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HYDRATION OF PORTLAND CEMENT CLINKER IN THE PRESENCE OF CARBONACEOUS MATERIALS

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ABSTRACT

An investigation of the hydration behaviour of ordinary Portland cement clinker in the presence of coal, coke, and charcoal has been carried out. The physico-chemical characteristics of cement are greatly influenced by these materials. The water requirement and setting times are increased. The 1-28 day compressive strength of the mortars are invariably lowered by the carbonaceous materials but the 90 day strength depends upon the nature of the materials. The hydration characteristics of different cementitious compositions have been investigated with the help of infrared spectroscopy, X-ray diffraction and SEM analysis.

Introduction

Portland cement or slag-cement can be used as a binder for making iron ore pellets used as burden material in blast furnace (1,2). The admissible limit of sulphur content in the burden is quite low and therefore gypsum free binder, i.e. cement clinker, is preferred for the purpose. Preparation of self-reducing pellets requires incorporation of reductants like coal, coke, charcoal, etc., into the pellet matrix. The setting time, hardening time, flow properties, etc., of cement are greatly influenced by the presence of various materials (3,4), and the effect is likely to be more when these materials are hydrophobic in nature like coal or coke. The surface activity of these materials changes with their structure, thermal history, ash content and other characteristics (5). However, literature reports on the hydration behaviour of cement in presence of carbonaceous materials are limited (6).

The physico-chemical properties of cementitious compositions containing Portland cement clinker and coal, coke and charcoal are reported in this paper. The hydration products have been characterized by infrared spectroscopy, X-ray diffraction and scanning electron microscopy.

Experimental

Materials

The materials used in this study were : ordinary Portland cement clinker (M/S. Orissa Cement Limited, India) having a fineness of 2950 cm^2/g (Blaine) and carbonaceous materials (particles below 44 micron size and surface area in the range of 1000 to 5600 cm^2 / cc) - (a) coal (Borgolai coal Field, North Eastern India), (b) coke(1) (Beehive coke prepared from the coal), (c) coke(2) (coke breeze from Rourkela Steel Plant, India), (d) charcoal(1) (wood charcoal) and (e) charcoal(2) (activated charcoal, M/S. E. Merck, India). In order to provide a comparison to the behaviour of conventional portland cement, analytical grade gypsum powder (M/S. E. Merck, India) was added to the

TABLE 1

Proximate analysis(wt.%) of carbonaceous materials

No.	Sample	Moisture	Ash	Volatile Matter	Fixed Carbon	Sulphur
1.	Coal	1.75	5.98	41.05	51.25	2.24
2.	Coke(1)	1.80	7.00	2.05	89.15	1.60
3.	Coke(2)	3.80	31.08	7.60	57.52	0.66
4.	Charcoal(1)	6.60	5.28	19.54	68.58	-
5.	Charcoal(2)	10.60	2.18	4.26	82.96	-

TABLE 2

Chemical analysis(wt.%) of ash and cement clinker

No.	Source	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	Others
1.	Coal	8.77	44.93	23.23	17.94	1.39	3.74
2.	Coke(1)	12.68	41.56	24.04	17.72	1.96	2.04
3.	Coke(2)	3.77	53.40	25.43	14.25	1.75	1.40
4.	Charcoal(1)	3.50	42.77	12.42	39.28	1.65	0.38
5.	Charcoal(2)	7.84	62.98	20.10	2.11	3.50	3.47
6.	Cement clinker	62.40	22.40	4.55	3.42	3.57	3.66

clinker. The proximate analyses of the carbonaceous materials are shown in Table 1 and the chemical analyses of the ash and clinker are shown in Table 2. The sulphur present in the coal is mostly in the organic form (7).

Methods

Cementitious compositions were prepared by mixing 85 parts by weight of the ground clinker with 15 parts by weight of each of the carbonaceous materials. Another composition was prepared by mixing 96 parts by weight of the clinker and 4 parts by weight of gypsum. Pastes were prepared by using different amounts of water (Table 3), sealed in polythene bags and allowed to hydrate at room temperature (25-30°C) for different periods. The samples were then ground in acetone for efficient moisture removal for about 5-10 minutes, washed with ether and finally dried in vacuum (0.1 mm Hg) for 1 hour and stored for analyses. Infrared spectra were recorded on KBr pellets using a Perkin Elmer Infrared Spectrophotometer, Model 580 B. XRD patterns were obtained using an X-ray Diffractometer, Model, JDX 11P3A, JEOL, Japan. Scanning electron micrographs were prepared with a JEOL, Model JSM-35 CF, (Ion Sputter JFC-1100, Gold coat).

