is decreased. This may be due to dilution effect and insignificant contribution of BHD towards heat evolution. However when 5% GBFS is added to R-2, the rate of heat evolution is decreased further and the peaks are broadened, distinguished and shifted to longer hydration times. Thus it appears that GBFS retards the hydration of silicate phase and delays the conversion of ettringite to monosulphate. However in the presence of GBFS, the heat of hydration varies widely and depend on the type of slag though they have almost the same glass content, hydraulic modulus and chemical composition. In the case of R-5 and R-6, the shoulder and the peak are more pronounced and shifted to lower hydration time with higher rate of heat evolution. The effect is more pronounced in cement R-6 since it contains larger amount of amorphous silica. This shows that the rice husk ash accelerates the hydration of silica phase as well as the conversion of ettringite to monosulphate. It appears that the amorphous silica provide nucleation sites for hydration products.

The $Ca^{++}$ ion concentrations in the liquid phase of the pastes of cements R-1, R-2, R-4 and R-6 (W/S=1.0) were determined as a function of time and values are given in Fig. 3.

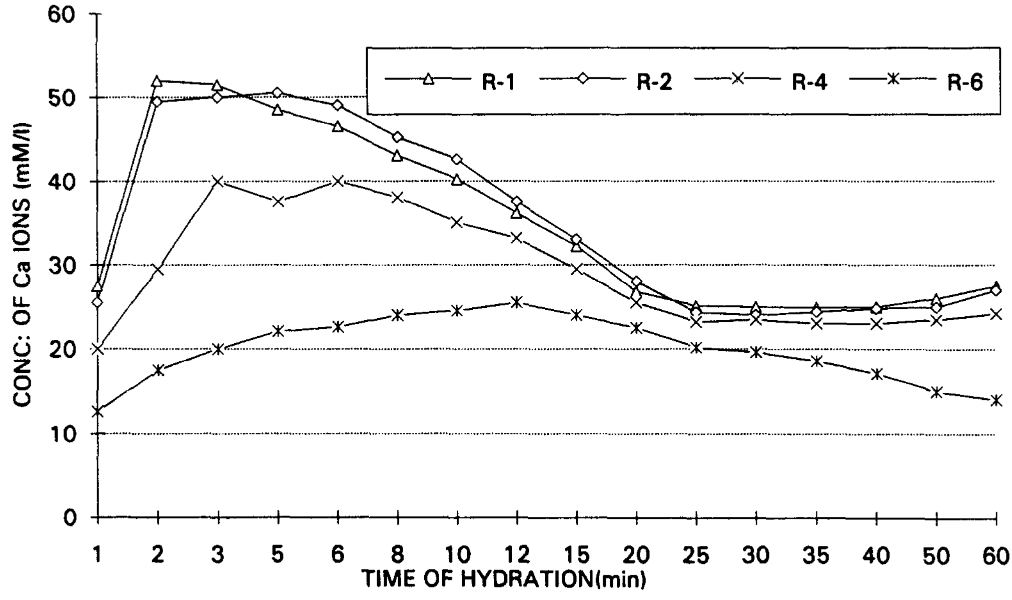

Fig. 3. Variation of $Ca^{++}$ ion concentration in solution with time

In the case of R-1, the $Ca^{++}$ ion concentration rises sharply to a peak value of about 52 mM/l after 2 minute and then drop to about 25 mM/l after 25 minutes. This value remains constant upto 50 minutes and then slowly increases. The results show that as soon as cement comes in contact to water, $Ca^{++}$ from $C_3A$, gypsum, silicates and free lime go into solution making the solution supersaturated with respect to $Ca(OH)_2$. The drop in $Ca^{++}$ ion concentrations after two minutes may be due to precipitation of ettringite, monosulphate, $Ca(OH)_2$ etc. During the dormant period the concentration remains practically constant but once the hydration accelerates the $Ca^{++}$ ion concentration starts increasing. In the case of R-2, the $Ca^{++}$ ion concentration variation is almost similar to that of R-1. The peak is slightly broadened and the concentration at the peak is slightly lower. It appears that $Ca^{++}$ ion comes