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Communication

Influence of mineral additives on the hydration characteristics of ordinary Portland cement

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Abstract

The effect of mineral additives such as fly ash, slags, limestone, and lime sludge on the hydration of ordinary Portland cement (OPC) has been studied. The samples of OPC with 10 wt% mineral additives were examined separately at 28 and 90 days of hydration by X-ray diffraction and differential thermal analysis. The hydration products in the OPC + slags and OPC + fly ash systems were found to be almost similar to that of pure OPC, except with the low quantity of $Ca(OH)_2$ during the early period of hydration (28 days). In the case of limestone and lime sludge addition, besides normal hydration phases of OPC, larger amount of $Ca(OH)_2$ and a little calcium carboaluminate hydrates were identified by X-ray diffraction and differential thermal analysis patterns.

Keywords: Hydration products; X-ray diffraction; Thermal analysis; $Ca(OH)_2$; Fly ash

1. Introduction

During recent years detailed investigations on the role of mineral additives, especially waste materials, on the hydration of ordinary Portland cement (OPC) have been made [1–4]. Attempts have been made to understand their role in strength development and to identify the reaction products [5–10]. However, the relative effectiveness of the waste materials in the formation of different hydration products has not been studied systematically. In this communication the effect of 10 wt% fly ash, ground granulated blast furnace slag (GGBFS), ground granulated phosphorous furnace slag (GGPFS), limestone, and lime sludge on the hydration of OPC have been studied and the hydration products characterised.

2. Experimental

OPC and five other mineral additives (fly ash, granulated blast furnace slag, granulated phosphorous furnace slag, powdered limestone, and lime sludge from paper industry) were procured from their respective sources in their original industrial form, and ground to a workable fineness in the laboratory ball mill. After examining their suitability by chemical, physical, and mineralogical characterisation (Table 1), the additives were mixed in OPC in 10% replacement ratio, and as many as five blends of samples with one control sample had no additive prepared. The X-ray diffraction (XRD) pattern of the OPC and mineral additives are given in Fig. 1.

OPC with and without 10% additives were allowed to hydrate in plastic vials at 27 ± 2°C at a water/cement ratio = 0.4. The hydrations were stopped with acetone at different intervals of time and stored in a vacuum desiccator. differential thermal analysis (DTA) of the hydrated samples (particle size <90 μm) were recorded with simultaneous TG-DTA-DTG apparatus (NETZ) from ambient to 1100°C in atmospheric air using α-Al_2O_3 as reference. XRD pattern of the hydrated samples (particle size <45 μm) were recorded with Rigaku X-ray diffractometer using Co K α radiation. Peak areas were calculated by millimetre graph paper.

3. Results and discussion

3.1. XRD

The XRD pattern of hydrated samples at 28 and 90 days are given in Fig. 2. For the comparison of reactivity of fly ash and slags at 28 days of hydration, Portlandite peaks at 21.17° and 39.29° have been selected in Fig. 2, whereas for

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Table 1
Chemical and physical properties of OPC and mineral additives

Contents	OPC	GGBFS	GGPFS	Fly ash	Limestone	Lime sludge
LOI	2.67	−0.83	0.24	3.50	37.5	38.17
SiO_2	21.14	32.06	41.29	59.64	10.91	8.45
CaO	61.20	32.05	48.55	1.98	48.0	45.45
MgO	2.67	10.05	1.92	0.85	0.79	3.20
Fe_2O_3	3.92	3.47	0.25	4.38	0.65	0.87
Al_2O_3	4.80	18.03	3.82	27.0	1.25	2.02
SO_3	2.08	–	–	–	0.20	0.10
Na_2O	0.20	0.7	0.65	0.23	0.08	0.68
K_2O	0.80	0.85	1.05	1.28	0.04	0.80
Cl	0.008	0.014	0.005	0.01	0.005	0.015
P_2O_5	0.32	0.17	1.08	0.45	traces	0.90
TiO_2	0.10	0.73	0.05	traces	0.05	0.12
Mn_2O_3	0.07	0.67	0.12	traces	traces	0.02
IR	3.06	0.96	1.26	90.41	11.38	12.50
Free CaO	0.50	–	–	–	–	–
Sulphide	–	0.75	0.09	–	–	–
Mineral composition		X-ray amorphous, a little FeS and crystalline material is also present	X-ray amorphous, small percent of crystalline phases also present, which are not identifiable	Quartz and mullite predominant phases, magnetite, hematite in small amount. Some X-ray amorphous material is also present	Calcite, quartz, muscovite	Calcite, dolomite, quartz, muscovite
C_3S	44.65					
C_2S	26.92					
C_3A	6.09					
C_4AF	11.93					
Glass content		93	94	32	–	–
Density	3.14	2.94	2.97	2.25	2.61	2.70
Fineness cm^2/g	3044	3850	4000	3650	4550	4650

LOI = loss on ignition at 1000°C, IR = insoluble residue.

