HYDRATION BEHAVIOUR OF FLYASH /SLAG BASED COMPOSITE CEMENT

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Abstract:

The study aimed to look into the hydration behaviour of composite cement based on different percentages of lime, flyash/slag as per EN197-2000. Degree of hydration has been compared by evaluating the non-evaporable and calcium content with compressive strength of 1:3 mortar cubes. The higher non-evaporable content and less lime content in case of lime slag composite cement compare to lime flyash composite cement indicates higher degree of hydration in former case and hence higher compressive strength. Further it has been observed that with 5 & 10% lime early stage of hydration is either more or comparable to control mix which indicates that C_3S dissolution is more.

Keywords: composite cement, lime, flyash, slag, hydration

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Introduction:

It is well established that proper use of mineral admixtures individually or blended with portland cement offers beneficial effects to mortars/concrete. The improvement in durability properties with the addition of mineral admixtures is either through the pozzolanic activity or hydraulic [1-3]. The use of mineral admixtures has technical and economical/environmental reasons. The technical reasons are satisfactory physical and mechanical properties of hydrated cement paste, and the economic/environmental reasons include energy saving during the decreased clinker production and consequently the reduction of environmental pollution by carbon dioxide [4-6]. The European standard EN 197-part2 CEM VA allow up to 64 wt % of clinker and rest limestone and pozzolanic materials in cement [7]. During the hydration of Portland cement clinker minerals react with water yielding a complex microstructure consisting mainly of amorphous calcium silicate hydrate gel, ettringite, portlandite, carbonated phases and calcite. When limestone is present in portland cement, the rate and degree of hydration change, as does the composition of the hydrated cement paste. The literature findings on the effect of limestone on the composition of hydrated cement paste are not always in close agreement but the general conclusion is that limestone participates to a certain extent in chemical reactions during hydration, not being only inert filler [8-12]. The increase in the rate of hydration of the clinker has been attributed to the formation of mono-carboaluminates, and the modification of the microstructure. Further, addition of $CaCO_3$ accelerates the hydration of C_3S, especially at the early age. This is due to the modification of the hydrating C_3S surface and its nucleation effect. [13-15].

The addition of mineral admixtures enhances the cement hydration, whereas others decrease the hydration rate [16-27]. The substitution of mineral admixtures for portland cement will depend upon the chemical composition of both. Since fly ash is a pozzolana while slag is classified as latent hydraulic material.

The present study is aimed to study the hydration characteristics of flyash / slag replacement in the composite cement.

Materials and mixture proportioning:

Clinker:

Clinker used in the present study was supplied by M/s Ambuja cements Ltd.. The clinker was ground with gypsum in ball mill to prepare cement and then it was sieved through 75 micron sieve. The physical and chemical analysis of cement is given in Table No. 1.

Fly Ash:

Fly ash used in composing cement was procured by a thermal plant in Indraprastha, New Delhi from field 2. The fly ash is used as per BIS: 3812 (part 1). The physical and chemical analysis of fly ash is given in Table No. 2.

Sand:

The standard sand (Ennore) used in the present study conforms to BIS: 650-2005

Limestone:

Limestone was procured in raw form and was grounded in the ball mill followed by sieving through 75 micron sieve.

Superplasticiser (SP):

Super Plasticizer used in the present study was Sikament 170 conforming to BIS: 9103 – 2003. It is based on Sulphonated Naphthalene Formaldehyde Condensate (SNF). It is used 1% by weight of cement.

X-ray Analysis:

X-ray graphs of the control and hydrated samples of different mixes are shown in fig. Nos. 1-

Preparation of Sample Mixes:

The mixtures of cement, limestone and fly ash in different proportions were prepared and its composition is given in the Table No.3. The mixtures are mixed thoroughly in powder mixer for half an hour.