from BHD. However in presence of BHD and GBFS (R-4) the variation is similar but the peak is at a longer time and values are lower. This may be due to dilution effect and GBFS might not be contributing much $Ca^{++}$ ions in the solution. In the presence of BHD and rice husk ash (R-6) the values are much lower and the maxima is broad and shifted to longer time (12 minutes). It appears that RHA contains amorphous silica which is very reactive and combines with $Ca(OH)_2$ to give C-S-H precipitates at an early time of hydration or $Ca^{++}$ ions are adsorbed at the surface of amorphous silica. As a result the $Ca^{++}$ ion concentrations in the solution in presence of rice husk ash are decreased considerably. It has been reported that when $Ca(OH)_2$ is mixed with the rice husk ash having the specific surface area of 1.52 $m^2/g$, it is consumed at a rate of 20 to 120 (g/100g of rice husk ash) at 293 K within 3 hours(9). However the pozzolanic activity of RHA in portland cement is decreased considerably as compared to RHA in lime.

The variation of compressive strength with time is given in Fig.4. In the case of OPC (R-1) the compressive strength values increased with time as usual. However when 5% BHD is added to it (R-2) the compressive strength values at 1 and 3 days are higher than those of R-1 but at 7 and 28 days, the values are lower than those of R-1. It appears that during early days of hydration BHD might be changing the nature of hydration products but at later stages the effect may be insignificant and as a result of dilution the compressive strength becomes lower as compared to those of OPC (R-1) alone.

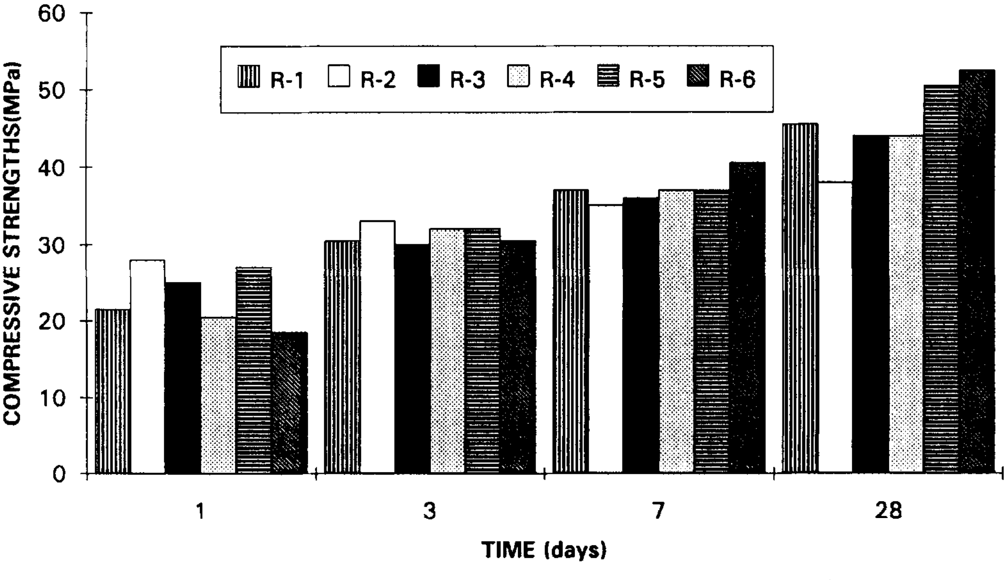

Fig.4. Variation of Compressive strength with hydration time

Cement (R-2) acts as control for other blended cements. When 5% BHD is added to R-2, the cement becomes R-3. The compressive strength values of R-3 are lower at

1 and 3 days and higher at 7 and 28 days as compared to those of R-2. The lower compressive strength values at 1 and 3 days may be due to dilution effect but at 7 and 28 days, BHD might be acting as a filler to reduce the porosity. Similar effects have been seen when 5% GBFS is added to R-2 (cement R-4). From the results it is difficult to say whether BHD activates GBFS or not.

