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Thermally Treated Local Sand is an Alternative of Fly Ash in Preparation of Composite Cement

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***Abstract*— Local sand was powered well using mini ball mill and then treated at 200, 400, 600, 800 and 1000 ^{0}C, separately. Infrared spectra were scanned of the treated and non-treated sand, and fly ash. The λ_3 band of silicate network of the non-treated sand appears at 1030 cm^{-1} with two shoulders at 1000 and 1080 cm^{-1}. On the other hand, the λ_3 band of the silicate network for the thermally treated sand (≥600 ^{0}C) shows single main band at approximately 1100 cm^{-1} that similar to fly ash. The Portland composite cements were prepared using clinker, additives and gypsum. The percentages of the additive were varied from 9 to 29%. 2.5% gypsum was used in all the preparations. The effects of the thermally treated local sand on the strength of the ordinary Portland cement (OPC) have been studied by measuring of compressive strengths. The results indicated that the strength of the composite cements was nicely satisfied with the respective American Society for Testing and Materials (ASTM) value recommended for different times of curing. It was observed that the strength of all the composite cements gradually increased with time of curing. Interestingly, thermally treated local sand (≥600 ^{0}C) composite cements showed same strengths at all ages (3, 7 and 28 days) compared to those prepared from fly ash. It has also been observed that the strengths were independent of the fineness of the composite cements.**

Keywords*— Local sand; Fly ash; IR spectra; Portland composite cement

1. INTRODUCTION

Portland composite cement (PCC), developed using traditional and up-to-date mineral addition, is considered to be state of art on cement production. PCCs are largely comparable to ordinary Portland cement (OPC) in terms of their construction properties and their inclusion in the setting of regulation. PCC has better characteristics than that of OPC. 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 of PCC is 15 to 20% higher than that of OPC [1]. The utilization of main constituents other than clinker reduces the CO_2 emission during cement manufacture in particular as the clinker content of PCCs is lower than that of OPC [2]. Furthermore, because it is characteristic of saving resources and power, utilizing industrial wastes as well as decreasing heat of hydration and improving durability of cement [3,4]. PCC is popular to the cement manufacturers and becomes a kind of cement for the sustainable development.

As far as the traditional composite cement properties are concerned, the literature review shows that the behavior of pozzolanas has been thoroughly investigated. The principal hydration product in PCCs are almost similar to those found in OPC but the added constituents may affect either hydration rate or the stoichiometry of the hydration products [3,4].

Pozzolanas, covers all the siliceous and aluminous materials, exhibit little or no cementitious properties. However, a finely divided form of pozzolanas react with lime ($Ca(OH)_2$) in the presence of water to form compounds with cementitious properties. The most pozzolanas are fly ash, ground granulated blast furnace slag, natural pozzolanas and microsilica.

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. Fly ash is siliceous compounds and the principal contents of fly ash are normally silica (70-80%), alumina (15-25%) with a few percent of iron oxide, magnesium oxide and very few amount of carbon. Fly ash improves concrete properties, lowers the cost of concrete production, and is ecologically beneficial. The utilization of fly ash is one of the popular methods proposed to reduce expansion due to alkali-silica reactivity. However, its behaviors are not completely understood.

In Bangladesh, a variety of pozzolanic and/ or hydraulic materials are used as cement main constituents. The main constituents are natural pozzolanas and fly ash. In our previous study [5], we have reported that slag and fly ash can be used as additives in production of Portland composite cement.

However, in Bangladesh, most of the additives imported from Thailand, Indonesia, Malaysia, China, etc.

Xu et al. [6] reported that addition of silica fume (silane-treated) to cement paste has been shown to increase the specific heat by 7% and decrease the thermal conductivity by 38 % relative to the cement paste without silica fume. Without the surface treatment with silane, the effect of silica fume on both specific heat and thermal conductivity are in the same direction, but less remarkable [6].

Sand is a much more common component in concrete than silica fume. It is different from silica fume in its relatively large particle size and negligible reactivity with cement. Therefore, addition of sand as an additive will be cost effective.

In the present paper, we have attempted to use thermally treated local sand as an additive in production of cost effective composite cement. We have investigated how the thermally treated local sand can be used as an alternative additive of fly ash in production of composite Portland cement. The results are expected to be useful to manufacture cost effective composite cement in under developing countries.