Preparation of cement cubes:

The mortar cubes were cast in constant temperature room maintained at temperature 27±2˚C. A mixture of 200gm. cement was mixed with 600g standard sand on a dry non porous table with 80cc of water (which is fixed for all the cement mixtures) for 3-4 min till uniform color of the mix was obtained. Then the mortar was filled in the iron moulds of 70.6mm as per BIS: 4031 through a hopper and prodded with rod to ensure elimination of air and vibrated for 2 min. The cubes were covered by wet gunny bag for 24 hours in the constant temperature room. After 24 hours the cubes were demoulded and cured in curing chamber maintained at temperature 27±2˚C and humidity 90±5%.

Compressive Strength:

The compressive strength of the cubes was determined at 1, 3,7,28 and 56 days. Minimum three cubes were tested for each set. The results are given in Table No. 4.

Determination of non-evaporable water and calcium hydroxide content:

The non-evaporable water and calcium content of the pastes of different composite cements at different time interval was calculated as described [28]. 1gm. of sample was dried at 105^{o}C for three hours and 1hr. at 950^{o}C to calculate weight loss due to the evaporation of free water and decomposition of chemically combined water. Further non-evaporable water was corrected by the loss of ignition of the dry binder powder at 950^{o}C with respect to its mass at 105^{o}C. The non-evaporable water per gm. of original binder was calculated by the equation of Powers and Brownyard modified [29] by Tang [28] as shown below:

$\underline{w_n} = \underline{W_{105}} (1-L_b) -1$

b W_{950}

Where w_n/b = non-evaporable water per gram original binder. $W_{105}{}^oC$ and $W_{950}{}^oC$ are sample weight at respective temperatures. L_b + loss on ignition of original binder (i.e., original fraction of cement x ignition loss of cement+ original fraction of mineral admixtures+ ignition loss of original mineral admixtures.

Calcium hydroxide content was calculated from the equation derived by Escalante etal., [30] as given below:

$$\frac{Wn_{450}}{b} - \frac{Wn_{550}}{b} = \frac{W_{450}-W_{550}}{W950}(1-Lb) - \left(\frac{b_{450}}{b} - \frac{b_{550}}{b}\right)$$

Where Wn_{450}/b and Wn_{550}/b 1s non-evaporable water content at 450^{o}C and 550^{o}C. W_{450} and W_{550} is sample weight at respective temperatures. b/450^{o}C andb/550^{o}C is weight of binder per gm. Original binder. The non-evaporable content and calcium hydroxide content of fly ash and slag based cements is given in table 5&6.

Table No. – 1 Physical and Chemical Analysis of Portland cement

Sl No.	Parameters	Result **(%)**
1.	Loss of ignition	0.32
2.	SO_3	0.73
3.	Insoluble Residue	0.17
4.	SiO_2	22.41
5.	Fe_2O_3	3.56
6.	Al_2O_3	4.72
7.	CaO	64.93
8.	MgO	1.49
9.	Na_2O	0.05
10.	K_2O	1.0
11.	Setting time* (mins.) Initial Final	 105 180
12.	Compressive strength (MPa)	
	1 day	6.58
	3day	30.12
	7day	39.16
	28day	51.0

***** ***As per BIS:4031(part-5) initial setting time must not be less than 30 min and for final setting time must not be more than 600 min.***

Table No. – 2 Chemical Analysis of Fly Ash

Sl.No	Property	Result (%)
1.	LOI	0.75
2.	SiO_2	16.8
3.	R_2O_3	28.20
4.	CaO	3.0
5.	R_2O ($MgO+CaO+SiO_2$)	75
6.	SO_3	1.25
7.	Surface area	$3400cm^2/g$
8.	Specific gravity	2.24

Table No. 3 Different Compositions Mixtures

System	Cement	Limestone	Fly Ash	Slag
Control	100	---	---	---
Mixture-1	60%	5%	35%	35%
Mixture-2	60%	10%	30%	30%
Mixture-3	60%	15%	25%	25%
Mixture-4	60%	20%	20%	20%