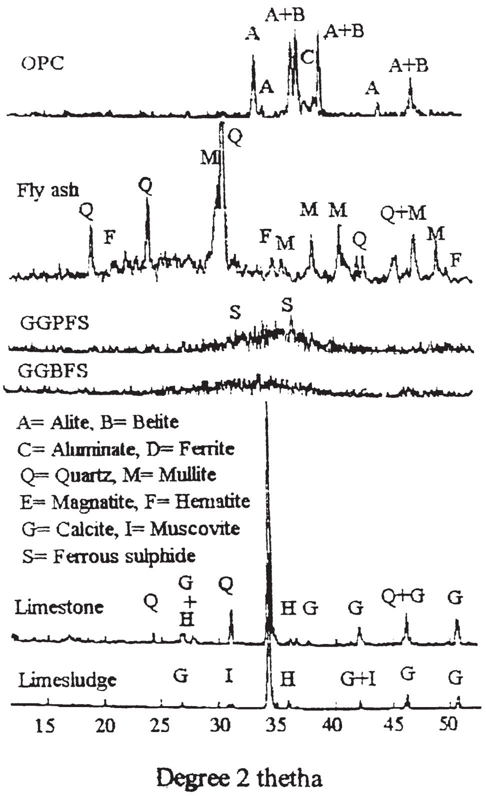

Fig. 1. X-ray diffractogram of OPC and mineral additives.

carbonate additives (limestone and lime sludge), the additional peaks of $CaCO_3$ at 34.11° and a characteristic peak of calcium carboaluminate at 13.24° are also chosen.

3.2. DTA

The results of DTA for hydrated OPC with and without mineral additives are given in Fig. 3. For the purpose of comparison, the endotherms at 140, 180, and 500°C are chosen, which are the dehydration temperature of CSH gel, monosulphate, and $Ca(OH)_2$, respectively. The endothermic peak between 700–800°C shows the decomposition of $CaCO_3$. A small hump at around 375°C shows the elimination of water molecules associated with tobermorite gel. The peak areas of the endotherms at ≈500°C are given in Table 2.

3.3. Hydration of OPC with fly ash

$Ca(OH)_2$ is one of the hydration product produced during the hydration of OPC. Fig. 2 and Table 2, showing XRD peak at $2\theta = 21.17$ Å, reveals that the amount of Portlandite formed in OPC +10% fly ash cement hydrated at 28 days is slightly more than that in neat OPC. However, in presence of fly ash the amount of Portlandite formed is expected to decrease as a result of pozzolanic reaction. There is an XRD peak at $2\theta = 21.17$ Å in the case of fly ash (Fig. 1), which interferes with the CH peak. As a result, the intensity of this