Physical properties of cements were tested according to Indian Standard methods (IS 4031-1968) which are similar to ASTM methods. The consistency i.e. the amount of water (%) required in respect to dry weight of cement to produce a cement paste of normal consistency is determined by Vicat apparatus. Setting times were determined by Vicat penetrometer test. Compressive strengths were determined on mortar cubes (7cm x 7cm x 7cm) prepared using a 1 : 3 ratio of the cementitious compositions and standard sand (IS 650 - 1966).

TABLE 3

Consistency and setting time of the compositions

No.	Composition	Consistency (%)	Setting time(min.)	
			Initial	Final
1.	Clinker*	24.50	19	39
2.	Clinker+4% Gypsum	20.00	48	73
3.	Clinker+15% Coal	24.50	43	56
4.	Clinker+15% Coke(1)	25.75	63	83
5.	Clinker+15% Coke(2)	30.50	26	96
6.	Clinker+15% Charcoal(1)	26.25	53	72
7.	Clinker+15% Charcoal(2)	44.28	192	224

* Phases(Wt.%) C_3S-53.82 C_2S-20.84 C_3A-6.27 and C_4AF - 10.0.

Results and Discussion

The consistency and setting times of the compositions are shown in Table 3. The consistency of the clinker is not affected by coal; coke(1) marginally increases the water requirement but the high ash coke(2) markedly increases it. Both charcoal(1) and charcoal(2) increase the water requirement. The effect of the latter is significantly high and may be due to its high adsorption properties.

The carbonaceous materials act as set retarders. The effect of the materials on the initial and final setting times followed the order(highest-lowest) : charcoal(2) > coke(1) > charcoal(1) > gypsum > coal > coke(2), and charcoal(2) > coke(2) > coke(1) > gypsum > charcoal(1) > coal, respectively. The differences between initial and final setting time were smallest in composition containing coal and greatest in the high ash coke(2) mixture. The setting time of the compositions were found to increase with the increase of carbonaceous material content. Fig. 1. shows the effect of high ash coke and high adsorptive charcoal on the setting properties. The setting times in compositions containing charcoal(2) increase considerably with the increase of carbonaceous materials. Charcoal(2) may not therefore be suitable for incorporation into the pellet matrix.

Set retardation by carbonaceous materials has been attributed to their hydrophobicity (6,8). These materials

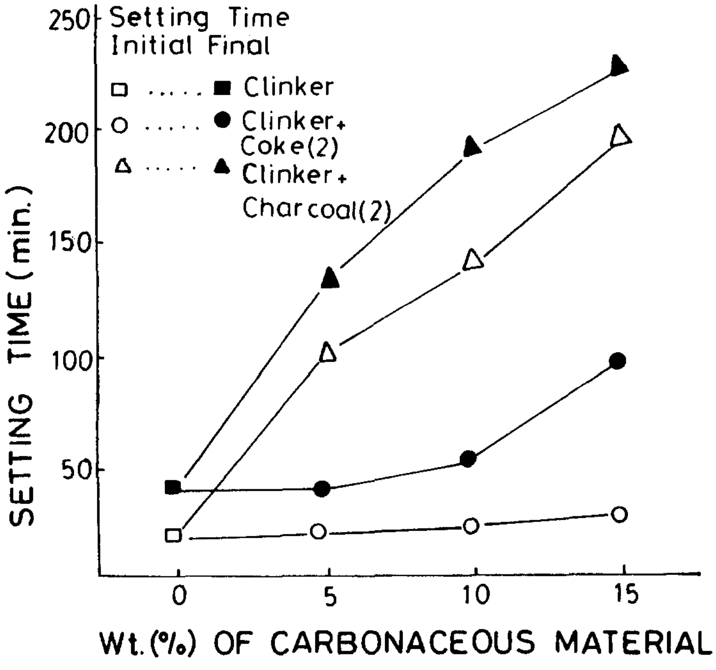


FIG. 1.

Influence of coke and charcoal on setting time disturb the wetting and therefore retard the hydration of the cement by being adsorbed on the particles and obstructing water diffusion to the cement surface. It appears from the moisture content (Table 1) that the hydrophobicity of coal is the greatest and that of charcoal(2) is the least , but the effect of coal on set retardation is the minimum. Therefore, apart from the hydrophobicity, other factors must influence the hydration characteristics. Setting is preceeded by formation of calcium rich surface layer on the clinker phases. In the case of charcoal(2) the delay in setting may be partly due to removal of calcium ions from the solution through chemisorption at the active surface of the charcoal or by the reaction with the ash constituents. This process may delay the nucleation and crystallization of $Ca(OH)_2$ and C-S-H phases. In general, both the surface characteristics and the inorganic constituents of the carbonaceous materials may be important in influencing the setting properties.