Table No. 4 Compressive Strength (MPa) of flyash based composite cement with and without super-plasticizer

System	1 Day	3 Day	7 Day	28 Day	56Day
Control	6.58	30.12	39.16	51.00	53.55
Mix-1	6.58	18.25	23.51	39.50	50.02
Mix-1(SP)	7.76	20.50	28.13	44.02	52.51
Mix-2	6.25	16.50	25.125	34.82	41.02
Mix-2(SP)	7.45	18.53	32.25	42.08	50.01
Mix-3	5.66	16.50	23.82	34.08	40.55
Mix-3(SP)	7.02	20.13	28.51	40.05	48.52
Mix-4	5.08	18.25	24.25	30.04	39.00
Mix-4(SP)	6.53	20.34	29.00	36.53	43.18

Table No. **5** Compressive Strength (MPa) of slag based composite cement with and without activator

System	1day	3day	7day	28day	56day
Control	6.6	30.1	39.2	51.0	53.5
Mix-1	6.8	22.5	32.9	48.3	54.0
Mix-1+Act	8.0	29.5	37.3	52.5	56.4
Mix-2	7.4	20.4	36.5	45.5	53.2
Mix-2+Act	8.4	30.3	37.8	48.0	54.5
Mix-3	9.0	23.3	34.4	42.4	53.0
Mix-3+Act	9.2	30.2	36.8	48.3	53.1
Mix-4	6.5	21.0	30.3	41.1	52.5
Mix-4+Act	9.7	31.0	39.0	52.5	55.6

Table No.6 Non-evaporable content of fly ash based composite cement

Age	control	Mix-1	Mix-2	Mix-3	Mix-4
1d	0.062	0.059	0.057	0.050	0.045
	*	0.068	0.065	0.069	0.063
3d	0.110	0.063	0.062	0.070	0.077
	*	0.086	0.081	0.073	0.080
7d	0.102	0.063	0.073	0.078	0.080
	*	0.069	0.070	0.080	0.083
28d	0.124	0.074	0.082	0.091	0.090
	*	0.076	0.085	0.094	0.092
56d	0.131	0.081	0.090	0.11	0.100
	*	0.130	0.127	0.120	0.115

* (with SP)

Table No.7 Non-evaporable content of Slag based composite cement

Age	control	Mix-1	Mix-2	Mix-3	Mix-4
1d	0.062	0.064	0.062	0.064	0.061
	**	0.070	0.069	0.075	0.068
3d	0.110	0.093	0.086	0.081	0.076
	**	0.110	0.111	0.109	0.111
7d	0.112	0.110	0.104	0.091	0.088
	**	0.113	0.109	0.105	0.101
28d	0.124	0.120	0.121	0.119	0.110
	**	0.122	0.123	0.120	0.114
56d	0.131	0.133	0.130	0.128	0.128
	**	0.135	0.132	0.130	0.131