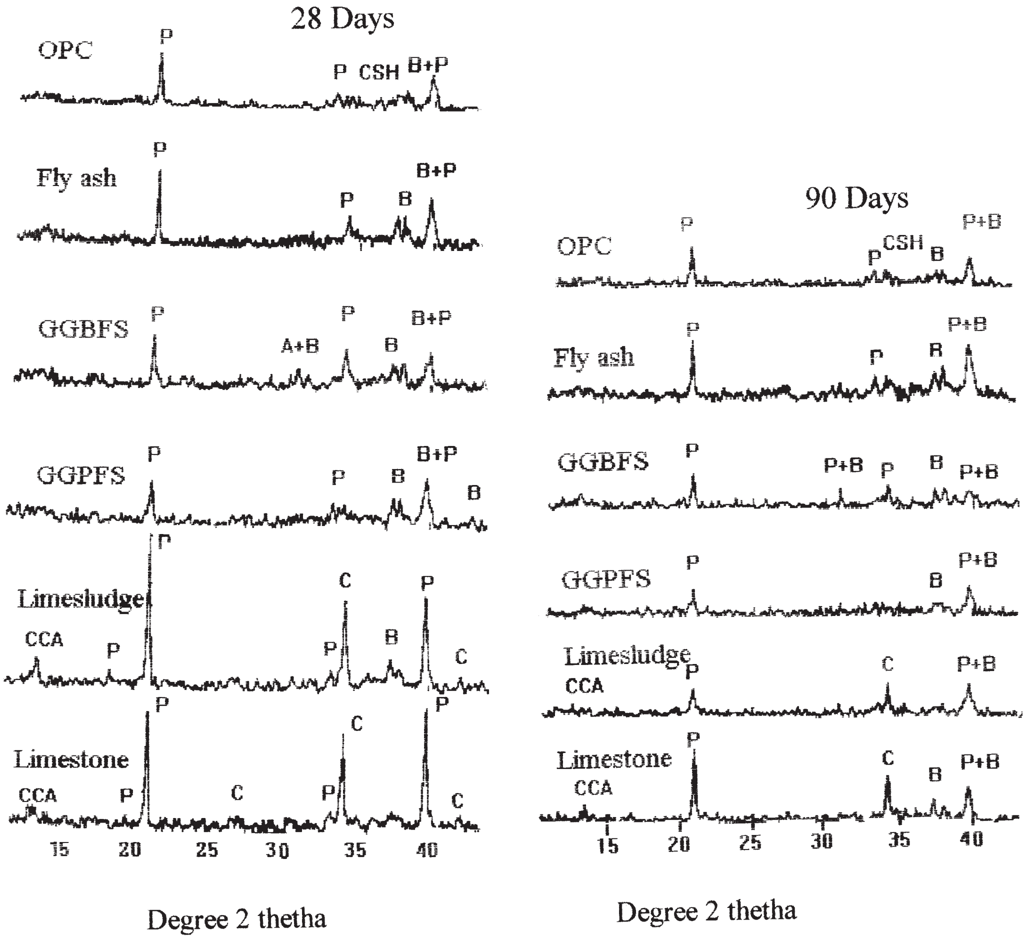

Fig. 2. XRD pattern of OPC hydrated in the presence of 10% mineral additives. A, alite; B, belite; C, calcium carbonate; CCA, calcium carboaluminate; CSH, calcium silicate hydrate; P, Portlandite.

peak in presence of fly ash becomes slightly greater than the CH peak in the control OPC, even though the pozzolanic reaction has taken place. The decrease of DTA peak area due to decomposition of CH at ≈500°C (Table 2, Fig. 3) in OPC + fly ash cement hydrated at 28 days compared to that of control confirms that pozzolanic reaction has taken place. In the case of control OPC, a smaller amount of CH (Table 2, Figs. 2 and 3) is present at 90 days of hydration, compared to that at 28 days. It is possible that a part of CH became carbonated. In the case of OPC + fly ash cement, a smaller amount of CH is present at 90 days of hydration. This indicates the presence of a pozzolanic reaction. The results show that although the pozzolanic reaction is in progress, the total amount of CH available for a pozzolanic reaction has not been consumed. The presence of belite peaks of relatively higher intensity and the absence of alite peaks indicate an almost complete hydration of alite but an incomplete hydration of the belite phase even at 90 days of hydration.

3.4. Hydration of OPC with slags

XRD pattern of granulated blast furnace slag and phosphorous furnace slag mixed cement (Table 2 and Fig. 2) show a distinct pozzolanic reactivity at 28 days of hydration. The reactivity of slags at this stage of hydration is better than that of fly ash. From the DTA pattern in Fig. 3, it is evident that the peak area (Table 2) of $Ca(OH)_2$ endotherms of cement samples with slags added are lower than that of control, which is due to an increased pozzolanic reactivity of slags with lime.

