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Studies on the Effect of Additives on the Strength of Ordinary Portland Cement

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Abstract

The effects of additives, such as slag, limestone and fly ash on the strength of ordinary Portland cement (OPC) have been studied. The percentages of the additives were varied from 9 to 29%. 2.5% gypsum was used in all preparations. The influence of the additives on the strength of OPC was monitored by measuring compressive strengths. The results indicated that the strengths of all the composite cements were nicely satisfied the respective American Society for Testing and Materials (ASTM) values recommended for different times of curing. It was observed that the strengths of the all composite cements gradually increased with time of curing. Interestingly, slag composite cements showed higher strengths at all ages (3, 7 and 28 days). On the other hand, limestone composite cements showed comparatively lower strengths but higher than that of ASTM recommended values. It has also been observed that the strengths are independent of the fineness of the composite cements.

Keywords: Ordinary Portland Cement (OPC), Additives, Composite Cement.

Introduction

Portland composite cement results from milling 40-64 parts (by weight) of Portland cement clinker together with a corresponding amount (60-36 parts) of pozzolans or other suitable additives [1-5]. Composite cements are largely comparable to Portland cement in terms of their construction properties and their inclusion in the setting of regulation. Portland composite cement has better characteristics than the ordinary Portland cement. This kind of cement is suitable to construct buildings, bridges and other commercial structures in coastal area and saline environmental area. The long-term strength is 15 to 20% higher than the ordinary Portland cement [6]. The use of Portland composite cements enhances the ecological efficiency of concrete construction. The utilization of main constituents other than clinker reduces the CO_2 emission during cement manufacture in particular as the clinker content of Portland composite cements is lower than that of Portland cements [7]. Composite being slow setting was hot very popular in earlier times but gradually it has become an acceptable building material [8].

Slag is a non-metallic product consisting essentially of glass silicates, alumino-silicates of lime and other bases and is obtained as a by-product in the manufacture of pig-iron in blast furnace**.** Fly ash or pulverized fuel ash is formed as a result of burning pulverized coal. It is a very fine material about 60-70% of which has a size below 0.076 mm. The principal contents of fly ash are normally silica (30-60%), alumina (15-30%), iron oxide and carbon in the form of unburnt fuel up to 20%, lime 7% and small quantities of magnesium oxide and sulphate. Limestone occurs in nature and is widely distributed as minerals known by various names as limestone, marble, chalk, Iceland spar, coral etc. There are two forms of crystals of calcium carbonate: Calcite and Aragonite.

From the beginning, there was only one cement factory in Bangladesh and the production of cement was not enough as per demand. At that time cement was imported from Thailand, Indonesia, Malaysia, China etc. To fulfillment the demand, a group of industrialists set up some cement factories in Bangladesh. After that cement price was very much controlled in our country. Latter, the price of clinker became higher and eventually the price of cement was increased. Now the time has come to carry out a research to develop a process to manufacture low cost cement.

In the present research, we have attempted to use some additives (slag, limestone and fly ash) with clinker to produce composite cements, which are cost effective compare to ordinary Portland cement (OPC). We have investigated the effects of additives on the strength of ordinary Portland cement. The results are expected to be useful in the manufacturing of composite cements in Bangladesh.

Experimental

Reagents

Ethylenediaminetetraacetate (EDTA), Triethanolamine (TEA), Ammonium chloride, Sodium-potassium tartarate, Ammonium hydroxide, pentahydrate copper sulphate, Methylthymol Blue (MTB), Mixed indicator (KB), Silver Nitrate, 1-(2-pyridilazo)-2-naphthol (PAN) were purchased from E. Merck, India. Potassium hydroxide, Hydrochloric acid, Sulphuric acid, Sodium salicylsulfonate were purchased from BDH. Standard sand (BS EN 196 Part I) was purchased from England.

Preparation and Procedure

Preparation of composite cements

All the materials were dried in an oven at 105 ^{0}C about 1 hour. The dried materials were taken according to the following composition as shown in Table 1 and ground in the mini ball mill (Model No. TCL 175, China) for 25-30 minutes. The total weight of composition was 5 kg. Another sample ‘d’ was prepared by grinding 97.5% clinker and 2.5% gypsum.

Physical Parameters

All the physical properties were measured according to the following procedures.