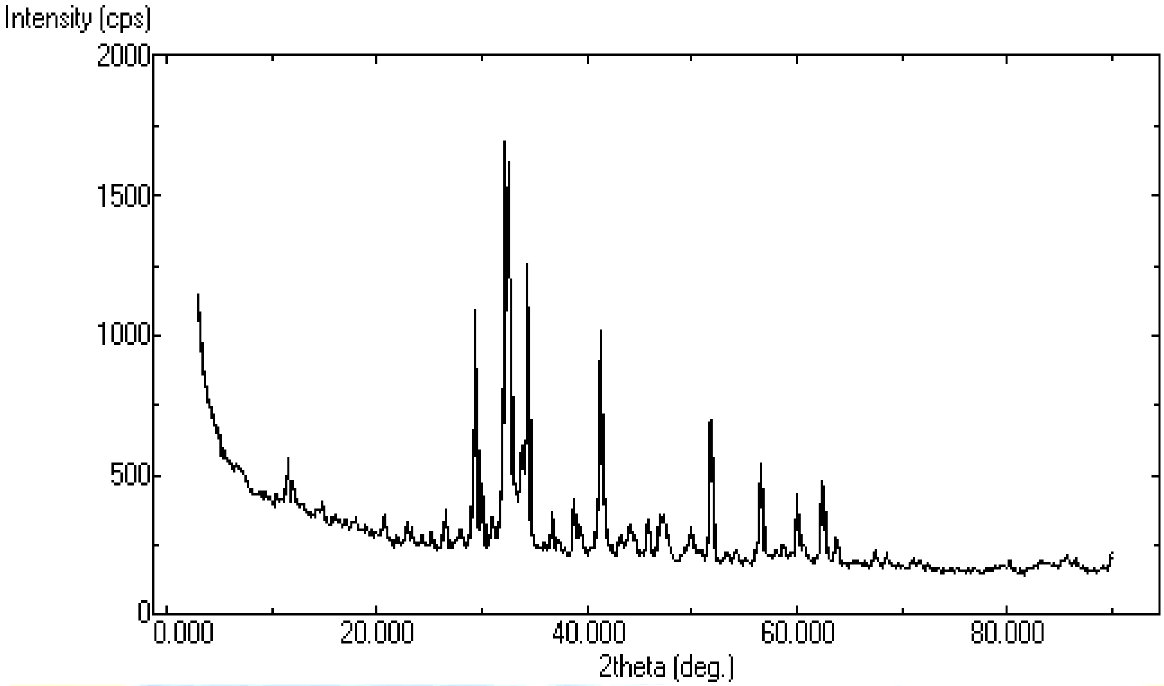
** (with Activator)

Table No.8 Calcium Hydroxide Content of fly ash based composite cement

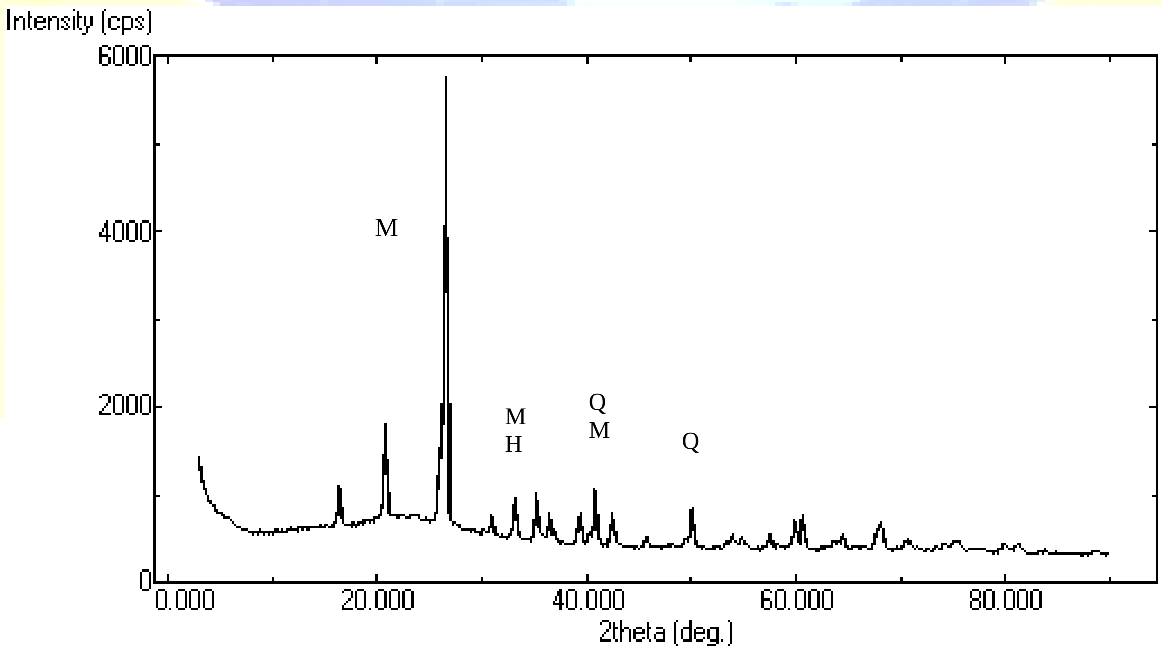
Age	control	Mix-1	Mix-2	Mix-3	Mix-4
1d	0.008	0.108	0.153	0.157	0.161
3d	0.007	0.014	0.018	0.022	0.024
7d	0.017	0.019	0.019	0.023	0.028
28d	0.011	0.009	0.011	0.015	0.012
56d	0.005	0.004	0.009	0.006	0.005