2. EXPERIMENTAL

2.1 Reagents

Disodium ethylenediaminetetraacetate (Na_2EDTA), triethanolamine (TEA), ammonium chloride, sodium-potassium tartrate, ammonium hydroxide, pentahydrate copper sulfate, methylthymol blue, silver nitrate and 1-(2-pyridilazo)-2-naphthol (PAN) were purchased from E. Merck, India. Potassium hydroxide, hydrochloric acid, sulfuric acid and sodium salicylsulfonate were purchased from BDH (England); Standard sand was purchased from BS EN 196 Part I, England.

2.2 Preparation of composite cements

The local sand was powered well using mini ball mill and then thermally treated at 200, 400, 600, 800 and 1000 ^{0}C. Then a series of composite cements were prepared according to the following composition as shown in Table 1 and ground in the mini ball mill for 25-30 minutes. The total weight of composition was 5 kg. A cement sample 'I' was prepared by only grinding 97.5% clinker and 2.5% gypsum.

Table 1. Composition of the prepared composite Portland cements.

Sample	Clinker %	Fly ash %	Gypsum %	*NTS %	200 °C %	400 °C %	600 °C %	800 °C %	1000 °C %
a_1	68.5	29.0	2.5	-	-	-	-	-	-
a_2	78.5	19.0	2.5	-	-	-	-	-	-
a_3	88.5	9.0	2.5	-	-	-	-	-	-
b_1	68.5	-	2.5	29.0	-	-	-	-	-
b_2	78.5	-	2.5	19.0	-	-	-	-	-
b_3	88.5	-	2.5	9.0	-	-	-	-	-
c_1	68.5	-	2.5	-	29.0	-	-	-	-
c_2	78.5	-	2.5	-	19.0	-	-	-	-
c_3	88.5	-	2.5	-	9.0	-	-	-	-
d_1	68.5	-	2.5	-	-	29.0	-	-	-
d_2	78.5	-	2.5	-	-	19.0	-	-	-
d_3	88.5	-	2.5	-	-	9.0	-	-	-
e_1	68.5	-	2.5	-	-	-	29.0	-	-
e_2	78.5	-	2.5	-	-	-	19.0	-	-
e_3	88.5	-	2.5	-	-	-	9.0	-	-
f_1	68.5	-	2.5	-	-	-	-	29.0	
f_2	78.5	-	2.5	-	-	-	-	19.0	-
f_3	88.5	-	2.5	-	-	-	-	9.0	-
g_1	68.5	-	2.5	-	-	-	-	-	29.0
g_2	78.5	-	2.5	-	-	-	-	-	19.0
g_3	88.5	-	2.5	-	-	-	-	-	9.0
d	97.5	-	2.5	-	-	-	-	-	-

2.3 Measurement of physical properties

2.3.1 Fineness. Fineness of the composite cements was measured using air permeability method and sieve tests.

2.31.1. 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 steady conditions and then specific surface was calculated [7].

2.3.1.2 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 [7].

2.3.2 Determination of water consistency. 500 g of cement was taken and prepared a paste with a weighed quantity of water (i.e. 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, it 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 water/cement ratios until the plunger penetrates to a depth of 33-35 mm from the top. This particular percentage of water was the percentage of water required to produce a cement paste of standard consistency [8].

2.3.3 Determination of setting time**.** 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. 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.

2.3.3.1 Initial setting time: The needle was lowered gently and brought it in contact with the surface of the test block and quickly released and penetrated 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.

2.3.3.2 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 [7].

2.4. Determination of compressive strength. Standard sand and composite cement with a weight ratio of 1:3 was mixed with water in a non-porous enamel tray using a trowel for one minute. Further mixing with different ingredients was continued until the mixtures were uniformed in color. 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 [7, 9-12].

2.2.3 IR spectroscopy study
The IR spectra of fly ash containing cement, sand containing non treated cement and thermally treated cement were recorded on an IR-470, Shimadzu, Japan in the range of 400-4000 cm^{-1}.

2.2.4 Chemical Analysis
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 as confirmed by silver nitrate solution. A 250 mL volumetric flask was used to collect the filtrate. The filtrate was made up to the mark with distill water and then analyzed according to standard methods [13]. Similarly, stock solutions of additive, gypsum and finished products were prepared and analyzed according to standard methods [13].
All the physical and chemical experiments were conducted at the laboratory of Tiger Cement, MTC Cement Industries Ltd., Meghnaghat, Narayanganj, Bangladesh.