The compressive strengths of mortars prepared from different cementitious compositions are presented in Fig. 2.for

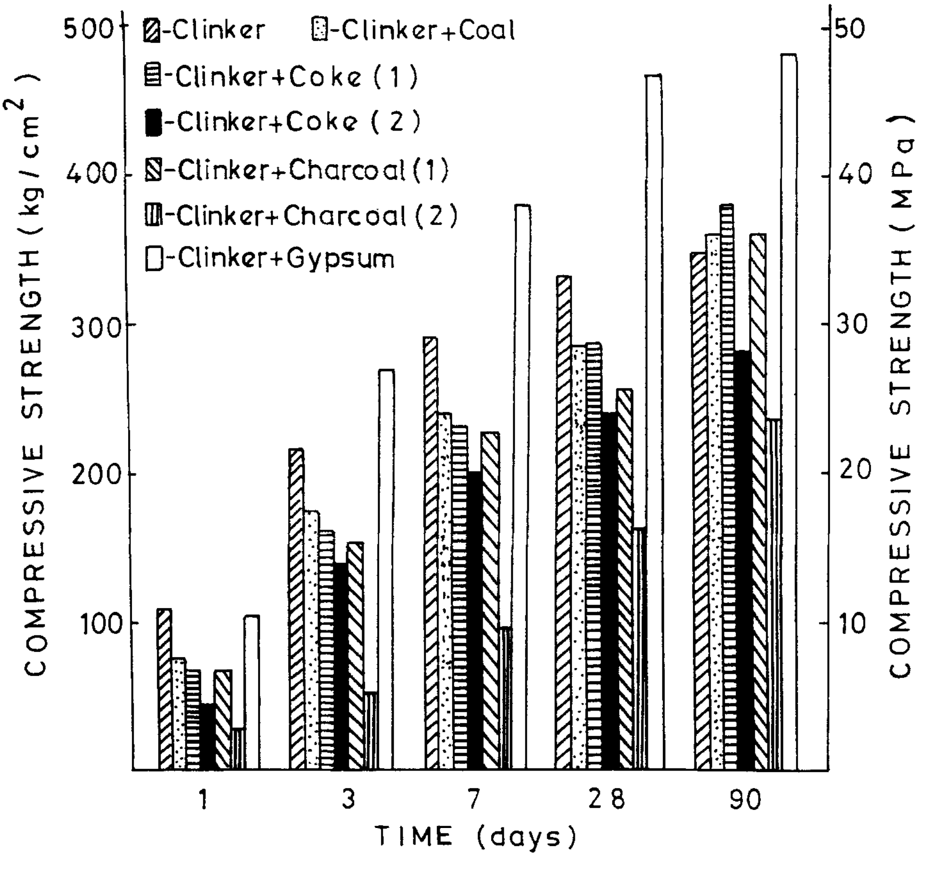


FIG.2.

Effect of carbonaceous materials on the compressive strength various curing times. The 1 day srength of the compositions containing carbonaceous materials was lower than that of the clinker and clinker-gypsum compositions. The composition containing charcoal(2) exhibited the lowest strength at all ages of curing followed by the one containing coke(2). This trend parallels to that observed for water requirement and setting time of the compositions. The 1 day strength of the paste containing coke(1) was lower than that of the one containing charcoal(1) or coal, but at 3,7 and 28 days, the composition containing charcoal(1) exhibited lower strength than the others. The 90 day strength of compositions containing different materials followed the trend : gypsum > coke(1) > charcoal(1) > coal > clinker > coke(2) > charcoal(2). It is possible that silica present in the carbonaceous materials may react with the lime liberated during hydration of cement to form C-S-H phase and thus contribute to strength enhancement.

Infrared Spectroscopic Studies

The IR spectra in the regions 400-1800 and 3000-3800 cm^{-1} of all the compositions are similar; intense bands are observed in the compositions containing charcoal(2) and gypsum. The clinker exhibits bands at 1430, 875 and 710 cm^{-1} due to carbonate (calcite) indicating that aeration of the clinker has occured. The intensity of the bands at 1430 and 875 cm^{-1} in the hydrated products increases slightly in the early ages of hydration indicating carbonation of a certain amount of lime liberated during hydration. The carbonation is probably caused by atmospheric carbon dioxide during grinding and preparation of the samples.

With the progress of hydration, the silicate band at 922 cm^{-1} of the clinker shifts towards higher wave number, revealing formation of the C-S-H phase (9). The 28 day hydration product of clinker shows the maximum shift (up to 993 cm^{-1}) and the minimum shift (up to 973 cm^{-1}) is found in composition containing coke(2). The order of shifting of the bands of the compositions containing different materials is, clinker > coal $\simeq$ charcoal(1) > coke(1) $\simeq$ gypsum > charcoal(2) > coke(2).