(a) Fineness: Fineness of the composite cements was measured using air permeability method and sieve tests.

Air Permeability Method

5 g of cement was placed in the permeability cell in a standard manner. Then air was slowly passed on through the cement bed at a constant velocity. The rate of airflow was adjusted until the flow meter shows a difference in level of 30-50 cm .The difference in level of manometer and the difference in level of the flow meter was recorded. These observations were repeated to ensure that steady conditions had been obtained and then specific surface was calculated [1].

Table 1. Percentages of clinker, additives and gypsum in the composite cements.

Cementitious materials (%)	Sample No.								
	a_1	a_2	a_3	b_1	b_2	b_3	c_1	c_2	c_3
Clinker	68.5	78.5	88.5	68.5	78.5	88.5	68.5	78.5	88.5
Slag	29	19	9	—	—	—	—	—	—
Limestone	—	—	—	29	19	9	—	—	—
Flyash	—	—	—	—	—	—	29	19	9
Gypsum	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5

Sieve Test.

100 g of Cement was weighed out and taken it on a standard IS Sieve No. 9 (90 micron). The air-set lumps in the sample were broken down with spatula. Then the sample was continuously sieved, giving circular and vertical motion for a period of 15 minutes. The residue left on the sieve was then weighed and calculated [1].

(b) Standard Consistency Test: 500 g of cement was taken and prepared a paste with a weighed quantity of water (say 24 percent by weight of cement) for the first trial. The paste was made in a standard manner and filled into the Vicat mould within 3-5 minutes. After completely filling the mould, the mould was shacked to expel air. A standard plunger, 10 mm diameter, 50 mm long was attached and brought down to touch the surface of the paste in the test lock and quickly released allowing it to sink into the paste by its own weight. Then the reading was taken by noting the depth of penetration of the plunger. Similarly, more trials were conducted with higher and higher water/cement ratios until such time the plunger penetrates to a depth of 33-35 mm from the top. That particular percentage of water, which allowed the plunger to penetrate only to a depth of 33-35 mm from the top, was the percentage of water required to produce a cement paste of standard consistency [9].

(c) Setting Time Test: 500 g of cement sample was taken in a pot and paste it with requisite amount of water to prepare cement paste of standard consistency. The paste was gauged and filled into the Vicat mould in specified manner within 3-5 minutes. A stopwatch (Diamond-788645, China) was started the moment water is added to the cement. The temperature of water and that of the test room, at the time of gauging was maintained within 27±2 ^{0}C. A water bath (Model-HHS, China) was used to control the temperature of water at 27±2^{0}C.

Initial setting time: The needle was lowered gently and brought it in contact with the surface of the test block and quickly released and to penetrate into the test block. The period elapsing between the time when water was added to the cement and the time at which the needle penetrates the test block to a depth equal to 33-35 mm from the top was taken as initial setting time.

Final setting time: The needle of the Vicat apparatus was replaced by a circular attachment. The cement was considered as finally set when, upon lowering the attachment gently cover the surface of the test block, the center needle makes an impression, while the circular cutting edge of the attachment fails to do so. This could indicate a hardened state, which the center needle did not pierce through more than 0.5mm [1].

(d) Compressive Strength Test: 1375 g portions of standard sand, 500 g portions of composite cements (i.e. ratio of ~1:3) and 242 mL water were taken on a non-porous enamel tray and each sample was mixed with a trowel for one minute. Further mixing with different ingredients was continued until the mixtures were of uniform color. The time of mixing was between 3 to 4 minutes. Immediately after mixing, cube moulds of size 7.06 cm were filled with the mortars. The mortars were compacted by taking the moulds on the vibrating table. The compacted cubes were kept in a curing box at a temperature of 20±2 ^{0}C with at least 90 percent relative humidity for 24 hours. The cubes were removed from the curing box and immersed in clean fresh water until taken out for testing. Three cubes were tested for compressive strength at the periods of 2, 7 and 28 days [1, 10-12].