2.3 Apparatus
Mini Grinding Ball Mill, (Model No. TCL 175,China) was used to grind local sand and clinker. A Muffle furnace (Model No. KXX-4-10A, FX-4-10, China) was used for thermal treatment of the powered sand. Shimadzu-470, Japan infrared (IR) spectrometer was used for IR spectra. 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).

3.0 RESULTS AND DISCUSSION

3.1 Chemical Composition. Table 2 indicates the chemical compositions of clinker, additives and gypsum. Local sand and fly ash are enriched with SiO_2. 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 compounds 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 so significant. The proportions of these five compounds in clinker were determined using a standard procedure [13]. Furthermore, the chemical compositions of all the additives and gypsum were determined using the same standard procedures which are shown in Table 2.

Table 2. Chemical compositions of clinker, additives (flyash, thermally treated local sand (600^{0}C) and gypsum.

Chemical composition (%)	Cementitious materials (%)			
	Clinker	Sand	Fly ash	Gypsum
SiO_2	22.00	85.02	92.66	6.00
CaO	64.78	3.53	1.56	31.46
MgO	4.08	0.48	1.26	0.24
Fe_2O_3	3.00	3.47	0.96	0.50
Al_2O_3	4.20	2.29	1.15	0.23

3.2 Physical Parameters
3.2.1 Fineness. Table 3 indicates the fineness of all the 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 American Society for Testing and Materials (ASTM) is 2800 cm^2/g.

Table 3. Percentage of residue, Blaine and water consistency of the prepared composite cements.

Sample No	Residue (%)	Blaine (sq.cm/g)	Water Consistency (%)
a_1	3.7	4753	26.00
a_2	3.0	4353	26.25
a_3	4.3	3194	24.50
b_1	6.5	4100	24.00
b_2	8.8	3724	24.75
b_3	4.5	3700	25.25
c_1	5.6	4081	25.50
c_2	5.3	3952	25.25
c_3	5.1	3939	25.00
d_1	4.6	4293	27.00
d_2	4.8	4094	26.50
d_3	4.3	4107	26.00
e_1	3.6	4743	26.50
e_2	3.1	4348	26.00
e_3	5.4	3384	24.25
f_1	3.8	4448	26.25
f_2	3.2	4389	26.50
f_3	5.3	3460	24.50
g_1	3.9	4506	26.25
g_2	3.4	4030	26.50
g_3	5.1	3535	24.75
I	6.6	3749	25.50

3.2.2 Setting time. Table 4 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 4. Setting times of the prepared composite cements.

Sample No.	Setting time (min)	
	Initial	Final
a_1	105	235
a_2	110	245
a_3	95	220
b_1	75	230
b_2	90	245
b_3	95	255
c_1	80	240
c_2	85	250
c_3	85	255
d_1	95	280
d_2	90	270
d_3	85	270
e_1	101	230
e_2	105	236
e_3	98	228
f_1	100	240
f_2	105	245
f_3	100	230
g_1	100	245
g_2	110	250
g_3	95	240
1	80	225

Table 5. Compressive strengths of the prepared composite Portland cement.

Sample No.	Compressive strength (MPa)		
	Age (days)		
	3	7	28
a_1	20.13	33.00	53.03
a_2	20.90	33.69	52.16
a_3	21.00	34.12	52.41
b_1	12.18	24.31	35.48
b_2	14.58	28.52	42.21
b_3	15.87	30.28	45.24
c_1	14.10	25.93	38.98
c_2	15.20	29.17	43.59
c_3	16.12	31.86	46.36
d_1	16.24	29.83	43.62
d_2	17.61	31.02	45.72
d_3	18.06	32.55	48.20
e_1	20.15	33.05	53.01
e_2	20.94	33.77	52.11
e_3	21.02	34.20	52.31
f_1	20.10	33.10	53.02
f_2	20.82	33.87	52.23
f_3	21.05	34.45	52.39
g_1	20.32	33.13	53.05
g_2	20.91	33.89	52.19
g_3	21.09	34.32	52.29
1	14.73	29.52	43.65

3.2.3 Compressive Strength.. Table 5 indicates the compressive strengths of the prepared composite cements and ordinary Portland cement. The results show that the strengths of the composite cements at all ages are higher than those for ordinary Portland cement.

Interestingly, thermally treated local sand (600 ºC or above) composite cement of all ratios show approximately same strengths at all ages compared to that of fly ash. But composite cements of thermally treated local sand of 200 or 400 ºC show higher strength compared to that of non-treated local sand but show lower strength than that of fly ash and treated local sand (600 ºC or above).