When 5% RHA is added to R-2, the compressive strength values of cement R-5 are again lower at 1 and 3 days of hydration as compared to those of R-2 whereas at 7 and 28 days, the values are higher. It appears that pozzolanic activity of RHA starts after 3 days and hence the compressive strength values increase. The unburnt carbon particles present in RHA might also act as a filler in the pores. However when 5% RHA-700 is added to R-2 (cement R-6), the compressive strength values at 1 and 3 days decreased as compared to those of R-2 and R-5. This may be due to the fact that pozzolanic activity of RHA-700 may not be appreciable during this period and due to dilution effect the compressive strength values are lower. The compressive strength values at 7 and 28 days of hydration are much higher as compared to other cements including the control. It has already been reported(10) that in silica blended (30%) portland cement, the volume of large pore size is small as compared with that of ordinary portland cement paste even at early age of 7 days. Reduction of capillary pore space and threshold pore diameter in silica cement paste with silica fume in early age may be considered to be caused by filler effect of fine particles and rapid initiation of pozzolanic reaction. Since RHA-700 contains amorphous silica, it might be reducing the pore size as a result of pozzolanic reaction and acting as a filler. Further in presence of BHD, the pozzolanic activity might increase. It has already been reported that coal fly ash dust enhances the activity of rice husk ash(11). In separate study we found that the compressive strengths of the non-portland blended cement made from BHD and RHA-700 are much higher than the other blends. Thus it appears that combination of BHD with different pozzolanic materials in portland cement is responsible for the increased compressive strengths of the blended cements.

The compressive strength values can not be correlated with the other hydration characteristics. The structural defects of glass in the pozzolanic materials affect the texture formed by the hydrates produced rather the reacted amount of pozzolanic material especially slag.

## CONCLUSIONS

From the results it is inferred that it is difficult to correlate the results obtained from different measurements. However the following conclusions can be made: (1) the non-evaporable water contents are always lower in presence of the waste materials as compared to the portland cement, (2) BHD reduces the rate of heat evolution without affecting the hydration characteristics, whereas GBFS in presence of BHD retards the hydration of silicate phase and delays the conversion of ettringite to monosulphate.

Rice husk ash on the other hand accelerates the hydration and increases the rate of heat evolution, (3) BHD, GBFS and RHA-700 decrease the $Ca^{++}$ ion concentrations in solution and the decrease is maximum in presence of RHA-700, (4) RHA-700 in combination with BHD gives maximum strength at 7 and 28 days of hydration, (5) it is possible to have better cements when appropriate waste materials in appropriate proportions are added to the portland cement.

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## REFERENCES

1. H. Uchikawa, Proc. 8th Int. Cong. Chem. Cem., Brazil, 3,2,249(1986).
2. R. Sersale, Proc. 9th Int. Cong. Chem. Cem., New Delhi, 1,261(1992).
3. K.C. Narang, ibid, 1,213(1992).
4. P.K. Mehta, Proc. Int. Workshop on the use of fly ash, slag, silica fume and other siliceous Materials in concrete, 337(1988).
5. K. Tori and M. Kawamura, Cem. Concr. Res., 24,361(1994).
6. N.B. Singh, M.P. Dwivedi and N.P. Singh, ibid, 22,121(1992).
7. N.B. Singh, K.N. Bhattacharjee and A.K. Shukla, ibid, (In Press).
8. M.H. Zhang and O.E. Gjorv, Cem. Concr. Res., 21,800(1991).
9. D.J. Cook and P. Suwanvitaya, "Properties and behaviour of lime-rice husk ash cement", Ist Int. Conf., The use of fly ash, silica fume, slag and other mineral byproducts in concrete, Montebello, II, 831(1983).
10. M. Relis and I. Soroka, J. Am. Ceram. Soc., 63, 690(1980).
11. N.B. Singh, R. Sarvahi, S. Prabha Singh and A.K. Shukla, Advances in Cement Research, 6,1(1994).
12. M.F. Pistille, G. Rau and R. Cechner, Cem. Concr. Aggr., 6,33(1984).