The IR bands near 3440 and 3640 cm^{-1} are attributed to the stretching of hydroxyl groups associated with the C-S-H phase and $Ca(OH)_2$ respectively. As hydration progresses, the intensity of the band at 3640 cm^{-1} increases indicating liberation of more lime. The effect is more pronounced in compositions containing carbonaceous materials. The broad bands near 3500 cm^{-1} are intensified as the hydration progresses, indicating that hydrated products associated with water increase. The bands near 1650 cm^{-1} are attributed to internal bending vibration of the water molecule (10).

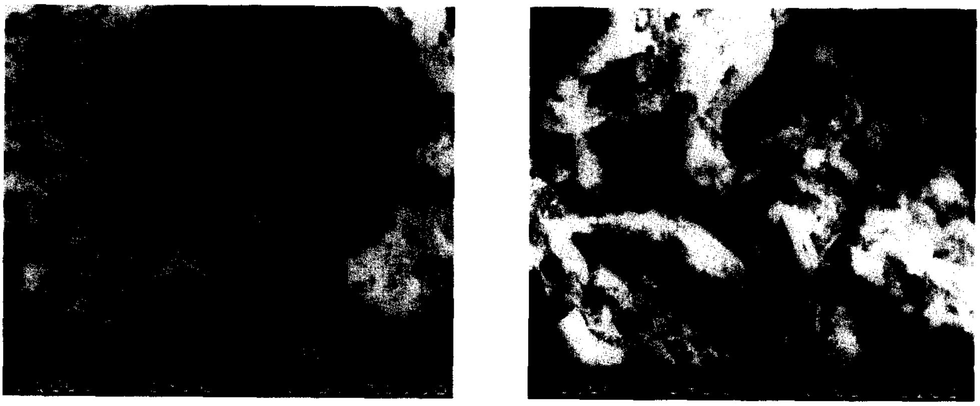
Acetone (used in sample preparation) is reported to show some complex reactions under alkaline condition to form several nonvolatile organic compounds like mesityl oxide, phorone, etc. (11). The hydrated products do not show any characteristic IR peaks of the organic compounds and hence, reaction of the hydrated phases with acetone under the experimental conditions employed is unlikely.

X-ray Diffraction Studies

Most of the carbonaceous materials exibit a peak at d = 3.35 Å in the XRD patterns which may be due to quartz or protographite or some related phases (12). The peak is very much depleted in the hydration products because the compositions contain a small amount of the carbonaceous materials. The reflection at d = 3.03 Å indicates the presence of calcite in the unhydrated cement clinker and is in conformity with the IR bands. The intensity of the peak remains almost constant in the 1 day hydration products. The 1 day hydration products of different compositions contain considerable amounts of $Ca(OH)_2$ (d = 4.90 and 2.62 Å). These peaks persist even in the 90 day hydration products indicating the presence of a considerable amount of unreacted $Ca(OH)_2$. The intensity of the peaks, (d = 2.78 and 2.74 Å) of the 90 day hydration products indicates that a considerable amount of C_3S and C_2S still remain unhydrated.

Scanning Electron Microscopy

The SEM micrographs of 90 days cured pastes of different compositions show the usual features of the hydrated products of clinker, namely amorphous C-S-H and crystalline $Ca(OH)_2$. In Fig. 3A, the rod shaped bodies are probably due to elongated fibrous particles of wood charcoal and not due to ettringite, since gypsum is absent in the composition. In composition containing charcoal(2) (Fig.3B), the voids are very irregular and bigger, and this may be due to higher water content (Table 3) and surface activity of the carbon particles. The hydration products of the compositions containing carbonaceous materials



A B

FIG. 3.

SEM of 90 day hydrated products, A-charcoal(1) and B-charcoal(2).

are found to exhibit hydrophobic nature and similar behaviour was also reported earlier (13) where coal tar pitch fines were used.

Conclusions

1. The water requirement and setting time, in general, are found to increase with the incorporation of carbonaceous materials in cementitious compositions. The setting time increases with increase in quantity of these materials.
2. The compressive strength of mortars prepared using compositions containing high ash coke and activated charcoal at all ages of curing are found to be lower than that of mortars made with the clinker alone. The compositions containing coal, low ash coke and low absorptive charcoal show comparable or higher strength than that of the clinker at 90 days.
3. IR spectroscopic study suggests that hydrated products of compositions containing carbonaceous materials in general are richer in $Ca(OH)_2$ than that of the clinker.
4. SEM micrographs of 90 day cured pastes show presence of irregular and larger voids in compositions containing carbonaceous materials compared to those made with the clinker alone.
5. For preparation of self-reducing iron ore pellets which require larger quantity of carbonaceous reductant, further investigation is necessary.

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