The higher strength of the composite cement made from treated local sand (600 ºC or above) is due to the formation of extra Calcium-silicate-hydrate (CSH). The strength of cement is due to the hydration and hydrolysis 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 developed in normal Portland cement. The reactive silica present in fly ash or treated local sand reacts with calcium hydroxide (a by-product of the hydrolysis of Bogue's compounds) *in situ* and form extra calcium-silicate-hydrate (C-S-H) gel. This in turns leads to a denser, harder cementitious paste, which increases ultimate strength as compared to 100% Portland cement systems. Moreover, the excess silica in composite cement forms sodium silicate through the reaction between reactive silica and Na^+ present in saline environment resulting protecting from the effects of salinity of cement made materials/concrete. The higher reactivity of the thermally treated local sand (600 or above) is due to the presence of reactive silica as in fly ash. The formation of reactive silica in the treated local sand could be phase transfer of silica.

IR spectral studies suggest the phase transfer of silica through thermal treatment. It has also been investigated that the strengths are irrespective of the fineness of the composite cements.

3.3 IR Spectral Studies

The IR spectra of local sand (non-treated and treated, 600 ^{0}C) and fly ash are shown in Fig. 1.

The major band (λ_3) of the silicate network for different siliceous materials is shown in Table 6.

The λ_3 band of non-treated local sand appears at 1030 cm^{-1} with two shoulders at 1000 and 1080 cm^{-1}. Interestingly, the λ_3 band for thermally treated local sand (600 to 1000^{0}C) shows single main band at approximately 1100 cm^{-1}. The same band for fly ash appears at 1110 cm^{-1}. Therefore, the IR spectral studies suggesting the phase transformation of silica through thermal treatment, resulting in formation of reactive silica as in fly ash.

Figure 1. IR spectra of (a) Non-treated local sand, (b) treated local sand (≥600 °C), and (c) fly ash.

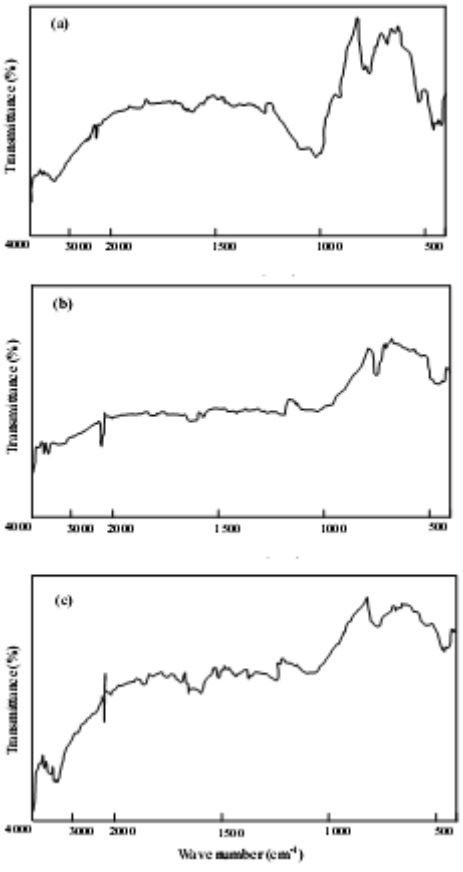

Table 6. Major λ_s band of the silicate network of fly ash and sand.

Name of the siliceous materials	Major band (λ_s) cm^{-1}
Non-treated local sand	1030 (m) 1000 & 1080 (s)
200 ^{0}C treated local sand	1030 (m) 1090 (s)
400 ^{0}C treated local sand	1080 (m) 1040 (s)
600 ^{0}C treated local sand	1080 (m)
800 ^{0}C treated local sand	1100 (m)
1000 ^{0}C treated local sand	1100 (m)
Fly ash	1110 (m)

CONCLUSION

Therefore, it is concluded that the thermally treated local sand (600 ºC or above) can be used in preparation of cost effective composite cement. The strength of the composite cements made from thermally treated local sand (600 ºC or above) is comparable to that made from fly ash. The comparative strength of the cement made from fly ash and thermally treated local sand (600 ºC or above) suggesting the presence of reactive silica in all the additives. Infrared spectral studies suggesting the phase transformation of silica through thermal treatment. Further study is under consideration.

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