Table No.9 Calcium Hydroxide Content of Slag based composite cement

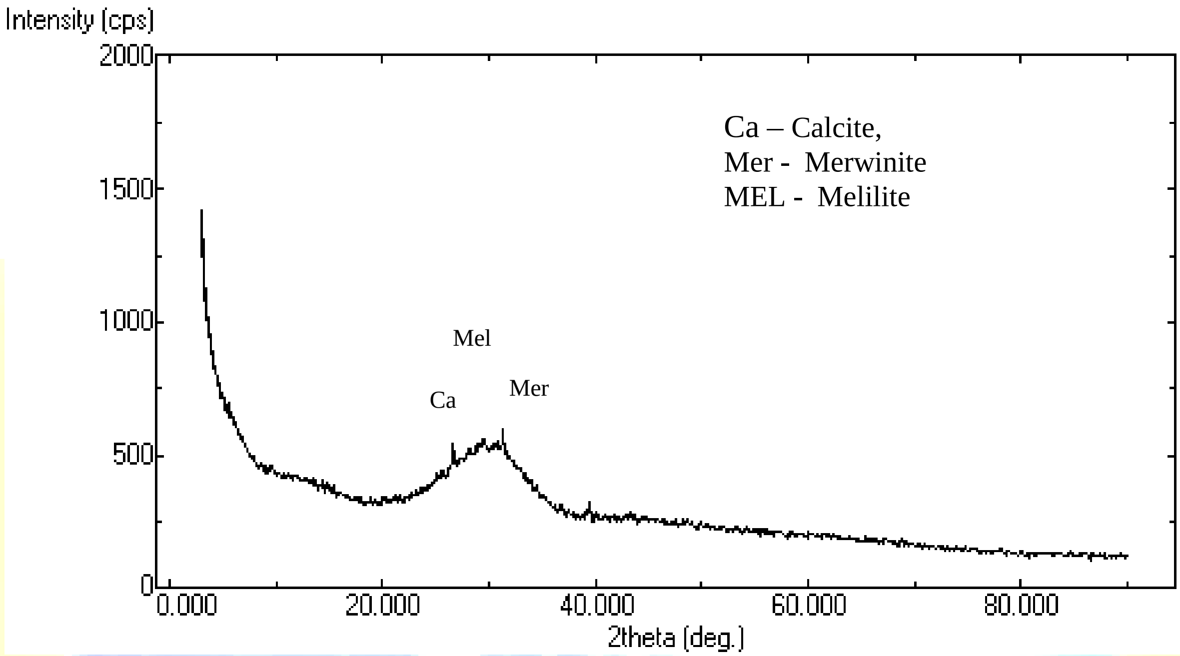
Age	control	Mix-1	Mix-2	Mix-3	Mix-4
1d	0.008	0.007	0.007	0.008	0.008
3d	0.007	0.009	0.011	0.012	0.012
7d	0.017	0.014	0.015	0.016	0.016
28d	0.011	0.010	0.009	0.009	0.009
56d	0.005	0.007	0.008	0.008	0.008



XRD Profile of Clinker



XRD profile of flyash



XRD profile of slag

Results and Discussion:

The compressive strength of fly ash and slag based composite system at various time intervals are given in table Nos. 4&5. Each value for compressive strength at 1, 3, 7, 28 and 56 days is the average of three test results. At 1 day compressive strength of Mix-1 is same as that of control and for other mixes there is drop in strength upto the age of 28days. However at 56 days for Mix 1&2 the strength is comparable to control. With the use of superplasticizer 1 day strength of all the mixes are either more or equal to control. The notable observation is the strength at 56 days which is comparable to control for Mix-1 to Mix-3.