In 90-day hydrated samples both the slags have shown good pozzolanic reactivity. The comparatively smaller peaks of Portlandite, with almost disappearing belite peaks, indicate an improved reactivity of slags at this period of hydration. The XRD pattern is almost similar to that of control OPC with comparatively smaller intensities of characteristic peaks. At 90 days of hydration, the pozzolanic reactivity of slags is better than that of fly ash. The corresponding peak areas of the endotherms of $Ca(OH)_2$ in DTA patterns of

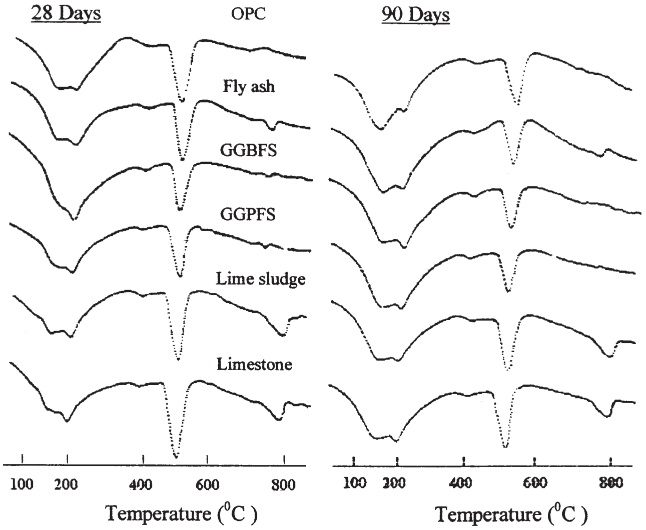

Fig. 3. DTA curve of OPC hydrated in the presence of 10% mineral additives.

GGBFS and GGPFS mixed samples are still lower, indicating the advancement of the pozzolanic reaction (Fig. 3, Table 2).

3.5. Hydration of OPC with limestone and lime sludge

At 28 days of hydration, the XRD pattern of OPC samples with limestone and lime sludge added shows relatively larger peaks of Portlandite at the respective 2θ values, which indicates an enhancement of the hydration of OPC (Fig. 2). The relatively low intensity of belite peaks in sludge and limestone-mixed samples also supports the view that the hydration of C_3S and C_2S present in ordinary Portland cement is accelerated in the presence of fine calcite ($CaCO_3$) particles. The appearance of a peak at 13.24° indicates the presence of the carbonate analogue of ettringite. The larger intensity of Portlandite and calcium carboaluminate peaks in the lime sludge-mixed sample indicates a faster hydration of the clinker phases in this sample.

The samples with carbonate additions hydrated at 90 days still show the characteristic peaks of calcium carboaluminate but with a lower intensity compared to that of 28-day hydrated sample. This may be due to the conversion of the primarily formed calcium carboaluminate into more stable monocarboaluminate form. The reduced intensity of $CaCO_3$ peaks in both the samples and particularly in the lime sludge-added sample shows the dissolution of $CaCO_3$ during the formation of hydration products. DTA pattern of the samples with limestone and lime sludge addition (Fig. 3) shows higher intensities of the $Ca(OH)_2$ endotherm, confirming a greater $Ca(OH)_2$ formation in the presence of calcium carbonate, which is in line with the results of XRD. The broadening of endotherms at lower temperature range from 140–180°C in all the samples indicates the presence of a higher amount of combined water associated with increased quantity of calcium silicate hydrate and other hydrated minerals.

Table 2
Peak areas

Sample	Peak area (mm^2) of XRD at 2θ = 21.17 Å for CH		Peak area (mm^2) of DTA endothermic peak at ≈500°C for CH	
	28 days	90 days	28 days	90 days
OPC	8.0	5.8	82	62
OPC + 10% fly ash	8.5	5.5	75	50
OPC + 10% GGBFS	7.0	5.0	65	47
OPC + 10% GGPFS	7.0	5.0	63	49
OPC + 10% lime sludge	25.0	5.5	90	68
OPC + 10% limestone	18.5	10.5	116	80

4. Conclusion

From the hydration study of OPC with mineral additives at the selected level of addition (10%), it is concluded that the hydration products of OPC with fly ash and slags are almost similar. The hydration reaction of OPC in the presence of slags has been observed to be enhanced compared to fly ash. With the addition of powdered limestone and lime sludge, the hydration of OPC accelerates and greater amounts of $Ca(OH)_2$ are liberated. The formation of the ettringite analogue of calcium carboaluminate hydrate takes place during the initial period, which can be observed up to the age of 28 days of hydration. After that it converts into more stable monocarboaluminate hydrate. The hydration of OPC with lime sludge is better than that with limestone due to the better crystallinity and fineness of powdered sludge.

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