Chemical Analysis

Preparation of stock solution. 0.5 g of clinker was taken in a beaker. 2-3 g of ammonium chloride was added and mixed well. This mixture was treated with 3 drops of conc. HNO_3 and 3 mL of conc. HCl and heated on sand bath to make paste and it was then dried for digestion. After completion of digestion it was cooled to room temperature. Then 125 mL of HCl (97:3) was added to make a solution. The residue was then filtered through Whatman paper no. 40 and washed thoroughly with hot distilled water until the filtrate was freed from chloride. A 250 mL volumetric flask was used to collect the filtrate. The filtrate was made upto the mark with distill water. This was the stock solution of clinker. Similarly, stock solutions of additives, gypsum and finished products were made [13, 14].

Apparatus

A mixture machine (Model No. 160A, China) was used to prepare a cement paste with sand and water. Fineness of the prepared cements was monitored using Vicat Needle Permeability Apparatus (Model No. VN-01, China). Setting time was recorded using Lea and Nurse Permeability Apparatus (ID No.BRTC 0604/04/CE, China). Compressive strengths of the cement cubes were measured using Compression Testing Machine (Model No. 82446/2004, China). The prepared cubes were cured in a Standard Cement Curing Cabinet (Model No. YH-40B, China).

Results and Discussion

Chemical Composition

Table 2 indicates the chemical compositions of clinker, additives and gypsum. Limestone is rich in CaO and fly ash is enriched with SiO_2. On the other hand, slag contains high amount of both SiO_2 and CaO. The five major compounds such as SiO_2, CaO, MgO, Al_2O_3 and Fe_2O_3 were tested because the relative proportions of these oxides responsible for influencing the various properties of cement. There may have many minor compounds but their influence on the properties of cement or hydrated compounds is not significant. The proportions of these five compounds in clinker were determined in the standard manner. Furthermore, the chemical compositions of all the composite cements are shown in Table 3.

Table 2. Chemical compositions of clinker, additives and gypsum.

Chemical composition	Cementitious materials (%)				
	Clinker	Slag	Limestone	Flyash	Gypsum
SiO_2	22.00	32.20	7.36	44.05	6.00
CaO	64.78	37.35	42.91	2.25	31.46
MgO	4.08	6.60	0.96	0.36	0.24
Fe_2O_3	3.00	0.72	1.07	0.84	0.50
Al_2O_3	4.20	0.62	1.50	19.45	0.23

Table 3. Chemical composition of the composite cements.

Chemical composition %)	Sample No									
	a_1	a_2	a_3	b_1	b_2	b_3	c_1	c_2	c_3	d
SiO_2	24.5	23.27	22.52	17.35	18.82	20.28	27.95	25.69	23.52	21.52
CaO	55.34	58.24	61.29	57.01	59.32	61.55	45.09	51.87	58.12	63.78
MgO	4.65	4.36	4.15	3.02	3.29	3.60	2.80	3.23	3.69	3.95
Fe_2O_3	2.21	2.45	2.65	2.30	2.51	2.71	2.25	2.28	2.53	2.75
Al_2O_3	3.01	3.42	3.72	3.27	3.55	3.81	8.47	6.95	5.42	4.04

Physical Parameters

Fineness

Table 4 indicates the fineness of all prepared composites. Fineness of cements was tested in two ways: 1) by sieve test and 2) by air-permeability method. An average (4.55 ± 0.85) percent of residue was present in each sample. According to the air permeability method, a range of surface area (3200 — 4800 cm^2/g) was observed where the standard surface area according to ASTM is 2800 cm^2/g.

Table 4. Percentage of residue, Blaine and water consistency of the composite cements.

Sample No	Residue (%)	Blaine (sq.cm/g)	Water Consistency (%)
a_1	3.6	3872	24.50
a_2	4.6	3399	24.00
a_3	4.0	3804	23.50
b_1	3.8	4840	22.00
b_2	5.2	4764	21.50
b_3	3.4	3490	22.50
c_1	3.7	4753	26.00
c_2	3.0	4353	26.25
c_3	4.3	3194	24.50
d	5.4	3384	24.00

Setting time

Table 5 indicates the initial and final setting times of all cement composites. The results of both the initial and final setting times satisfied the ASTM standard (initial setting is not less than 45 minutes and final setting time is not more than 375 minutes).

Table 5. Setting times of the composite cements.

Sample No.	Setting time (min)	
	Initial	*Final*
a_1	125	285
a_2	100	200
a_3	65	170
b_1	55	160
b_2	65	185
b_3	90	215
c_1	105	235
c_2	110	245
c_3	95	220
d	75	220

Compressive Strength

Table 6 indicates the compressive strengths of the composite cements as well as ordinary Portland cement. The results show that the strengths of the composite cements at all ages are higher than those for ordinary Portland cement.