In case of slag based composite system, compressive strength of Mix-1 to Mix-4 is more or comparable to control without activator. With the use of activator 28 days strength is comparable to control and at 56 days it is equivalent to control. Since slag is most like portland cement and least like a pozzolana. In contrast with early strength development of the blended paste is better than the reference paste.

The mechanism of activation by sodium sulfate on blended cement can be explained by assuming that the sulfate ions reacts with the calcium ions dissolved from the cement minerals results in the formation of gypsum, which act as nuclei for ettringite and CSH gel. During this process calcium ions depletes and thus accelerates the dissolution of cement minerals such as alite and belite. The function of sodium ions is to increase the pH of the paste, which helps in the dissolution of amorphous silica oxide and aluminum oxide. The dissolved oxides react with calcium hydroxide to form CSH gel.

The results of non-evaporable water of pastes at different ages are given in table Nos. 6&7 The results clearly show that the value of w_n of all the mixes increases with age. The maximum value of 0.14 against 0.13 in control mix has been found to be observed with S-1 and S-2 mix at 56 days. At 28 days the w_n values in case of slag based composite cement is comparable to control which is found to be in agreement with the compressive strength. The notable w_n value of 0.6 of control at 1day has been found to observe in case of mix-1 and mix-2 of fly ash and slag containing 35% and 30% pozzolana. The same trend is found in compressive strength. It is known that 5 to 10% lime stone powder increases the rate of hydration due to the formation of mono-carboaluminates, and the modification of the microstructure. Further, addition of $CaCO_3$ accelerates the hydration of C_3S, especially at the early age. This is due to the modification of the hydrating C_3S surface and its nucleation effect. [30-32]. At 56 days the w_n of mix-1 & mix-2 is comparable to control suggesting thereby that the strength values for these mixes are comparable to control and has been observed practically. In the presence of superplasticizer w_n of flyash based composite cement is more for mix 1&2 and comparable to control for mix 3&4. At 1day the values of w_n have been found to more in all the mixes compare to control suggesting thereby that early hydration of C_3S.

The CH content of control and mix-1 and mix-2 at 7days are almost similar as mix-1 and mix-2 contains 35% and 30% fly ash and seems to consume insignificant amount of CH. From 7 to 28 days however the pozzolanic reaction consumes part of CH and thus drops.

For mix-3 and mix-4 at 7days CH value has been found to be slightly higher because fly ash content in these mixes is 25% and 20% and consumes little CH. From 7days to 28 days there is drop in CH content and at 56 days CH content is almost similar in control and composite mixes.

In case of slag from 7 to 28 days the pozzolanic reaction consumes a part of the CH in paste and obviously there is drop in CH content. However beyond 28 days of hydration there is little change.

Conclusion:

1. From the present study it can be concluded that with the use of superplasticizer it is possible to have strength of Mix-1 and Mix-2 at 56 days comparable to control and for Mix-3 and Mix-4 there is only 10% drop indicating thereby that it is possible to develop composite cement using 20% each lime stone powder and fly ash.
2. In case of slag based composite cement with the use of activator it is possible to achieve 28 days strength of Mix-1 to Mix-3 equivalent to control and at 56 days the strength is more than control.
3. Thus it is possible to save 40% clinker and saving equivalent amount of carbon dioxide which helps the reduction in green gas house emission.

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