Table 6. Compressive strengths of the composite cements.

Sample No.	Compressive strength (MPa)		
	Age (days)		
	3	**7**	**28**
a_1	15.75	33.25	51.75
a_2	17.25	34.31	53.78
a_3	22.50	43.25	55.78
b_1	15.87	27.25	34.96
b_2	18.25	31.81	37.03
b_3	21.31	34.81	37.68
c_1	14.62	29.68	43.70
c_2	15.62	29.80	44.06
c_3	17.00	30.50	44.87
d	17.93	30.75	39.62
Portland Composite cement (ASTM Standard)	12.00	19.00	28.00

Interestingly, sag cements of all ratios show higher strengths at all ages. The early (3 and 8 days) strength is due to the hydration reaction between Portland cement and water, resulting in the formation of calcium-silicate-hydrate (CSH) and calcium hydroxide [$Ca(OH)_2$]. CSH is a gel that is responsible for strength development in Portland cement pastes. $Ca(OH)_2$ is a by-product of the hydration process that does not significantly contribute to strength development in normal Portland cement. Silicates in slag cement combine with the calcium hydroxide by-product of hydration and form additional CSH. This in turns leads to a denser, harder cementitious paste, which increases ultimate strength as compared to 100% Portland cement systems.

On the other hand, although fly ash cements show higher strength than that of ordinary Portland cement but show lower strength compared to slag cement. In the case of fly ash cement, hydration reaction also occur and results in the formation of calcium-silicate-hydrate(CSH) and $Ca(OH)_2$. Eventually, the usual strength of cement is due to the formation of CSH gel. The higher strength of fly ash cement is due to the formation of additional CSH from the reaction of $Ca(OH)_2$ and silica in fly ash. But the lower strength compared to slag cement may due to the inadequate amount of CaO needed for the formation of CSH.

Limestone cements show comparative strengths at 3 and 7 days but show lower strength at 28 days compared to any one of the composite cements as well as ordinary Portland cement. The early higher strength is due to the formation of calcium-silicate-hydrate during the hydration reaction. But at higher ages (28 days) no further formation of CSH is possible since limestone does not contain adequate quantity of SiO_2.

Slag cement does not contain carbon and will not cause fluctuation in air content. The percentage of slag cement to get highest flexural strength varies depending on the specific mix design and constituents used. However, slag cement used at replacement rates greater than 25% can cause a dramatic increase in time of set. The lower heat evolution characteristic of slag cement in the summer can be beneficial because it allows more time for placing and finishing concrete. In spring and fall, the delayed set may cause problems with joint sawing, texturing and secondary paving operations. A rule of thumb is that the set time is delayed 3 minutes for every 10% slag replacement of Portland cement. Slag cements demonstrate improved workability and finishability compared to ordinary Portland cement. This is due to the several factors including increased paste cohesiveness, glassy structure of slag cement, and low initial water absorption.

Fly ash cement also produces less heat of hydration and offers greater resistance to the attack of aggressive waters compared to ordinary Portland cement. Moreover, it reduces the leaching of calcium hydroxide when used in hydraulic structures [1]. The main problem of utilization of fly ash comes from the unburnt carbon in it as it has no binding force. Carbon content variability in fly ash is one of the major causes of fluctuating air contents. The addition of fly ash increases the paste volume, drying shrinkage may be increased slightly if the water content remains constant [11]. At normally specified replacement levels, concrete made with slag cement have lower permeability than concrete made with fly ash.

Limestone is a plasticizing material. The addition of limestone with Portland cement reduces setting time and facilitate workability. It is primarily used for spreading onto walls to make exterior stucco, as Portland cement would have poor spreadability.

It has also been investigated that the strengths are irrespective of the fineness of the composite cements.

Conclusion

The composite cements of all ratios of slag and fly ash showed better results upto 28 days compared to ordinary Portland cement. In addition, slag containing composite cements showed much better strengths compared to ordinary Portland cement and other composite cements. On the other hand, limestone containing composite cements showed slightly lower strengths compared to ordinary Portland cement. However, this strength is higher than that recommended by ASTM standard.

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